Supporting Information for:

Heck Cyclization Strategy for Preparation of Erythrinan Alkaloids: asymmetric Synthesis of Unnatural (-)-Erysotramidine from *L*-Tartaric Acid

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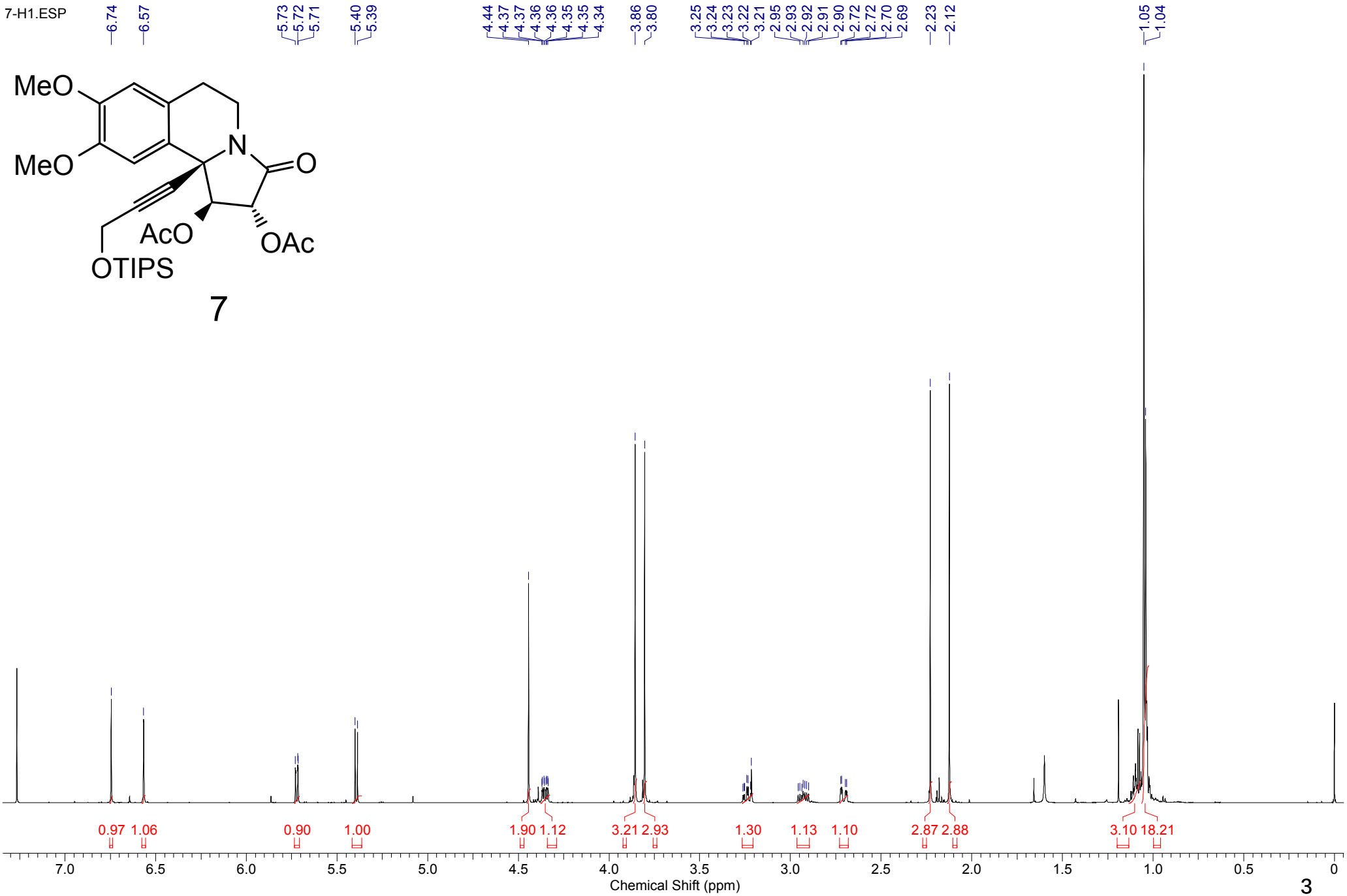
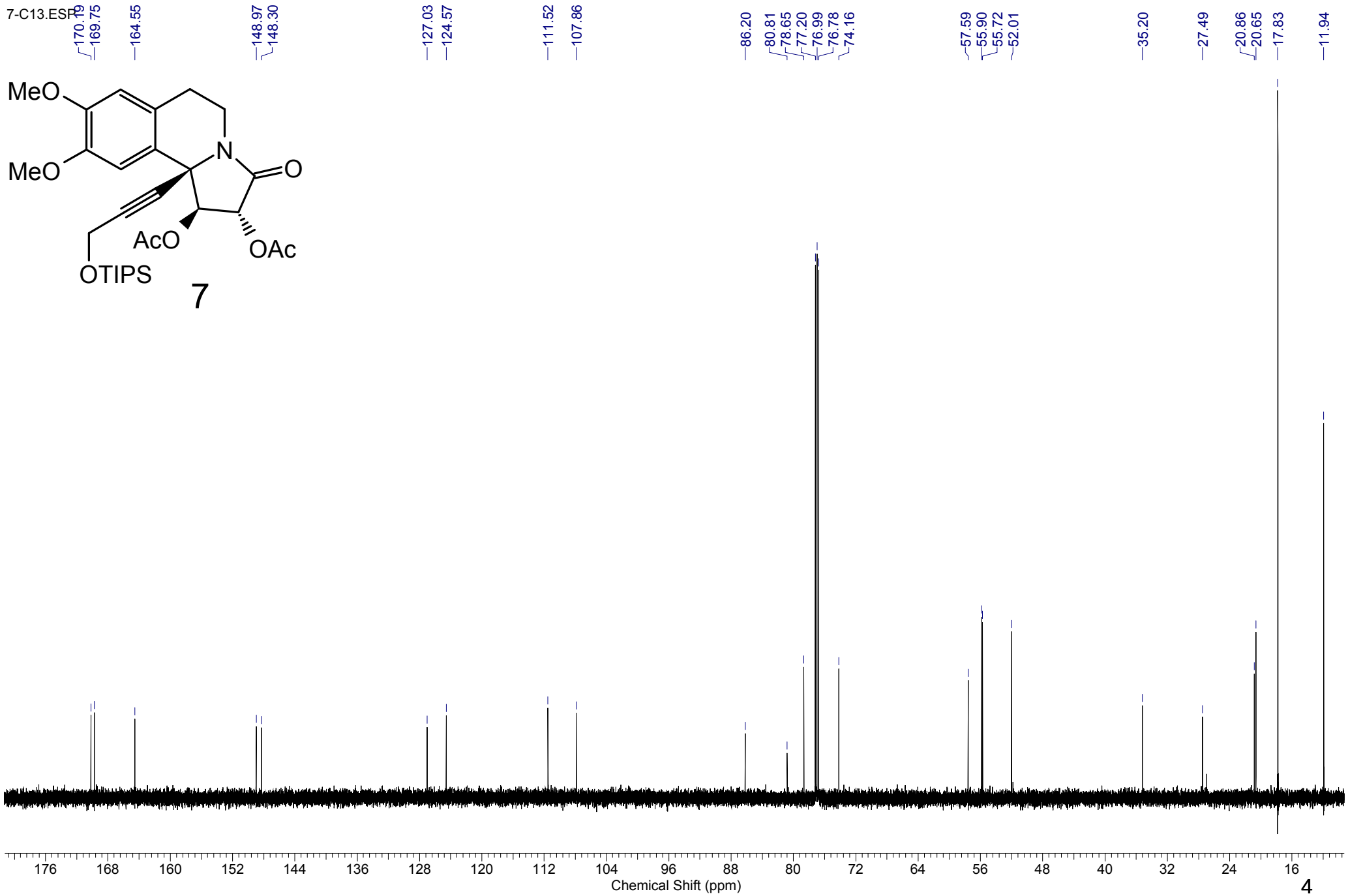
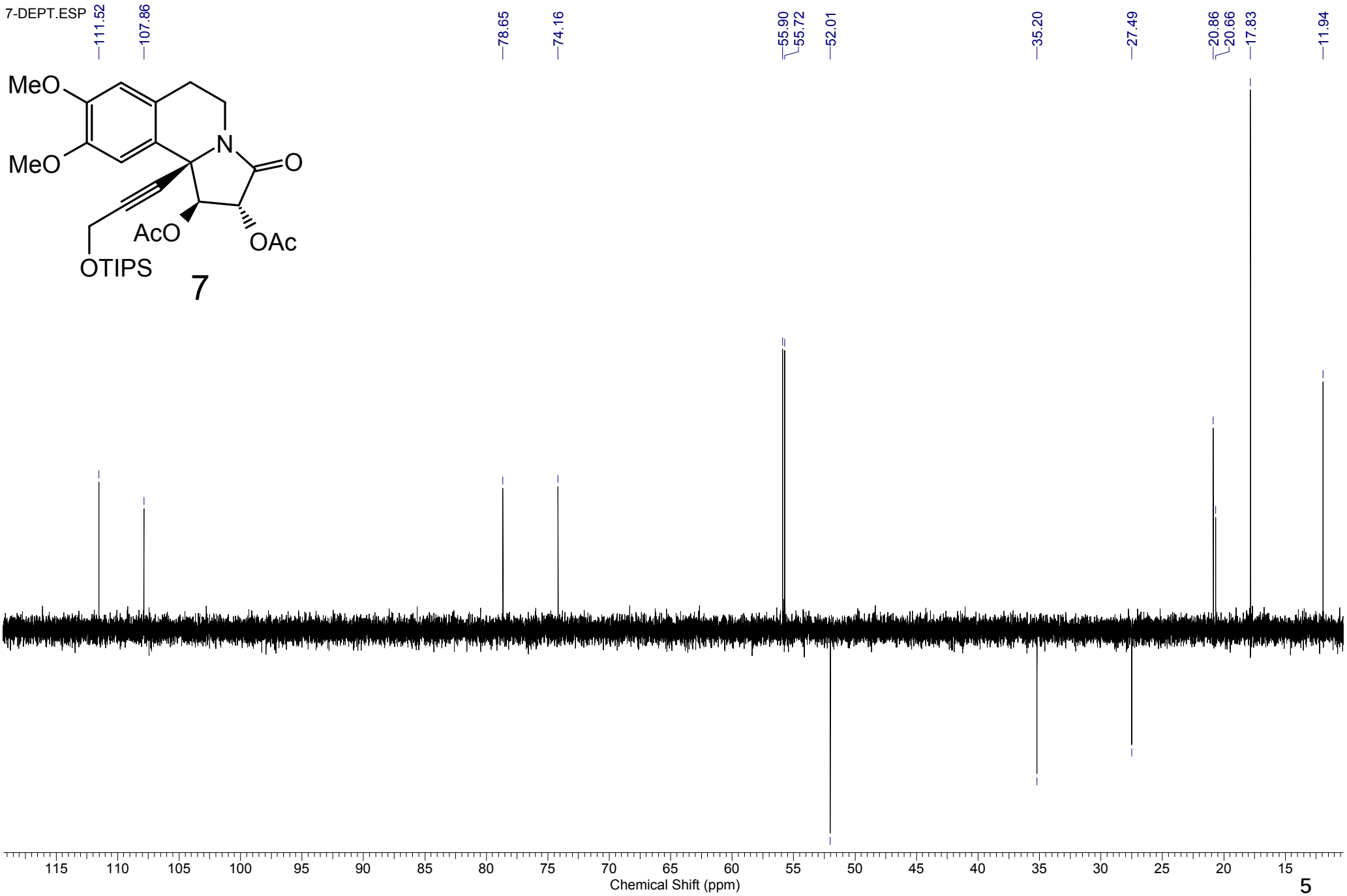
1. General information

NMR spectra were acquired on commercial instruments (500 MHz) at room temperature (except where indicated otherwise). Chemical shifts are quoted in parts per million (ppm) relative to TMS for ^{1}H and $CDCl_3$ for ^{13}C NMR. Coupling constants J are reported in Hertz (Hz). IR spectra were obtained using a FTIR commercial instrument and reported in reciprocal centimeters (cm^{-1}). HRMS mass spectra were recorded on a magnetic sector mass spectrometer, equipped with an electron impact (EI) ion source and the EBE double focusing geometry mass analyzer or on mass spectrometer equipped with an electrospray ion source and q-TOF type mass analyzer. Optical rotations were measured at 23 °C using commercial digital polarimeter. Thin-layer chromatography was carried out on precoated silica gel (Kieselgel 60 F254, 0.2 mm layer thickness). Visualization of the developed chromatogram was done either by UV absorbance or by spraying with cerium molybdate water solution or ninhidrine ethanol solution. Flash column chromatography was performed using silica gel (Kieselgel 230–400 mesh). All air and moisture sensitive reactions were carried out under an argon atmosphere in a flame-dried glassware using anhydrous solvents. Most reagents were obtained from commercial suppliers and were used without further purification, unless otherwise noted. THF was distilled from Na and benzophenone, dichloromethane and toluene were distilled from CaH_2.

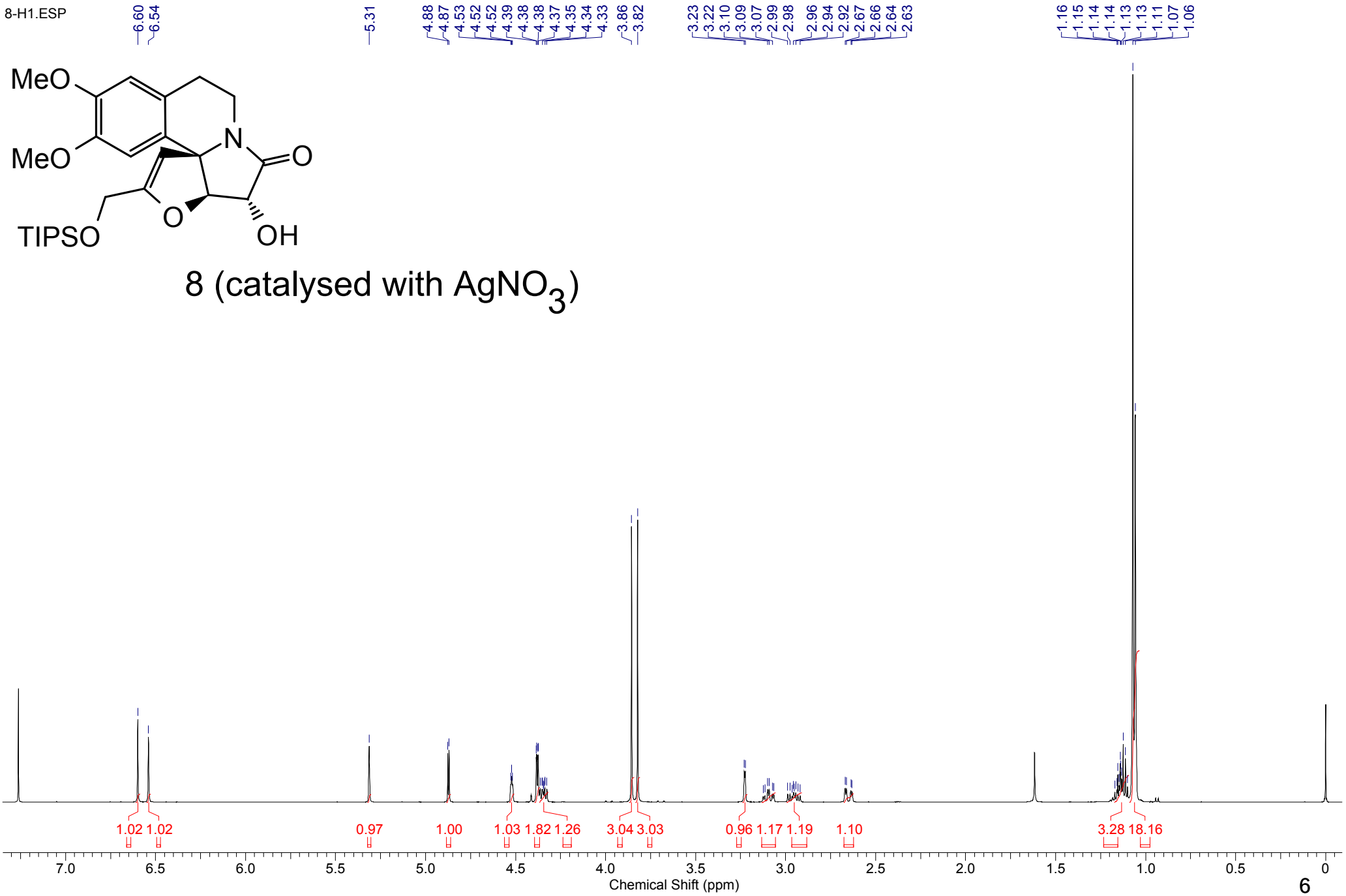
2. ^{1}H-NMR and ^{13}C-NMR spectra for all products


7-H1.ESP
6.74
6.57
5.73
5.72
5.71
5.40
5.39
4.44
4.37
4.37
4.36
4.36
4.35
4.35
4.34
3.86
3.80
3.25
3.24
3.23
3.22
3.21
2.95
2.93
2.92
2.91
2.90
2.72
2.72
2.70
2.69
2.23
2.12
1.05
1.04
MeO
MeO
N
O
AcO
OAc
OTIPS
7
0.97 1.06
0.90
1.00
1.90 1.12
3.21 2.93
1.30
1.13
1.10
2.87 2.88
3.10 18.21
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
Chemical Shift (ppm)

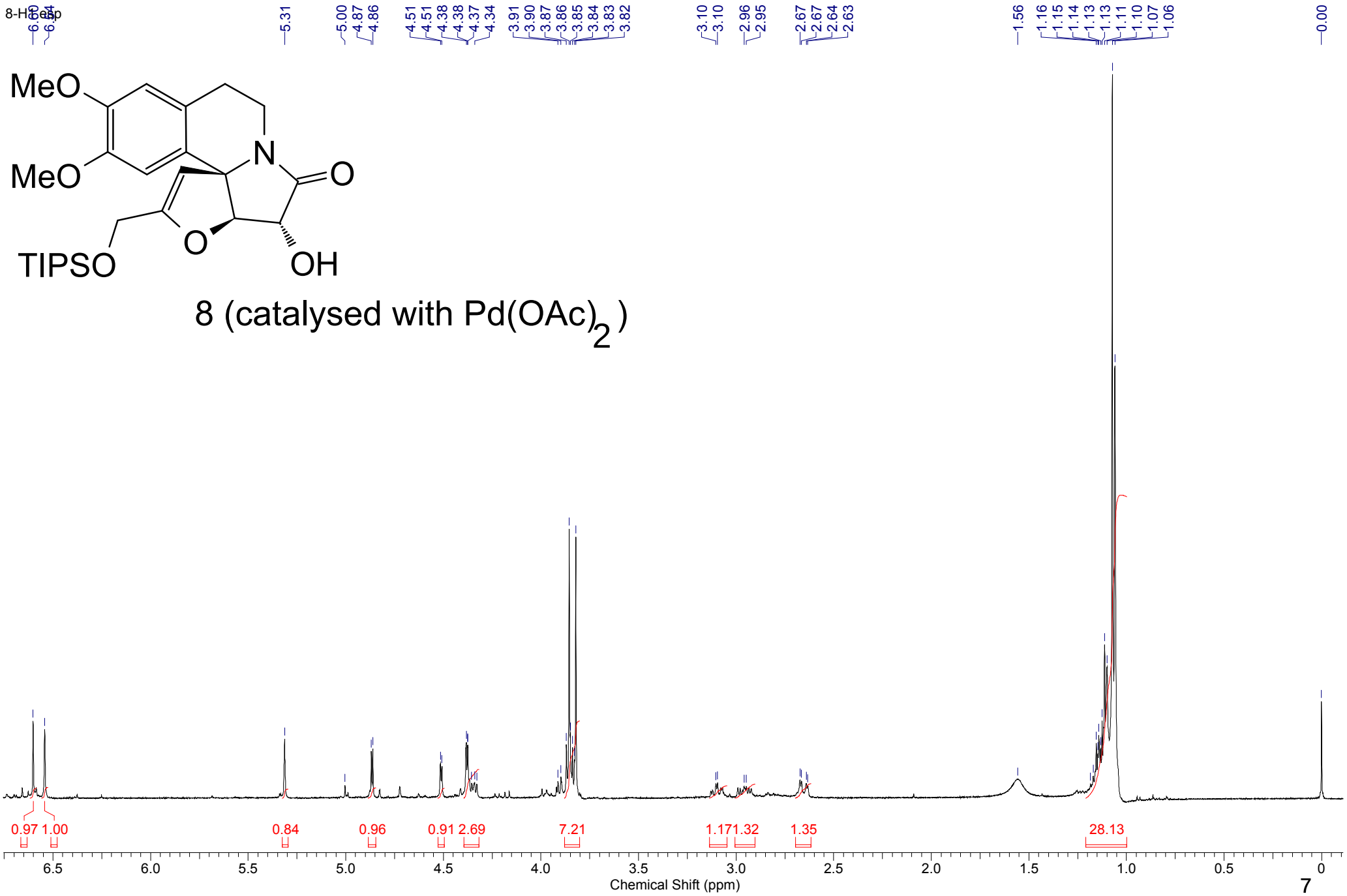

7-C13.ESP
170.19
169.75
164.55
148.97
148.30
127.03
124.57
111.52
107.86
86.20
80.81
78.65
77.20
76.99
76.78
74.16
57.59
55.90
55.72
52.01
35.20
27.49
20.86
20.65
17.83
11.94
MeO
MeO
N
O
AcO
OAc
OTIPS
7
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)

