Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Electronic Supporting Information

Diboron Reagents in the Deoxygenation of Nitrones

Emily L. Vargas,[a] Mario Franco,[a] Inés Alonso, [a,b] Mariola Tortosa,*[a,b] M. Belén Cid*[a,b]

[a]Department of Organic Chemistry, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid (Spain).

[b]Institute for Advanced Research in Chemical Sciences (IAdCHEM), Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid (Spain).

Corresponding Authors: belen.cid@uam.es, mariolatortosa@uam.es

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Experiments to evaluate the role of methoxide as additive

We also considered of interest to evaluate the role of an alkoxide as an additive in the reduction of nitrones, since it is known to activate the B-B bond for the cleavage of the N-O bond in nitrocompounds (see ref 13 of the manuscript). To this end, we calculated the energies of the possible transition states responsible for the deoxygenation of the model nitrone **1b** with diboron reagents in presence of MeOK as additive (Figure S1). According to the calculations, the reactions should be clearly faster in the presence of an alkoxide either by using B_2pin_2 or B_2nep_2 (compare a with b and c with d). In parentheses are shown the difference of energies regarding the previous nitrone-diboron complexes. Potassium methoxide induces electronic and conformational changes that would favor the interaction with nitrone in the TS.

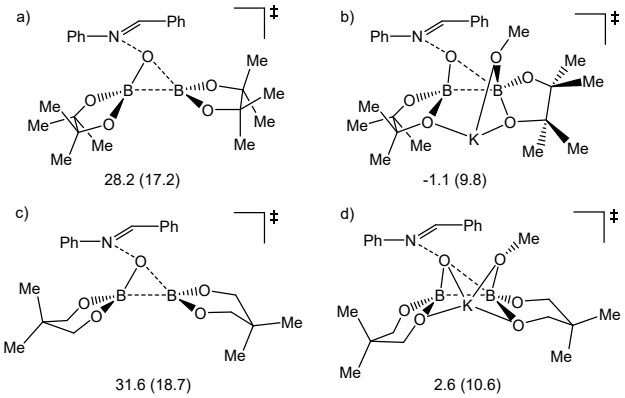


Figure S1. Calculated transition states structures for the deoxygenation step of the model nitrone **1b** using B_2nep_2 or B_2pin_2, with or without MeOK ($M062X_{SMD(benzene)}$/6-311+G(d,p)//($M062X_{SMD(benzene)}$/6-31+G(d). Relative G values at 298 K (kcal·mol^{-1}) with respect to separated starting materials. The difference of energies regarding the previous nitrone-diboron complexes are shown in parentheses).

Therefore, we carried out a set of experiments using different deuterated solvents and base equivalents of MeOK to assess the effect on the reactivity of diboron compounds towards nitrone deoxygenation (Figure S2). Nevertheless, as can be observed in the graph, although the results do not seem to follow a clear tendence, the presence of the alkoxide do slow down the deoxygenation reaction.

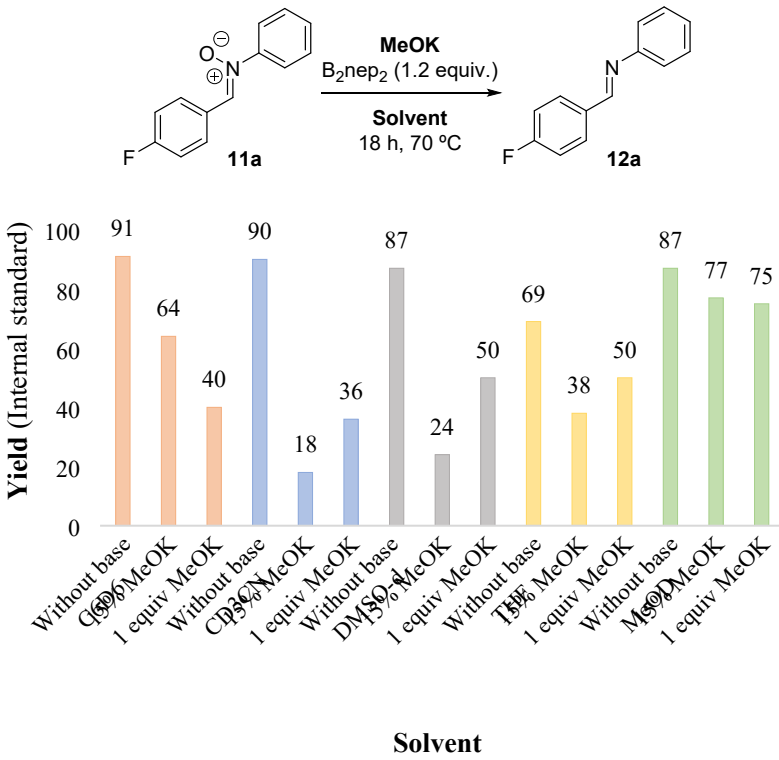
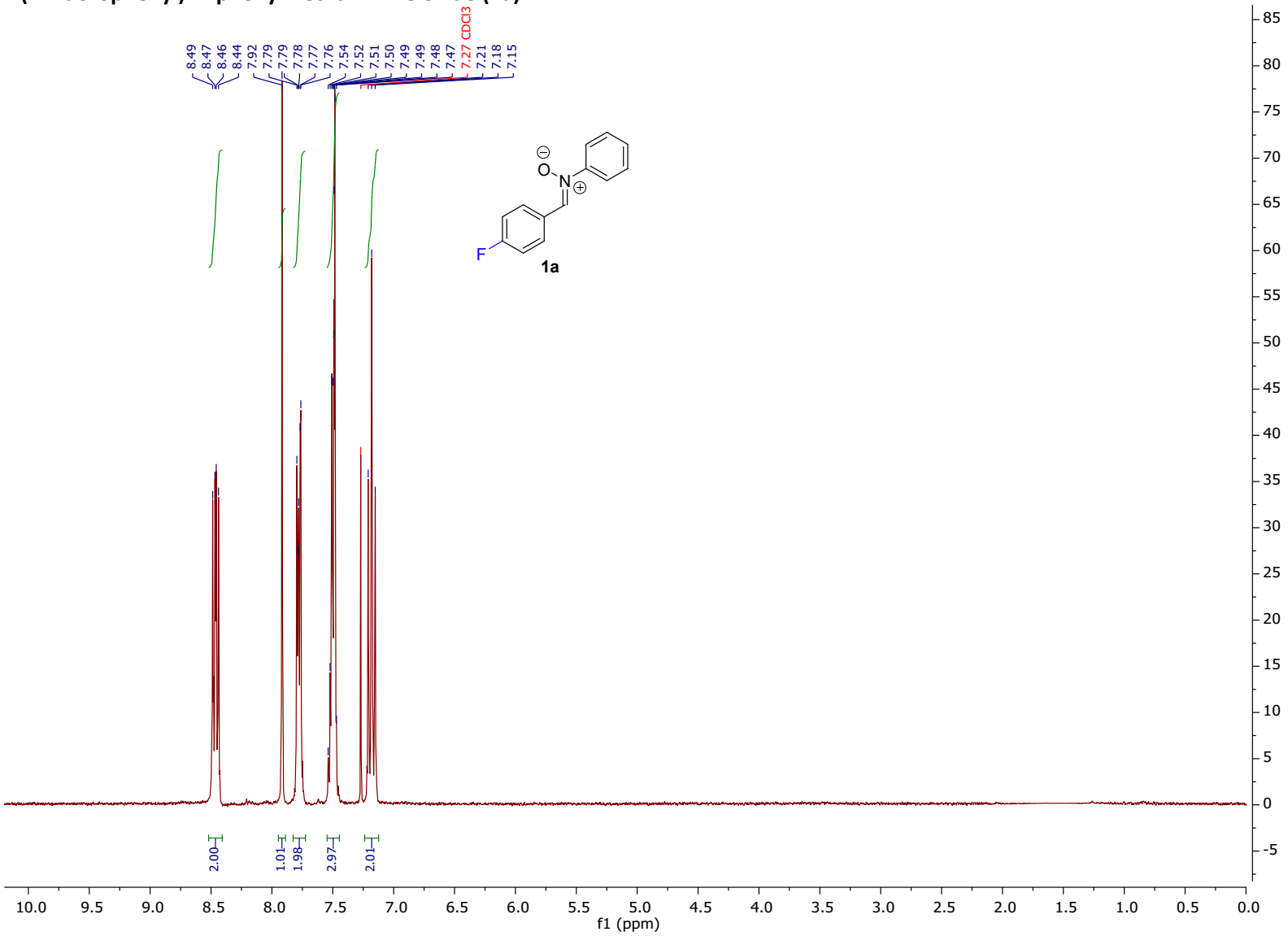


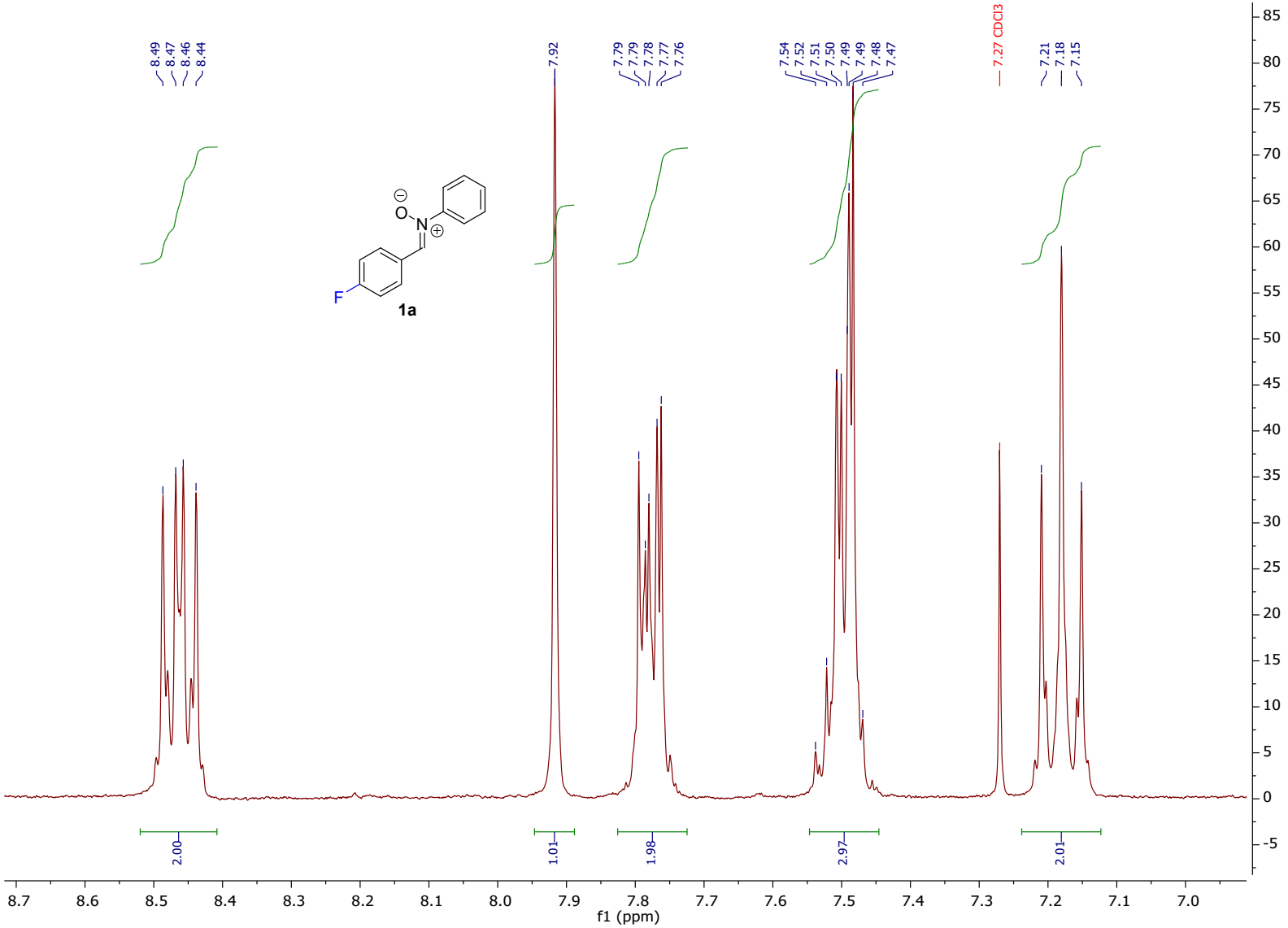
Figure S2. *Nitrone reactivity in presence of base-activated diborons.*

We hypothesize that these apparent anarchical experimental results could be a consequence of several factors such as the base **solubility** and the **stability** of the diboron reagent. The poor solubility of the base in non-polar solvents could inhibit its participation in the reaction. B_2nep_2 is a more labile diboron compound that could undergo exchange of alcohols in the presence of MeOK more easily than the bulkier B_2pin_2.

Spectra of nitrones and imines

(*Z*)-1-(4-Fluorophenyl)-*N*-phenylmethanimine oxide (1a)

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7.78
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7.76
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7.52
7.51
7.50
7.49
7.49
7.48
7.47
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7.21
7.18
7.15
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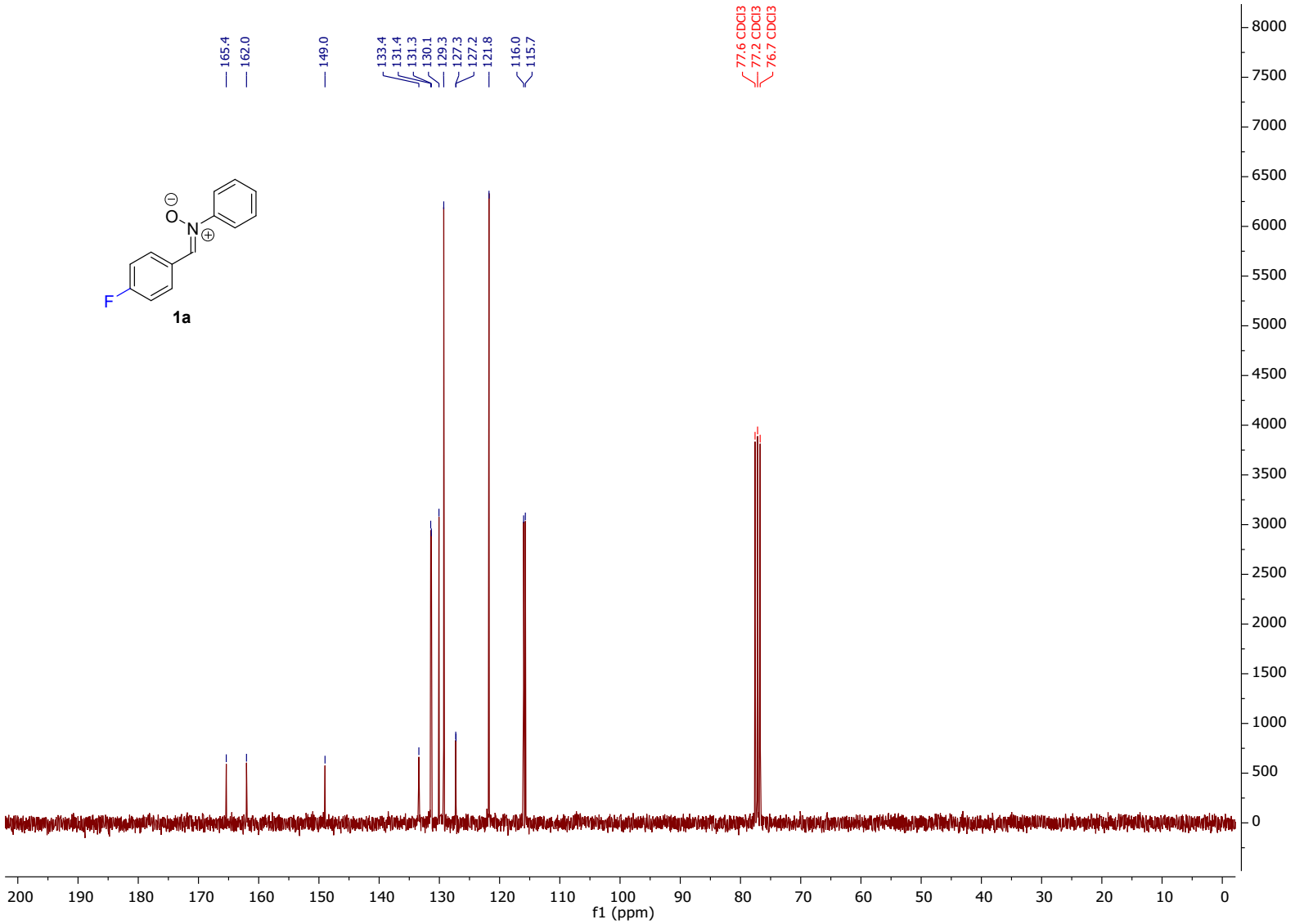
1.01
1.98
2.97
2.01
f1 (ppm)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149.0
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131.4
131.3
130.1
129.3
127.3
127.2
121.8
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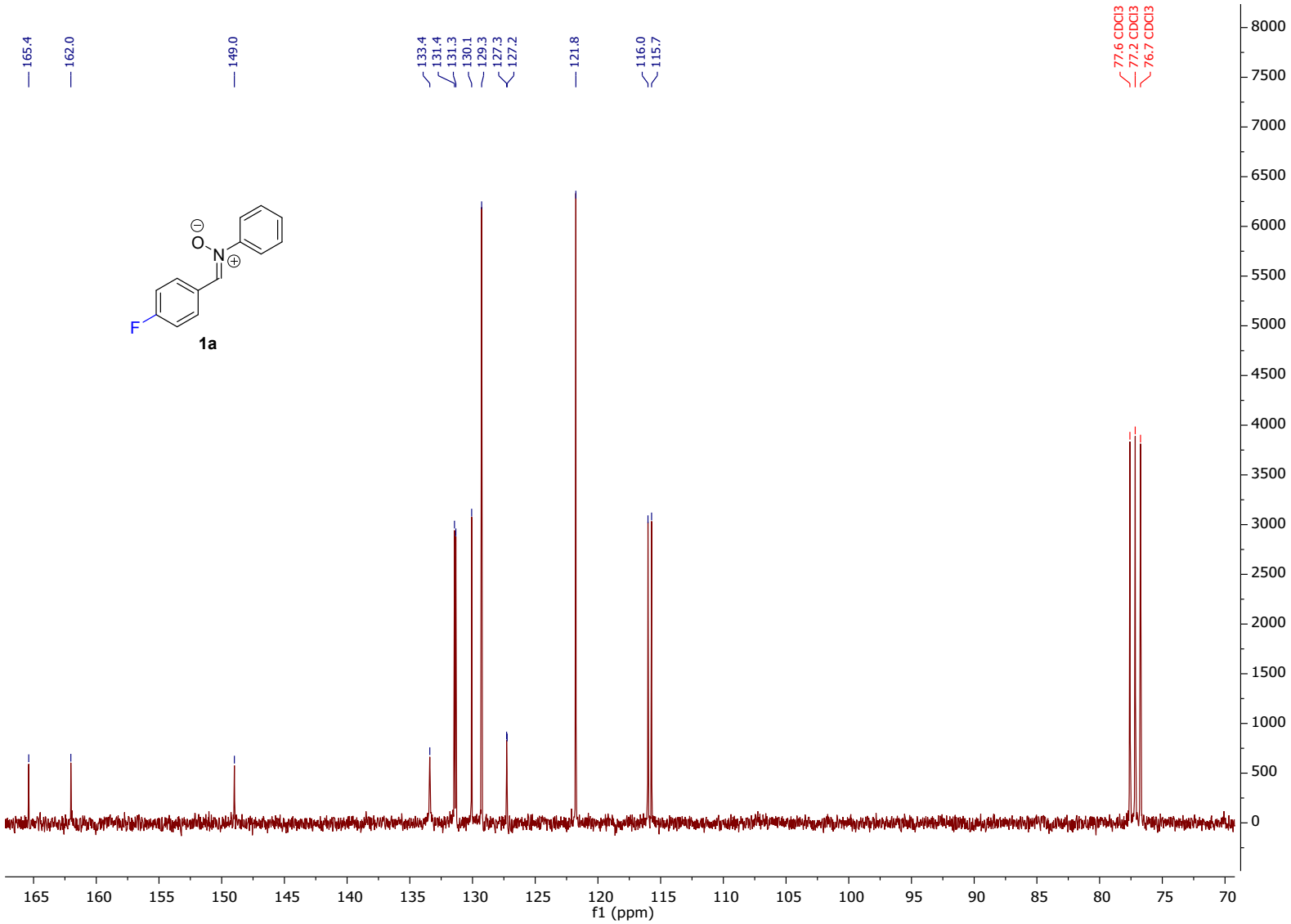
115.7
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
O
N
F
1a
f1 (ppm)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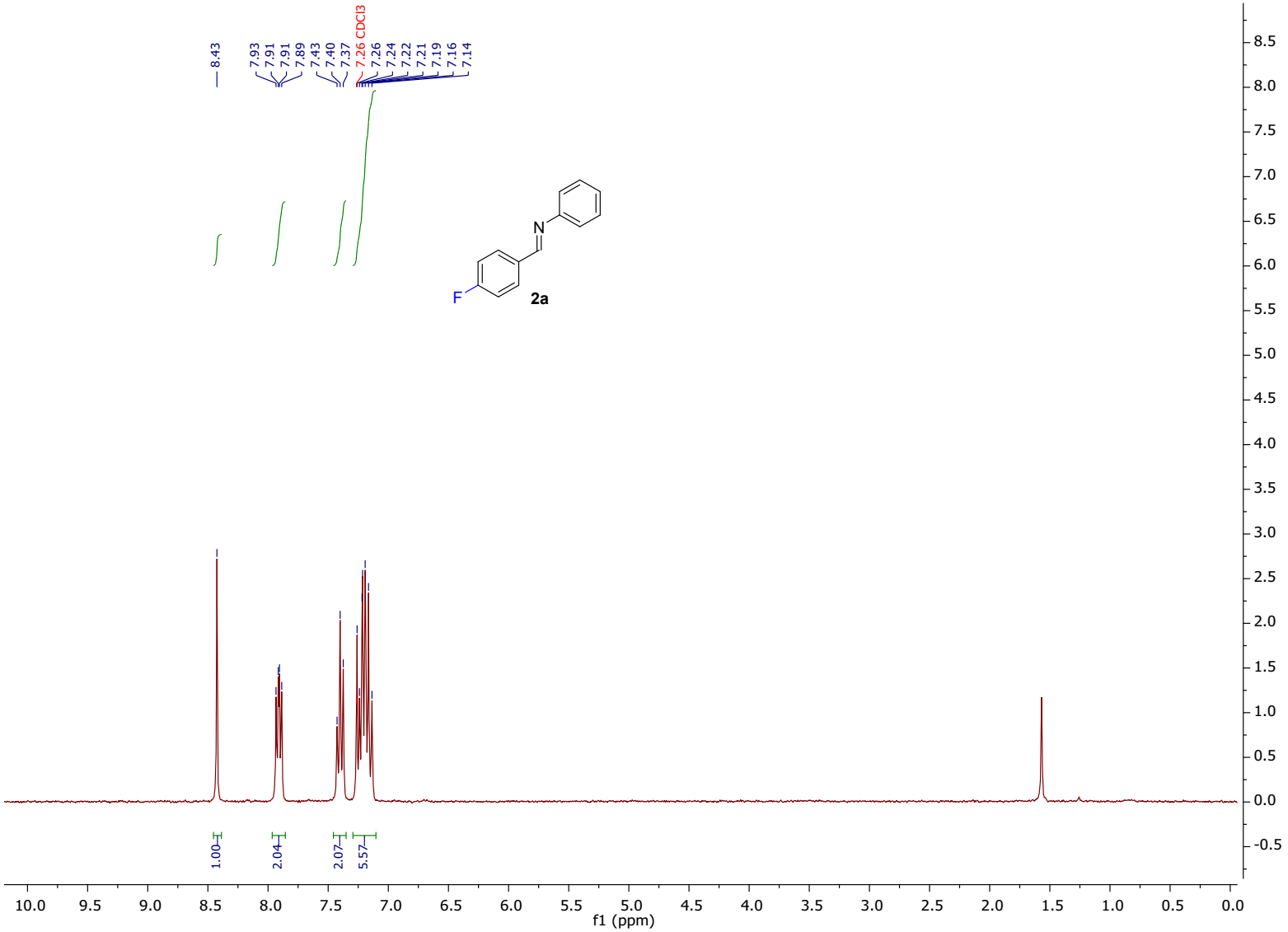
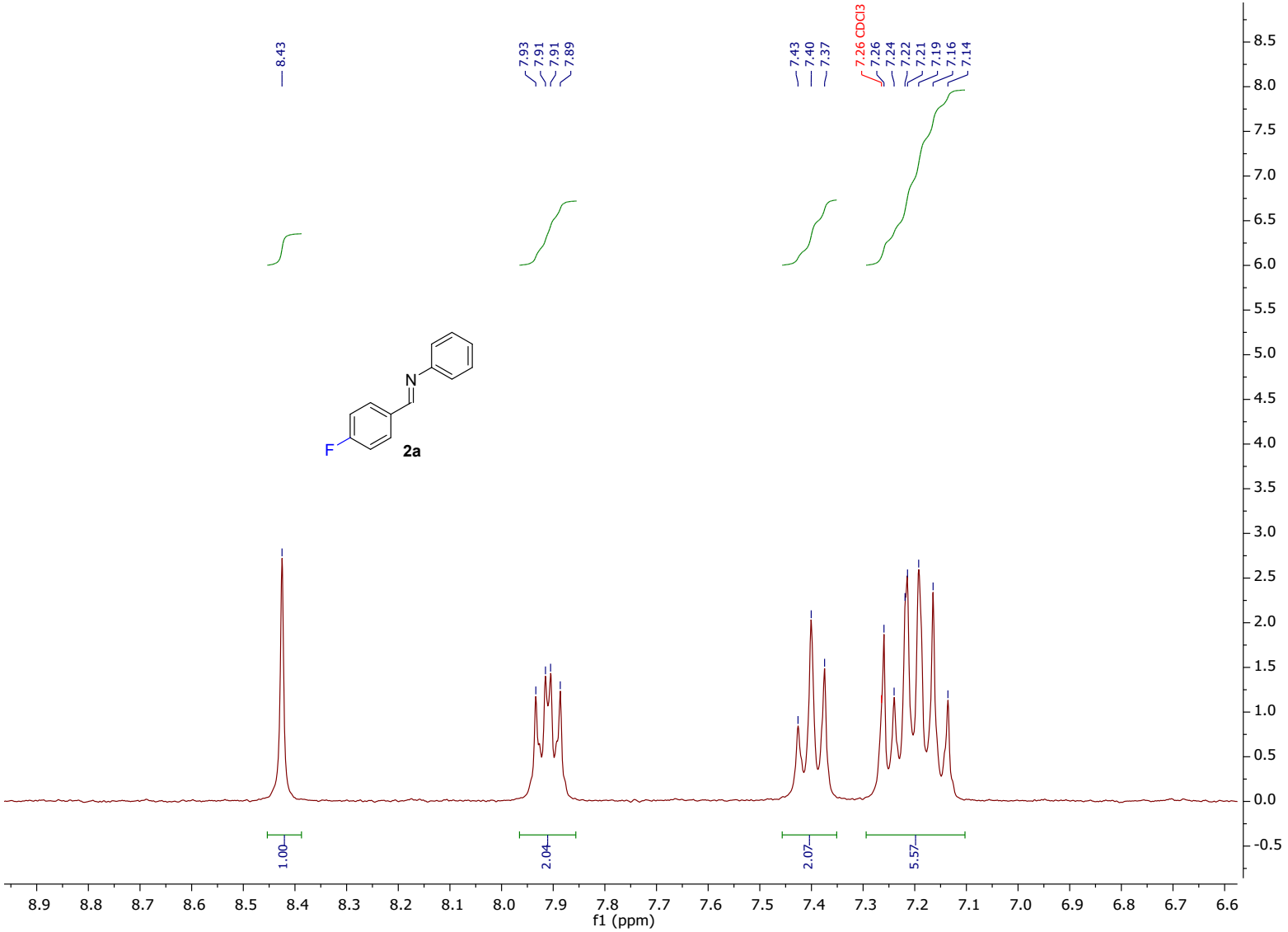
129.3
127.3
127.2
121.8
116.0
115.7
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
1a
f1 (ppm)

(*E*)-*N*-(4-fluorobenzylidene) aniline (2a)

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F
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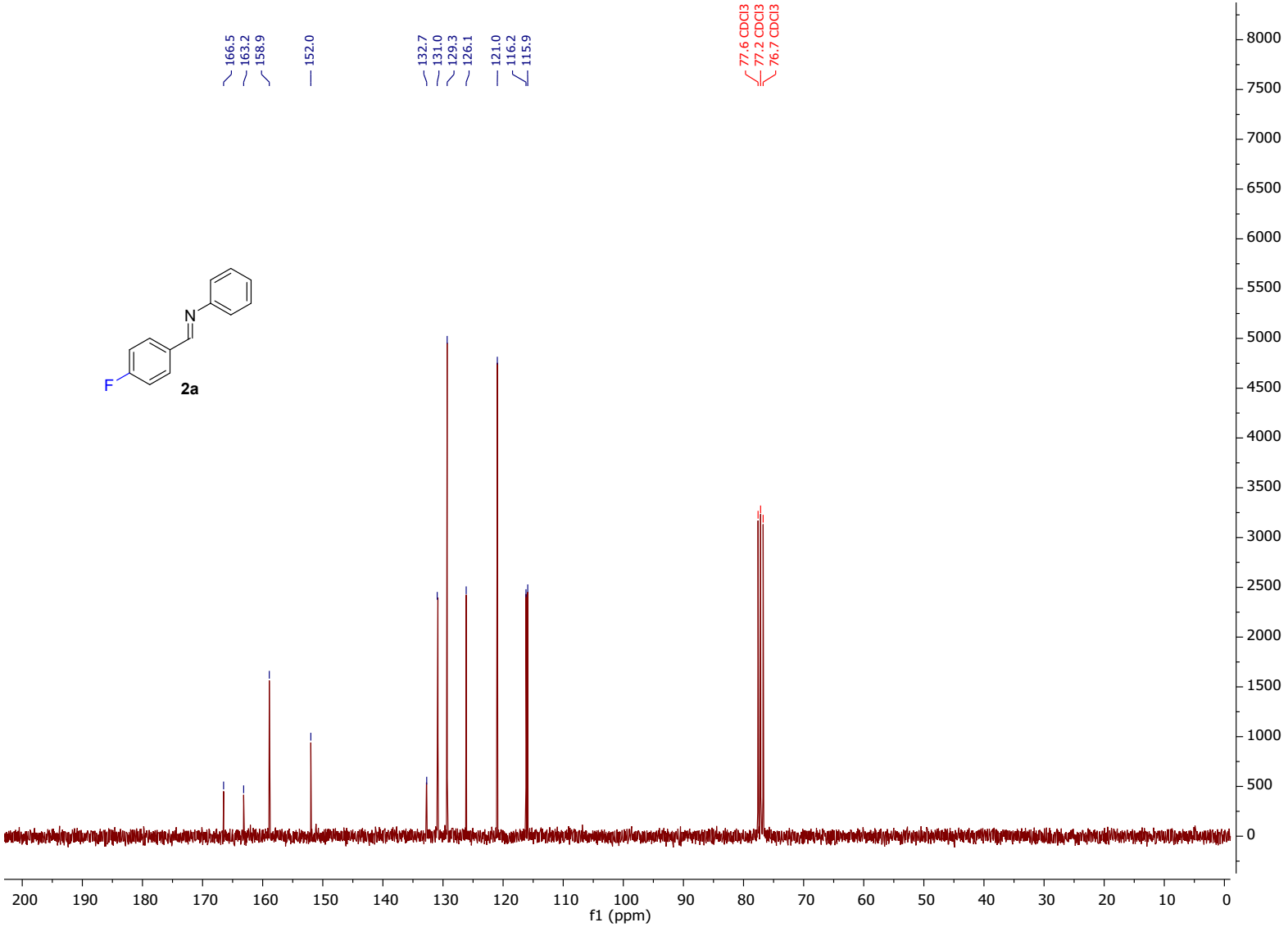
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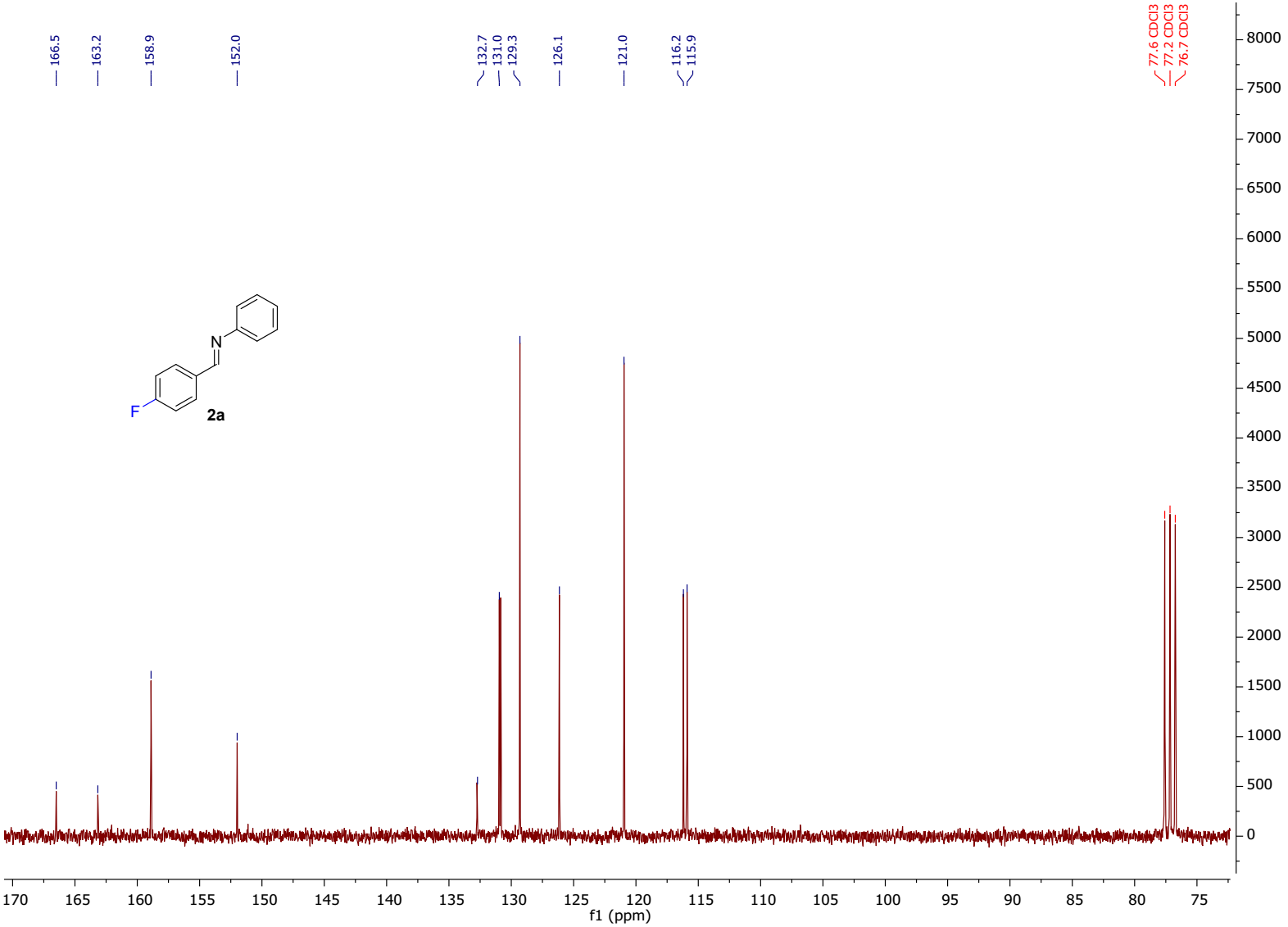
77.2 CDCl3
76.7 CDCl3
N
F
2a
f1 (ppm)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115.9
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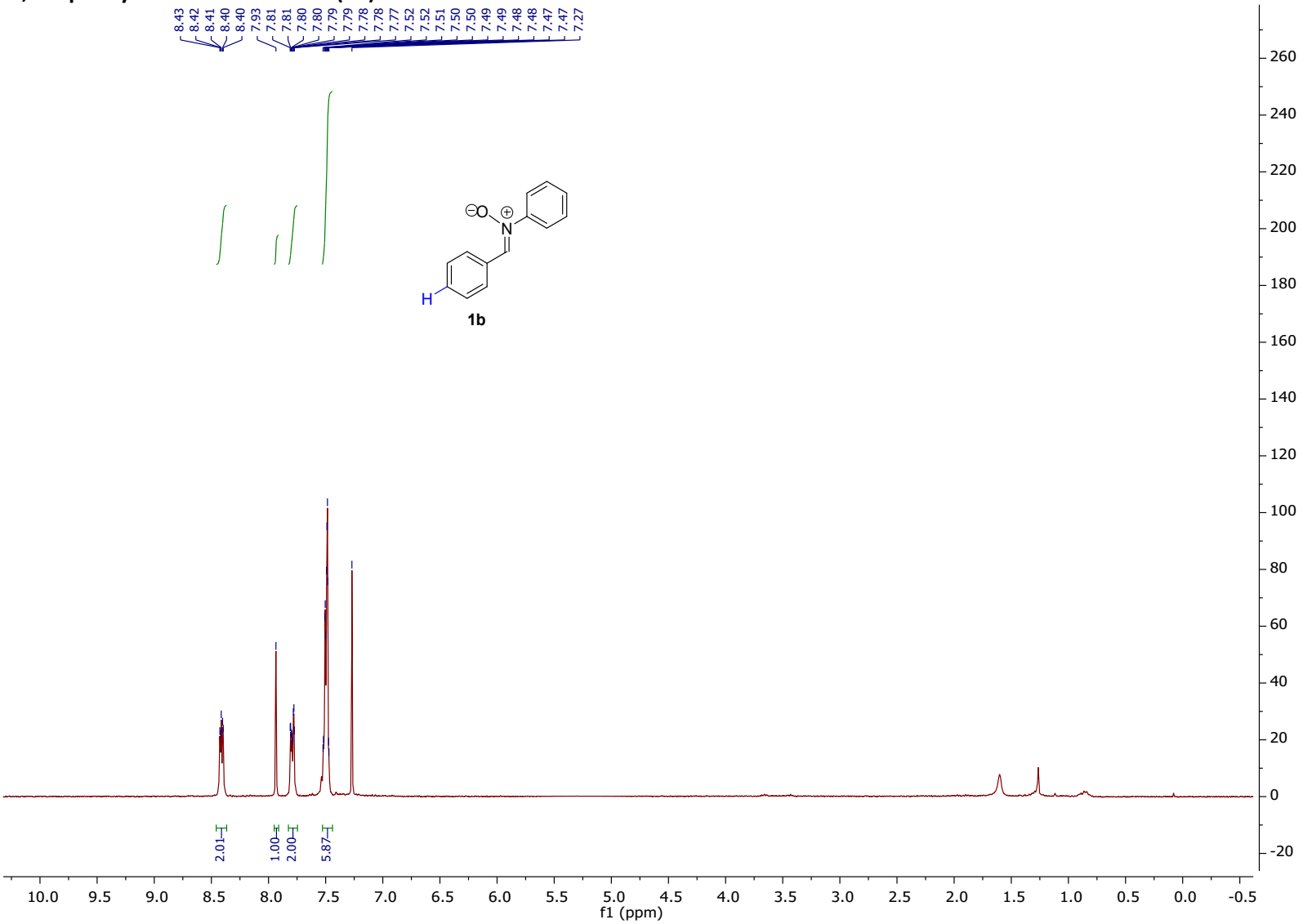
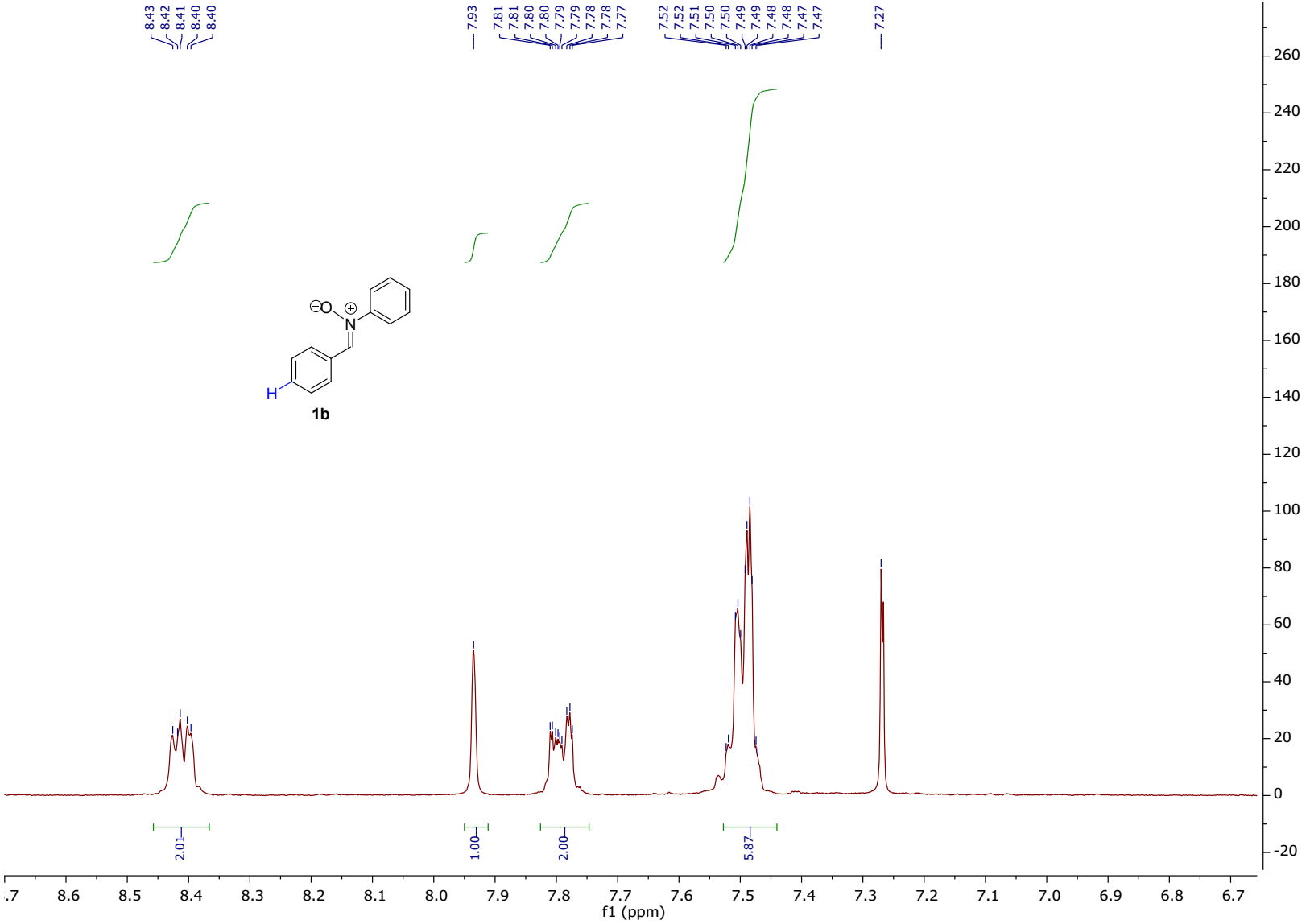
76.7 CDCl3
N
F
2a
f1 (ppm)

(*Z*)-*N*,1-Diphenylmethanimine oxide (1b)

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7.51
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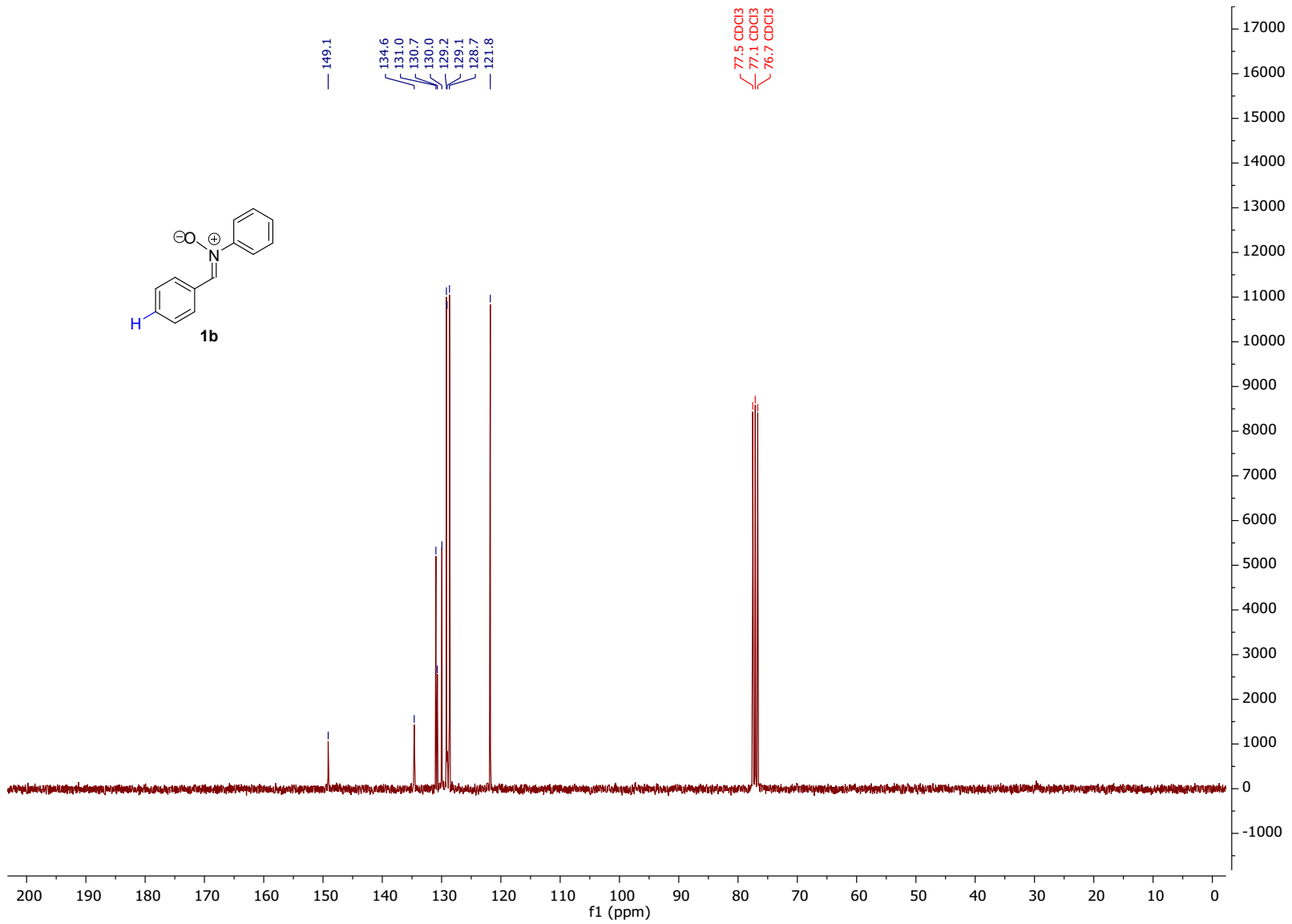
5.87
f1 (ppm)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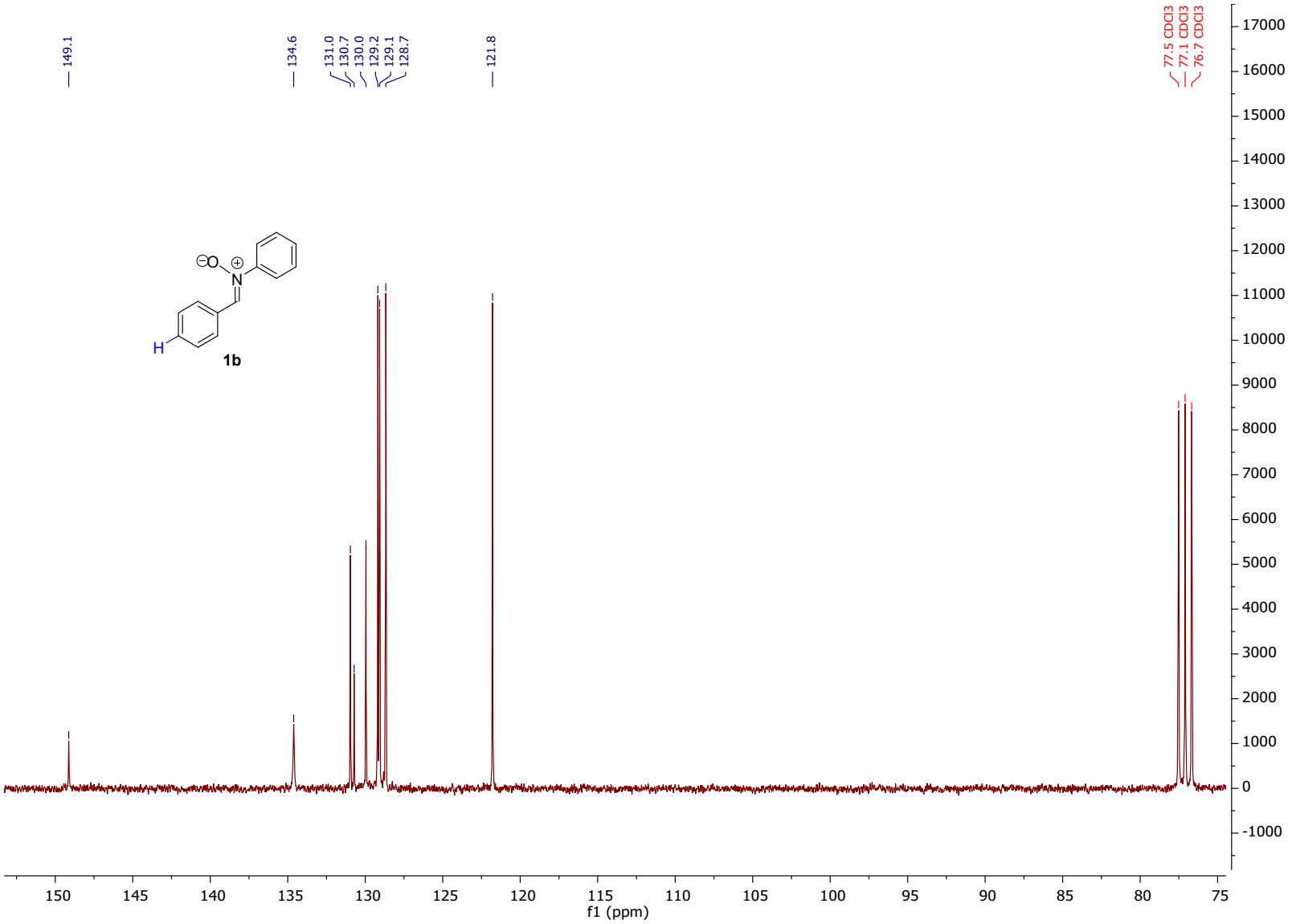
77.1 CDCl3
76.7 CDCl3
1b
f1 (ppm)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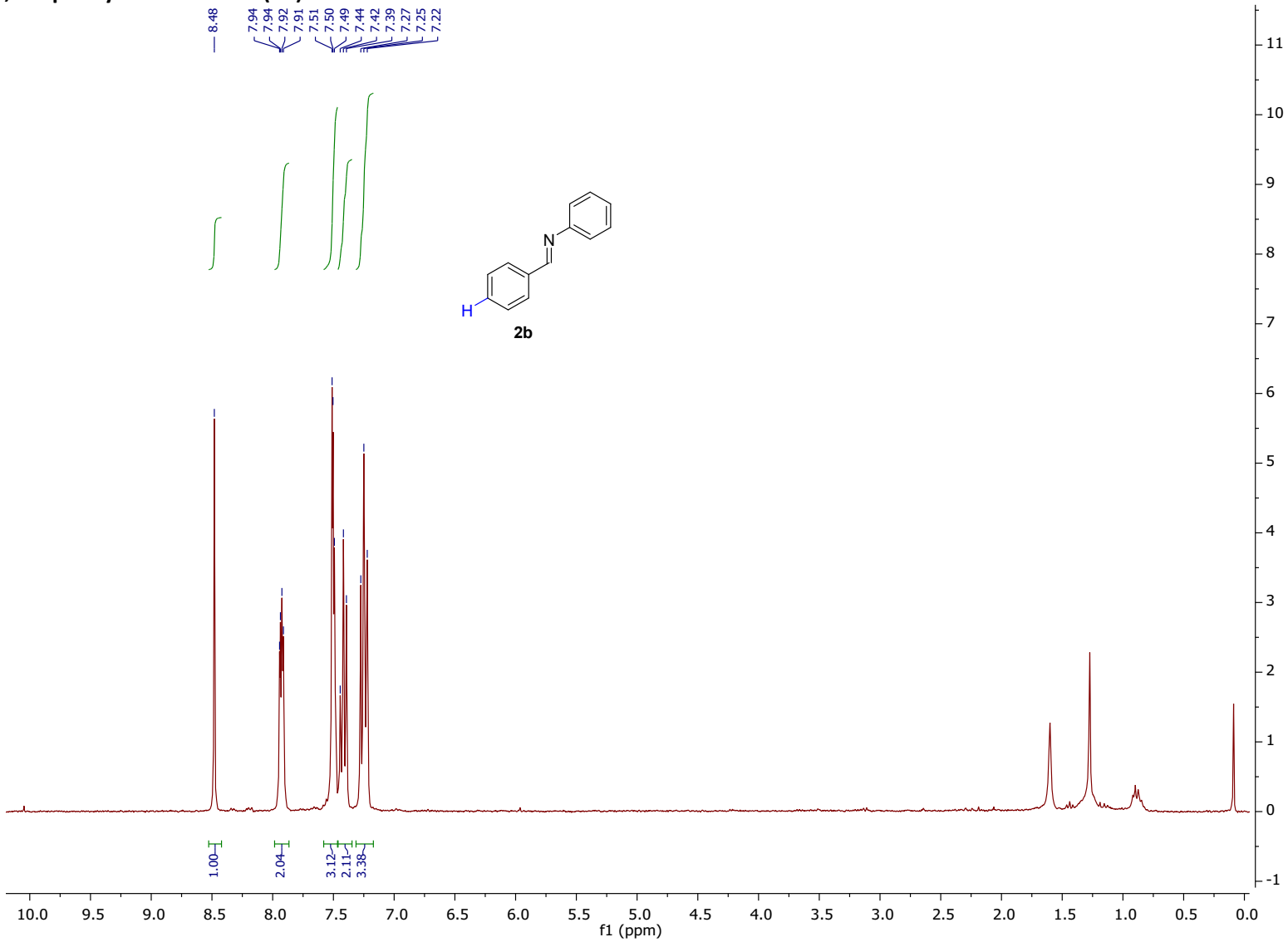
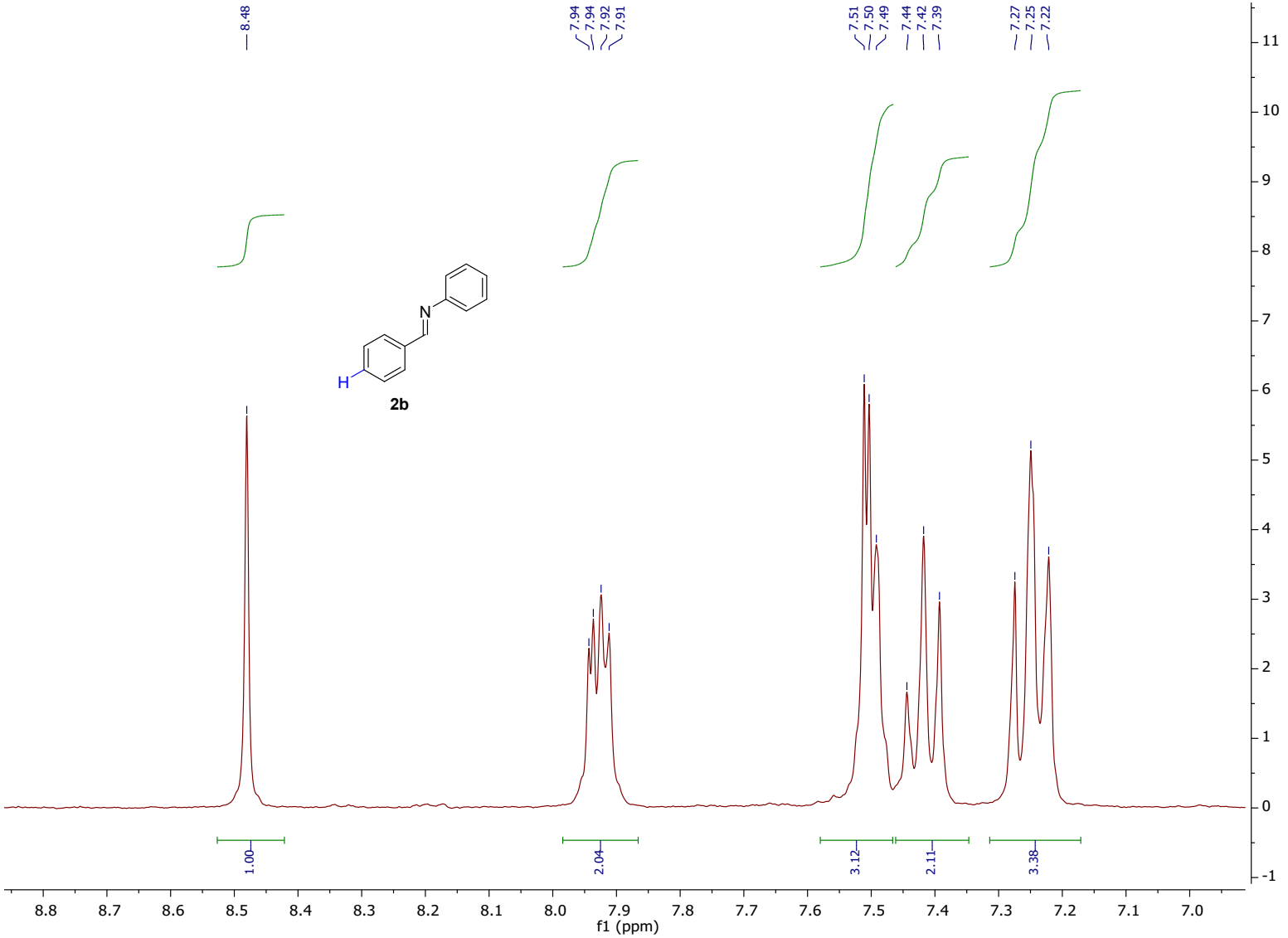
1b
f1 (ppm)

(*E*)-*N*,1-Diphenylmethanimine (2b)

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N
H
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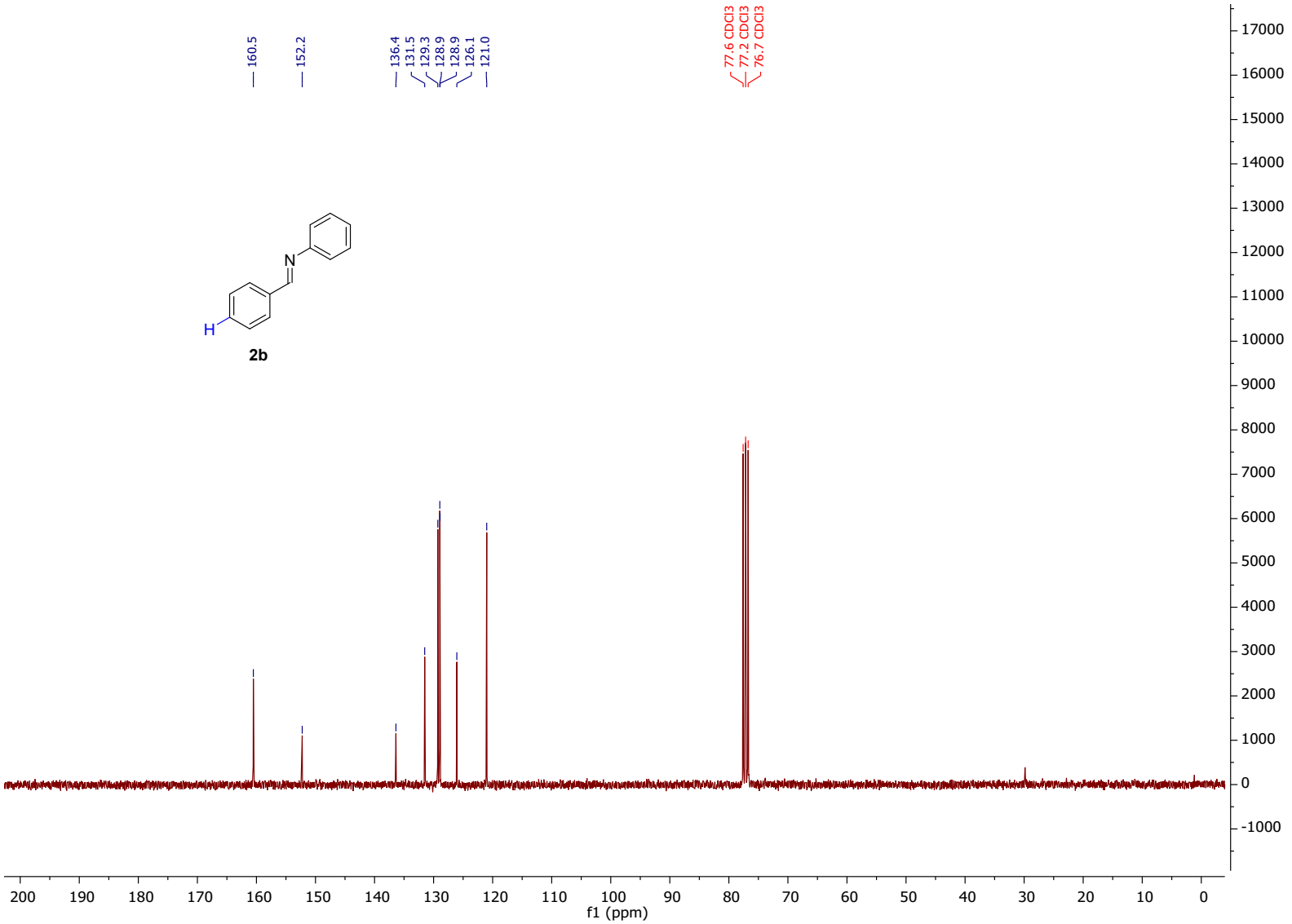
3.12
2.11
3.38
f1 (ppm)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126.1
121.0
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77.2 CDCl3
76.7 CDCl3
N
H
2b
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
200
190
180
170
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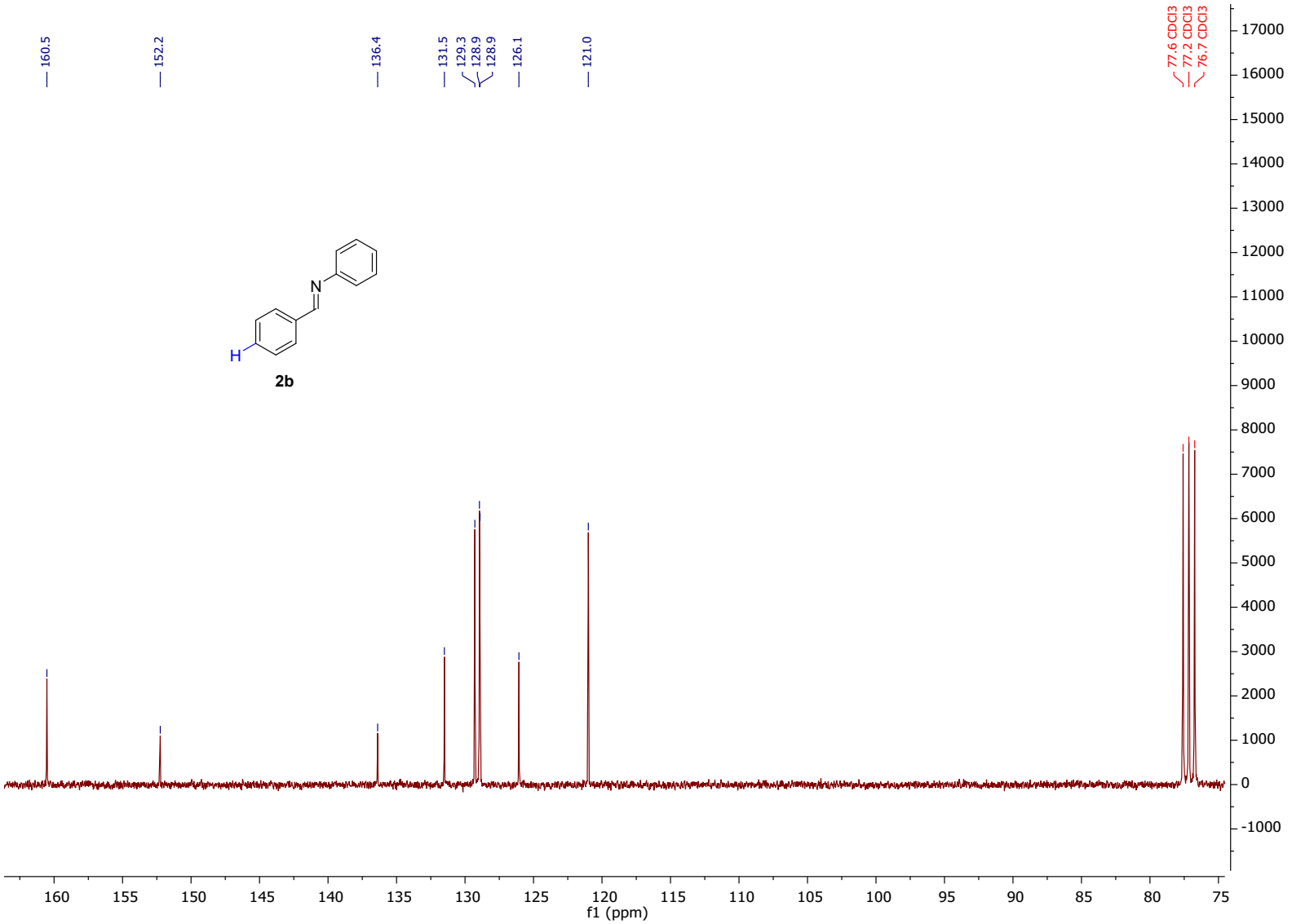
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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129.3
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121.0
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77.2 CDCl3
76.7 CDCl3
N
H
2b
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
160
155
150
145
140
135
130
125
120
115
110
105
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95
90
85
80
75
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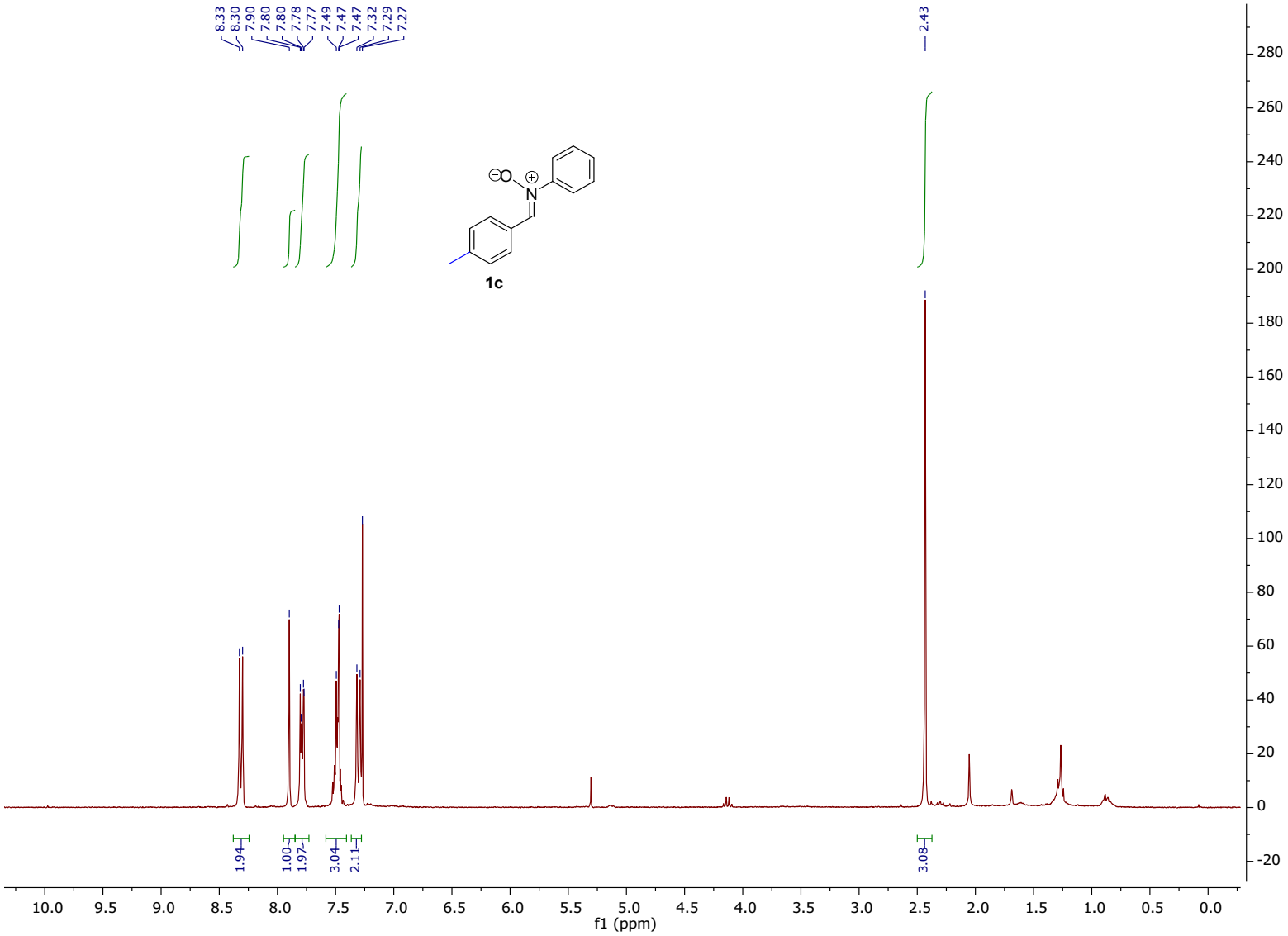
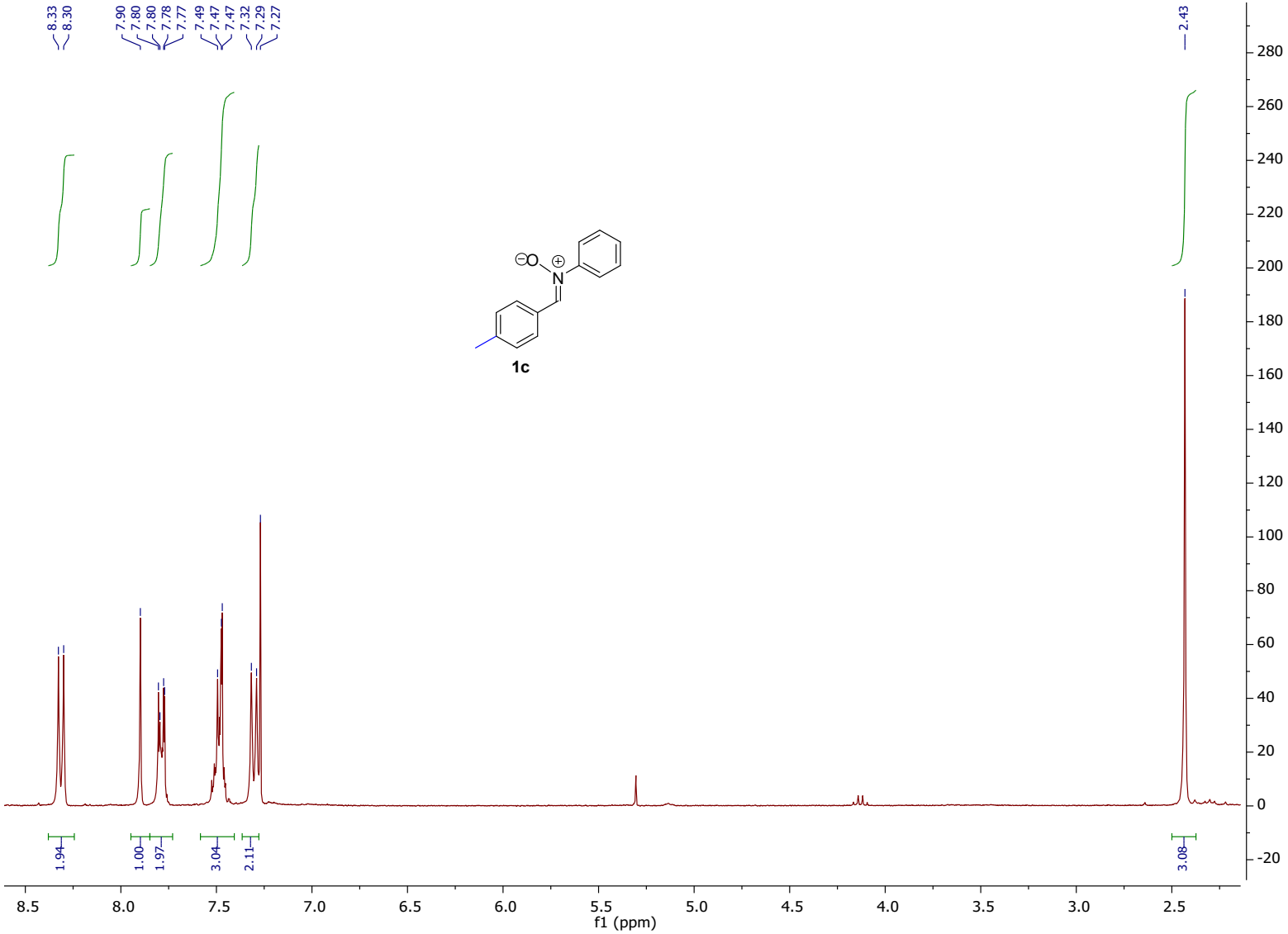
(*Z*)-*N*-phenyl-1-(*p*-tolyl)methanimine oxide (1c)

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7.80
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7.77
7.49
7.47
7.47
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7.27
2.43
1c
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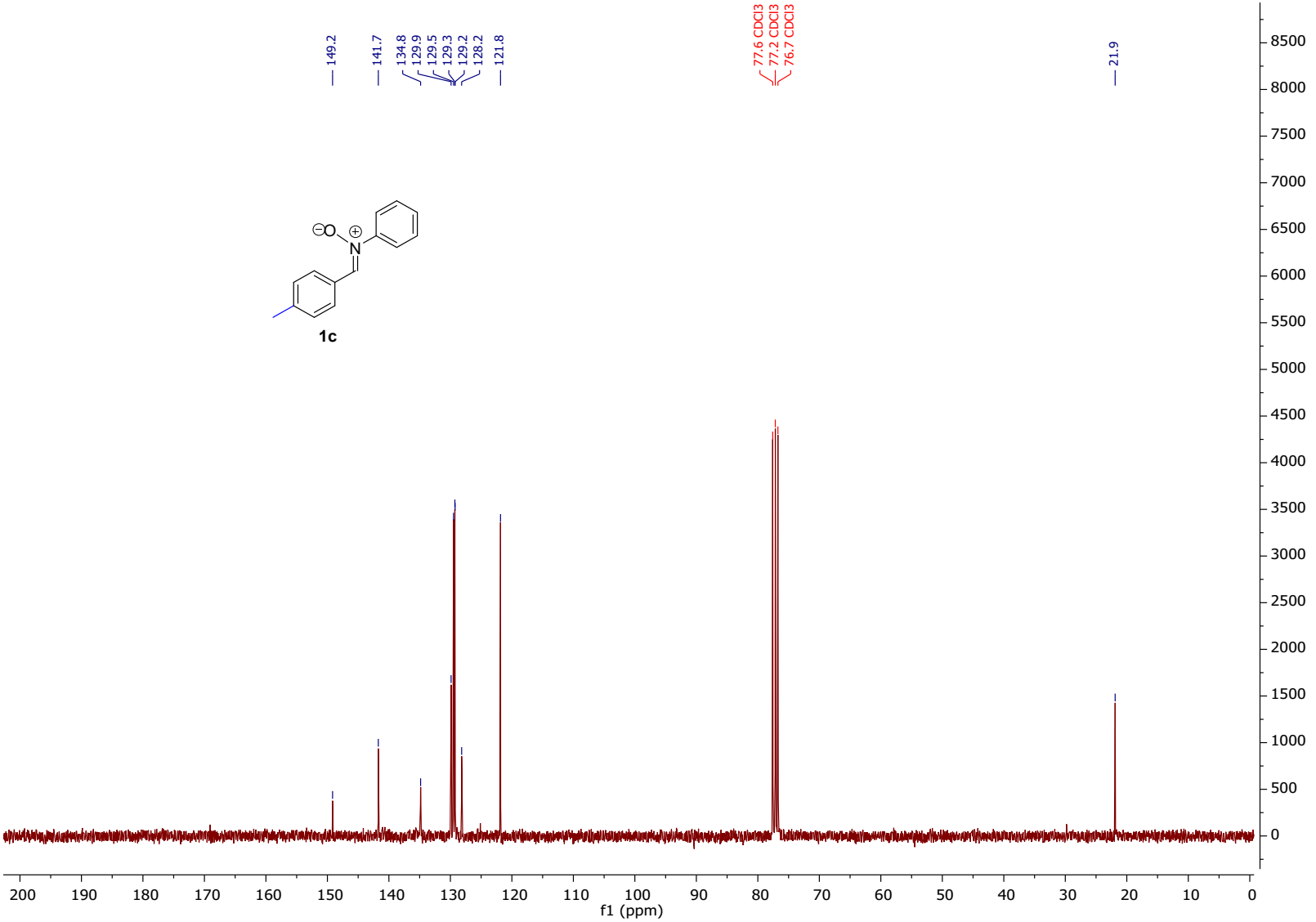
1.00
1.97
3.04
2.11
3.08
f1 (ppm)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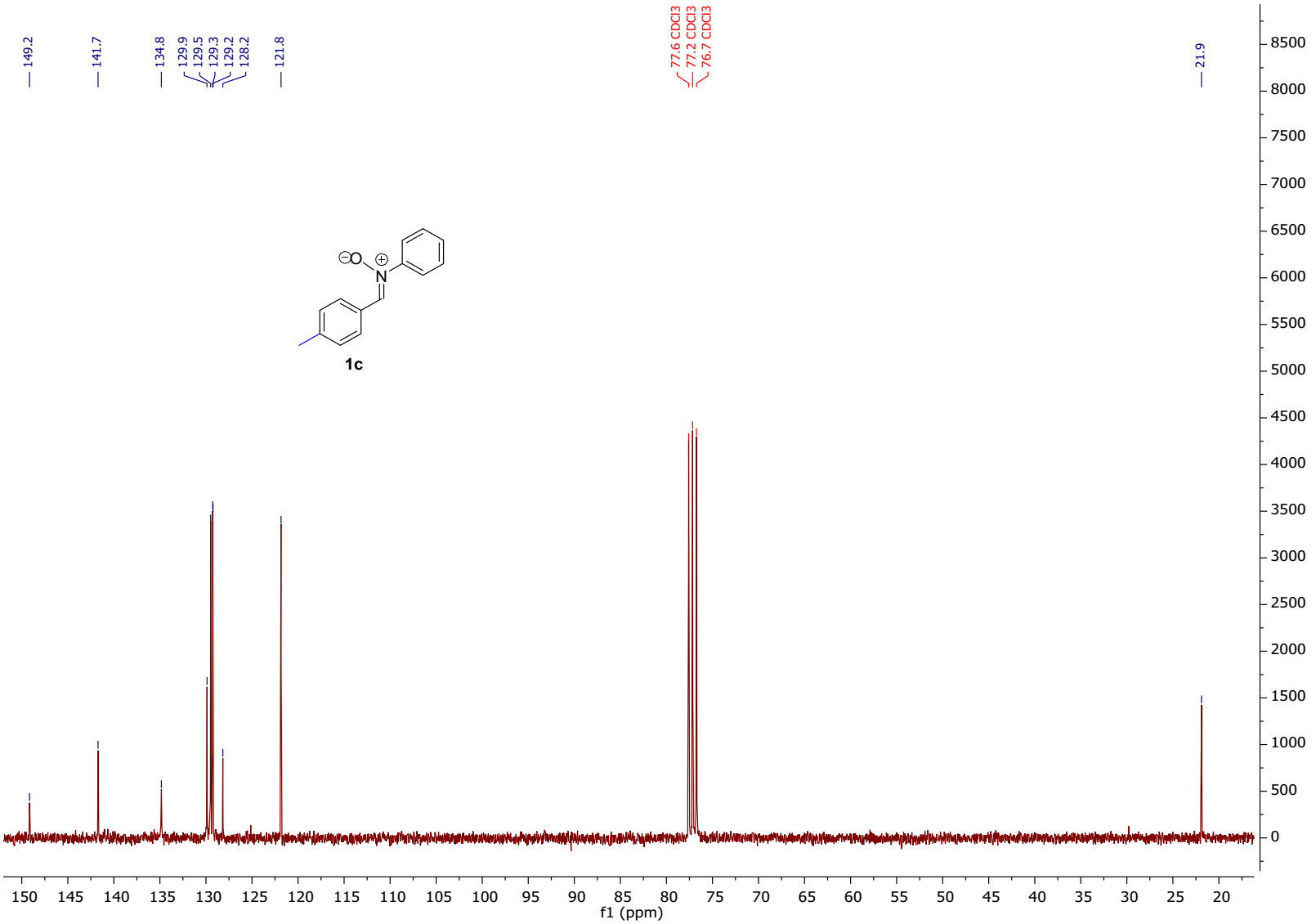
21.9
1c
f1 (ppm)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129.5
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129.2
128.2
121.8
77.6 CDCl3
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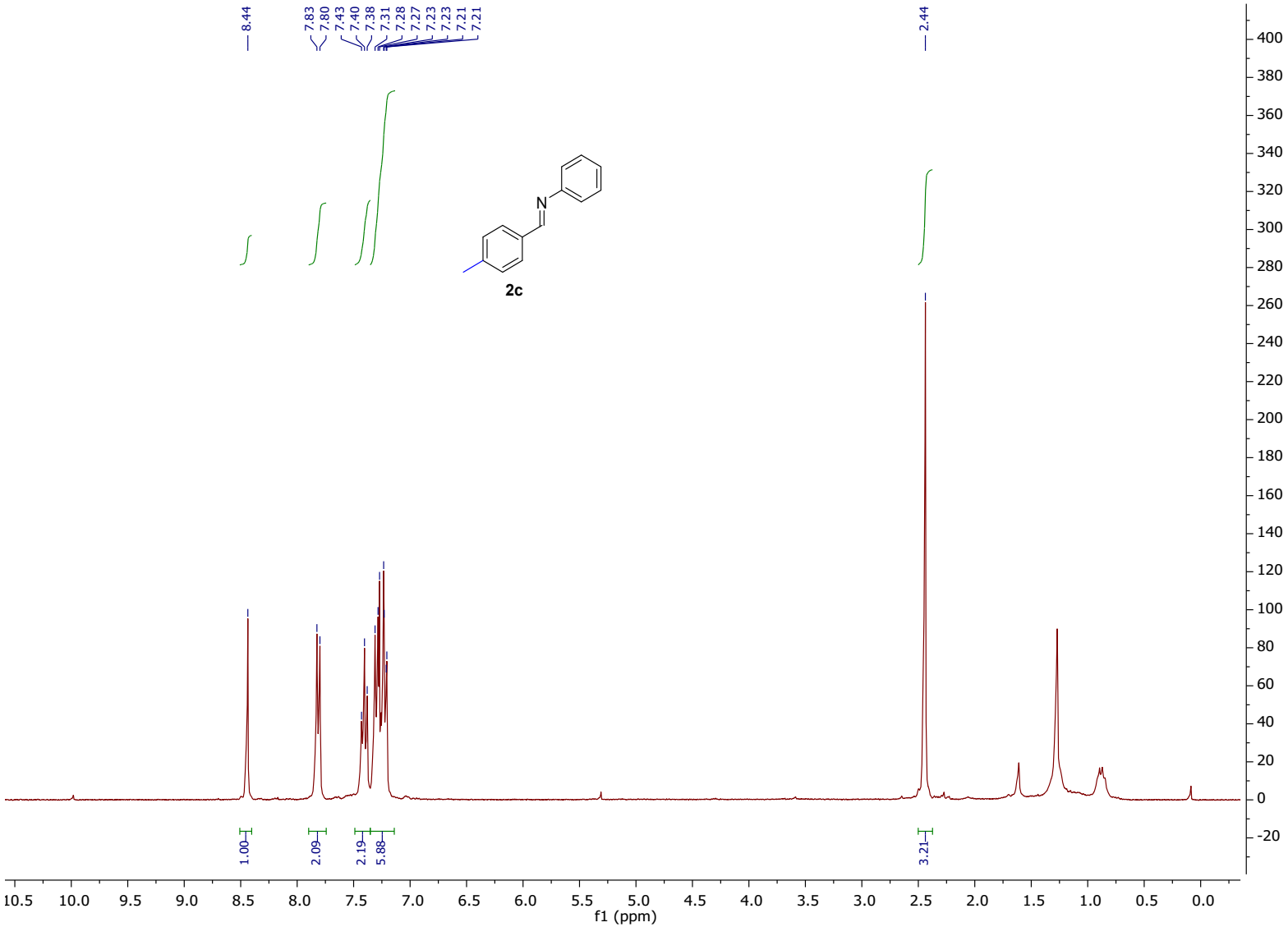
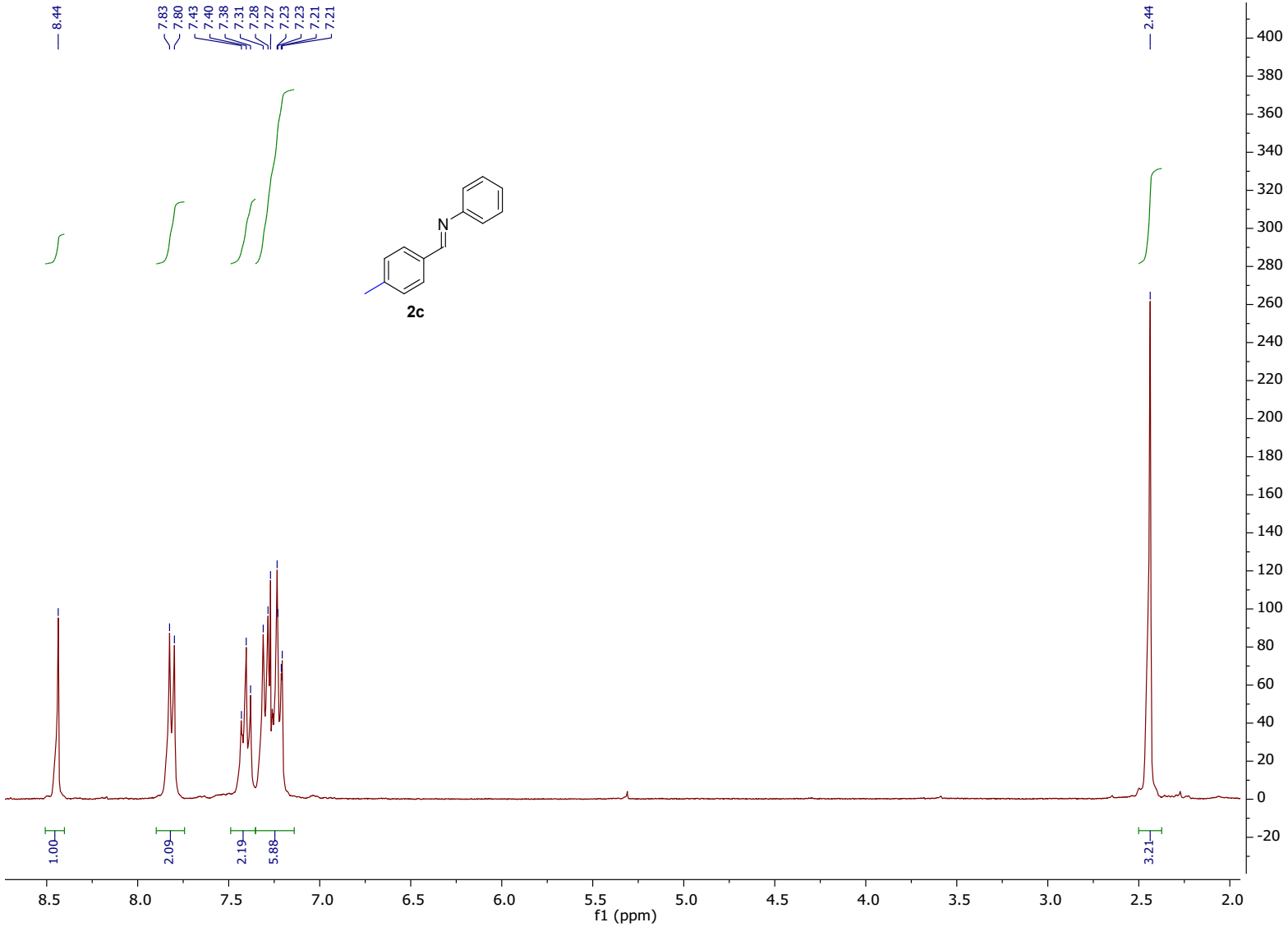
1c
f1 (ppm)

