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*Supplement of*

# Technical note: Preparation and purification of atmospherically relevant $\alpha$-hydroxynitrate esters of monoterpenes

**Elena Ali McKnight et al.**

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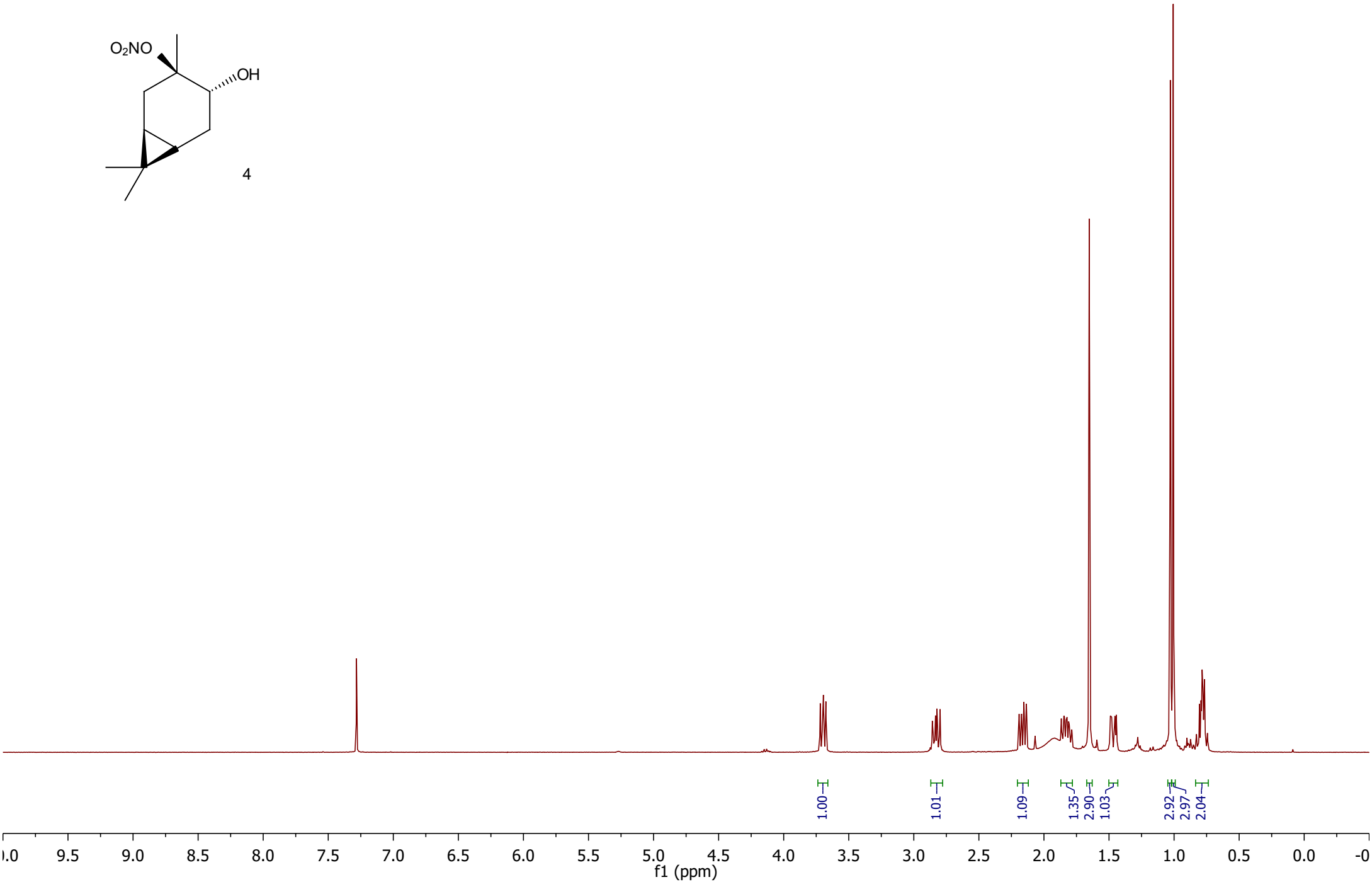
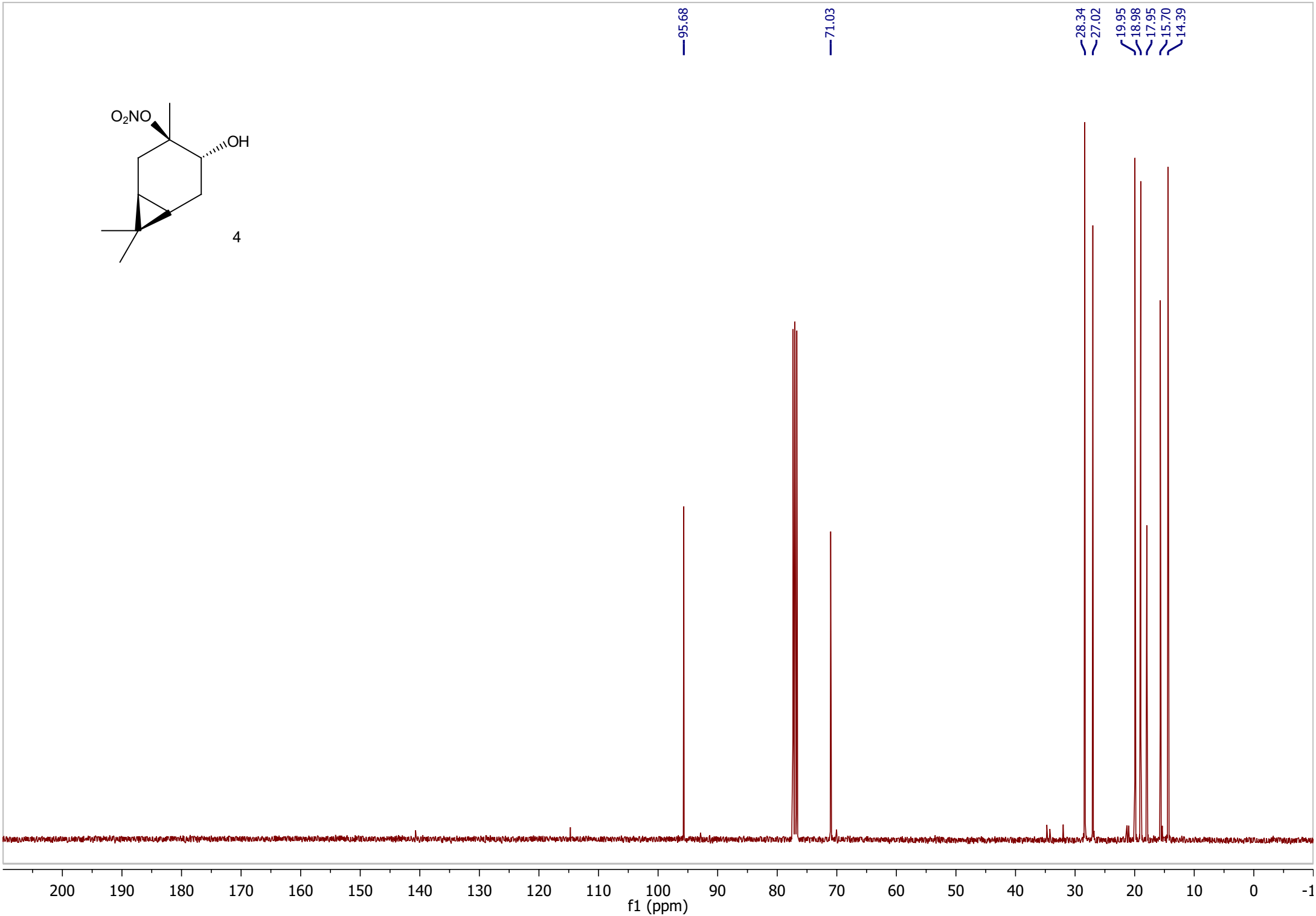
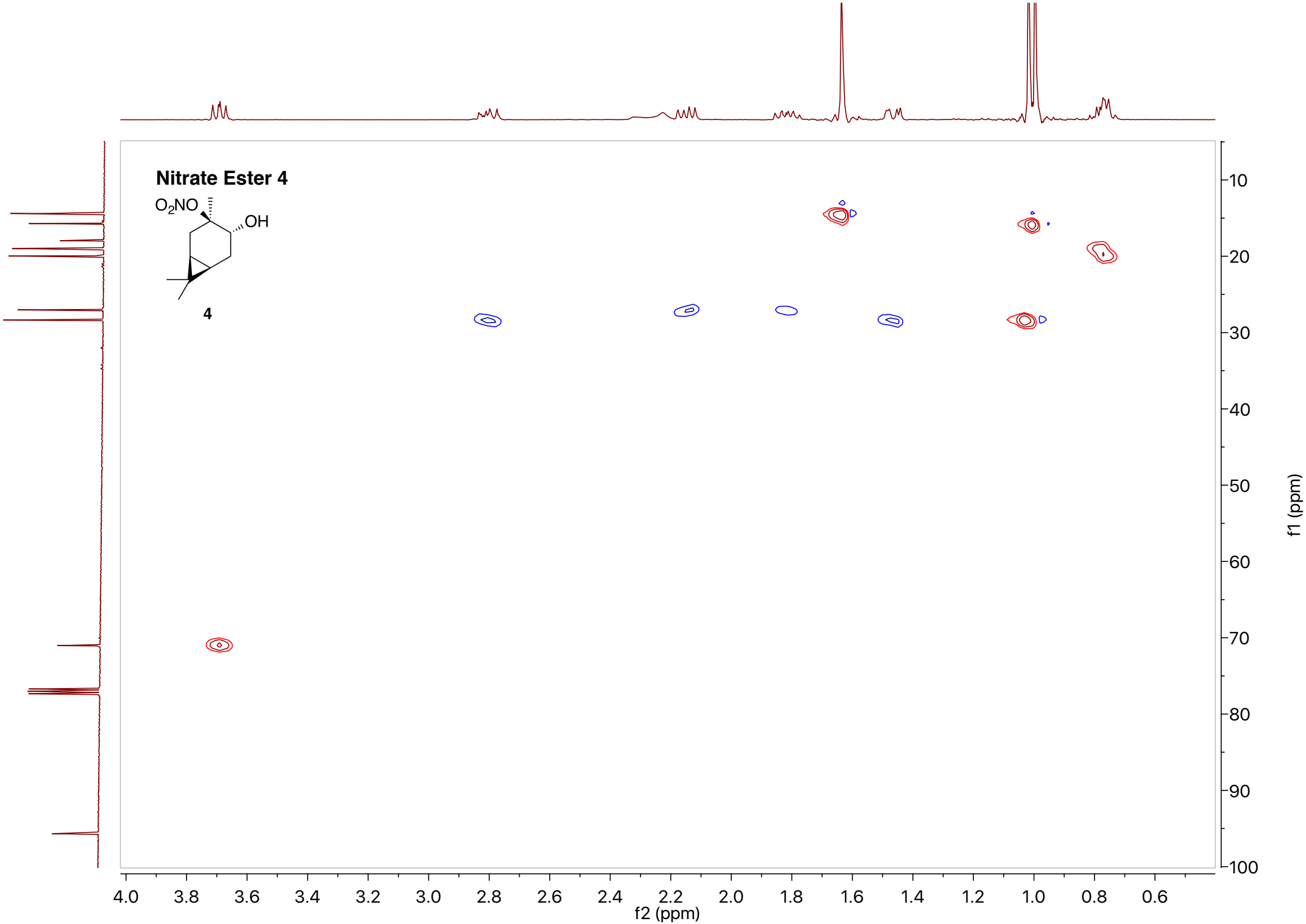
O2NO
OH

4


1.00
1.01
1.09
1.35
2.90
1.03
2.92
2.97
2.04
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)


95.68
71.03
28.34
27.02
19.95
18.98
17.95
15.70
14.39
O2NO
OH
4
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


Nitrate Ester 4
O2NO
OH
4
f2 (ppm)
f1 (ppm)
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
10
20
30
40
50
60
70
80
90
100

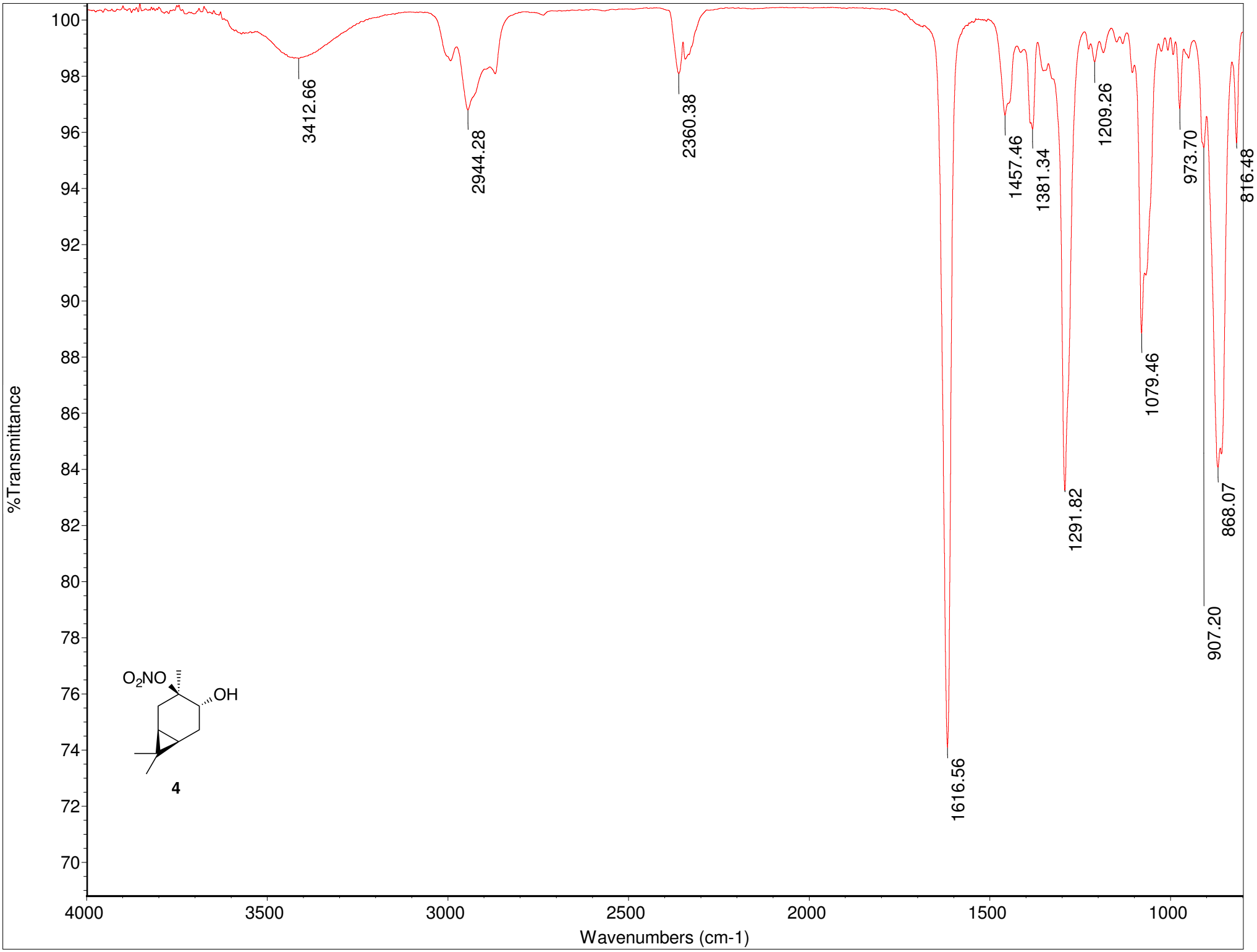

%Transmittance
Wavenumbers (cm-1)
3412.66
2944.28
2360.38
1616.56
1457.46
1381.34
1291.82
1209.26
1079.46
973.70
907.20
868.07
816.48
O2NO
OH
4

**Table 1**. $^{1}$H NMR data for aldehyde **11**

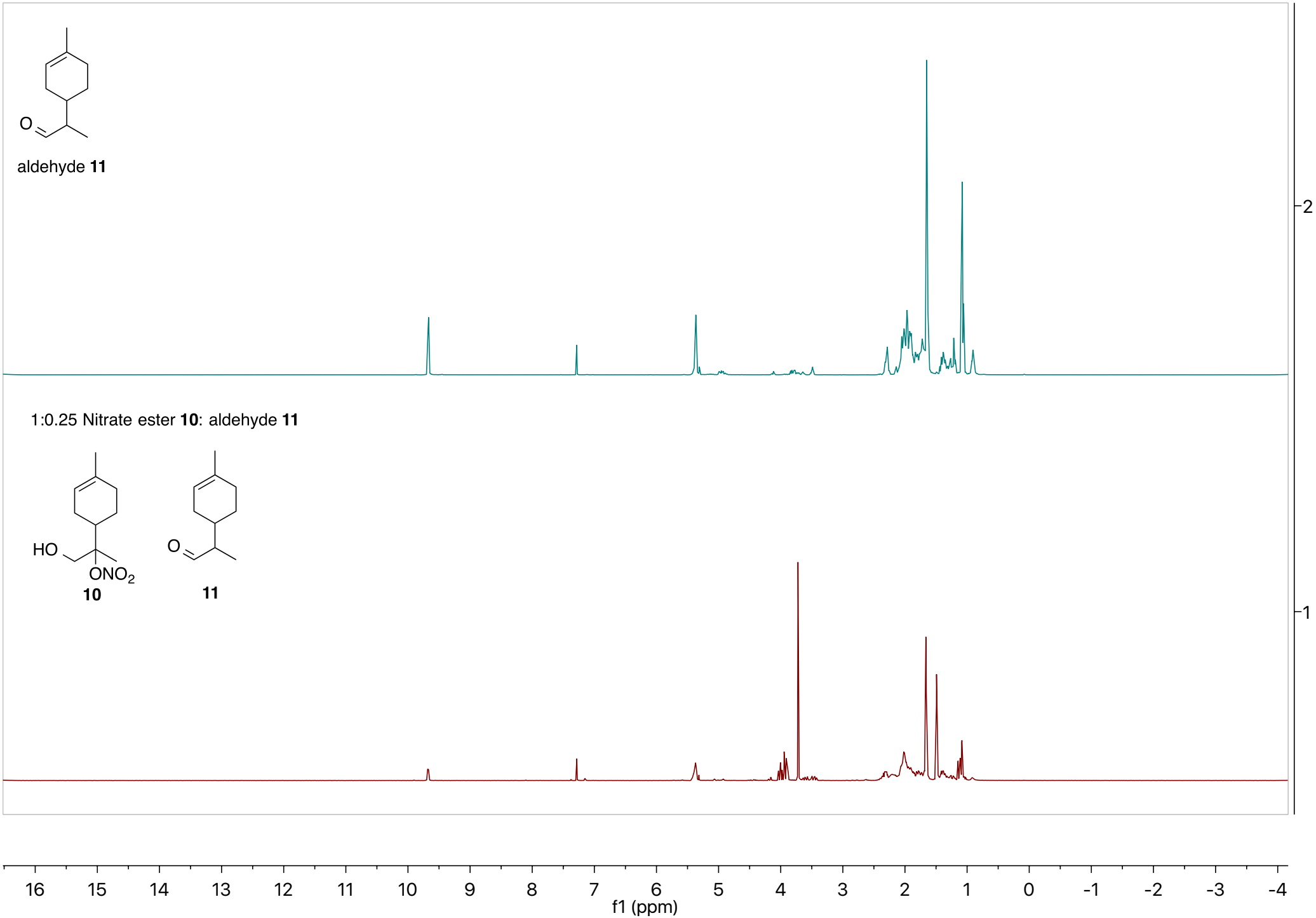
| Uehara, 2017 | Reid and Watson, 2018 | This report (1:1 diastereomers) |
|---|---|---|
| 9.61 - 9.57 (m, 1H) | 9.66 (dd, J = 5.5, 2.5 Hz, 1H) | 9.69 (d, *J* = 2.4 Hz, 0.5H)<br>9.68 (d, *J* = 2.7 Hz, 0.5H) |
| 5.29 (s, 1H) | 5.36 (s, 1H) | 5.42 – 5.35 (m, 1H) |
| 2.27 - 2.18 (m, 1H) | 2.37 – 2.21 (m, 1H) | 2.35 – 2.25 (m, 1H) |
| 2.03 - 1.77 (m, 6H) | 2.10 – 1.66 (m, 6H) | 2.10 – 1.73 (m, 6H) |
| 1.71 - 1.59 (m, 1H) | 1.64 (s, 3H) | 1.68 – 1.62 (br s, 3H) |
| 1.57 (s, 3H) | 1.45 – 1.29 (m, 1H) | 1.46 – 1.32 (m, 1H) |
| 1.00 (t, J ¼ 6.9 Hz, 3H) | 1.07 (dd, J = 7.0, 5.2 Hz, 3H) | 1.10 (d, *J* = 5.2 Hz, 1.5H)<br>1.08 (d, *J* = 5.3 Hz, 1.5H) |

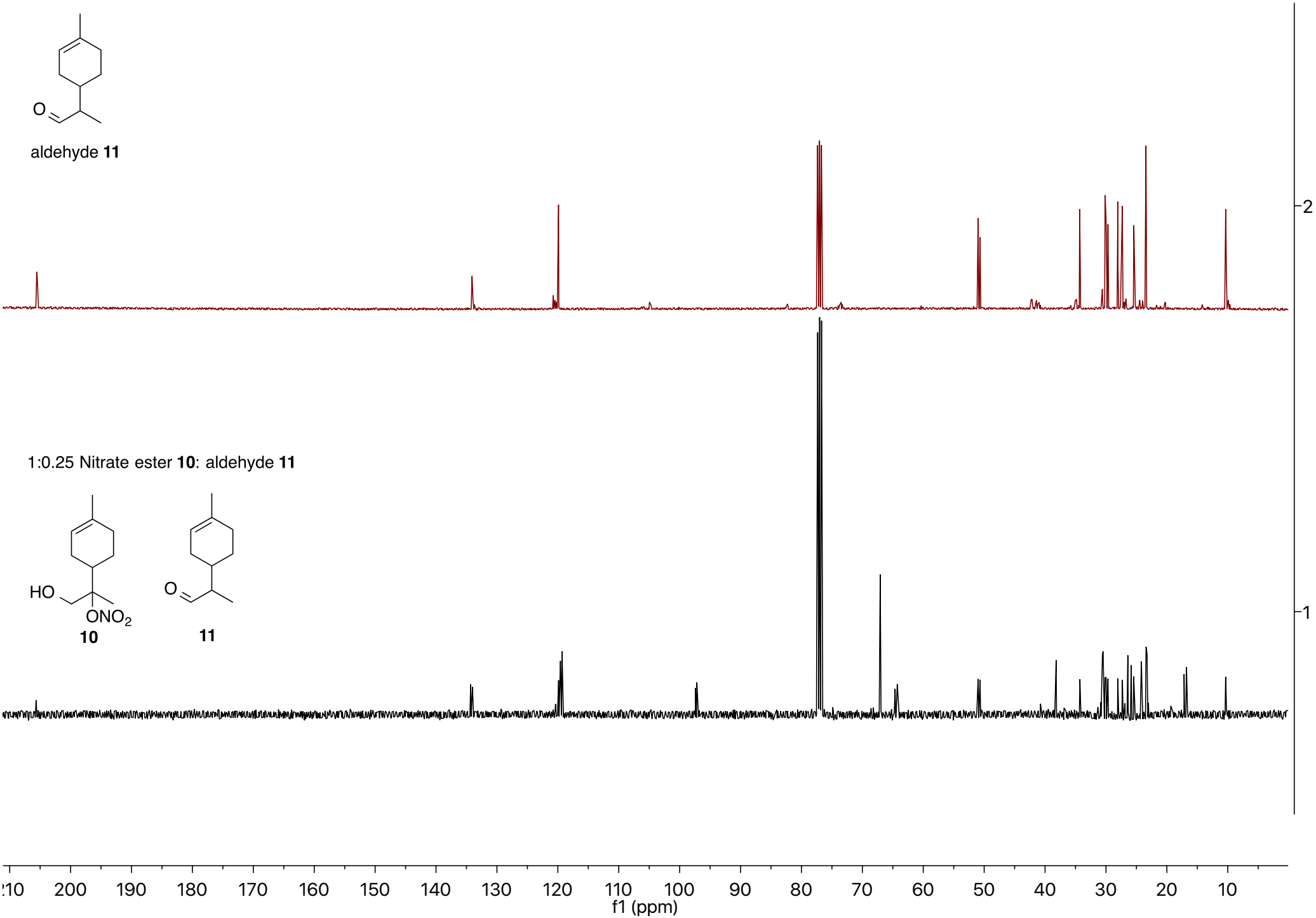
**Table 2.** $^{13}$C NMR data for aldehyde **11**