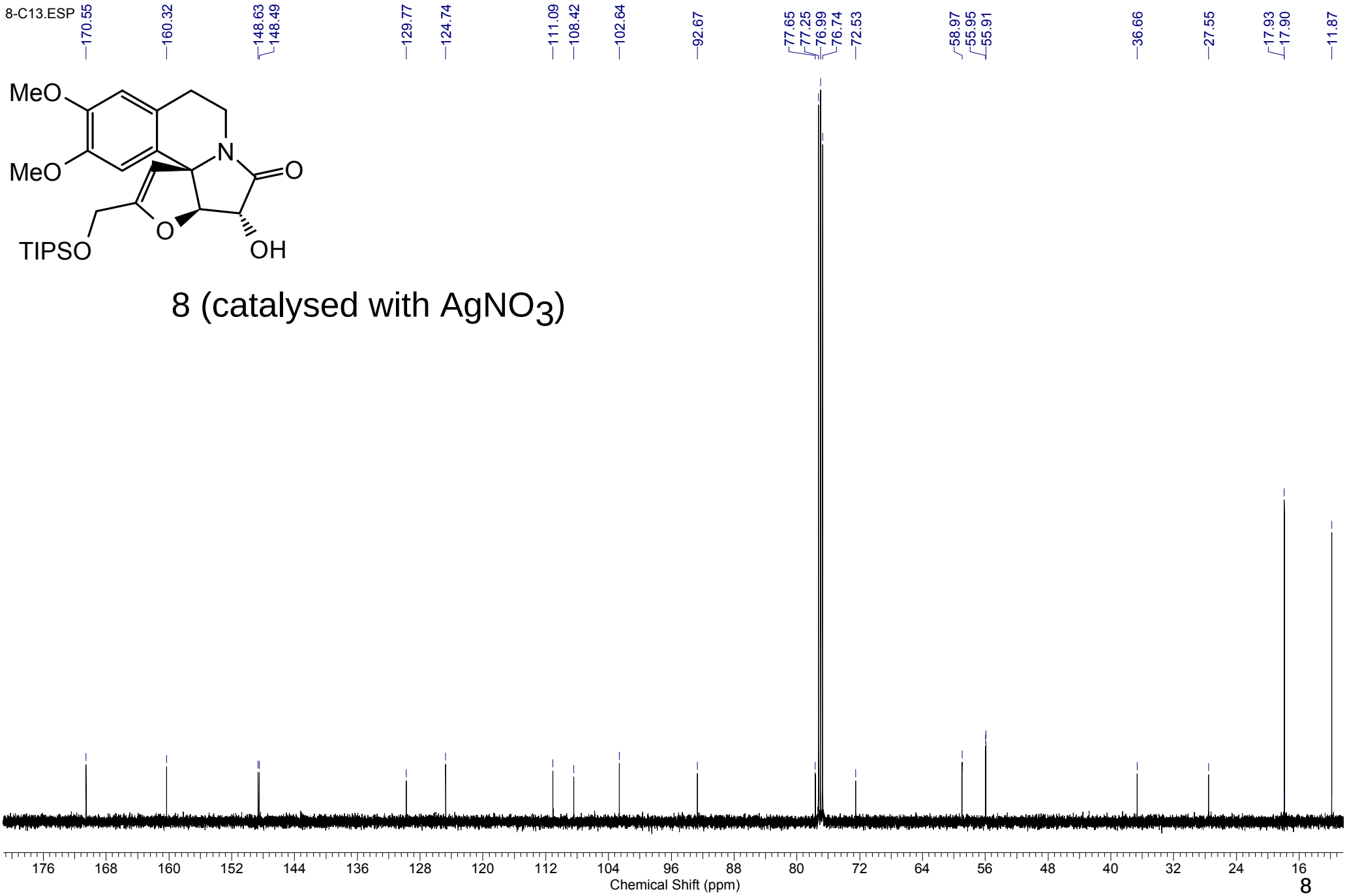

7-DEPT.ESP
111.52
107.86
78.65
74.16
55.90
55.72
52.01
35.20
27.49
20.86
20.66
17.83
11.94
MeO
MeO
N
O
AcO
OAc
OTIPS
7
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
Chemical Shift (ppm)

8-H1.ESP

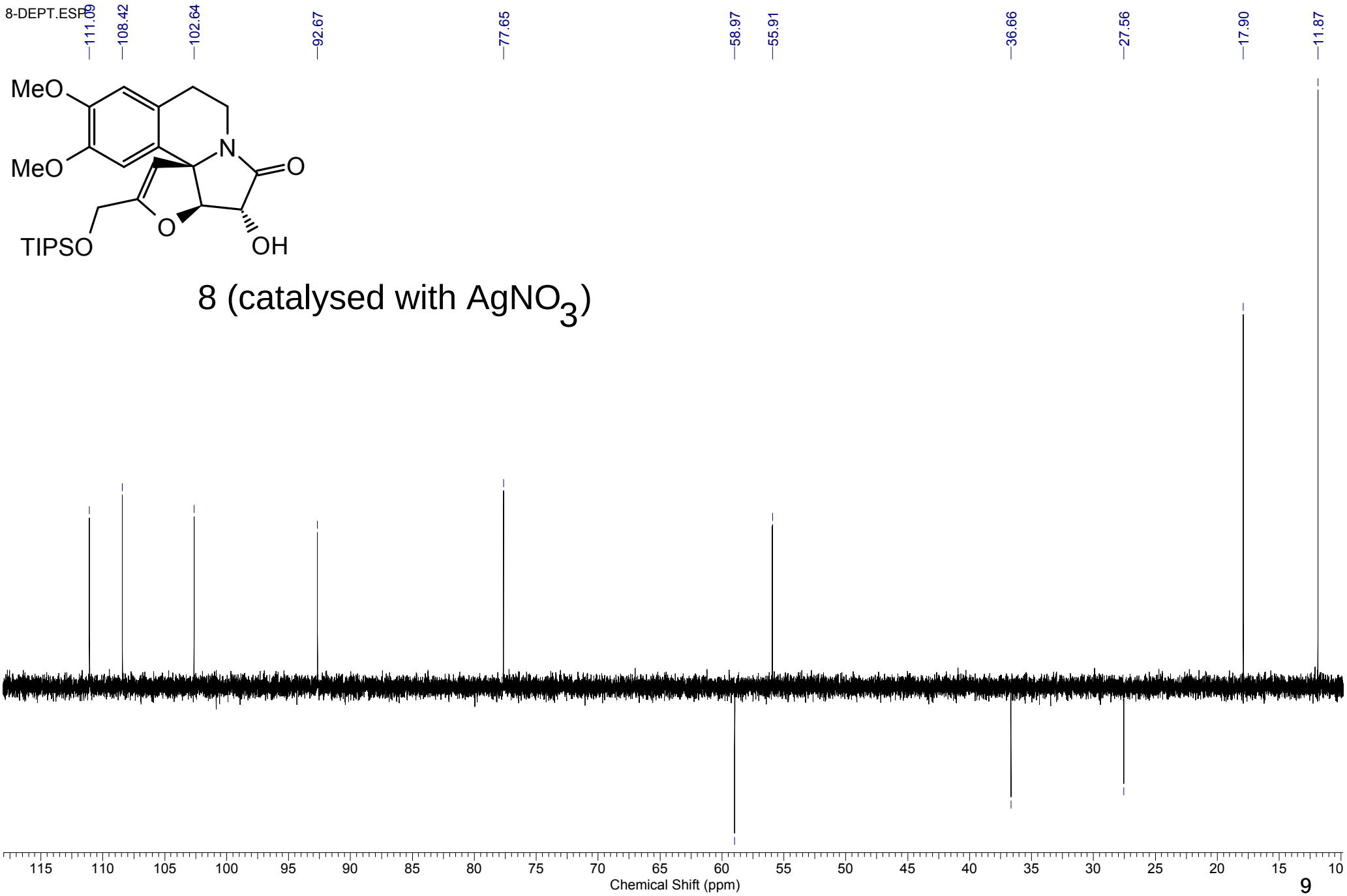


8 (catalysed with $AgNO_3$)

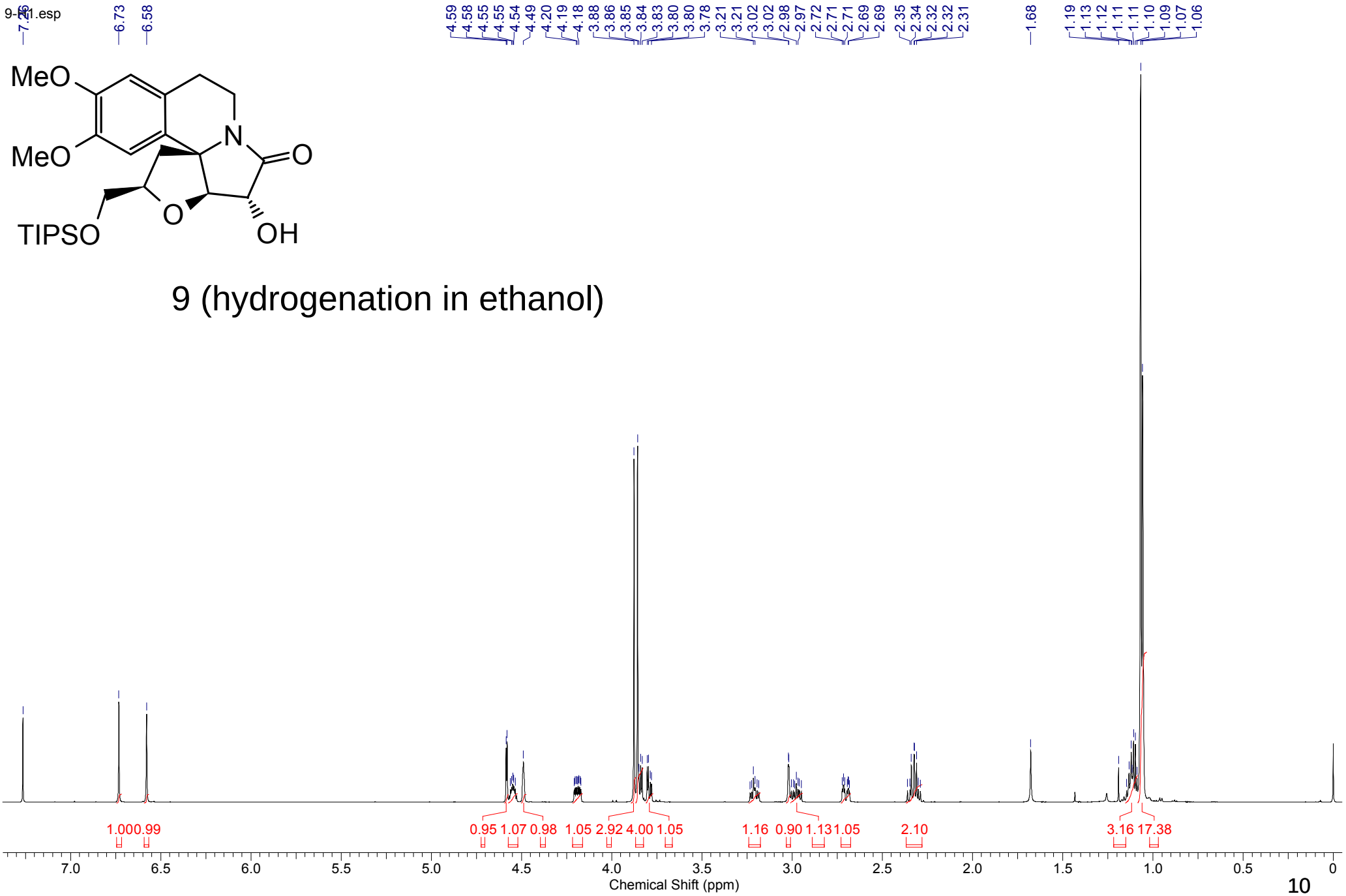

8-Hcasp
MeO
MeO
N
O
O
TIPSO
OH
8 (catalysed with Pd(OAc)2)
6.60 6.54 5.31 5.00 4.87 4.86 4.51 4.51 4.38 4.38 4.37 4.34 3.91 3.90 3.87 3.86 3.85 3.84 3.83 3.82 3.10 3.10 2.96 2.95 2.67 2.67 2.64 2.63 1.56 1.16 1.15 1.14 1.13 1.13 1.11 1.10 1.07 1.06 0.00
0.97 1.00 0.84 0.96 0.91 2.69 7.21 1.17 1.32 1.35 28.13
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
Chemical Shift (ppm)

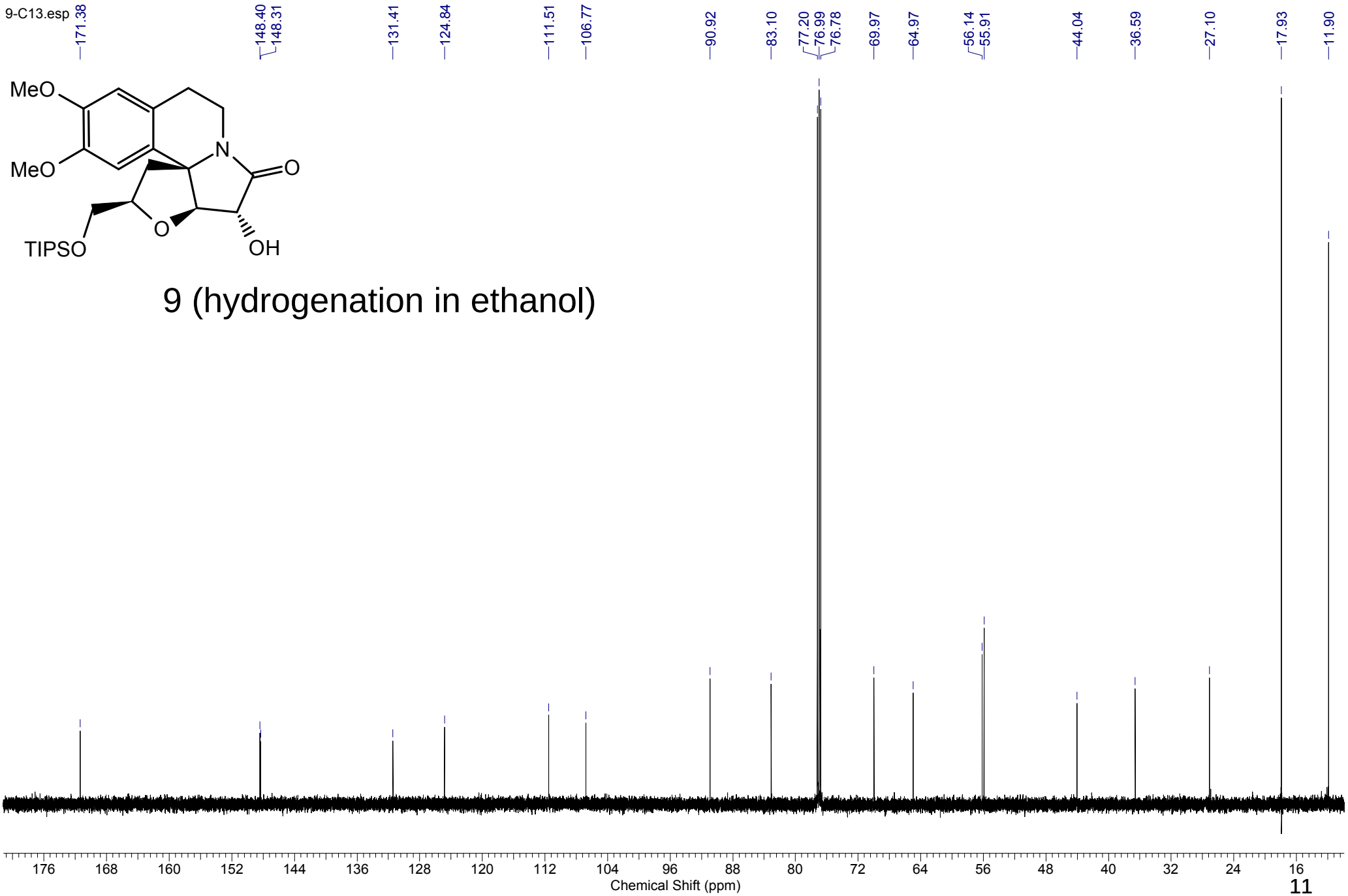


8 (catalysed with $AgNO_3$)



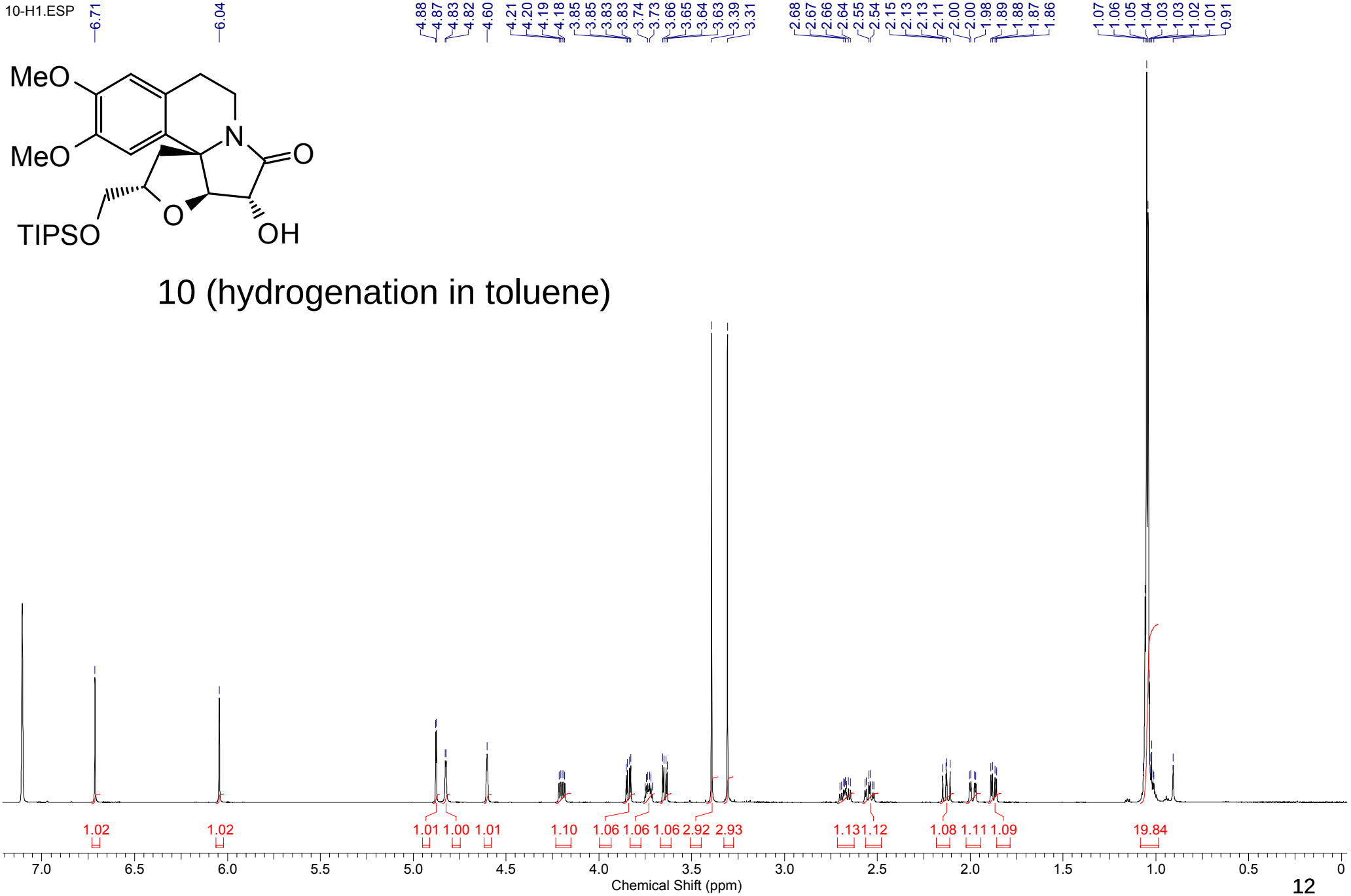
8 (catalysed with $AgNO_3$)


9-H1.esp
MeO
MeO
N
O
O
TIPSO
OH
9 (hydrogenation in ethanol)
7.26
6.73
6.58
4.59 4.58 4.55 4.55 4.54 4.49 4.20 4.19 4.18 3.88 3.86 3.85 3.84 3.83 3.80 3.80 3.78 3.21 3.21 3.02 3.02 2.98 2.97 2.72 2.71 2.71 2.69 2.69 2.35 2.34 2.32 2.32 2.31
1.68
1.19 1.13 1.12 1.11 1.11 1.10 1.09 1.07 1.06
1.00 0.99
0.95 1.07 0.98 1.05 2.92 4.00 1.05
1.16 0.90 1.13 1.05
2.10
3.16 17.38
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
Chemical Shift (ppm)

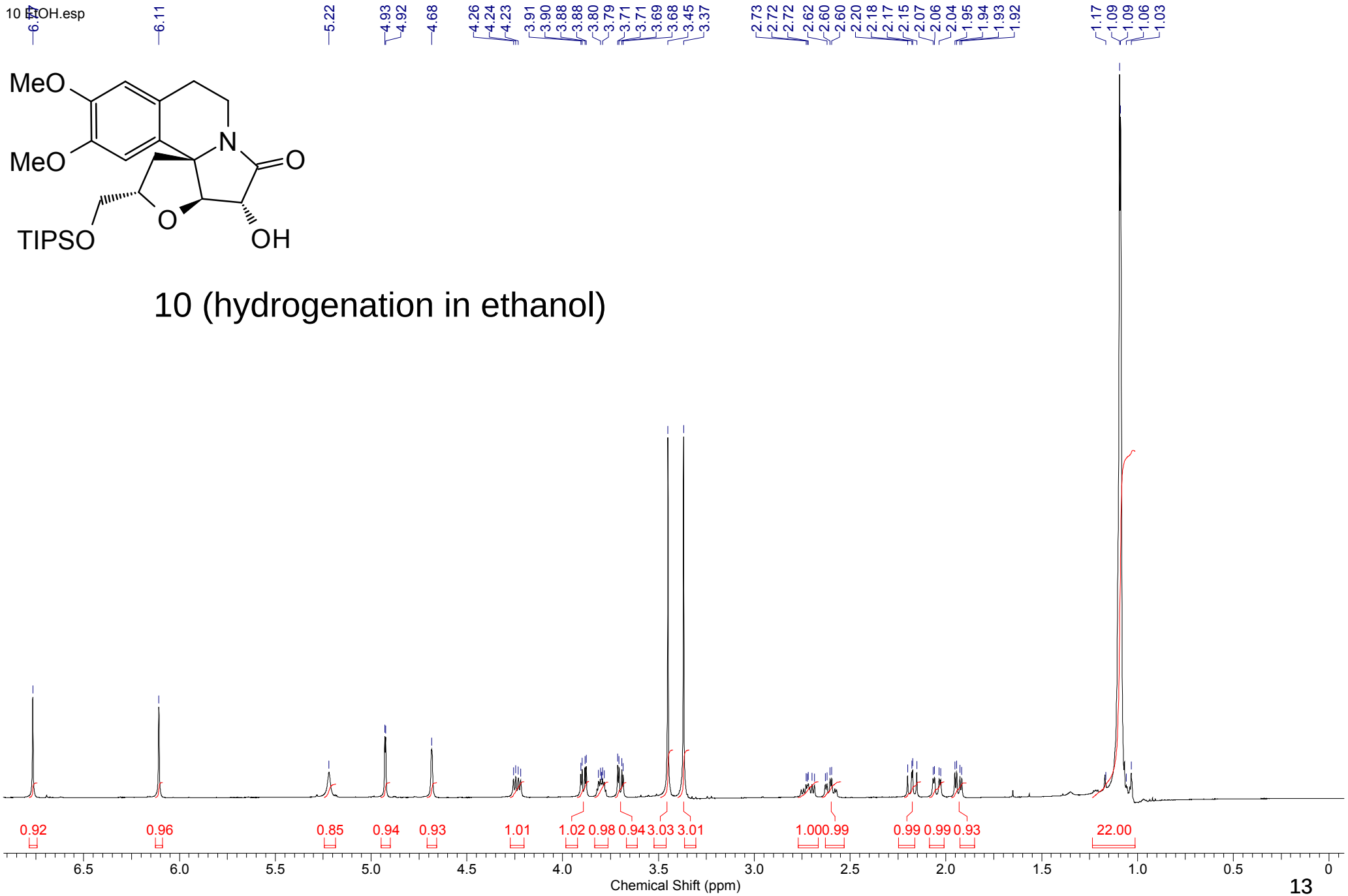


9 (hydrogenation in ethanol)