(*E*)-*N*-Phenyl-1-(p-tolyl)methanimine (2c)

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7.23
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7.21
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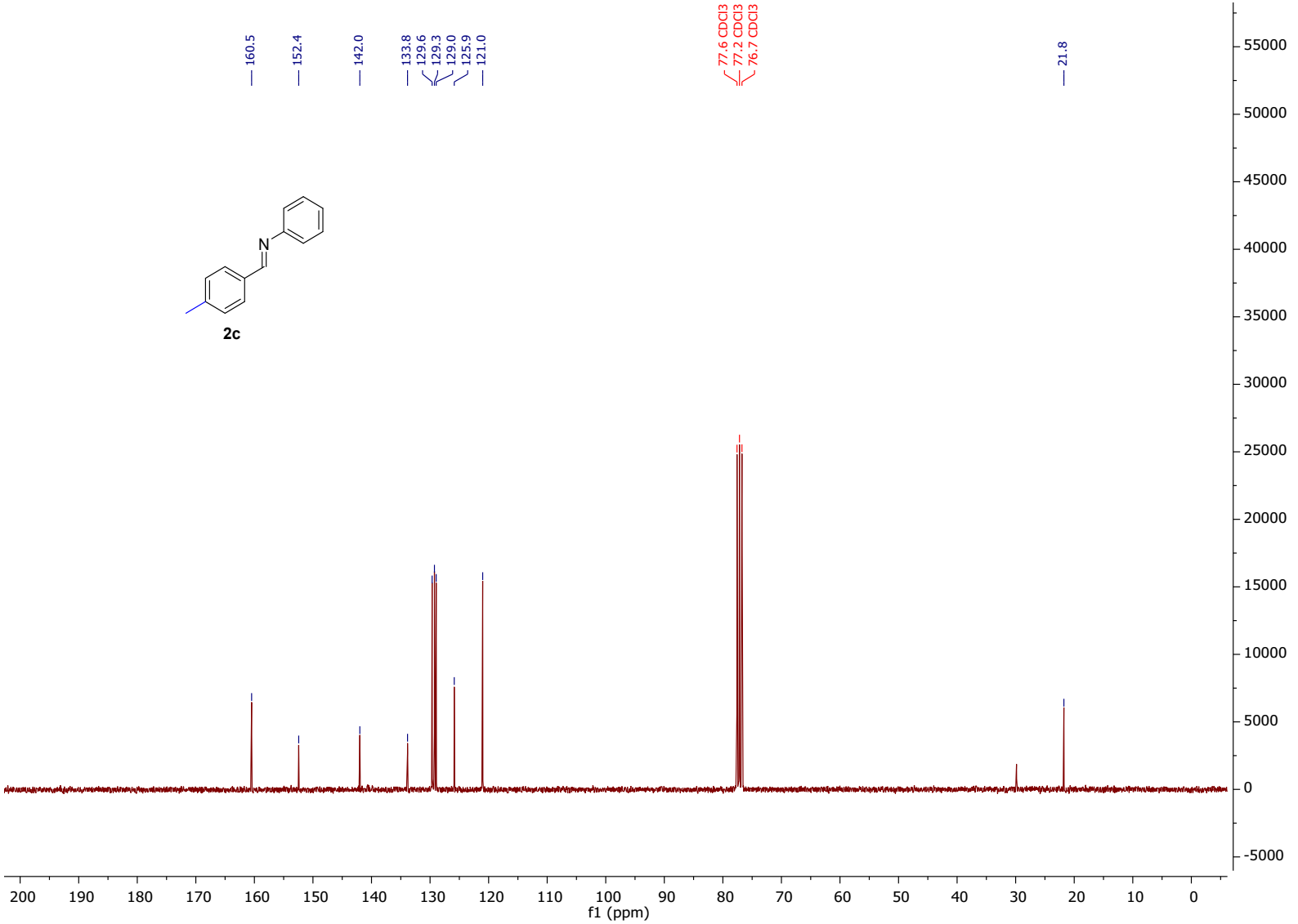
3.21
f1 (ppm)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129.0
125.9
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77.2 CDCl3
76.7 CDCl3
21.8
N
2c
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
200
190
180
170
160
150
140
130
120
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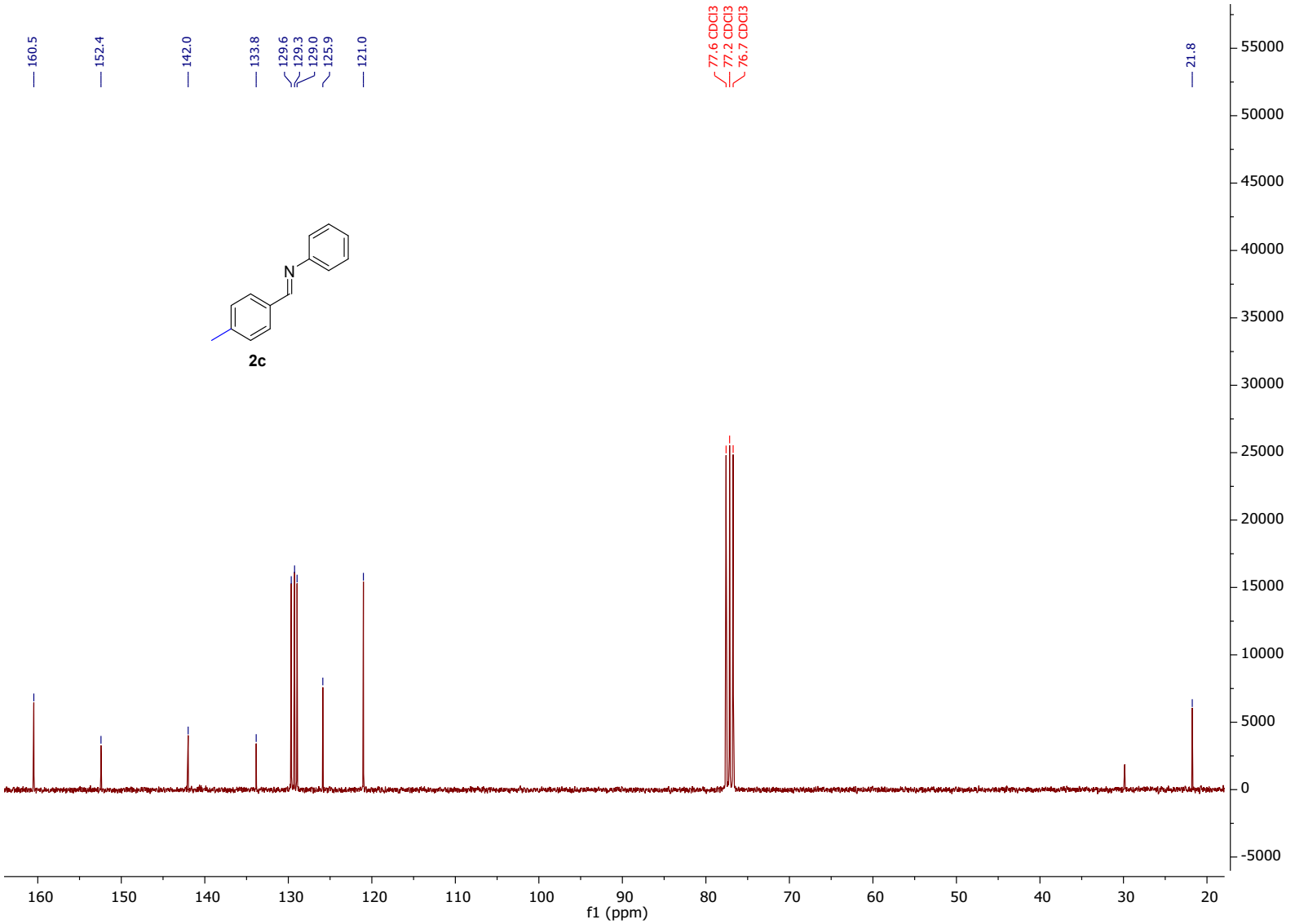
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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133.8
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125.9
121.0
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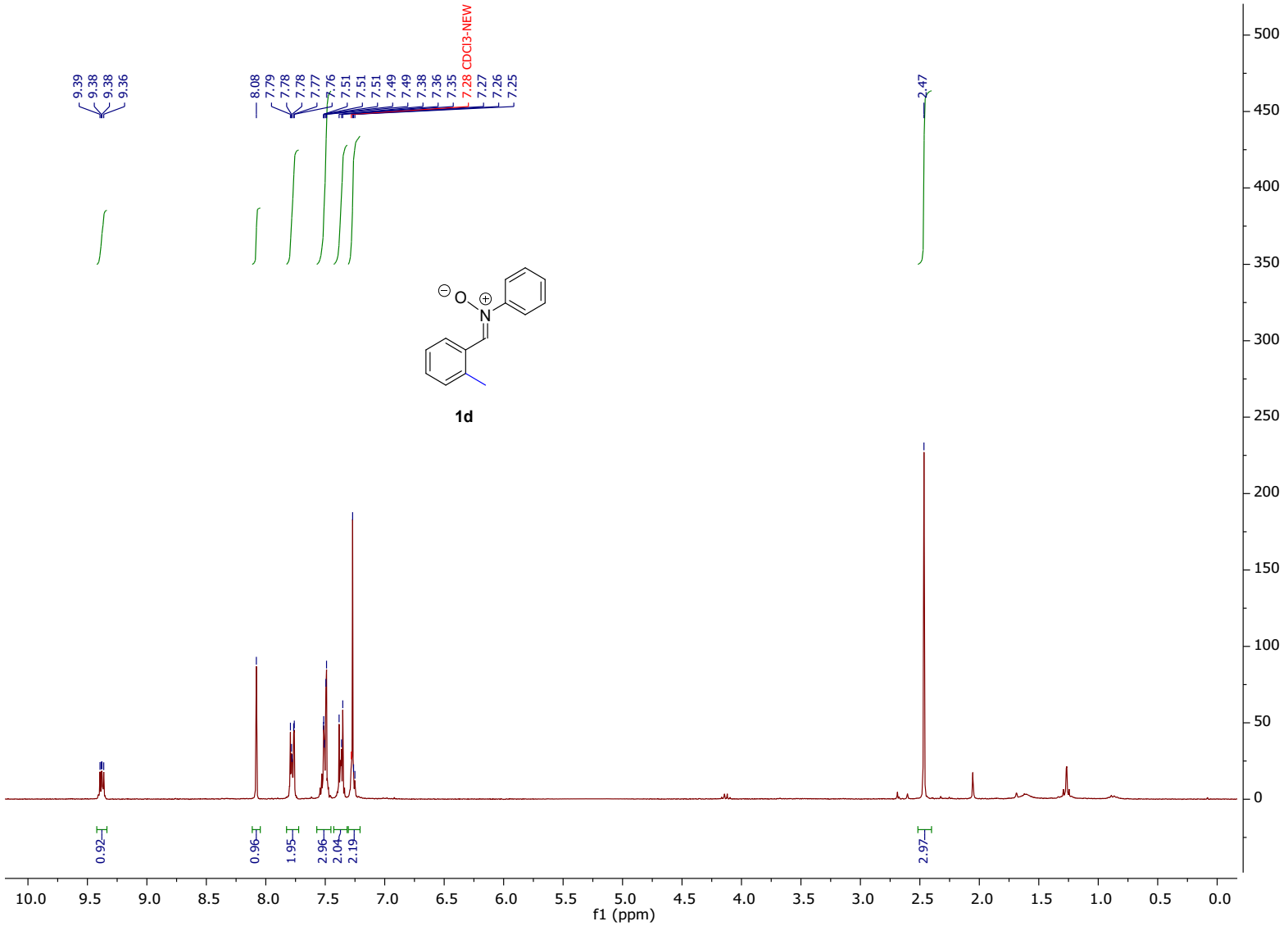
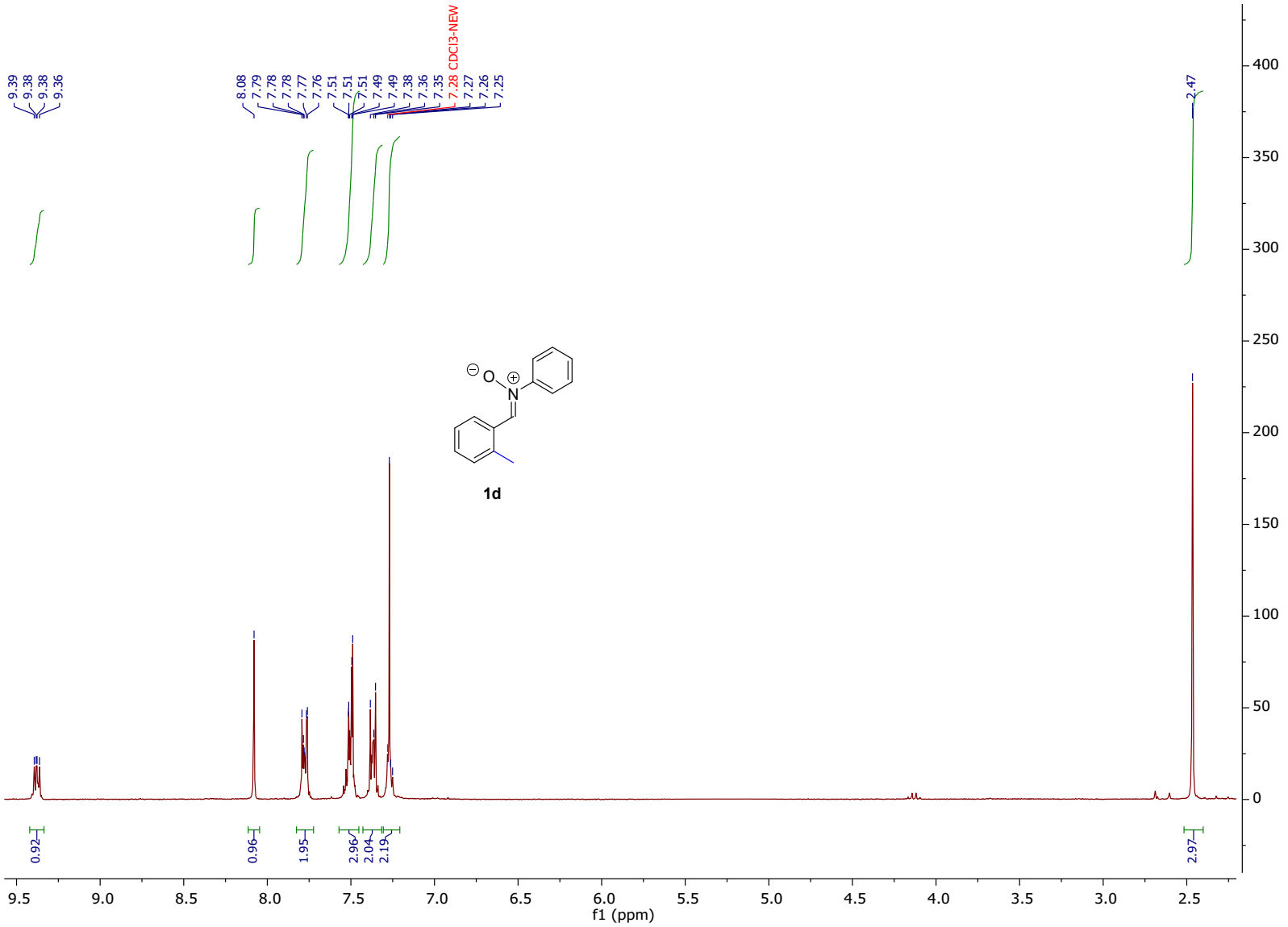
77.2 CDCl3
76.7 CDCl3
21.8
N
2c
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

(*Z*)-*N*-phenyl-1-(o-tolyl)methanimine oxide (1d)

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9.38
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8.08
7.79
7.78
7.78
7.77
7.76
7.51
7.51
7.51
7.49
7.49
7.38
7.36
7.35
7.28 CDCl3-NEW
7.27
7.26
7.25
2.47
1d
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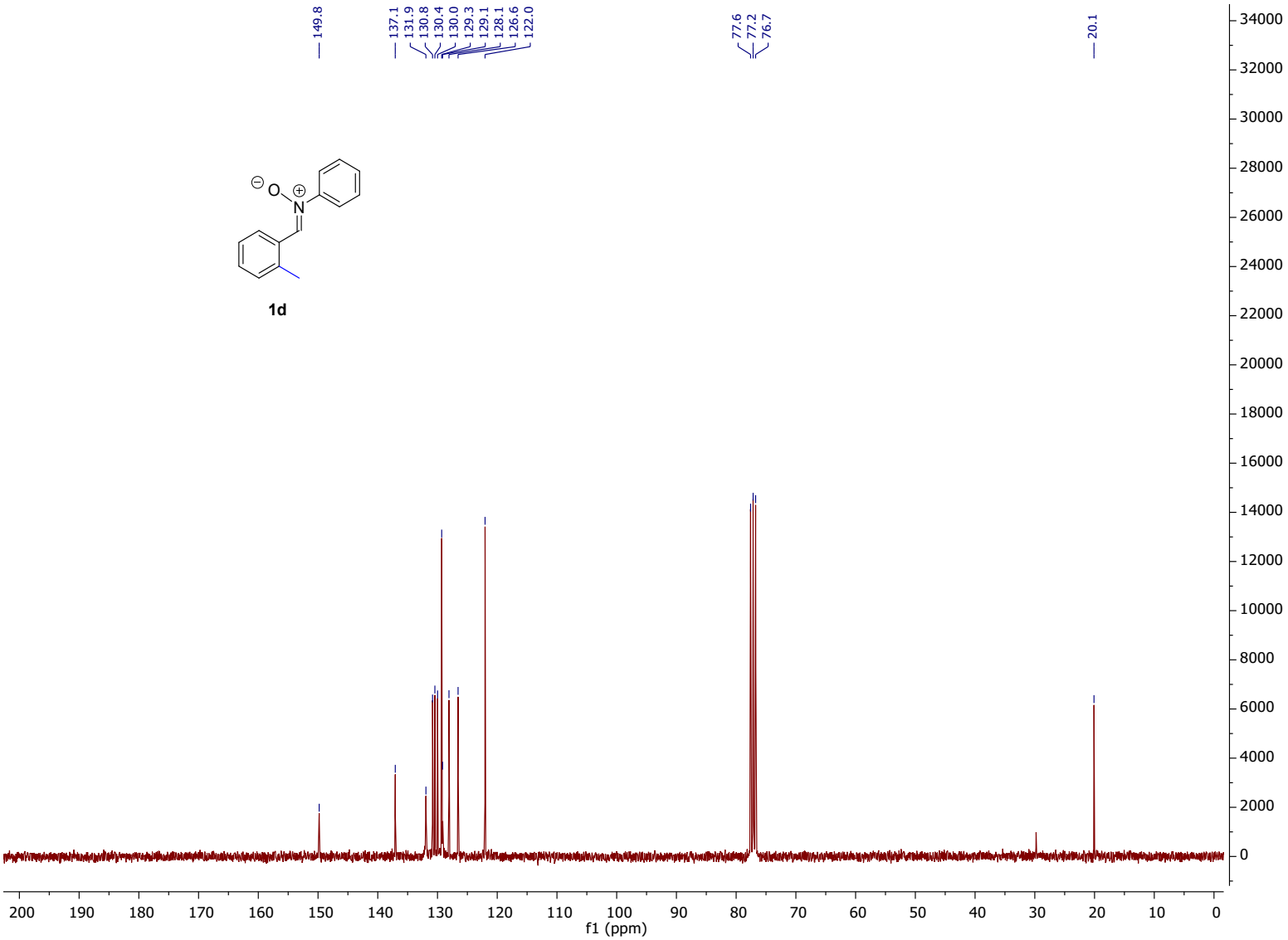
0.96
1.95
2.96
2.04
2.19
2.97
f1 (ppm)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130.4
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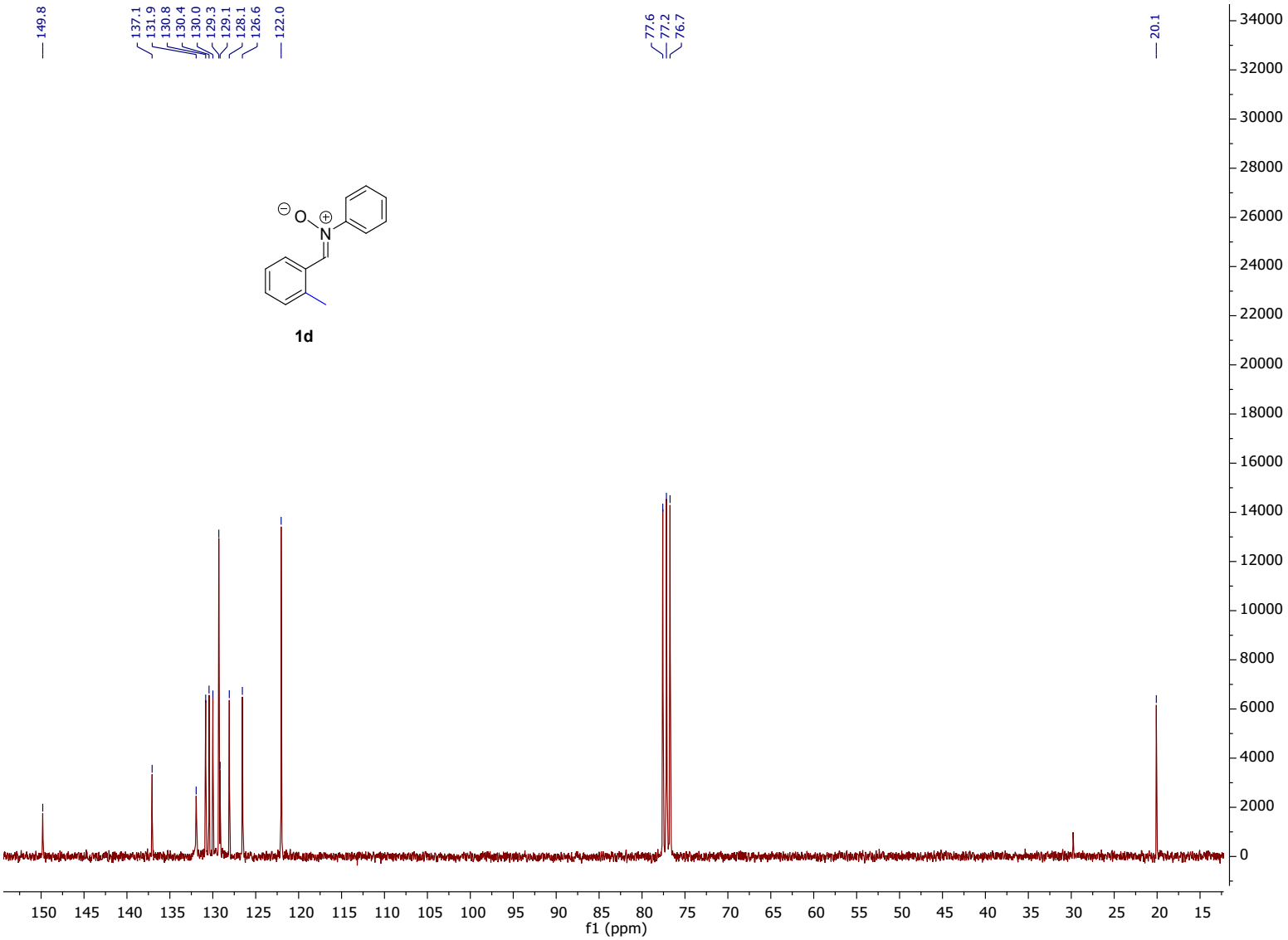
20.1
1d
f1 (ppm)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131.9
130.8
130.4
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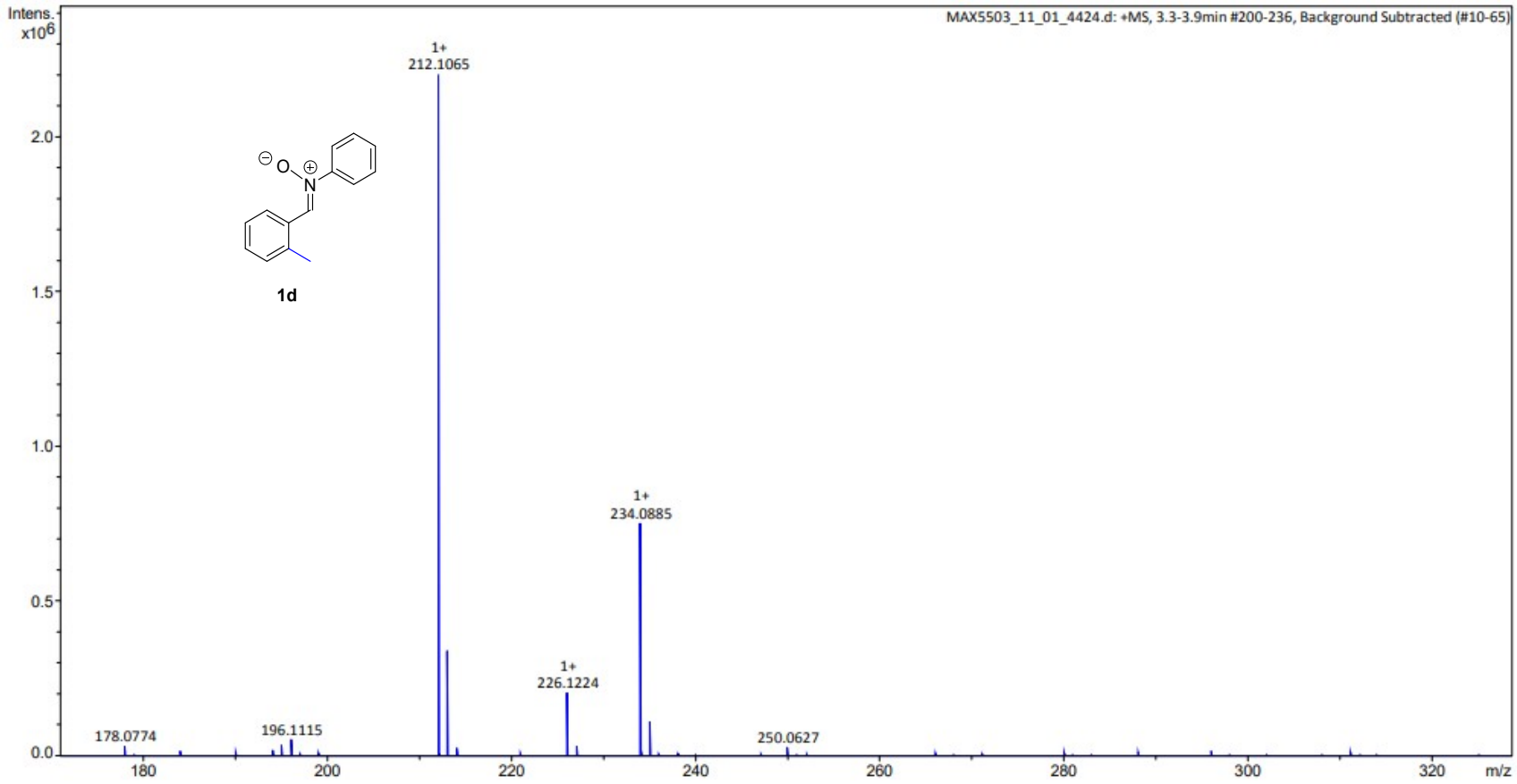
77.6
77.2
76.7
20.1
1d
f1 (ppm)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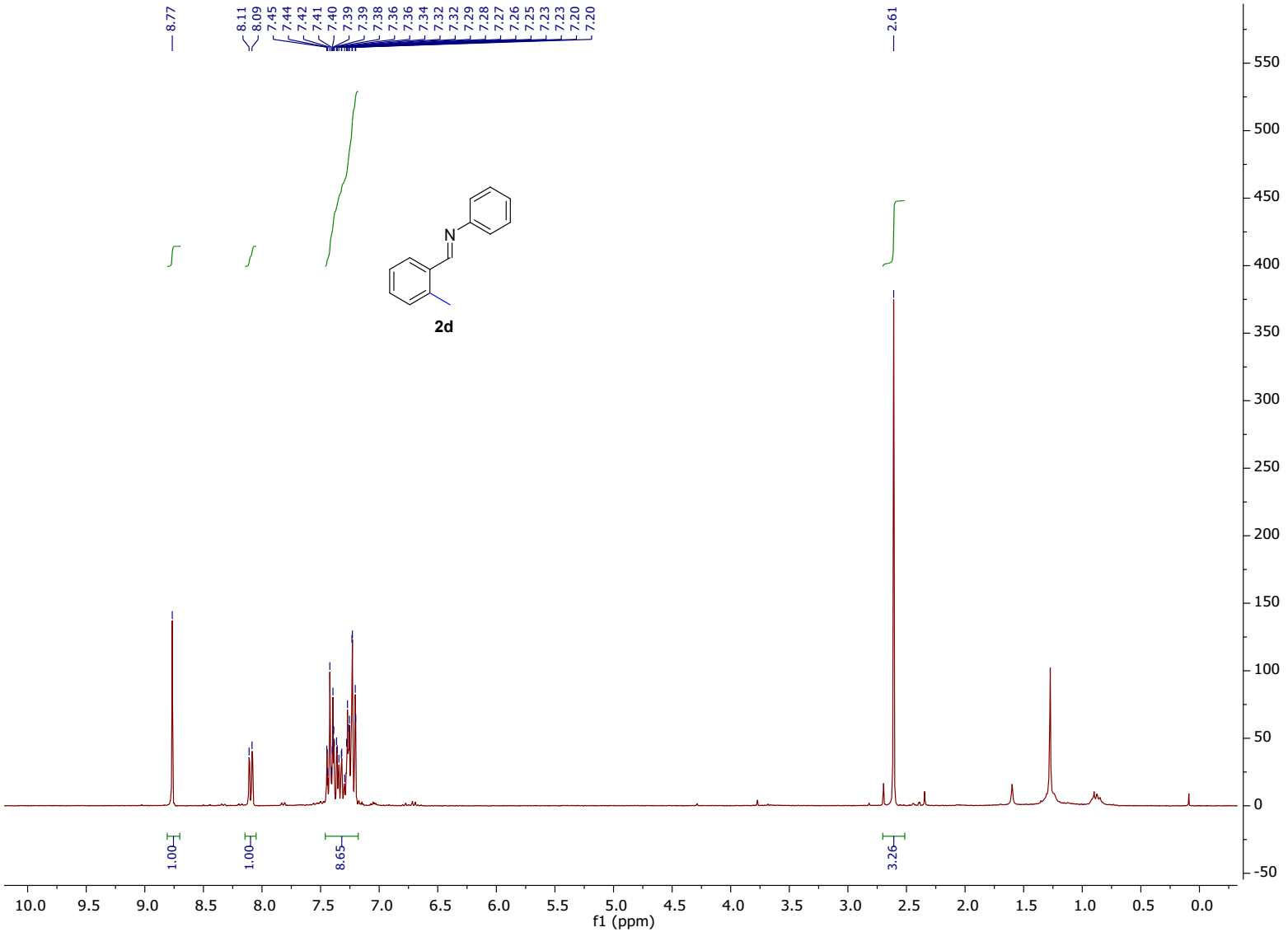
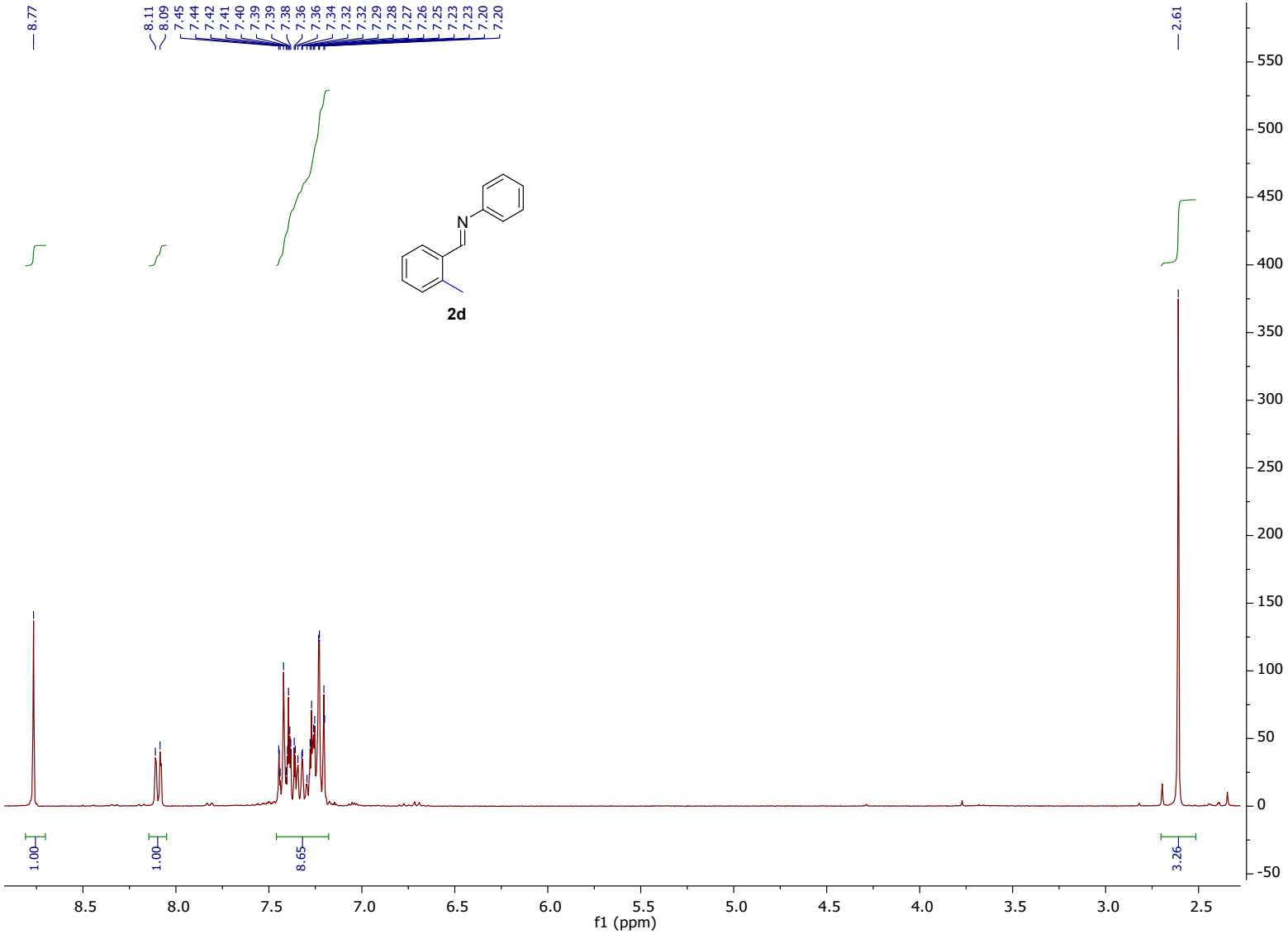
1.0
0.5
0.0
1+
212.1065
1+
234.0885
1+
226.1224
178.0774
196.1115
250.0627
180
200
220
240
260
280
300
320
m/z
1d

(*E*)-*N*-phenyl-1-(o-tolyl)methanimine (2d)

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7.28
7.27
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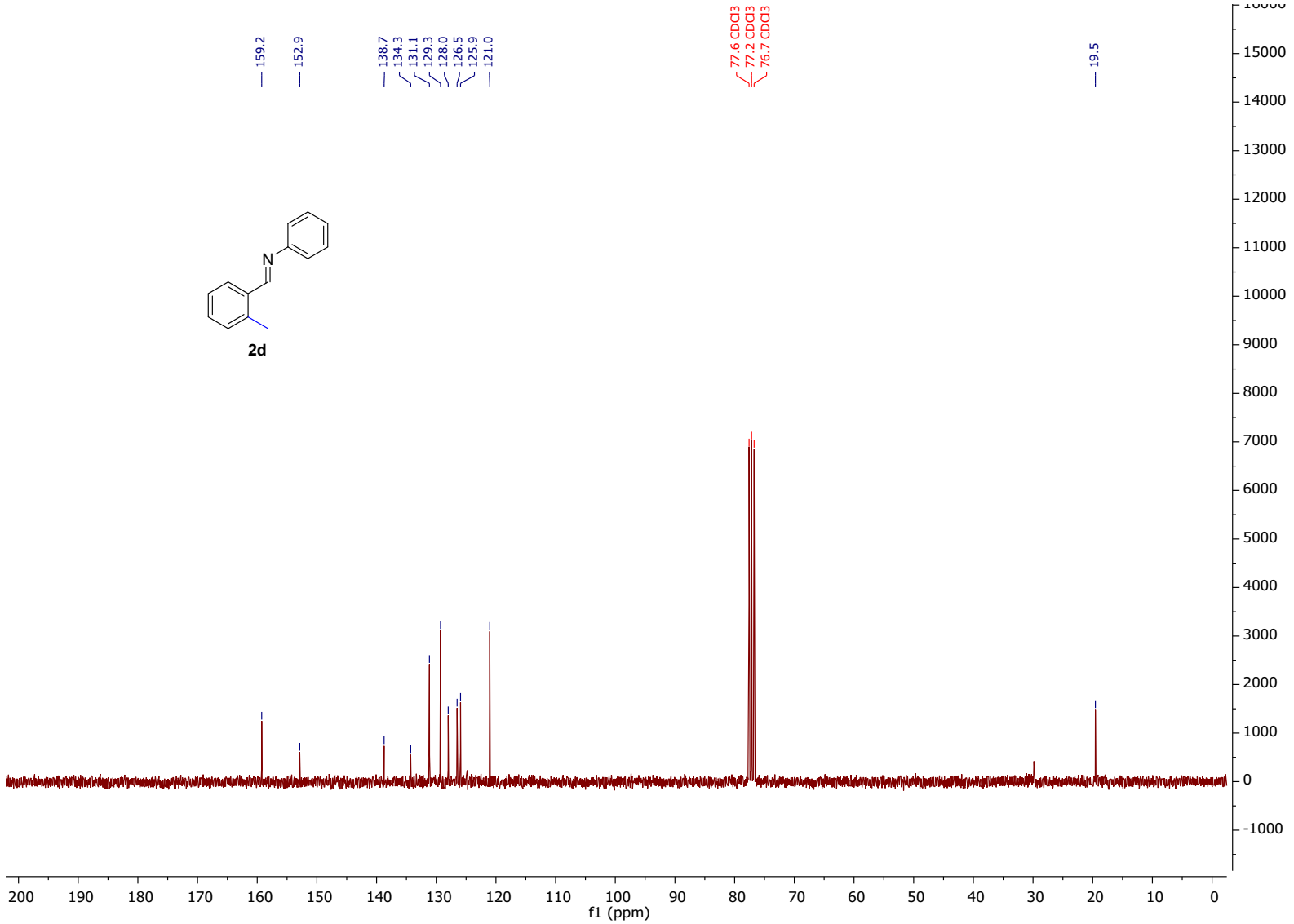
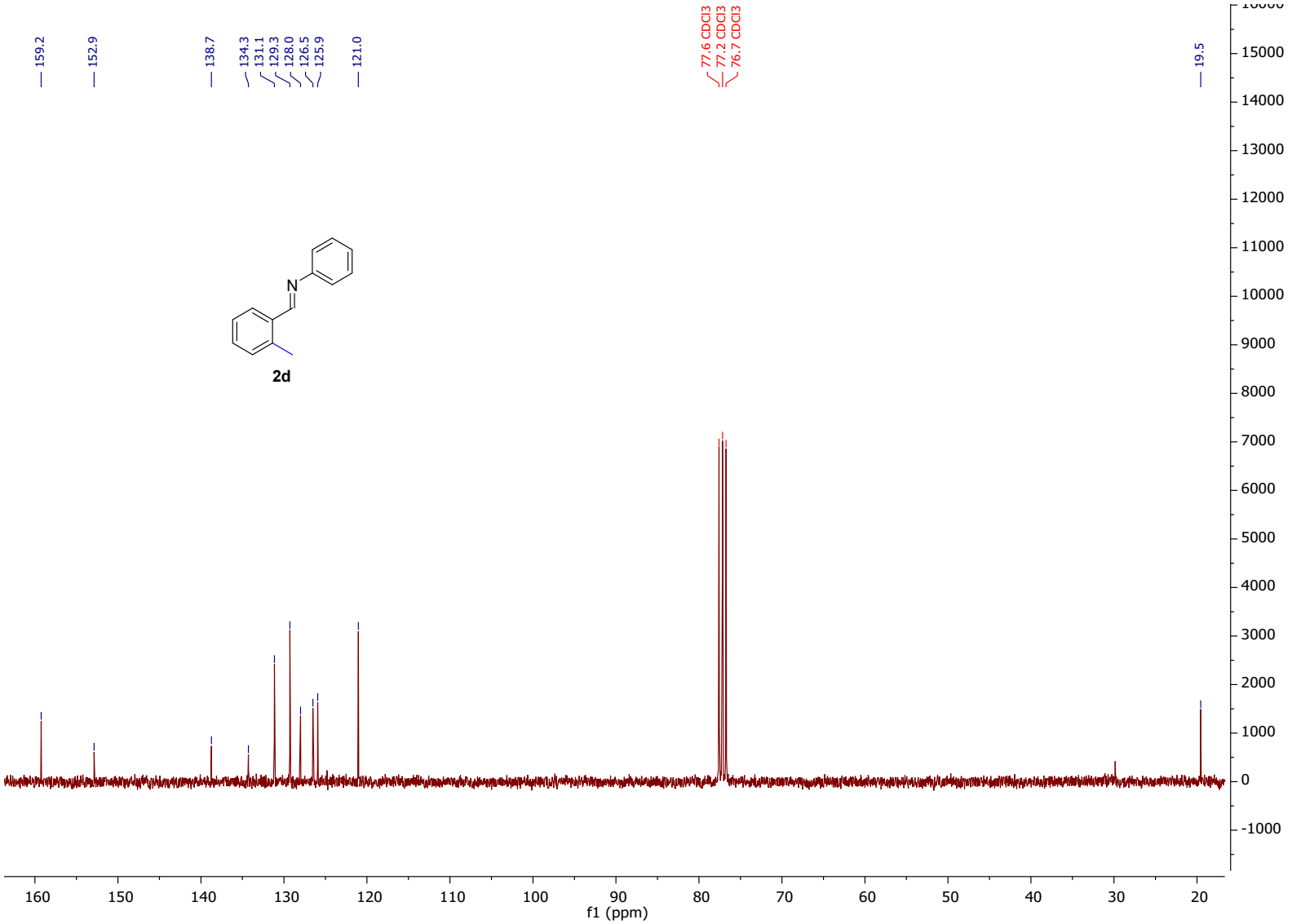
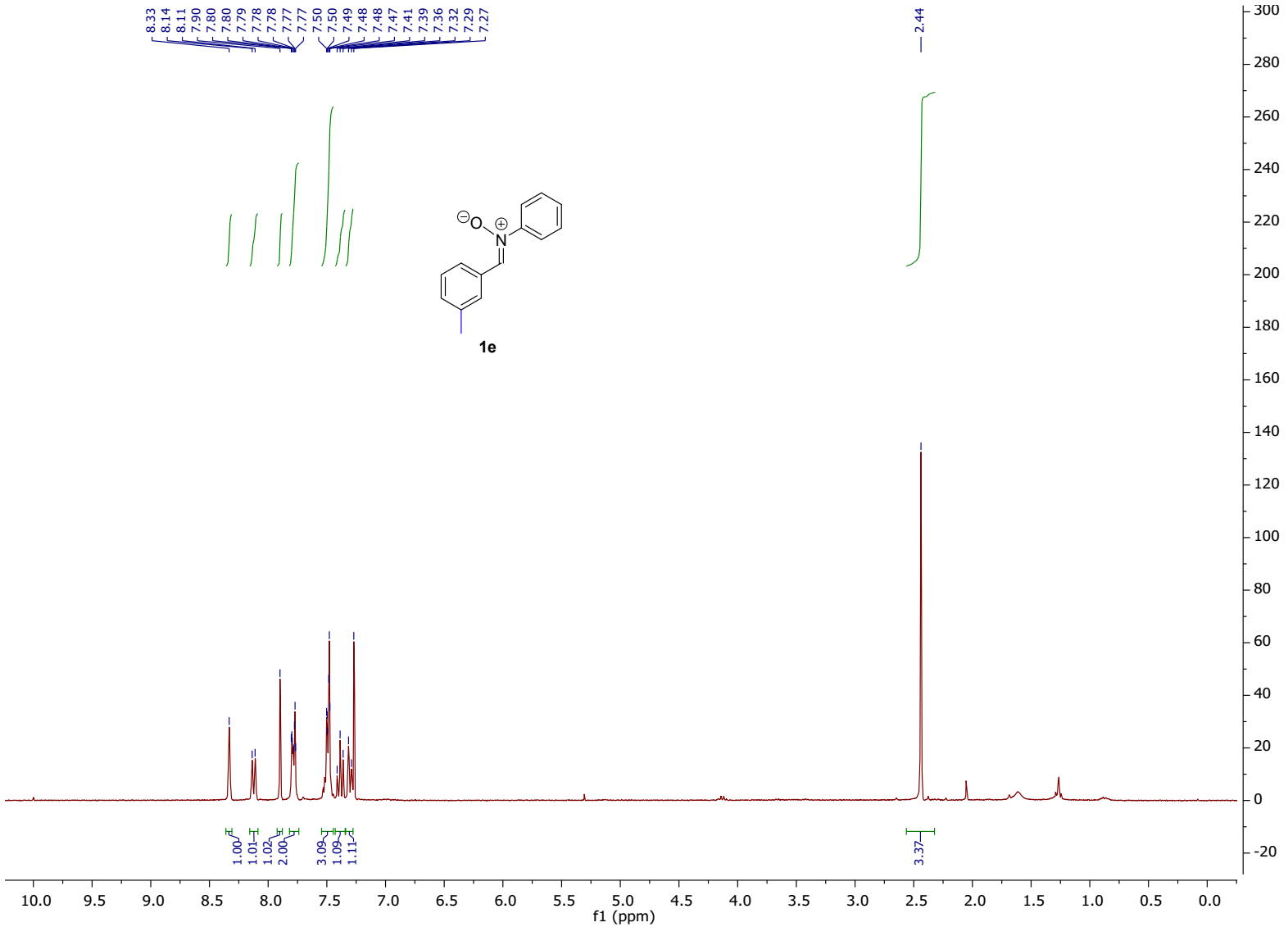
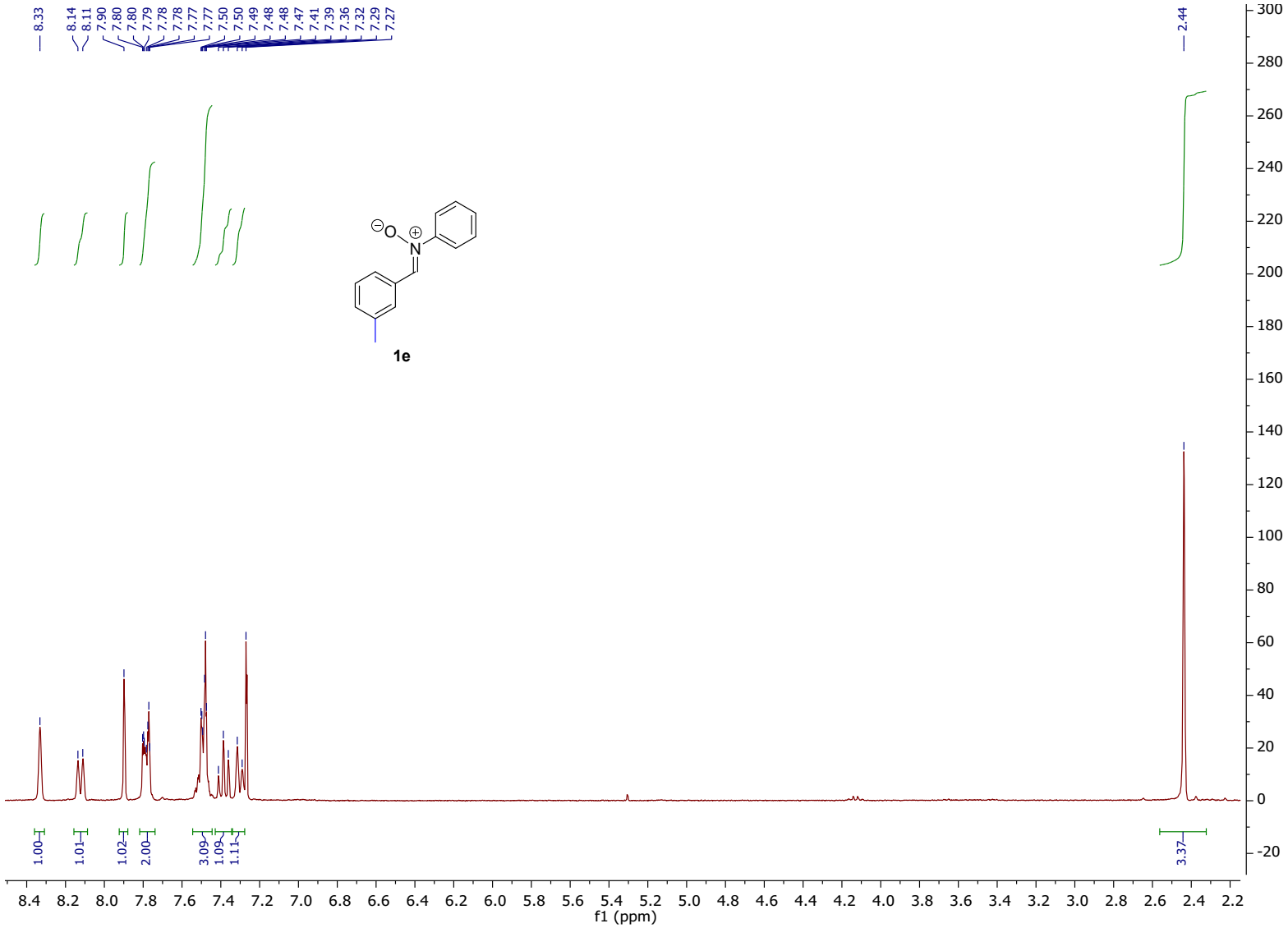
7.25
7.23
7.23
7.20
7.20
2.61
N
2d
1.00
1.00
8.65
3.26
f1 (ppm)

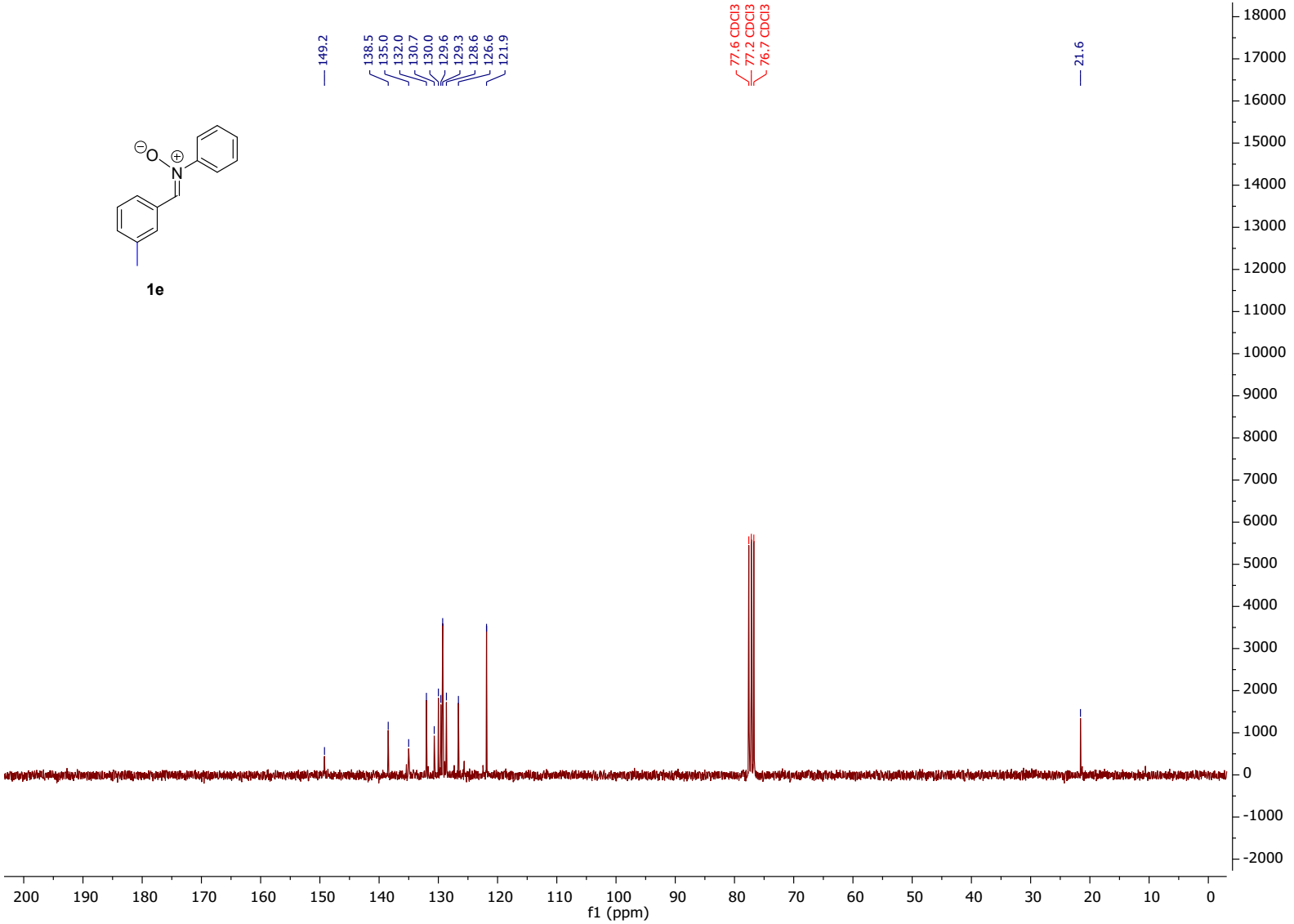

159.2
152.9
138.7
134.3
131.1
129.3
128.0
126.5
125.9
121.0
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
19.5
N
2d
f1 (ppm)

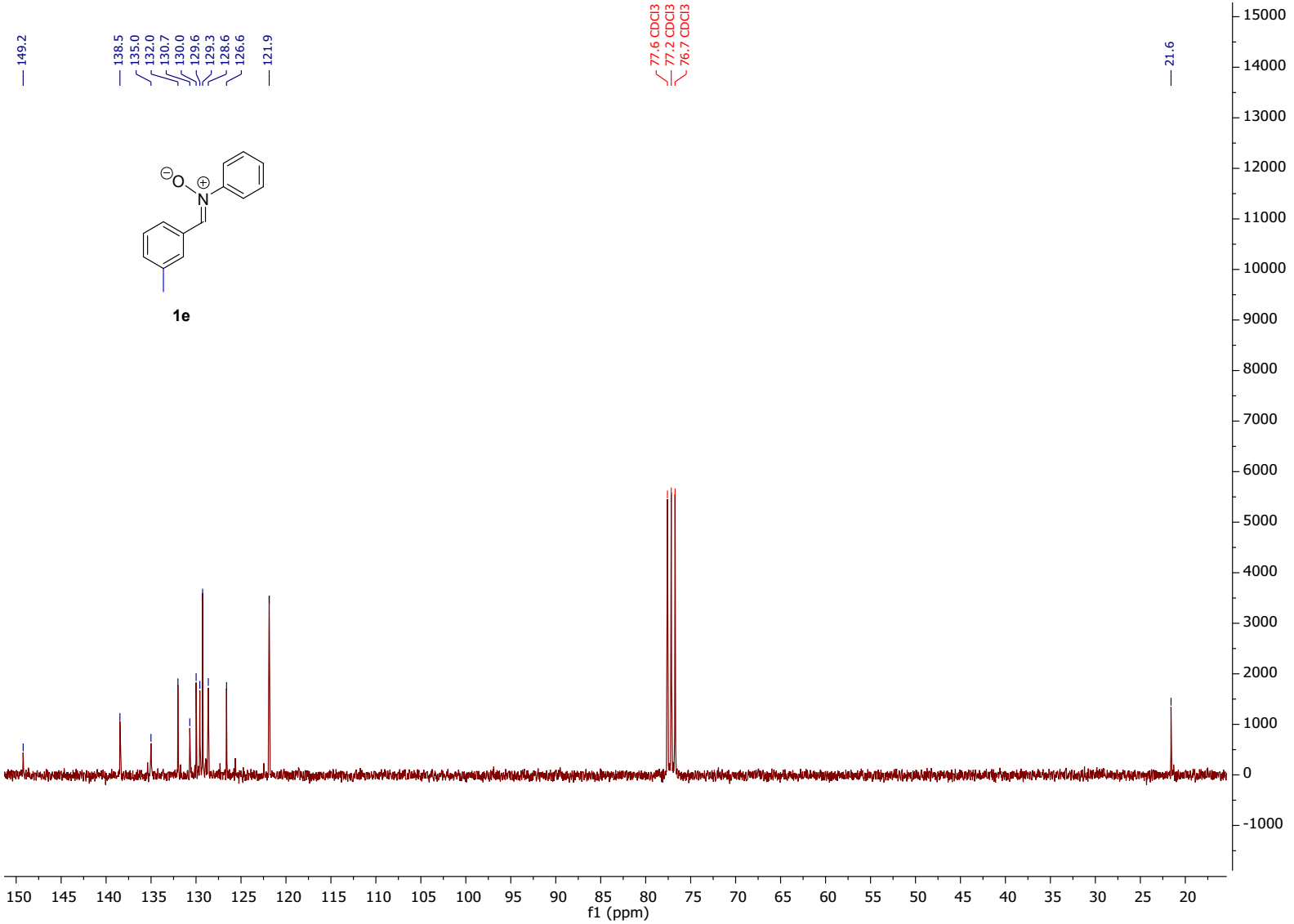

159.2
152.9
138.7
134.3
131.1
129.3
128.0
126.5
125.9
121.0
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
19.5
N
2d
f1 (ppm)

(*Z*)-*N*-phenyl-1-(m-tolyl)methanimine oxide (1e)

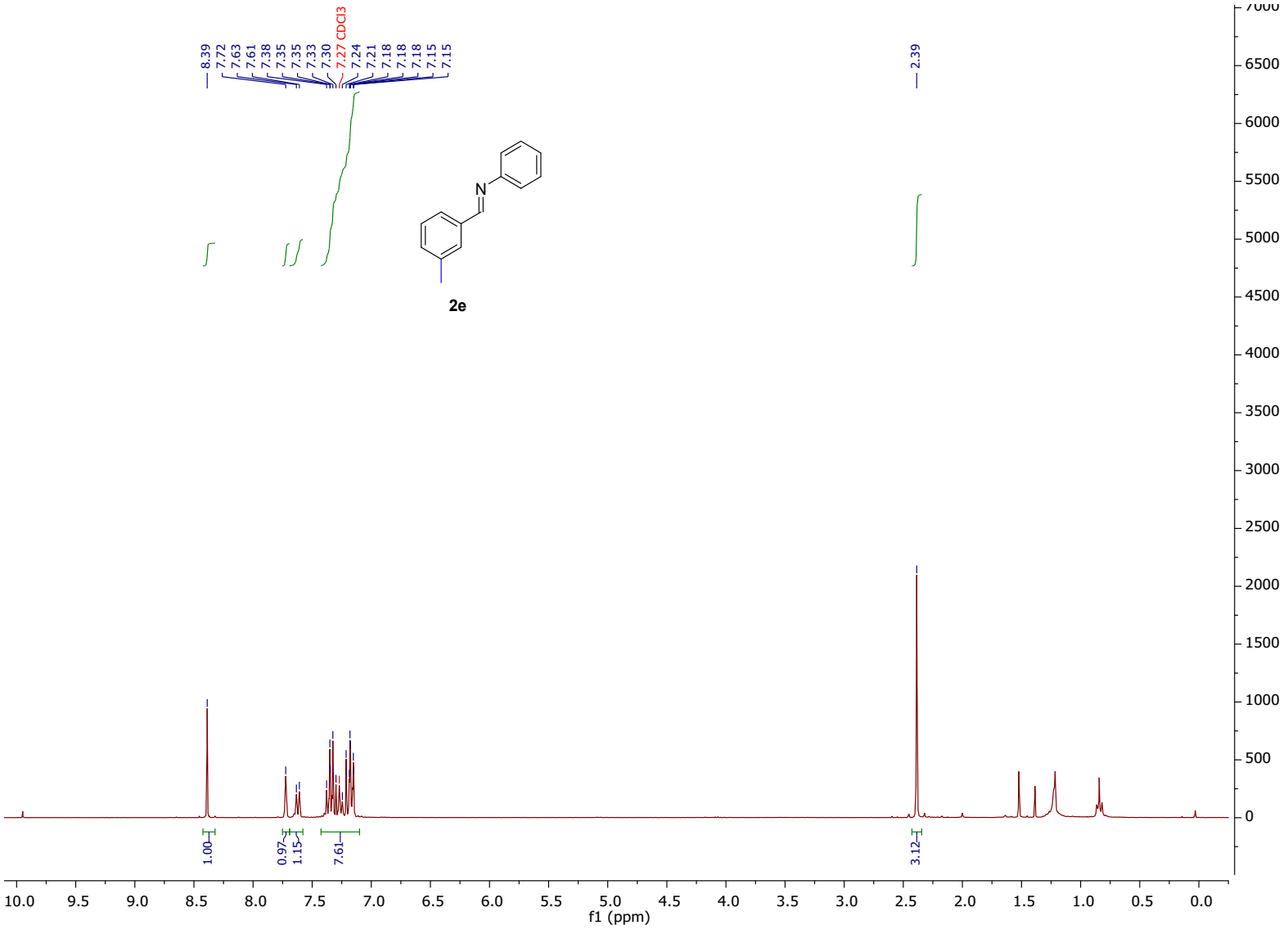


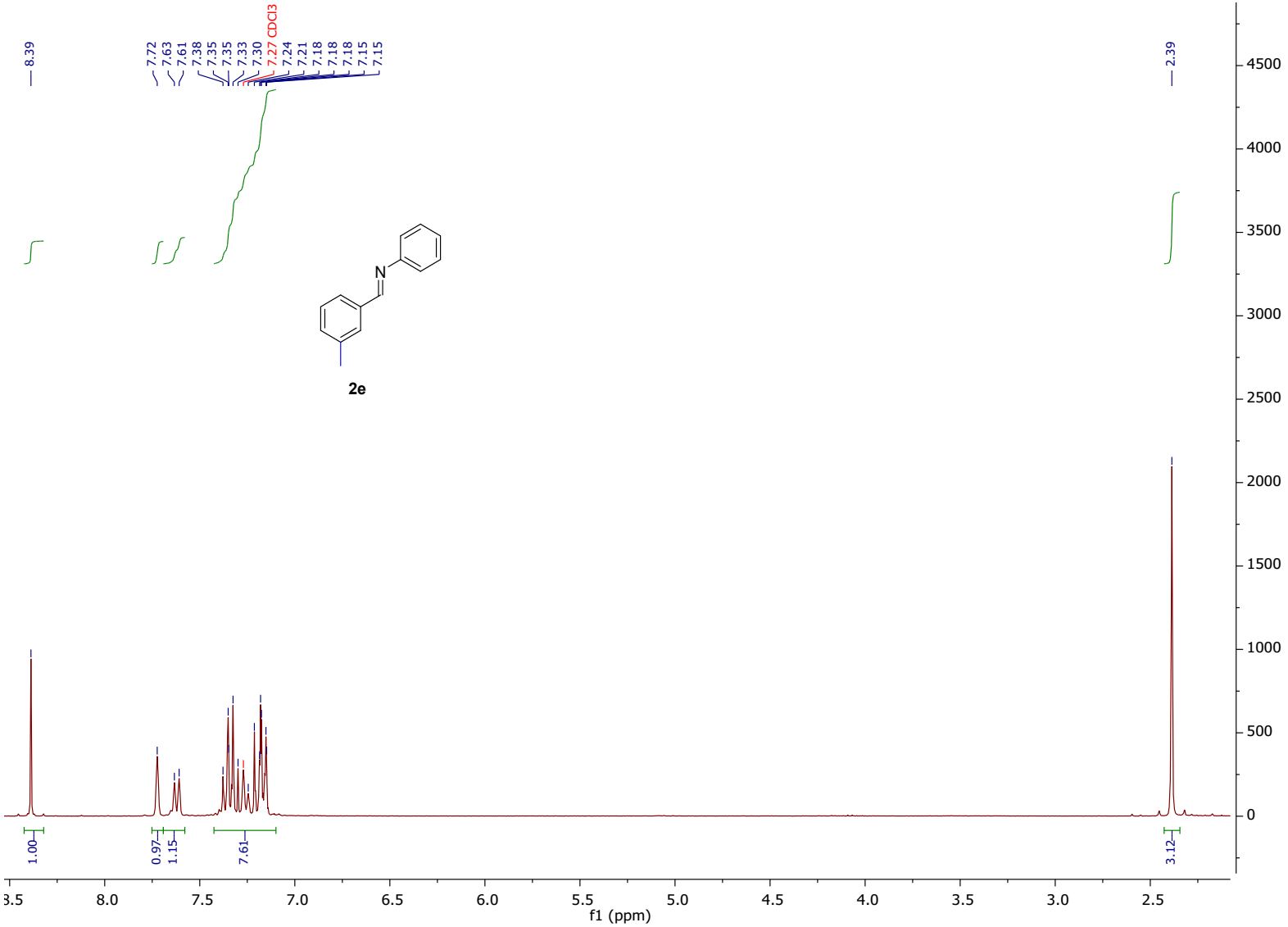

8.33
8.14
8.11
7.90
7.80
7.80
7.79
7.78
7.78
7.77
7.77
7.50
7.50
7.49
7.48
7.48
7.47
7.41
7.39
7.36
7.32
7.29
7.27
2.44
1e
1.00
1.01
1.02
2.00
3.09
1.09
1.11
3.37
f1 (ppm)

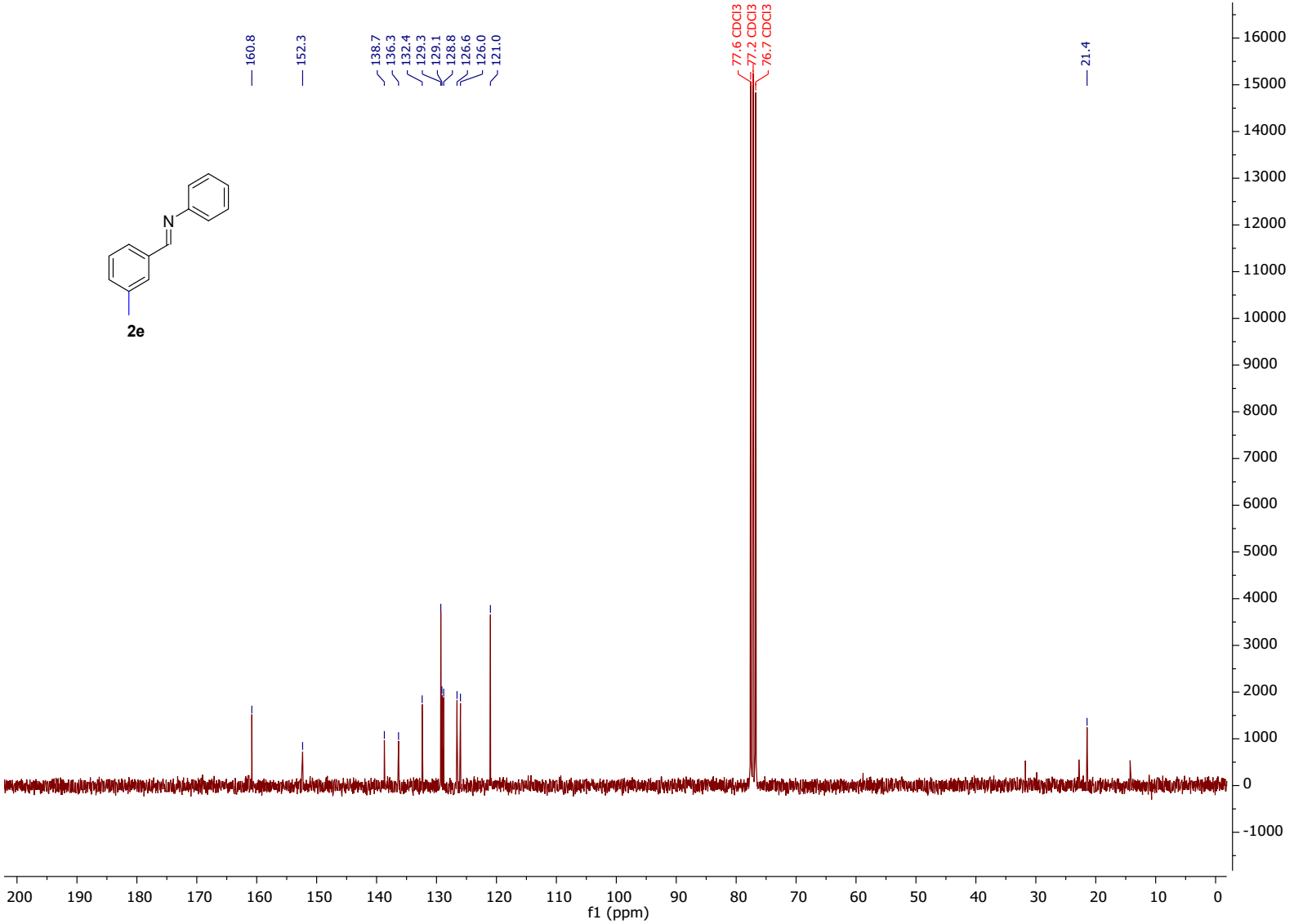

149.2
138.5
135.0
132.0
130.7
130.0
129.6
129.3
128.6
126.6
121.9
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
21.6
1e
f1 (ppm)

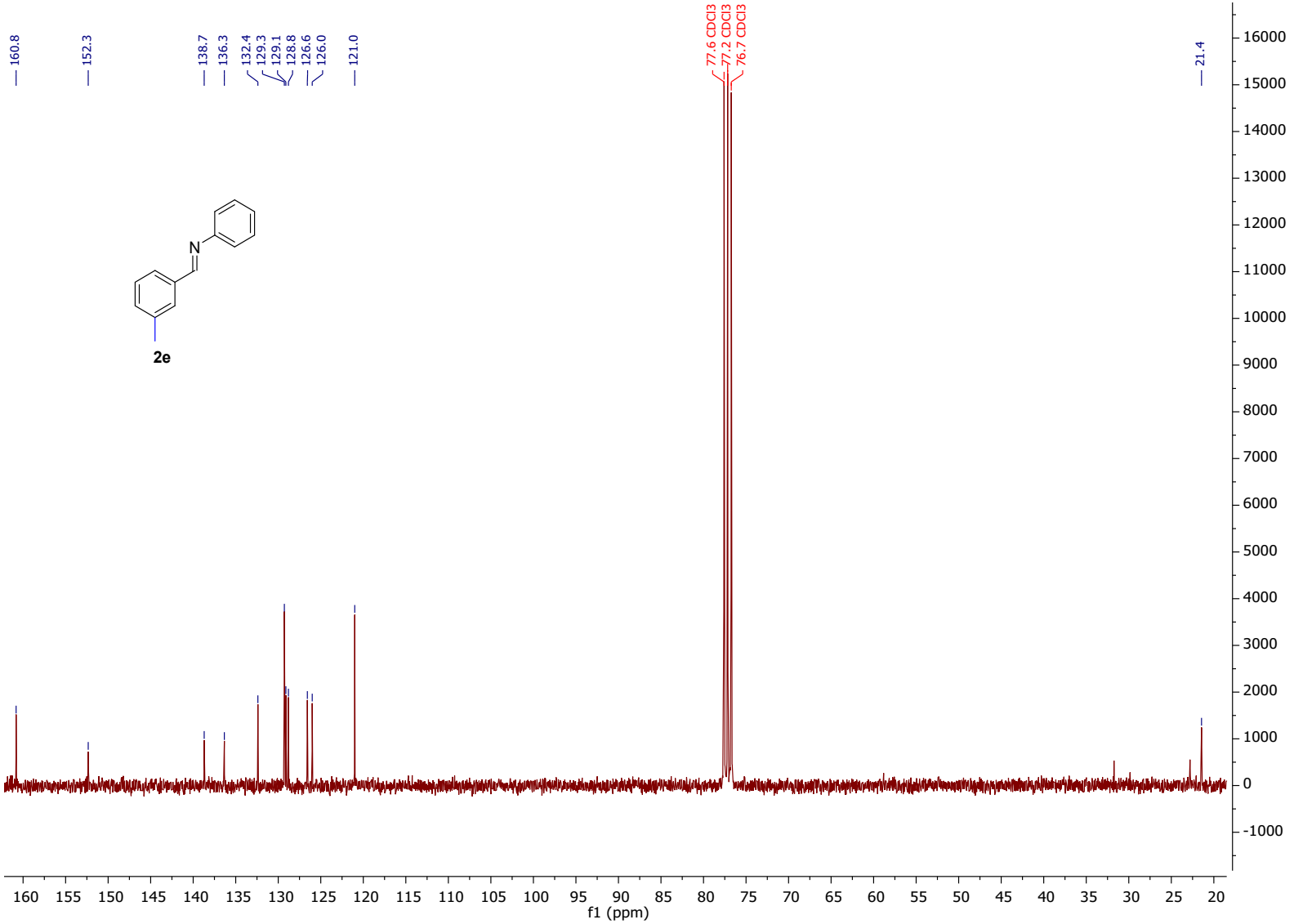

149.2
138.5
135.0
132.0
130.7
130.0
129.6
129.3
128.6
126.6
121.9
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
21.6
1e
f1 (ppm)

(*E*)-*N*-Phenyl-1-(m-tolyl)methanimine (2e)

