Supporting Information for:

Synthetic Approaches to Bicyclic Diazenium Salts

Wyman, J.; Javed, M.I.; Al-Bataineh, N.; Brewer, M.*

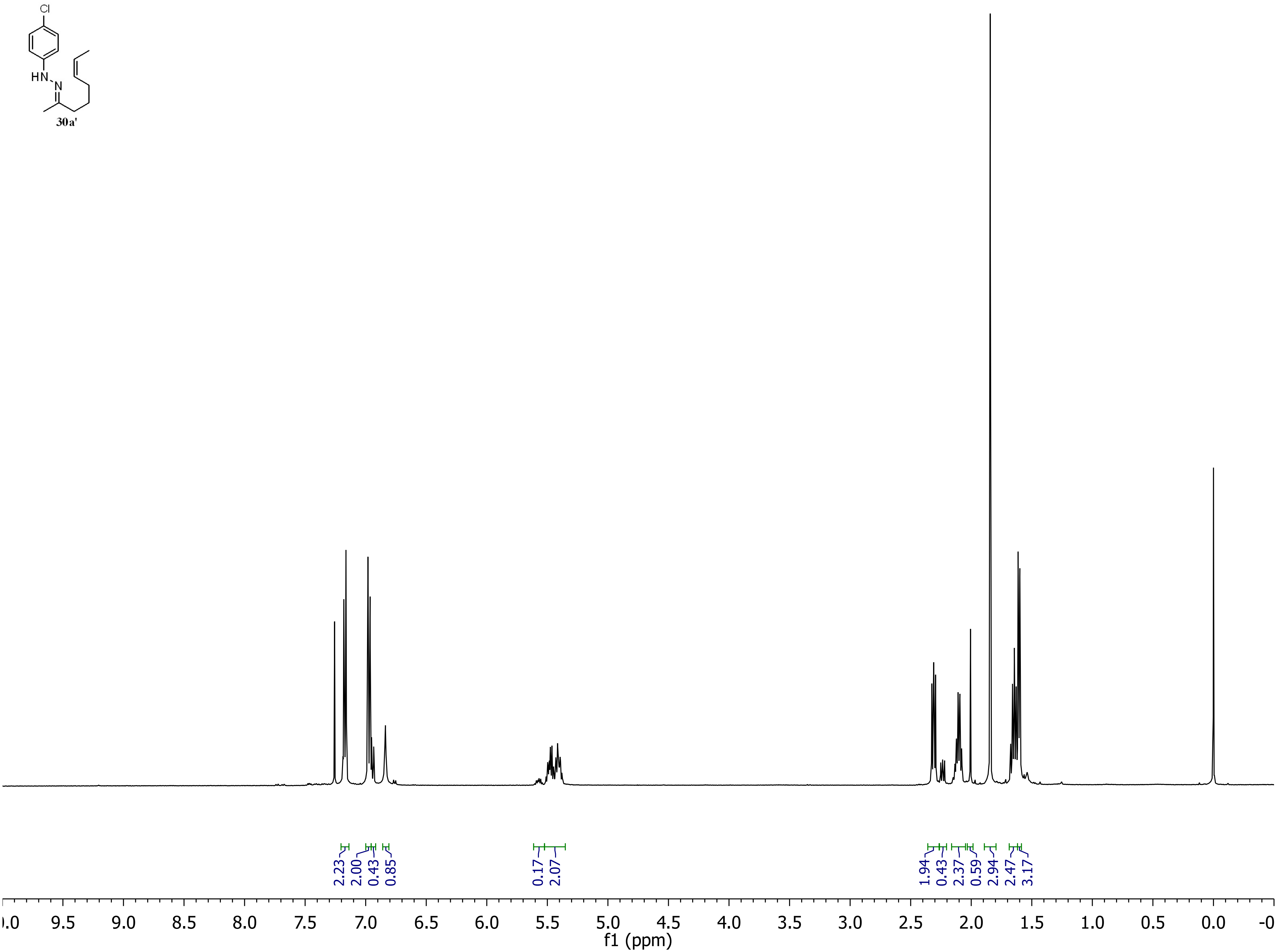
The University of Vermont, Department of Chemistry,
82 University Place, Burlington VT 05405
matthias.brewer@uvm.edu

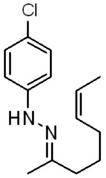
I) General experimental information:

All reactions were carried out under an atmosphere of nitrogen using flame-dried glassware. A rotary evaporator equipped with a water condenser and attached to a vacuum system was used to concentrate *in vacuo*. Samples were further dried under reduced pressure on a high vacuum line.

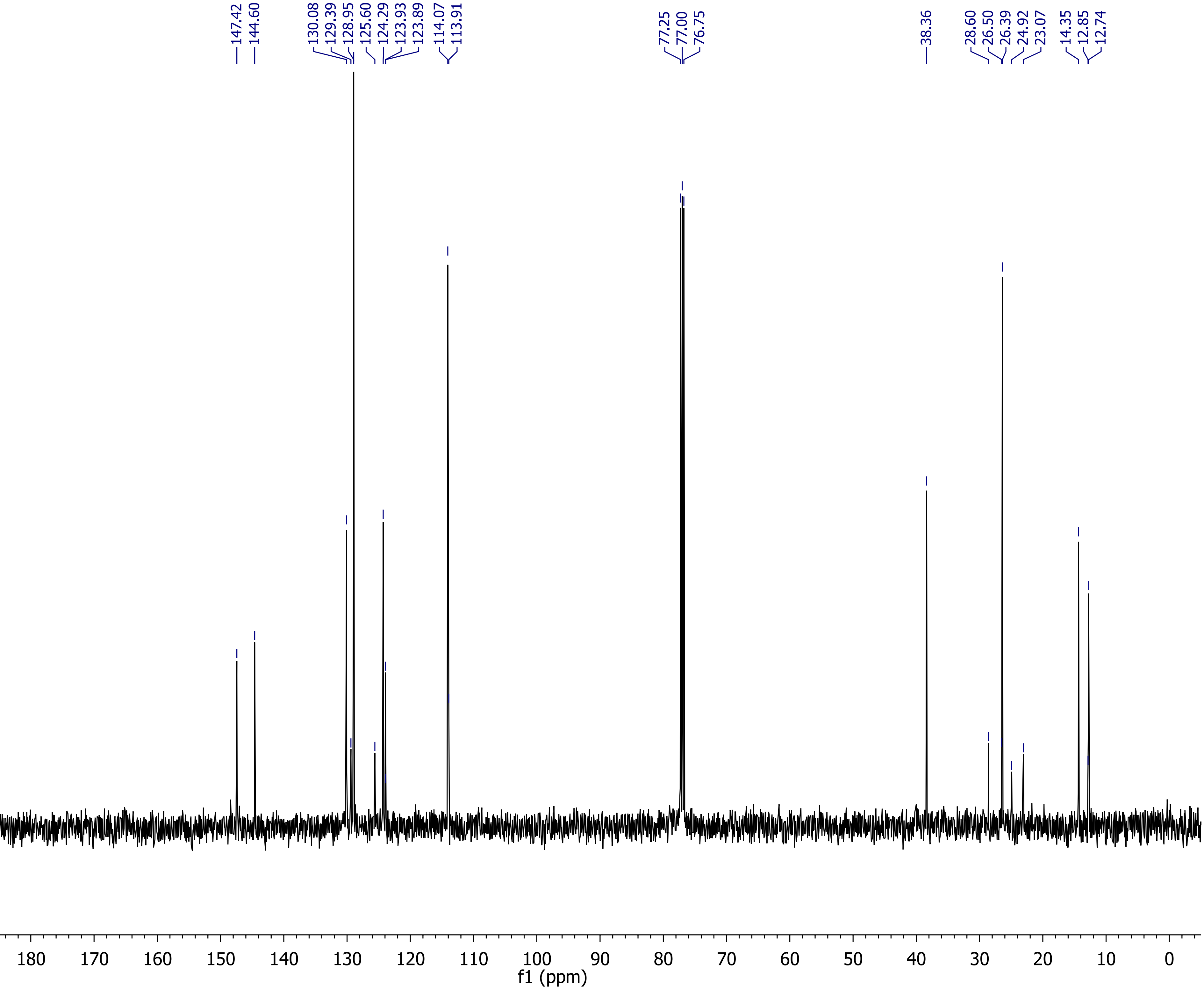
Tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), and diethyl ether (Et_2O) were dried via a solvent dispensing system. Triethylamine was freshly distilled from CaH_2 before use. Oxalyl chloride was distilled before use and stored in a sealable container under and atmosphere of dry nitrogen. Triflic Anhydride was distilled from P_2O_5 before use and stored for short periods in a sealable container under and atmosphere of dry nitrogen. Extra dry DMSO stored over molecular sieves was used as received. All hydrazones were freshly prepared before use as these materials could not be stored and underwent facile auto oxidation on standing in air.

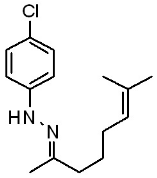
Reactions were cooled to –78 °C via dry ice-acetone baths. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or CD_3CN. ^{1}H chemical shifts are reported in ppm (δ units) downfield from tetramethylsilane. Solvent peaks were used as internal references for all ^{13}C NMR. Mass spectra were recorded in positive ion electrospray mode.


Cl
HN
N
30a'
2.23
2.00
0.43
0.85
0.17
2.07
1.94
0.43
2.37
0.59
2.94
2.47
3.17
10.0
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
-0
f1 (ppm)

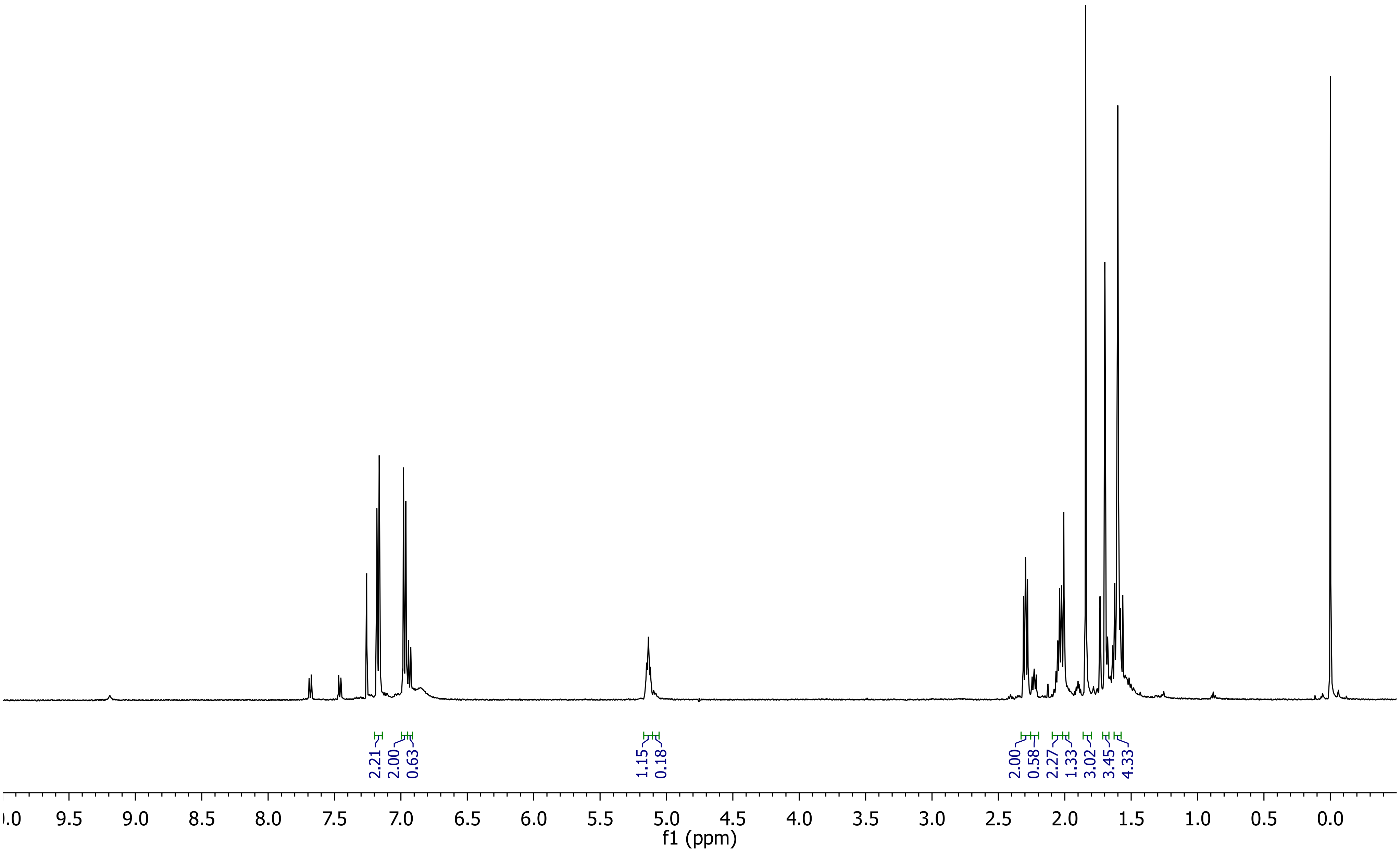


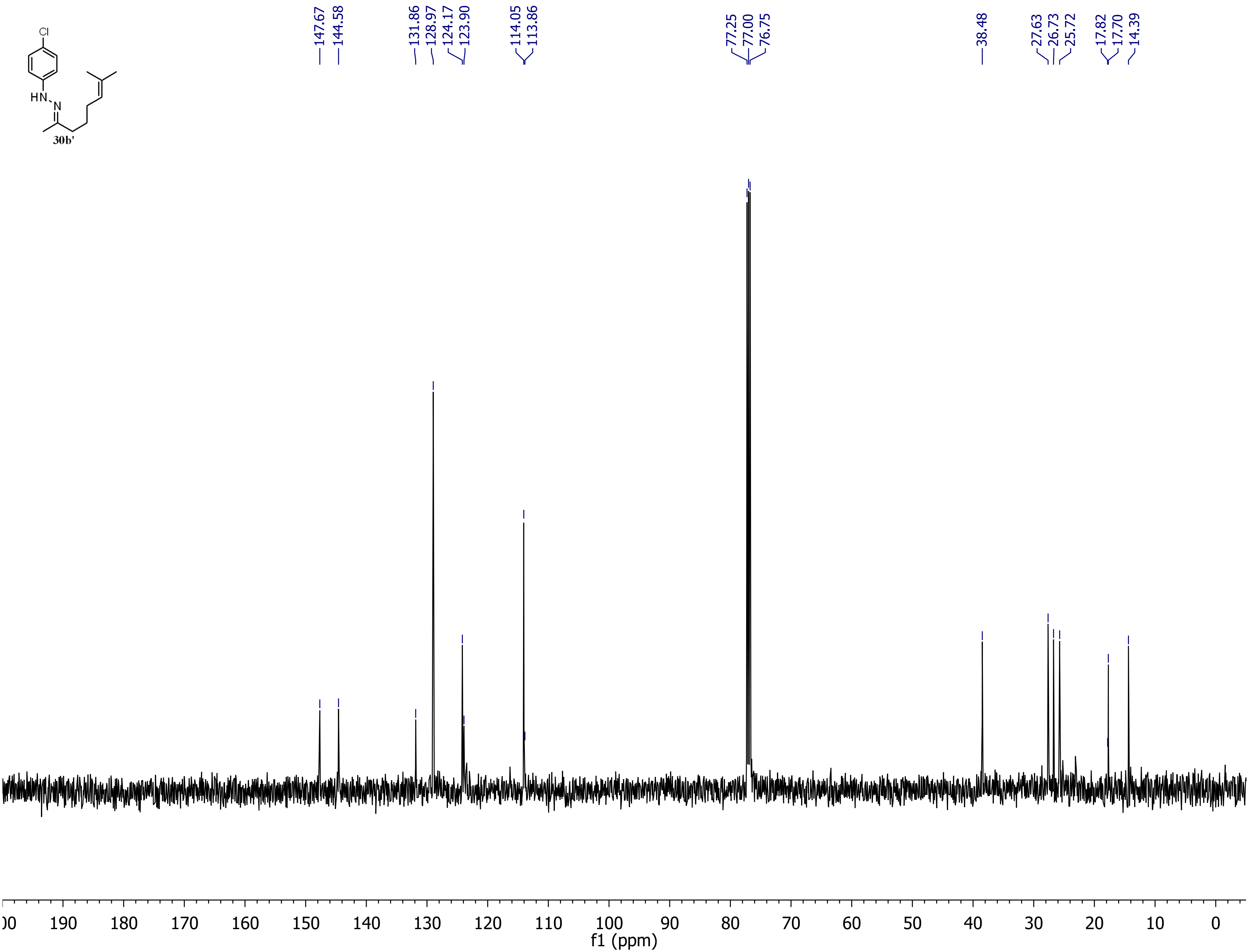
30a'

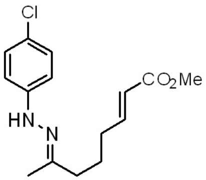

147.42
144.60
130.08
129.39
128.95
125.60
124.29
123.93
123.89
114.07
113.91
77.25
77.00
76.75
38.36
28.60
26.50
26.39
24.92
23.07
14.35
12.85
12.74
f1 (ppm)


Cl
HN
N

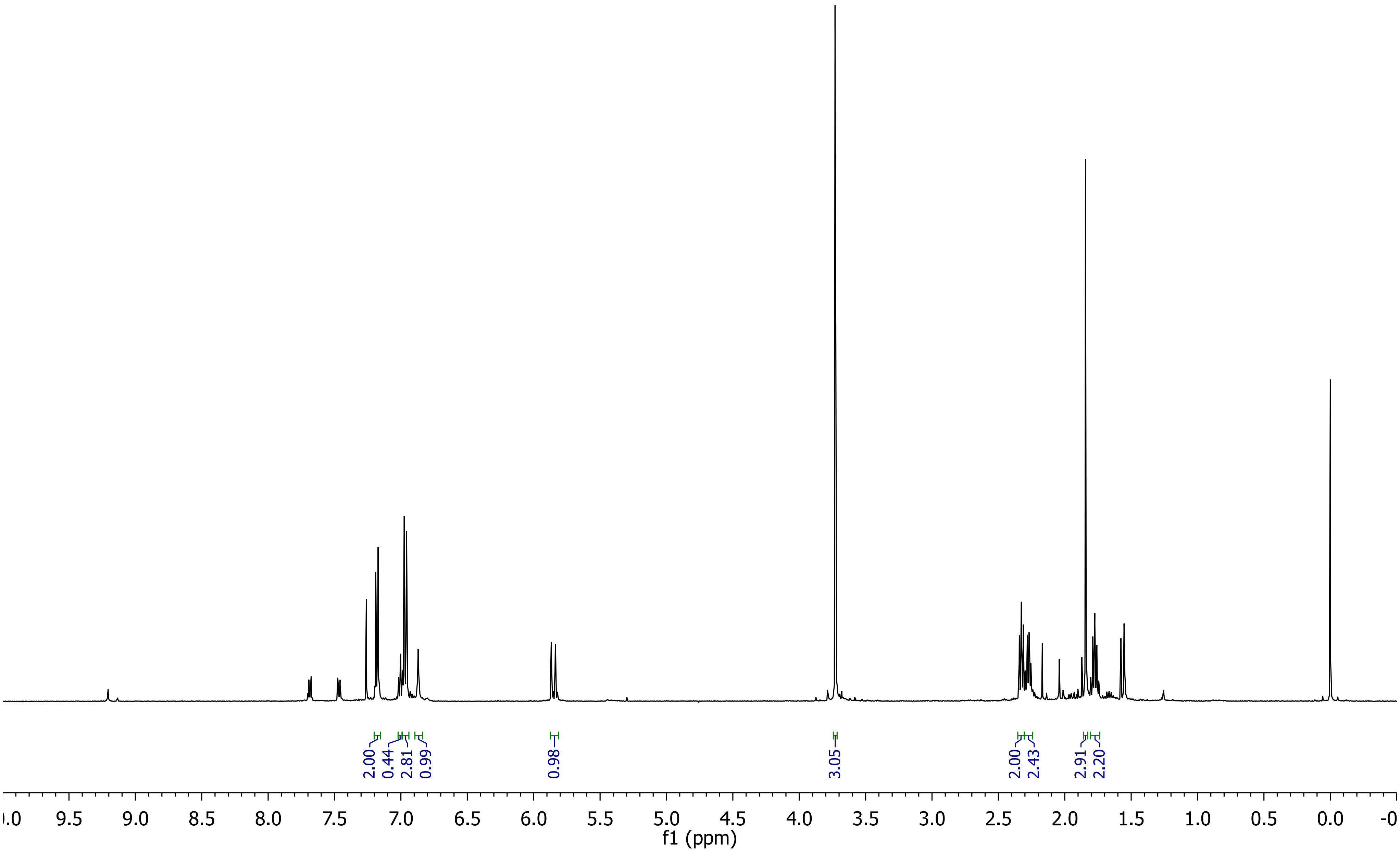
30b'

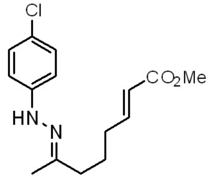

2.21
2.00
0.63
1.15
0.18
2.00
0.58
2.27
1.33
3.02
3.45
4.33
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


147.67
144.58
131.86
128.97
124.17
123.90
114.05
113.86
77.25
77.00
76.75
38.48
27.63
26.73
25.72
17.82
17.70
14.39
Cl
HN
N
30b'
f1 (ppm)

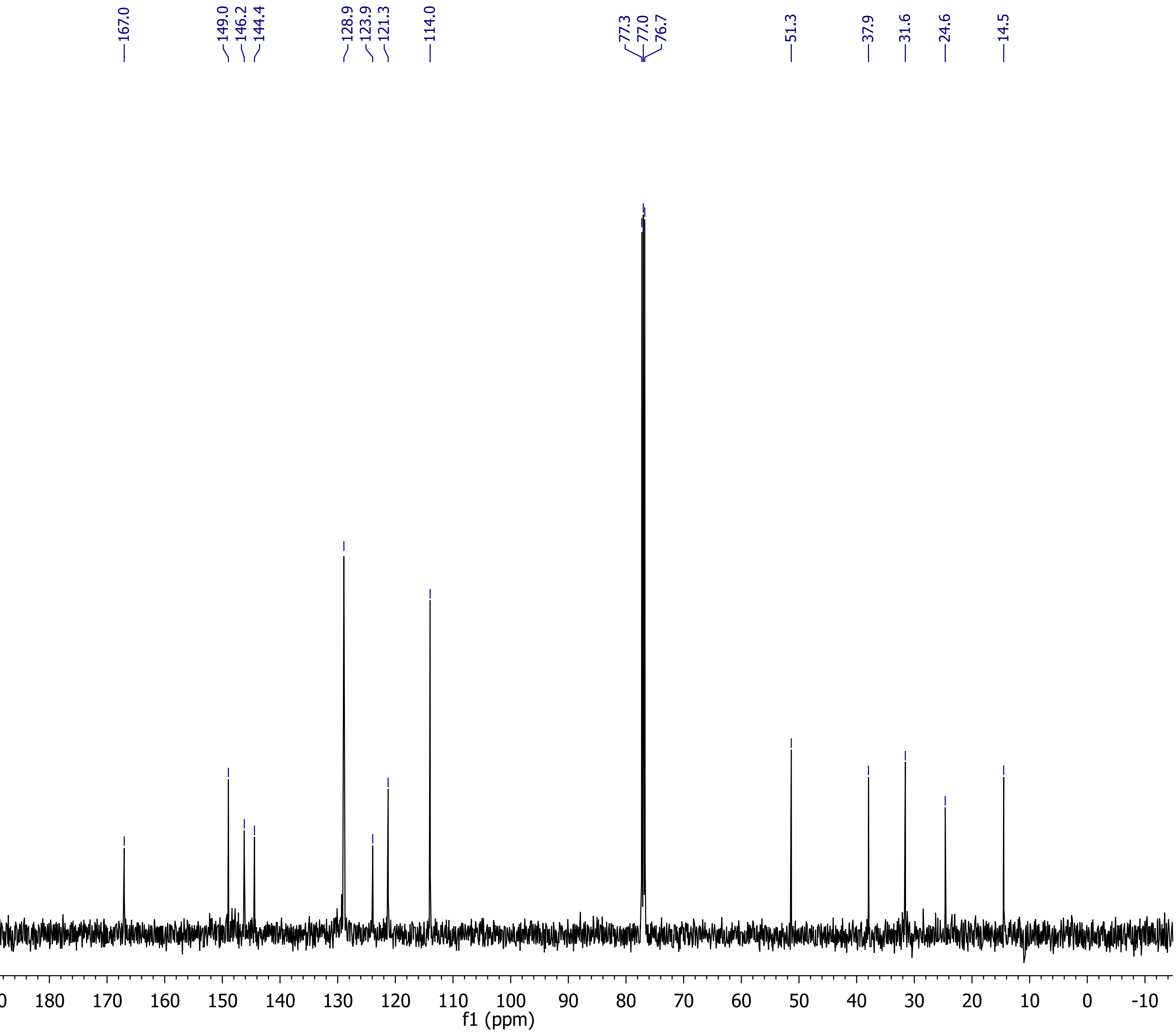


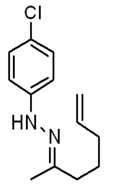
30c'



