Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information for:

Synthesis of Chiral Hexynones for Use as Precursors to Native Photosynthetic Hydroporphyrins

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(1) Detection of an epimer by ^{1}H NMR spectroscopy

The integrity of the stereogenic centers in **4** is contrasted with those in the mixture of **4** and **4-epi** upon examination by ^{1}H NMR spectroscopy. The spectra are displayed in Figure S1. In the most upfield region, two singlets (partially merged with each other) corresponding to the trimethylsilyl group of **4** and **4-epi** appear at 0.14 and 0.13 ppm, respectively. Each type of methyl group in **4** and **4-epi** appears at the same position, giving rise to two resonances, one triplet and one doublet, centered at 1.03 and 1.17 ppm, respectively. The methylene protons of the ethyl group from two epimers resonate at the range corresponding to the multiplet centered at 1.50 ppm. The multiplet centered at 2.40 ppm can be assigned to one methyne proton in **4** and the analogous one in **4-epi**. The other methyne protons in **4** and **4-epi** appear in the downfield region and are well resolved as two distinctive resonances at 2.55 and 2.76 ppm, respectively. The same scenario was also noted for the aldehydic resonances of the two epimers: the higher one (9.67 ppm) can be easily assigned to the major component, **4-epi**, while the smaller one at 9.76 ppm is assigned to the minor component, **4**.

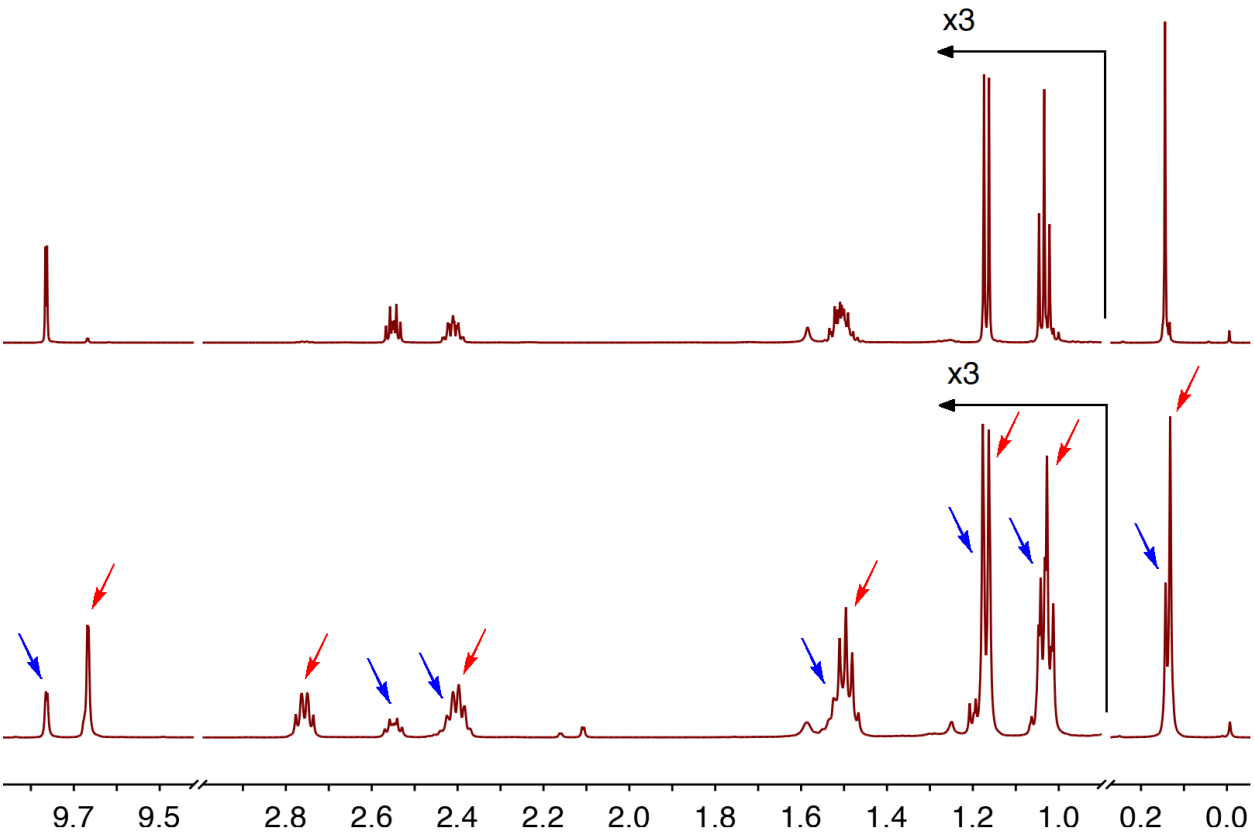


Figure S1. ^{1}H NMR spectra in $CDCl_3$ of **4** (top, 600 MHz instrument) obtained by exhaustive reduction followed by oxidation[10] and an inseparable mixture of **4** and **4-epi** (bottom, 500 MHz instrument) obtained by hydrolysis of **7**. Resonances corresponding to **4** and **4-epi** in the mixture are marked by blue and red arrows, respectively.

(2) Single-crystal X-ray diffraction data

Table S1. Data for compound **10.**

CCDC registry	2287122
Chemical formula	$C_{17}H_{31}NO_3Si$
Formula weight (g/mol)	325.52
Temperature (K)	100
Wavelength (Å)	0.71073
Crystal size (mm)	0.63 × 0.22 × 0.09
Crystal habit	Colorless plate
Crystal system	Monoclinic
Space group	P_{21}
Unit cell dimensions, *a* (Å)	6.1517 (11)
Unit cell dimensions, *b* (Å)	11.1177 (19)
Unit cell dimensions, *c* (Å)	14.455 (2)
α, deg	90
β, deg	91.786 (6)
γ, deg	90
Volume ($Å^3$)	988.1 (3)
Z	2
Density (calculated) (g/cm^3)	1.094
Absorption coefficient (mm^{-1})	0.13
F(000)	356
Theta range for data collection, deg	2.3 to 26.7
Index ranges	-6<=h<=7, -14<=k<=14, -18<=l<=18
Reflections collected	11928
Independent reflections	4010 [R(int) = 0.042]
R_1	0.0433
wR_2	0.0859
R_1 (all data)	0.0514
wR_2 (all data)	0.0900
Largest diff. peak and hole ($eÅ^{-3}$)	0.21, −0.28
R.M.S. deviation from mean ($eÅ^{-3}$)	0.041
Absolute structure parameter	−0.02 (9)

Table S2. Data for compound **11**.

CCDC registry	2287123
Chemical formula	$C_{25}H_{36}Co_2N_2O_{10}Si$
Formula weight (g/mol)	670.51
Temperature (K)	100
Wavelength (Å)	0.71073
Crystal size (mm)	0.253 × 0.065 × 0.024
Crystal habit	Clear dark red prism
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions, *a* (Å)	9.0216 (3)
Unit cell dimensions, *b* (Å)	13.8726 (5)
Unit cell dimensions, *c* (Å)	24.6824 (9)
α, deg	90
β, deg	90
γ, deg	90
Volume ($Å^3$)	3089.08 (19)
Z	4
Density (calculated) (g/cm^3)	1.442
Absorption coefficient (mm^{-1})	1.166
F(000)	1392
Theta range for data collection, deg	4.808 to 54.272
Index ranges	-11<=h<=11, -17<=k<=17, -31<=l<=31
Reflections collected	37149
Independent reflections	6743 [R(int) = 0.0656]
R_1	0.0303
wR_2	0.0639
R_1 (all data)	0.0367
wR_2 (all data)	0.0667
Largest diff. peak and hole ($eÅ^{-3}$)	0.41, –0.29
R.M.S. deviation from mean ($eÅ^{-3}$)	0.058
Absolute structure parameter	0.007(8)

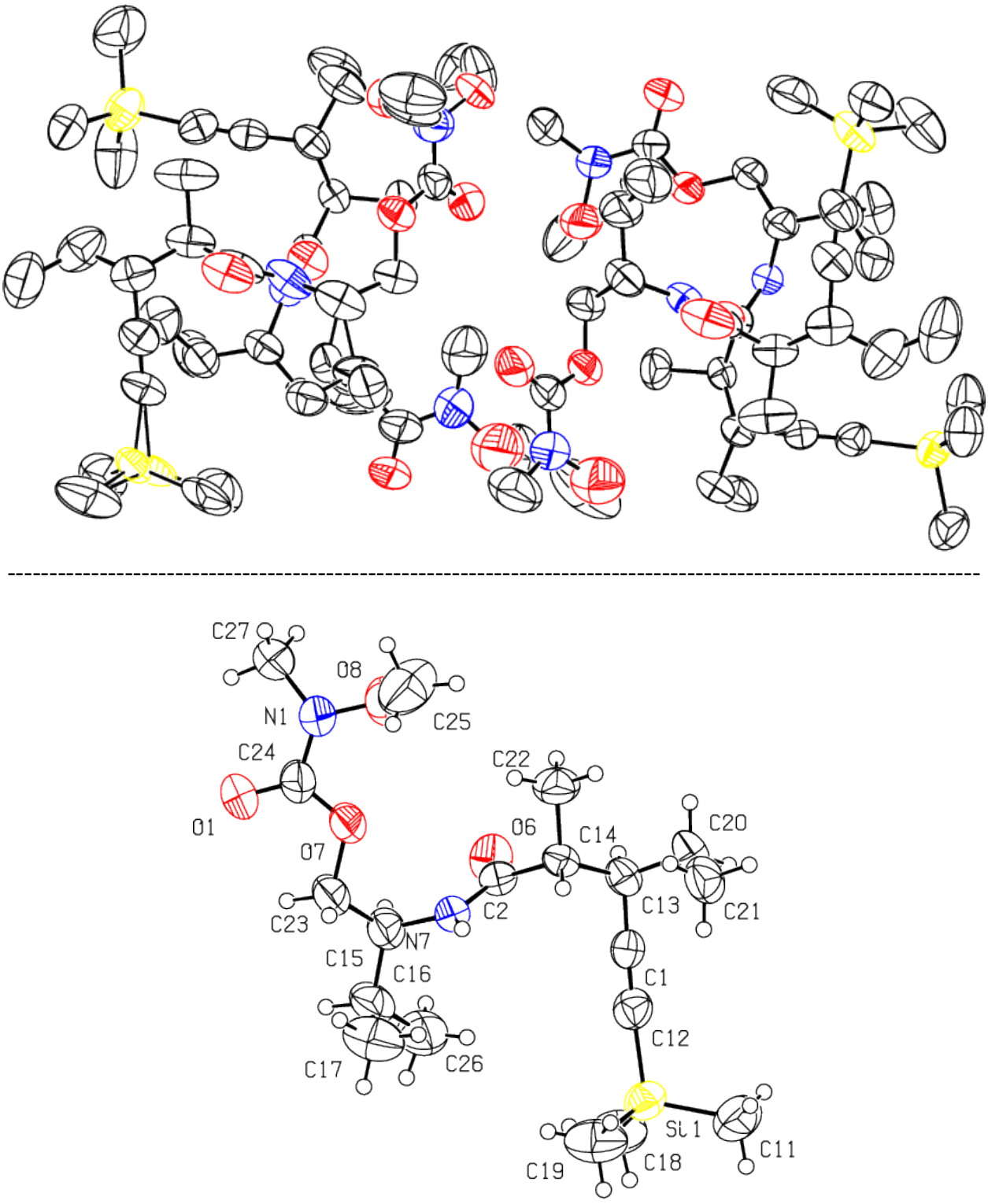
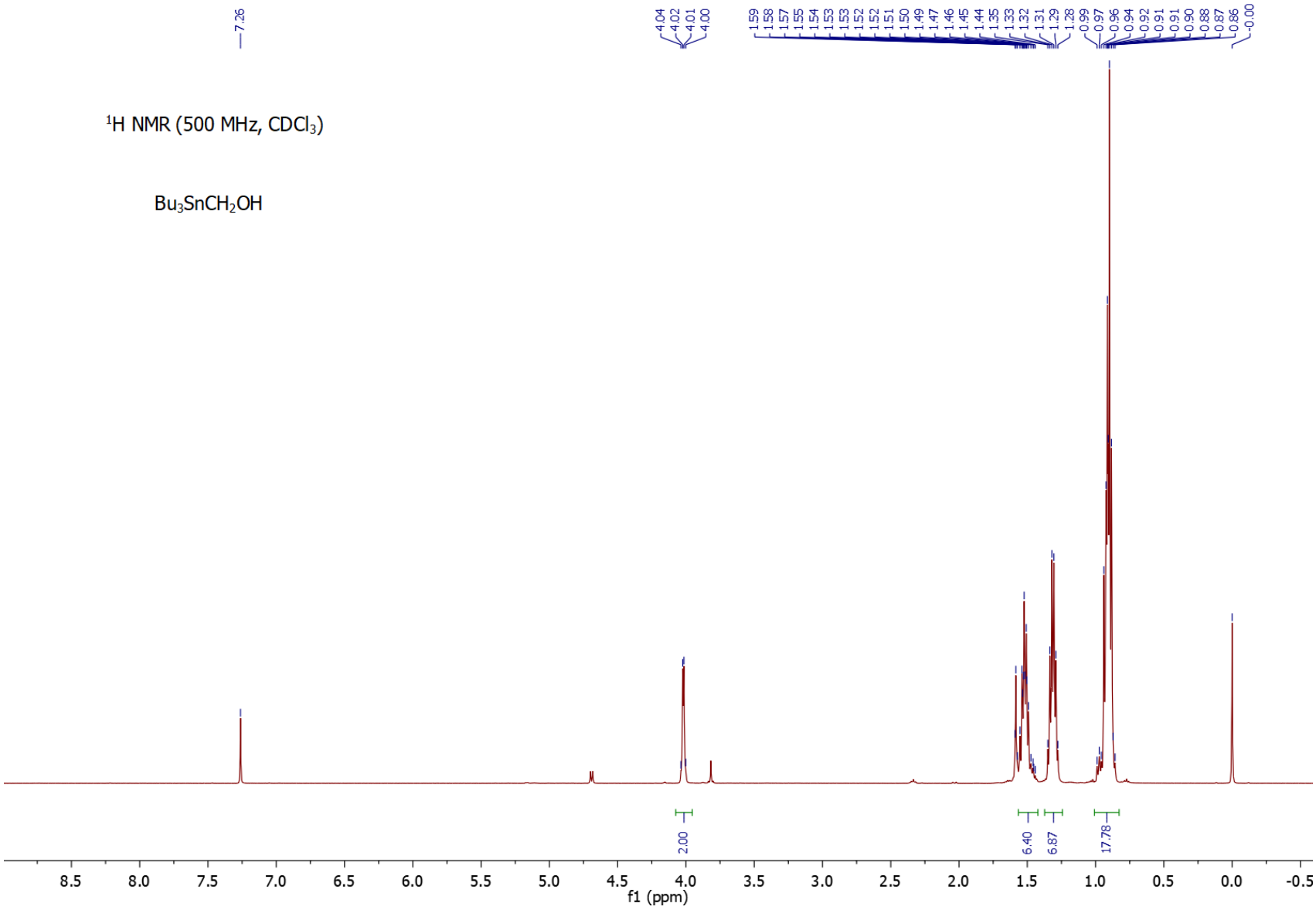


Figure S2. Top: ORTEP diagram of compound **12** containing four crystallographically independent moieties with thermal ellipsoids drawn at the 50% probability level and omitted H atoms for clarity; bottom: ORTEP diagram of the best moiety of compound **12** with thermal ellipsoids drawn at the 50% probability level.

Table S3. Data for compound **12**.

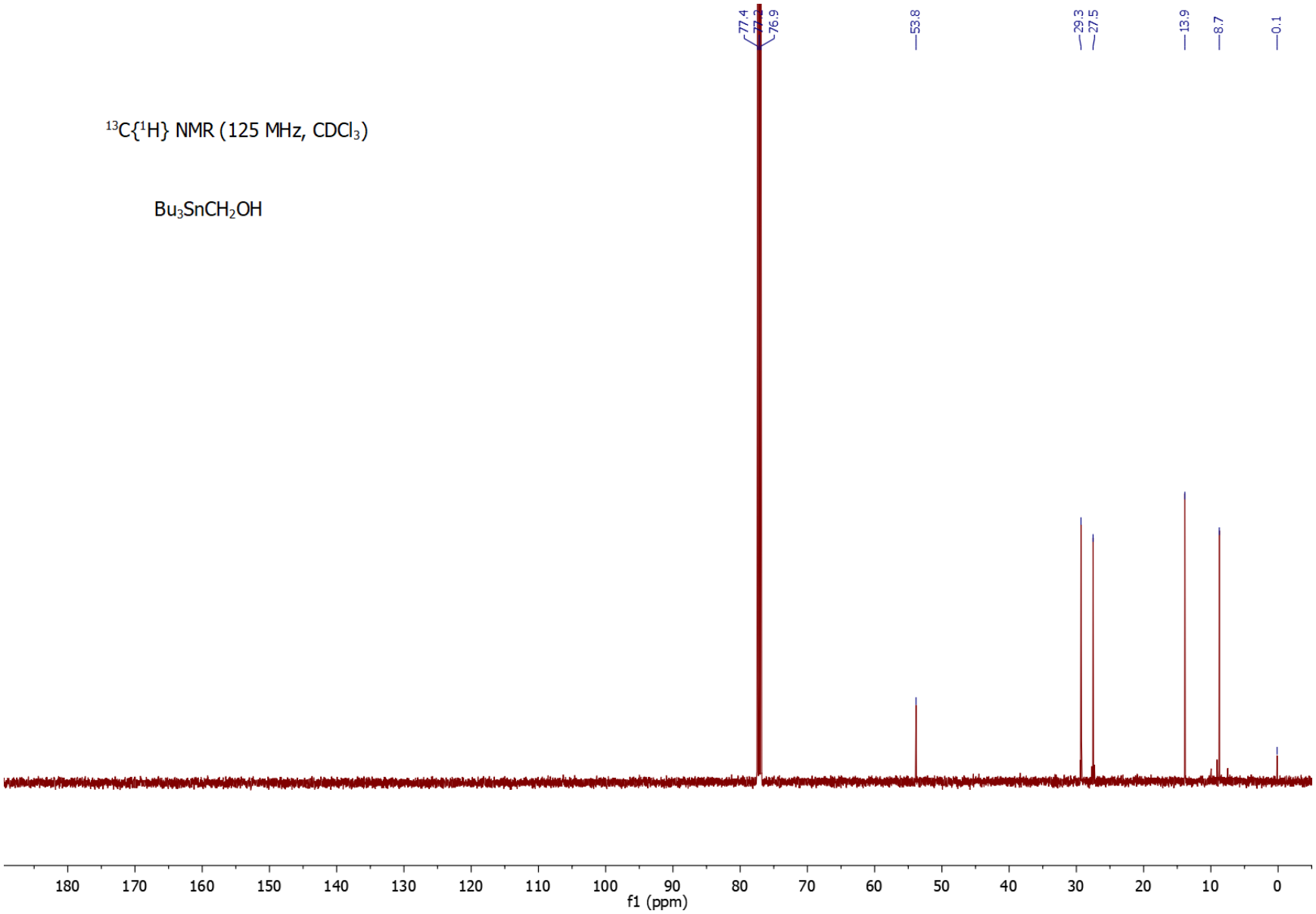
CCDC registry	2287124
Chemical formula	$C_{19}H_{36}N_2O_4Si$
Formula weight (g/mol)	384.59
Temperature (K)	100
Wavelength (Å)	1.54178
Crystal size (mm)	0.327 × 0.137 × 0.044
Crystal habit	Clear light colorless plate
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions, *a* (Å)	9.5029 (4)
Unit cell dimensions, *b* (Å)	44.825 (2)
Unit cell dimensions, *c* (Å)	11.1259 (6)
α, deg	90
β, deg	90.692 (3)
γ, deg	90
Volume ($Å^3$)	4739.0 (4)
Z	8
Density (calculated) (g/cm^3)	1.078
Absorption coefficient (mm^{-1})	1.06
F(000)	1680
Theta range for data collection, deg	3.945 to 66.592
Index ranges	-10<=h<=11, -53<=k<=53, -13<=l<=13
Reflections collected	60586
Independent reflections	16704 [R(int) = 0.056]
R_1	0.0799
wR_2	0.2241
R_1 (all data)	0.0918
wR_2 (all data)	0.2413
Largest diff. peak and hole ($eÅ^{-3}$)	0.861, –0.341
R.M.S. deviation from mean ($eÅ^{-3}$)	0.055
Absolute structure parameter	0.022 (15)

(3) Spectral data



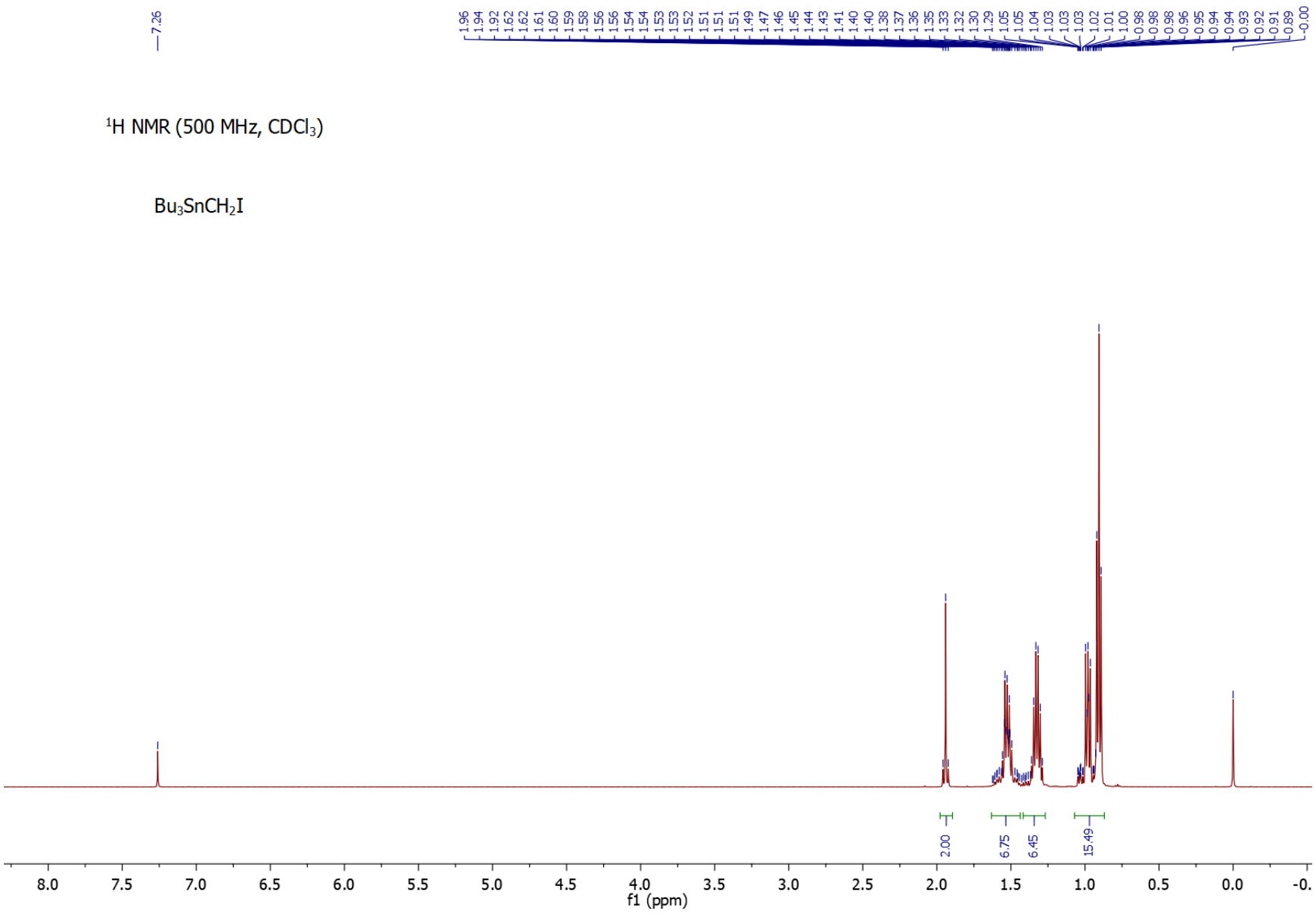
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

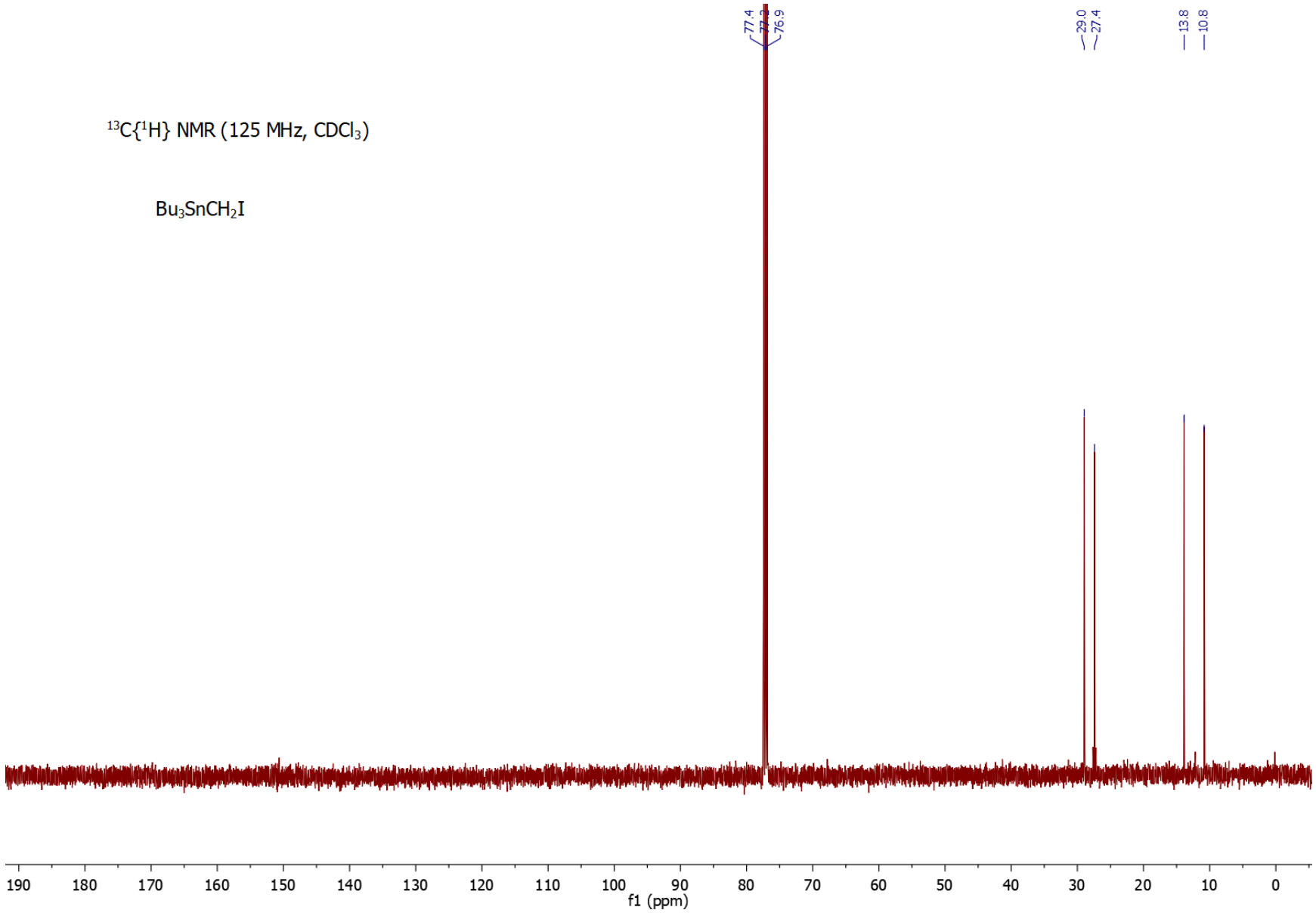
Bu_3SnCH_2OH



^{1}H NMR (500 MHz, $CDCl_3$)

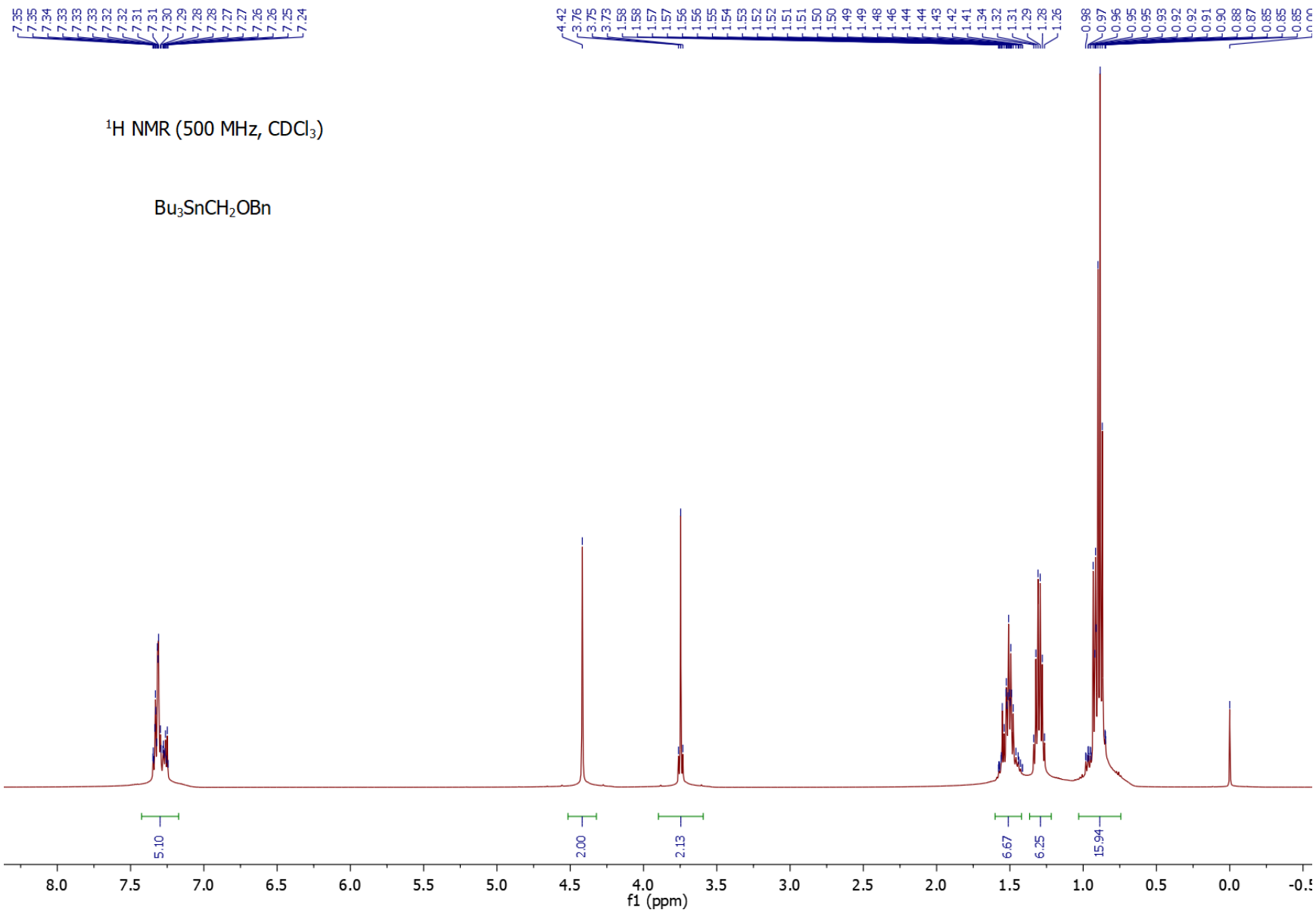
Bu_3SnCH_2I

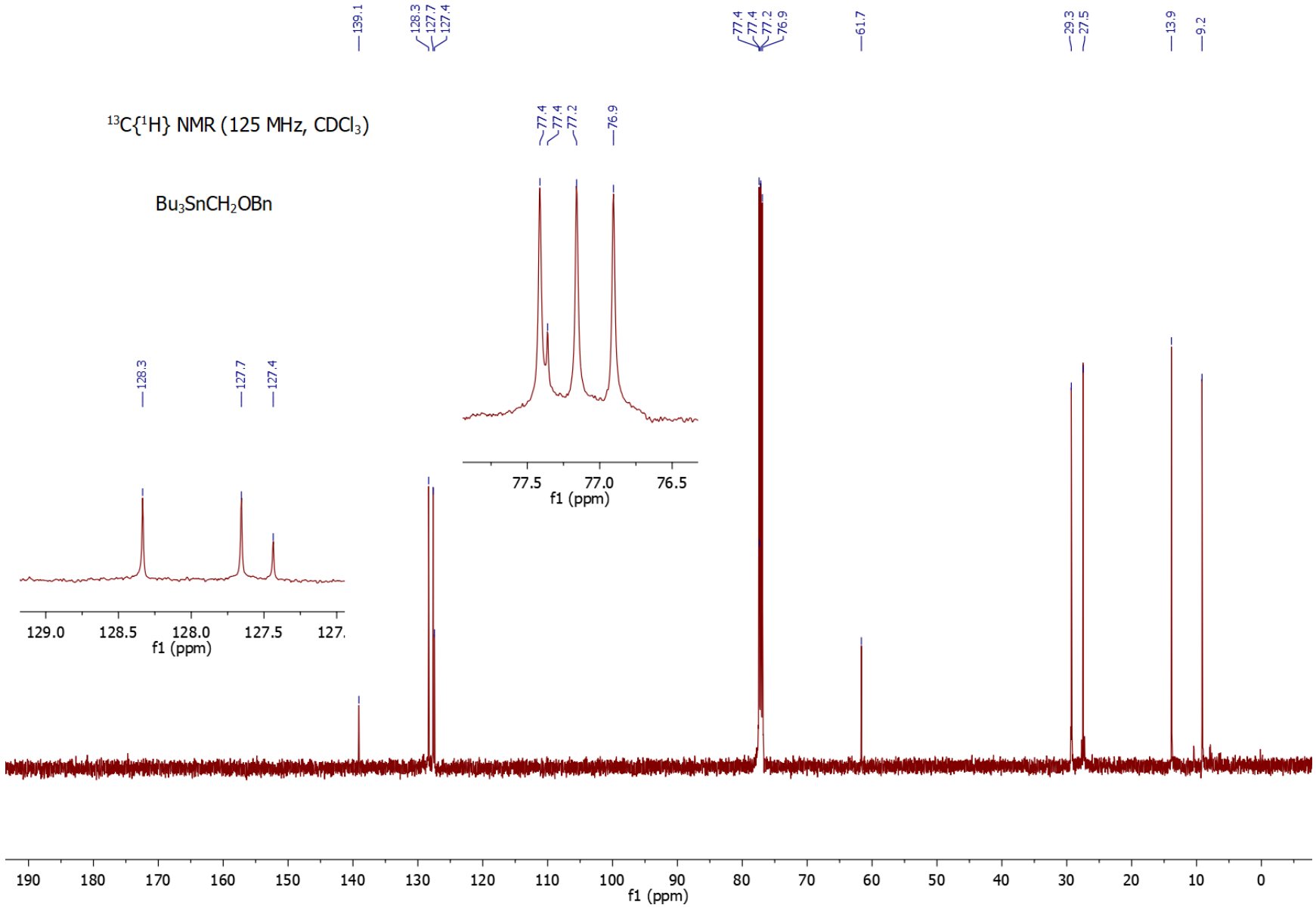


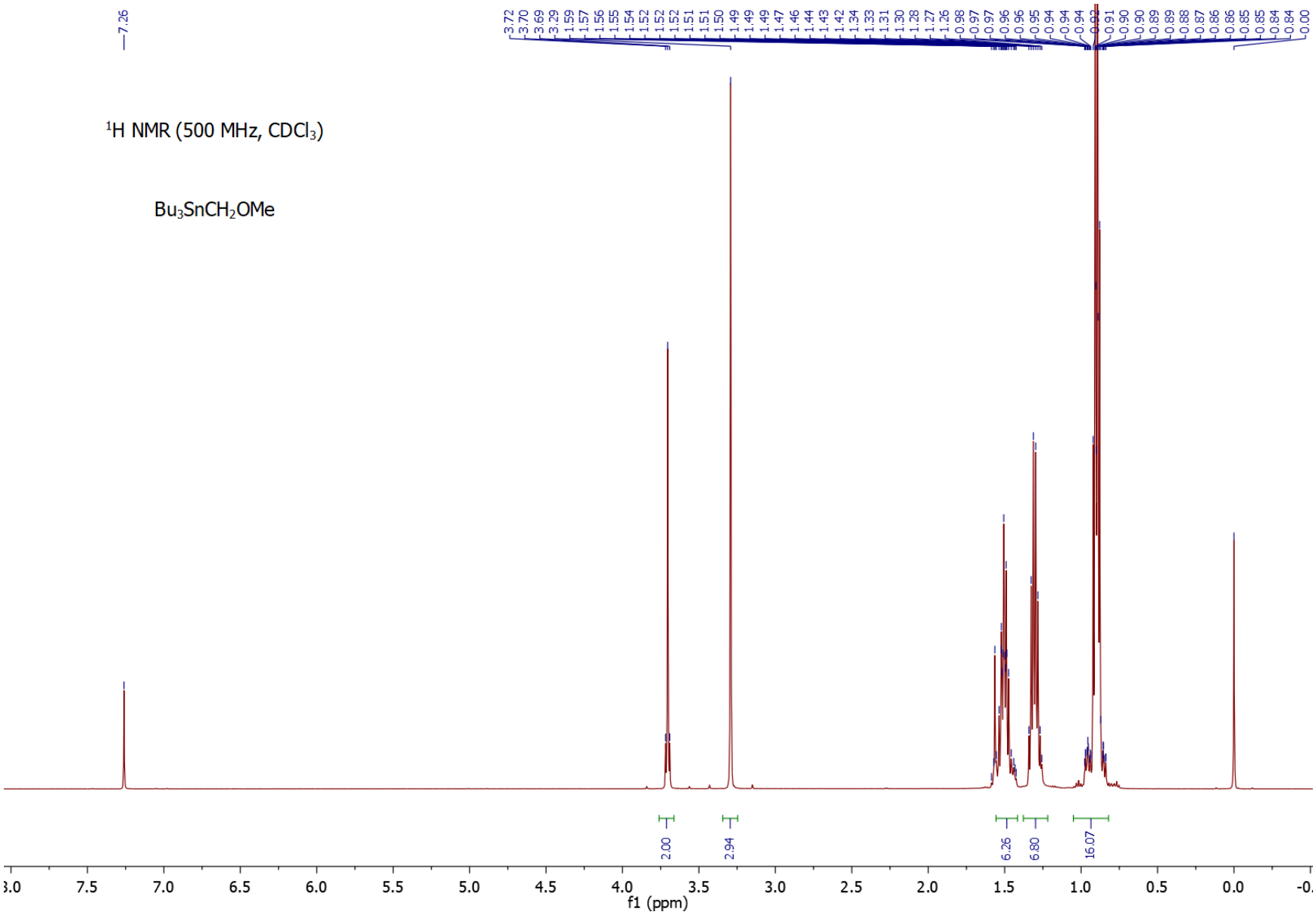


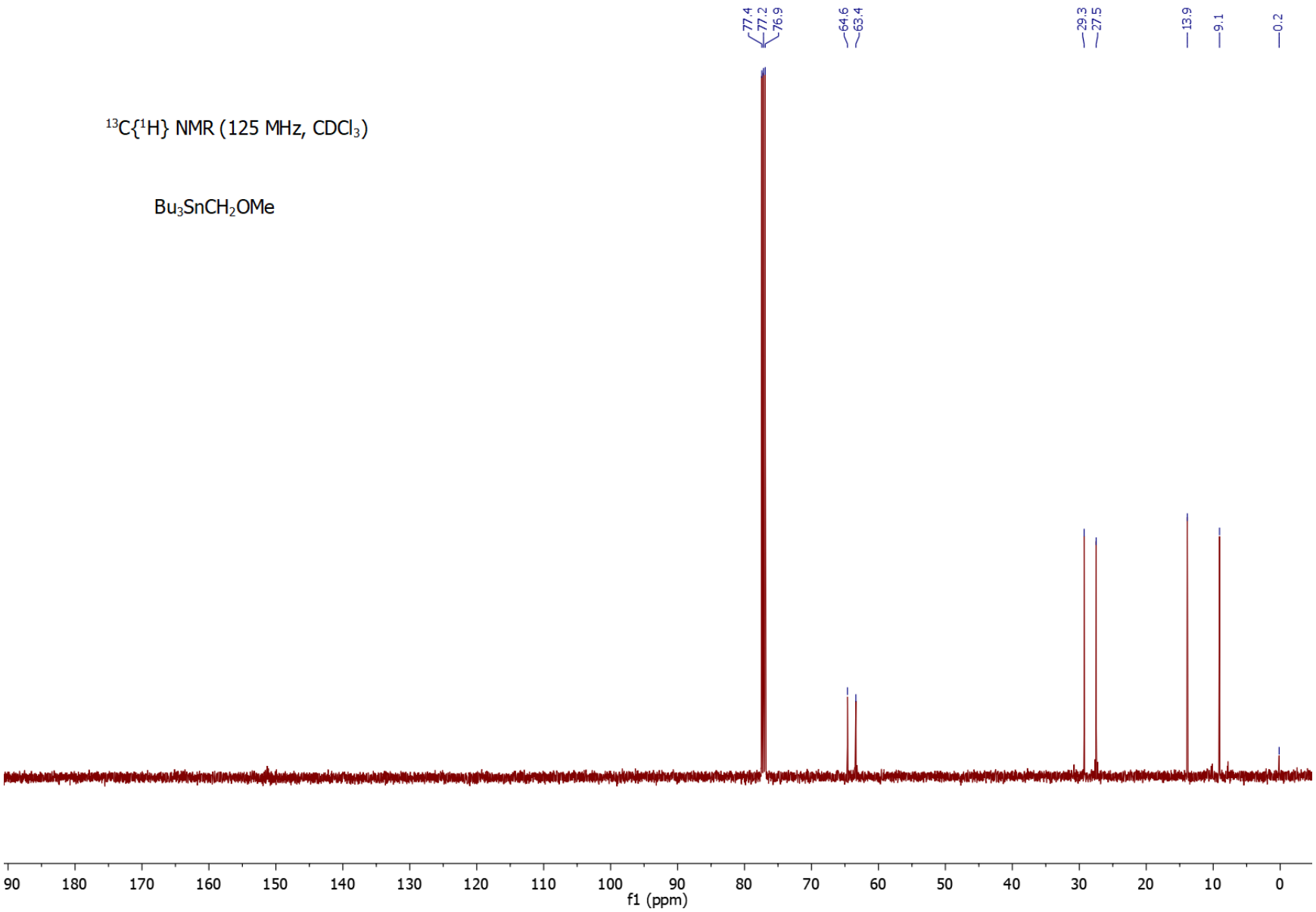
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