10-H1.ESP

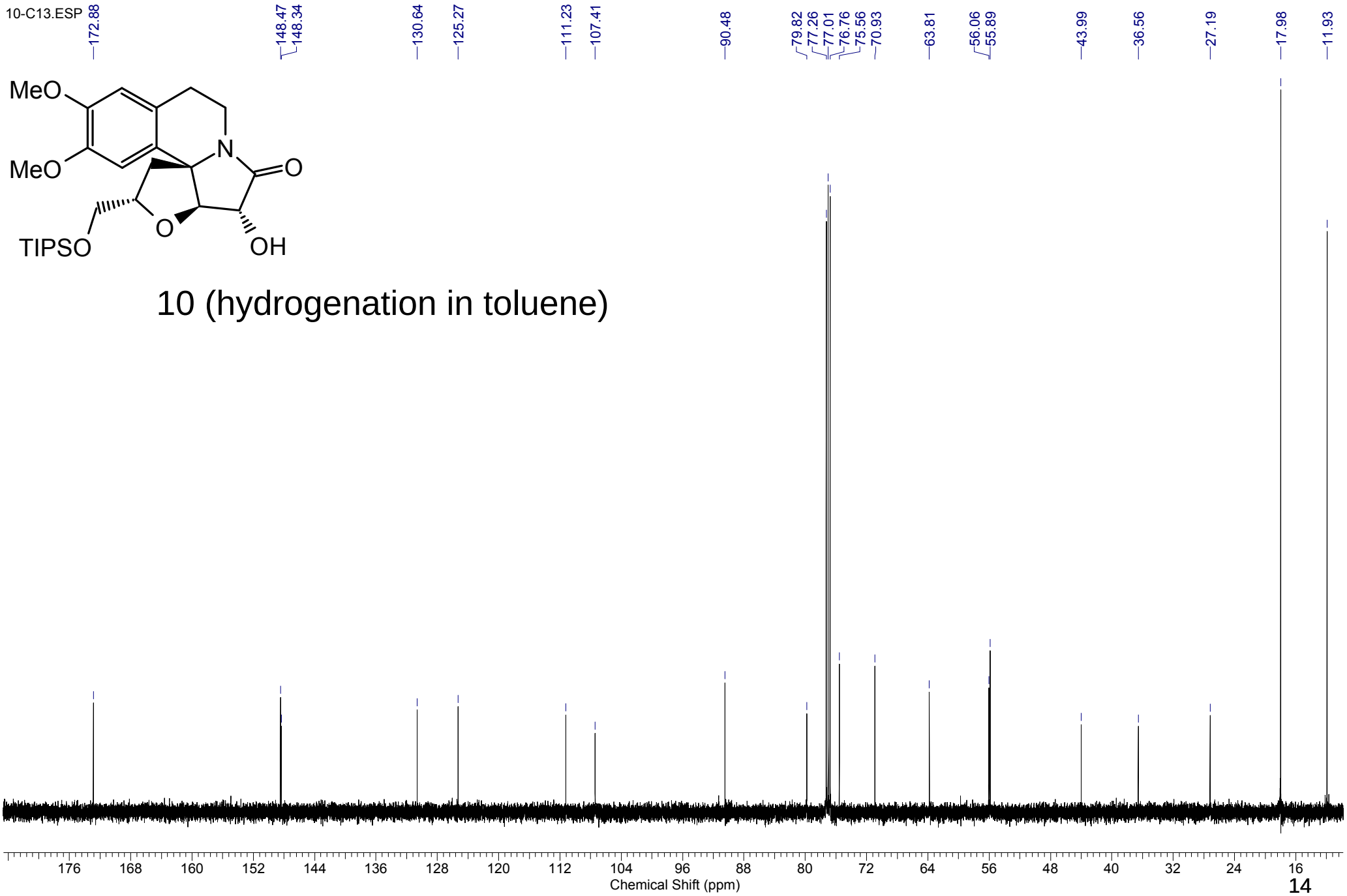


10 (hydrogenation in toluene)



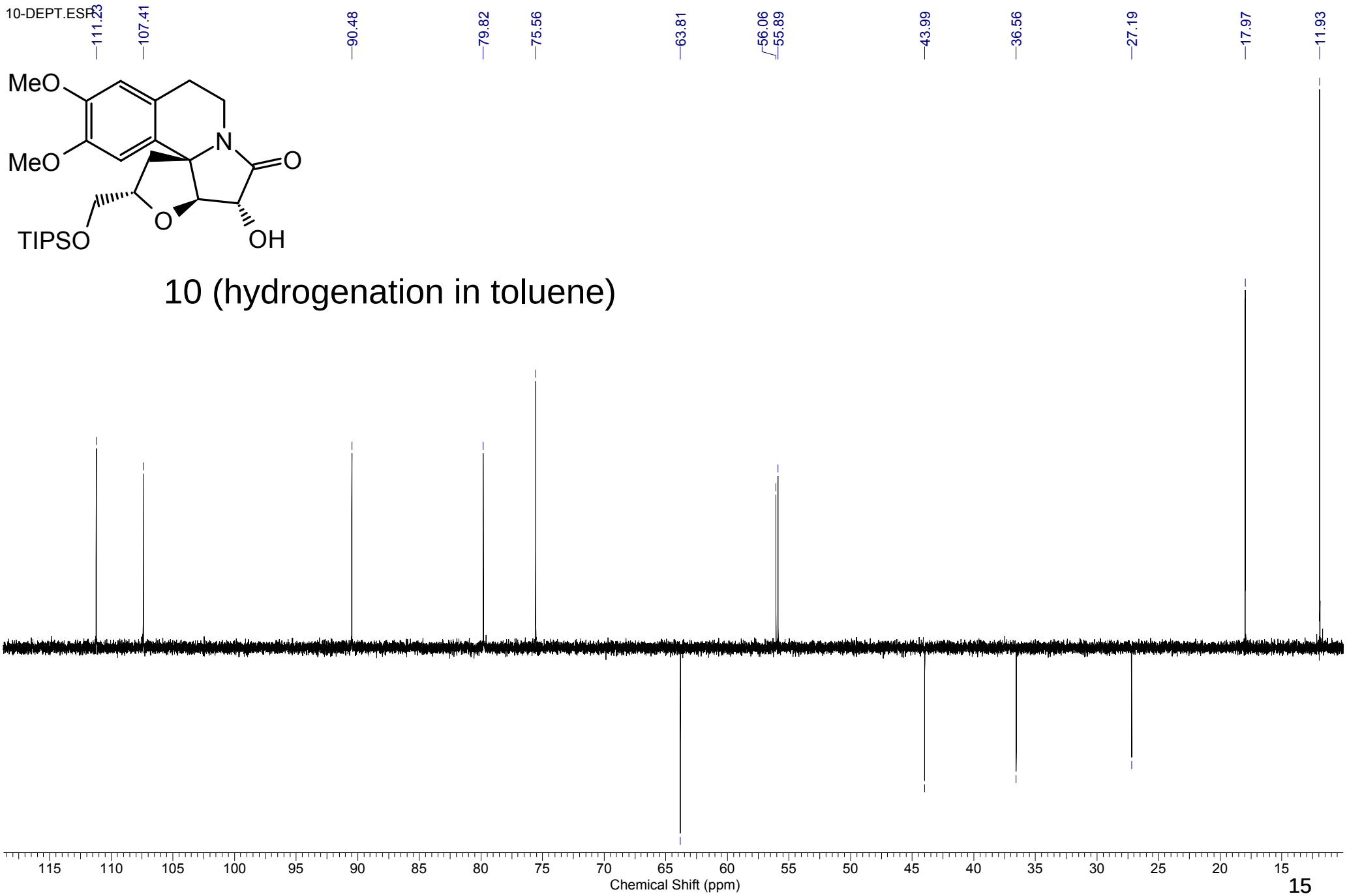
10 (hydrogenation in ethanol)

10-C13.ESP

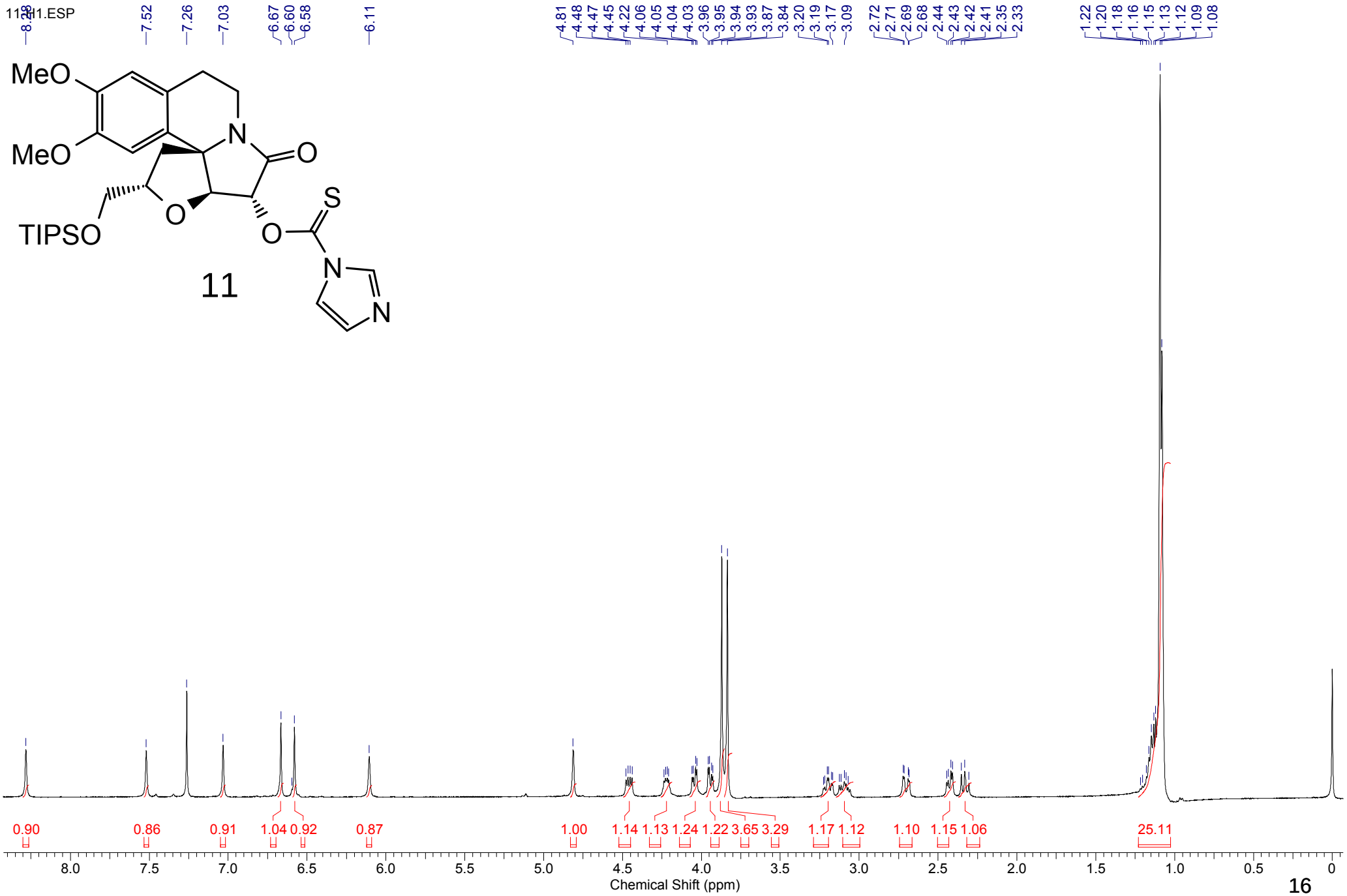


10 (hydrogenation in toluene)

10-DEPT.ESP



10 (hydrogenation in toluene)


11-H1.ESP
MeO
MeO
TIPSO
N
O
O
S
O
N
N
11
8.28
7.52
7.26
7.03
6.67
6.60
6.58
6.11
4.81
4.48
4.47
4.45
4.22
4.06
4.05
4.04
4.03
3.96
3.95
3.94
3.93
3.87
3.84
3.20
3.19
3.17
3.09
2.72
2.71
2.69
2.68
2.44
2.43
2.42
2.41
2.35
2.33
1.22
1.20
1.18
1.16
1.15
1.13
1.12
1.09
1.08
0.90
0.86
0.91
1.04
0.92
0.87
1.00
1.14
1.13
1.24
1.22
3.65
3.29
1.17
1.12
1.10
1.15
1.06
25.11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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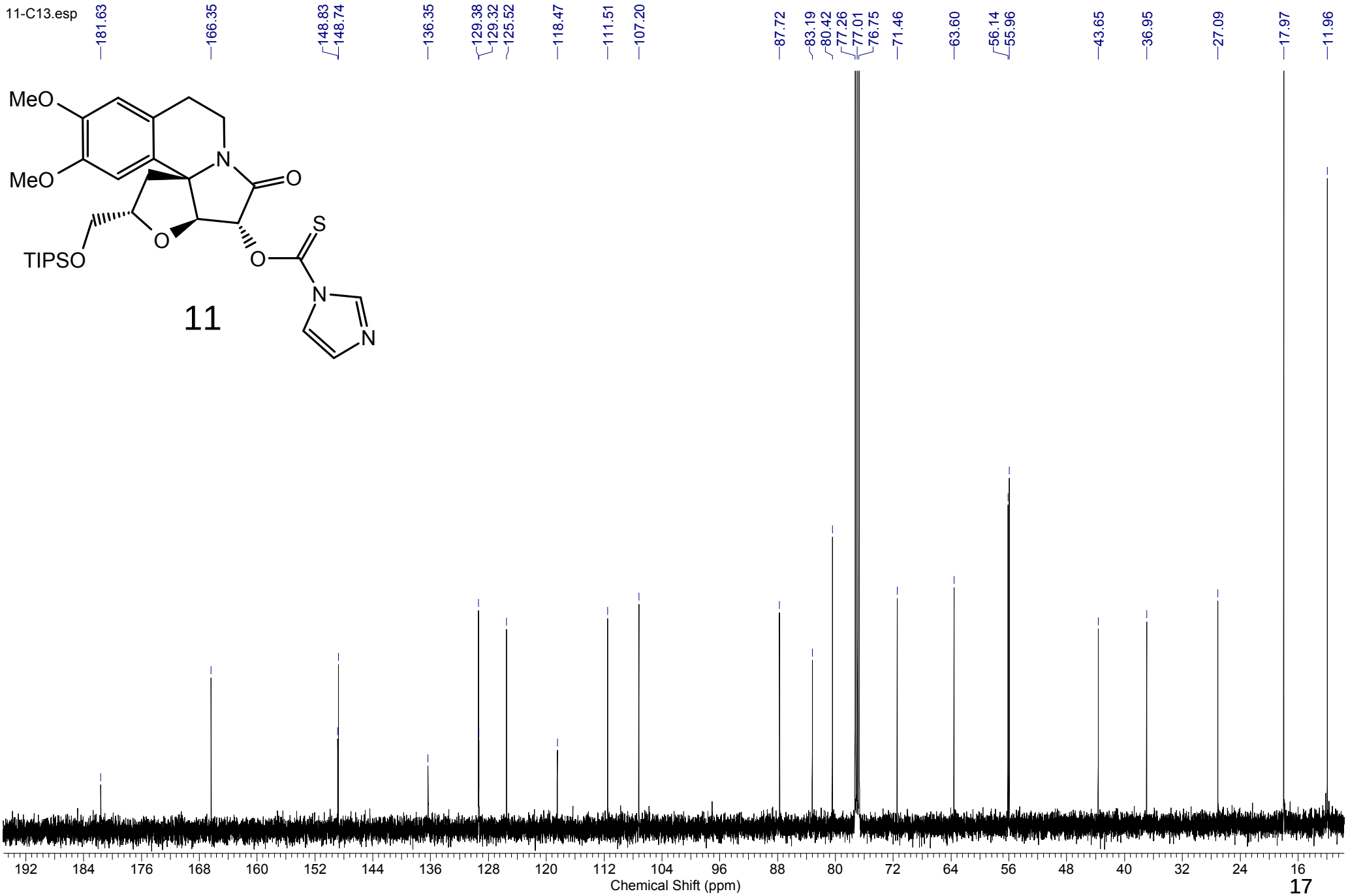
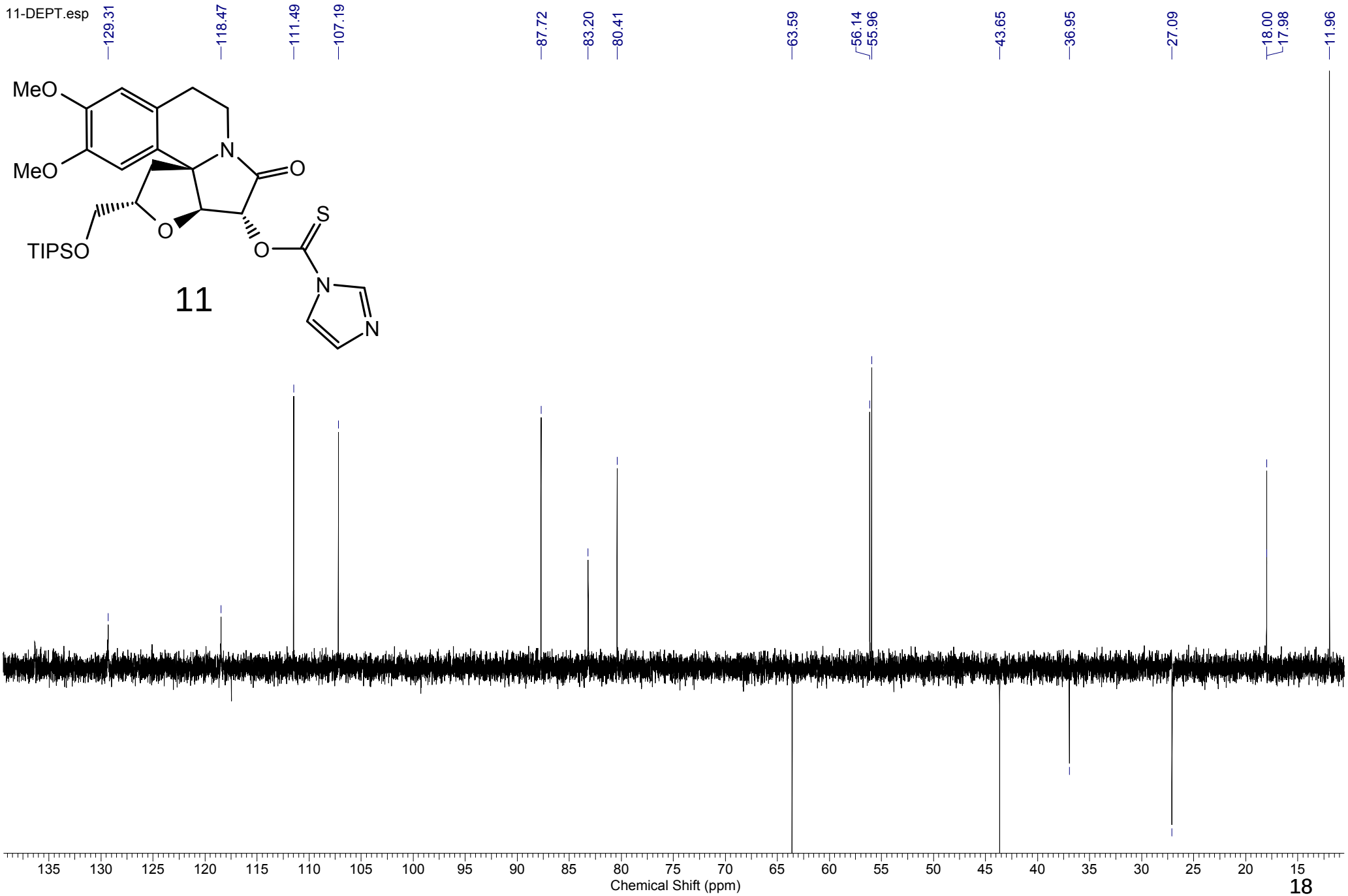
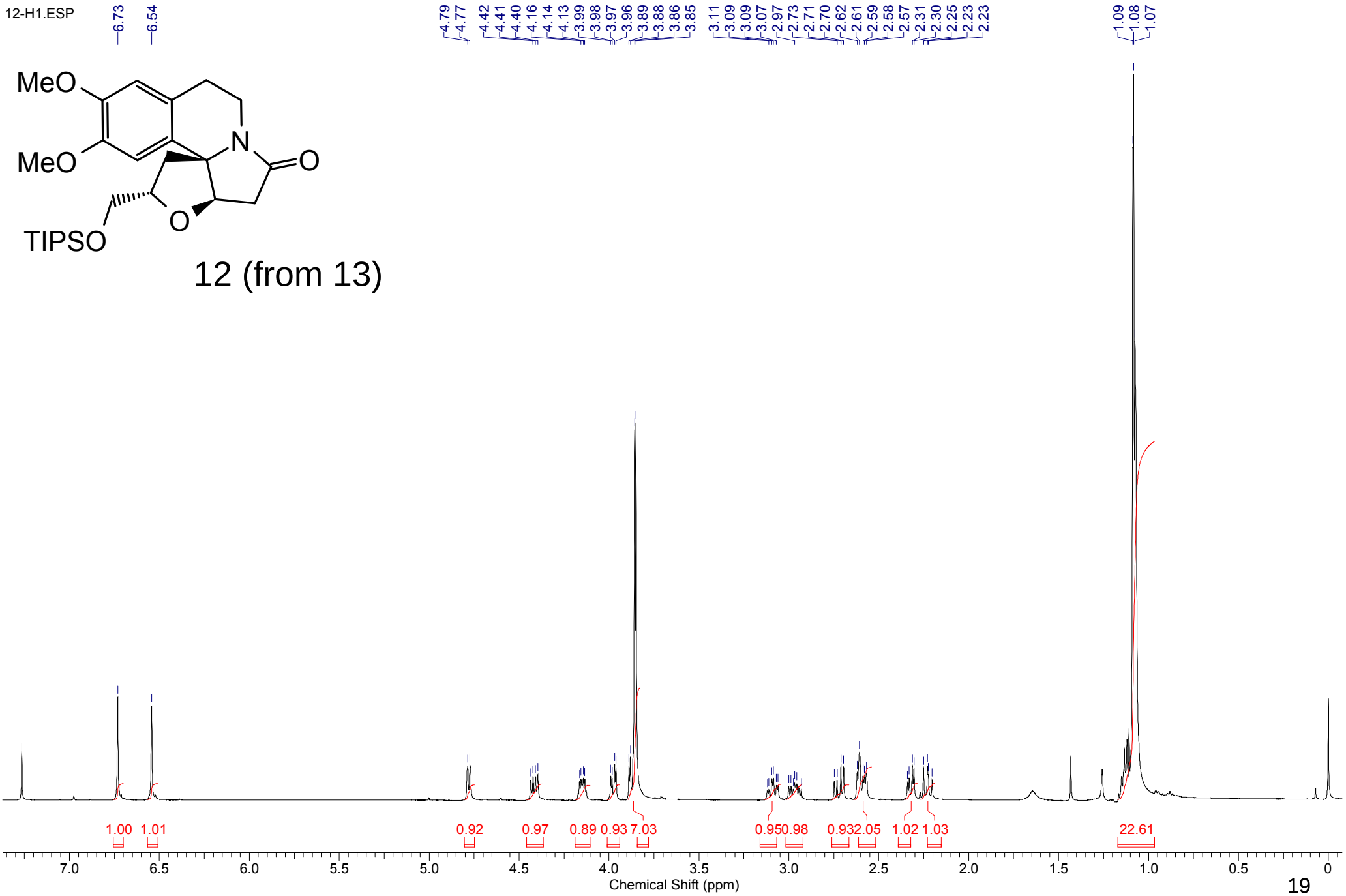
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


11-C13.esp
181.63
166.35
148.83
148.74
136.35
129.38
129.32
125.52
118.47
111.51
107.20
87.72
83.19
80.42
77.26
77.01
76.75
71.46
63.60
56.14
55.96
43.65
36.95
27.09
17.97
11.96
MeO
MeO
N
O
O
S
O
TIPSO
N
N
11
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)