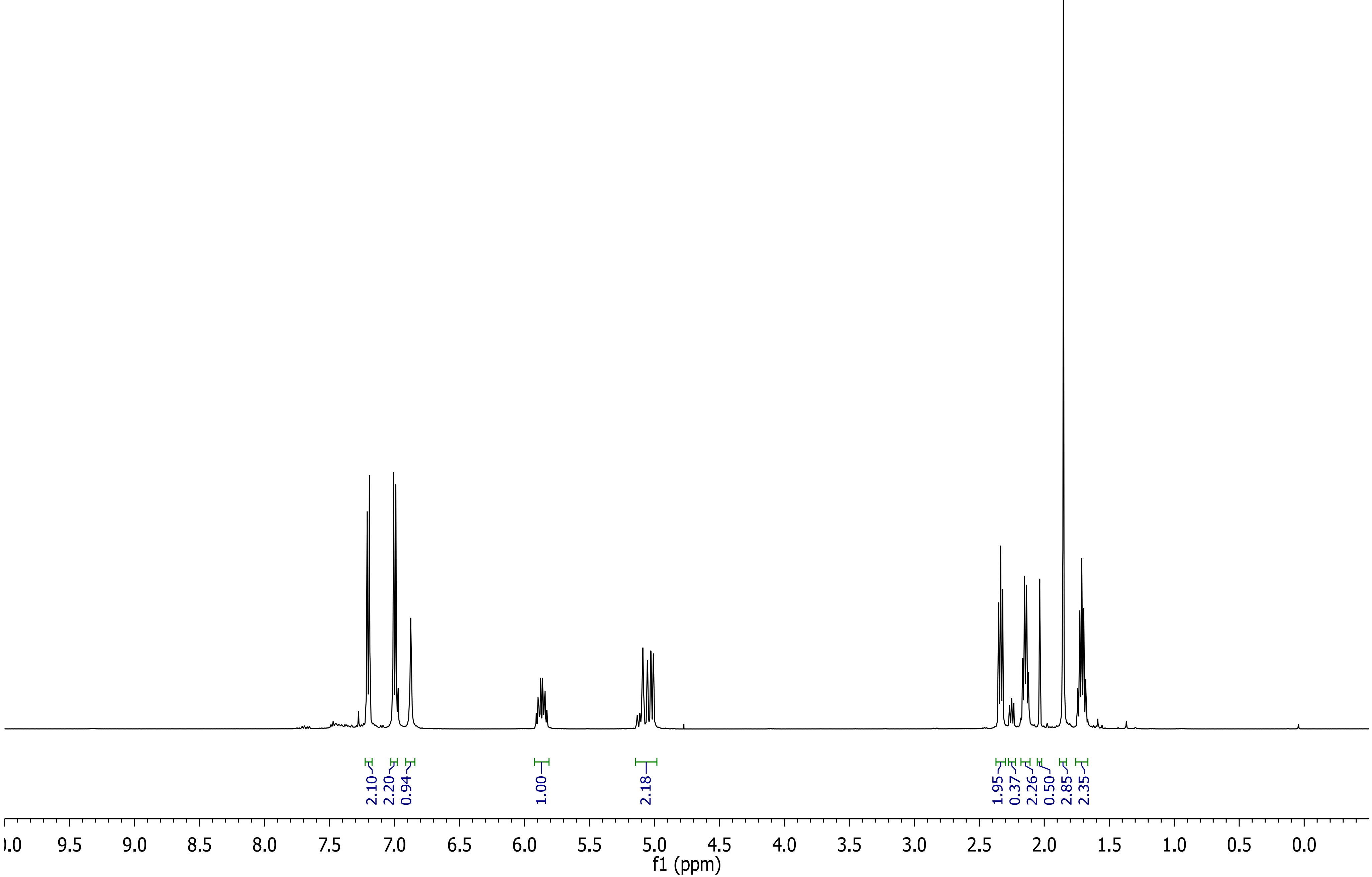

Cl
HN
N
CO2Me

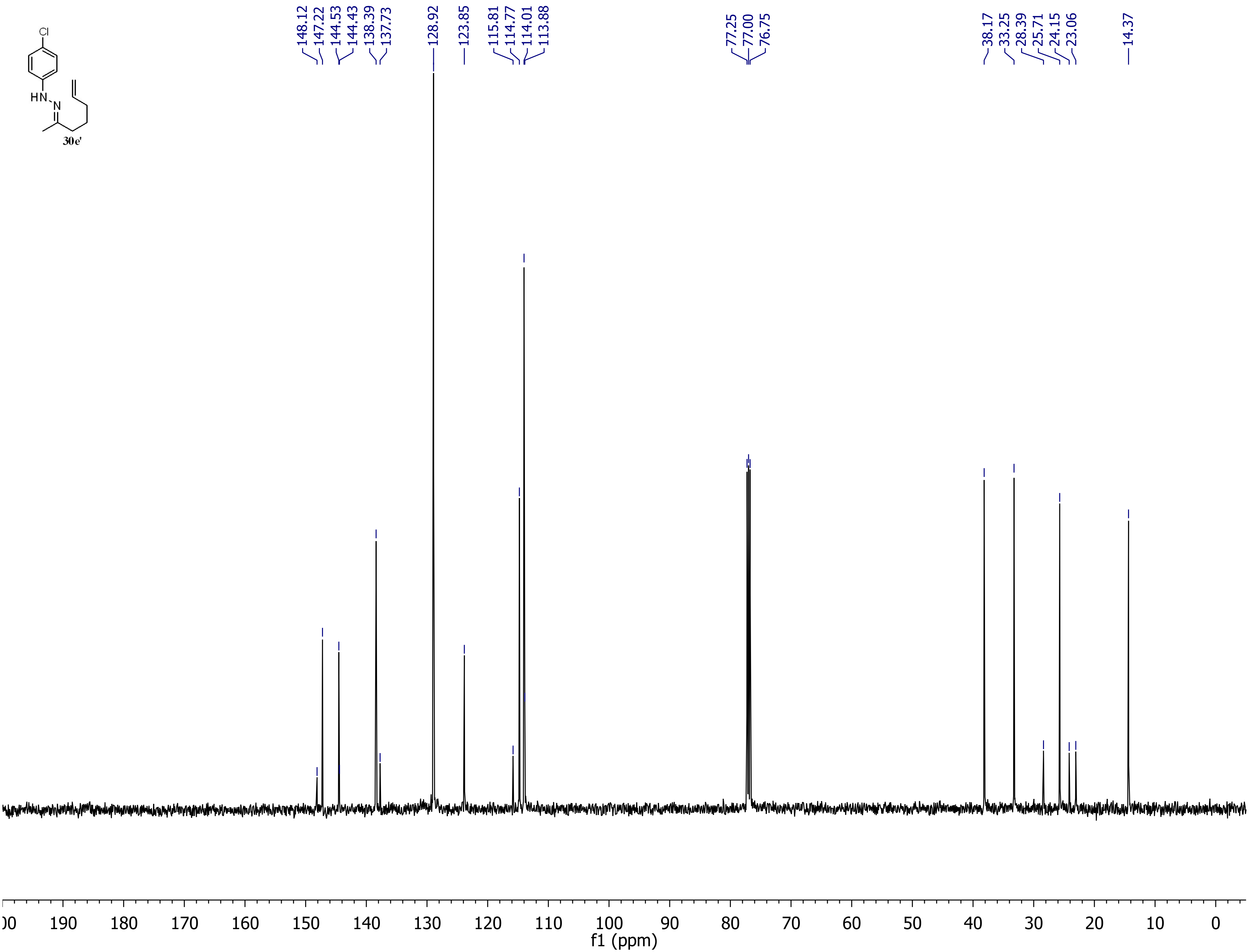
30c'


167.0
149.0
146.2
144.4
128.9
123.9
121.3
114.0
77.3
77.0
76.7
51.3
37.9
31.6
24.6
14.5
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

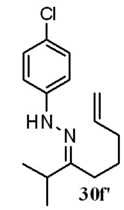

Cl
HN
N

30e'

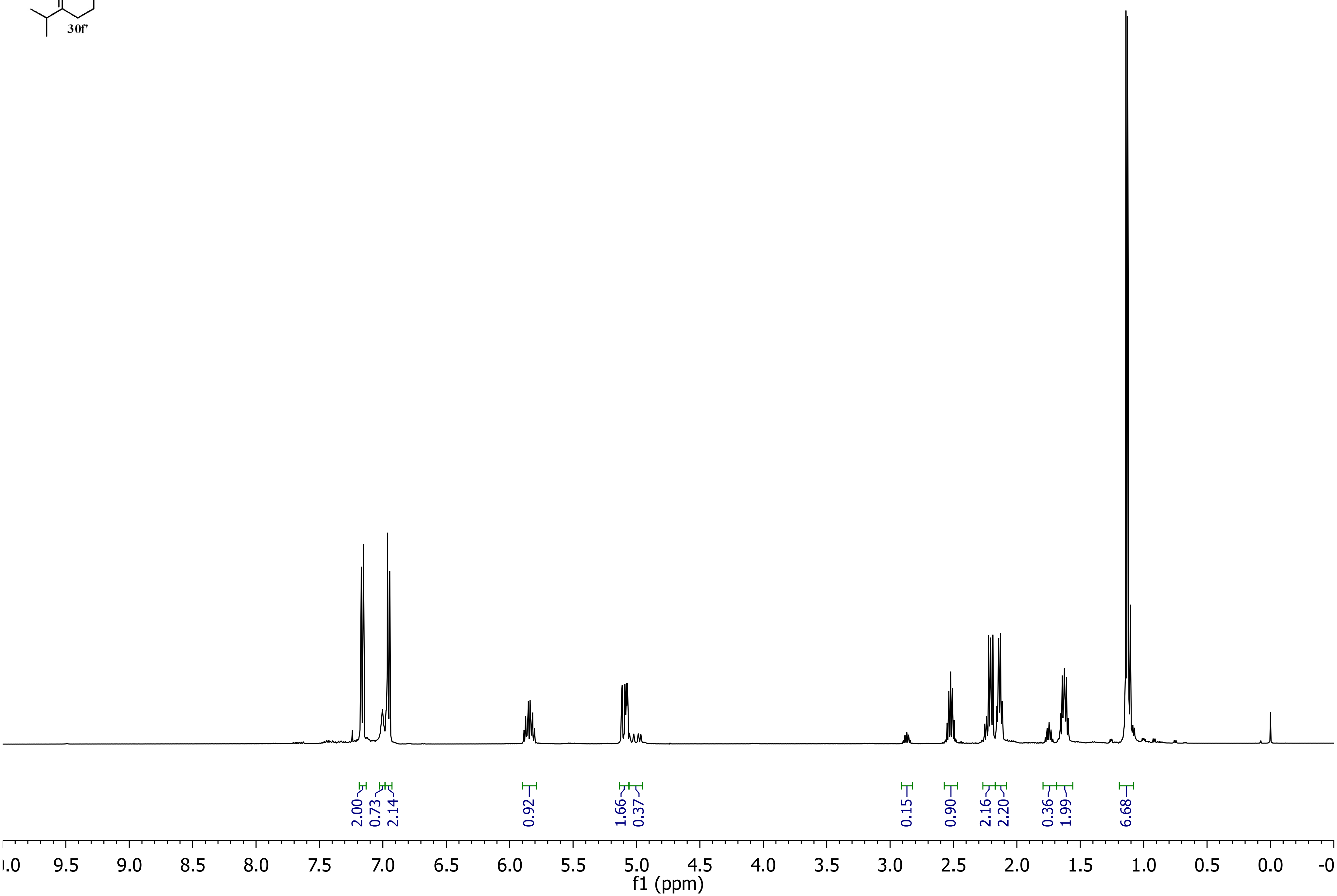

2.10
2.20
0.94
1.00
2.18
1.95
0.37
2.26
0.50
2.85
2.35
).0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



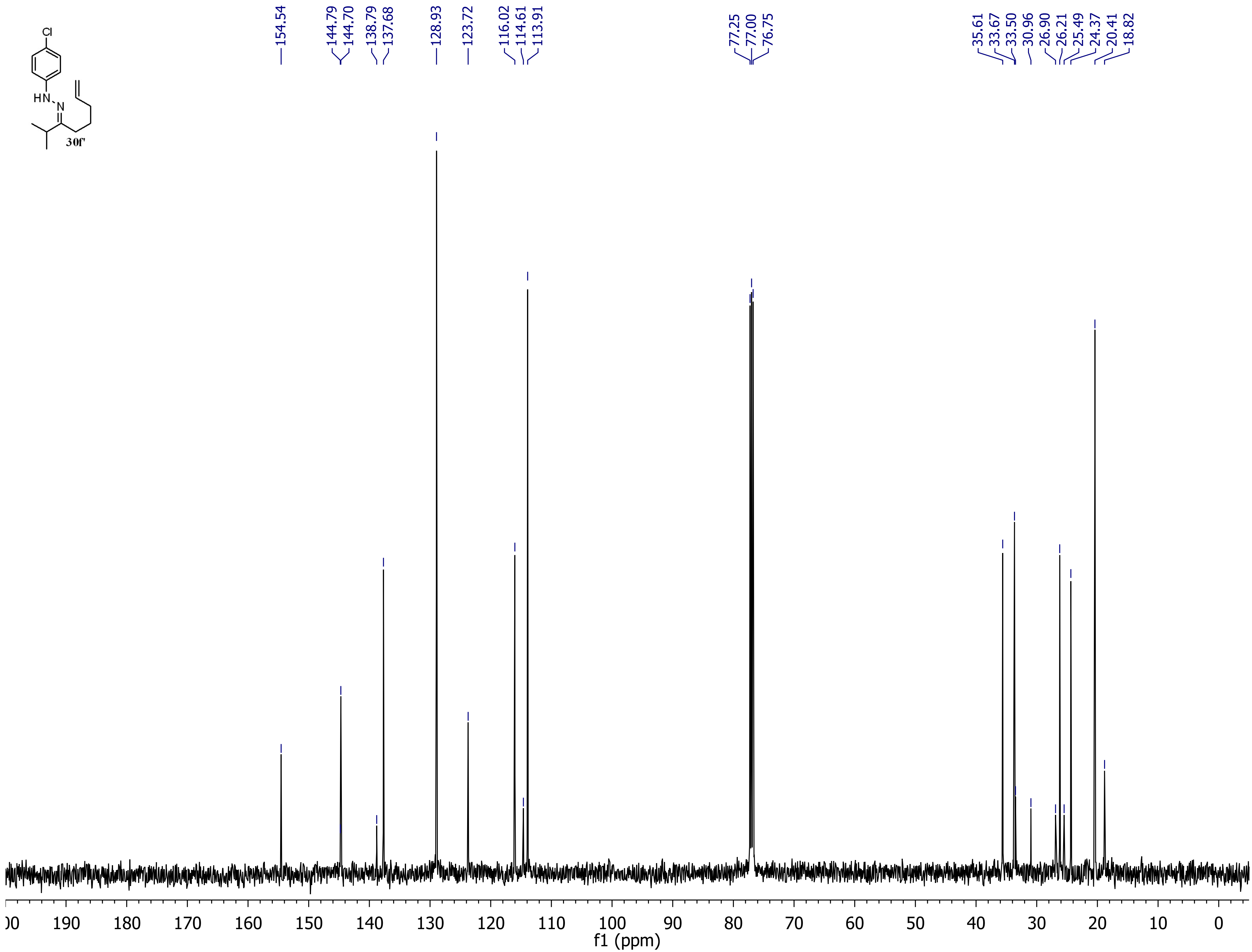
30e'
148.12
147.22
144.53
144.43
138.39
137.73
128.92
123.85
115.81
114.77
114.01
113.88
77.25
77.00
76.75
38.17
33.25
28.39
25.71
24.15
23.06
14.37
f1 (ppm)

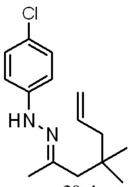


30f'

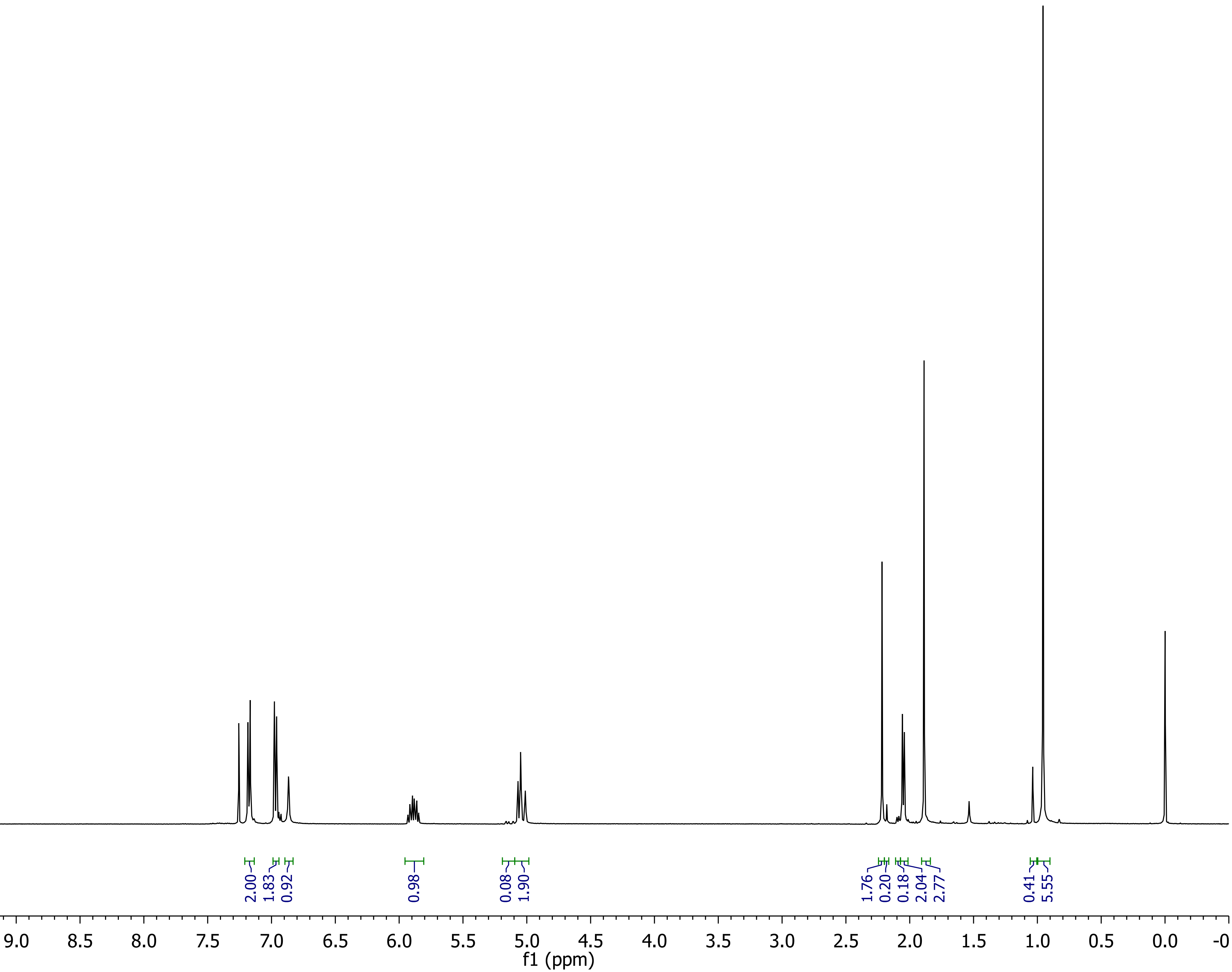


2.00
0.73
2.14
0.92
1.66
0.37
0.15
0.90
2.16
2.20
0.36
1.99
6.68
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

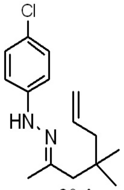

Cl
HN
N
30f'
154.54
144.79
144.70
138.79
137.68
128.93
123.72
116.02
114.61
113.91
77.25
77.00
76.75
35.61
33.67
33.50
30.96
26.90
26.21
25.49
24.37
20.41
18.82
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



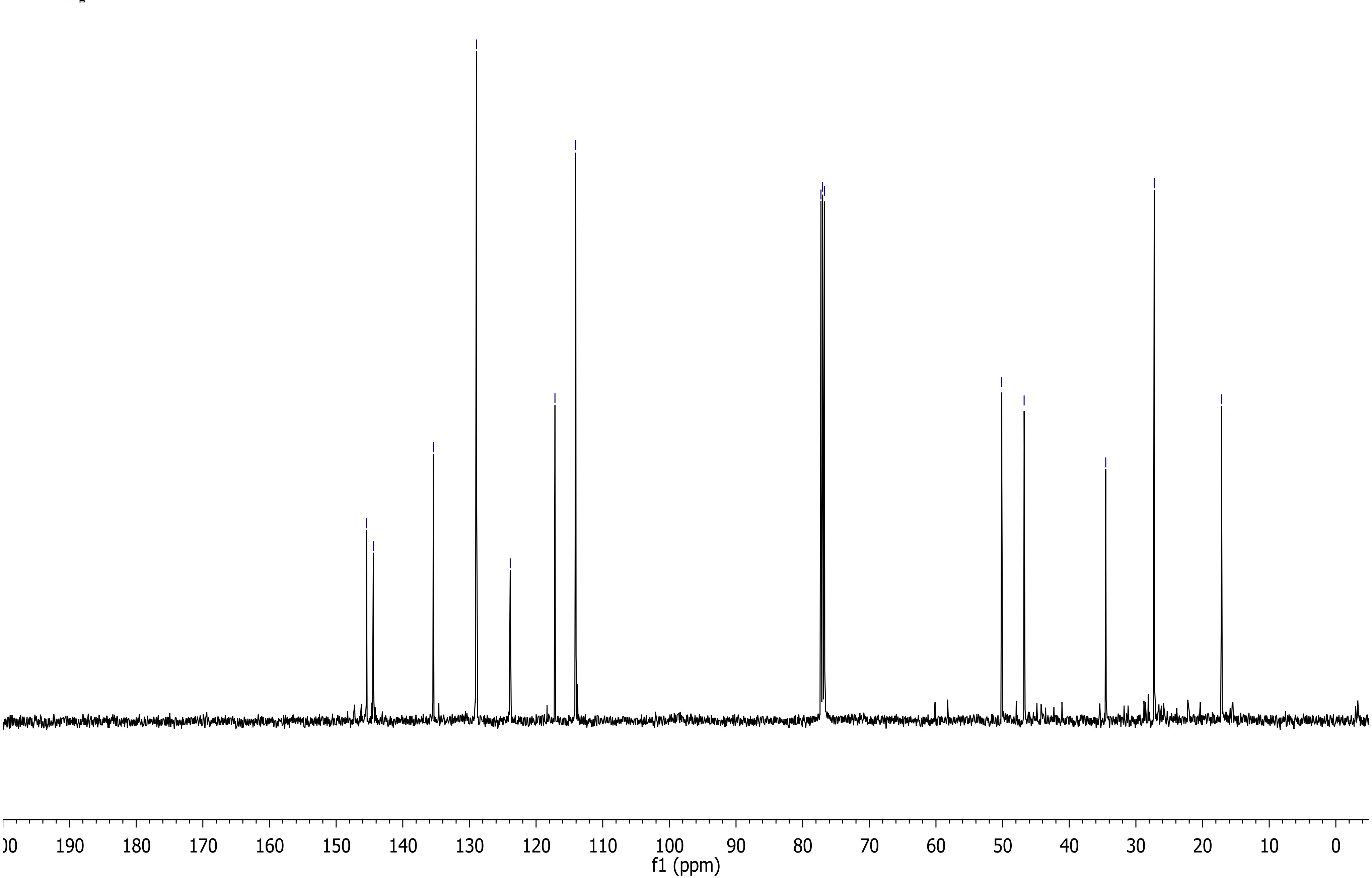
30g'

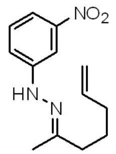


2.00
1.83
0.92
0.98
0.08
1.90
1.76
0.20
0.18
2.04
2.77
0.41
5.55
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

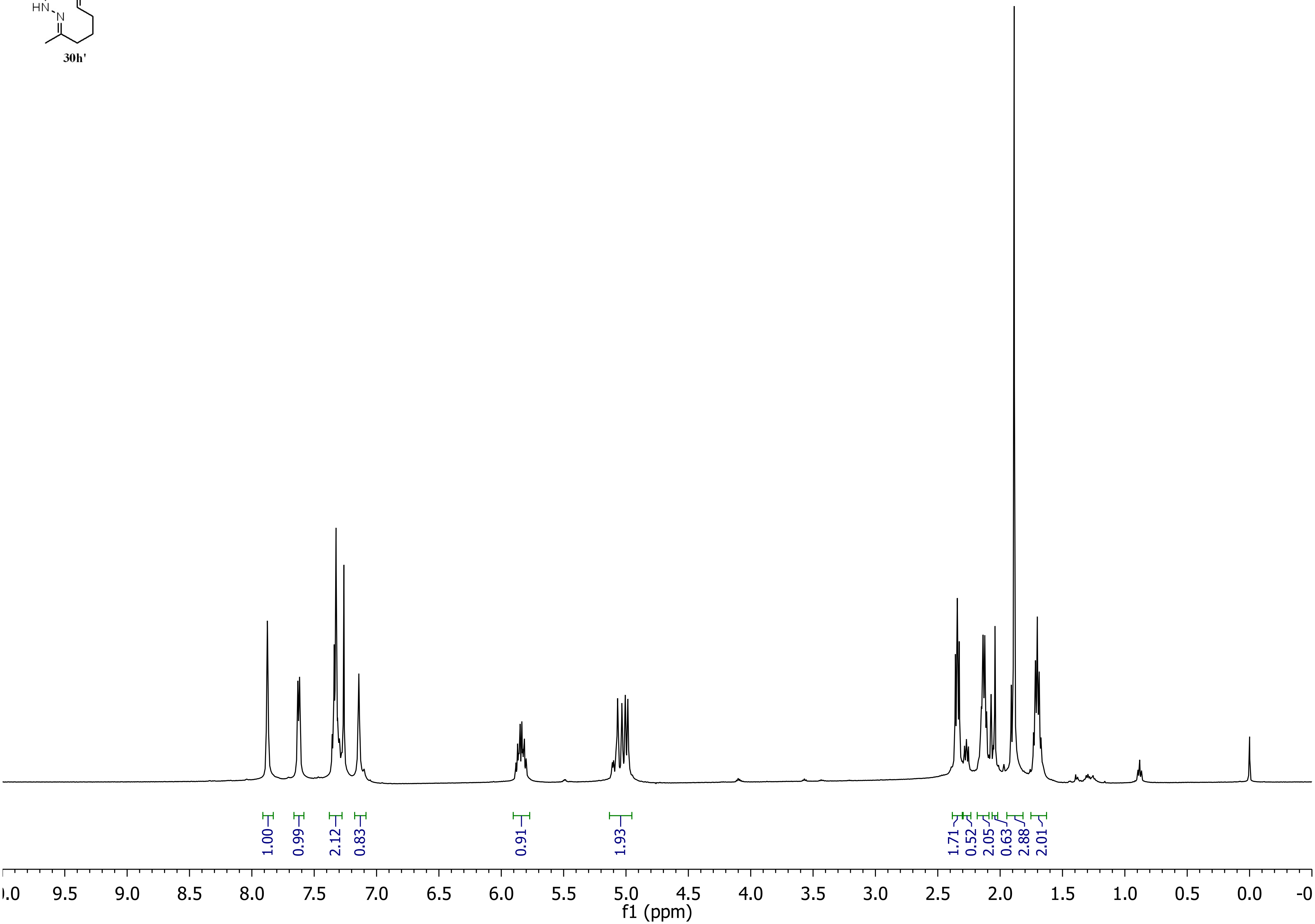


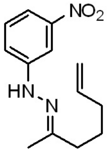
30g'


145.44
144.42
135.42
128.95
123.89
117.17
114.04
77.25
77.00
76.75
50.12
46.78
34.52
27.25
17.16
f1 (ppm)

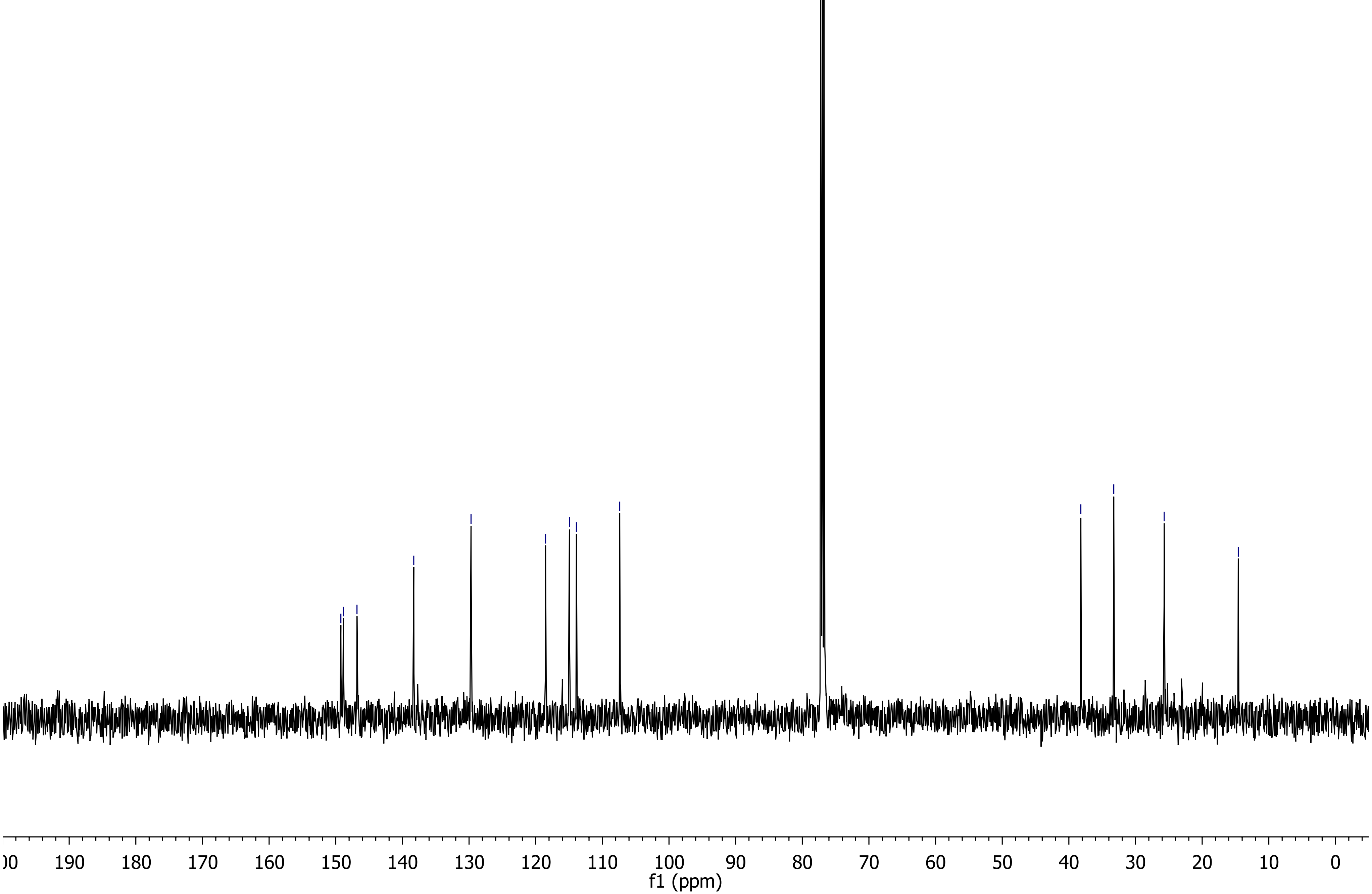


30h'