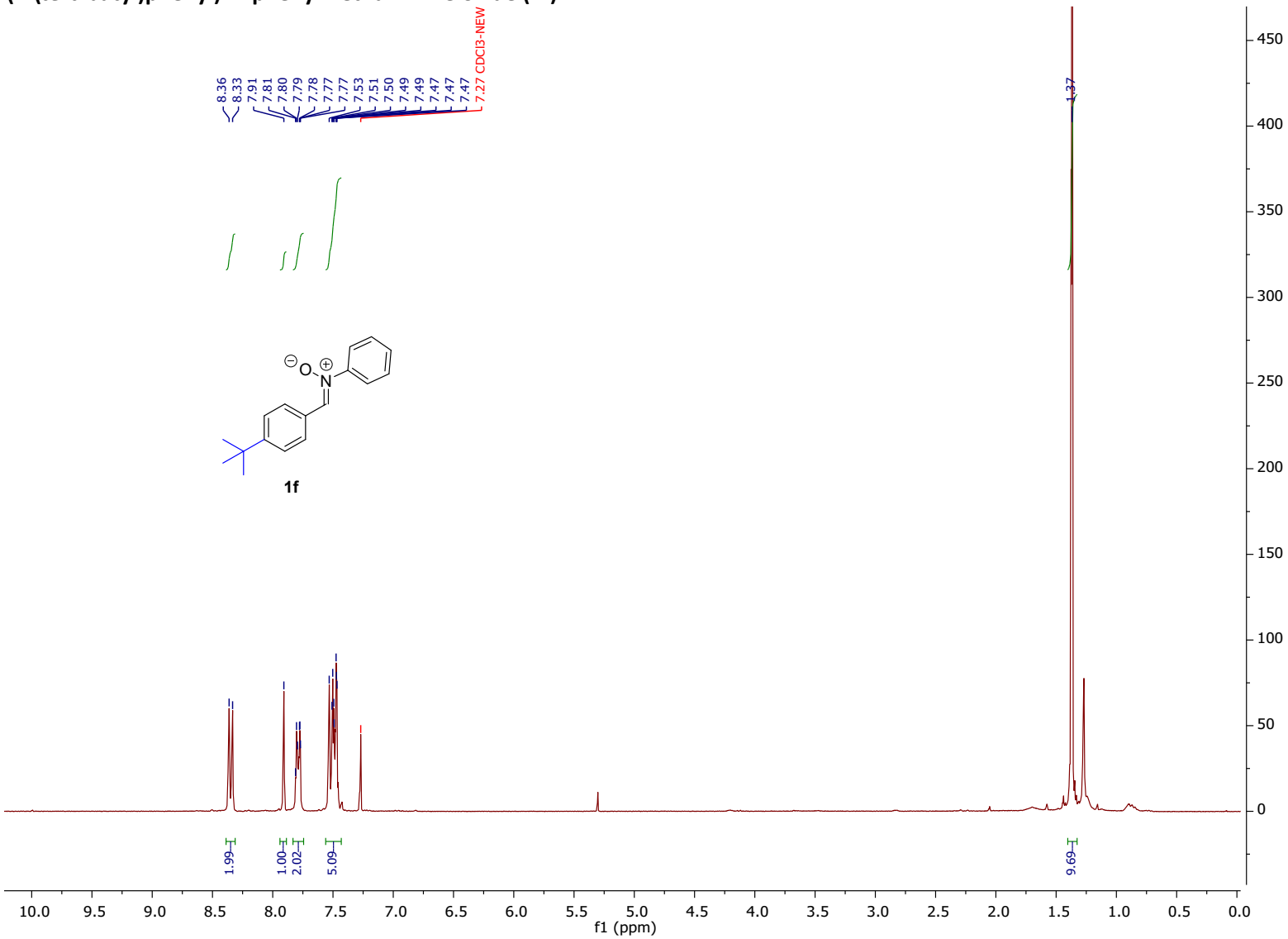


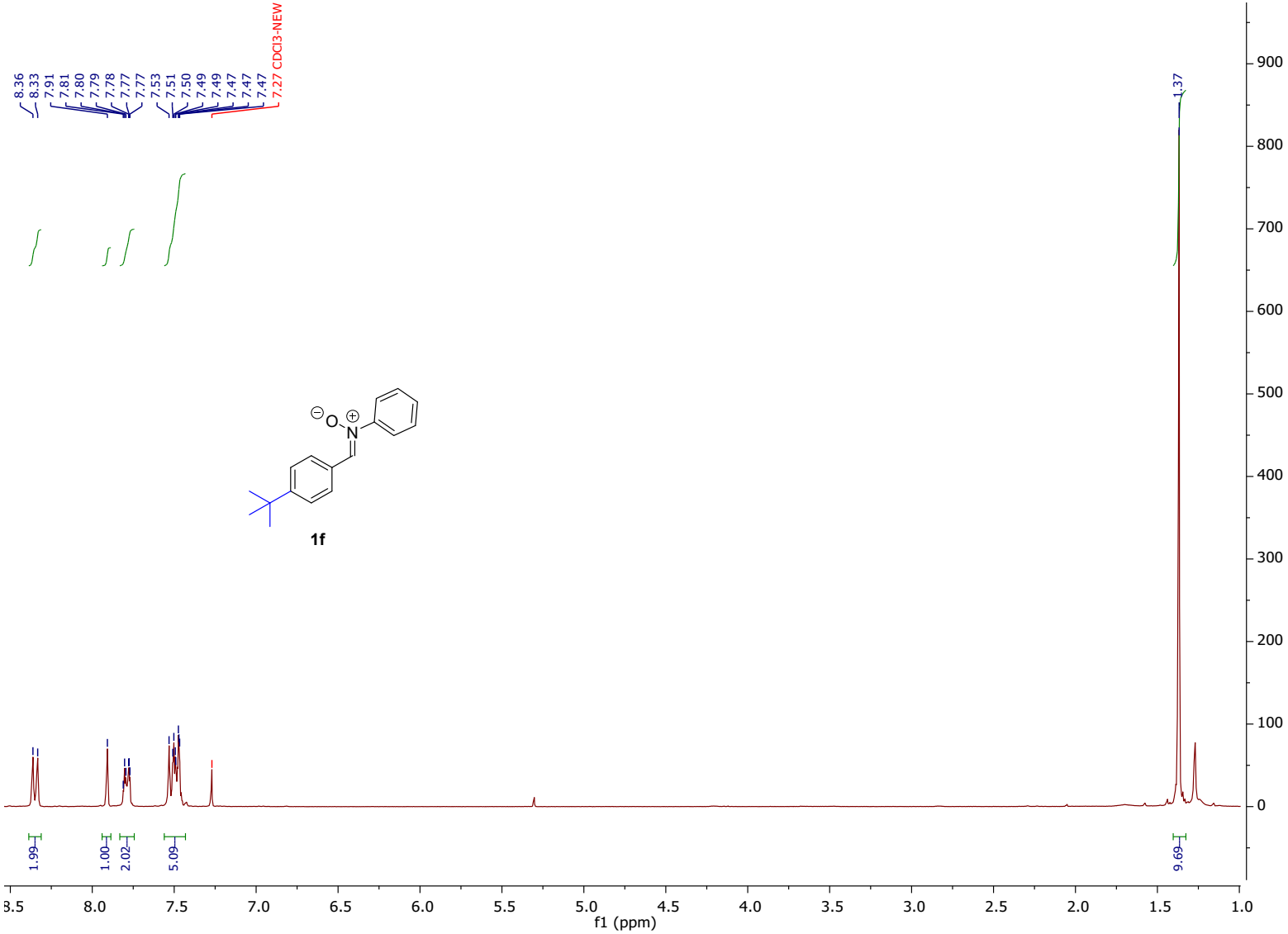

8.39
7.72
7.63
7.61
7.38
7.35
7.35
7.33
7.30
7.27 CDCl3
7.24
7.21
7.18
7.18
7.18
7.15
7.15
2.39
N
2e
1.00
0.97
1.15
7.61
3.12
4500
4000
3500
3000
2500
2000
1500
1000
500
0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)

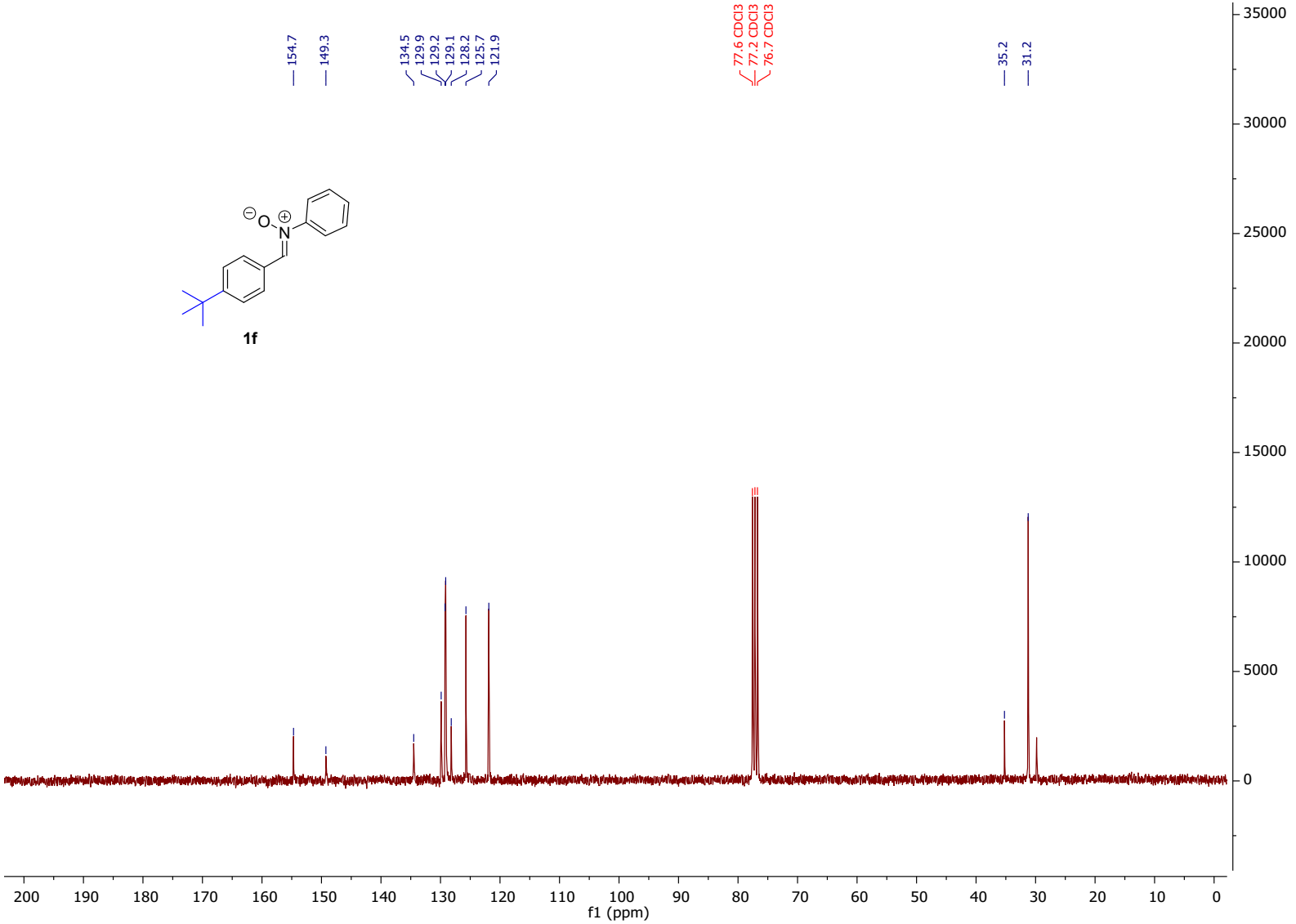

160.8
152.3
138.7
136.3
132.4
129.3
129.1
128.8
126.6
126.0
121.0
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
21.4
N
2e
f1 (ppm)

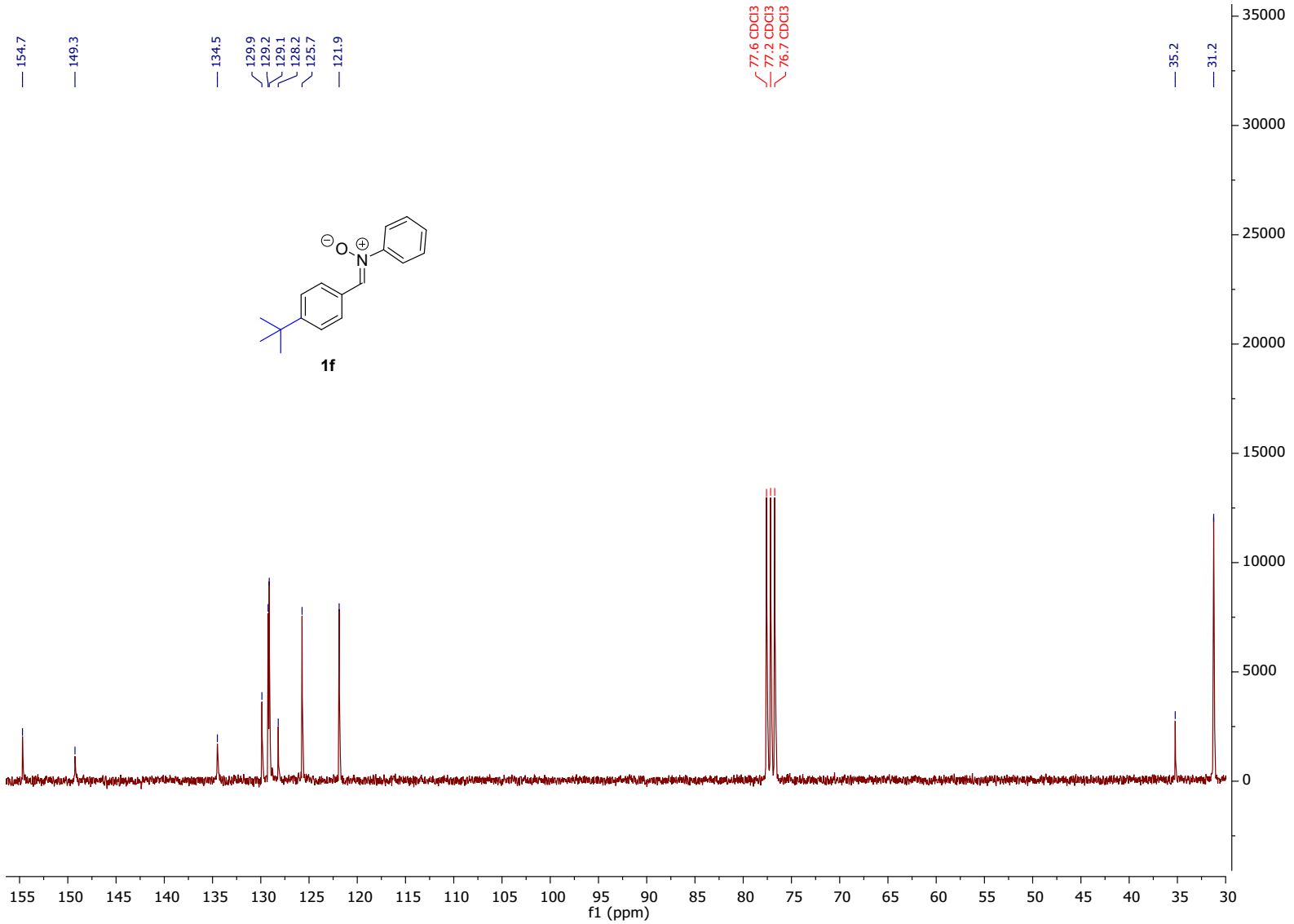

160.8
152.3
138.7
136.3
132.4
129.3
129.1
128.8
126.6
126.0
121.0
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
21.4
N
2e
f1 (ppm)

(*Z*)-1-(4-(*tert*-butyl)phenyl)-N-phenylmethanimine oxide (1f)

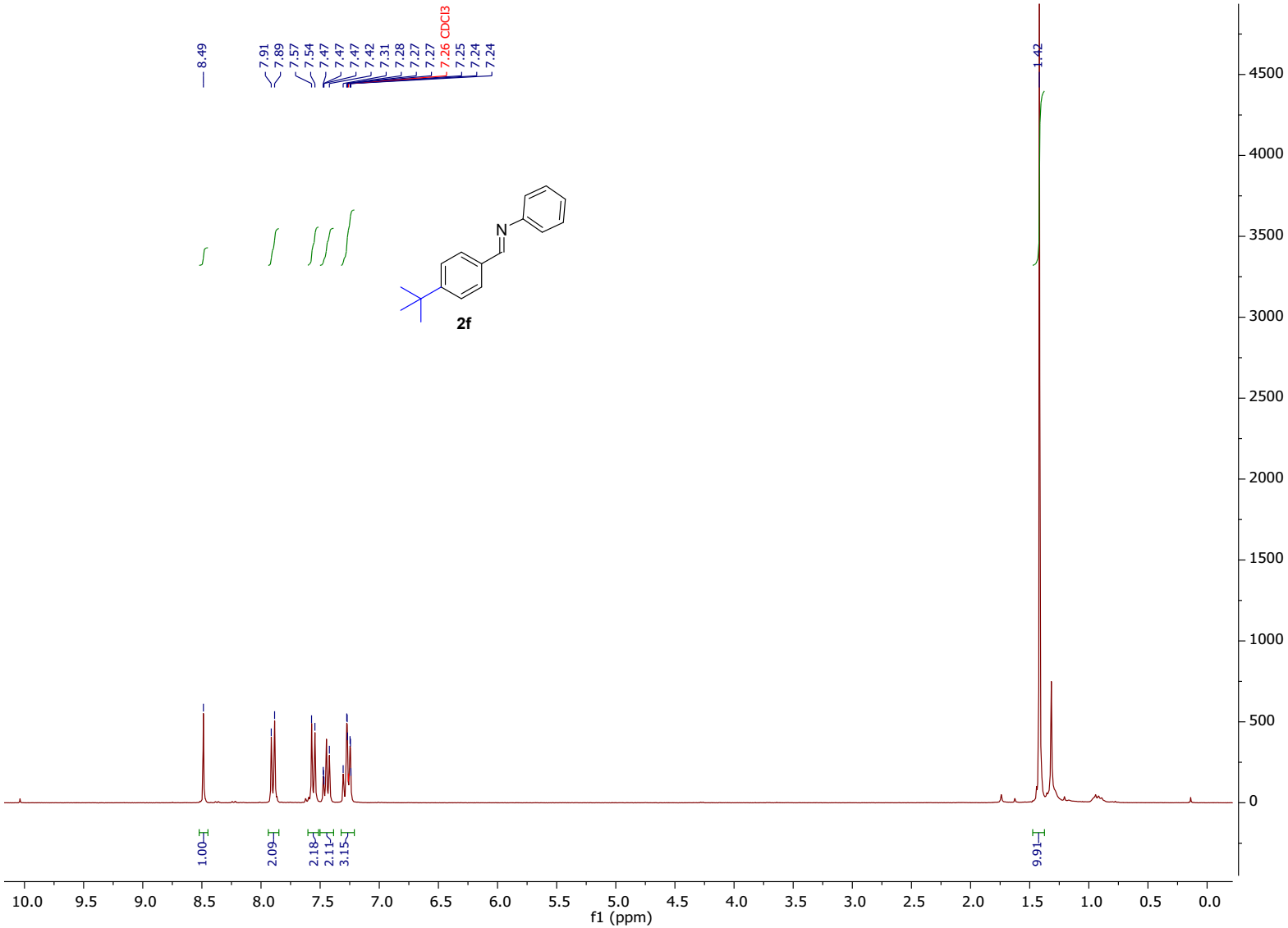


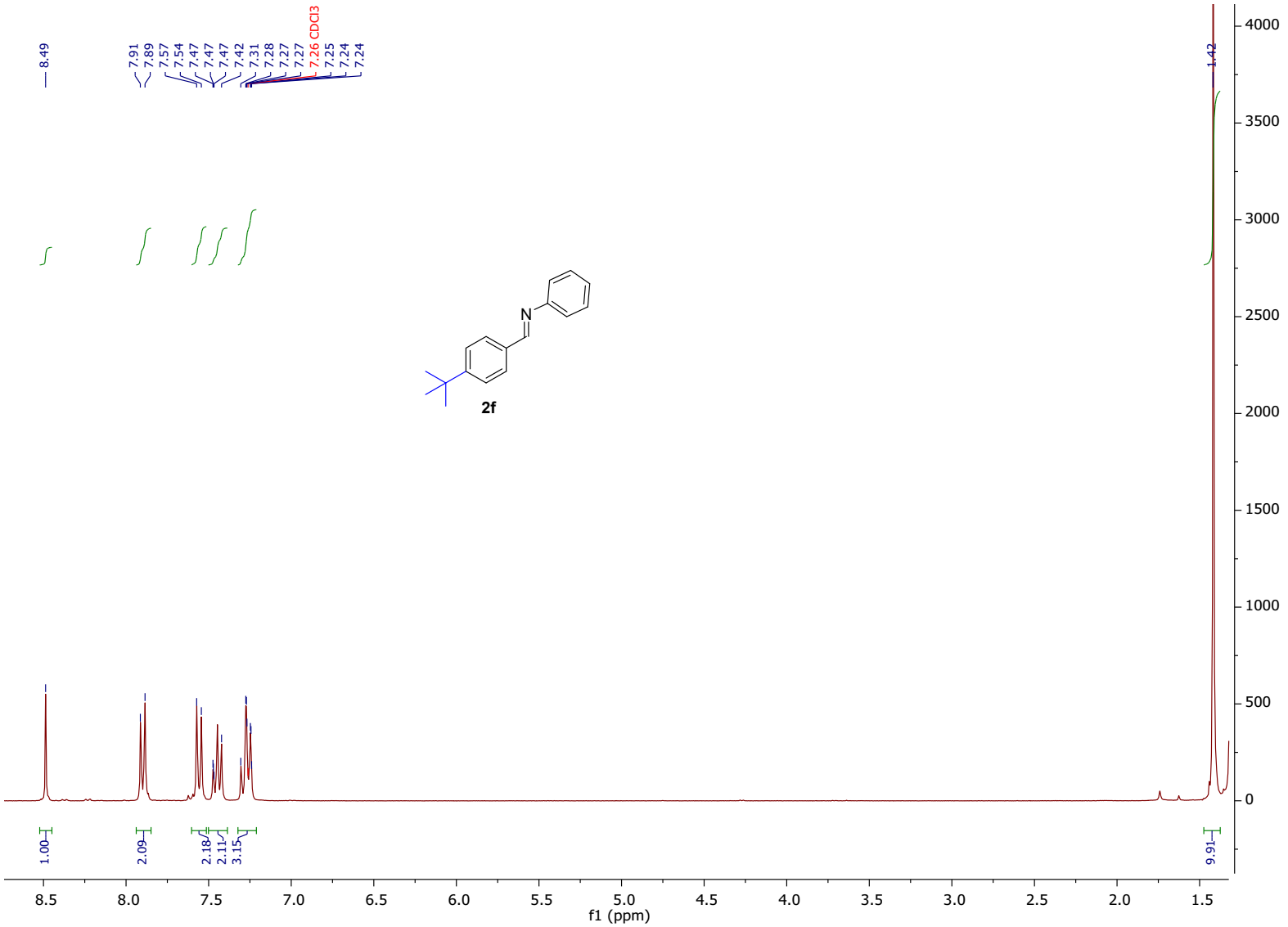

8.36
8.33
7.91
7.81
7.80
7.79
7.78
7.77
7.77
7.53
7.51
7.50
7.49
7.49
7.47
7.47
7.47
7.27 CDCl3-NEW
1.37
1f
1.99
1.00
2.02
5.09
9.69
f1 (ppm)

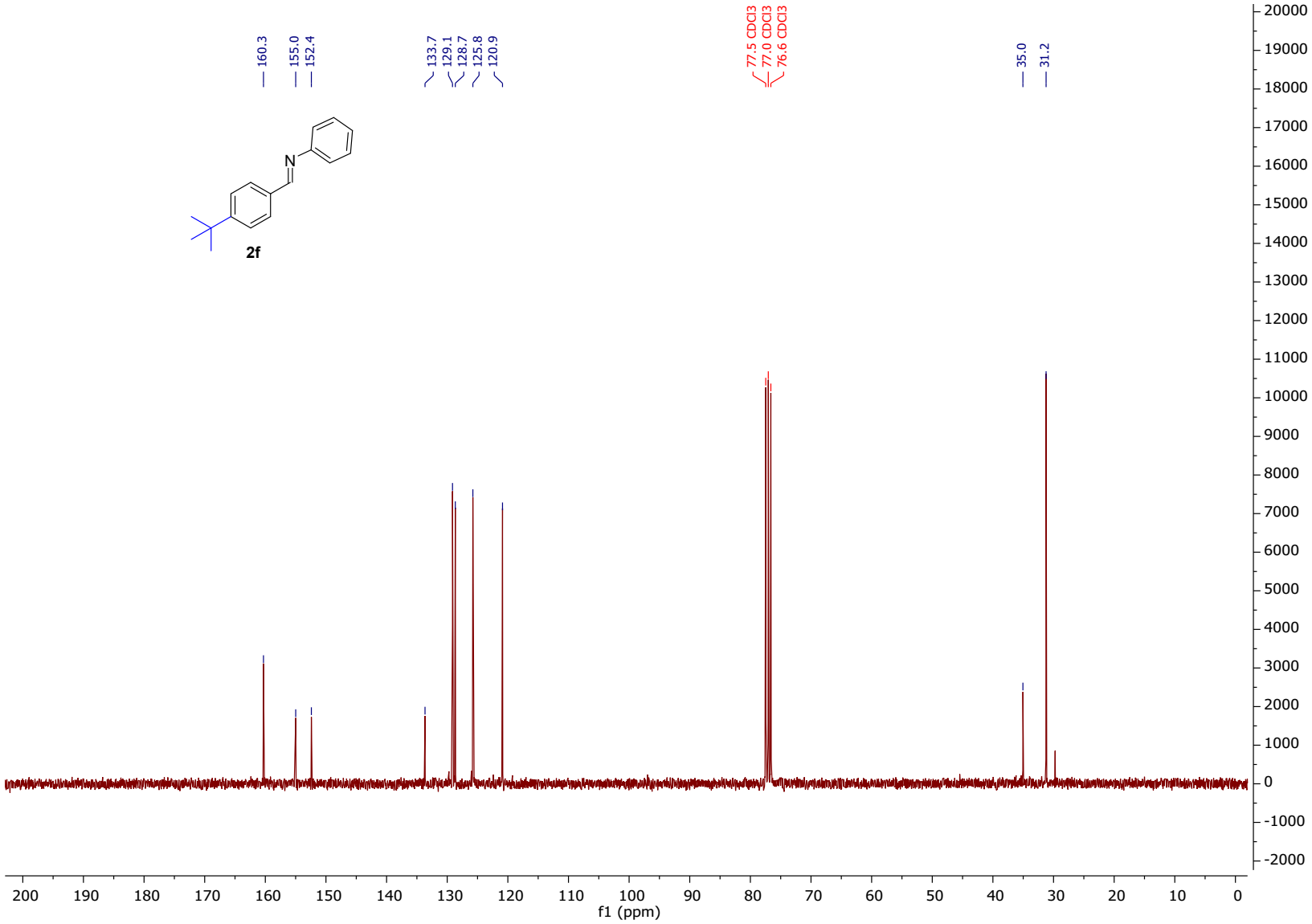

154.7
149.3
134.5
129.9
129.2
129.1
128.2
125.7
121.9
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
35.2
31.2
1f
35000
30000
25000
20000
15000
10000
5000
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

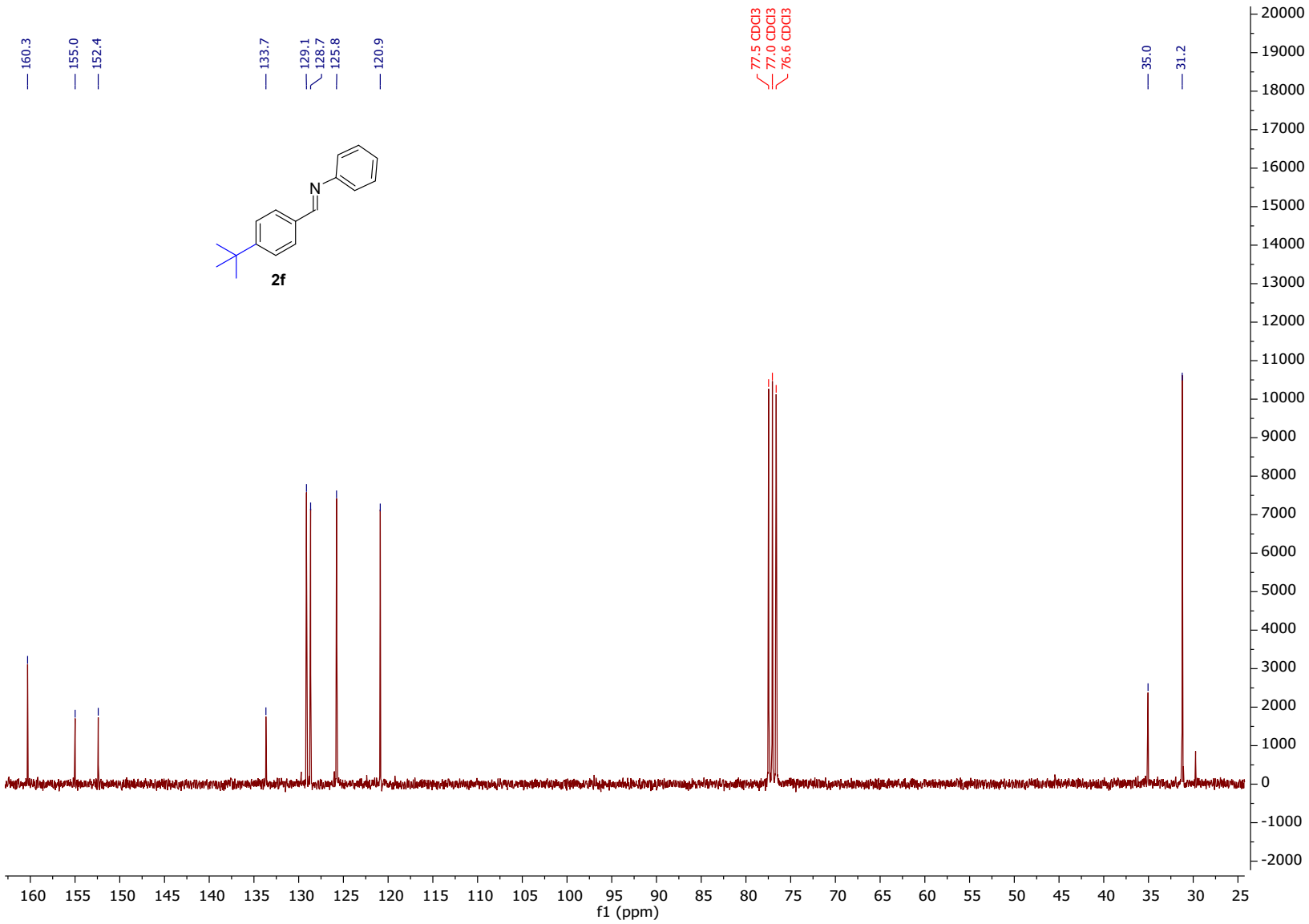

154.7
149.3
134.5
129.9
129.2
129.1
128.2
125.7
121.9
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
35.2
31.2
1f
f1 (ppm)

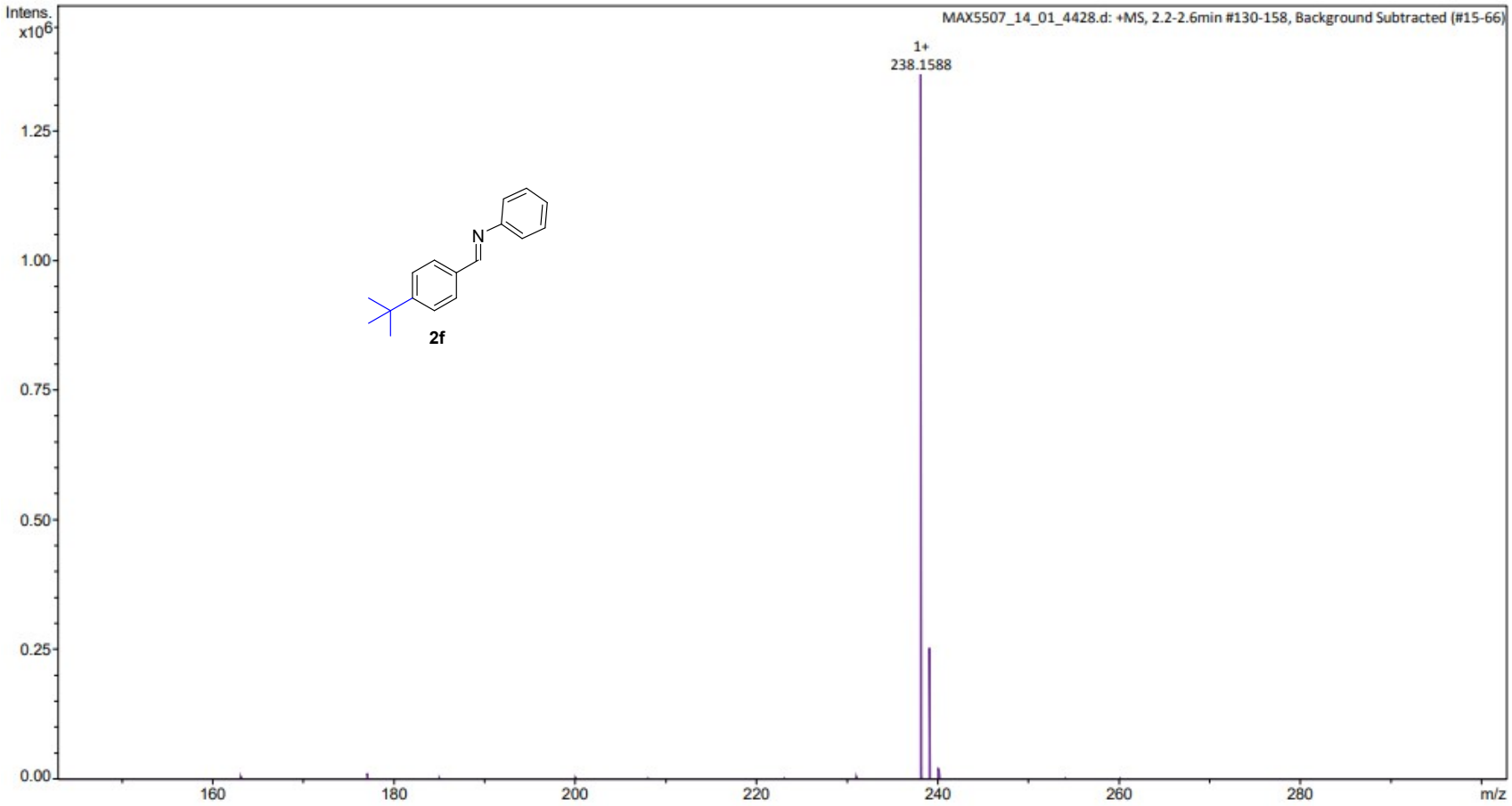
(E)-1-(4-(*tert*-butyl)phenyl)-N-phenylmethanimine (2f)



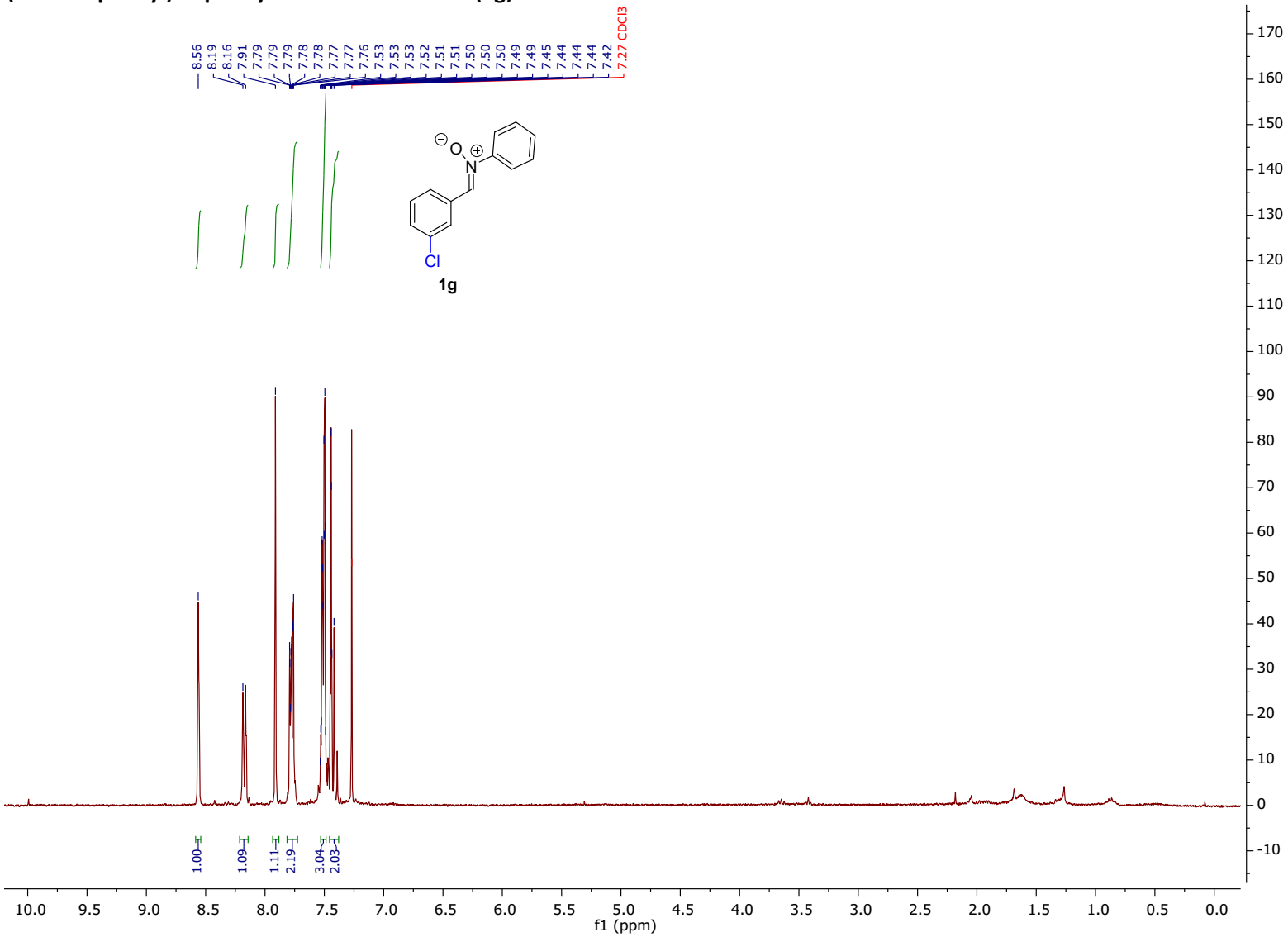

8.49
7.91
7.89
7.57
7.54
7.47
7.47
7.47
7.42
7.31
7.28
7.27
7.27
7.26 CDCl3
7.25
7.24
7.24
1.42
N
2f
1.00
2.09
2.18
2.11
3.15
9.91
f1 (ppm)

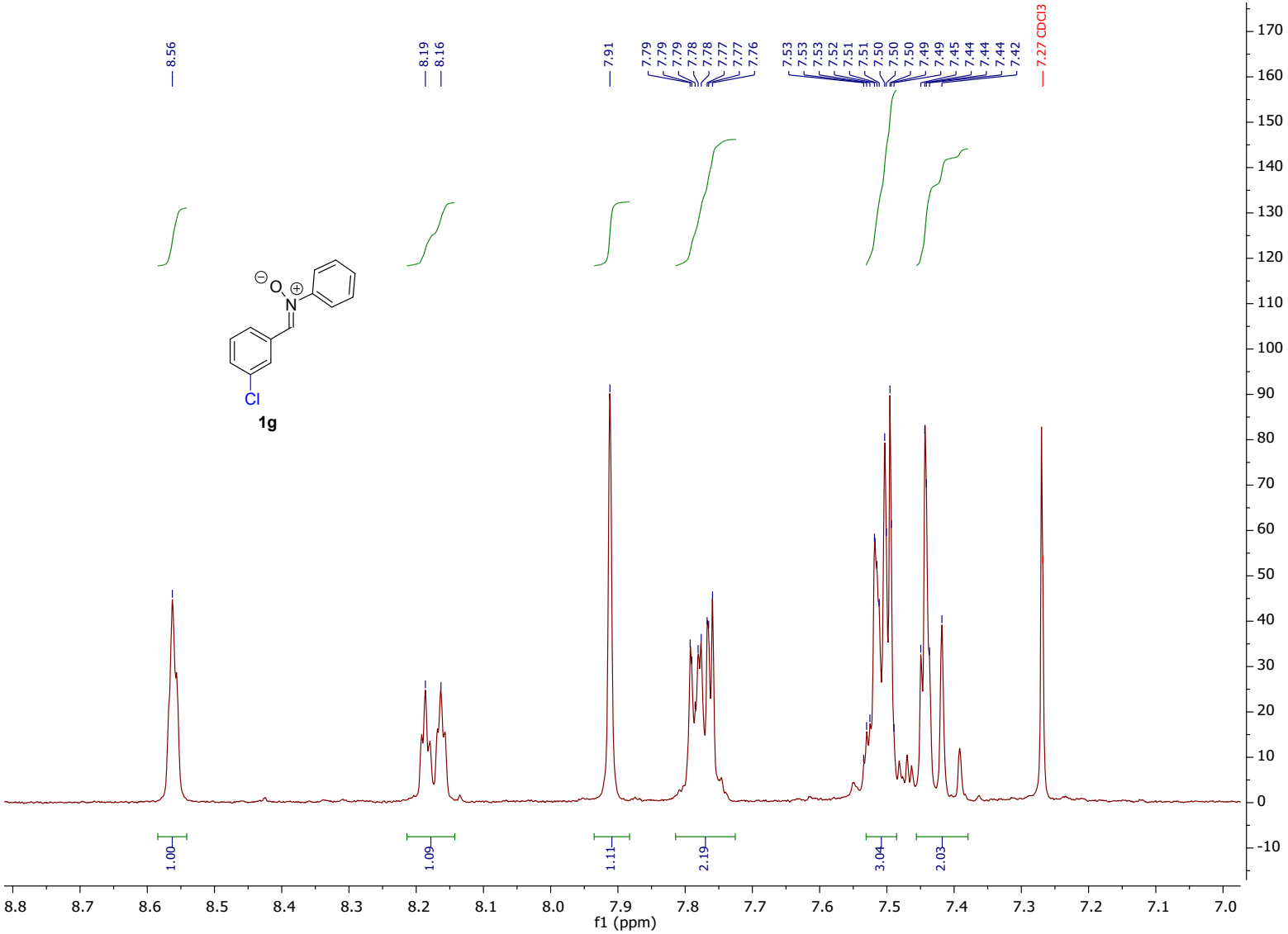

160.3
155.0
152.4
133.7
129.1
128.7
125.8
120.9
77.5 CDCl3
77.0 CDCl3
76.6 CDCl3
35.0
31.2
N
2f
f1 (ppm)

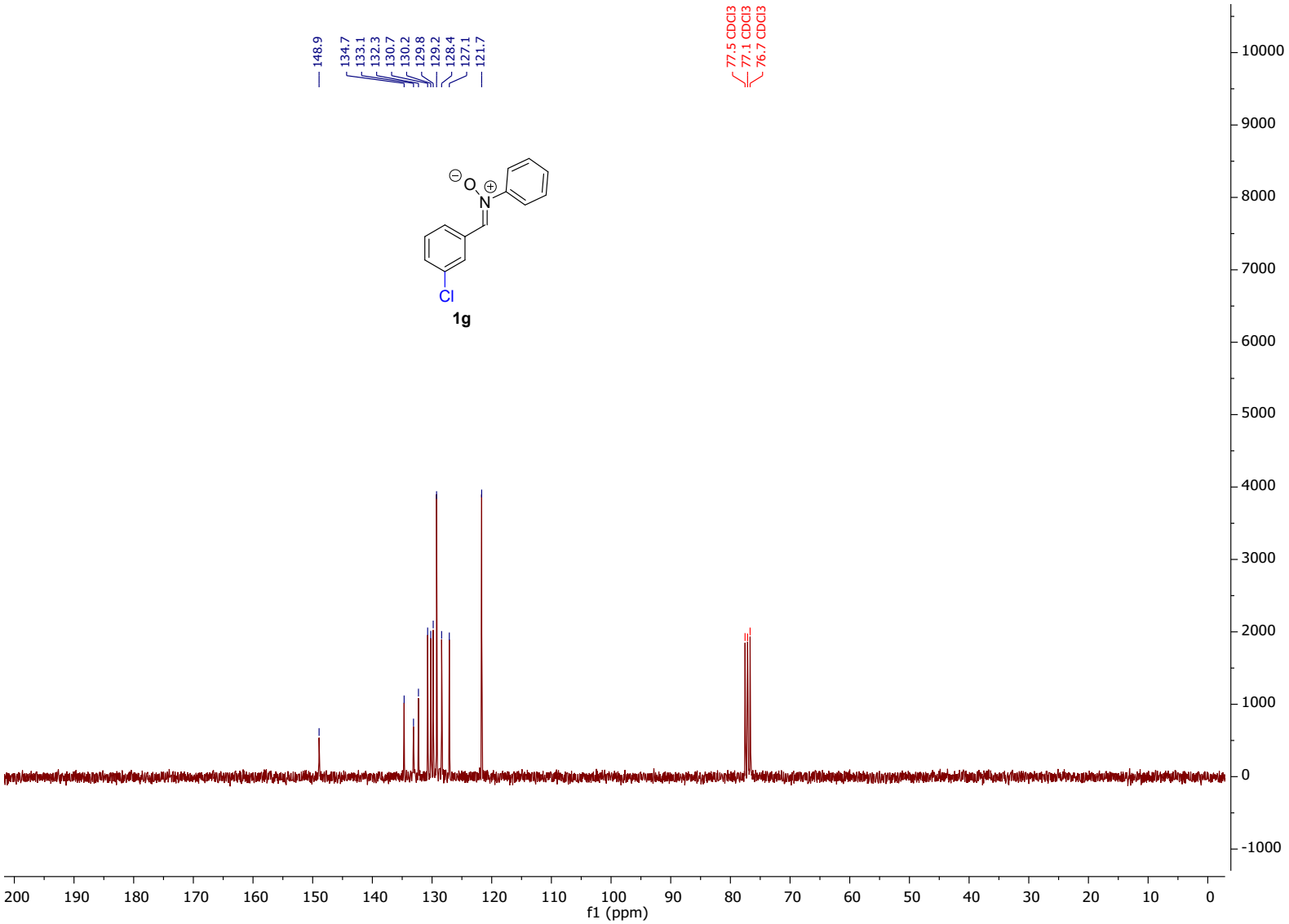

160.3
155.0
152.4
133.7
129.1
128.7
125.8
120.9
77.5 CDCl3
77.0 CDCl3
76.6 CDCl3
35.0
31.2
N
2f
f1 (ppm)

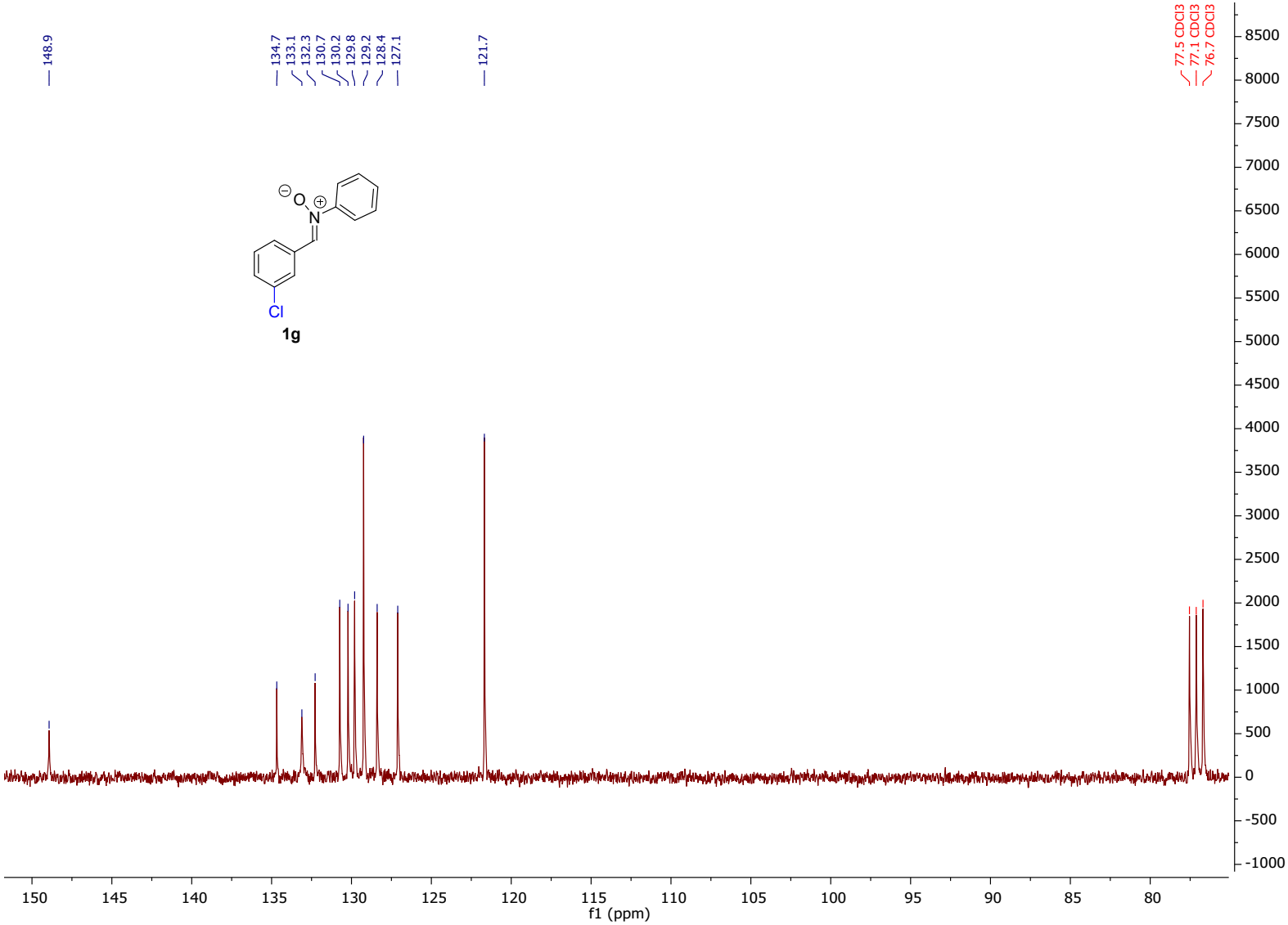

Intens.
x10^6
1.25
1.00
0.75
0.50
0.25
0.00
MAX5507_14_01_4428.d: +MS, 2.2-2.6min #130-158, Background Subtracted (#15-66)
1+
238.1588
N
2f
160
180
200
220
240
260
280
m/z

(*Z*)-1-(3-chlorophenyl)-N-phenylmethanimine oxide (1g)

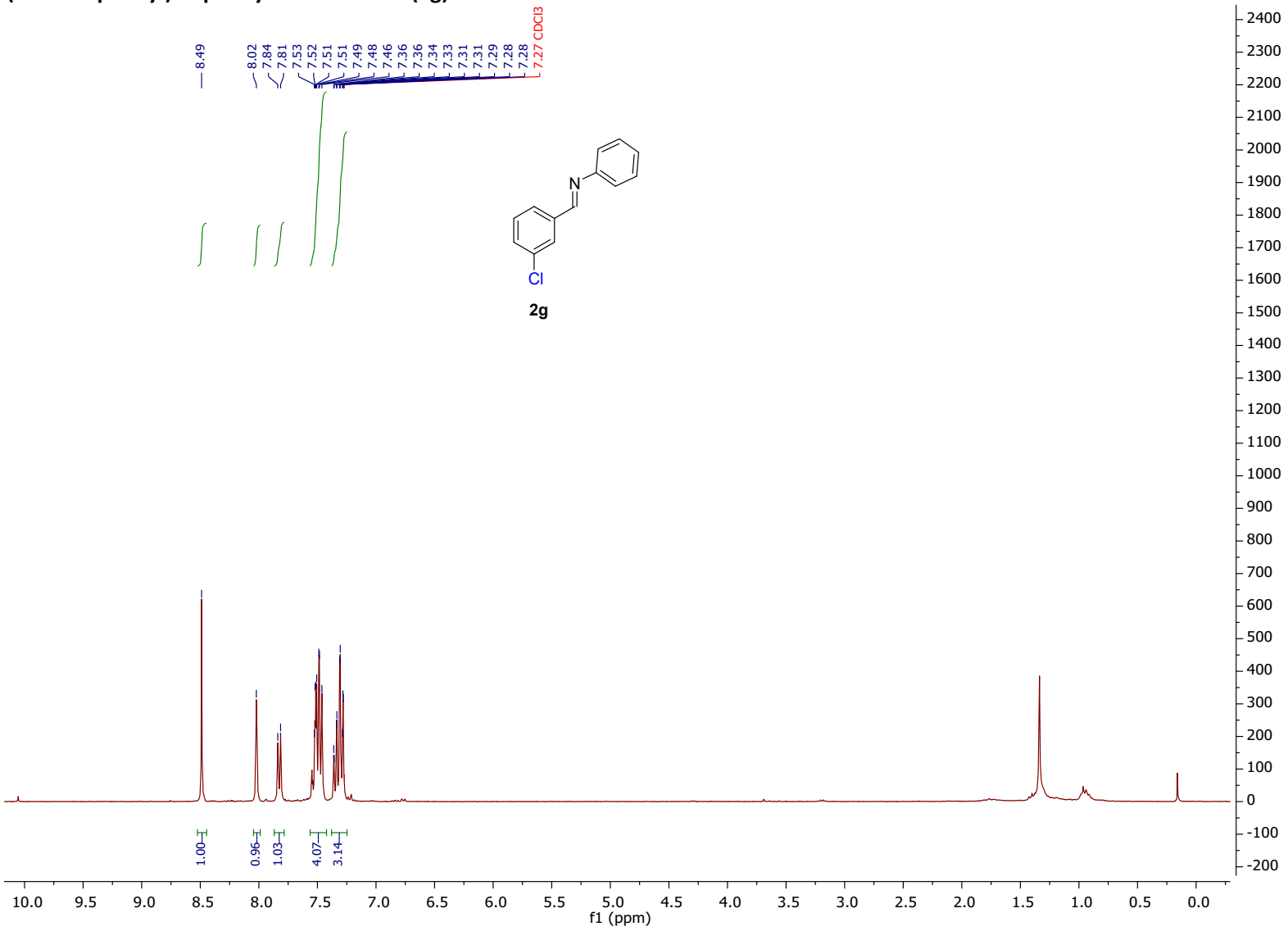


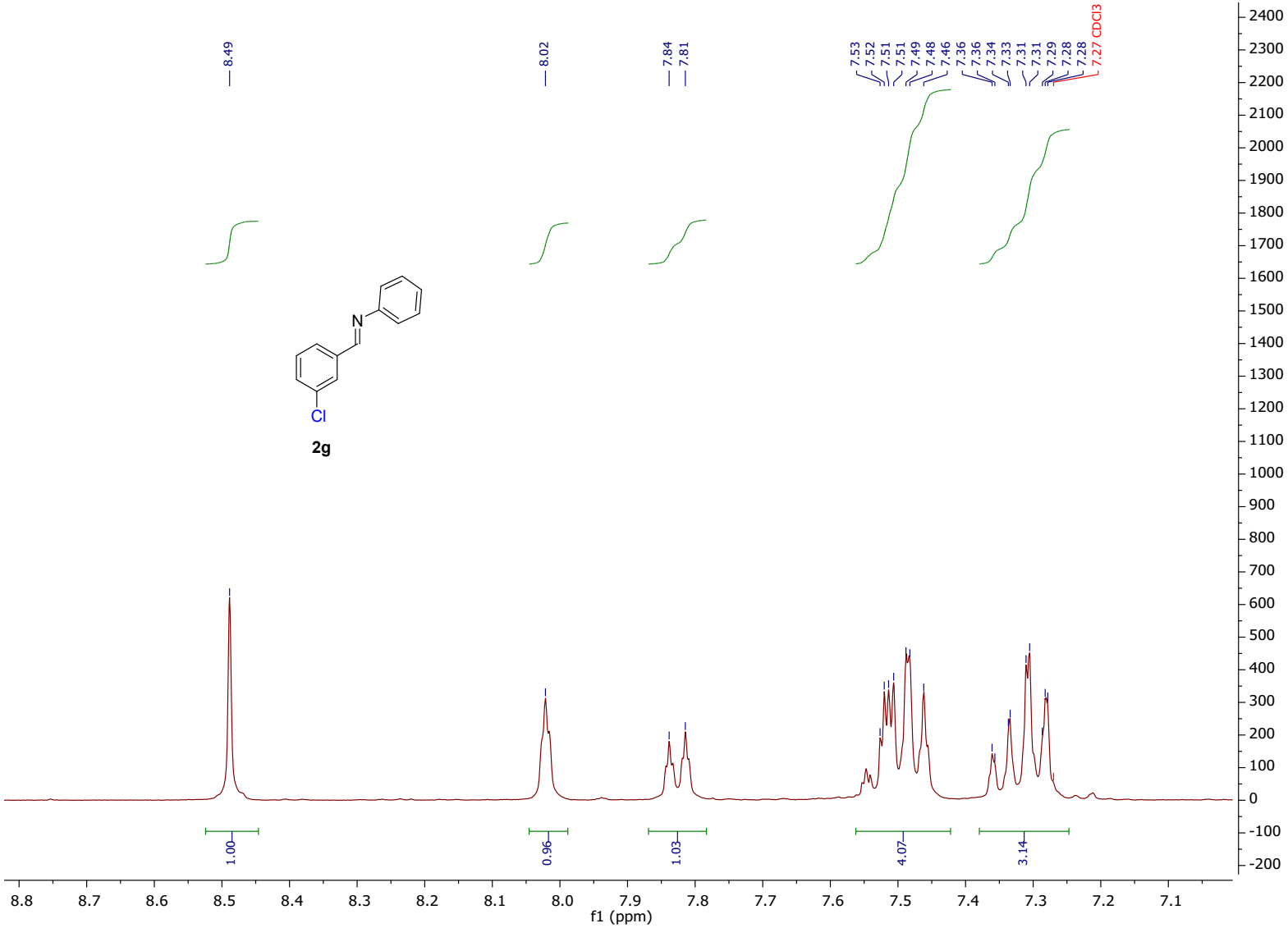

8.56
8.19
8.16
7.91
7.79
7.79
7.79
7.78
7.78
7.77
7.77
7.76
7.53
7.53
7.53
7.52
7.51
7.51
7.50
7.50
7.50
7.49
7.49
7.45
7.44
7.44
7.44
7.42
7.27 CDCl3
O
N
Cl
1g
1.00
1.09
1.11
2.19
3.04
2.03
f1 (ppm)

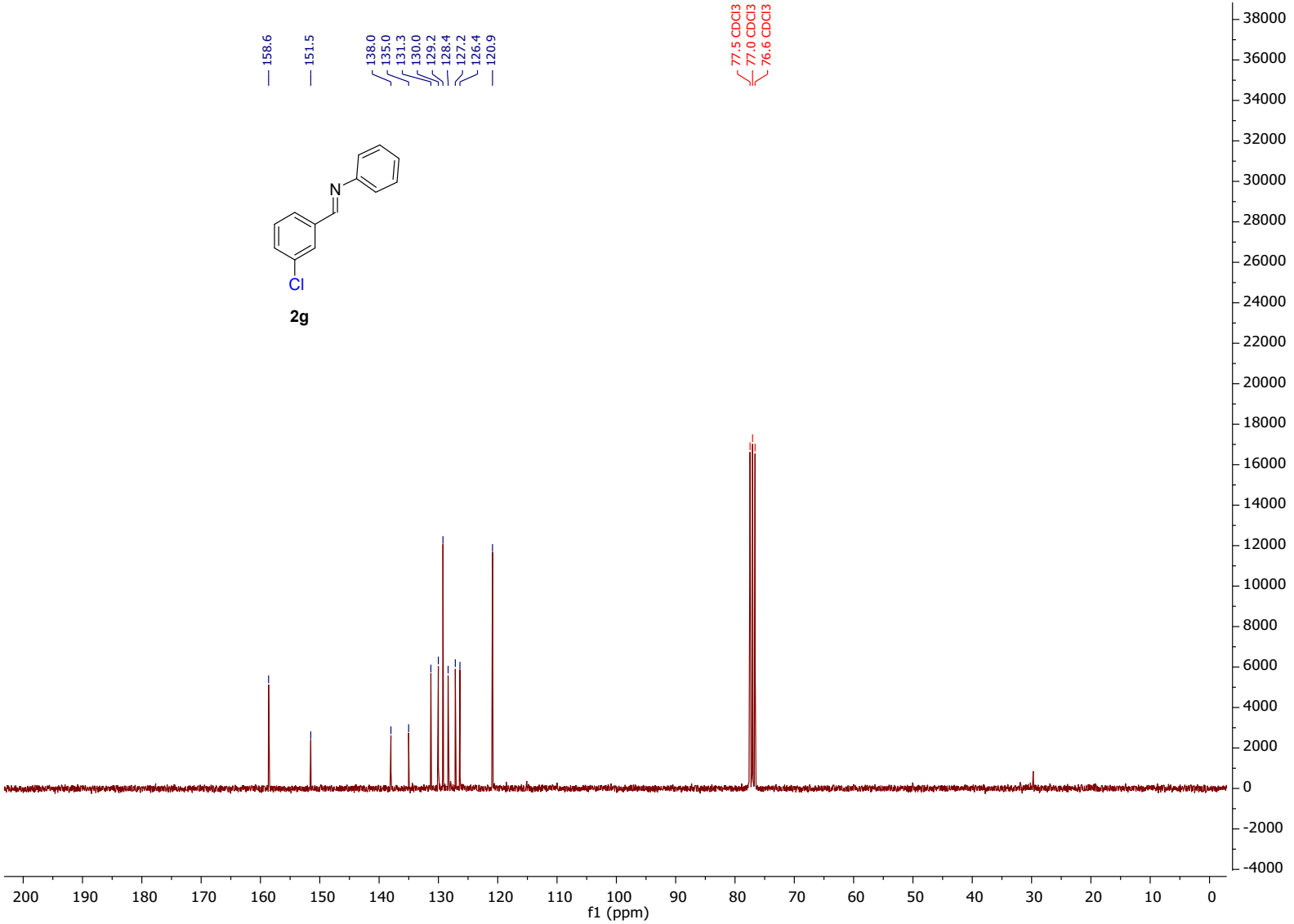

148.9
134.7
133.1
132.3
130.7
130.2
129.8
129.2
128.4
127.1
121.7
77.5 CDCl3
77.1 CDCl3
76.7 CDCl3
O
N
Cl
1g
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

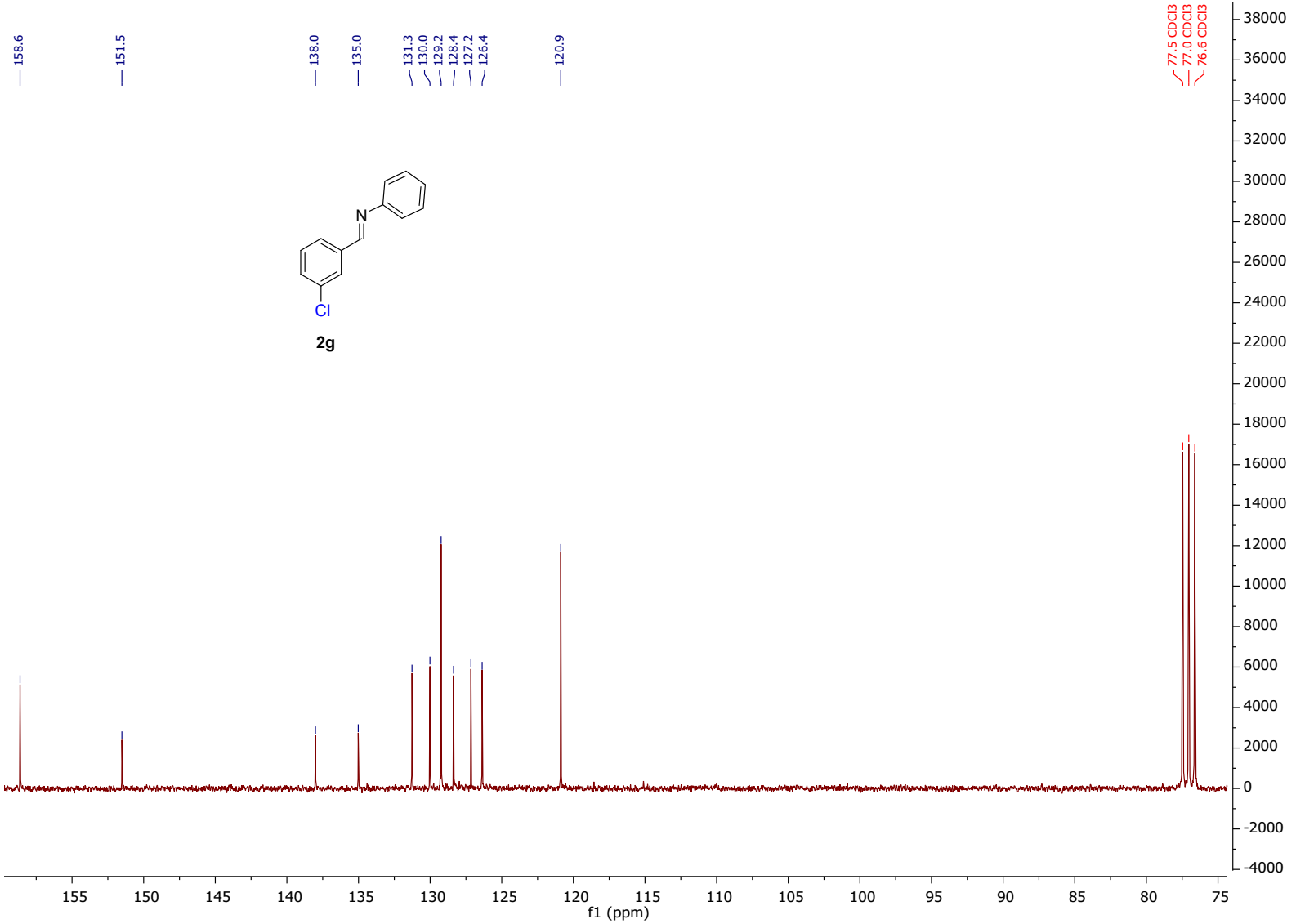

148.9
134.7
133.1
132.3
130.7
130.2
129.8
129.2
128.4
127.1
121.7
77.5 CDCl3
77.1 CDCl3
76.7 CDCl3
O
N
Cl
1g
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
f1 (ppm)

(*E*)-1-(3-chlorophenyl)-N-phenylmethanimine (2g)

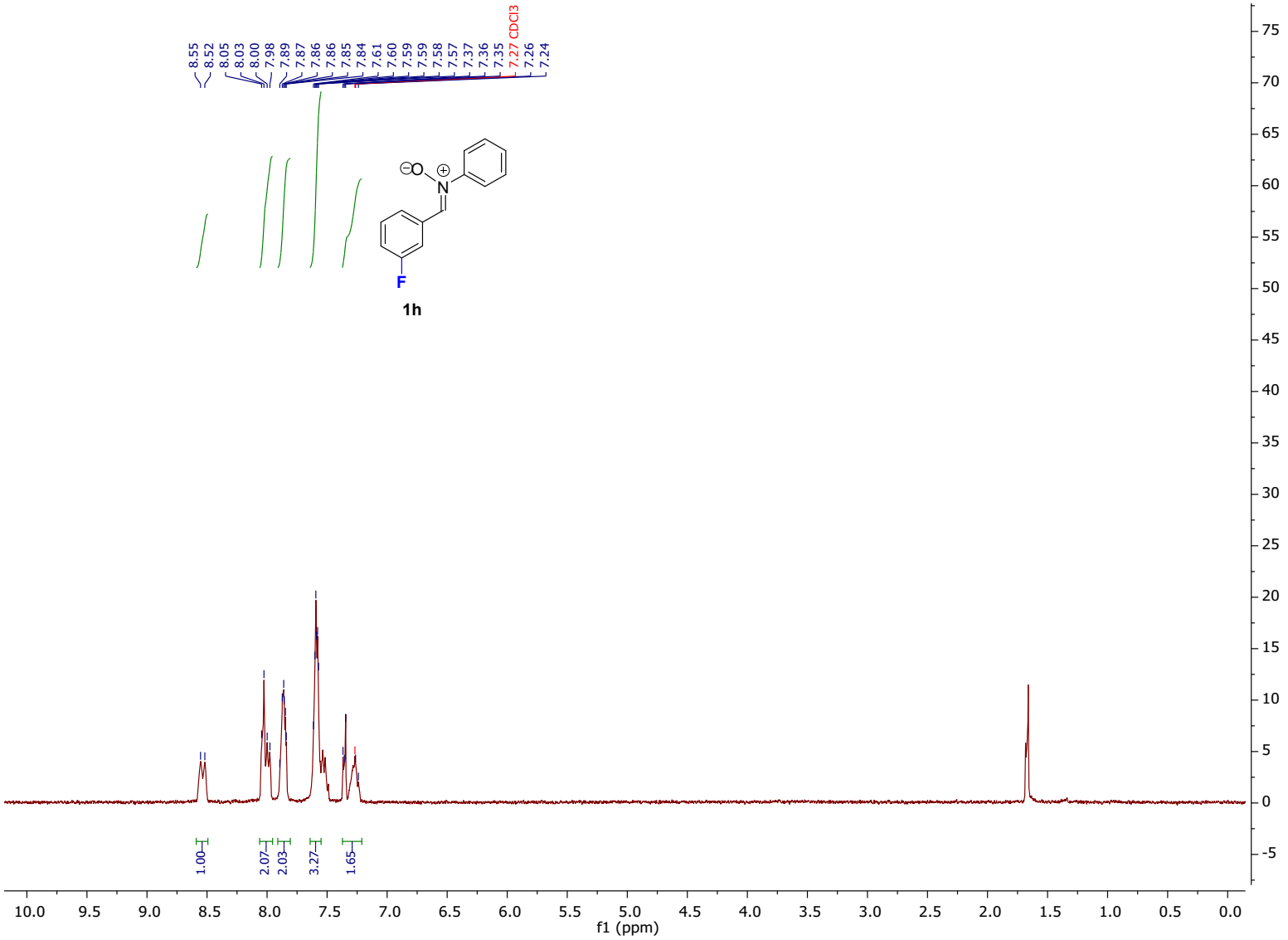


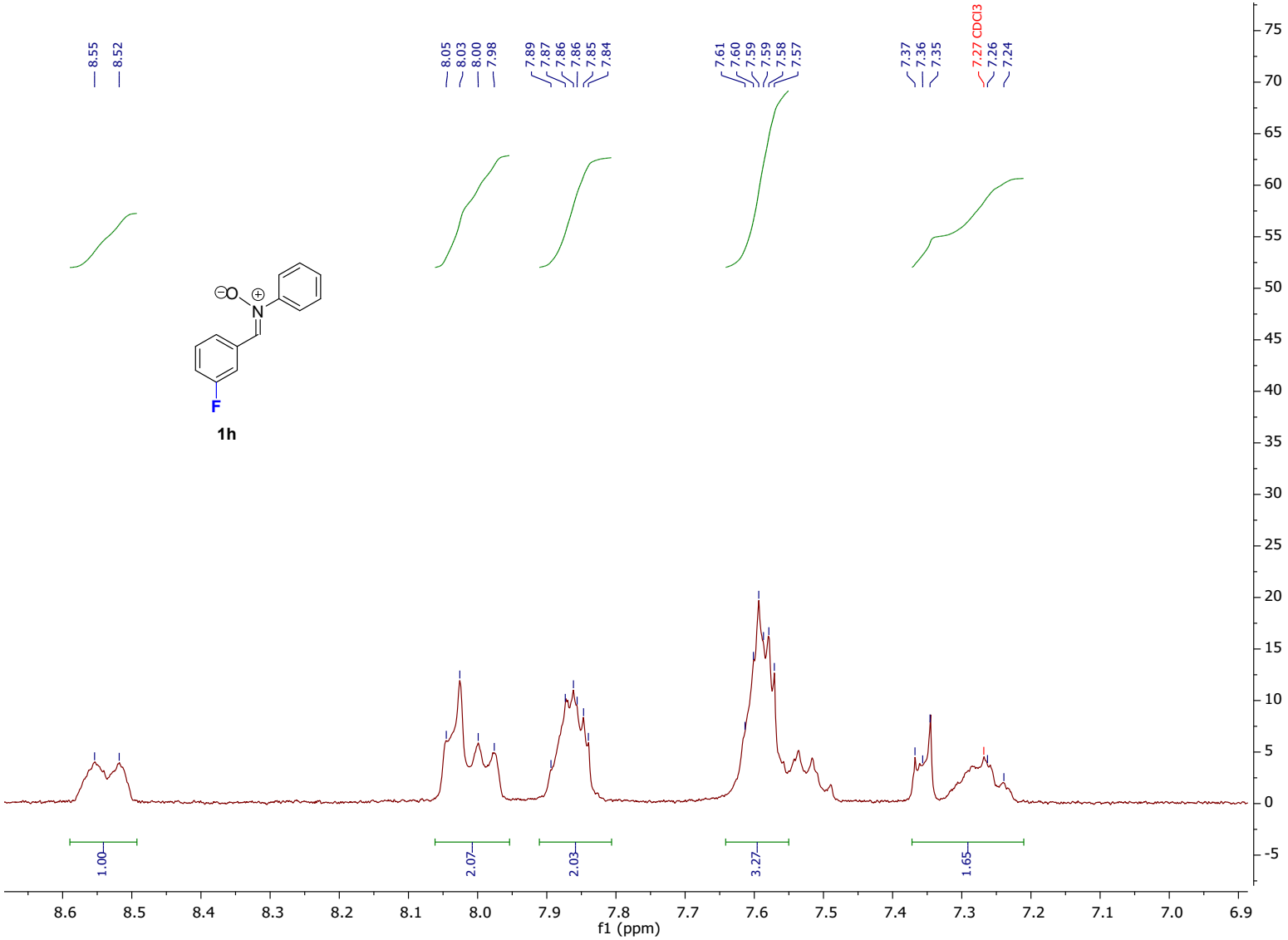

8.49
8.02
7.84
7.81
7.53
7.52
7.51
7.51
7.49
7.48
7.46
7.36
7.36
7.34
7.33
7.31
7.31
7.29
7.28
7.28
7.27 CDCl3
N
Cl
2g
1.00
0.96
1.03
4.07
3.14
f1 (ppm)

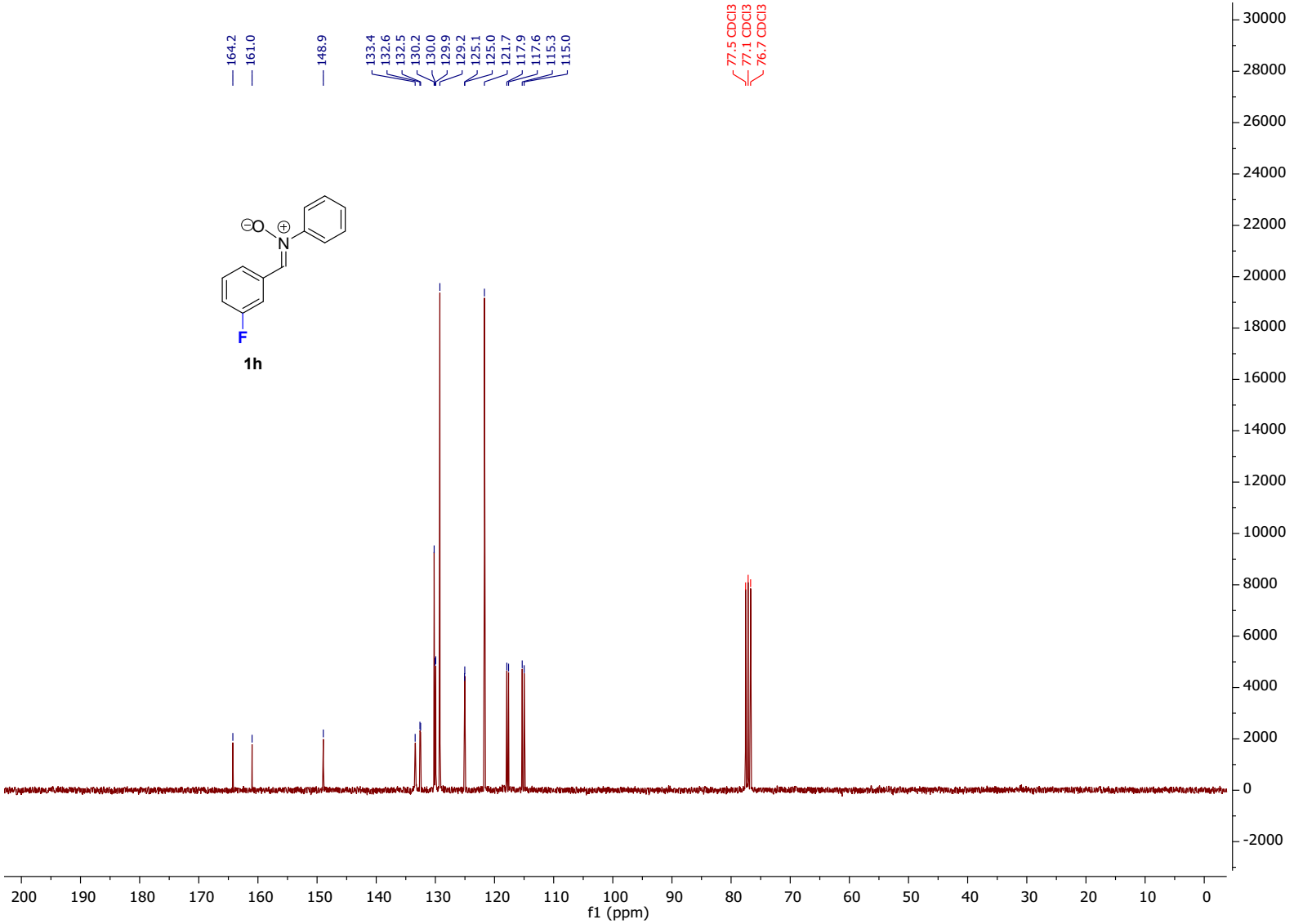

158.6
151.5
138.0
135.0
131.3
130.0
129.2
128.4
127.2
126.4
120.9
77.5 CDCl3
77.0 CDCl3
76.6 CDCl3
N
Cl
2g
f1 (ppm)

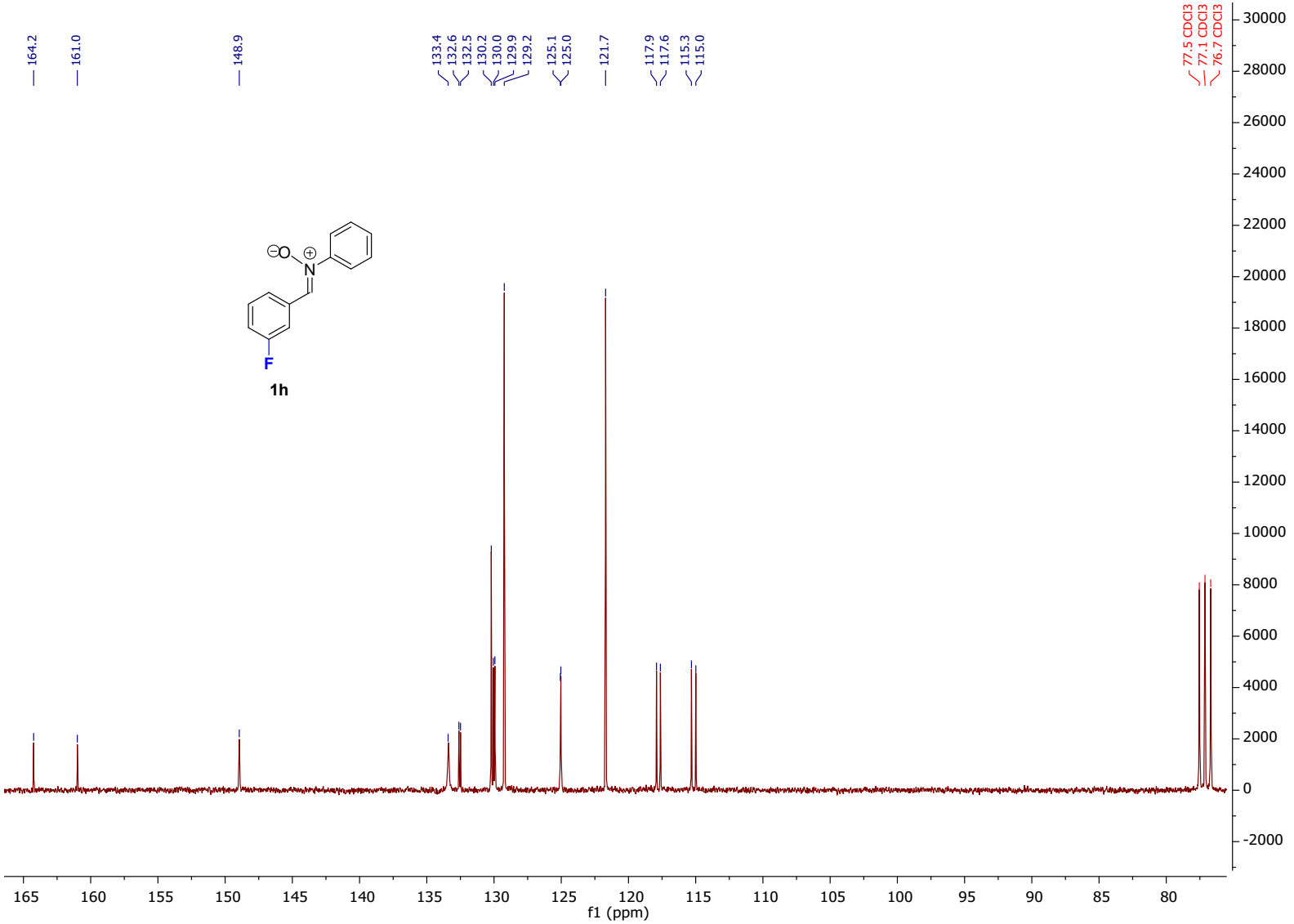

158.6
151.5
138.0
135.0
131.3
130.0
129.2
128.4
127.2
126.4
120.9
77.5 CDCl3
77.0 CDCl3
76.6 CDCl3
N
Cl
2g
f1 (ppm)