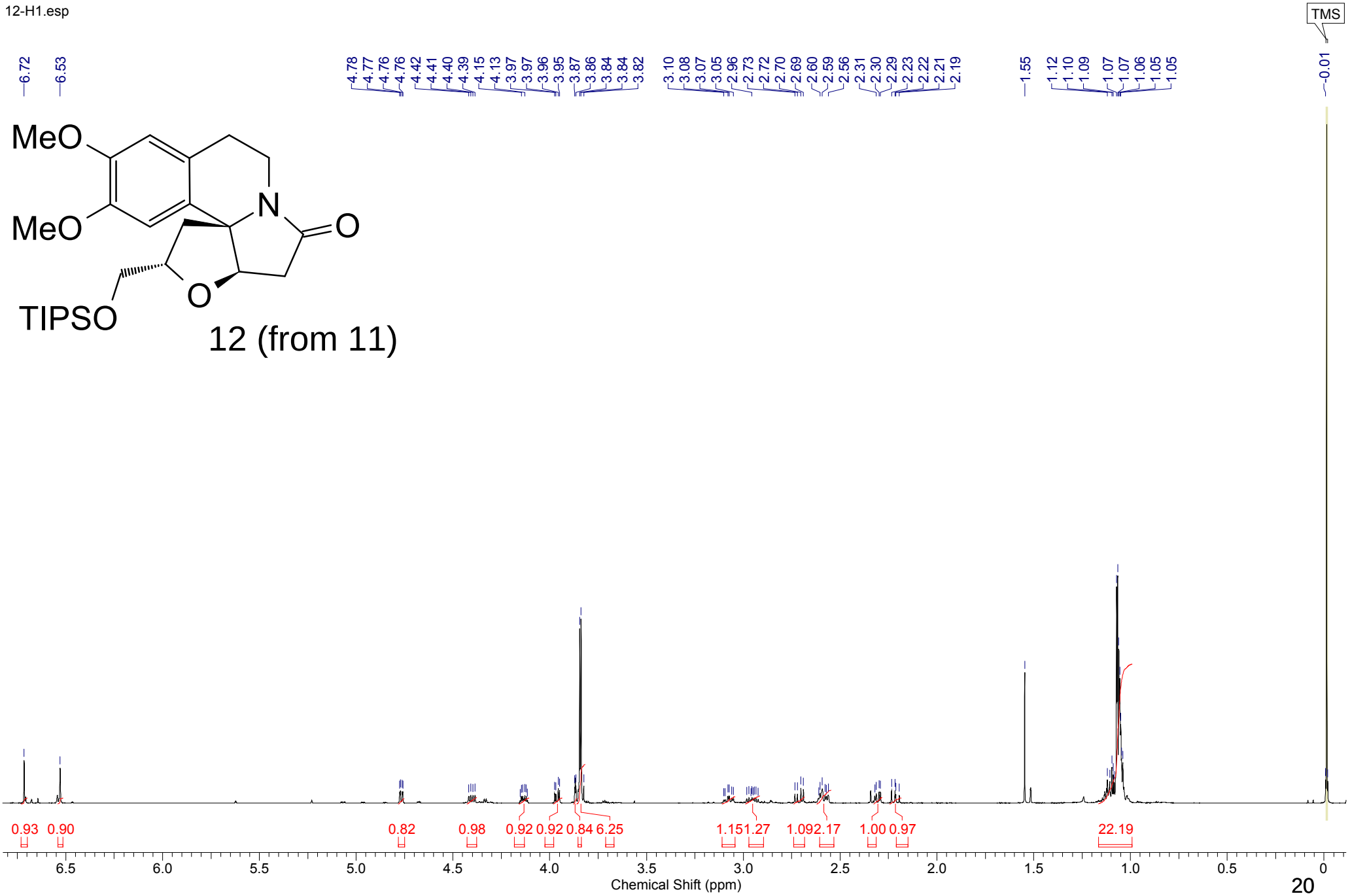

11-DEPT.esp
129.31
118.47
111.49
107.19
87.72
83.20
80.41
63.59
56.14
55.96
43.65
36.95
27.09
18.00
17.98
11.96
MeO
MeO
N
O
O
S
O
TIPSO
O
N
N
11
135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
Chemical Shift (ppm)

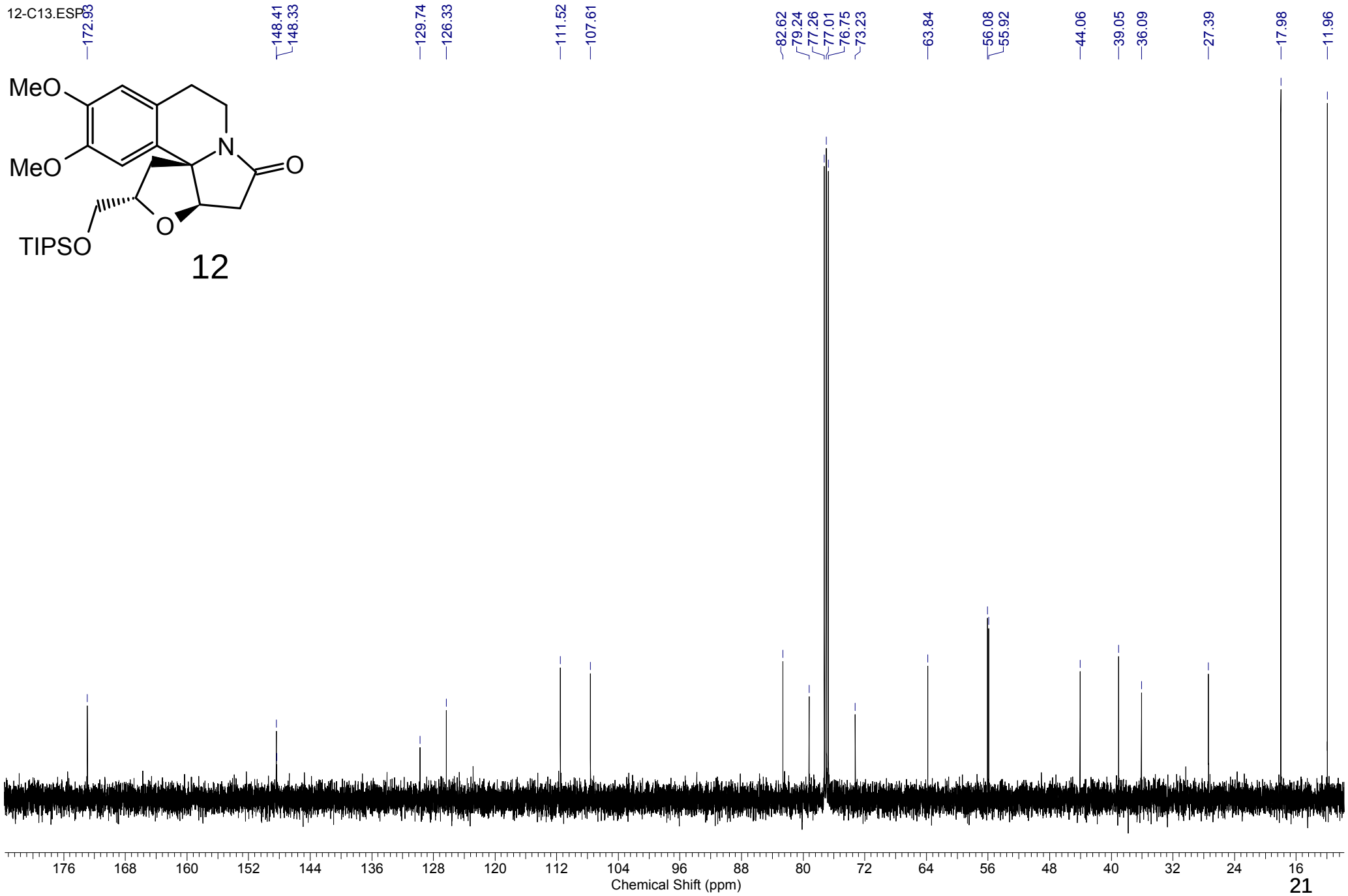
12-H1.ESP

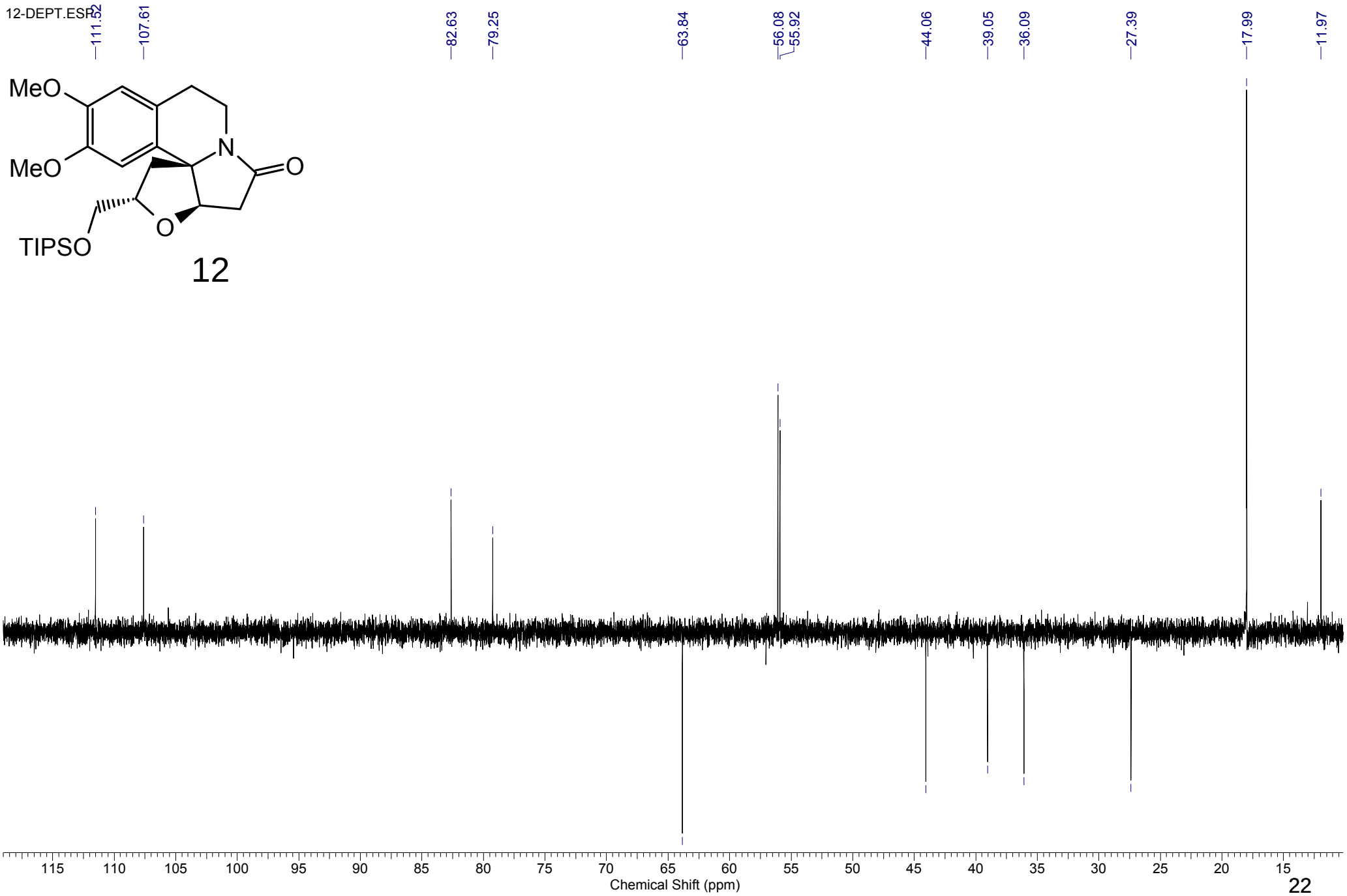


12 (from 13)

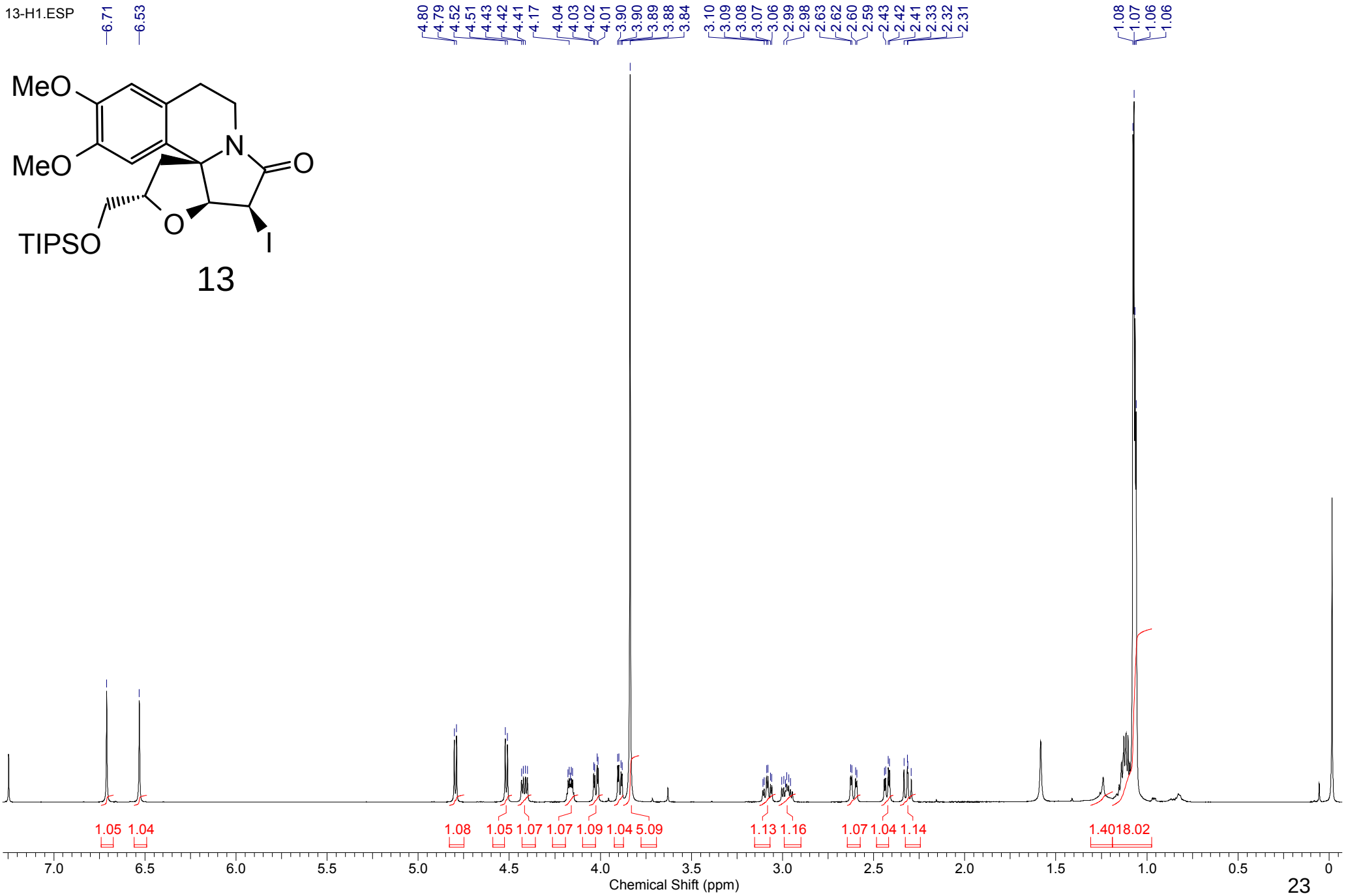
12-H1.esp

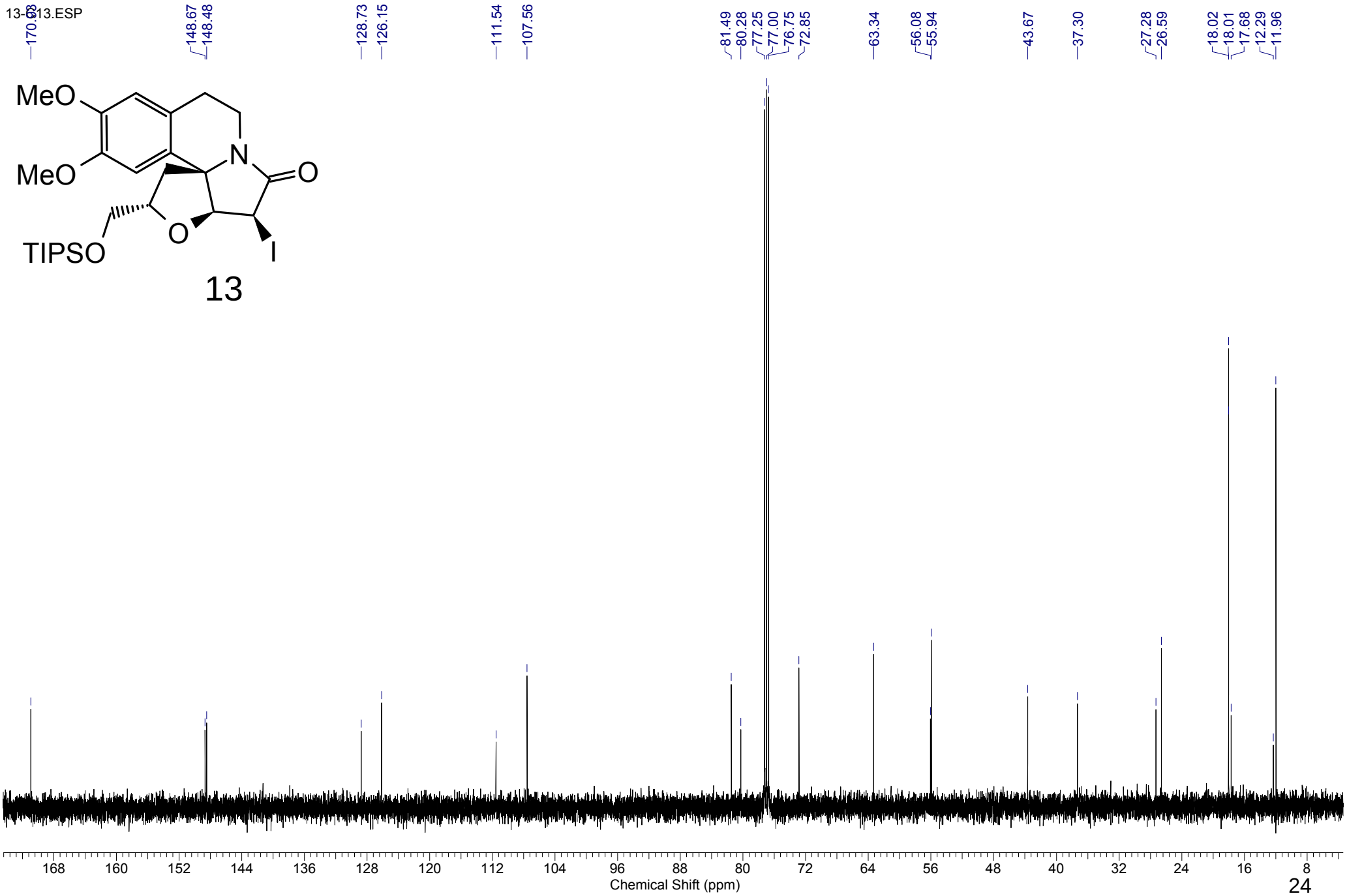

TMS
6.72
6.53
4.78 4.77 4.76 4.76 4.42 4.41 4.40 4.39 4.15 4.13 3.97 3.97 3.96 3.95 3.87 3.86 3.84 3.84 3.82
3.10 3.08 3.07 3.05 2.96 2.73 2.72 2.70 2.69 2.60 2.59 2.56 2.31 2.30 2.29 2.23 2.22 2.21 2.19
1.55
1.12 1.10 1.09 1.07 1.07 1.06 1.05 1.05
-0.01
MeO
MeO
N
O
O
TIPSO
12 (from 11)
0.93 0.90 0.82 0.98 0.92 0.92 0.84 6.25 1.15 1.27 1.09 2.17 1.00 0.97 22.19
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
Chemical Shift (ppm)

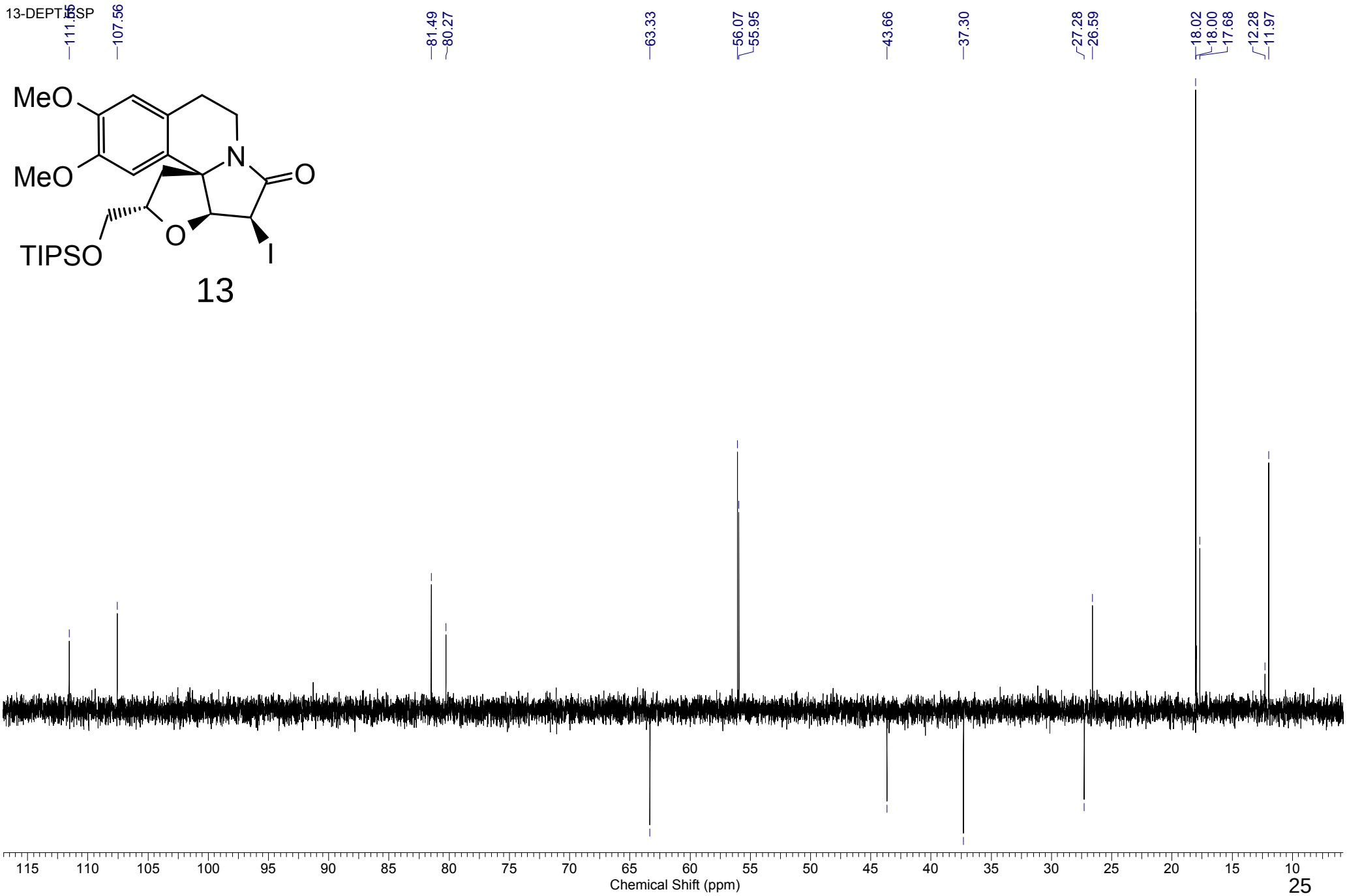

12-C13.ESP
172.93
148.41
148.33
129.74
126.33
111.52
107.61
82.62
79.24
77.26
77.01
76.75
73.23
63.84
56.08
55.92
44.06
39.05
36.09
27.39
17.98
11.96
MeO
MeO
N
O
O
TIPSO
12
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)