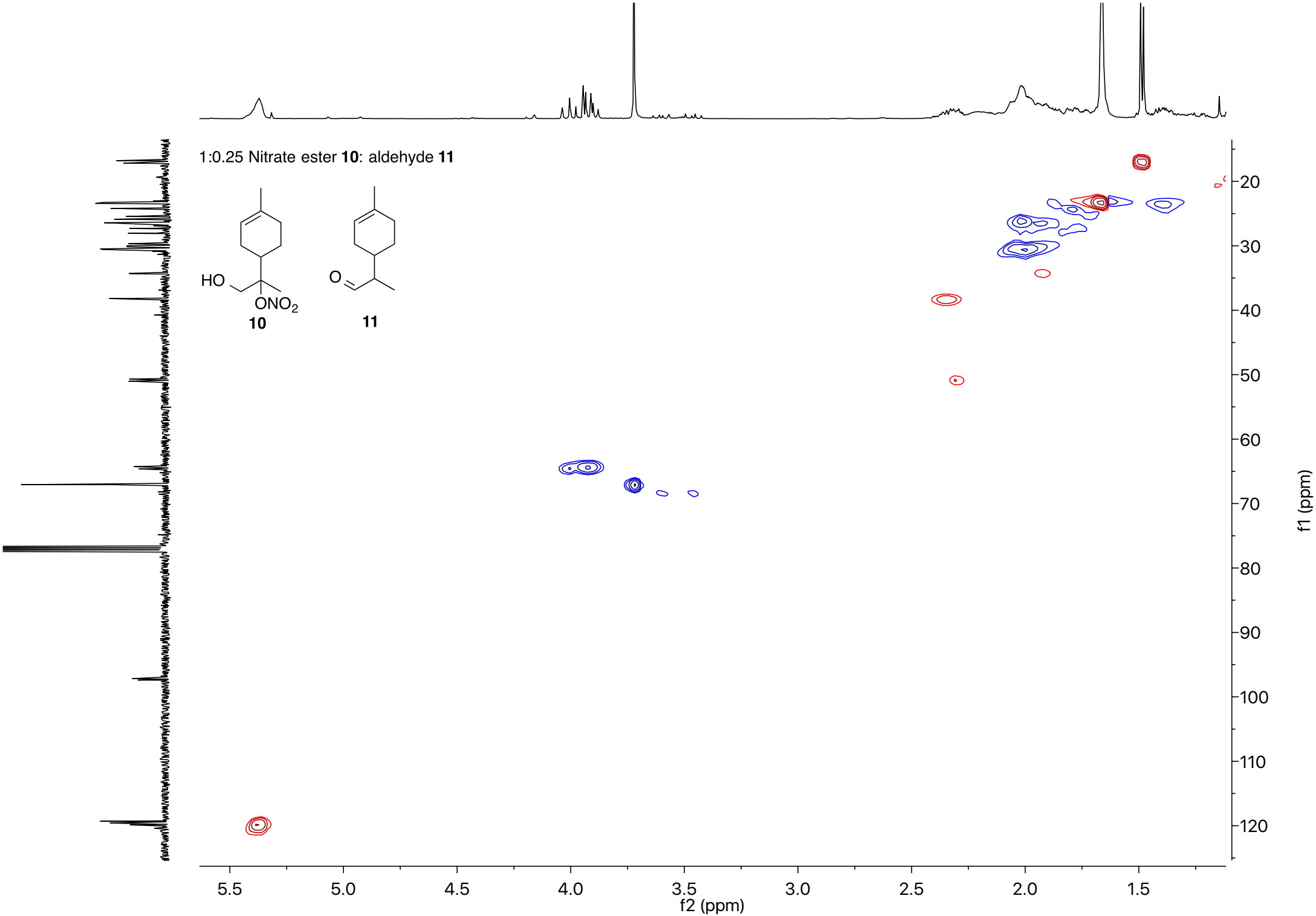
| Uehara, 2017 | Reid & Watson, 2018 | This report |
|---|---|---|
| 205.48, 205.40 | 205.8, 205.7 | 205.55, 205.47 |
| 134.04, 134.01 | 134.3, 134.2 | 134.09, 134.05 |
| 119.95, 119.88 | 120.1, 120.0 | 119.95, 119.88 |
| 50.96, 50.65 | 51.2, 50.8 | 51.00, 50.68 |
| 34.32, 34.25 | 34.43, 34.37 | 34.32, 34.25 |
| 30.13, 29.97 | 30.3, 30.1 | 30.15, 29.99 |
| 29.65 | 29.8 | 29.67 |
| 28.04, 27.29 | 28.2, 27.5 | 28.05, 27.31 |
| 25.43, 23.39 | 25.6, 23.6 | 25.43, 23.43 |
| 10.31,10.22 | 10.5, 10.4 | 10.34, 10.24 |
| | | |

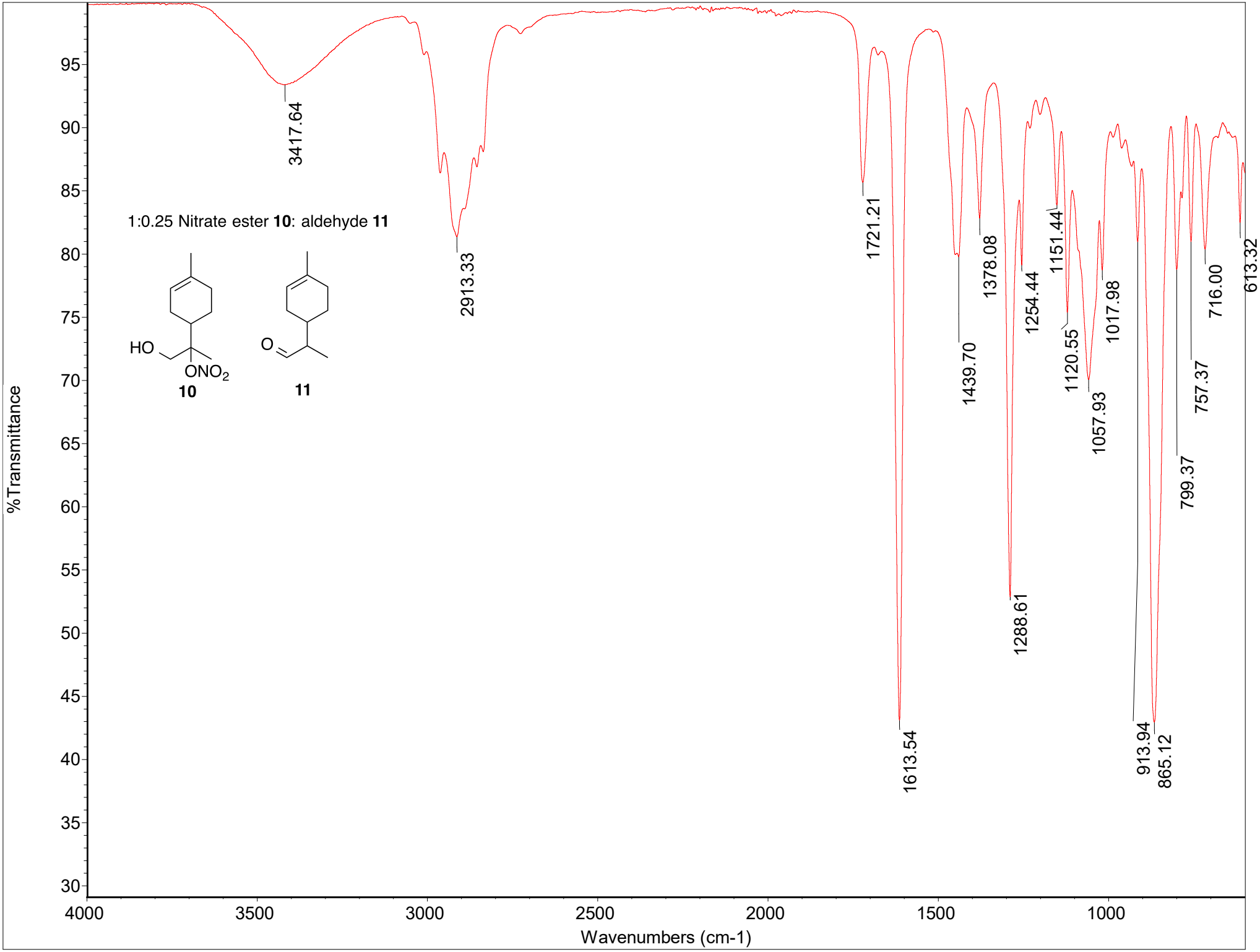
Uehara, A., Tommis, B., Belhassen, E., Satrani, B., Ghanmi, M. and Baldovini, N.: Odor-active constituents of Cedrus atlantica wood essential oil, Phytochemistry, 144 (J. Essent. Oil Res. 16 2004), 208–215, doi:10.1016/j.phytochem.2017.09.017, 2017.

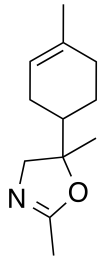
Reid, W. B. and Watson, D. A.: Synthesis of Trisubstituted Alkenyl Boronic Esters from Alkenes Using the Boryl-Heck Reaction, Org Lett, 20(21), 6832–6835, doi:10.1021/acs.orglett.8b02949, 2018.


O
aldehyde 11
2
1:0.25 Nitrate ester 10: aldehyde 11
HO
ONO2
10
O
11
1
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

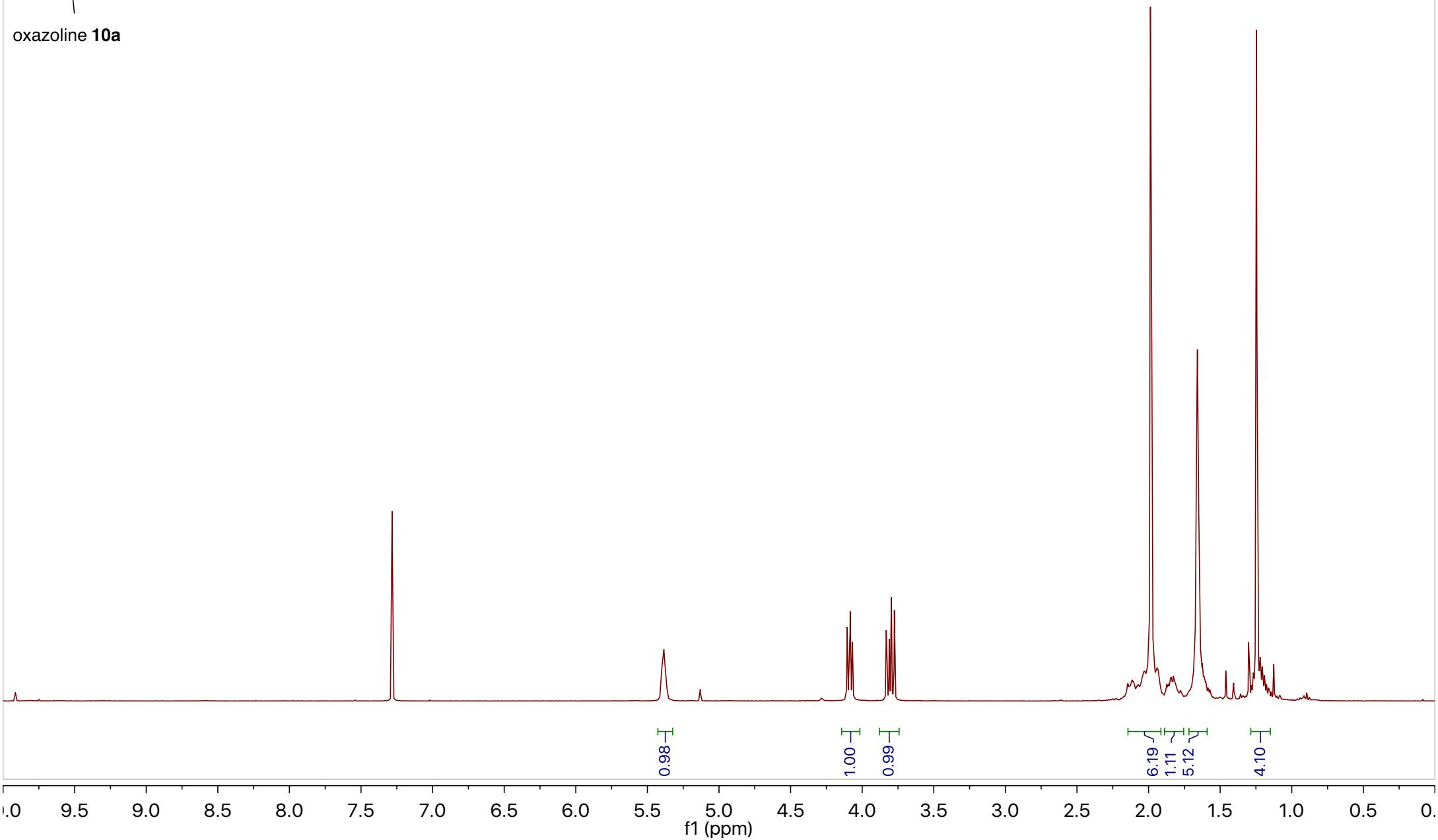

aldehyde 11
2
1:0.25 Nitrate ester 10: aldehyde 11
HO
ONO2
10
O
11
1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


1:0.25 Nitrate ester **10**: aldehyde **11**
HO
ONO2
10
O
11
f2 (ppm)
f1 (ppm)
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
20
30
40
50
60
70
80
90
100
110
120

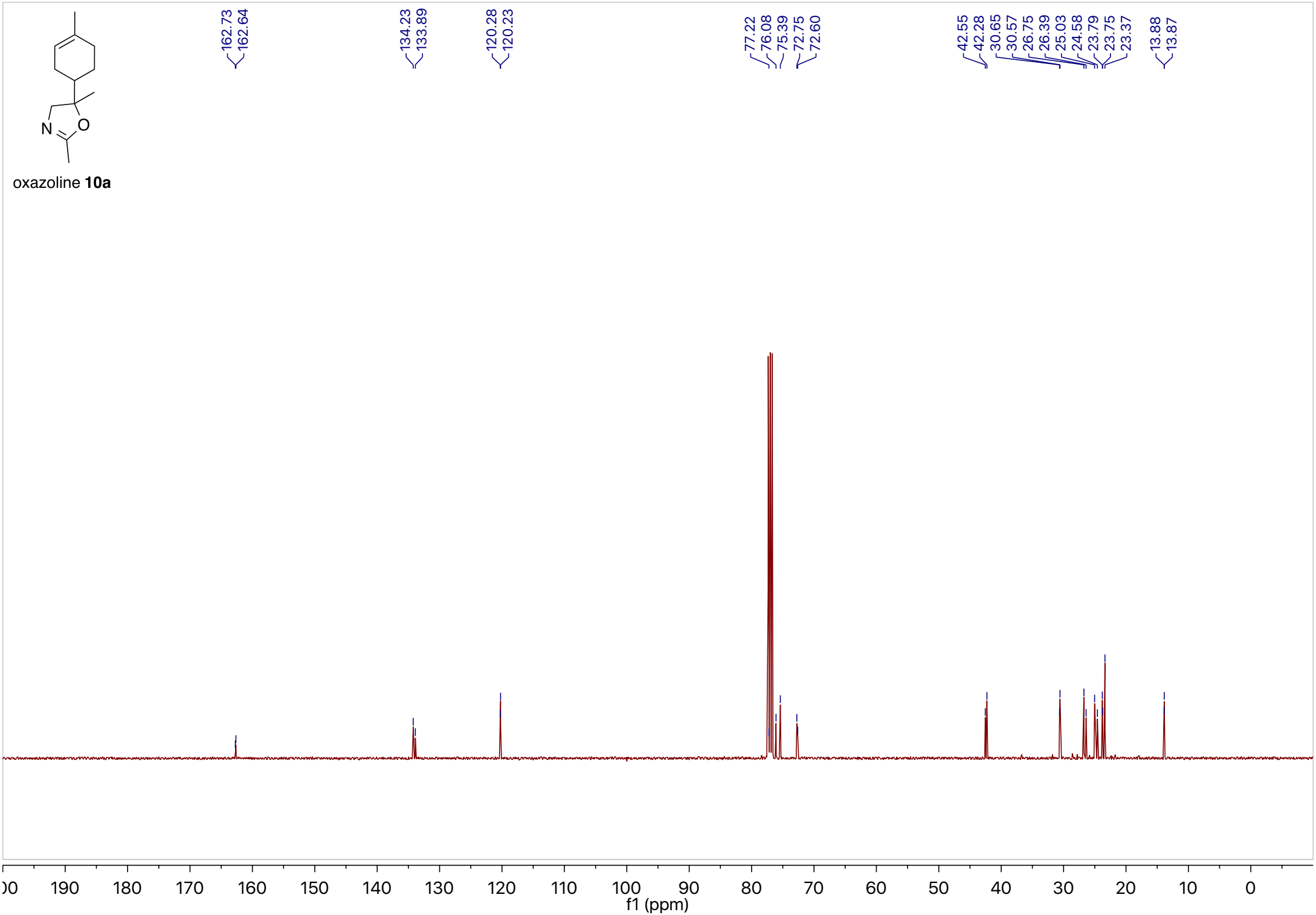

1:0.25 Nitrate ester 10: aldehyde 11
HO
ONO2
10
O
11
3417.64
2913.33
1721.21
1613.54
1439.70
1378.08
1288.61
1254.44
1151.44
1120.55
1057.93
1017.98
913.94
865.12
799.37
757.37
716.00
613.32
%Transmittance
Wavenumbers (cm-1)
95
90
85
80
75
70
65
60
55
50
45
40
35
30
4000
3500
3000
2500
2000
1500
1000