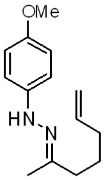

1.00
0.99
2.12
0.83
0.91
1.93
1.71
0.52
2.05
0.63
2.88
2.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)



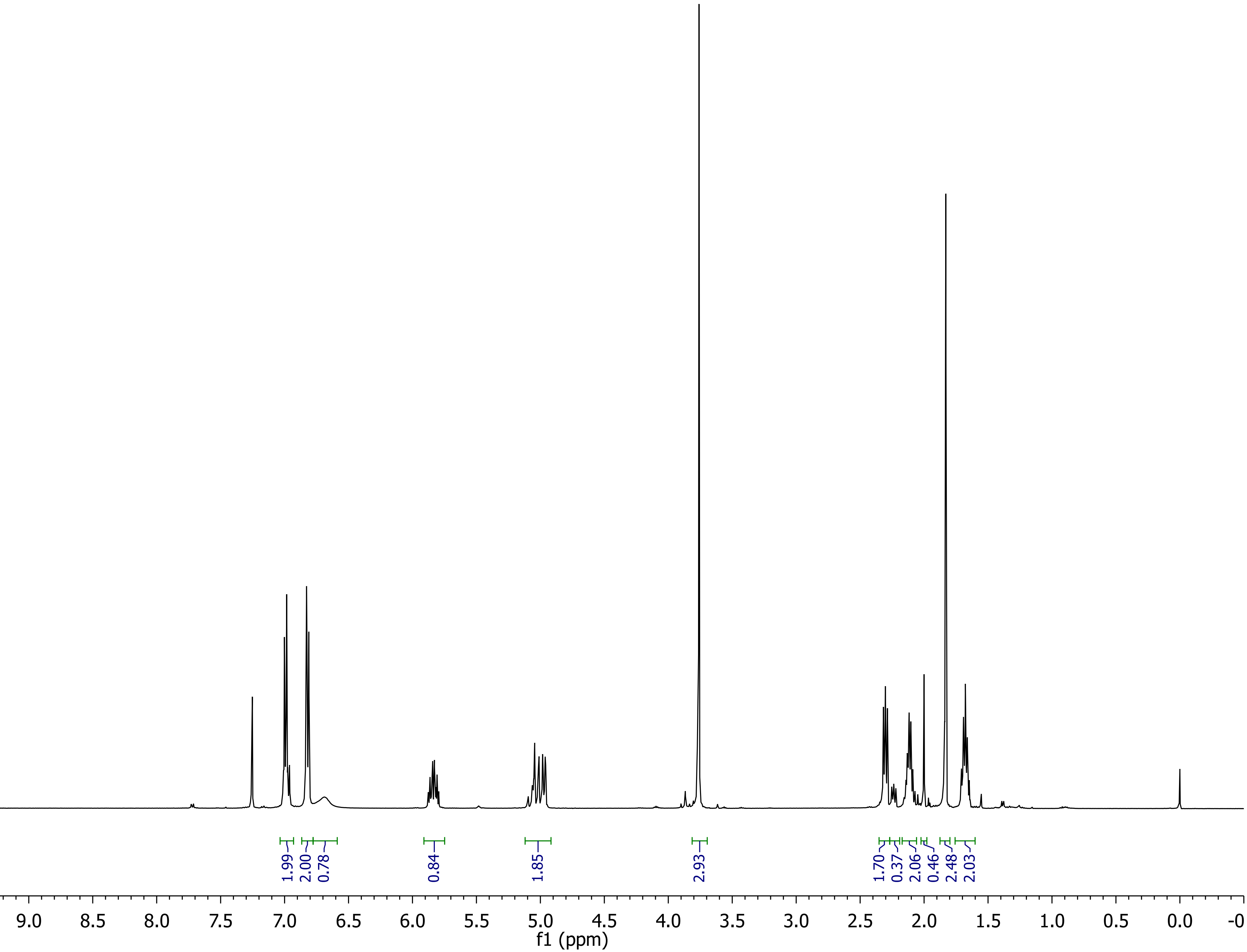
30h'

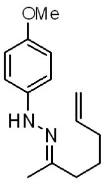


149.23
148.86
146.82
138.30
129.70
118.52
114.94
113.89
107.39
77.25
77.00
76.75
38.20
33.26
25.70
14.58
f1 (ppm)

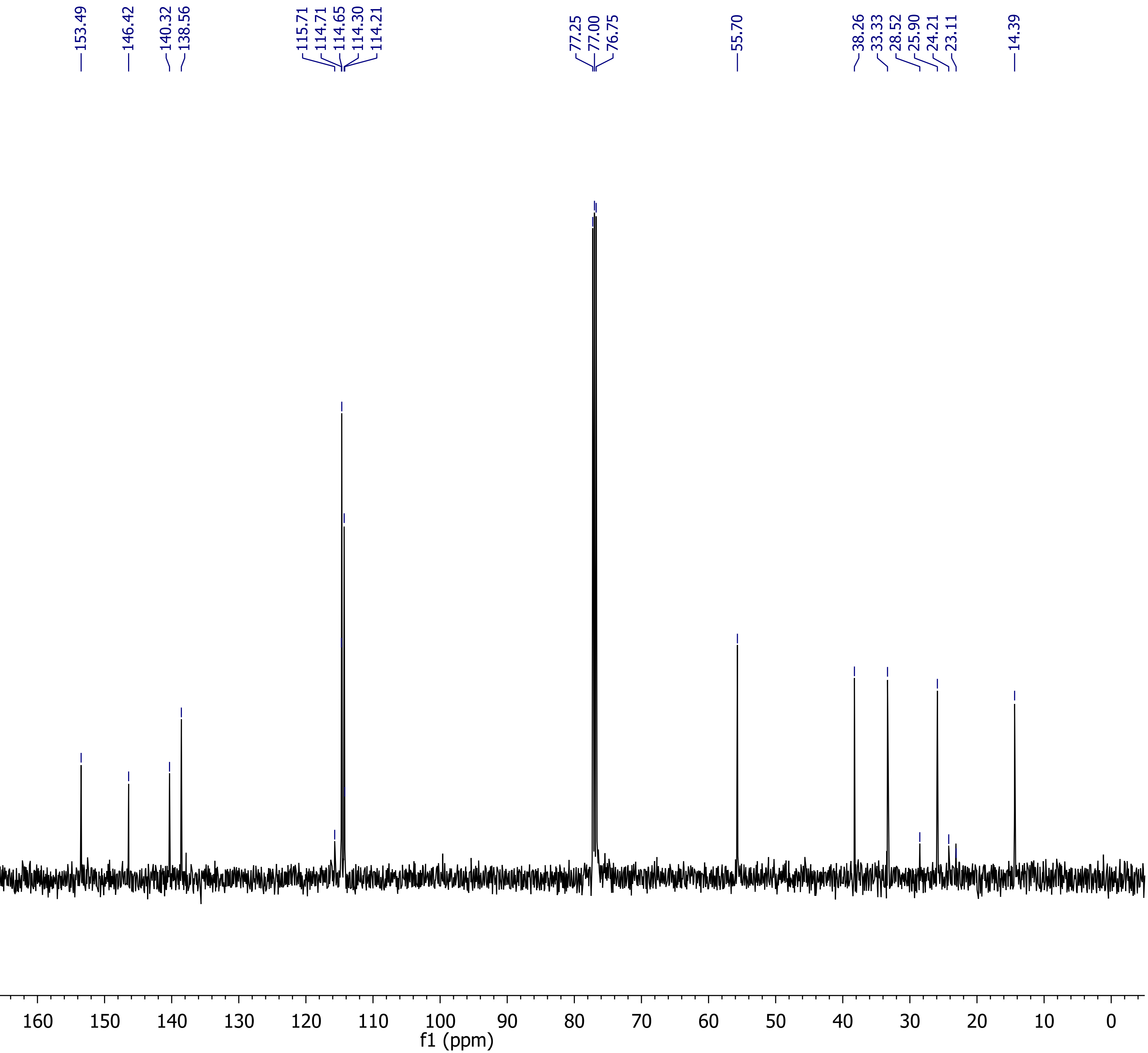

OMe
HN
N

30i'

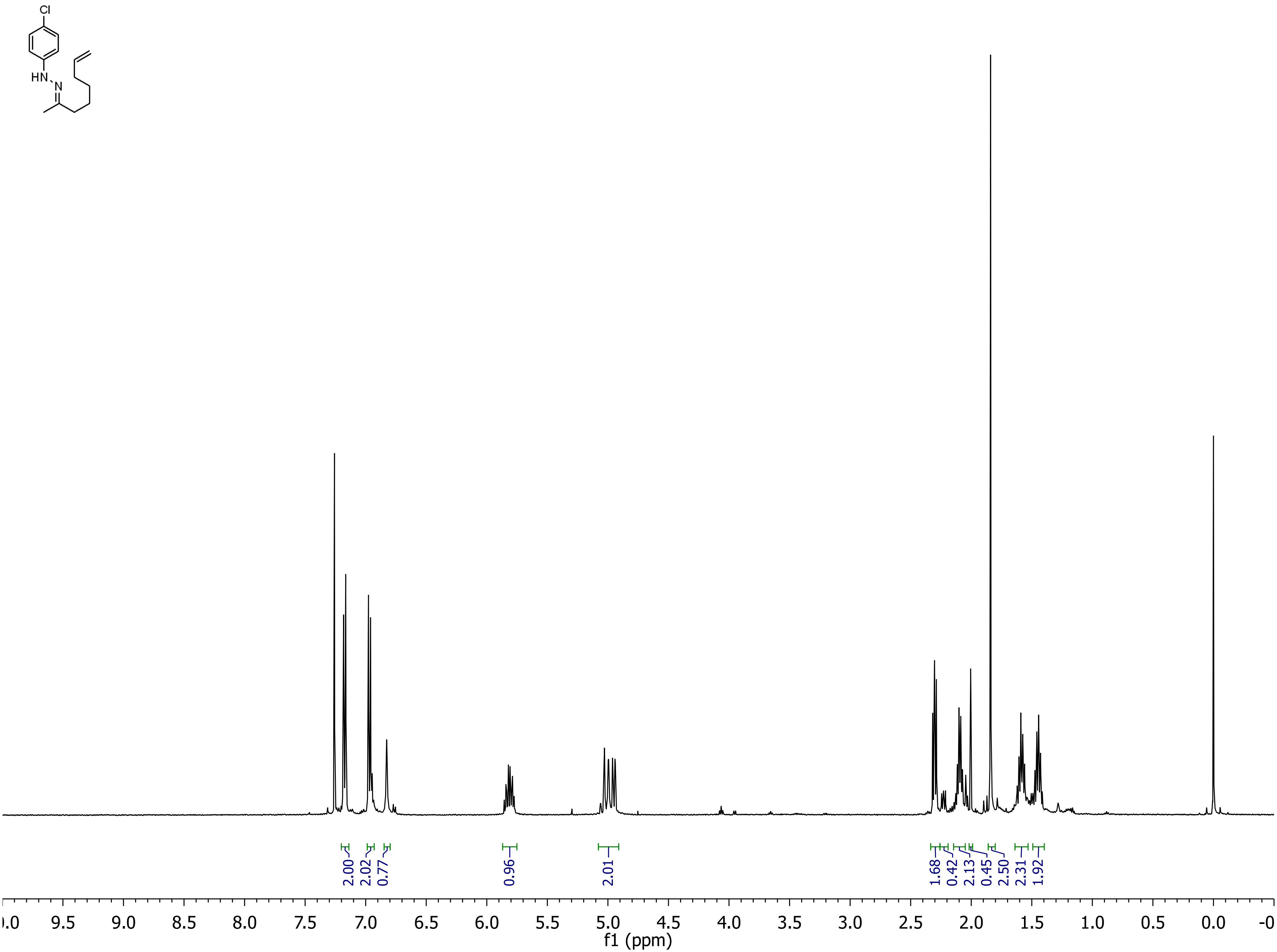

1.99
2.00
0.78
0.84
1.85
2.93
1.70
0.37
2.06
0.46
2.48
2.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

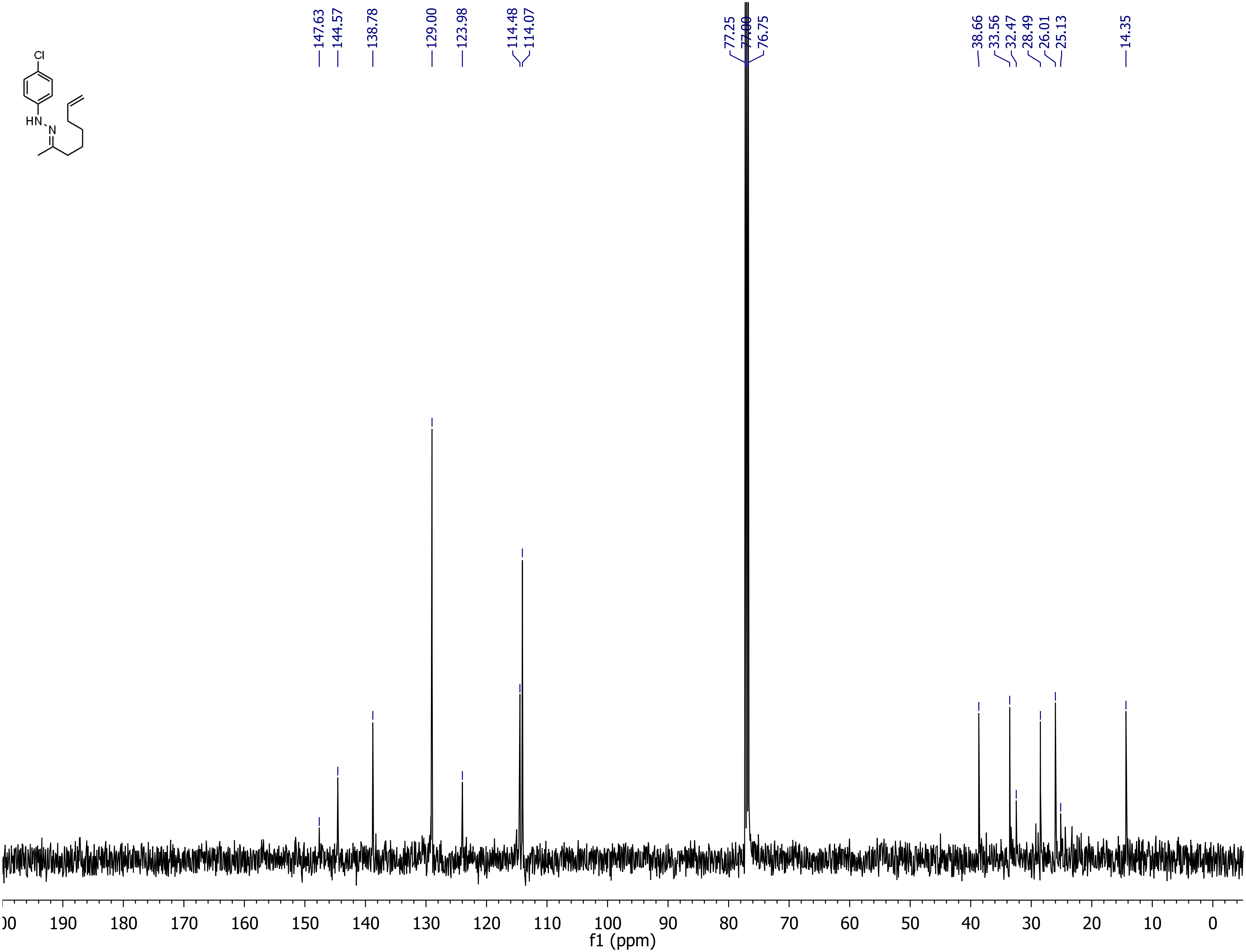


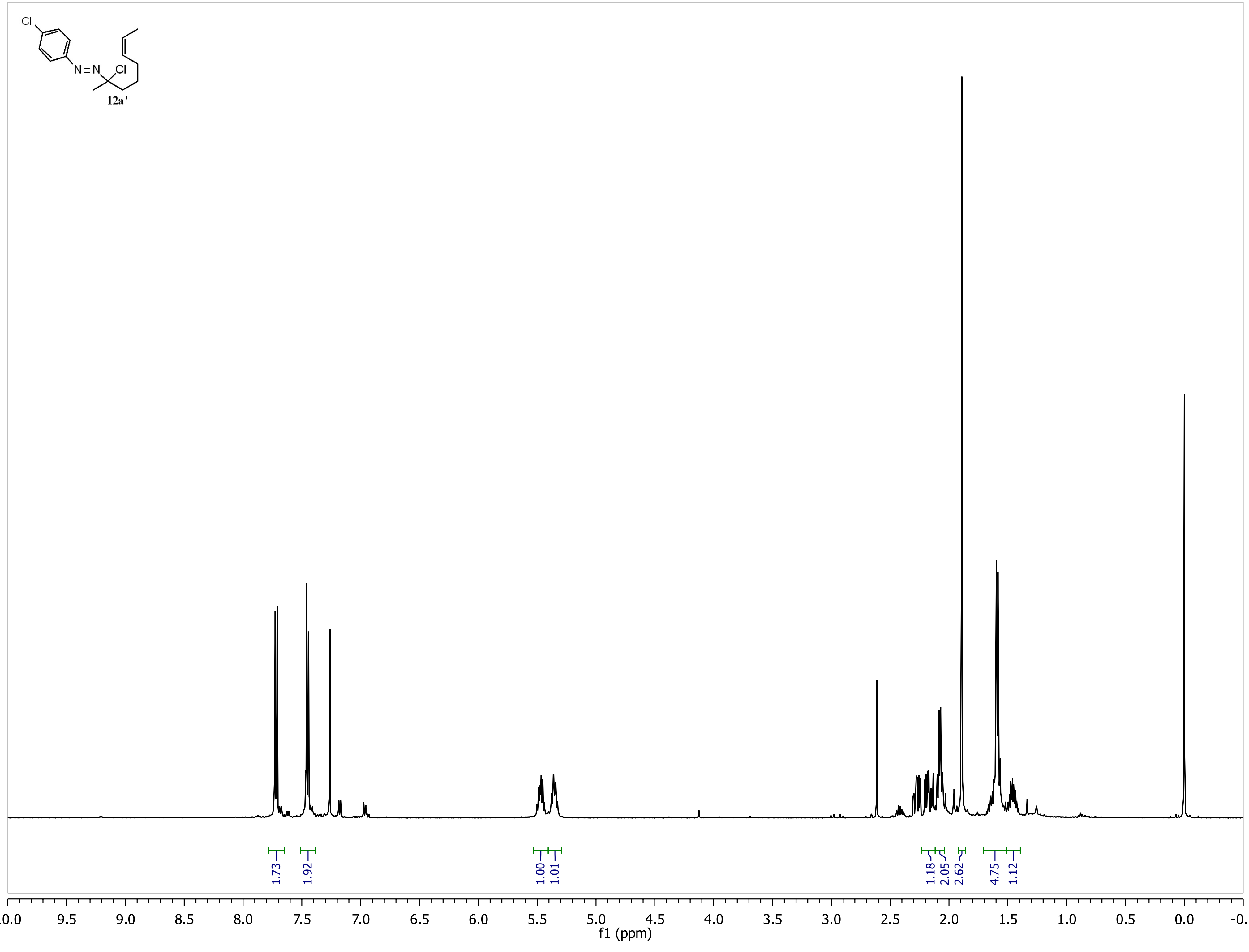
30i'

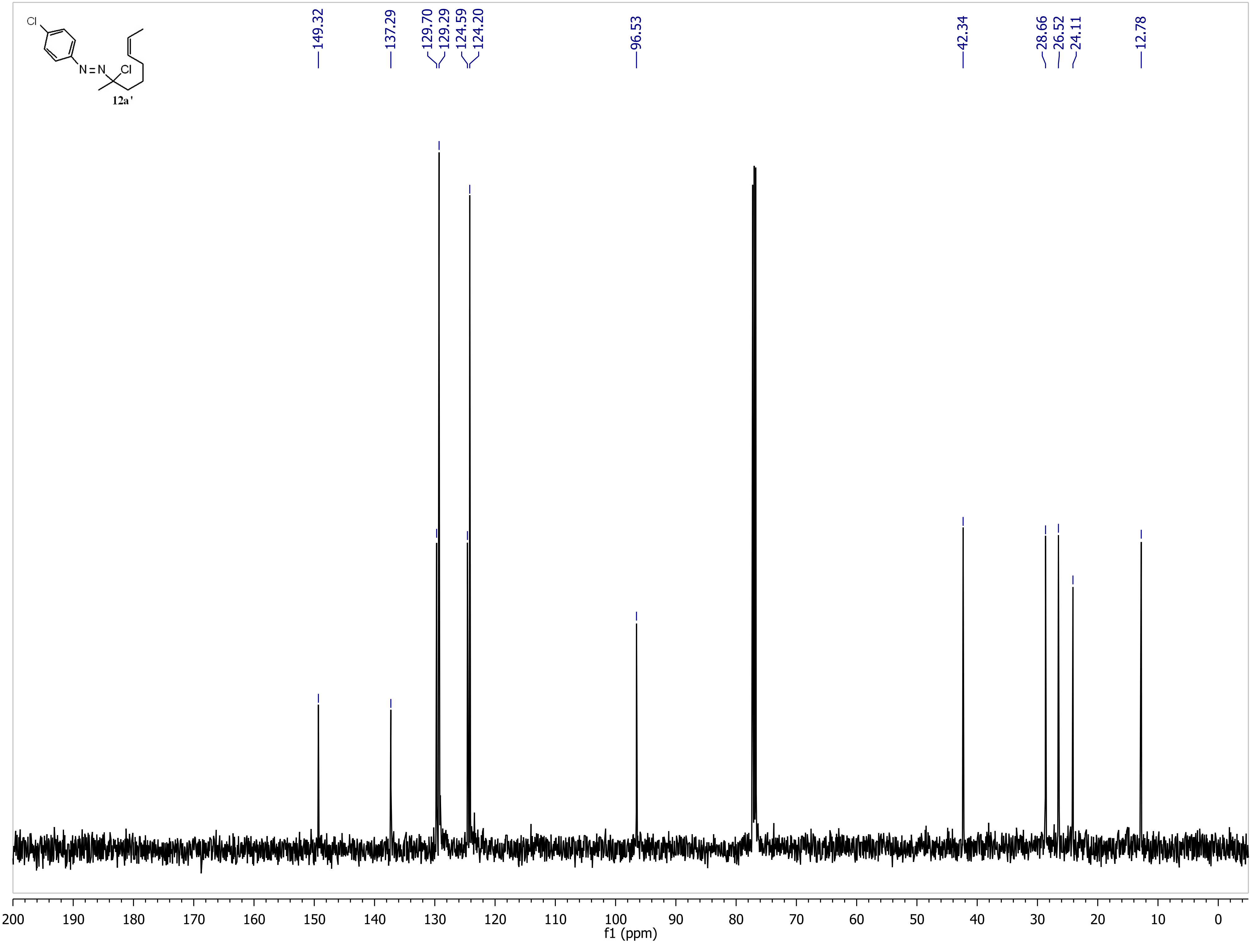


153.49
146.42
140.32
138.56
115.71
114.71
114.65
114.30
114.21
77.25
77.00
76.75
55.70
38.26
33.33
28.52
25.90
24.21
23.11
14.39
f1 (ppm)

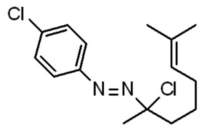

Cl
HN
N
2.00
2.02
0.77
0.96
2.01
1.68
0.42
2.13
0.45
2.50
2.31
1.92
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Cl
HN
N
147.63
144.57
138.78
129.00
123.98
114.48
114.07
77.25
77.00
76.75
38.66
33.56
32.47
28.49
26.01
25.13
14.35
f1 (ppm)

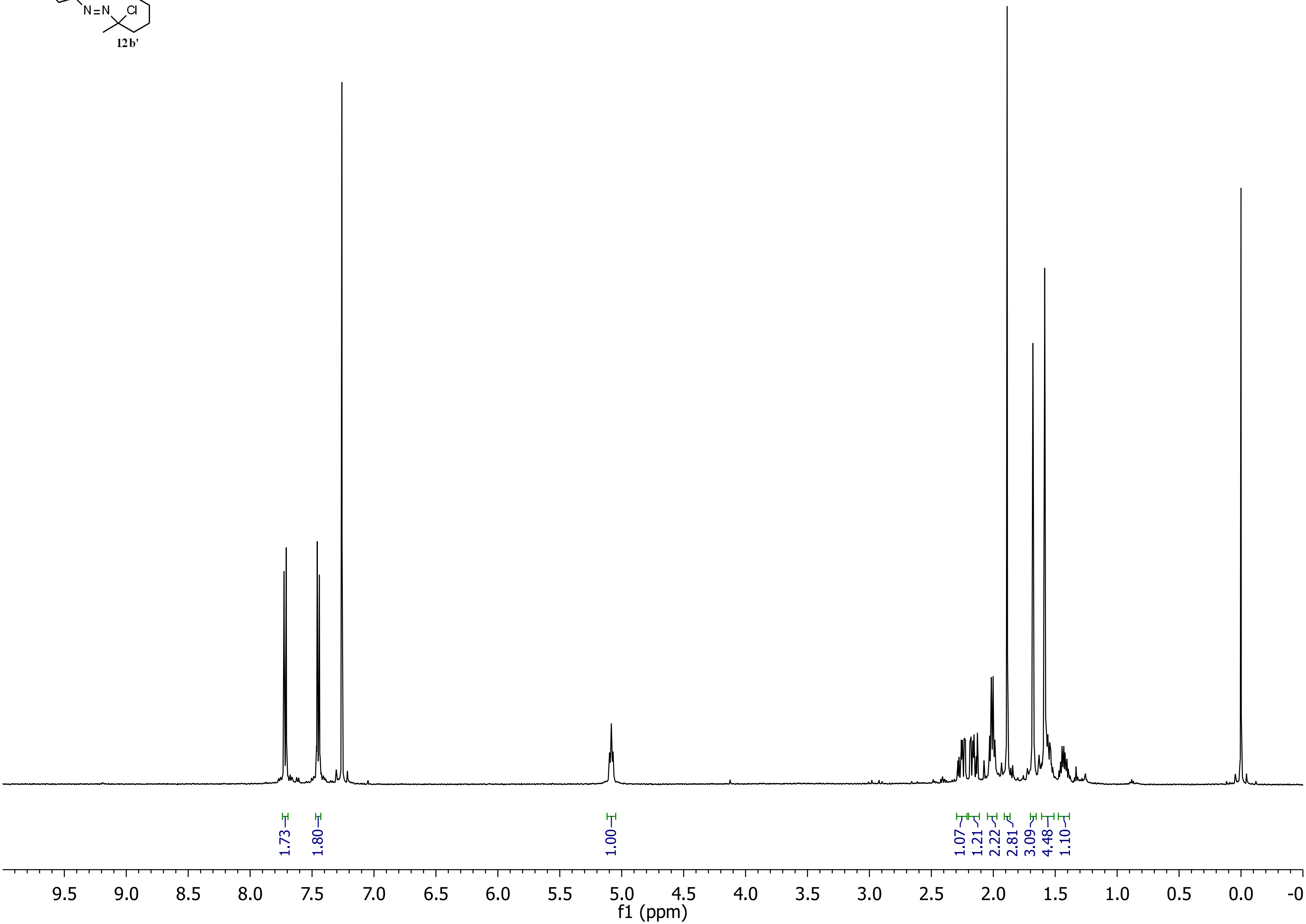

Cl
N=N
Cl
12a'
1.73
1.92
1.00
1.01
1.18
2.05
2.62
4.75
1.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