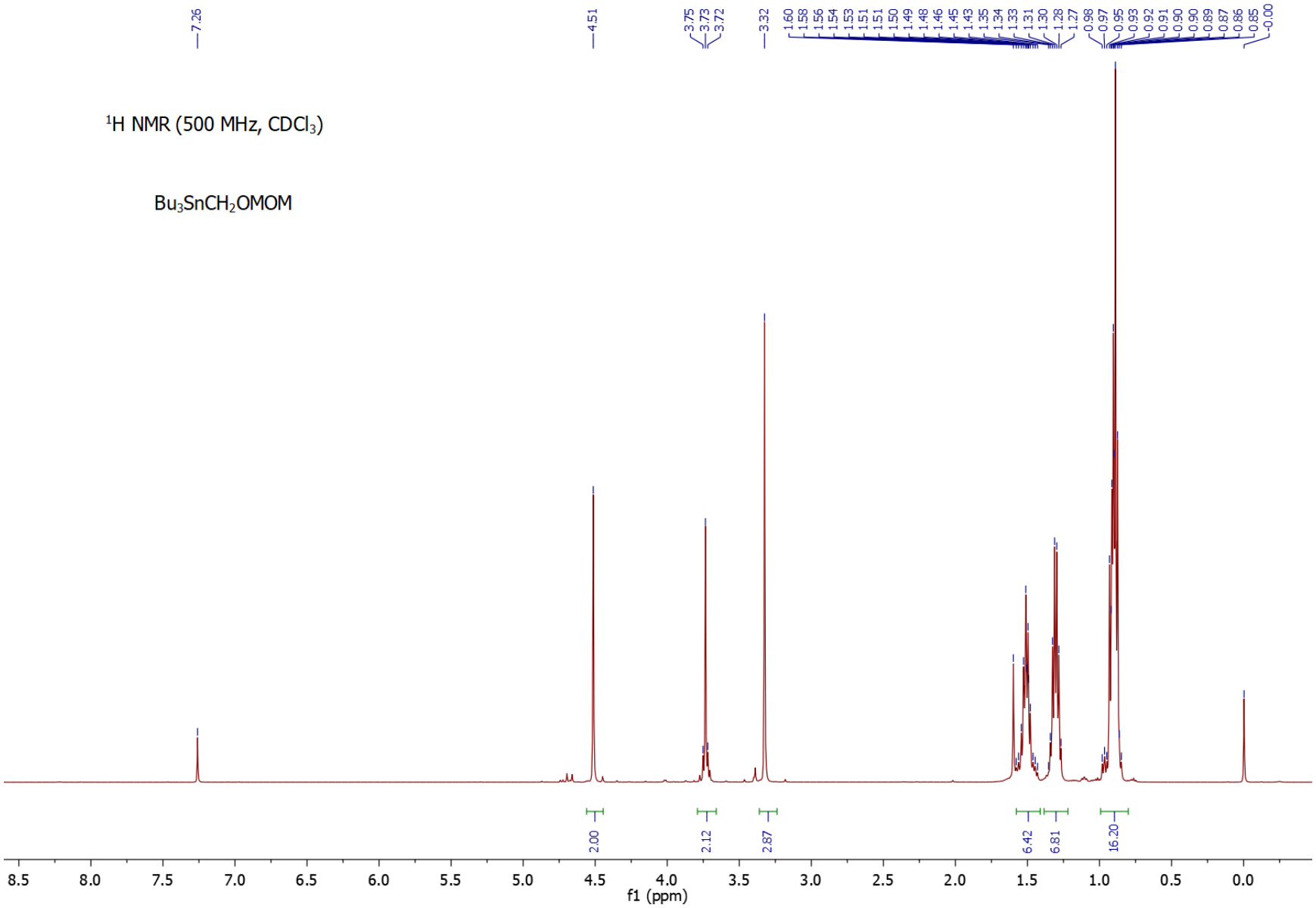
Bu_3SnCH_2I

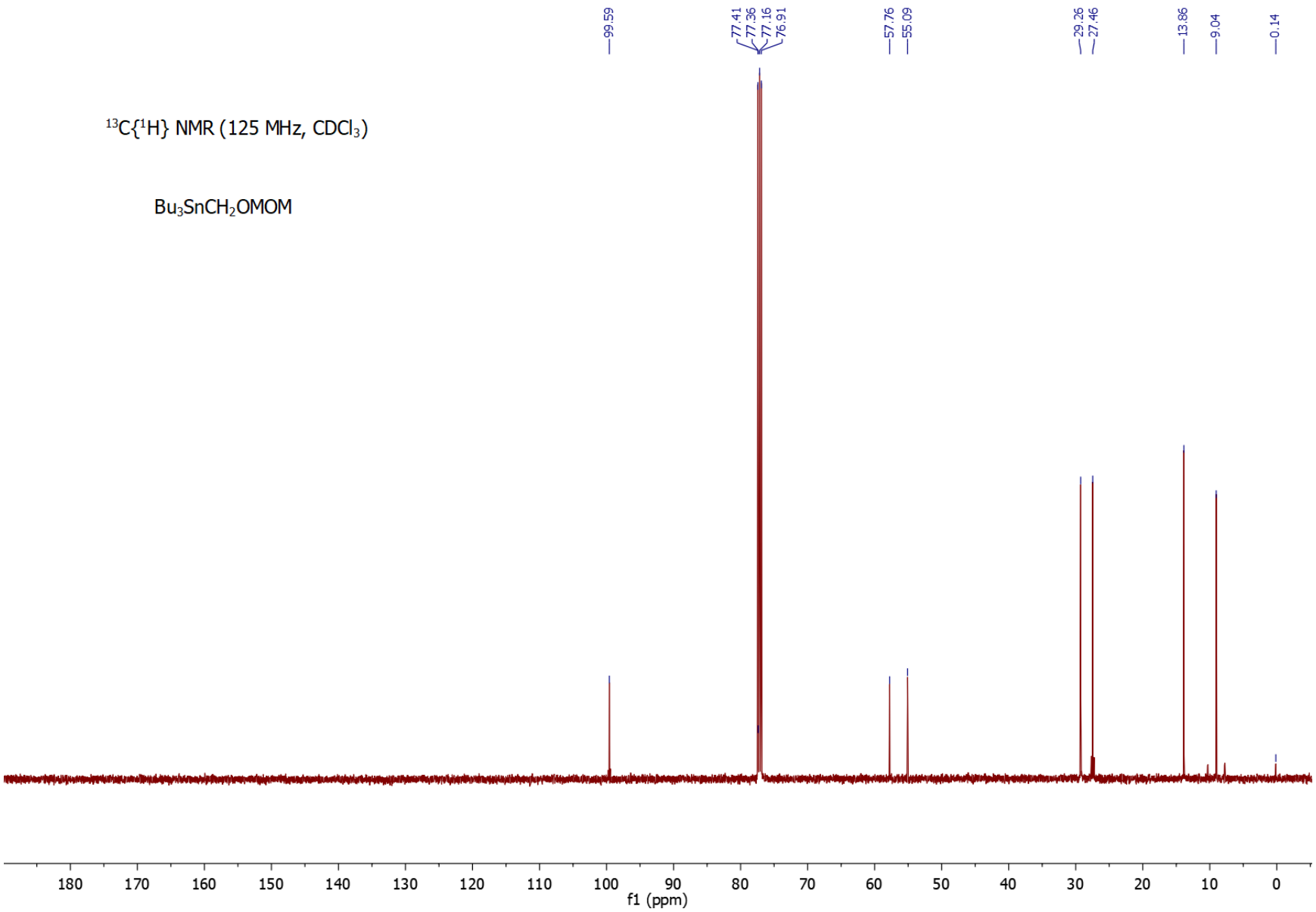

^{1}H NMR (500 MHz, $CDCl_3$)
Bu_3SnCH_2OBn
f1 (ppm)

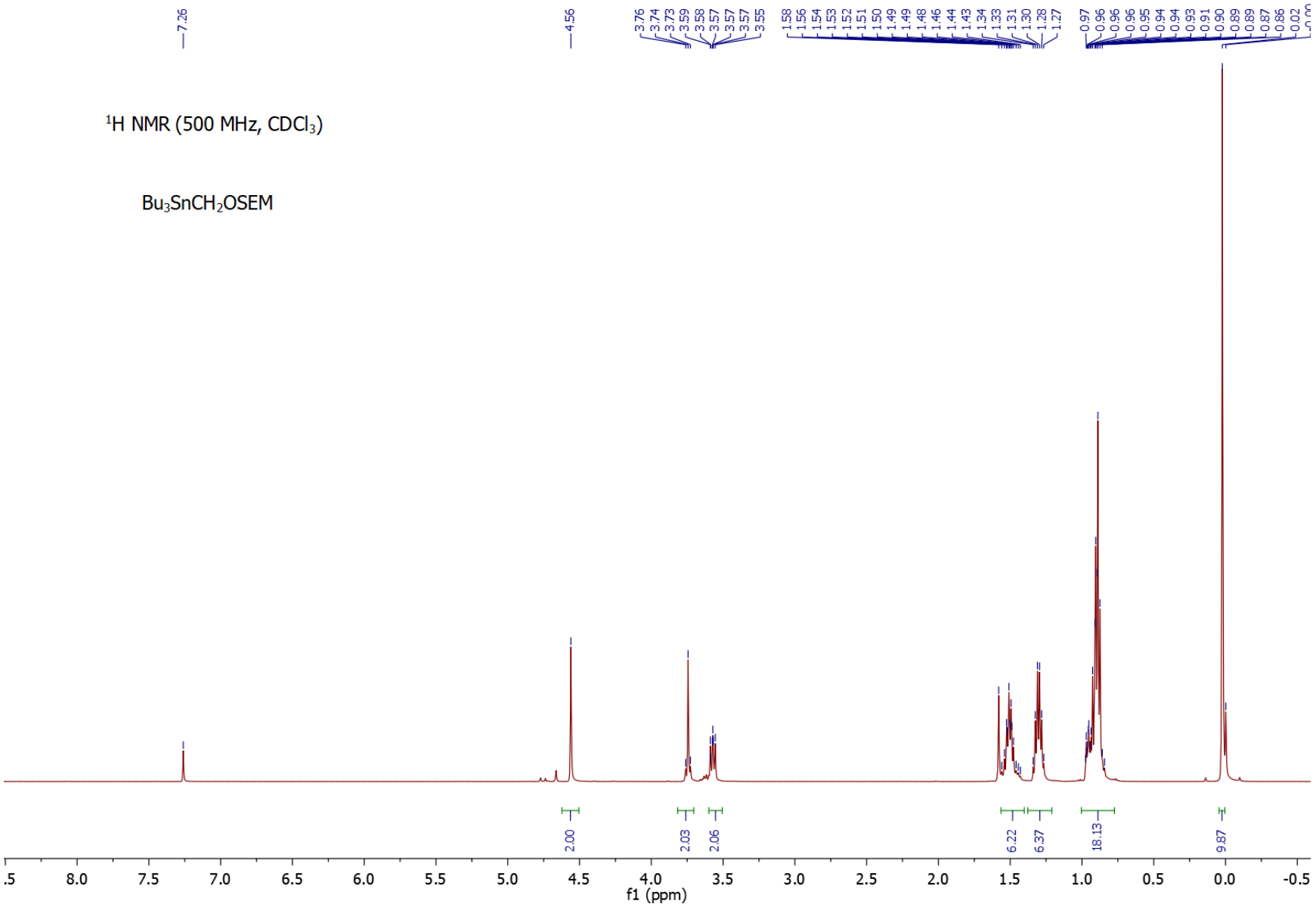

139.1
128.3
127.7
127.4
77.4
77.4
77.2
76.9
61.7
29.3
27.5
13.9
9.2
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
Bu_3SnCH_2OBn
77.5
77.0
76.5
f1 (ppm)
129.0
128.5
128.0
127.5
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

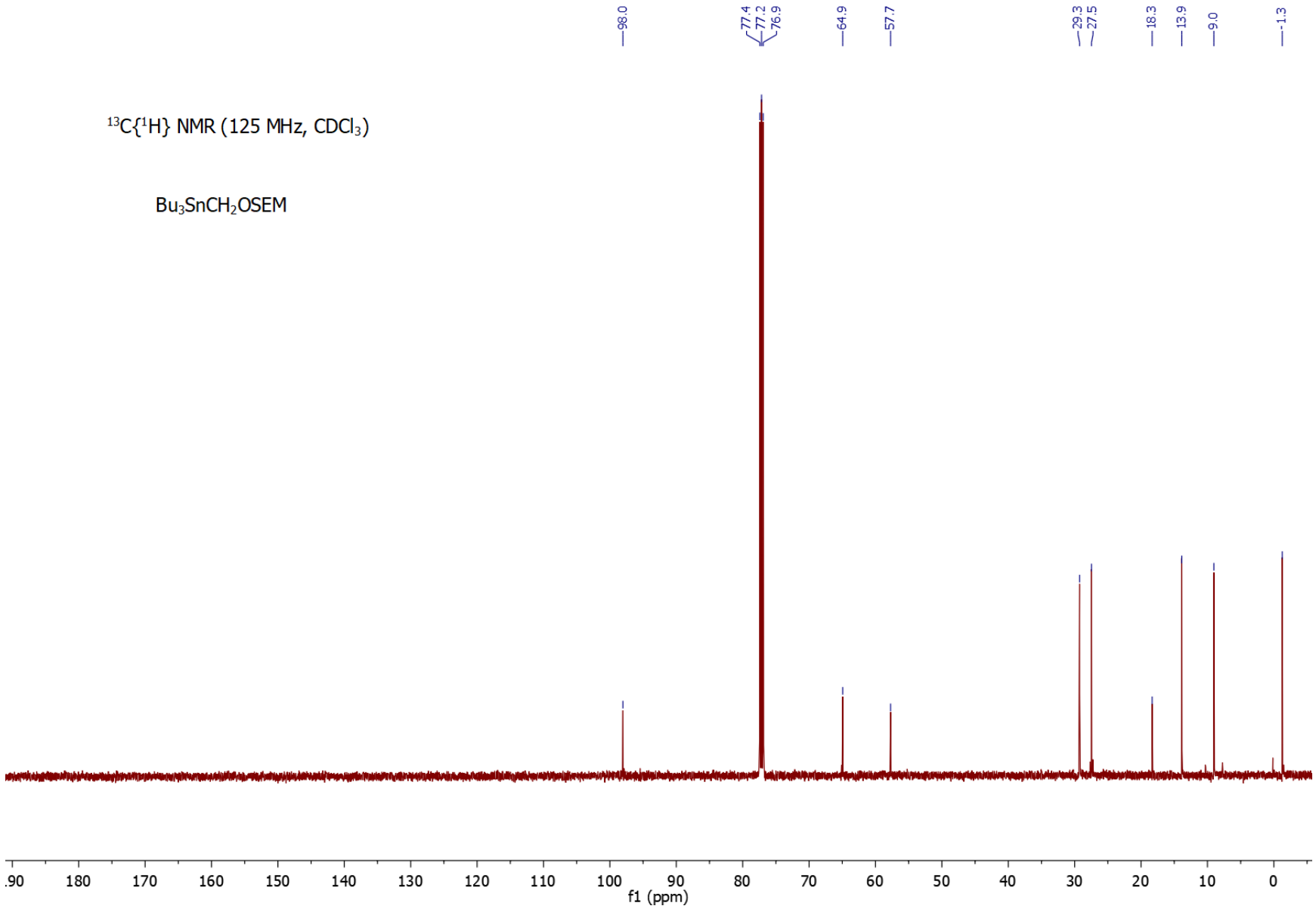

^{1}H NMR (500 MHz, $CDCl_3$)
Bu_3SnCH_2OMe
7.26
3.72
3.70
3.69
3.29
1.59
1.57
1.56
1.55
1.54
1.52
1.52
1.52
1.51
1.51
1.50
1.49
1.49
1.49
1.47
1.46
1.44
1.43
1.42
1.34
1.33
1.31
1.30
1.28
1.27
1.26
0.98
0.97
0.97
0.96
0.96
0.95
0.94
0.94
0.93
0.91
0.90
0.90
0.89
0.89
0.88
0.87
0.86
0.86
0.85
0.85
0.84
0.84
0.00
2.00
2.94
6.26
6.80
16.07
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)

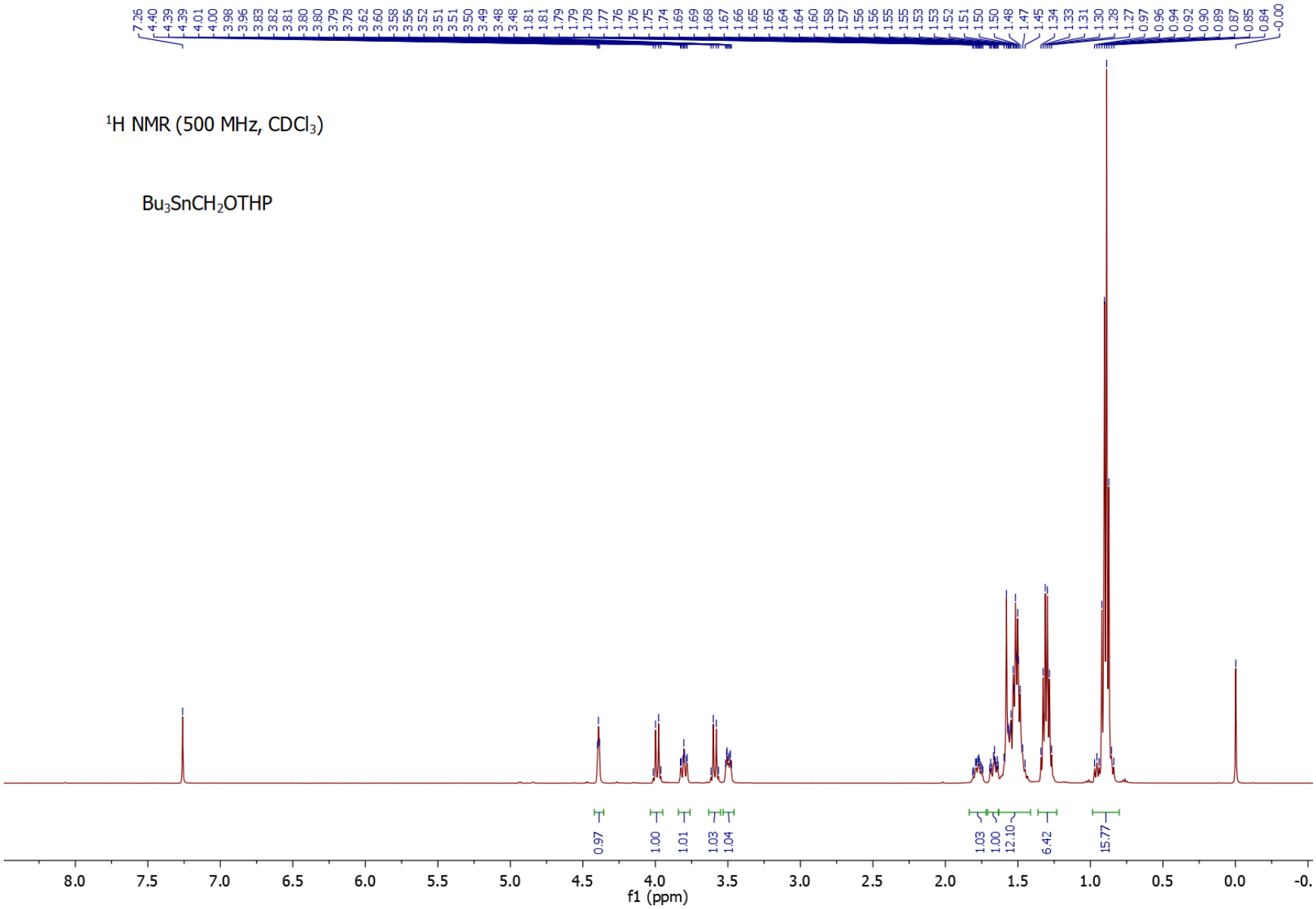

77.4
77.2
76.9
64.6
63.4
29.3
27.5
13.9
9.1
0.2
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
Bu_3SnCH_2OMe
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26
4.51
3.75
3.73
3.72
3.32
1.60
1.58
1.56
1.54
1.53
1.51
1.51
1.50
1.49
1.48
1.46
1.45
1.43
1.35
1.34
1.33
1.31
1.30
1.28
1.27
0.98
0.97
0.95
0.93
0.92
0.91
0.90
0.90
0.89
0.87
0.86
0.85
-0.00
^{1}H NMR (500 MHz, $CDCl_3$)
Bu_3SnCH_2OMOM
2.00
2.12
2.87
6.42
6.81
16.20
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)


99.59
77.41
77.36
77.16
76.91
57.76
55.09
29.26
27.46
13.86
9.04
0.14
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
Bu_3SnCH_2OMOM
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26
4.56
3.76
3.74
3.73
3.59
3.58
3.57
3.57
3.57
3.55
1.58
1.56
1.54
1.53
1.52
1.51
1.50
1.49
1.49
1.48
1.46
1.44
1.43
1.34
1.33
1.31
1.30
1.28
1.27
0.97
0.96
0.96
0.96
0.95
0.94
0.94
0.93
0.91
0.90
0.89
0.89
0.87
0.86
0.02
^{1}H NMR (500 MHz, $CDCl_3$)
Bu_3SnCH_2OSEM
2.00
2.03
2.06
6.22
6.37
18.13
9.87
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


98.0
77.4
77.2
76.9
64.9
57.7
29.3
27.5
18.3
13.9
9.0
-1.3
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
Bu_3SnCH_2OSEM
f1 (ppm)


7.26
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4.01
4.00
3.98
3.96
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3.82
3.81
3.80
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3.79
3.78
3.62
3.60
3.58
3.56
3.52
3.51
3.51
3.50
3.49
3.48
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1.78
1.77
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1.75
1.74
1.69
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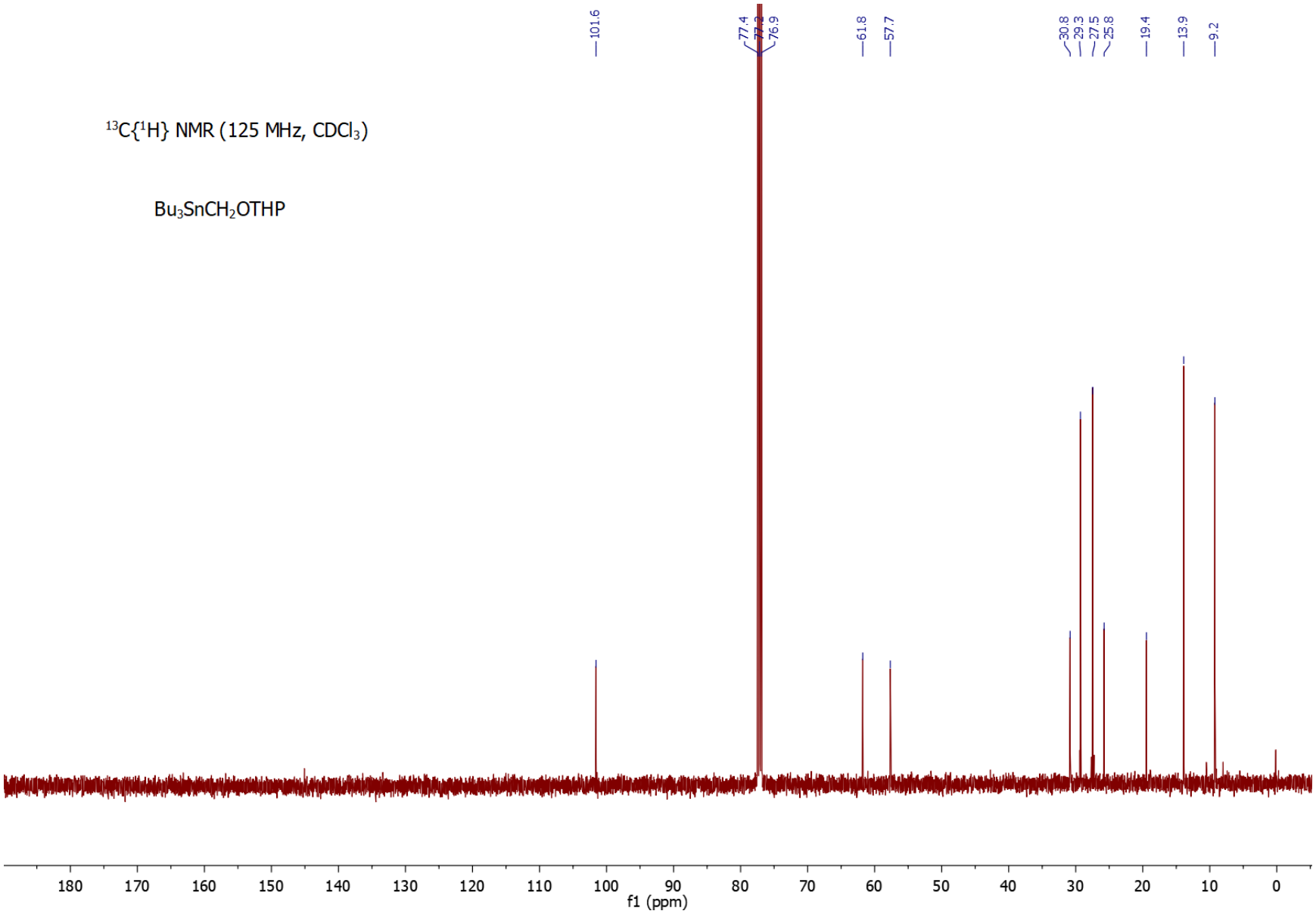
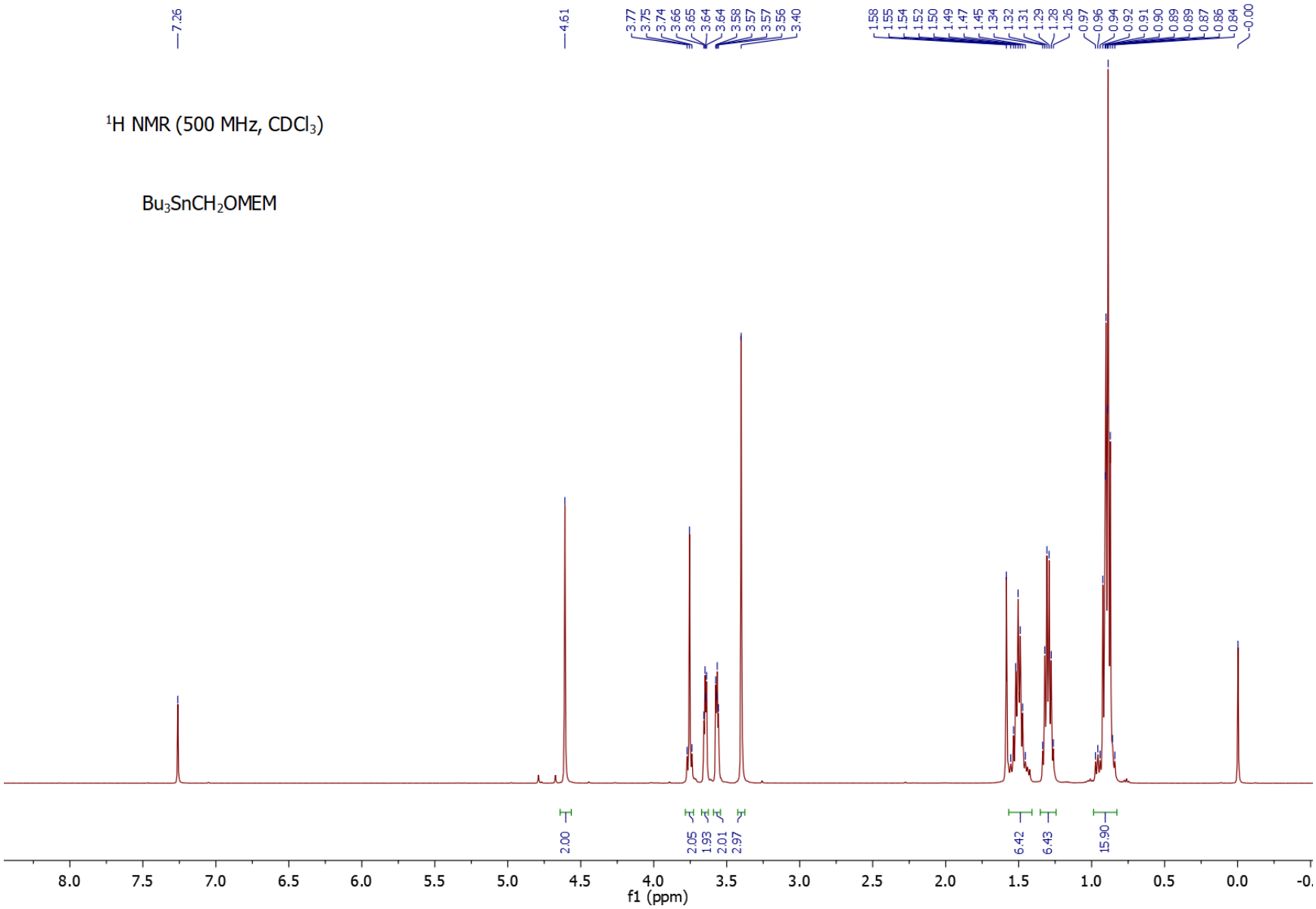
1.67
1.66
1.65
1.65
1.64
1.64
1.60
1.58
1.57
1.56
1.56
1.55
1.55
1.53
1.53
1.52
1.51
1.50
1.50
1.48
1.47
1.45
1.34
1.33
1.31
1.30
1.28
1.27
0.97
0.96
0.94
0.92
0.90
0.89
0.87
0.85
0.84
-0.00
^{1}H NMR (500 MHz, $CDCl_3$)
Bu_3SnCH_2OTHP
0.97
1.00
1.01
1.03
1.04
1.03
1.00
12.10
6.42
15.77
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)



$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

Bu_3SnCH_2OTHP


7.26
4.61
3.77
3.75
3.74
3.66
3.65
3.64
3.64
3.58
3.57
3.57
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3.40
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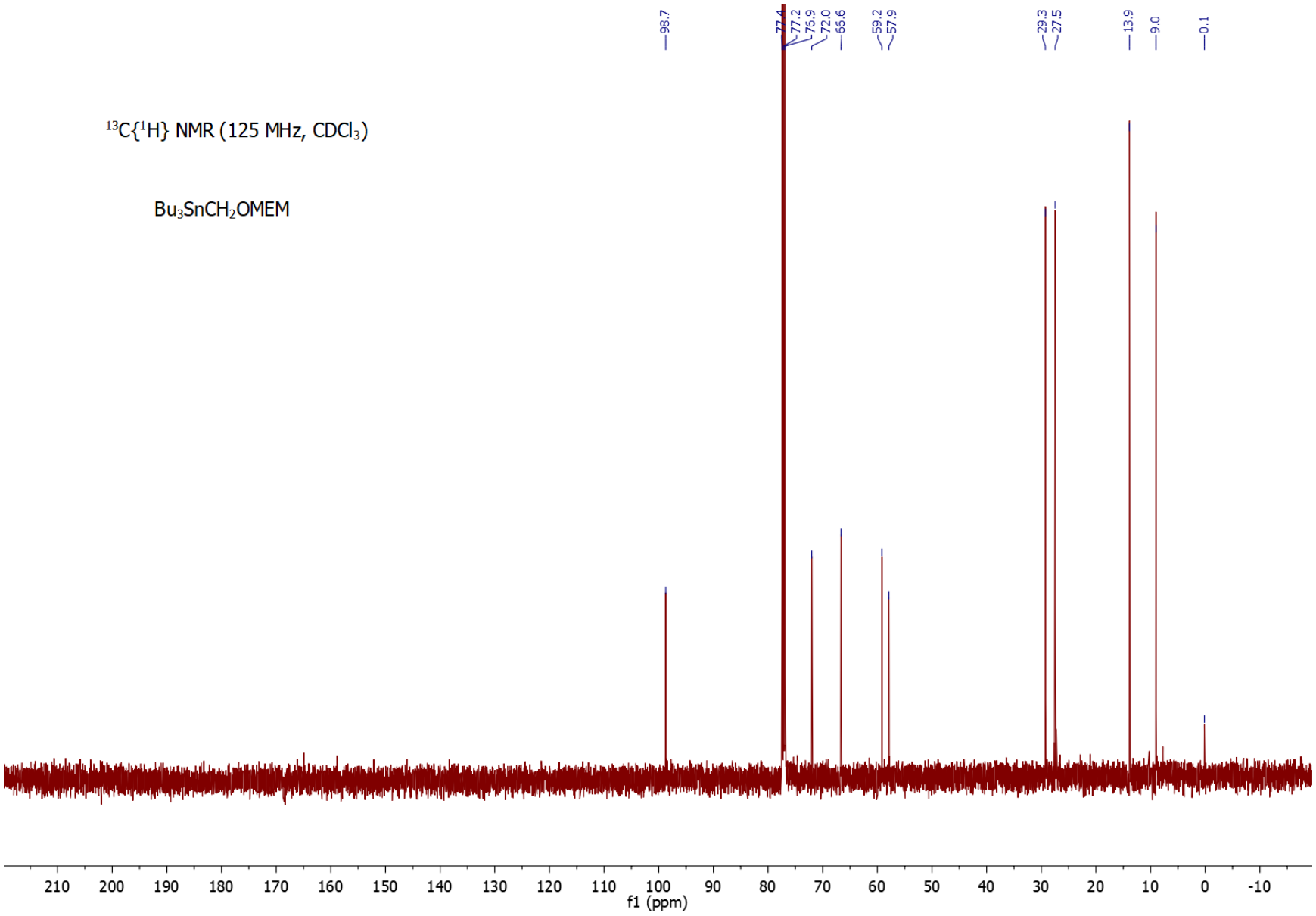
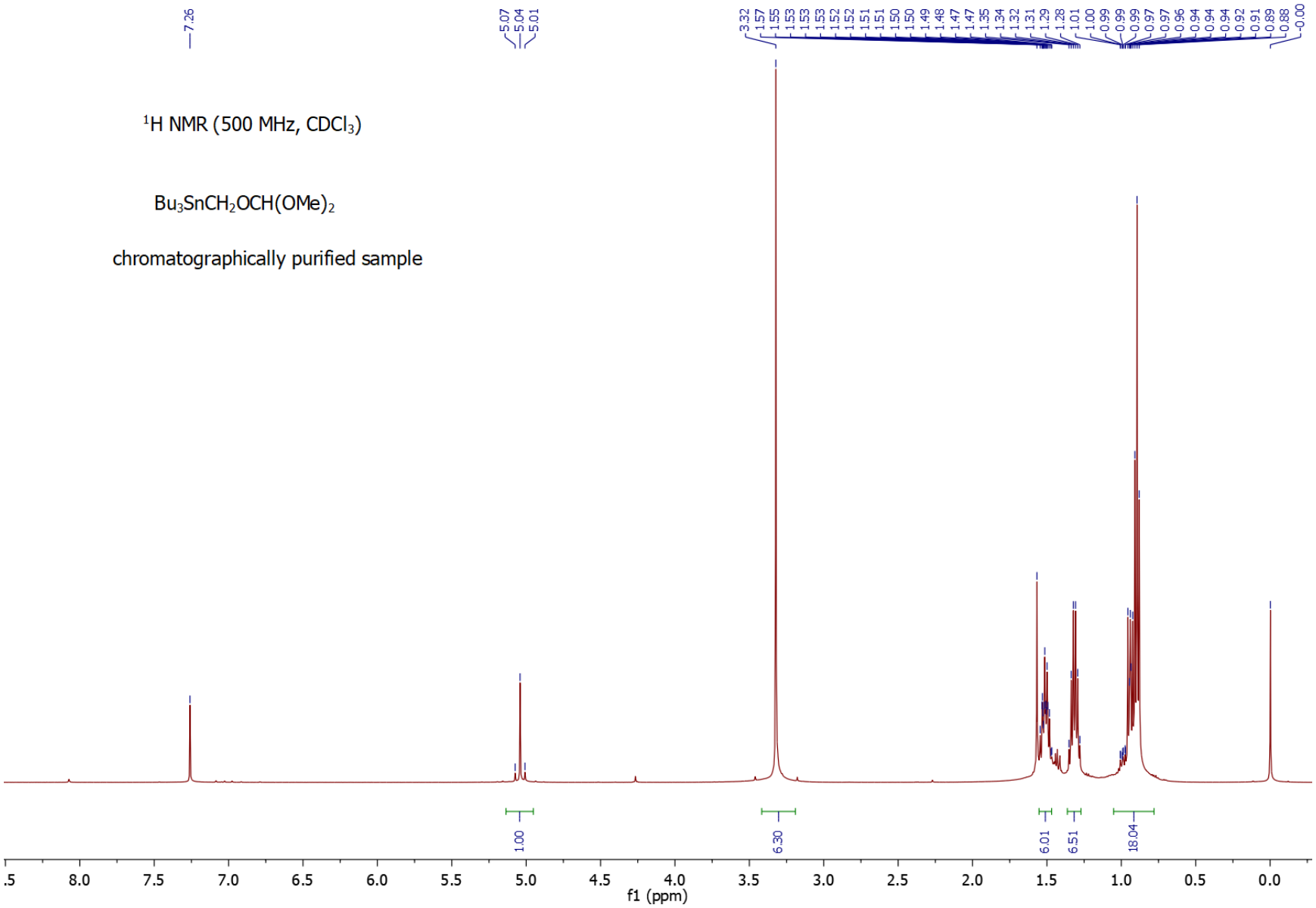
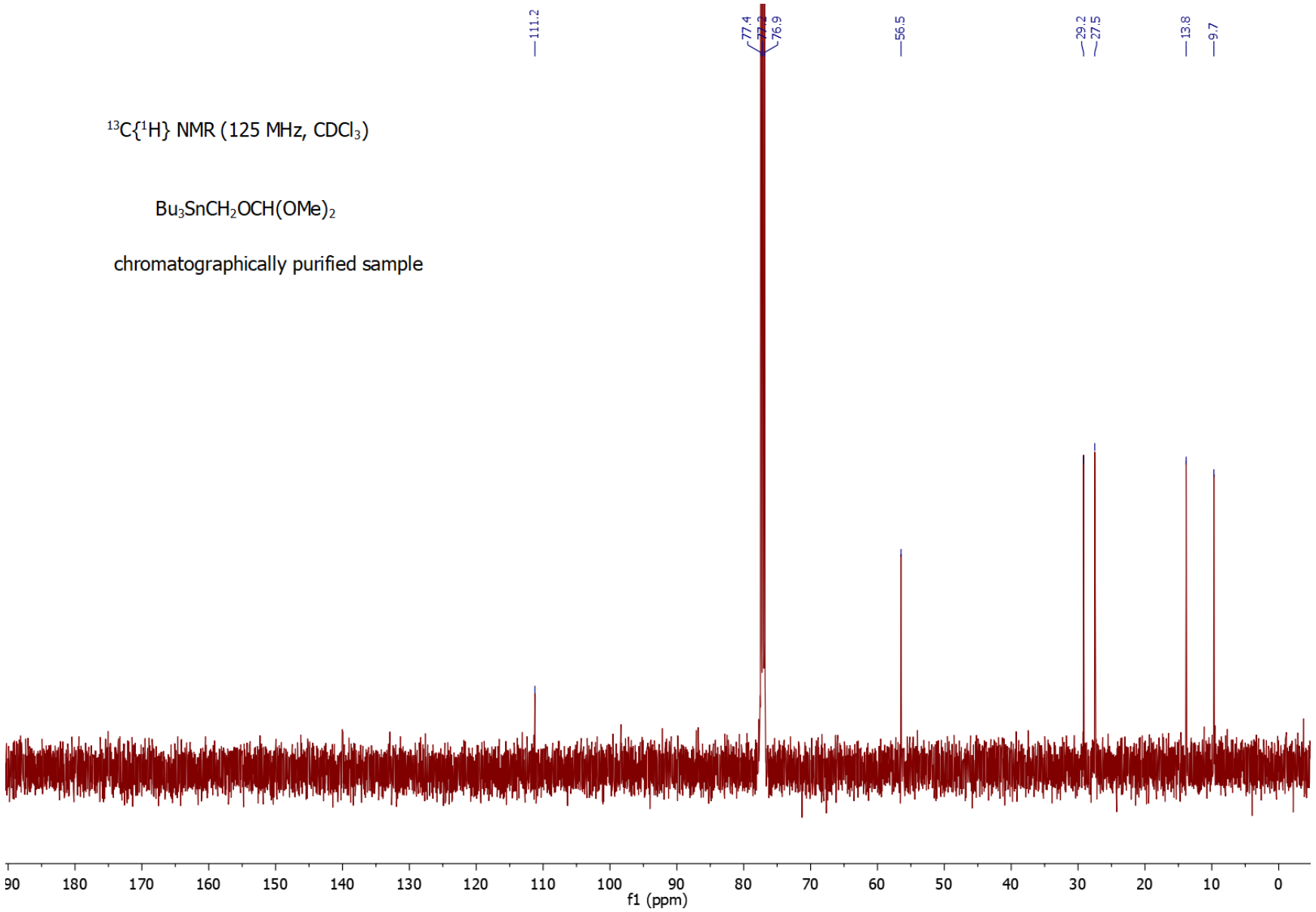
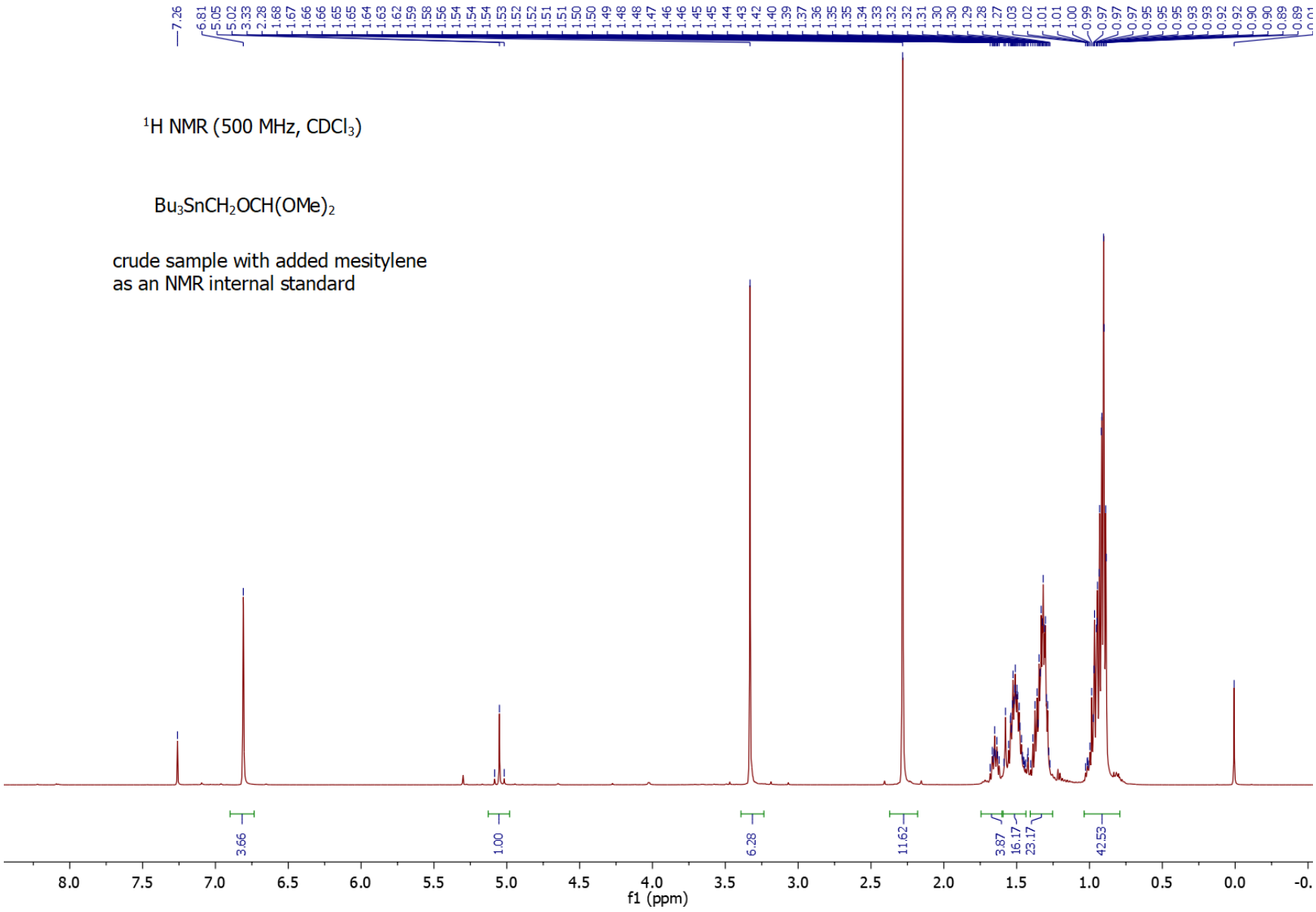
1.55
1.54
1.52
1.50
1.49
1.47
1.45
1.34
1.32
1.31
1.29
1.28
1.26
0.97
0.96
0.94
0.92
0.91
0.90
0.89
0.89
0.87
0.86
0.84
-0.00
^{1}H NMR (500 MHz, $CDCl_3$)
Bu_3SnCH_2OMEM
2.00
2.05
1.93
2.01
2.97
6.42
6.43
15.90
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