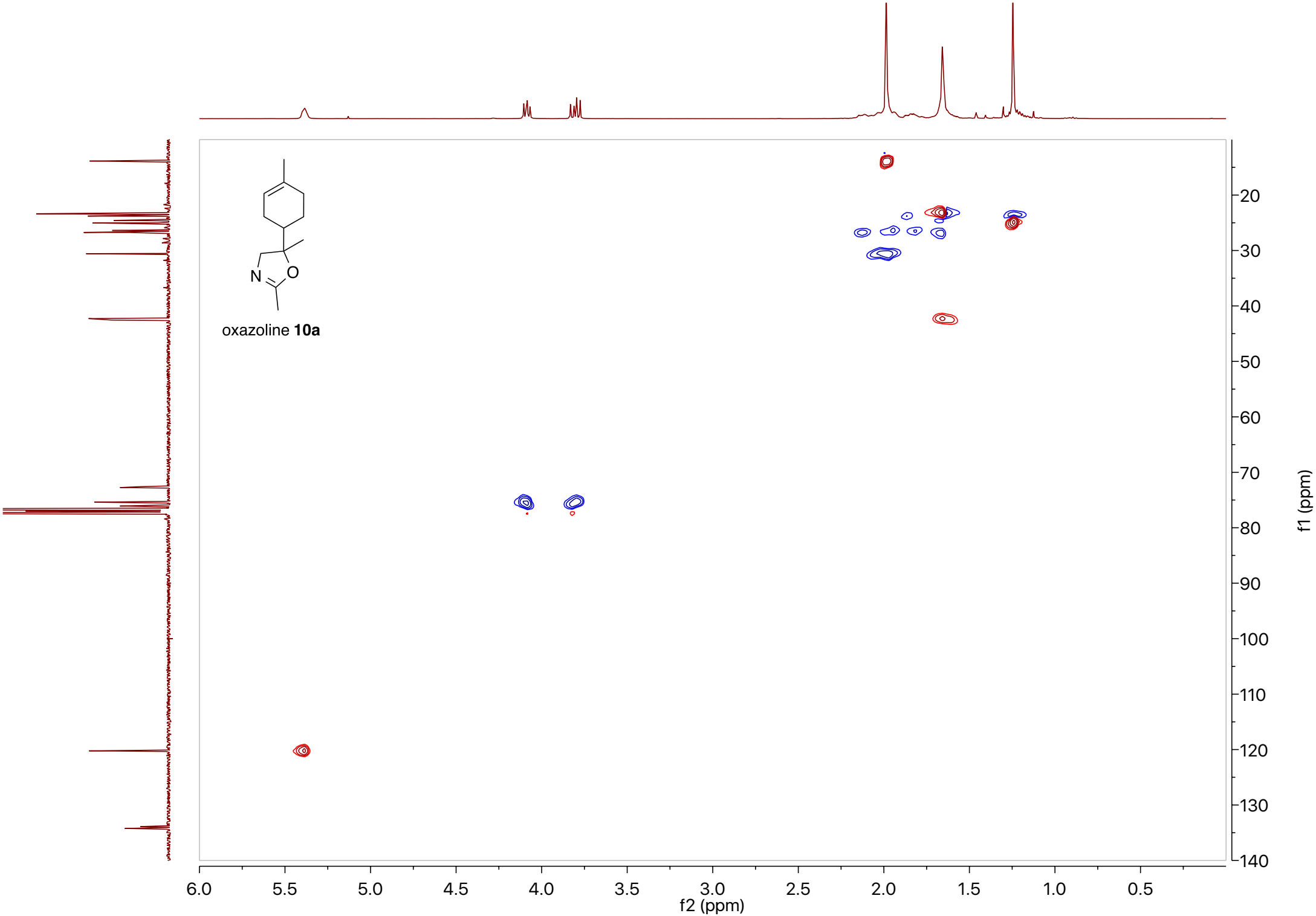


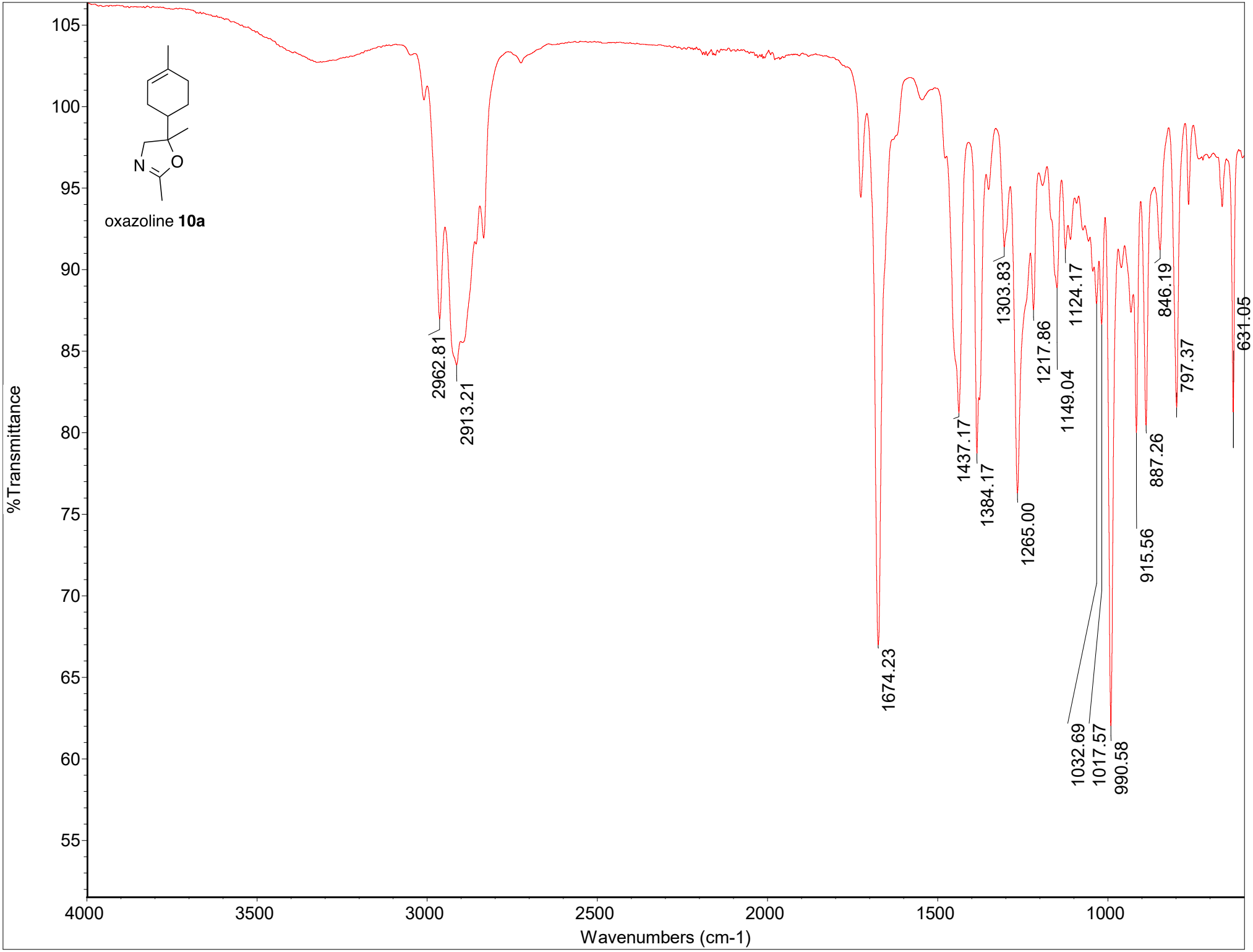

oxazoline **10a**



oxazoline **10a**

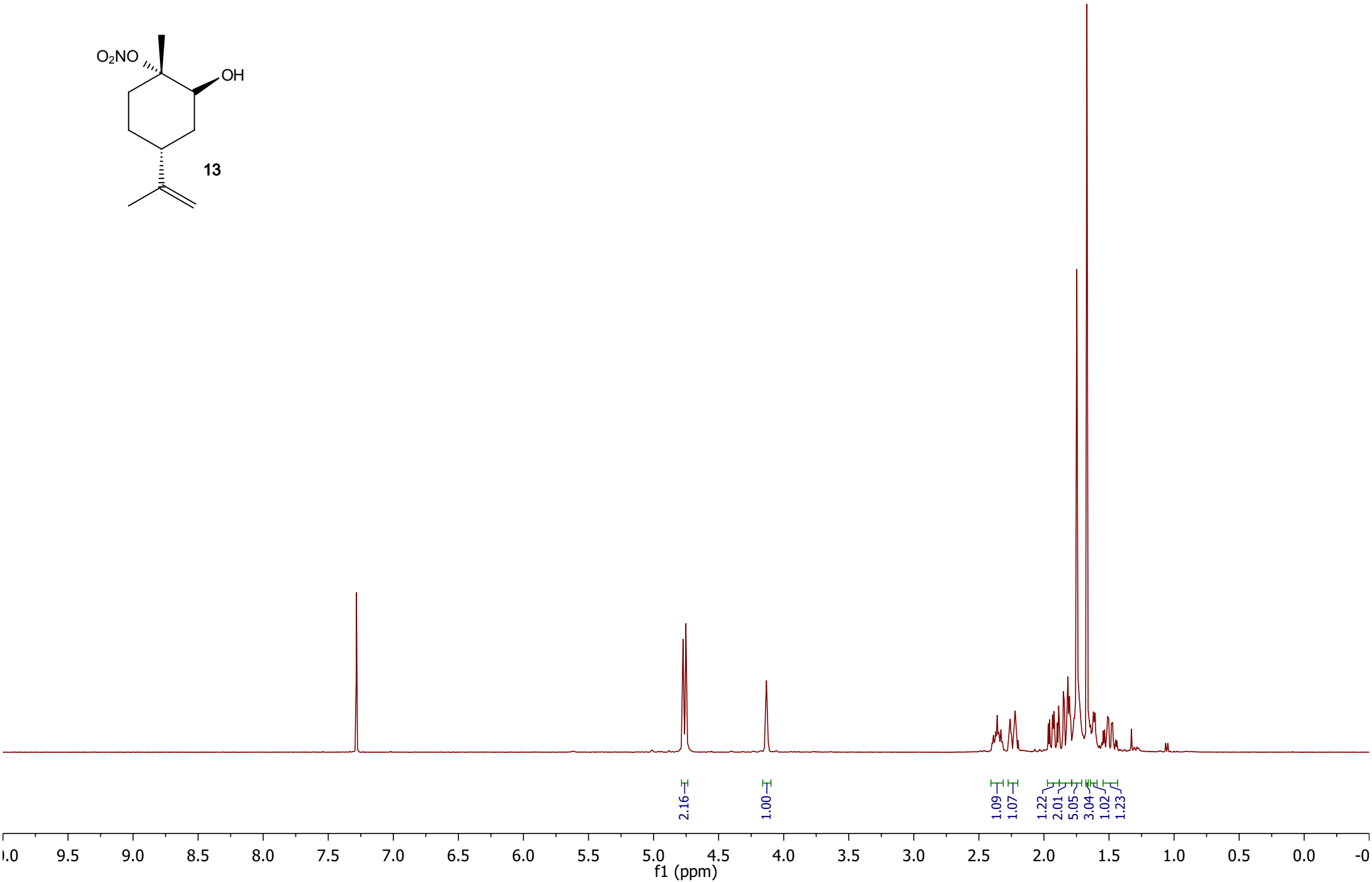


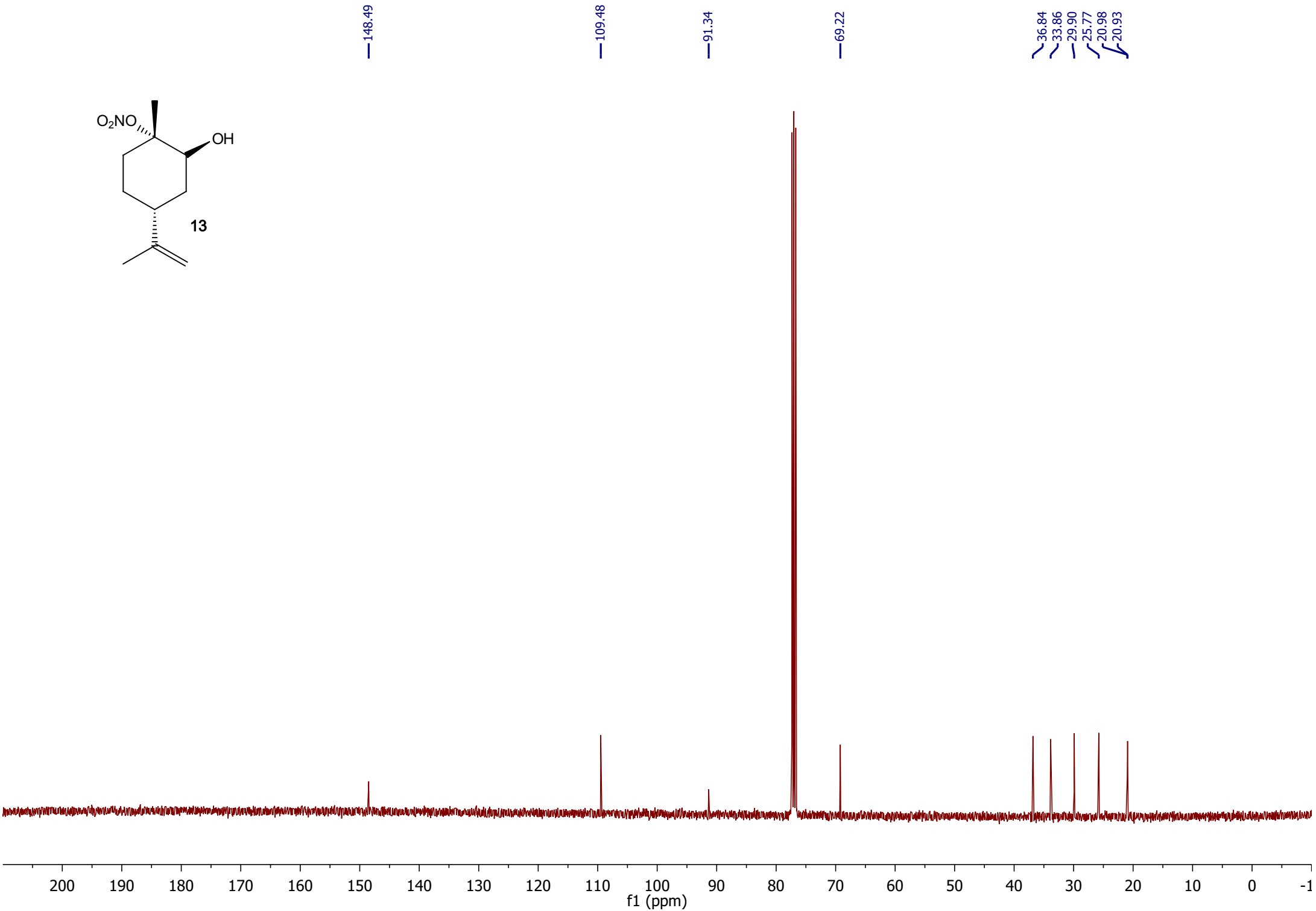

N
O
oxazoline **10a**
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
20
30
40
50
60
70
80
90
100
110
120
130
140
f1 (ppm)

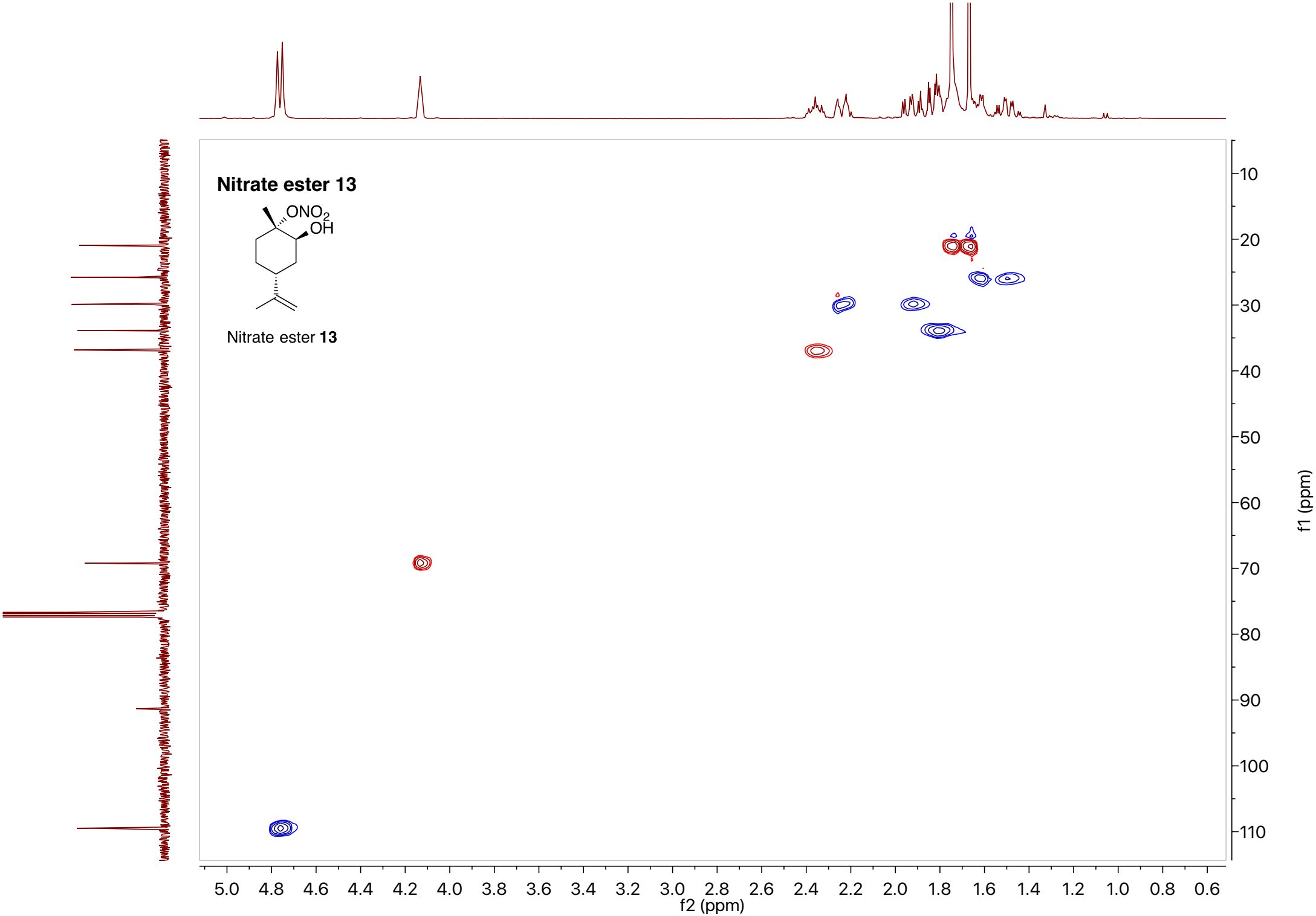

oxazoline **10a**
N
O
%Transmittance
Wavenumbers (cm-1)
105
100
95
90
85
80
75
70
65
60
55
4000
3500
3000
2500
2000
1500
1000
2962.81
2913.21
1674.23
1437.17
1384.17
1303.83
1265.00
1217.86
1149.04
1124.17
1032.69
1017.57
990.58
915.56
887.26
846.19
797.37
631.05

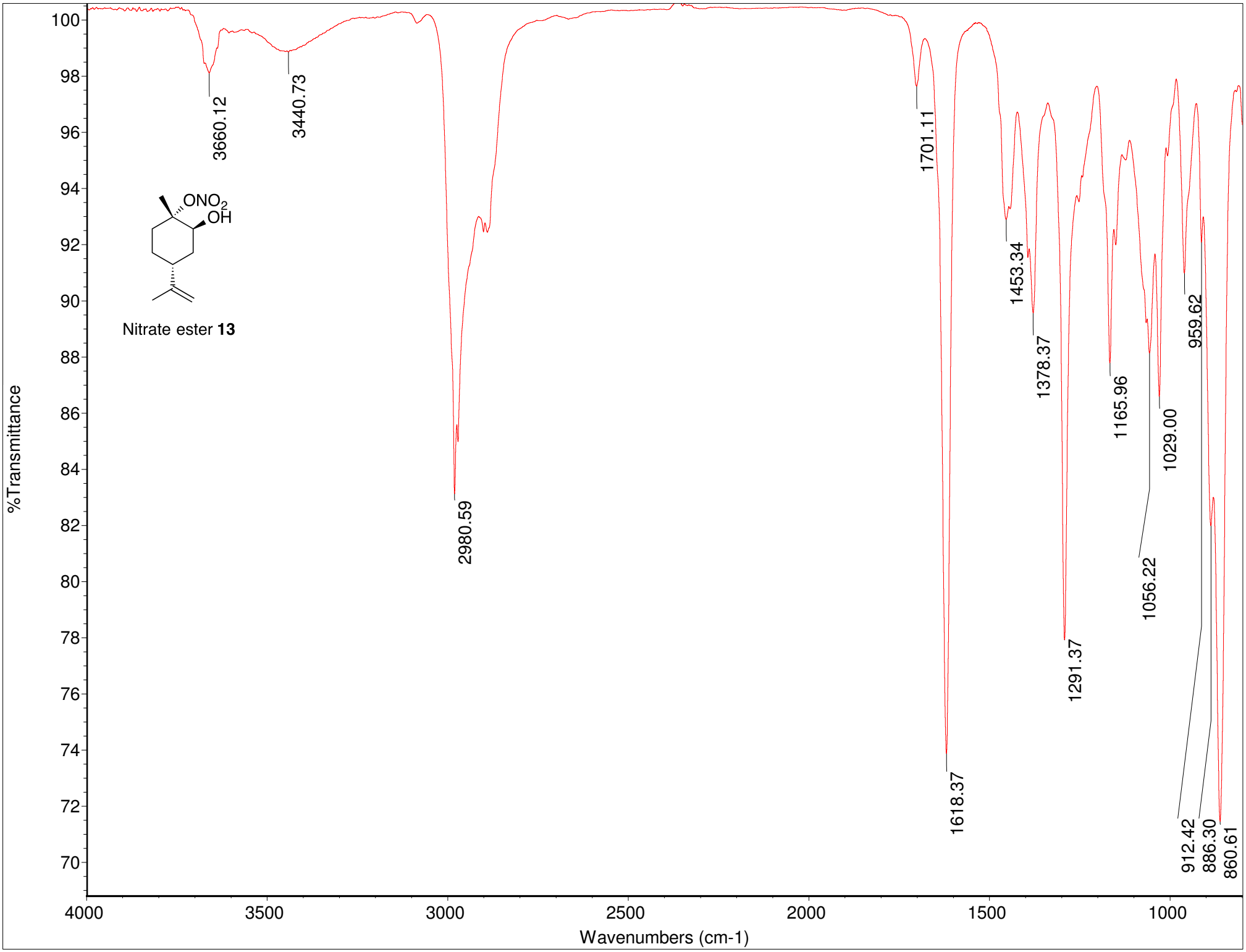
O2NO
OH

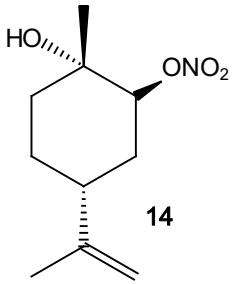
**13**


2.16
1.00
1.09
1.07
1.22
2.01
5.05
3.04
1.02
1.23
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)

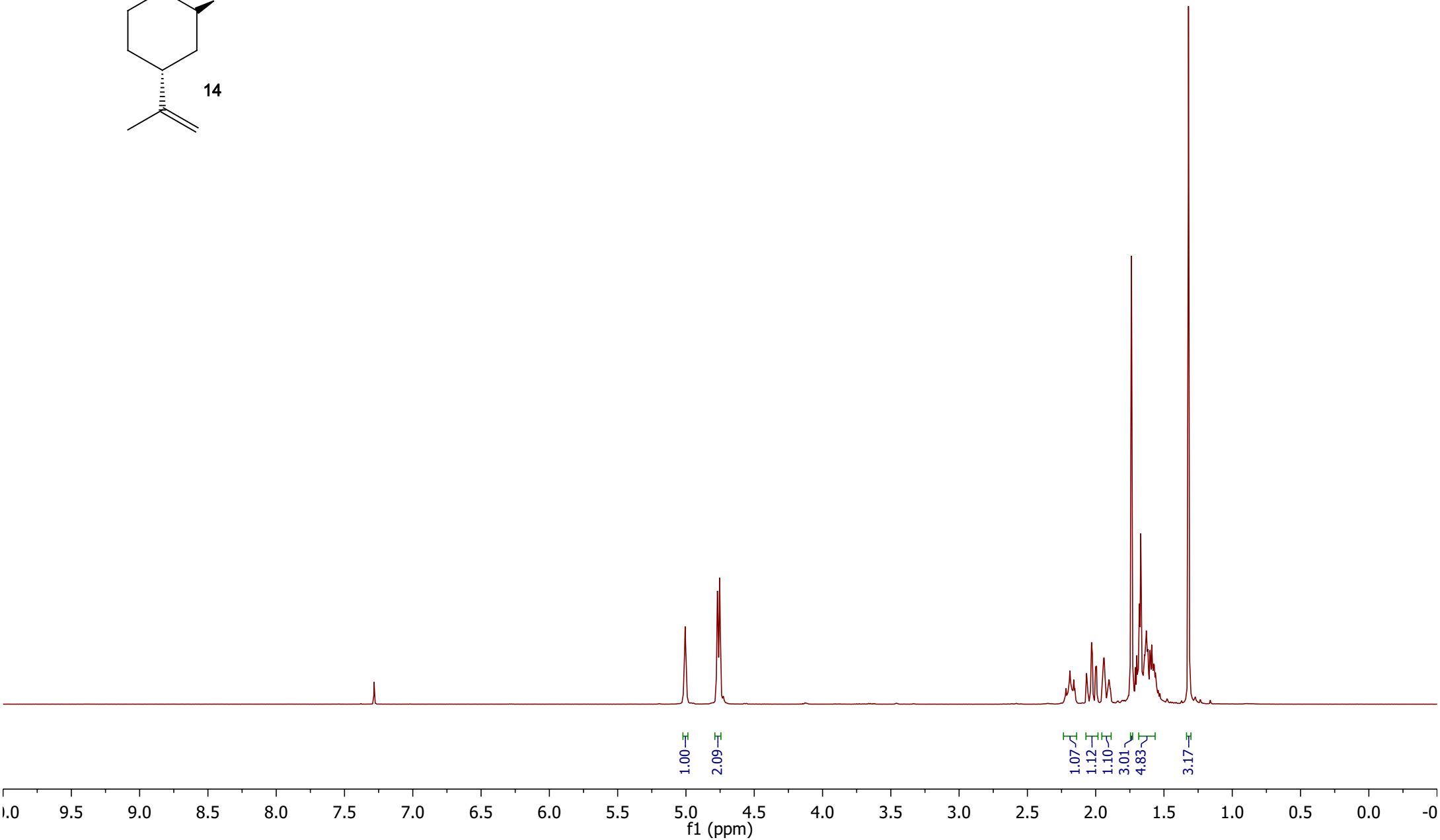

148.49
109.48
91.34
69.22
36.84
33.86
29.90
25.77
20.98
20.93
O2NO
OH
13
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

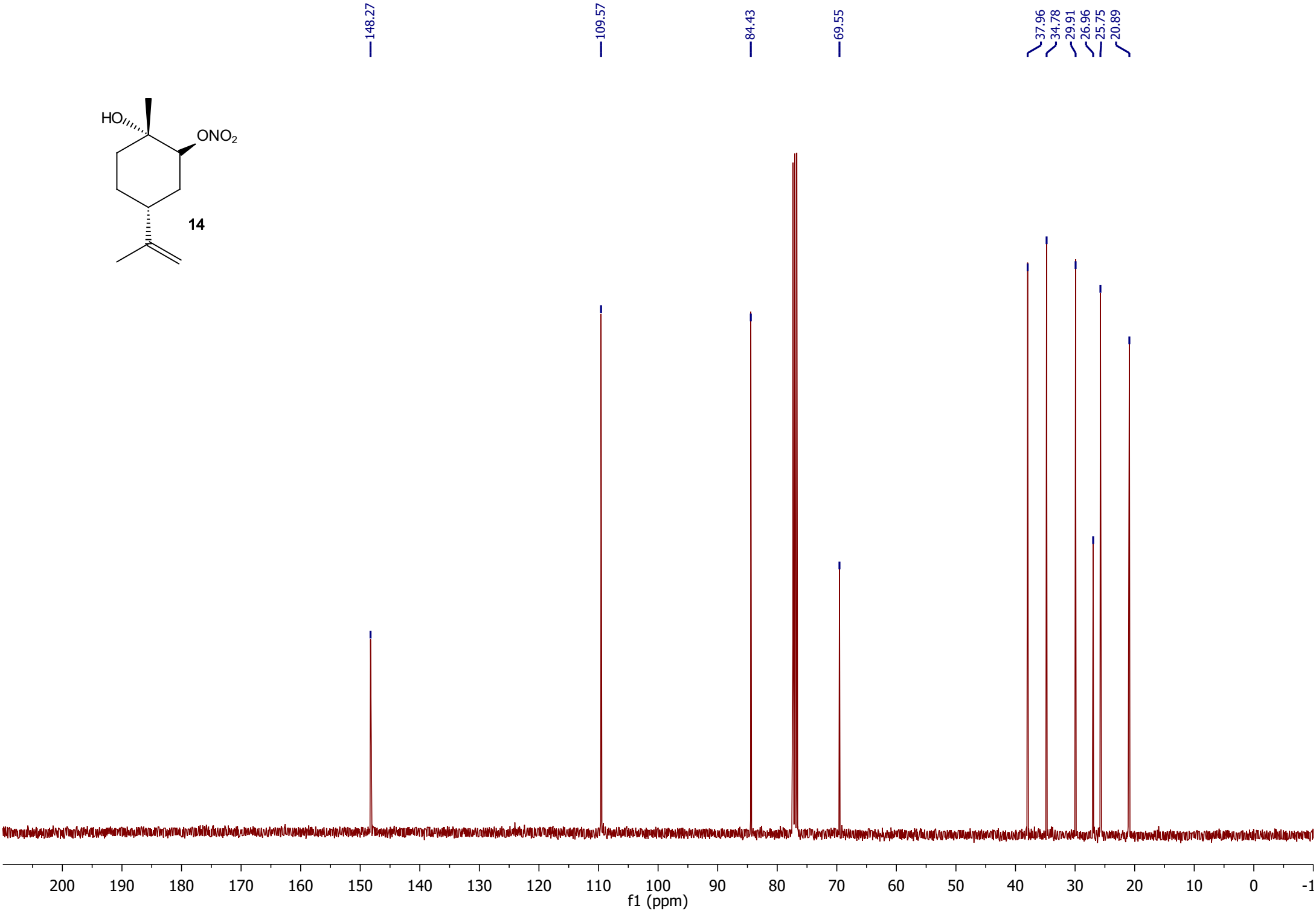

Nitrate ester 13
ONO2
OH
Nitrate ester 13
f2 (ppm)
f1 (ppm)