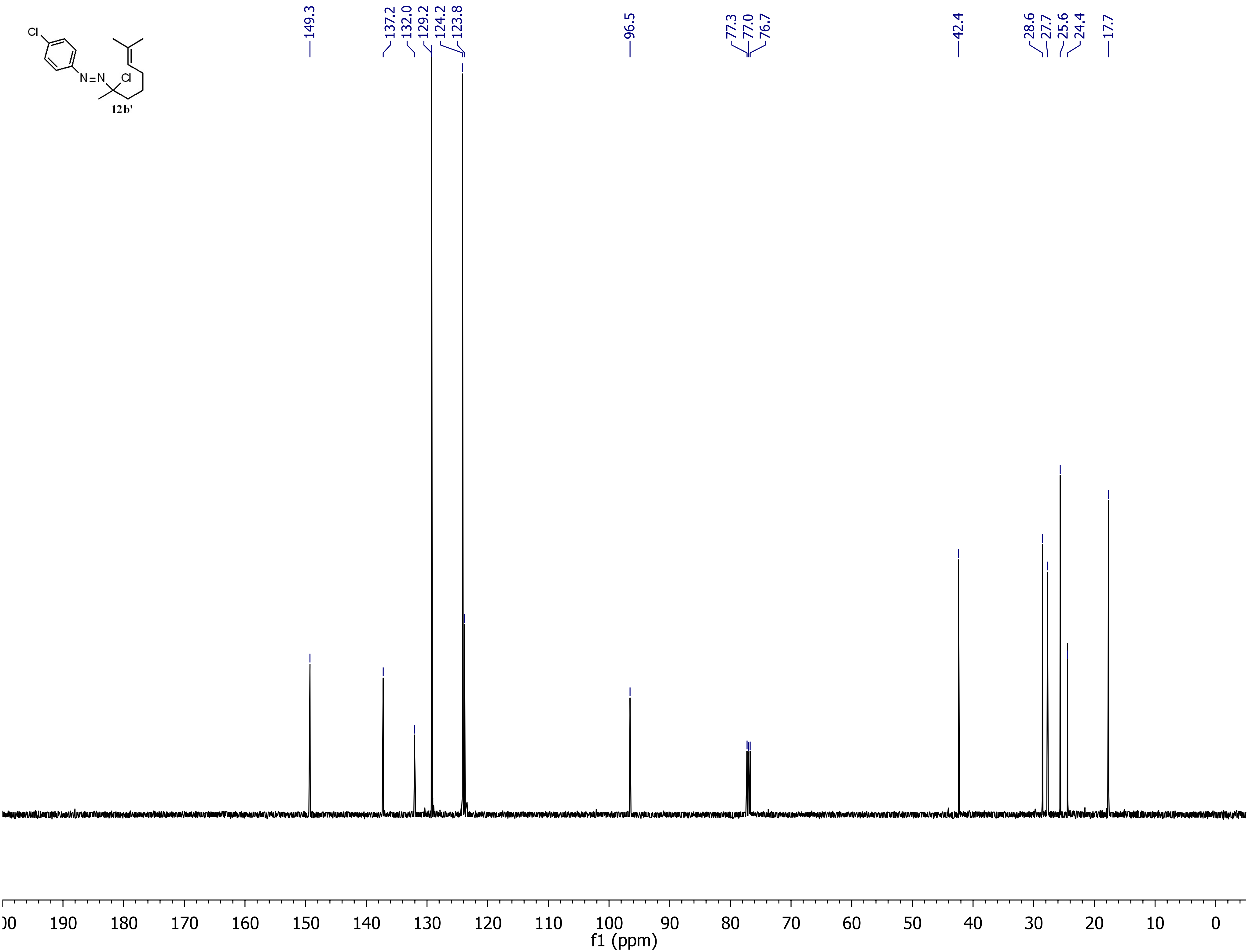


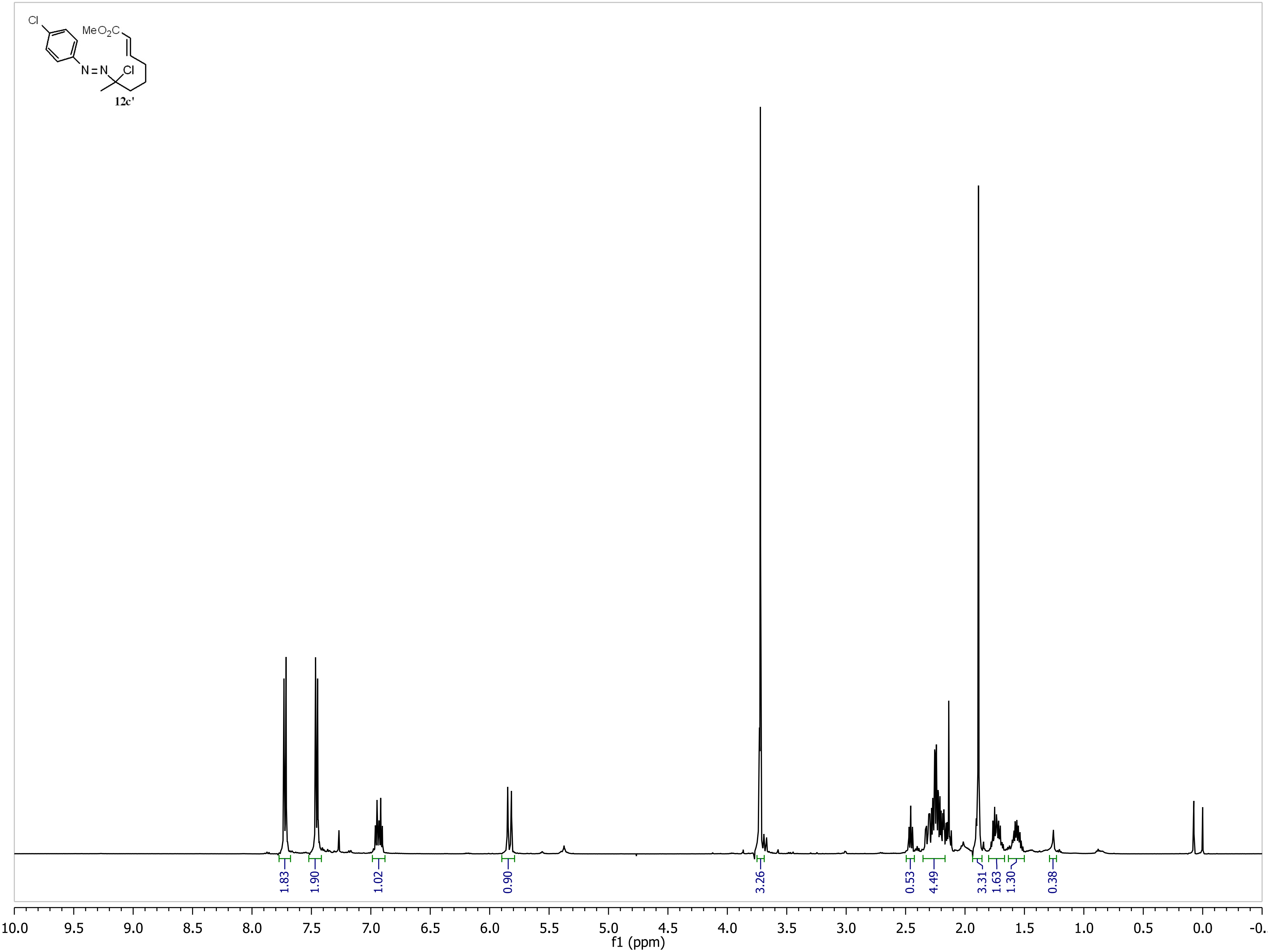
12a'
149.32
137.29
129.70
129.29
124.59
124.20
96.53
42.34
28.66
26.52
24.11
12.78
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Cl
N=N
Cl

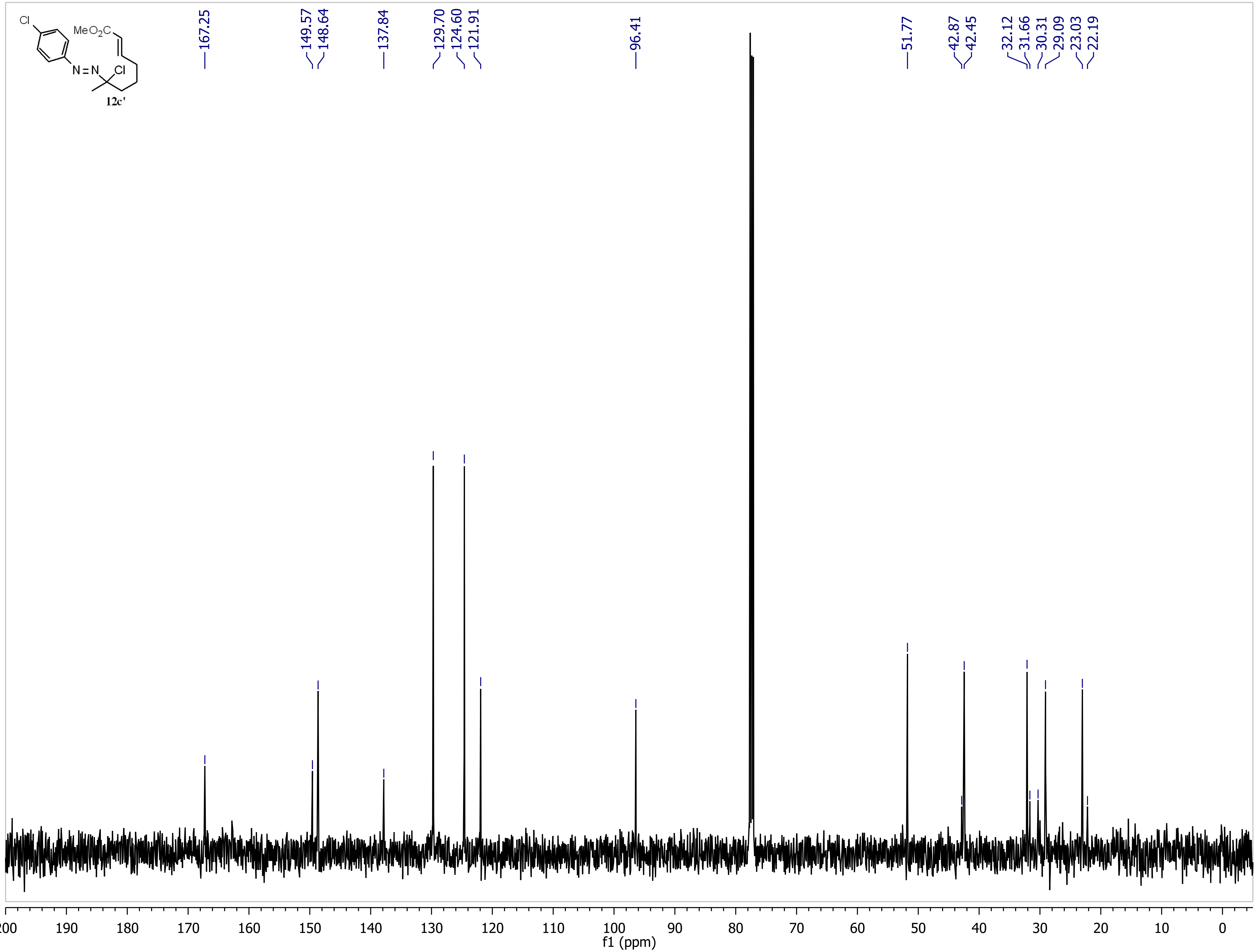
12b'

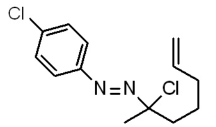

1.73
1.80
1.00
1.07
1.21
2.22
2.81
3.09
4.48
1.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


Cl
N=N
Cl
12b'
149.3
137.2
132.0
129.2
124.2
123.8
96.5
77.3
77.0
76.7
42.4
28.6
27.7
25.6
24.4
17.7
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

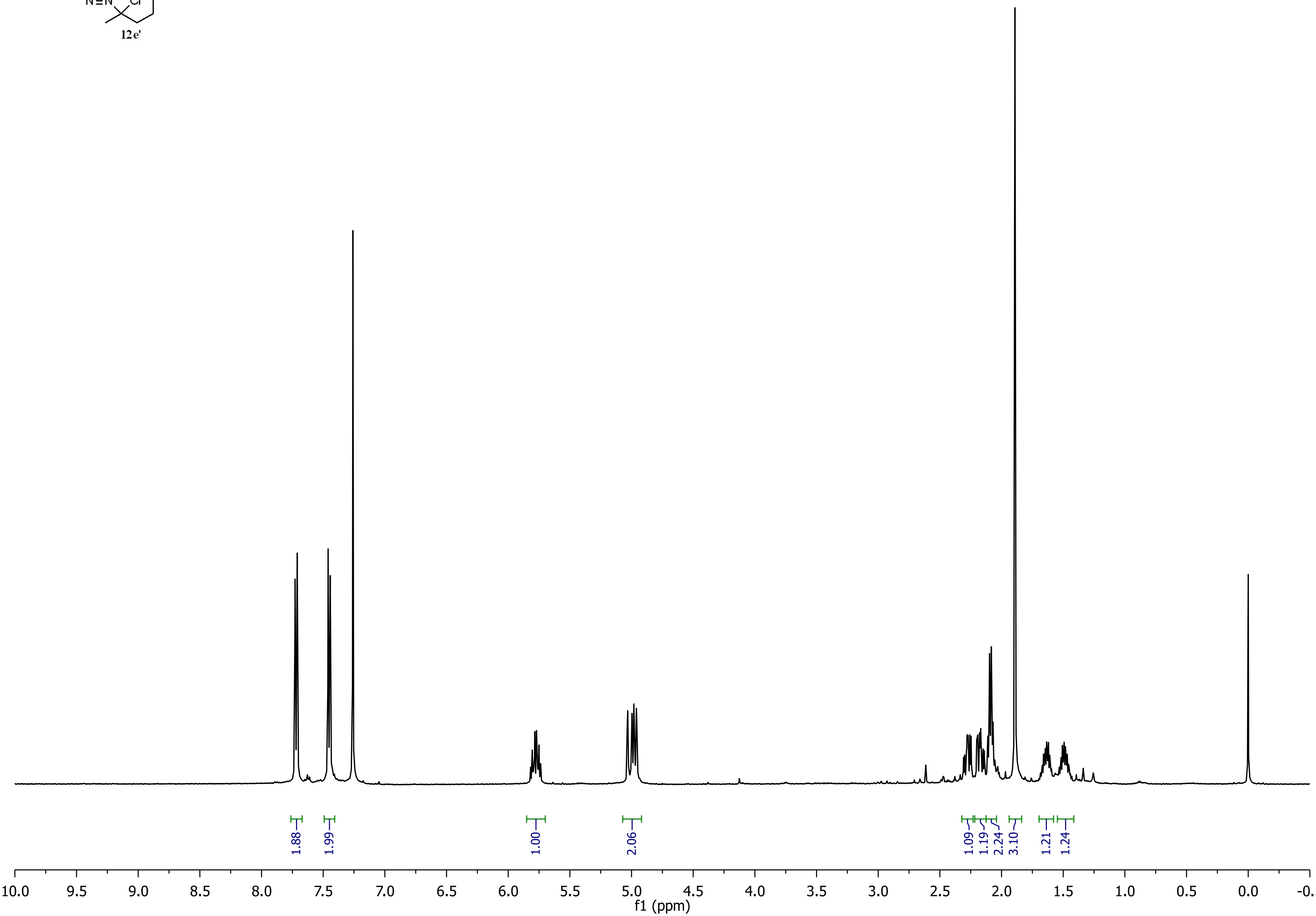


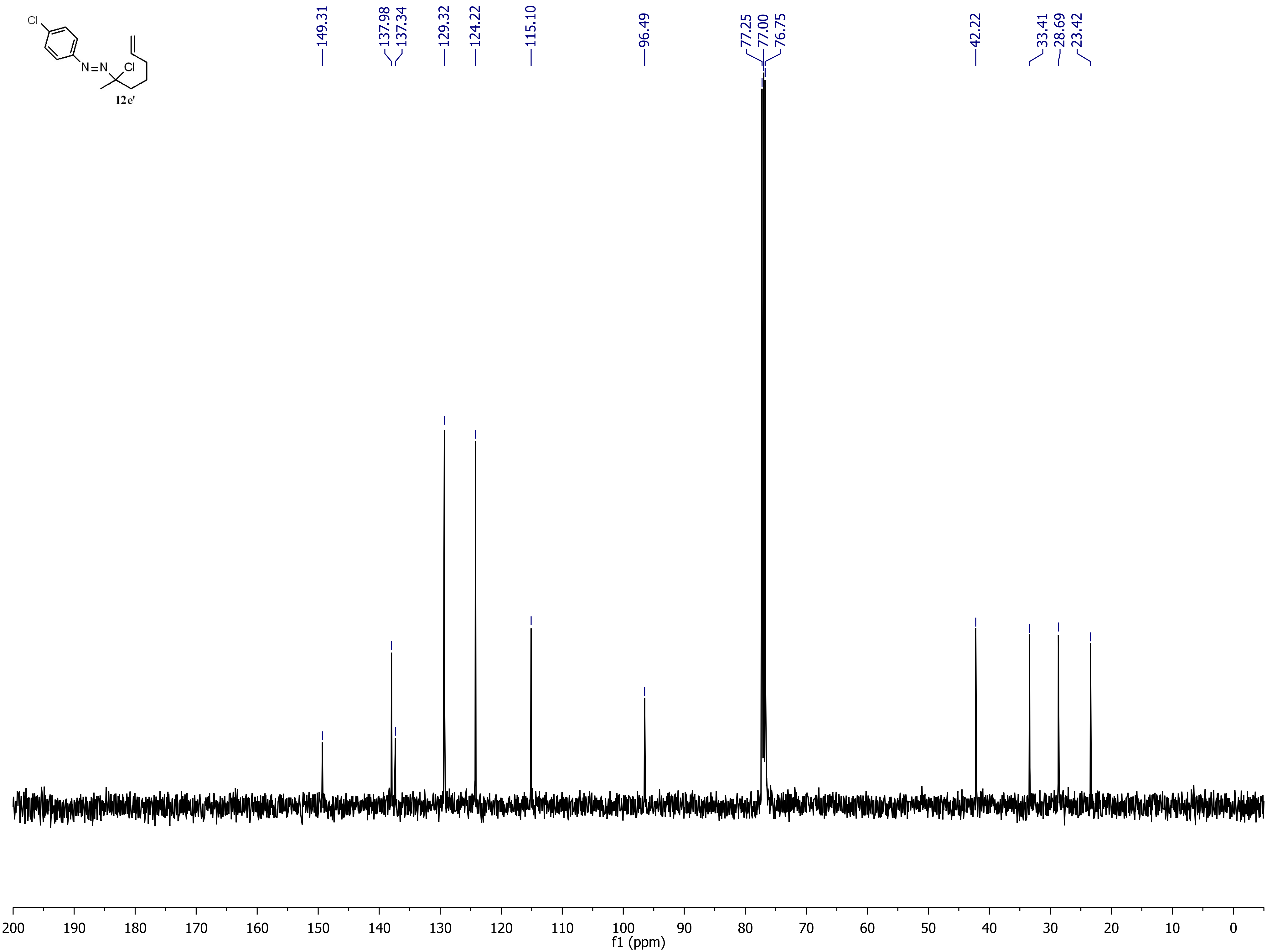
12c'
f1 (ppm)


Cl
MeO2C
N=N
Cl
12c'
167.25
149.57
148.64
137.84
129.70
124.60
121.91
96.41
51.77
42.87
42.45
32.12
31.66
30.31
29.09
23.03
22.19
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

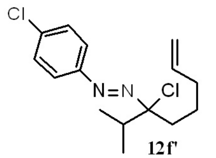


12e'

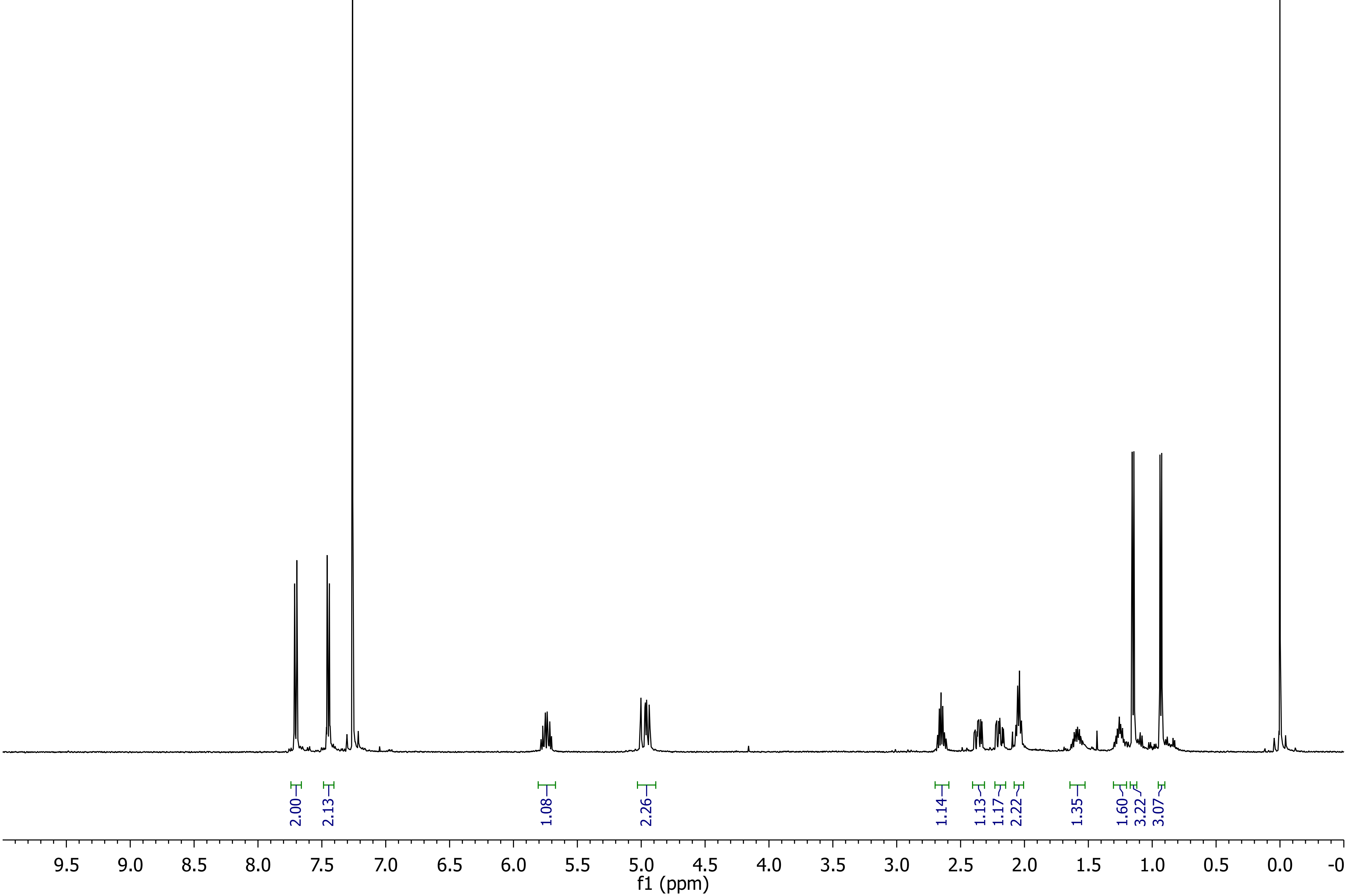

1.88
1.99
1.00
2.06
1.09
1.19
2.24
3.10
1.21
1.24
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

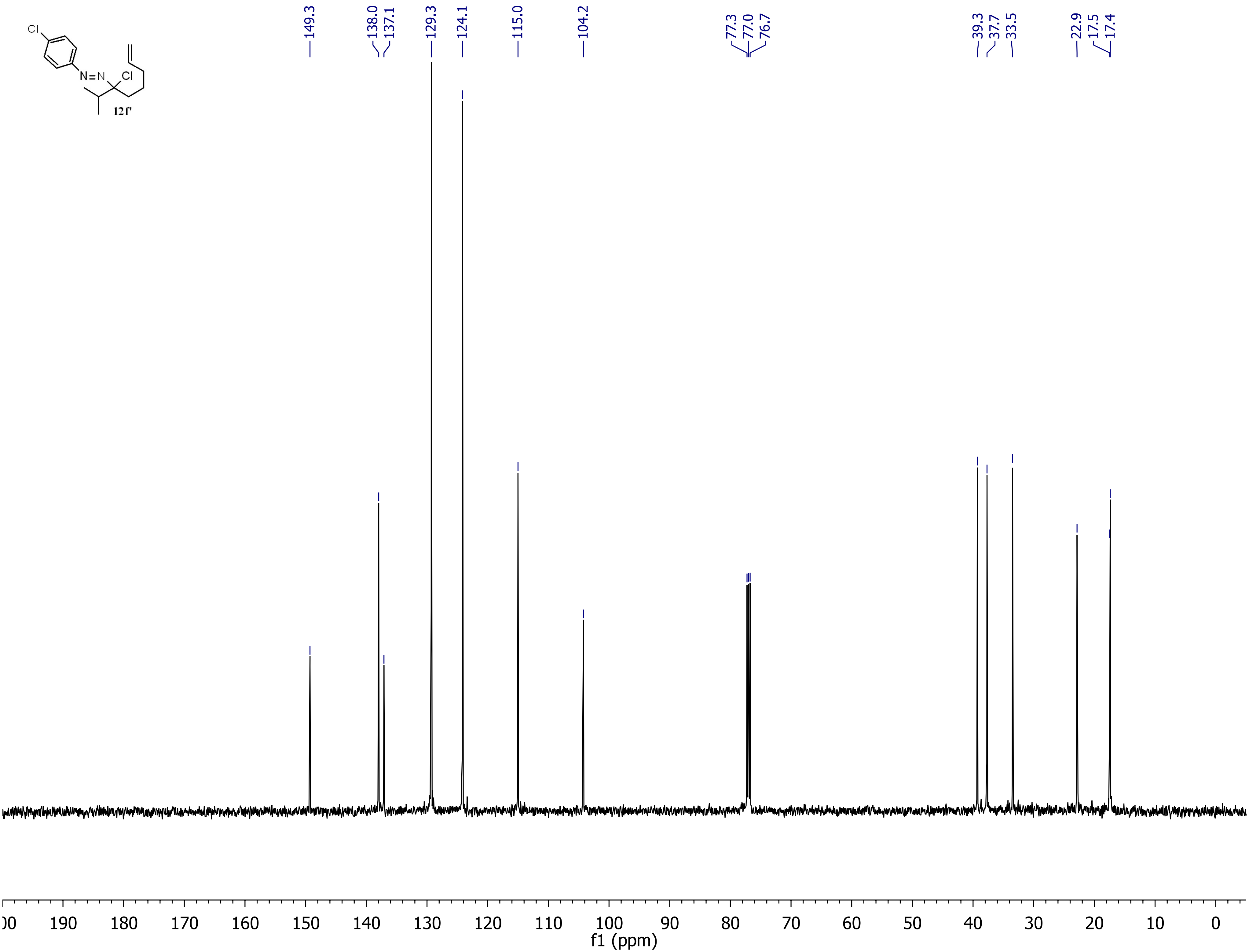


Cl
N=N
Cl
12e'
149.31
137.98
137.34
129.32
124.22
115.10
96.49
77.25
77.00
76.75
42.22
33.41
28.69
23.42
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

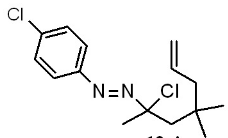


12f'