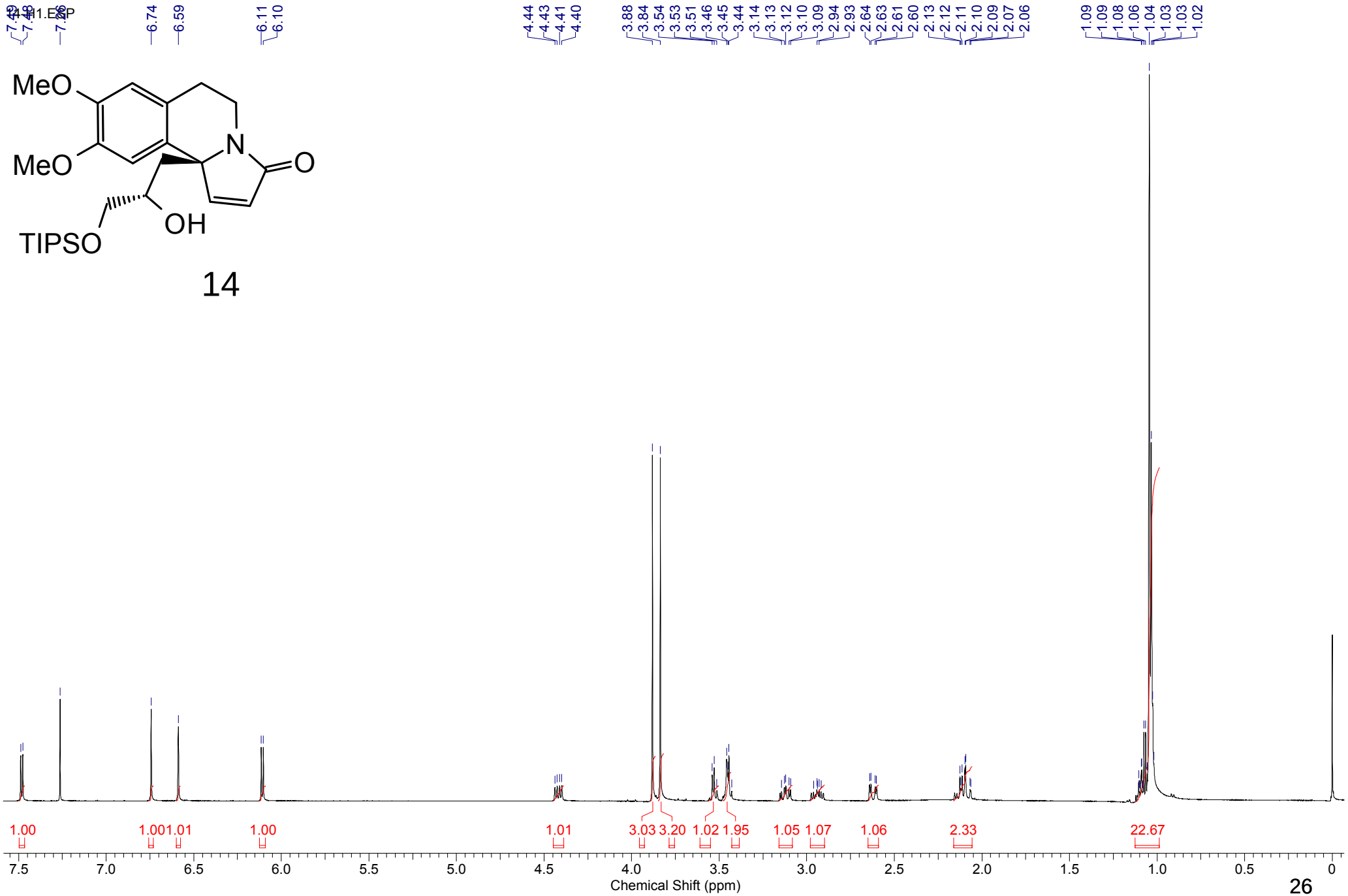

12-DEPT.ESP
111.52
107.61
82.63
79.25
63.84
56.08
55.92
44.06
39.05
36.09
27.39
17.99
11.97
MeO
MeO
N
O
O
TIPSO
12
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
Chemical Shift (ppm)

13-H1.ESP


6.71
6.53
4.80 4.79 4.52 4.51 4.43 4.42 4.41 4.17 4.04 4.03 4.02 4.01 3.90 3.90 3.89 3.88 3.84
3.10 3.09 3.08 3.07 3.06 2.99 2.98 2.63 2.62 2.60 2.59 2.43 2.42 2.41 2.33 2.32 2.31
1.08 1.07 1.06 1.06
MeO
MeO
N
O
O
TIPSO
I
13
1.05 1.04
1.08
1.05 1.07 1.07 1.09 1.04 5.09
1.13 1.16
1.07 1.04 1.14
1.40 18.02
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
Chemical Shift (ppm)


13-613.ESP
170.68
148.67
148.48
128.73
126.15
111.54
107.56
81.49
80.28
77.25
77.00
76.75
72.85
63.34
56.08
55.94
43.67
37.30
27.28
26.59
18.02
18.01
17.68
12.29
11.96
MeO
MeO
N
O
O
TIPSO
I
13
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


13-DEPTSP
111.55
107.56
81.49
80.27
63.33
56.07
55.95
43.66
37.30
27.28
26.59
18.02
18.00
17.68
12.28
11.97
MeO
MeO
N
O
O
TIPSO
I
13
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
Chemical Shift (ppm)


44H1.ESP
MeO
MeO
N
O
OH
TIPSO
14
7.49
7.48
7.46
6.74
6.59
6.11
6.10
4.44
4.43
4.41
4.40
3.88
3.84
3.54
3.53
3.51
3.46
3.45
3.44
3.14
3.13
3.12
3.10
3.09
2.94
2.93
2.64
2.63
2.61
2.60
2.13
2.12
2.11
2.10
2.09
2.07
2.06
1.09
1.09
1.08
1.06
1.04
1.03
1.03
1.02
1.00
1.00
1.01
1.00
1.01
3.03
3.20
1.02
1.95
1.05
1.07
1.06
2.33
22.67
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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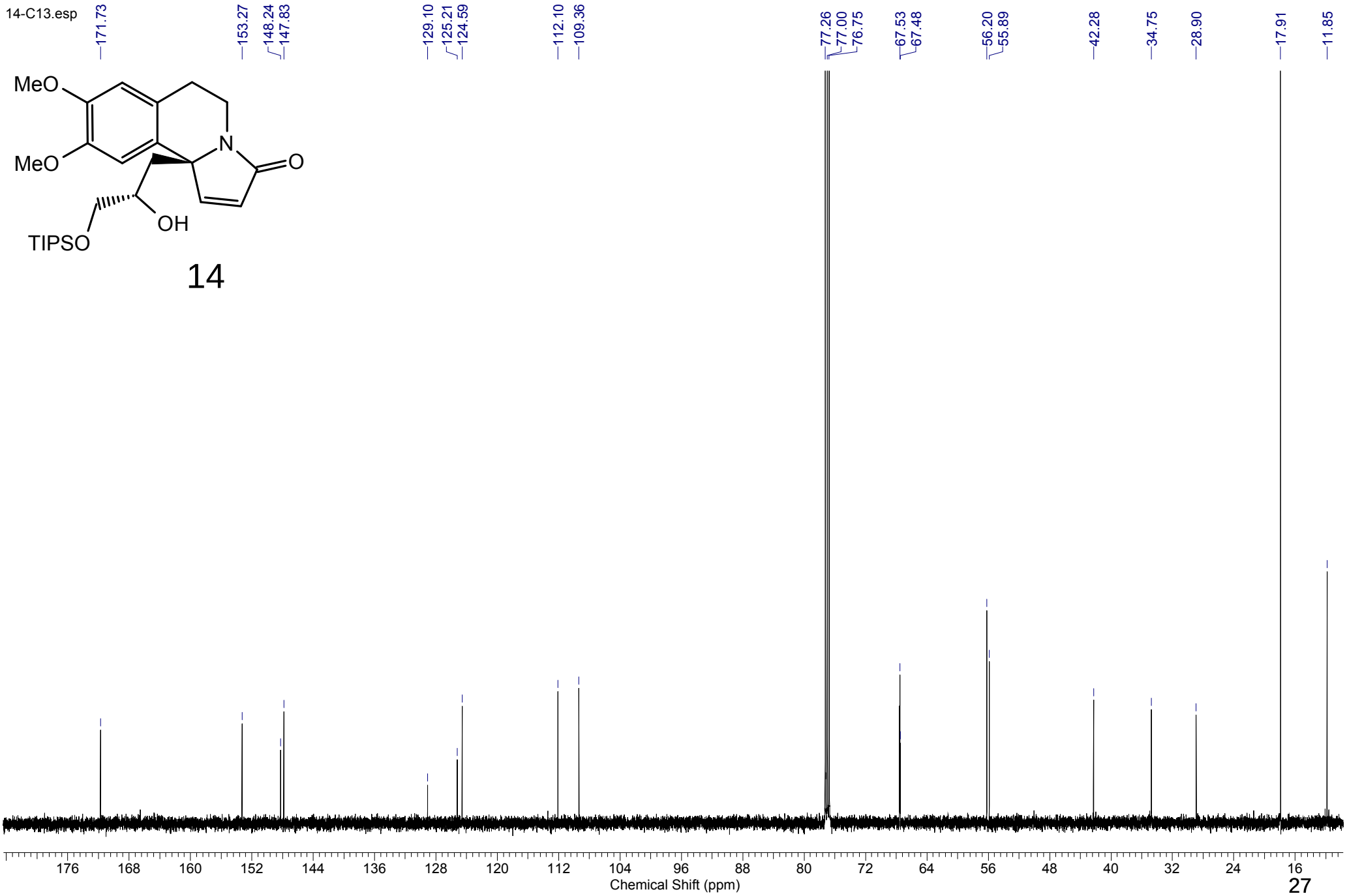
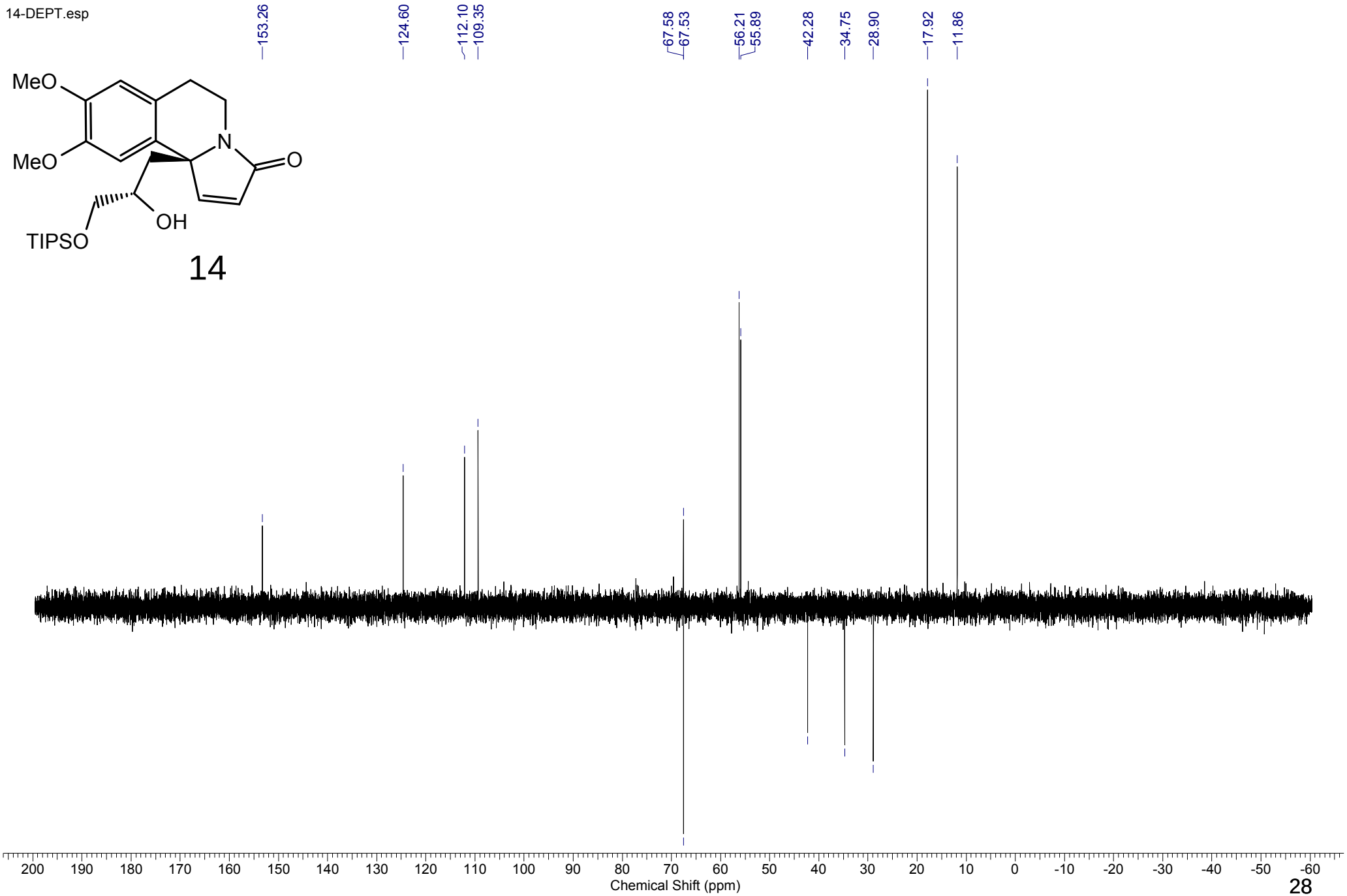
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

14-C13.esp

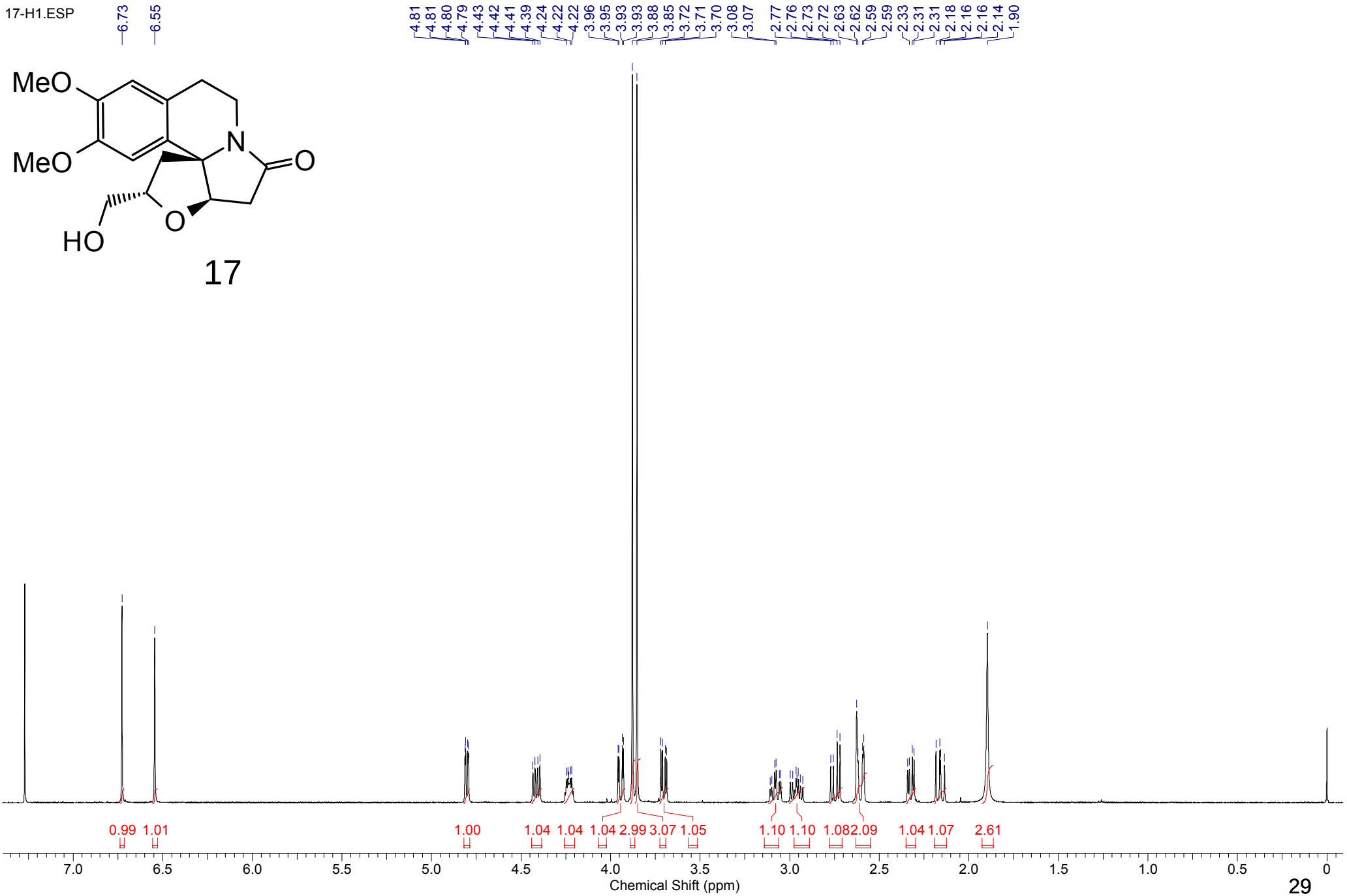

171.73
153.27
148.24
147.83
129.10
125.21
124.59
112.10
109.36
77.26
77.00
76.75
67.53
67.48
56.20
55.89
42.28
34.75
28.90
17.91
11.85
MeO
MeO
N
O
OH
TIPSO
14
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)