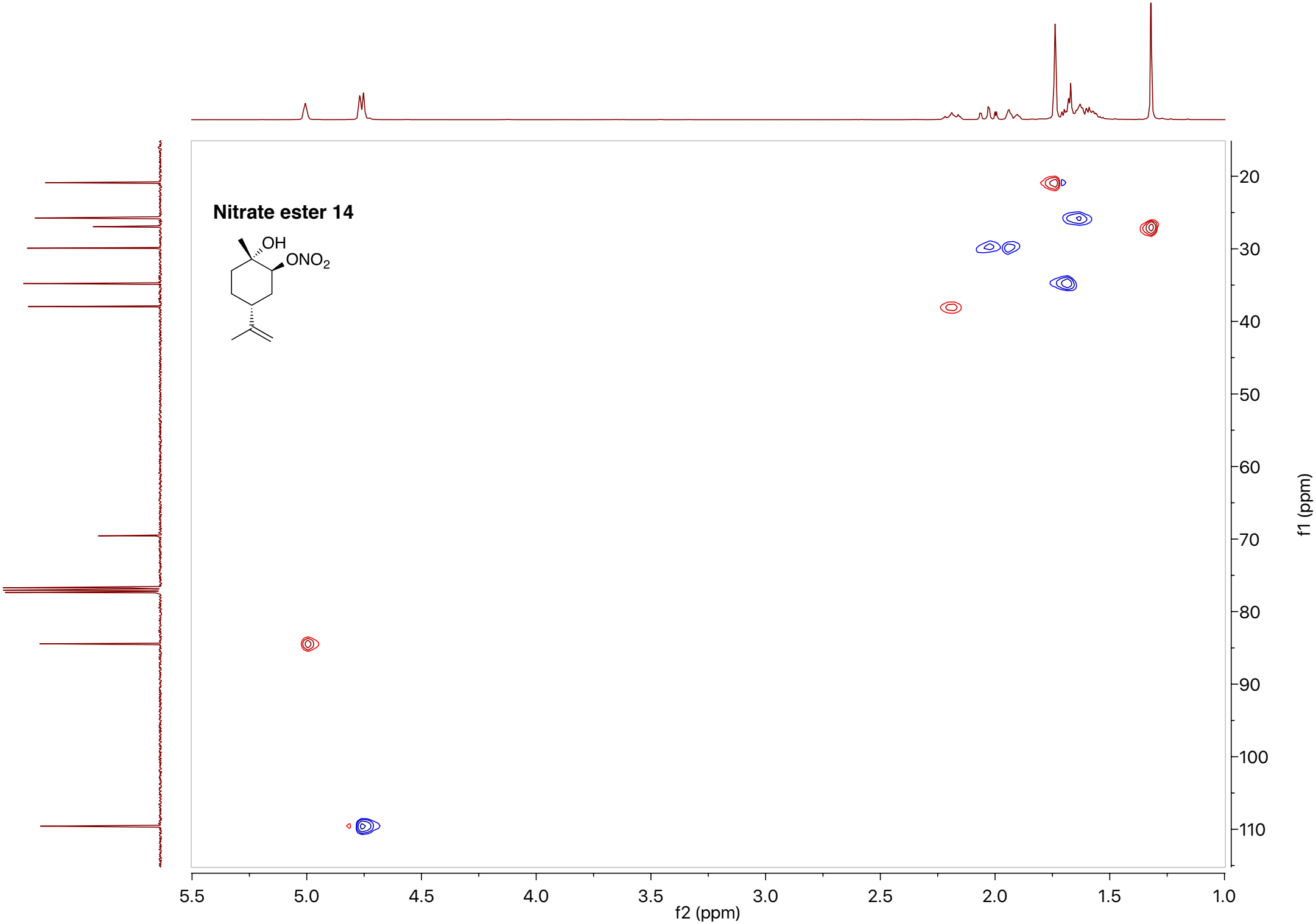

%Transmittance
Wavenumbers (cm-1)
3660.12
3440.73
2980.59
1701.11
1618.37
1453.34
1378.37
1291.37
1165.96
1056.22
1029.00
959.62
912.42
886.30
860.61
ONO2
OH
Nitrate ester 13

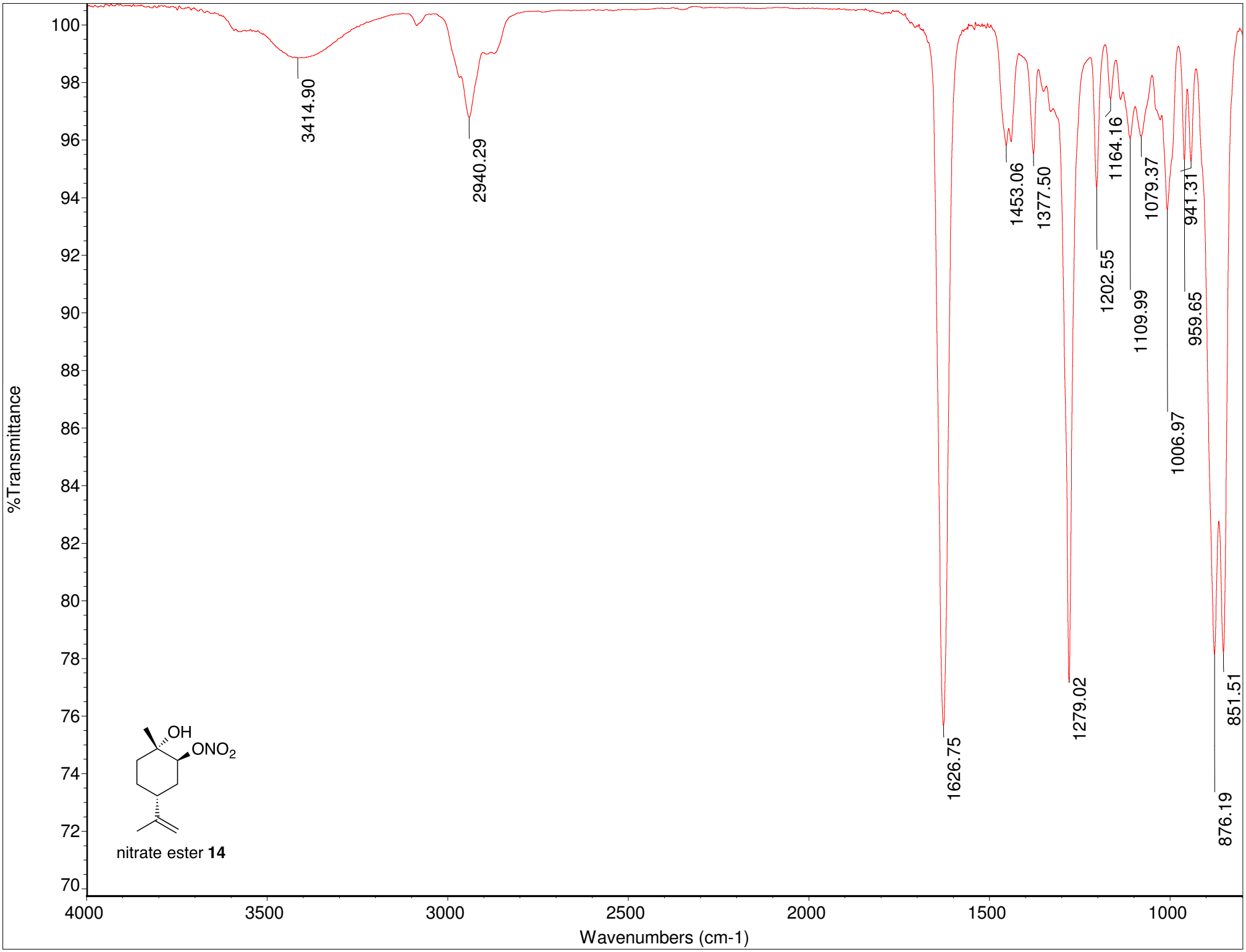

HO
ONO2

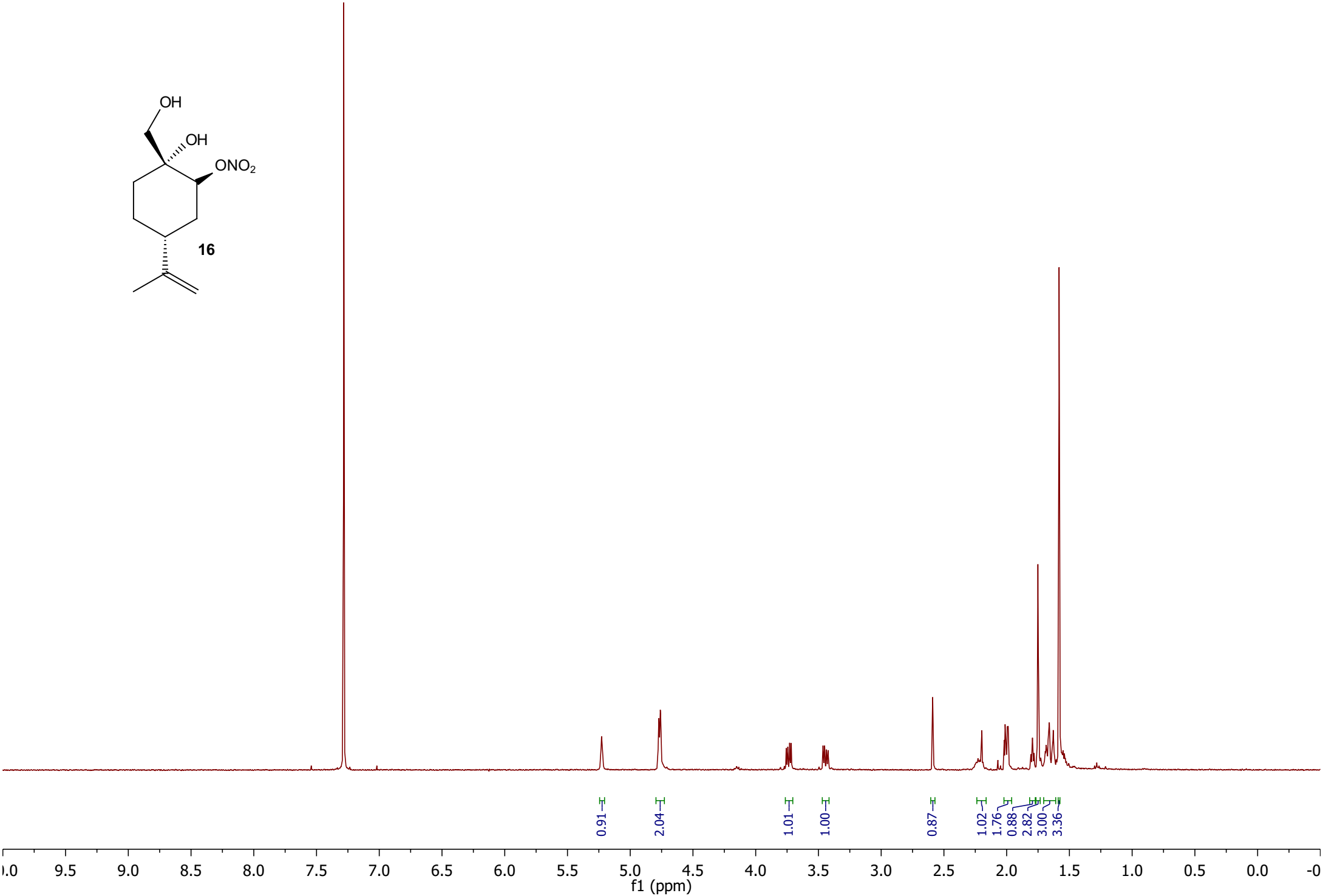
**14**

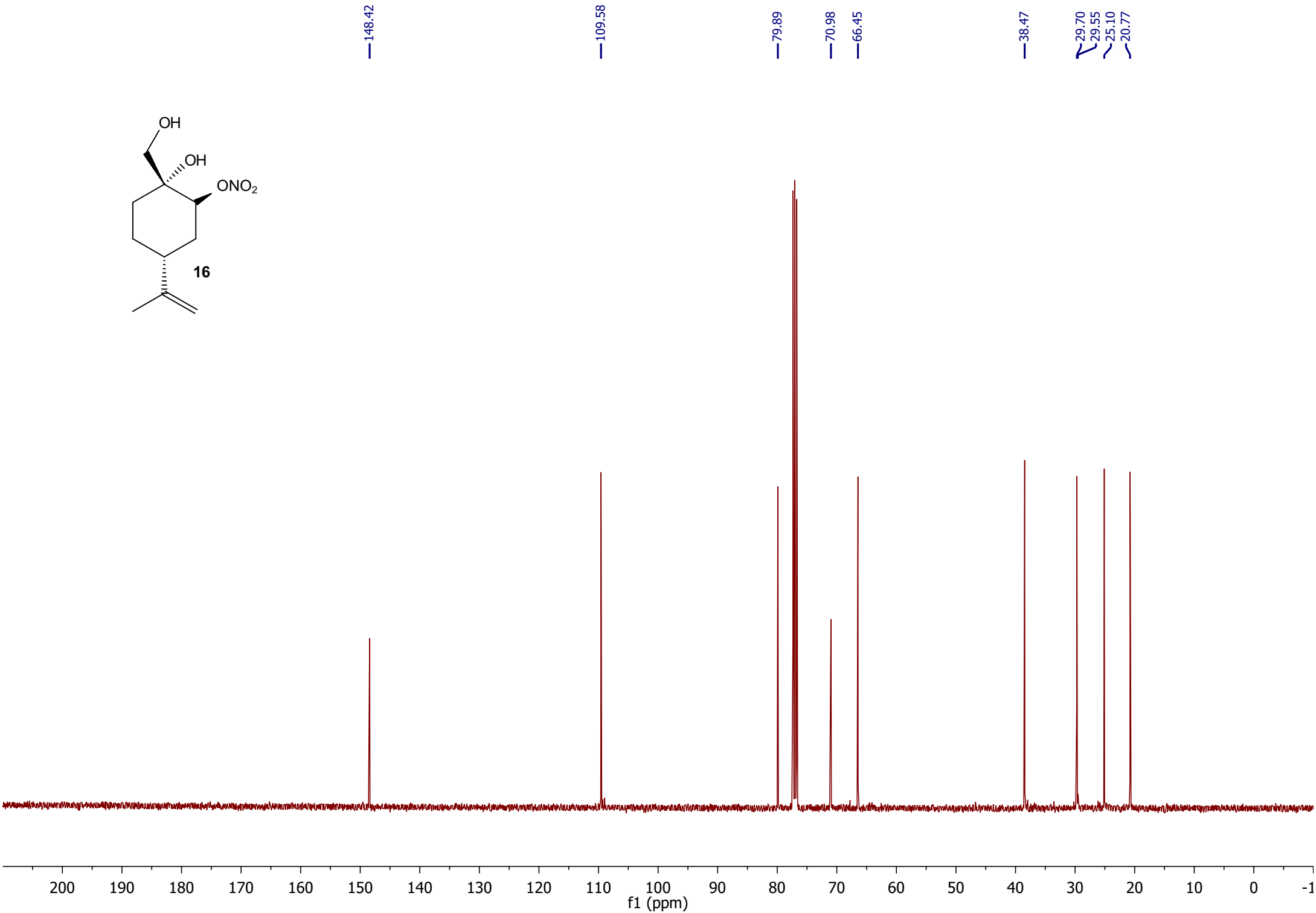

1.00
2.09
1.07
1.12
1.10
3.01
4.83
3.17
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

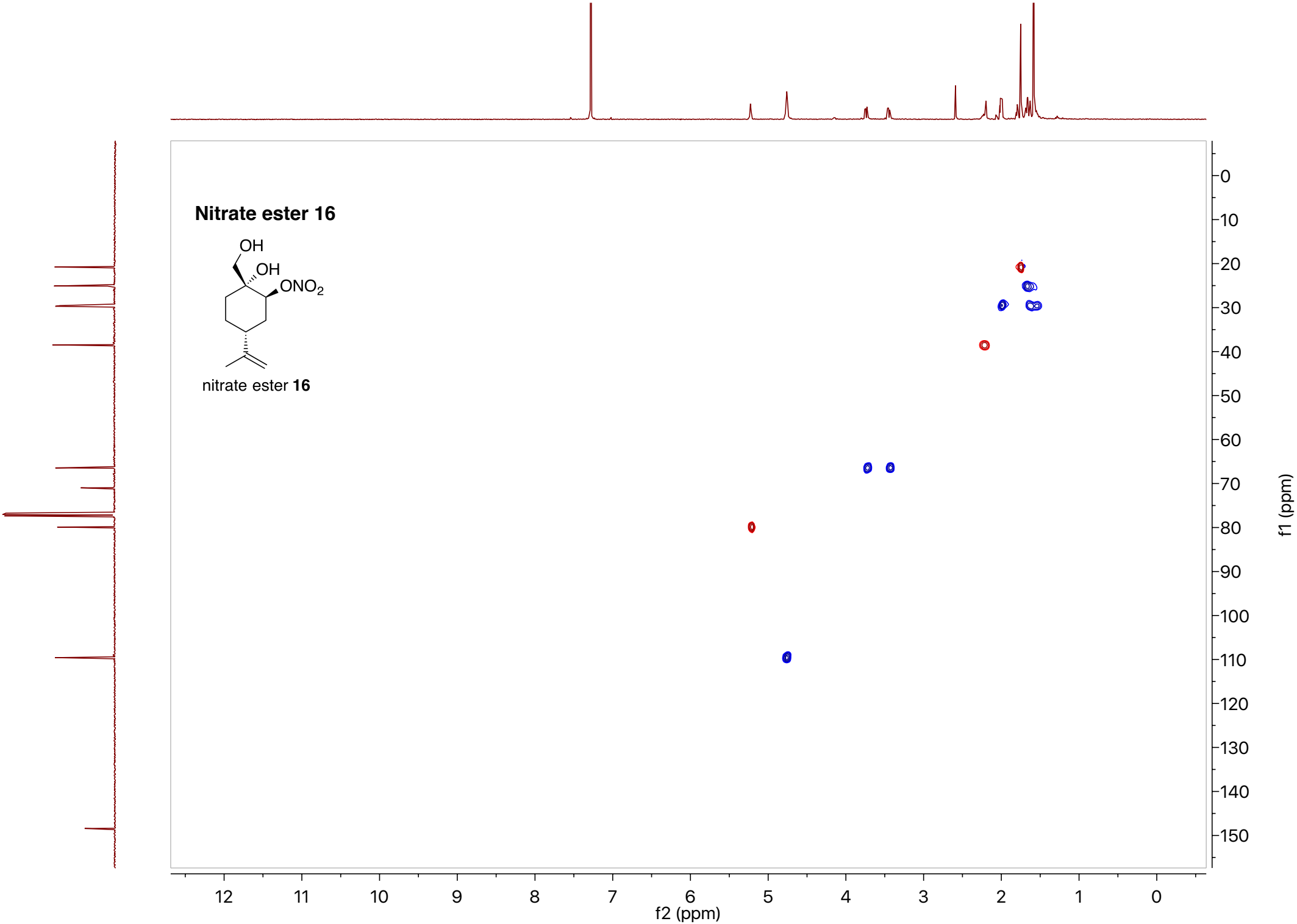

148.27
109.57
84.43
69.55
37.96
34.78
29.91
26.96
25.75
20.89
HO
ONO2
14
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

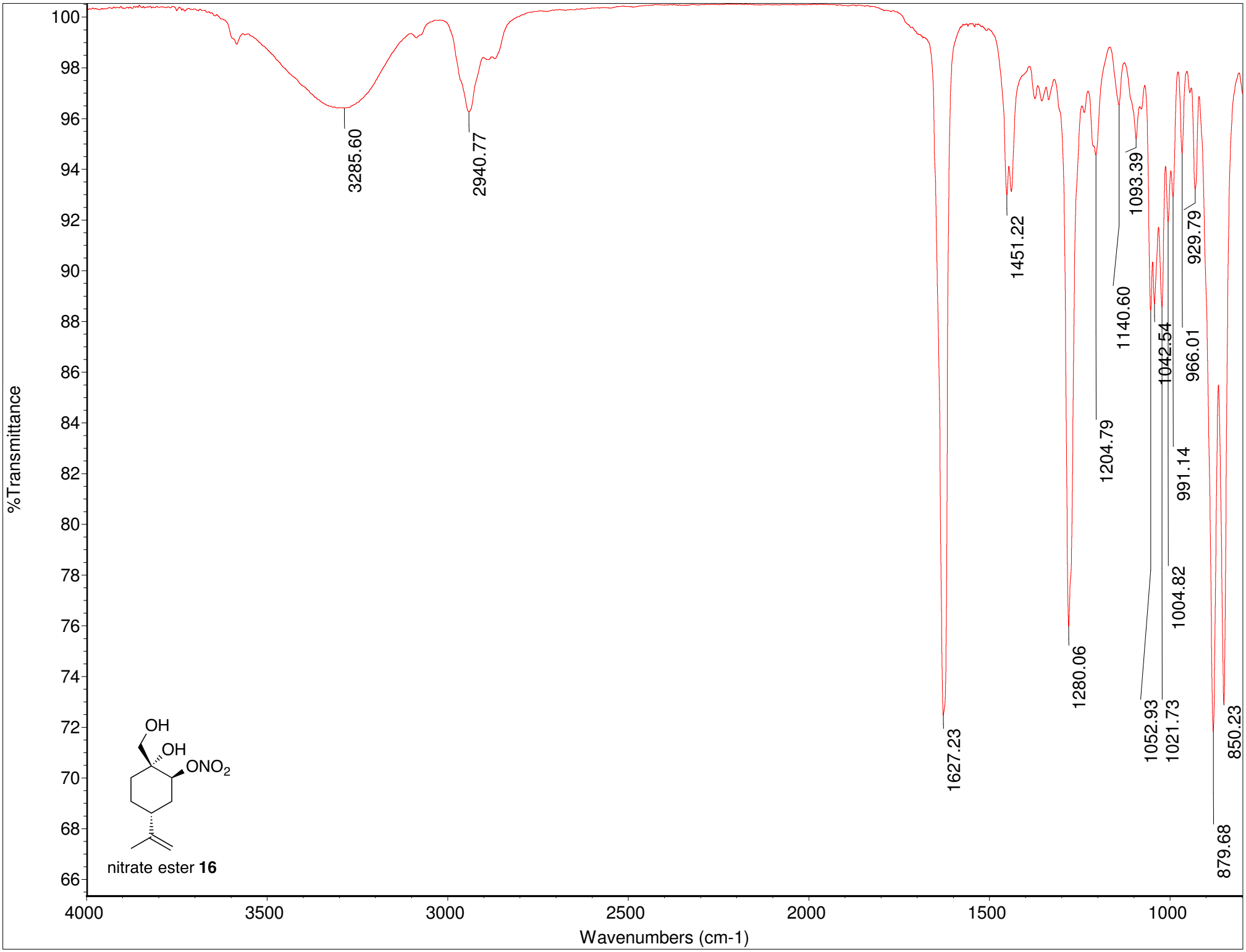

Nitrate ester 14
OH
ONO2
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
20
30
40
50
60
70
80
90
100
110
f1 (ppm)

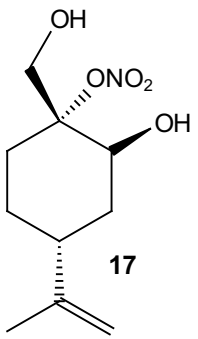

%Transmittance
Wavenumbers (cm-1)
3414.90
2940.29
1626.75
1453.06
1377.50
1279.02
1202.55
1164.16
1109.99
1079.37
1006.97
941.31
959.65
876.19
851.51
OH
ONO2
nitrate ester 14