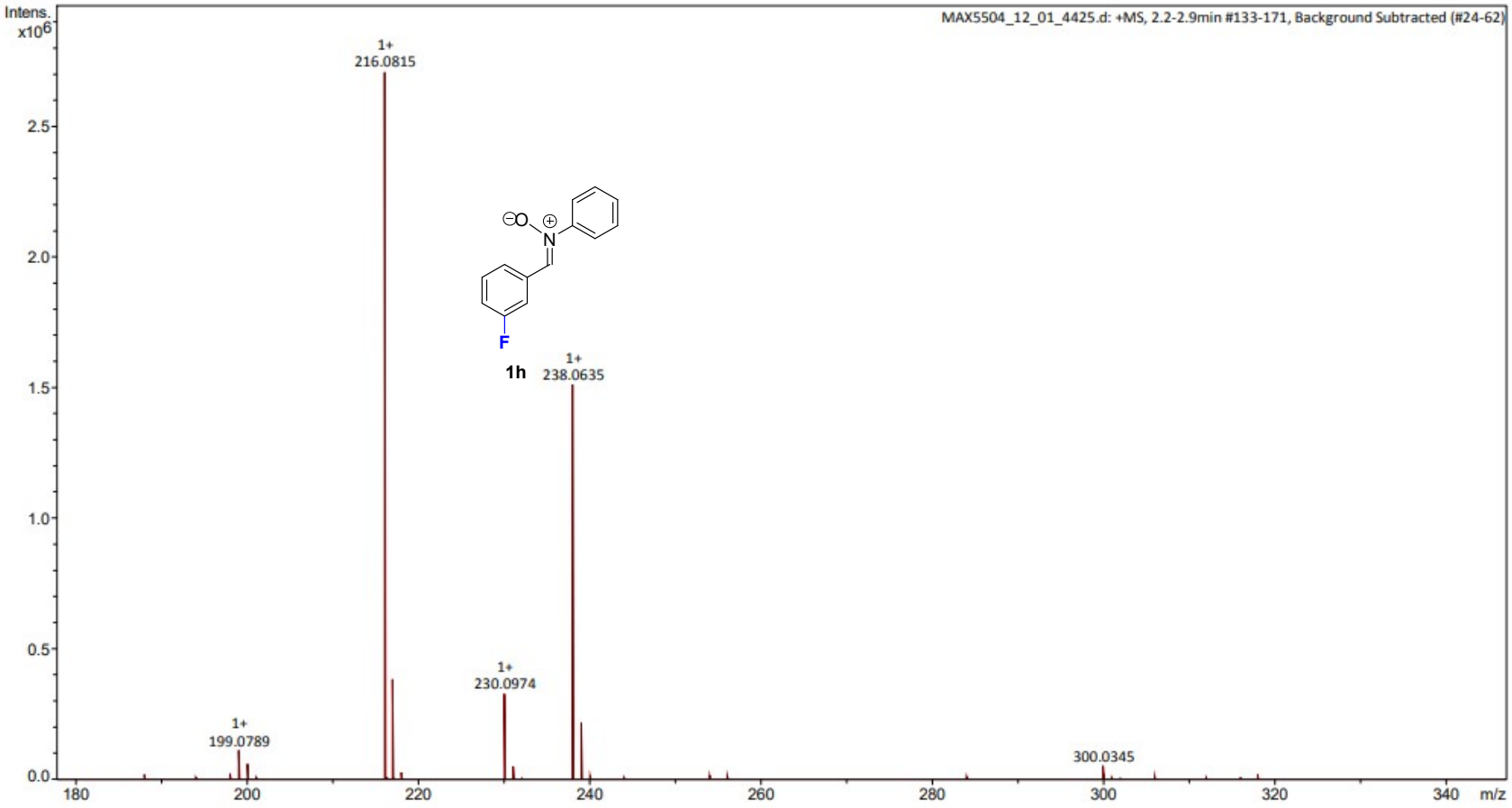
(*Z*)-1-(3-fluorophenyl)-*N*-phenylmethanimine oxide (1h)



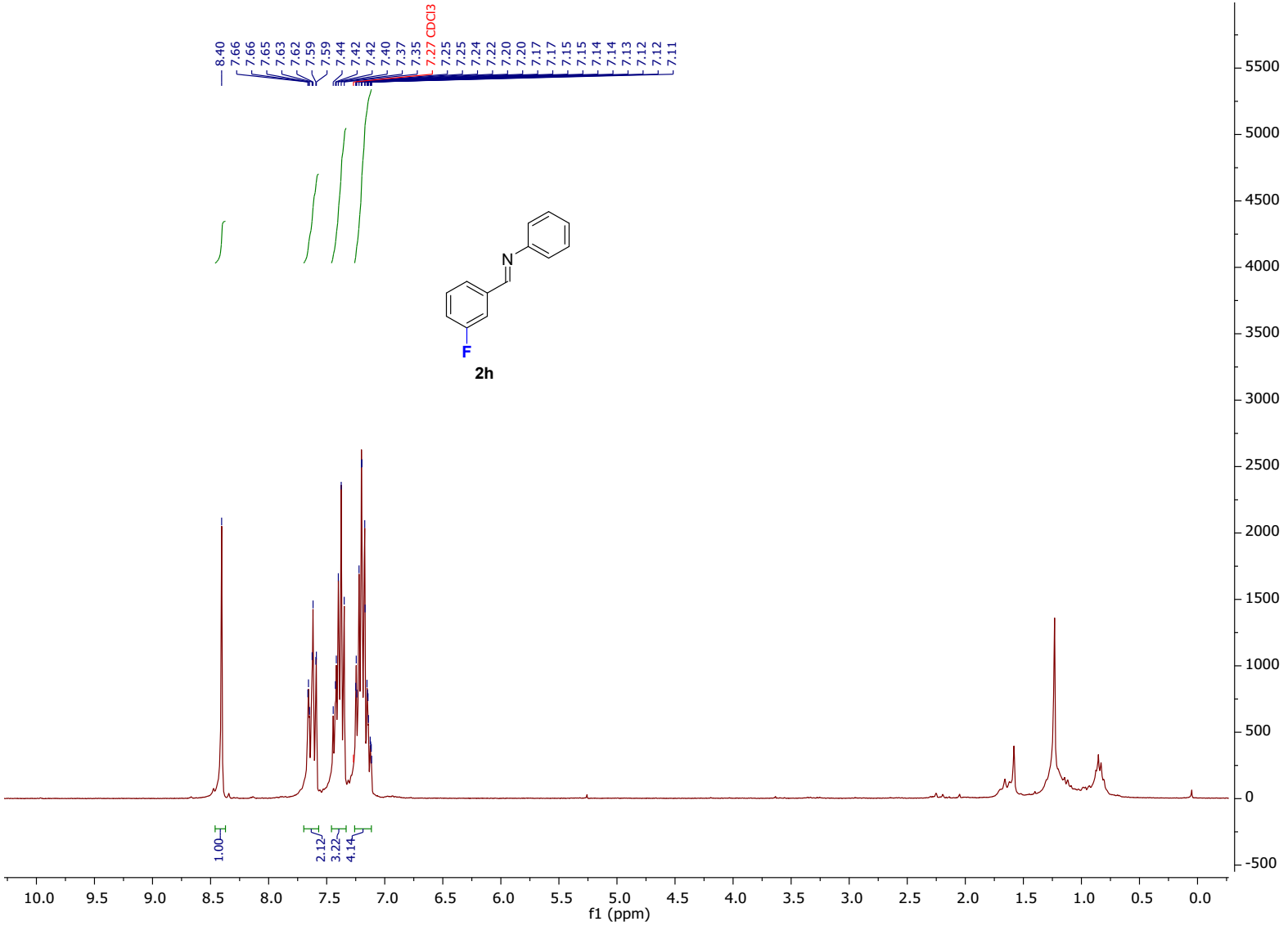

8.55
8.52
8.05
8.03
8.00
7.98
7.89
7.87
7.86
7.86
7.85
7.84
7.61
7.60
7.59
7.59
7.58
7.57
7.37
7.36
7.35
7.27 CDCl3
7.26
7.24
1h
1.00
2.07
2.03
3.27
1.65
f1 (ppm)

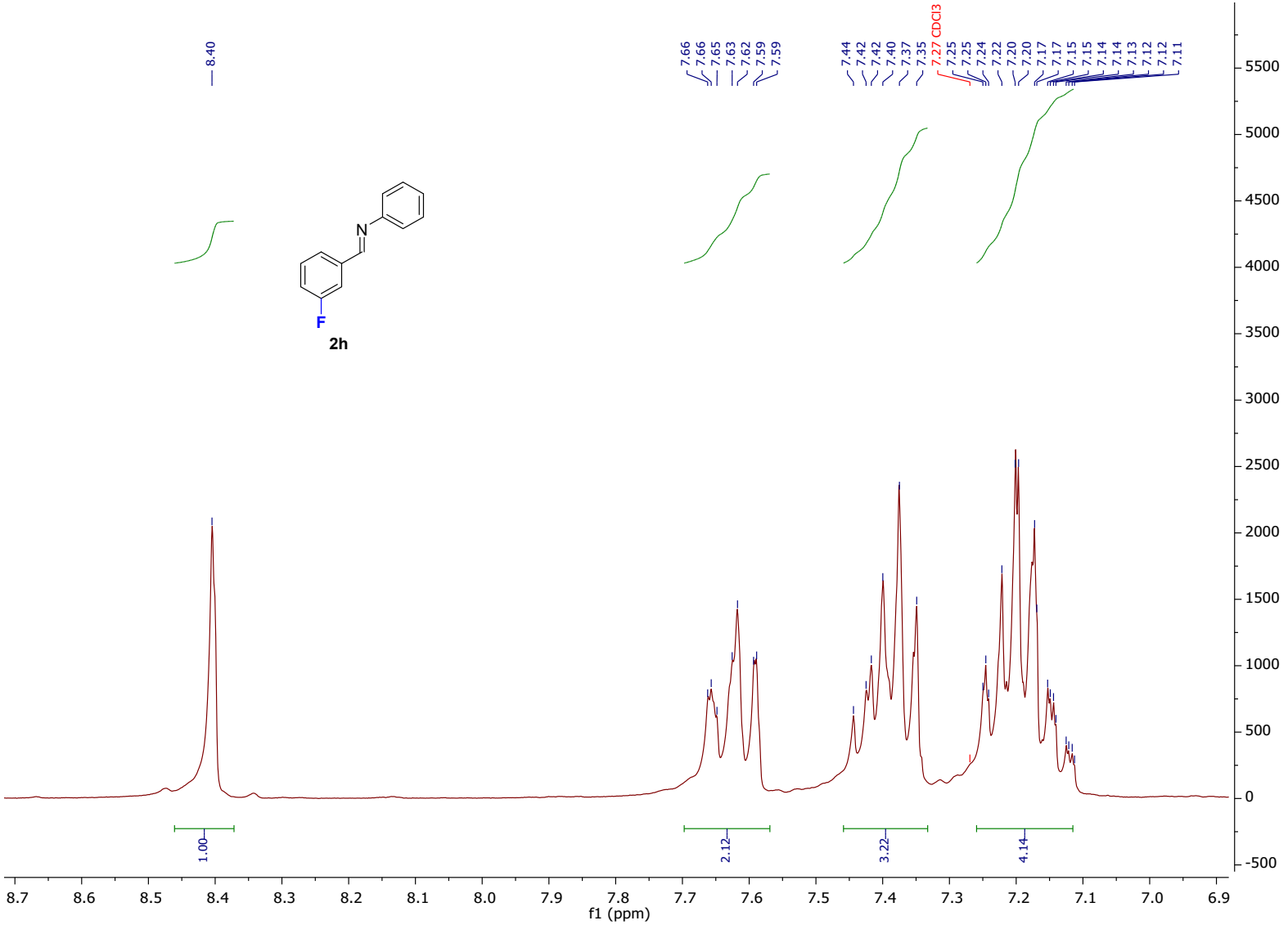

164.2
161.0
148.9
133.4
132.6
132.5
130.2
130.0
129.9
129.2
125.1
125.0
121.7
117.9
117.6
115.3
115.0
77.5 CDCl3
77.1 CDCl3
76.7 CDCl3
F
1h
f1 (ppm)

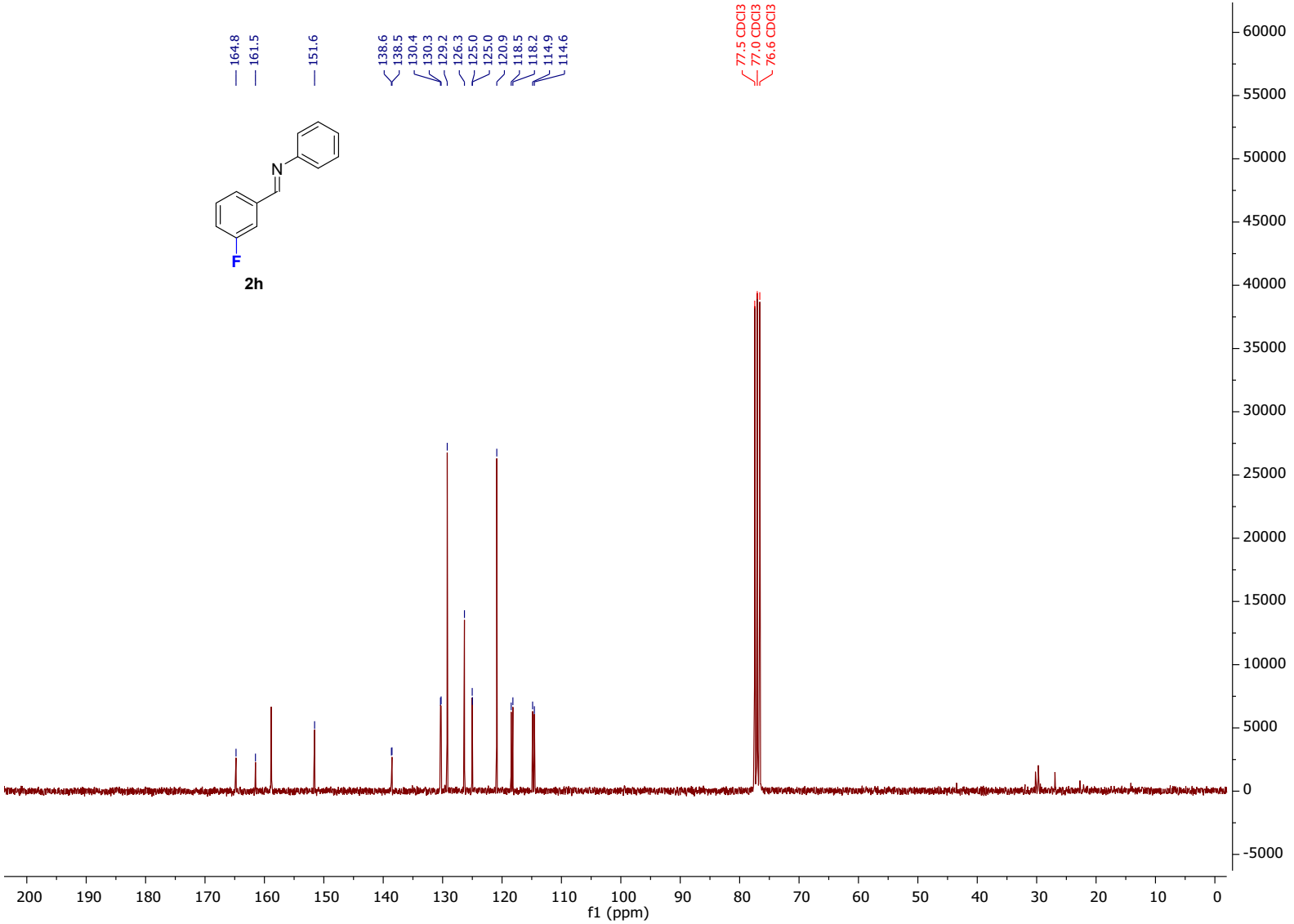

164.2
161.0
148.9
133.4
132.6
132.5
130.2
130.0
129.9
129.2
125.1
125.0
121.7
117.9
117.6
115.3
115.0
77.5 CDCl3
77.1 CDCl3
76.7 CDCl3
F
1h
f1 (ppm)

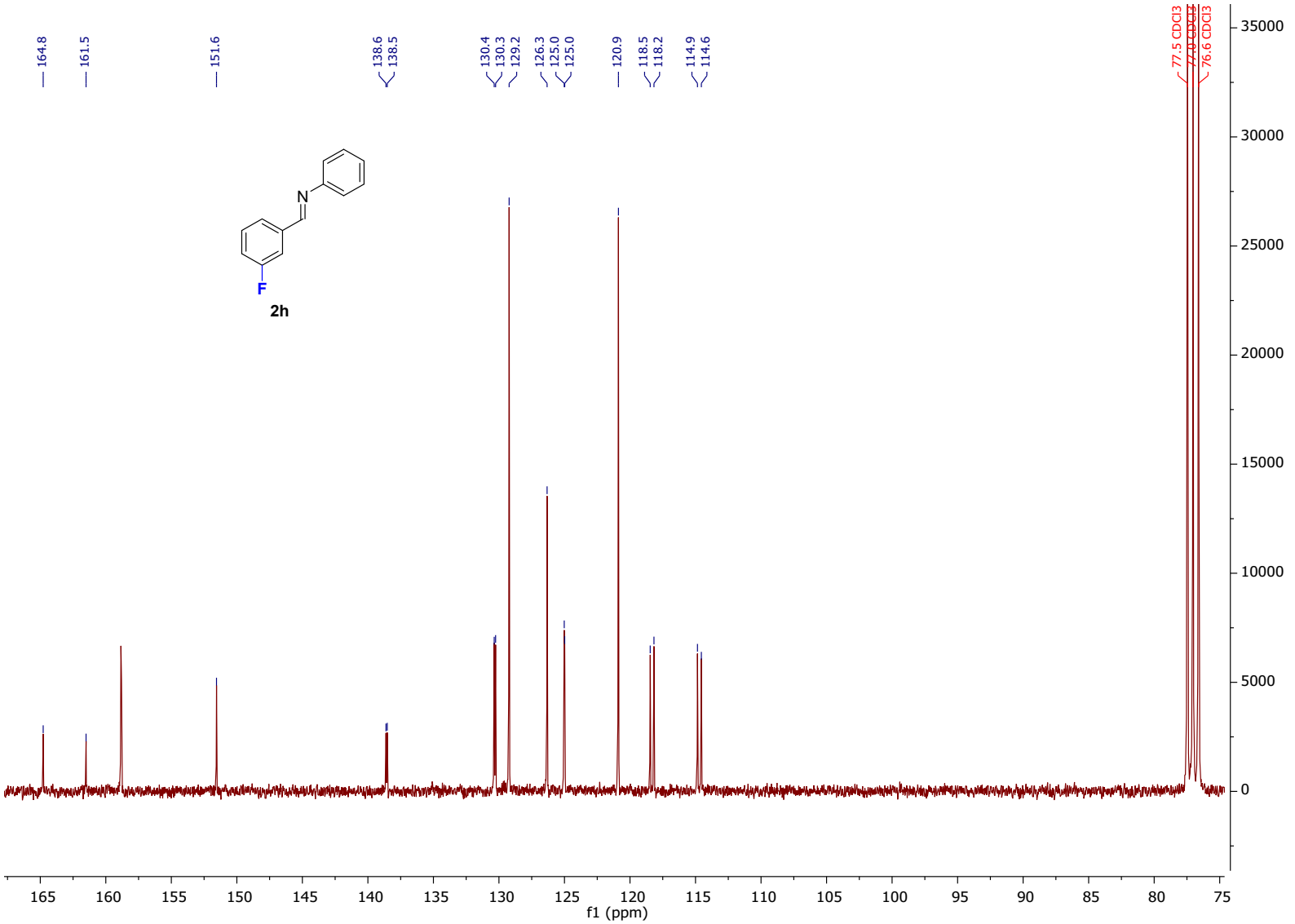

Intens.
x10^6
MAX5504_12_01_4425.d: +MS, 2.2-2.9min #133-171, Background Subtracted (#24-62)
1+
216.0815
1+
238.0635
1+
230.0974
1+
199.0789
300.0345
1h
2.5
2.0
1.5
1.0
0.5
0.0
180
200
220
240
260
280
300
320
340
m/z

(*E*)-1-(3-fluorophenyl)-N-phenylmethanimine (2h)

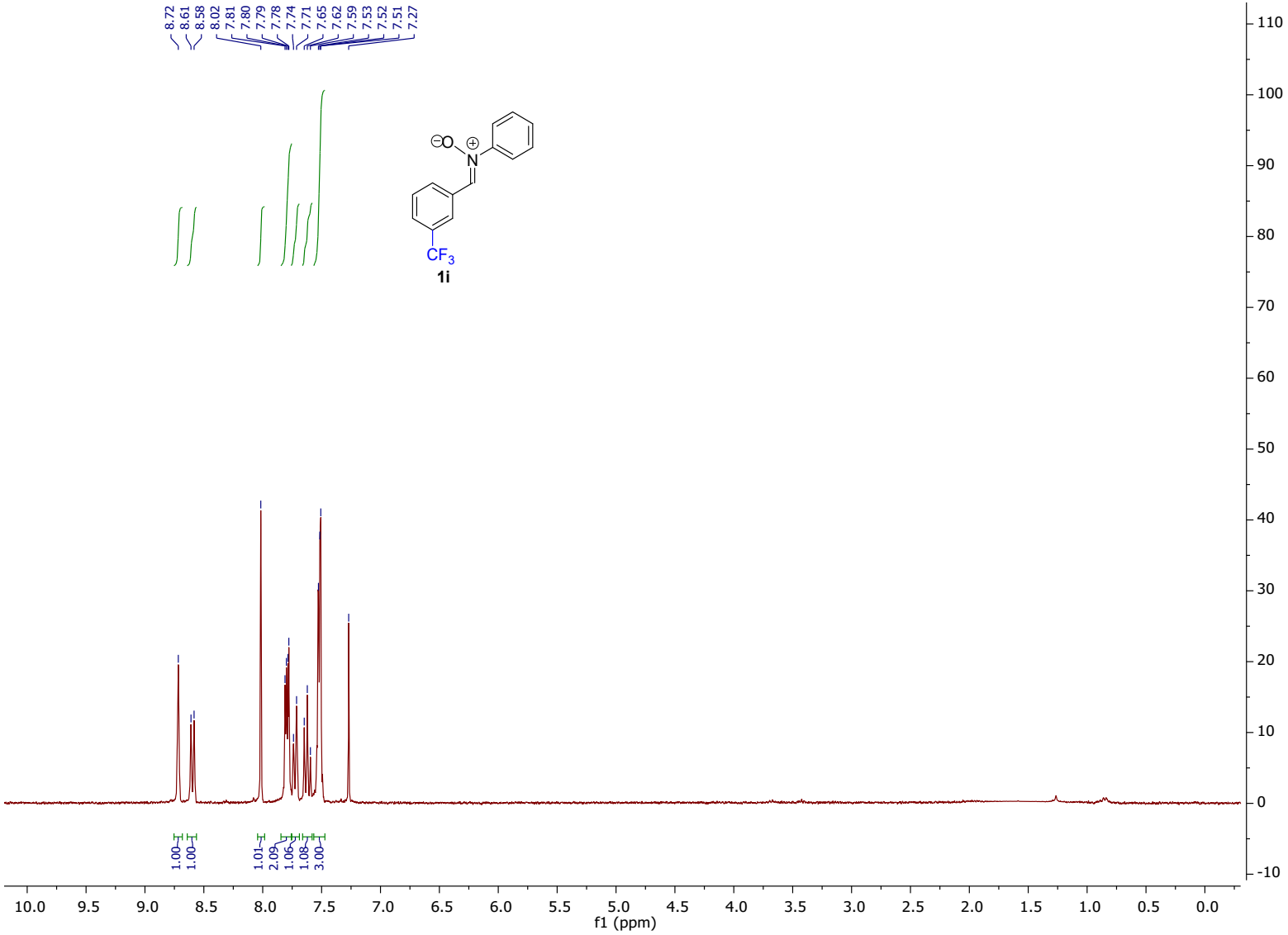


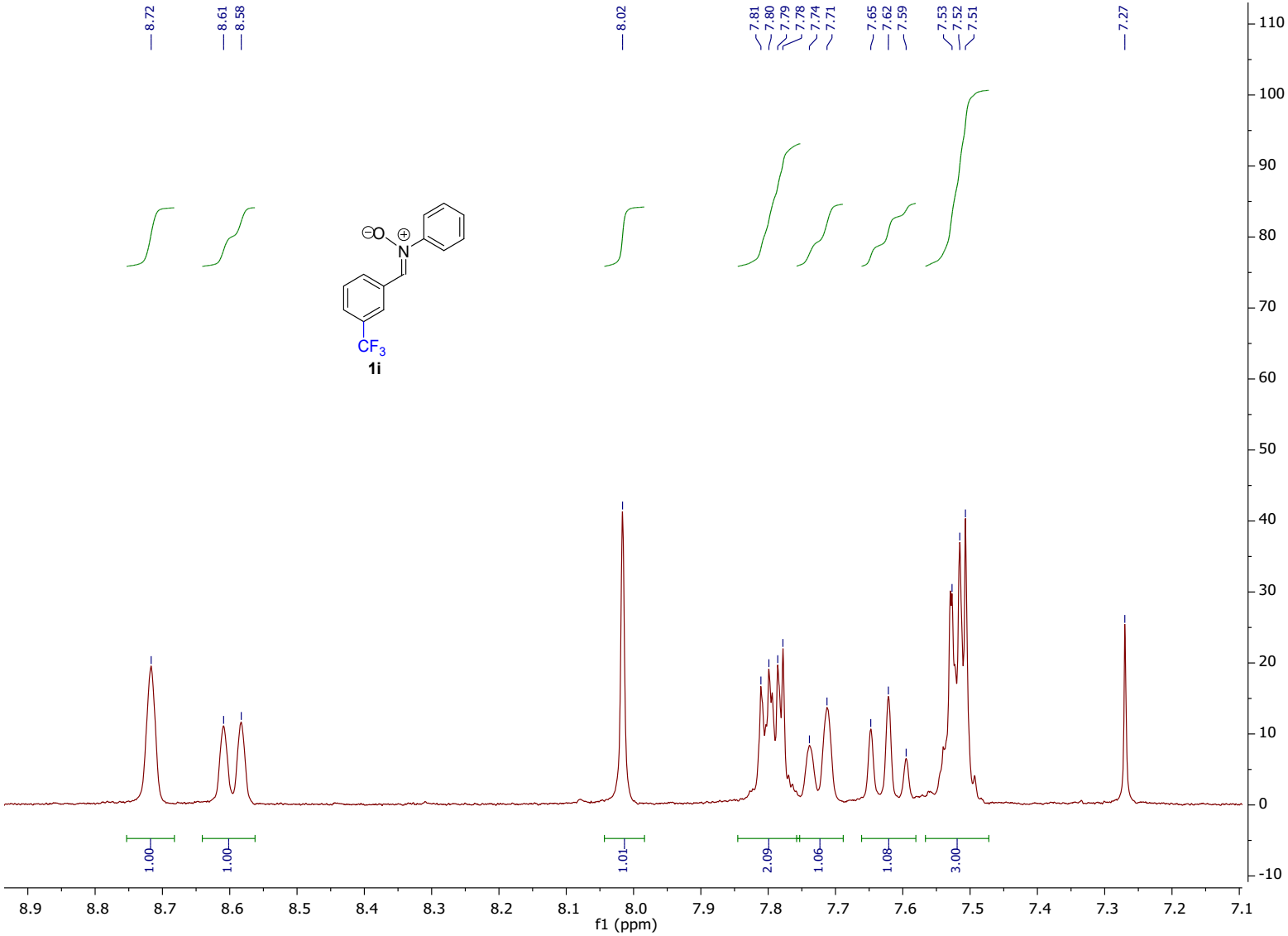

8.40
7.66
7.66
7.65
7.63
7.62
7.59
7.59
7.44
7.42
7.42
7.40
7.37
7.35
7.27 CDCl3
7.25
7.25
7.24
7.22
7.20
7.20
7.17
7.17
7.15
7.15
7.14
7.14
7.13
7.12
7.12
7.11
N
F
2h
1.00
2.12
3.22
4.14
f1 (ppm)

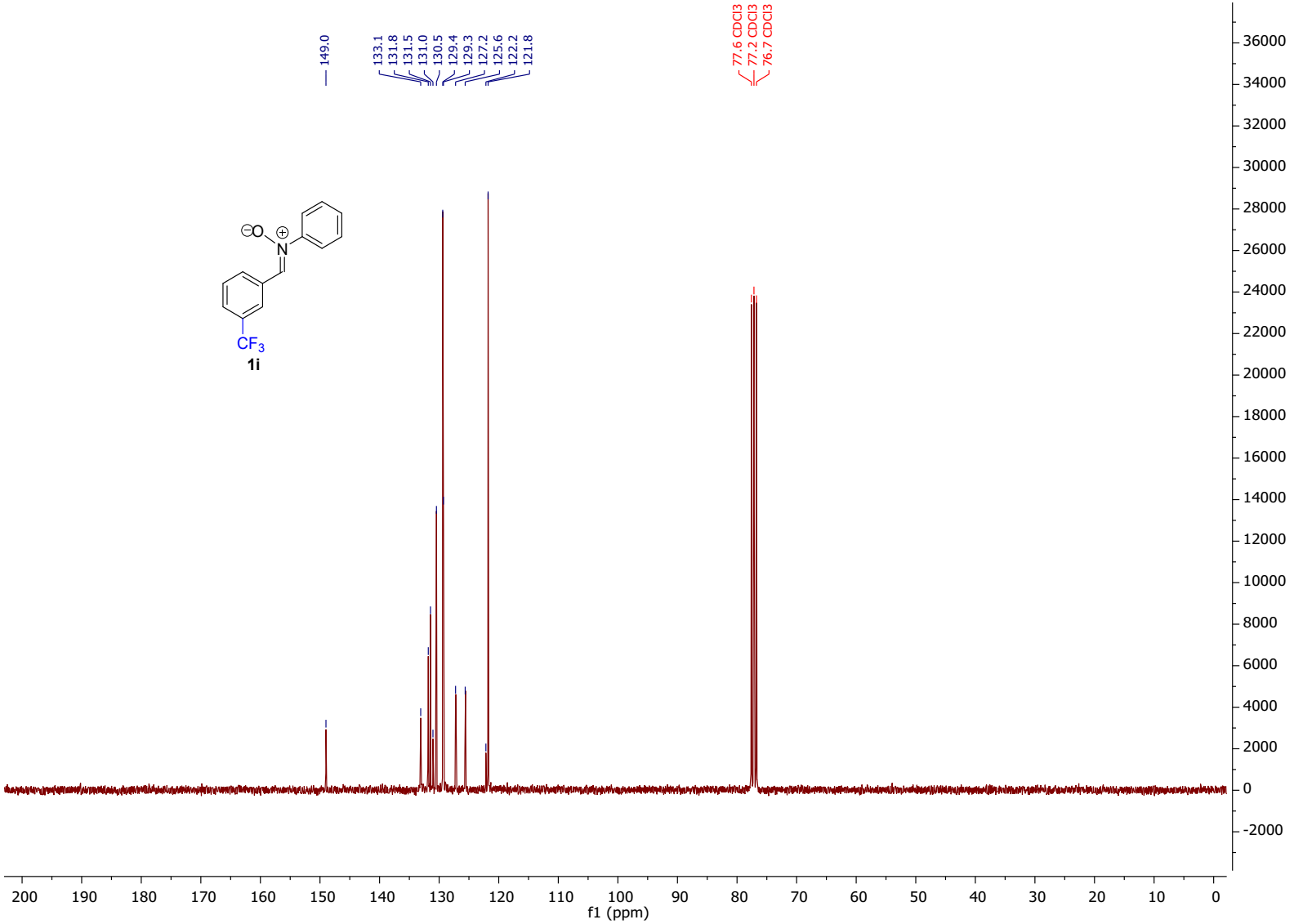

164.8
161.5
151.6
138.6
138.5
130.4
130.3
129.2
126.3
125.0
125.0
120.9
118.5
118.2
114.9
114.6
77.5 CDCl3
77.0 CDCl3
76.6 CDCl3
N
F
2h
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

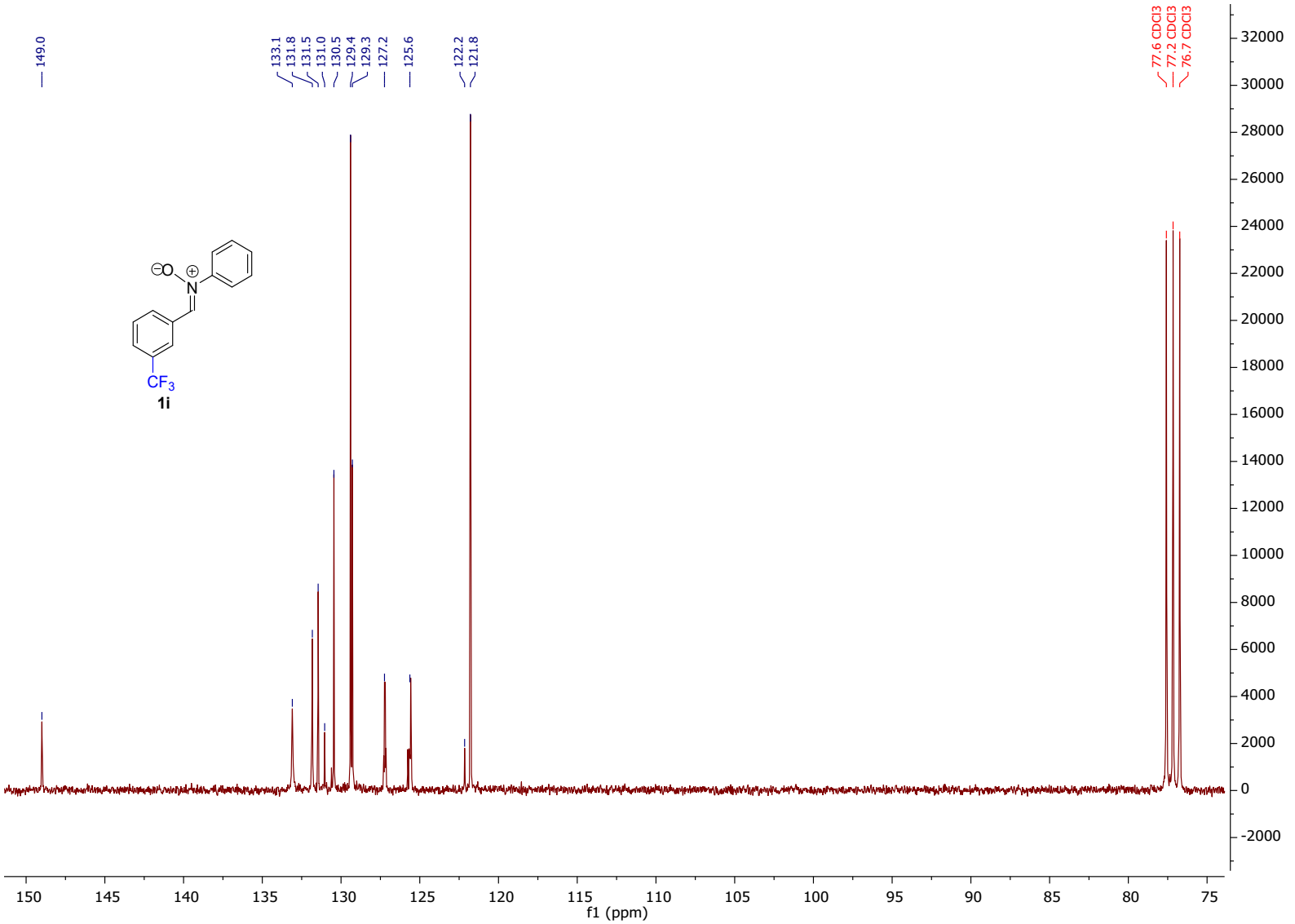

164.8
161.5
151.6
138.6
138.5
130.4
130.3
129.2
126.3
125.0
125.0
120.9
118.5
118.2
114.9
114.6
77.5 CDCl3
77.0 CDCl3
76.6 CDCl3
N
F
2h
35000
30000
25000
20000
15000
10000
5000
0
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
f1 (ppm)

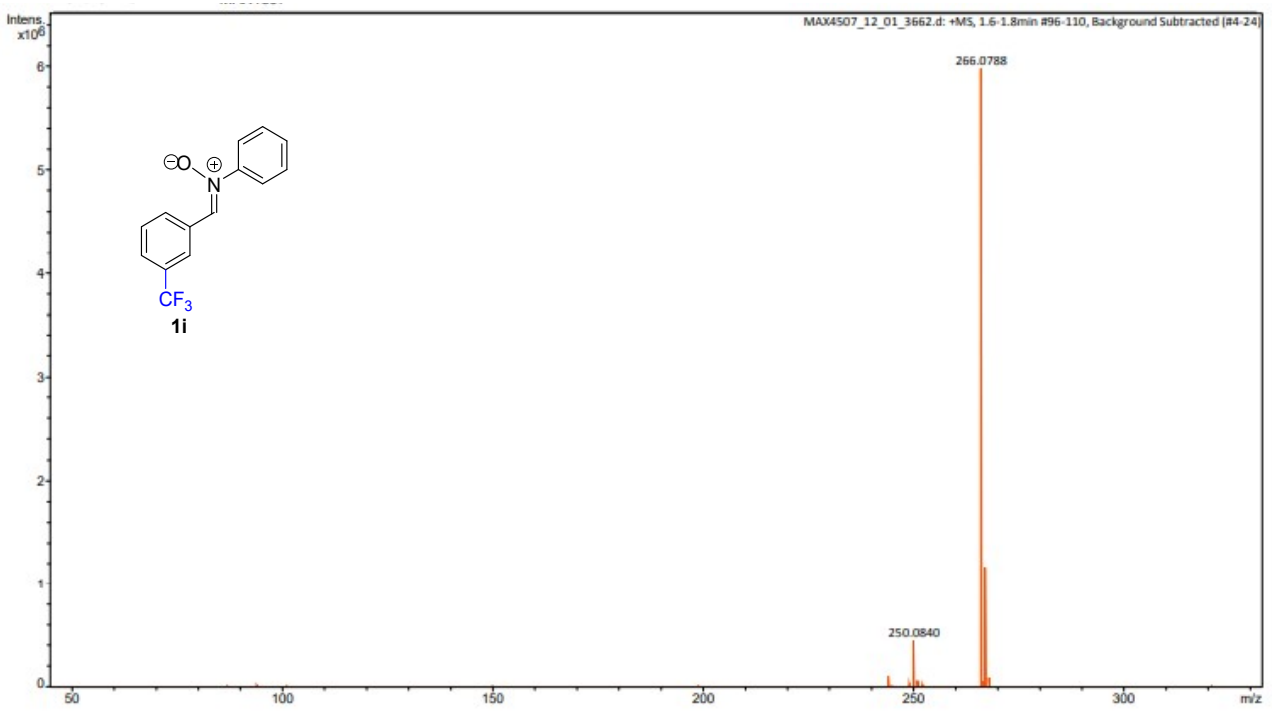
(*Z*)-*N*-phenyl-1-(3-(trifluoromethyl)phenyl)methanimine oxide (1i)



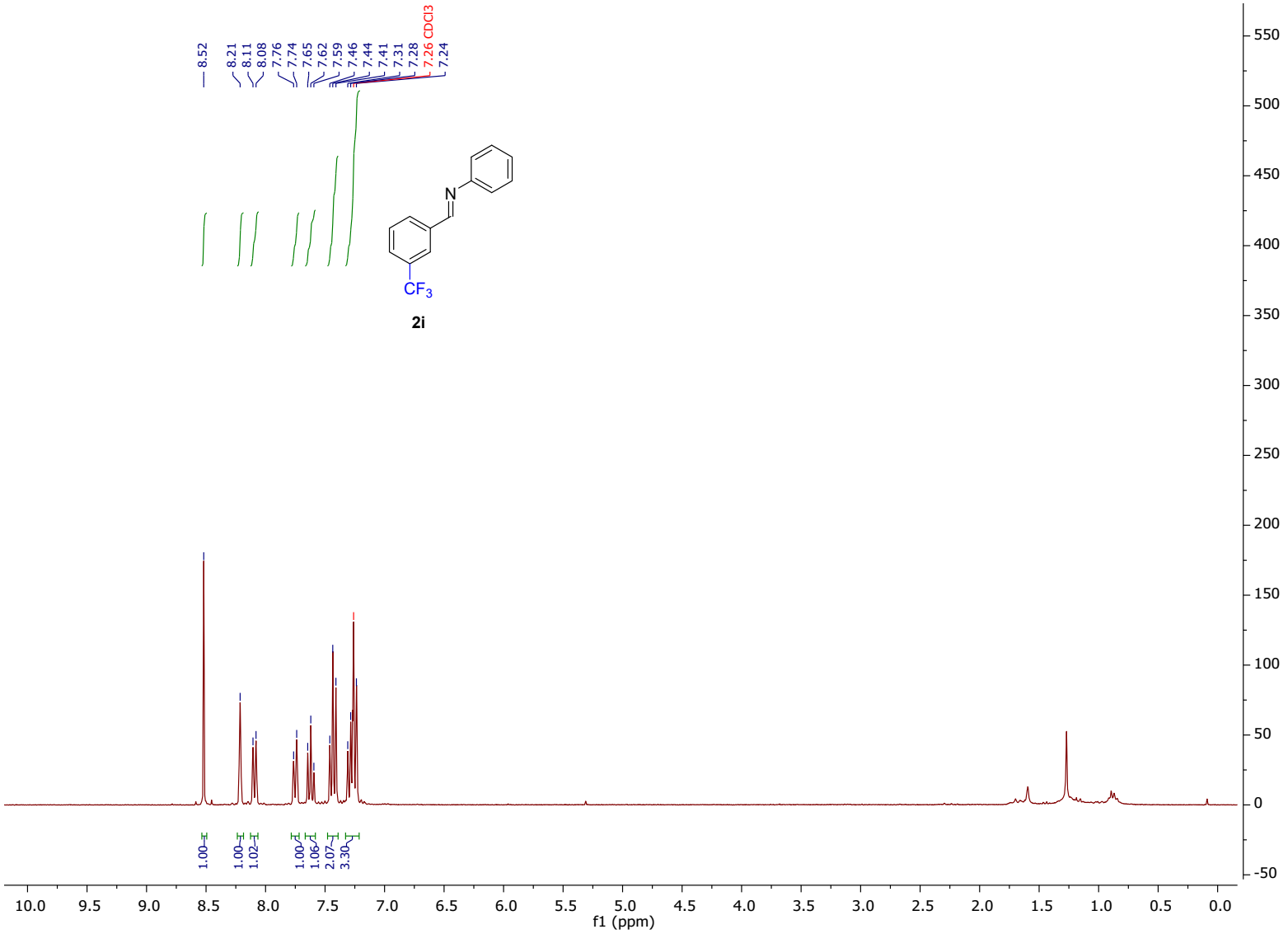

8.72
8.61
8.58
8.02
7.81
7.80
7.79
7.78
7.74
7.71
7.65
7.62
7.59
7.53
7.52
7.51
7.27
CF3
1i
1.00
1.00
1.01
2.09
1.06
1.08
3.00
f1 (ppm)

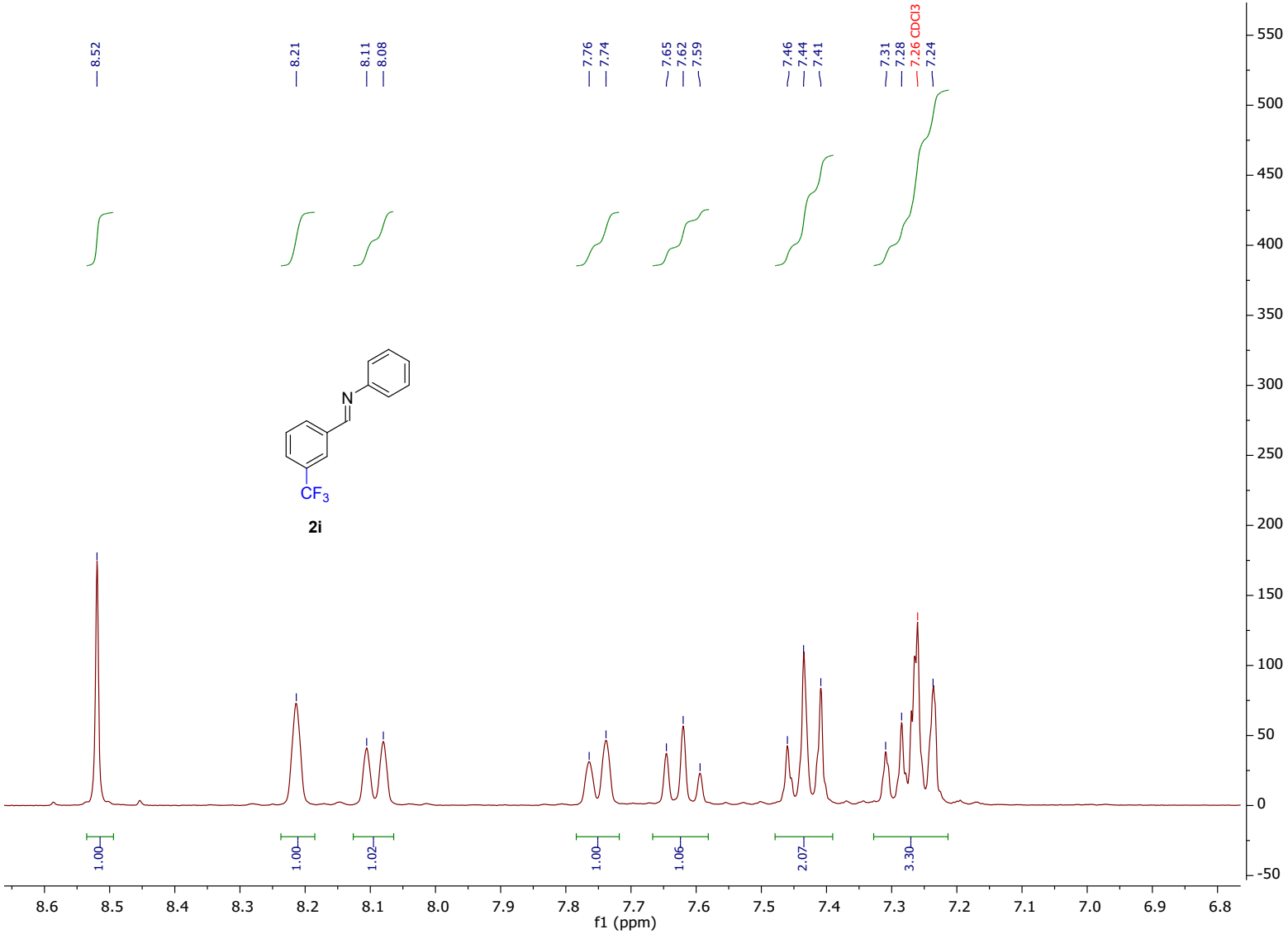

149.0
133.1
131.8
131.5
131.0
130.5
129.4
129.3
127.2
125.6
122.2
121.8
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
CF3
1i
f1 (ppm)

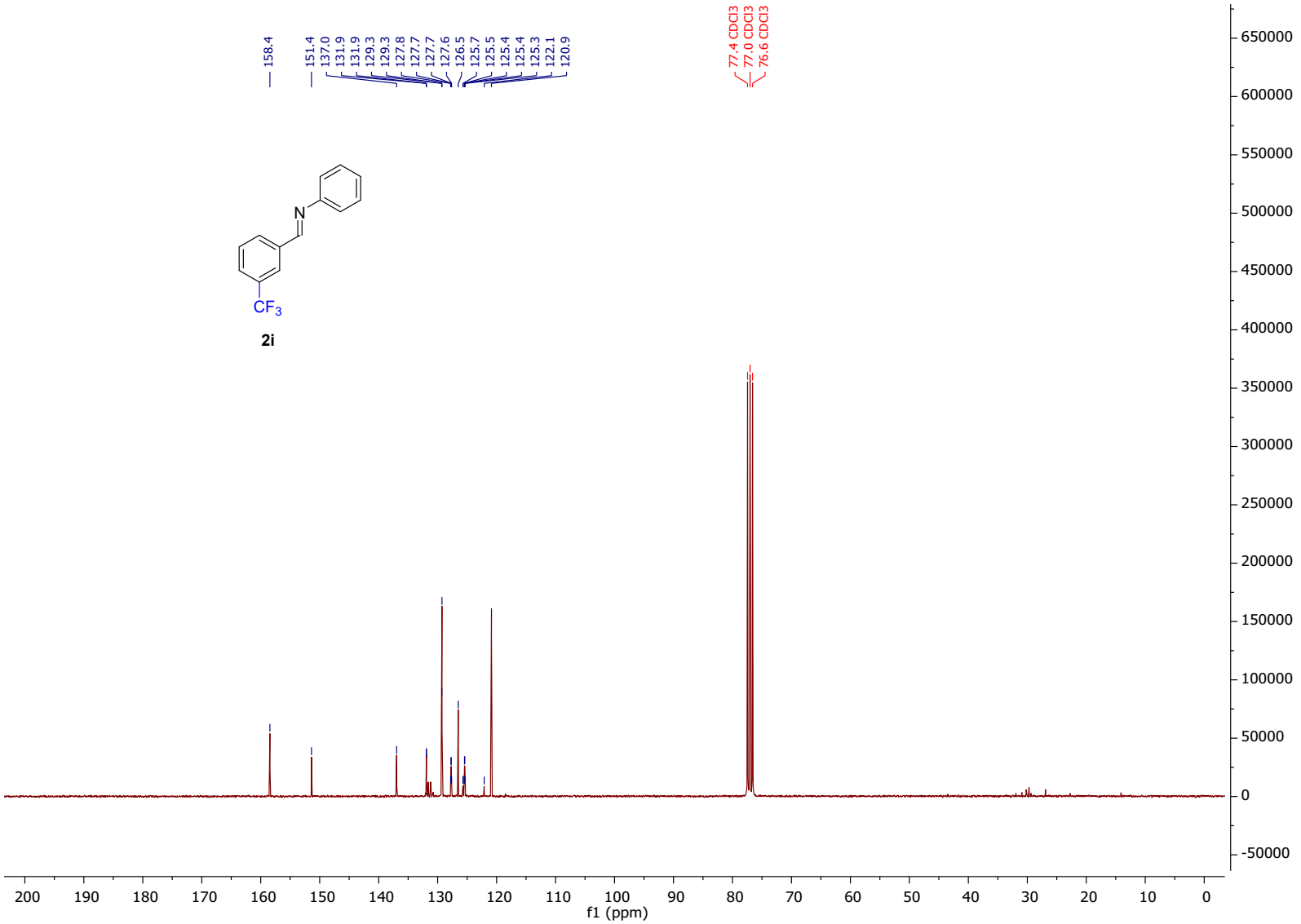

149.0
133.1
131.8
131.5
131.0
130.5
129.4
129.3
127.2
125.6
122.2
121.8
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
CF3
1i
f1 (ppm)

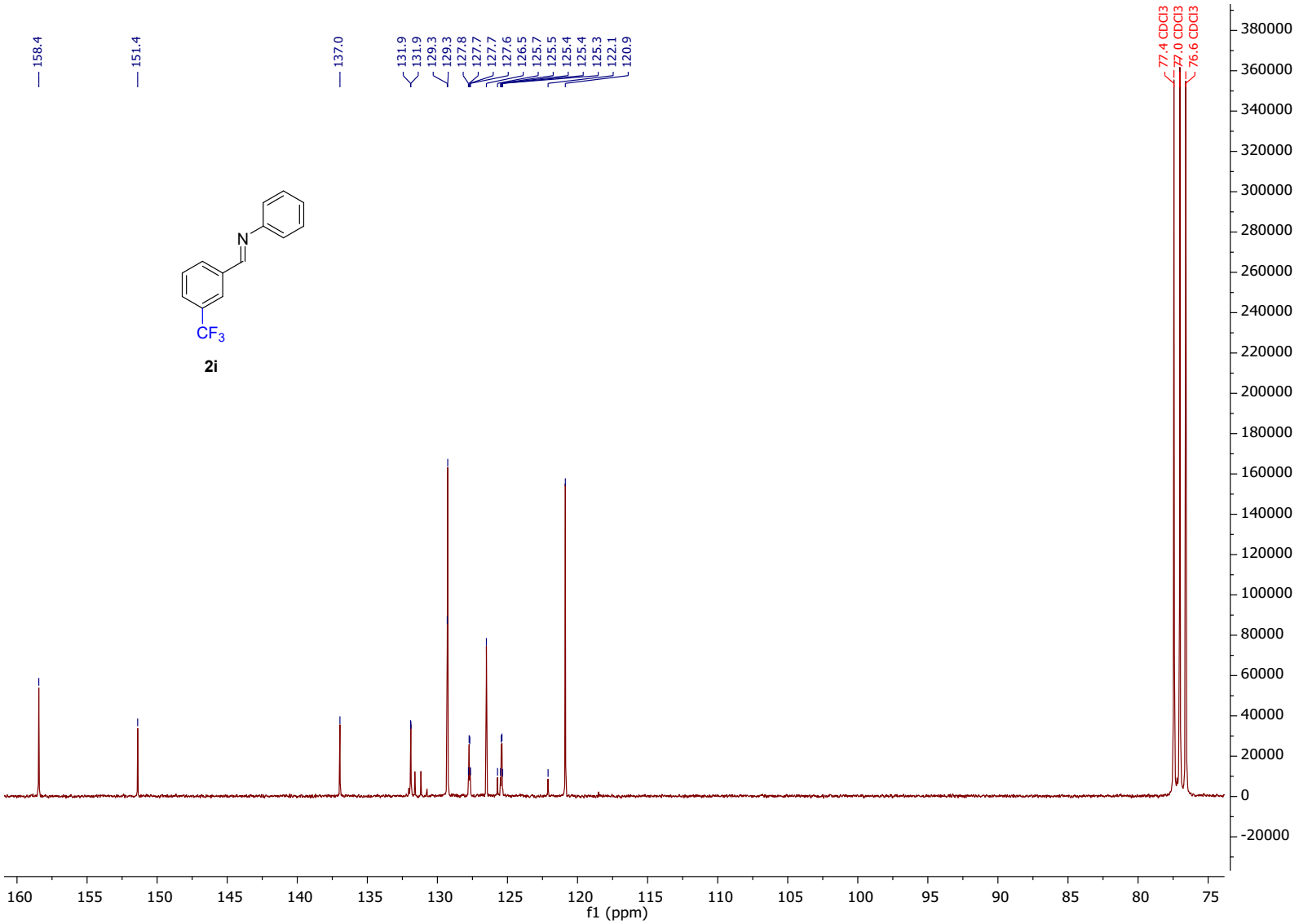

Intens.
x10^6
MAX4507_12_01_3662.d: +MS, 1.6-1.8min #96-110, Background Subtracted (#4-24)
266.0788
250.0840
m/z
CF3
1i

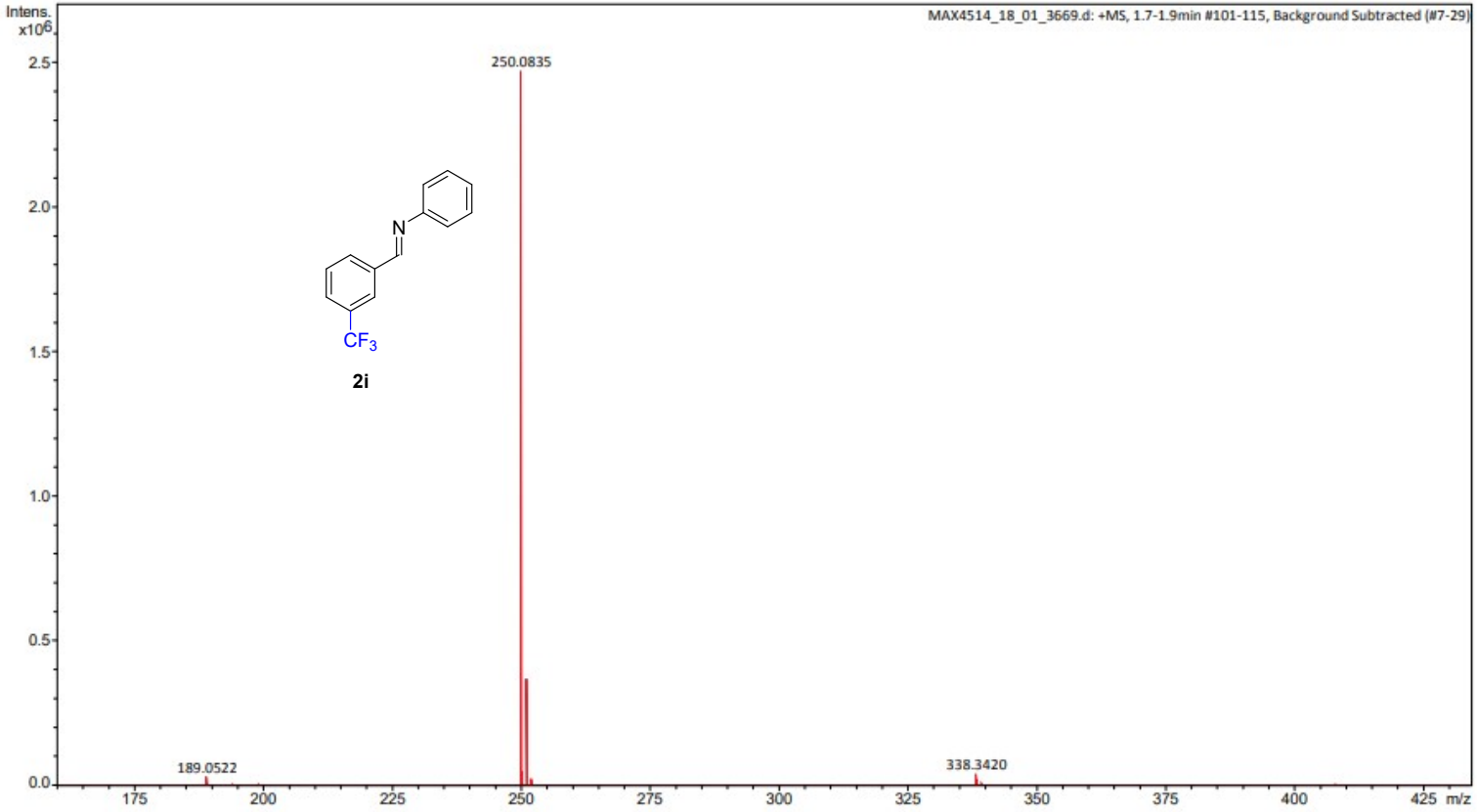
(*E*)-*N*-phenyl-1-(3-(trifluoromethyl)phenyl)methanimine (2i)




8.52
8.21
8.11
8.08
7.76
7.74
7.65
7.62
7.59
7.46
7.44
7.41
7.31
7.28
7.26 CDCl3
7.24
N
CF3
2i
1.00
1.00
1.02
1.00
1.06
2.07
3.30
f1 (ppm)

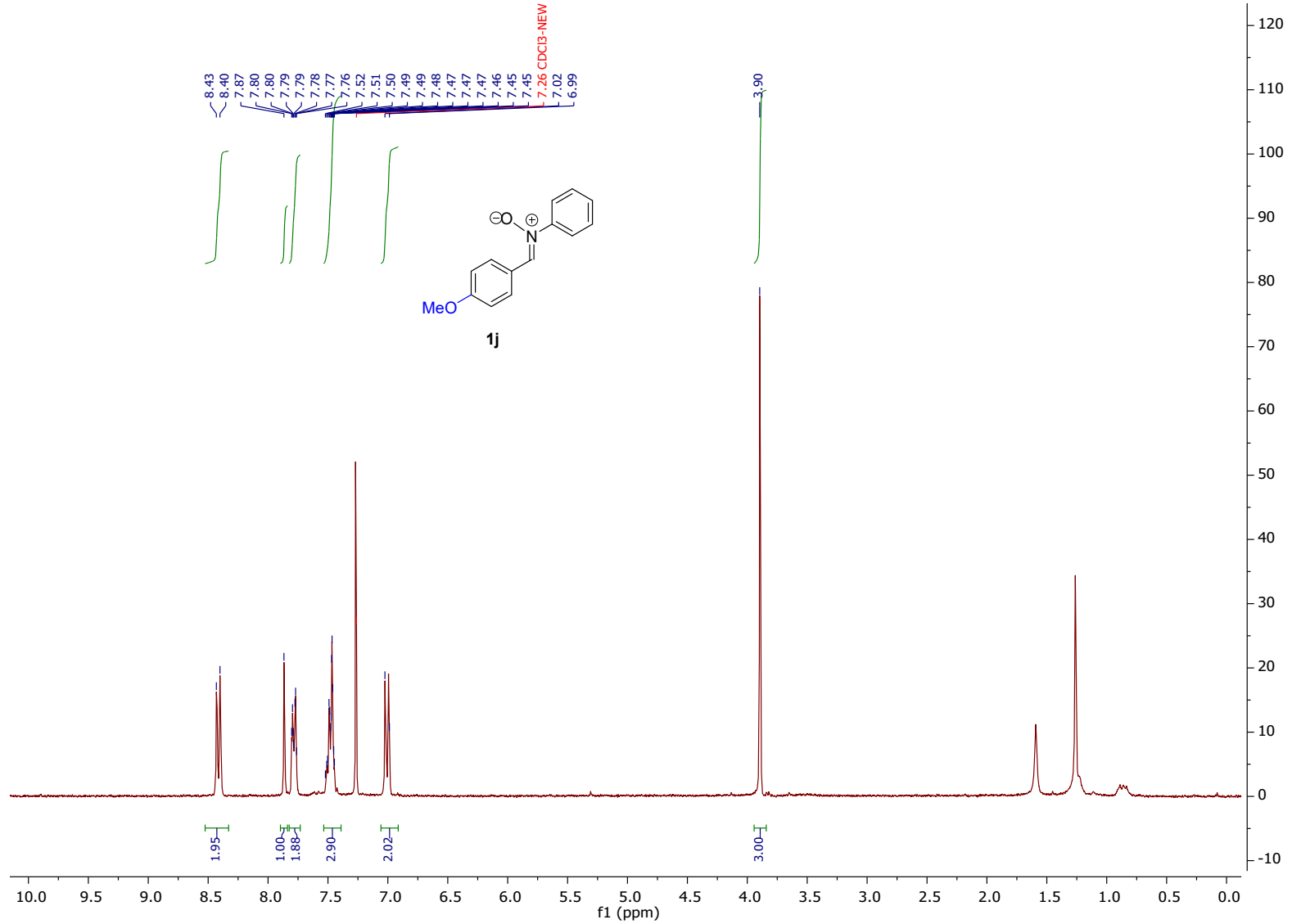

158.4
151.4
137.0
131.9
131.9
129.3
129.3
127.8
127.7
127.7
127.6
126.5
125.7
125.5
125.4
125.4
125.3
122.1
120.9
77.4 CDCl3
77.0 CDCl3
76.6 CDCl3
N
CF3
2i
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

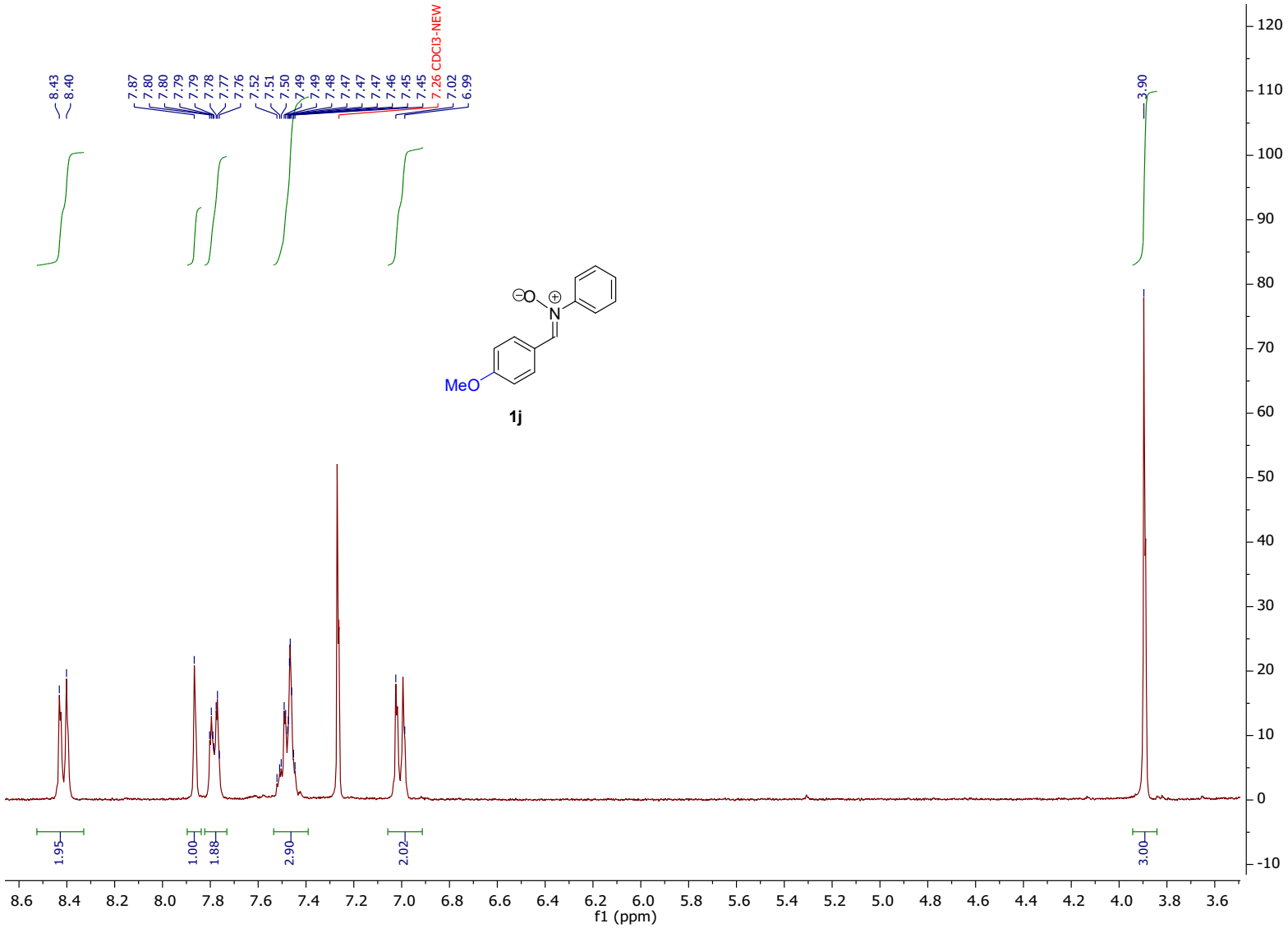

158.4
151.4
137.0
131.9
131.9
129.3
129.3
127.8
127.7
127.7
127.6
126.5
125.7
125.5
125.4
125.4
125.3
122.1
120.9
77.4 CDCl3
77.0 CDCl3
76.6 CDCl3
N
CF3
2i
f1 (ppm)

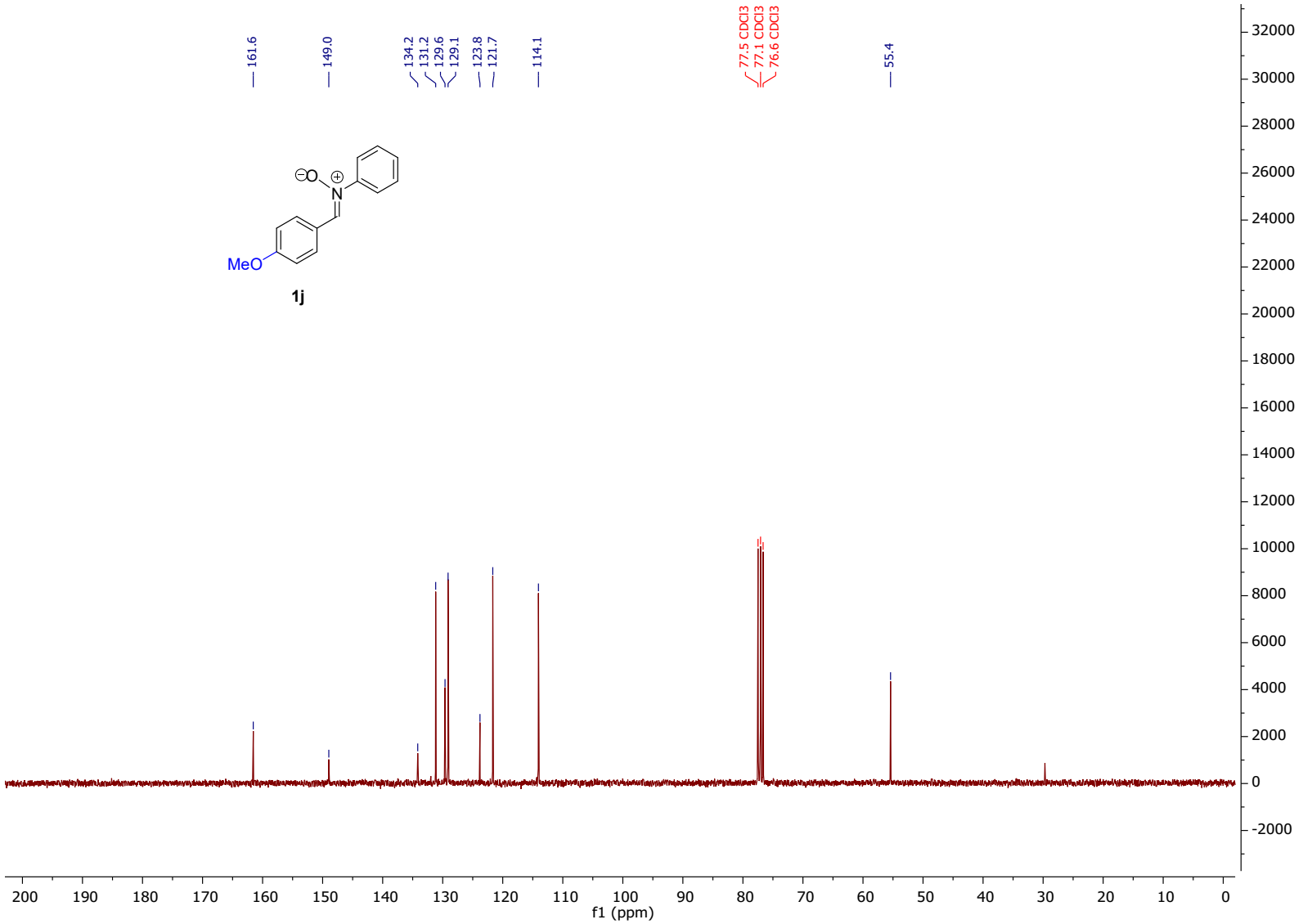

Intens.
x10^6
MAX4514_18_01_3669.d: +MS, 1.7-1.9min #101-115, Background Subtracted (#7-29)
250.0835
189.0522
338.3420
2.5
2.0
1.5
1.0
0.5
0.0
175
200
225
250
275
300
325
350
375
400
425 m/z
N
CF3

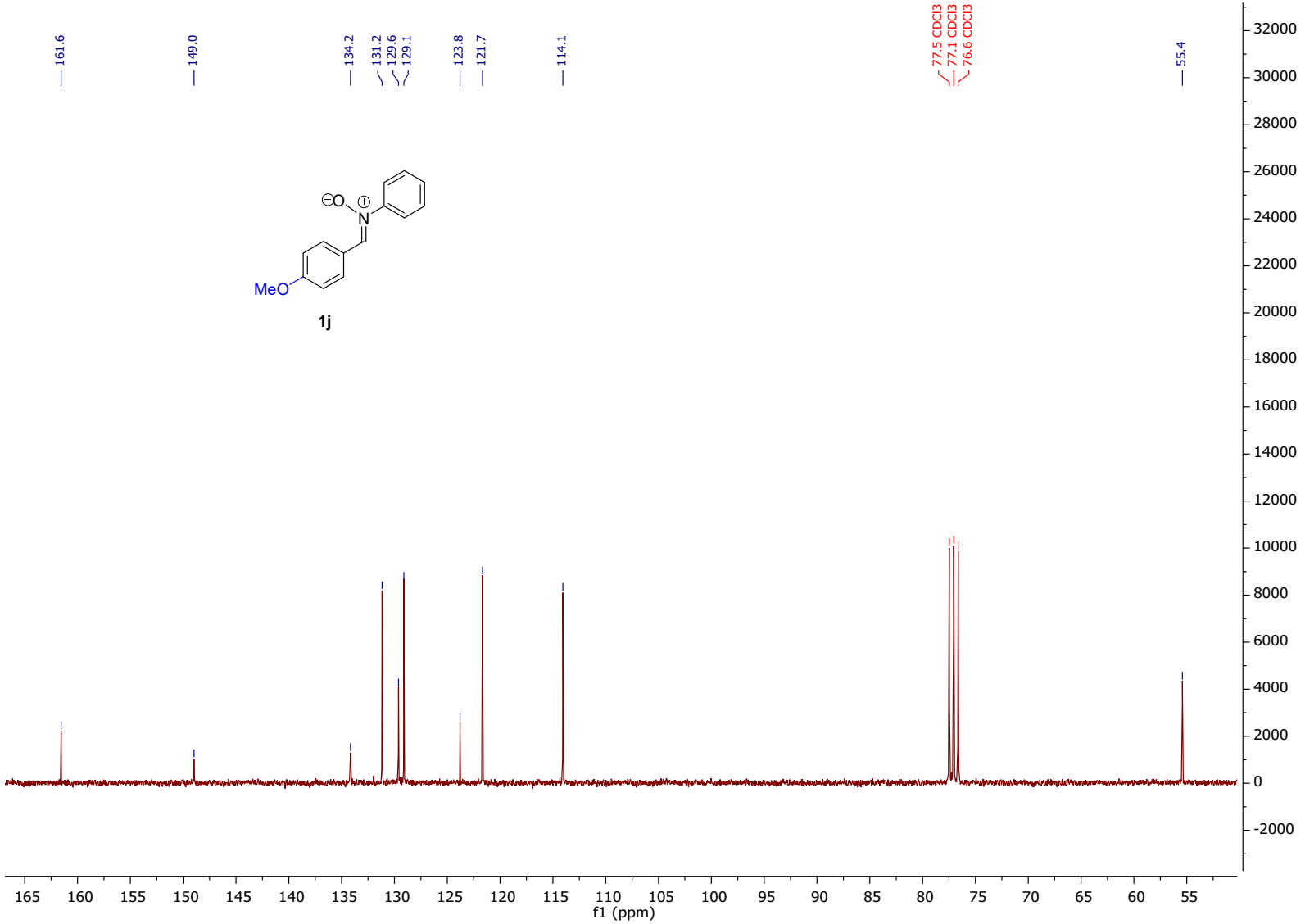
2i

(*Z*)-1-(4-Methoxyphenyl)-*N*-phenylmethanimine oxide (1j)

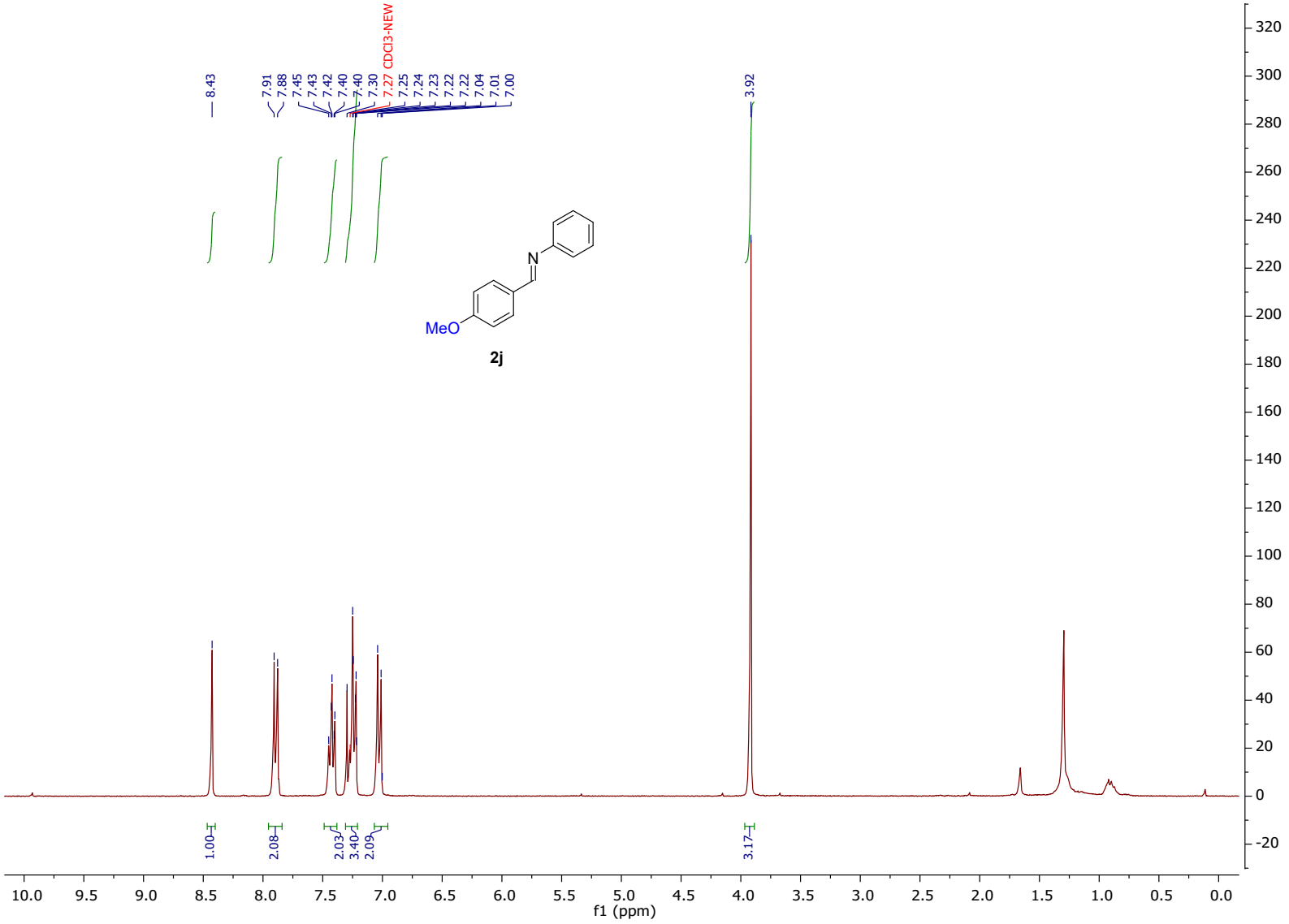


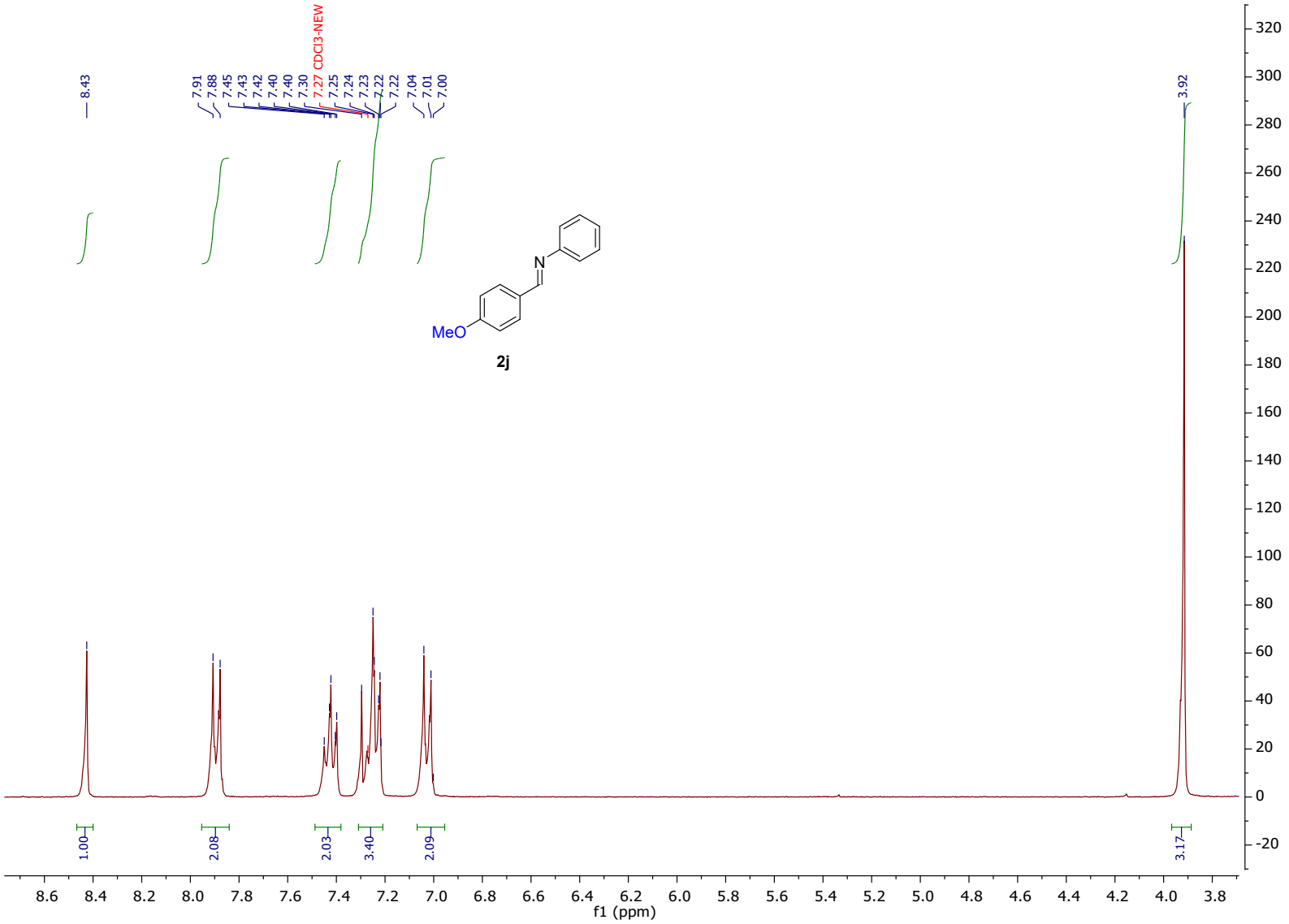

8.43
8.40
7.87
7.80
7.80
7.79
7.79
7.78
7.77
7.76
7.52
7.51
7.50
7.49
7.49
7.48
7.47
7.47
7.47
7.46
7.45
7.45
7.26 CDCl3-NEW
7.02
6.99
3.90
MeO
1j
1.95
1.00
1.88
2.90
2.02
3.00
f1 (ppm)


161.6
149.0
134.2
131.2
129.6
129.1
123.8
121.7
114.1
77.5 CDCl3
77.1 CDCl3
76.6 CDCl3
55.4
MeO
1j
f1 (ppm)