14-DEPT.esp

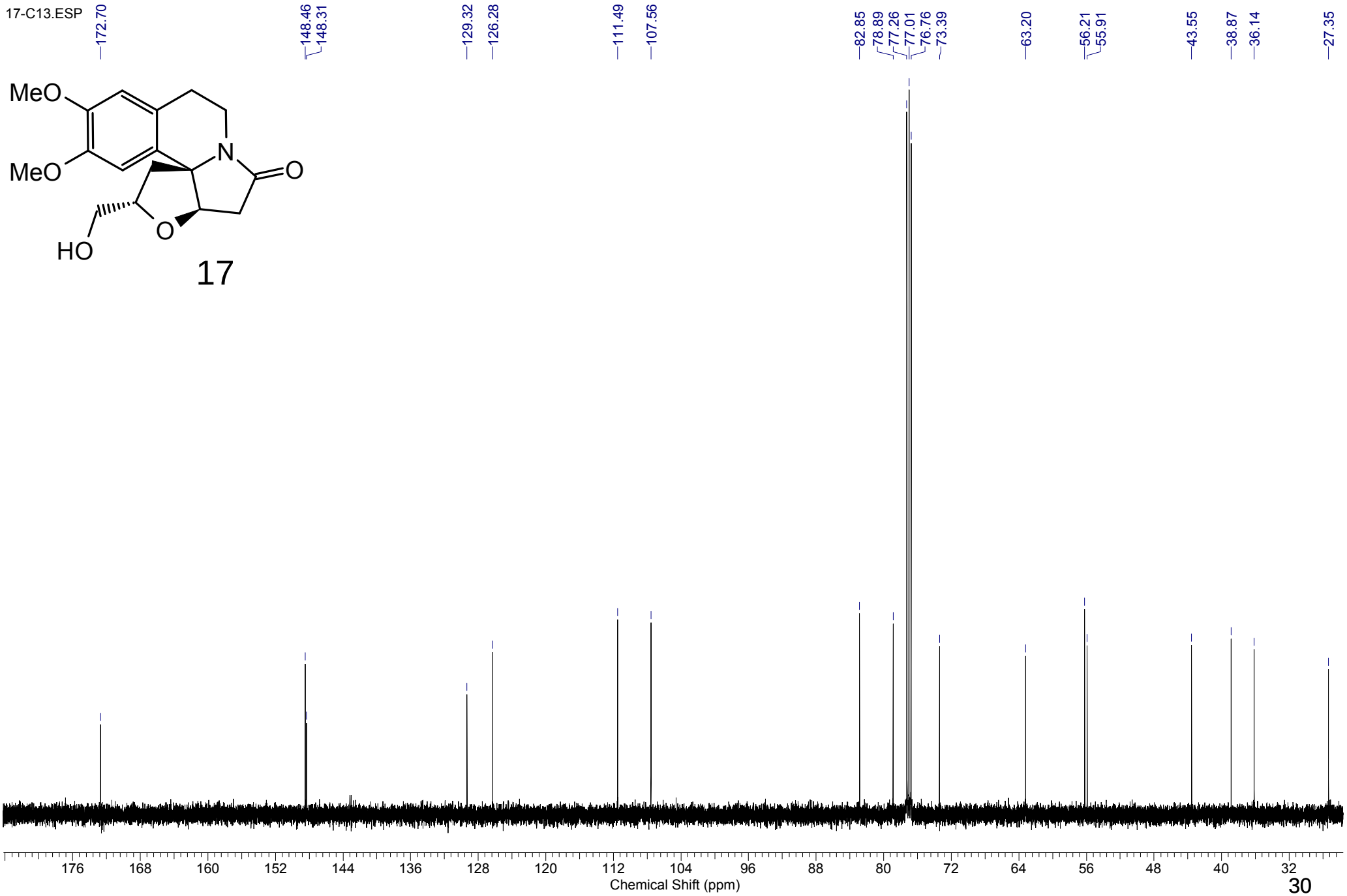
14

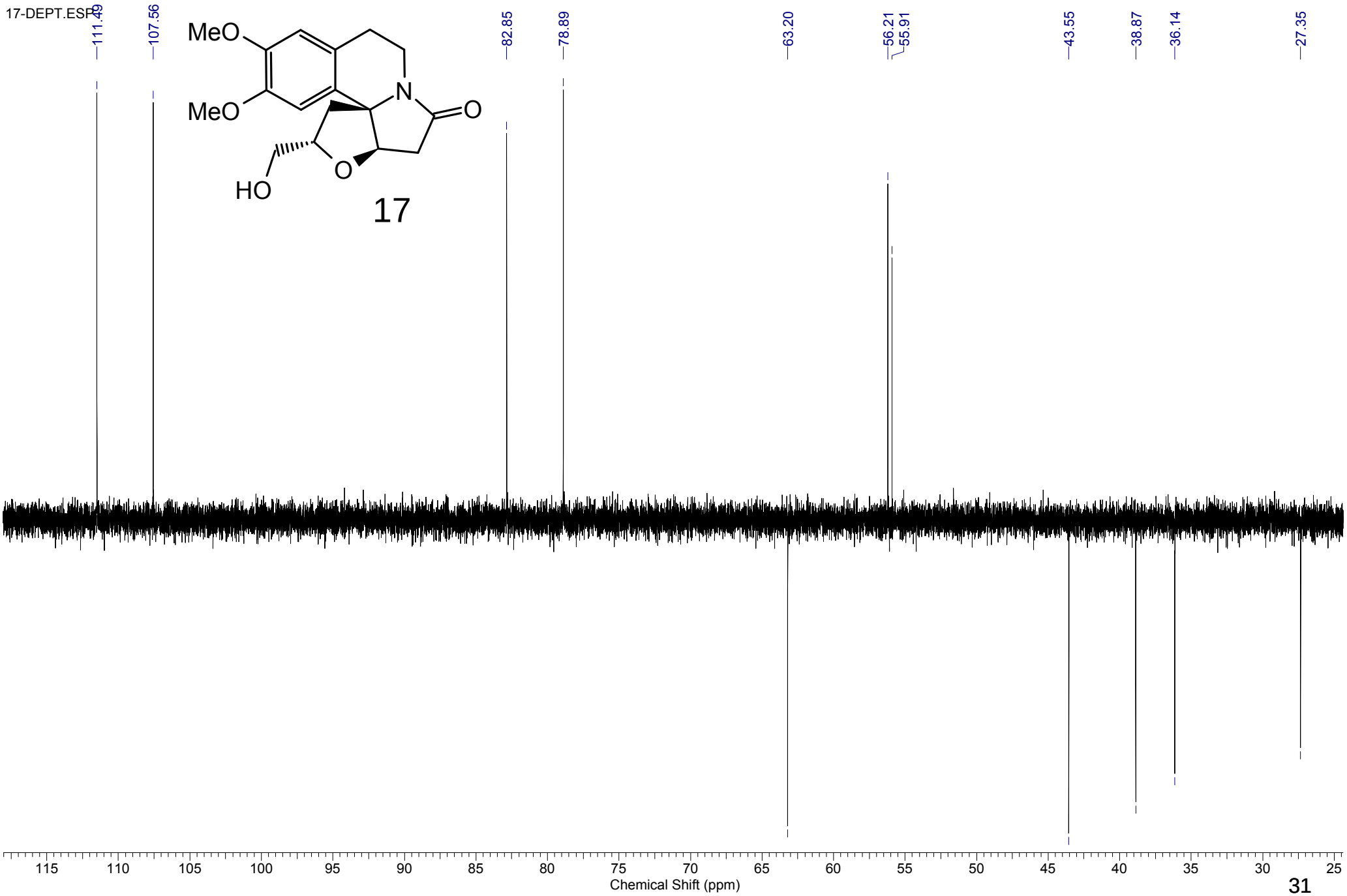


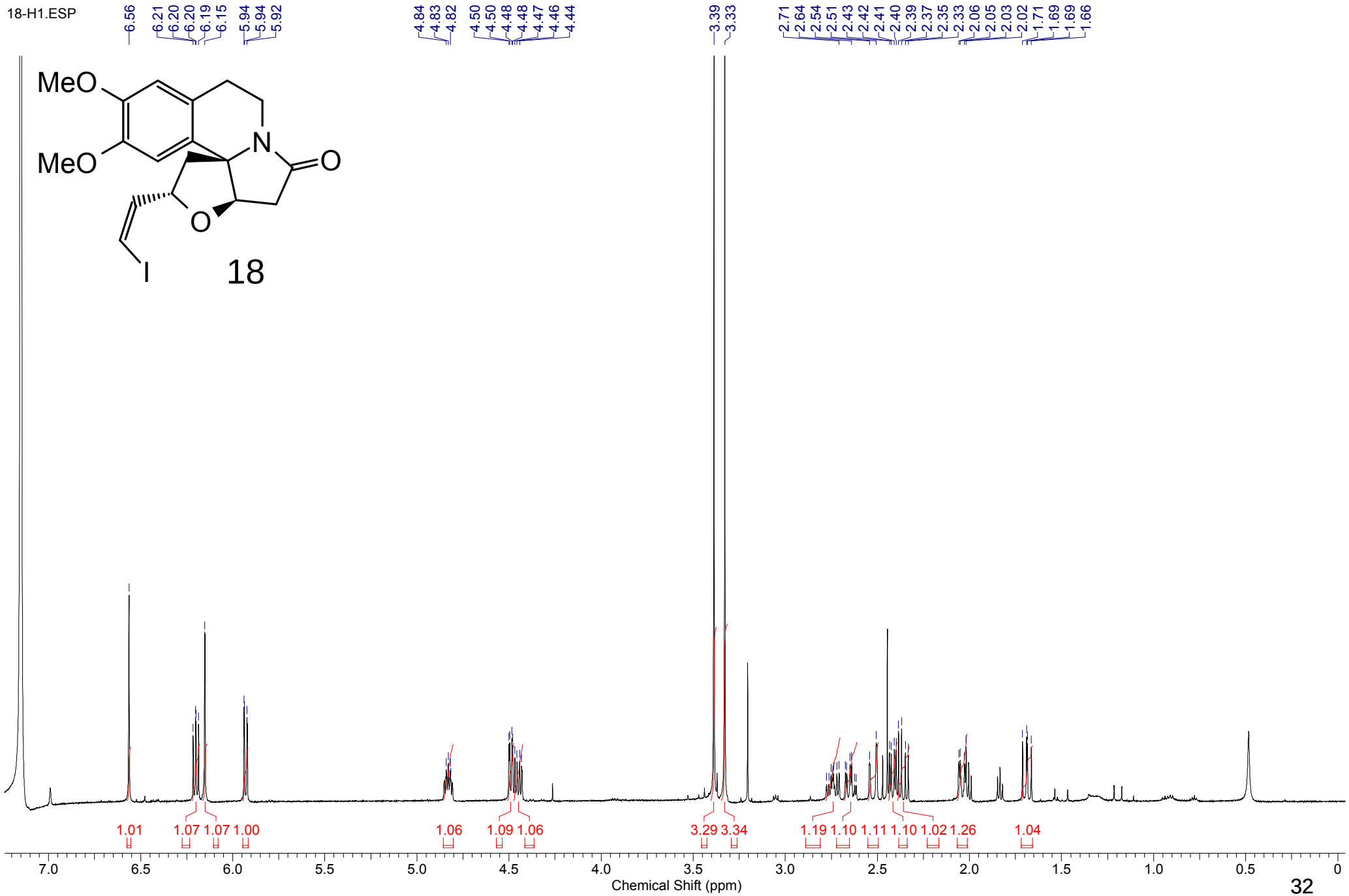
17-H1.ESP

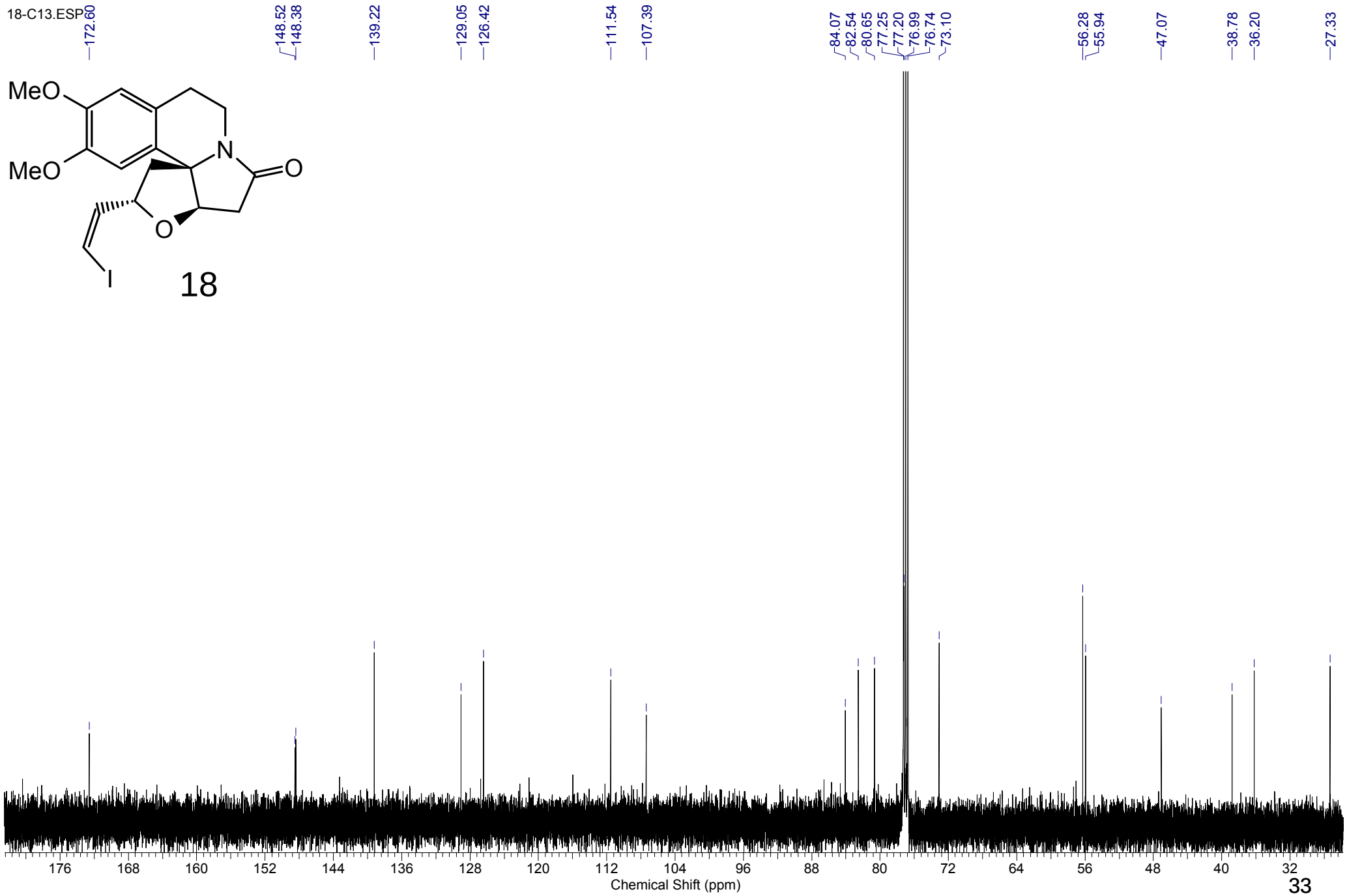

6.73
6.55
4.81
4.81
4.80
4.79
4.43
4.42
4.41
4.39
4.24
4.22
4.22
3.96
3.95
3.93
3.93
3.88
3.85
3.72
3.71
3.70
3.08
3.07
2.77
2.76
2.73
2.72
2.63
2.62
2.59
2.59
2.33
2.31
2.31
2.18
2.16
2.16
2.14
1.90
MeO
MeO
N
O
O
HO
17
0.99 1.01
1.00
1.04 1.04 1.04 2.99 3.07 1.05
1.10 1.10 1.08 2.09
1.04 1.07
2.61
7.0
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
Chemical Shift (ppm)

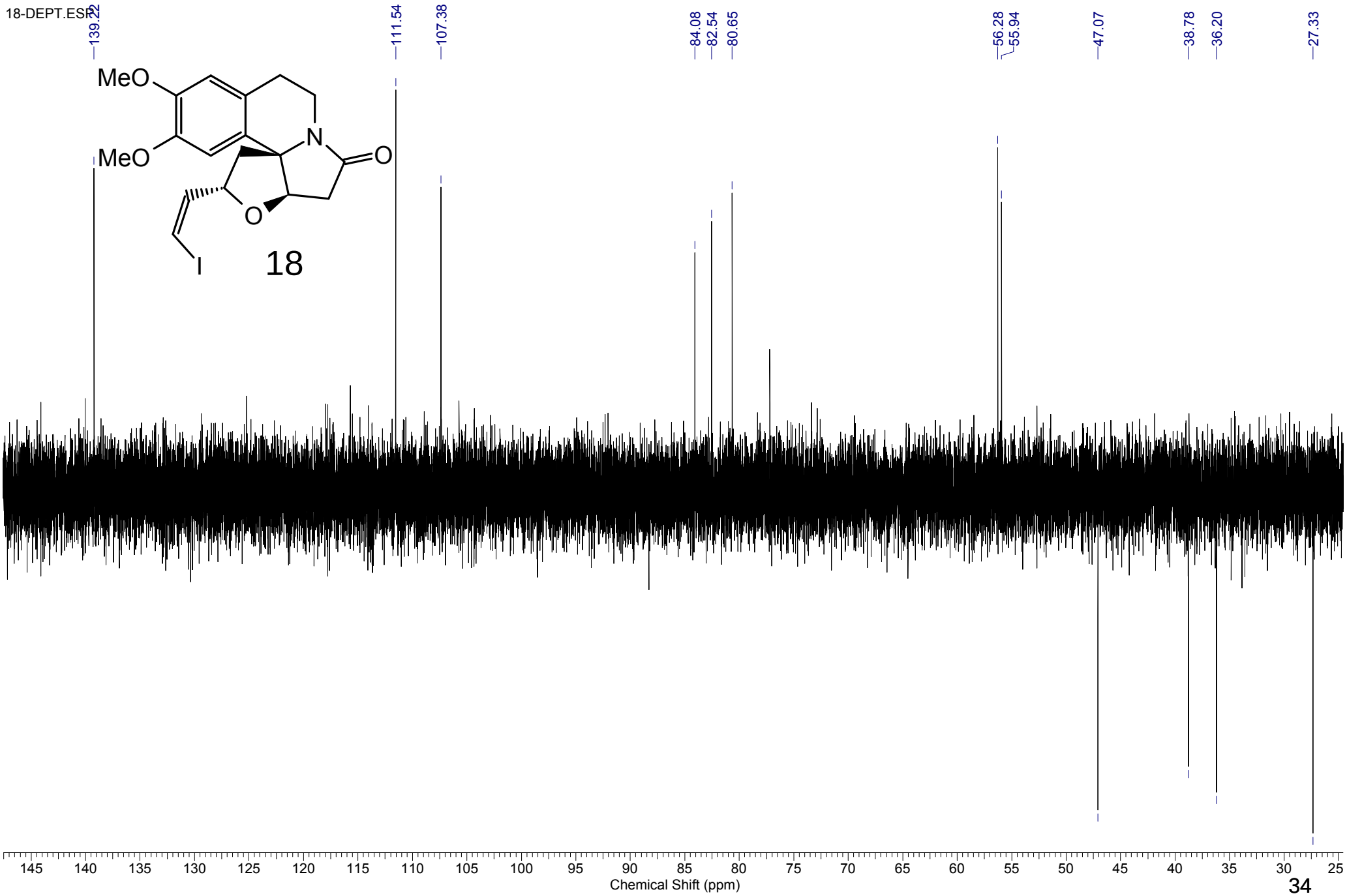
17-C13.ESP

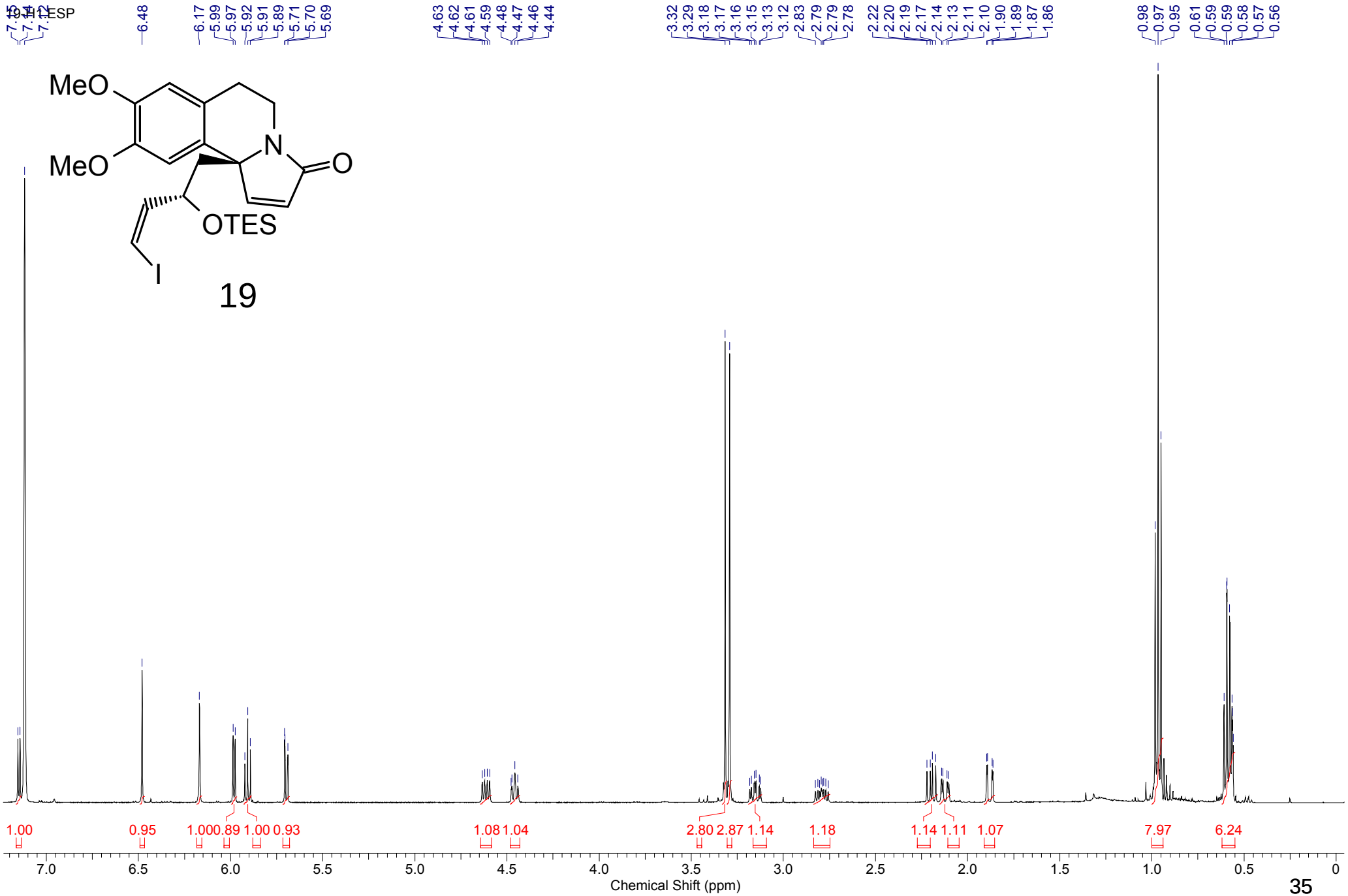

172.70
148.46
148.31
129.32
126.28
111.49
107.56
82.85
78.89
77.26
77.01
76.76
73.39
63.20
56.21
55.91
43.55
38.87
36.14
27.35
MeO
MeO
N
O
O
HO
17
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
Chemical Shift (ppm)

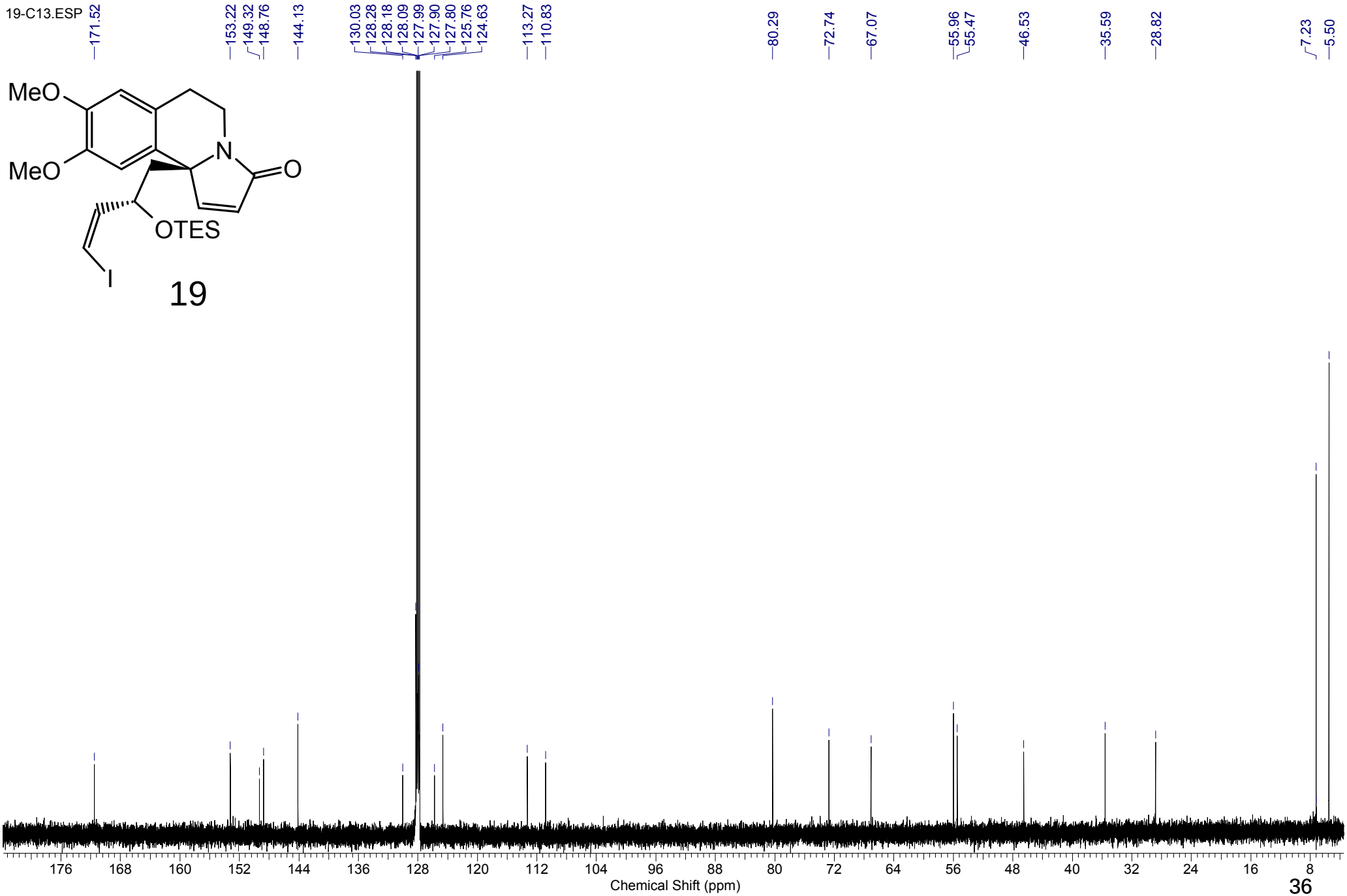

17-DEPT.ESP
111.49
107.56
82.85
78.89
63.20
56.21
55.91
43.55
38.87
36.14
27.35
MeO
MeO
N
O
O
HO
17
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
Chemical Shift (ppm)