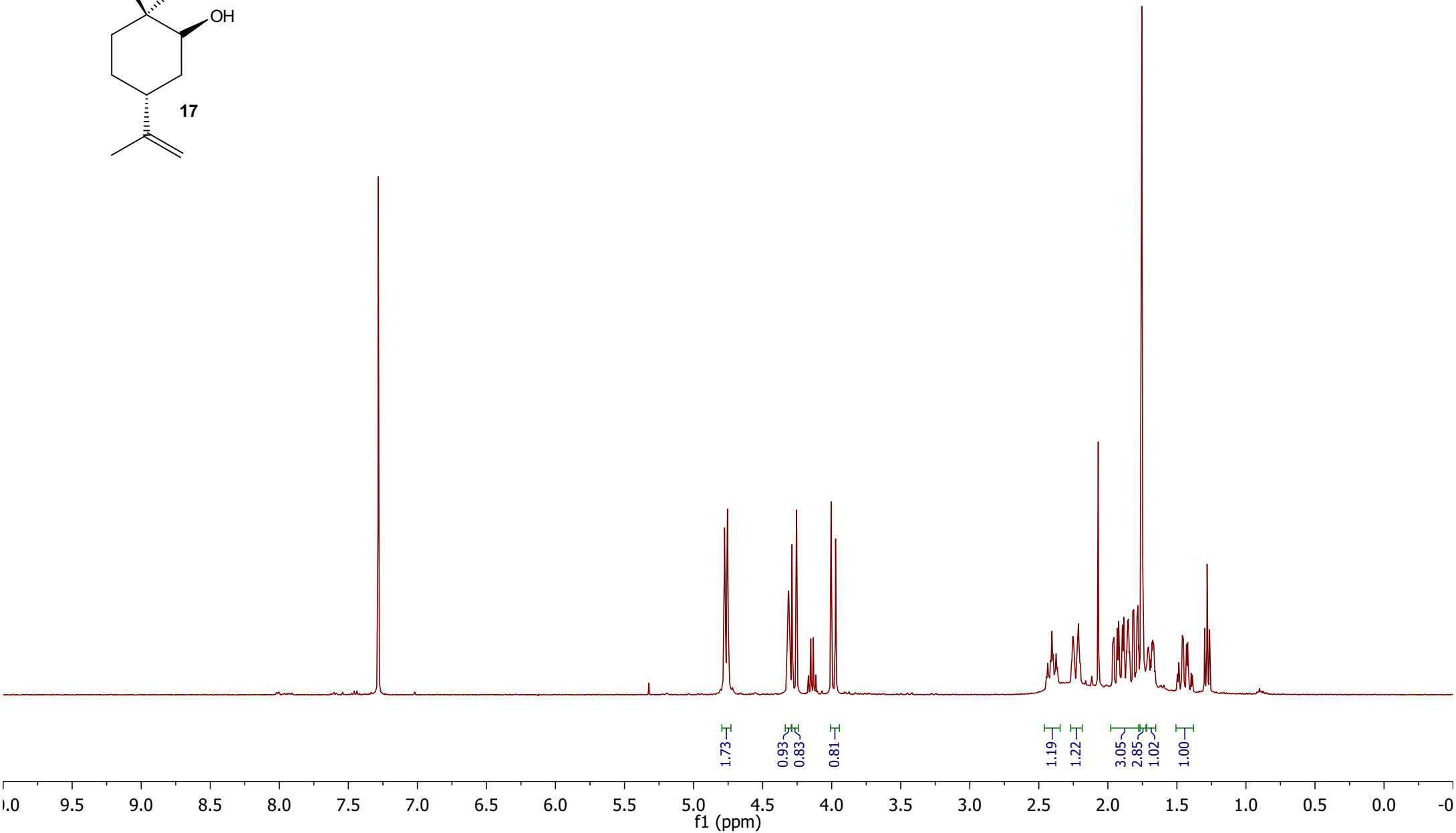

OH
OH
ONO2
16
0.91
2.04
1.01
1.00
0.87
1.02
1.76
0.88
2.82
3.00
3.36
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

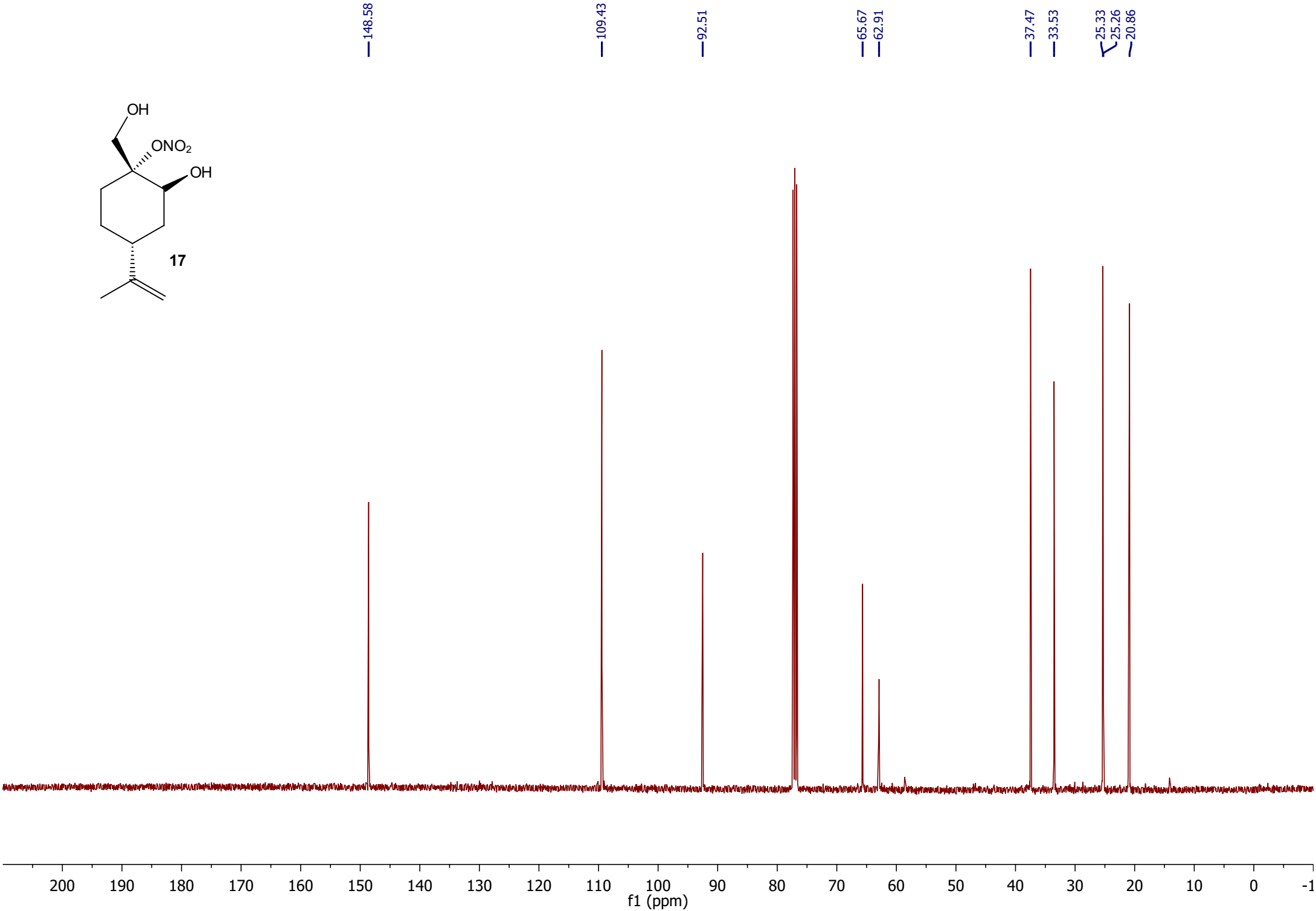

148.42
109.58
79.89
70.98
66.45
38.47
29.70
29.55
25.10
20.77
OH
OH
ONO2
16
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

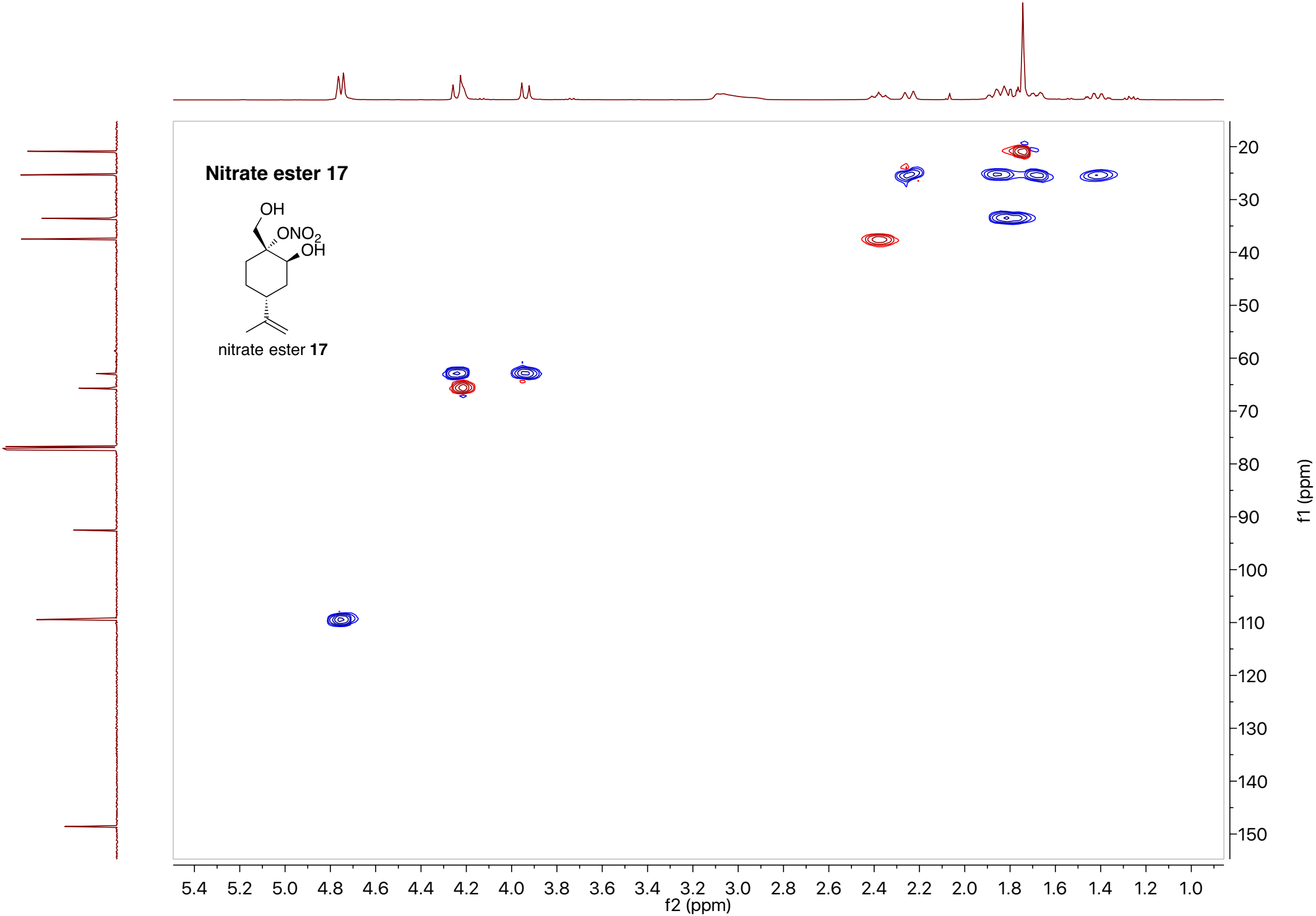

Nitrate ester 16
OH
OH
ONO2
nitrate ester 16
f2 (ppm)
f1 (ppm)

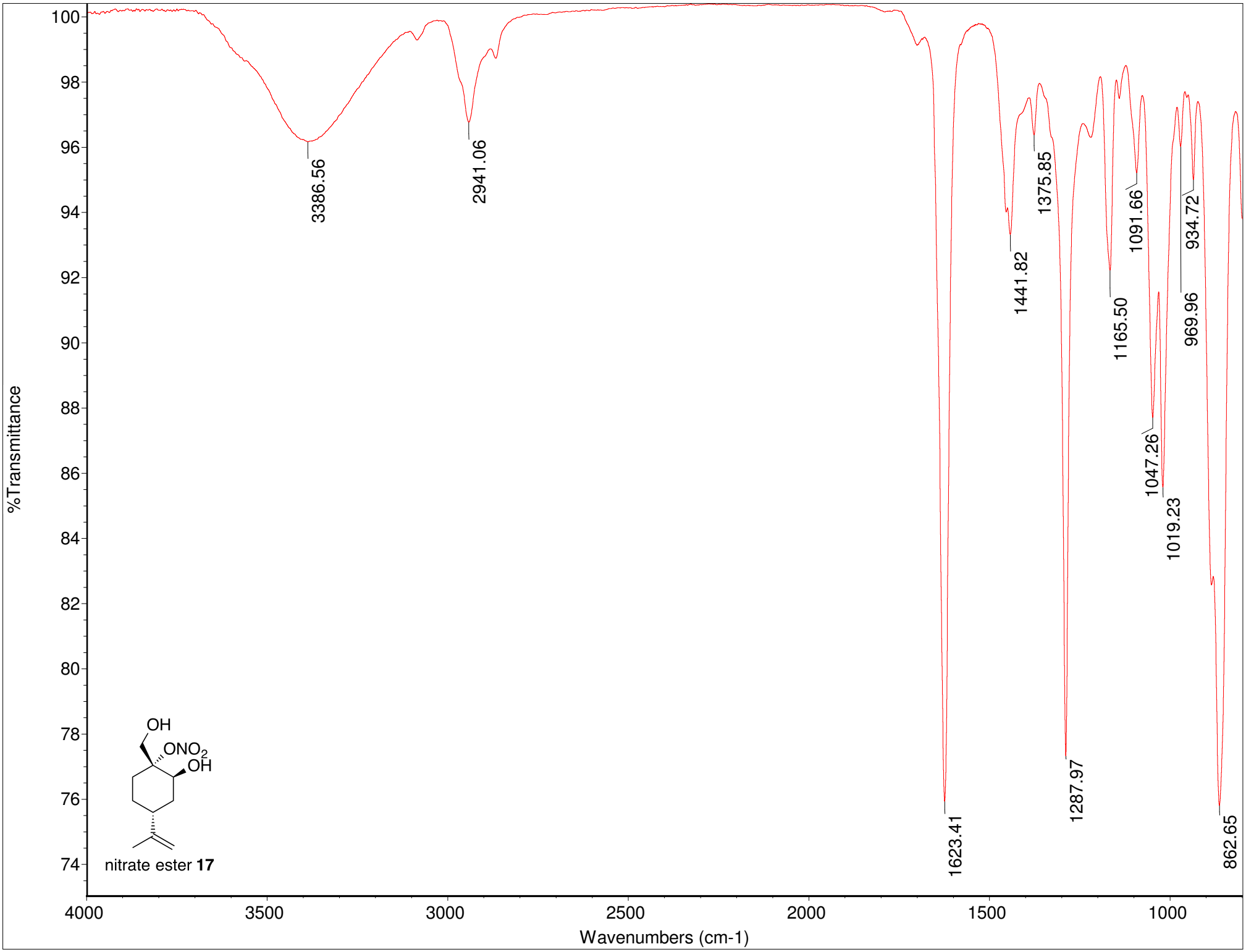

%Transmittance
Wavenumbers (cm-1)
3285.60
2940.77
1627.23
1451.22
1280.06
1204.79
1140.60
1093.39
1052.93
1042.54
1021.73
1004.82
991.14
966.01
929.79
879.68
850.23
OH
OH
ONO2
nitrate ester 16


OH
ONO2
OH
17


1.73
0.93
0.83
0.81
1.19
1.22
3.05
2.85
1.02
1.00
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
f1 (ppm)

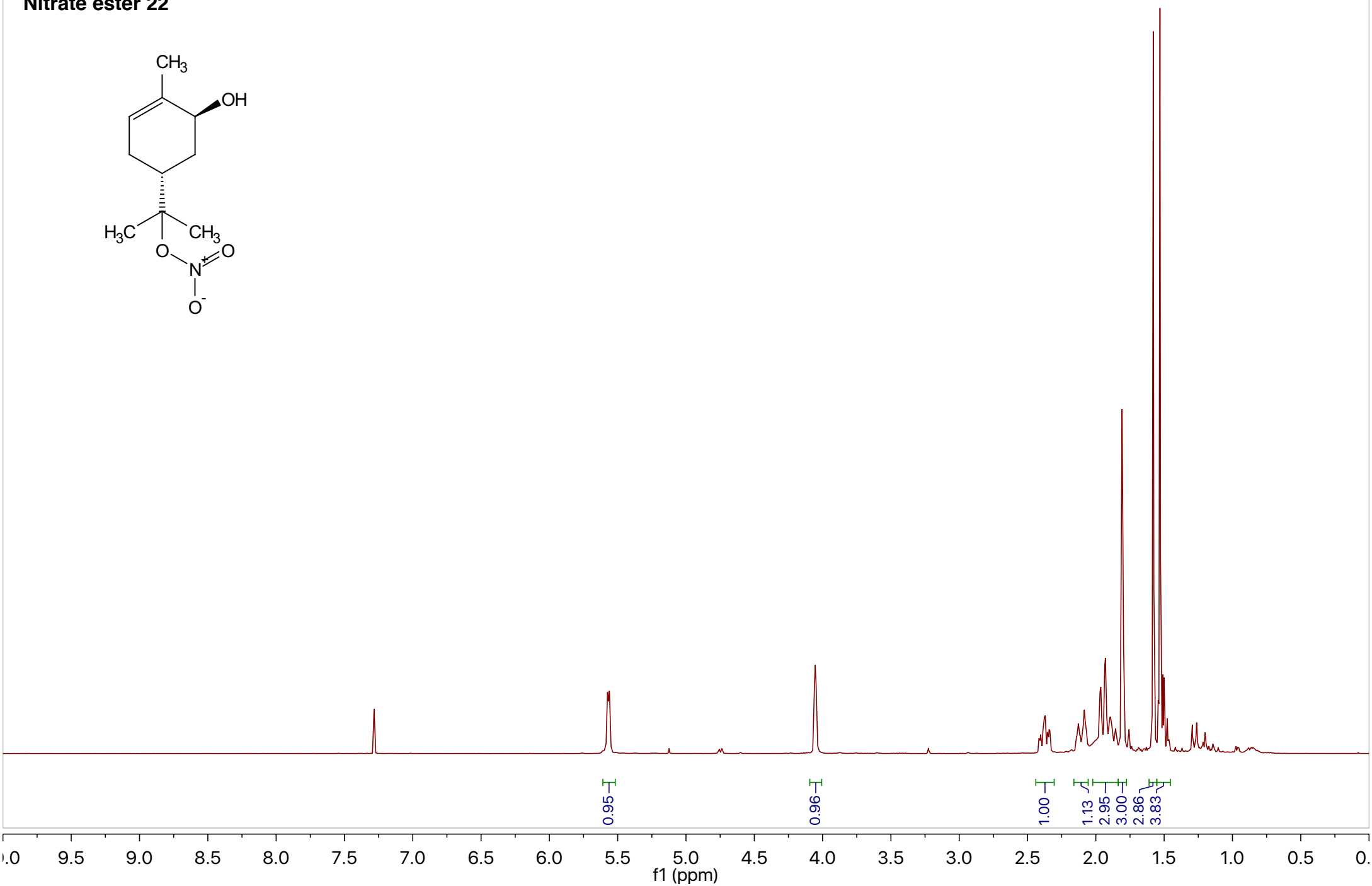

148.58
109.43
92.51
65.67
62.91
37.47
33.53
25.33
25.26
20.86
OH
ONO2
OH
17
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


Nitrate ester 17
OH
ONO2
OH
nitrate ester 17
f2 (ppm)
f1 (ppm)


%Transmittance
Wavenumbers (cm-1)
3386.56
2941.06
1441.82
1375.85
1091.66
934.72
1165.50
969.96
1047.26
1019.23
1623.41
1287.97
862.65
OH
ONO2
OH
nitrate ester 17