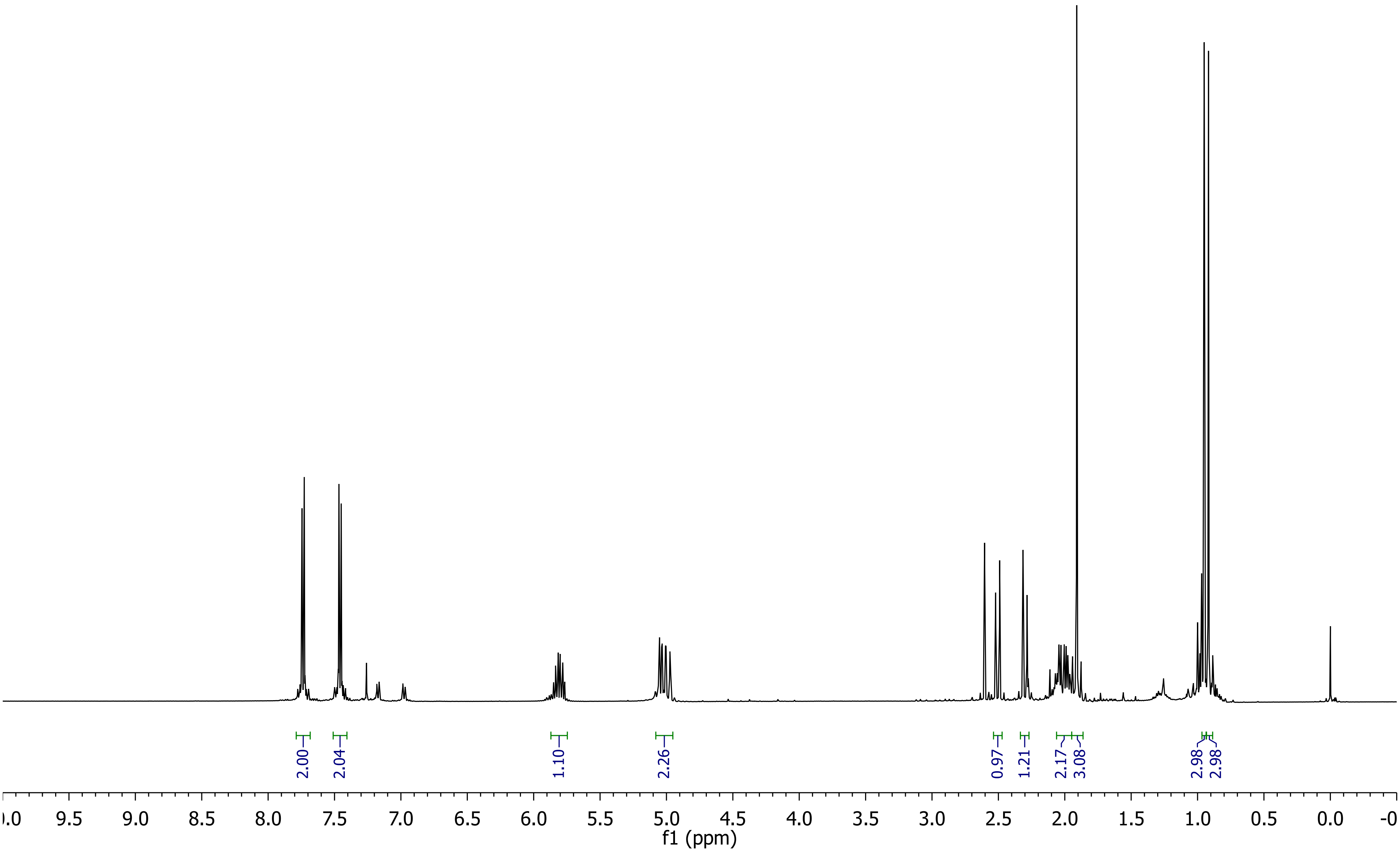

2.00
2.13
1.08
2.26
1.14
1.13
1.17
2.22
1.35
1.60
3.22
3.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)



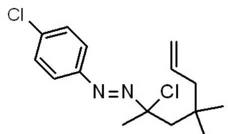
12f'
149.3
138.0
137.1
129.3
124.1
115.0
104.2
77.3
77.0
76.7
39.3
37.7
33.5
22.9
17.5
17.4
f1 (ppm)



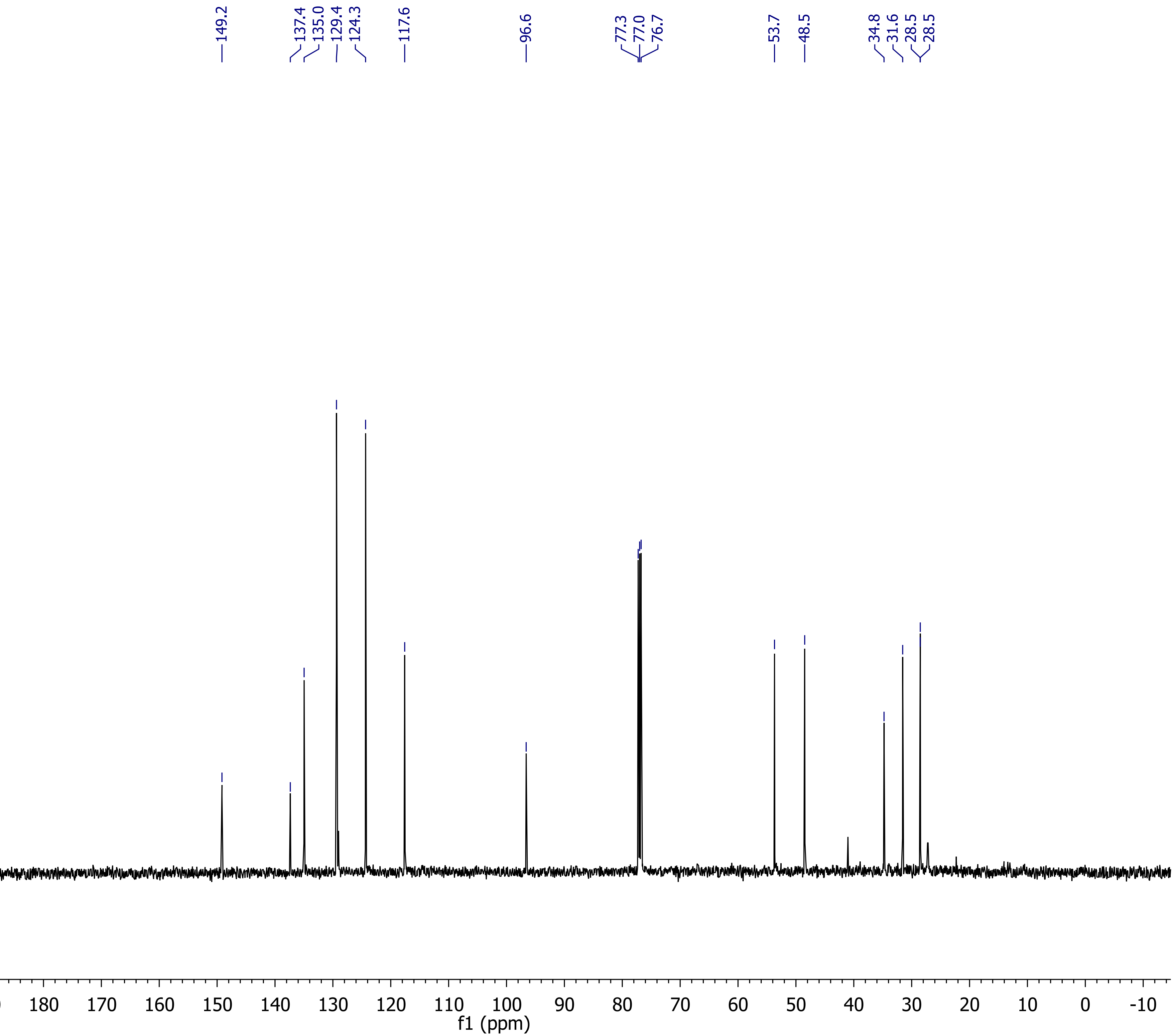
12g'

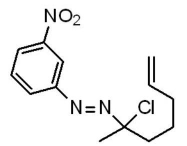


2.00
2.04
1.10
2.26
0.97
1.21
2.17
3.08
2.98
2.98
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

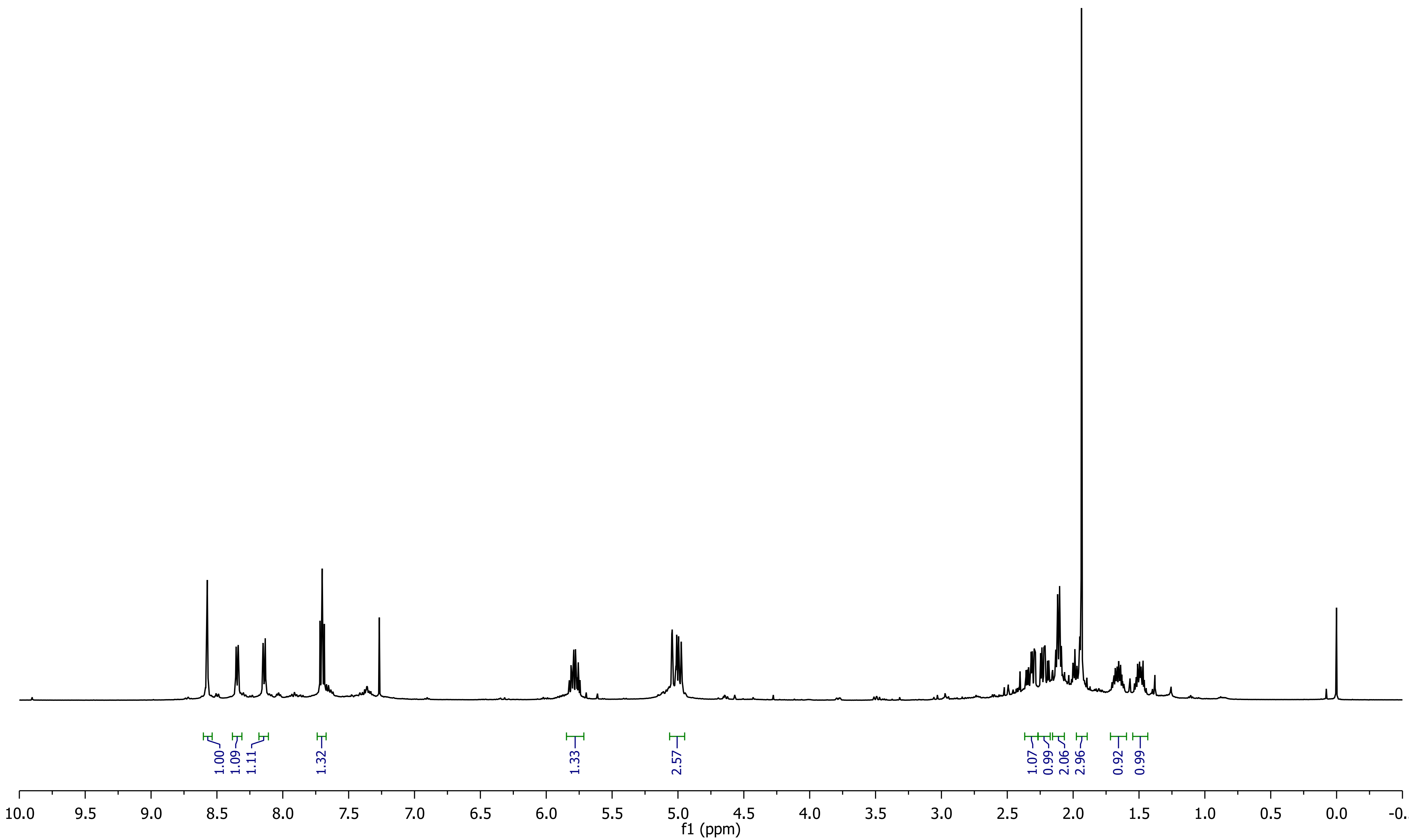


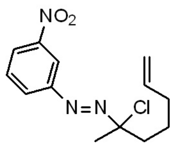
12g'


149.2
137.4
135.0
129.4
124.3
117.6
96.6
77.3
77.0
76.7
53.7
48.5
34.8
31.6
28.5
28.5
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

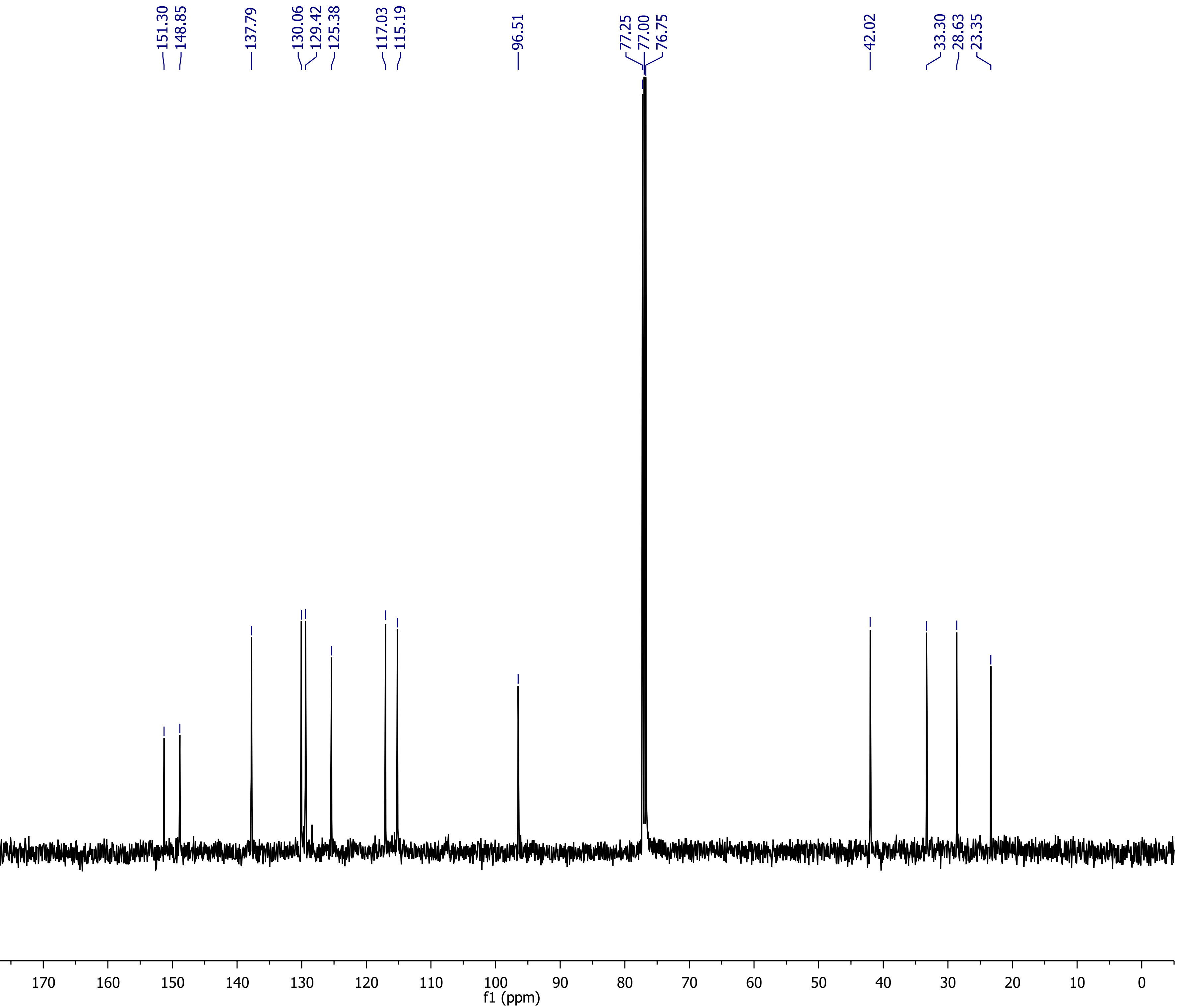

NO2
N=N
Cl

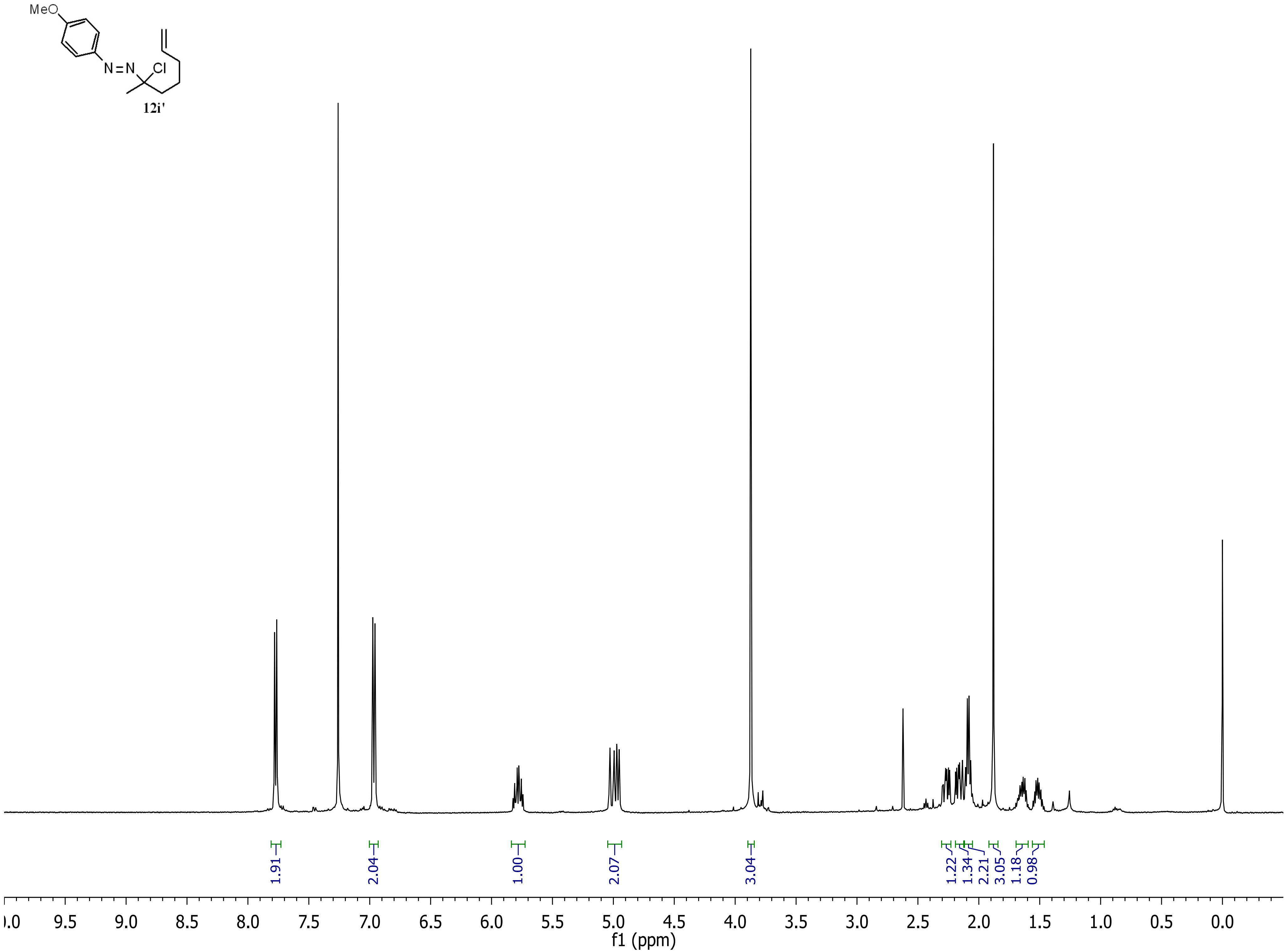
12h'

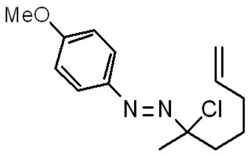

1.00
1.09
1.11
1.32
1.33
2.57
1.07
0.99
2.06
2.96
0.92
0.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



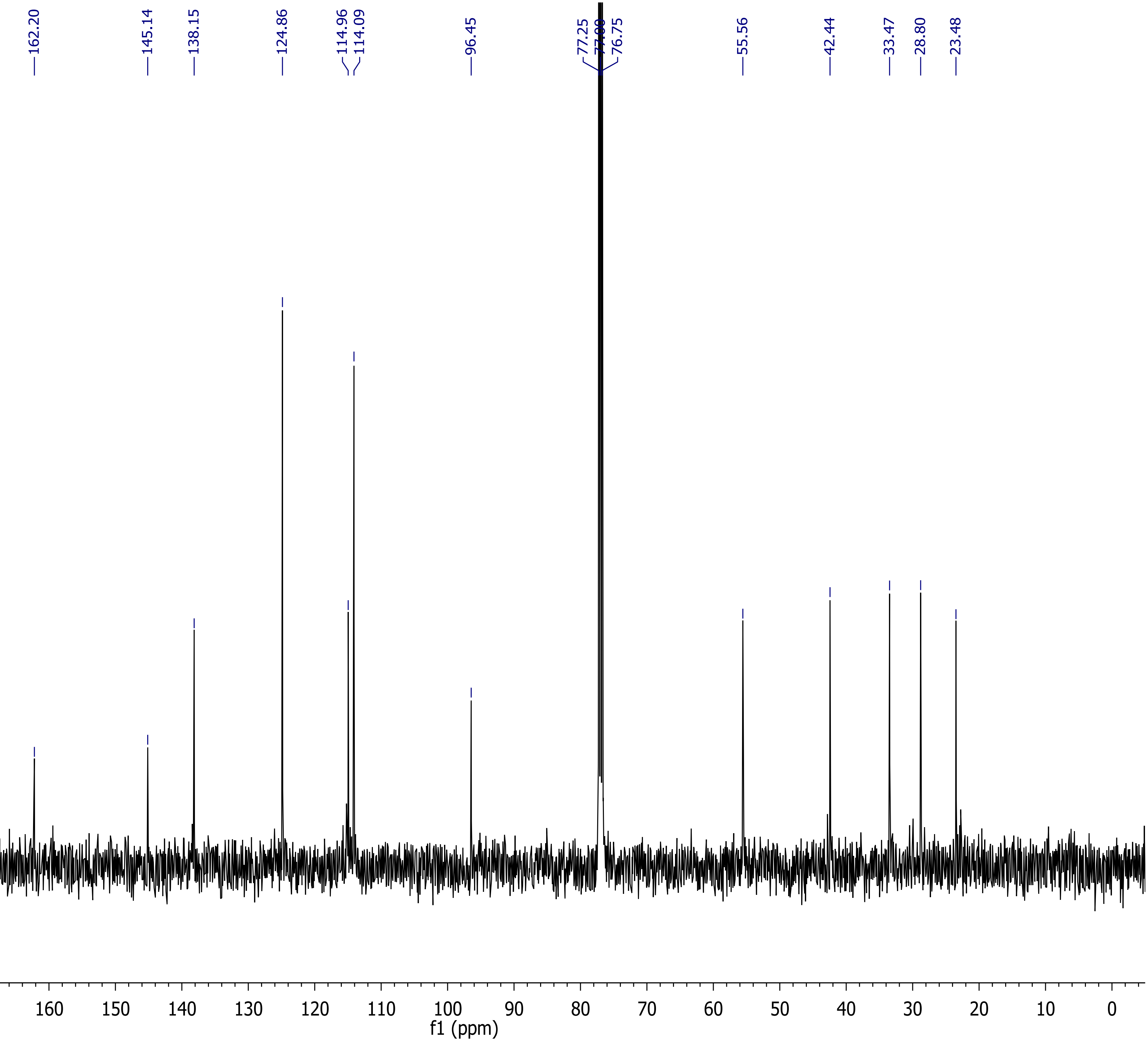
12h'

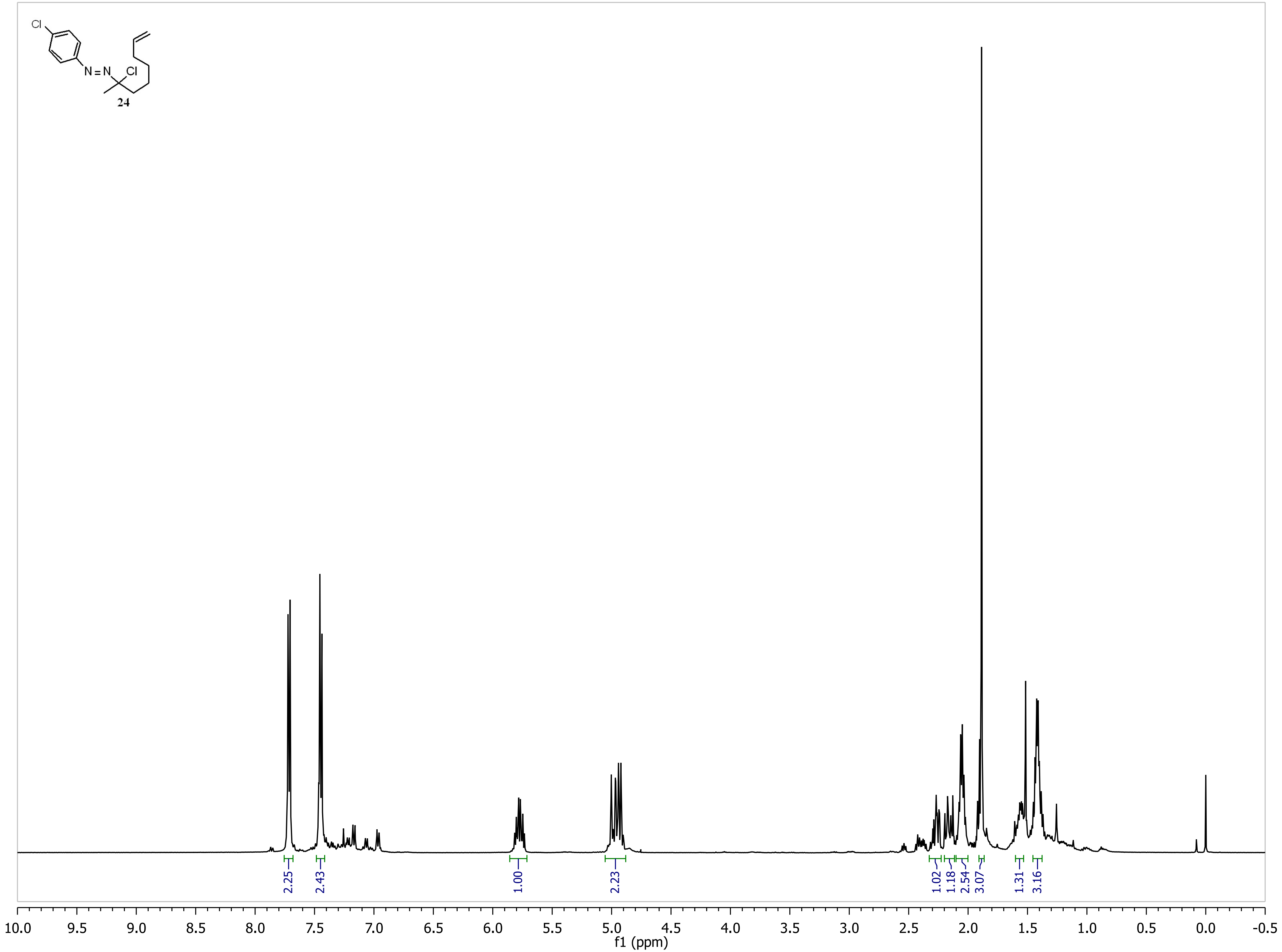

151.30
148.85
137.79
130.06
129.42
125.38
117.03
115.19
96.51
77.25
77.00
76.75
42.02
33.30
28.63
23.35
f1 (ppm)

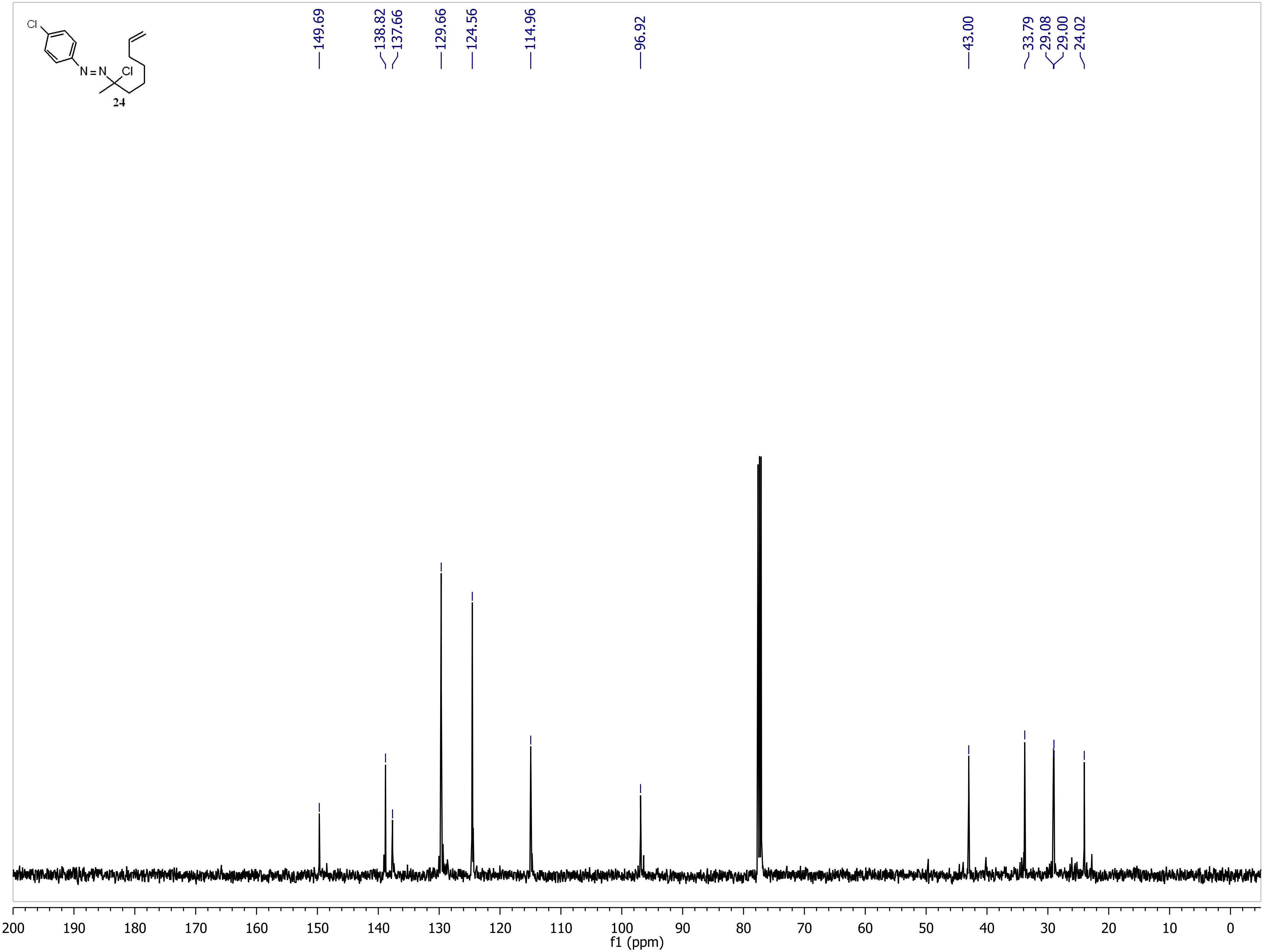

MeO
N=N
Cl
12i'
1.91
2.04
1.00
2.07
3.04
1.22
1.34
2.21
3.05
1.18
0.98
f1 (ppm)