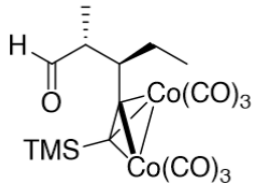

98.7
77.4
77.2
76.9
72.0
66.6
59.2
57.9
29.3
27.5
13.9
9.0
0.1
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
Bu_3SnCH_2OMEM
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.26
5.07
5.04
5.01
3.32
1.57
1.55
1.53
1.53
1.53
1.52
1.52
1.51
1.51
1.50
1.50
1.49
1.48
1.47
1.47
1.35
1.34
1.32
1.31
1.29
1.28
1.01
1.00
0.99
0.99
0.99
0.97
0.97
0.96
0.94
0.94
0.94
0.92
0.91
0.89
0.88
-0.00
1H NMR (500 MHz, CDCl3)
Bu3SnCH2OCH(OMe)2
chromatographically purified sample
1.00
6.30
6.01
6.51
18.04
.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)

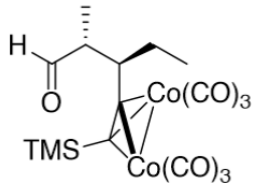

111.2
77.4
77.2
76.9
56.5
29.2
27.5
13.8
9.7
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
$Bu_3SnCH_2OCH(OMe)_2$
chromatographically purified sample
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

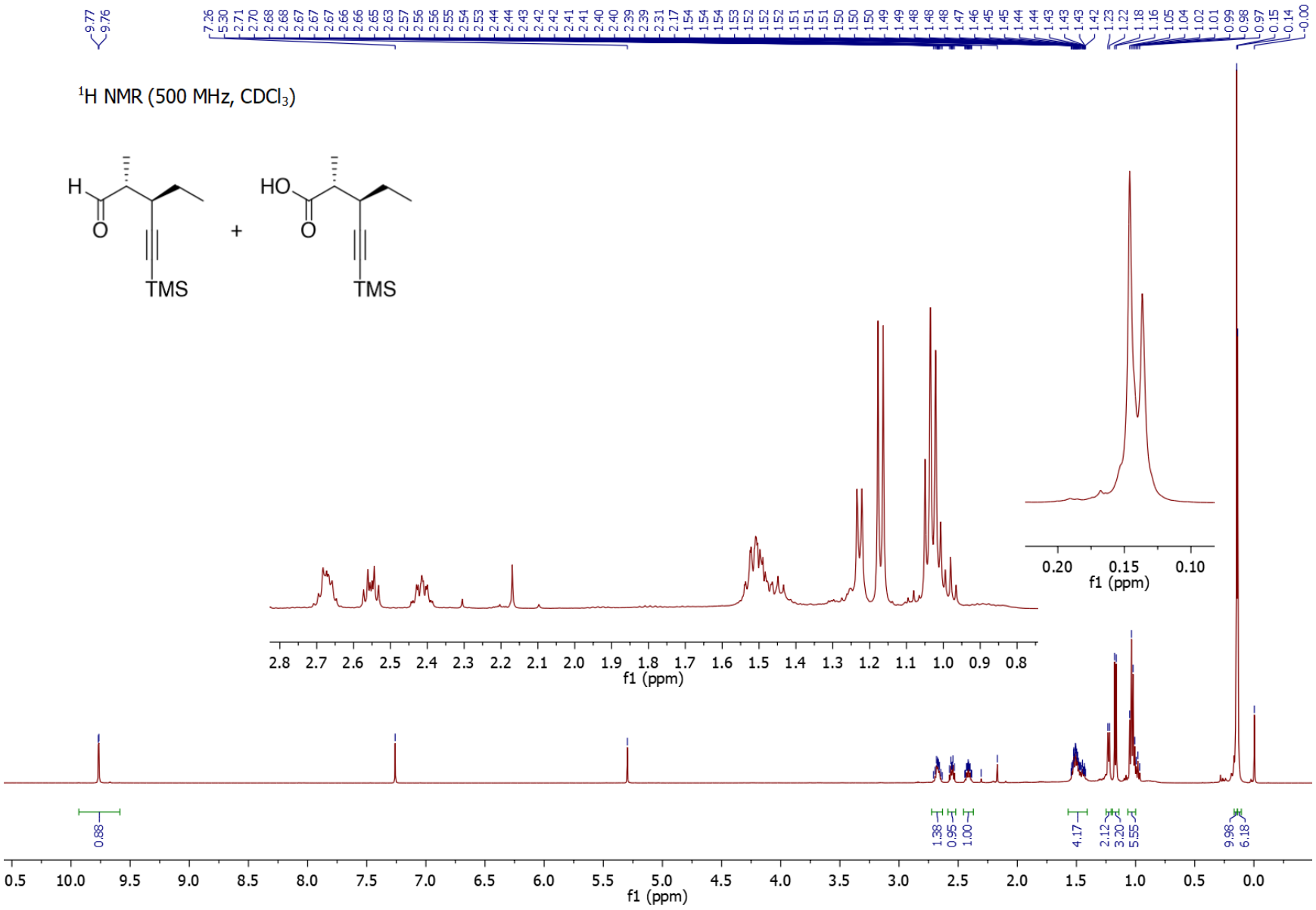

^{1}H NMR (500 MHz, $CDCl_3$)
$Bu_3SnCH_2OCH(OMe)_2$
crude sample with added mesitylene
as an NMR internal standard
f1 (ppm)

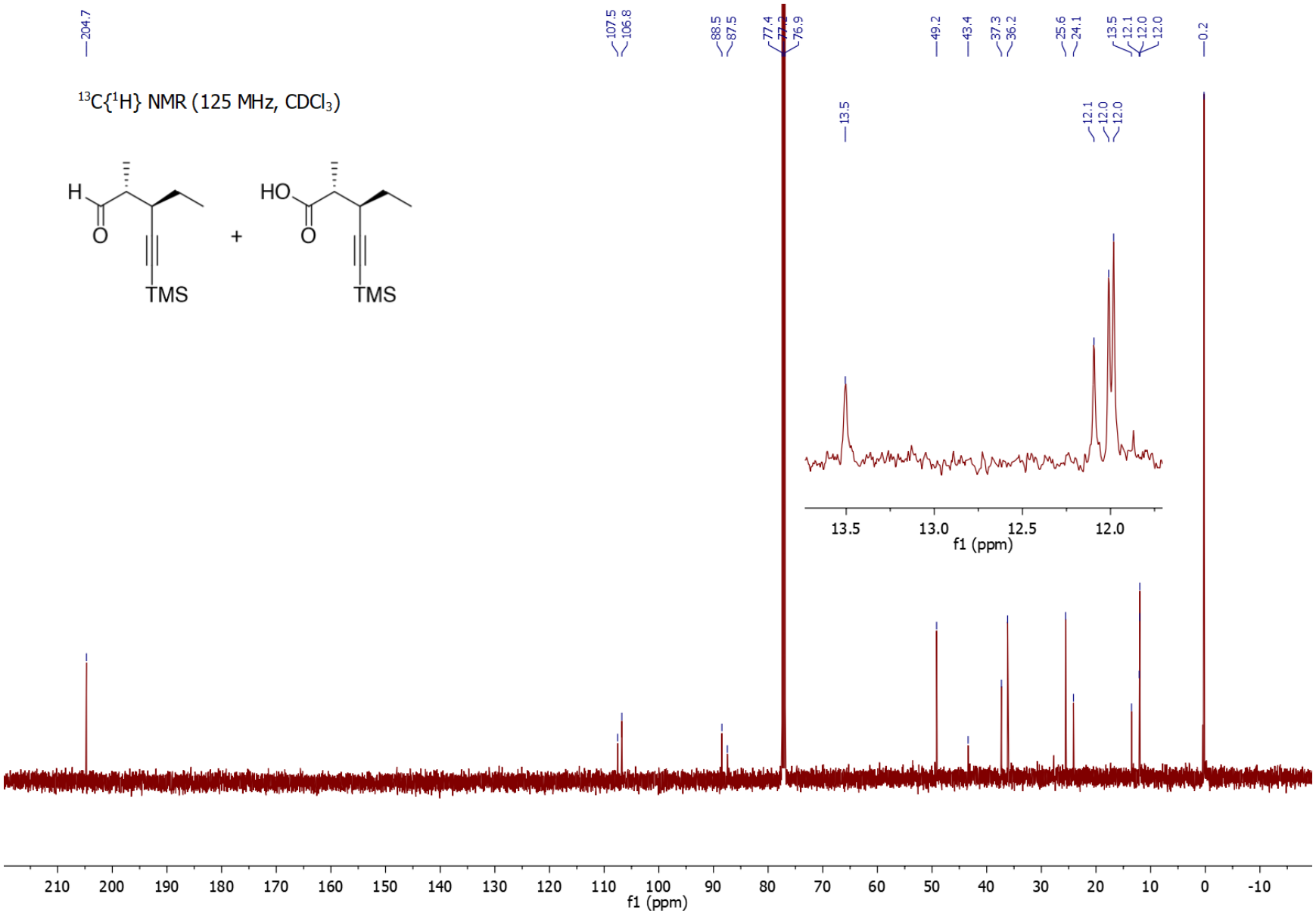
^{1}H NMR (500 MHz, $CDCl_3$)

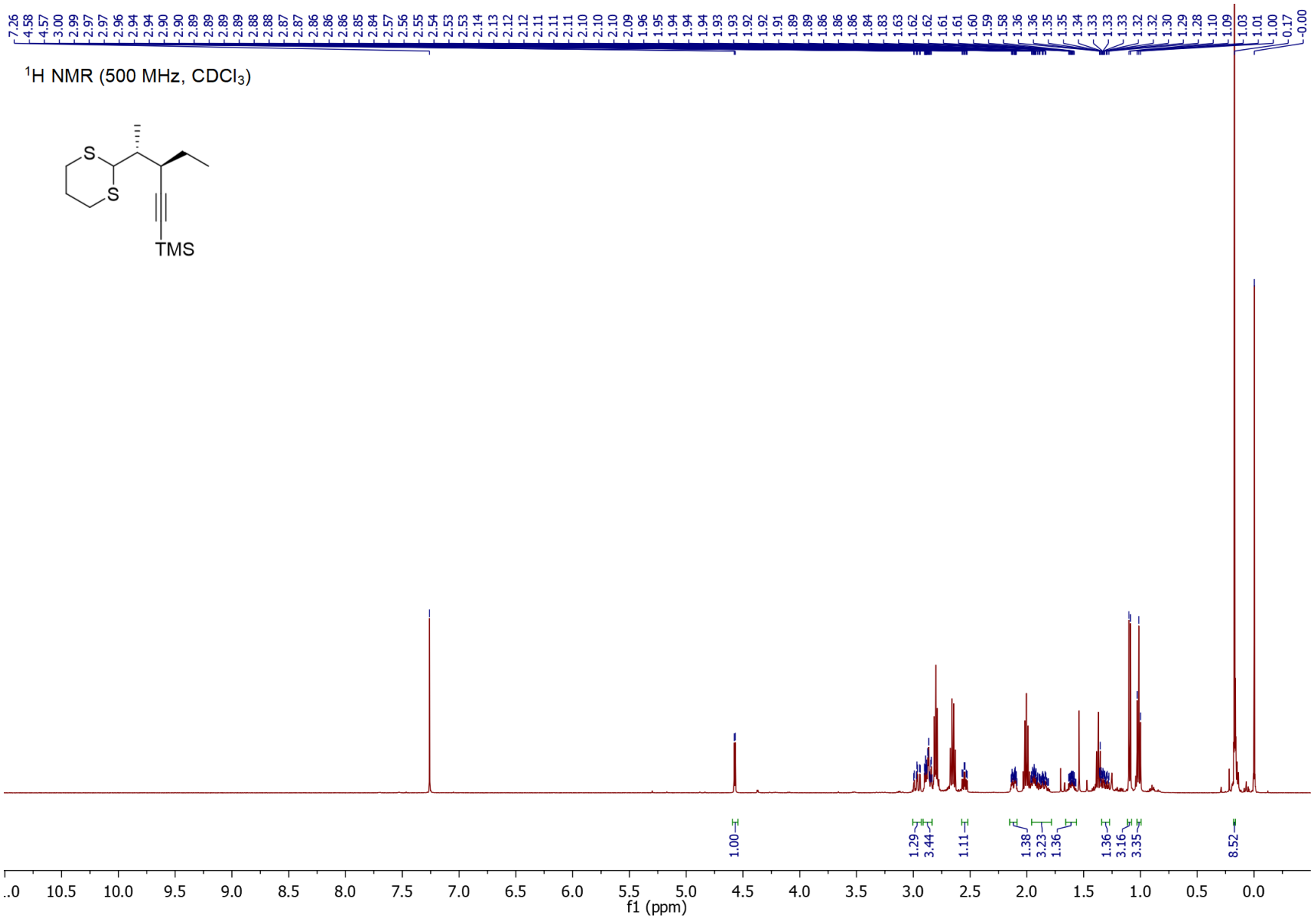


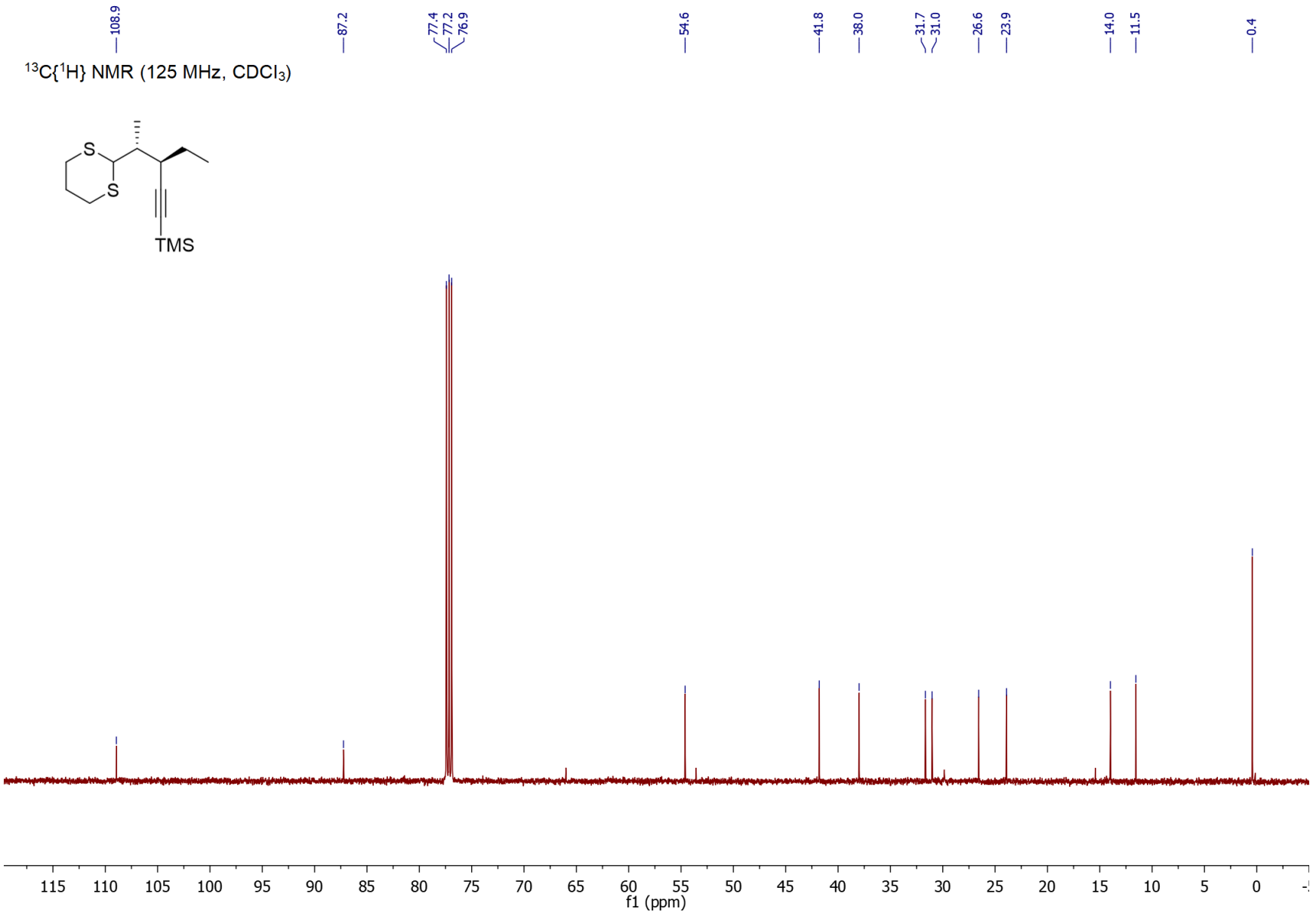
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

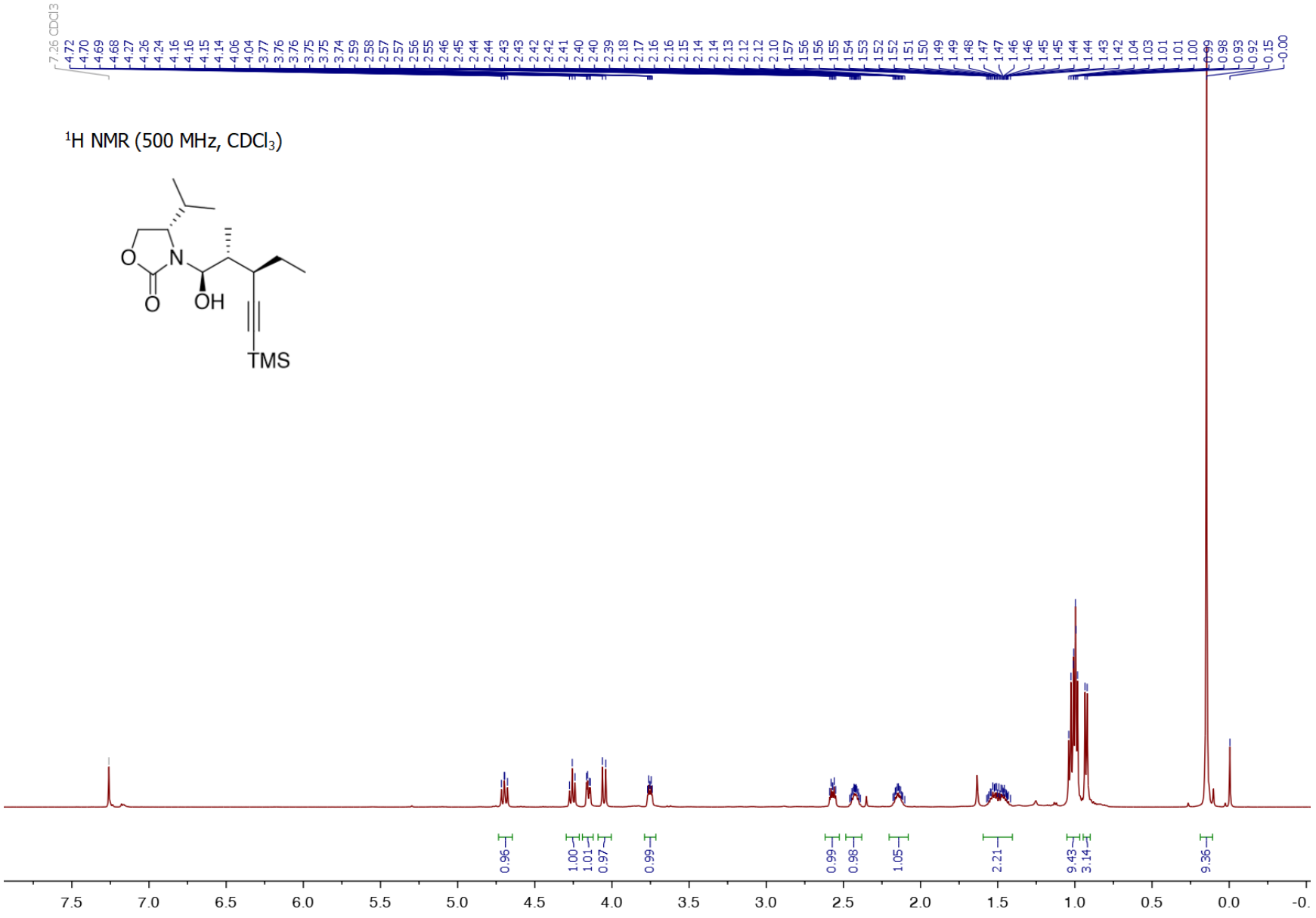


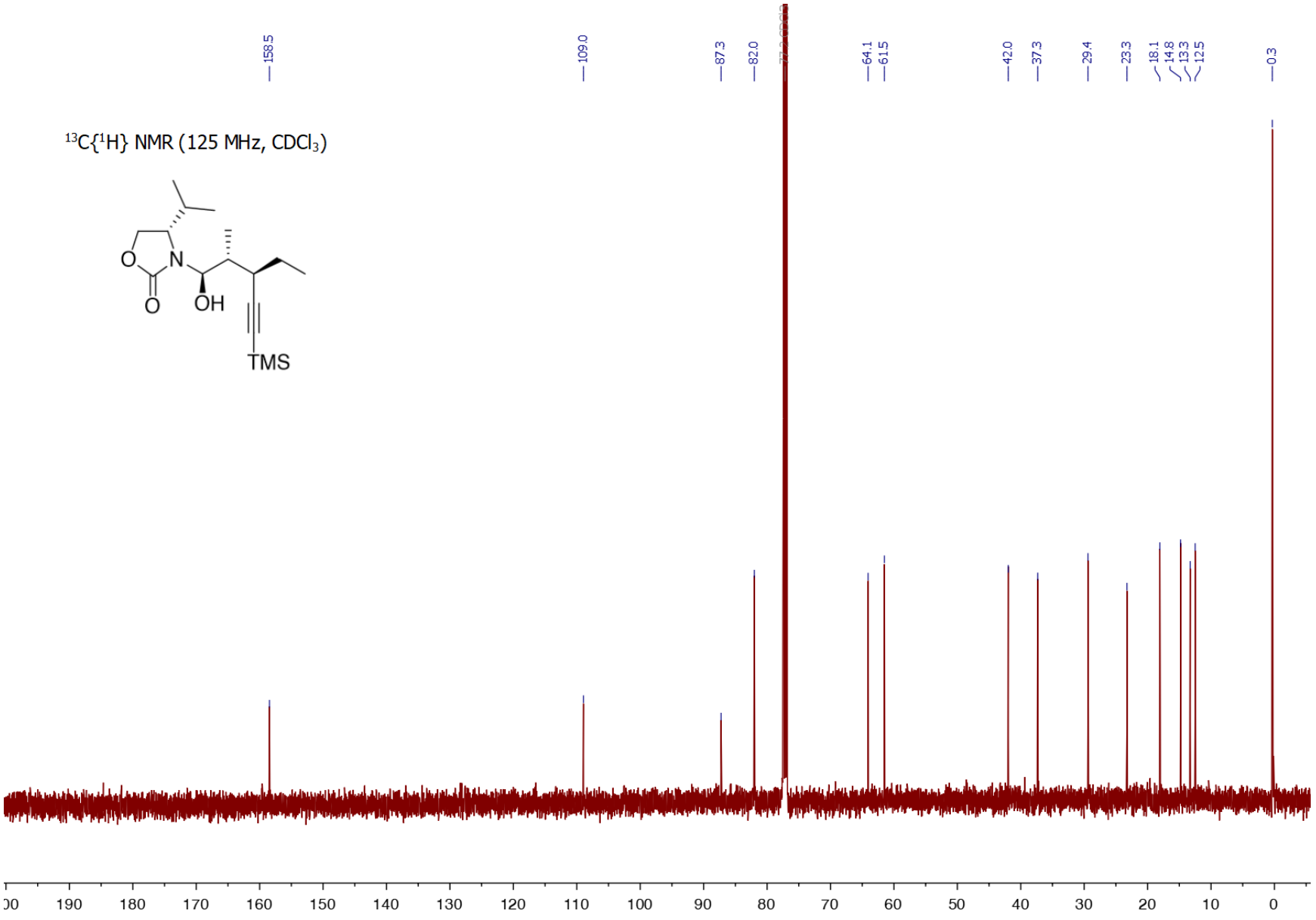

^{1}H NMR (500 MHz, $CDCl_3$)
H
O
TMS
+
HO
O
TMS
f1 (ppm)
f1 (ppm)
f1 (ppm)


$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
H
O
TMS
+
HO
O
TMS
204.7
107.5
106.8
88.5
87.5
77.4
77.0
76.9
49.2
43.4
37.3
36.2
25.6
24.1
13.5
12.1
12.0
12.0
0.2
13.5
12.1
12.0
12.0
13.5
13.0
12.5
12.0
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

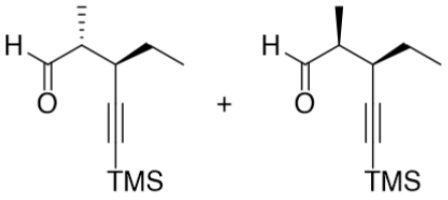

^{1}H NMR (500 MHz, $CDCl_3$)
S
S
TMS
f1 (ppm)

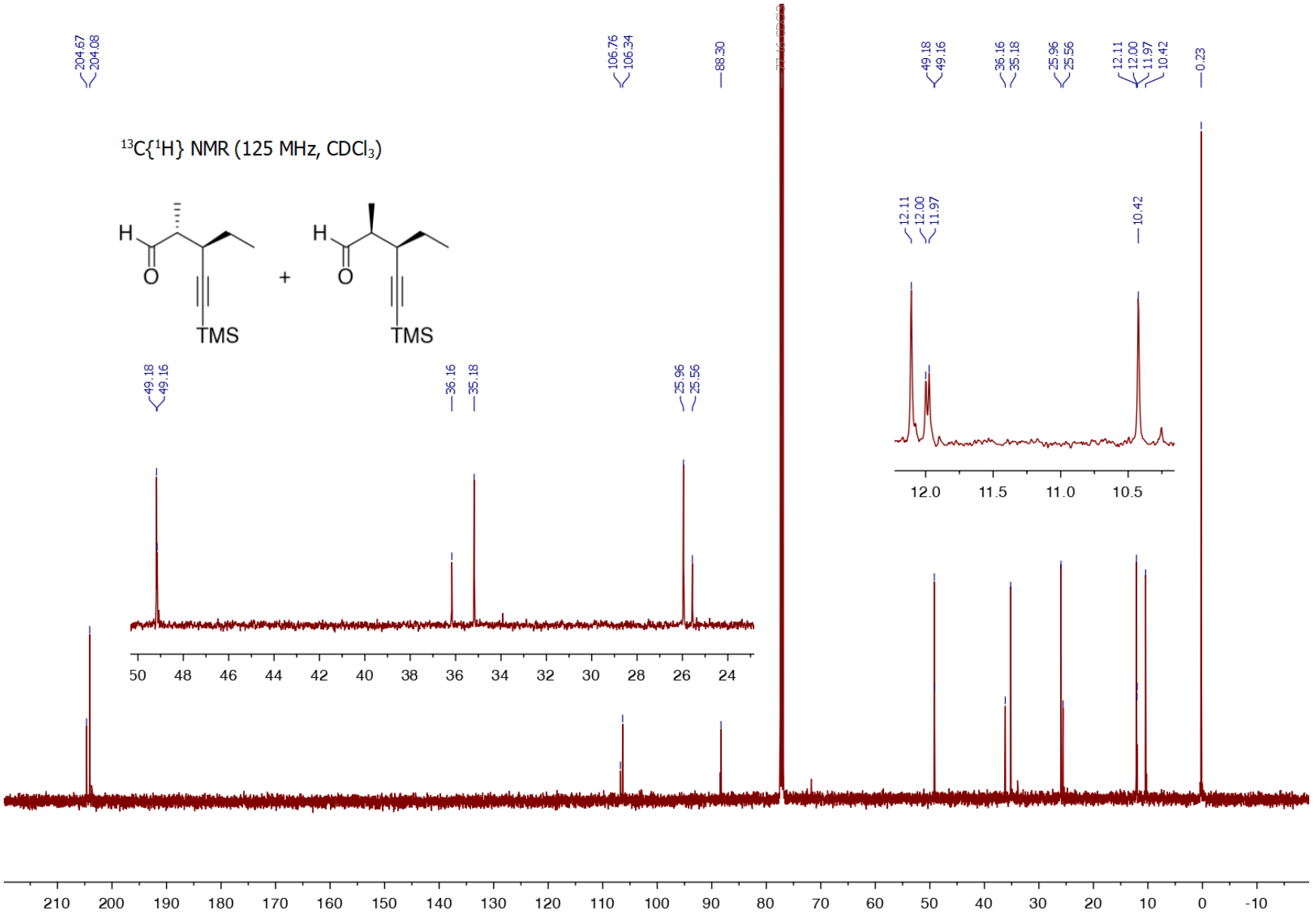

108.9
87.2
77.4
77.2
76.9
54.6
41.8
38.0
31.7
31.0
26.6
23.9
14.0
11.5
0.4
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
S
S
TMS
115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

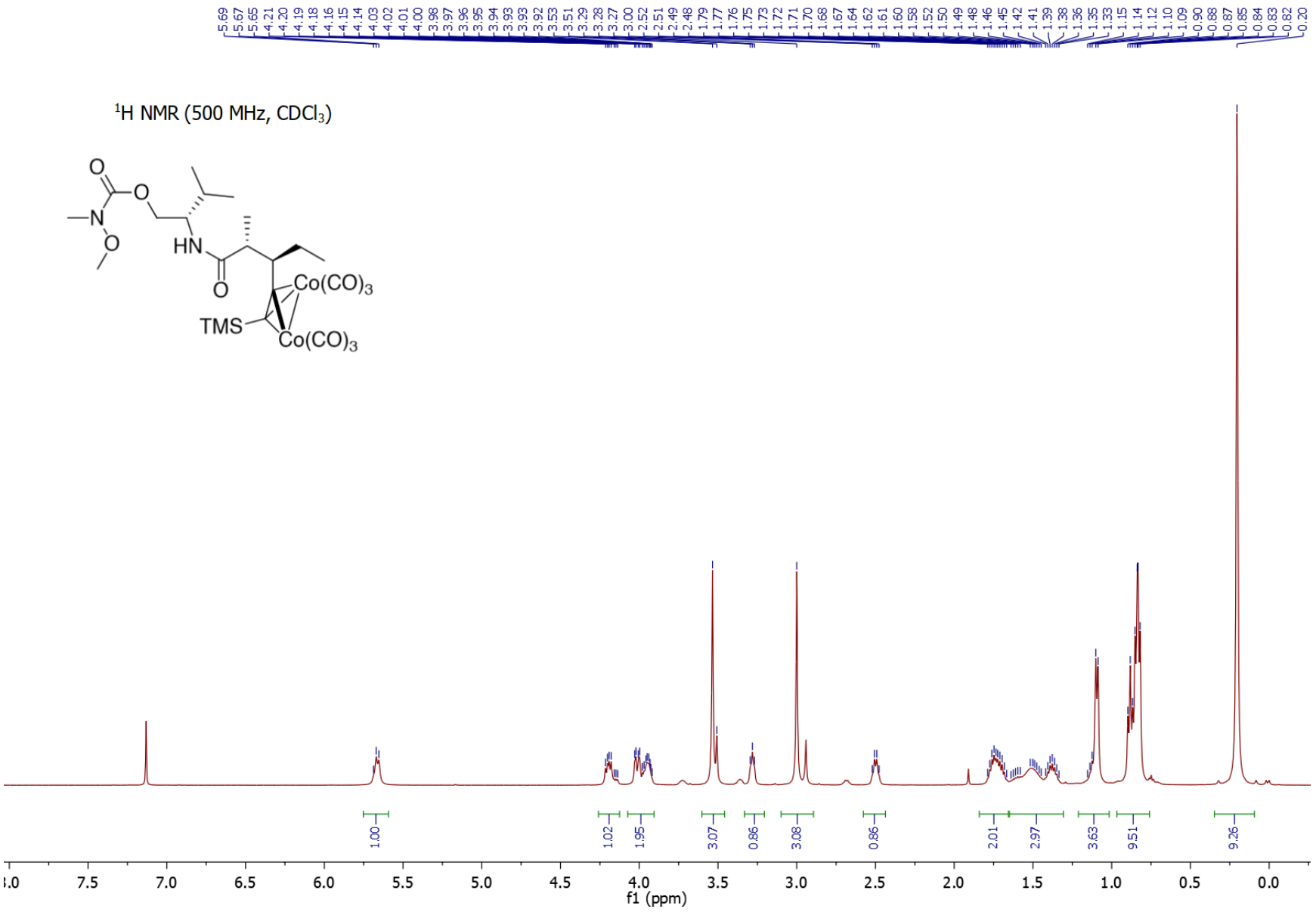

7.26 CDCl3
4.72 4.70 4.69 4.68 4.27 4.26 4.24 4.16 4.16 4.15 4.14 4.06 4.04 3.77 3.76 3.76 3.75 3.75 3.74 2.59 2.58 2.57 2.57 2.56 2.55 2.46 2.45 2.44 2.44 2.43 2.43 2.42 2.42 2.41 2.40 2.40 2.39 2.18 2.17 2.16 2.16 2.15 2.14 2.14 2.13 2.12 2.12 2.10 1.57 1.56 1.56 1.55 1.54 1.53 1.52 1.52 1.51 1.50 1.49 1.49 1.48 1.47 1.47 1.46 1.46 1.45 1.45 1.44 1.44 1.43 1.42 1.04 1.03 1.01 1.01 1.00 0.99 0.98 0.93 0.92 0.15 -0.00
1H NMR (500 MHz, CDCl3)
O
N
O
OH
TMS
0.96 1.00 1.01 0.97 0.99 0.99 0.98 1.05 2.21 9.43 3.14 9.36
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.

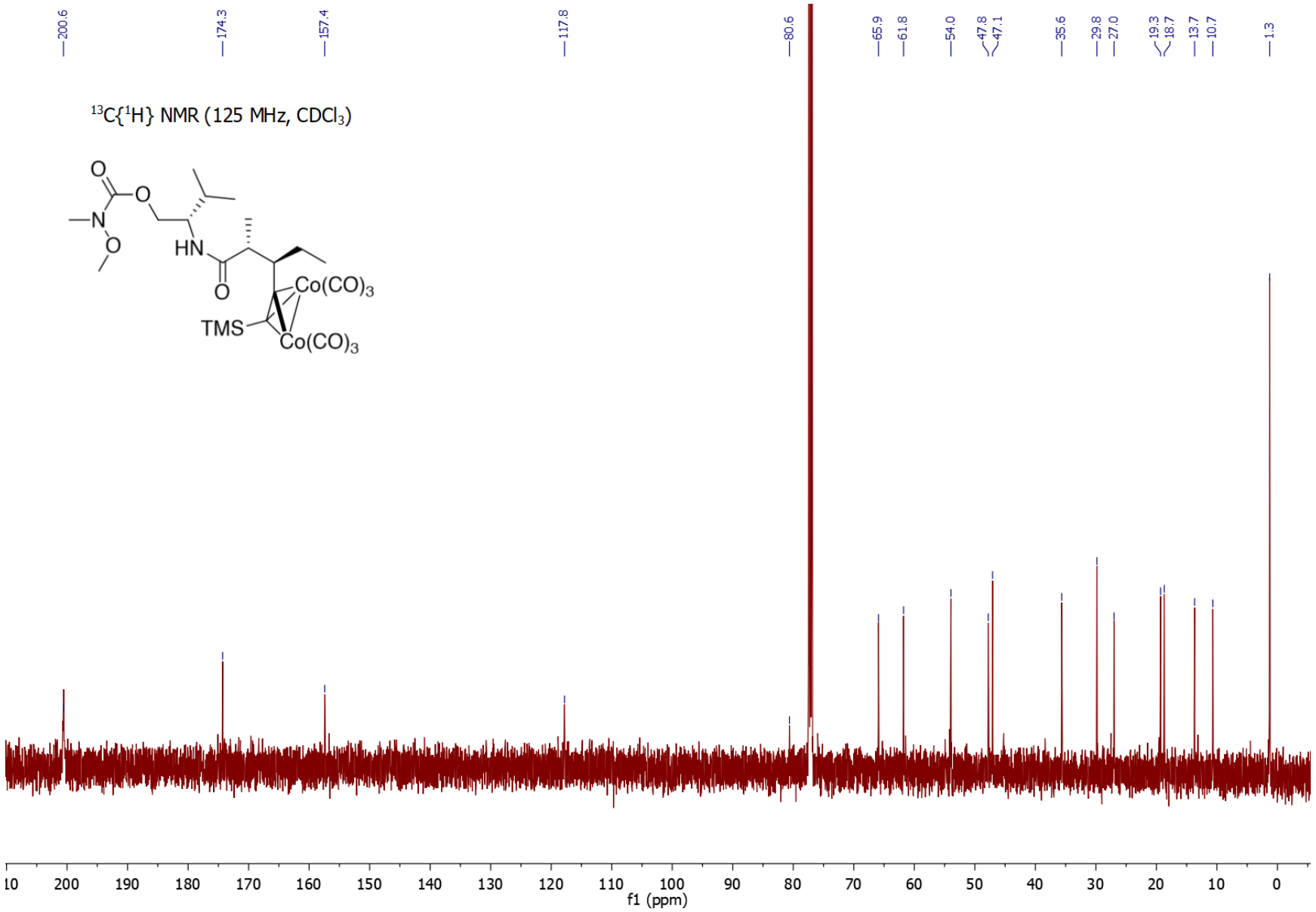

158.5
109.0
87.3
82.0
77.0
64.1
61.5
42.0
37.3
29.4
23.3
18.1
14.8
13.3
12.5
0.3
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
O
N
O
OH
TMS
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

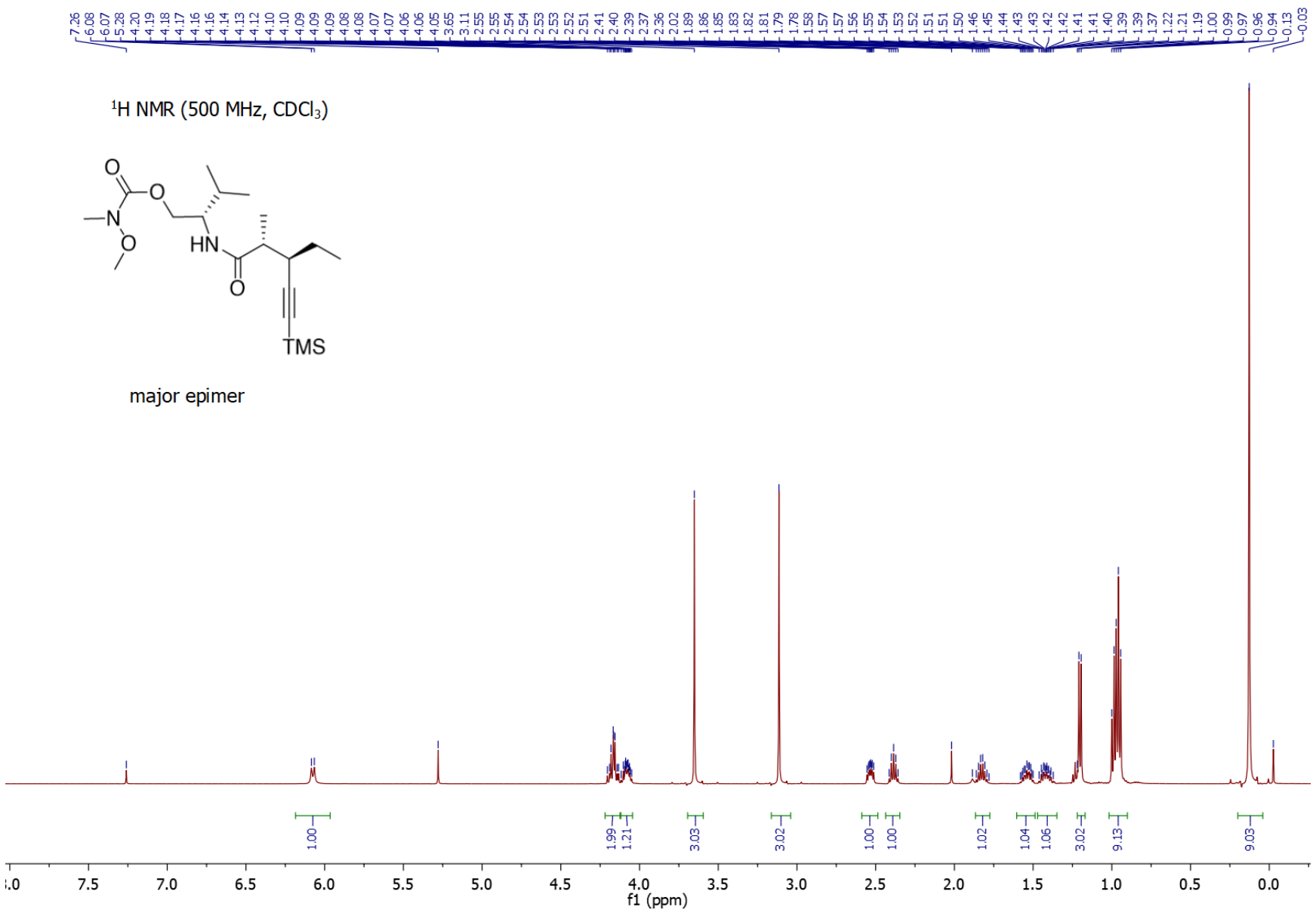
^{1}H NMR (500 MHz, $CDCl_3$)