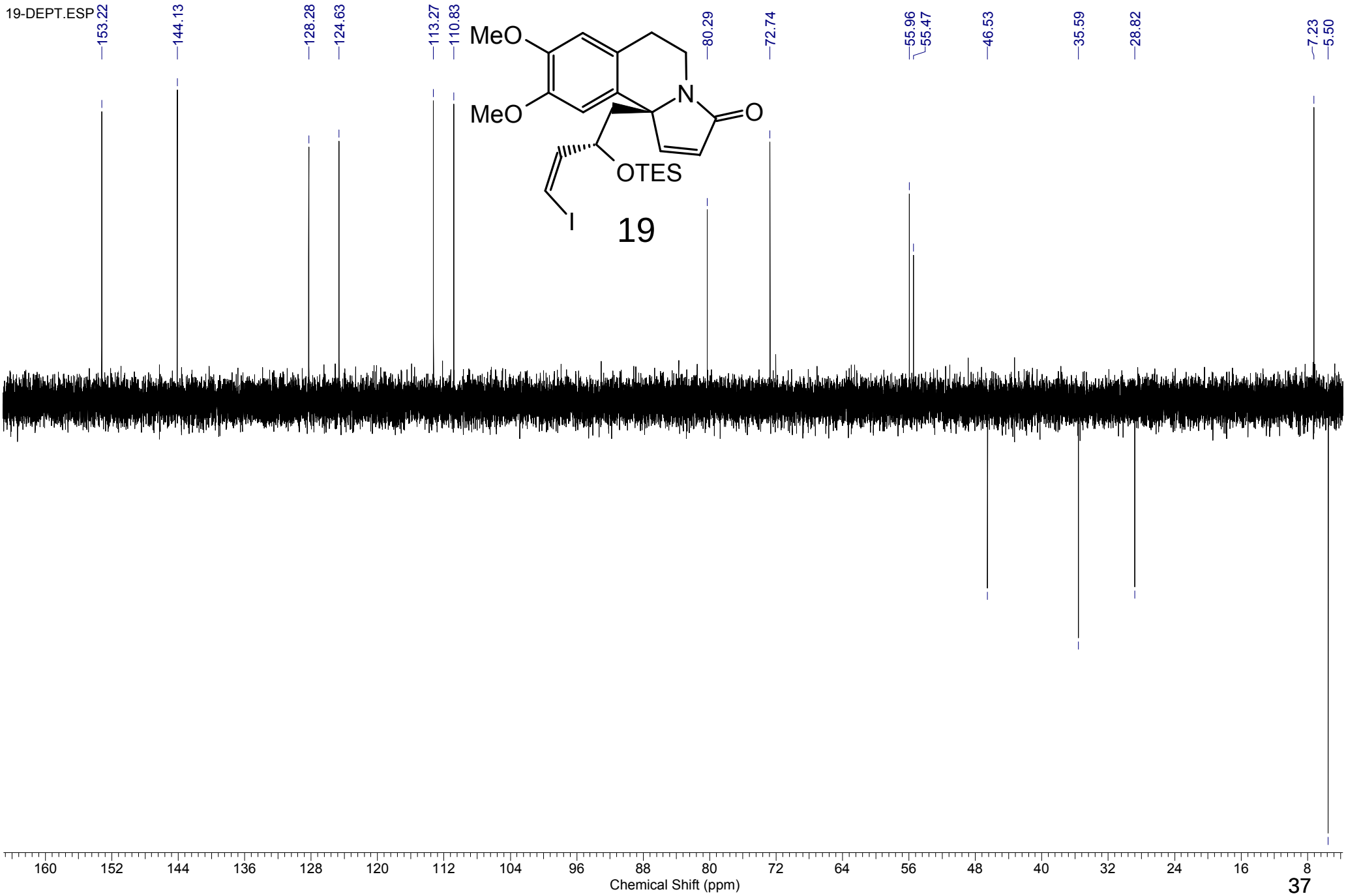

18-H1.ESP
6.56
6.21
6.20
6.20
6.19
6.15
5.94
5.94
5.92
4.84
4.83
4.82
4.50
4.50
4.48
4.48
4.47
4.46
4.44
3.39
3.33
2.71
2.64
2.54
2.51
2.43
2.42
2.41
2.40
2.39
2.37
2.35
2.33
2.06
2.05
2.03
2.02
1.71
1.69
1.69
1.66
MeO
MeO
N
O
O
I
18
1.01
1.07
1.07
1.00
1.06
1.09
1.06
3.29
3.34
1.19
1.10
1.11
1.10
1.02
1.26
1.04
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
Chemical Shift (ppm)

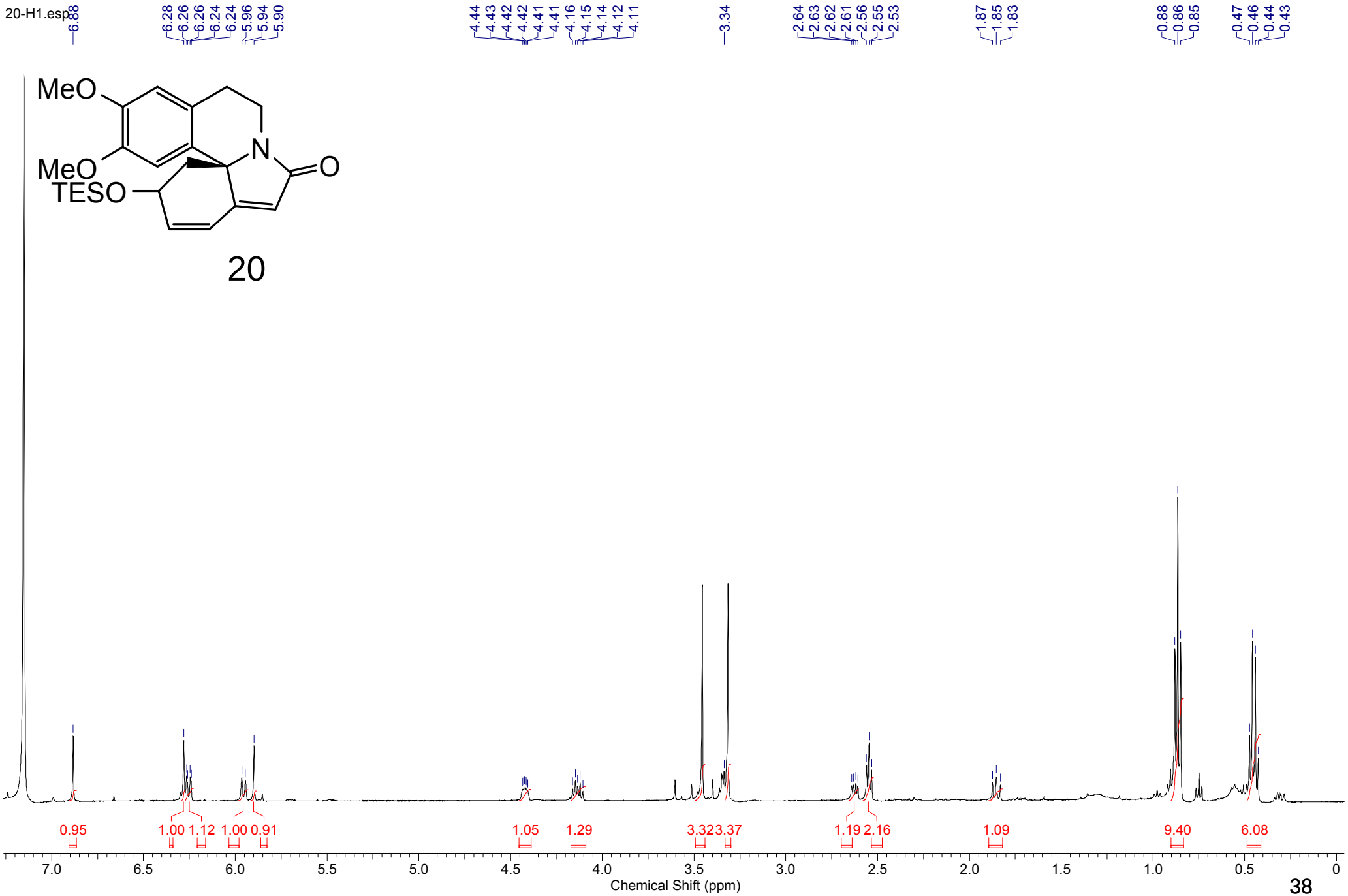

18-C13.ESP
172.60
148.52
148.38
139.22
129.05
126.42
111.54
107.39
84.07
82.54
80.65
77.25
77.20
76.99
76.74
73.10
56.28
55.94
47.07
38.78
36.20
27.33
MeO
MeO
N
O
O
I
18
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
Chemical Shift (ppm)

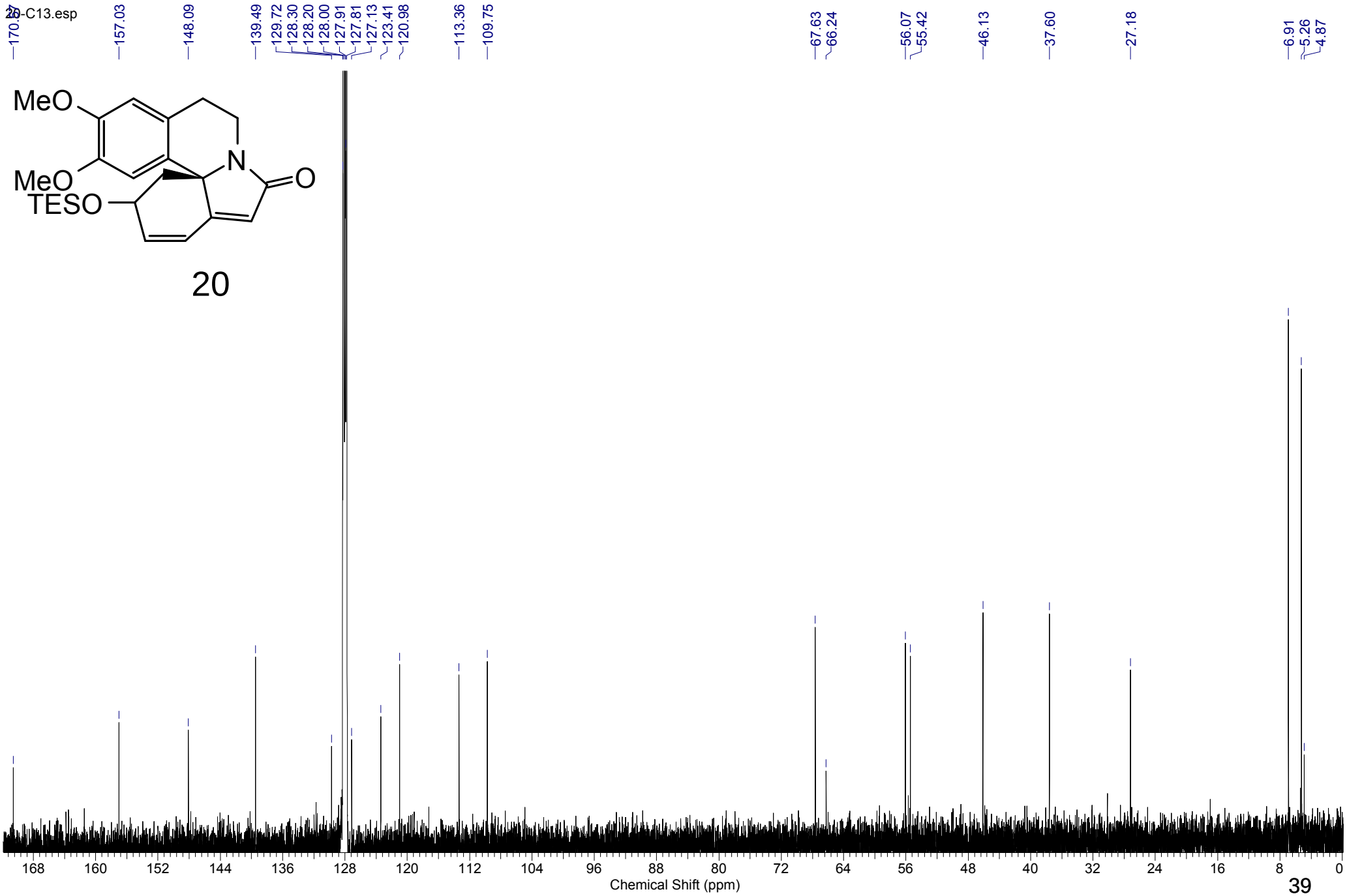

18-DEPT.ESP
139.22
111.54
107.38
84.08
82.54
80.65
56.28
55.94
47.07
38.78
36.20
27.33
MeO
MeO
N
O
O
I
18
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
Chemical Shift (ppm)

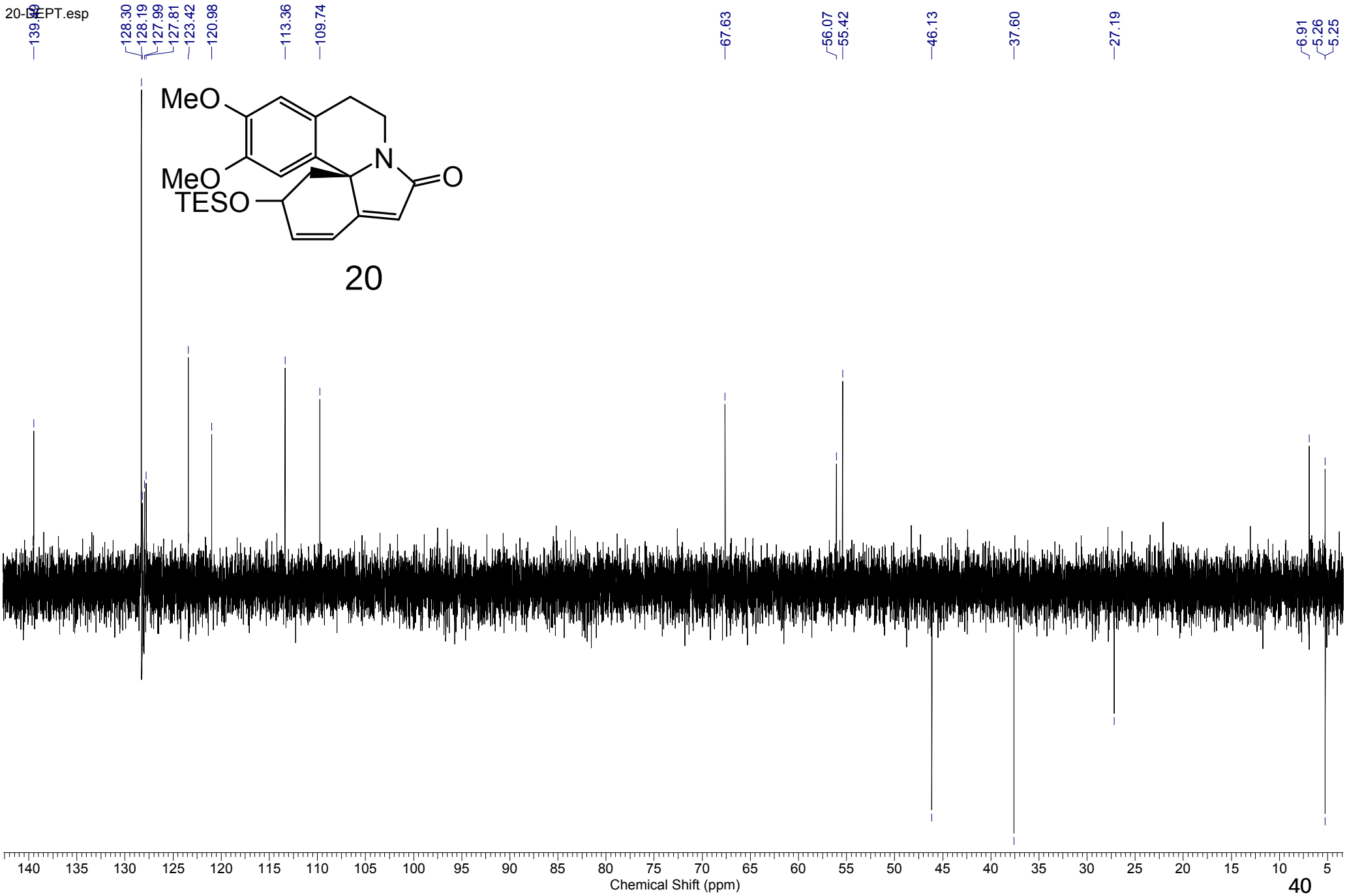

19-H1.ESP
MeO
MeO
N
O
OTES
I
19
7.34 7.32 7.12 6.48 6.17 5.99 5.97 5.92 5.91 5.89 5.71 5.70 5.69 4.63 4.62 4.61 4.59 4.48 4.47 4.46 4.44 3.32 3.29 3.18 3.17 3.16 3.15 3.13 3.12 2.83 2.79 2.79 2.78 2.22 2.20 2.19 2.17 2.14 2.13 2.11 2.10 1.90 1.89 1.87 1.86 0.98 0.97 0.95 0.61 0.59 0.59 0.58 0.57 0.56
1.00 0.95 1.00 0.89 1.00 0.93 1.08 1.04 2.80 2.87 1.14 1.18 1.14 1.11 1.07 7.97 6.24
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
Chemical Shift (ppm)


19-C13.ESP
171.52
153.22
149.32
148.76
144.13
130.03
128.28
128.18
128.09
127.99
127.90
127.80
125.76
124.63
113.27
110.83
80.29
72.74
67.07
55.96
55.47
46.53
35.59
28.82
7.23
5.50
MeO
MeO
N
O
OTES
I
19
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

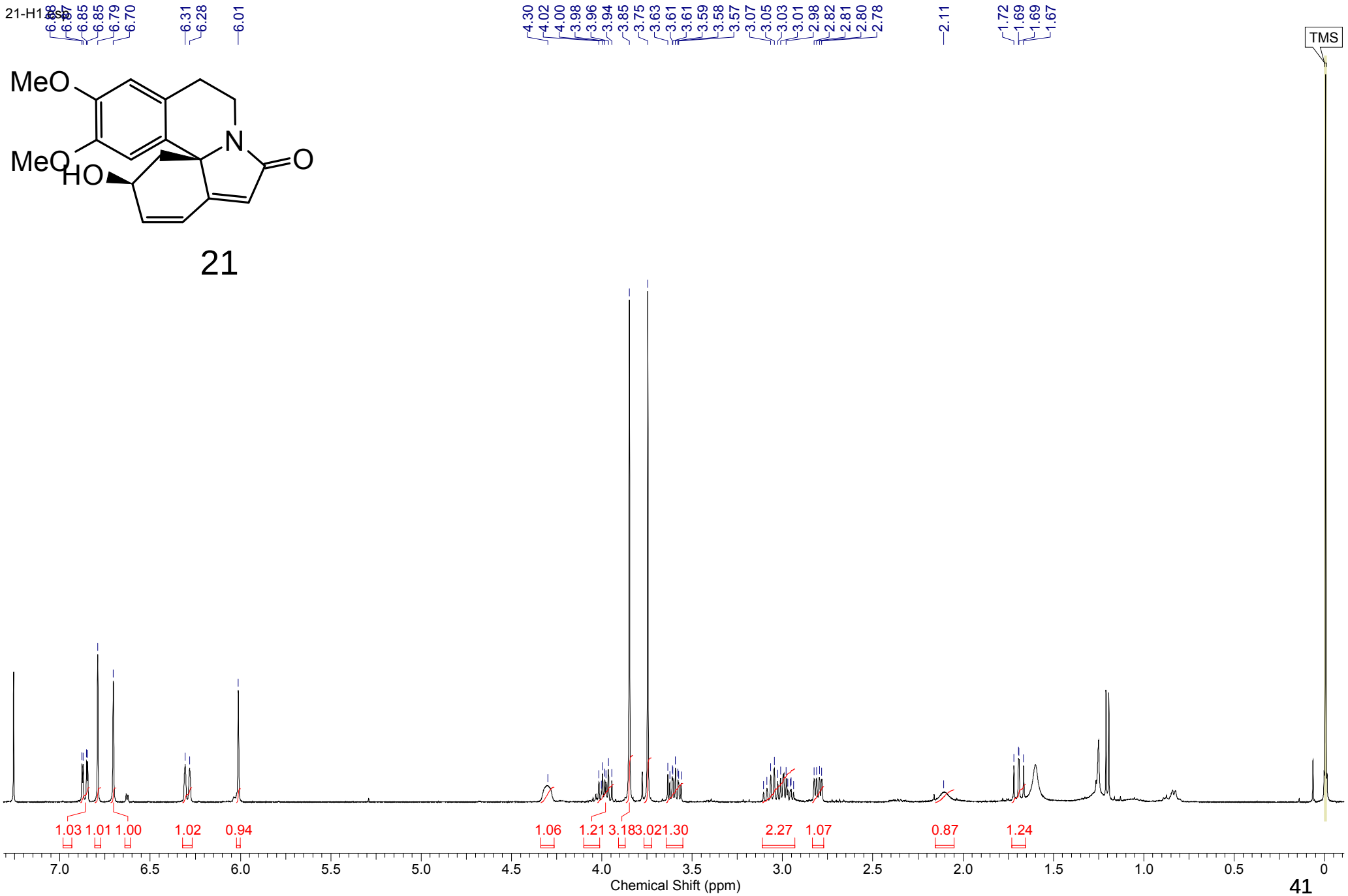

19-DEPT.ESP
153.22
144.13
128.28
124.63
113.27
110.83
80.29
72.74
55.96
55.47
46.53
35.59
28.82
7.23
5.50
MeO
MeO
N
O
OTES
I
19
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


20-H1.esp
6.88
6.28
6.26
6.26
6.24
6.24
5.96
5.94
5.90
4.44
4.43
4.42
4.42
4.41
4.41
4.16
4.15
4.14
4.12
4.11
3.34
2.64
2.63
2.62
2.61
2.56
2.55
2.53
1.87
1.85
1.83
0.88
0.86
0.85
0.47
0.46
0.44
0.43
MeO
MeO
TESO
N
O
20
0.95
1.00
1.12
1.00
0.91
1.05
1.29
3.32
3.37
1.19
2.16
1.09
9.40
6.08
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
Chemical Shift (ppm)

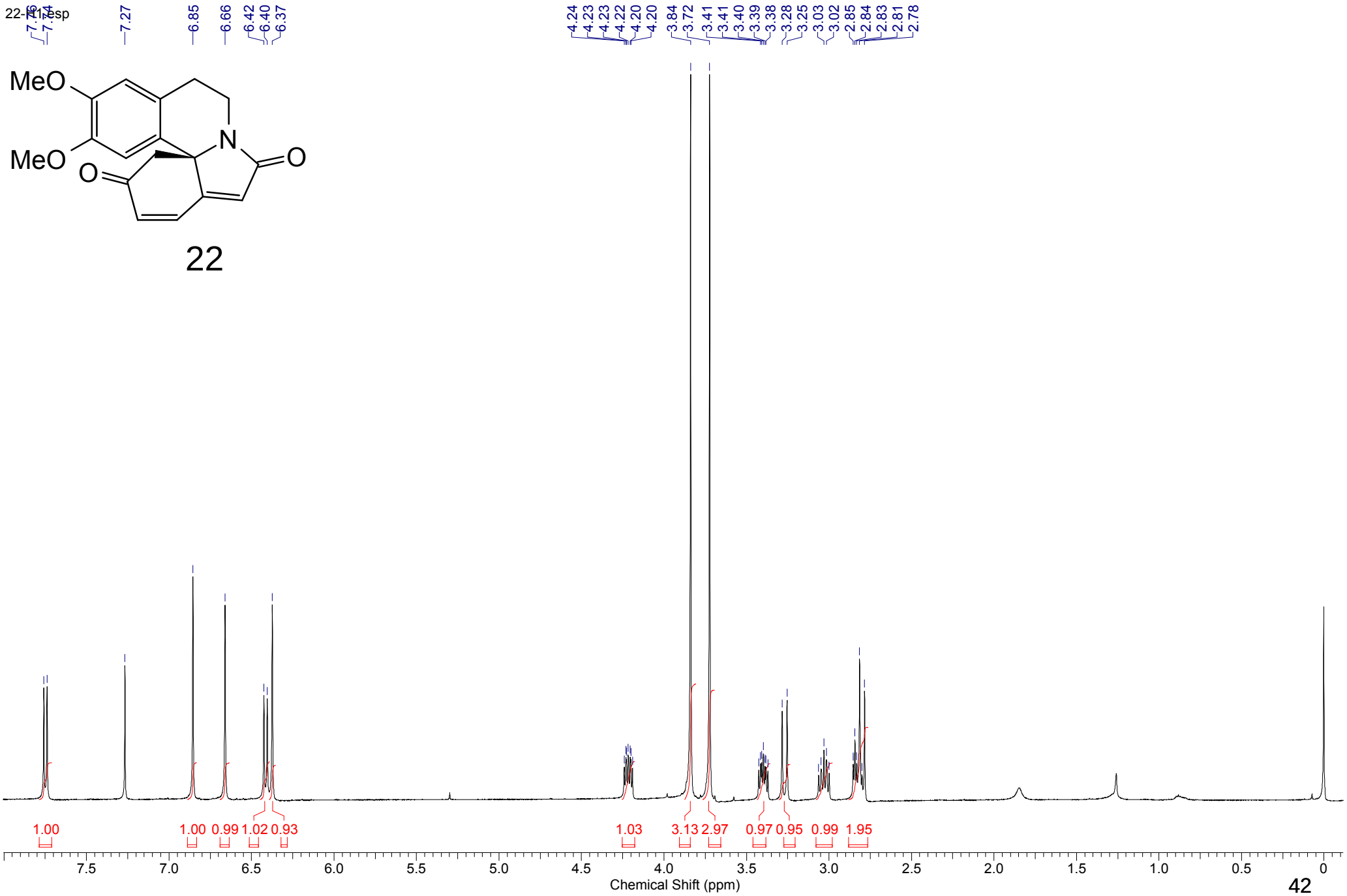

20-C13.esp
170.07
157.03
148.09
139.49
129.72
128.30
128.20
128.00
127.91
127.81
127.13
123.41
120.98
113.36
109.75
67.63
66.24
56.07
55.42
46.13
37.60
27.18
6.91
5.26
4.87
MeO
MeO
TESO
N
O
20
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