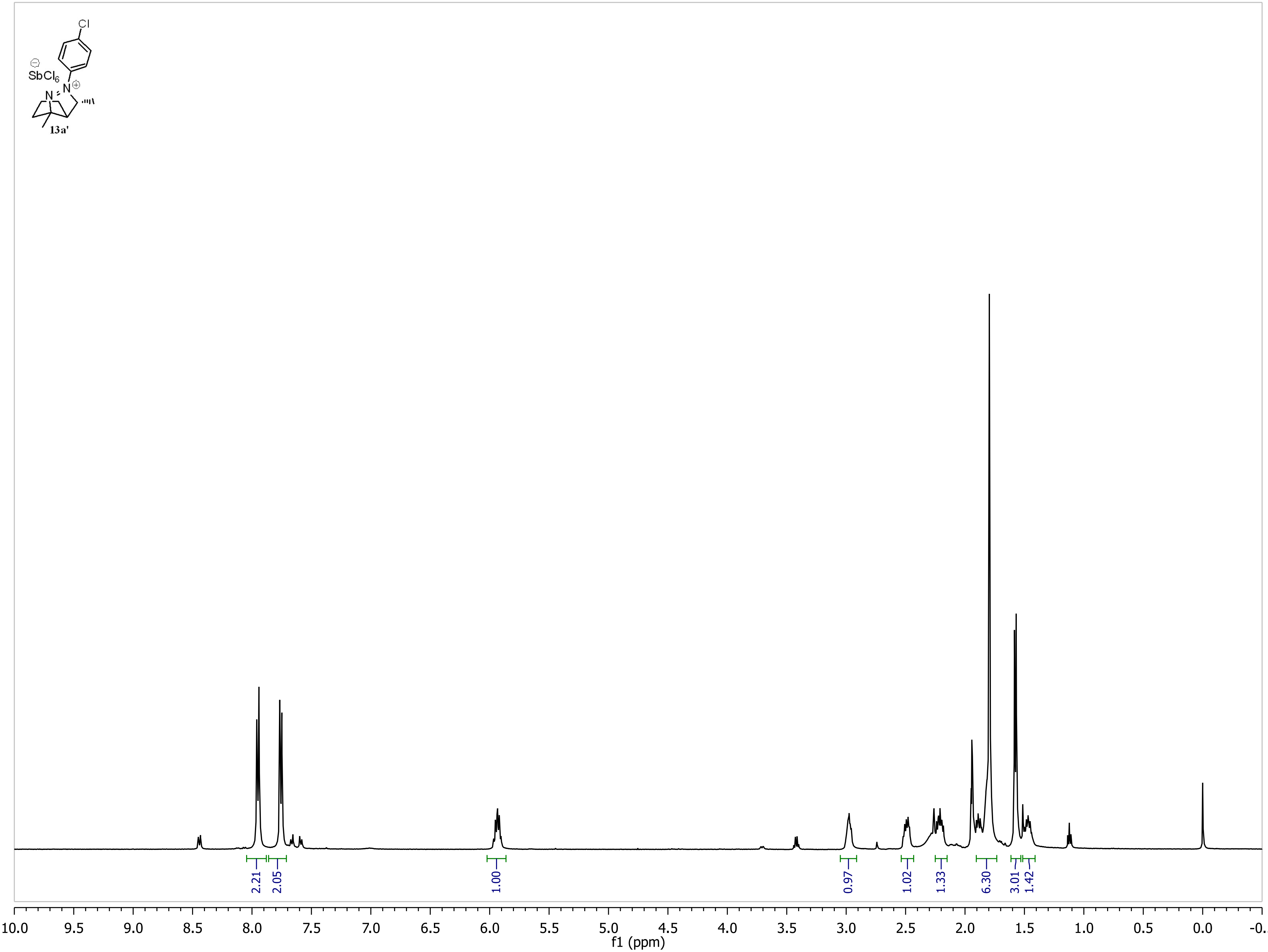

MeO
N=N
Cl

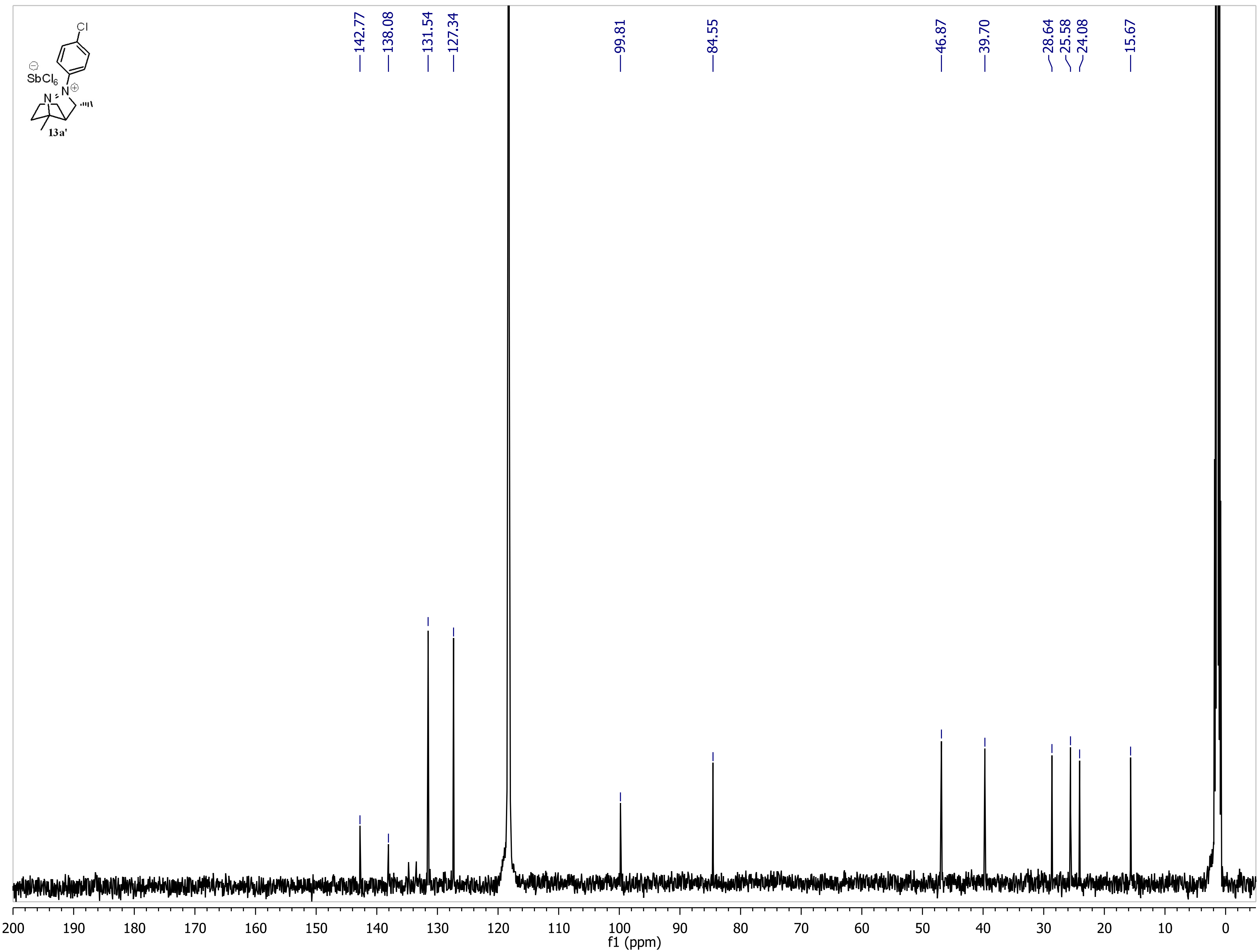
12i'


162.20
145.14
138.15
124.86
114.96
114.09
96.45
77.25
77.00
76.75
55.56
42.44
33.47
28.80
23.48
f1 (ppm)

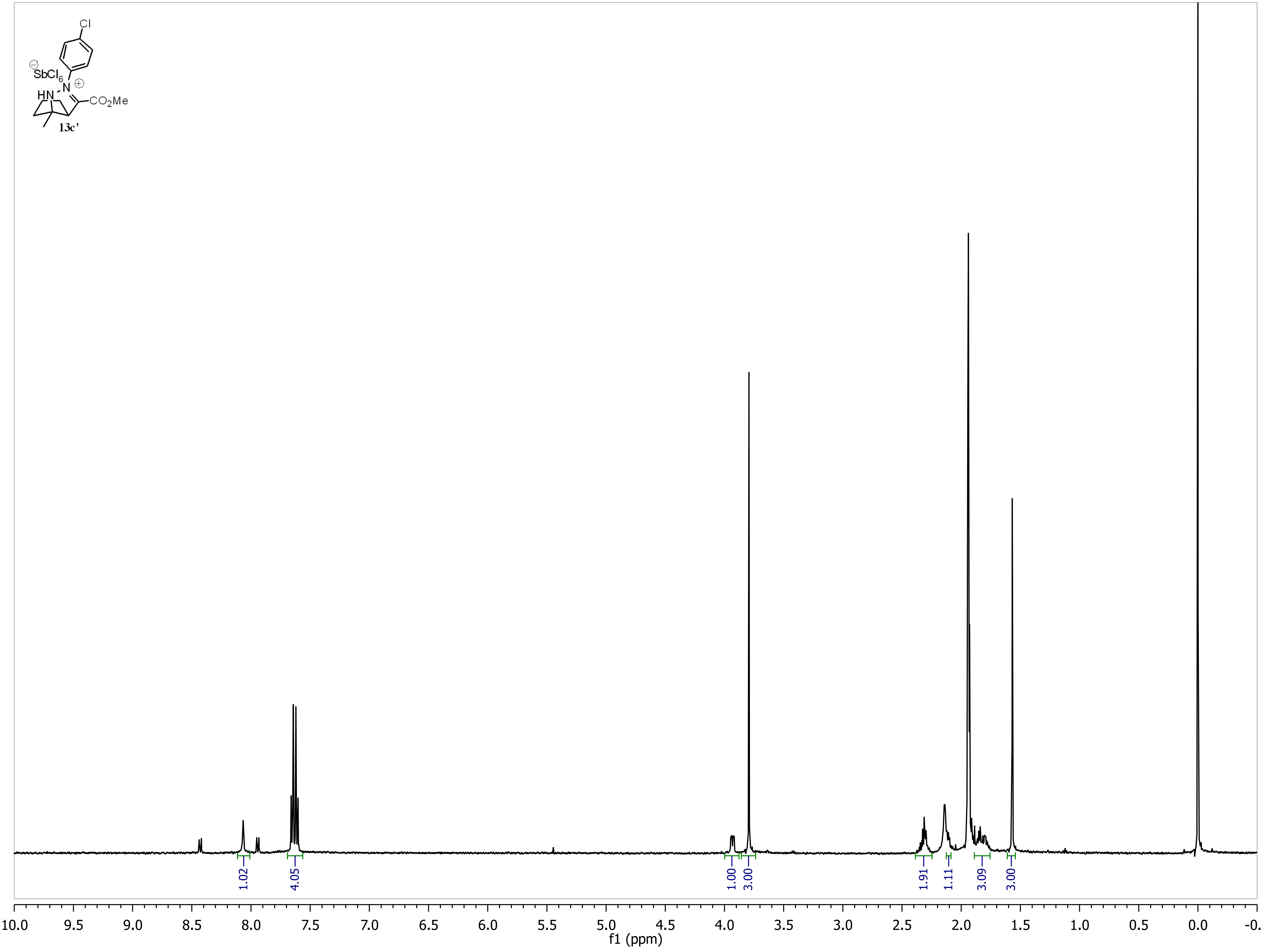

Cl
N=N
Cl
24
2.25
2.43
1.00
2.23
1.02
1.18
2.54
3.07
1.31
3.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

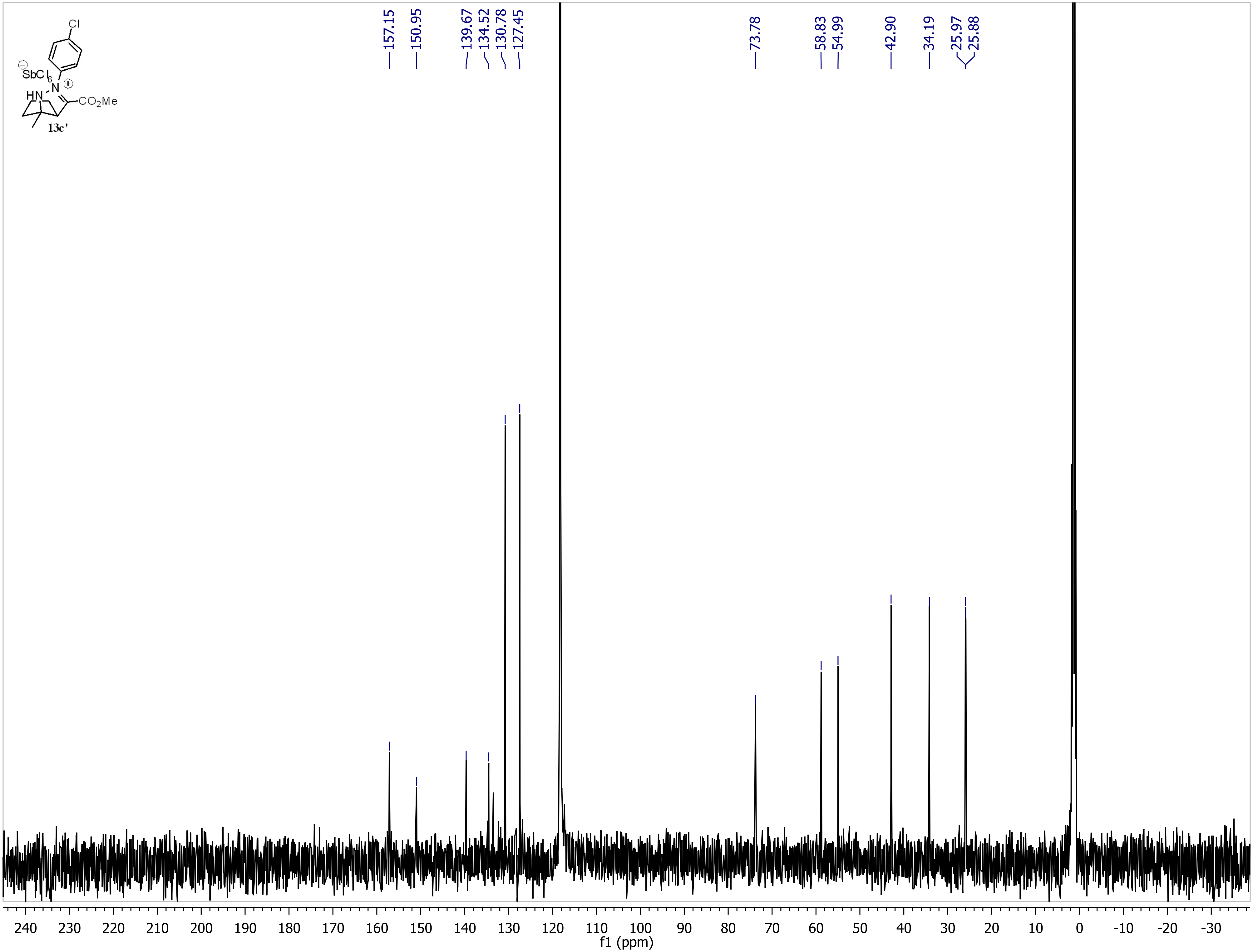

Cl
N=N
Cl
24
149.69
138.82
137.66
129.66
124.56
114.96
96.92
43.00
33.79
29.08
29.00
24.02
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

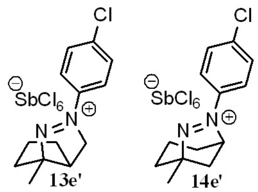

Cl
SbCl6
N
N
13a'
2.21
2.05
1.00
0.97
1.02
1.33
6.30
3.01
1.42
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

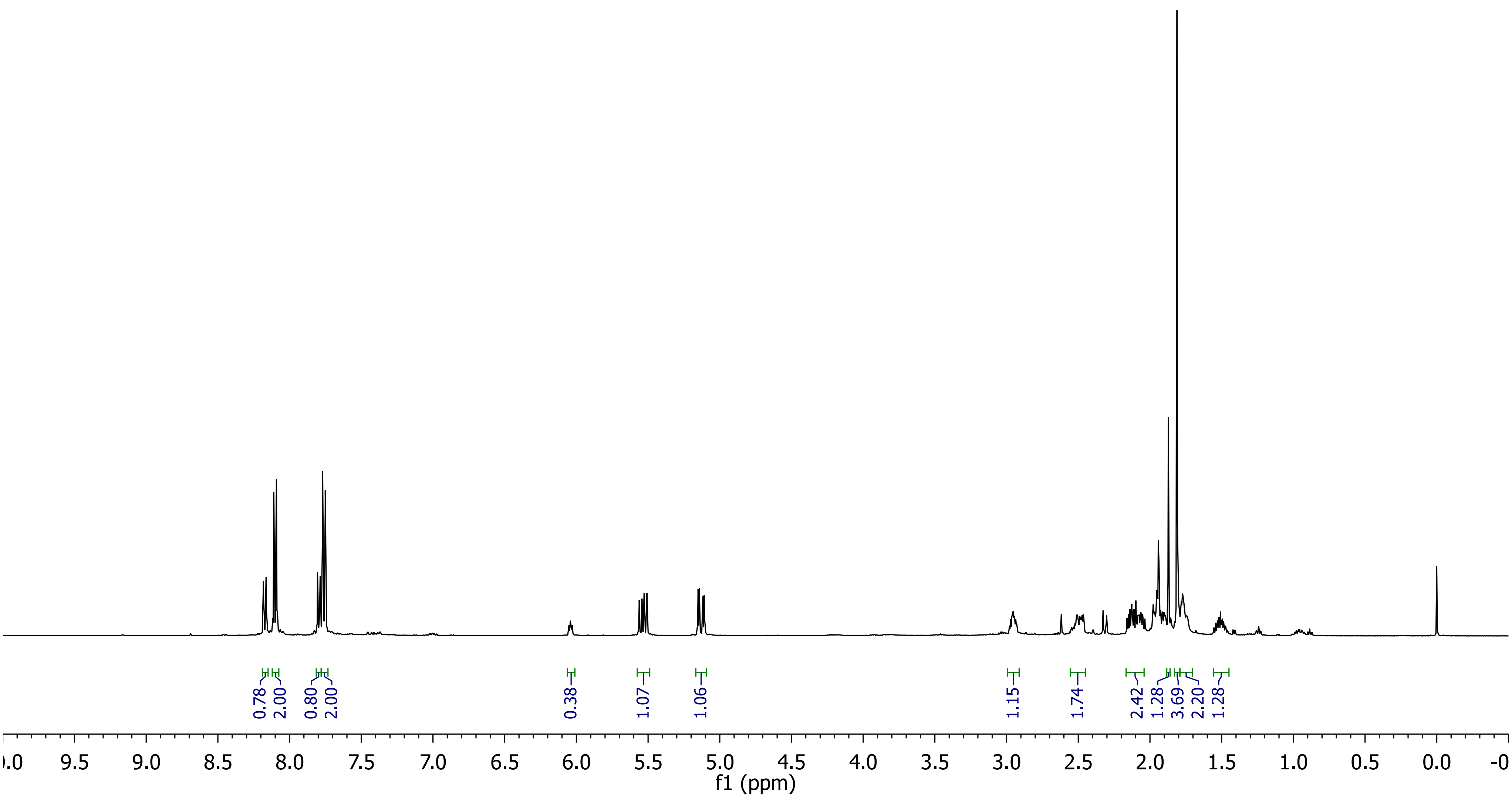


Cl
SbCl6
N
N
13a'
142.77
138.08
131.54
127.34
99.81
84.55
46.87
39.70
28.64
25.58
24.08
15.67
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

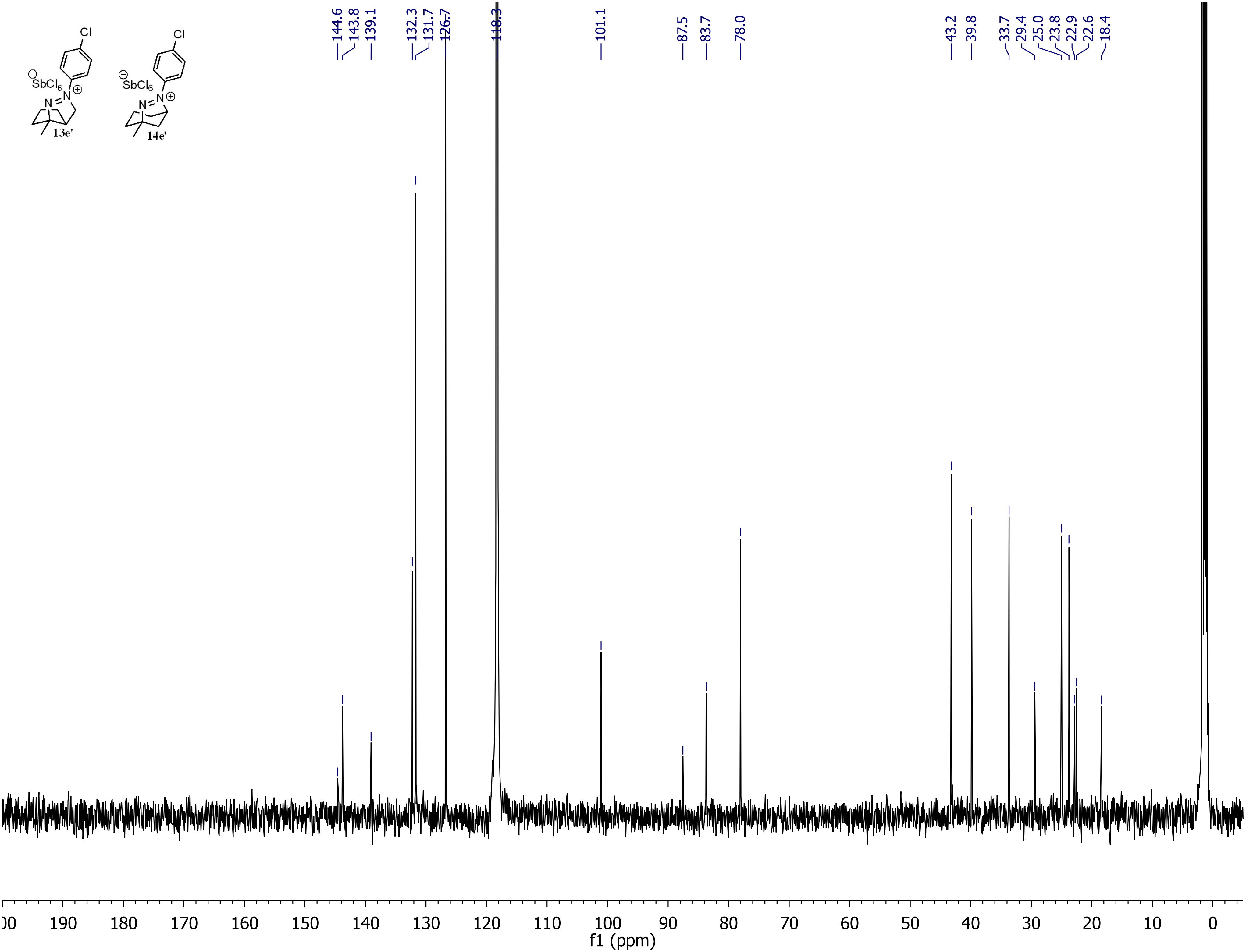

Cl
SbCl6
HN
N
CO2Me
13c'
1.02
4.05
1.00
3.00
1.91
1.11
3.09
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

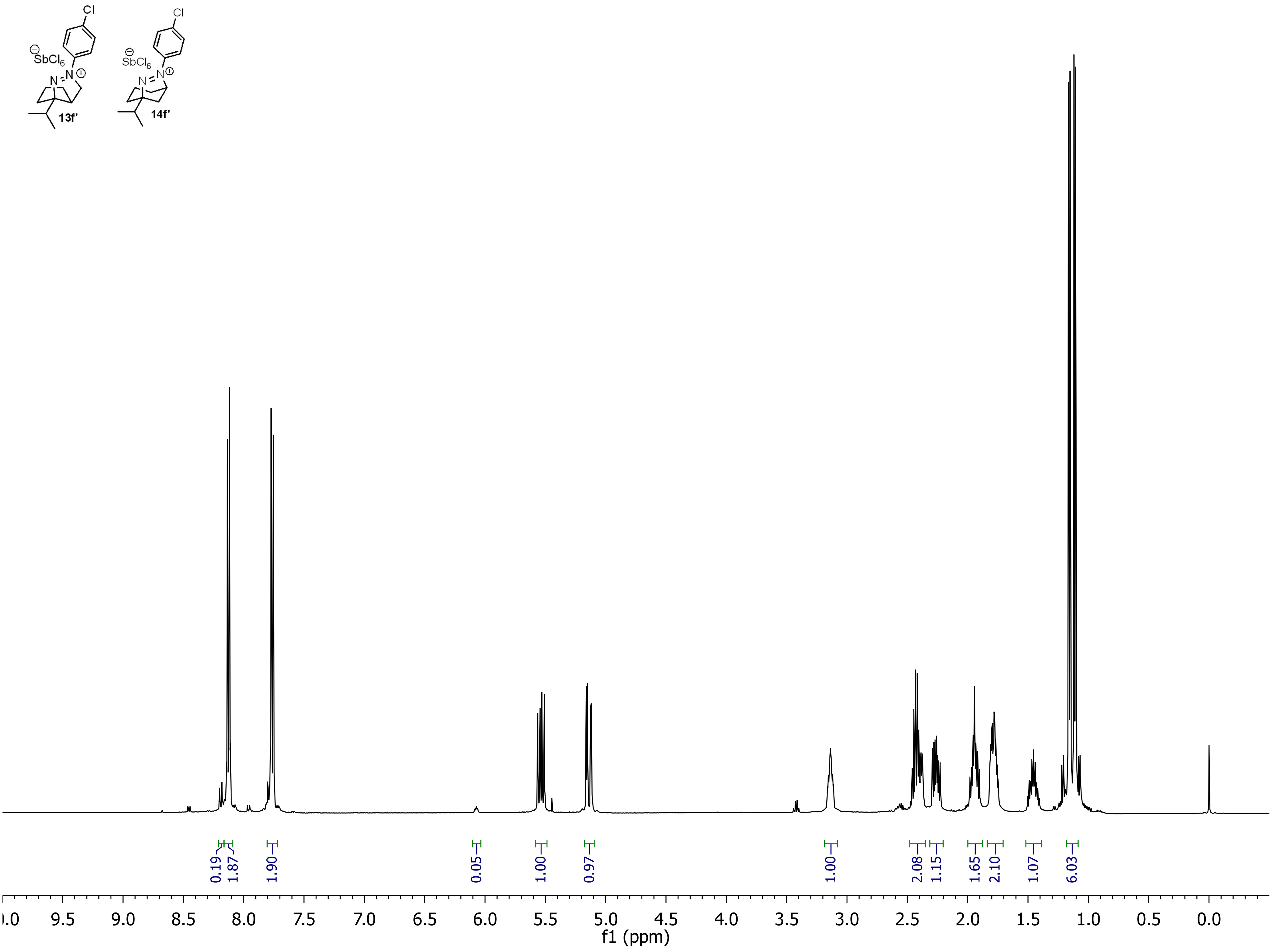

13c'
157.15
150.95
139.67
134.52
130.78
127.45
73.78
58.83
54.99
42.90
34.19
25.97
25.88
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)