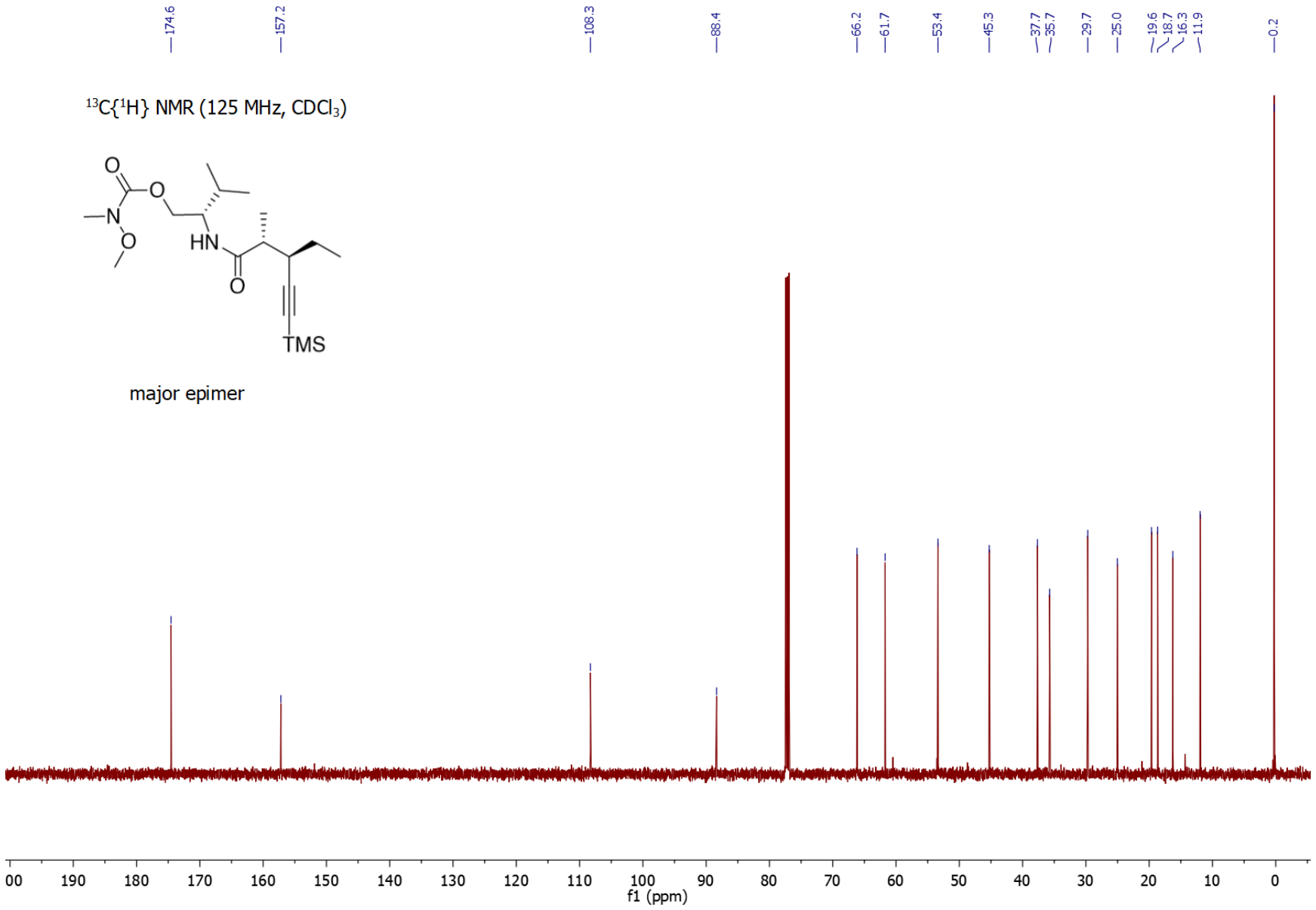


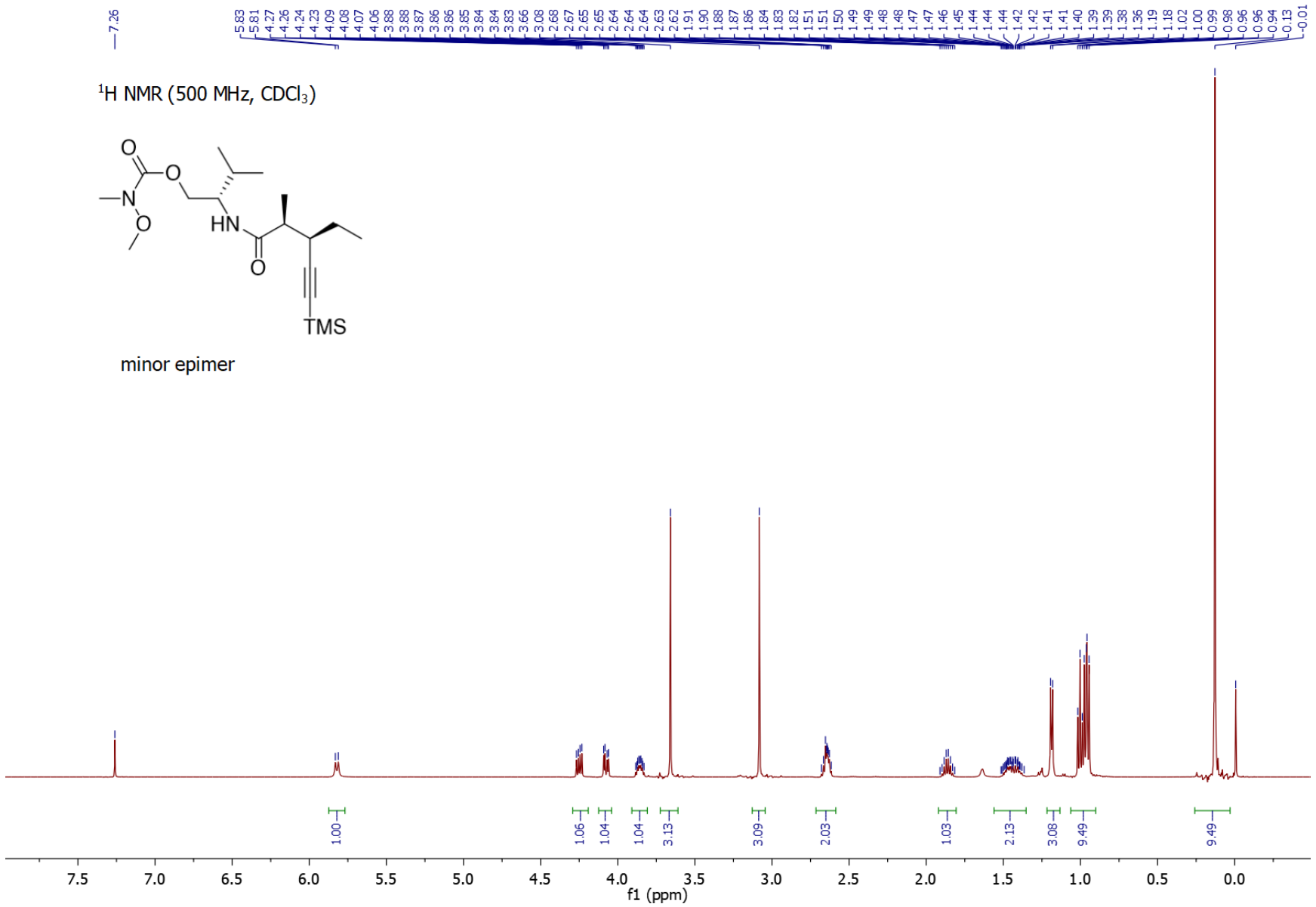

204.67
204.08
106.76
106.34
88.30
77.46
49.18
49.16
36.16
35.18
25.96
25.56
12.11
12.00
11.97
10.42
0.23
13C{1H} NMR (125 MHz, CDCl3)
H
O
TMS
+
H
O
TMS
49.18
49.16
36.16
35.18
25.96
25.56
50 48 46 44 42 40 38 36 34 32 30 28 26 24
12.11
12.00
11.97
10.42
12.0 11.5 11.0 10.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

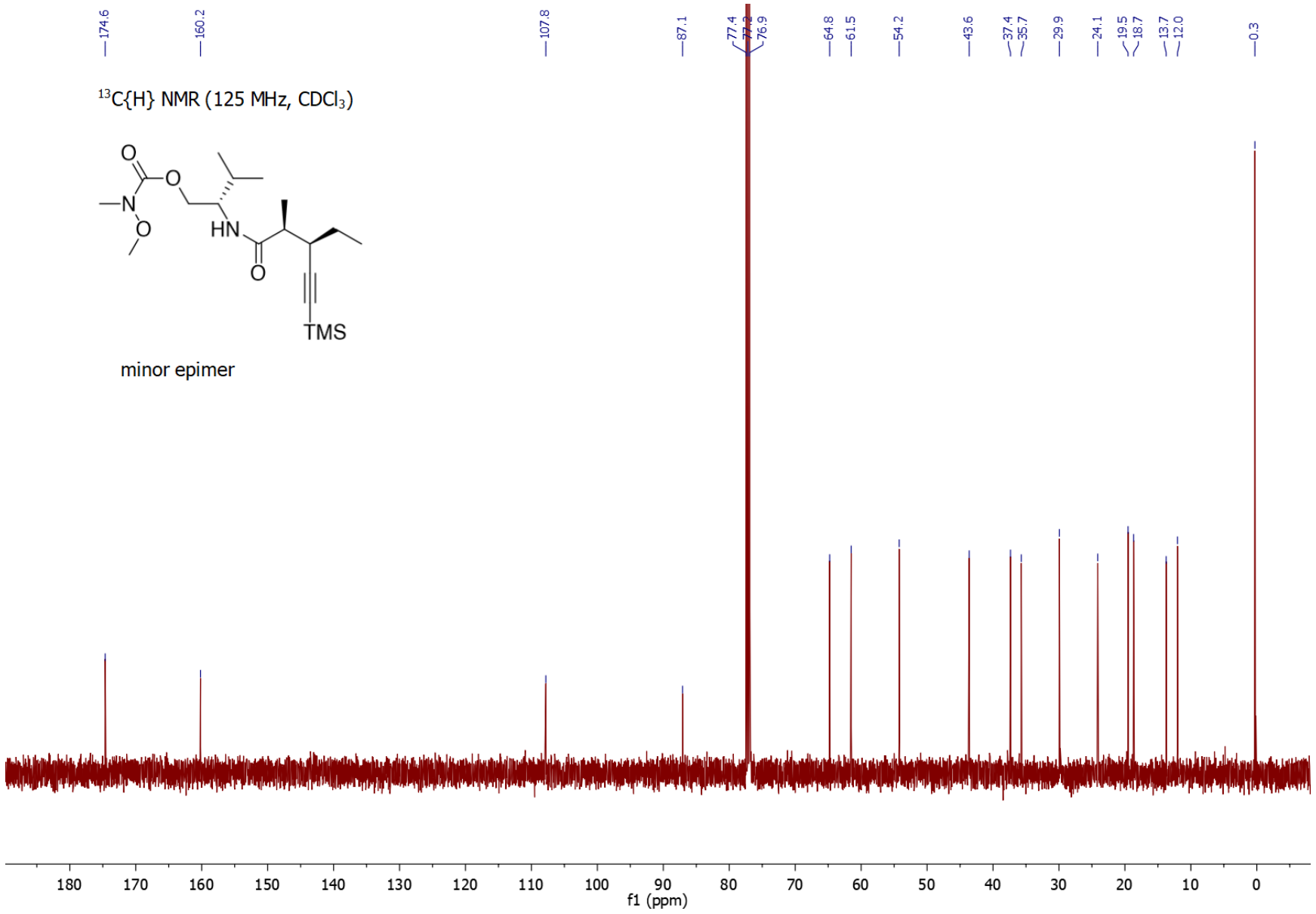

5.69 5.67 5.65 4.21 4.20 4.19 4.18 4.16 4.15 4.14 4.03 4.02 4.01 4.00 3.98 3.97 3.96 3.95 3.94 3.93 3.93 3.92 3.53 3.51 3.29 3.28 3.27 3.00 2.52 2.51 2.49 2.48 1.79 1.77 1.76 1.75 1.73 1.72 1.71 1.70 1.68 1.67 1.64 1.62 1.61 1.60 1.58 1.52 1.50 1.49 1.48 1.46 1.45 1.42 1.41 1.39 1.38 1.36 1.35 1.33 1.15 1.14 1.12 1.10 1.09 0.90 0.88 0.87 0.85 0.84 0.83 0.82 0.20
^{1}H NMR (500 MHz, $CDCl_3$)
O
O
N
O
HN
O
Co(CO)3
TMS
Co(CO)3
1.00 1.02 1.95 3.07 0.86 3.08 0.86 2.01 2.97 3.63 9.51 9.26
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)


200.6
174.3
157.4
117.8
80.6
65.9
61.8
54.0
47.8
47.1
35.6
29.8
27.0
19.3
18.7
13.7
10.7
1.3
13C{1H} NMR (125 MHz, CDCl3)
O
O
N
O
HN
O
Co(CO)3
TMS
Co(CO)3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

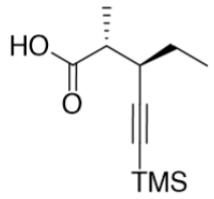

7.26 6.08 6.07 5.28 4.20 4.19 4.18 4.17 4.16 4.16 4.14 4.13 4.12 4.10 4.10 4.09 4.09 4.09 4.08 4.08 4.07 4.07 4.06 4.06 4.05 3.65 3.11 2.55 2.55 2.54 2.54 2.53 2.53 2.52 2.51 2.41 2.40 2.39 2.37 2.36 2.02 1.89 1.86 1.85 1.83 1.82 1.81 1.79 1.78 1.58 1.57 1.57 1.56 1.55 1.54 1.53 1.52 1.51 1.51 1.50 1.46 1.45 1.44 1.43 1.43 1.42 1.42 1.41 1.41 1.40 1.39 1.39 1.37 1.22 1.21 1.19 1.00 0.99 0.97 0.96 0.94 0.13 -0.03
^{1}H NMR (500 MHz, $CDCl_3$)
O
O
N
O
HN
O
TMS
major epimer
1.00 1.99 1.21 3.03 3.02 1.00 1.00 1.02 1.04 1.06 3.02 9.13 9.03
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)

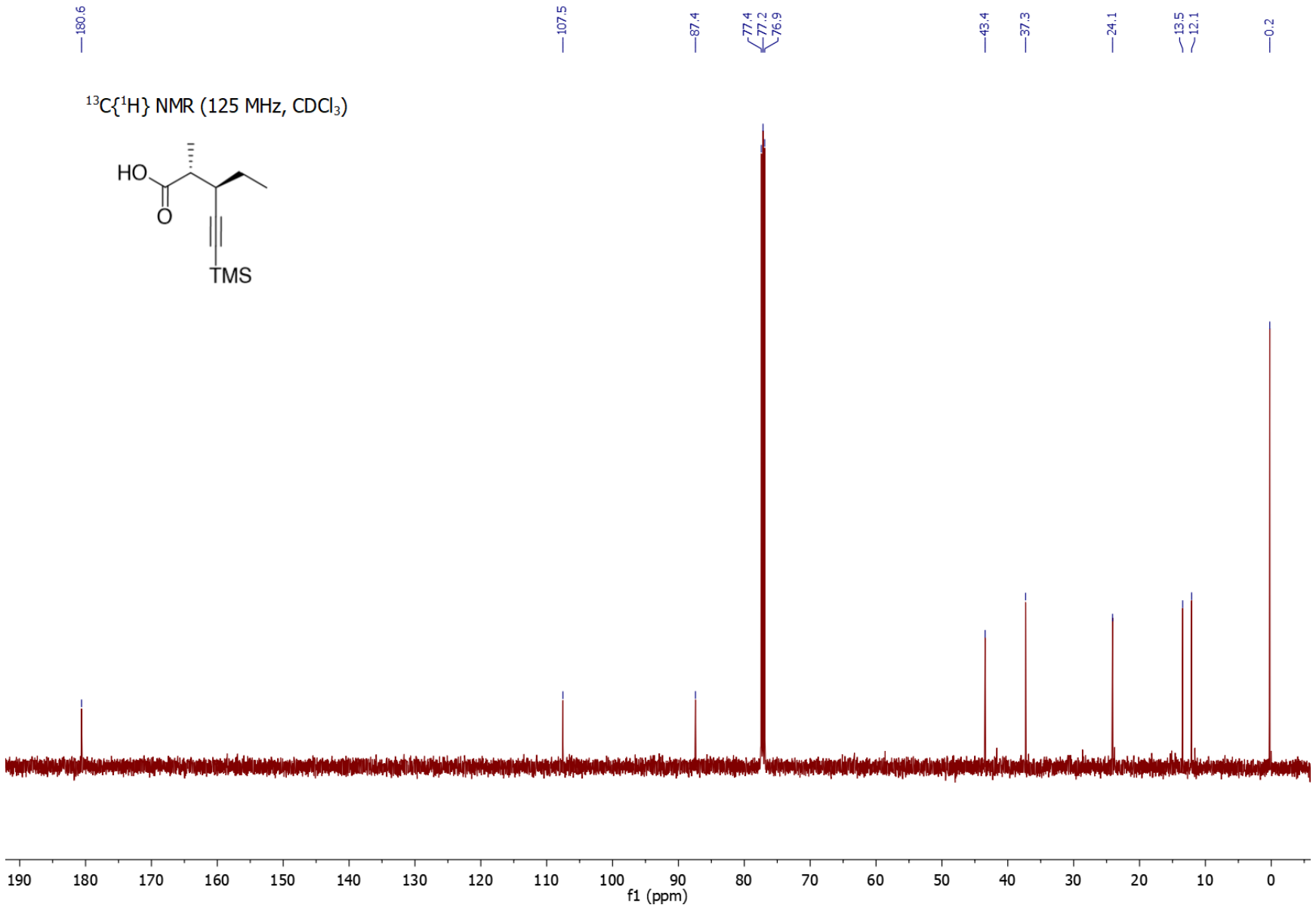

174.6
157.2
108.3
88.4
66.2
61.7
53.4
45.3
37.7
35.7
29.7
25.0
19.6
18.7
16.3
11.9
0.2
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
O
O
N
O
HN
O
TMS
major epimer
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26
5.83 5.81 4.27 4.26 4.24 4.23 4.09 4.08 4.07 4.06 3.88 3.88 3.87 3.86 3.86 3.85 3.84 3.84 3.83 3.66 3.08 2.68 2.67 2.65 2.65 2.64 2.64 2.64 2.63 2.62 1.91 1.90 1.88 1.87 1.86 1.84 1.83 1.82 1.51 1.51 1.50 1.49 1.49 1.48 1.48 1.47 1.47 1.46 1.45 1.44 1.44 1.44 1.42 1.42 1.41 1.41 1.40 1.39 1.39 1.38 1.36 1.19 1.18 1.02 1.00 0.99 0.98 0.96 0.96 0.94 0.13 -0.01
1H NMR (500 MHz, CDCl3)
O
O
N
O
HN
O
TMS
minor epimer
1.00
1.06
1.04
1.04
3.13
3.09
2.03
1.03
2.13
3.08
9.49
9.49
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)

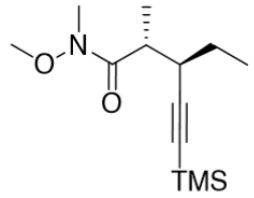

174.6
160.2
107.8
87.1
77.4
76.9
64.8
61.5
54.2
43.6
37.4
35.7
29.9
24.1
19.5
18.7
13.7
12.0
0.3
13C{H} NMR (125 MHz, CDCl3)
O
O
N
O
HN
O
TMS
minor epimer
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}H NMR (500 MHz, $CDCl_3$)

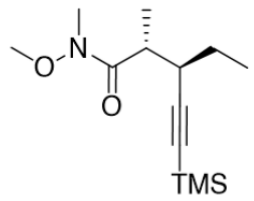


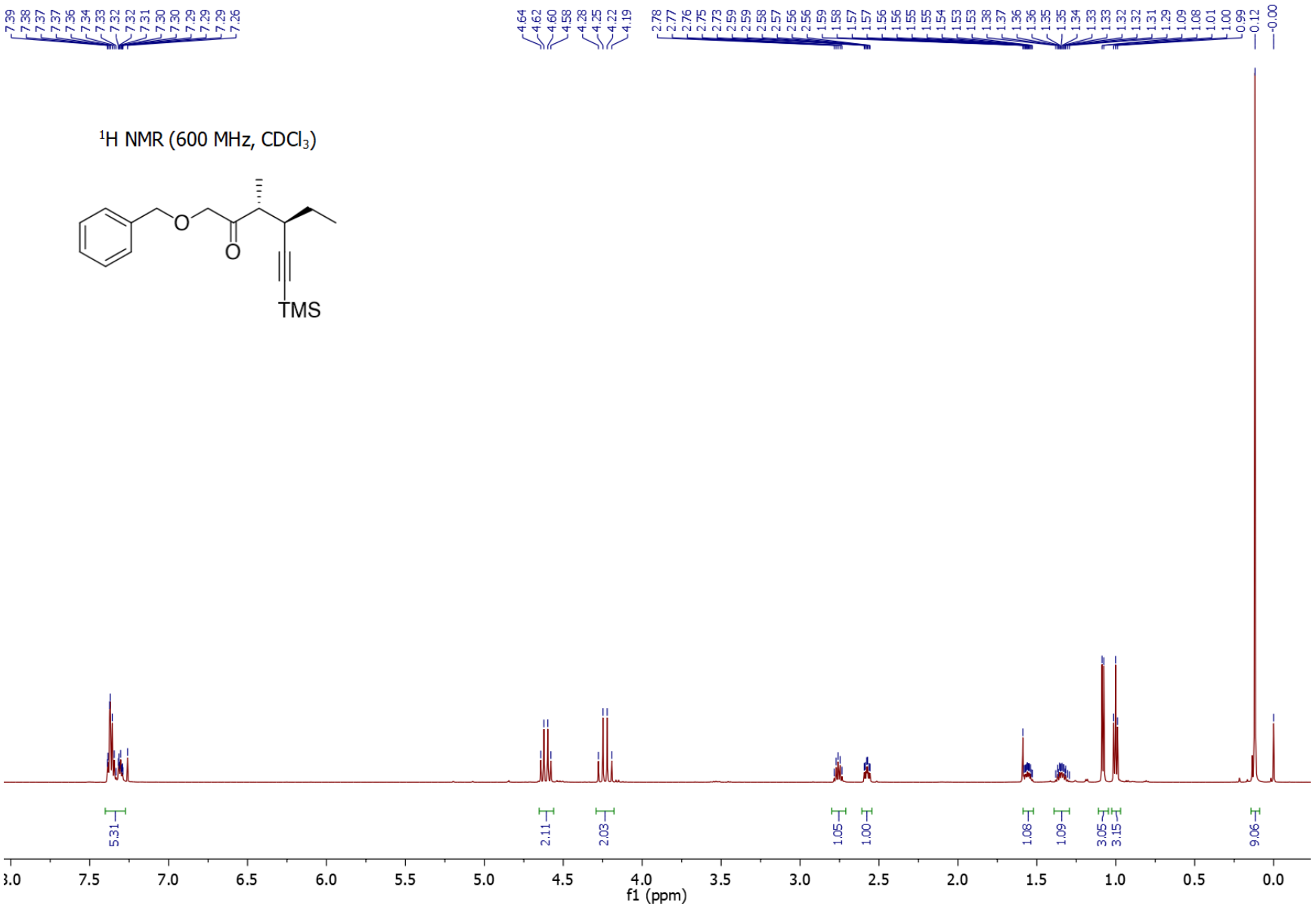

180.6
107.5
87.4
77.4
77.2
76.9
43.4
37.3
24.1
13.5
12.1
0.2
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
HO
O
TMS
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

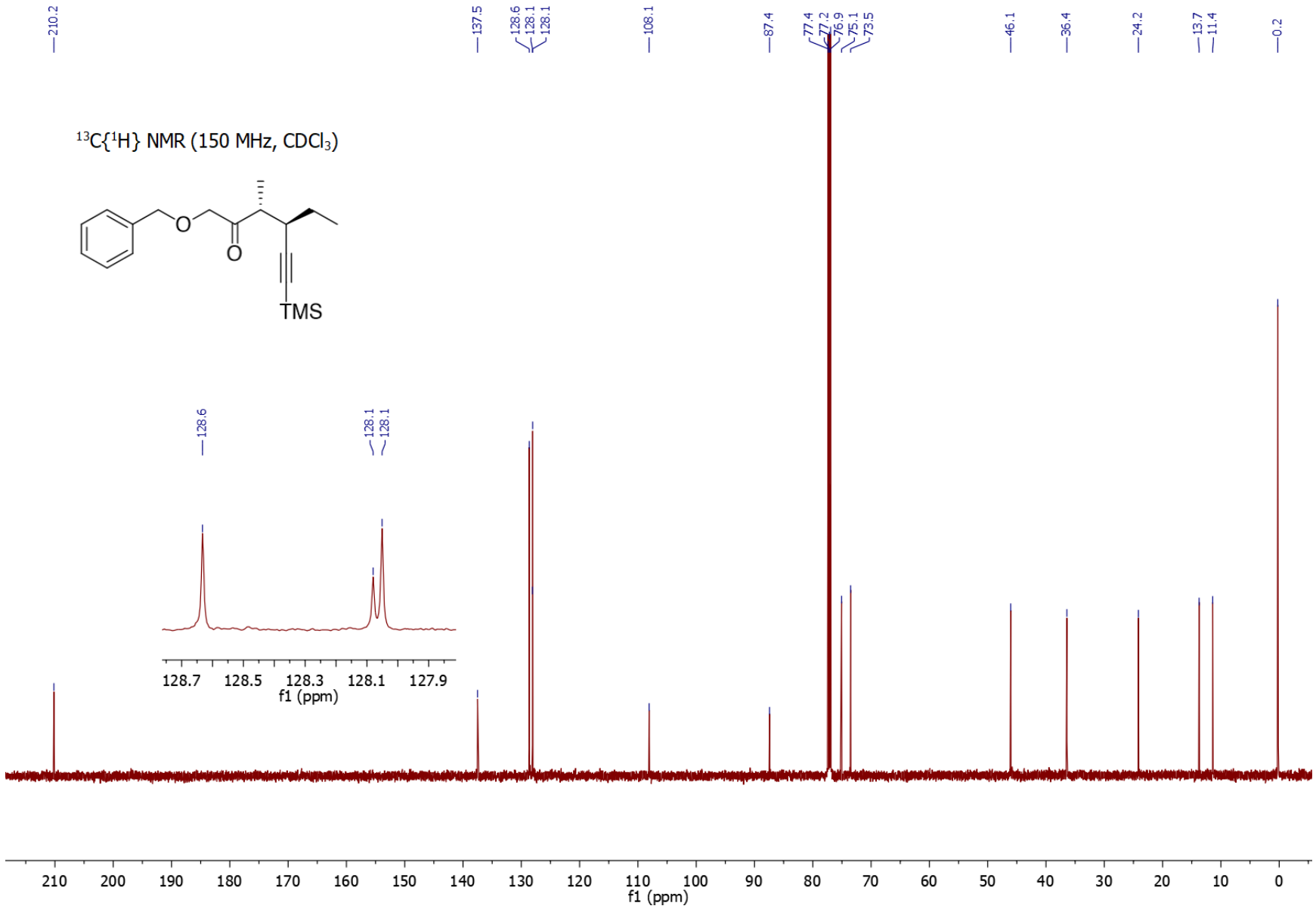
^{1}H NMR (500 MHz, $CDCl_3$)



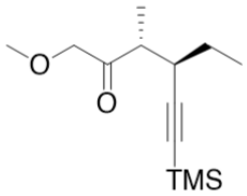
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

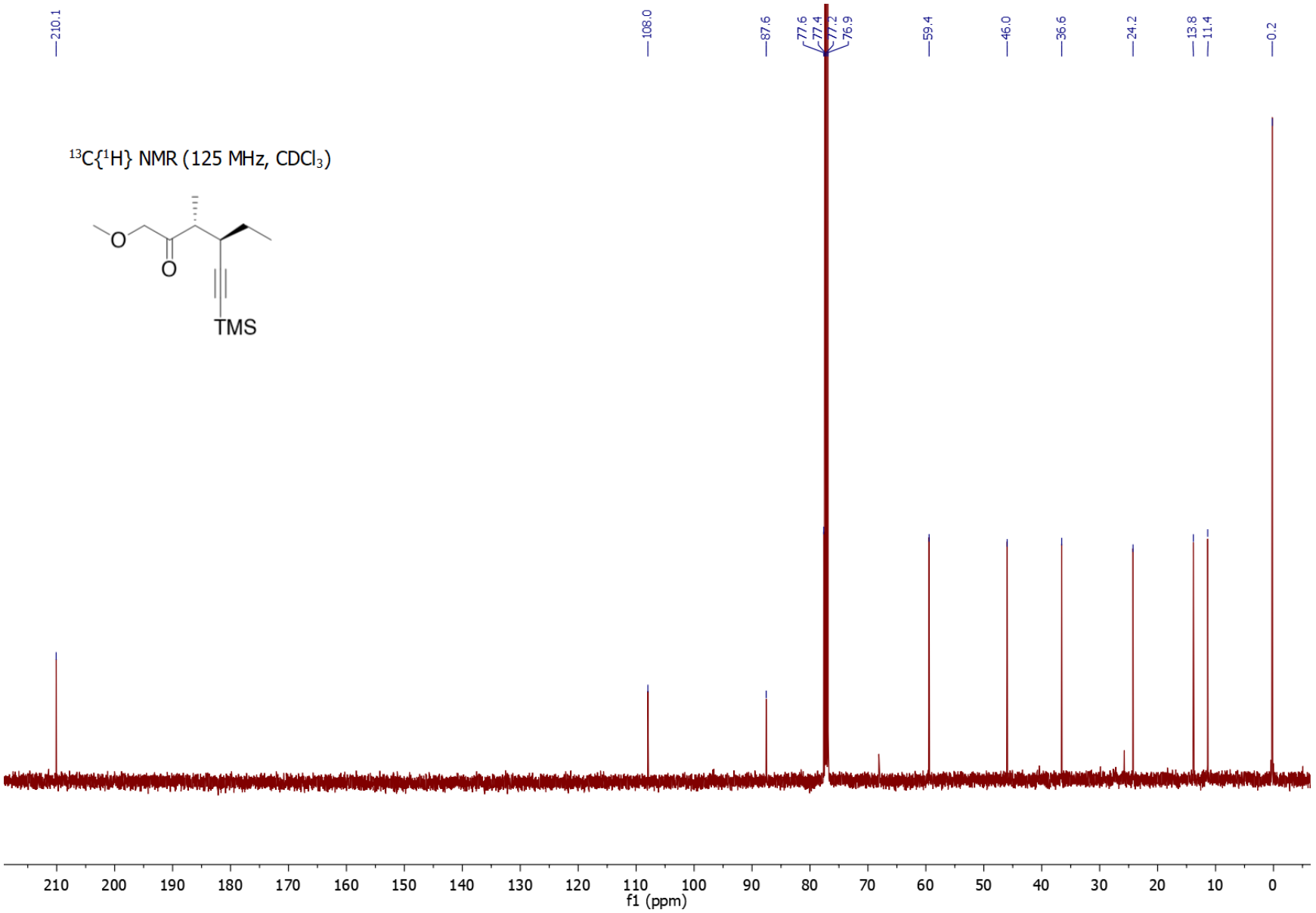


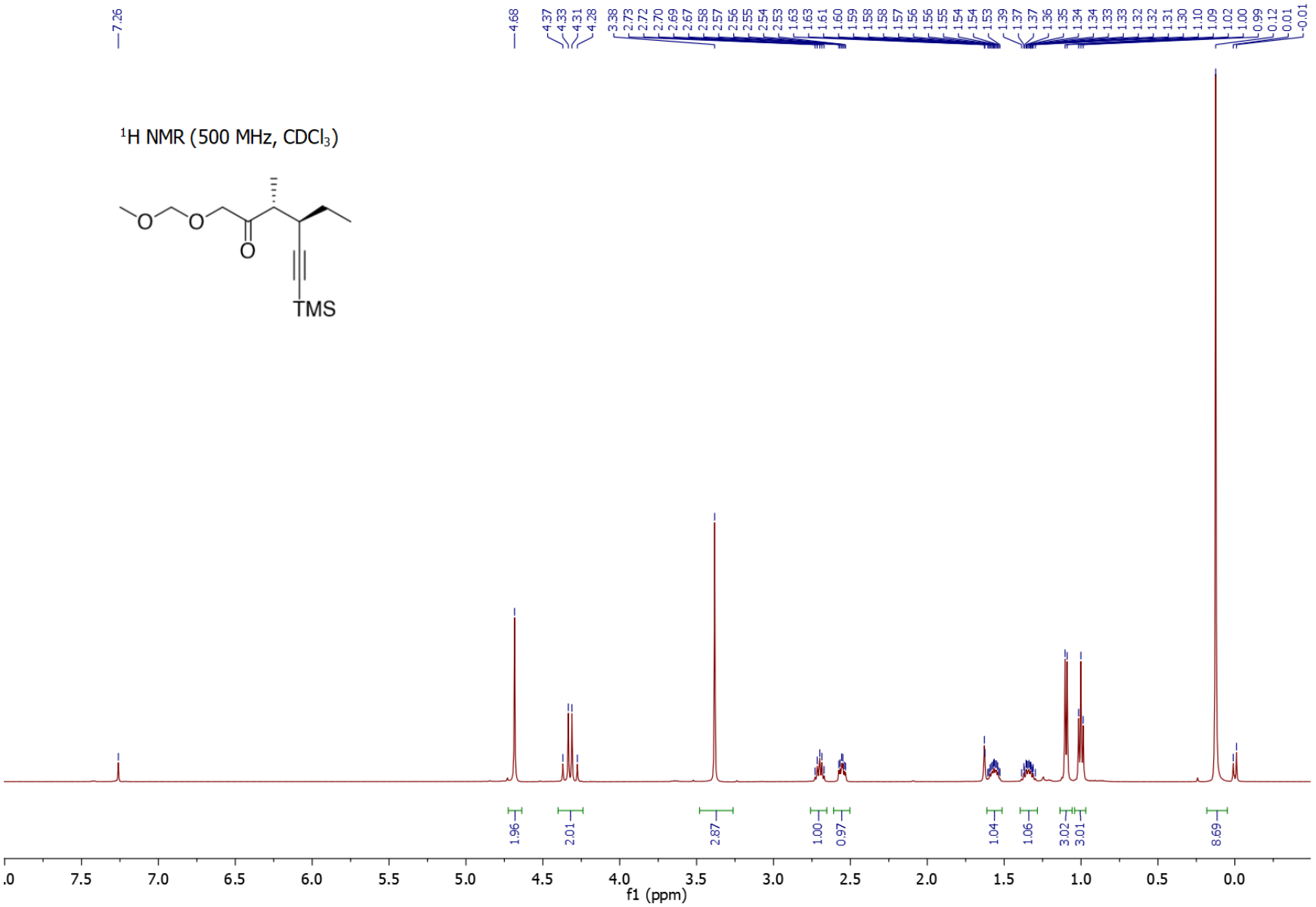

7.39 7.38 7.37 7.37 7.36 7.34 7.33 7.32 7.32 7.31 7.30 7.30 7.29 7.29 7.29 7.26
4.64 4.62 4.60 4.58 4.28 4.25 4.22 4.19
2.78 2.77 2.76 2.75 2.73 2.59 2.59 2.58 2.57 2.56 2.56 1.59 1.58 1.57 1.57 1.56 1.56 1.55 1.55 1.54 1.53 1.53 1.38 1.37 1.36 1.36 1.35 1.35 1.34 1.33 1.33 1.32 1.32 1.31 1.29 1.09 1.08 1.01 1.00 0.99 0.12 -0.00
1H NMR (600 MHz, CDCl3)
O
O
TMS
5.31
2.11
2.03
1.05
1.00
1.08
1.09
3.05
3.15
9.06
3.0 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)

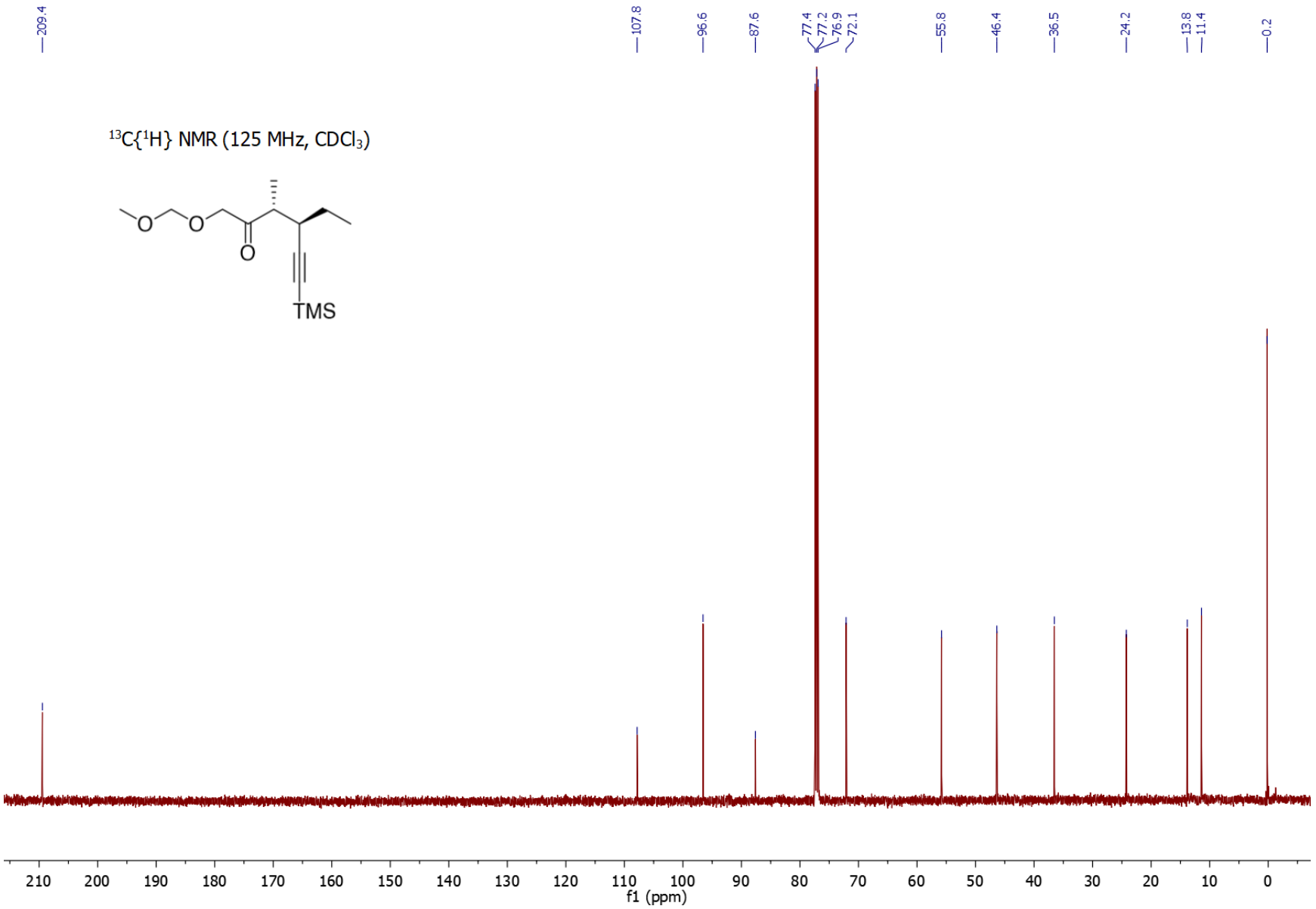

$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)
TMS
210.2
137.5
128.6
128.1
128.1
108.1
87.4
77.4
77.2
76.9
75.1
73.5
46.1
36.4
24.2
13.7
11.4
0.2
128.7
128.5
128.3
128.1
127.9
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

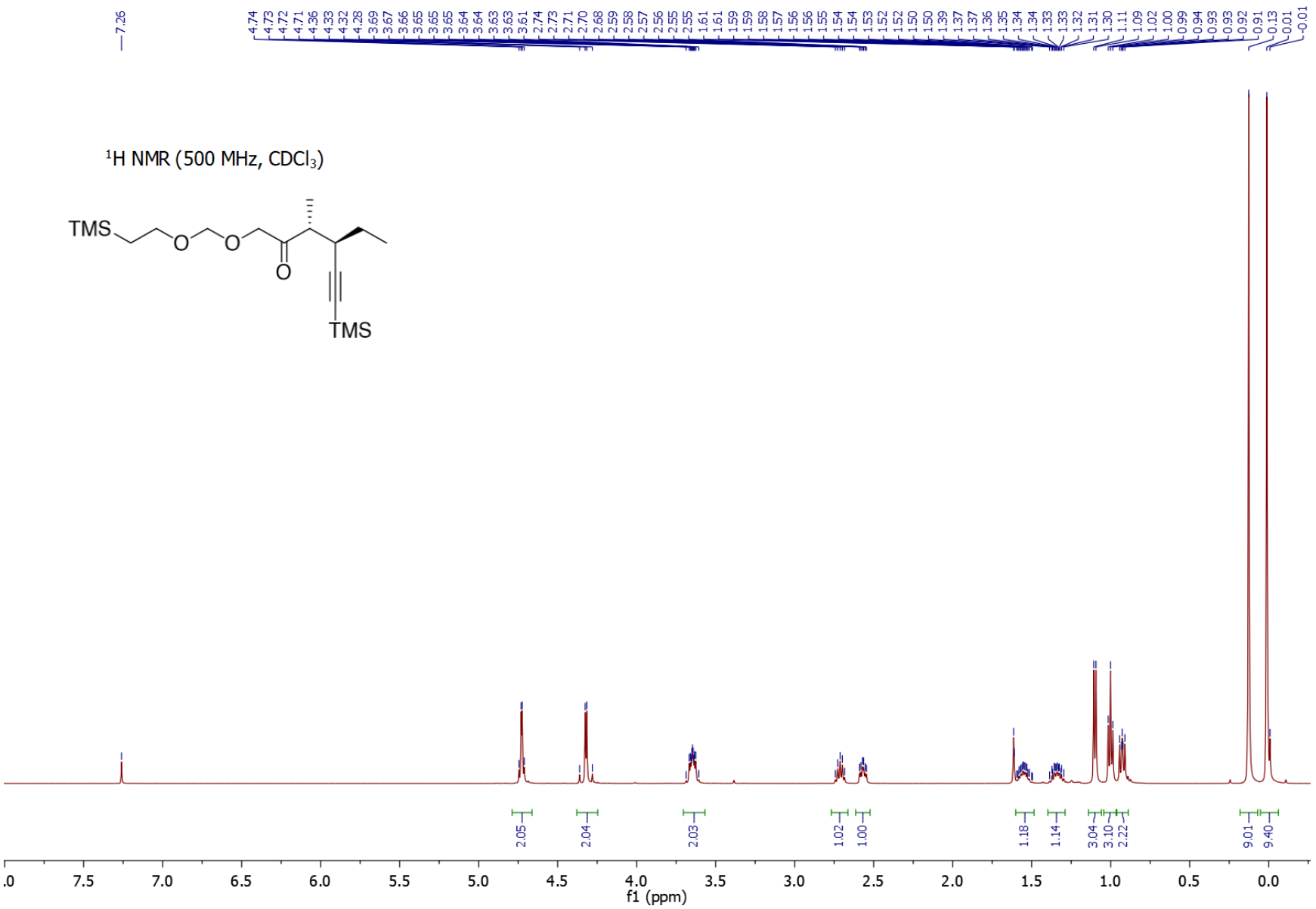
^{1}H NMR (500 MHz, $CDCl_3$)