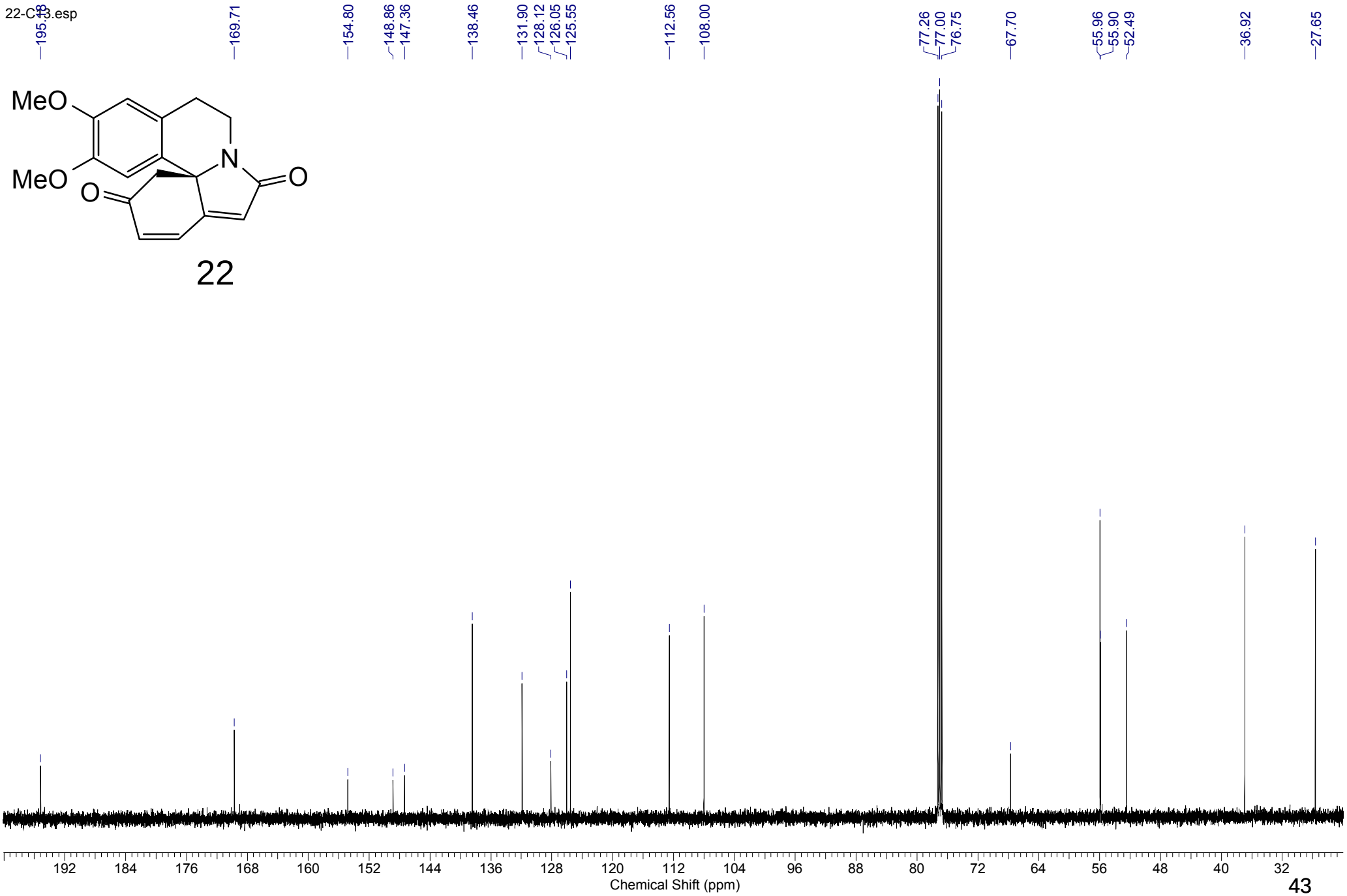

20-DEPT.esp
139.49
128.30
128.19
127.99
127.81
123.42
120.98
113.36
109.74
67.63
56.07
55.42
46.13
37.60
27.19
6.91
5.26
5.25
MeO
MeO
TESO
N
O
20
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
Chemical Shift (ppm)

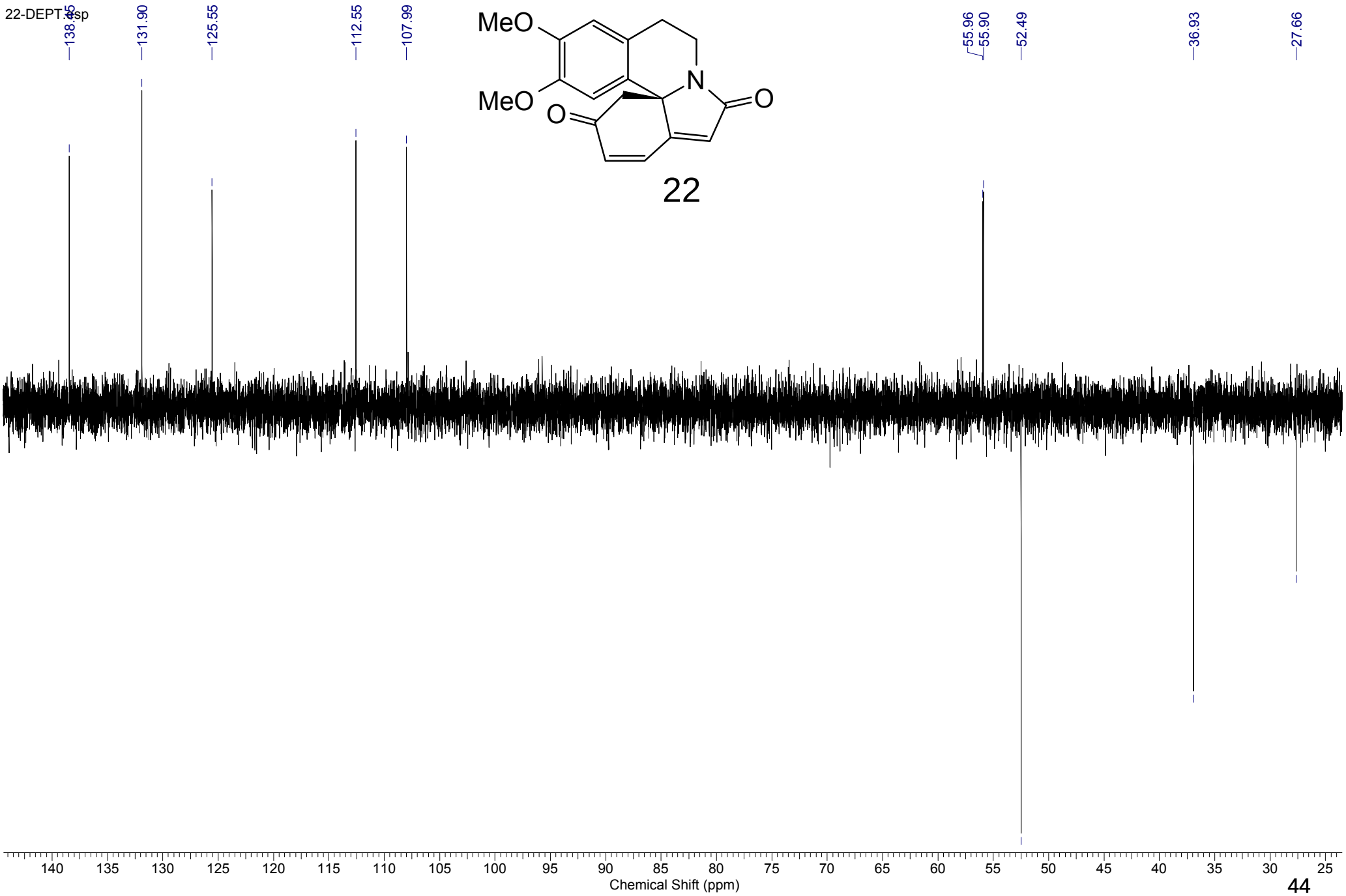
21-H1.esp

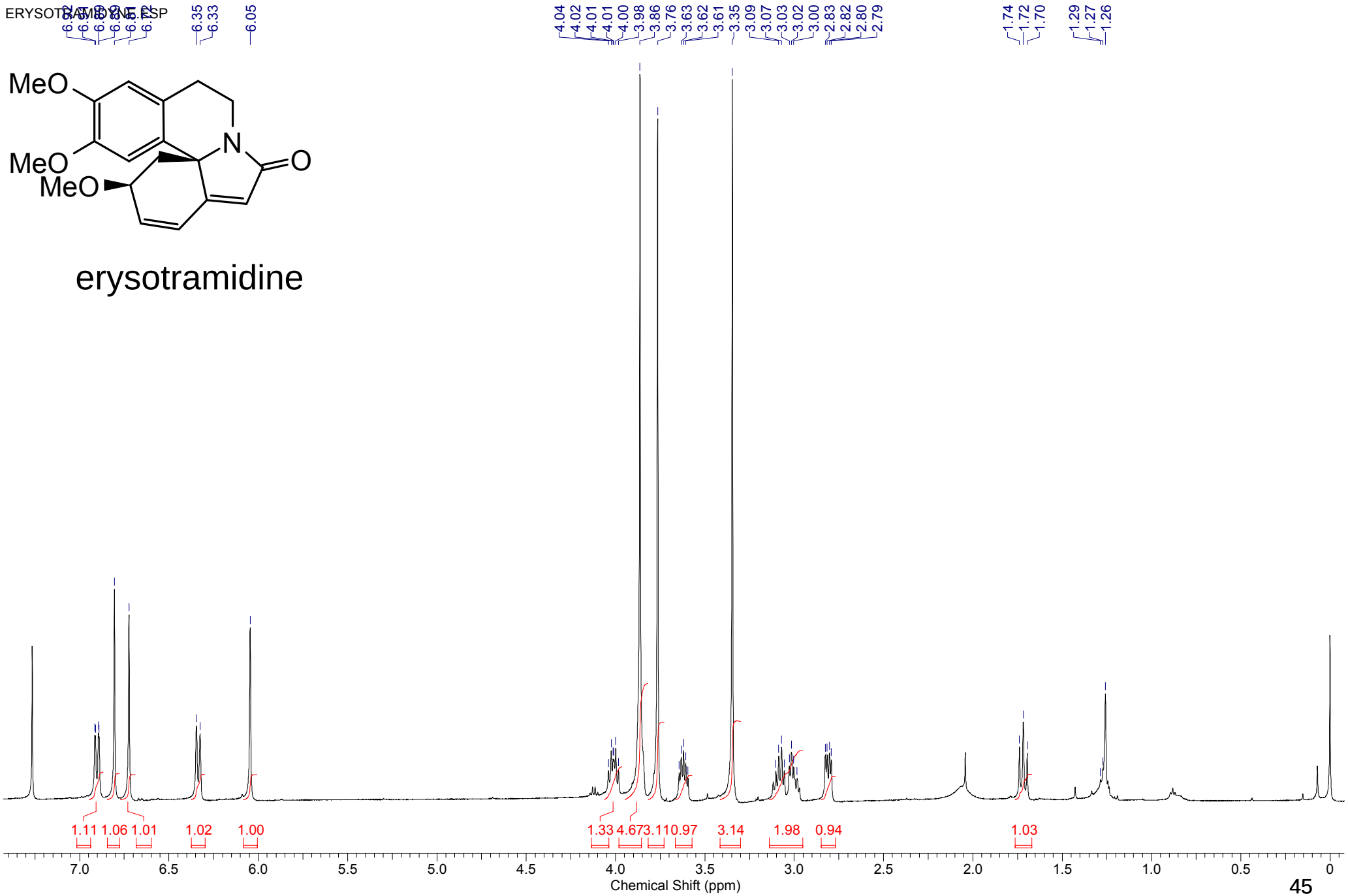

6.98
6.97
6.85
6.85
6.79
6.70
6.31
6.28
6.01
4.30
4.02
4.00
3.98
3.96
3.94
3.85
3.75
3.63
3.61
3.61
3.59
3.58
3.57
3.07
3.05
3.03
3.01
2.98
2.82
2.81
2.80
2.78
2.11
1.72
1.69
1.69
1.67
TMS
MeO
MeO
HO
N
O
1.03 1.01 1.00
1.02
0.94
1.06
1.21 3.18 3.02 1.30
2.27
1.07
0.87
1.24
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

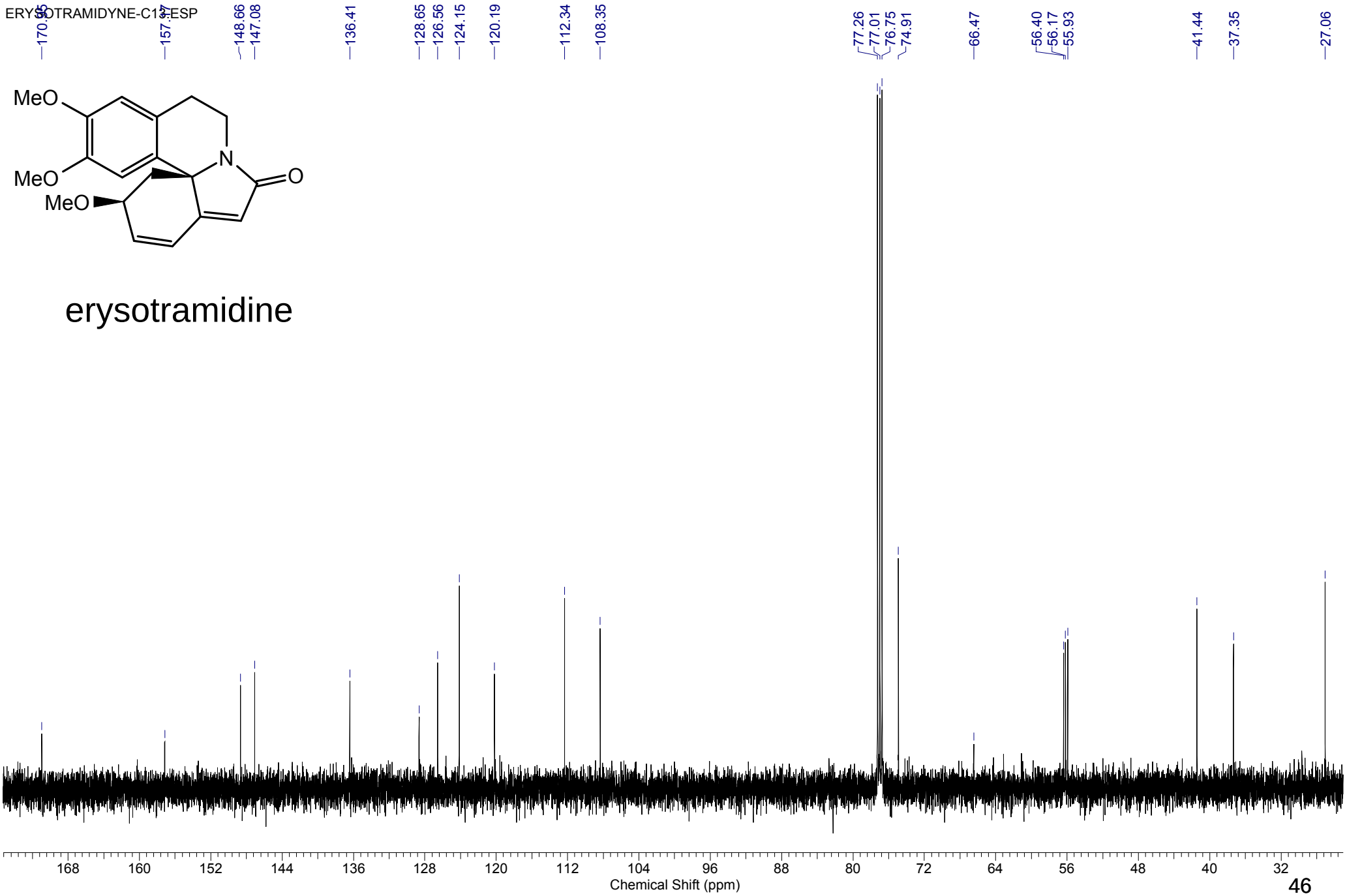
21

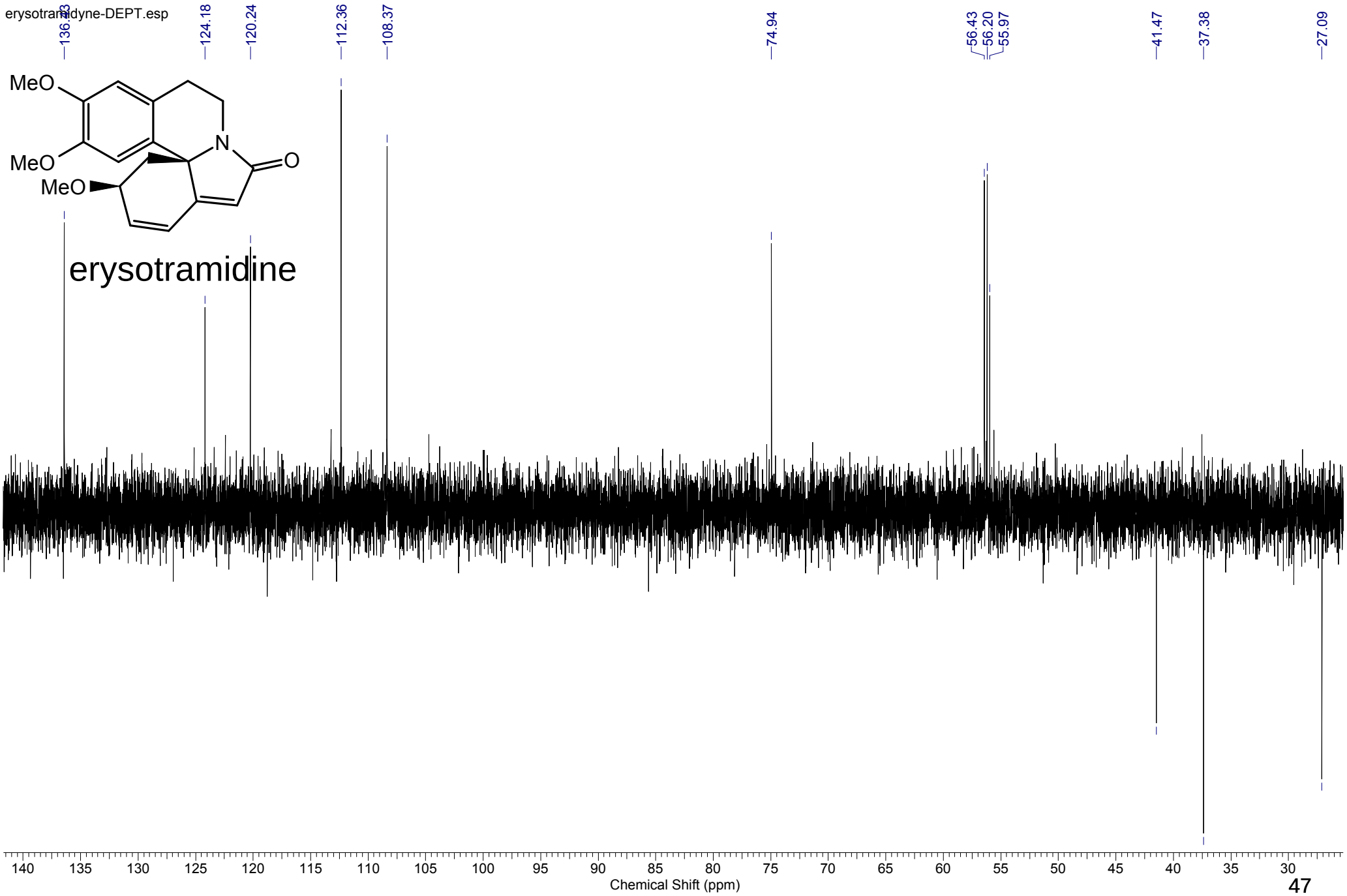

22-711.esp
7.76
7.74
7.27
6.85
6.66
6.42
6.40
6.37
4.24
4.23
4.23
4.22
4.20
4.20
3.84
3.72
3.41
3.41
3.40
3.39
3.38
3.28
3.25
3.03
3.02
2.85
2.84
2.83
2.81
2.78
MeO
MeO
N
O
O
22
1.00
1.00
0.99
1.02
0.93
1.03
3.13
2.97
0.97
0.95
0.99
1.95
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


22-C13.esp
195.18
169.71
154.80
148.86
147.36
138.46
131.90
128.12
126.05
125.55
112.56
108.00
77.26
77.00
76.75
67.70
55.96
55.90
52.49
36.92
27.65
MeO
MeO
N
O
O
22
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
Chemical Shift (ppm)


22-DEPT.esp
138.45
131.90
125.55
112.55
107.99
55.96
55.90
52.49
36.93
27.66
MeO
MeO
N
O
O
22
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
Chemical Shift (ppm)


ERYSOTRAMIDINE.ESP
MeO
MeO
MeO
N
O
erysotramidine
6.89 6.87 6.85 6.83 6.81 6.35 6.33 6.05
4.04 4.02 4.01 4.01 4.00 3.98 3.86 3.76 3.63 3.62 3.61 3.35 3.09 3.07 3.03 3.02 3.00 2.83 2.82 2.80 2.79
1.74 1.72 1.70 1.29 1.27 1.26
1.11 1.06 1.01 1.02 1.00 1.33 4.67 3.11 0.97 3.14 1.98 0.94 1.03
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
Chemical Shift (ppm)


ERYSOTRAMIDYNE-C13-ESP
170.55
157.77
148.66
147.08
136.41
128.65
126.56
124.15
120.19
112.34
108.35
77.26
77.01
76.75
74.91
66.47
56.40
56.17
55.93
41.44
37.35
27.06
MeO
MeO
MeO
N
O
erysotramidine
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
Chemical Shift (ppm)


erysotramidyne-DEPT.esp
136.23
124.18
120.24
112.36
108.37
74.94
56.43
56.20
55.97
41.47
37.38
27.09
MeO
MeO
MeO
N
O
erysotramidine
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
Chemical Shift (ppm)