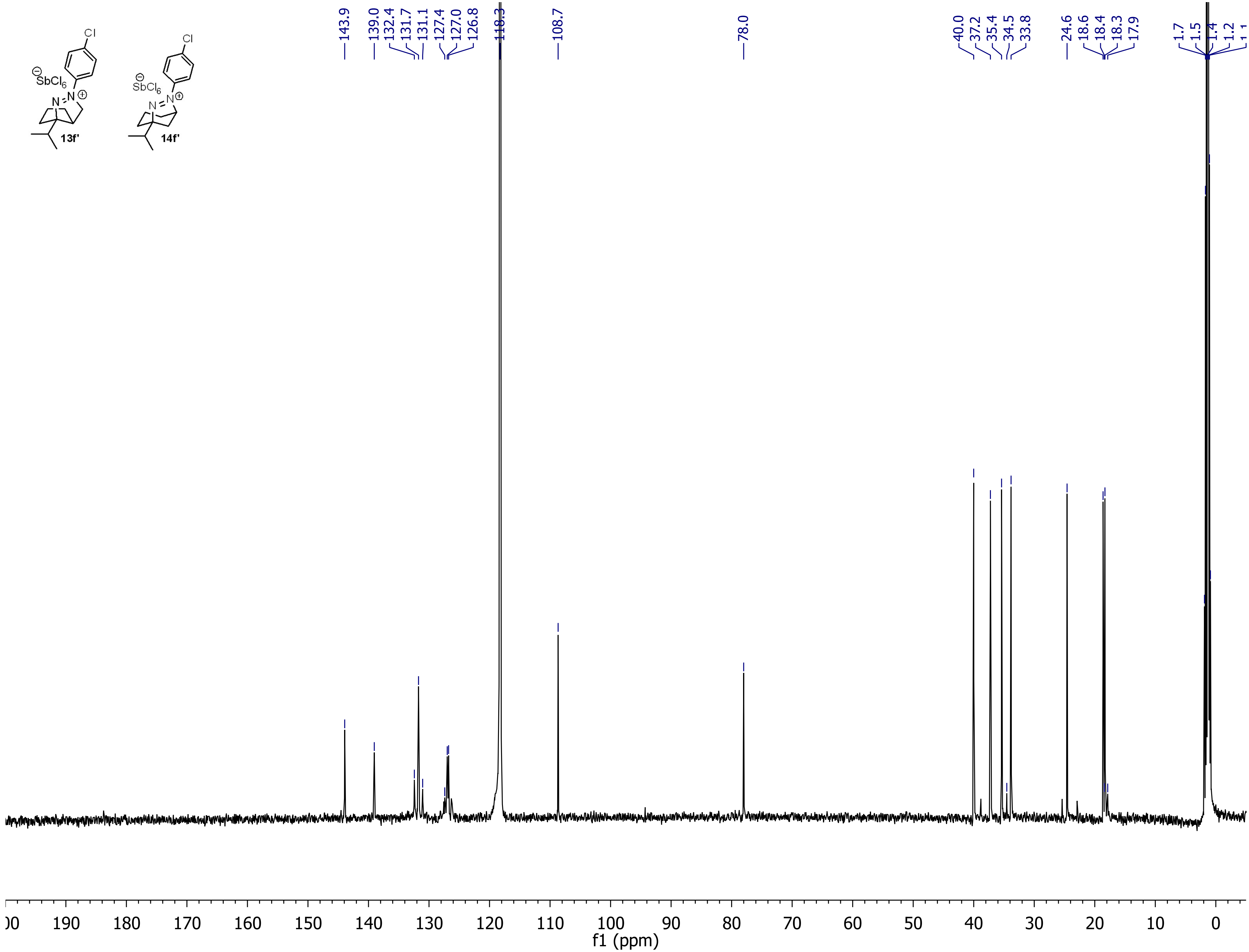


0.78
2.00
0.80
2.00
0.38
1.07
1.06
1.15
1.74
2.42
1.28
3.69
2.20
1.28
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


144.6
143.8
139.1
132.3
131.7
126.7
118.3
101.1
87.5
83.7
78.0
43.2
39.8
33.7
29.4
25.0
23.8
22.9
22.6
18.4
Cl
$SbCl_6$
13e'
14e'
f1 (ppm)

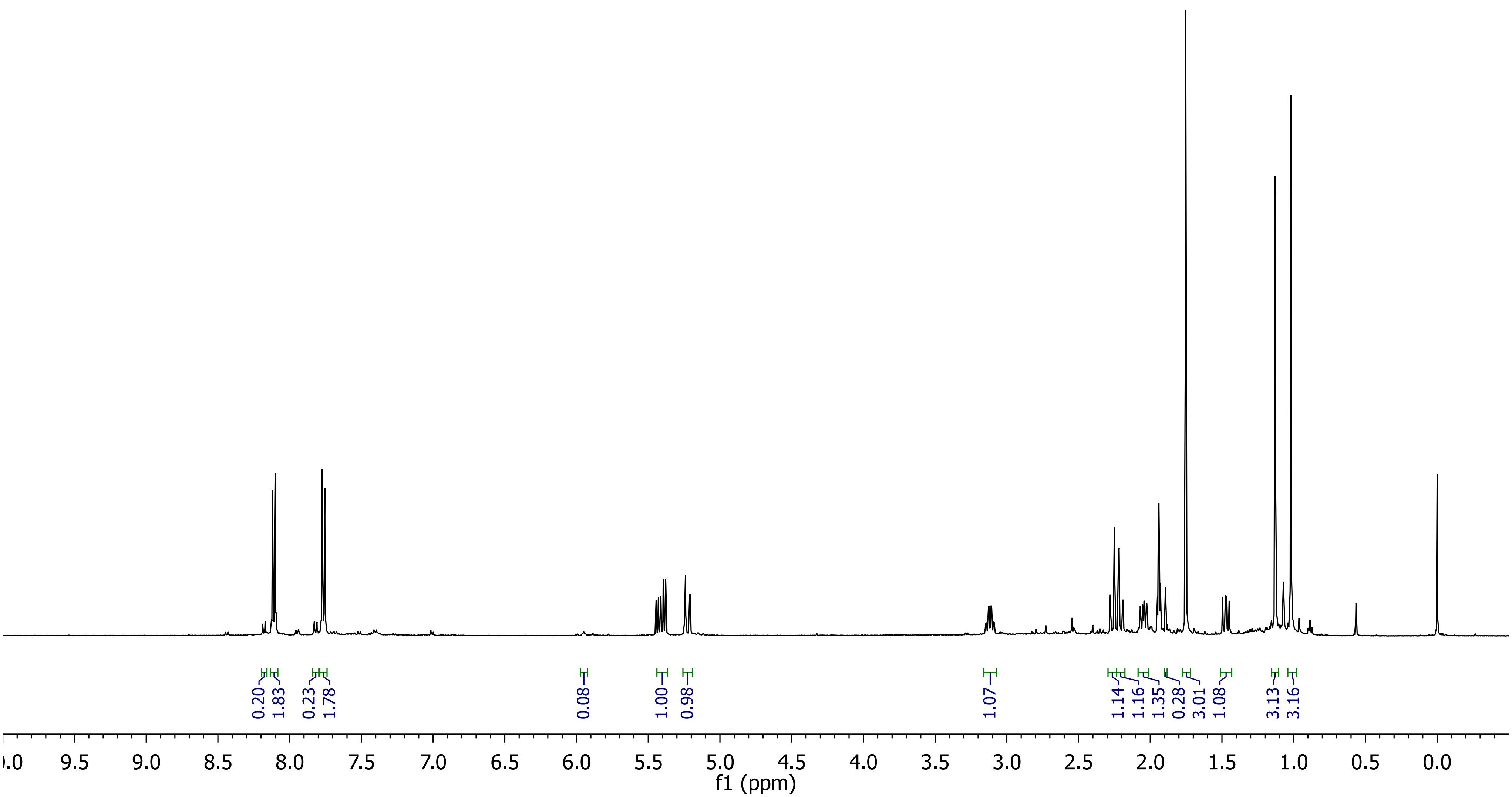


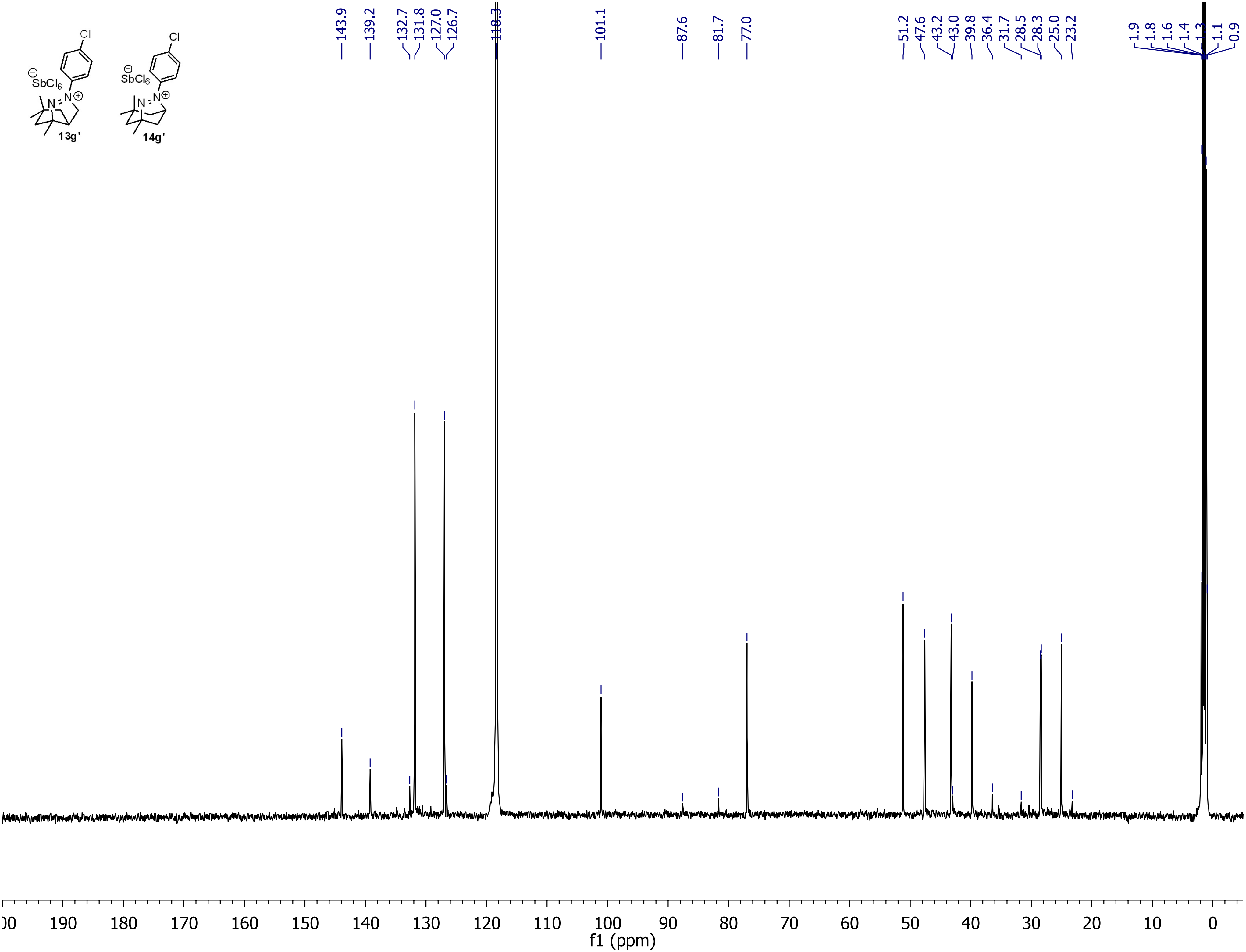
13f'
14f'
0.19
1.87
1.90
0.05
1.00
0.97
1.00
2.08
1.15
1.65
2.10
1.07
6.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

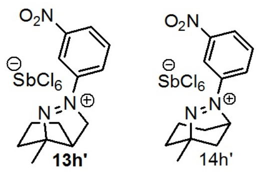

Cl
SbCl6
N
N
13f'
Cl
SbCl6
N
N
14f'
143.9
139.0
132.4
131.7
131.1
127.4
127.0
126.8
118.3
108.7
78.0
40.0
37.2
35.4
34.5
33.8
24.6
18.6
18.4
18.3
17.9
1.7
1.5
1.4
1.2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

13g'

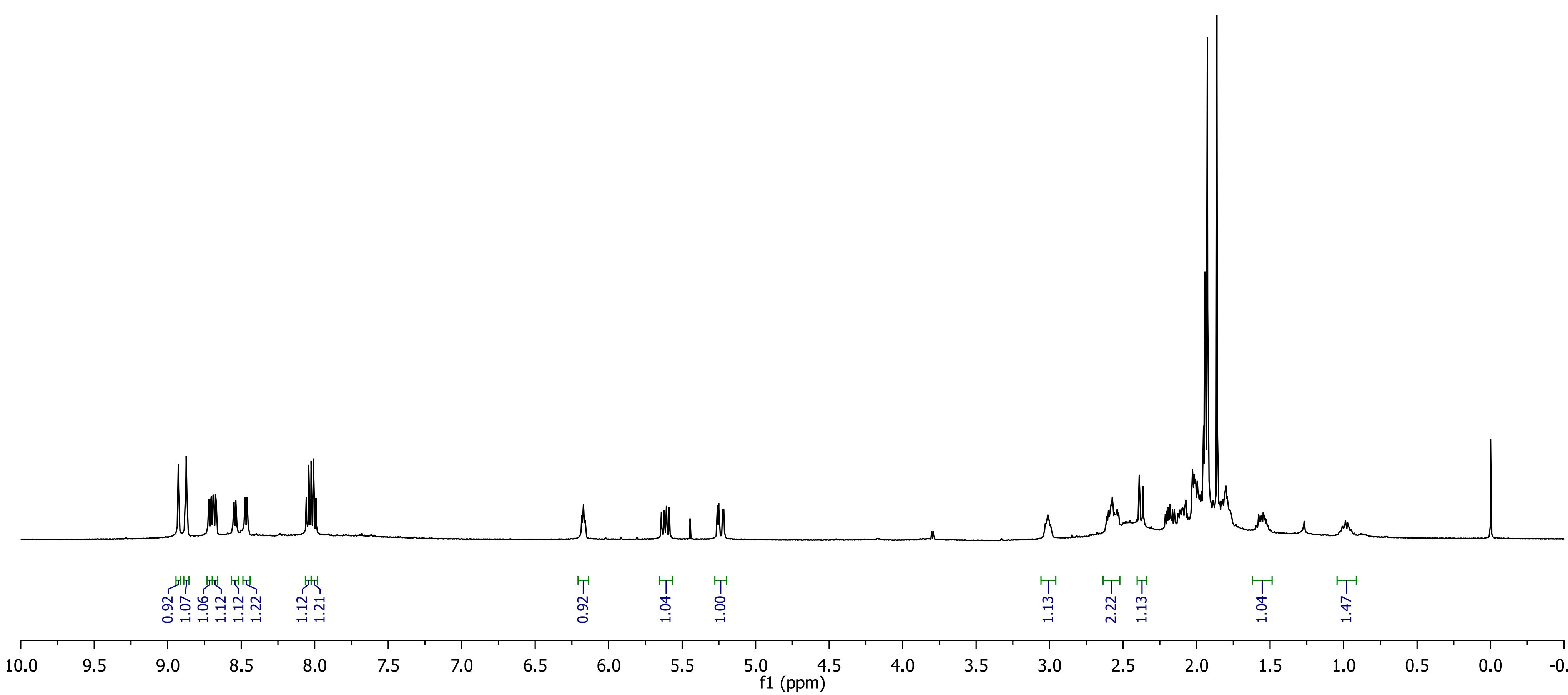
14g'


0.20
1.83
0.23
1.78
0.08
1.00
0.98
1.07
1.14
1.16
1.35
0.28
3.01
1.08
3.13
3.16
10.0
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
f1 (ppm)

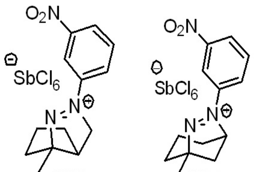

SbCl6
Cl
13g'
SbCl6
Cl
14g'
143.9
139.2
132.7
131.8
127.0
126.7
118.3
101.1
87.6
81.7
77.0
51.2
47.6
43.2
43.0
39.8
36.4
31.7
28.5
28.3
25.0
23.2
1.9
1.8
1.6
1.4
1.3
1.1
0.9
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



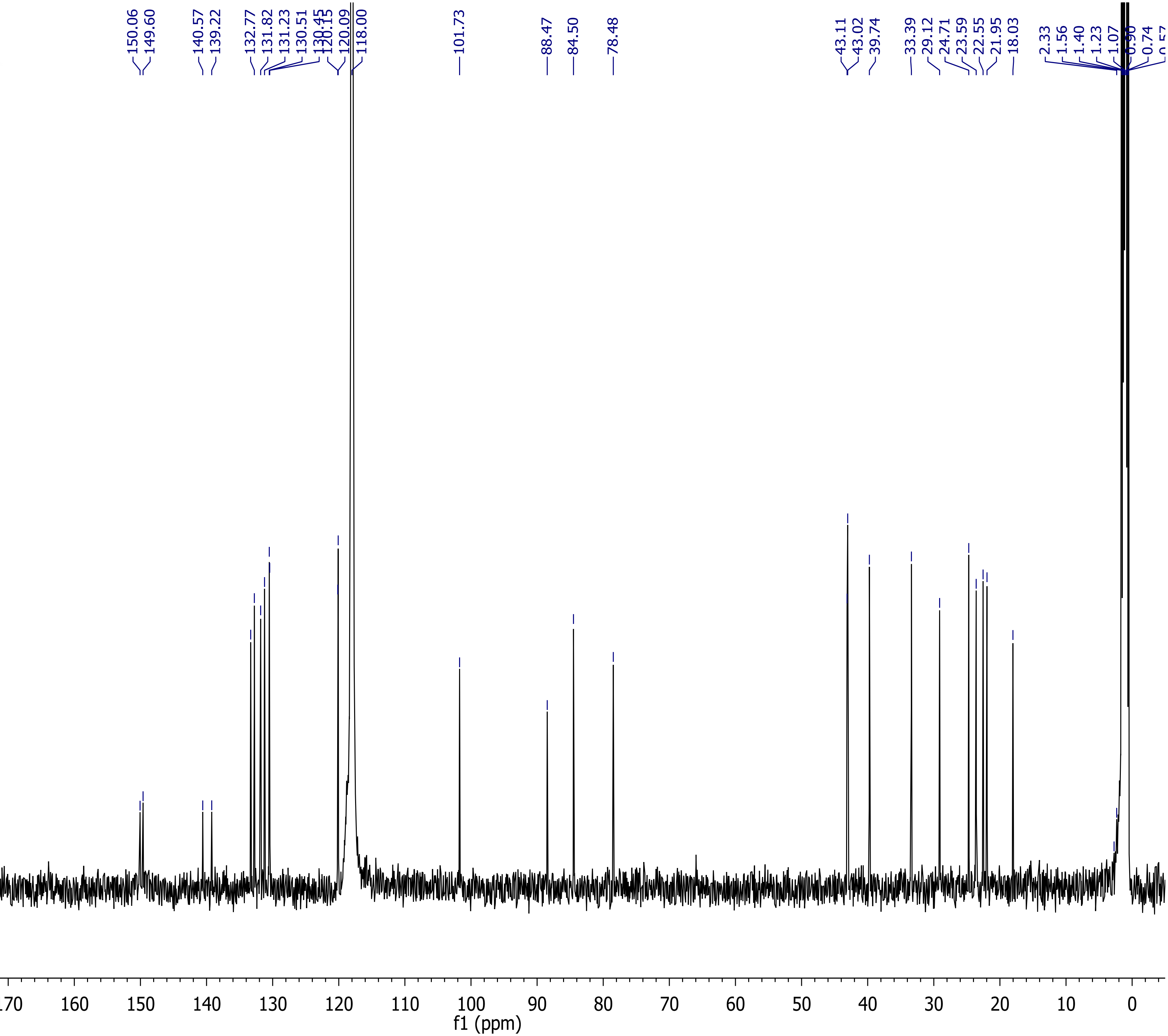
O_2N
$SbCl_6$
13h'
14h'



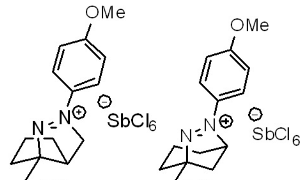
0.92
1.07
1.06
1.12
1.12
1.22
1.12
1.21
0.92
1.04
1.00
1.13
2.22
1.13
1.04
1.47
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



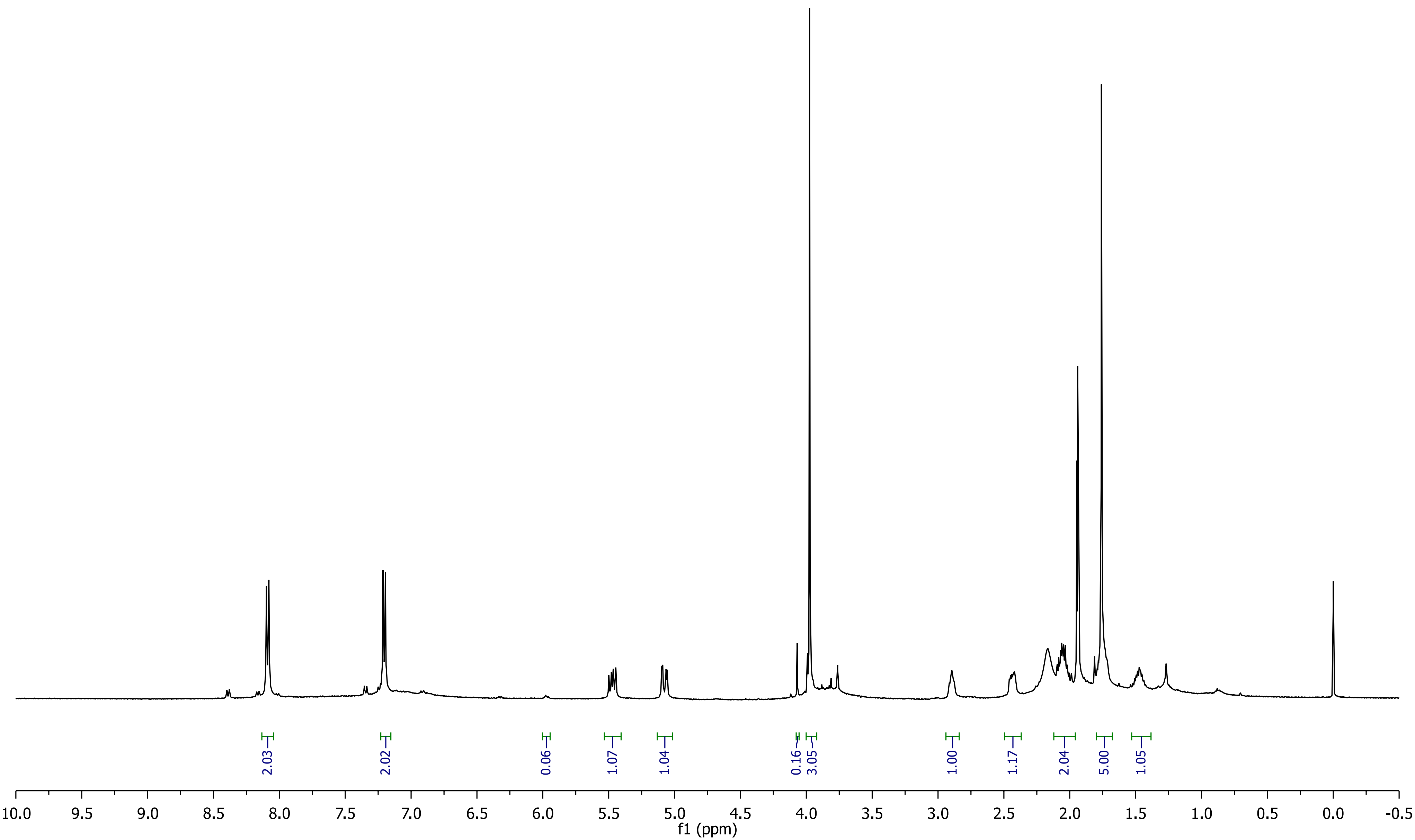
13h' 14h'

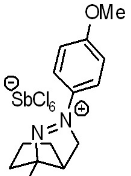


150.06
149.60
140.57
139.22
132.77
131.82
131.23
130.51
130.45
120.15
120.09
118.00
101.73
88.47
84.50
78.48
43.11
43.02
39.74
33.39
29.12
24.71
23.59
22.55
21.95
18.03
2.33
1.56
1.40
1.23
1.07
0.90
0.74
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OMe
SbCl6
OMe
SbCl6

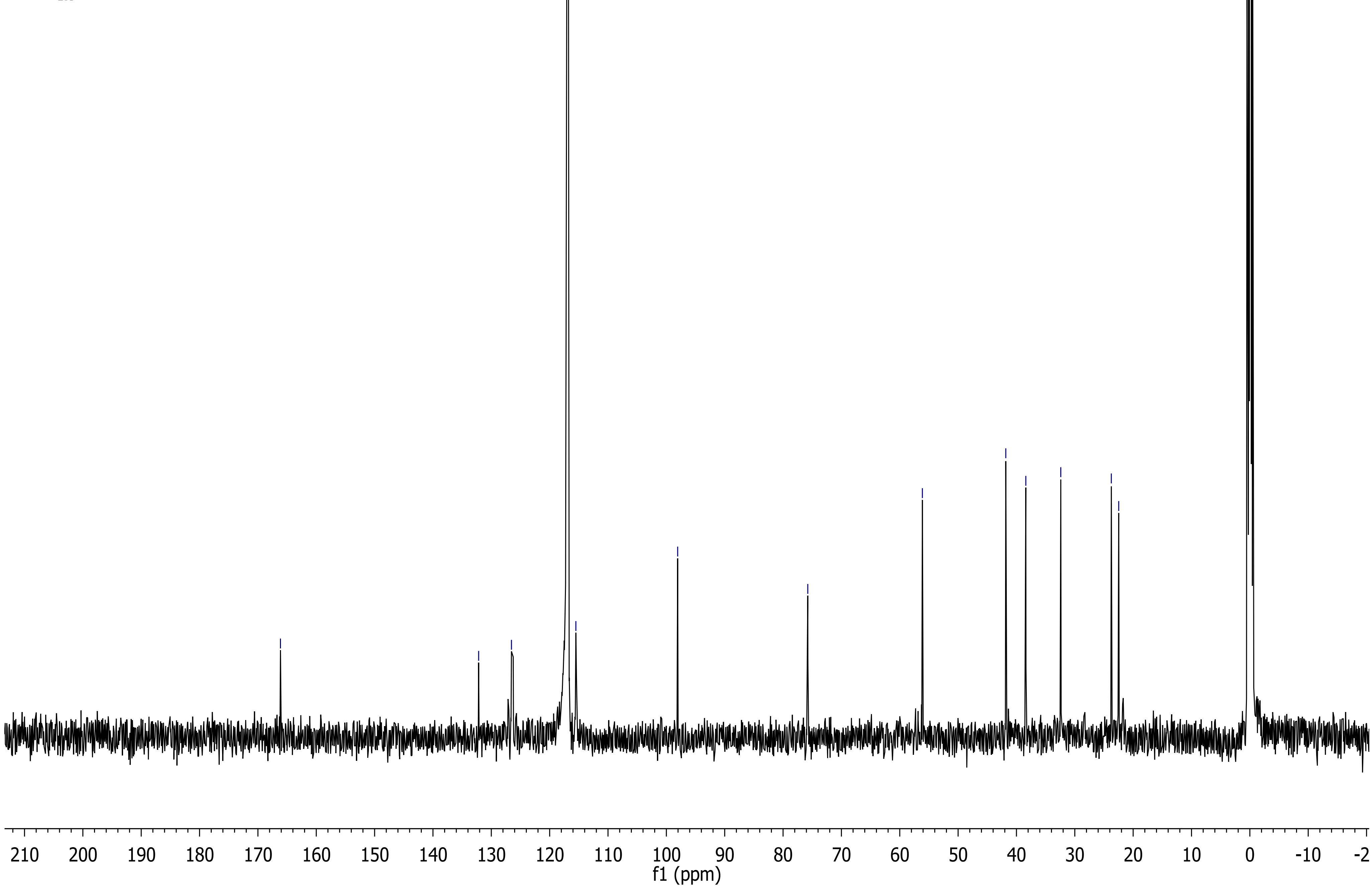
13i' 14i'