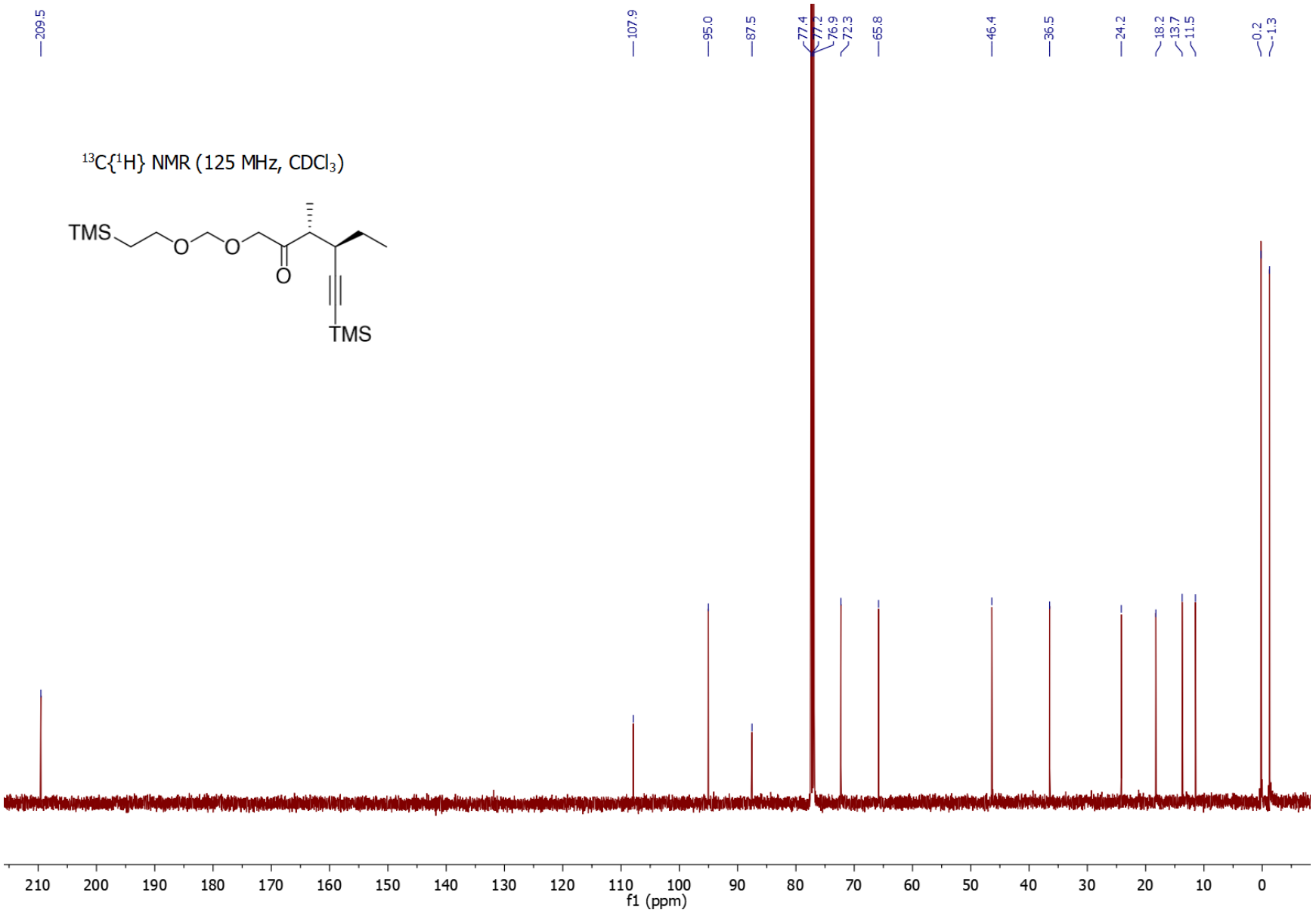


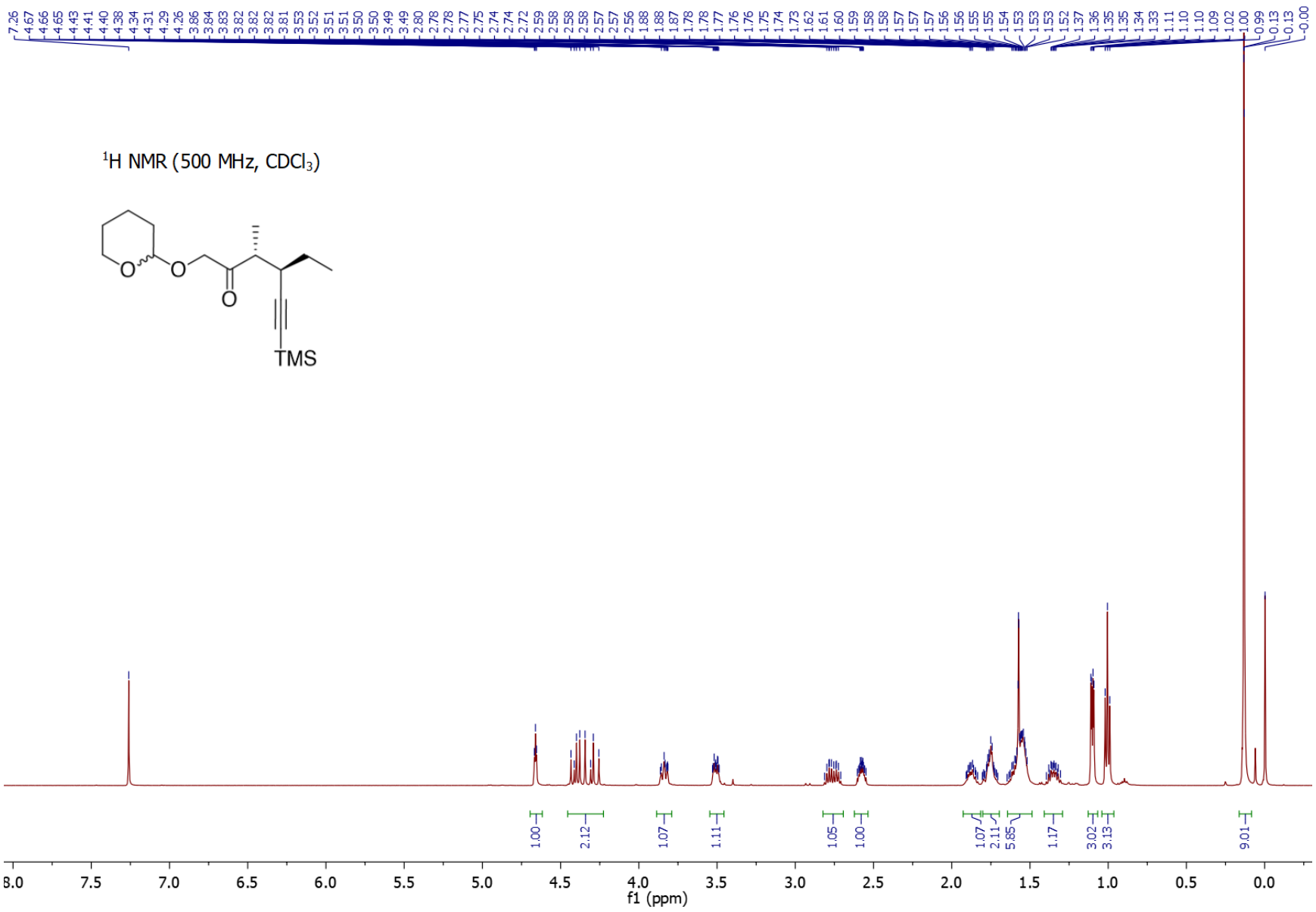

210.1
108.0
87.6
77.6
77.4
77.2
76.9
59.4
46.0
36.6
24.2
13.8
11.4
0.2
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
O
O
TMS
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

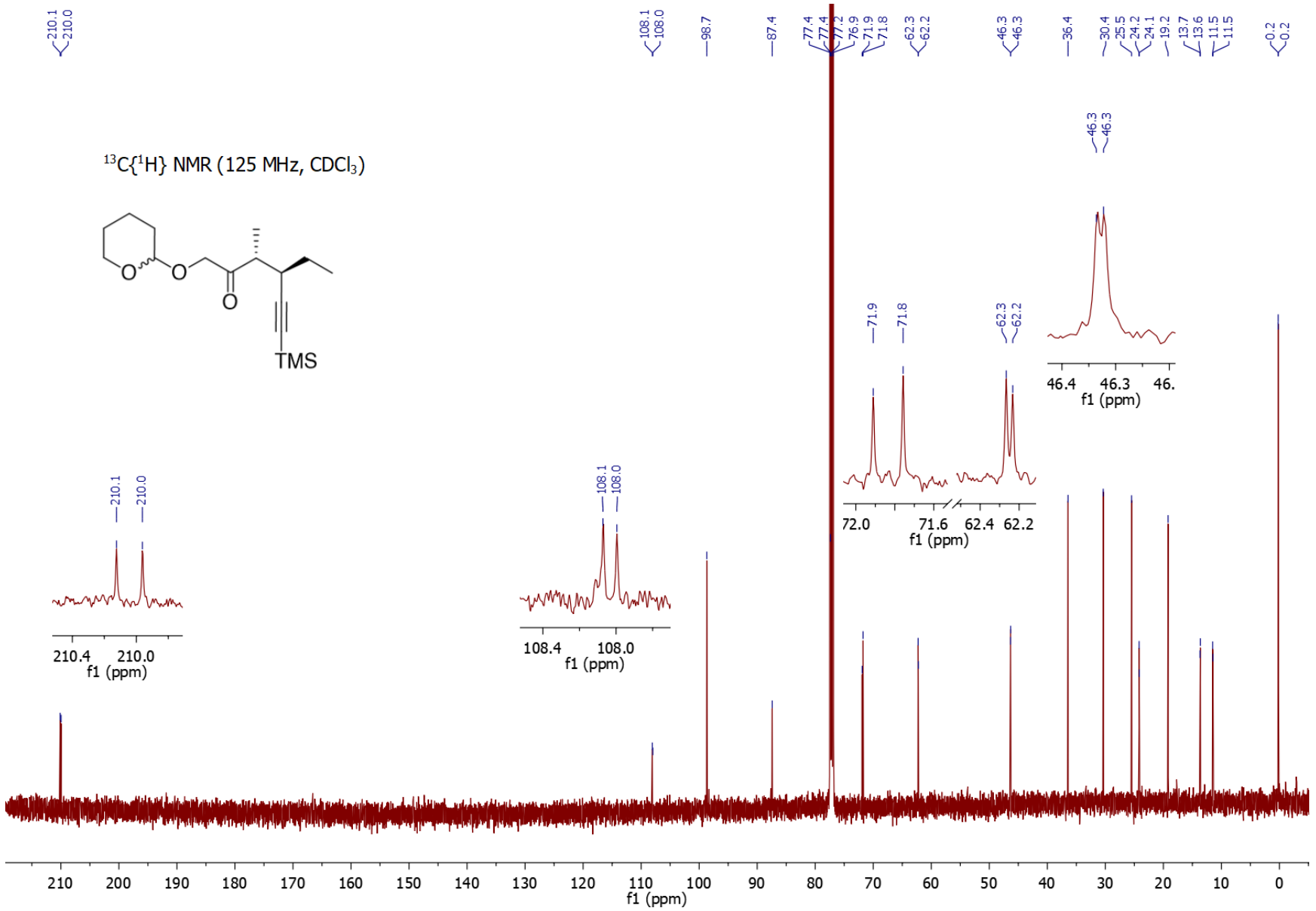

^{1}H NMR (500 MHz, $CDCl_3$)
TMS
f1 (ppm)


209.4
107.8
96.6
87.6
77.4
77.2
76.9
72.1
55.8
46.4
36.5
24.2
13.8
11.4
0.2
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
O
O
O
TMS
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

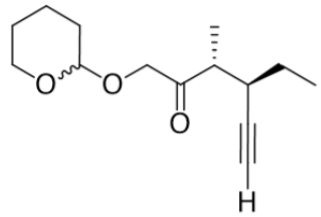

7.26
4.74 4.73 4.72 4.71 4.36 4.33 4.32 4.28 3.69 3.67 3.66 3.65 3.65 3.65 3.64 3.64 3.63 3.63 3.61 2.74 2.73 2.71 2.70 2.68 2.59 2.58 2.57 2.56 2.55 2.55 1.61 1.61 1.59 1.59 1.58 1.57 1.56 1.56 1.55 1.54 1.54 1.53 1.52 1.52 1.50 1.50 1.39 1.37 1.37 1.36 1.35 1.34 1.34 1.33 1.33 1.32 1.31 1.30 1.11 1.09 1.02 1.00 0.99 0.94 0.93 0.93 0.92 0.91 0.13 0.01 -0.01
1H NMR (500 MHz, CDCl3)
TMS
O
O
O
TMS
2.05 2.04 2.03 1.02 1.00 1.18 1.14 3.04 3.10 2.22 9.01 9.40
.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)

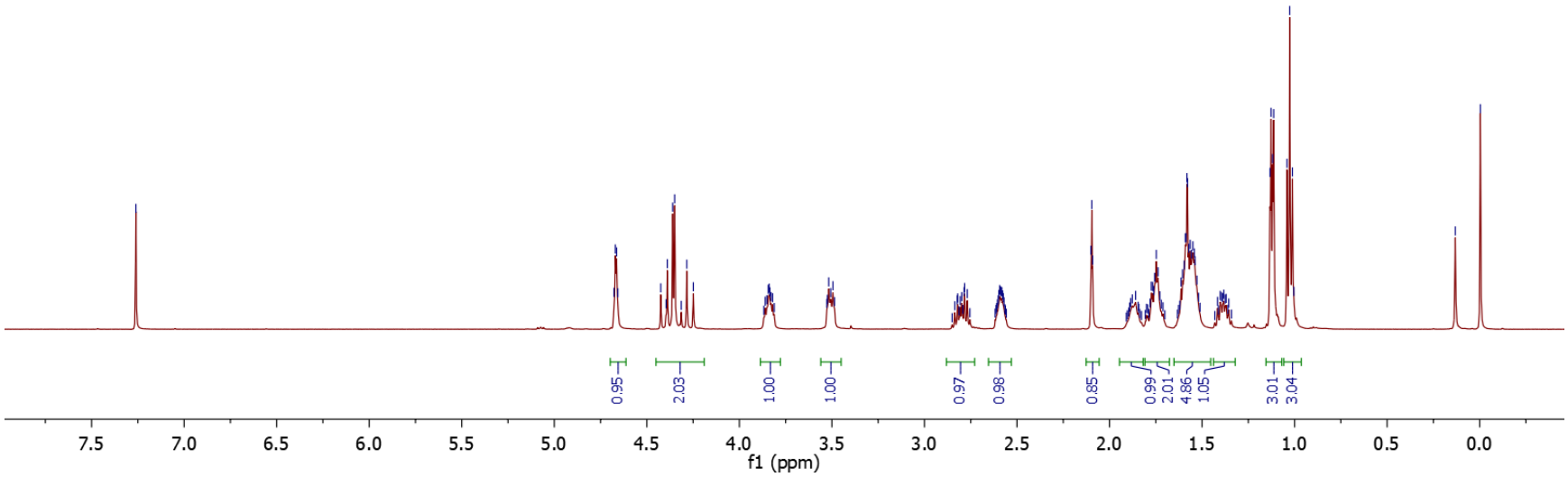

209.5
107.9
95.0
87.5
77.4
77.2
76.9
72.3
65.8
46.4
36.5
24.2
18.2
13.7
11.5
0.2
-1.3
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
TMS
O
O
O
TMS
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

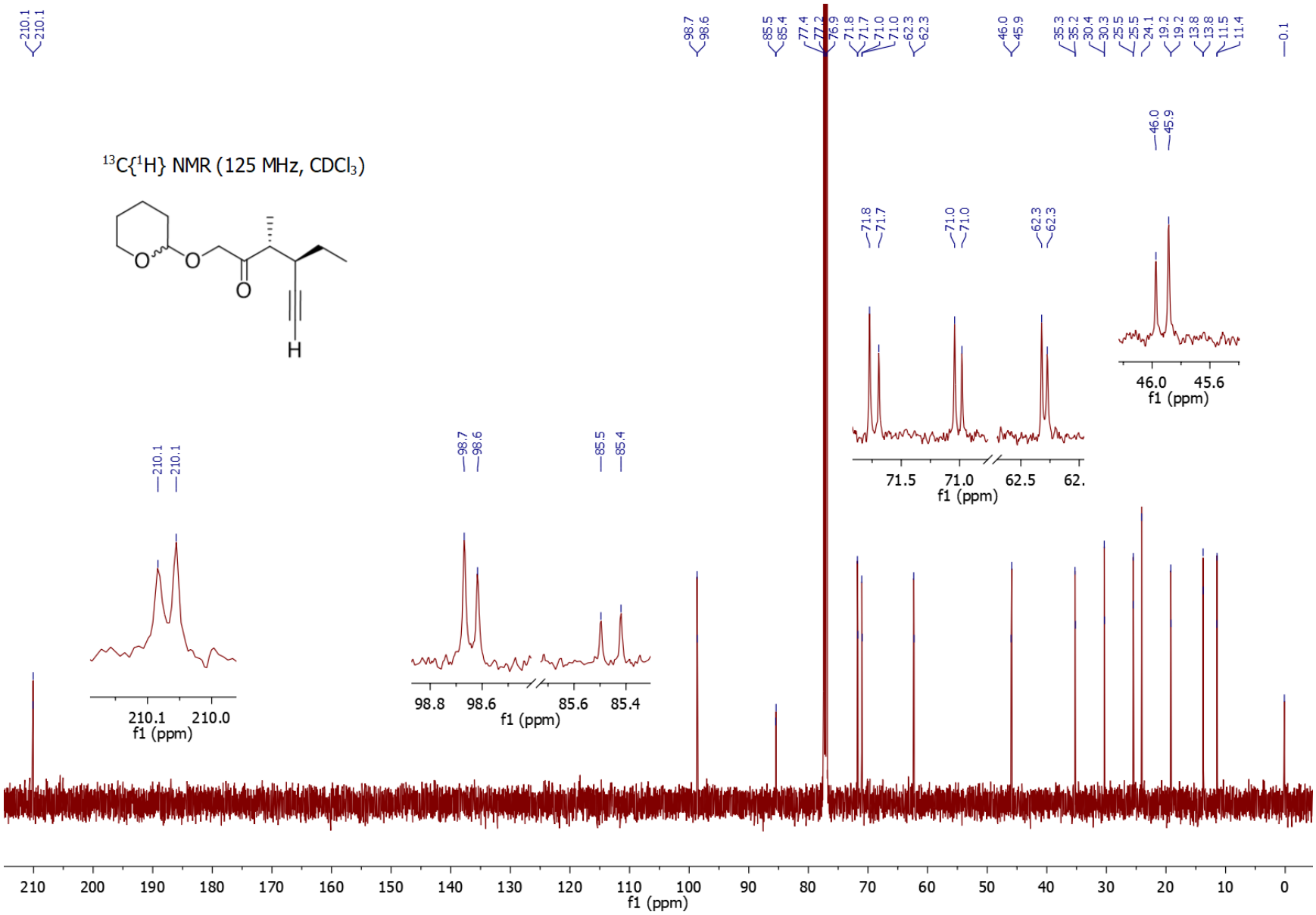

^{1}H NMR (500 MHz, $CDCl_3$)
O
O
O
TMS
f1 (ppm)


$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
TMS
f1 (ppm)

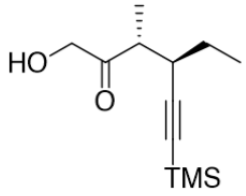
^{1}H NMR (500 MHz, $CDCl_3$)



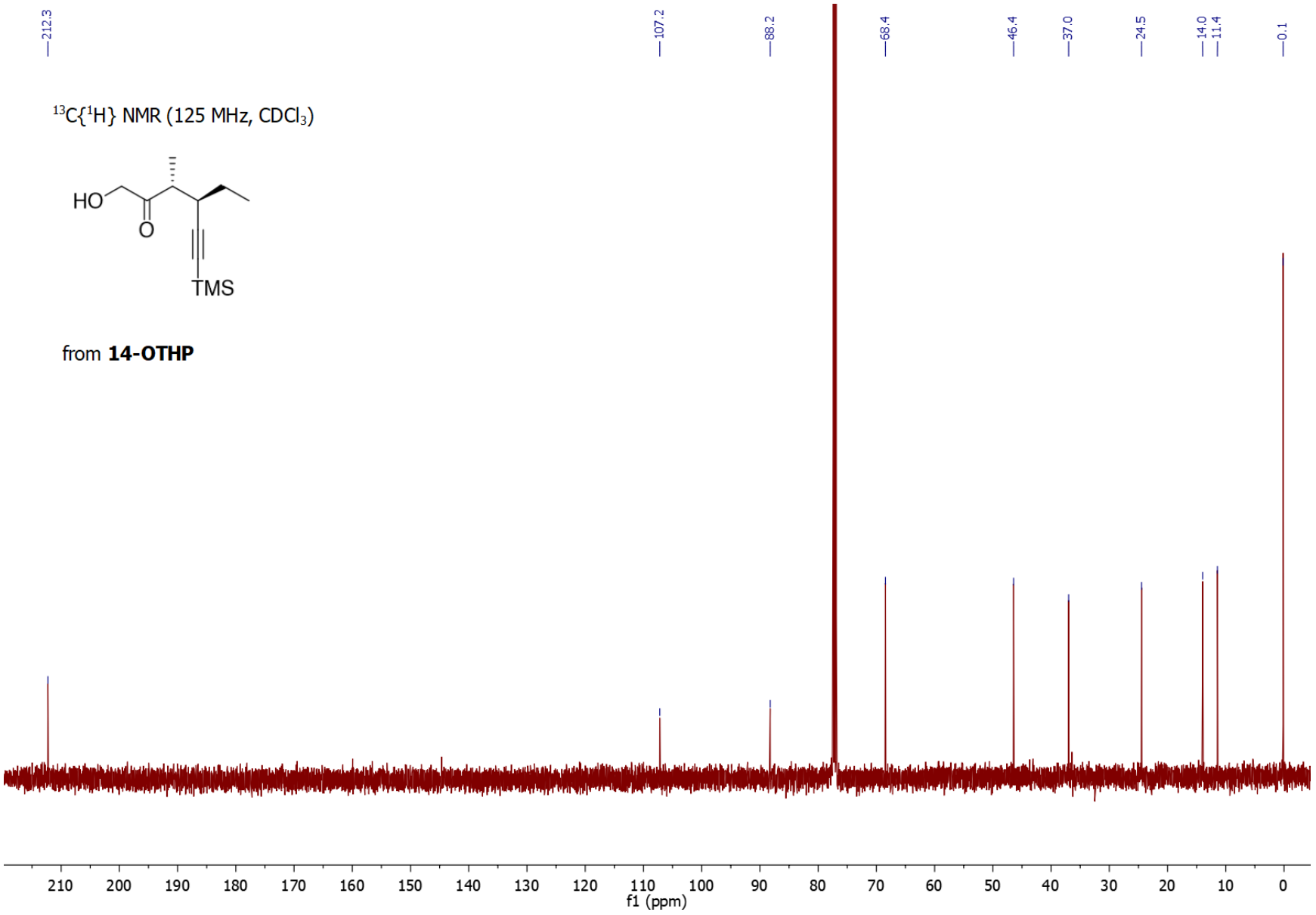


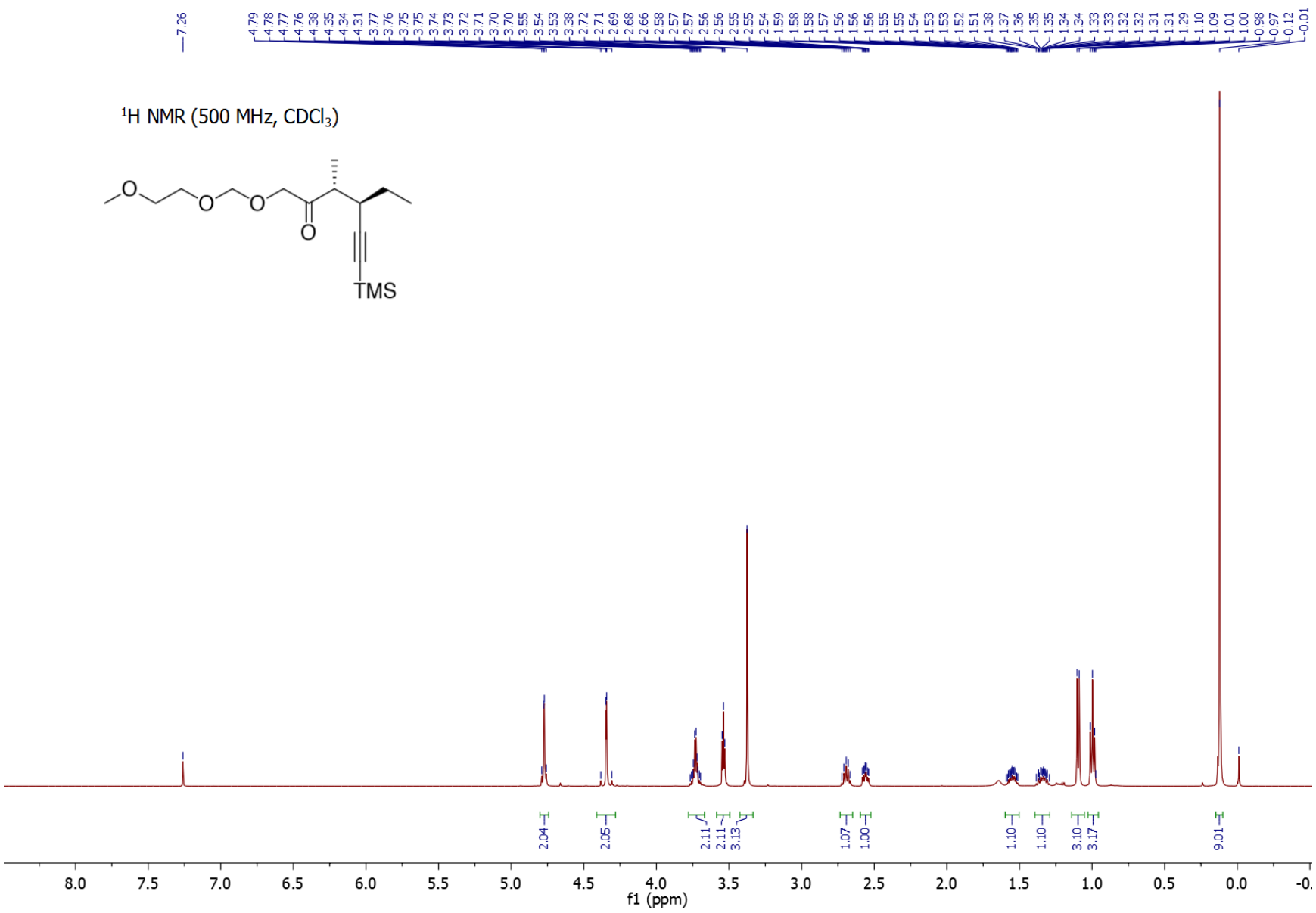

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
O
O
O
H
210.1
210.1
98.7
98.6
85.5
85.4
77.4
77.2
76.9
71.8
71.7
71.0
71.0
62.3
62.3
46.0
45.9
35.3
35.2
30.4
30.3
25.5
24.1
19.2
19.2
13.8
13.8
11.5
11.4
0.1
f1 (ppm)

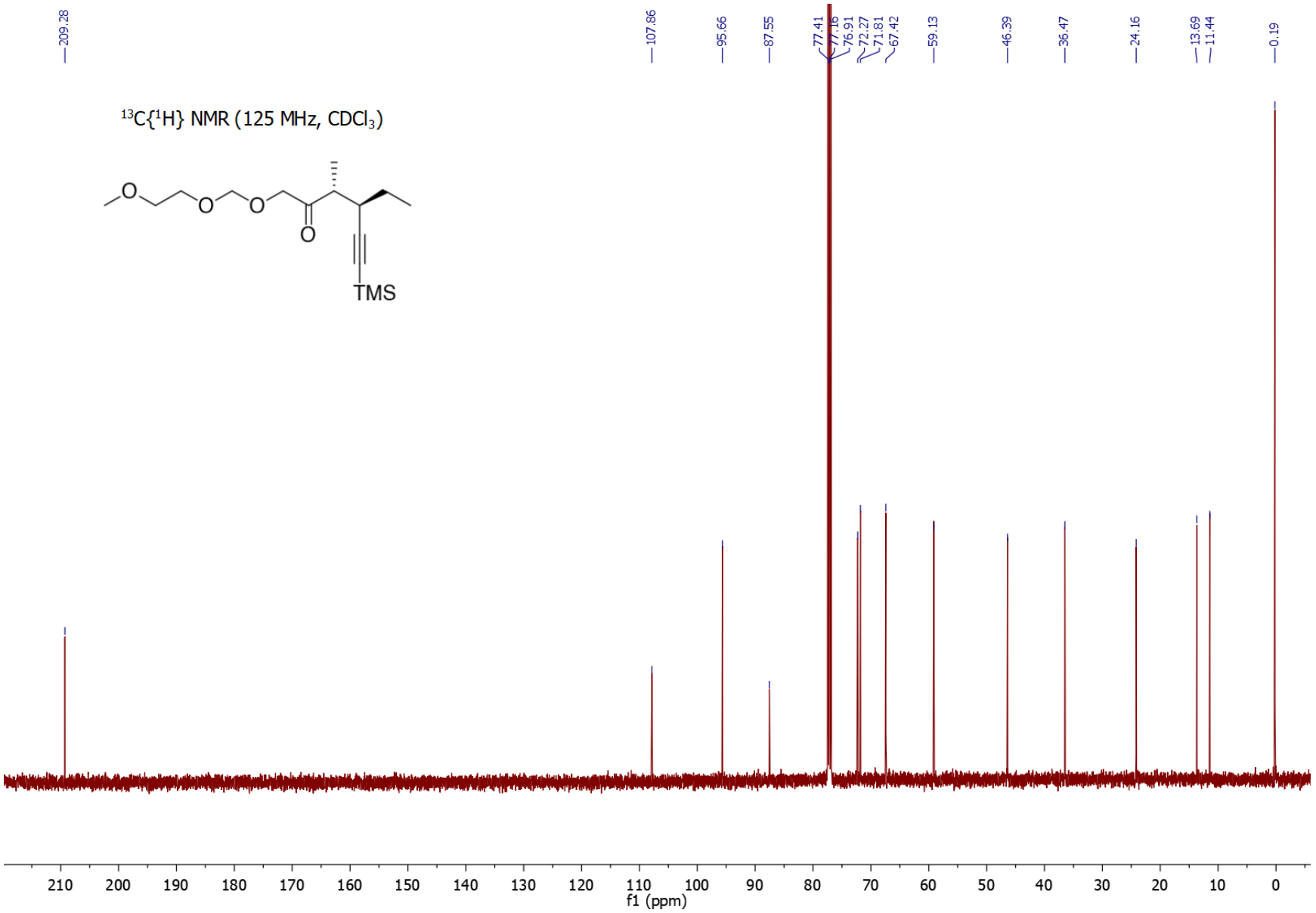
^{1}H NMR (500 MHz, $CDCl_3$)



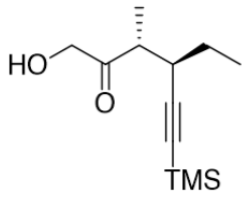
from **14-OTHP**


212.3
107.2
88.2
68.4
46.4
37.0
24.5
14.0
11.4
0.1
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
HO
O
TMS
from **14-OTHP**
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


^{1}H NMR (500 MHz, $CDCl_3$)
TMS
f1 (ppm)

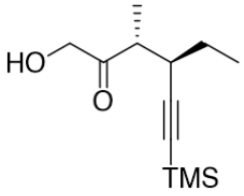

209.28
107.86
95.66
87.55
77.41
77.16
76.91
72.27
71.81
67.42
59.13
46.39
36.47
24.16
13.69
11.44
0.19
13C{1H} NMR (125 MHz, CDCl3)
O
O
O
O
TMS
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}H NMR (500 MHz, $CDCl_3$)

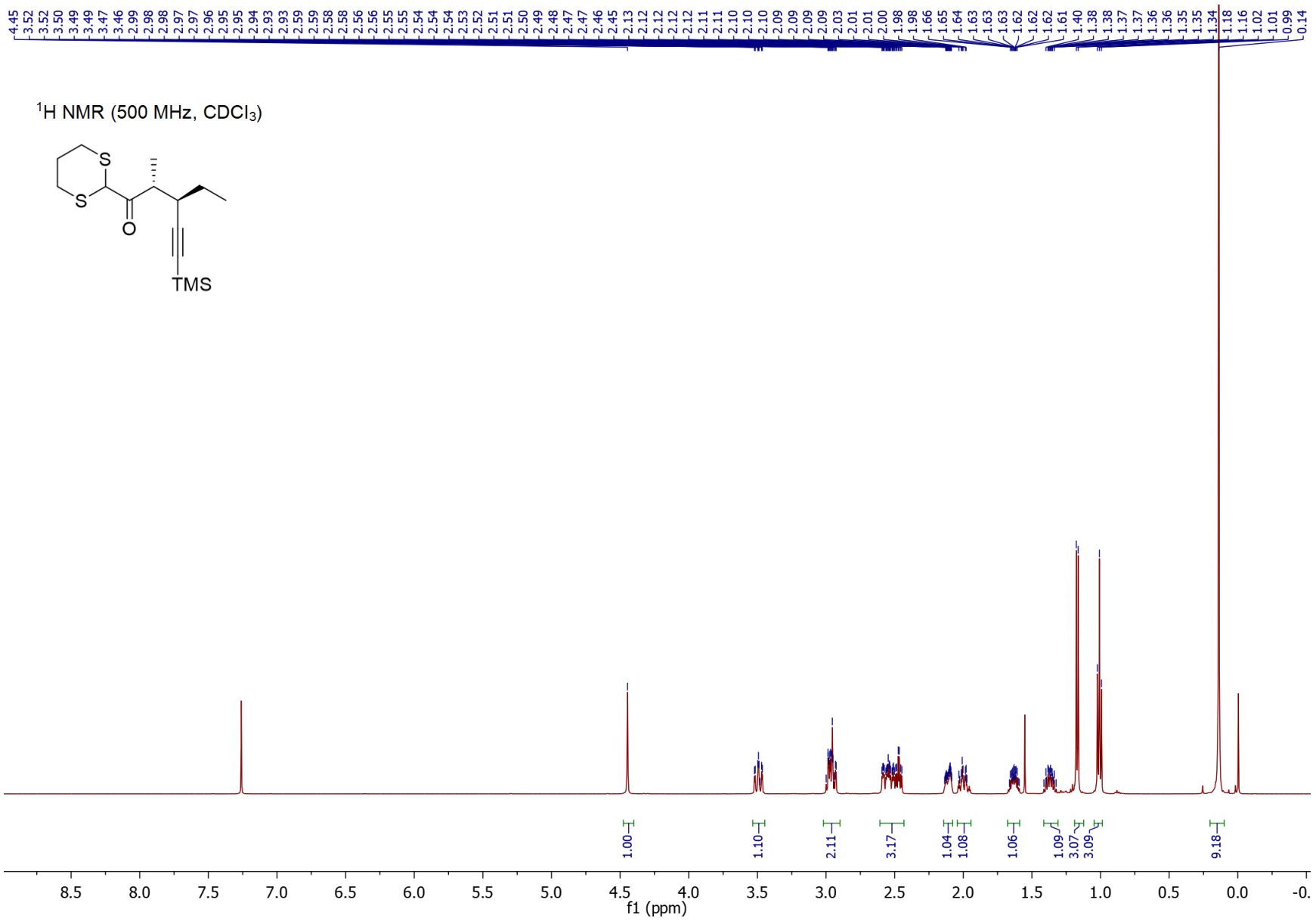


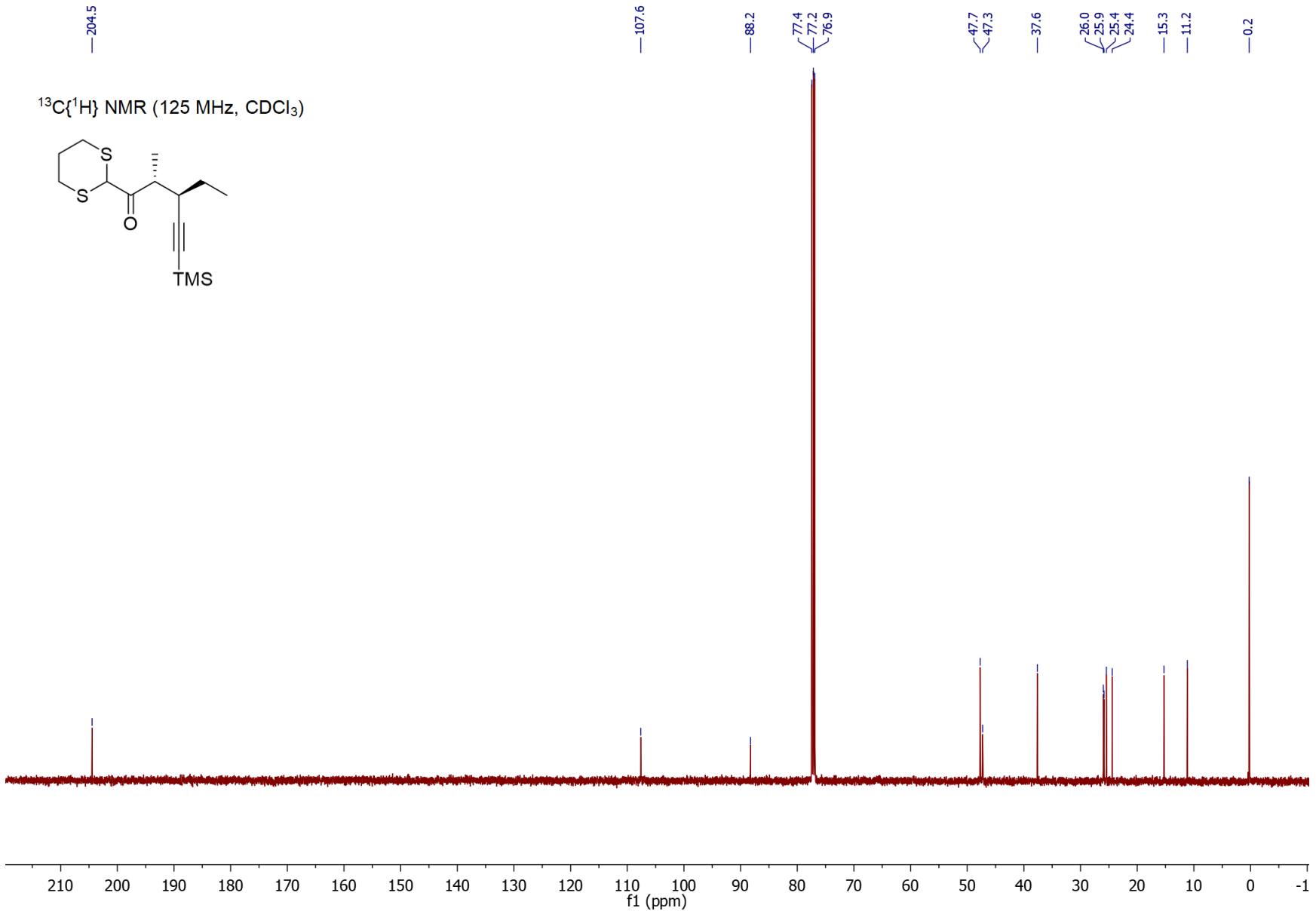
from **14-OMEM**

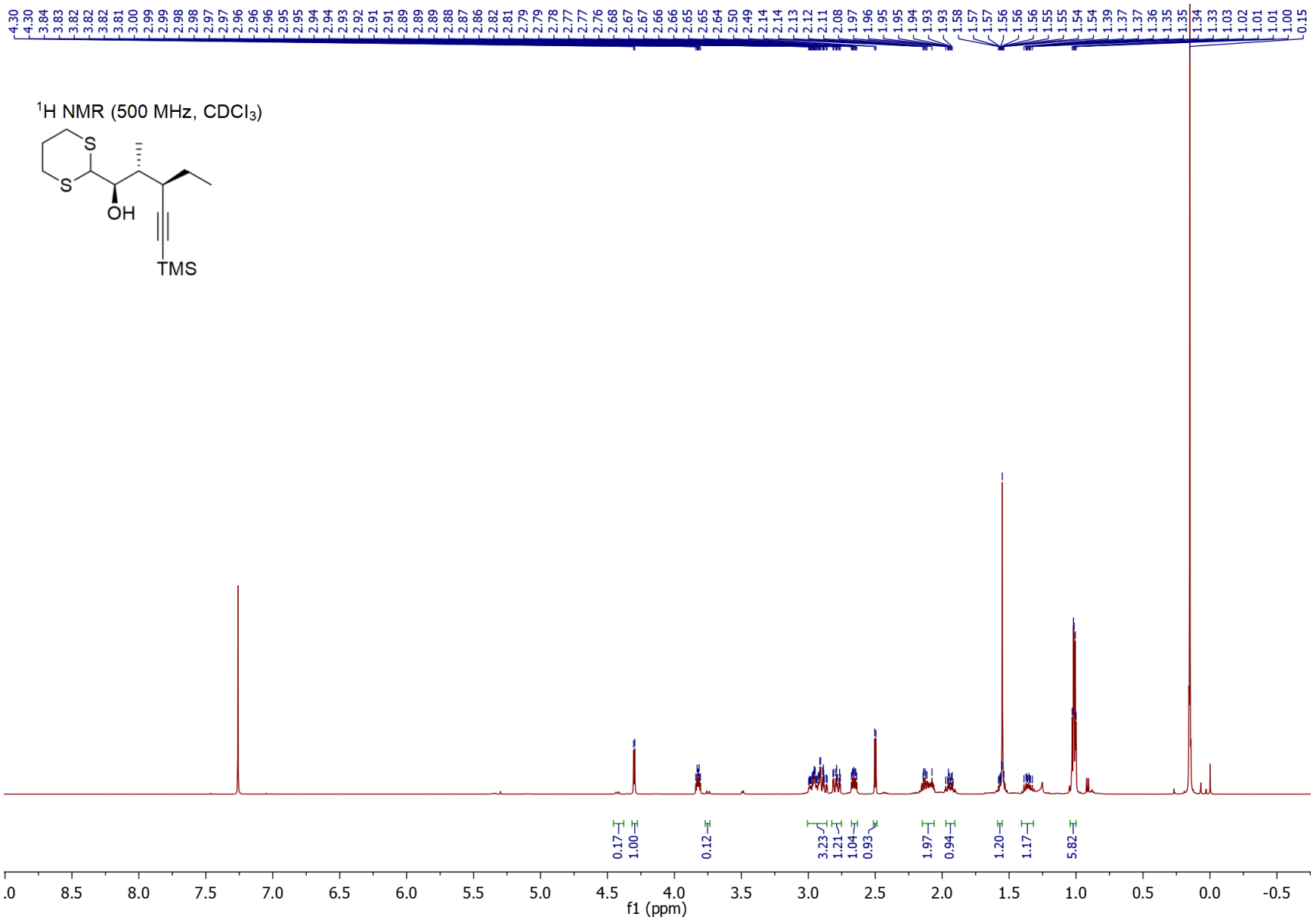
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