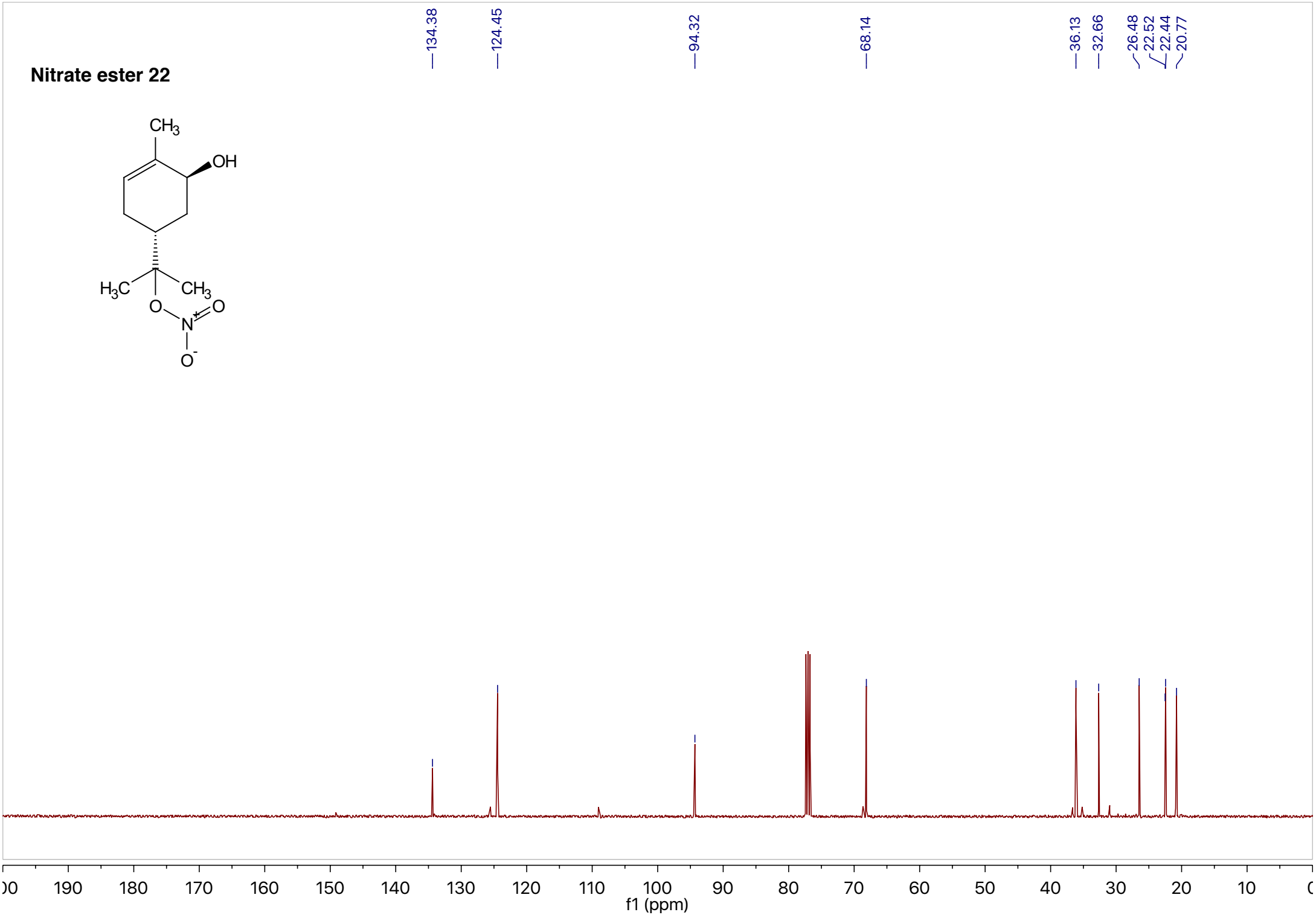
**Nitrate ester 22**

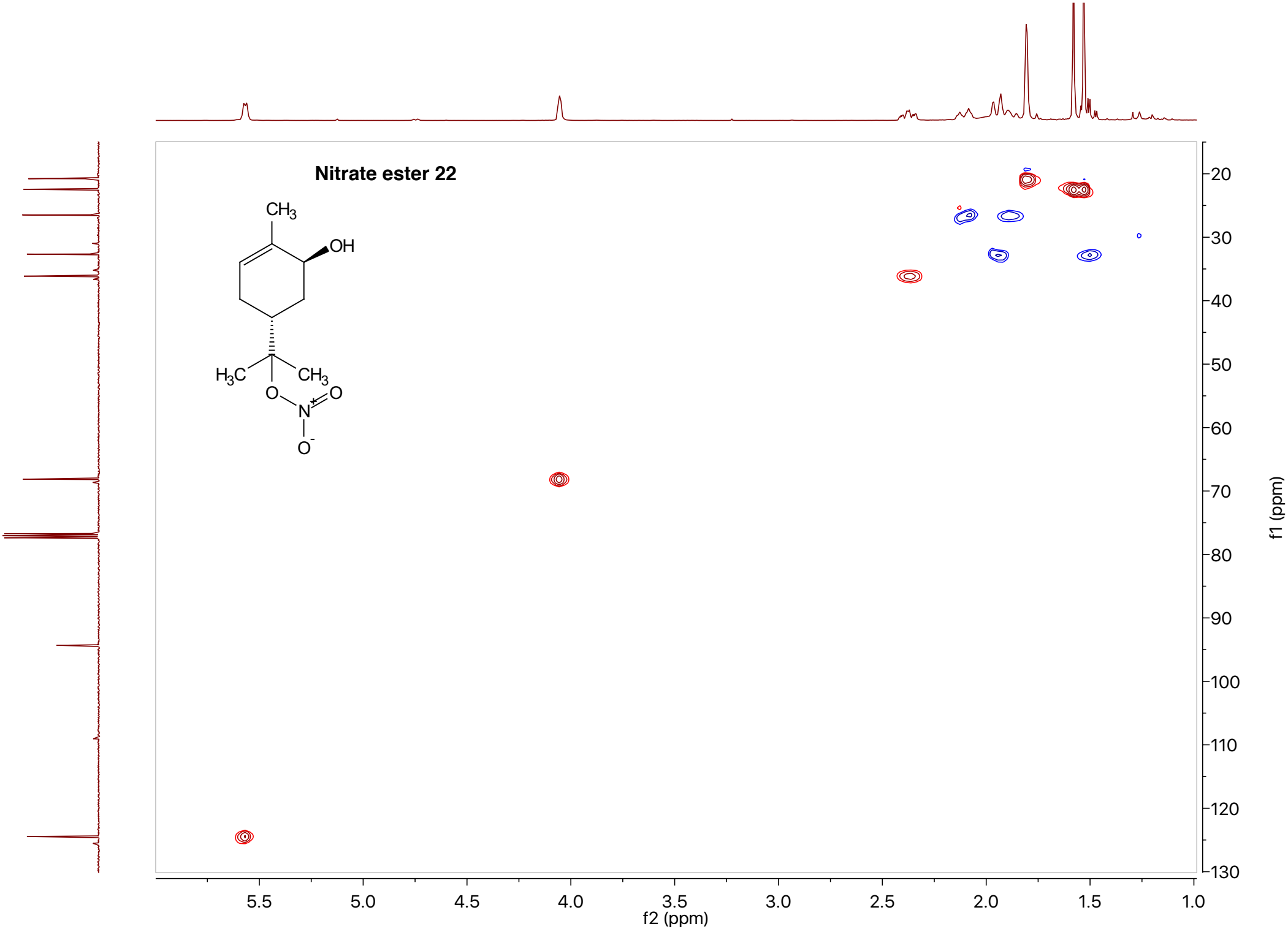


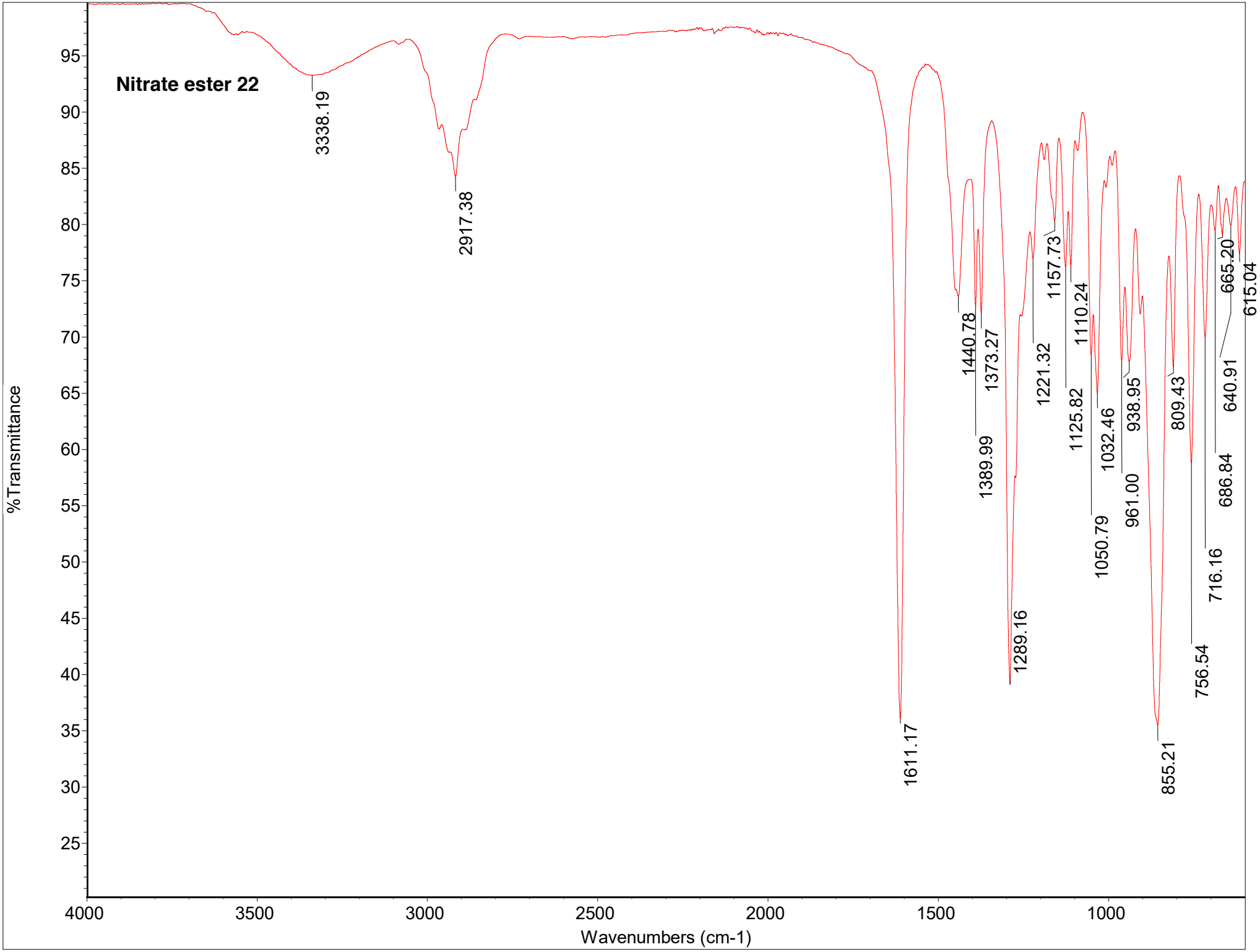



**Nitrate ester 22**



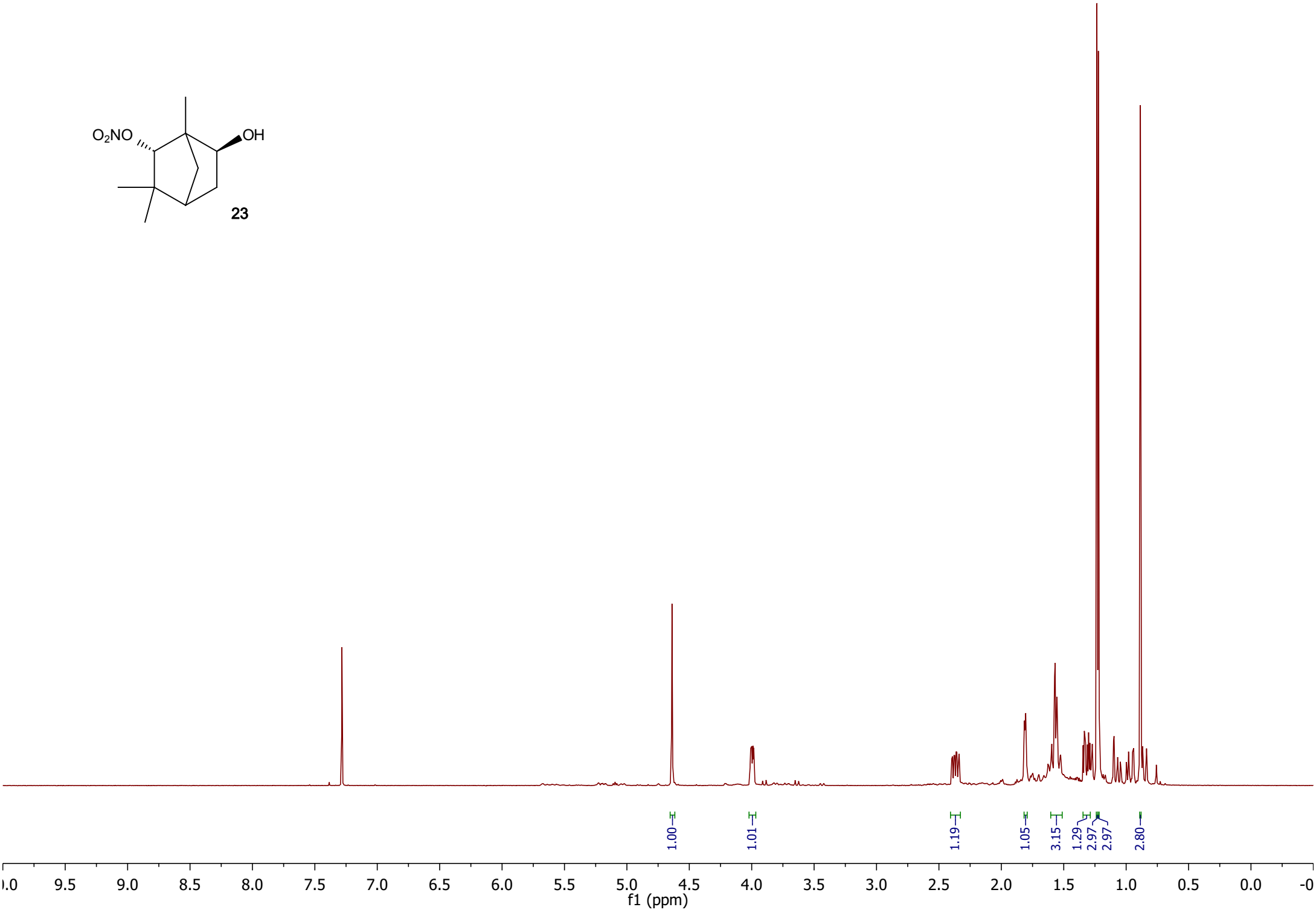




Nitrate ester 22
CH3
OH
H3C
CH3
O
N
O
O-
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
20
30
40
50
60
70
80
90
100
110
120
130
f1 (ppm)


Nitrate ester 22
%Transmittance
Wavenumbers (cm-1)
3338.19
2917.38
1611.17
1440.78
1389.99
1373.27
1289.16
1221.32
1157.73
1125.82
1110.24
1050.79
1032.46
961.00
938.95
855.21
809.43
756.54
716.16
686.84
665.20
640.91
615.04

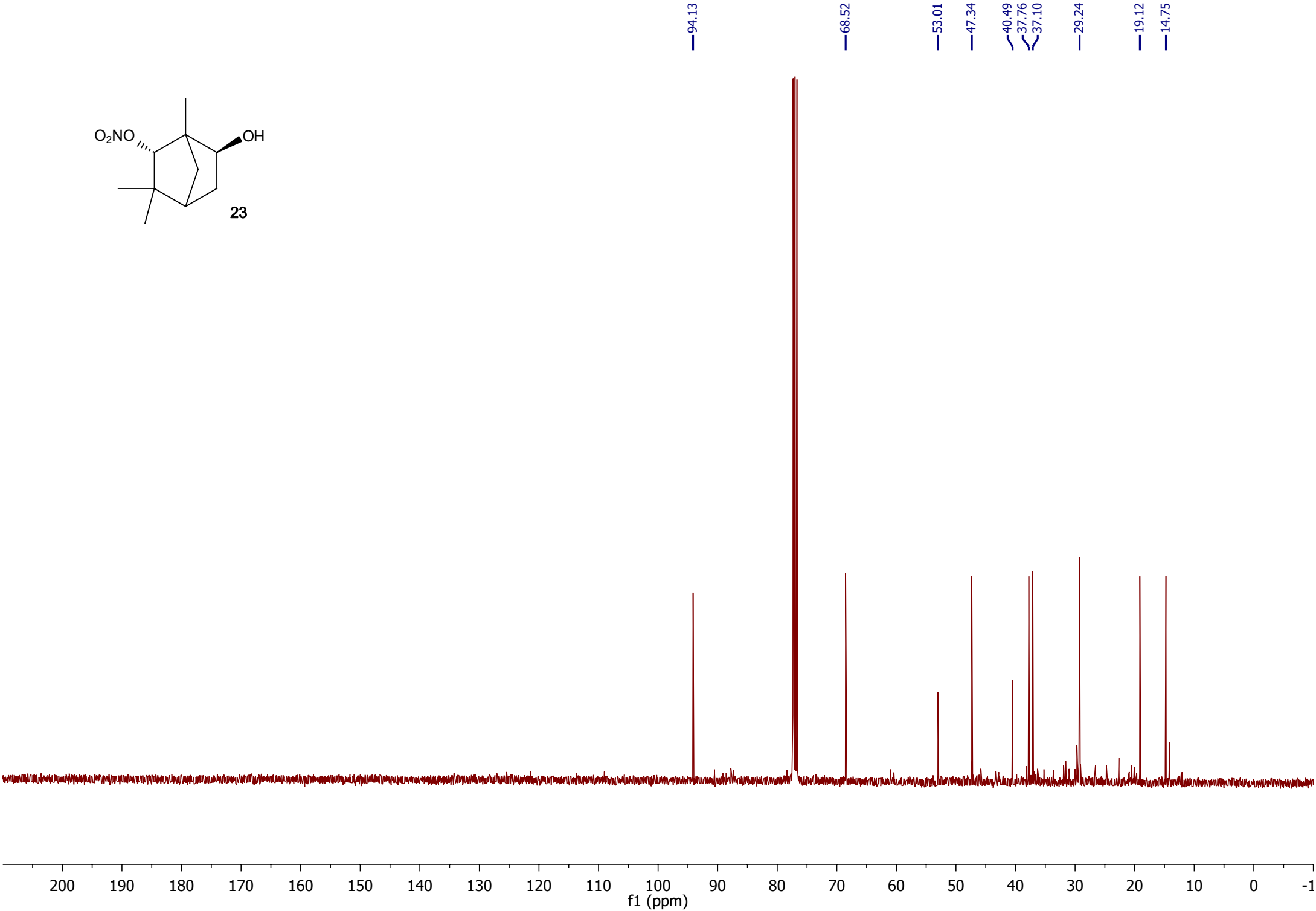
O2NO
OH

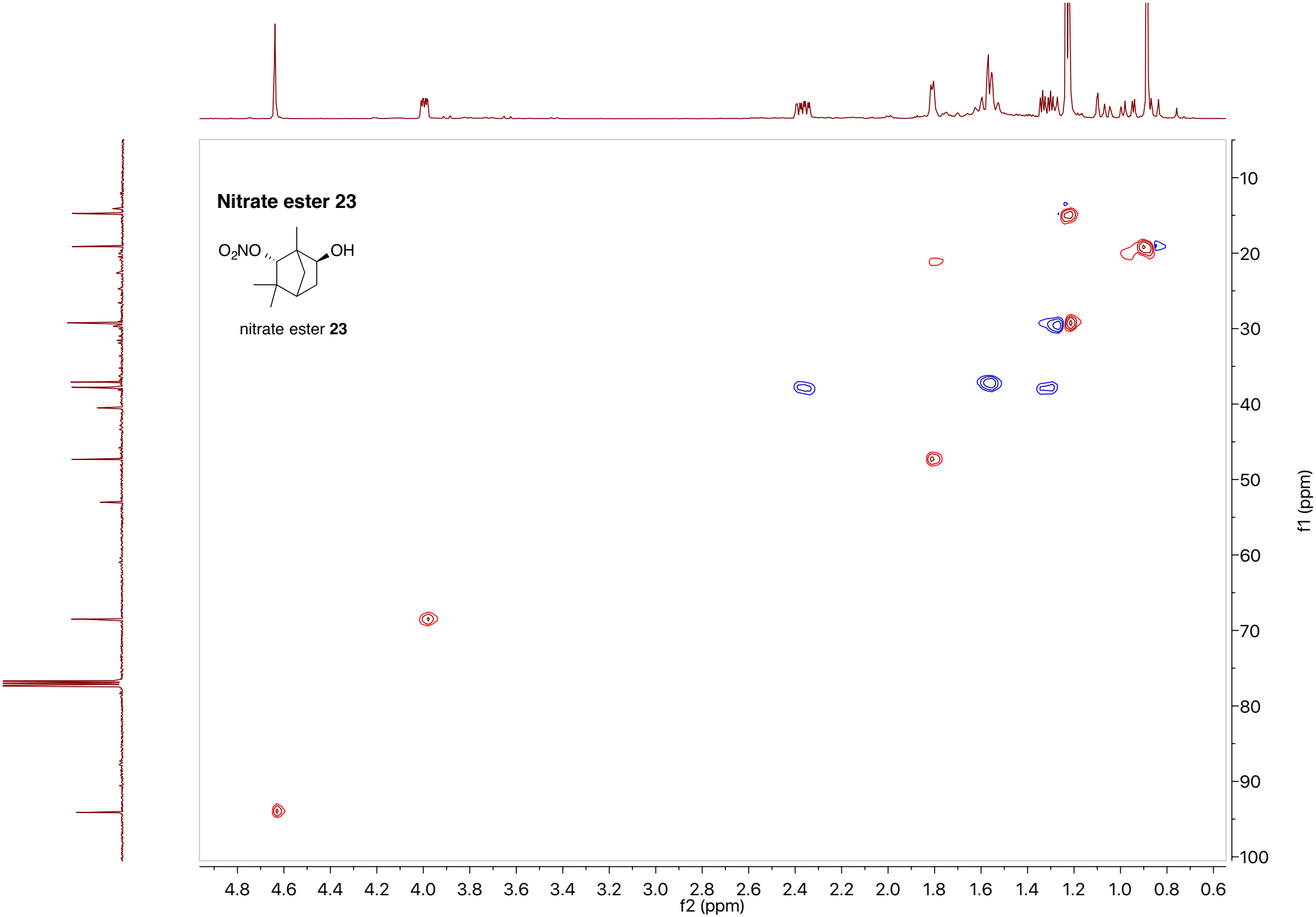
**23**

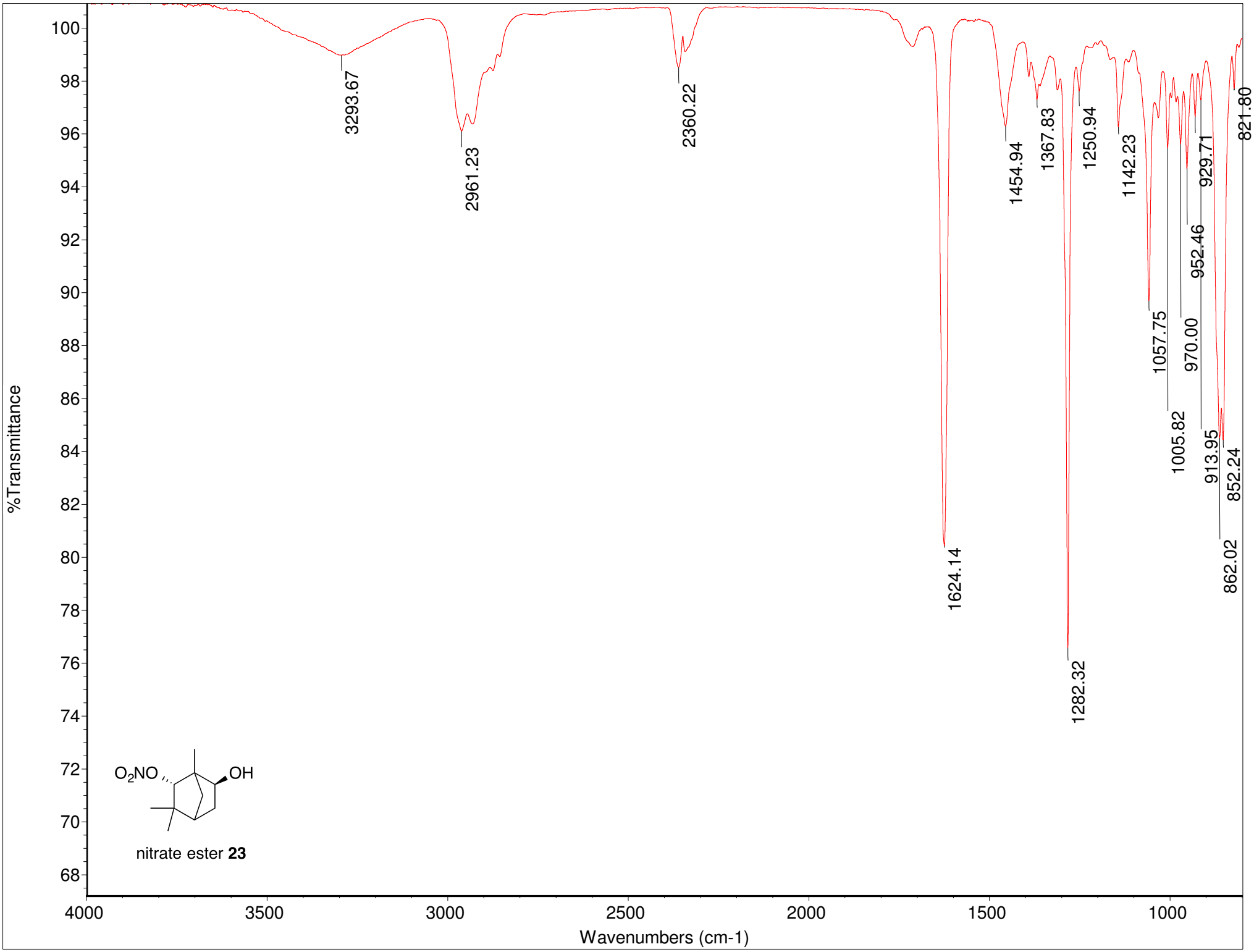

1.00
1.01
1.19
1.05
3.15
1.29
2.97
2.97
2.80
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

O2NO
OH

23

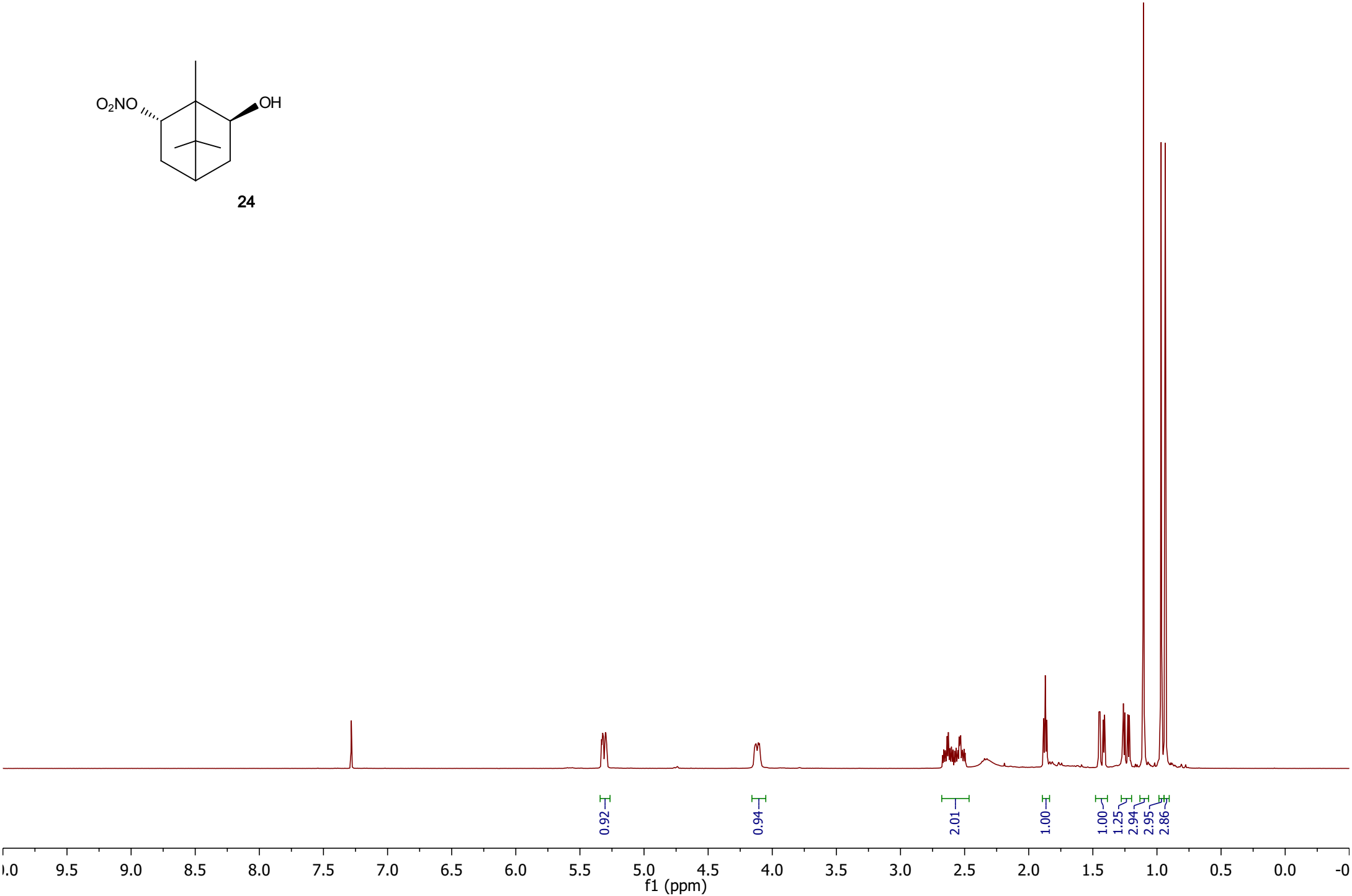

94.13
68.52
53.01
47.34
40.49
37.76
37.10
29.24
19.12
14.75
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