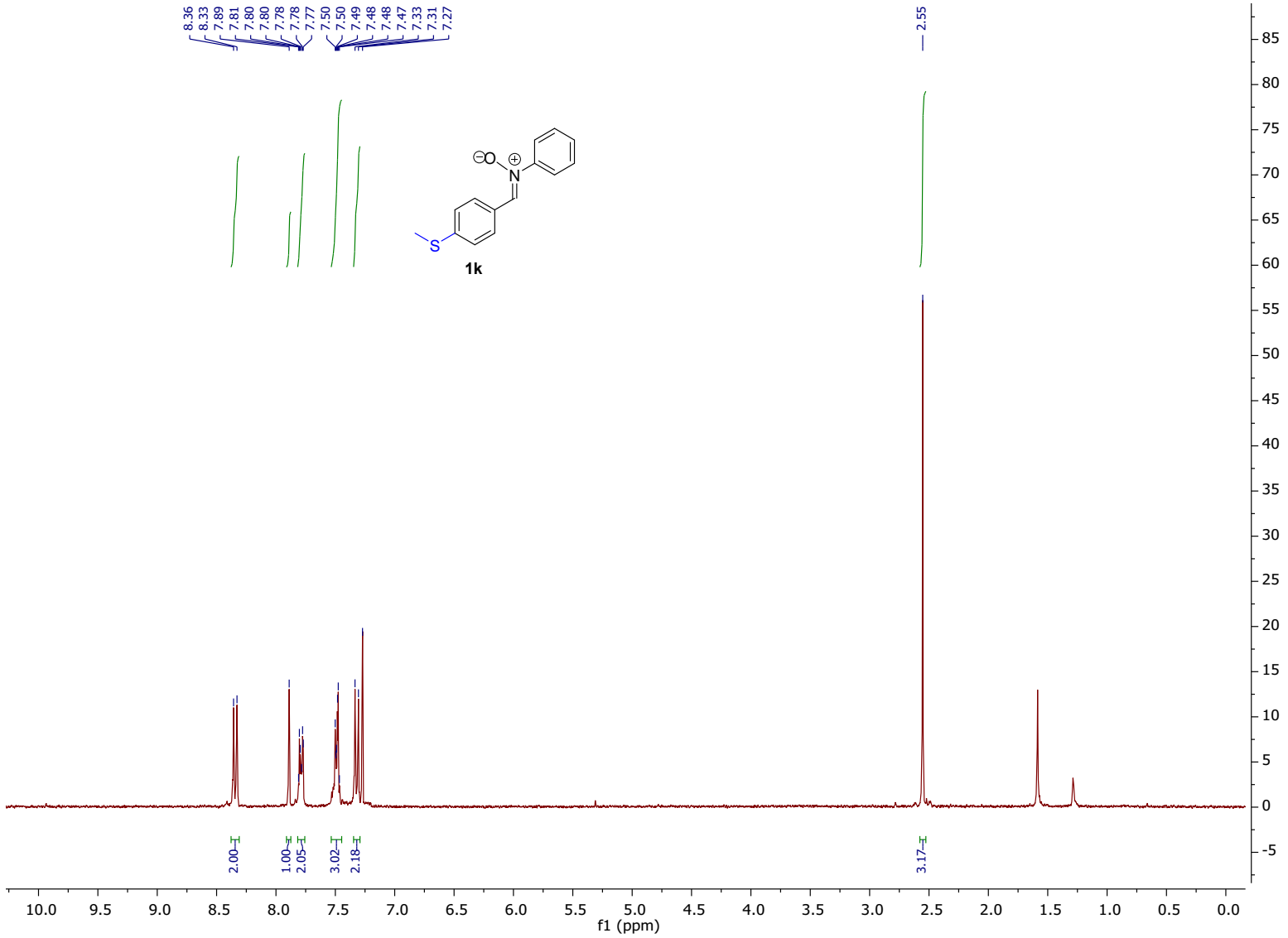

161.6
149.0
134.2
131.2
129.6
129.1
123.8
121.7
114.1
77.5 CDCl3
77.1 CDCl3
76.6 CDCl3
55.4
MeO
1j
f1 (ppm)

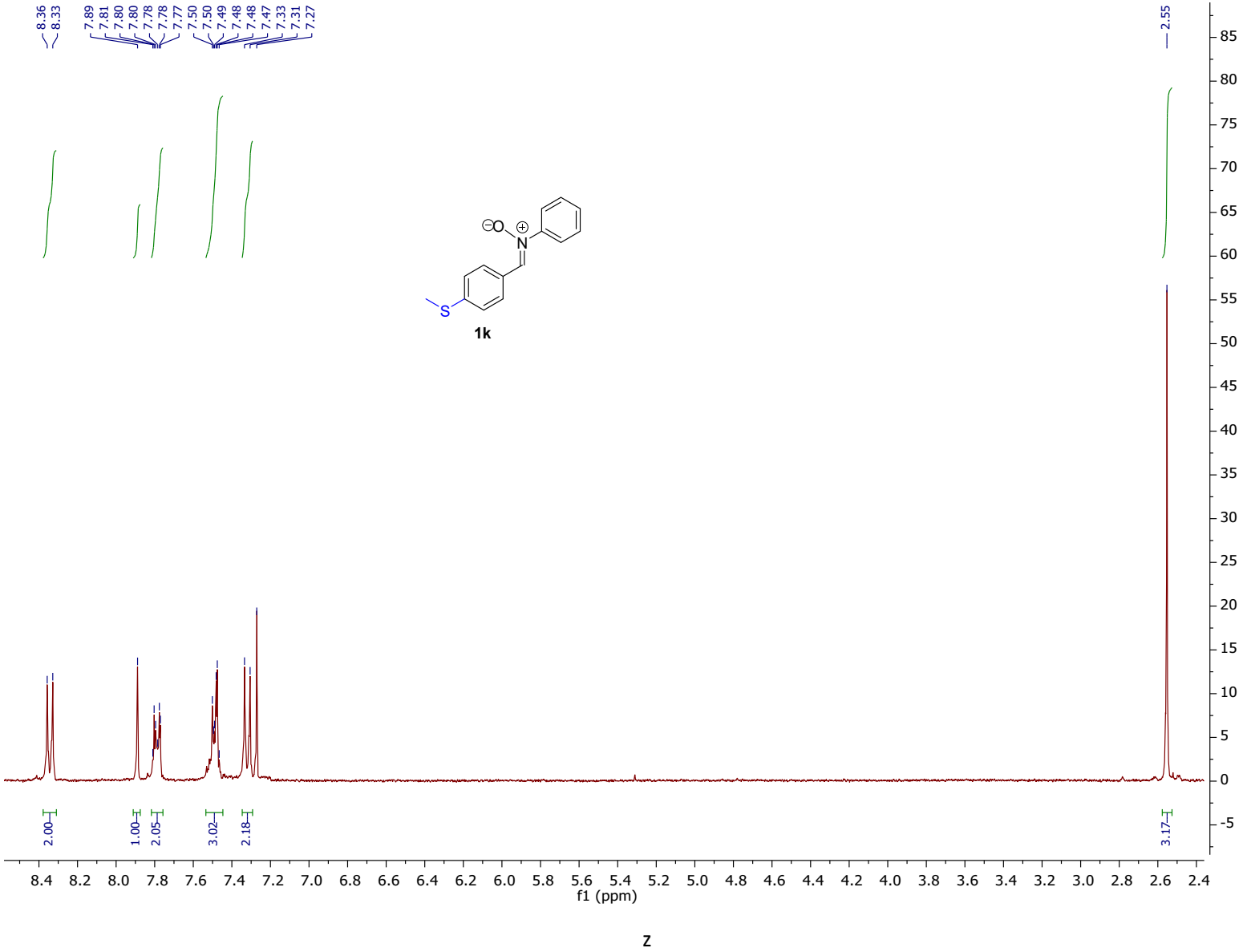
(*E*)-1-(4-Methoxyphenyl)-*N*-phenylmethanimine (2j)



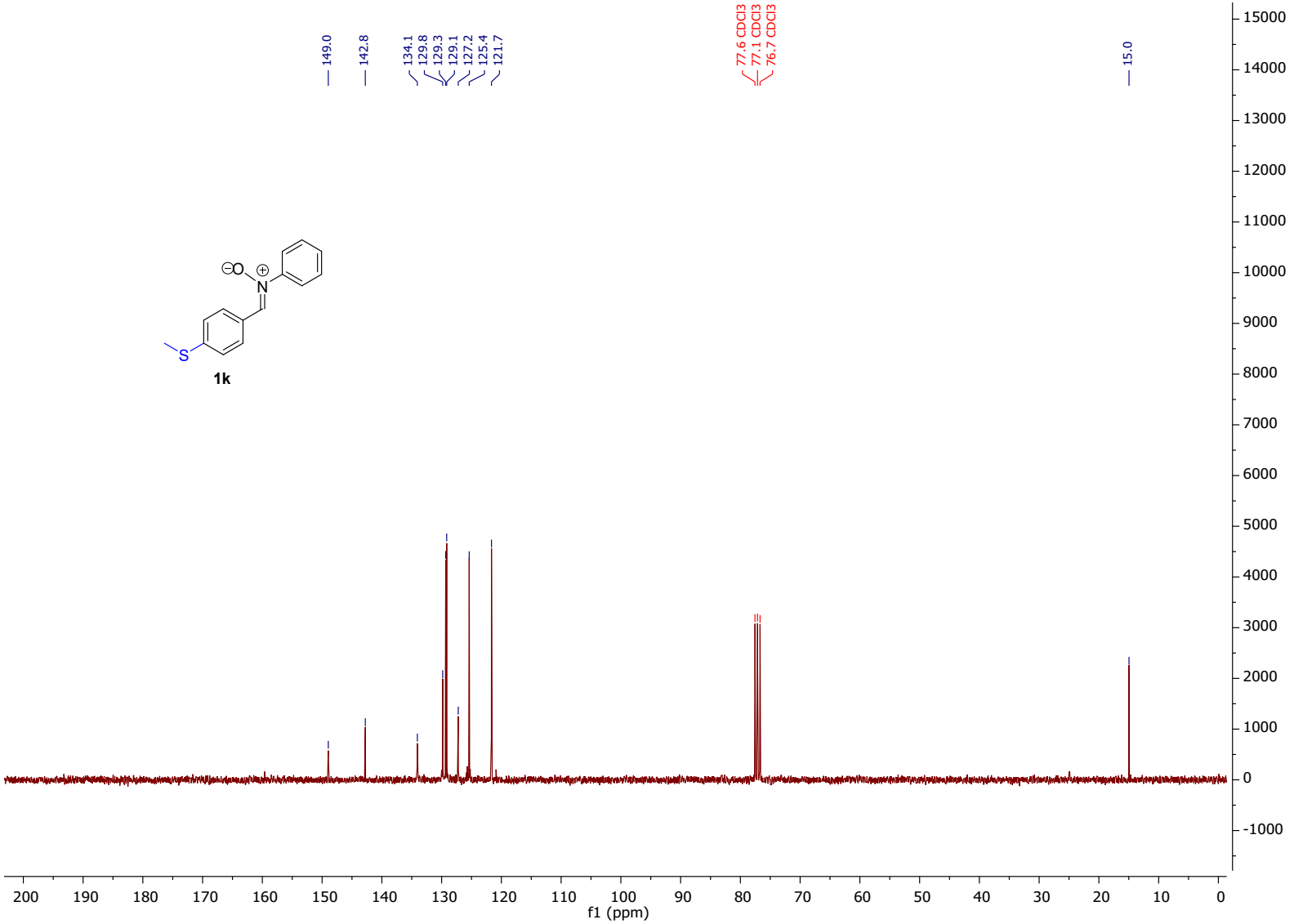

8.43
7.91
7.88
7.45
7.43
7.42
7.40
7.40
7.30
7.27 CDCl3-NEW
7.25
7.24
7.23
7.22
7.22
7.04
7.01
7.00
3.92
N
MeO
2j
1.00
2.08
2.03
3.40
2.09
3.17
f1 (ppm)

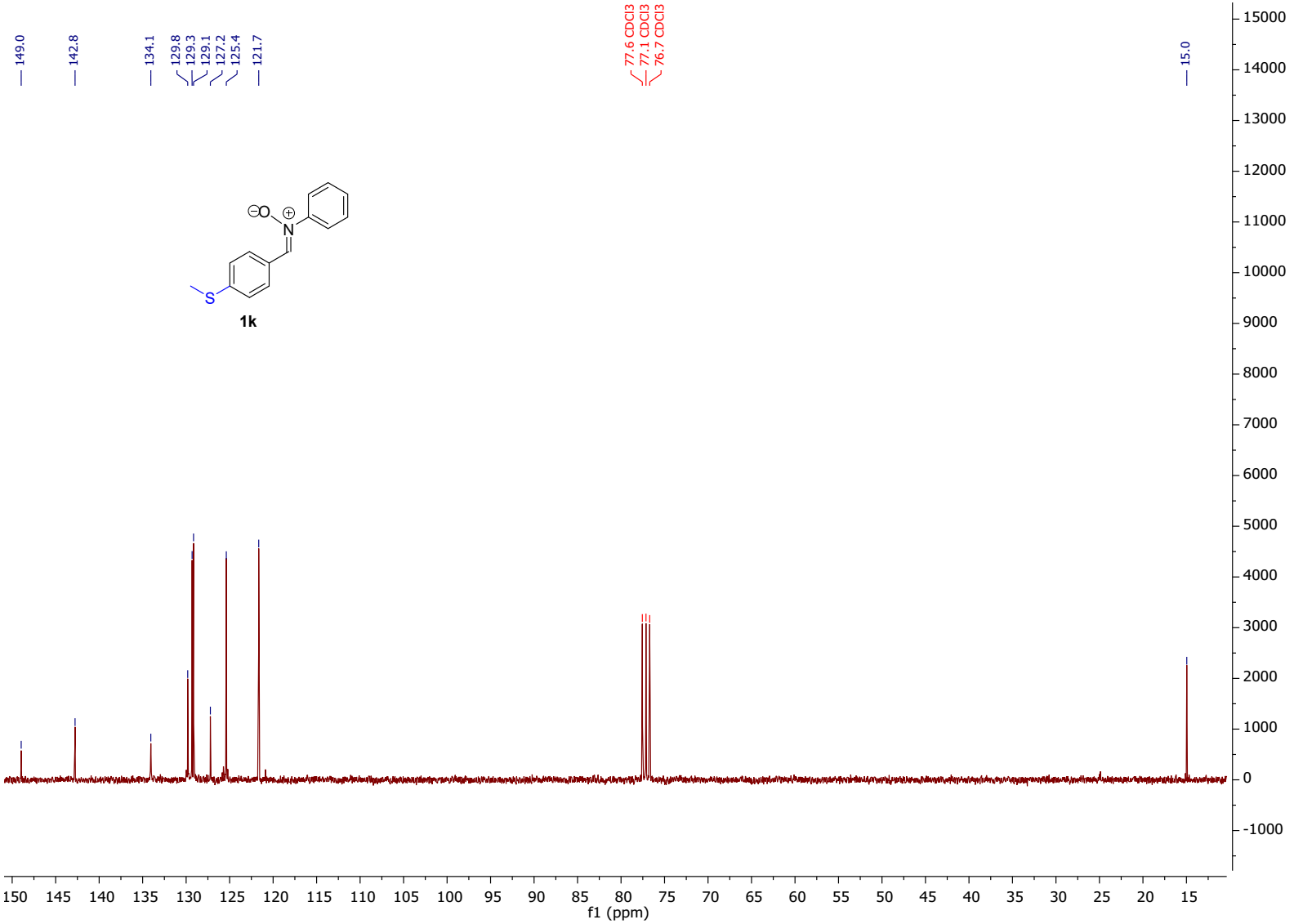
(*Z*)-1-(4-(methylthio)phenyl)-*N*-phenylmethanimine oxide (1k)

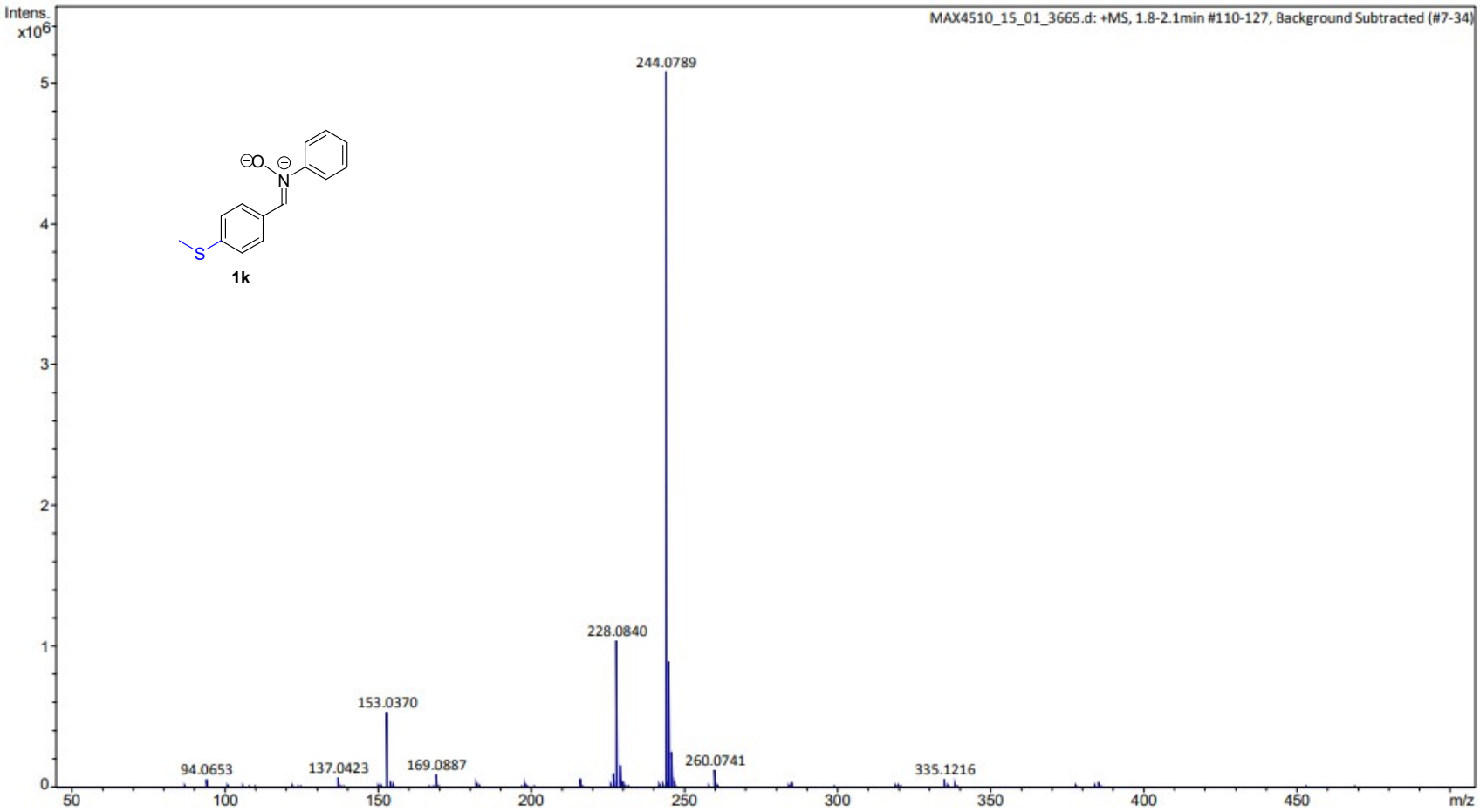



8.36
8.33
7.89
7.81
7.80
7.80
7.78
7.78
7.77
7.50
7.50
7.49
7.48
7.48
7.47
7.33
7.31
7.27
2.55
O
N
S
1k
2.00
1.00
2.05
3.02
2.18
3.17
f1 (ppm)

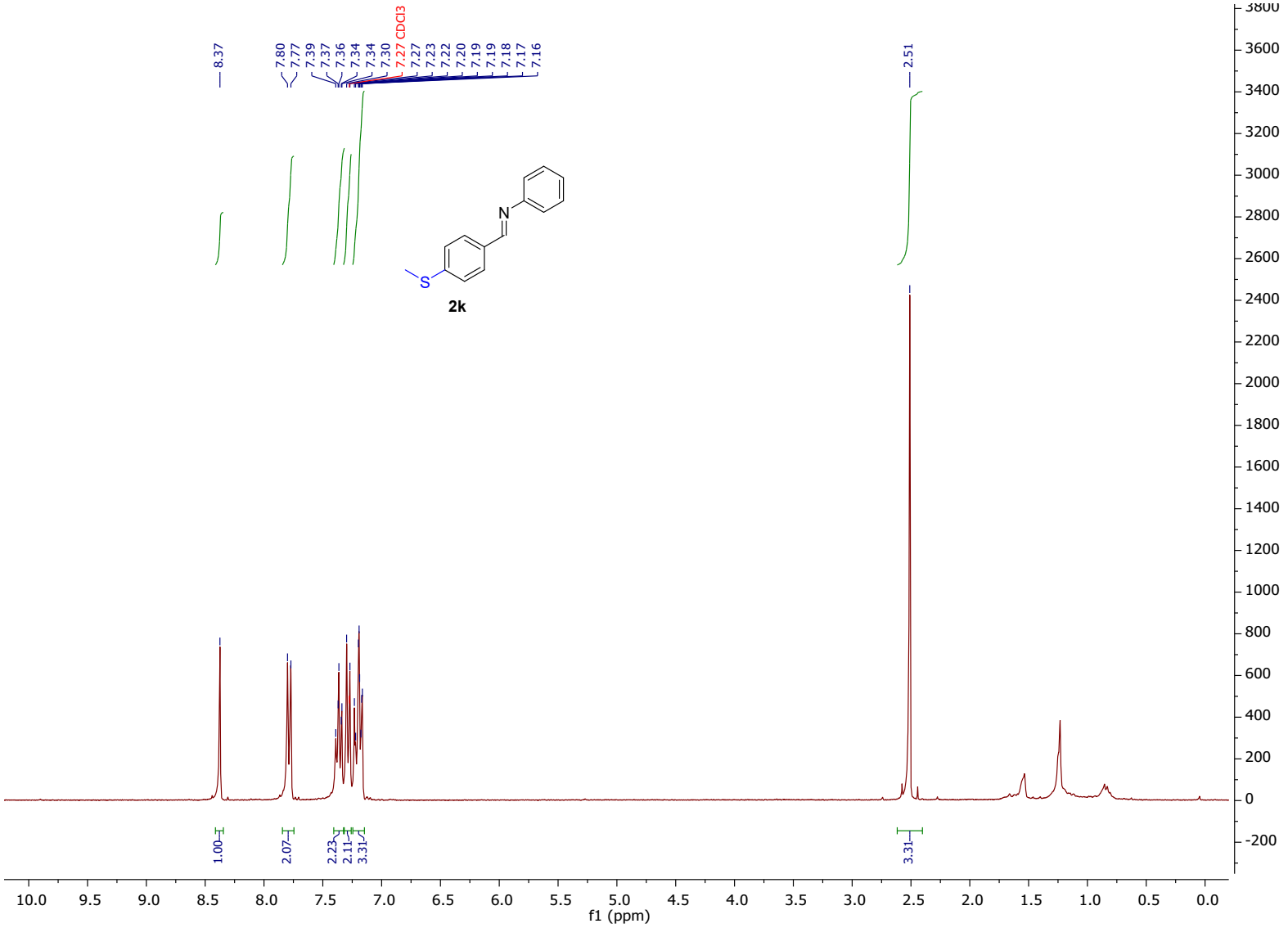
Z

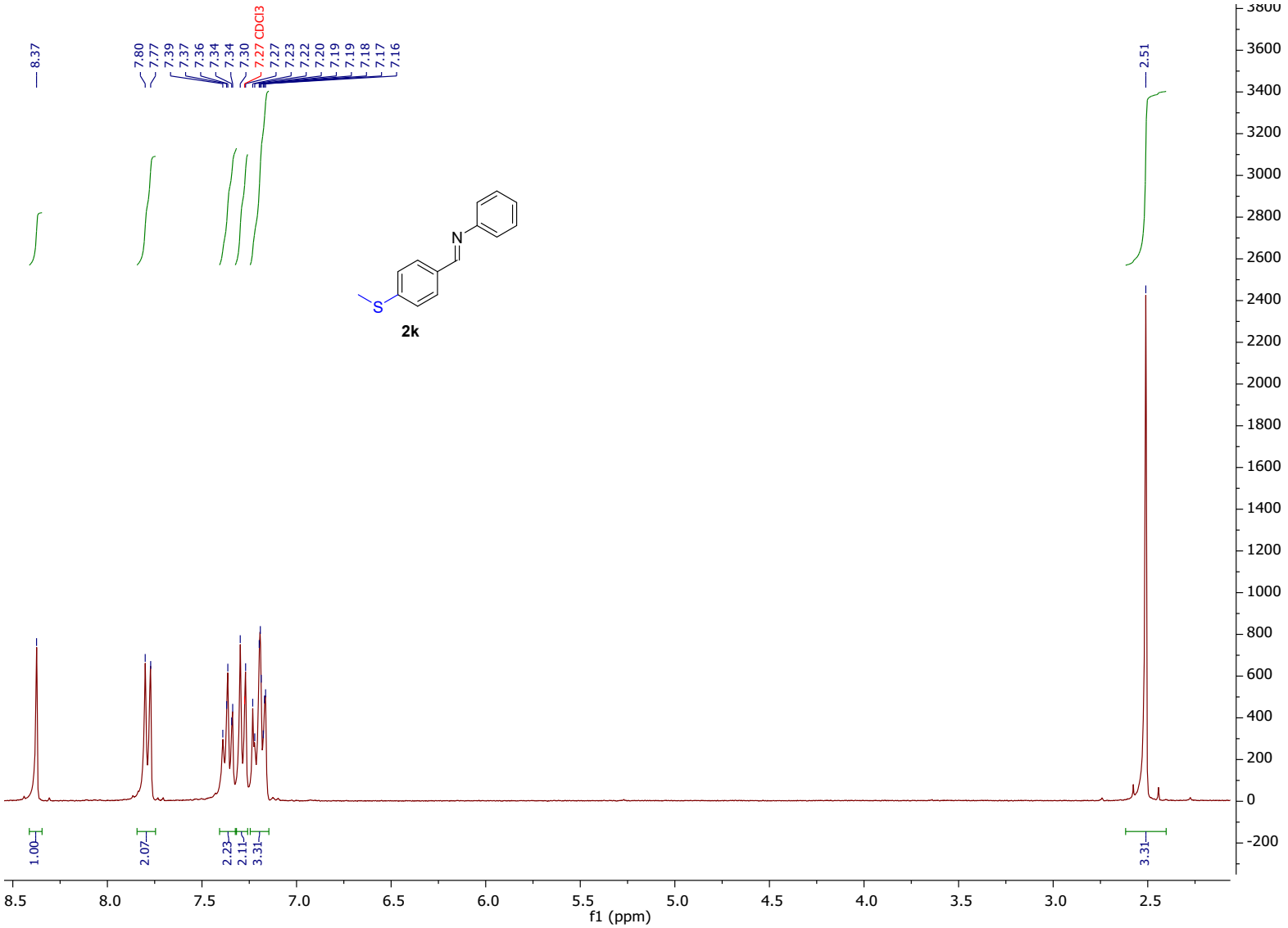

149.0
142.8
134.1
129.8
129.3
129.1
127.2
125.4
121.7
77.6 CDCl3
77.1 CDCl3
76.7 CDCl3
15.0
1k
f1 (ppm)

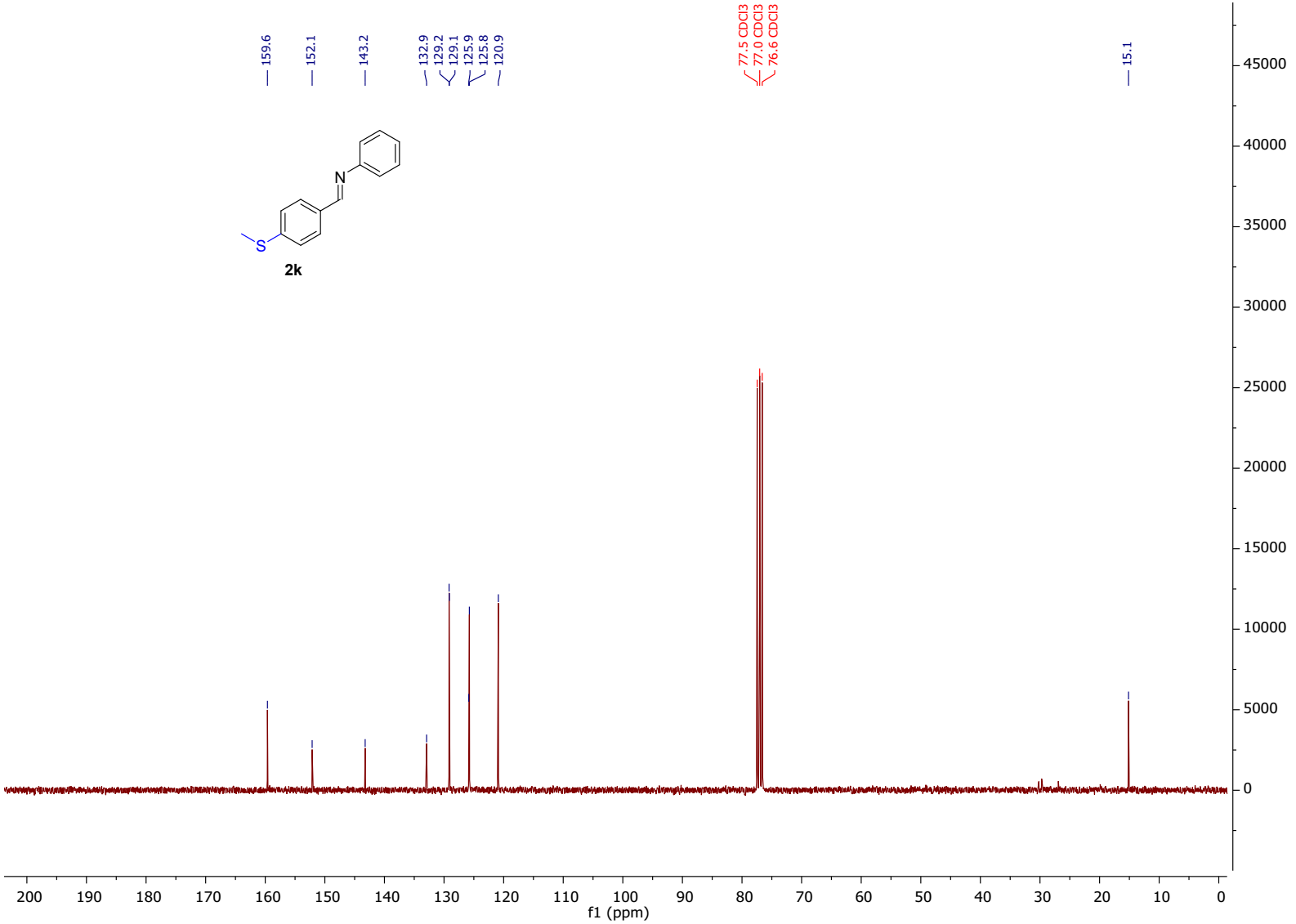

149.0
142.8
134.1
129.8
129.3
129.1
127.2
125.4
121.7
77.6 CDCl3
77.1 CDCl3
76.7 CDCl3
15.0
1k
f1 (ppm)

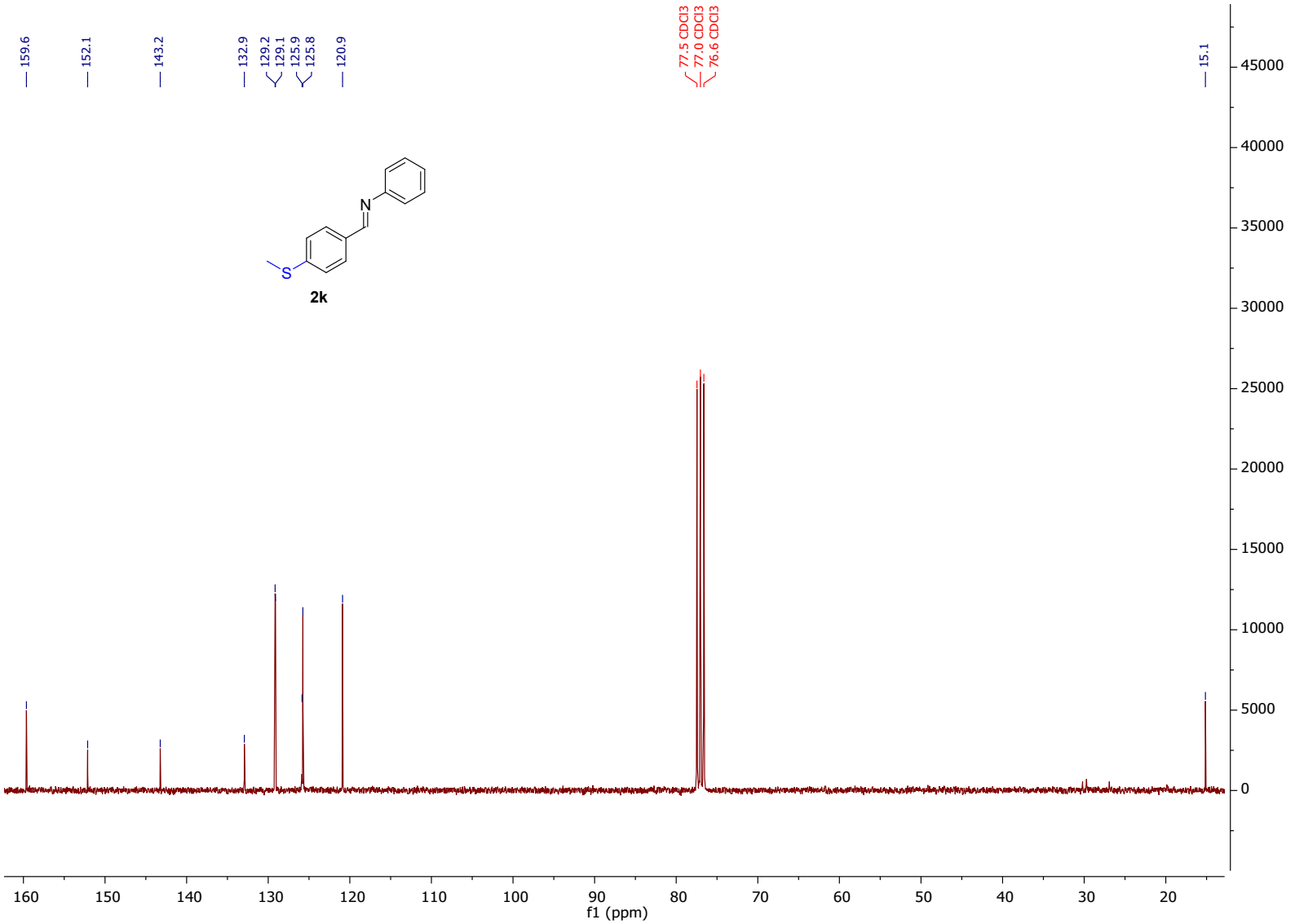

Intens.
x10^6
MAX4510_15_01_3665.d: +MS, 1.8-2.1min #110-127, Background Subtracted (#7-34)
244.0789
228.0840
153.0370
94.0653
137.0423
169.0887
260.0741
335.1216
m/z
1k

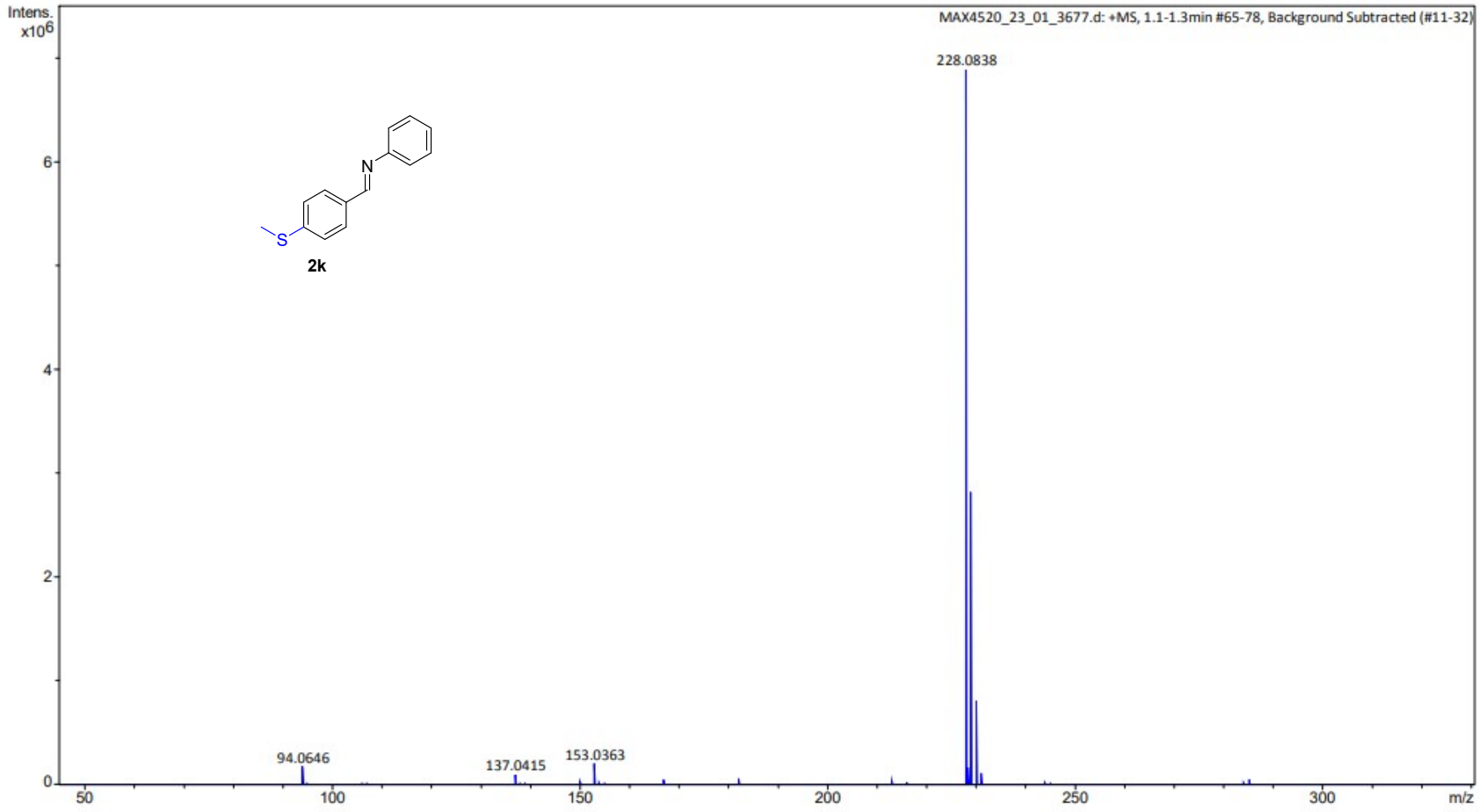
(*E*)-1-(4-(Methylthio)phenyl)-*N*-phenylmethanimine (2k)



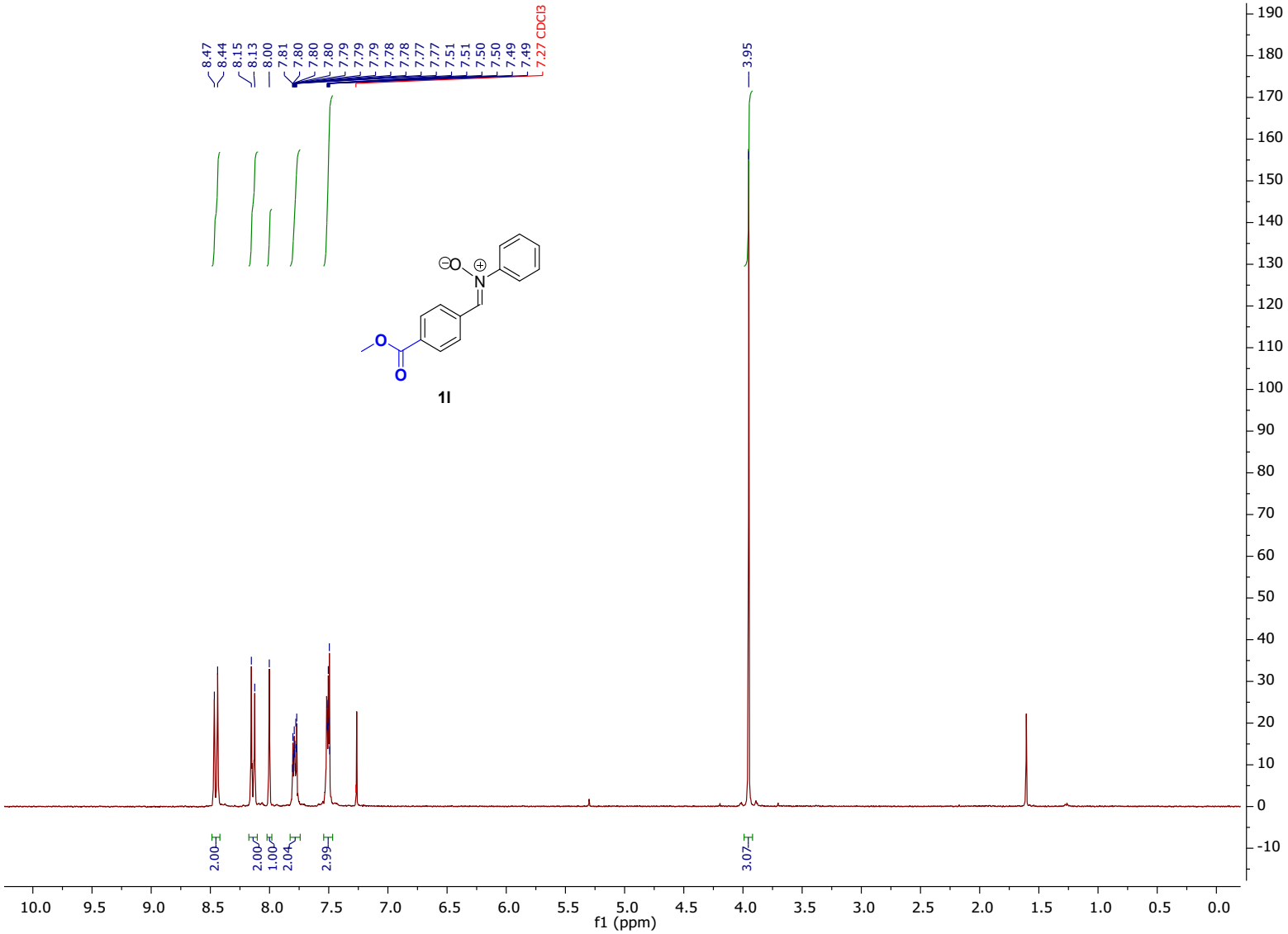

8.37
7.80
7.77
7.39
7.37
7.36
7.34
7.34
7.30
7.27 CDCl3
7.27
7.23
7.22
7.20
7.19
7.19
7.18
7.17
7.16
2.51
N
S
2k
1.00
2.07
2.23
2.11
3.31
3.31
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

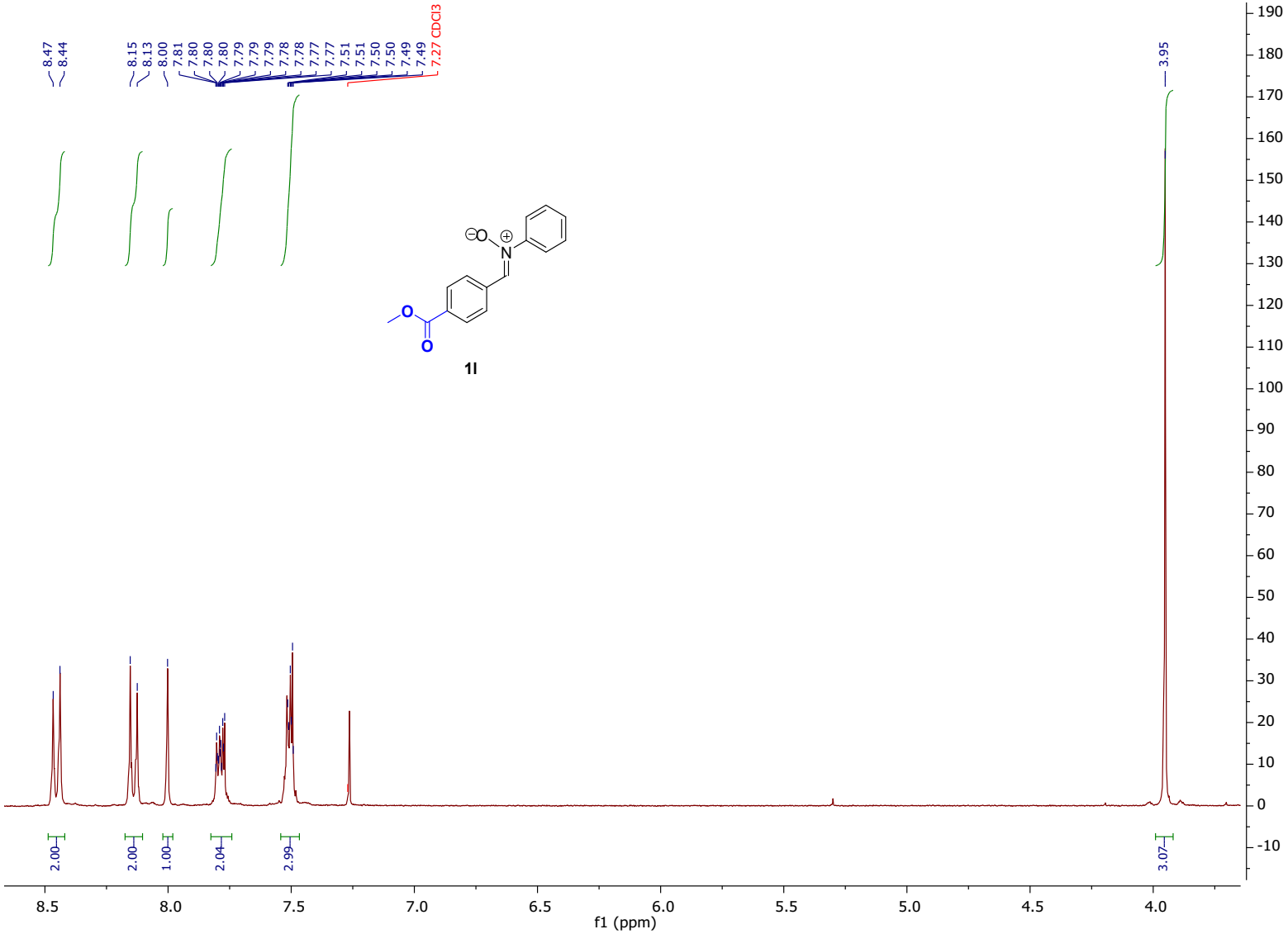

159.6
152.1
143.2
132.9
129.2
129.1
125.9
125.8
120.9
77.5 CDCl3
77.0 CDCl3
76.6 CDCl3
15.1
N
S
2k
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

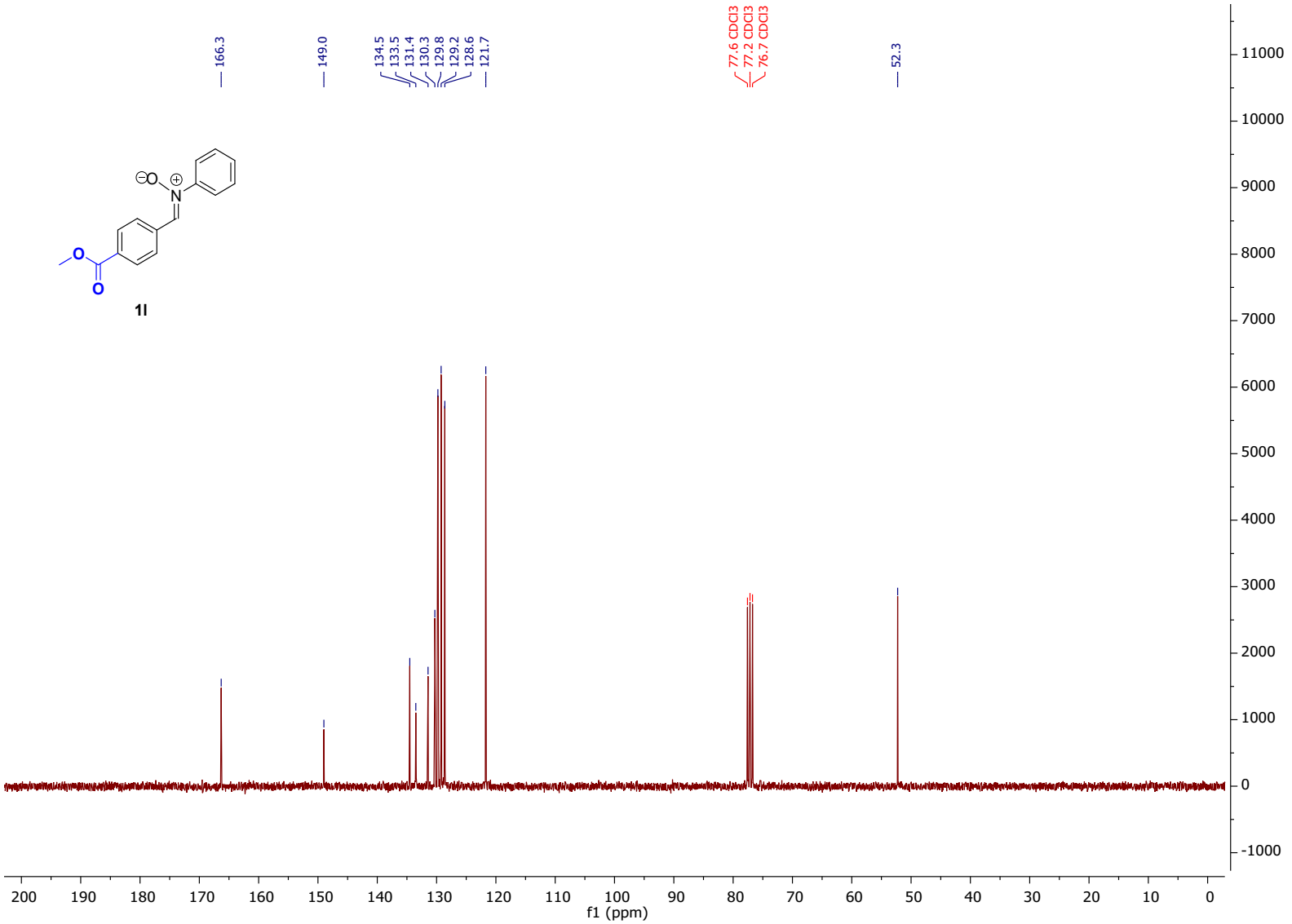

159.6
152.1
143.2
132.9
129.2
129.1
125.9
125.8
120.9
77.5 CDCl3
77.0 CDCl3
76.6 CDCl3
15.1
N
S
2k
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

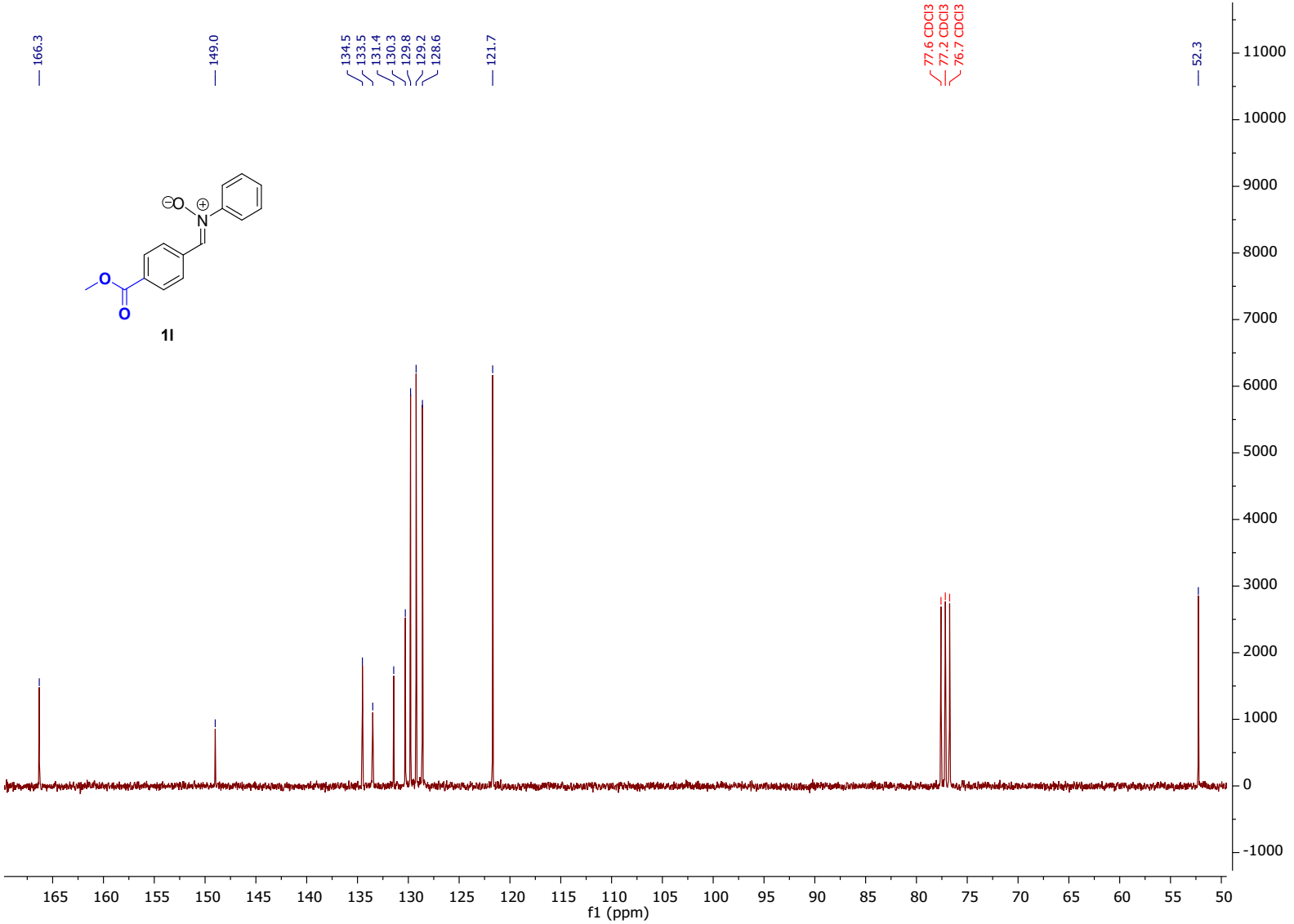

Intens.
x10^6
MAX4520_23_01_3677.d: +MS, 1.1-1.3min #65-78, Background Subtracted (#11-32)
228.0838
6
4
2
0
94.0646
137.0415
153.0363
50
100
150
200
250
300
m/z
N
S
2k

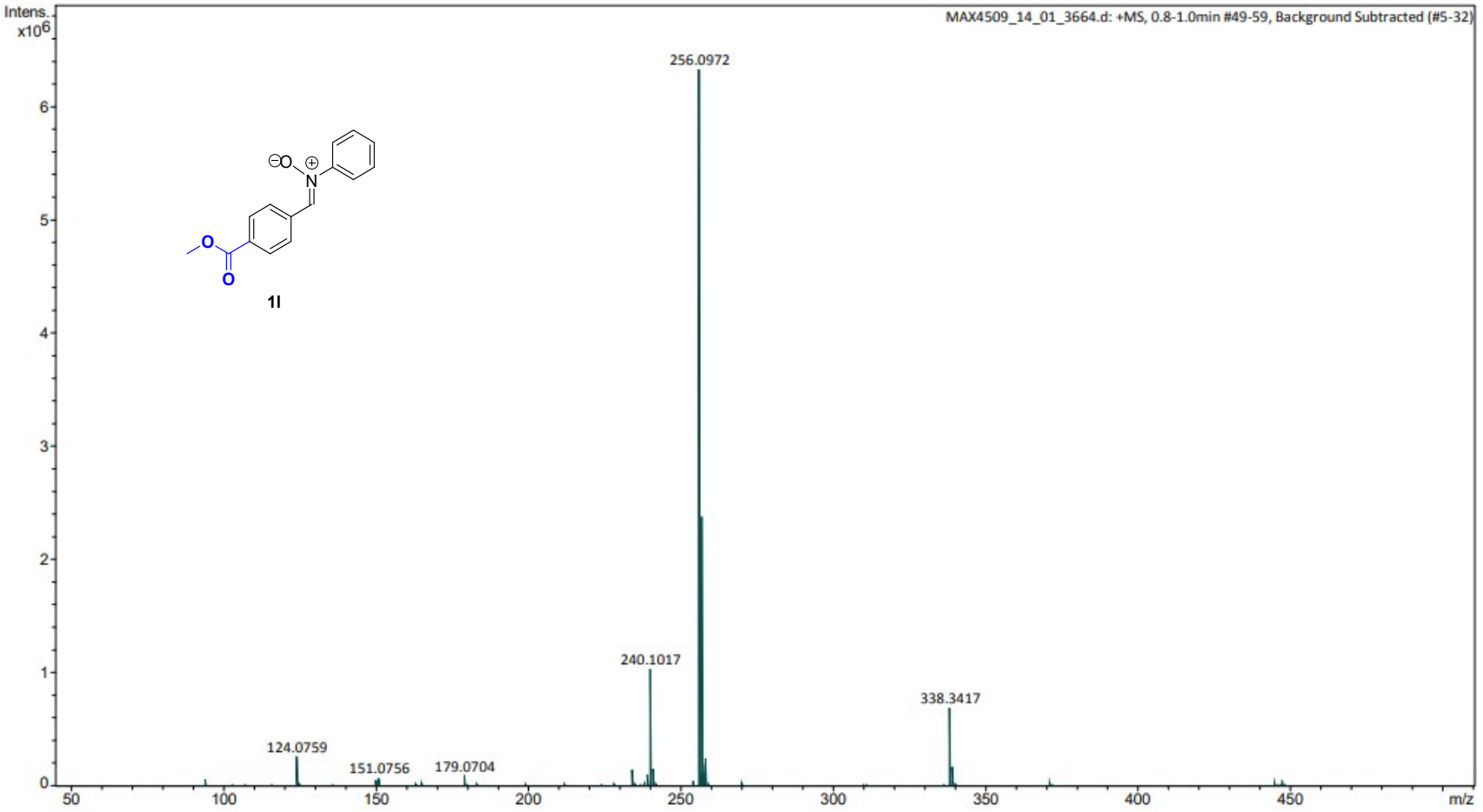
(*Z*)-1-(4-(methoxycarbonyl)phenyl)-*N*-phenylmethanimine oxide (1l)



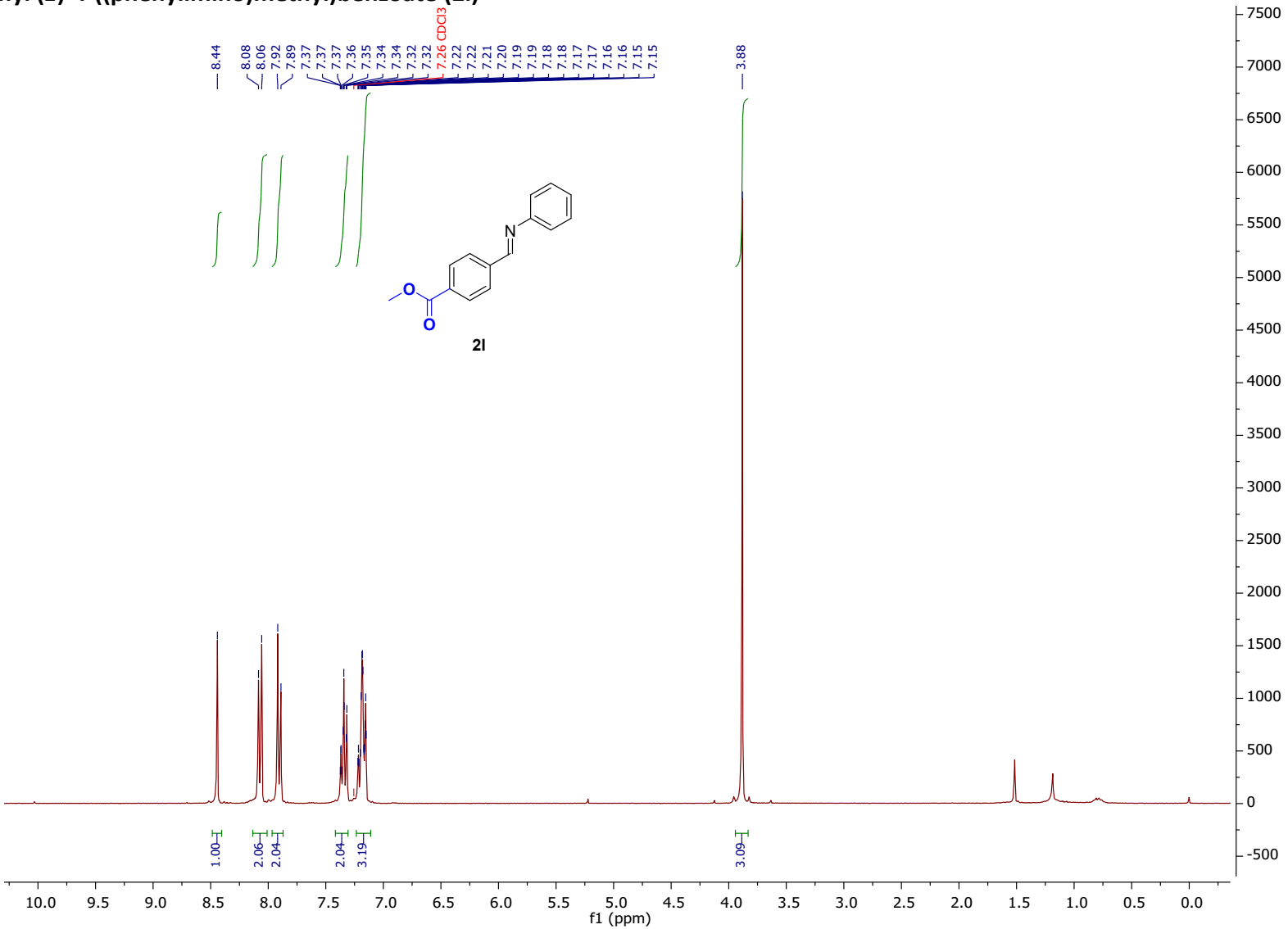

8.47
8.44
8.15
8.13
8.00
7.81
7.80
7.80
7.80
7.79
7.79
7.79
7.78
7.78
7.77
7.77
7.51
7.51
7.50
7.50
7.49
7.49
7.27 CDCl3
3.95
1l
2.00
2.00
1.00
2.04
2.99
3.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

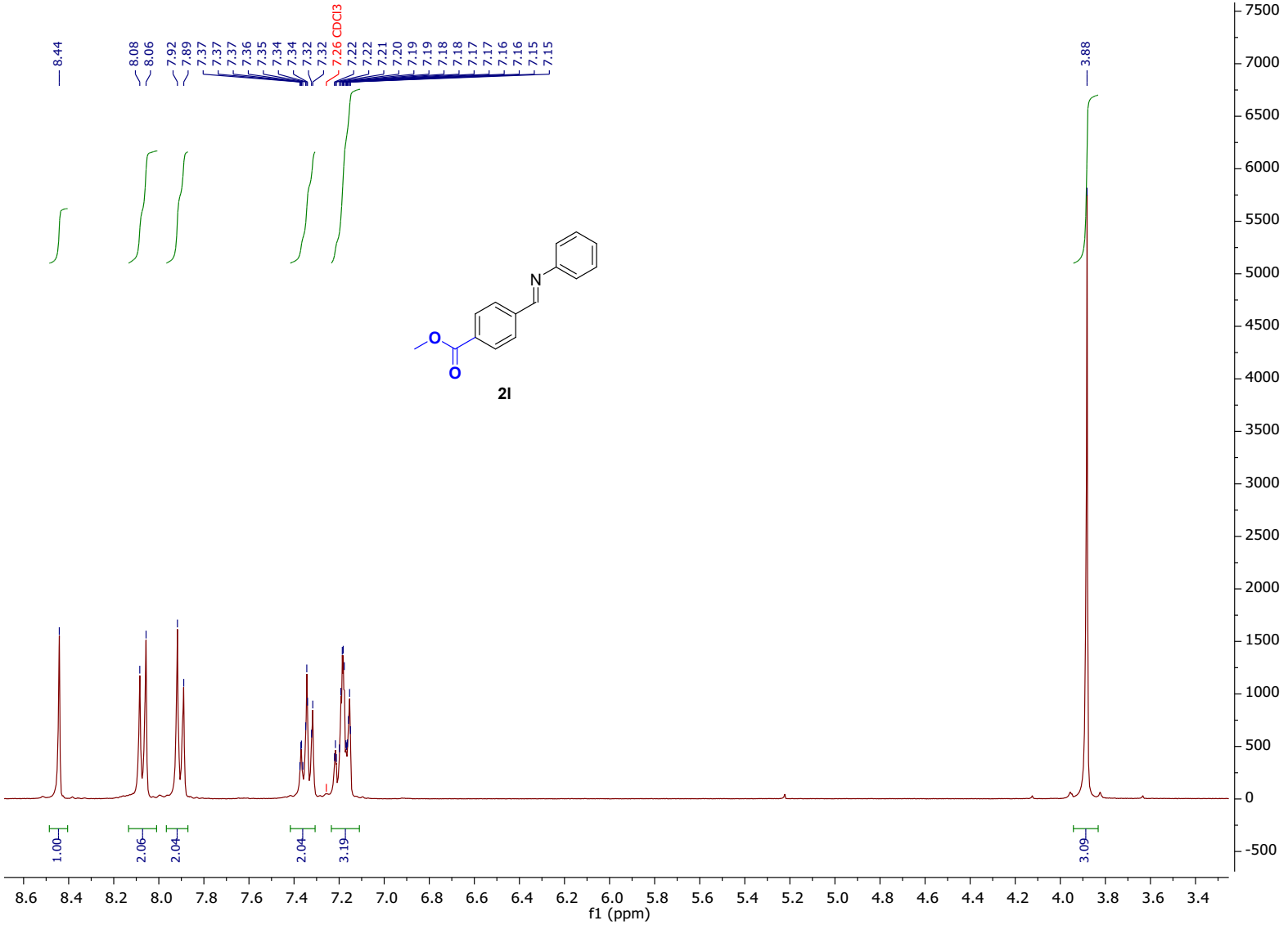

166.3
149.0
134.5
133.5
131.4
130.3
129.8
129.2
128.6
121.7
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
52.3
1l
f1 (ppm)

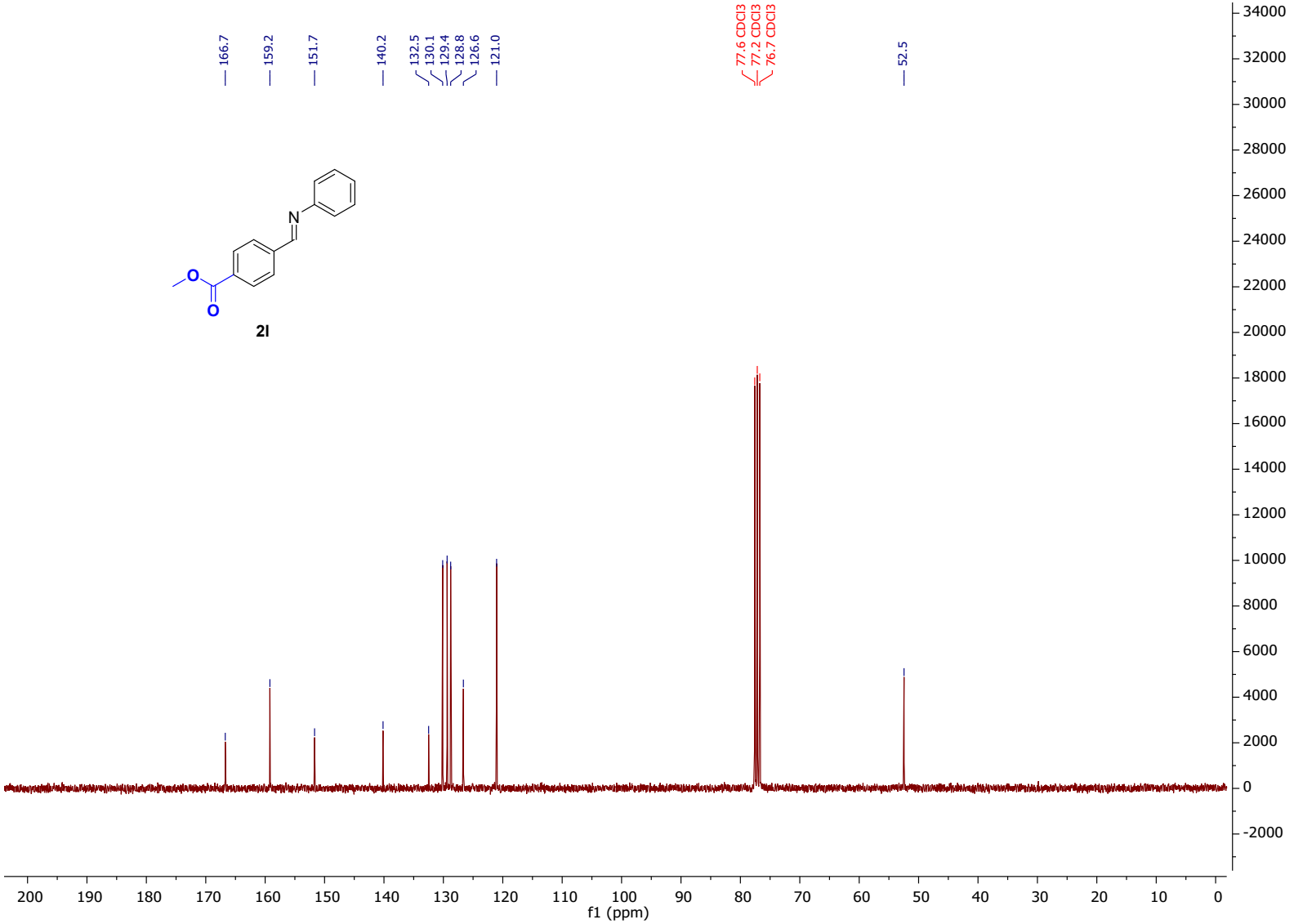

166.3
149.0
134.5
133.5
131.4
130.3
129.8
129.2
128.6
121.7
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
52.3
1l
f1 (ppm)

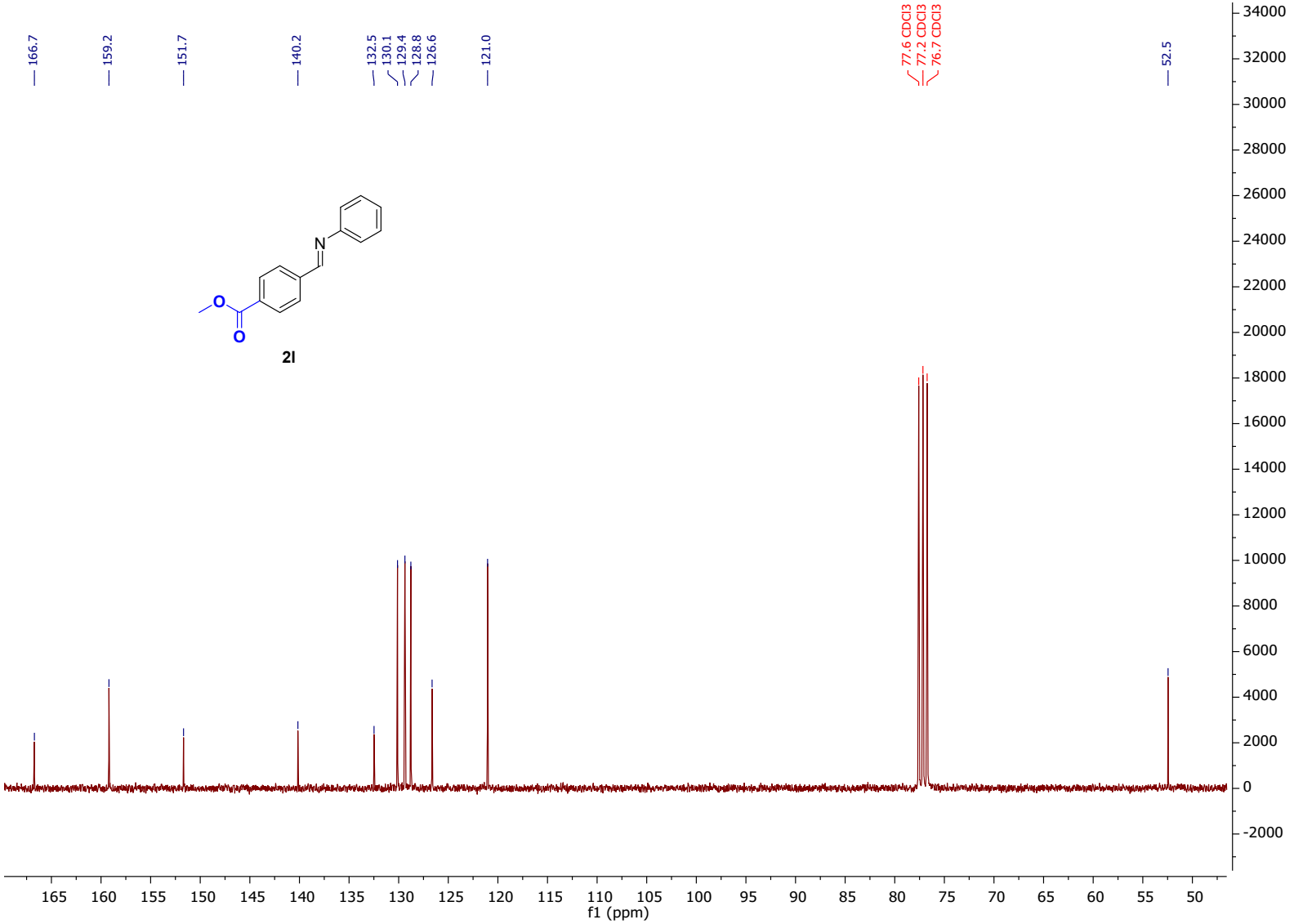

Intens.
x10^6
MAX4509_14_01_3664.d: +MS, 0.8-1.0min #49-59, Background Subtracted (#5-32)
256.0972
240.1017
338.3417
124.0759
151.0756
179.0704
m/z
1l

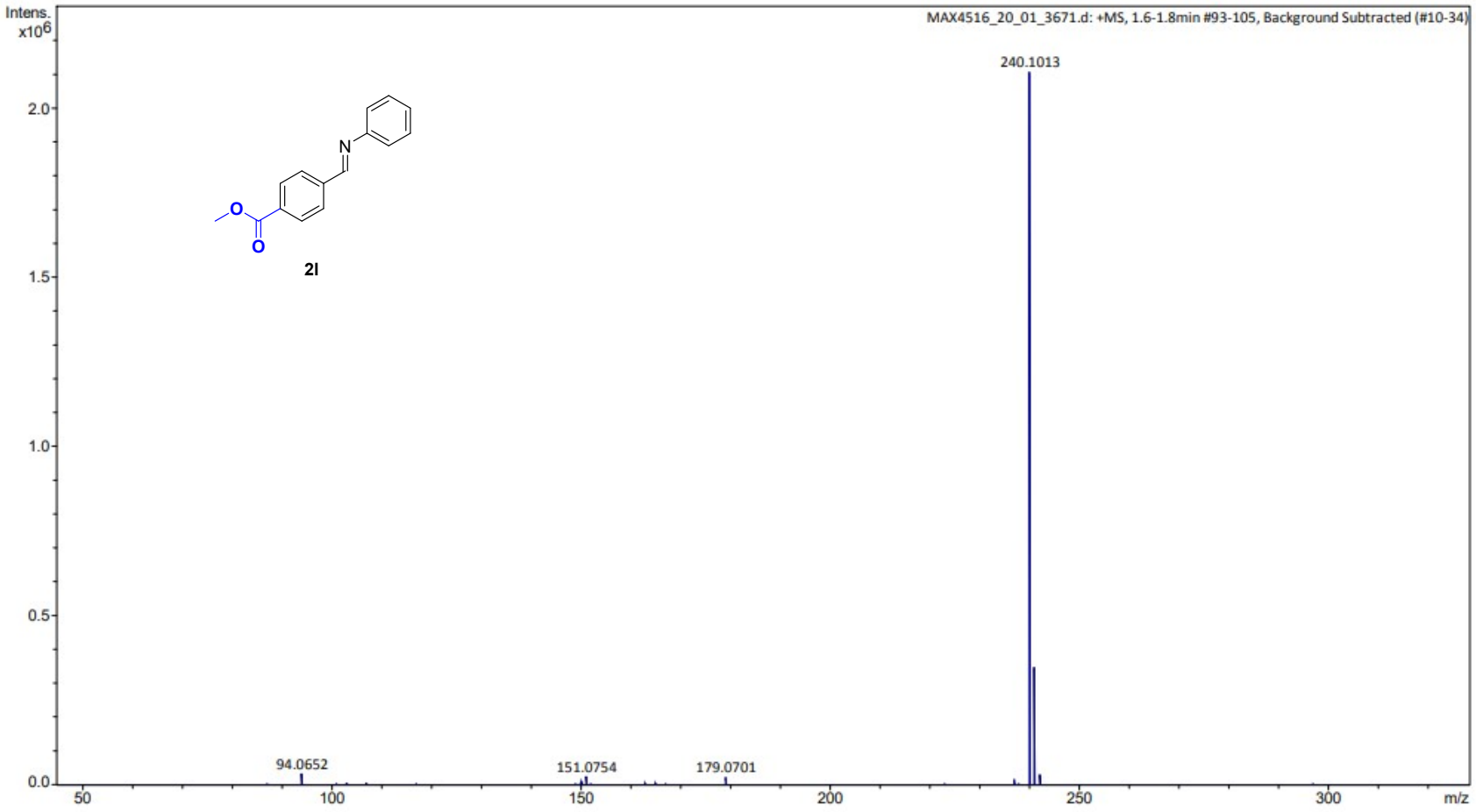
Methyl (*E*)-4-((phenylimino)methyl)benzoate (2l)




8.44
8.08
8.06
7.92
7.89
7.37
7.37
7.37
7.36
7.35
7.34
7.34
7.32
7.32
7.26 CDCl3
7.22
7.22
7.21
7.20
7.19
7.19
7.18
7.18
7.17
7.17
7.16
7.16
7.15
7.15
3.88
N
O
O
2l
1.00
2.06
2.04
2.04
3.19
3.09
f1 (ppm)

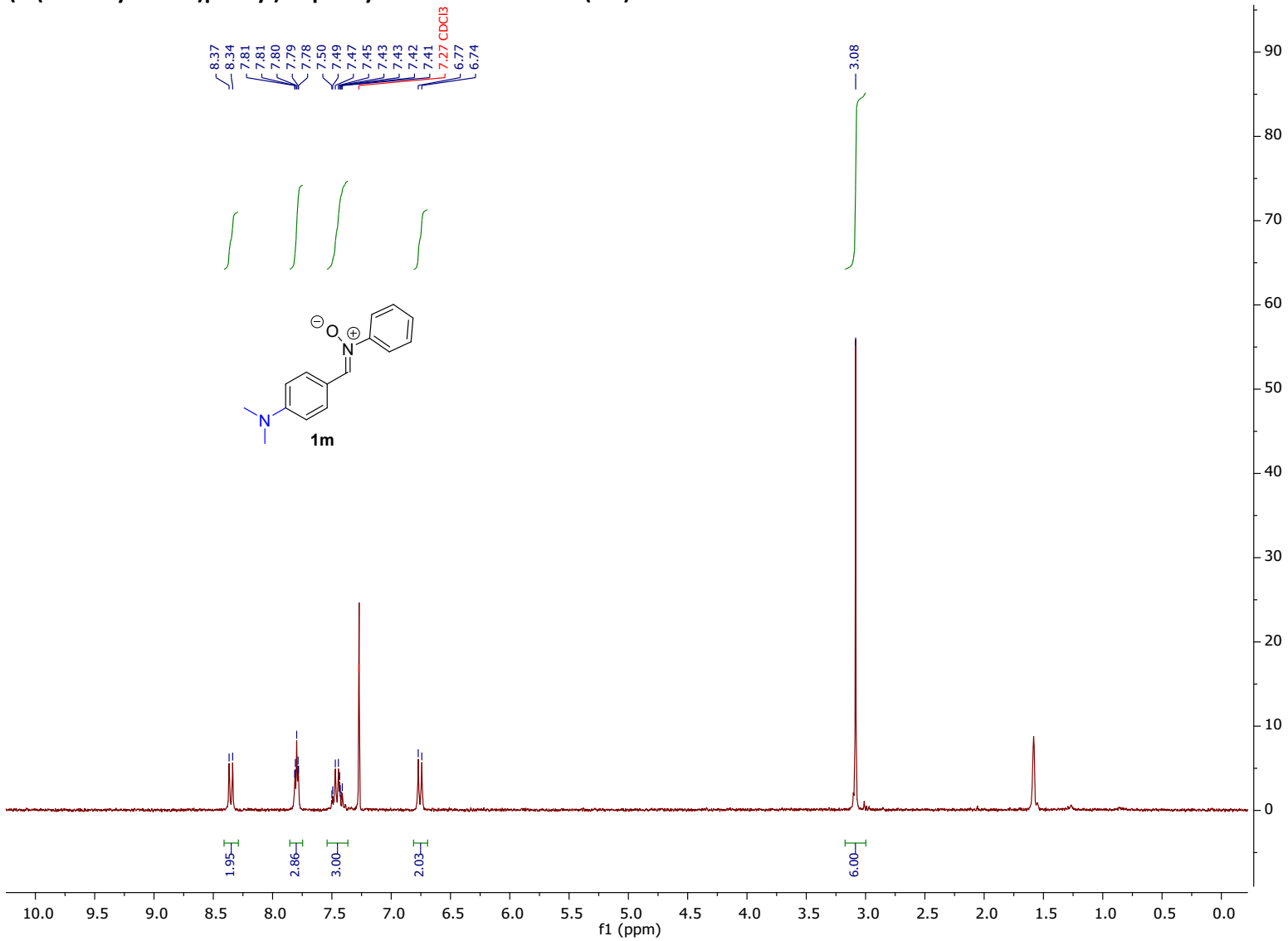

166.7
159.2
151.7
140.2
132.5
130.1
129.4
128.8
126.6
121.0
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
52.5
N
O
O
2l
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