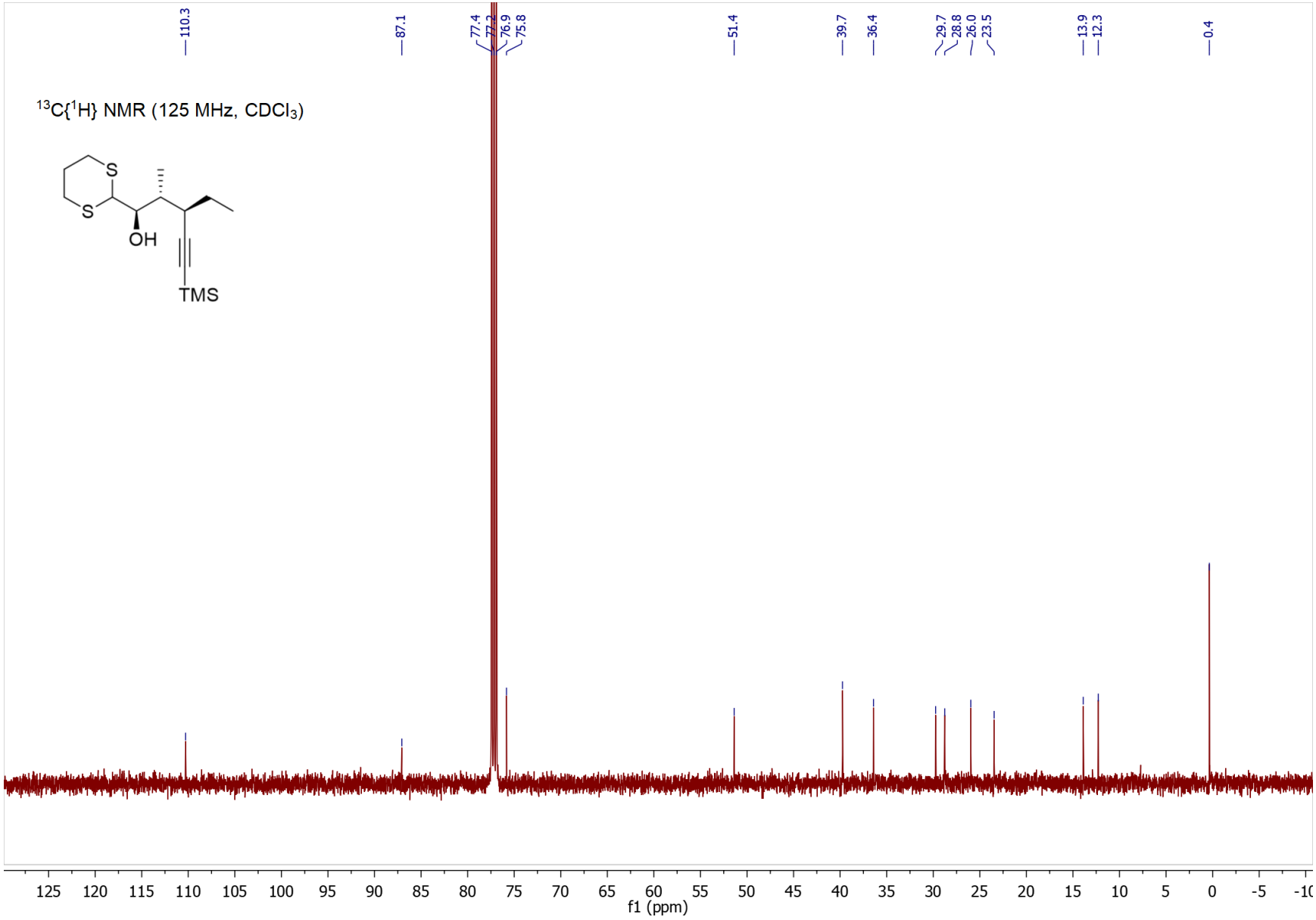


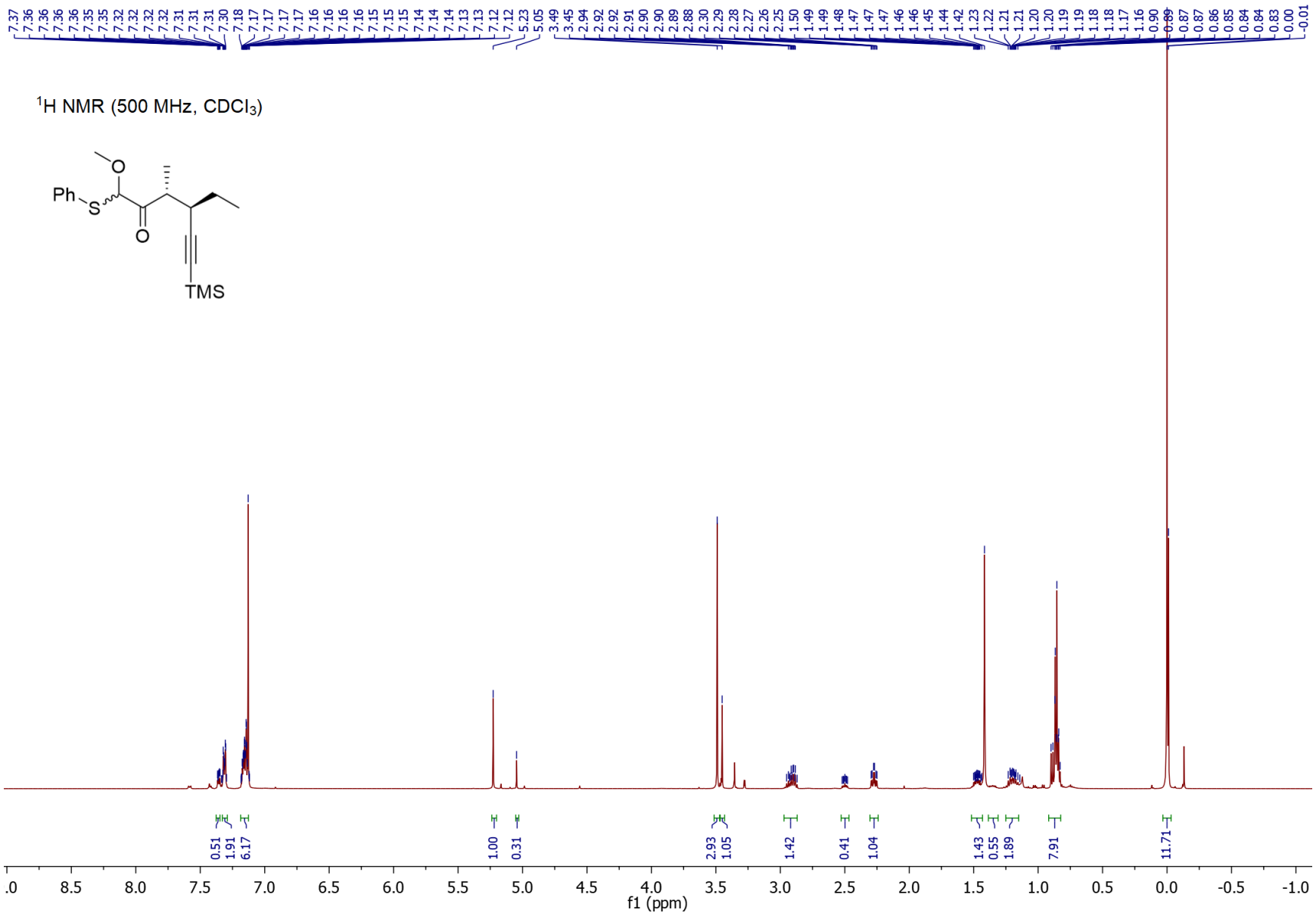
from **14-OMEM**

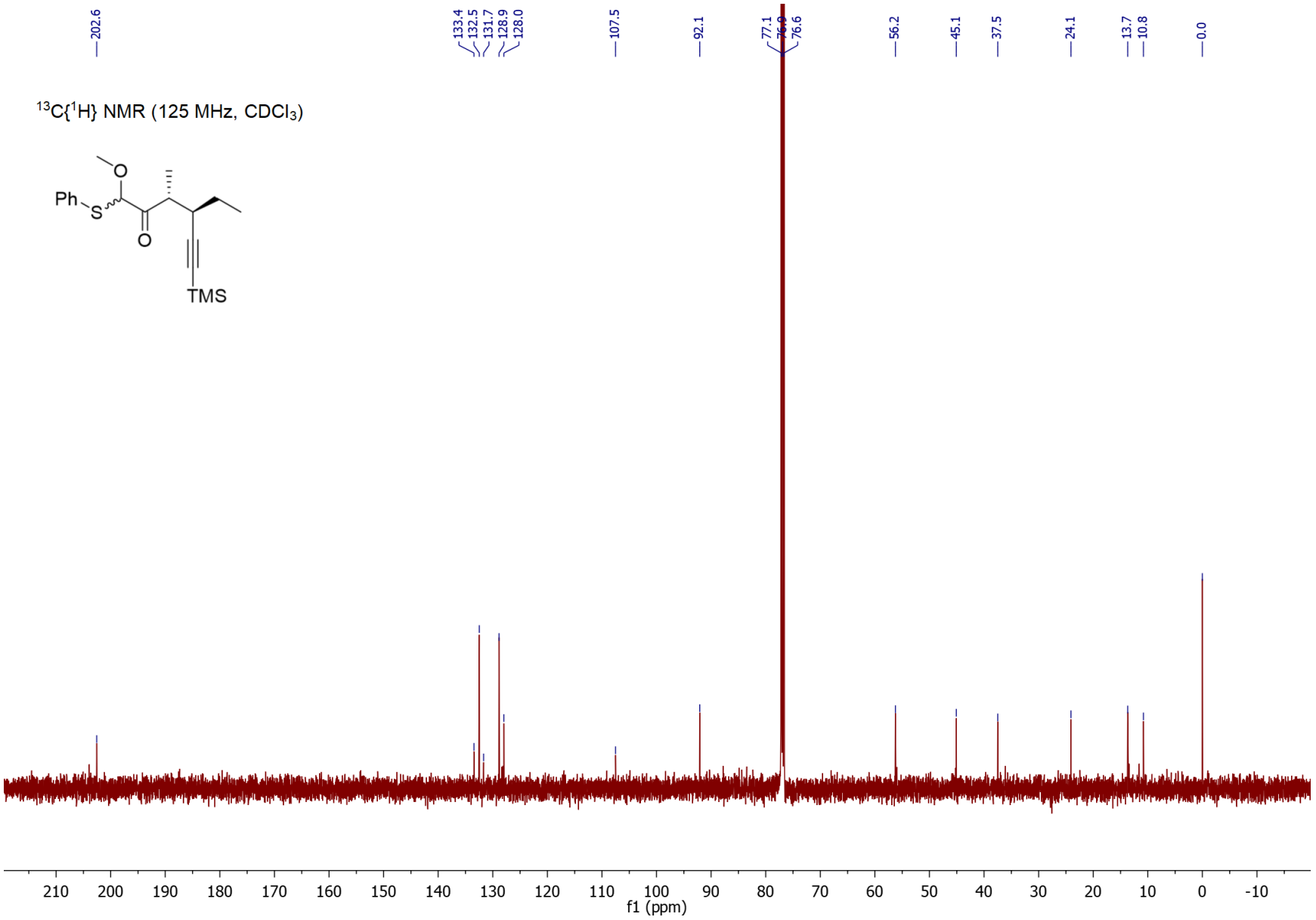

4.45 3.52 3.52 3.50 3.49 3.49 3.47 3.46 2.99 2.98 2.98 2.97 2.97 2.96 2.95 2.95 2.94 2.93 2.93 2.59 2.59 2.58 2.58 2.56 2.56 2.55 2.55 2.54 2.54 2.54 2.53 2.52 2.51 2.51 2.50 2.49 2.48 2.47 2.47 2.46 2.45 2.13 2.12 2.12 2.12 2.11 2.11 2.10 2.10 2.09 2.09 2.09 2.09 2.03 2.01 2.01 2.00 1.98 1.98 1.66 1.65 1.64 1.63 1.63 1.63 1.62 1.62 1.62 1.61 1.40 1.38 1.38 1.37 1.37 1.36 1.36 1.35 1.35 1.34 1.18 1.16 1.02 1.01 0.99 0.14
^{1}H NMR (500 MHz, $CDCl_3$)
S
S
O
TMS
1.00 1.10 2.11 3.17 1.04 1.08 1.06 1.09 3.07 3.09 9.18
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

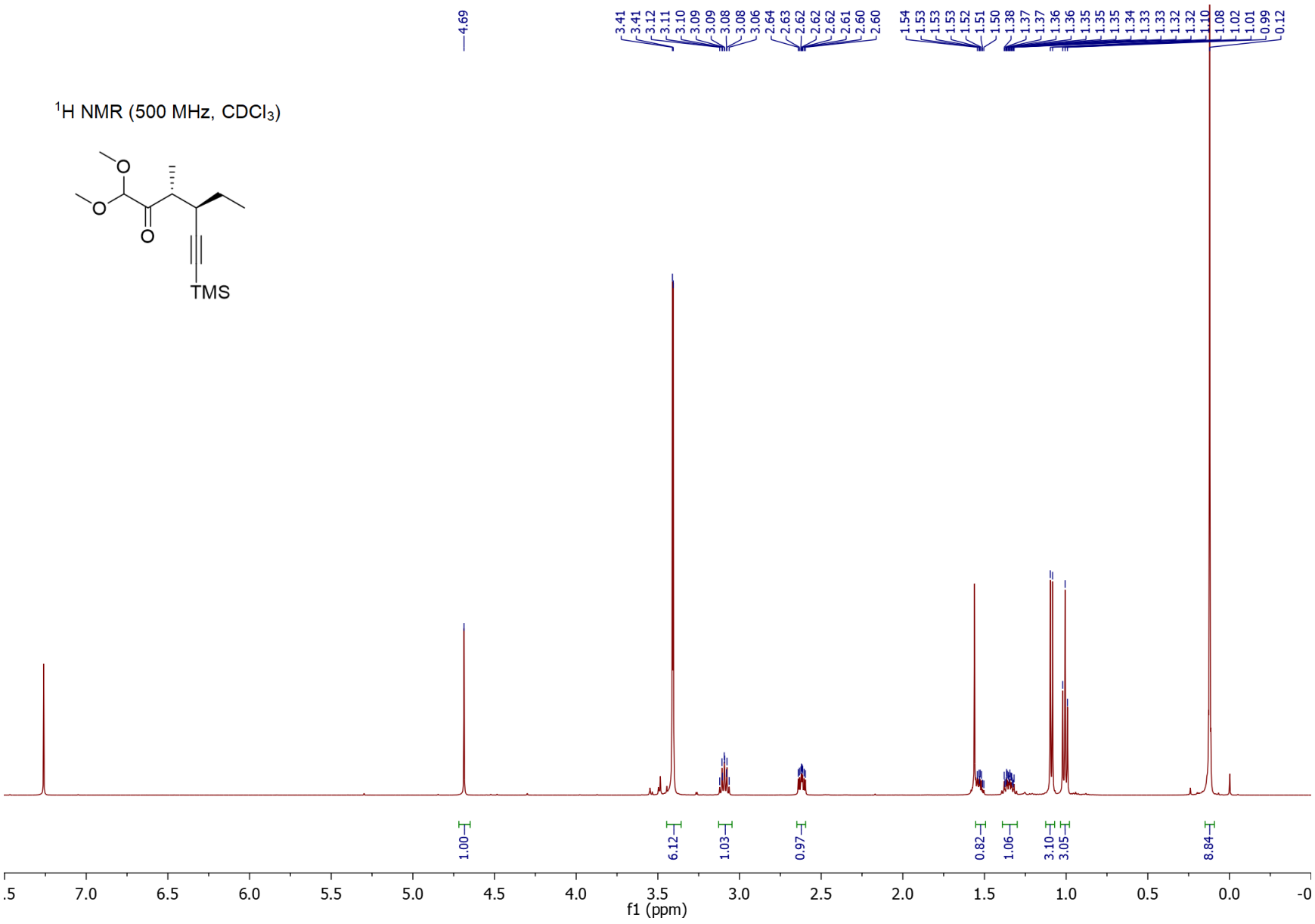

204.5
107.6
88.2
77.4
77.2
76.9
47.7
47.3
37.6
26.0
25.9
25.4
24.4
15.3
11.2
0.2
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
S
S
O
TMS
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

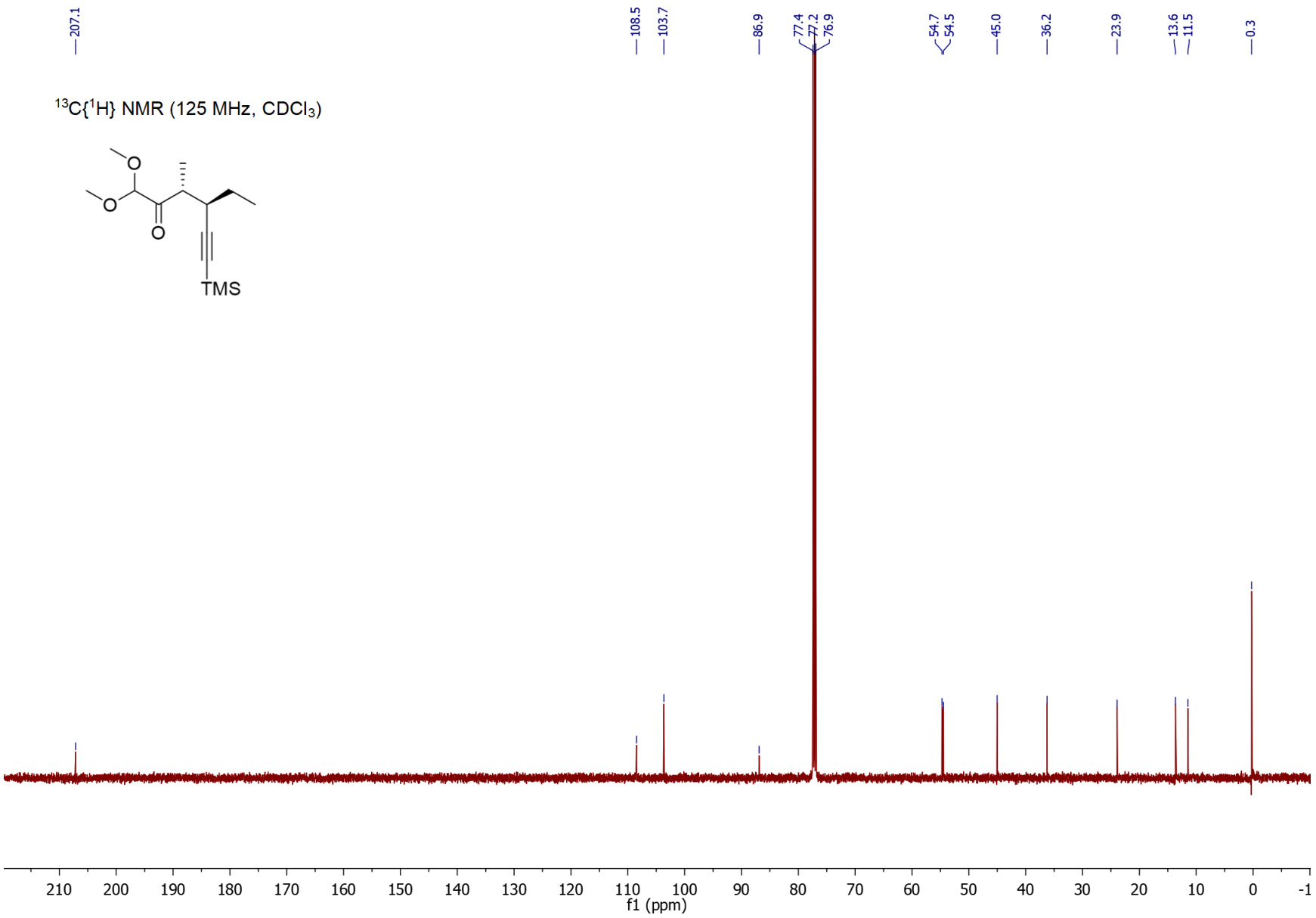

4.30 4.30 3.84 3.83 3.82 3.82 3.81 3.00 2.99 2.99 2.98 2.98 2.97 2.97 2.96 2.96 2.96 2.95 2.95 2.94 2.94 2.93 2.92 2.91 2.91 2.89 2.89 2.89 2.88 2.87 2.86 2.82 2.81 2.79 2.79 2.78 2.77 2.77 2.76 2.68 2.67 2.67 2.66 2.66 2.65 2.65 2.64 2.50 2.49 2.14 2.14 2.13 2.12 2.11 2.08 1.97 1.96 1.95 1.95 1.94 1.93 1.93 1.58 1.57 1.57 1.56 1.56 1.56 1.55 1.55 1.54 1.54 1.39 1.37 1.37 1.36 1.35 1.35 1.34 1.33 1.03 1.02 1.01 1.01 1.00 0.15
^{1}H NMR (500 MHz, CDCl$_3$)
S
S
OH
TMS
0.17 1.00 0.12 3.23 1.21 1.04 0.93 1.97 0.94 1.20 1.17 5.82
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

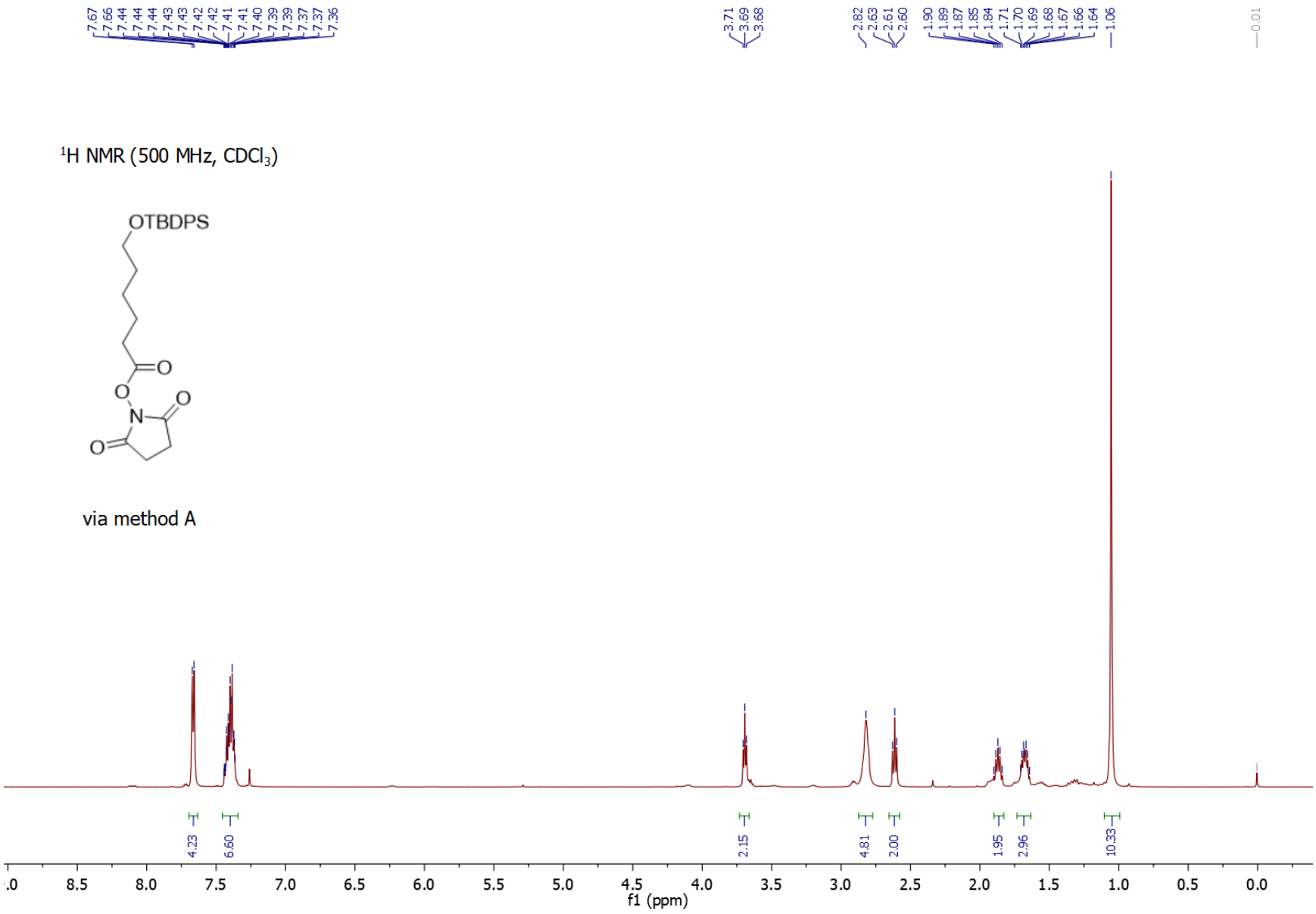

110.3
87.1
77.4
77.2
76.9
75.8
51.4
39.7
36.4
29.7
28.8
26.0
23.5
13.9
12.3
0.4
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
S
S
OH
TMS
125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10
f1 (ppm)

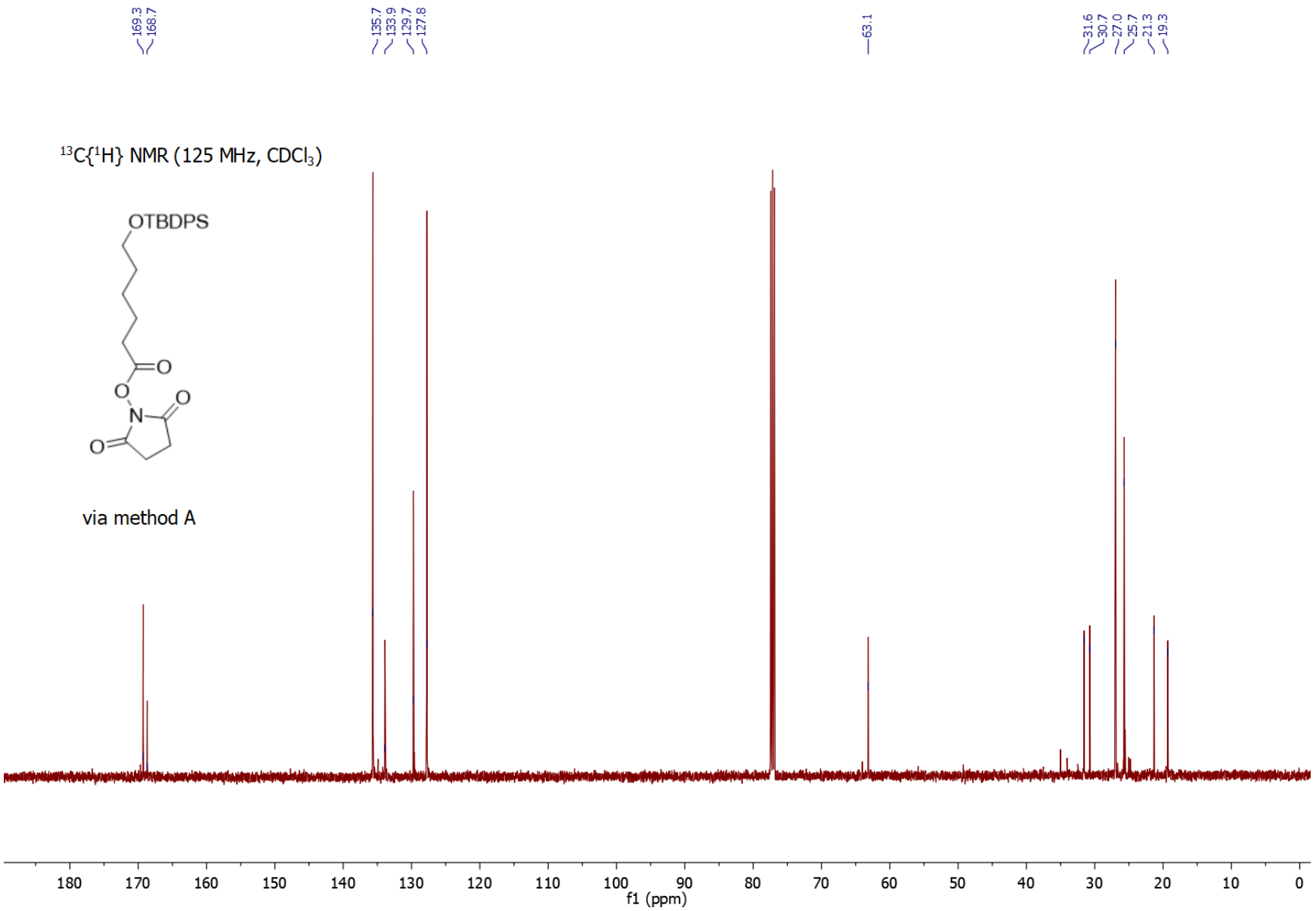

7.37 7.36 7.36 7.36 7.36 7.35 7.35 7.32 7.32 7.32 7.32 7.31 7.31 7.31 7.30 7.18 7.17 7.17 7.17 7.17 7.16 7.16 7.16 7.16 7.15 7.15 7.15 7.14 7.14 7.14 7.13 7.13 7.12 7.12 5.23 5.05 3.49 3.45 2.94 2.92 2.92 2.91 2.90 2.90 2.89 2.88 2.30 2.29 2.28 2.27 2.26 2.25 1.50 1.49 1.49 1.48 1.47 1.47 1.47 1.46 1.46 1.45 1.44 1.42 1.23 1.22 1.21 1.21 1.20 1.20 1.19 1.19 1.18 1.18 1.17 1.16 0.90 0.89 0.87 0.87 0.86 0.85 0.84 0.84 0.83 0.00 -0.01
^{1}H NMR (500 MHz, CDCl$_3$)
Ph
S
O
O
TMS
0.51 1.91 6.17 1.00 0.31 2.93 1.05 1.42 0.41 1.04 1.43 0.55 1.89 7.91 11.71
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

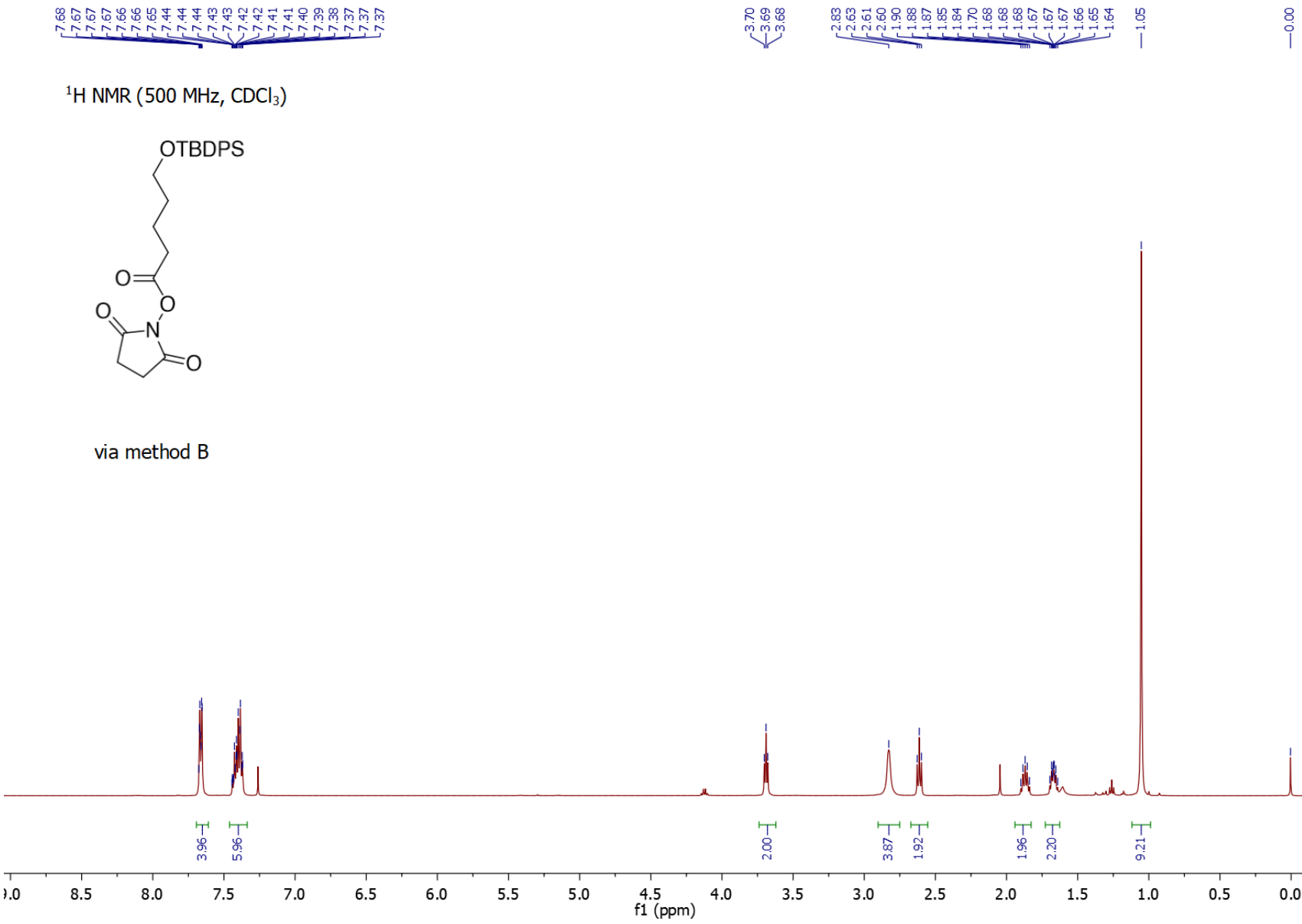

202.6
133.4
132.5
131.7
128.9
128.0
107.5
92.1
77.1
76.9
76.6
56.2
45.1
37.5
24.1
13.7
10.8
0.0
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
Ph
S
O
O
TMS
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

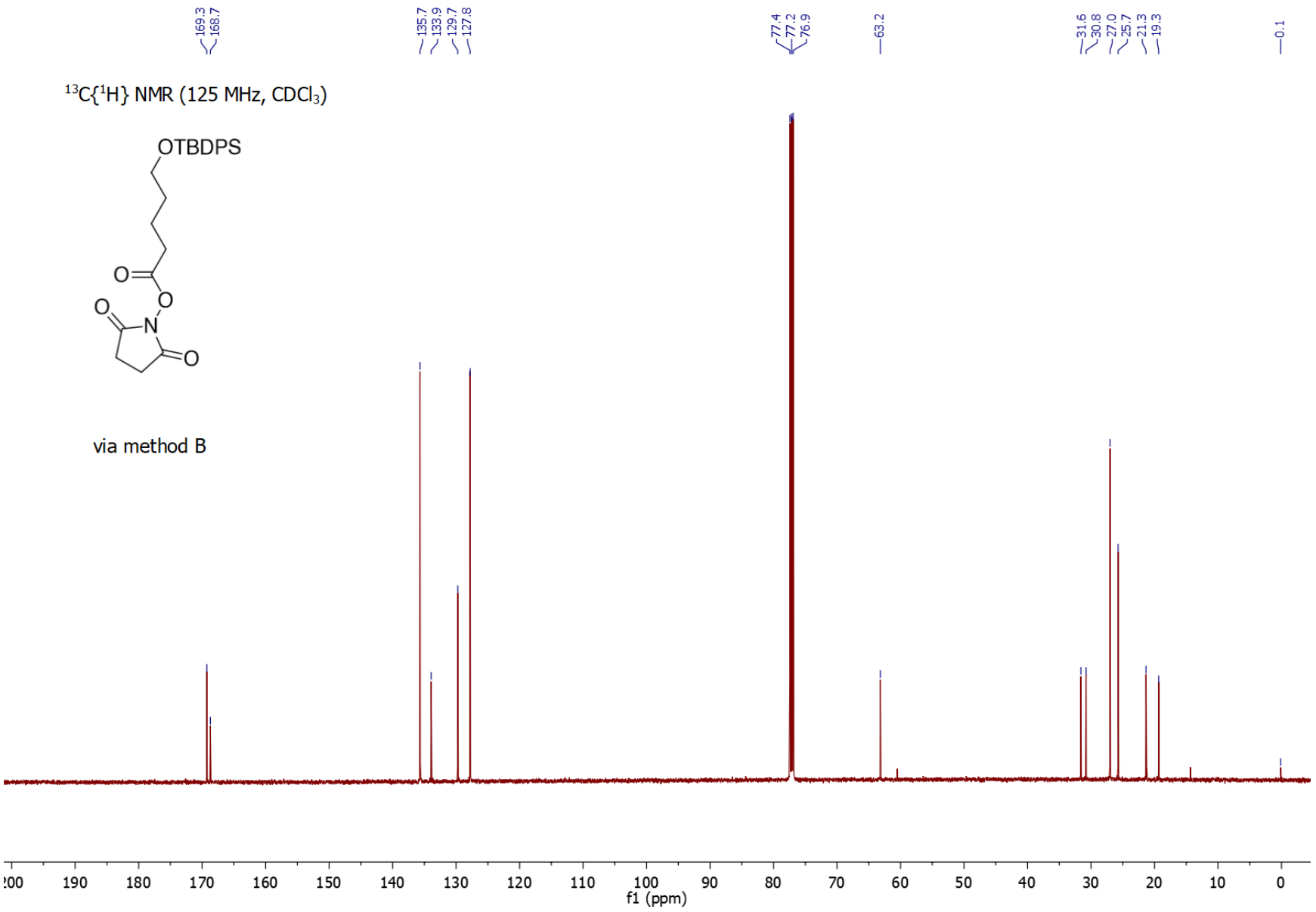

1H NMR (500 MHz, CDCl3)
TMS
4.69
3.41 3.41 3.12 3.11 3.10 3.09 3.09 3.08 3.08 3.06 2.64 2.63 2.62 2.62 2.62 2.61 2.60 2.60
1.54 1.53 1.53 1.53 1.52 1.51 1.50 1.38 1.37 1.37 1.36 1.36 1.35 1.35 1.35 1.34 1.33 1.33 1.32 1.32 1.10 1.08 1.02 1.01 0.99 0.12
1.00 6.12 1.03 0.97 0.82 1.06 3.10 3.05 8.84
f1 (ppm)


207.1
108.5
103.7
86.9
77.4
77.2
76.9
54.7
54.5
45.0
36.2
23.9
13.6
11.5
0.3
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
O
O
O
TMS
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

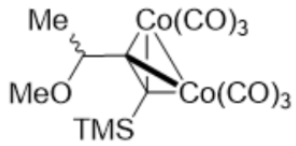

7.67
7.66
7.44
7.44
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.39
7.39
7.37
7.37
7.36
3.71
3.69
3.68
2.82
2.63
2.61
2.60
1.90
1.89
1.87
1.85
1.84
1.71
1.70
1.69
1.68
1.67
1.66
1.64
1.06
0.01
^{1}H NMR (500 MHz, $CDCl_3$)
OTBDPS
O
O
N
O
O
via method A
4.23
6.60
2.15
4.81
2.00
1.95
2.96
10.33
8.5
8.0
7.5
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)

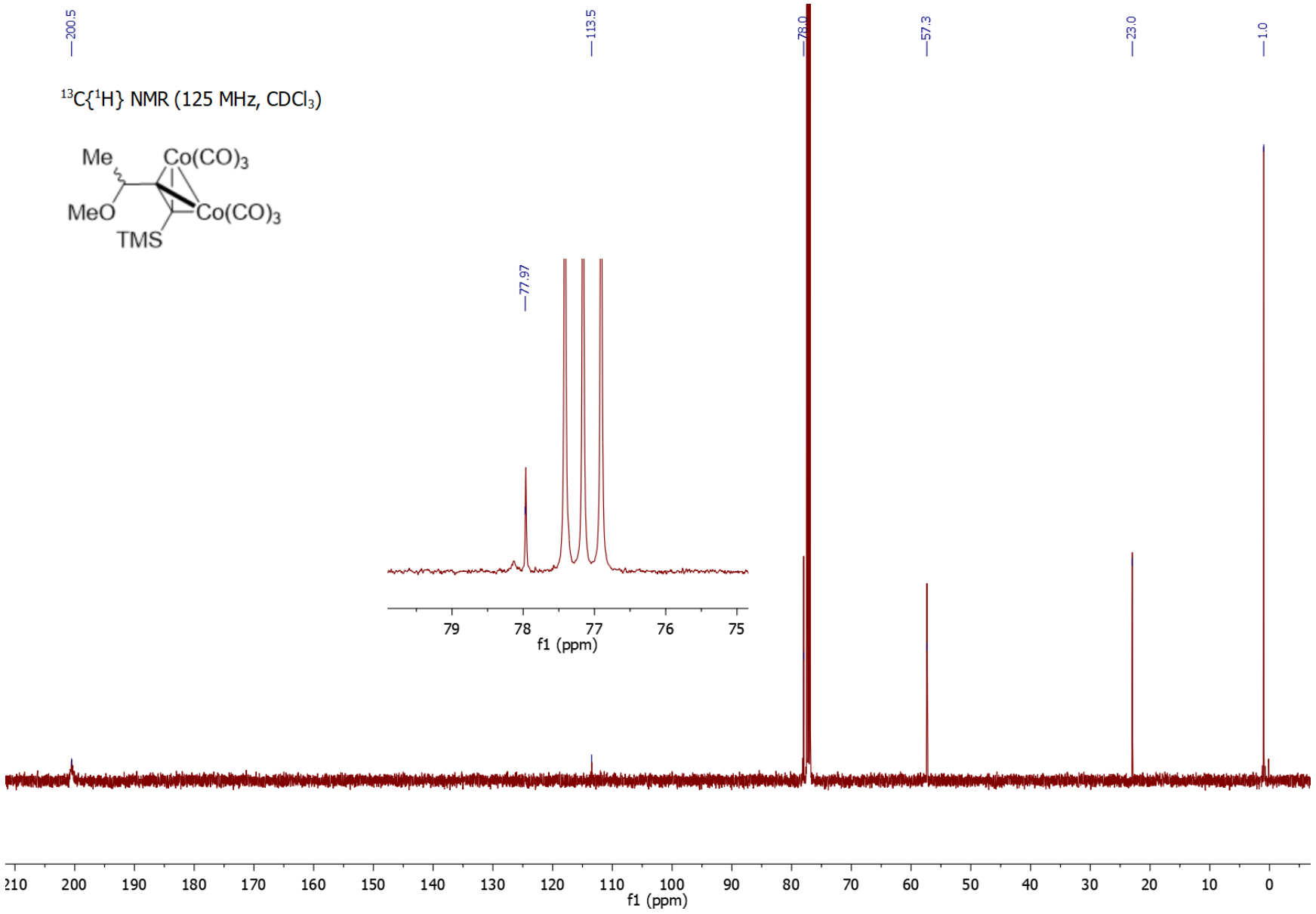

169.3
168.7
135.7
133.9
129.7
127.8
63.1
31.6
30.7
27.0
25.7
21.3
19.3
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
OTBDPS
O
O
N
O
O
via method A
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

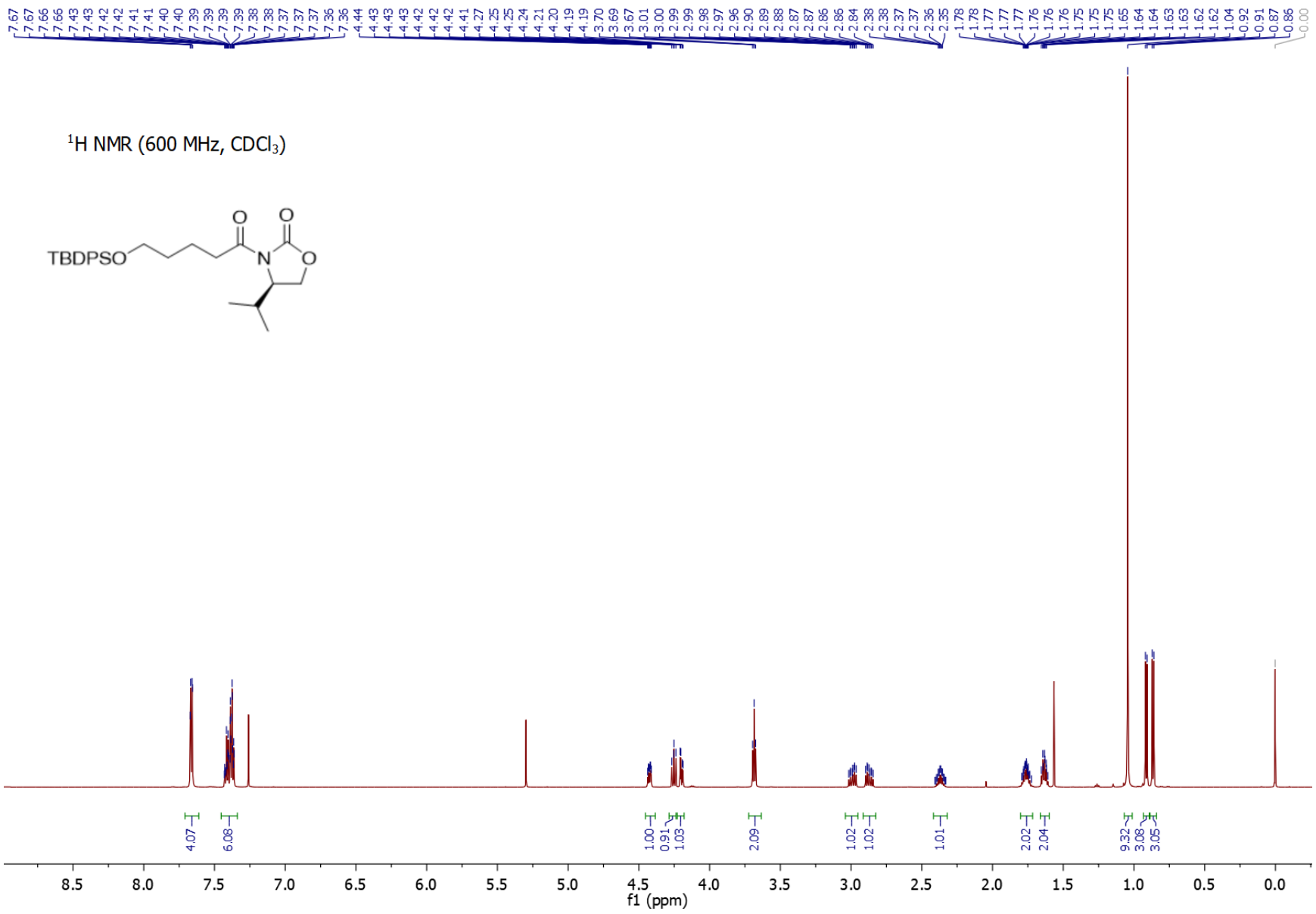

7.68
7.67
7.67
7.67
7.66
7.66
7.65
7.44
7.44
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.39
7.38
7.37
7.37
7.37
3.70
3.69
3.68
2.83
2.63
2.61
2.60
1.90
1.88
1.87
1.85
1.84
1.70
1.68
1.68
1.68
1.67
1.67
1.67
1.66
1.65
1.64
1.05
0.00
^{1}H NMR (500 MHz, $CDCl_3$)
OTBDPS
O
O
O
N
O
via method B
3.96
5.96
2.00
3.87
1.92
1.96
2.20
9.21
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)