2.03
2.02
0.06
1.07
1.04
0.16
3.05
1.00
1.17
2.04
5.00
1.05
10.0 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 -0.5
f1 (ppm)

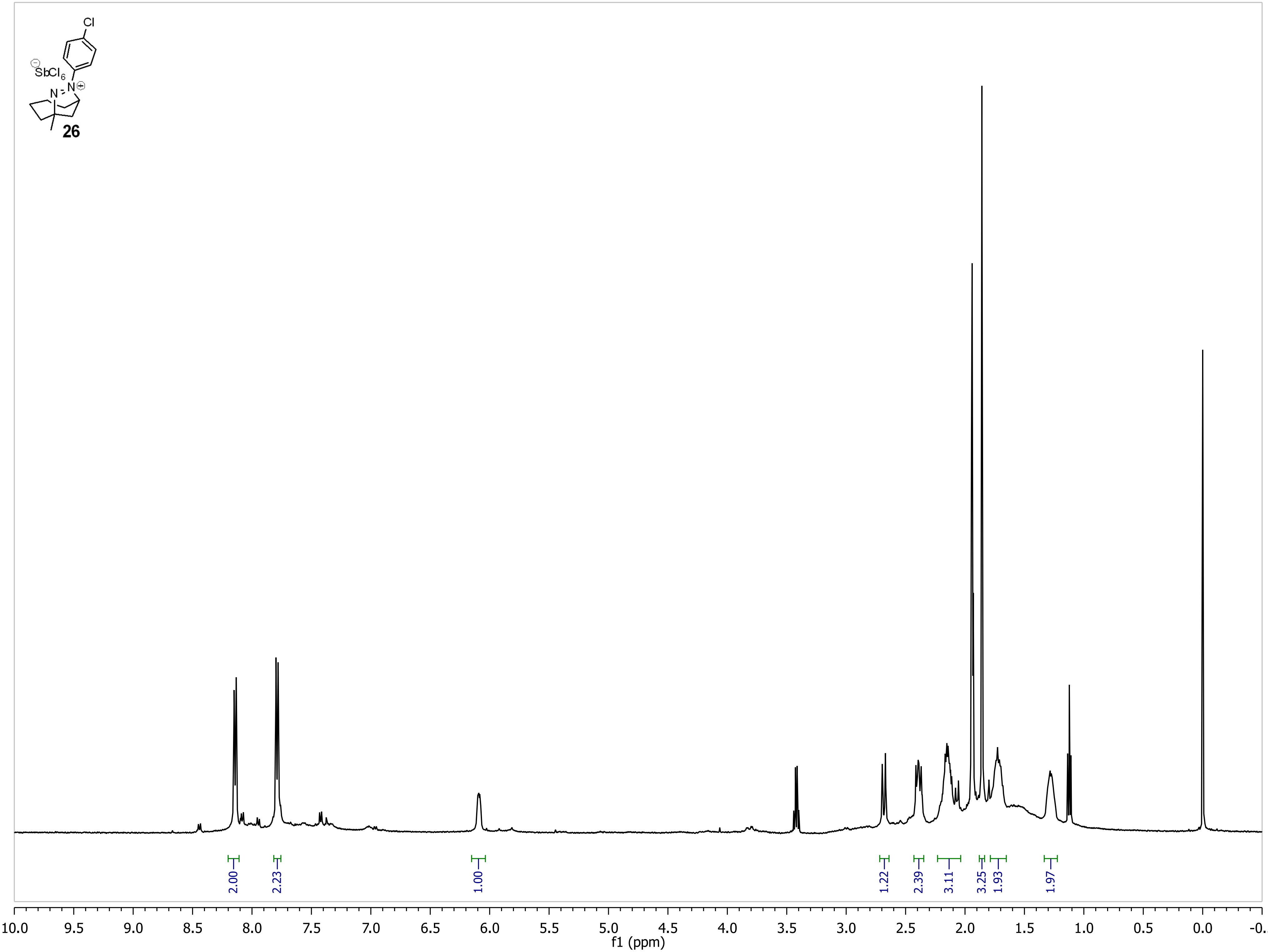


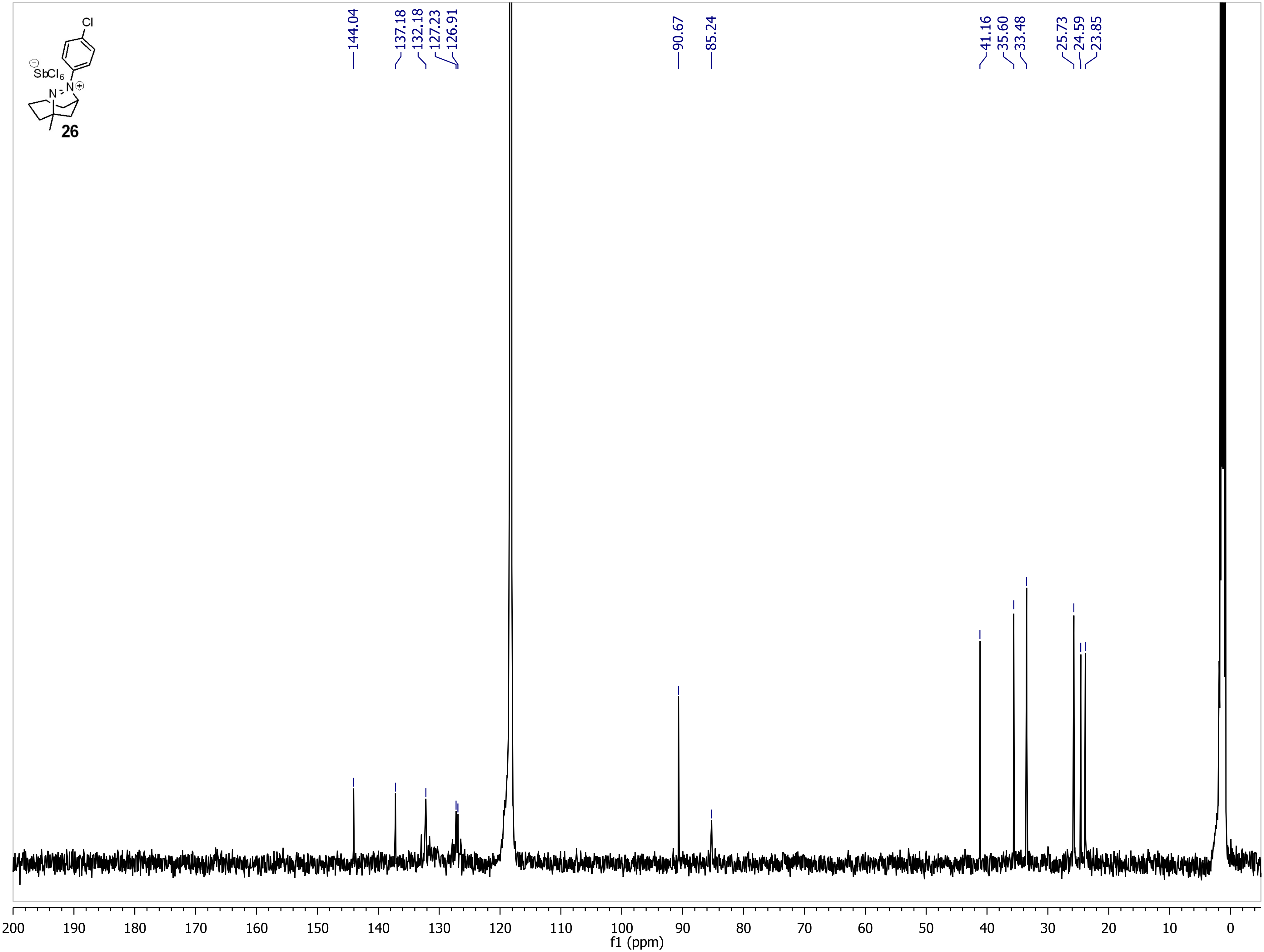
OMe
SbCl6
N
N

13i'

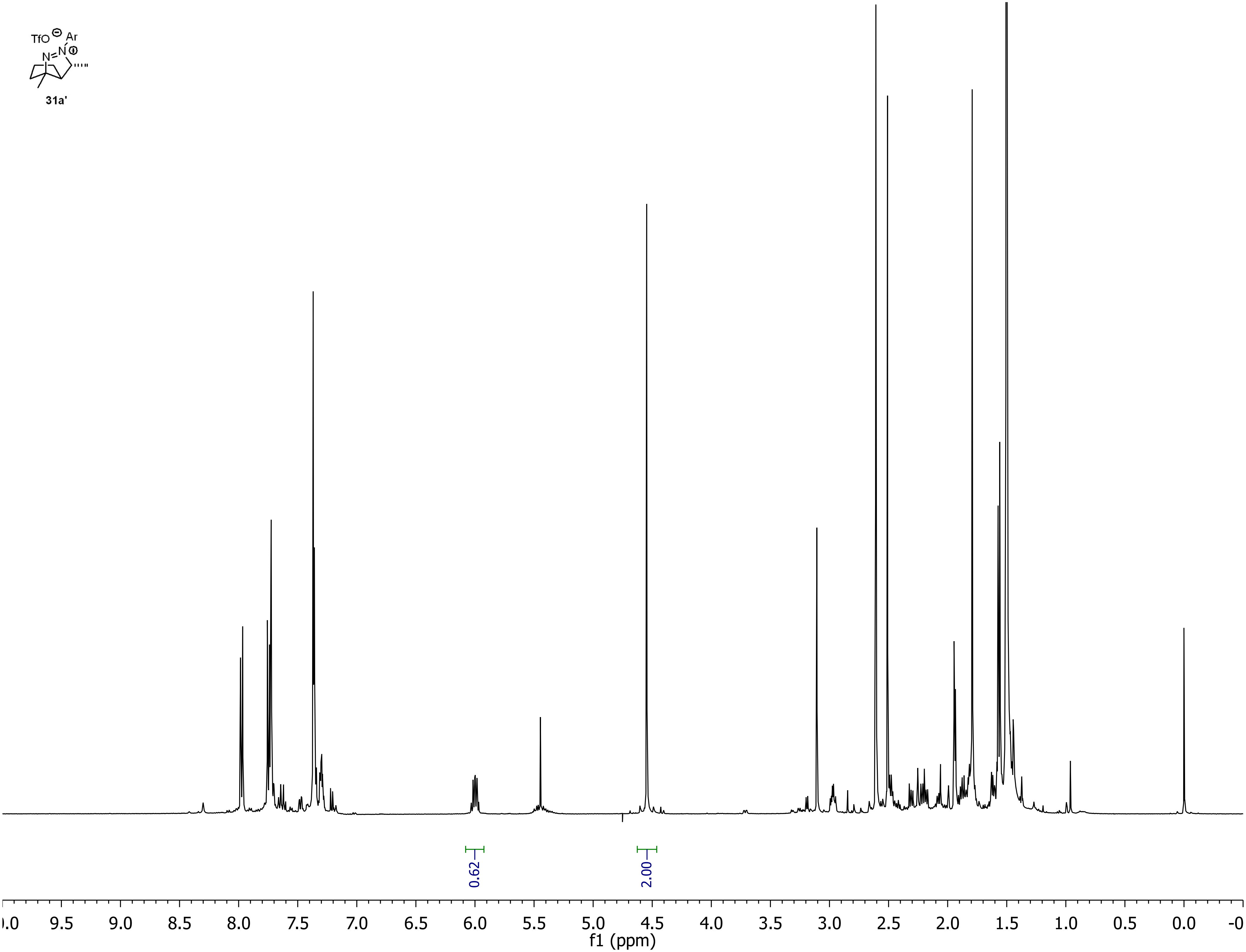


166.14
132.17
126.55
116.94
115.51
98.06
75.76
56.12
41.83
38.40
32.40
23.74
22.47
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)

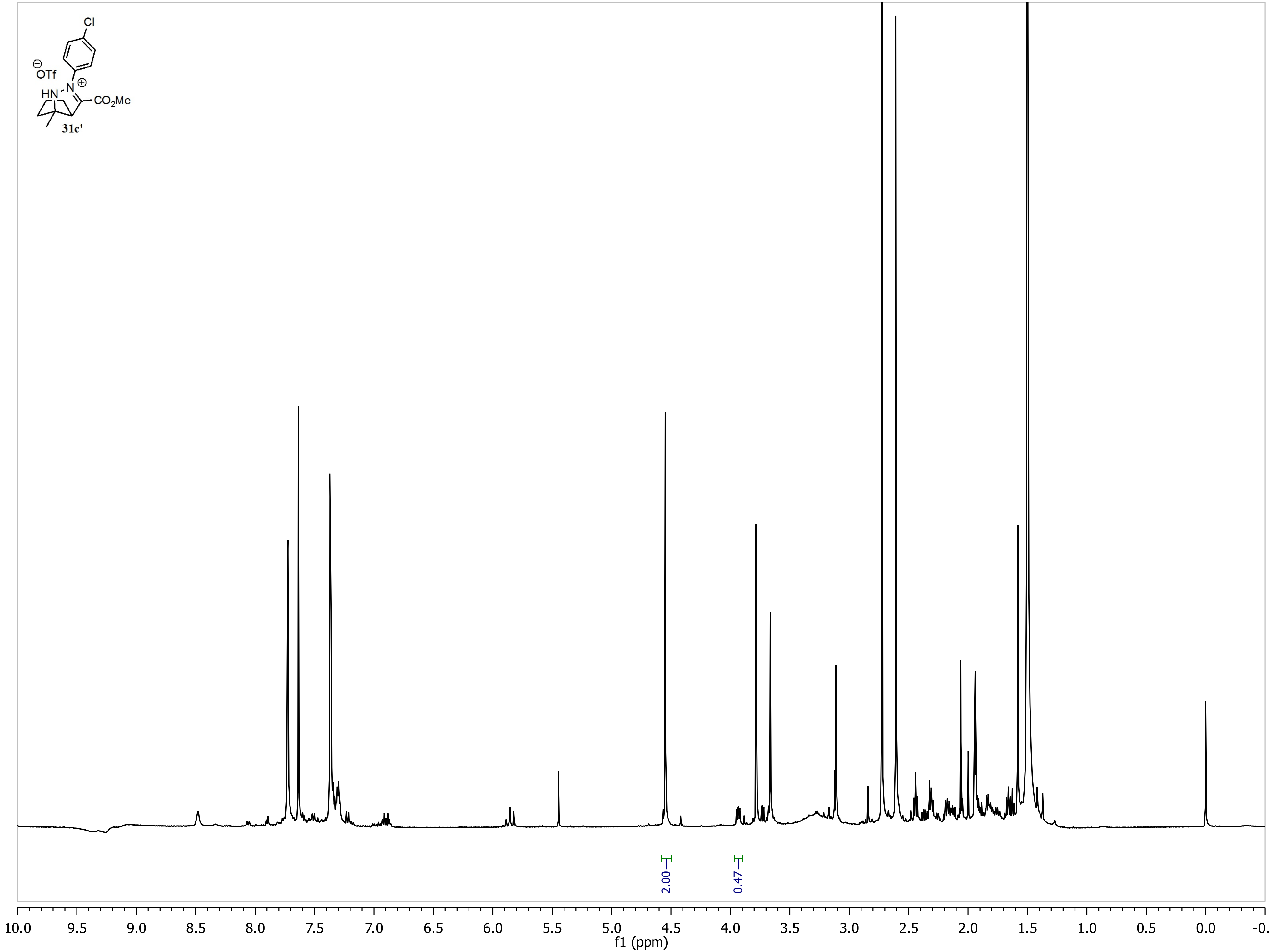

Cl
SbCl6
N
N
26
2.00
2.23
1.00
1.22
2.39
3.11
3.25
1.93
1.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



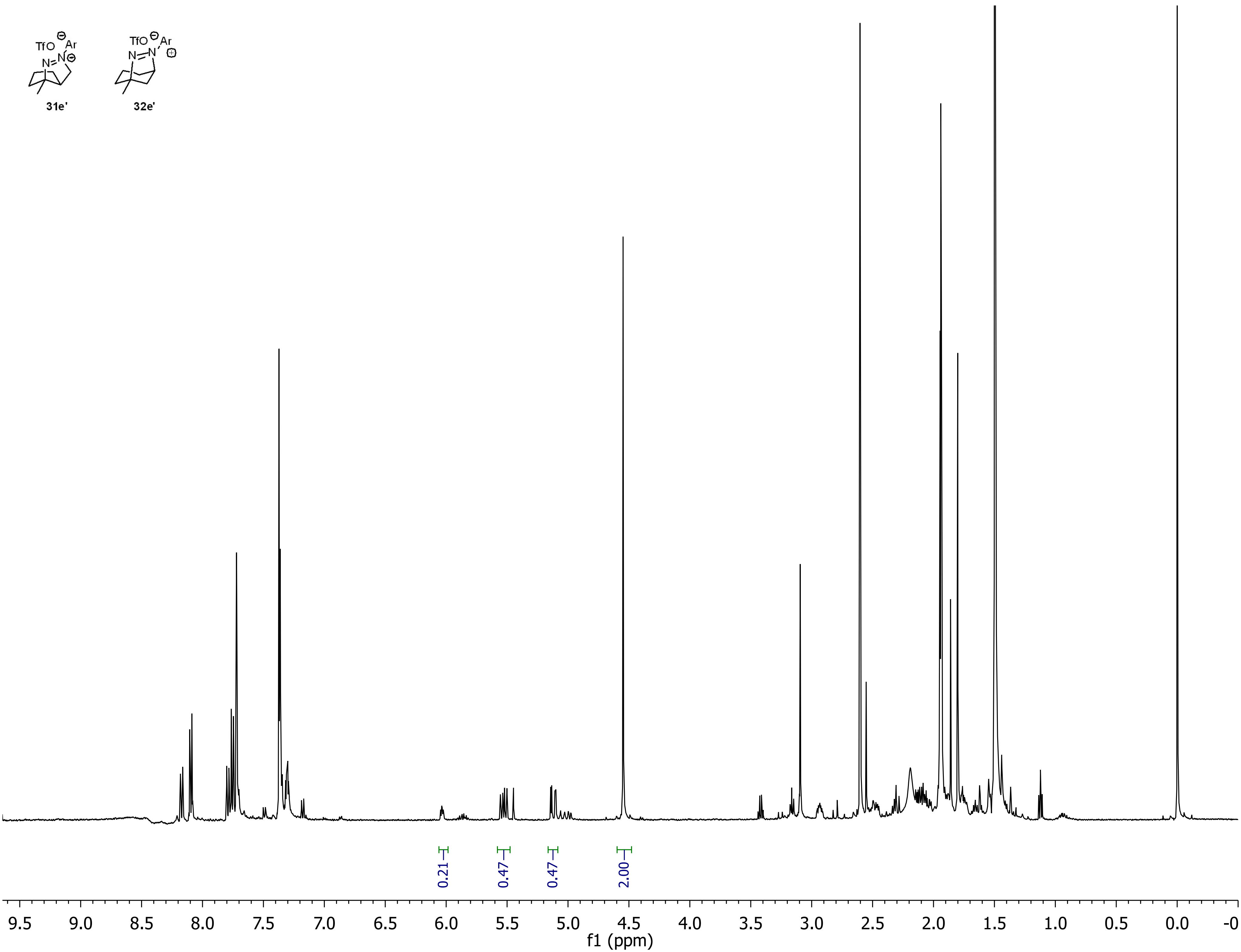
Cl
SbCl6
N
N
26
144.04
137.18
132.18
127.23
126.91
90.67
85.24
41.16
35.60
33.48
25.73
24.59
23.85
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



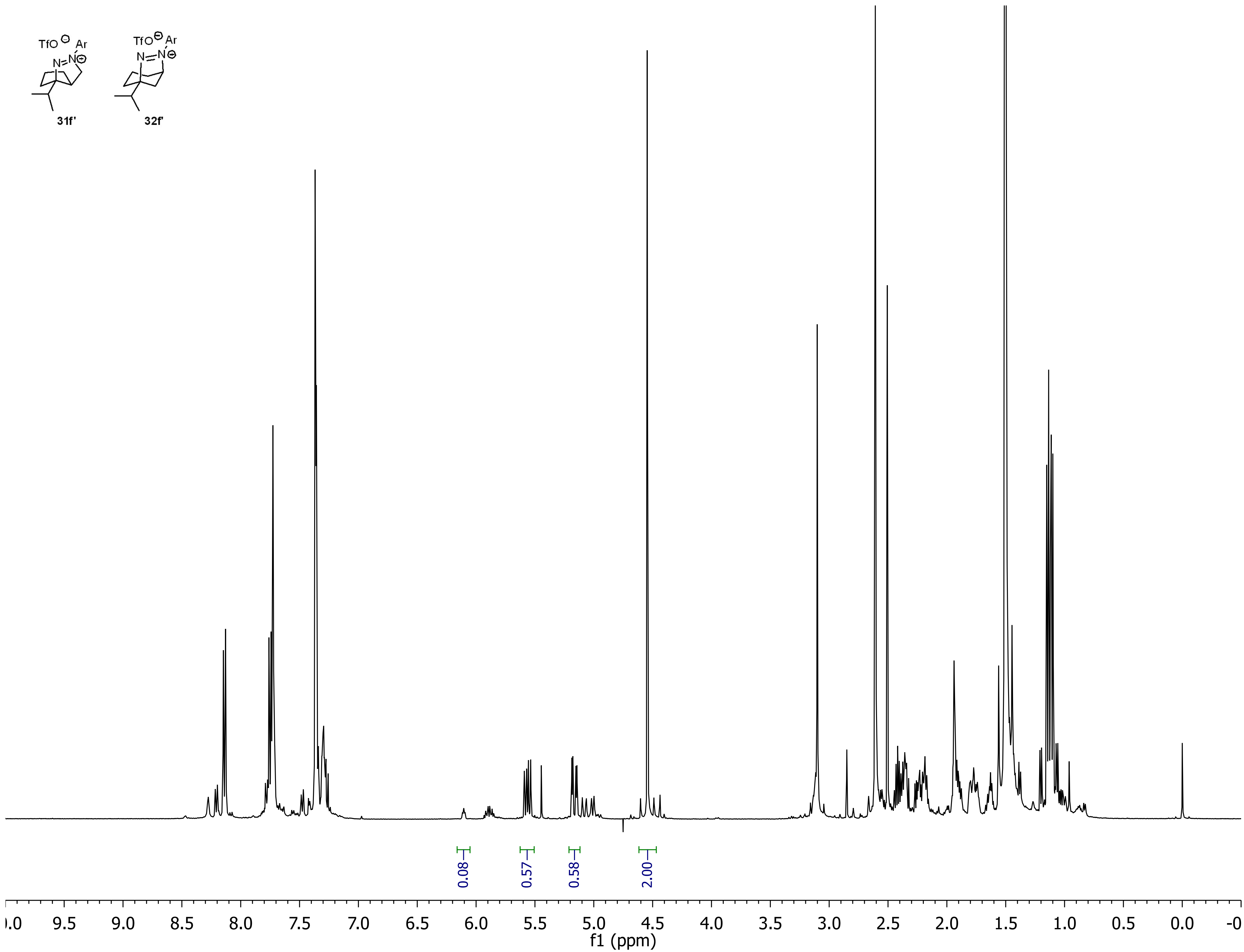
TfO
Ar
N
N
31a'
0.62
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

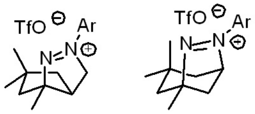


Cl
OTf
HN
N
CO2Me
31c'
2.00
0.47
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

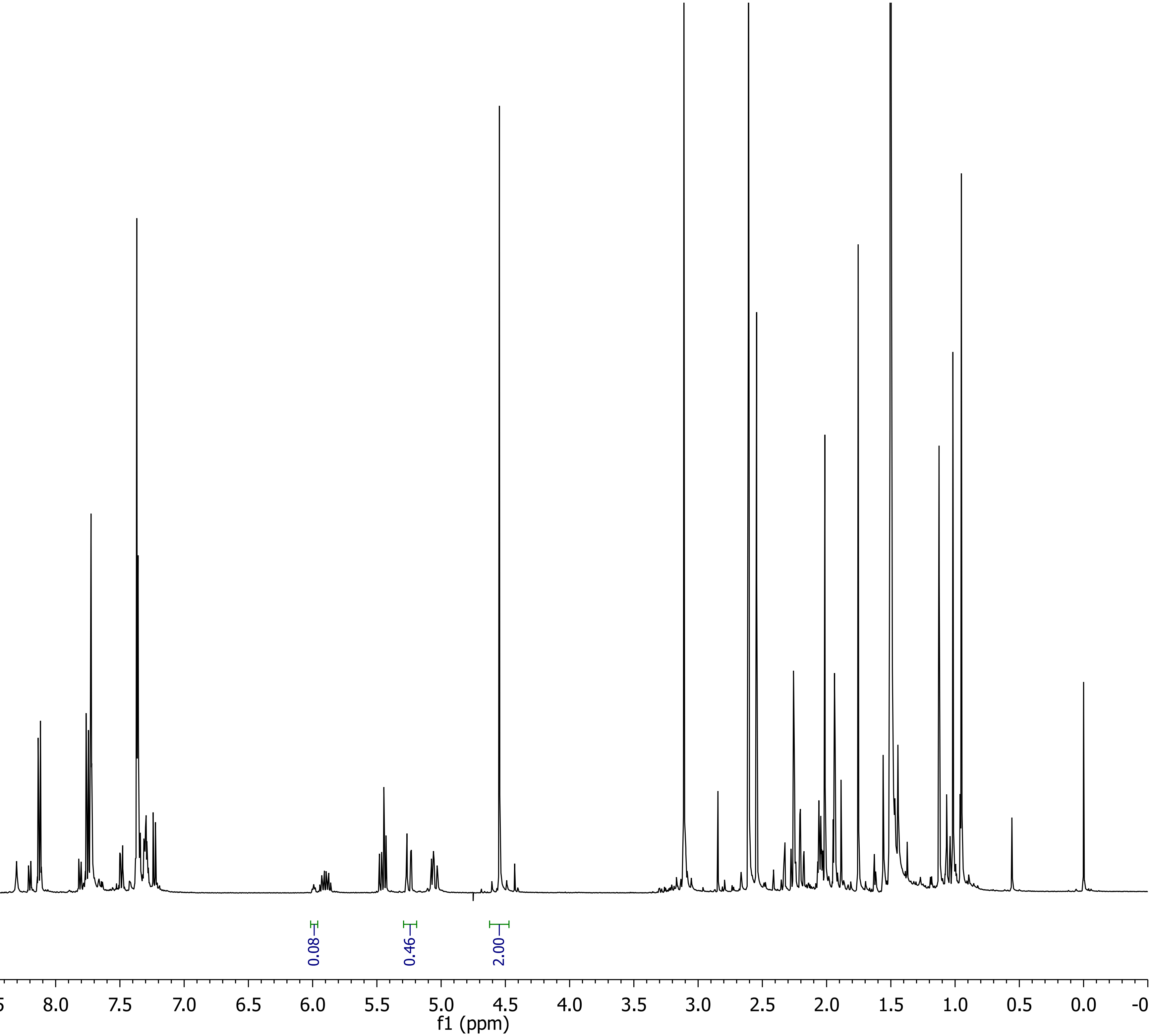


TfO
Ar
N
31e'
32e'
0.21
0.47
0.47
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


TfO
Ar
N
N
31f'
TfO
Ar
N
N
32f'
0.08
0.57
0.58
2.00
f1 (ppm)


TfO
Ar
N
N
TfO
Ar
N
N

31g' **32g'**


0.08
0.46
2.00
0.0 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 -0
f1 (ppm)