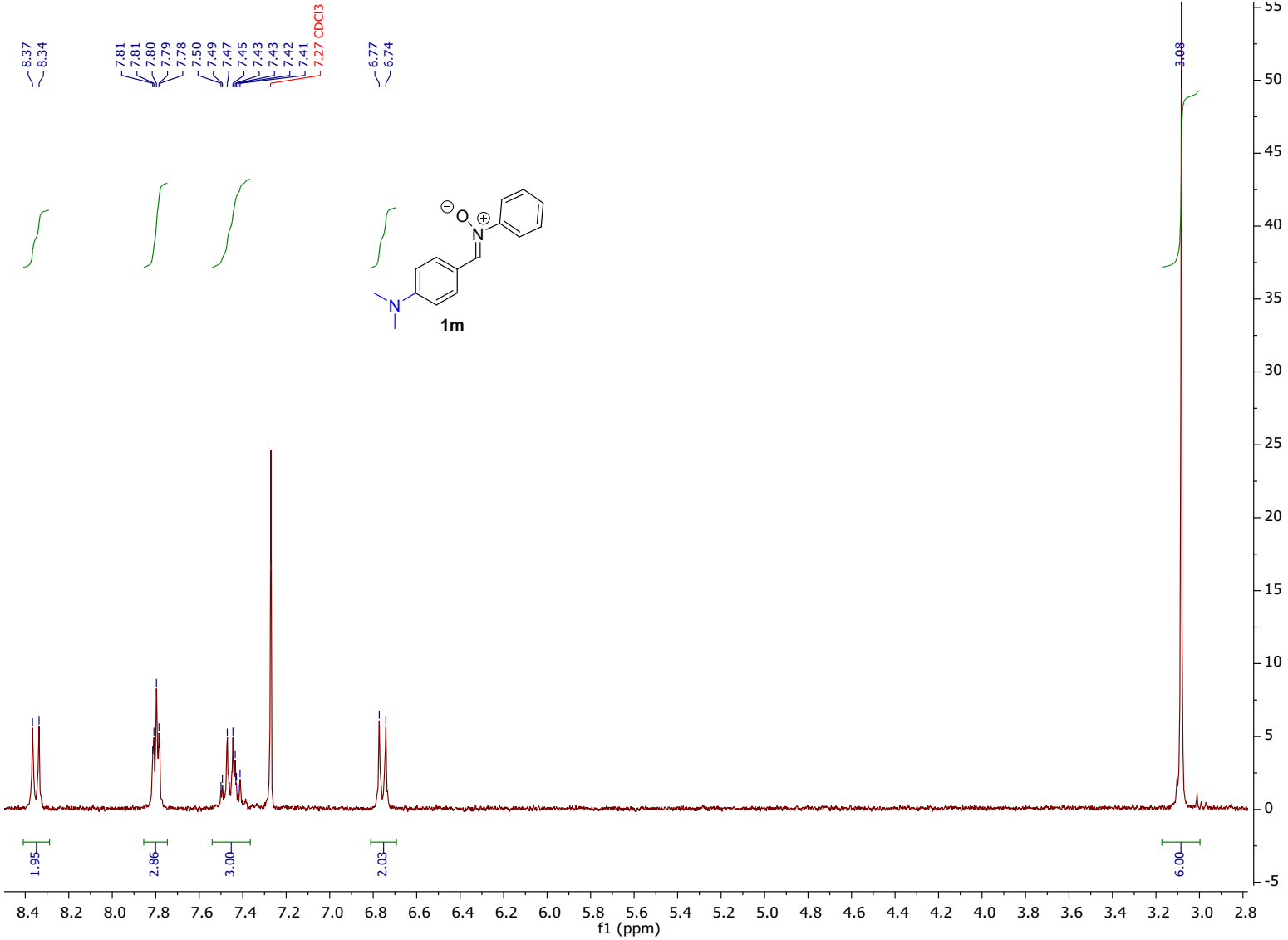

166.7
159.2
151.7
140.2
132.5
130.1
129.4
128.8
126.6
121.0
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
52.5
N
O
O
2l
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50
f1 (ppm)

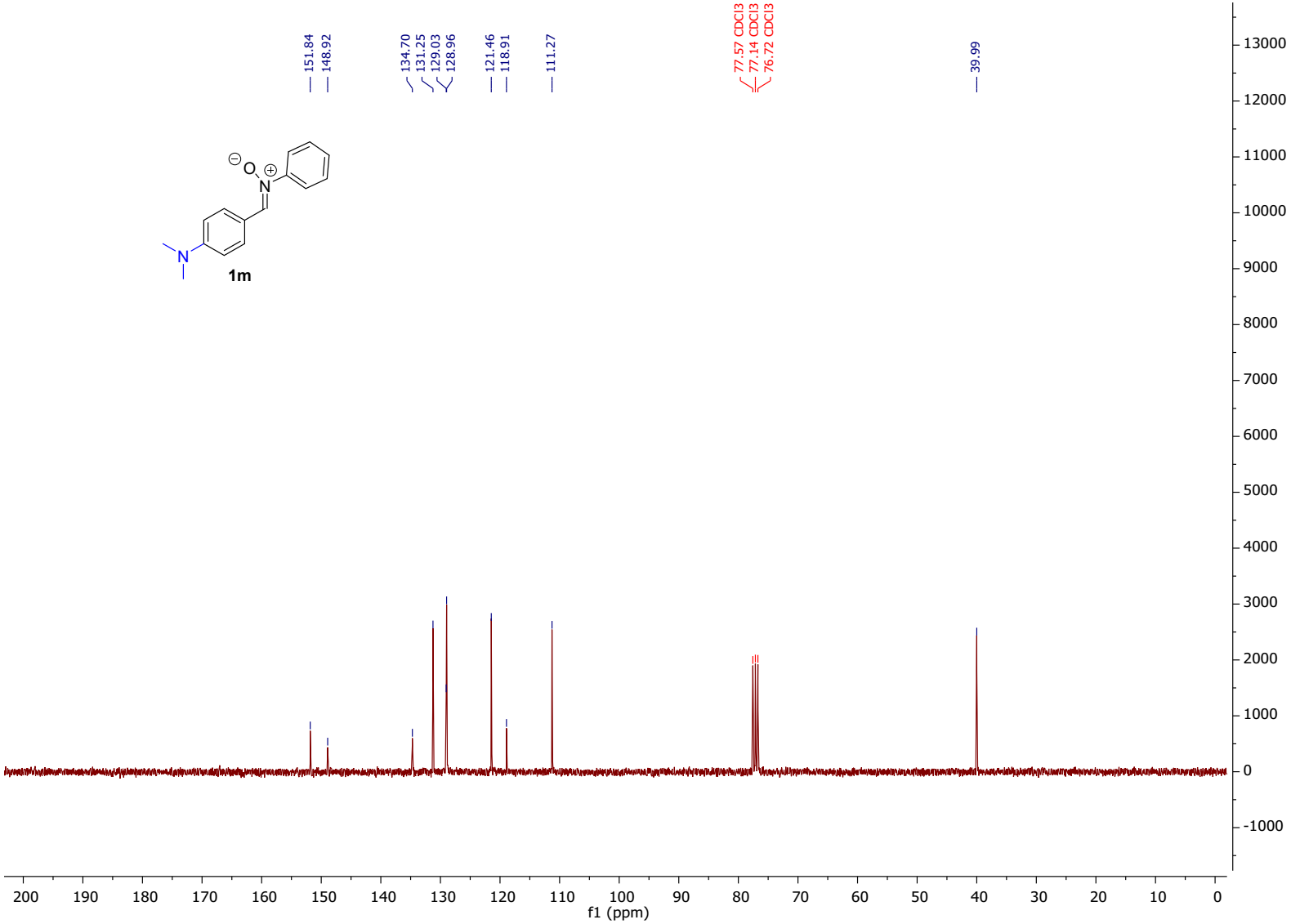

Intens.
x10^6
MAX4516_20_01_3671.d: +MS, 1.6-1.8min #93-105, Background Subtracted (#10-34)
240.1013
2.0
1.5
1.0
0.5
0.0
94.0652
151.0754
179.0701
50
100
150
200
250
300
m/z
N
O
O

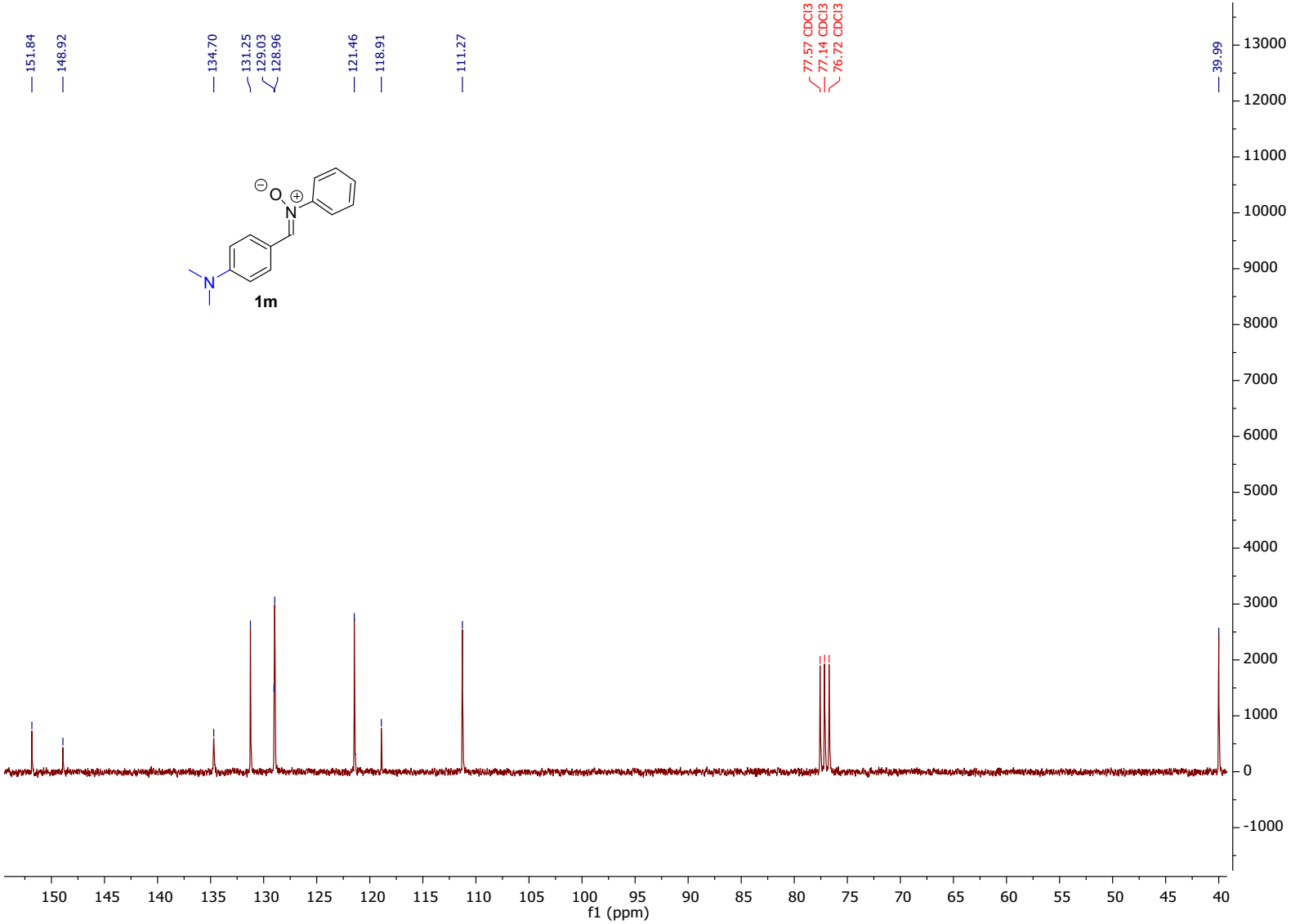
2l

(Z)-1-(4-(dimethylamino)phenyl)-N-phenylmethanimine oxide (1m)

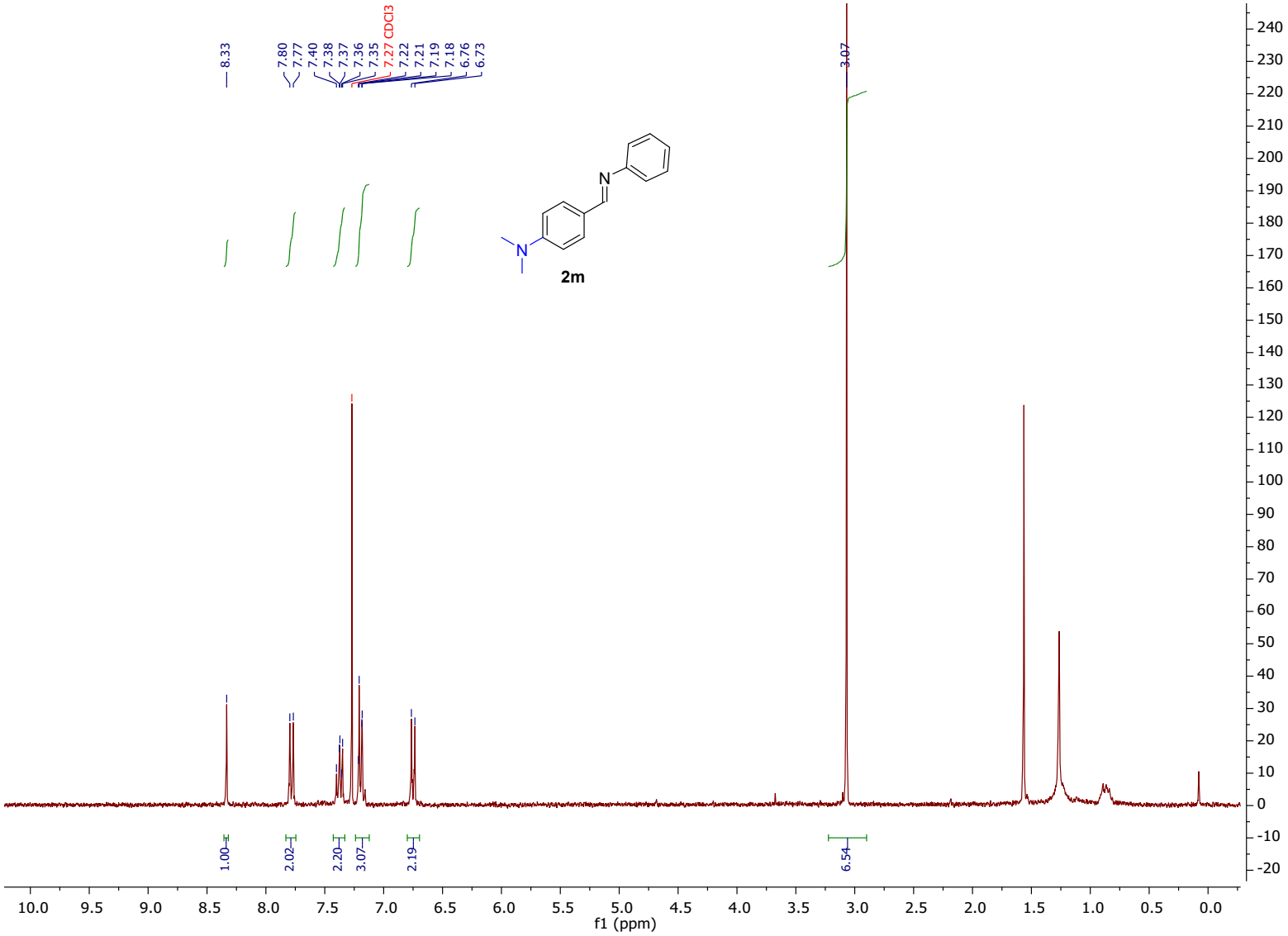


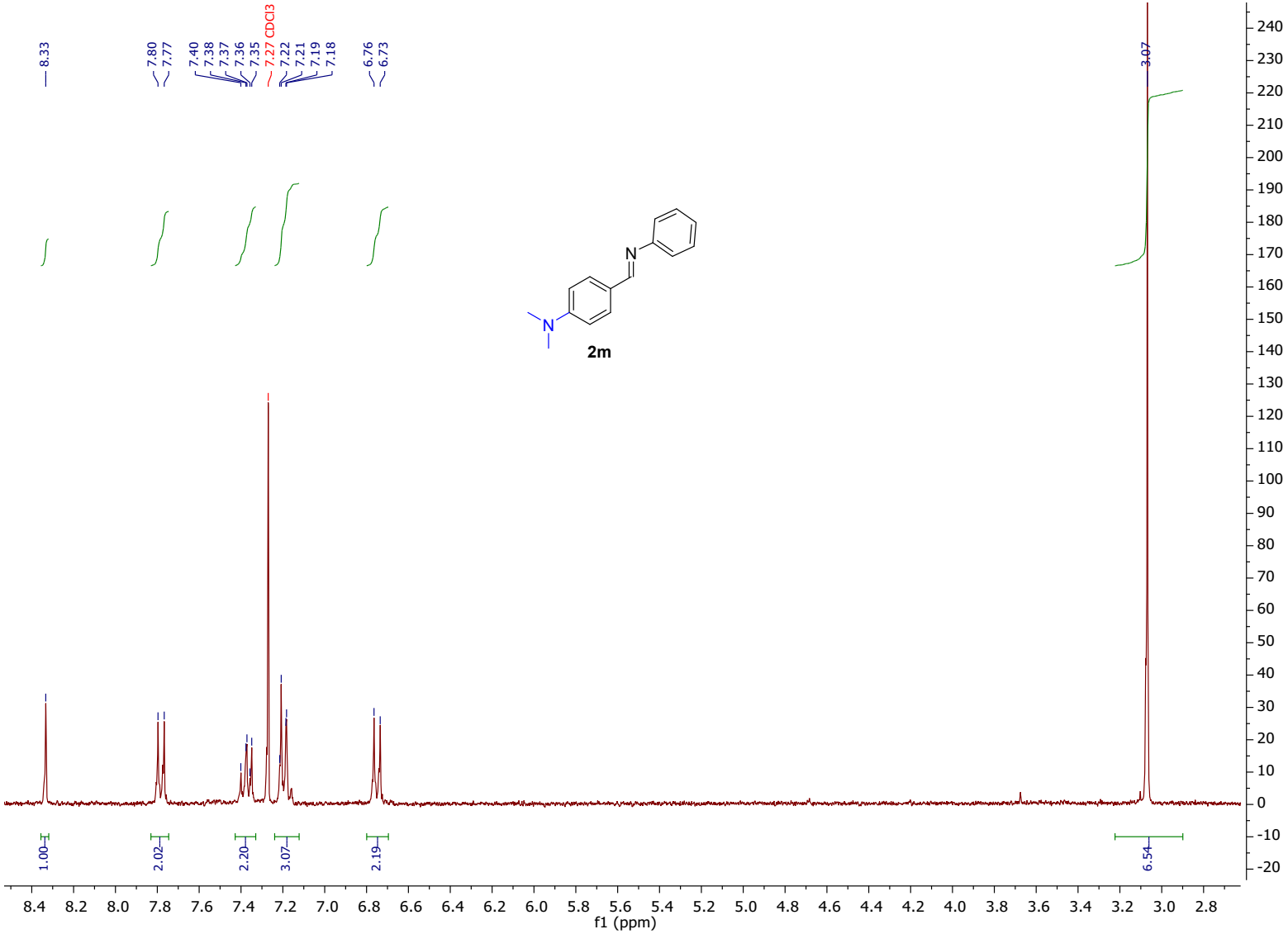

8.37
8.34
7.81
7.81
7.80
7.79
7.78
7.50
7.49
7.47
7.45
7.43
7.43
7.42
7.41
7.27 CDCl3
6.77
6.74
3.08
1m
1.95
2.86
3.00
2.03
6.00
f1 (ppm)


151.84
148.92
134.70
131.25
129.03
128.96
121.46
118.91
111.27
77.57 CDCl3
77.14 CDCl3
76.72 CDCl3
39.99
1m
f1 (ppm)

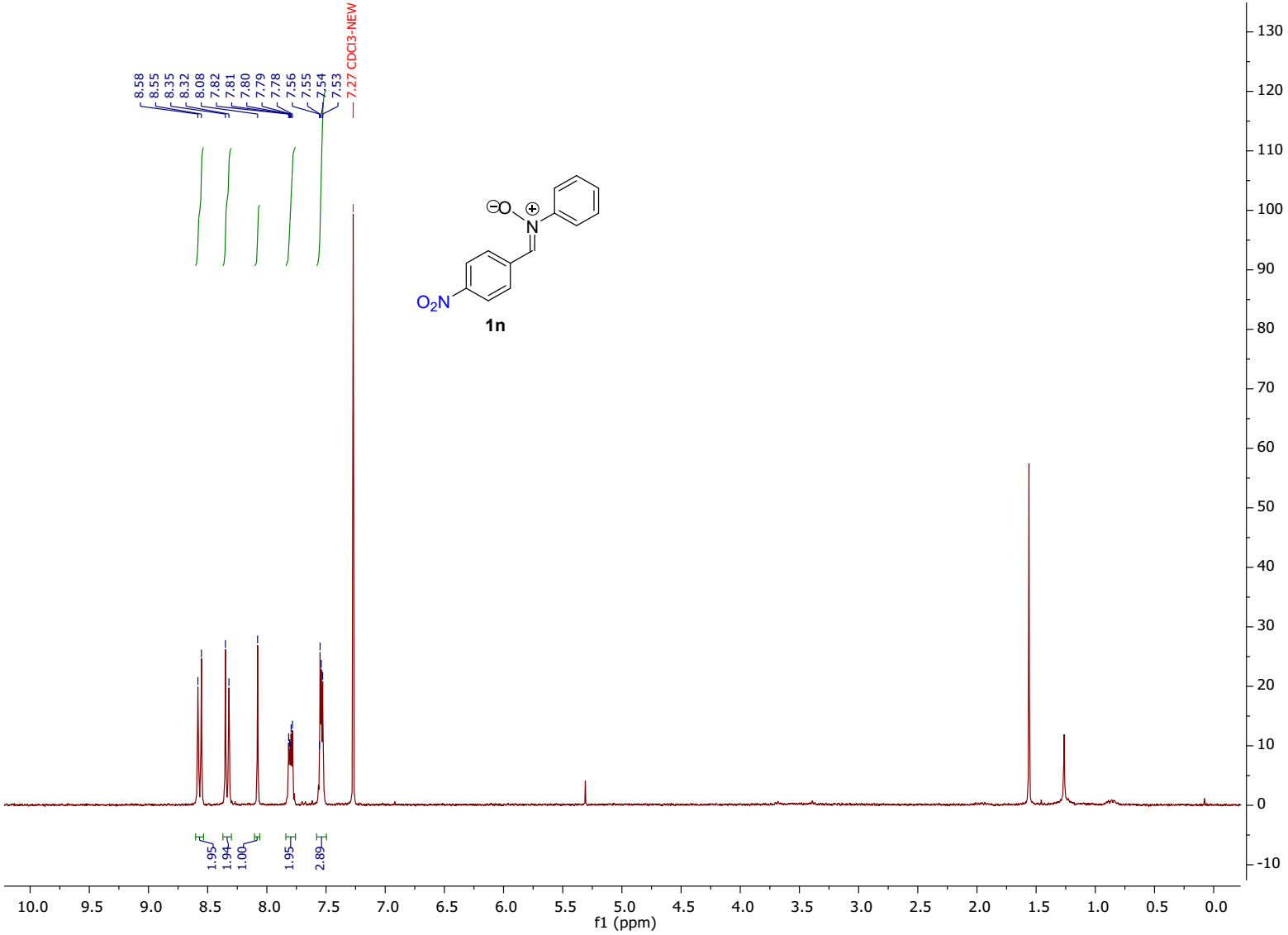

151.84
148.92
134.70
131.25
129.03
128.96
121.46
118.91
111.27
77.57 CDCl3
77.14 CDCl3
76.72 CDCl3
39.99
1m
f1 (ppm)

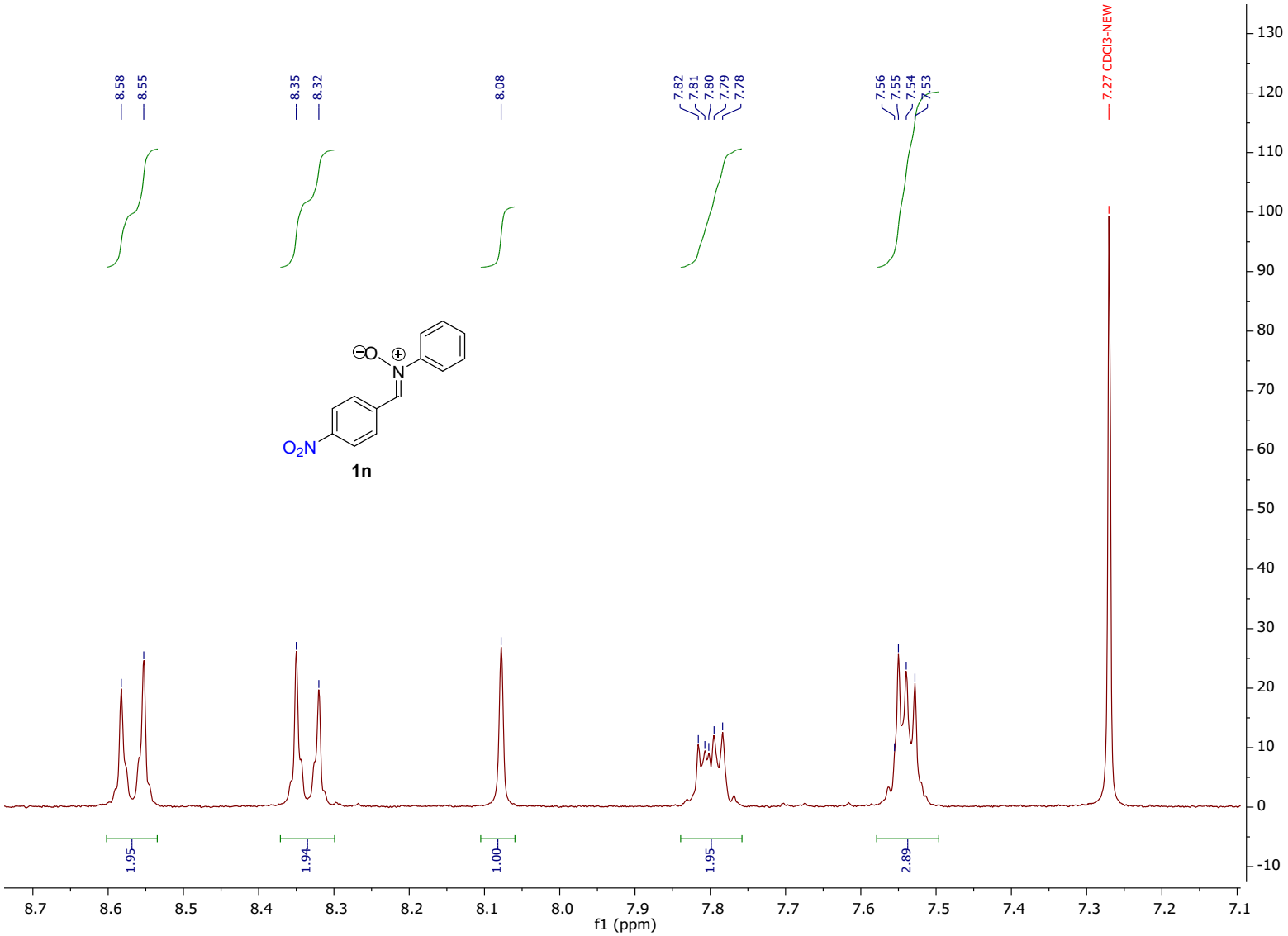
(*E*)-*N*,*N*-dimethyl-4-((phenylimino)methyl)aniline (2m)

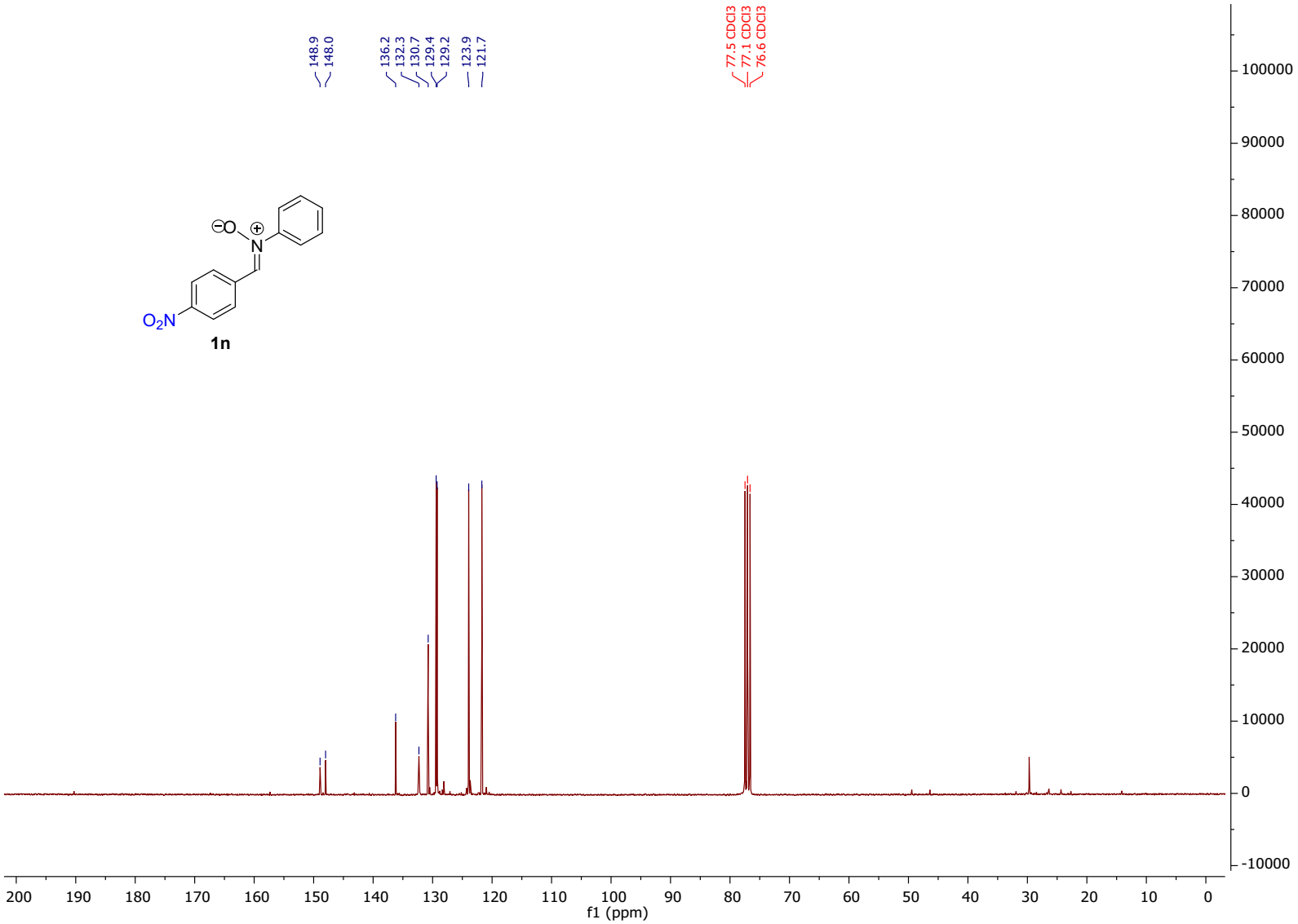


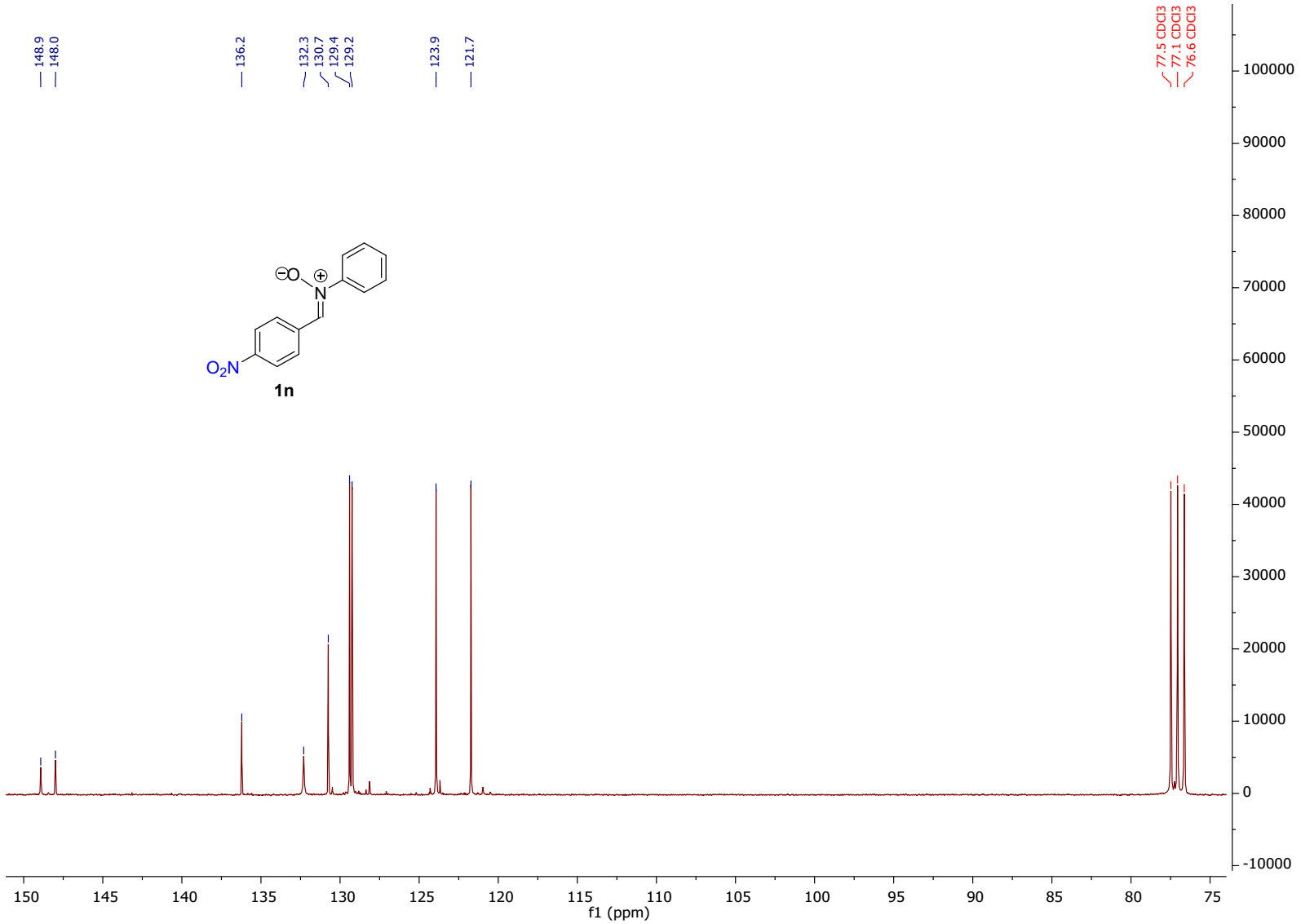

8.33
7.80
7.77
7.40
7.38
7.37
7.36
7.35
7.27 CDCl3
7.22
7.21
7.19
7.18
6.76
6.73
3.07
N
N
2m
1.00
2.02
2.20
3.07
2.19
6.54
f1 (ppm)

(*Z*)-1-(4-Nitrophenyl)-*N*-phenylmethanimine oxide (1n)

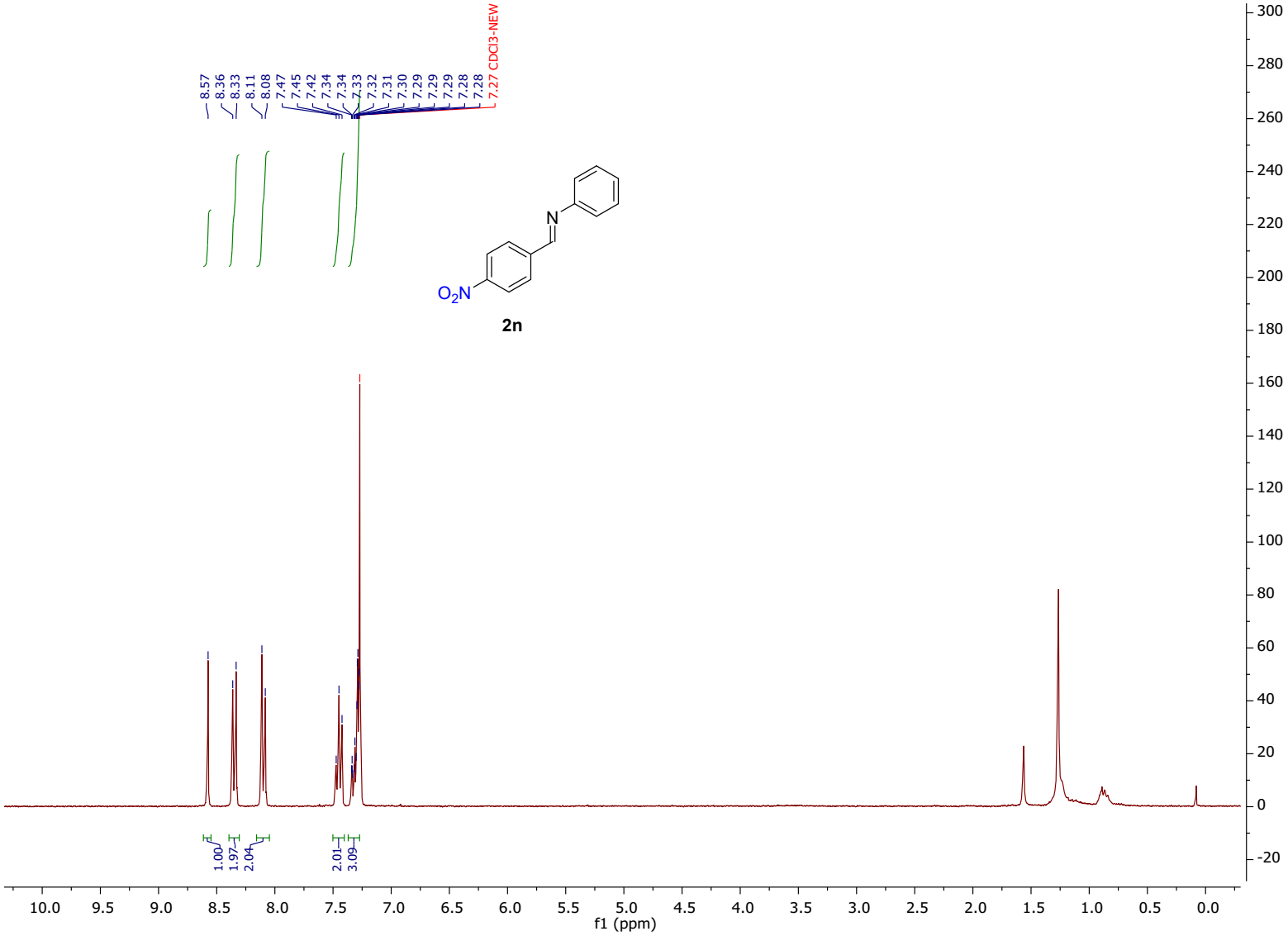


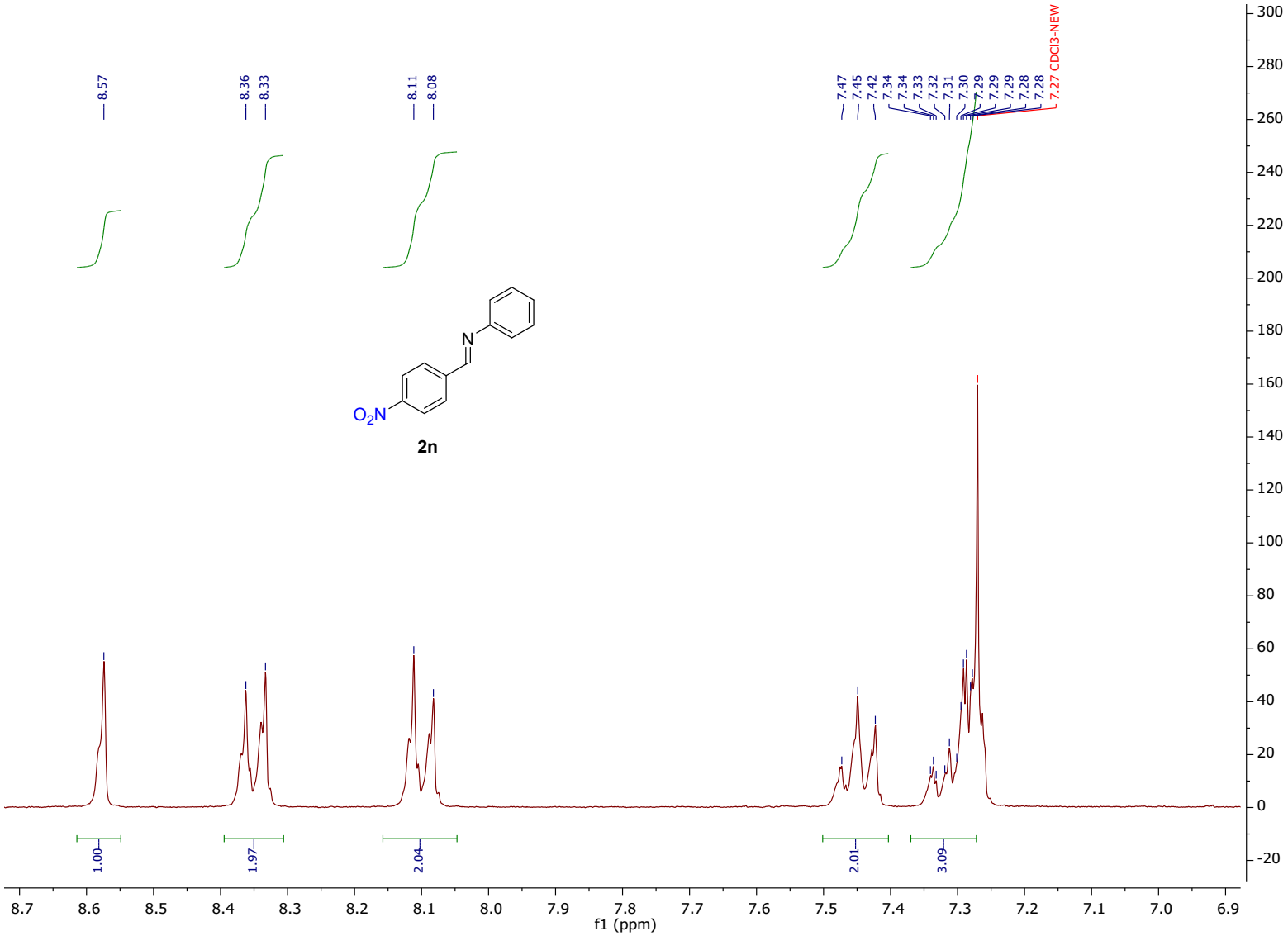

8.58
8.55
8.35
8.32
8.08
7.82
7.81
7.80
7.79
7.78
7.56
7.55
7.54
7.53
7.27 CDCl3-NEW
O2N
1n
1.95
1.94
1.00
1.95
2.89
f1 (ppm)

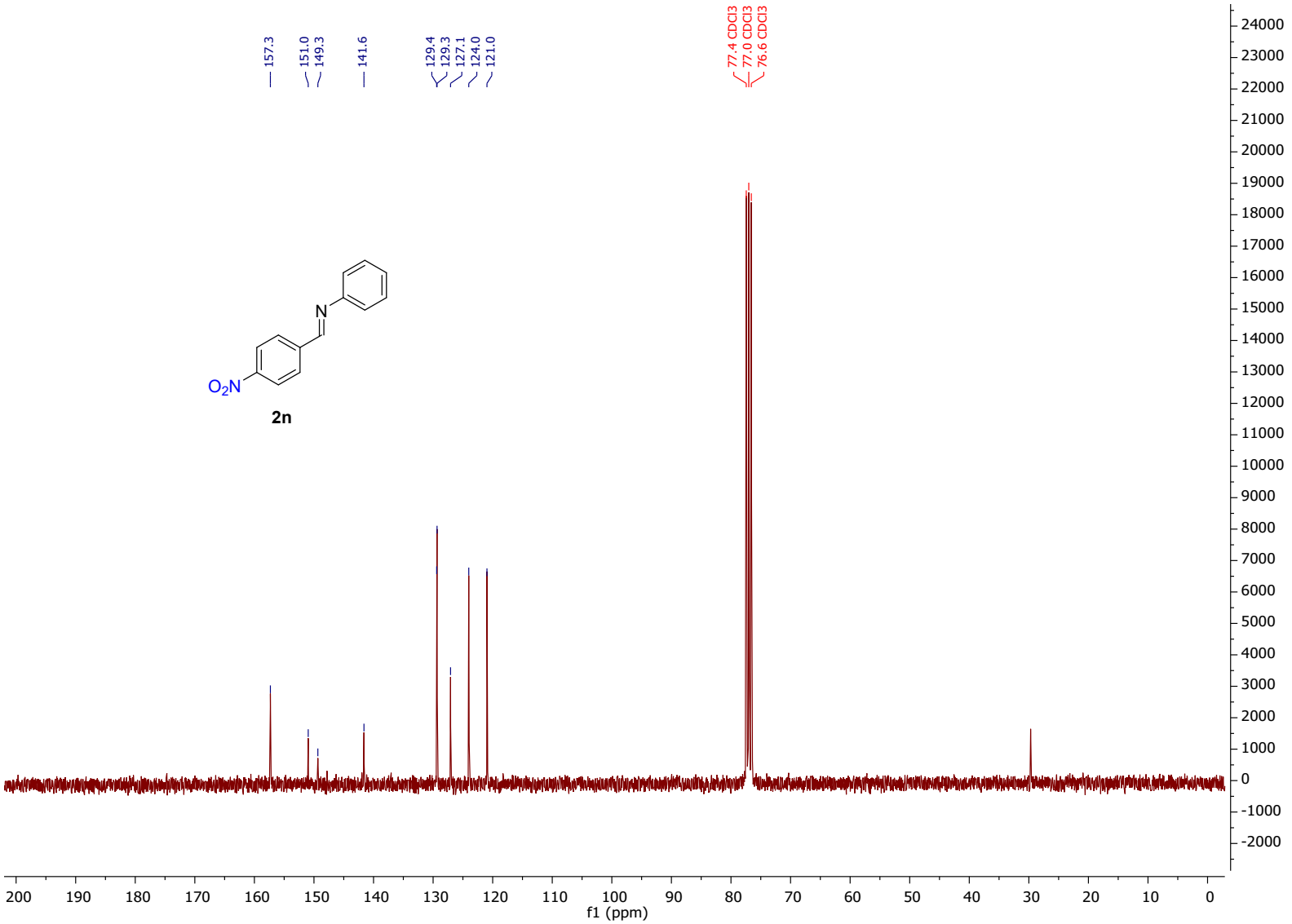

148.9
148.0
136.2
132.3
130.7
129.4
129.2
123.9
121.7
77.5 CDCl3
77.1 CDCl3
76.6 CDCl3
O2N
1n
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

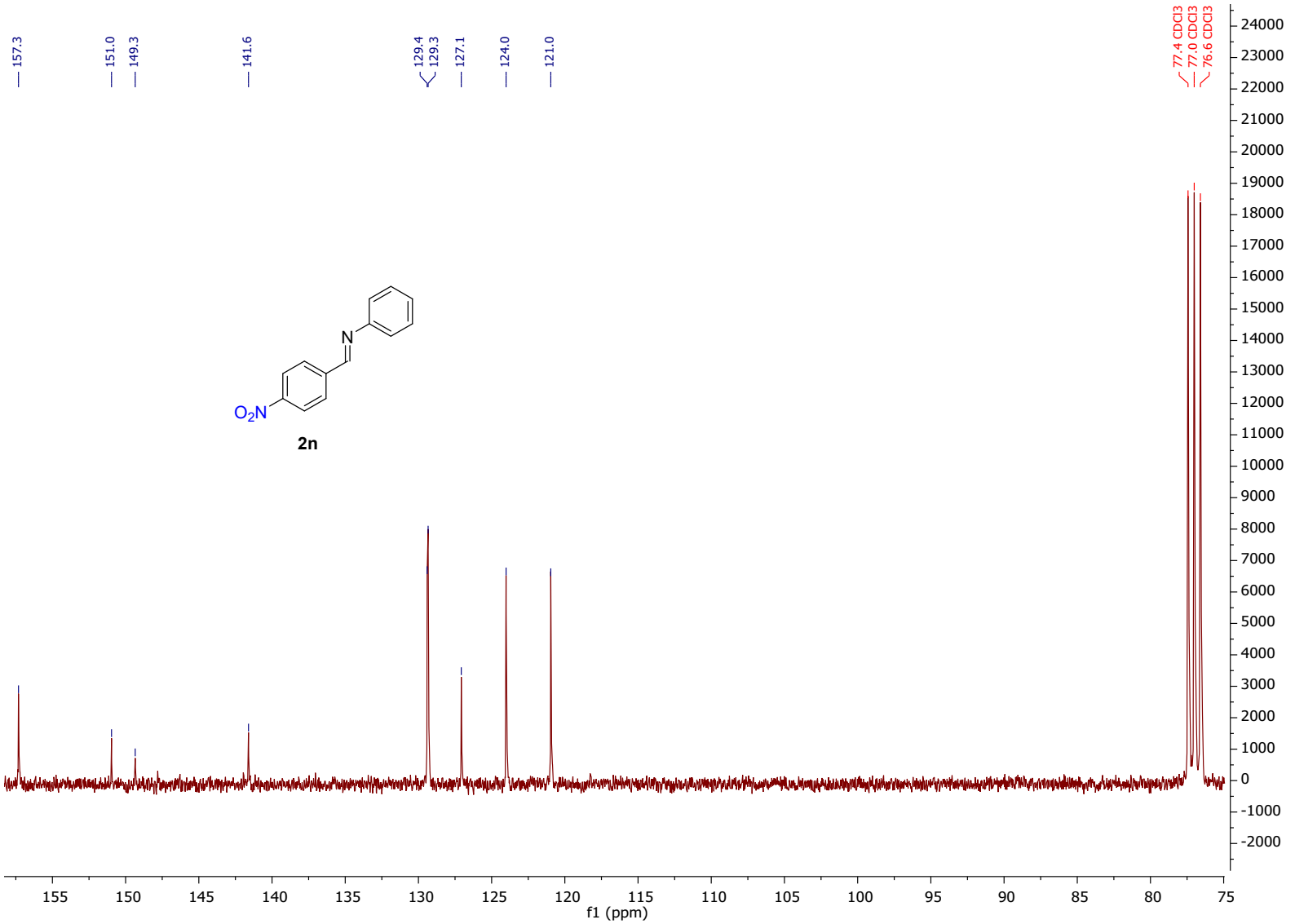

148.9
148.0
136.2
132.3
130.7
129.4
129.2
123.9
121.7
77.5 CDCl3
77.1 CDCl3
76.6 CDCl3
1n
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
f1 (ppm)

(*E*)-1-(4-Nitrophenyl)-*N*-phenylmethanimine (2n)

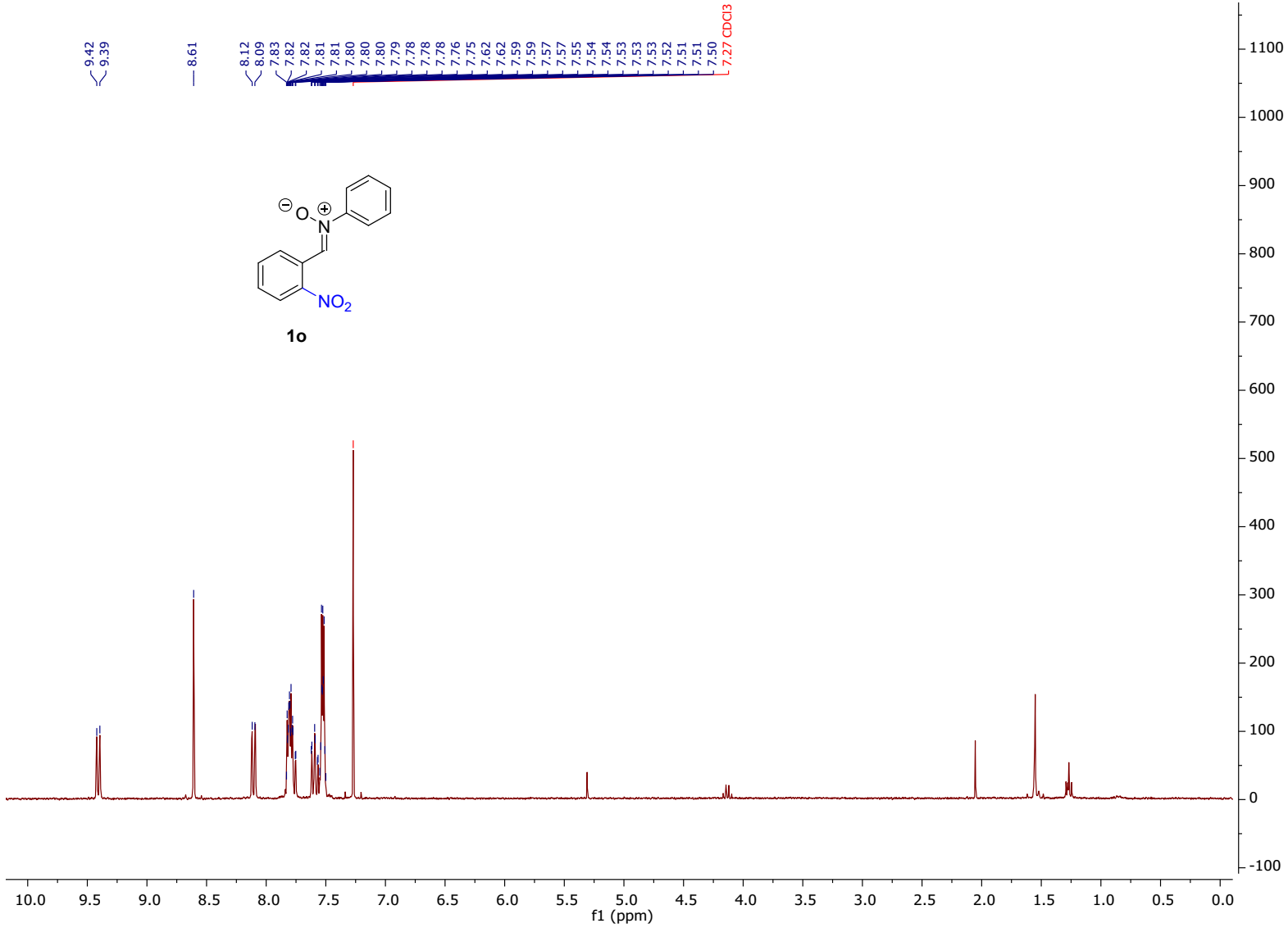


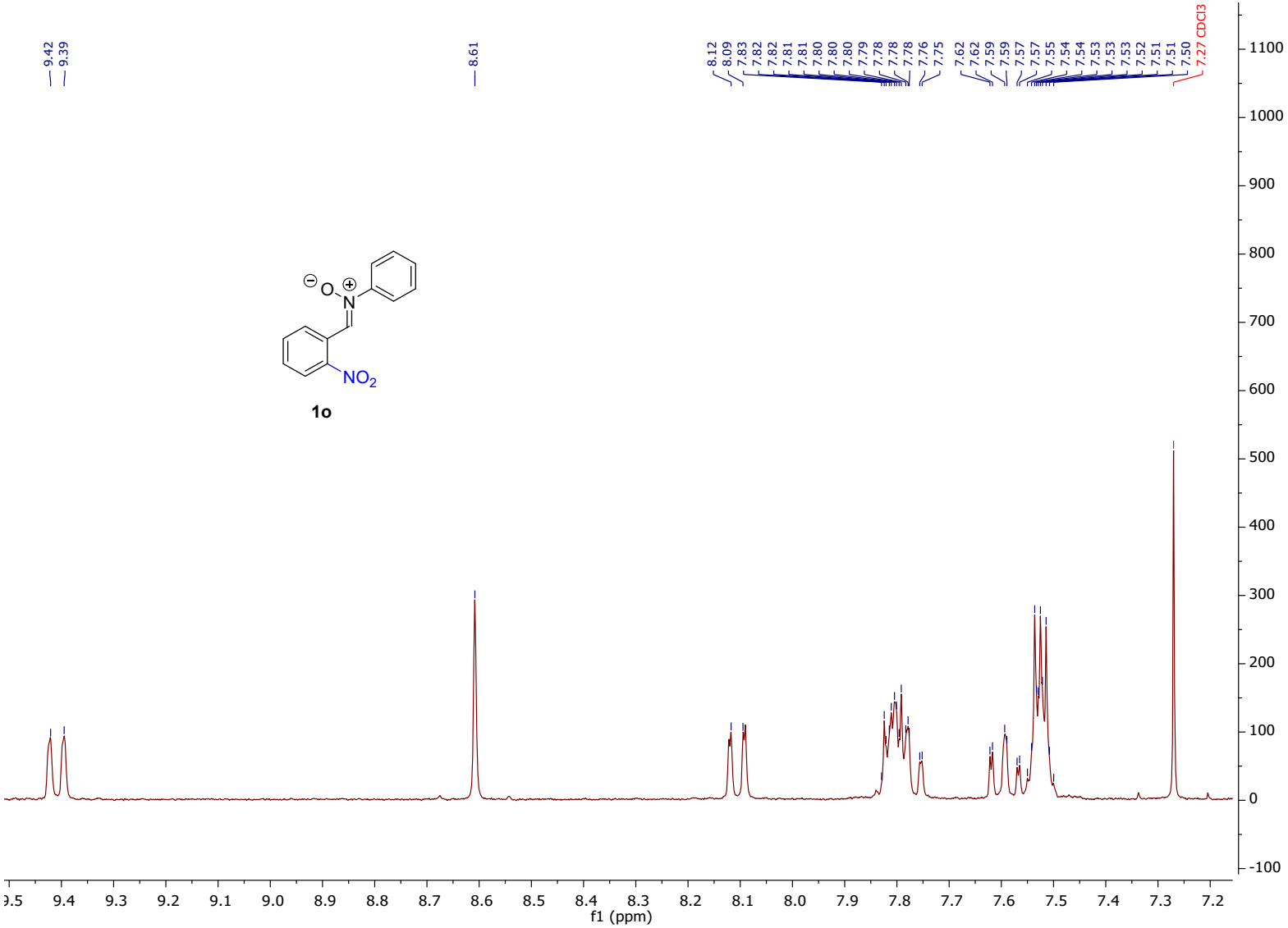

8.57
8.36
8.33
8.11
8.08
7.47
7.45
7.42
7.34
7.34
7.33
7.32
7.31
7.30
7.29
7.29
7.29
7.28
7.28
7.27 CDCl3-NEW
N
O2N
2n
1.00
1.97
2.04
2.01
3.09
f1 (ppm)

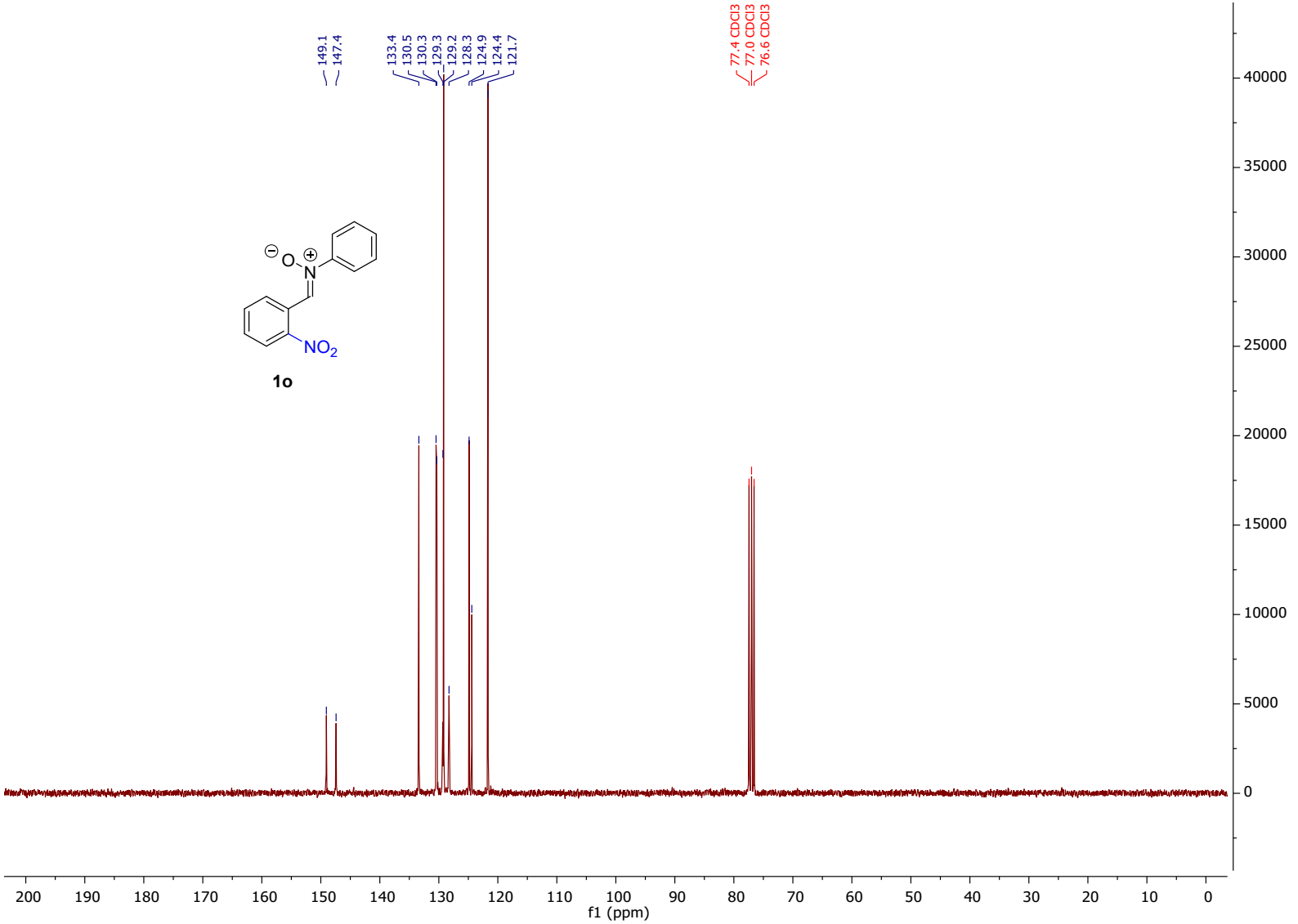

157.3
151.0
149.3
141.6
129.4
129.3
127.1
124.0
121.0
77.4 CDCl3
77.0 CDCl3
76.6 CDCl3
N
O2N
2n
f1 (ppm)

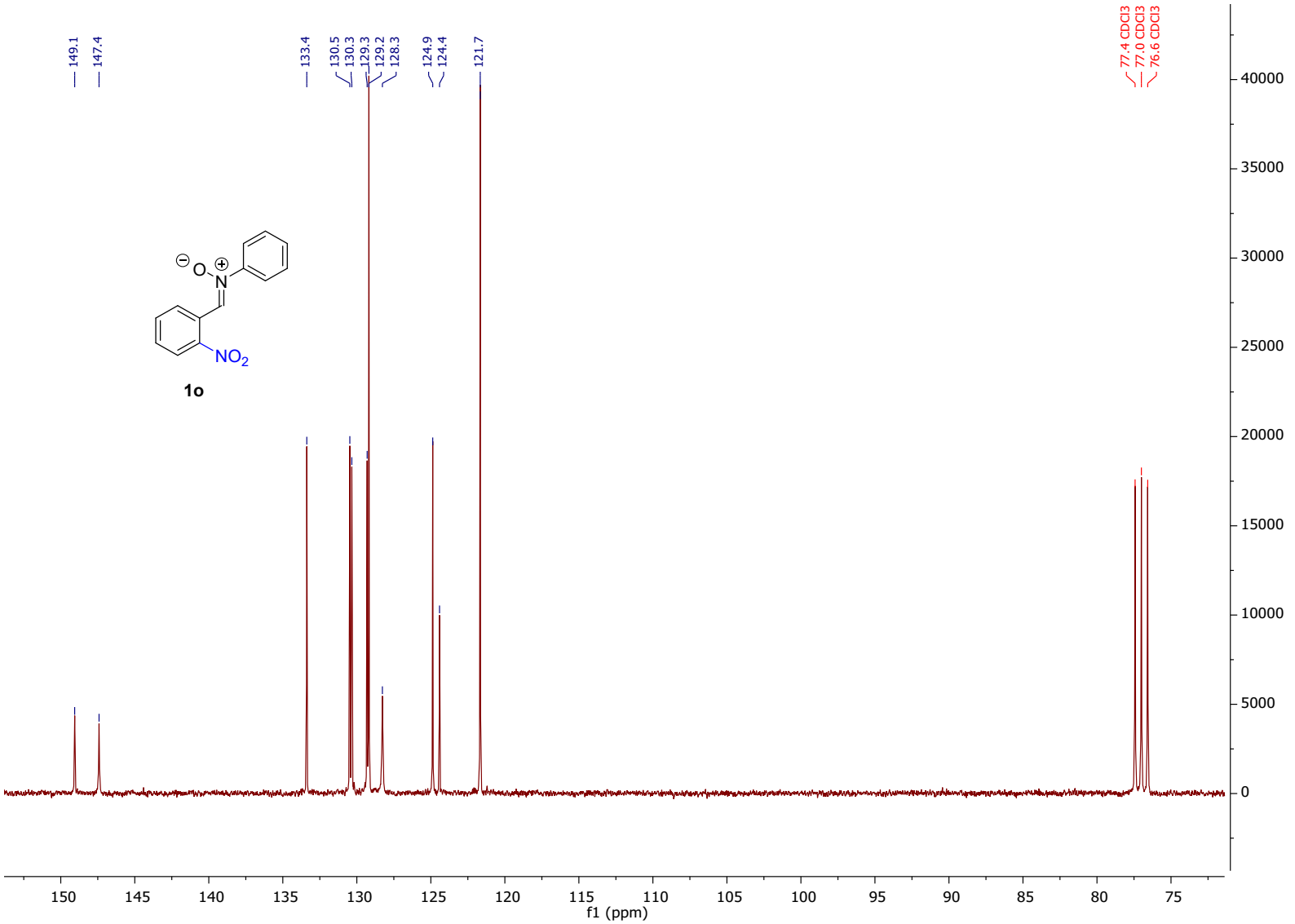

157.3
151.0
149.3
141.6
129.4
129.3
127.1
124.0
121.0
77.4 CDCl3
77.0 CDCl3
76.6 CDCl3
N
O2N
2n
f1 (ppm)

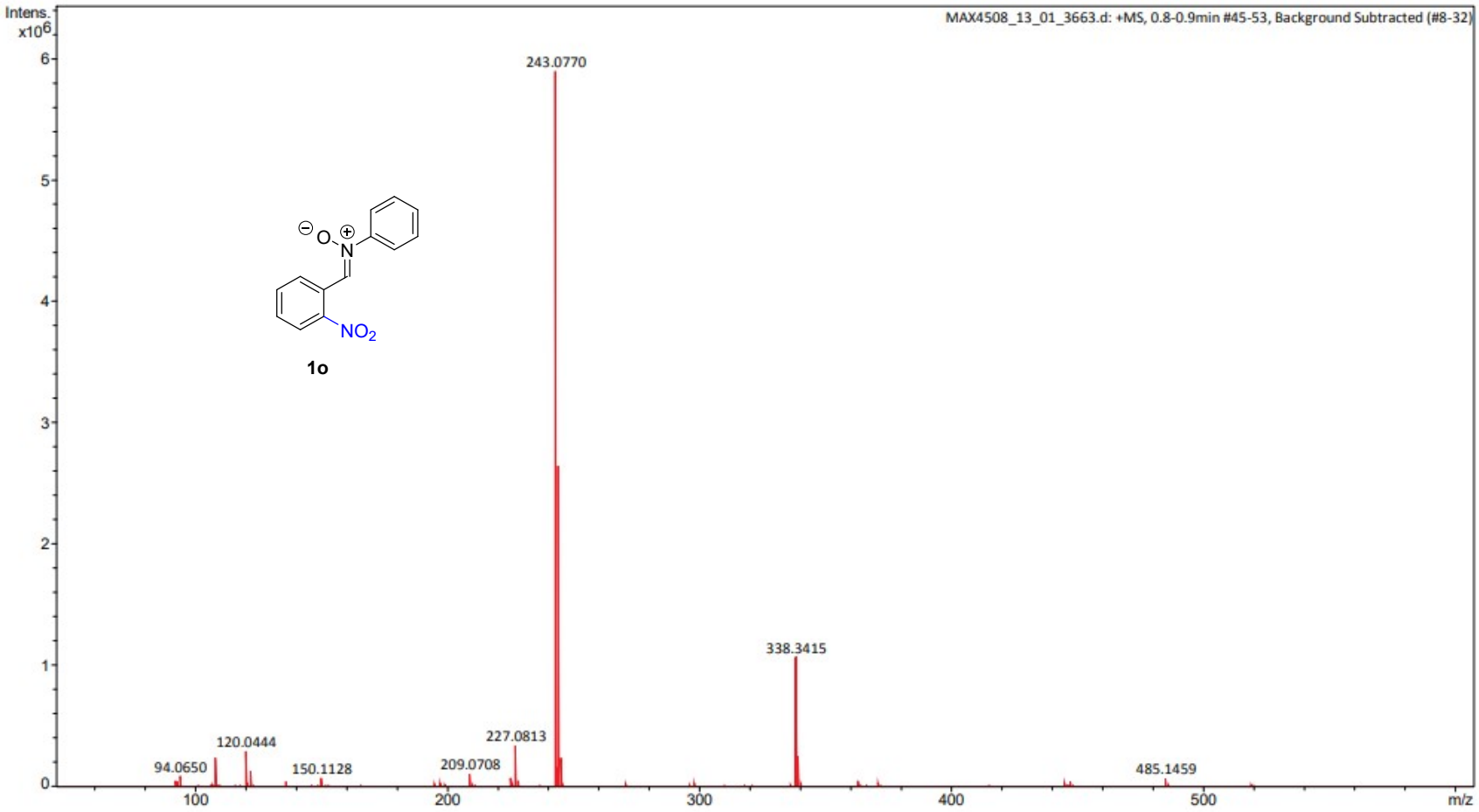
(*Z*)-1-(2-Nitrophenyl)-*N*-phenylmethanimine oxide (1o)



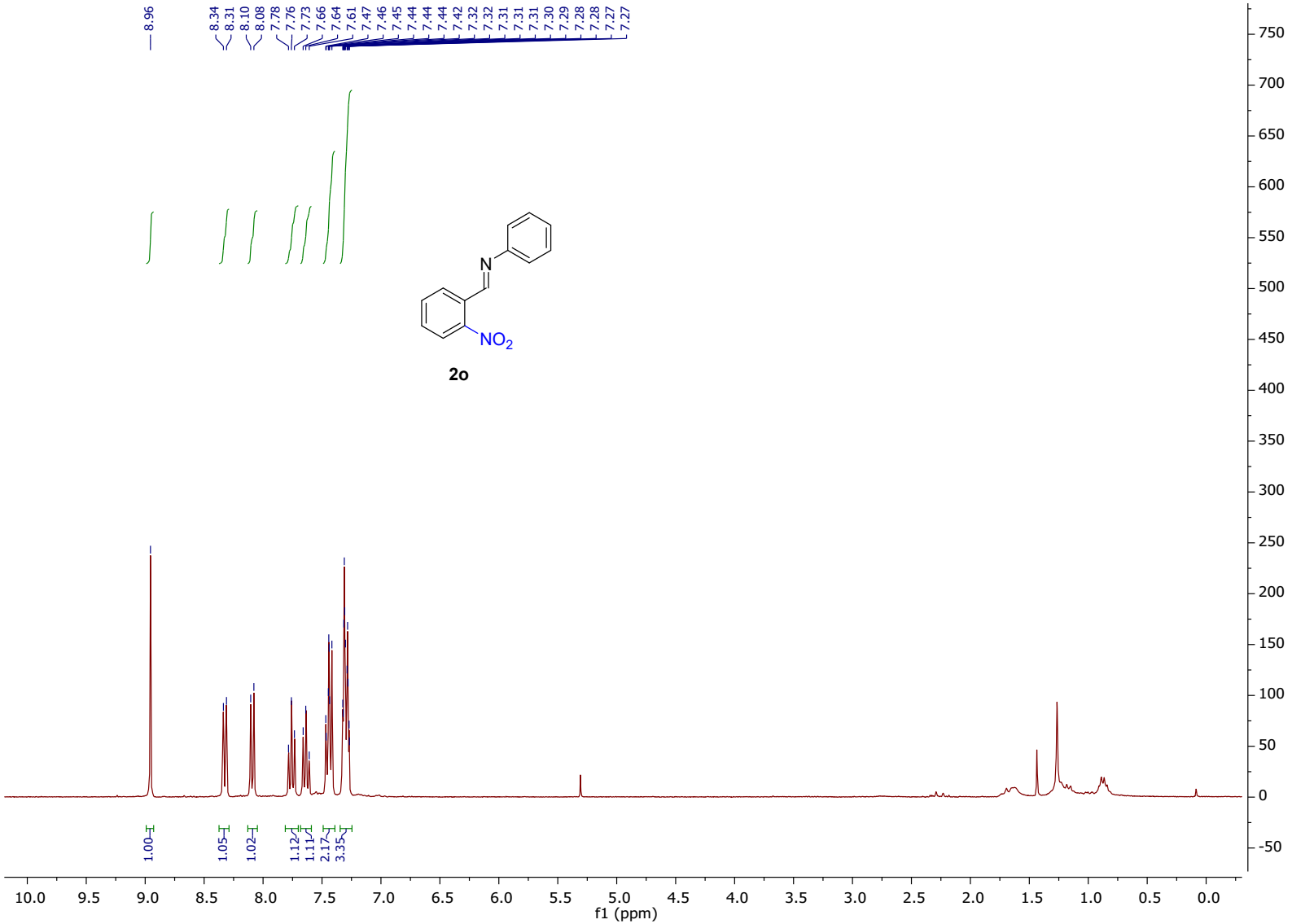

9.42
9.39
8.61
8.12
8.09
7.83
7.82
7.82
7.81
7.81
7.80
7.80
7.80
7.79
7.78
7.78
7.78
7.76
7.75
7.62
7.62
7.59
7.59
7.57
7.57
7.55
7.54
7.54
7.53
7.53
7.52
7.51
7.51
7.50
7.27 CDCl3
O
N
NO2
1o
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
9.5
9.4
9.3
9.2
9.1
9.0
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
f1 (ppm)

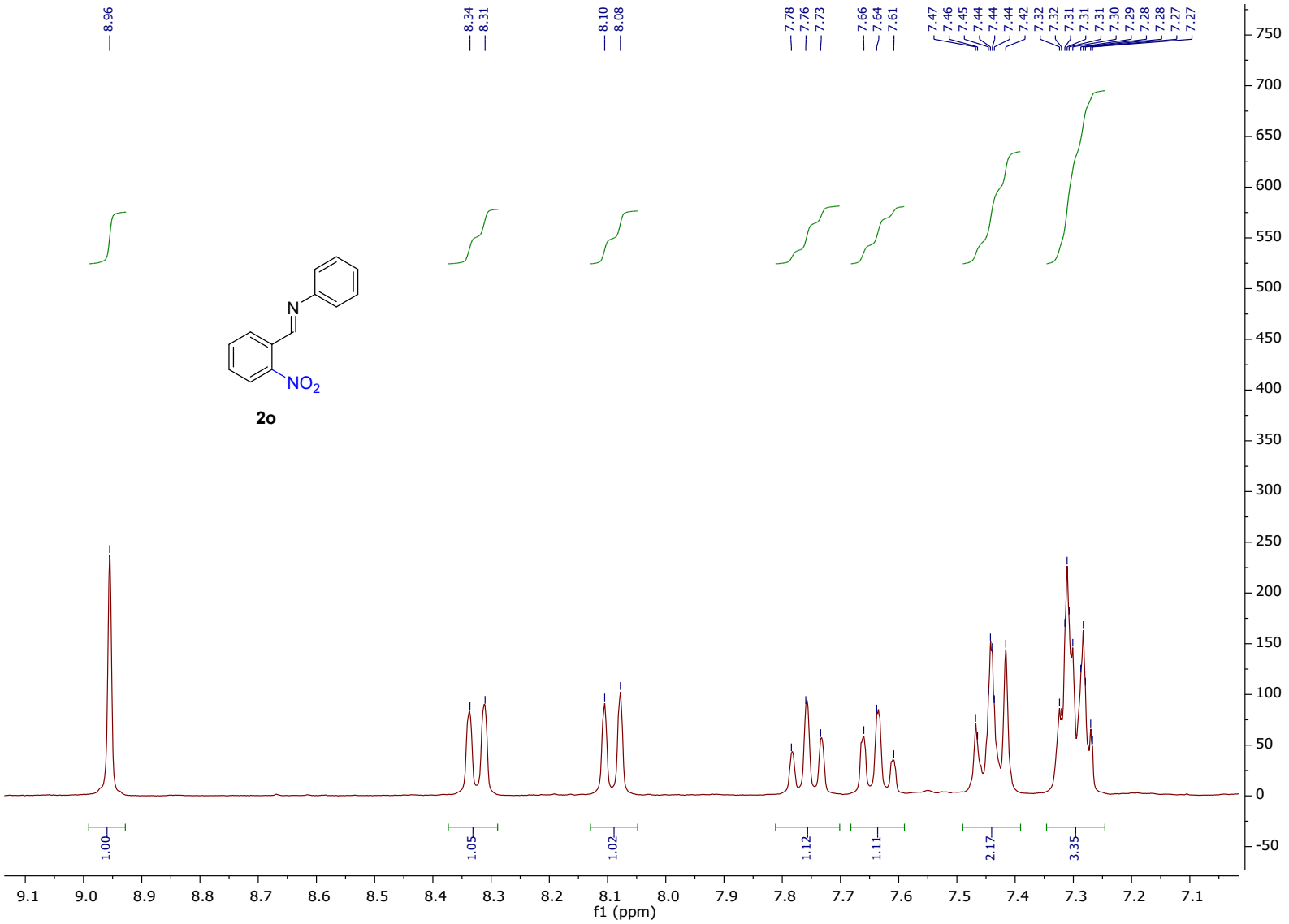

149.1
147.4
133.4
130.5
130.3
129.3
129.2
128.3
124.9
124.4
121.7
77.4 CDCl3
77.0 CDCl3
76.6 CDCl3
NO2
1o
40000
35000
30000
25000
20000
15000
10000
5000
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

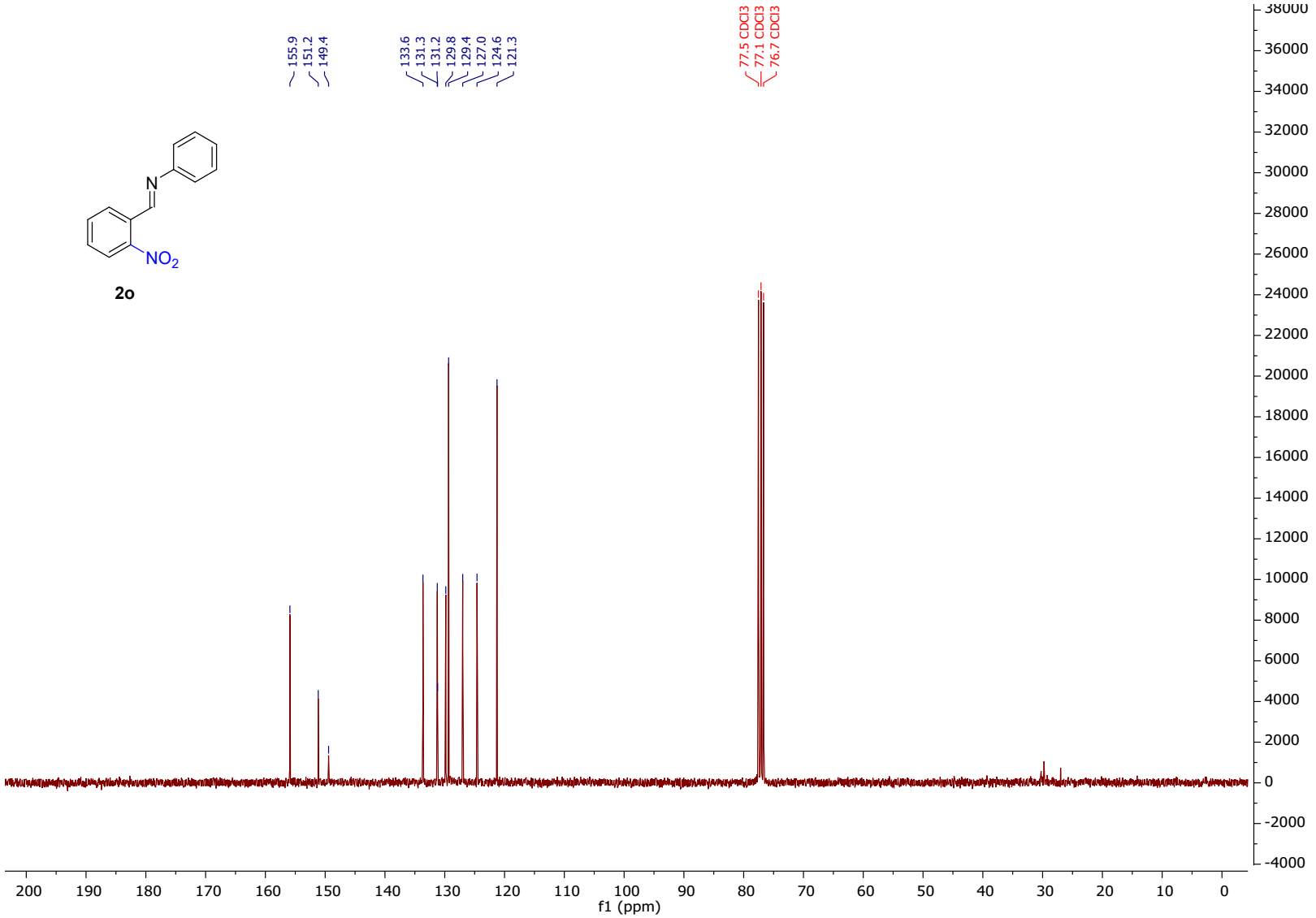

149.1
147.4
133.4
130.5
130.3
129.3
129.2
128.3
124.9
124.4
121.7
77.4 CDCl3
77.0 CDCl3
76.6 CDCl3
NO2
1o
40000
35000
30000
25000
20000
15000
10000
5000
0
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
f1 (ppm)