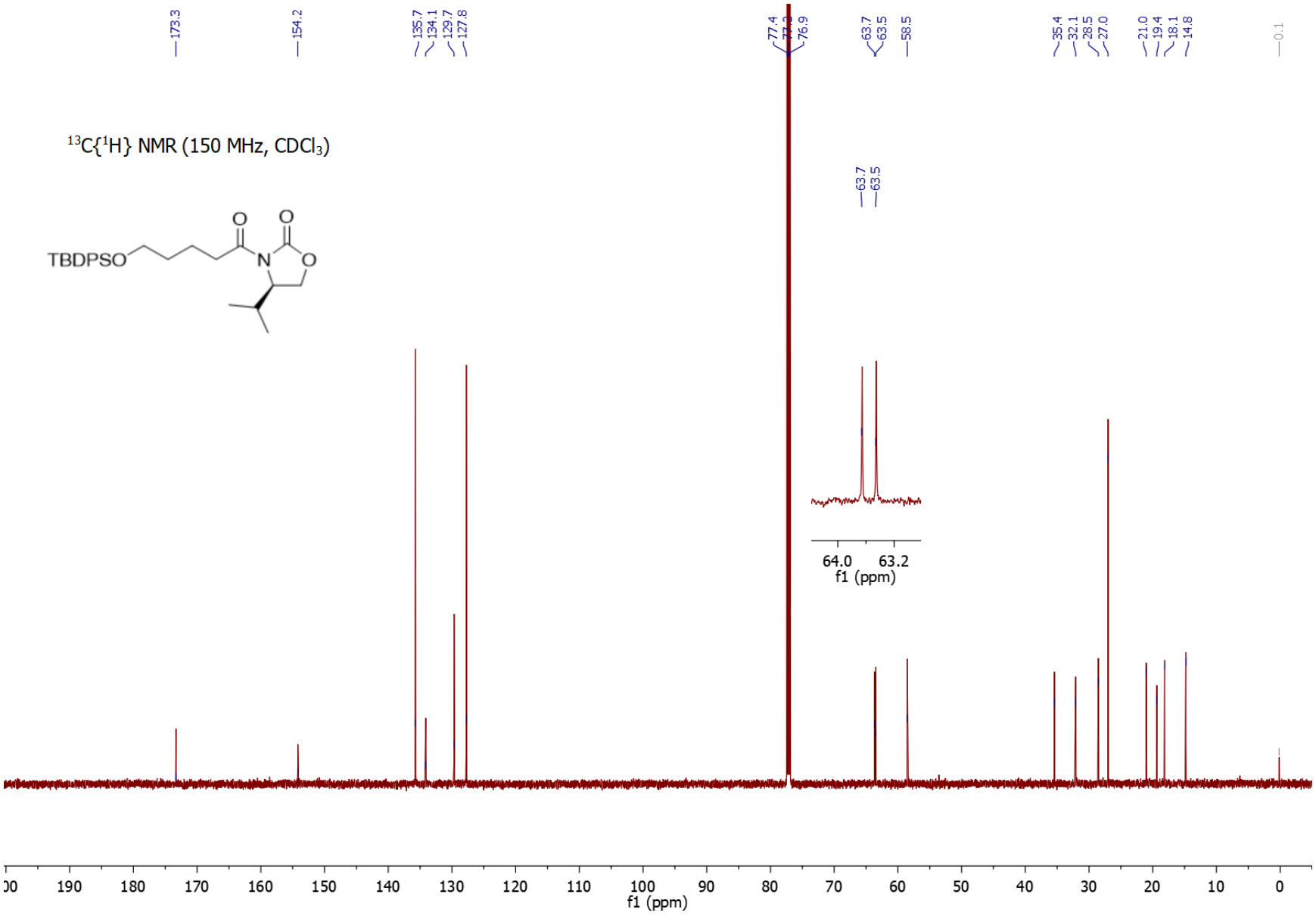

169.3
168.7
135.7
133.9
129.7
127.8
77.4
77.2
76.9
63.2
31.6
30.8
27.0
25.7
21.3
19.3
0.1
13C{1H} NMR (125 MHz, CDCl3)
OTBDPS
O
O
O
N
O
via method B
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

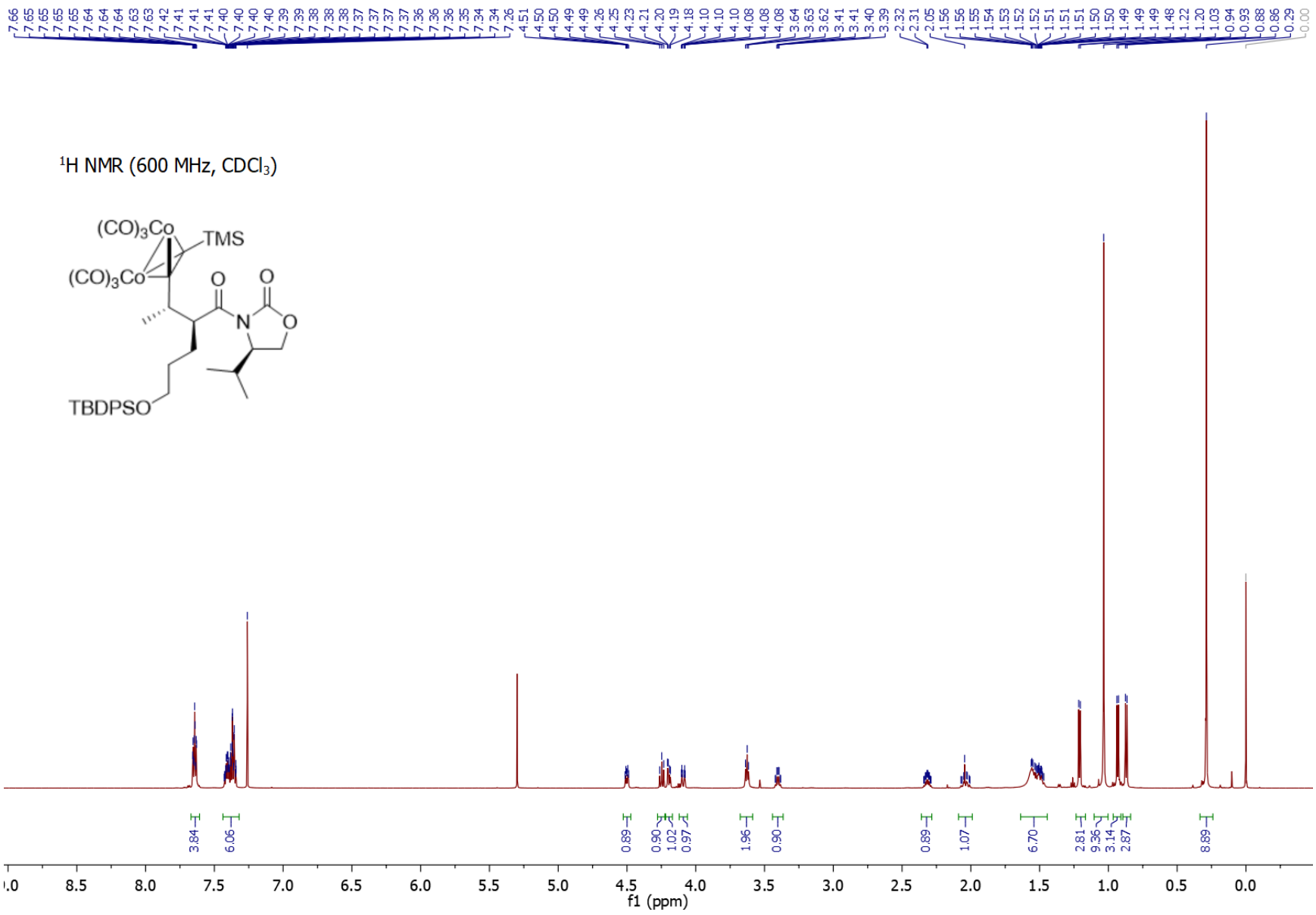
^{1}H NMR (500 MHz, $CDCl_3$)

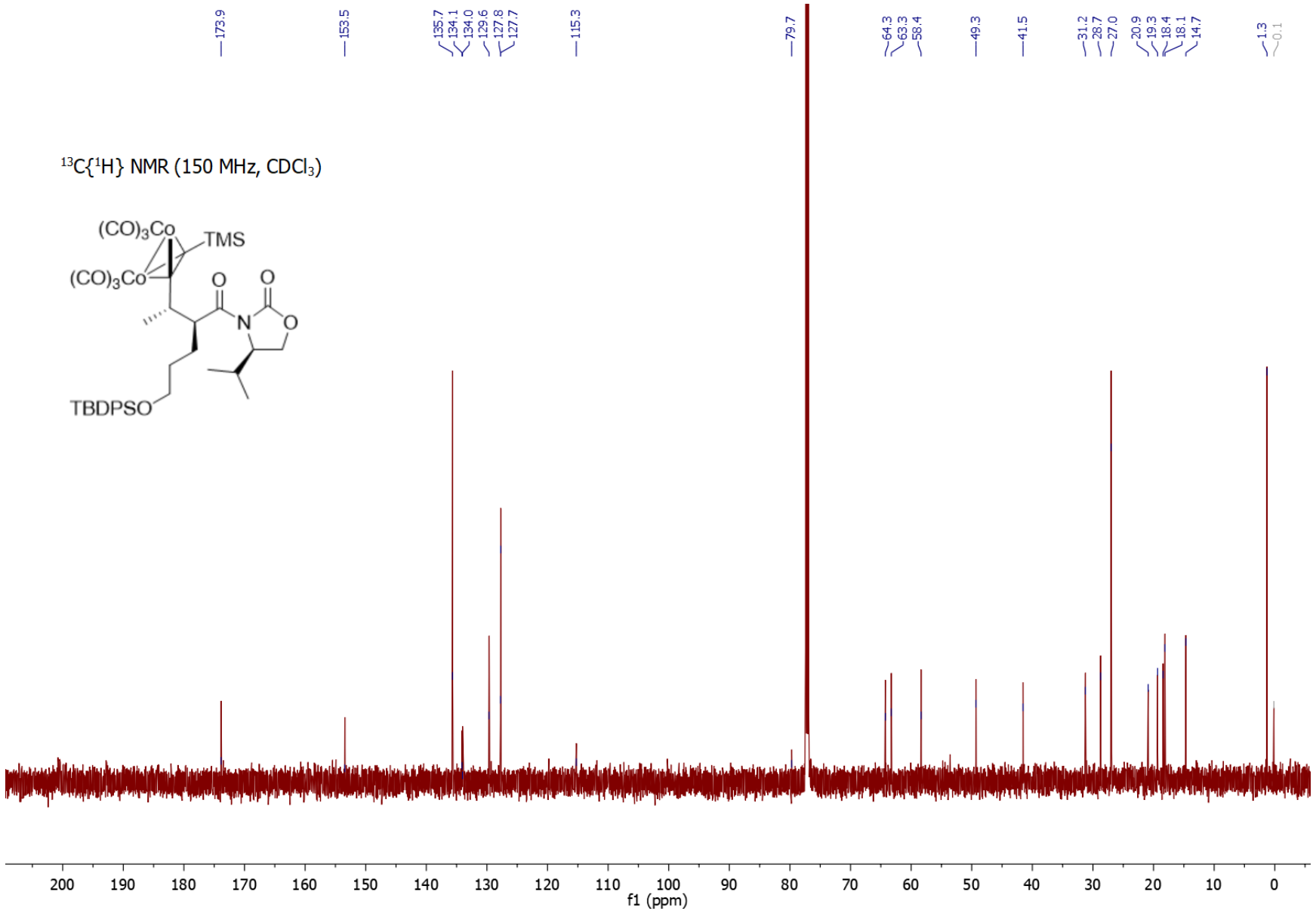


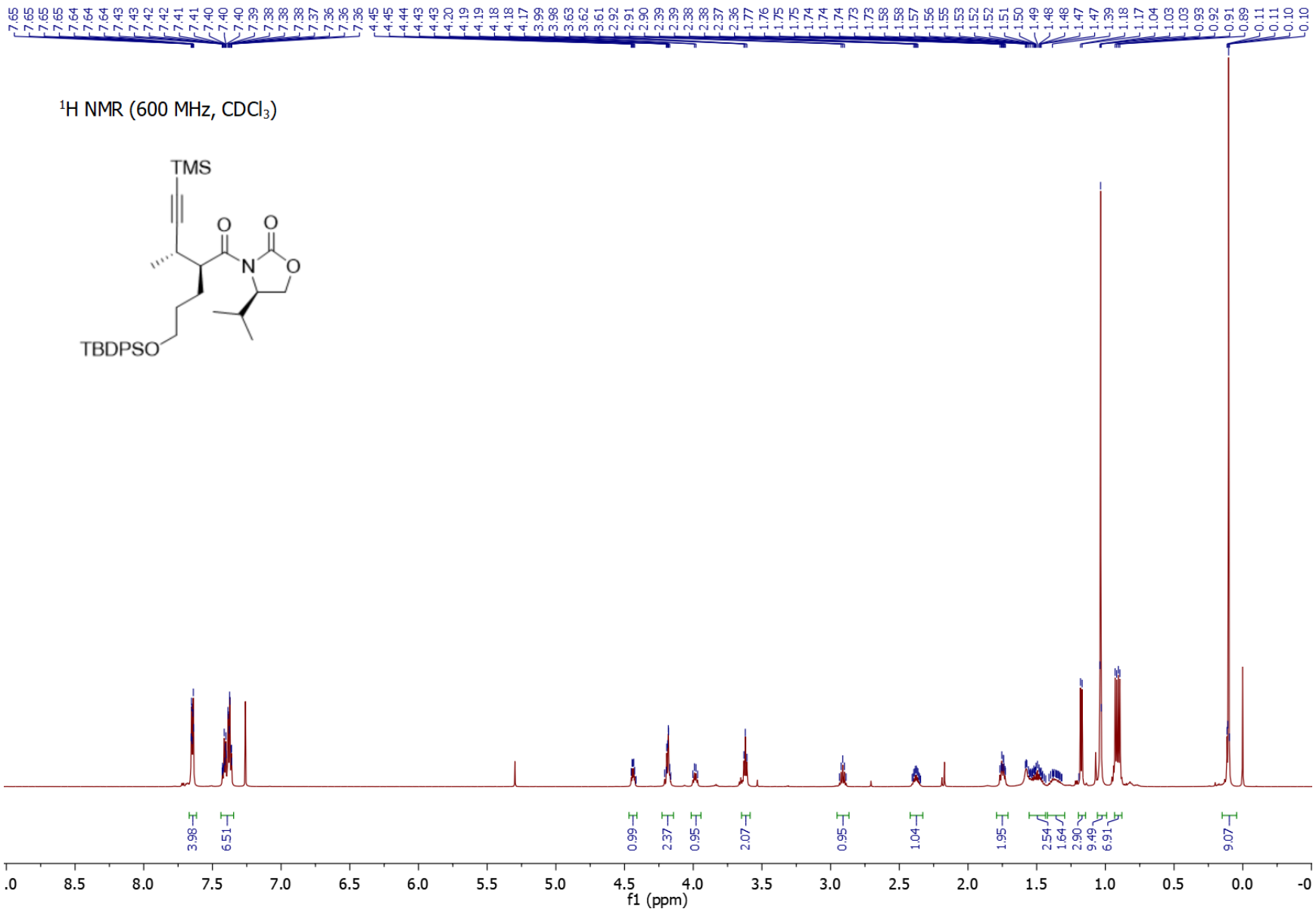

200.5
113.5
78.0
57.3
23.0
1.0
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
Me
$Co(CO)_3$
MeO
$Co(CO)_3$
TMS
77.97
79
78
77
76
75
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

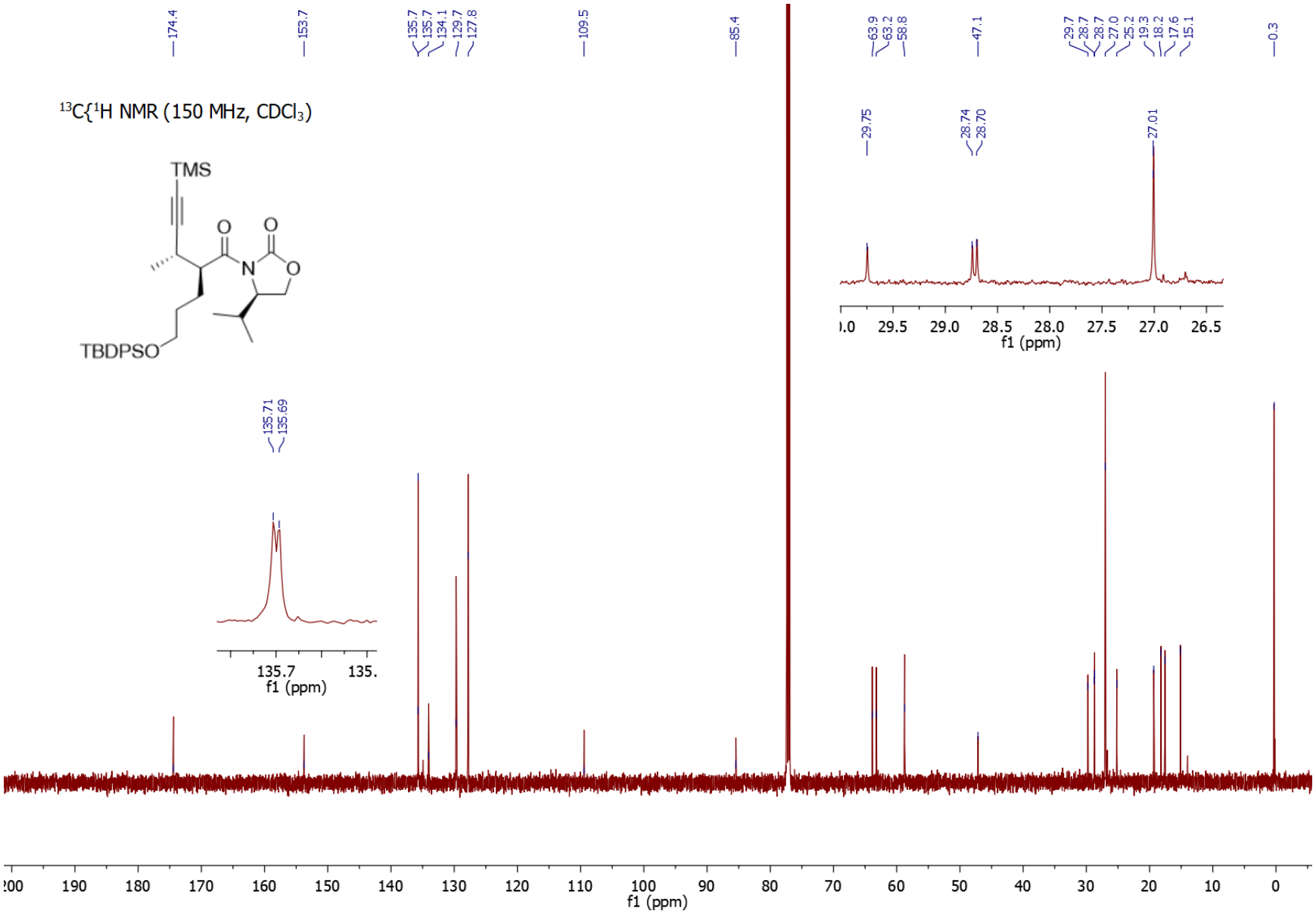

7.67 7.67 7.66 7.66 7.43 7.43 7.42 7.42 7.41 7.41 7.40 7.40 7.39 7.39 7.39 7.39 7.38 7.38 7.37 7.37 7.37 7.37 7.36 7.36
4.44 4.43 4.43 4.43 4.42 4.42 4.42 4.41 4.27 4.25 4.25 4.24 4.21 4.20 4.19 4.19 3.70 3.69 3.67 3.01 3.00 2.99 2.99 2.98 2.97 2.96 2.90 2.89 2.88 2.87 2.87 2.86 2.86 2.84 2.38 2.38 2.37 2.37 2.36 2.35
1.78 1.78 1.77 1.77 1.77 1.76 1.76 1.76 1.75 1.75 1.75 1.65 1.64 1.64 1.63 1.63 1.62 1.62 1.04 0.92 0.91 0.87 0.86 0.00
^{1}H NMR (600 MHz, $CDCl_3$)
TBDPSO
O
O
N
O
4.07
6.08
1.00
0.91
1.03
2.09
1.02
1.02
1.01
2.02
2.04
9.32
3.08
3.05
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)

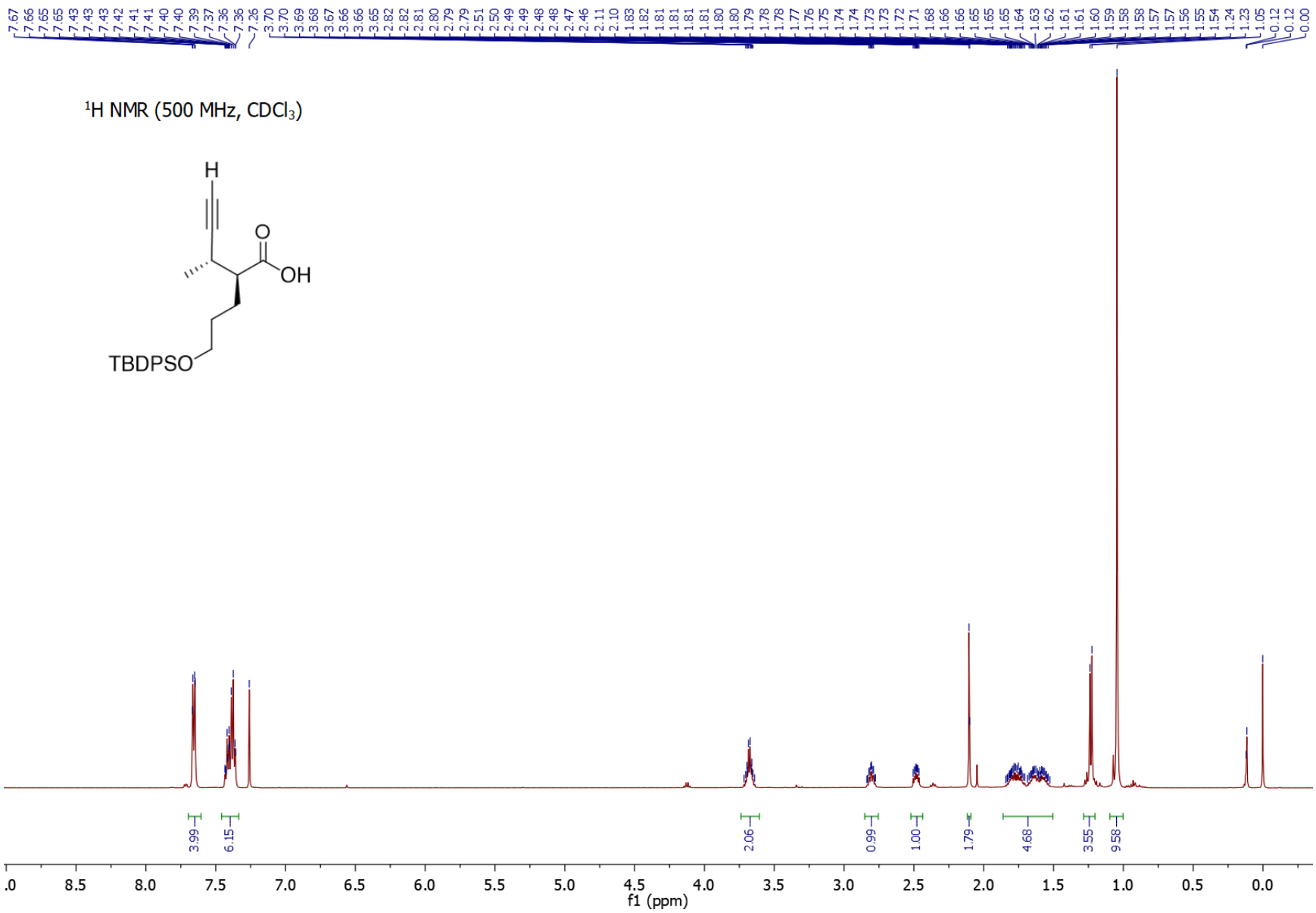

173.3
154.2
135.7
134.1
129.7
127.8
77.4
77.2
76.9
63.7
63.5
58.5
35.4
32.1
28.5
27.0
21.0
19.4
18.1
14.8
0.1
13C{1H} NMR (150 MHz, CDCl3)
TBDPSO
O
O
N
O
63.7
63.5
64.0
63.2
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

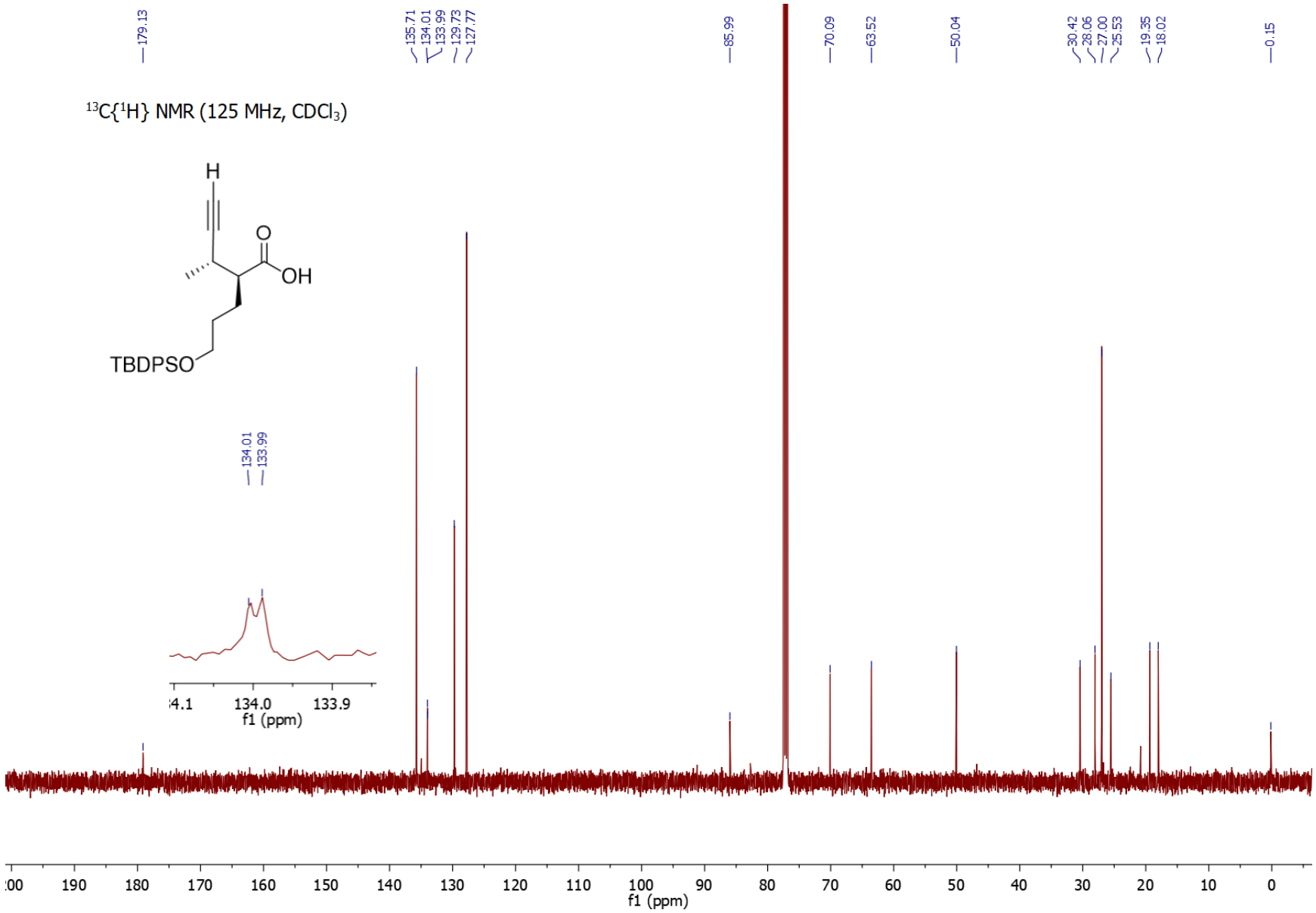

^{1}H NMR (600 MHz, $CDCl_3$)
$(CO)_3Co$
TMS
$(CO)_3Co$
O
O
N
O
TBDPSO
f1 (ppm)

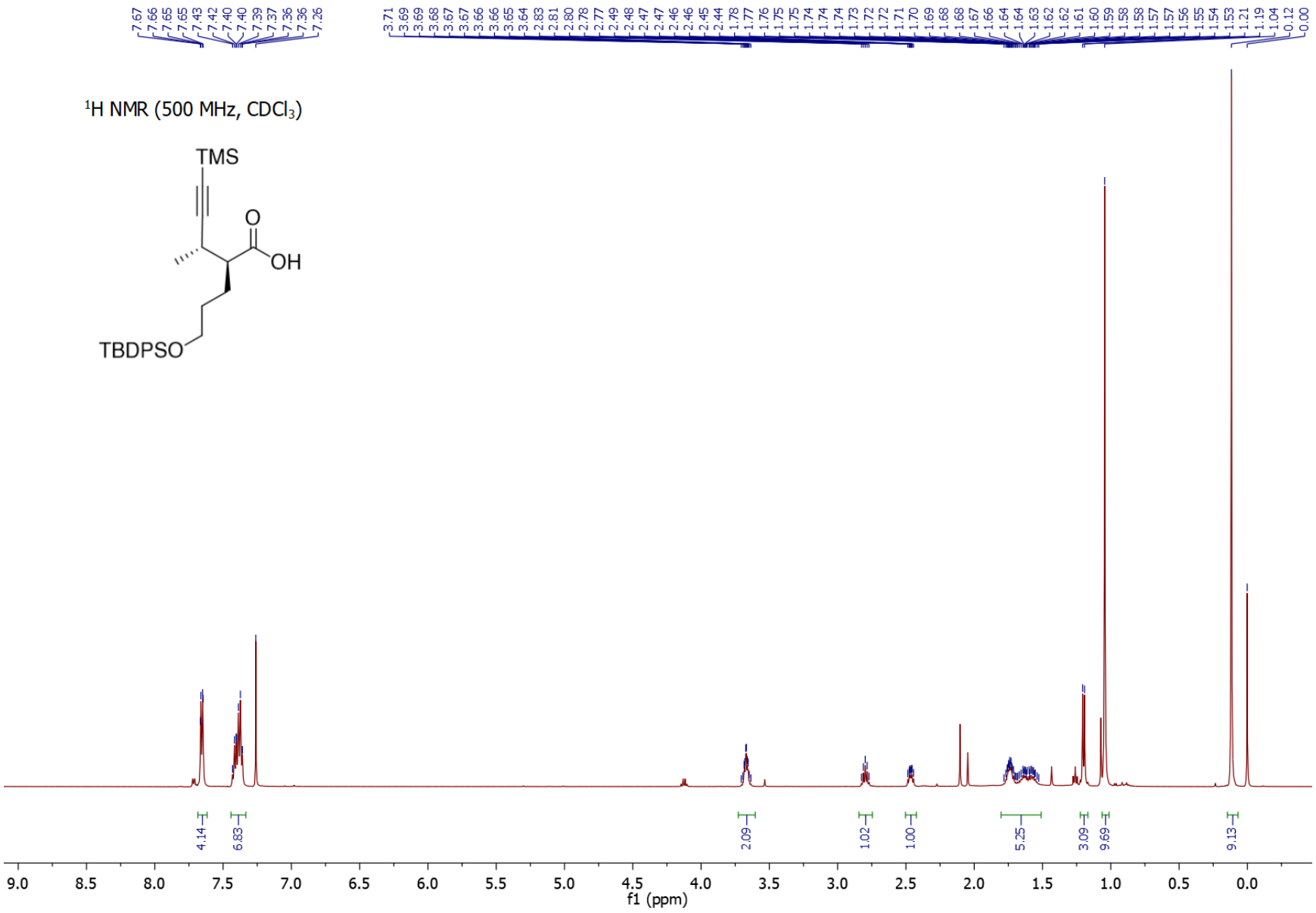

$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)
$(CO)_3Co$
TMS
$(CO)_3Co$
O
O
N
O
TBDPSO
173.9
153.5
135.7
134.1
134.0
129.6
127.8
127.7
115.3
79.7
64.3
63.3
58.4
49.3
41.5
31.2
28.7
27.0
20.9
19.3
18.4
18.1
14.7
1.3
-0.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

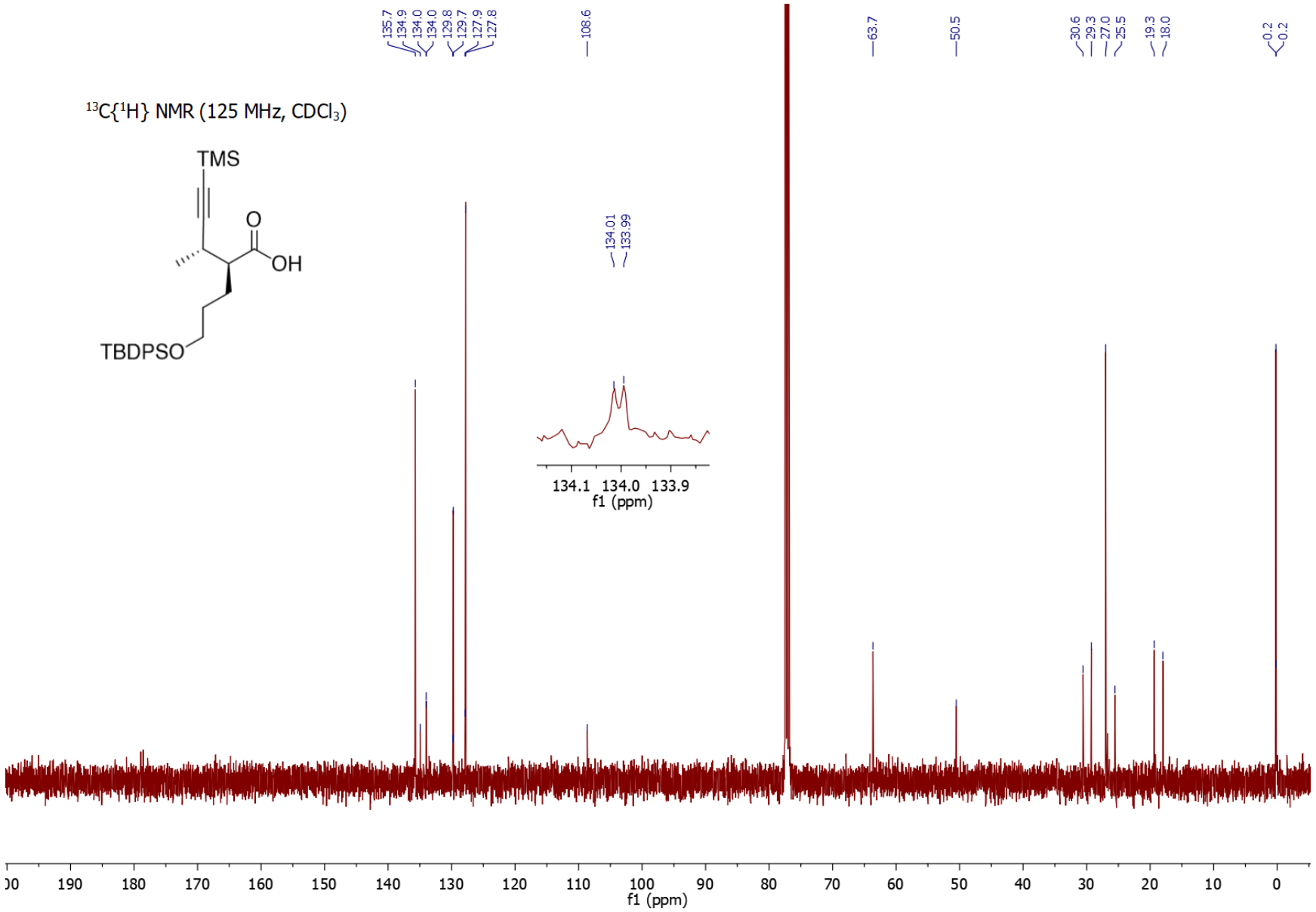

^{1}H NMR (600 MHz, $CDCl_3$)
TMS
O
O
N
O
TBDPSO
f1 (ppm)

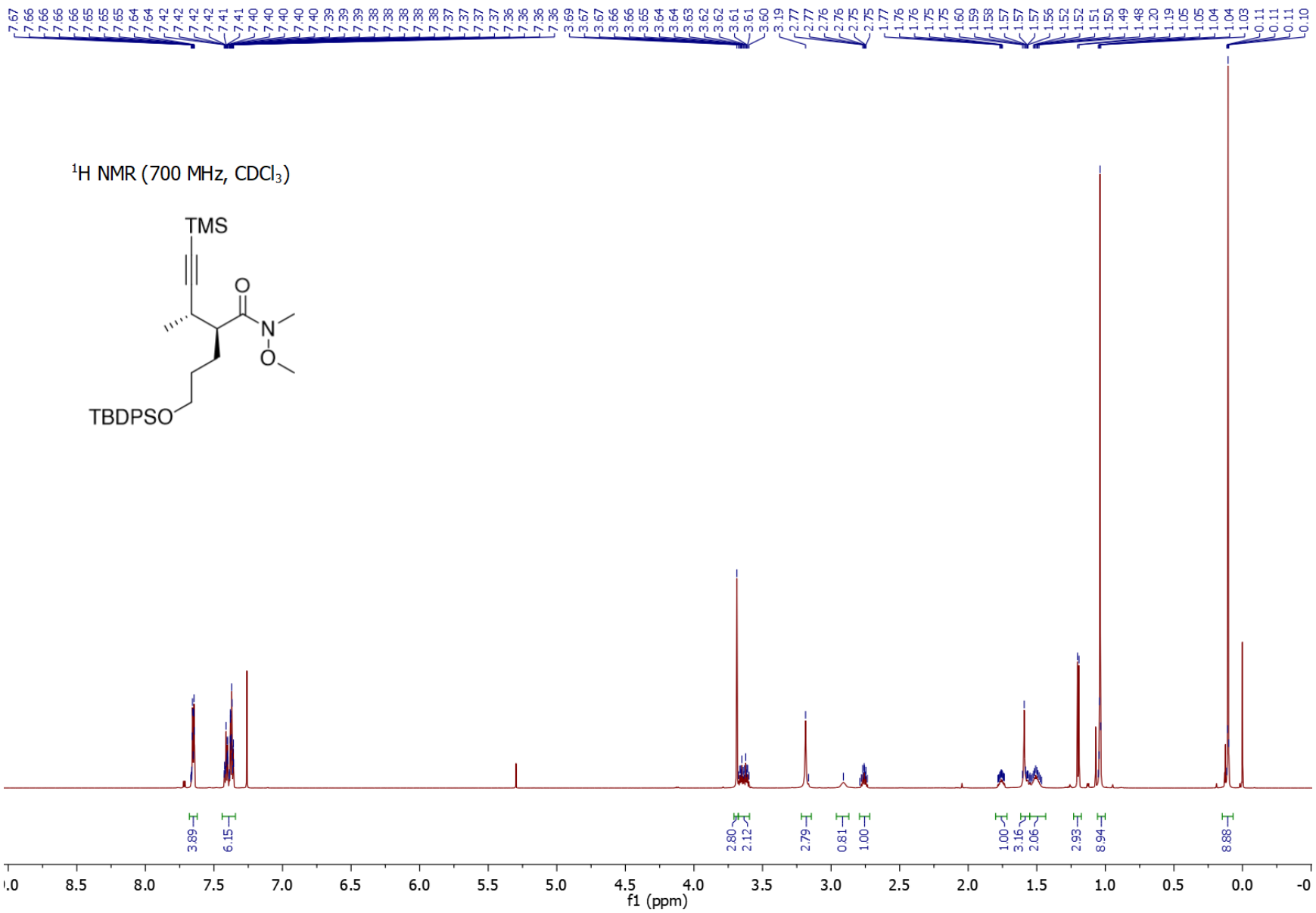

174.4
153.7
135.7
135.7
134.1
129.7
127.8
109.5
85.4
63.9
63.2
58.8
47.1
29.7
28.7
28.7
27.0
25.2
19.3
18.2
17.6
15.1
0.3
13C{1H NMR (150 MHz, CDCl3)
TMS
TBDPSO
O
O
N
O
29.75
28.74
28.70
27.01
f1 (ppm)
135.71
135.69
135.7
135.
f1 (ppm)
f1 (ppm)