Nitrate ester 23
O2NO
OH
nitrate ester 23
f2 (ppm)
f1 (ppm)
4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
10 20 30 40 50 60 70 80 90 100

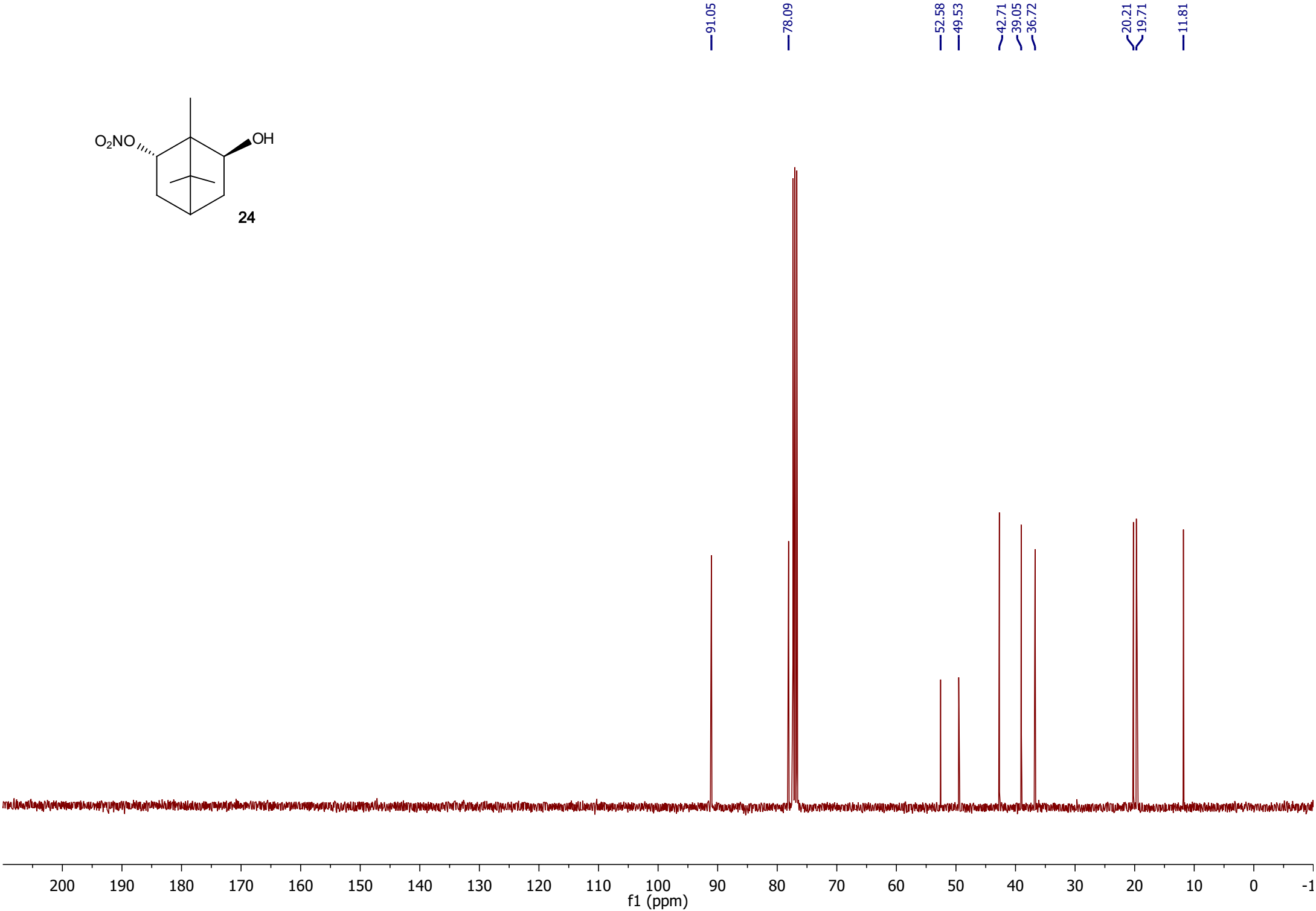

%Transmittance
Wavenumbers (cm-1)
3293.67
2961.23
2360.22
1624.14
1454.94
1367.83
1282.32
1250.94
1142.23
1057.75
1005.82
970.00
952.46
929.71
913.95
862.02
852.24
821.80
O2NO
OH
nitrate ester 23

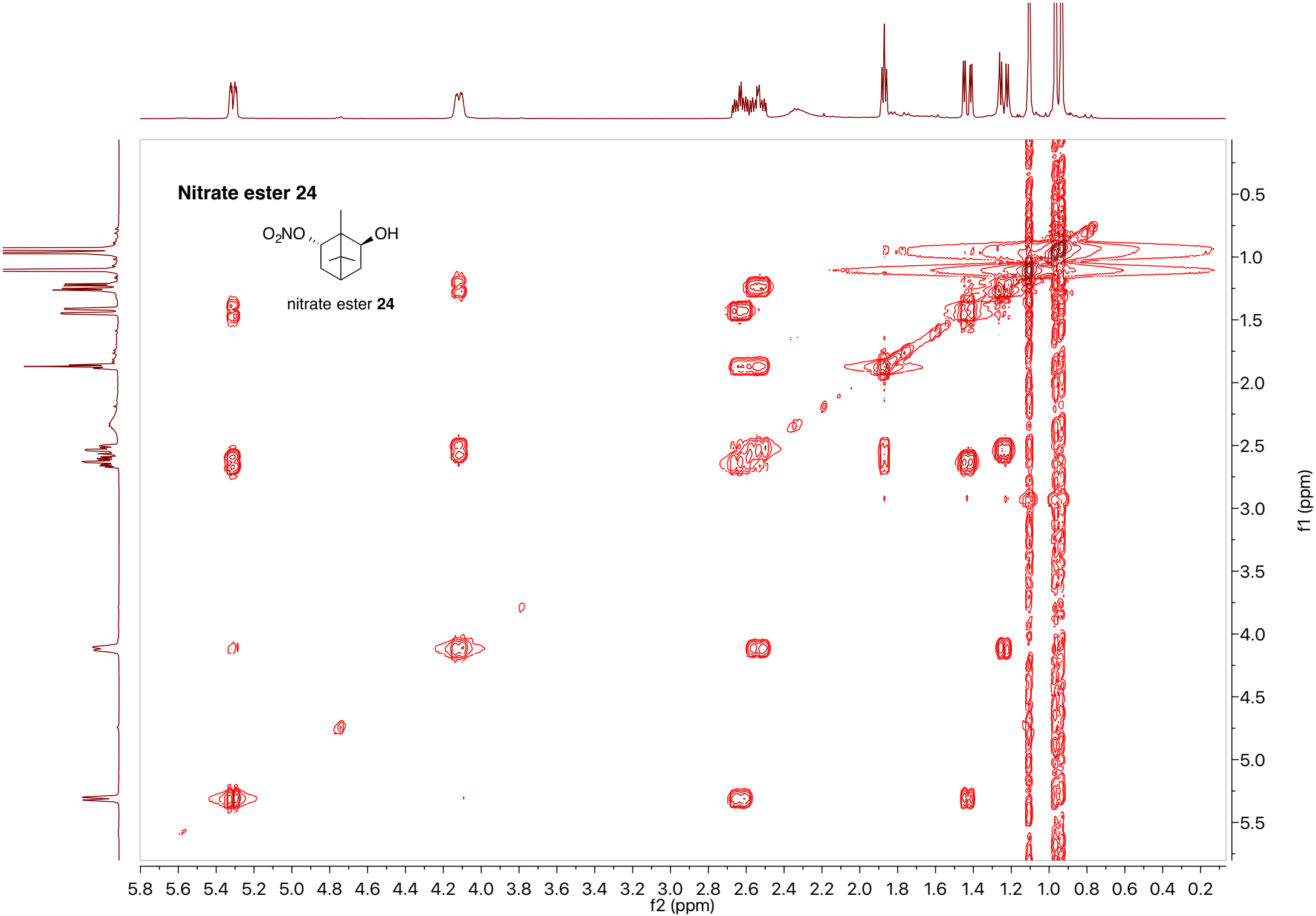
O2NO
OH

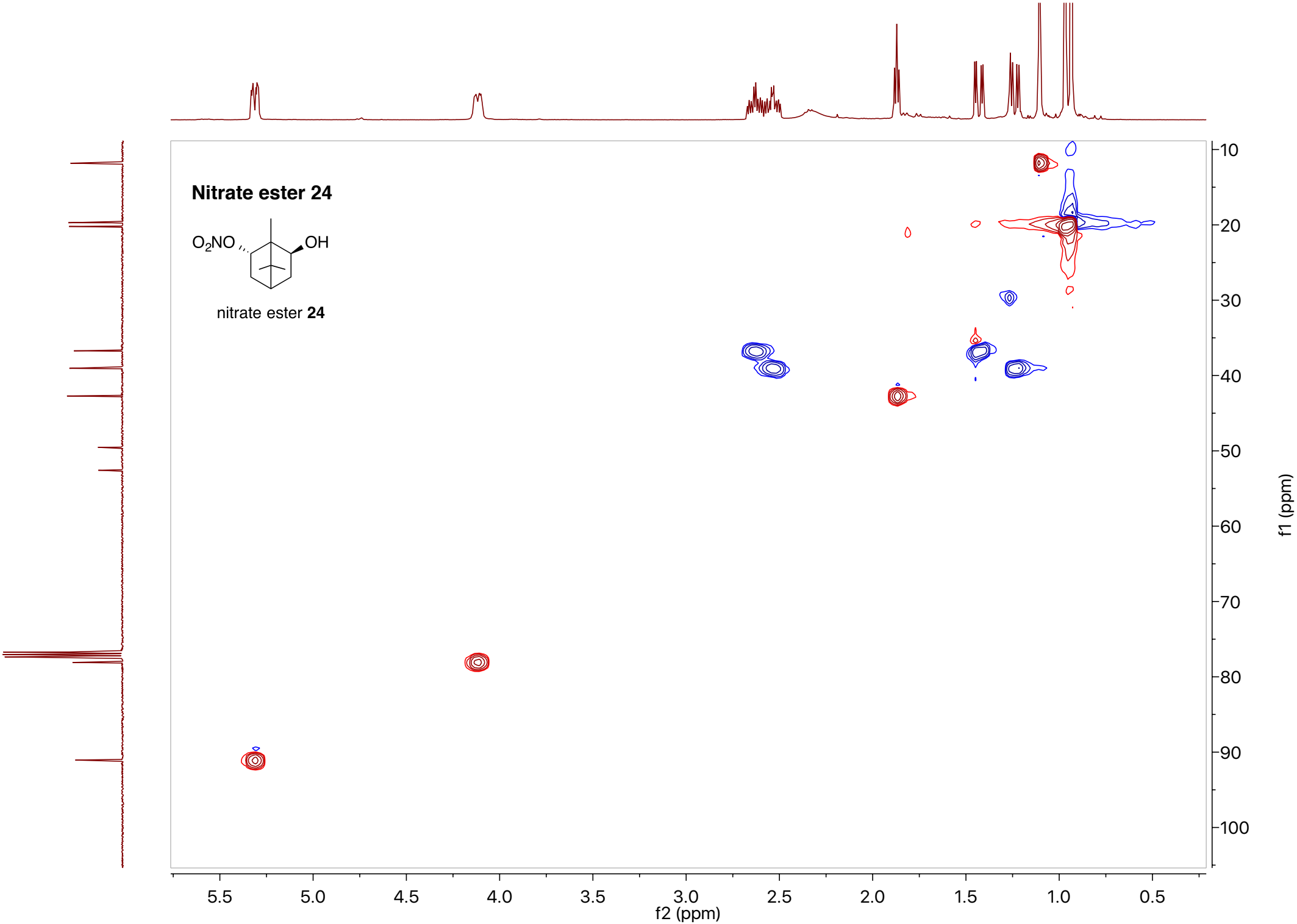
**24**

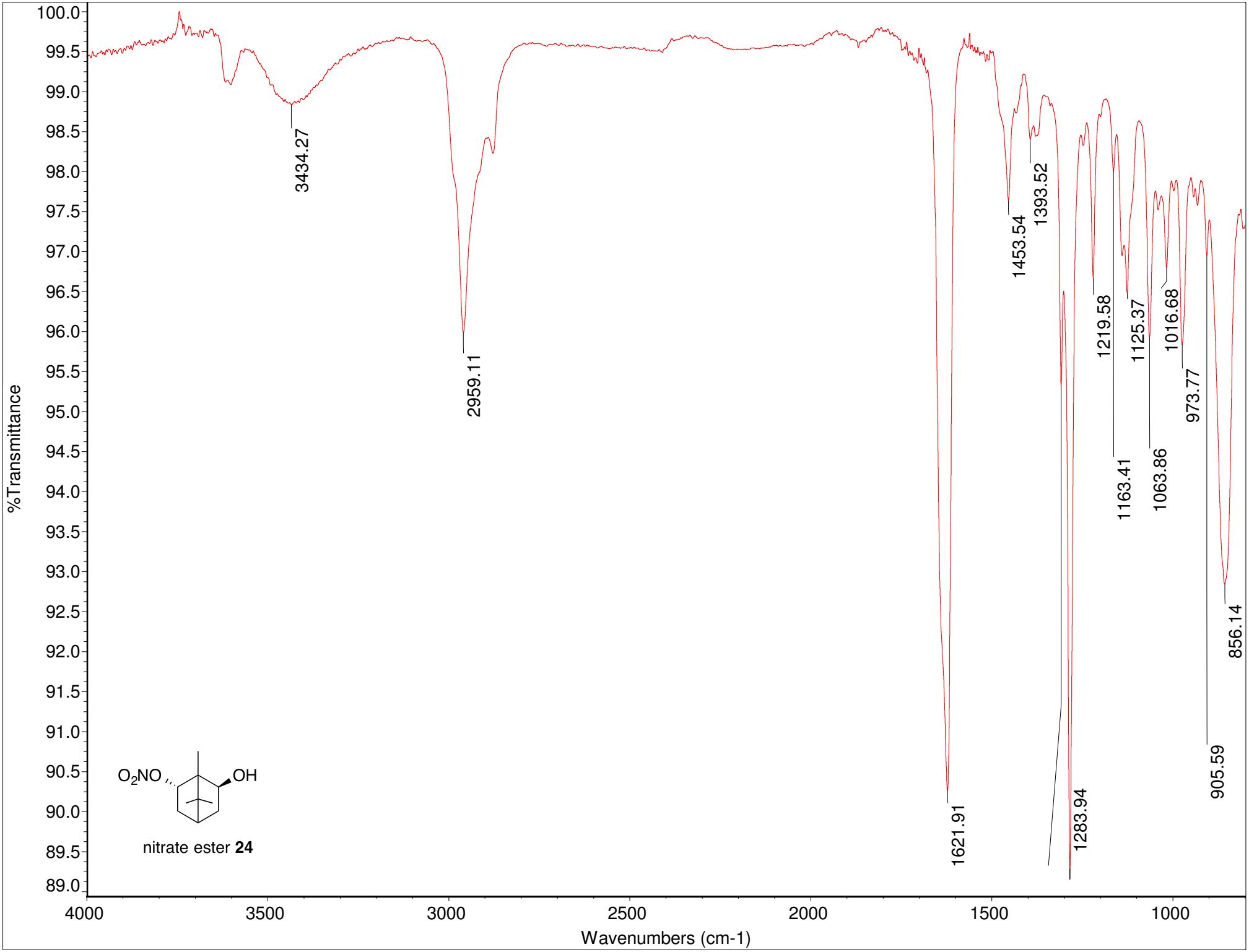

0.92
0.94
2.01
1.00
1.00
1.25
2.94
2.95
2.86
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

O2NO
OH
24

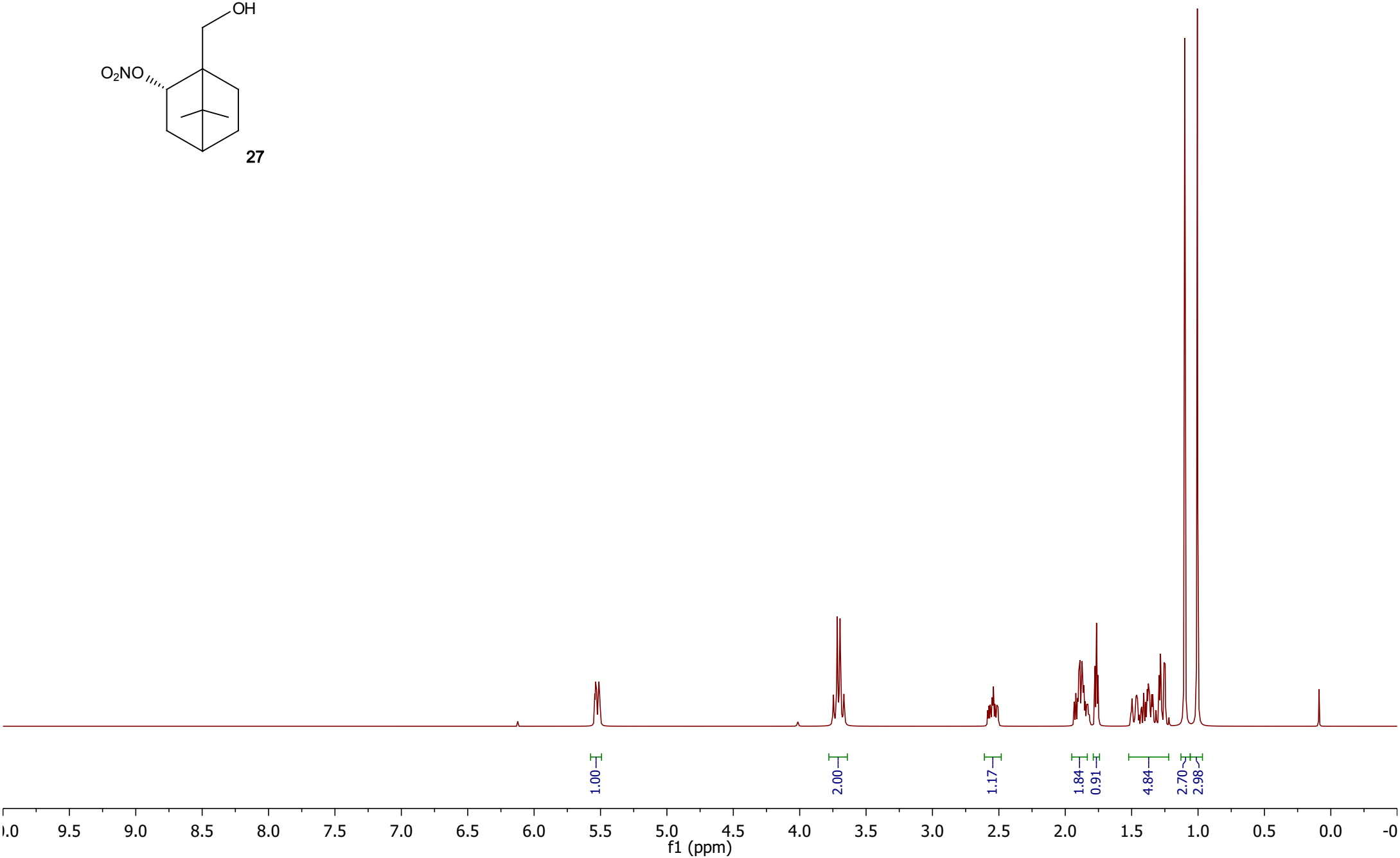

91.05
78.09
52.58
49.53
42.71
39.05
36.72
20.21
19.71
11.81
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


Nitrate ester 24
$O_2NO$
OH
nitrate ester **24**
f2 (ppm)
f1 (ppm)

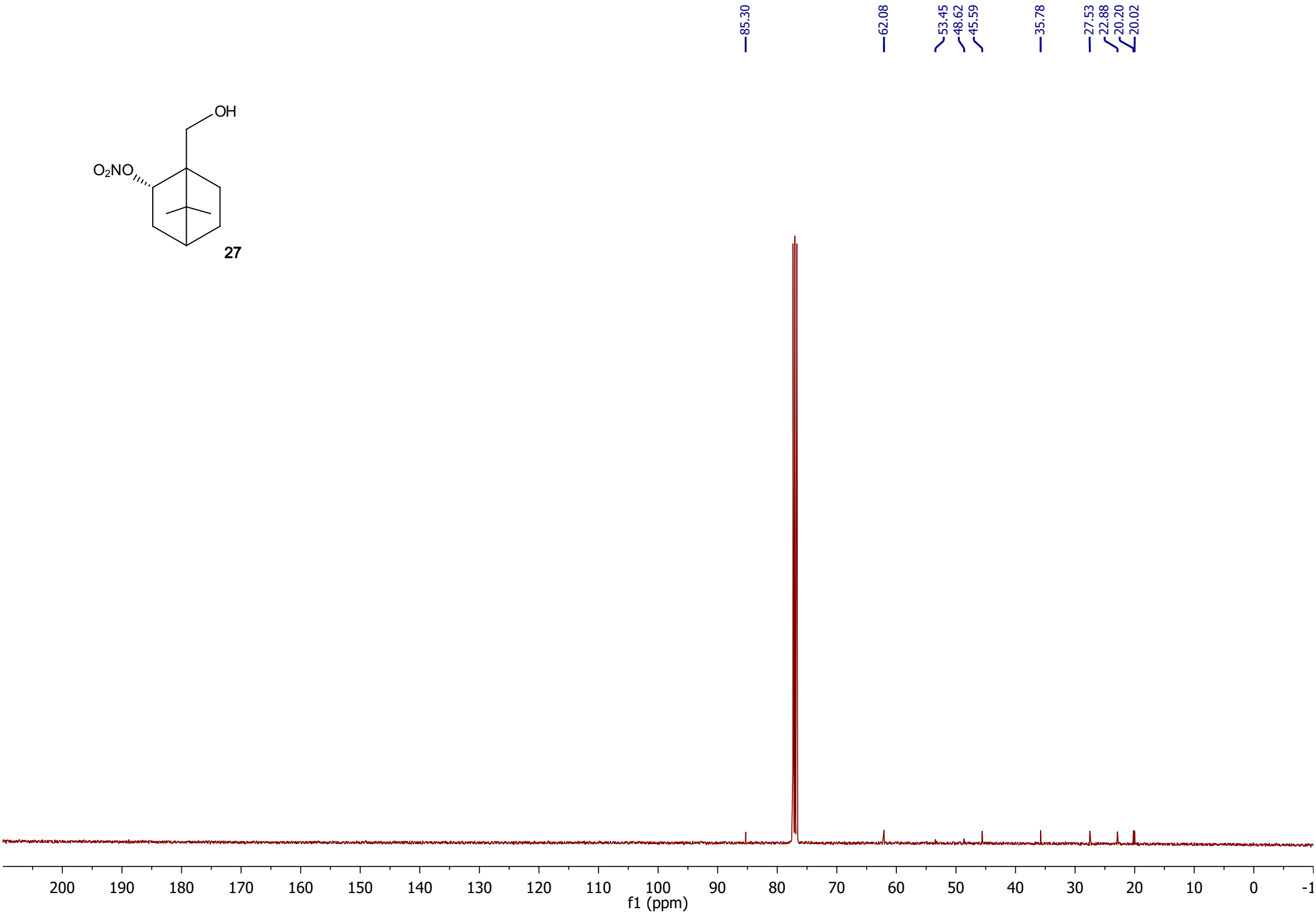

Nitrate ester 24
O2NO
OH
nitrate ester 24
f2 (ppm)
f1 (ppm)
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
10
20
30
40
50
60
70
80
90
100