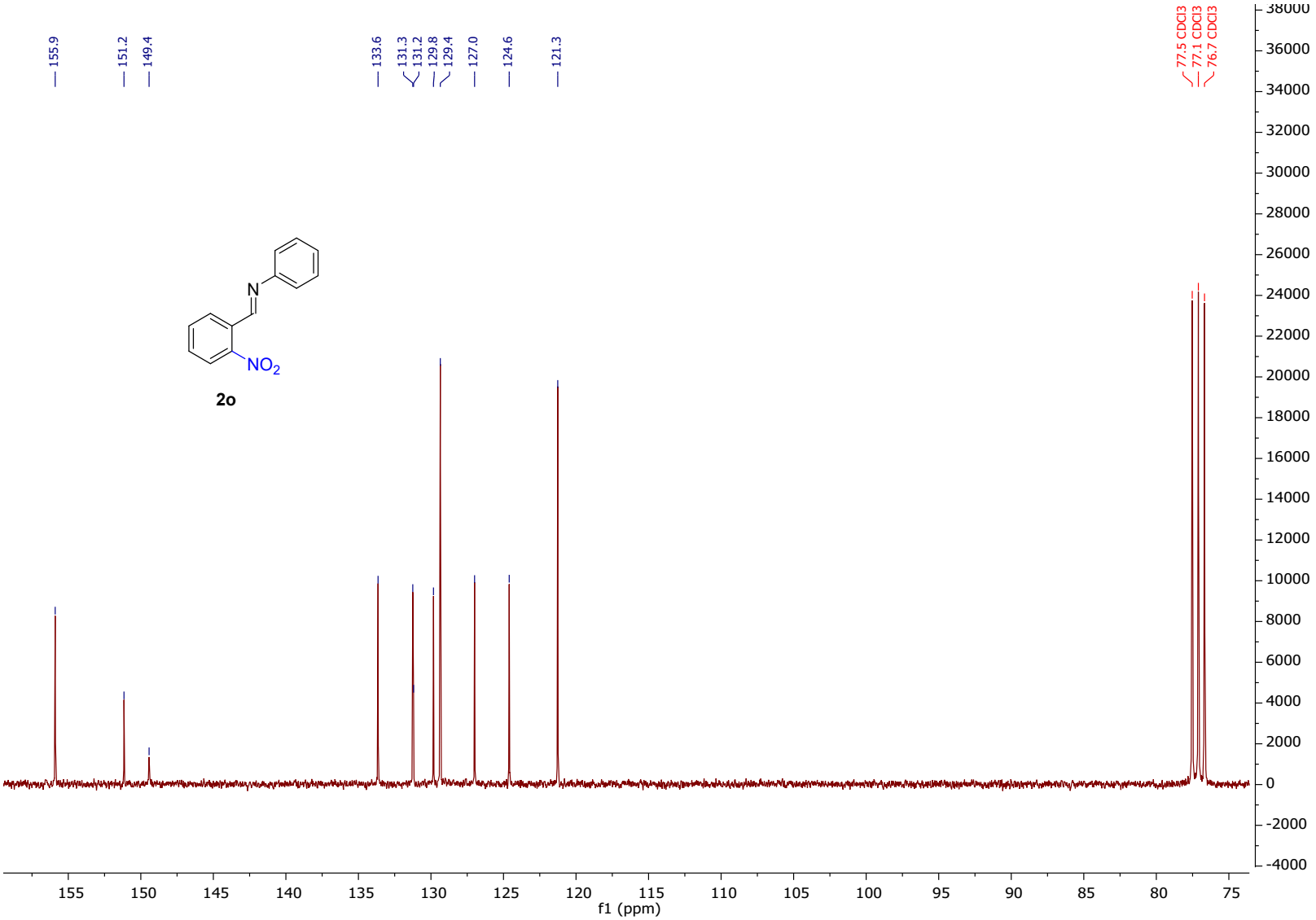

Intens.
x10^6
MAX4508_13_01_3663.d: +MS, 0.8-0.9min #45-53, Background Subtracted (#8-32)
243.0770
338.3415
120.0444
227.0813
94.0650
150.1128
209.0708
485.1459
m/z
1o

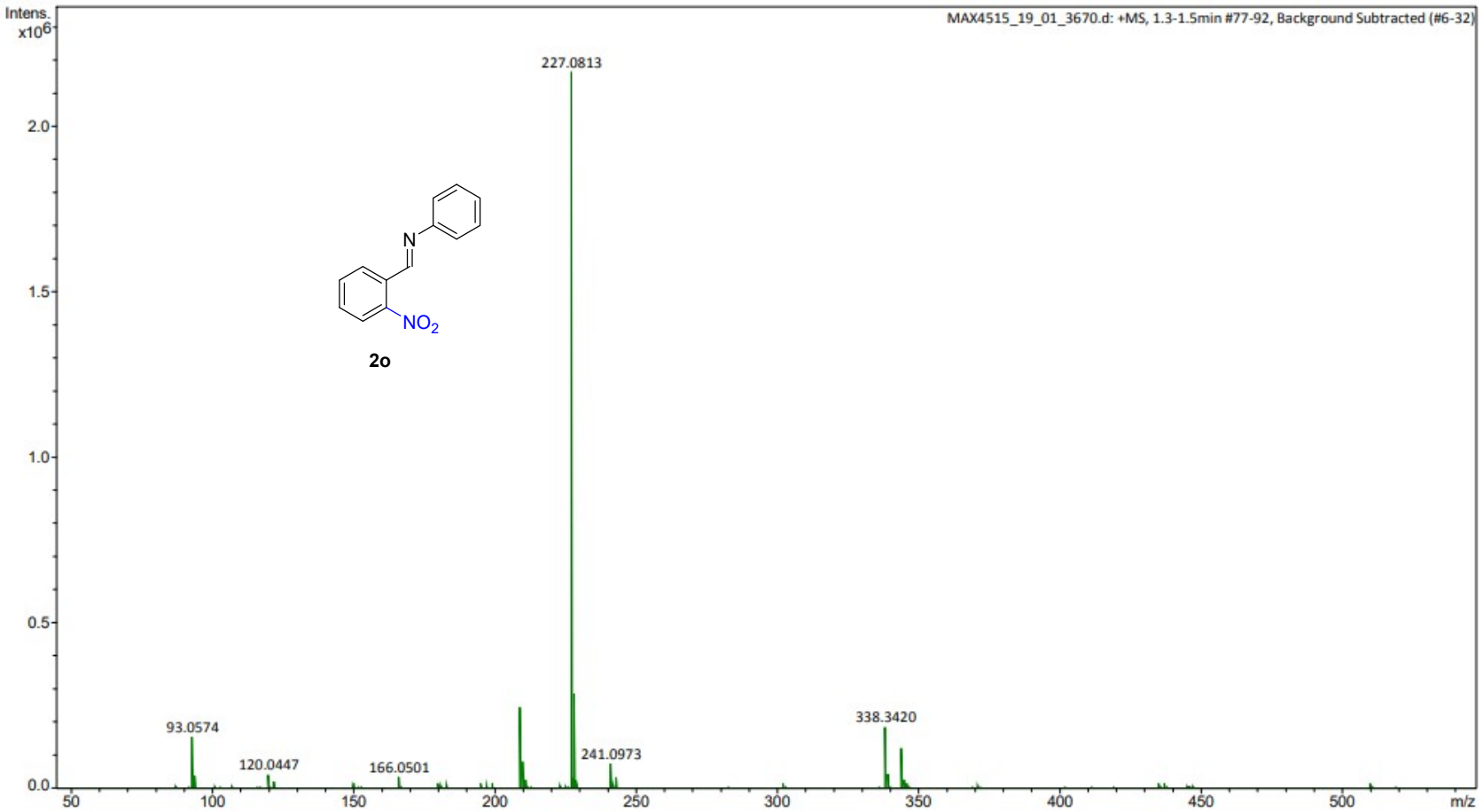
(*E*)-1-(2-Nitrophenyl)-*N*-phenylmethanimine (2o)




8.96
8.34
8.31
8.10
8.08
7.78
7.76
7.73
7.66
7.64
7.61
7.47
7.46
7.45
7.44
7.44
7.44
7.42
7.32
7.32
7.31
7.31
7.31
7.30
7.29
7.28
7.28
7.27
7.27
N
NO2
2o
1.00
1.05
1.02
1.12
1.11
2.17
3.35
f1 (ppm)

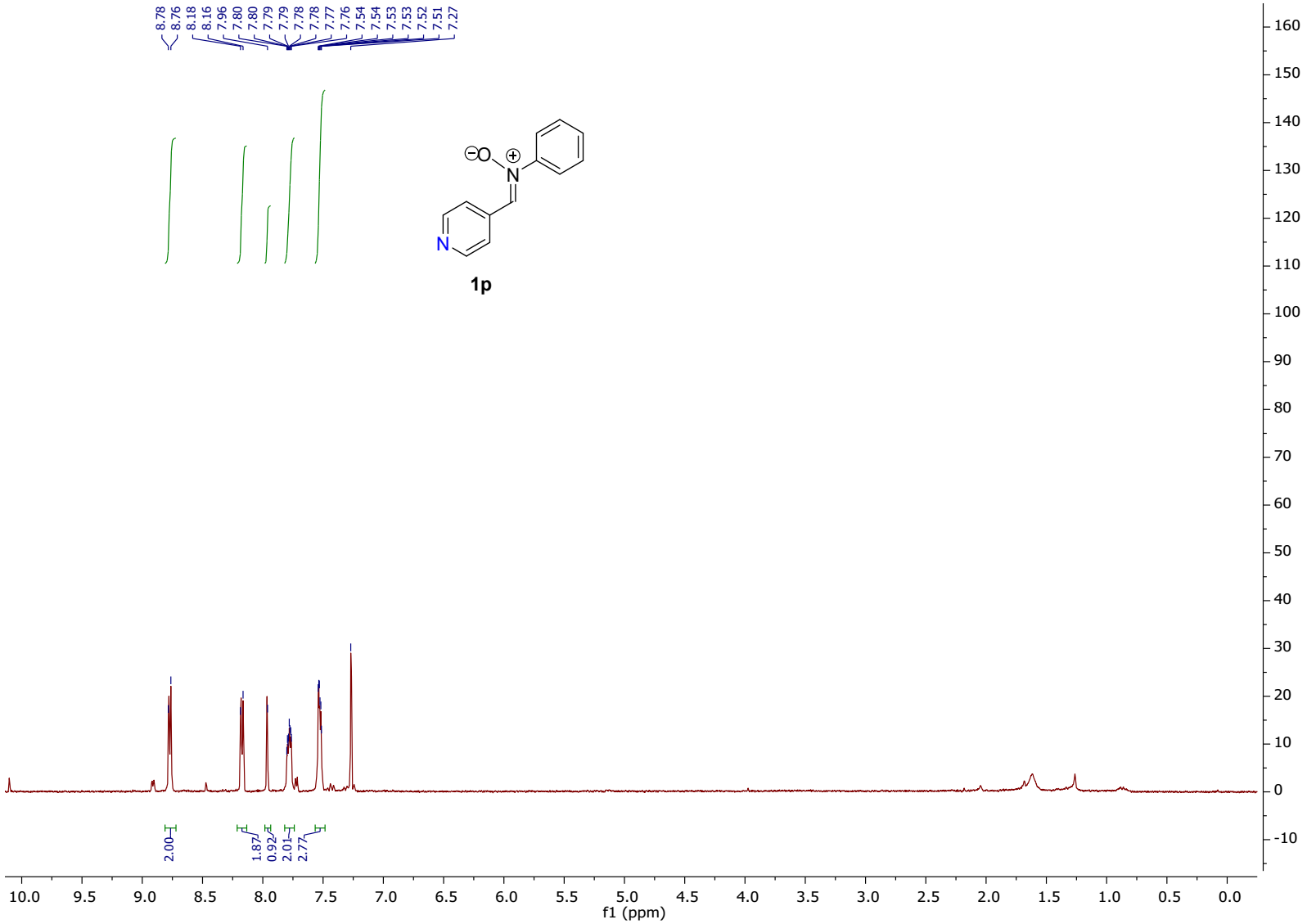

155.9
151.2
149.4
133.6
131.3
131.2
129.8
129.4
127.0
124.6
121.3
77.5 CDCl3
77.1 CDCl3
76.7 CDCl3
N
NO2
2o
f1 (ppm)

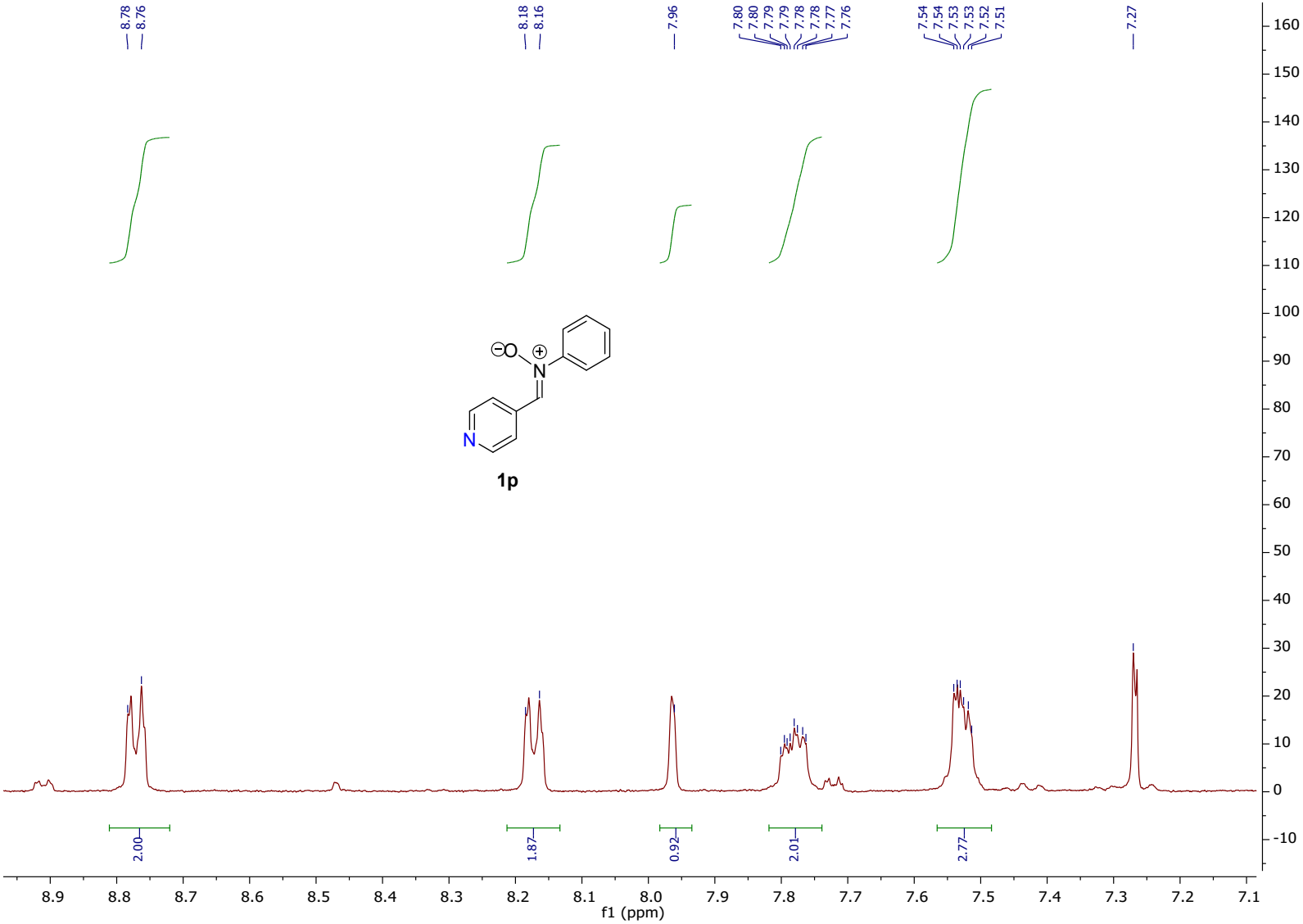

155.9
151.2
149.4
133.6
131.3
131.2
129.8
129.4
127.0
124.6
121.3
77.5 CDCl3
77.1 CDCl3
76.7 CDCl3
N
NO2
2o
f1 (ppm)

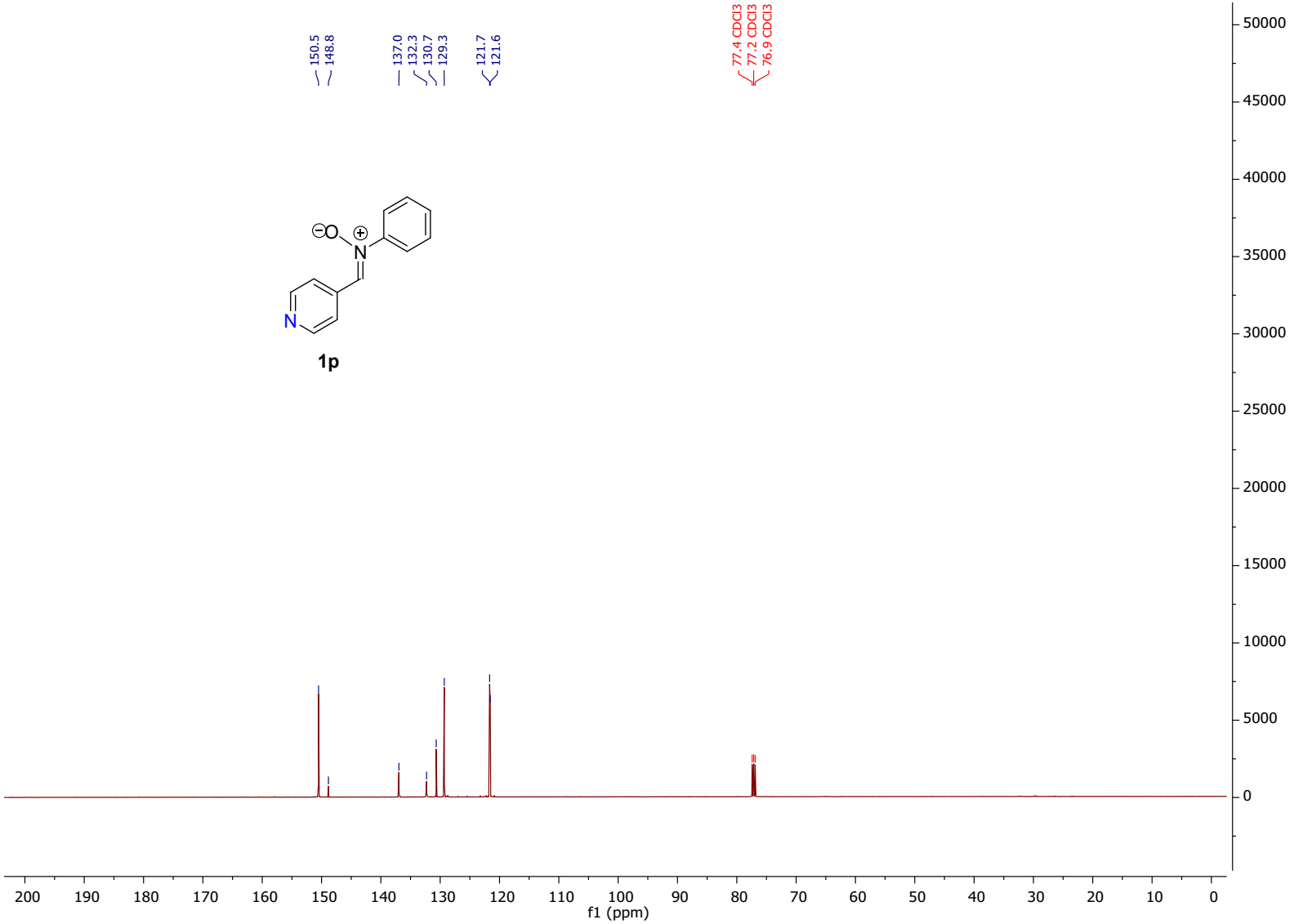

Intens.
x10^6
MAX4515_19_01_3670.d: +MS, 1.3-1.5min #77-92, Background Subtracted (#6-32)
227.0813
2.0
1.5
1.0
0.5
0.0
N
NO2
93.0574
120.0447
166.0501
241.0973
338.3420
50
100
150
200
250
300
350
400
450
500
m/z

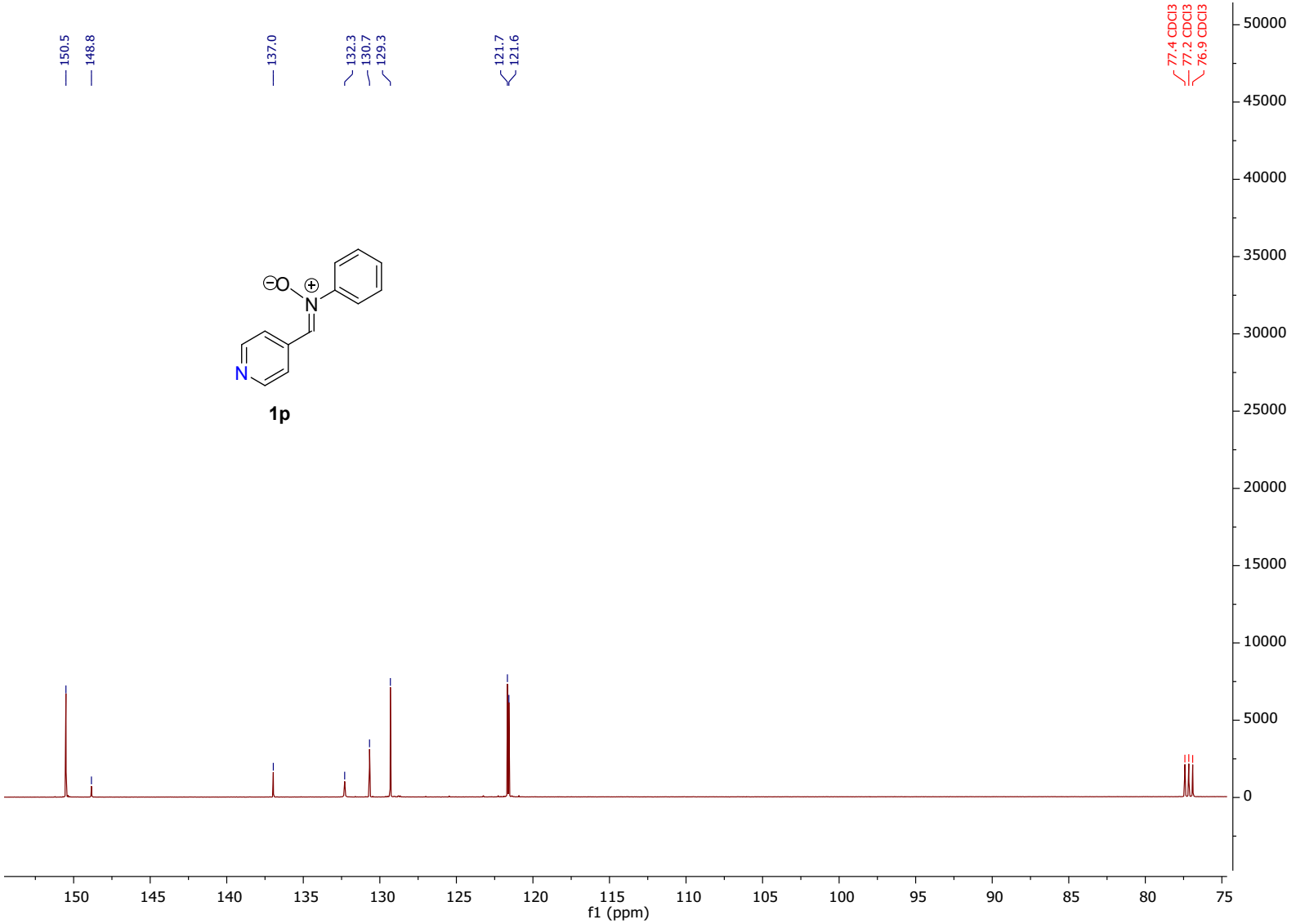
2o

(*Z*)-*N*-Phenyl-1-(pyridin-4-yl)methanimine oxide (1p)

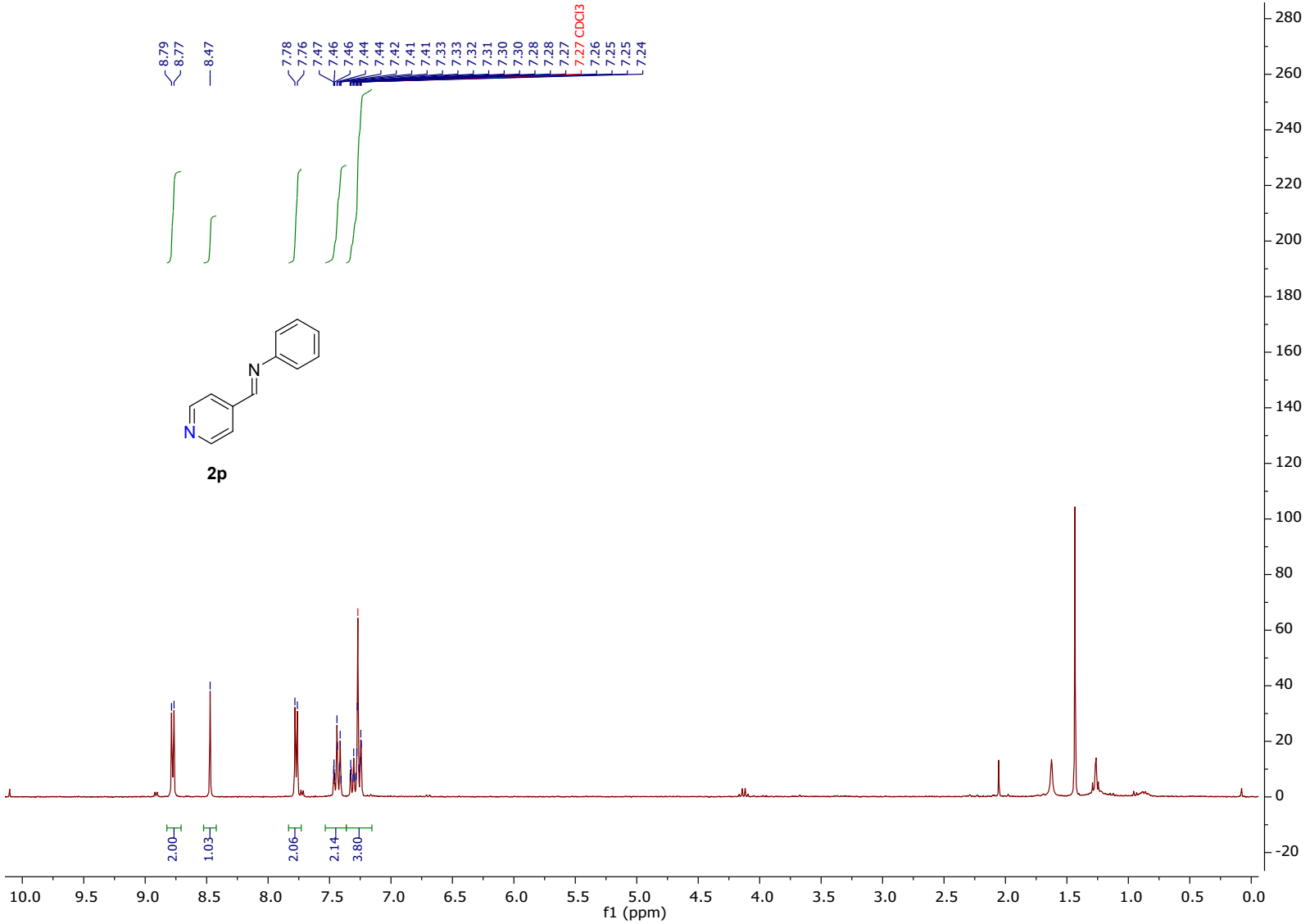


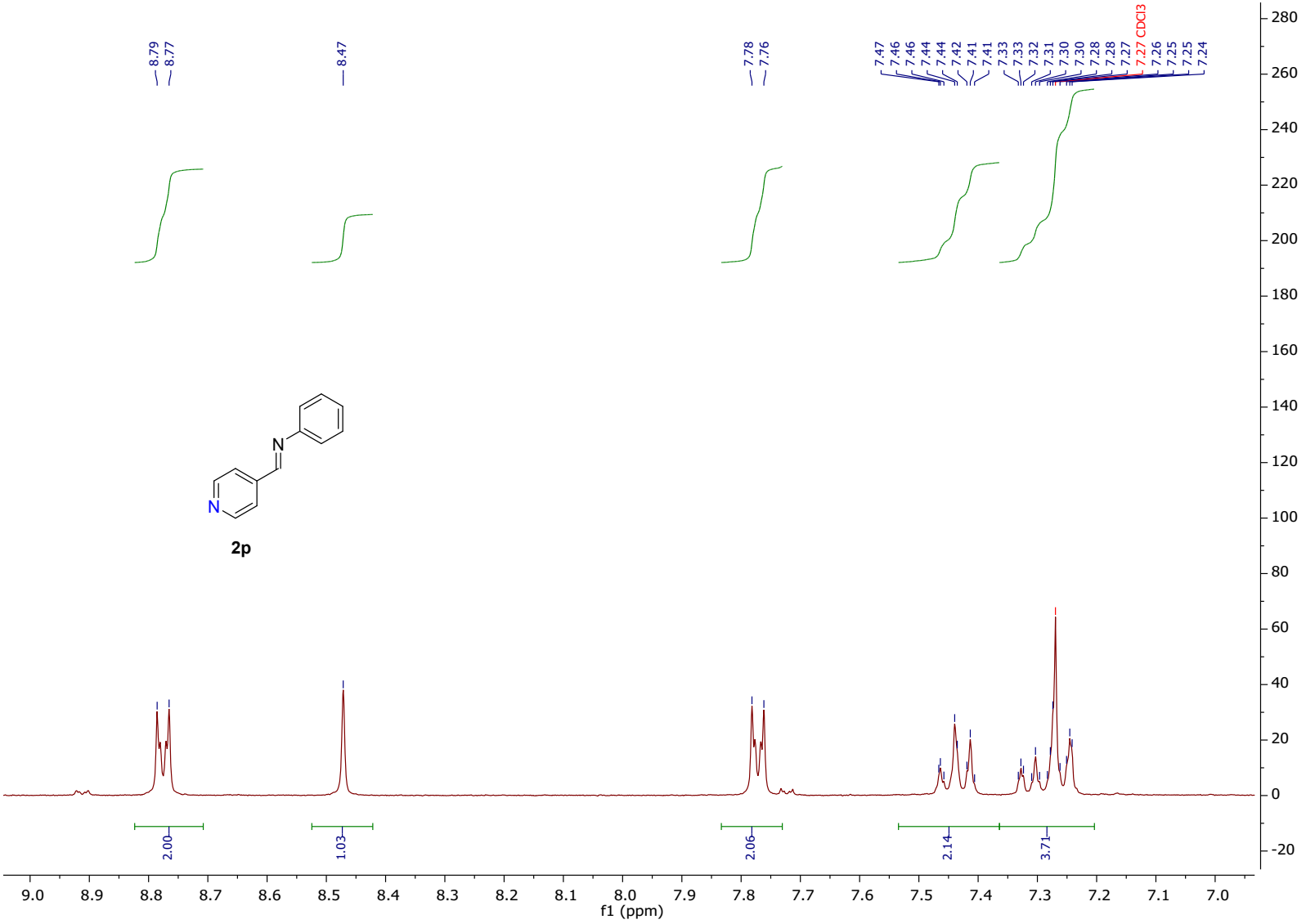

8.78
8.76
8.18
8.16
7.96
7.80
7.80
7.79
7.79
7.78
7.78
7.77
7.76
7.54
7.54
7.53
7.53
7.52
7.51
7.27
1p
2.00
1.87
0.92
2.01
2.77
f1 (ppm)

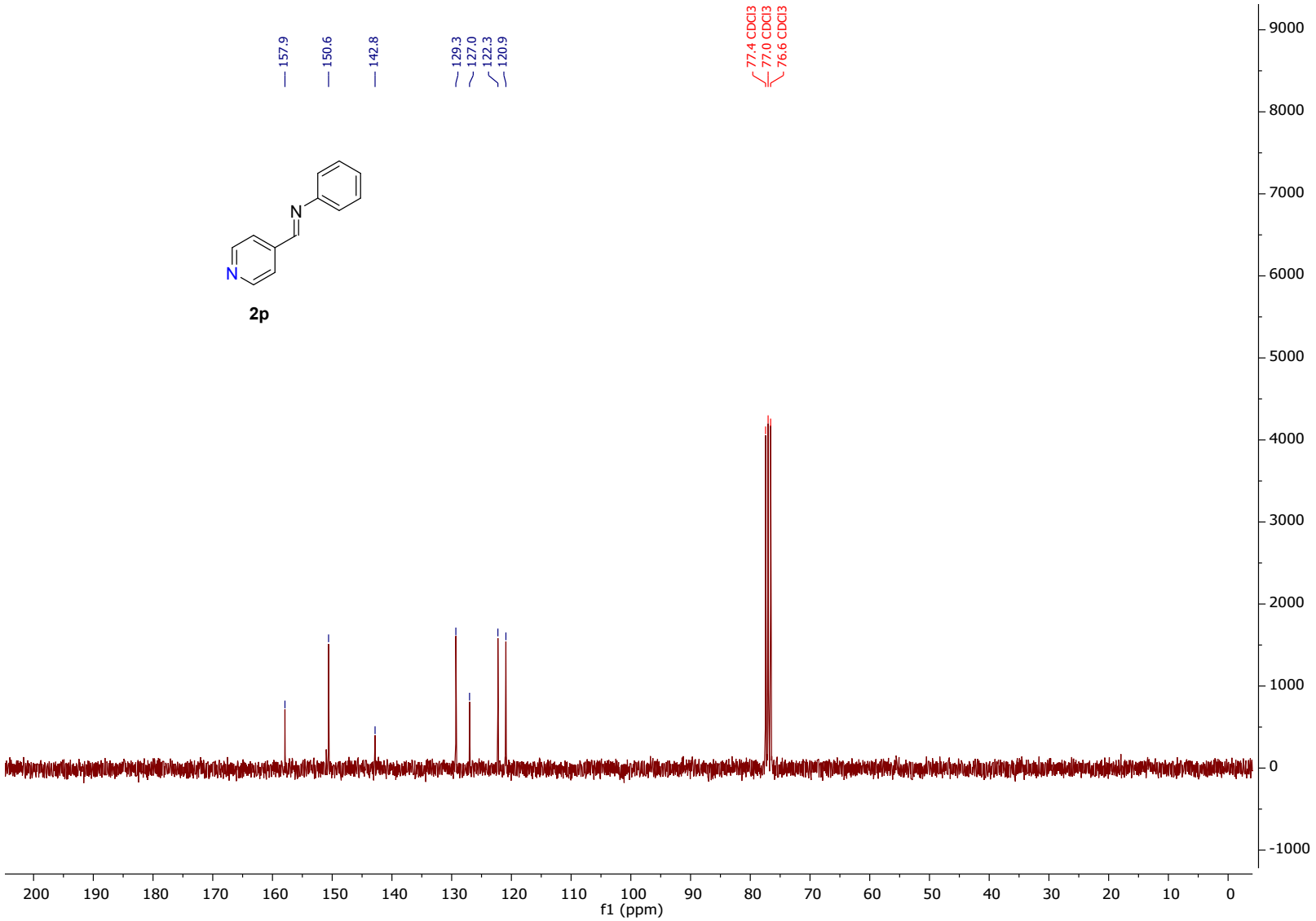

150.5
148.8
137.0
132.3
130.7
129.3
121.7
121.6
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
1p
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

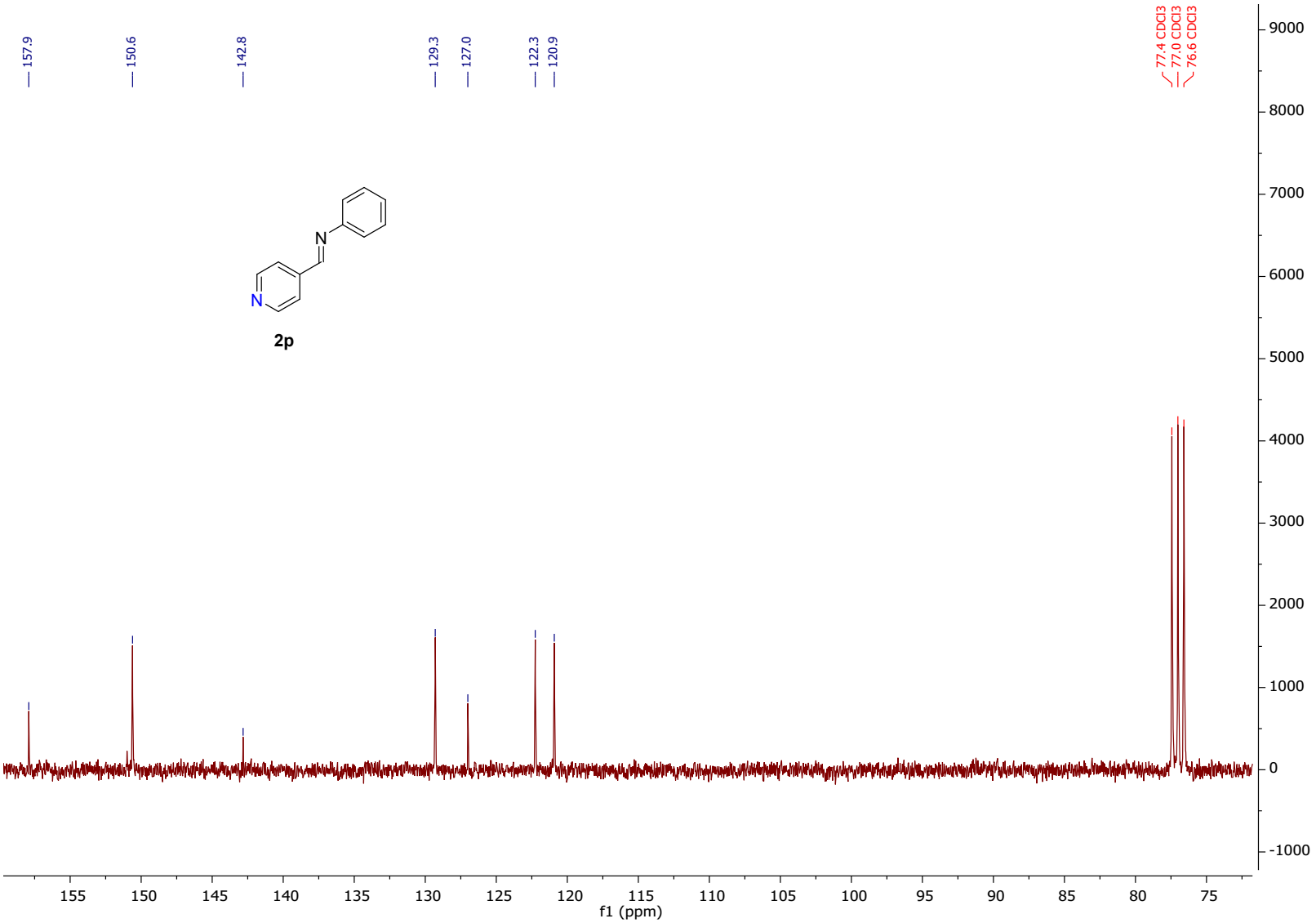

150.5
148.8
137.0
132.3
130.7
129.3
121.7
121.6
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
1p
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
f1 (ppm)

(*E*)-*N*-Phenyl-1-(pyridin-4-yl)methanimine (2p)

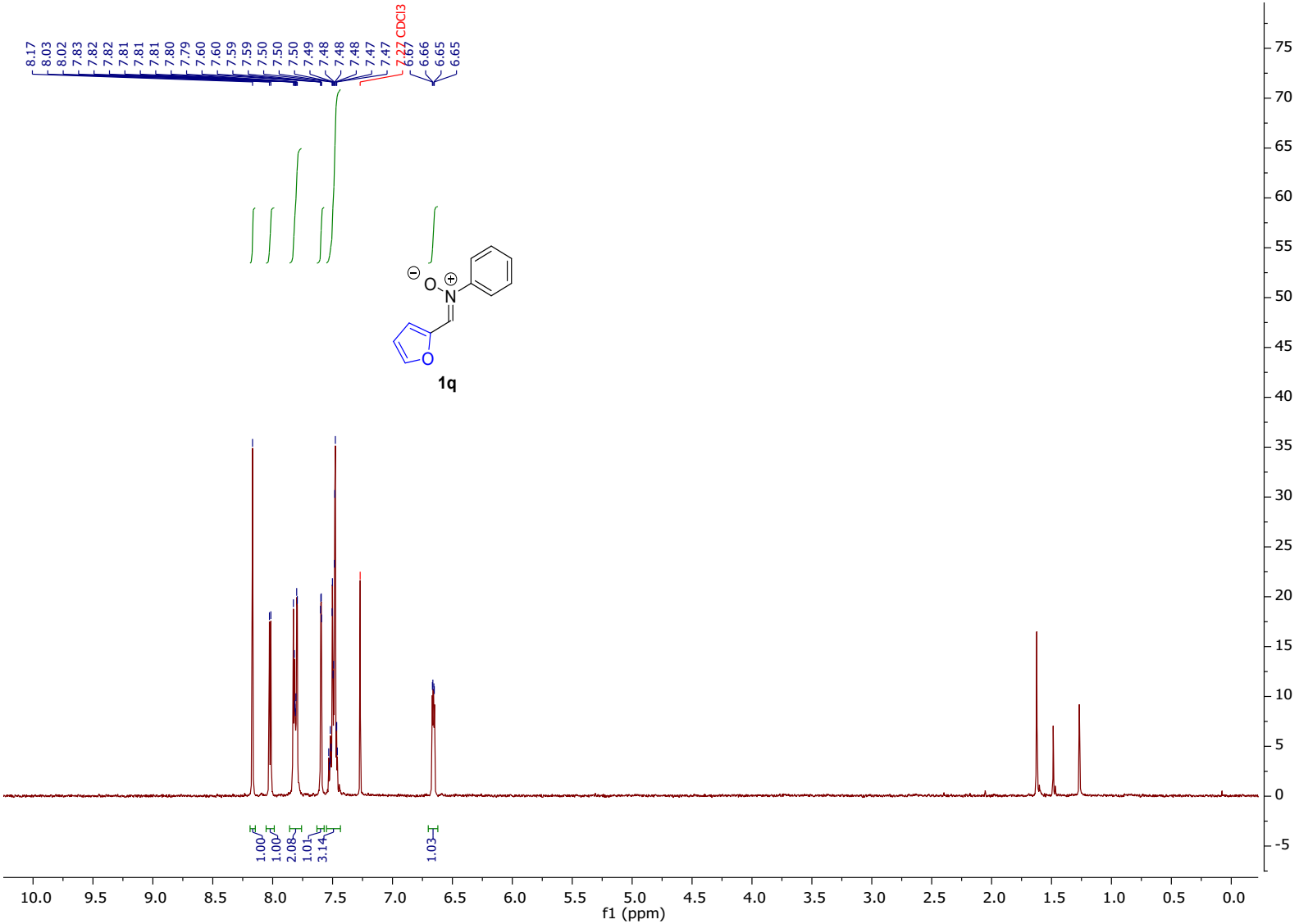


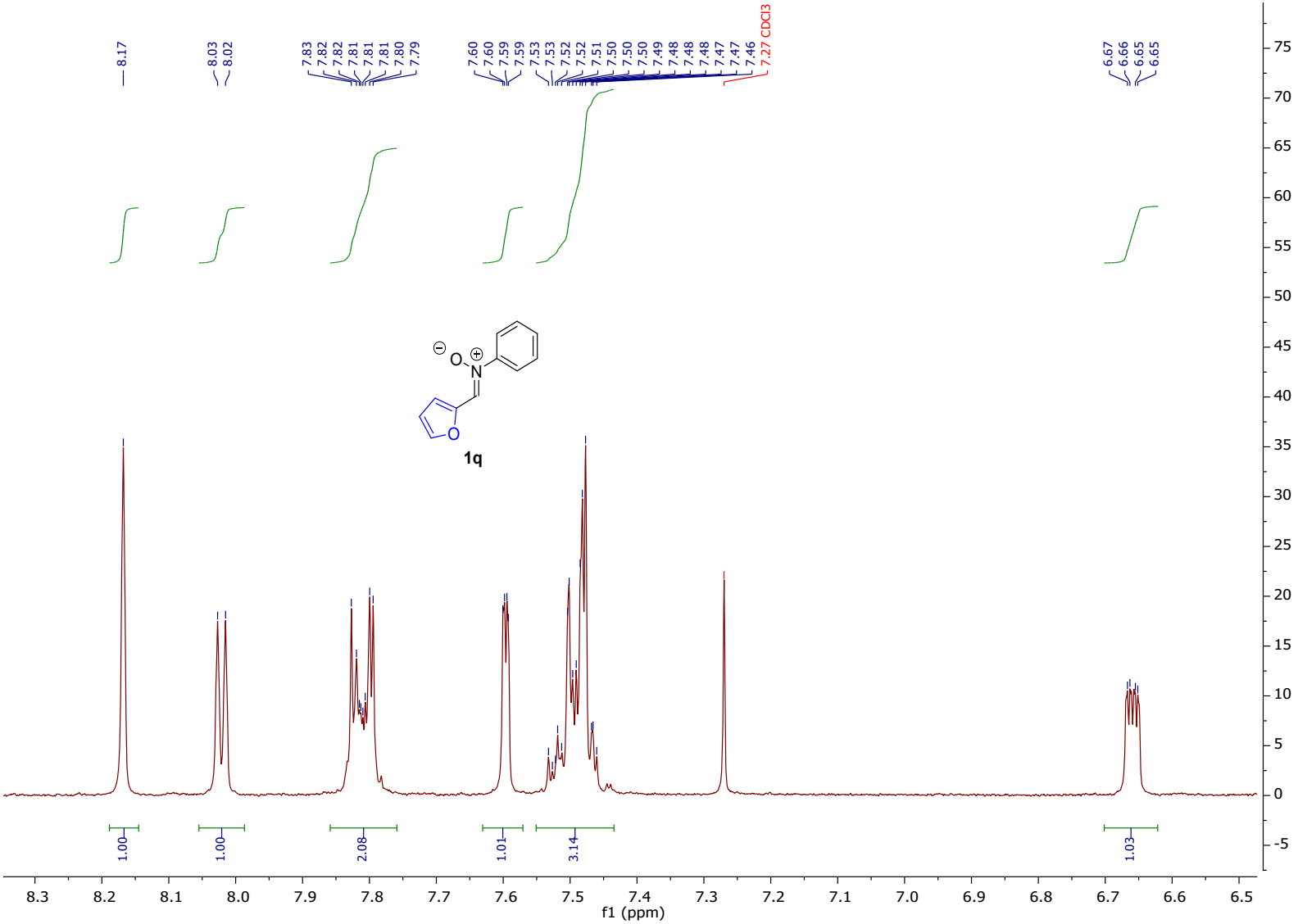

8.79
8.77
8.47
7.78
7.76
7.47
7.46
7.46
7.44
7.44
7.42
7.41
7.41
7.33
7.33
7.32
7.31
7.30
7.30
7.28
7.28
7.27
7.27 CDCl3
7.26
7.25
7.25
7.24
N
N
2p
2.00
1.03
2.06
2.14
3.71
f1 (ppm)

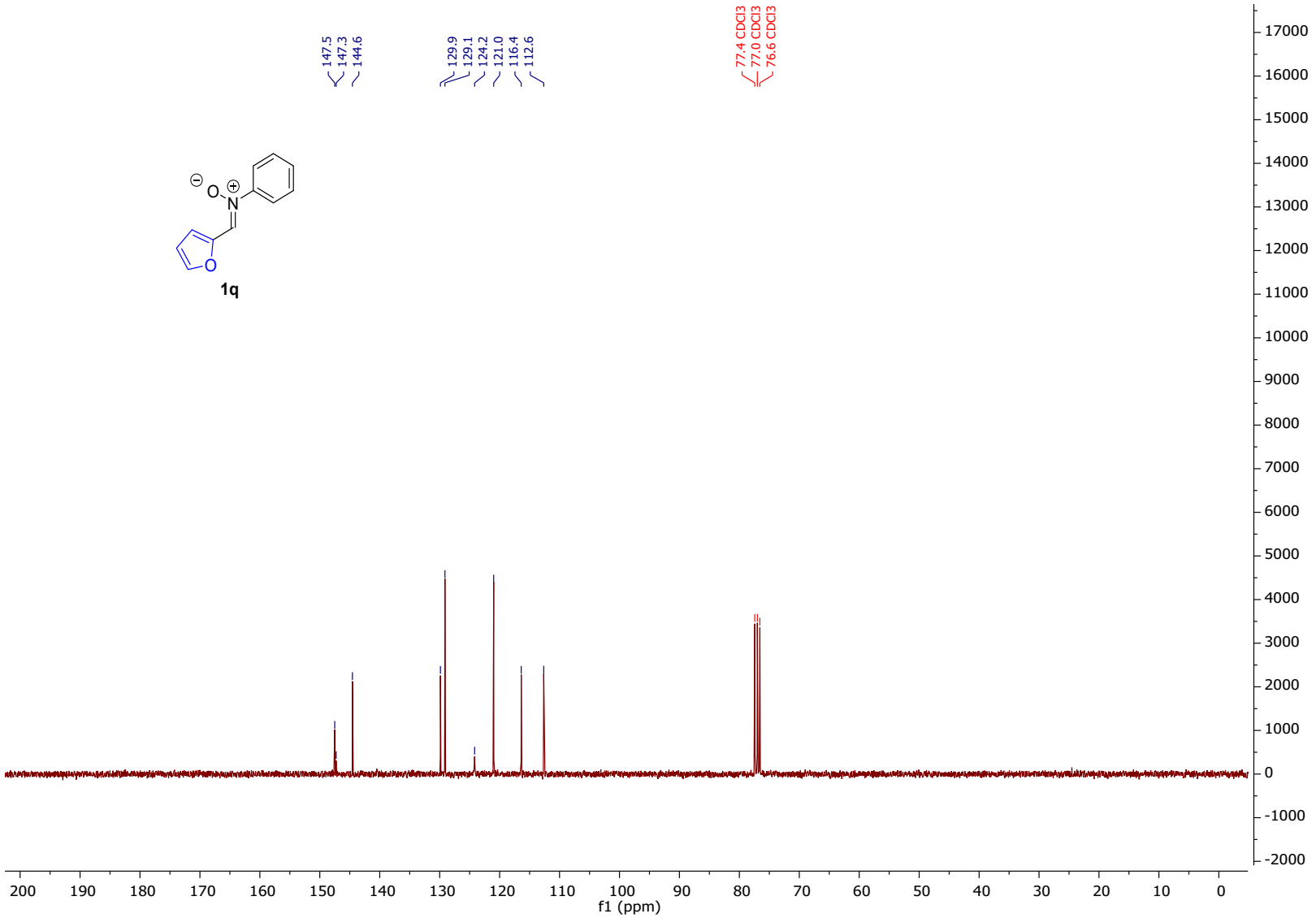

157.9
150.6
142.8
129.3
127.0
122.3
120.9
77.4 CDCl3
77.0 CDCl3
76.6 CDCl3
N
N
2p
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

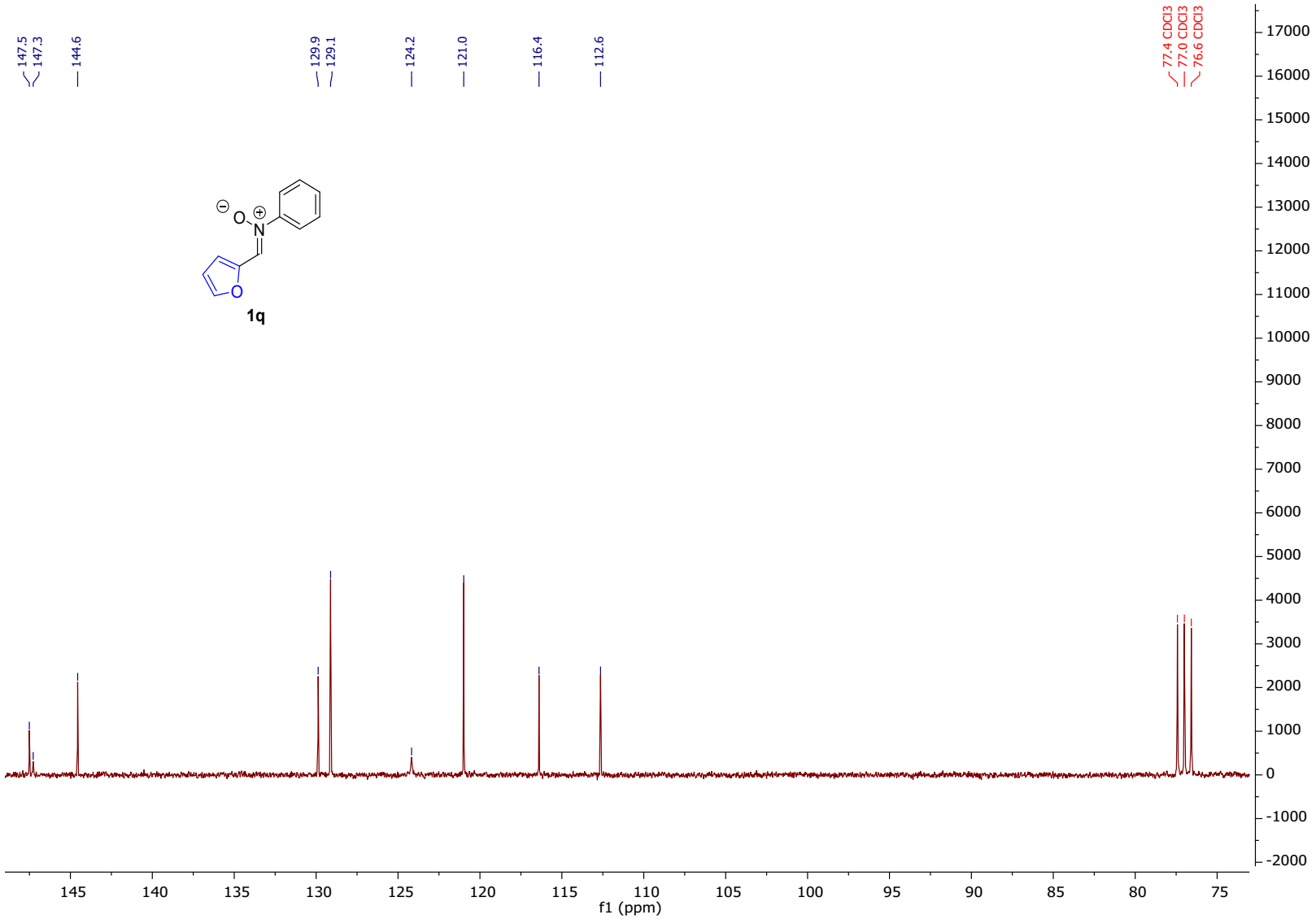

157.9
150.6
142.8
129.3
127.0
122.3
120.9
77.4 CDCl3
77.0 CDCl3
76.6 CDCl3
N
N
2p
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
f1 (ppm)

(*Z*)-1-(furan-2-yl)-N-phenylmethanimine oxide (1q)

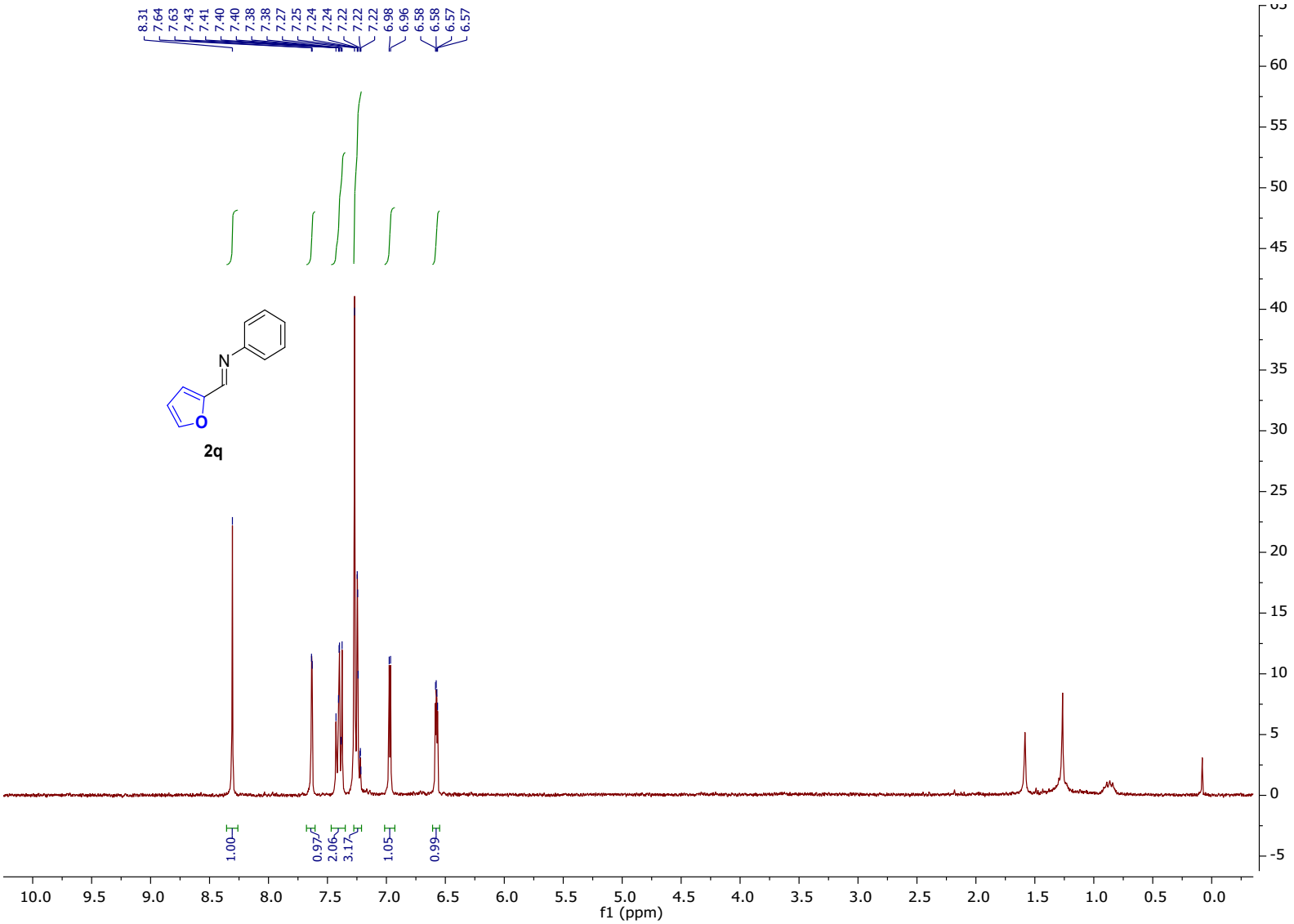


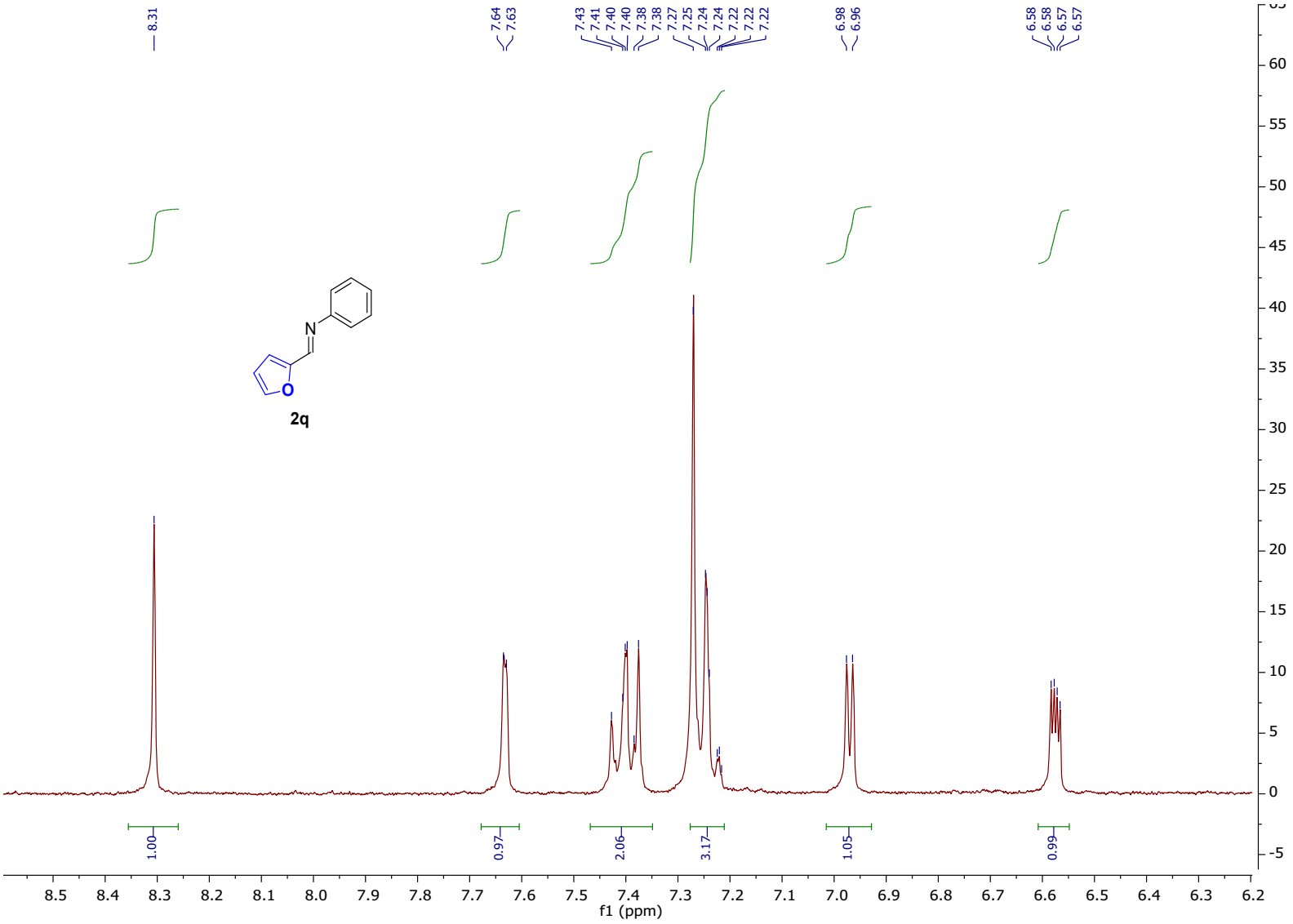

8.17
8.03
8.02
7.83
7.82
7.82
7.81
7.81
7.81
7.80
7.79
7.60
7.60
7.59
7.59
7.53
7.53
7.52
7.52
7.51
7.50
7.50
7.50
7.49
7.48
7.48
7.48
7.47
7.47
7.46
7.27 CDCl3
6.67
6.66
6.65
6.65
1q
1.00
1.00
2.08
1.01
3.14
1.03
f1 (ppm)

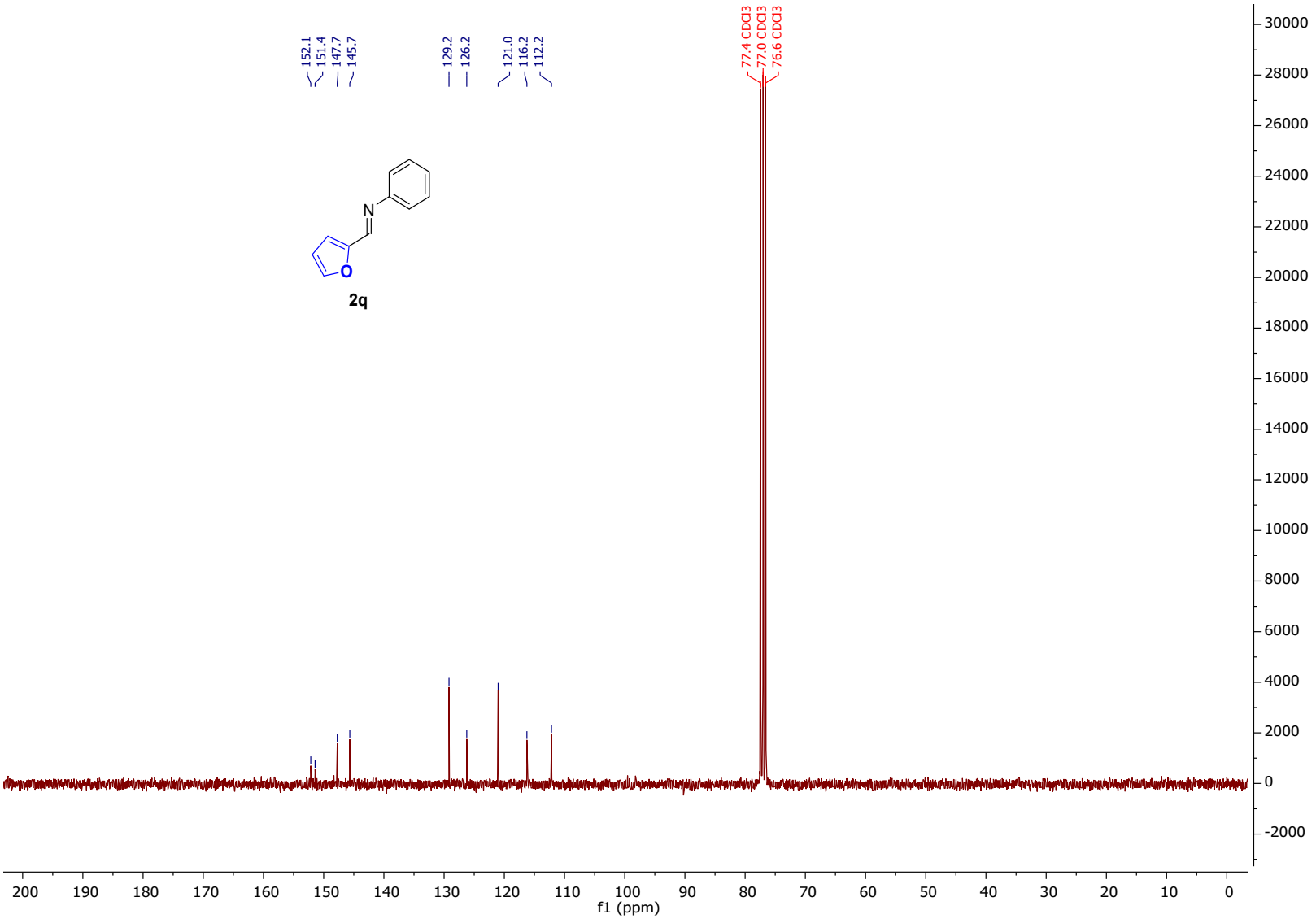

147.5
147.3
144.6
129.9
129.1
124.2
121.0
116.4
112.6
77.4 CDCl3
77.0 CDCl3
76.6 CDCl3
1q
f1 (ppm)

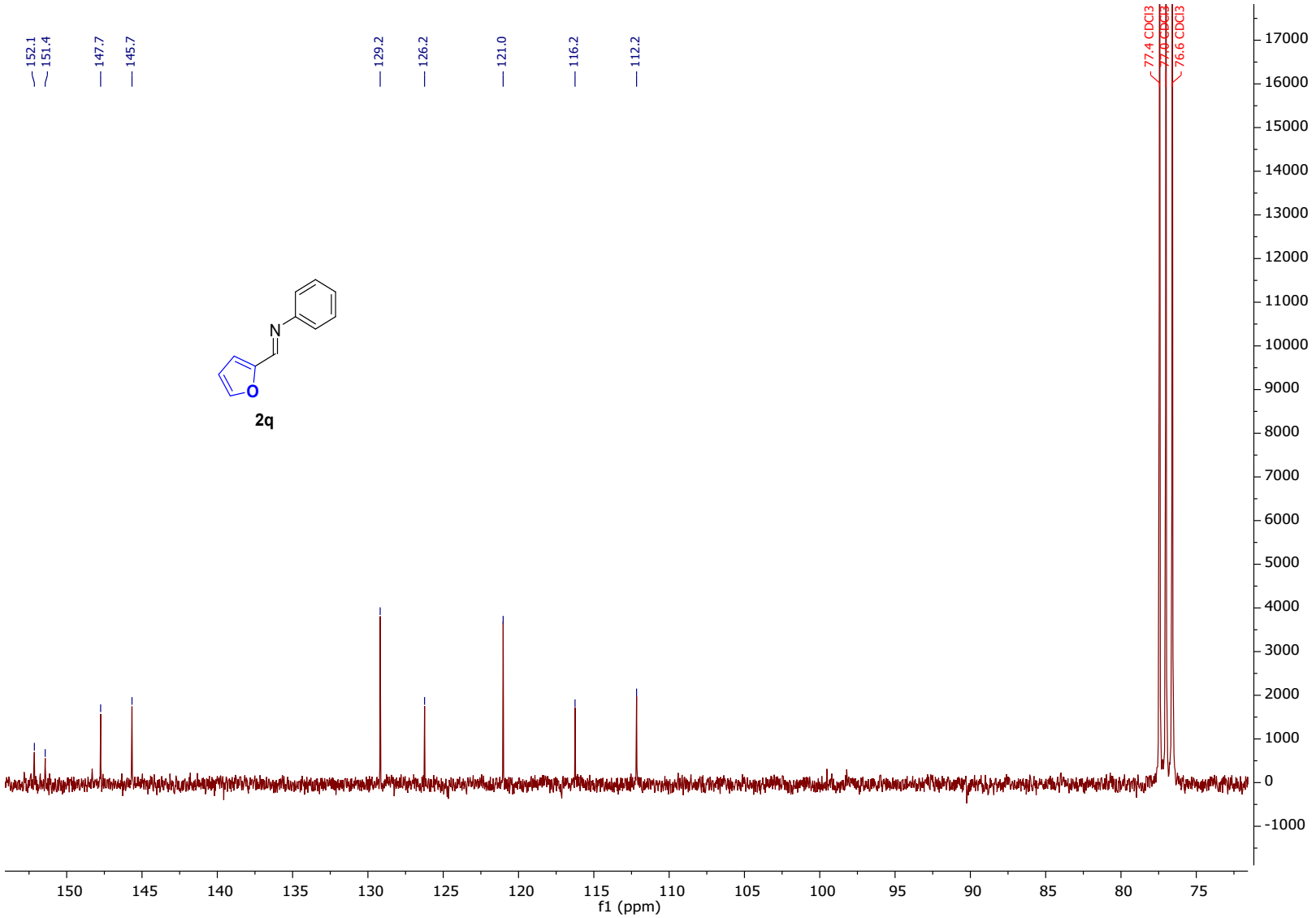

147.5
147.3
144.6
129.9
129.1
124.2
121.0
116.4
112.6
77.4 CDCl3
77.0 CDCl3
76.6 CDCl3
1q
f1 (ppm)

(*E*)-1-(furan-2-yl)-*N*-phenylmethanimine (2q)

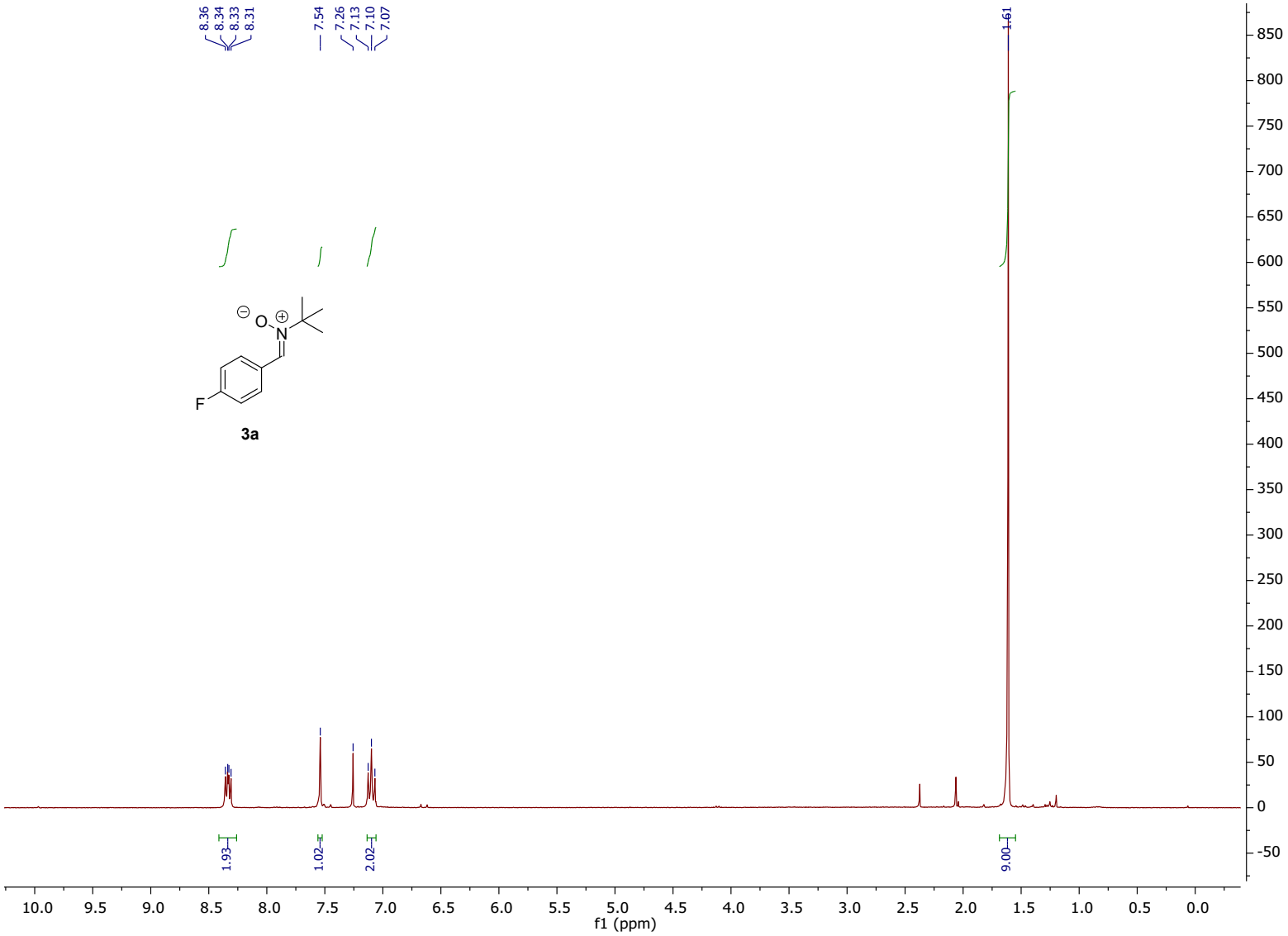


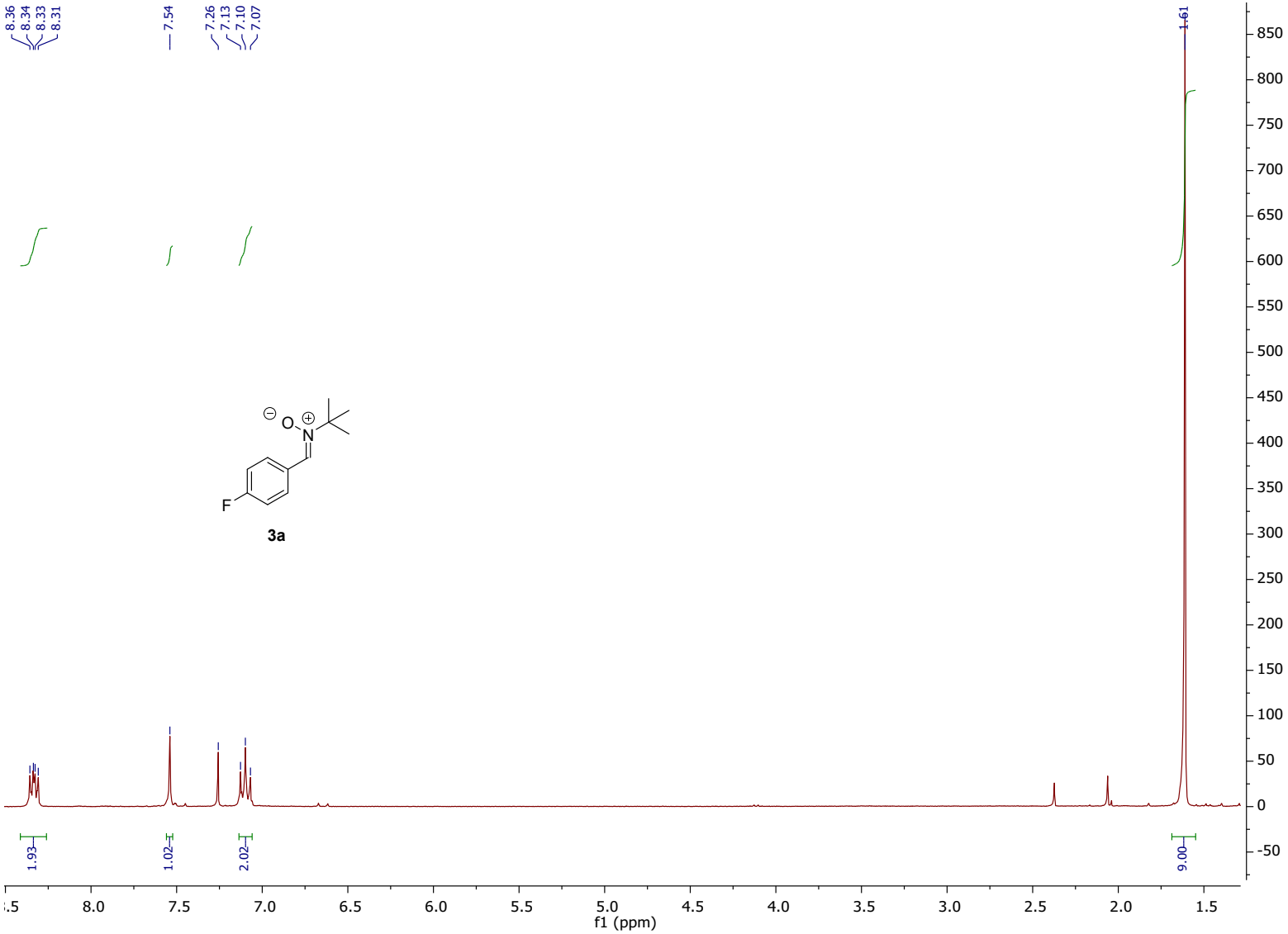

8.31
7.64
7.63
7.43
7.41
7.40
7.40
7.38
7.38
7.27
7.25
7.24
7.24
7.22
7.22
7.22
6.98
6.96
6.58
6.58
6.57
6.57
N
O
2q
1.00
0.97
2.06
3.17
1.05
0.99
f1 (ppm)

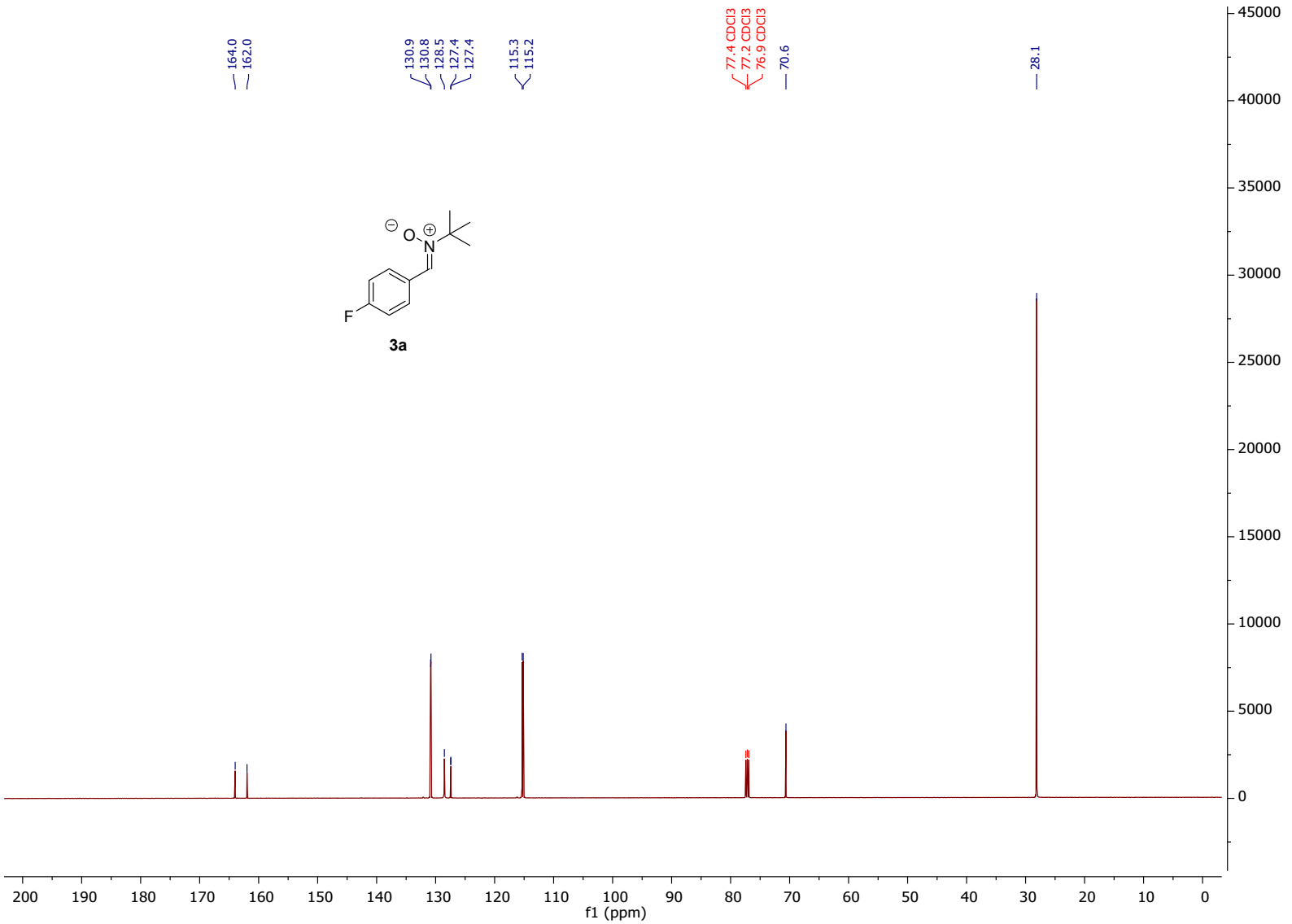

152.1
151.4
147.7
145.7
129.2
126.2
121.0
116.2
112.2
77.4 CDCl3
77.0 CDCl3
76.6 CDCl3
N
O
2q
f1 (ppm)

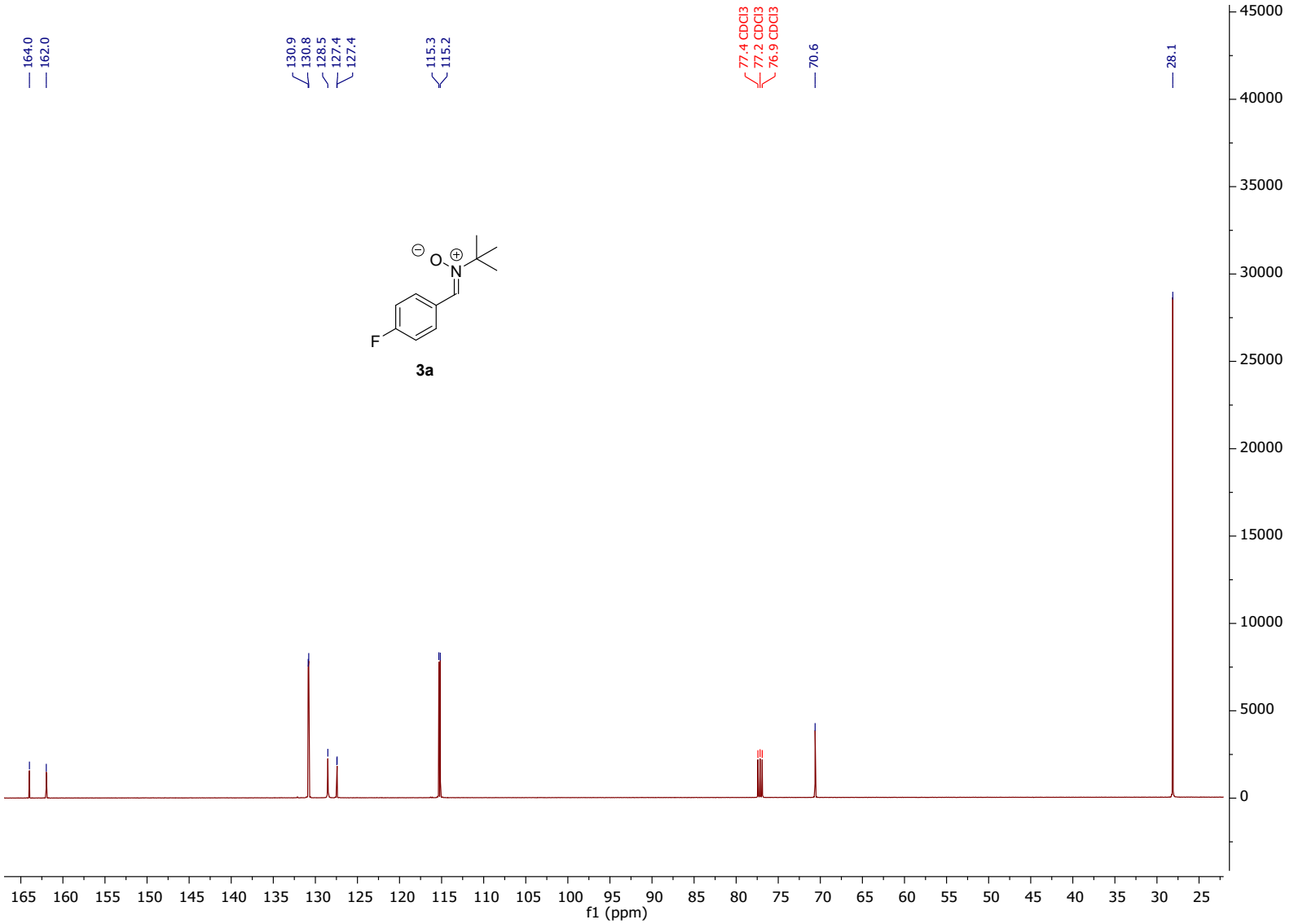

152.1
151.4
147.7
145.7
129.2
126.2
121.0
116.2
112.2
77.4 CDCl3
77.0 CDCl3
76.6 CDCl3
N
O
2q
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
f1 (ppm)

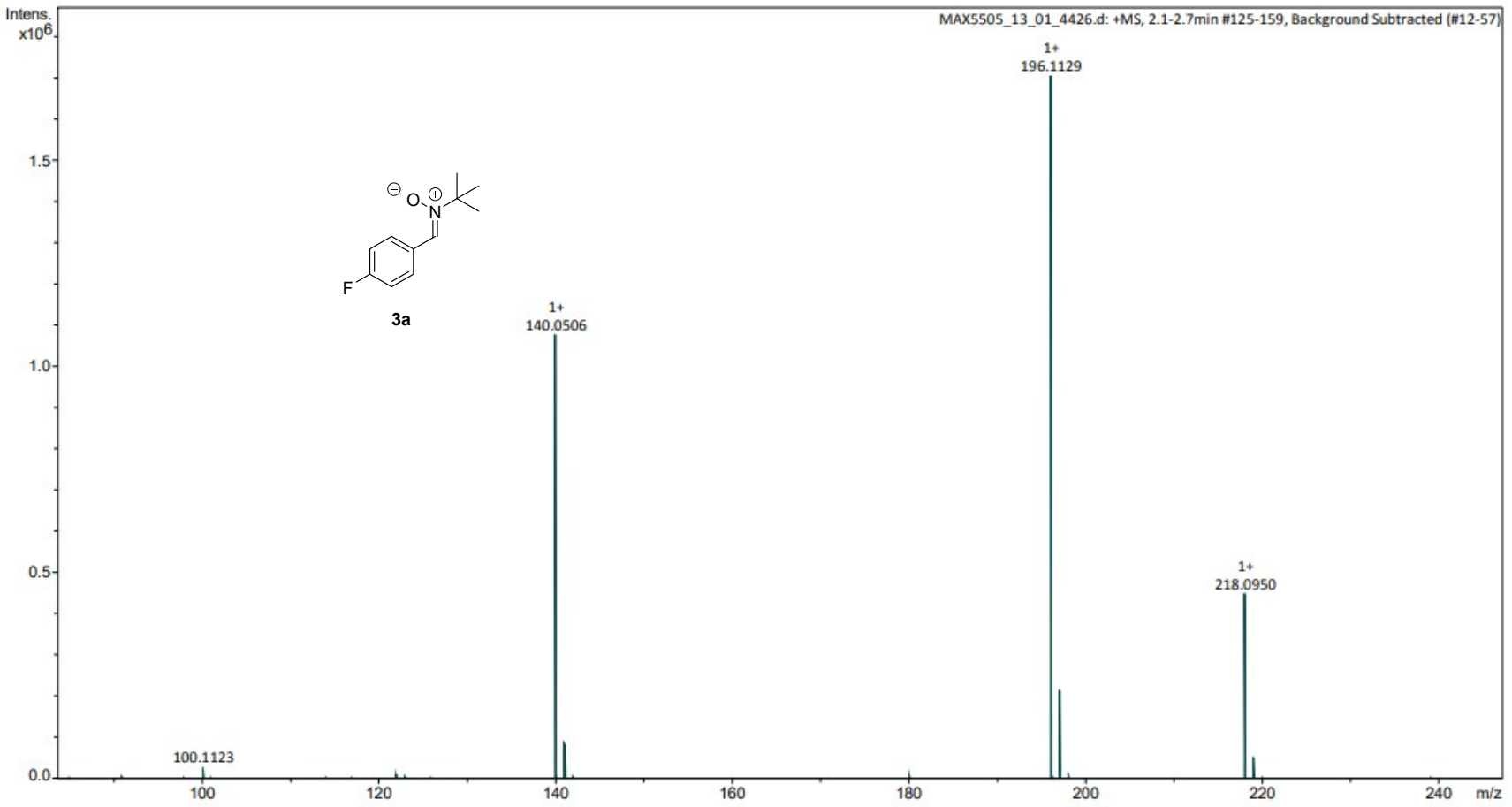
(*Z*)-*N*-tert-butyl-1-(4-fluorophenyl)methanimine oxide (3a)



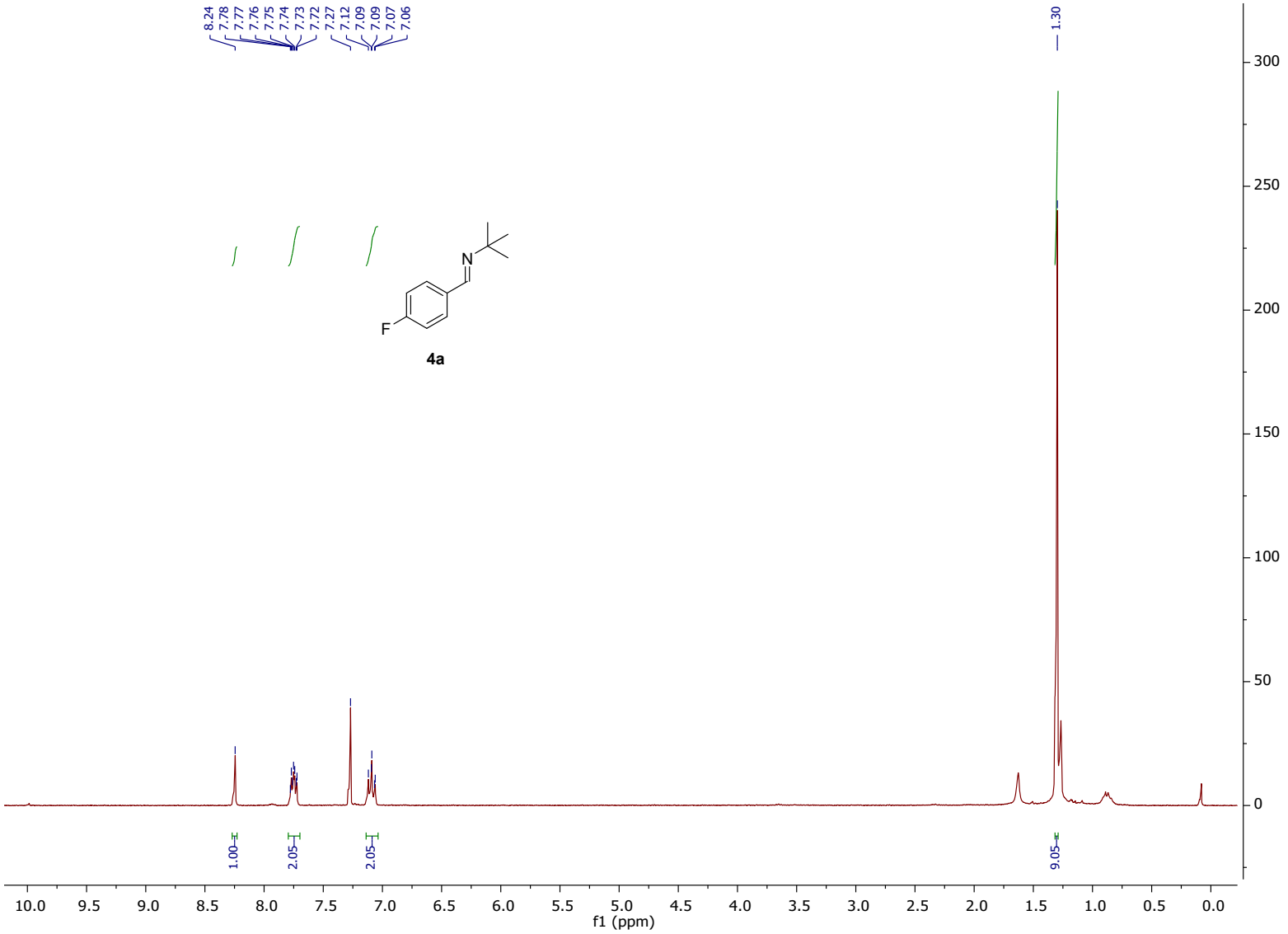

8.36
8.34
8.33
8.31
7.54
7.26
7.13
7.10
7.07
1.61
O
N
F
3a
1.93
1.02
2.02
9.00
f1 (ppm)

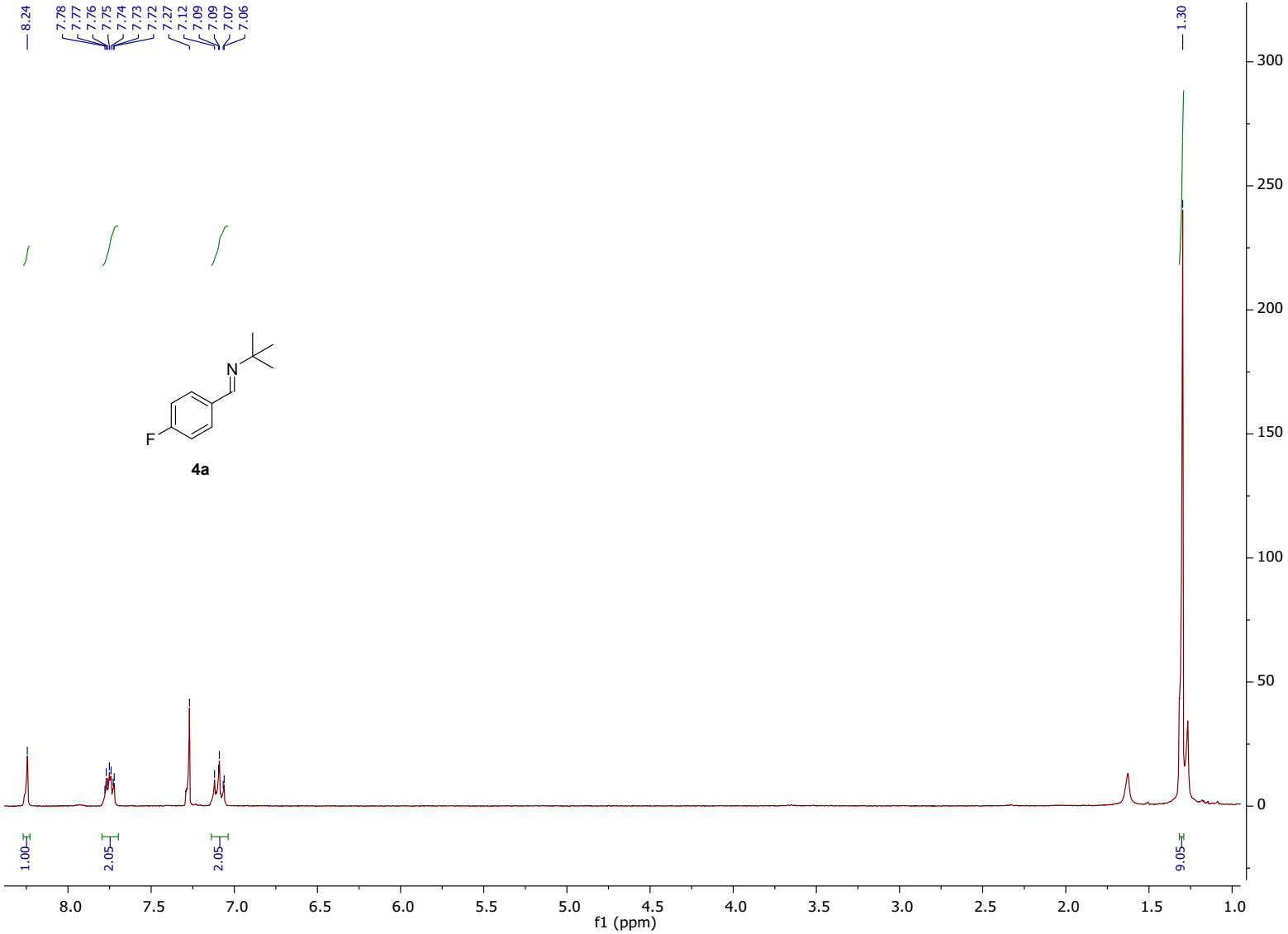

164.0
162.0
130.9
130.8
128.5
127.4
127.4
115.3
115.2
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
70.6
28.1
O
N
F
3a
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


164.0
162.0
130.9
130.8
128.5
127.4
127.4
115.3
115.2
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
70.6
28.1
O
N
F
3a
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
f1 (ppm)

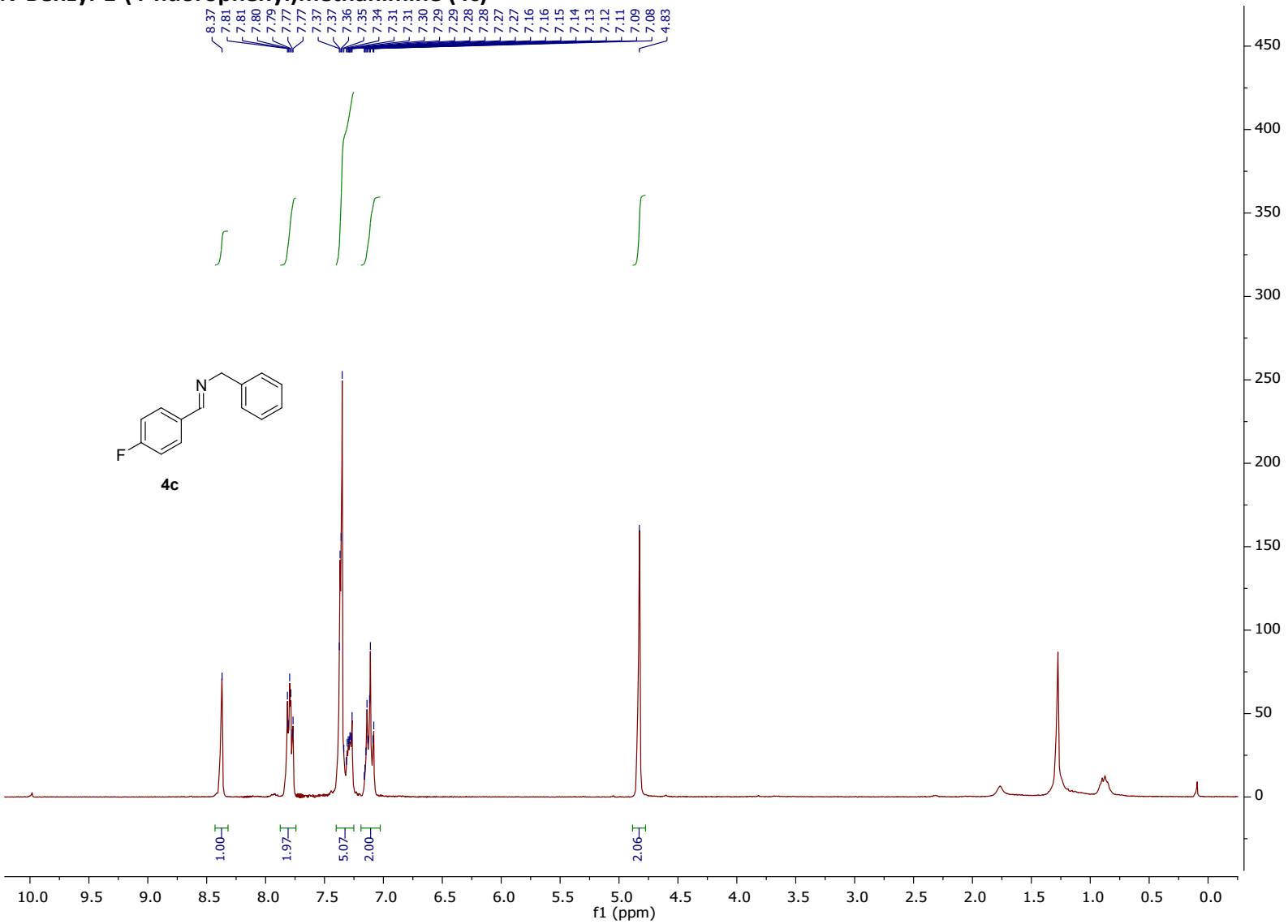

Intens.
x10^6
MAX5505_13_01_4426.d: +MS, 2.1-2.7min #125-159, Background Subtracted (#12-57)
1+
196.1129
1+
140.0506
1+
218.0950
100.1123
3a
1.5
1.0
0.5
0.0
100
120
140
160
180
200
220
240
m/z

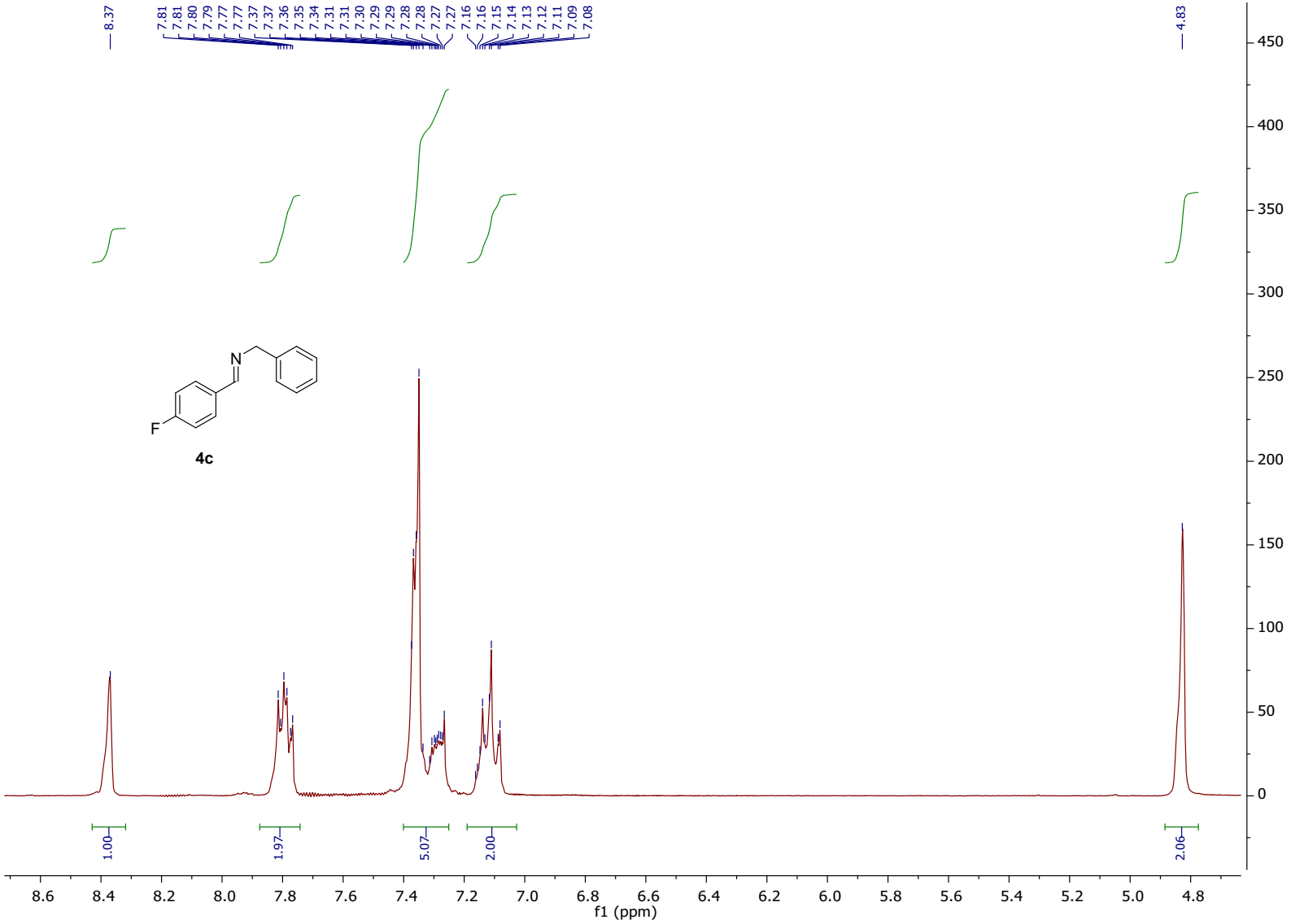
(*E*)-*N*-t*ert*-butyl-1-(4-fluorophenyl)methanimine (4a)

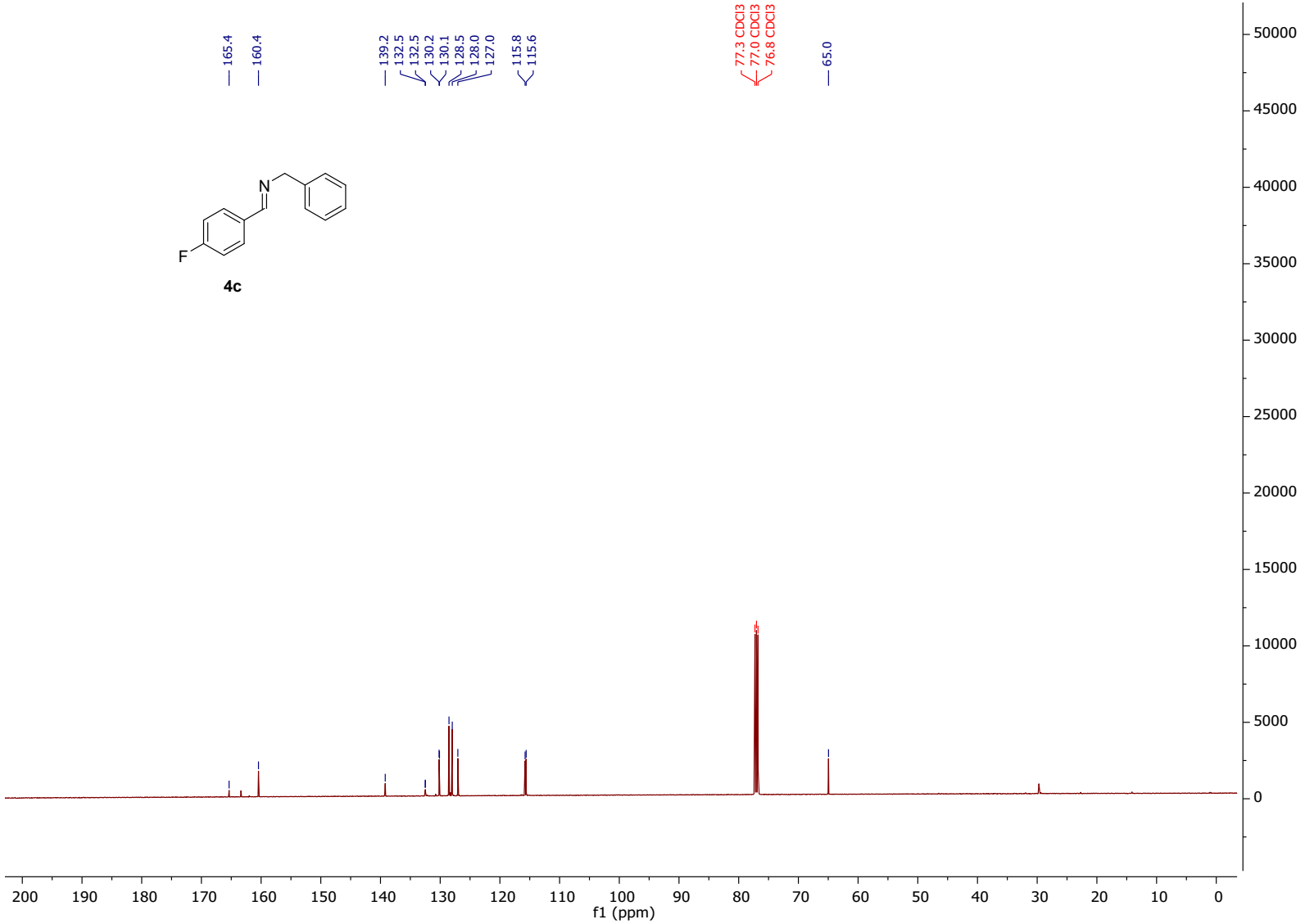


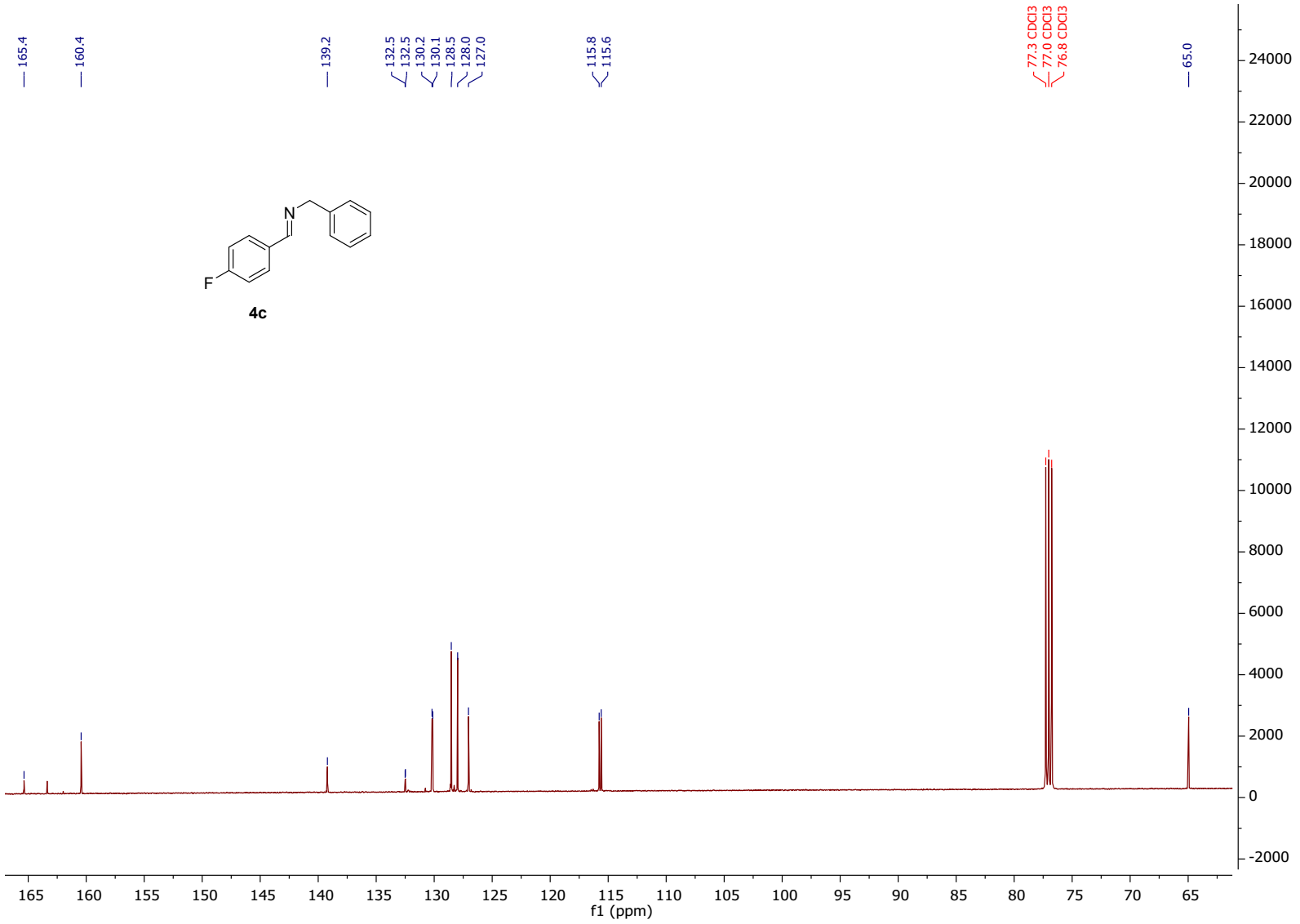

8.24
7.78
7.77
7.76
7.75
7.74
7.73
7.72
7.27
7.12
7.09
7.09
7.07
7.06
1.30
N
F
4a
1.00
2.05
2.05
9.05
f1 (ppm)

(*E*)-*N*-Benzyl-1-(4-fluorophenyl)methanimine (4c)

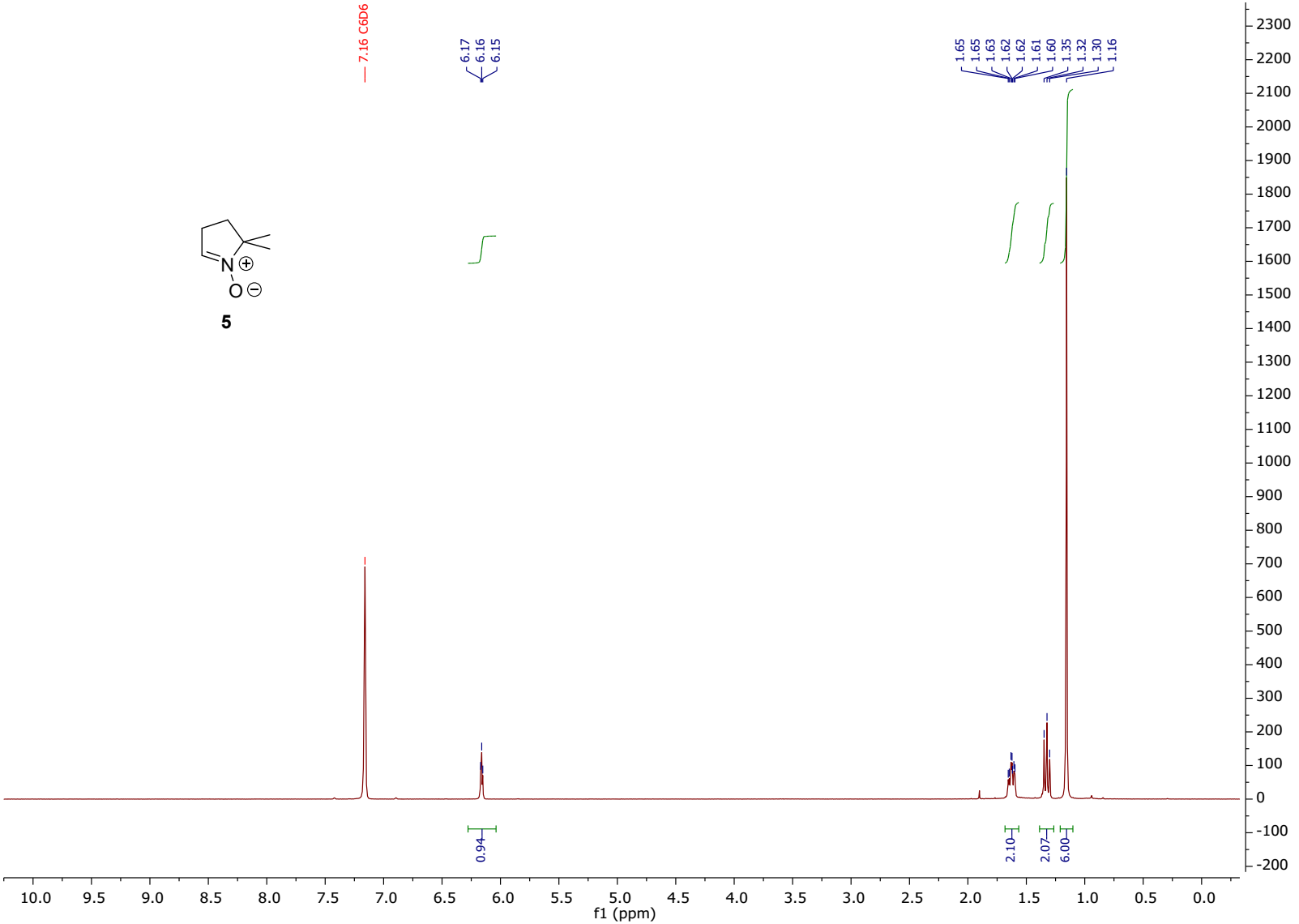



8.37
7.81
7.81
7.80
7.79
7.77
7.77
7.37
7.37
7.36
7.35
7.34
7.31
7.31
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.16
7.16
7.15
7.14
7.13
7.12
7.11
7.09
7.08
4.83
N
F
4c
1.00
1.97
5.07
2.00
2.06
f1 (ppm)

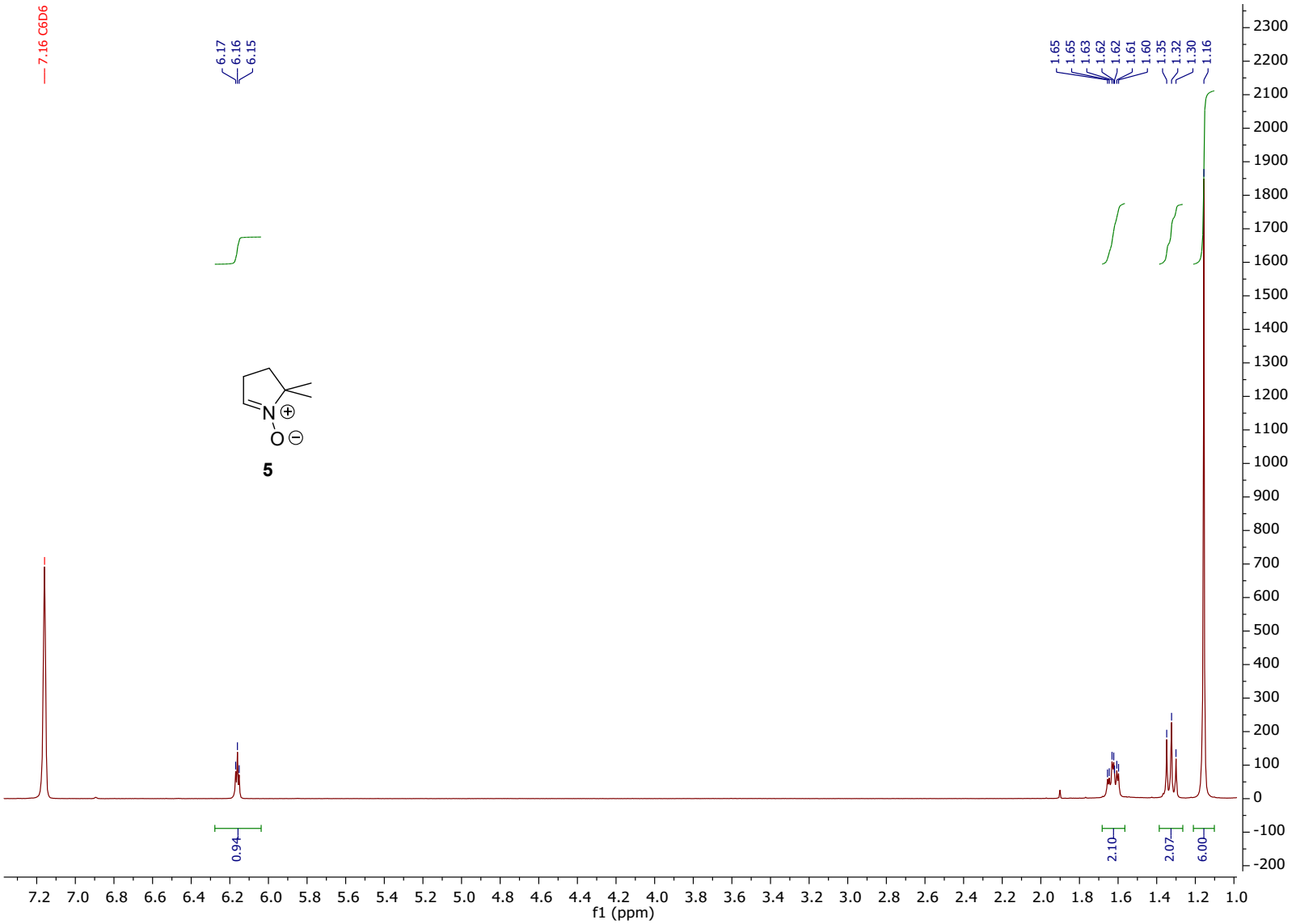

165.4
160.4
139.2
132.5
132.5
130.2
130.1
128.5
128.0
127.0
115.8
115.6
77.3 CDCl3
77.0 CDCl3
76.8 CDCl3
65.0
N
F
4c
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


165.4
160.4
139.2
132.5
132.5
130.2
130.1
128.5
128.0
127.0
115.8
115.6
77.3 CDCl3
77.0 CDCl3
76.8 CDCl3
65.0
N
F
4c
f1 (ppm)

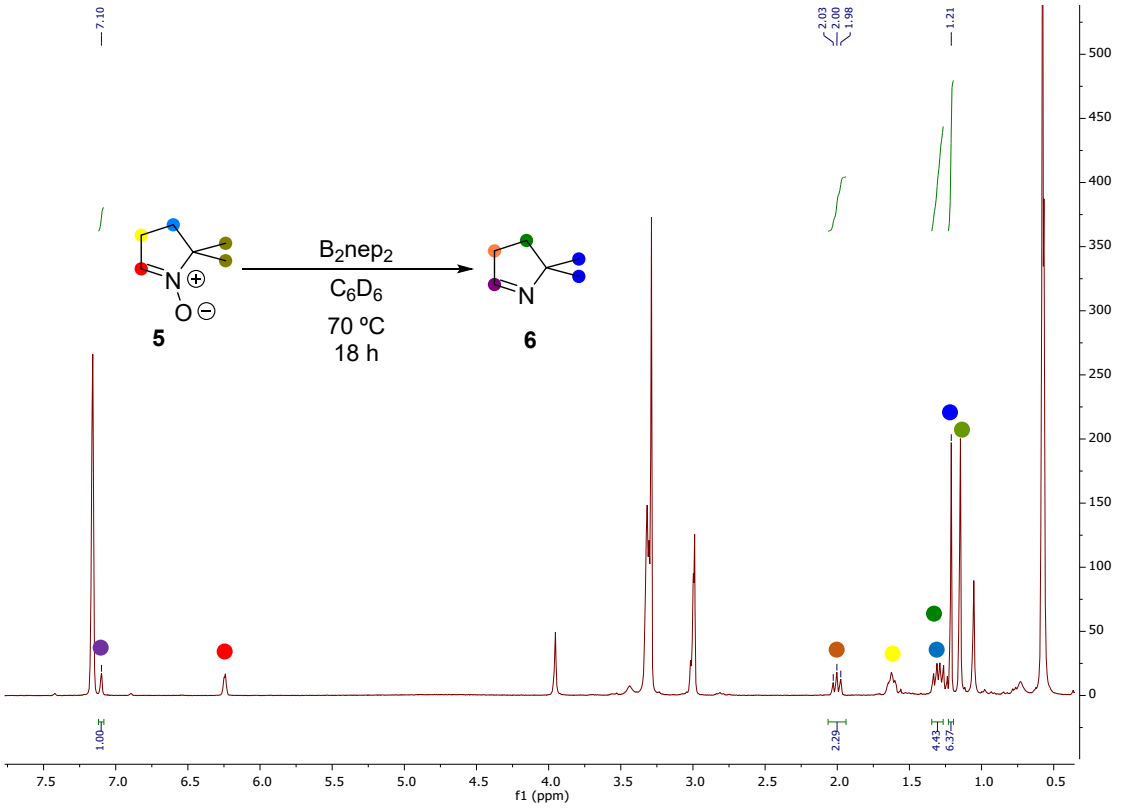
NMR of cyclic nitrone **5**



5

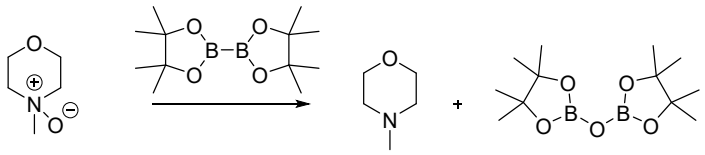

7.16 C6D6
6.17
6.16
6.15
1.65
1.65
1.63
1.62
1.62
1.61
1.60
1.35
1.32
1.30
1.16
5
0.94
2.10
2.07
6.00
f1 (ppm)

^{1}H NMR of the crude of the reduction of the cyclic nitrone **5** to imine **6** using B_2nep_2 after 18 h



Identification of RB-O-BR

PinB-O-Bpin and nepB-O-Bnep (**7**) were detected when apply the general procedure to reduce nitrones and the crude was analyzed. To be sure that our assignation was correct we did the three experiments (1-3) showed below (Schemes S2-S5) and detailed in the experimental part of the manuscript. To design these experiments, we were based on the publication that described the reduction of amine *N*-oxides using bis(pinacolato)diboron (B_2pin_2) and proposed the formation of pinB-O-Bpin (Scheme S1).[1]



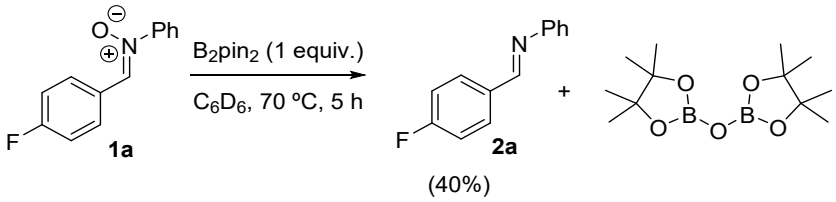
J. Org. Chem., 2011, 76, 7842.

Scheme S1. Reduction of 4-methylmorpholine N-oxide using bis(pinacolato)diboron.[1]

Description of the experiments:

Reduction of nitrone 1a using bis(pinacolato)diboron (Experiment 1)

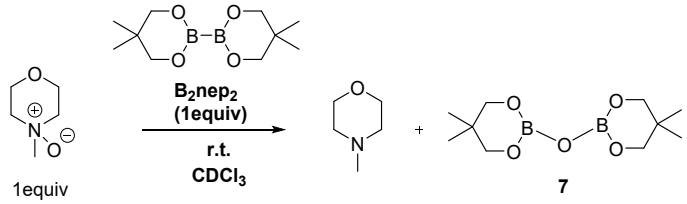
The reaction of the nitrone **1a** using B_2pin_2 allowed us to demonstrate that pinB-O-Bpin is also formed in the reduction of nitrones (Scheme S2). Although conversion was not complete, pinB-O-Bpin was unequivocally identified by ^1H, ^{13}C and ^{11}B NMR (see below).



Scheme S2. Reduction of nitrone **1a** using bis(pinacolato)diboron

Reduction of 4-methylmorpholine N-oxide using B_2nep_2 (Experiment 2)

The reaction of 4-methylmorpholine N-oxide using B_2nep_2 to unequivocally identify nepB-O-Bnep **7** (Scheme S3) by ^1H and ^{13}C NMR as well as mass spectrometry (see below).

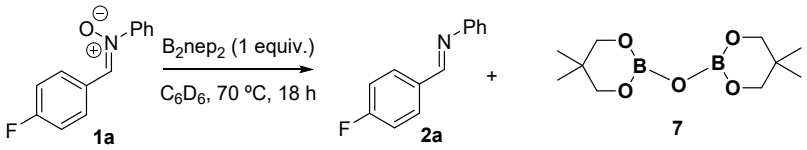


Scheme S3. Reduction of 4-methylmorpholine N-oxide using B_2nep_2

[1] H. P. Kokatla, P. F. Thomson, S. Bae, S. V. R. Doddi and M. K. Lakshman, *J. Org. Chem.*, 2011, **76**, 7842 (reference 9 in the manuscript).

Reduction of nitrone 1a using B_2nep_2 (Experiment 3)

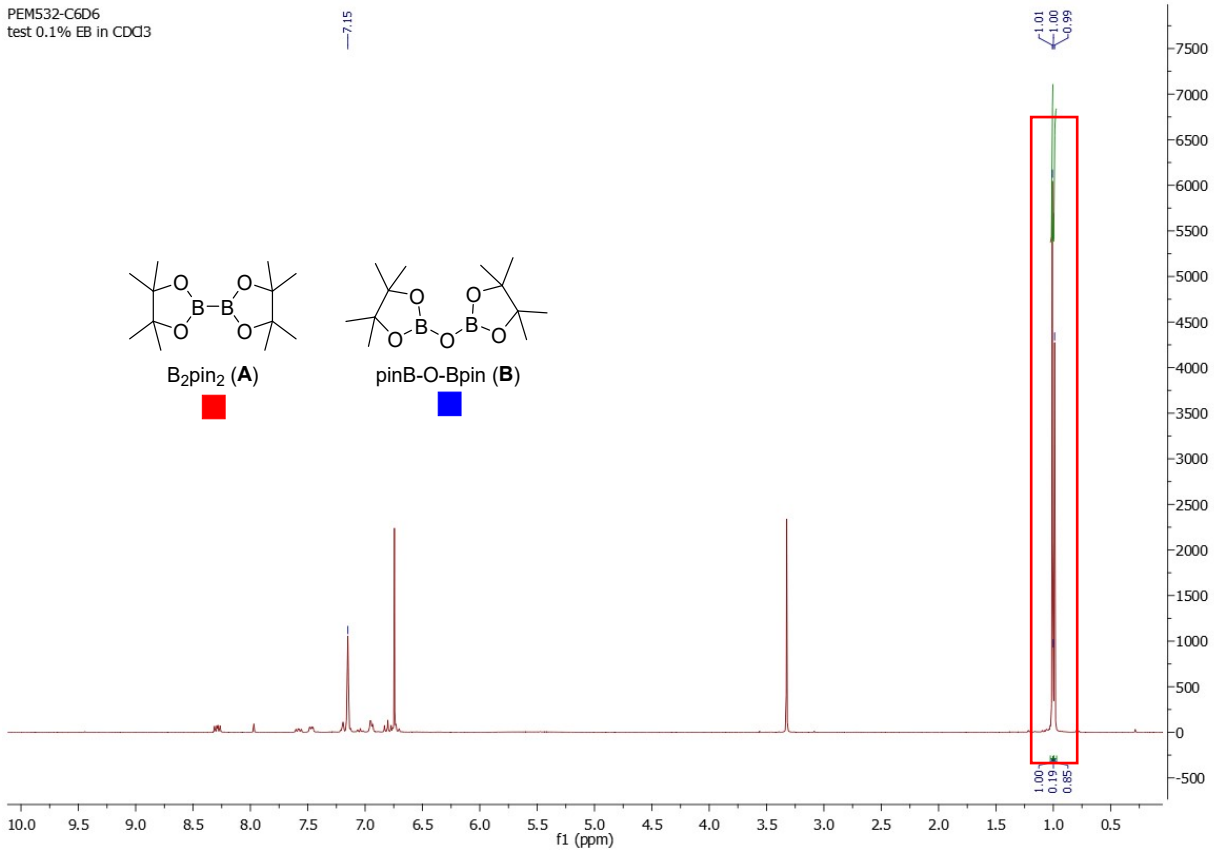
Finally, we treated nitrone **1a** with B_2nep_2 and analyzed the crude by ^1H and ^{13}C NMR where we could also identify nepB-O-Bnep (**7**) (Scheme S4).

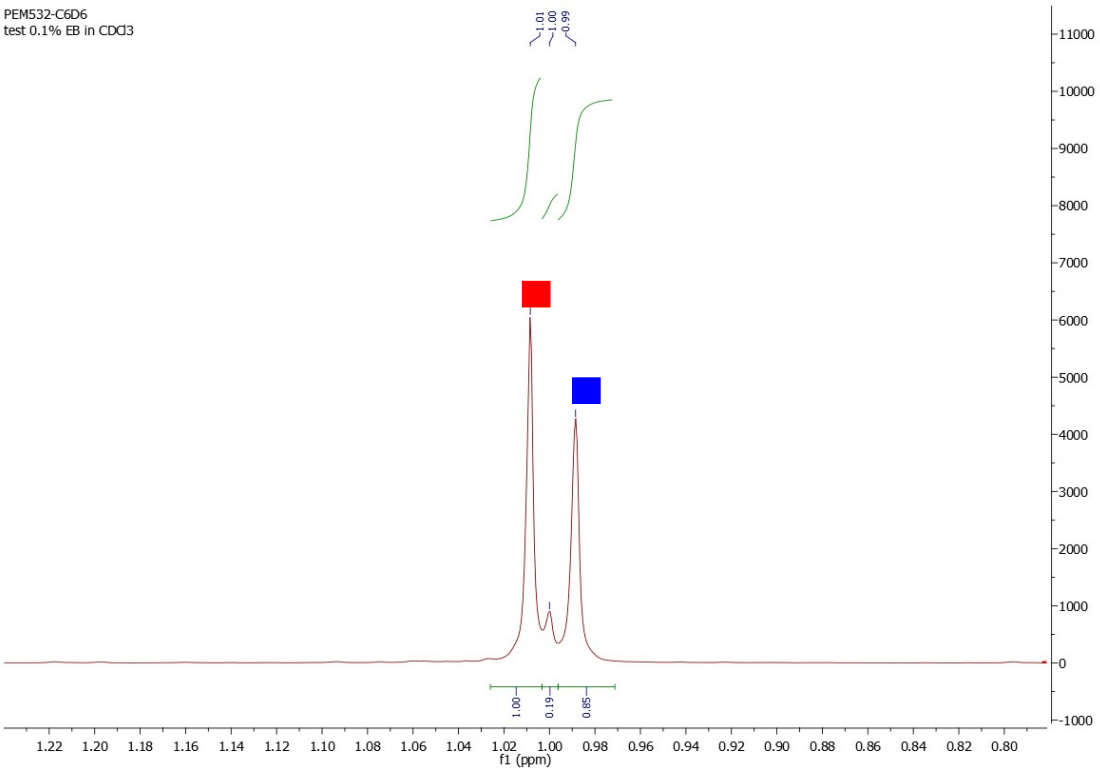


Scheme S4. Reduction of nitrone **1a** using B_2nep_2

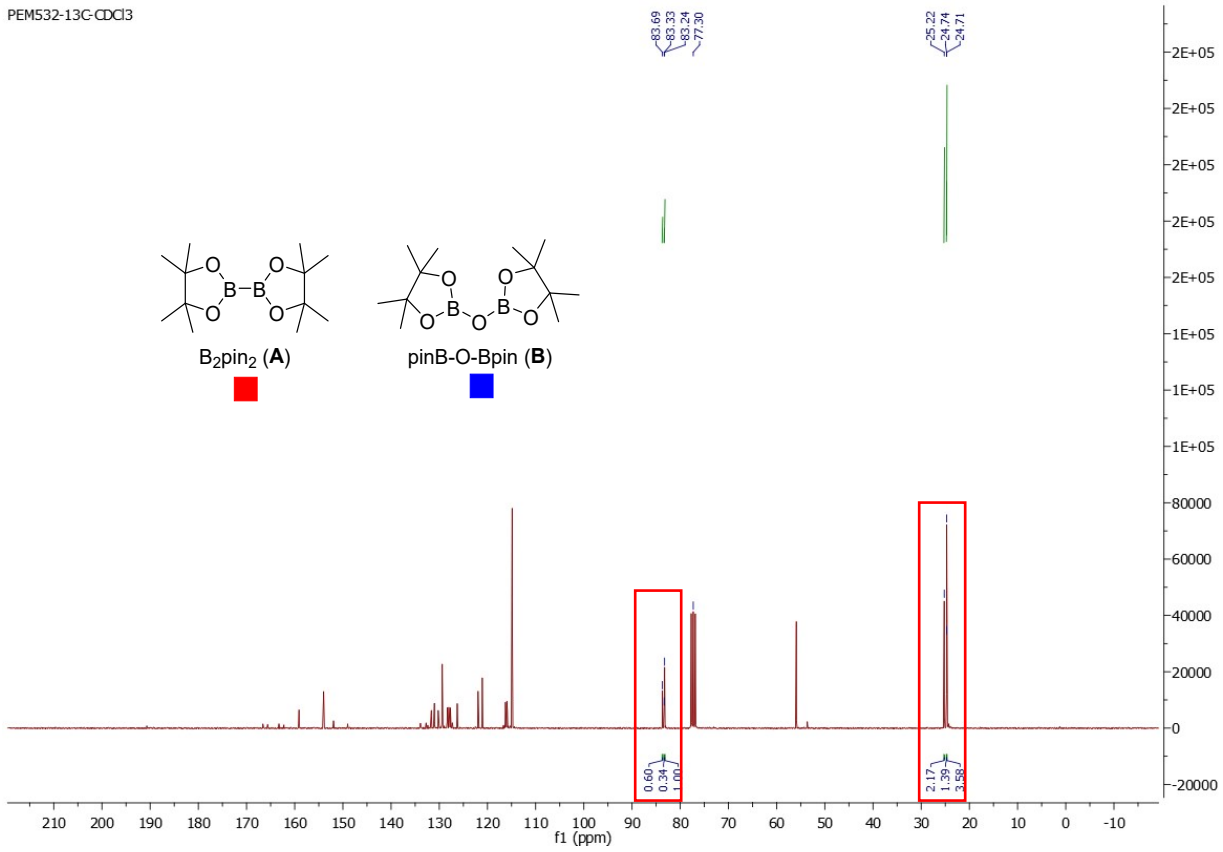
Spectra of the reduction of nitrone 1a using bis(pinacolato)diboron (Experiment 1)

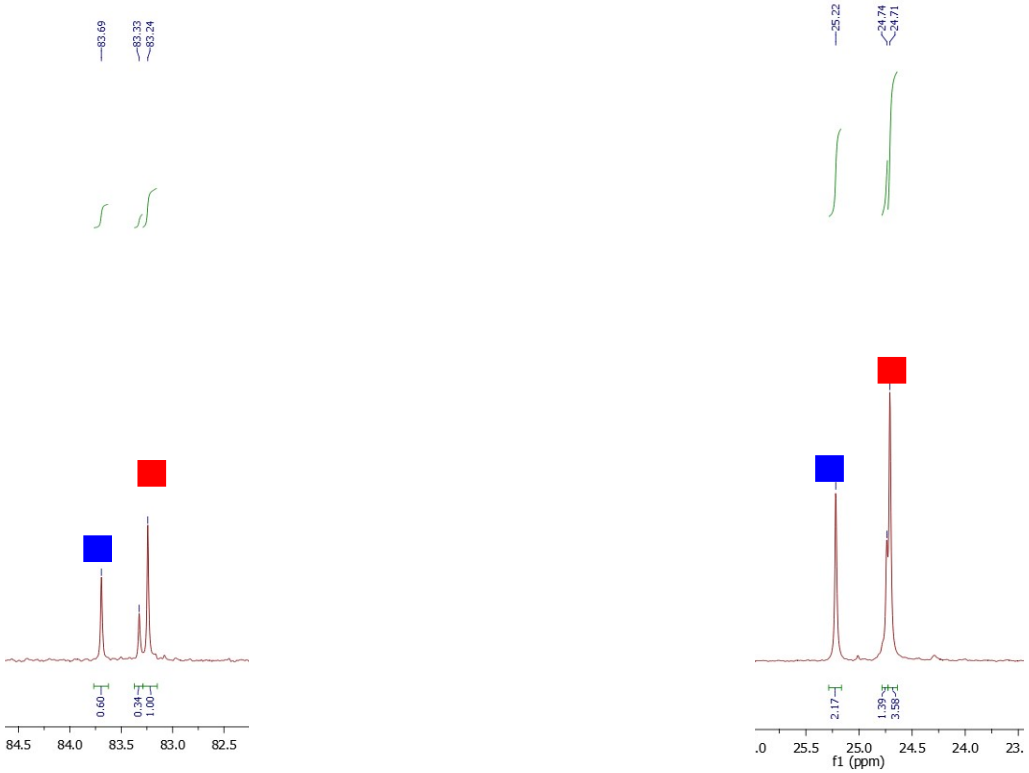
^{1}H-NMR



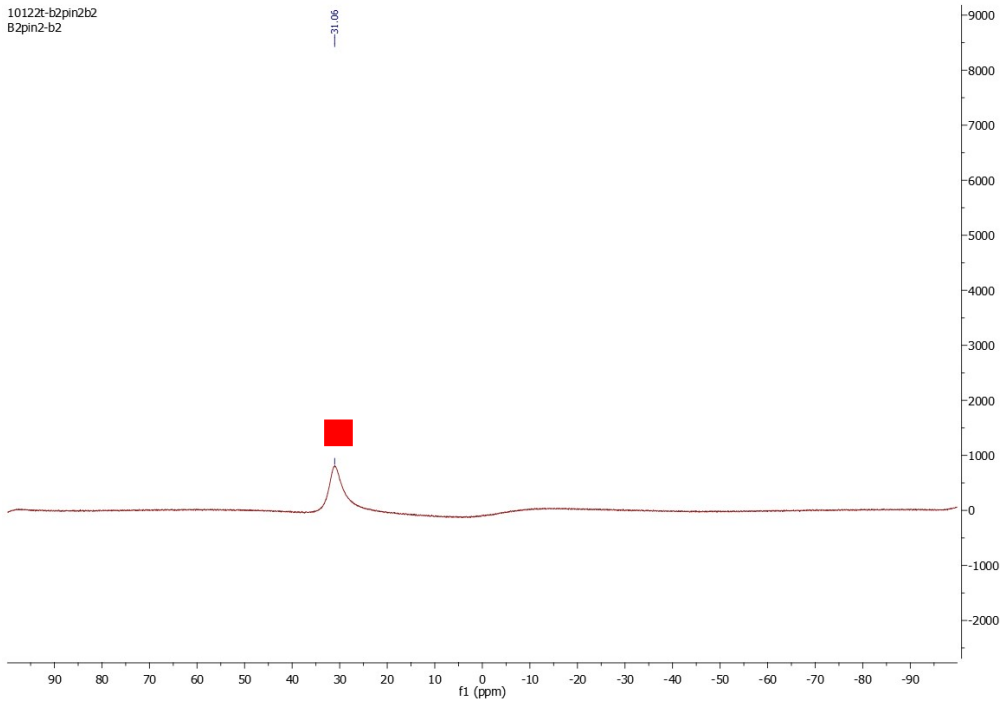

PEM532-C6D6
test 0.1% EB in CDCl3
1.01
1.00
0.99
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
1.00
0.19
0.85
1.22 1.20 1.18 1.16 1.14 1.12 1.10 1.08 1.06 1.04 1.02 1.00 0.98 0.96 0.94 0.92 0.90 0.88 0.86 0.84 0.82 0.80
f1 (ppm)

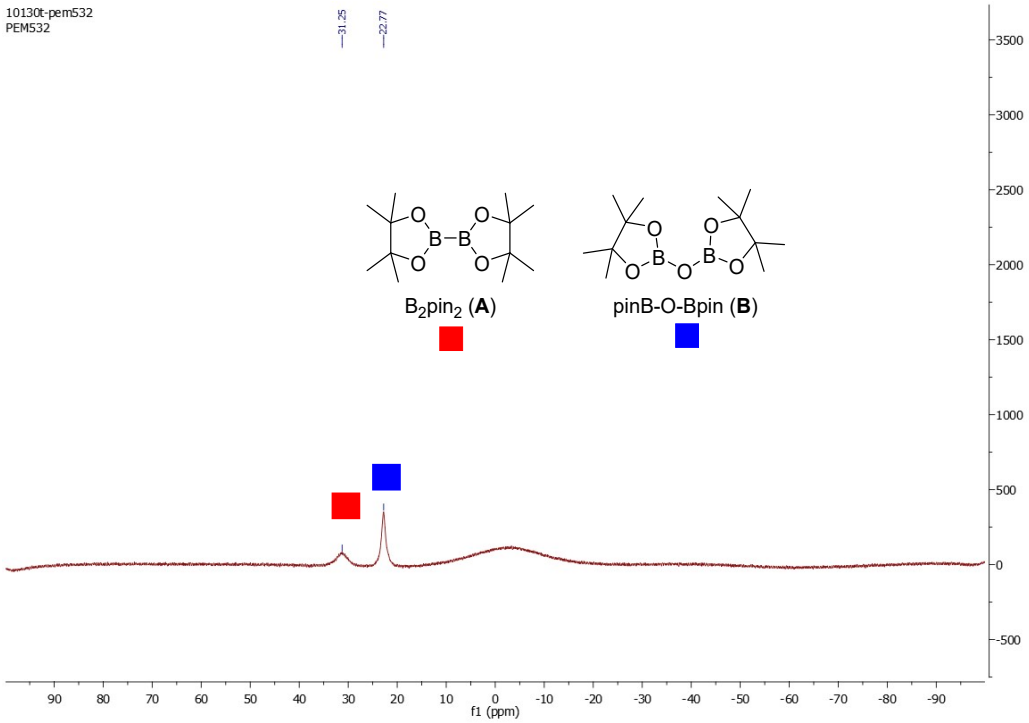
^{13}C-NMR


PEM532-13C-CDCl3
83.69
83.33
83.24
77.30
25.22
24.74
24.71
B2pin2 (A)
pinB-O-Bpin (B)
0.60
0.34
1.00
2.17
1.39
3.58
f1 (ppm)


83.69
83.33
83.24
25.22
24.74
24.71
0.60
0.34
1.00
2.17
1.39
3.58
f1 (ppm)

^{11}B-NMR (C_6D_6)

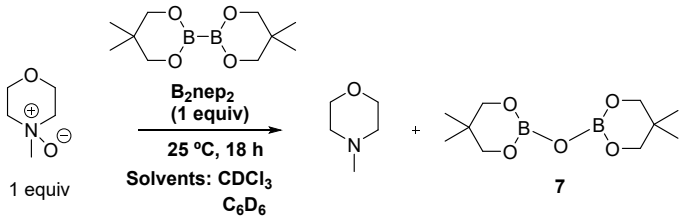




B_2pin_2 (**A**)

pinB-O-Bpin (**B**)

Spectra of the reaction of 4-methylmorpholine N-oxide and B_2nep_2 (Experiment 2)

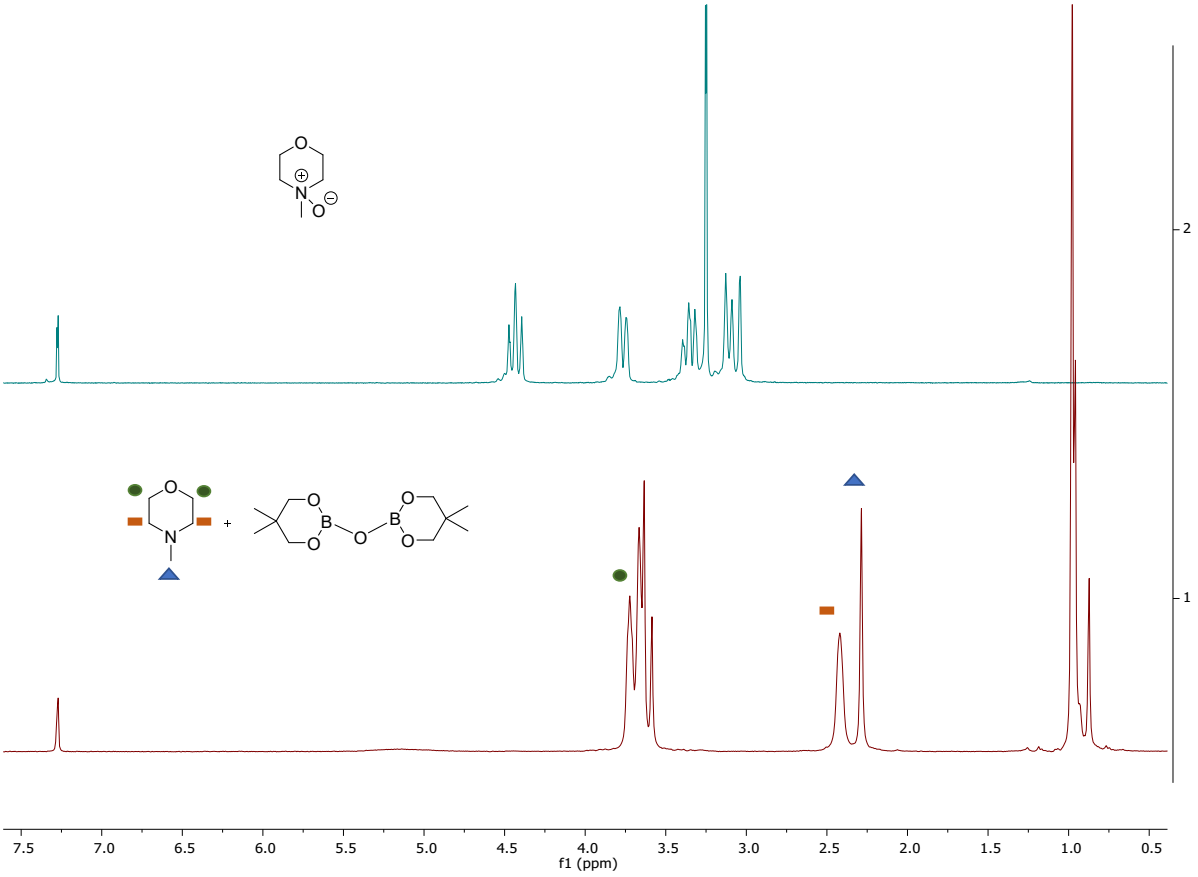


Scheme S3. Reduction of 4-methylmorpholine N-oxide using B_2nep_2

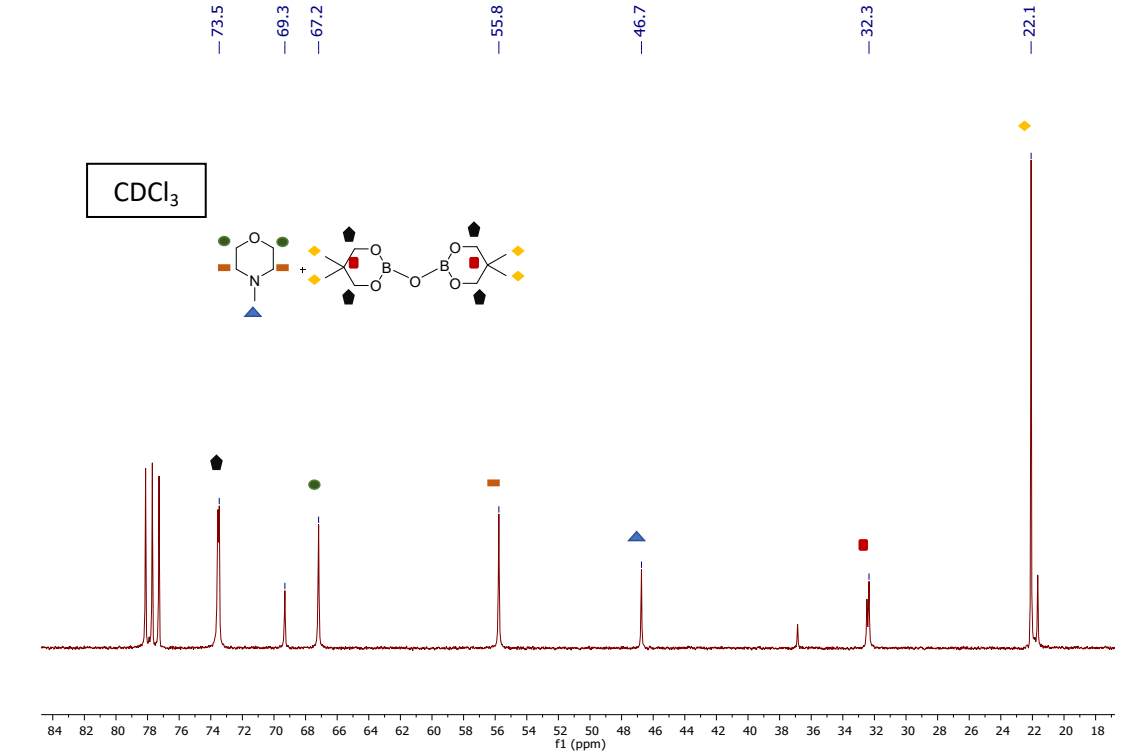
The reaction was performed in both $CDCl_3$ and C_6D_6.

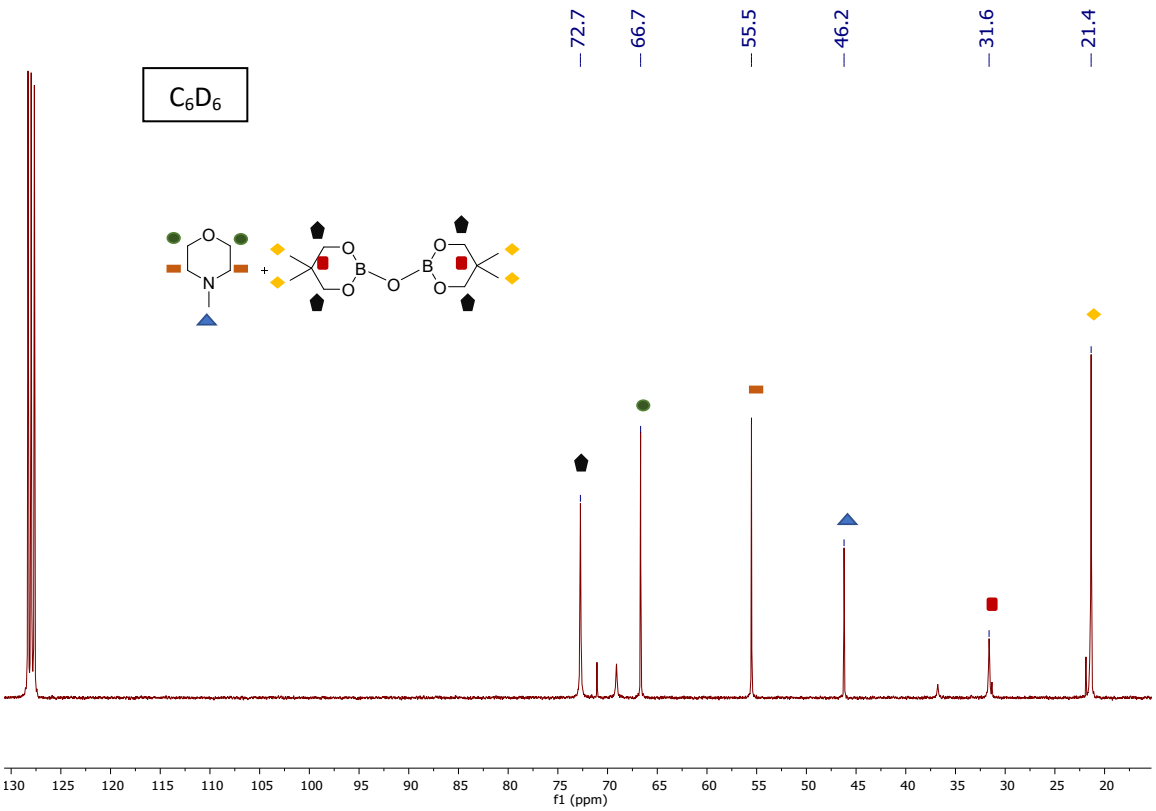
^{1}H-NMR

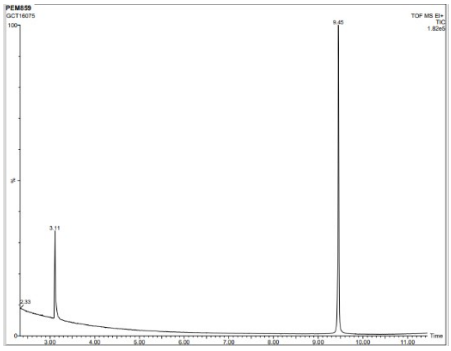
$CDCl_3$



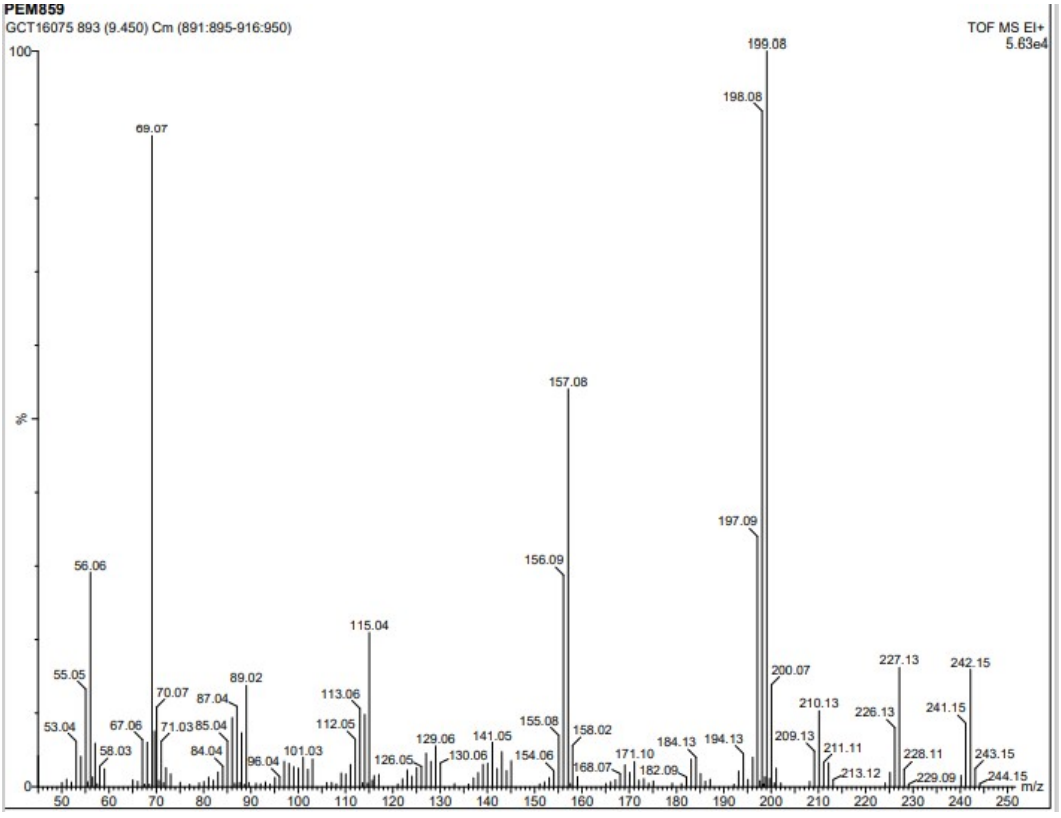
^{13}C-NMR


73.5
69.3
67.2
55.8
46.7
32.3
22.1
CDCl3
84 82 80 78 76 74 72 70 68 66 64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18
f1 (ppm)


72.7
66.7
55.5
46.2
31.6
21.4
C6D6
130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)

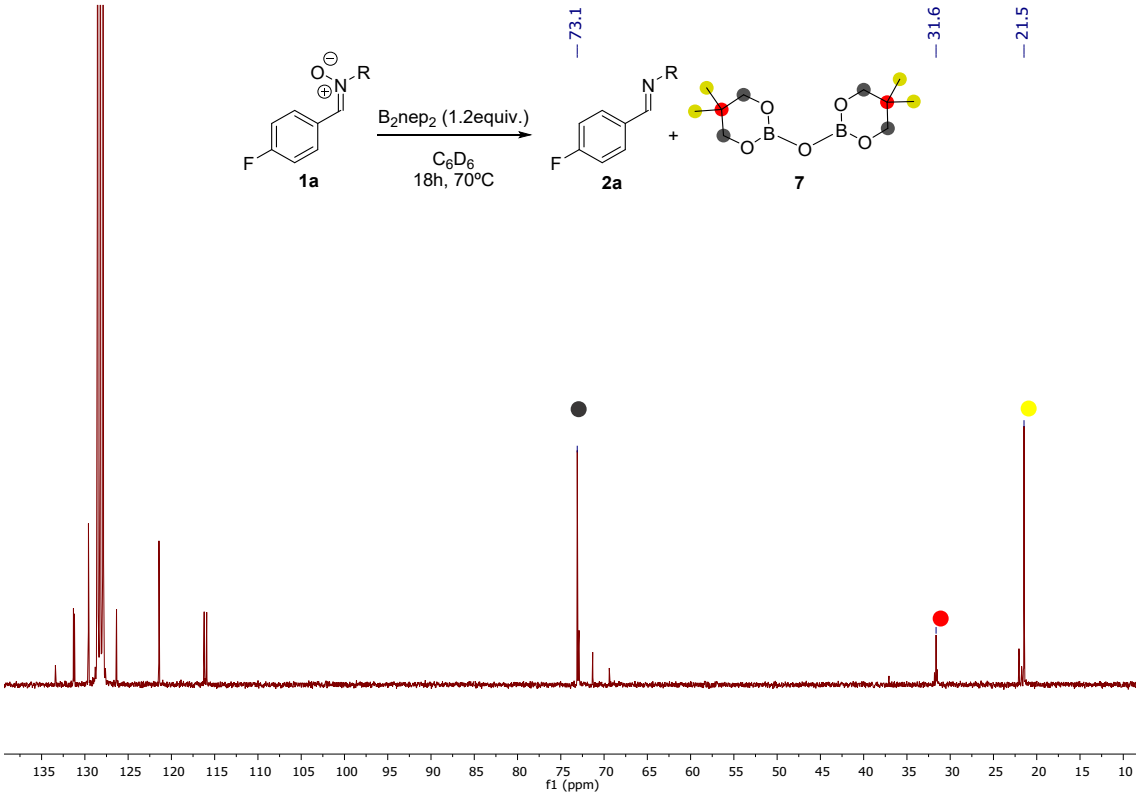


When we analized the crude by GC-MS we could detect a peak with m/z 242 assigned to compound 7.



Spectra of the reduction of nitrone 1a using B_2nep_2 (Experiment 3)

^{13}C-NMR (C_6D_6)



The following figure show the evolution of B_2nep_2 into nepB-Bnep (**7**) in the reduction of nitrone **1a** followed by ^{1}HNMR over time.