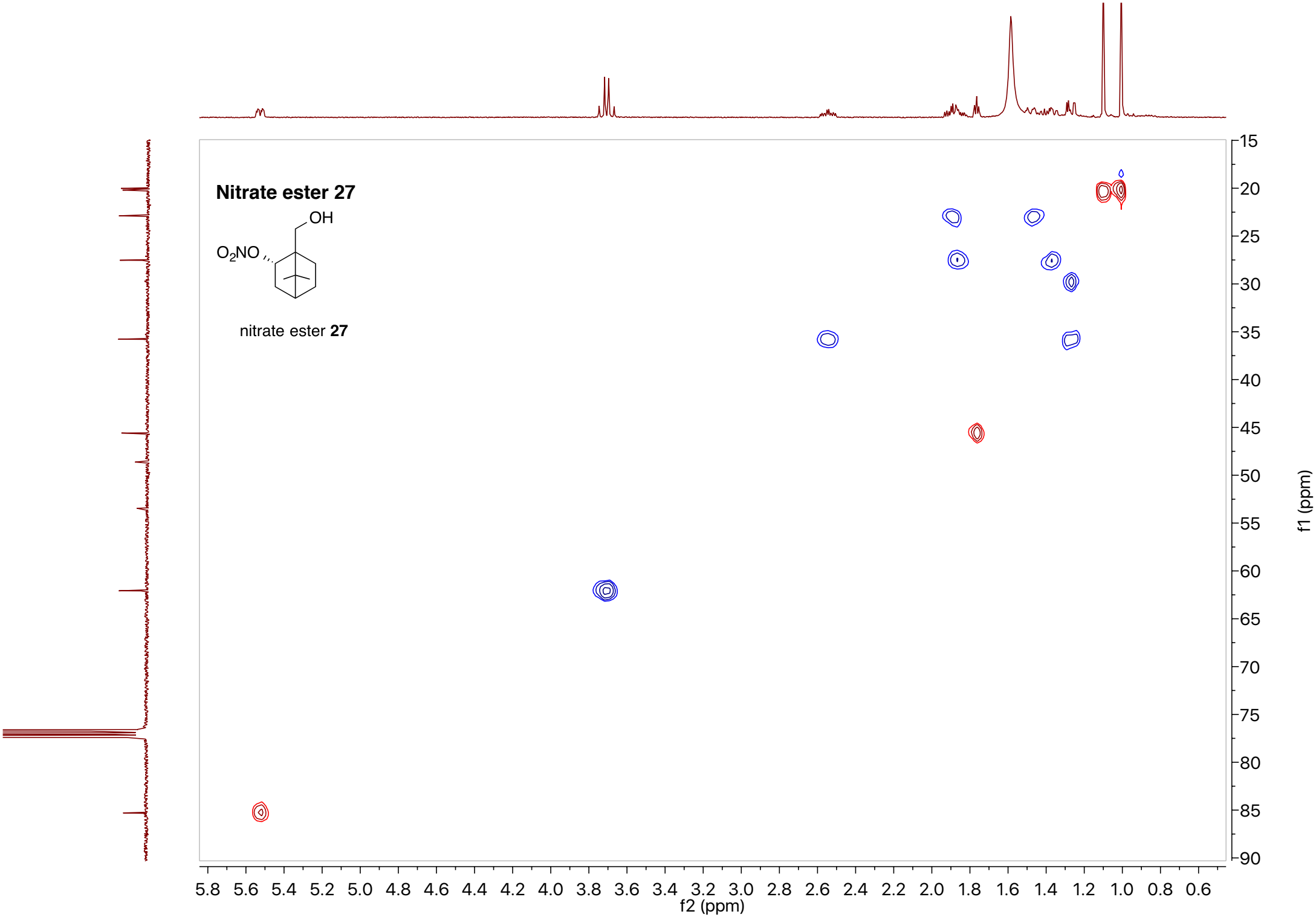

%Transmittance
Wavenumbers (cm-1)
3434.27
2959.11
1621.91
1453.54
1393.52
1283.94
1219.58
1163.41
1125.37
1063.86
1016.68
973.77
905.59
856.14
O2NO
OH
nitrate ester 24

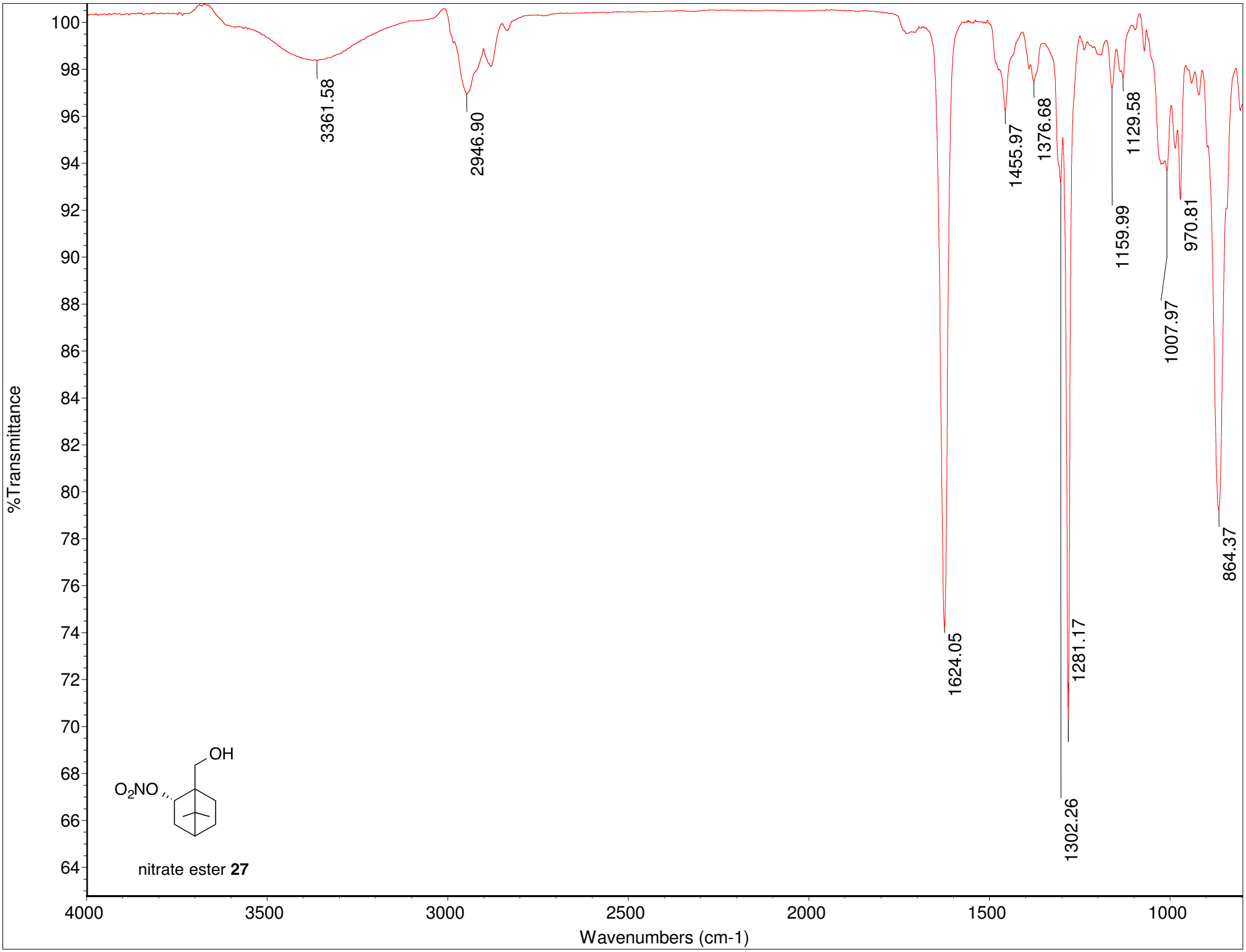
OH
$O_2NO$
27


1.00
2.00
1.17
1.84
0.91
4.84
2.70
2.98
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)

OH
$O_2NO$
27

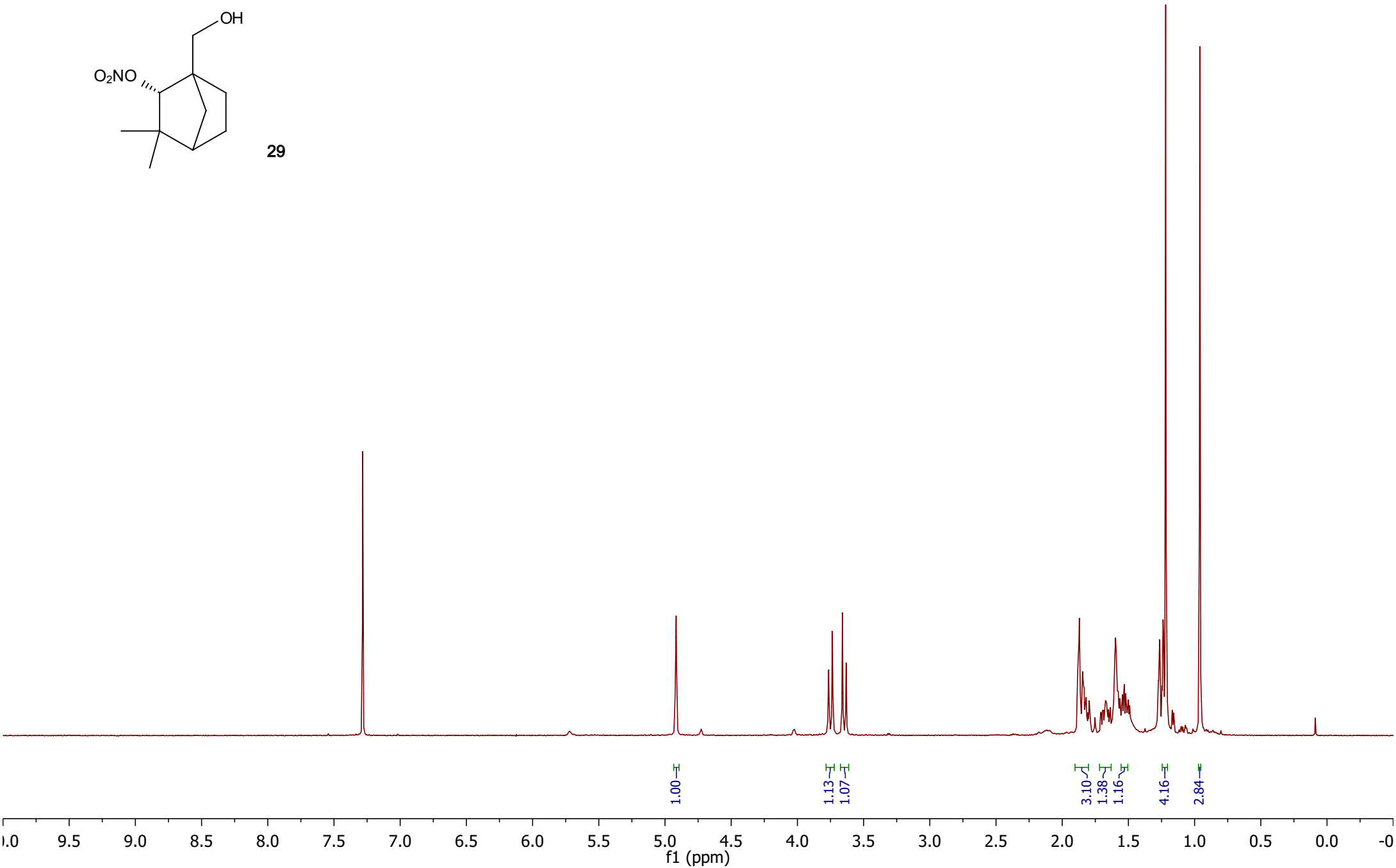

85.30
62.08
53.45
48.62
45.59
35.78
27.53
22.88
20.20
20.02
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


Nitrate ester 27
OH
$O_2NO$
nitrate ester **27**
f2 (ppm)
f1 (ppm)


%Transmittance
Wavenumbers (cm-1)
3361.58
2946.90
1624.05
1455.97
1376.68
1302.26
1281.17
1159.99
1129.58
1007.97
970.81
864.37
OH
O2NO
nitrate ester 27

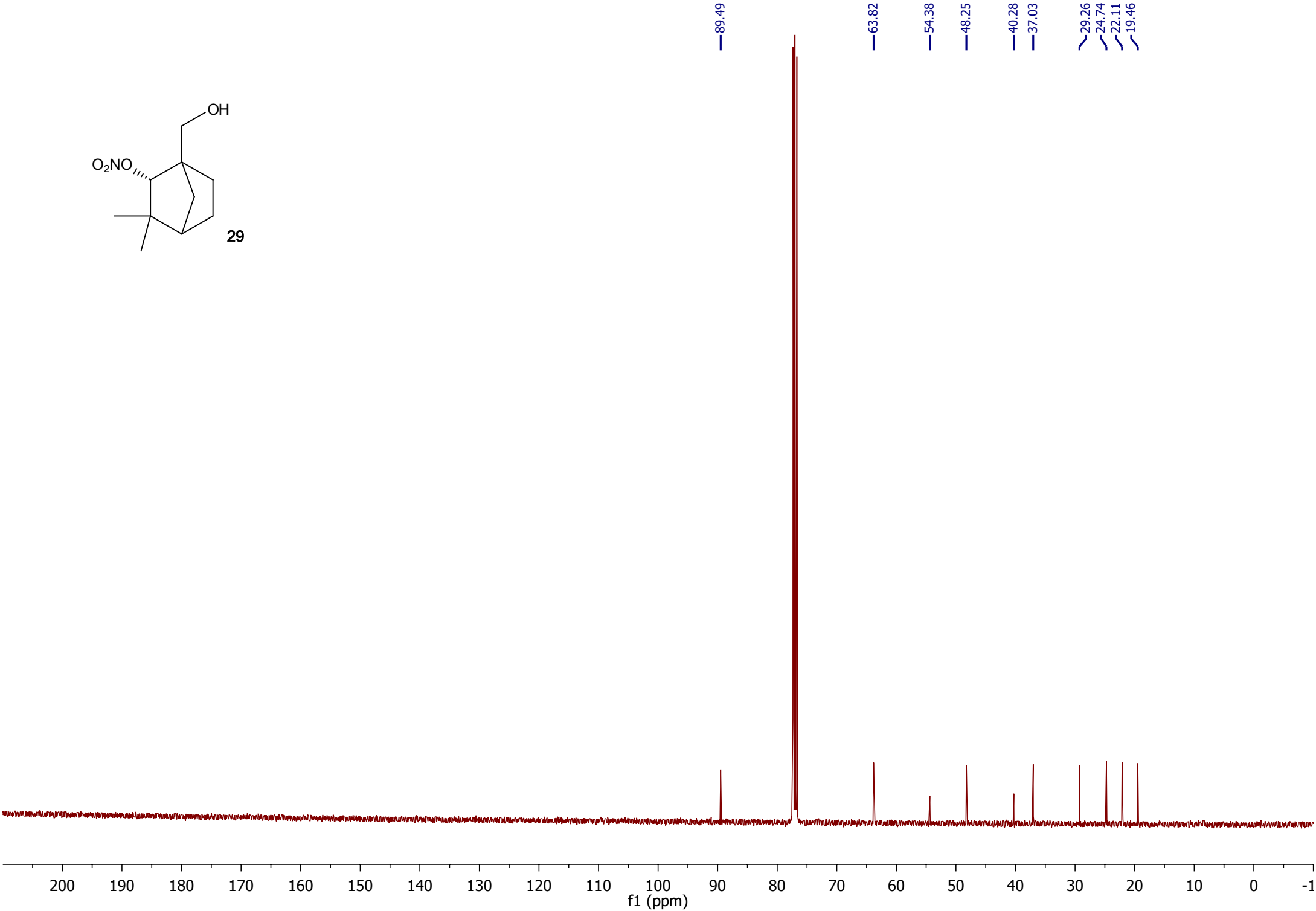
OH
O2NO

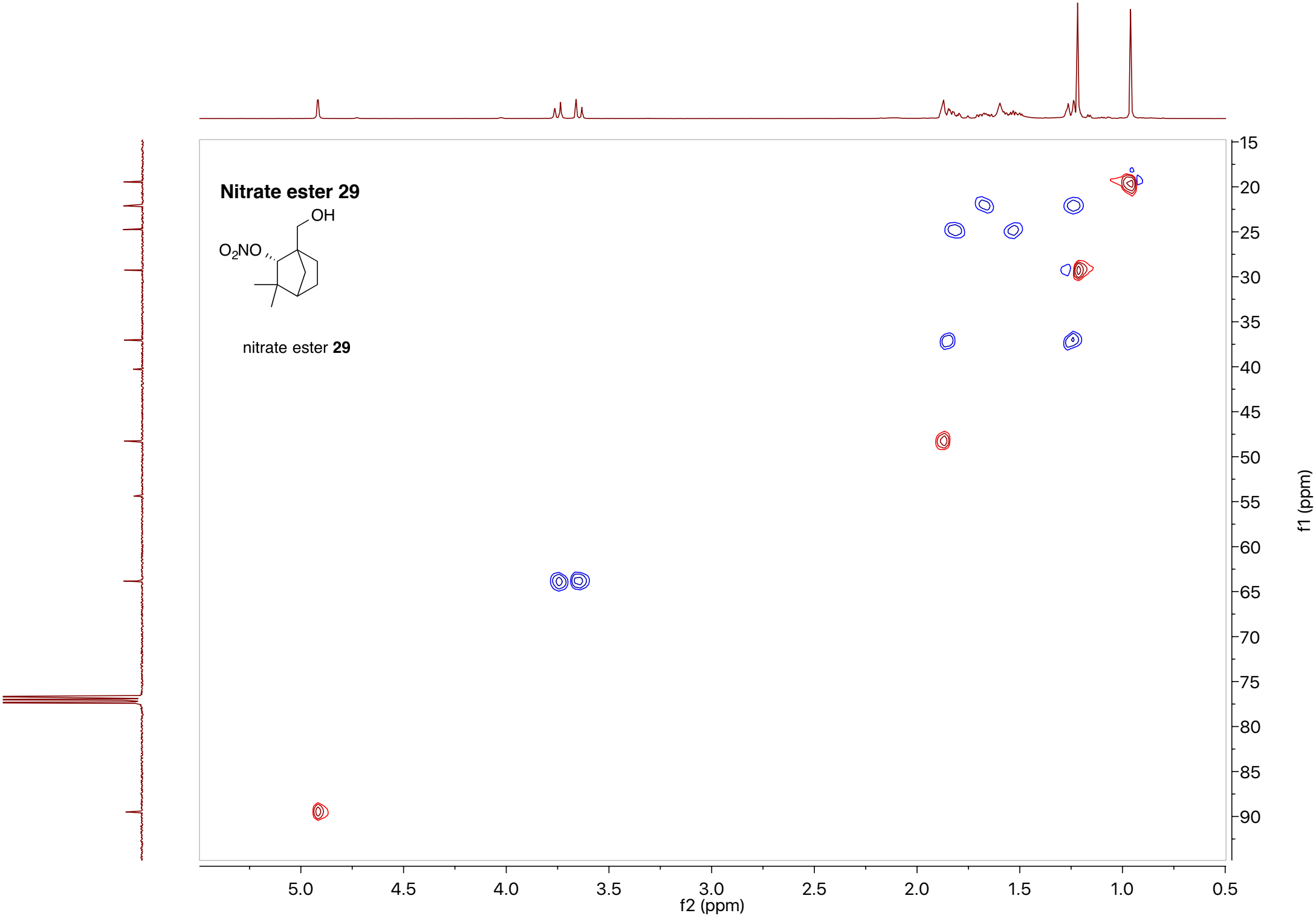
**29**

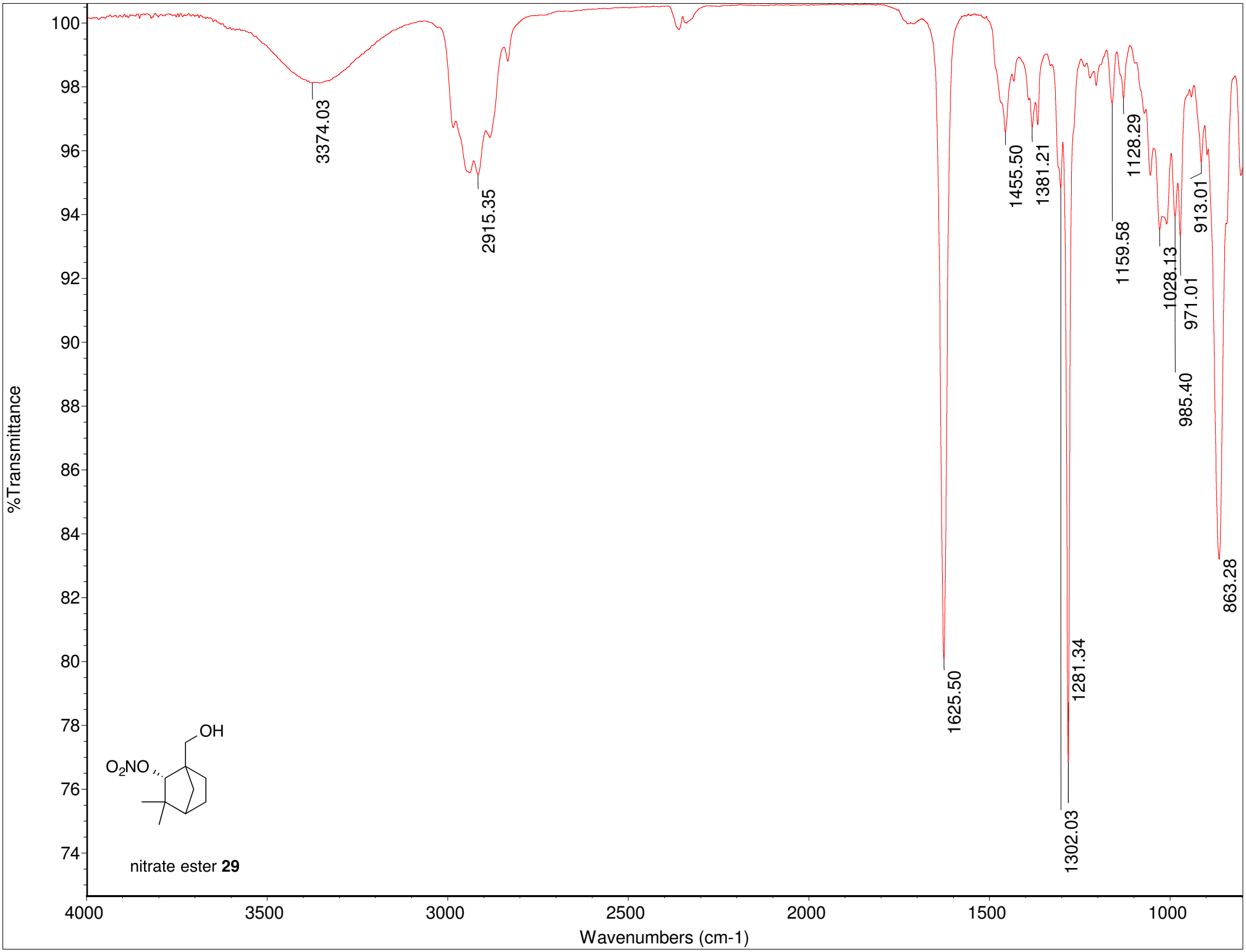

1.00
1.13
1.07
3.10
1.38
1.16
4.16
2.84
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

OH
$O_2NO$

29


89.49
63.82
54.38
48.25
40.28
37.03
29.26
24.74
22.11
19.46
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


Nitrate ester 29
OH
$O_2NO$
nitrate ester **29**
f2 (ppm)
f1 (ppm)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90


%Transmittance
Wavenumbers (cm-1)
3374.03
2915.35
1625.50
1455.50
1381.21
1302.03
1281.34
1159.58
1128.29
1028.13
985.40
971.01
913.01
863.28
OH
$O_2NO$
nitrate ester **29**