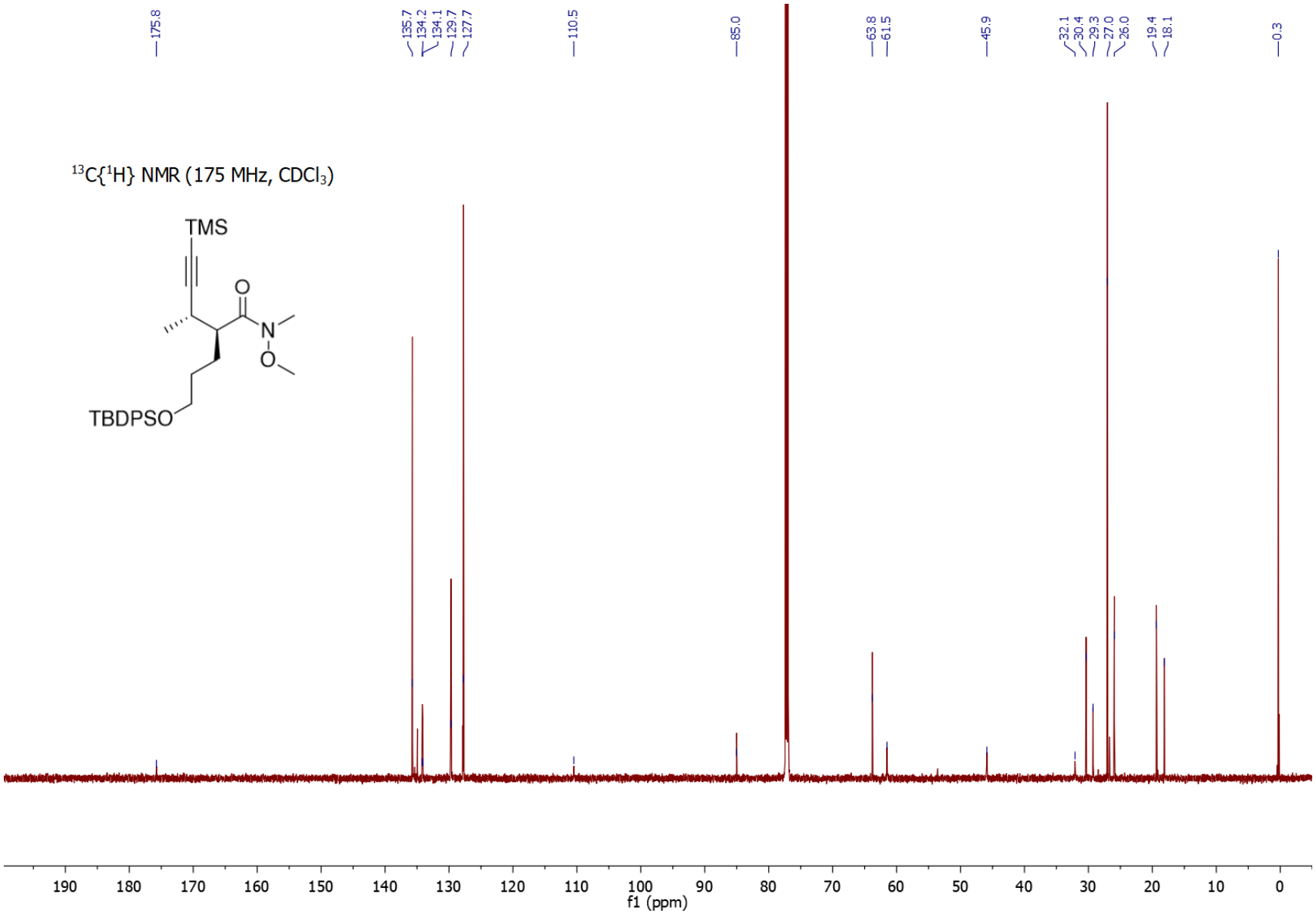

7.67 7.66 7.65 7.65 7.43 7.43 7.43 7.42 7.41 7.41 7.40 7.40 7.39 7.37 7.36 7.36 7.26 3.70 3.70 3.69 3.68 3.67 3.66 3.66 3.65 2.82 2.82 2.81 2.80 2.79 2.79 2.51 2.50 2.49 2.49 2.48 2.48 2.47 2.46 2.11 2.10 1.83 1.82 1.81 1.81 1.81 1.81 1.80 1.80 1.79 1.78 1.78 1.77 1.76 1.75 1.74 1.74 1.73 1.73 1.72 1.71 1.68 1.66 1.66 1.65 1.65 1.65 1.64 1.63 1.62 1.61 1.61 1.60 1.59 1.58 1.58 1.57 1.57 1.56 1.55 1.54 1.24 1.23 1.05 0.12 0.12 0.00
^{1}H NMR (500 MHz, $CDCl_3$)
H
O
OH
TBDPSO
3.99
6.15
2.06
0.99
1.00
1.79
4.68
3.55
9.58
.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)

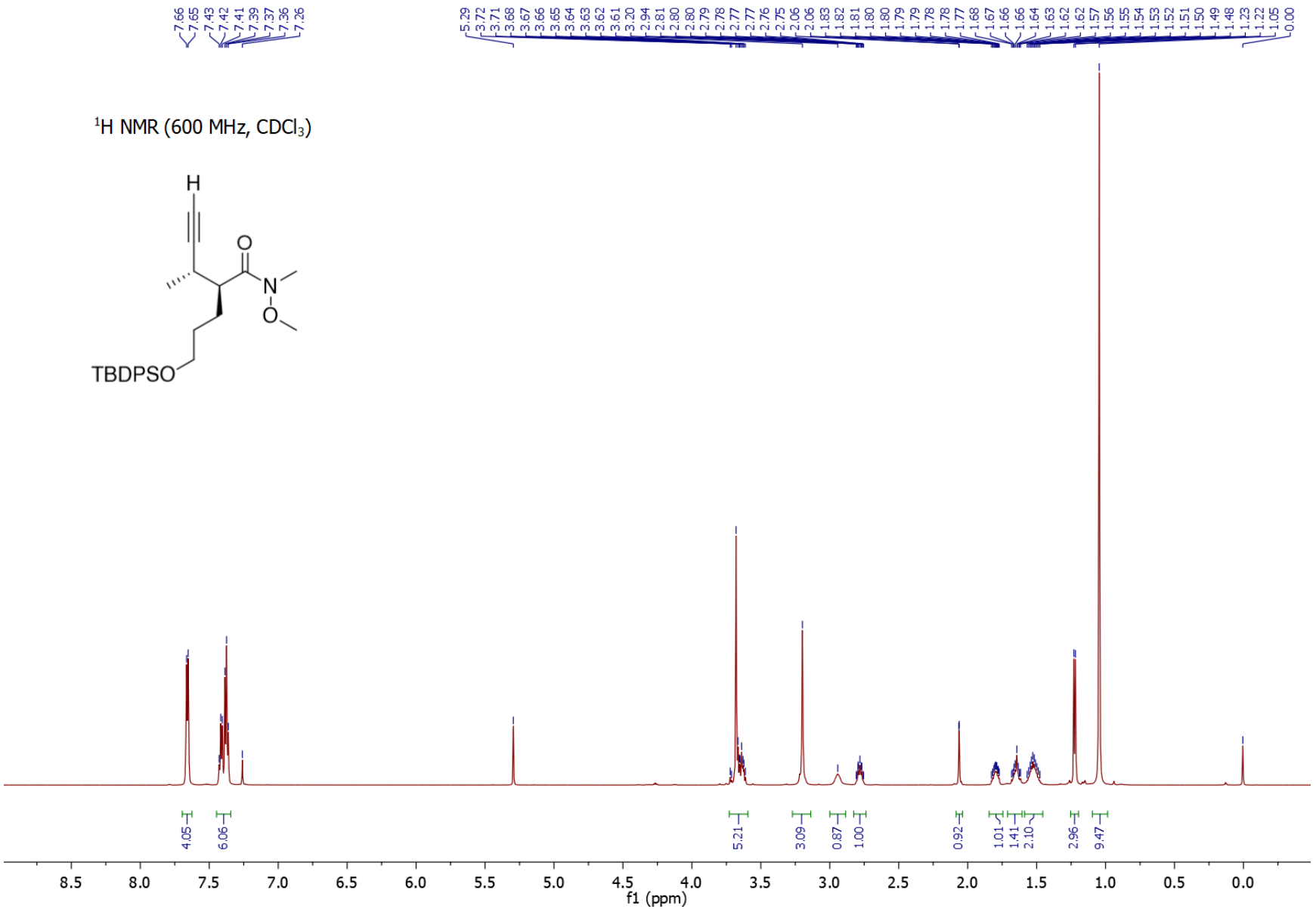

179.13
135.71
134.01
133.99
129.73
127.77
85.99
70.09
63.52
50.04
30.42
28.06
27.00
25.53
19.35
18.02
0.15
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
H
O
OH
TBDPSO
134.01
133.99
134.0
133.9
f1 (ppm)
f1 (ppm)

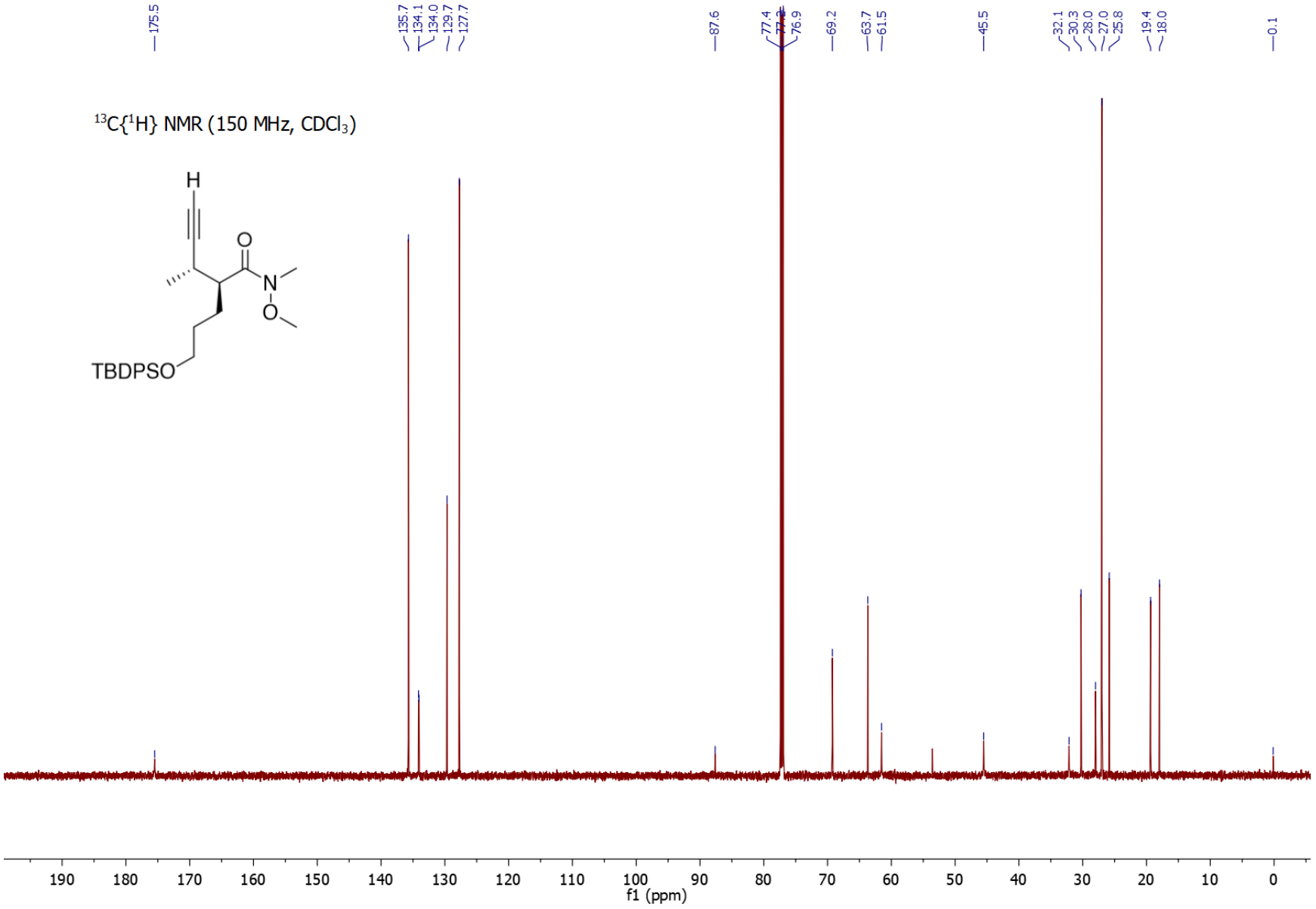

7.67
7.66
7.65
7.65
7.43
7.42
7.40
7.40
7.39
7.37
7.36
7.36
7.26
3.71
3.69
3.69
3.68
3.67
3.67
3.66
3.65
3.64
2.83
2.81
2.80
2.78
2.77
2.49
2.48
2.47
2.47
2.46
2.46
2.45
2.44
1.78
1.77
1.76
1.75
1.75
1.74
1.74
1.74
1.73
1.72
1.72
1.71
1.70
1.69
1.68
1.68
1.67
1.66
1.64
1.64
1.63
1.62
1.62
1.61
1.60
1.59
1.58
1.58
1.57
1.57
1.56
1.55
1.54
1.53
1.21
1.19
1.04
0.12
0.00
1H NMR (500 MHz, CDCl3)
TMS
O
OH
TBDPSO
4.14
6.83
2.09
1.02
1.00
5.25
3.09
9.69
9.13
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)

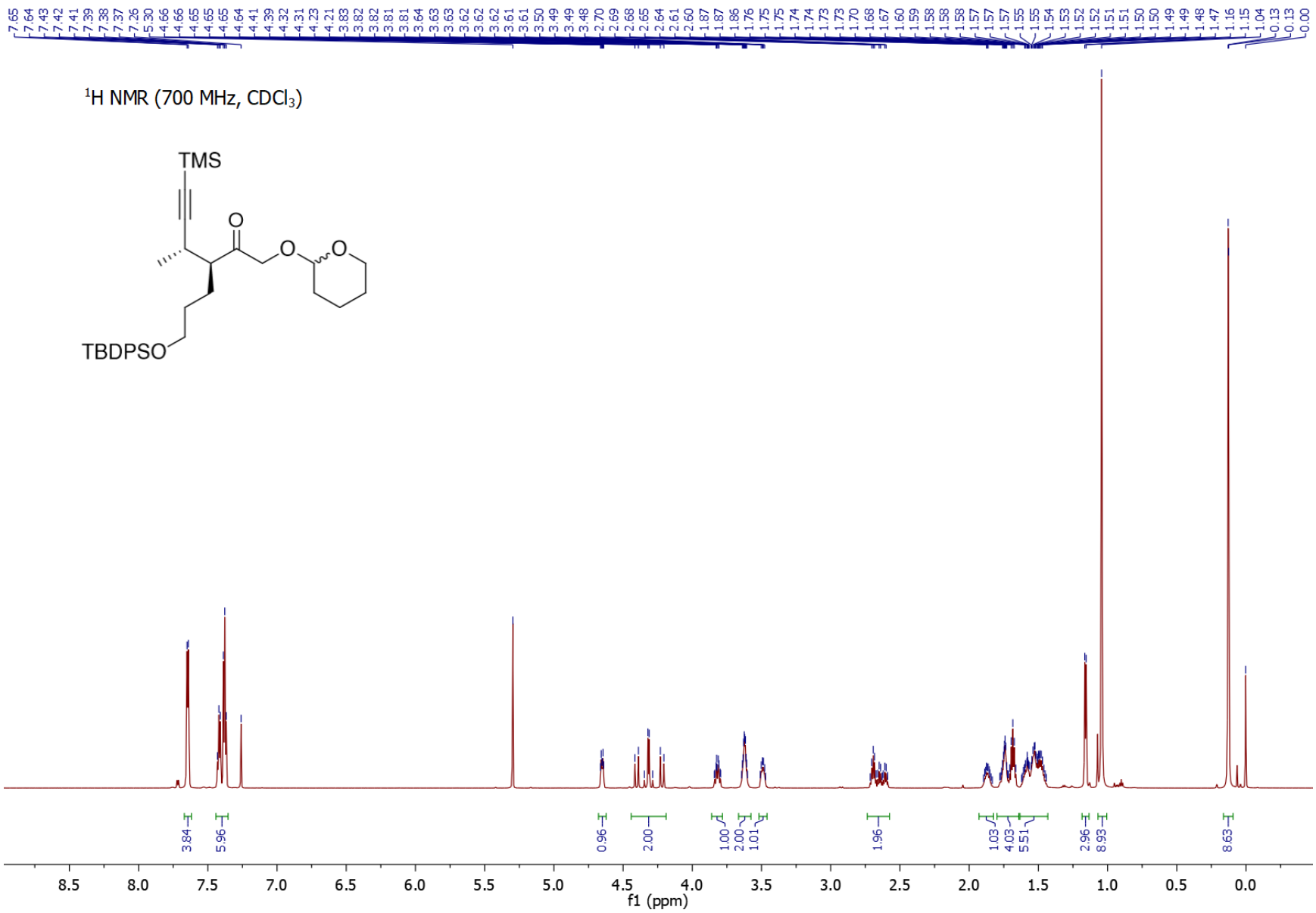

135.7
134.9
134.0
134.0
129.8
129.7
127.9
127.8
108.6
63.7
50.5
30.6
29.3
27.0
25.5
19.3
18.0
0.2
0.2
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
TMS
O
OH
TBDPSO
134.01
133.99
134.1 134.0 133.9
f1 (ppm)
f1 (ppm)

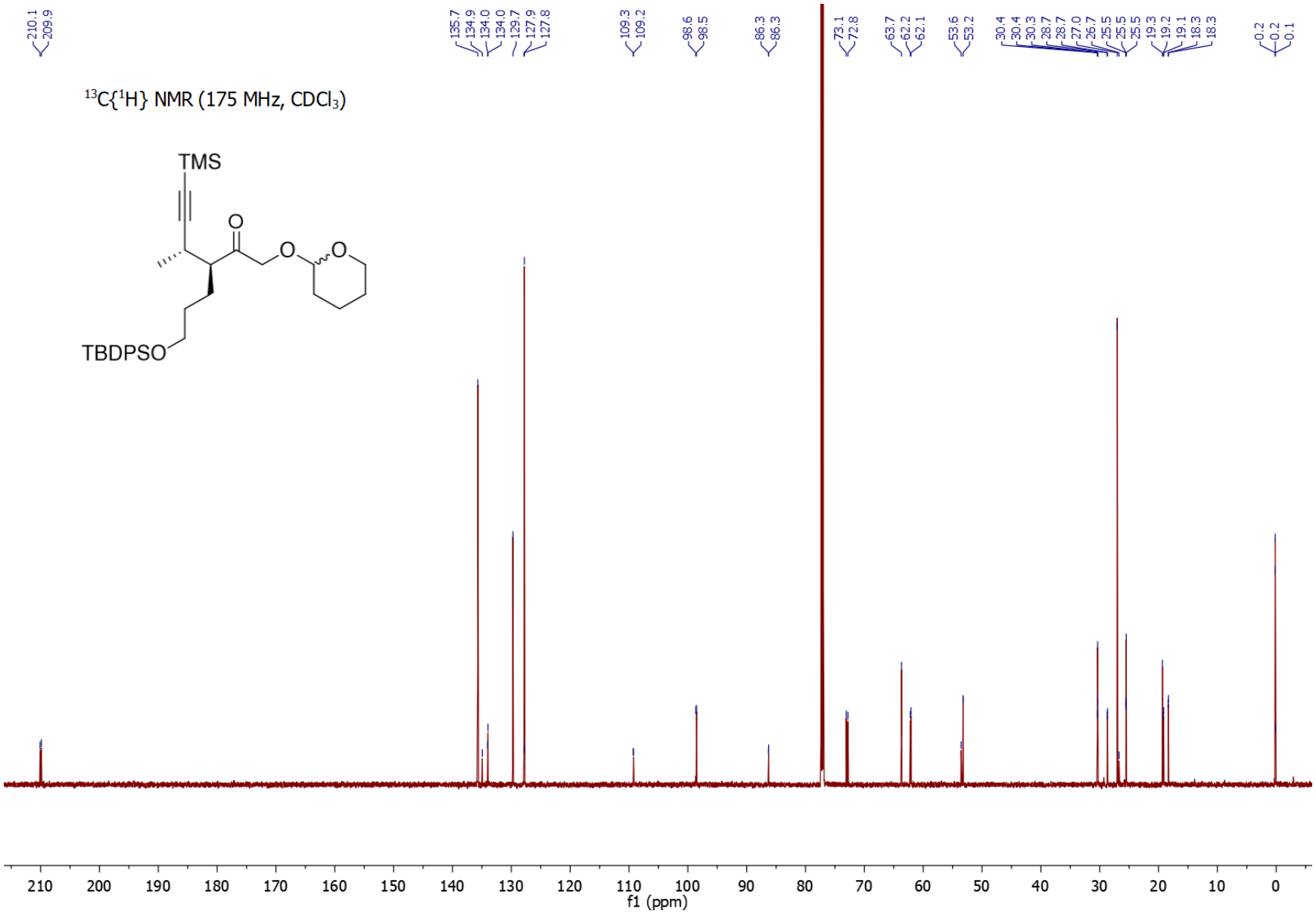

^{1}H NMR (700 MHz, $CDCl_3$)
TMS
O
N
O
TBDPSO
f1 (ppm)

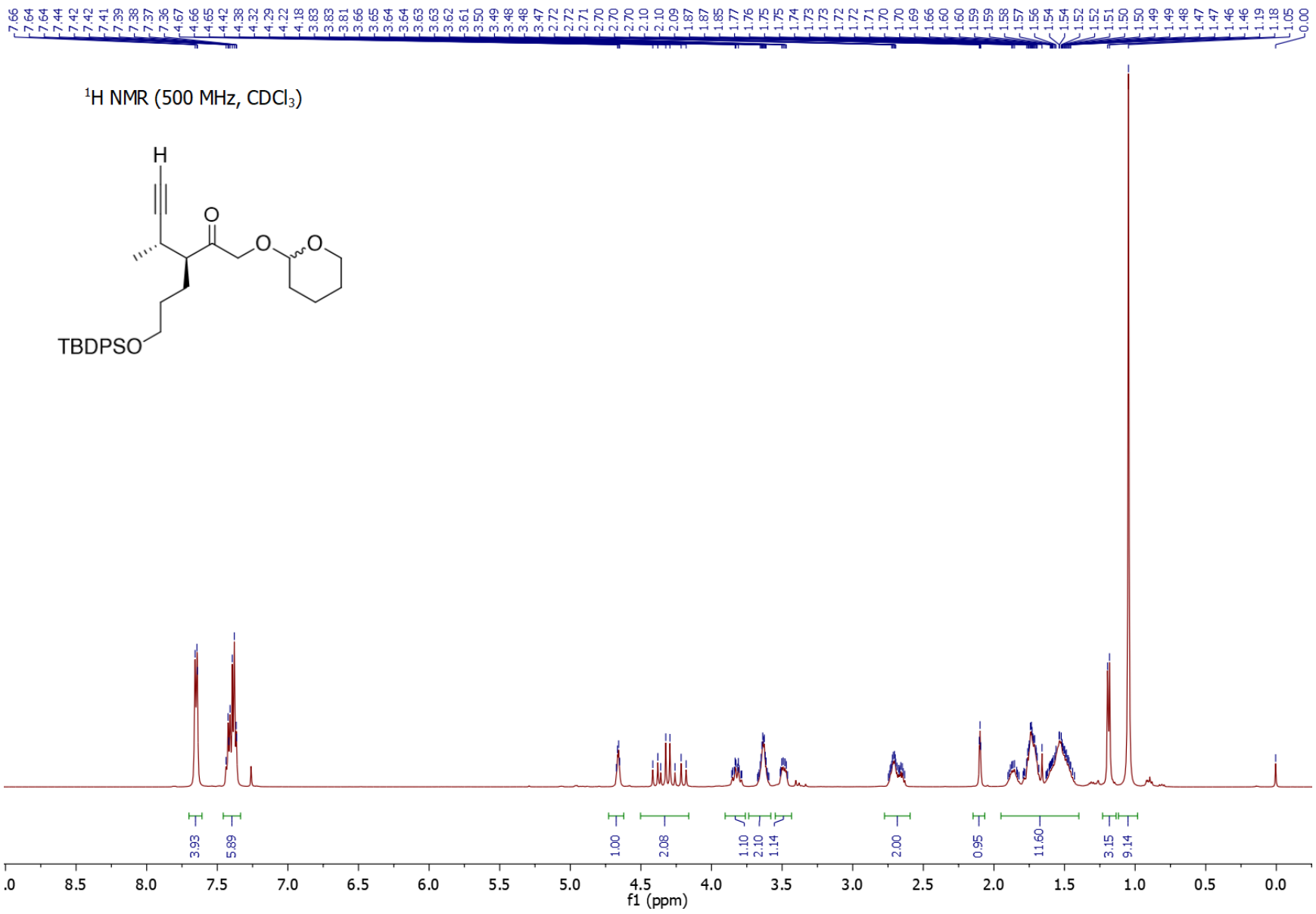

175.8
135.7
134.2
134.1
129.7
127.7
110.5
85.0
63.8
61.5
45.9
32.1
30.4
29.3
27.0
26.0
19.4
18.1
0.3
$^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$)
TMS
O
N
O
TBDPSO
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

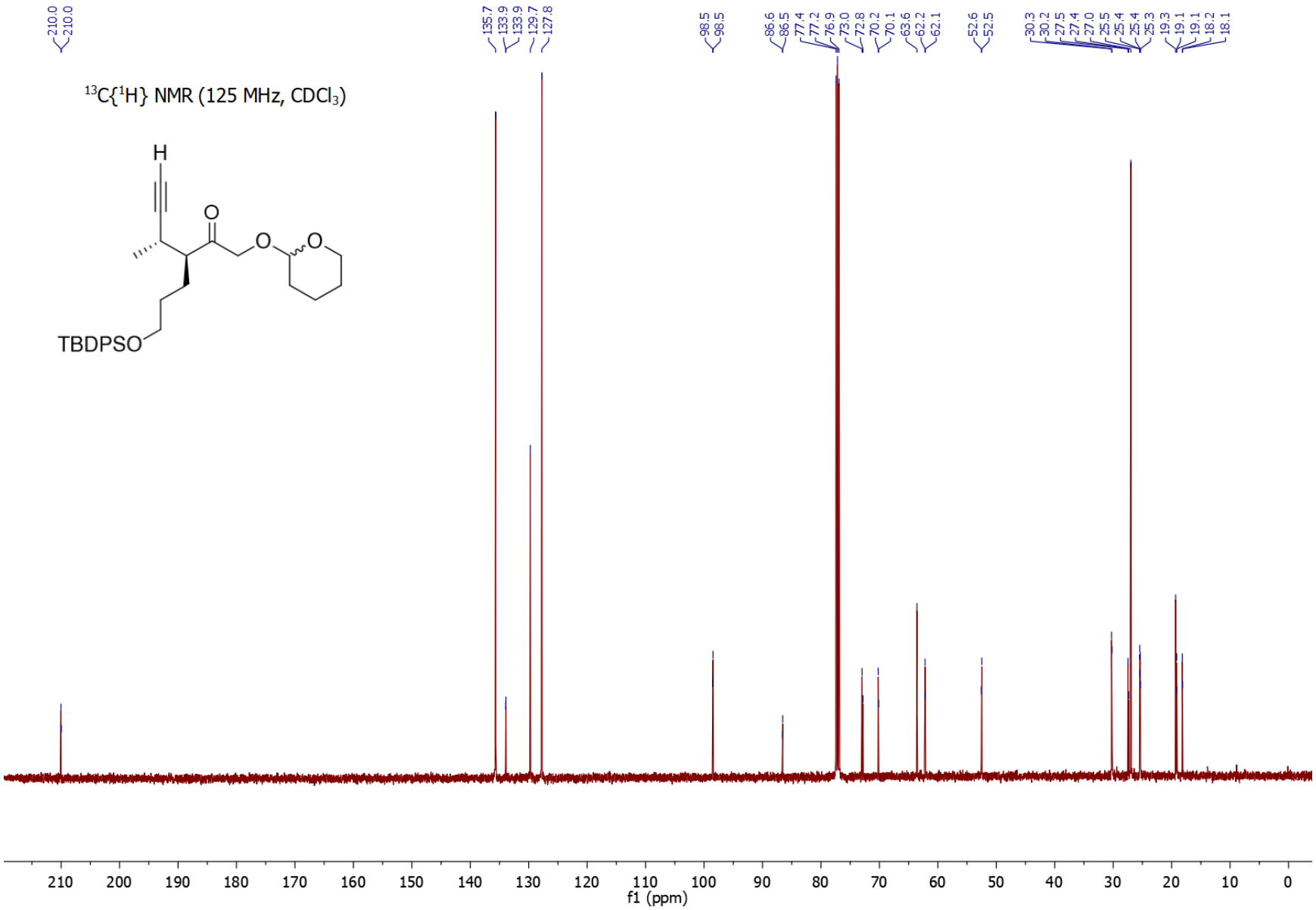

7.66
7.65
7.43
7.42
7.41
7.39
7.37
7.36
7.26
5.29
3.72
3.71
3.68
3.67
3.66
3.65
3.64
3.63
3.62
3.61
3.20
2.94
2.81
2.80
2.80
2.79
2.78
2.77
2.77
2.76
2.75
2.06
2.06
1.83
1.82
1.81
1.80
1.80
1.79
1.79
1.78
1.78
1.77
1.68
1.67
1.66
1.66
1.64
1.63
1.62
1.62
1.57
1.56
1.55
1.54
1.53
1.52
1.51
1.50
1.49
1.48
1.23
1.22
1.05
0.00
^{1}H NMR (600 MHz, $CDCl_3$)
H
O
N
O
TBDPSO
4.05
6.06
5.21
3.09
0.87
1.00
0.92
1.01
1.41
2.10
2.96
9.47
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)

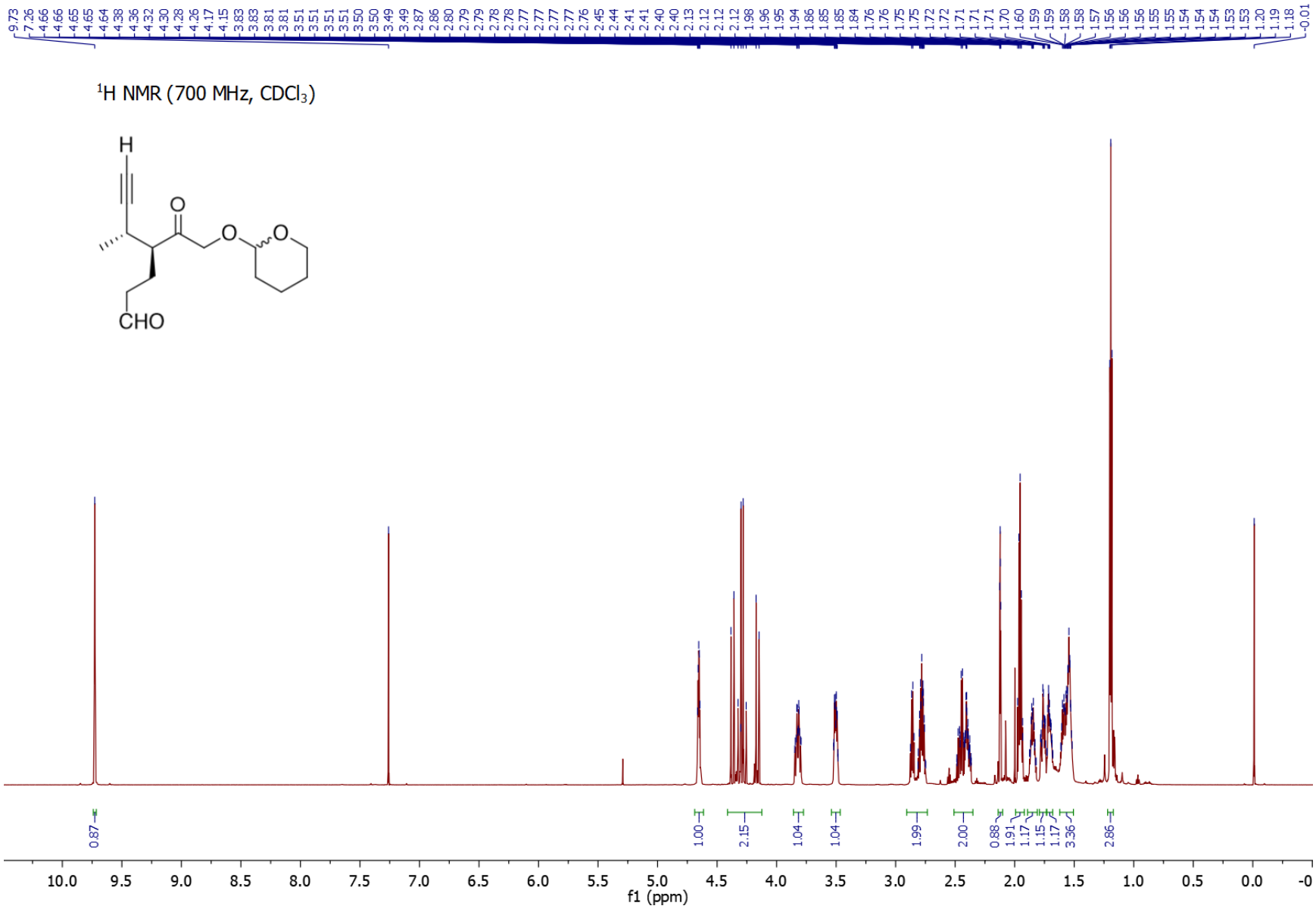

175.5
135.7
134.1
134.0
129.7
127.7
87.6
77.4
77.2
76.9
69.2
63.7
61.5
45.5
32.1
30.3
28.0
27.0
25.8
19.4
18.0
0.1
13C{1H} NMR (150 MHz, CDCl3)
H
O
N
O
TBDPSO
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

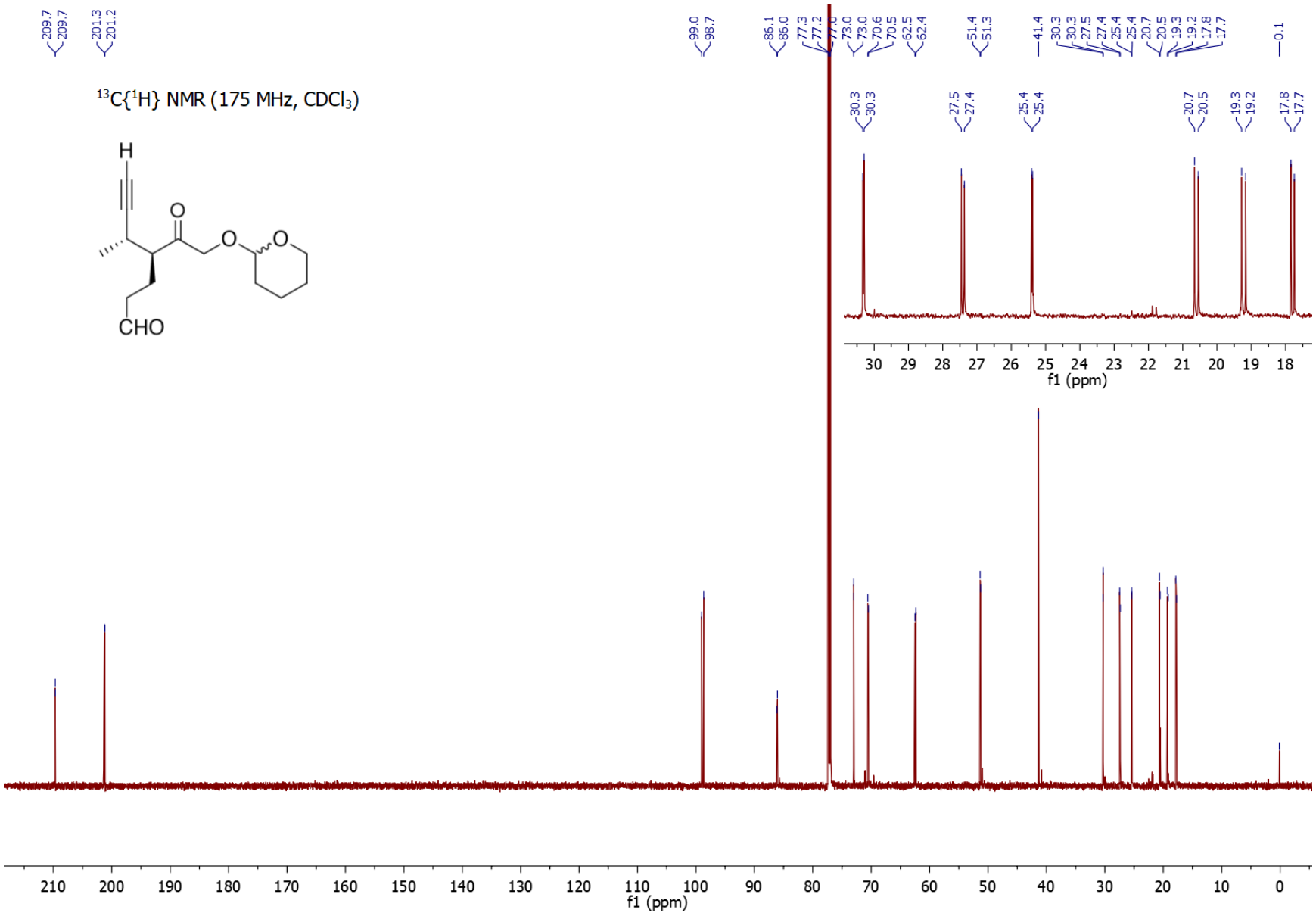

^{1}H NMR (700 MHz, $CDCl_3$)
TMS
O
O
O
TBDPSO
f1 (ppm)

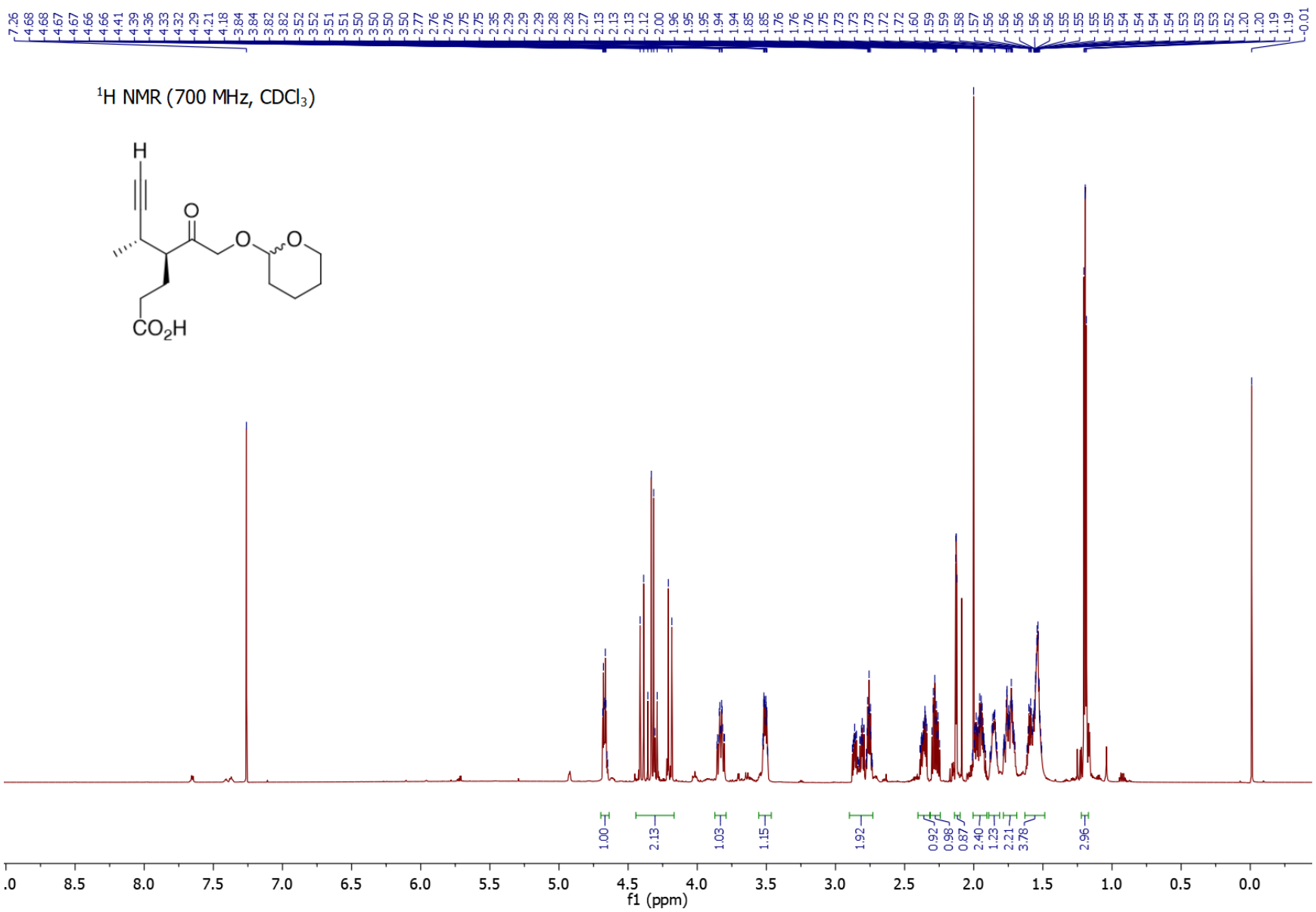

210.1
209.9
135.7
134.9
134.0
134.0
129.7
127.9
127.8
109.3
109.2
98.6
98.5
86.3
86.3
73.1
72.8
63.7
62.2
62.1
53.6
53.2
30.4
30.4
30.3
28.7
28.7
27.0
26.7
25.5
25.5
25.5
19.3
19.2
19.1
18.3
18.3
0.2
0.2
0.1
$^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$)
TMS
O
O
O
TBDPSO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

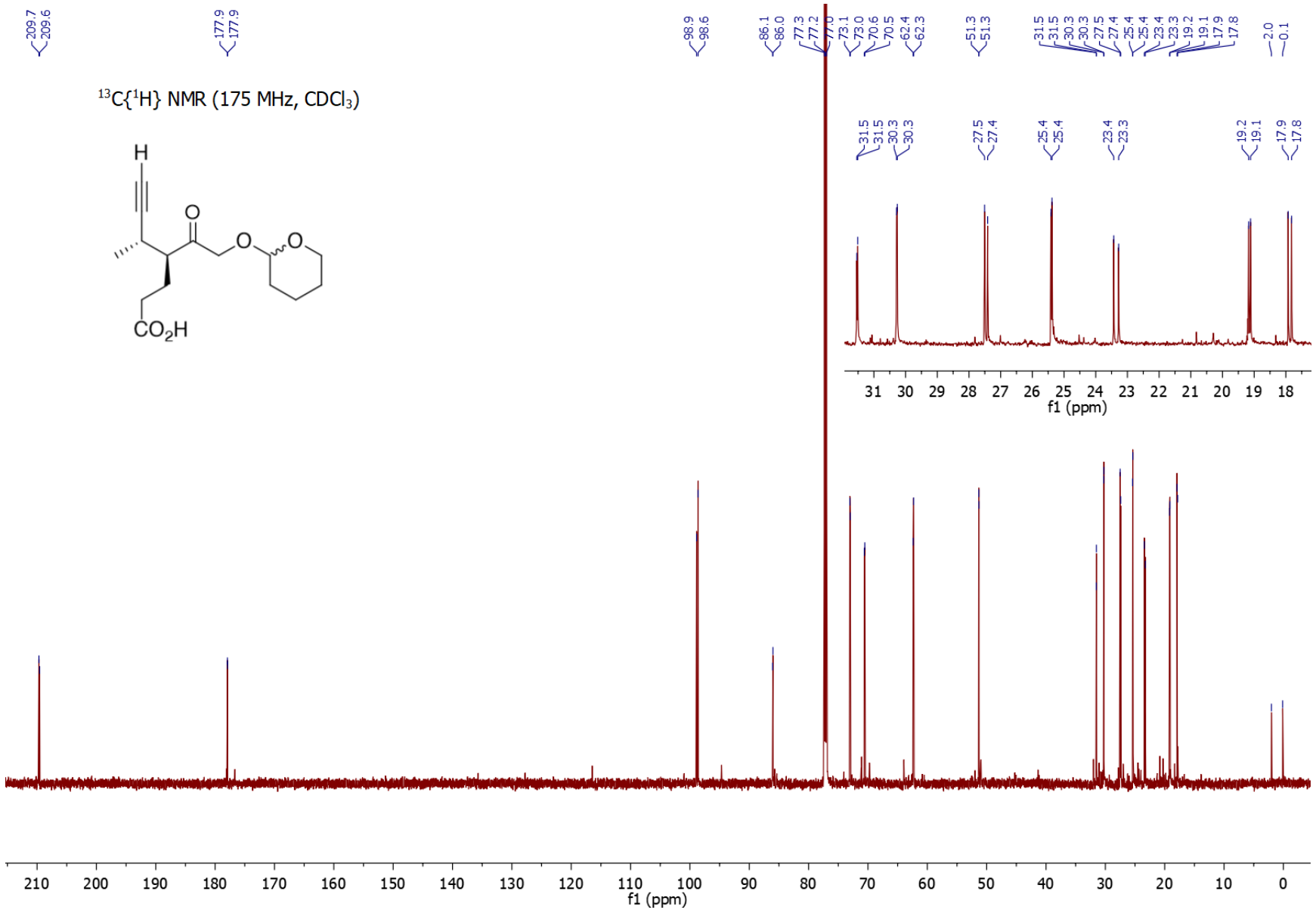

7.66 7.64 7.64 7.44 7.42 7.42 7.41 7.39 7.38 7.37 7.36 4.67 4.66 4.65 4.42 4.38 4.32 4.29 4.22 4.18 3.83 3.83 3.81 3.66 3.65 3.64 3.64 3.63 3.63 3.62 3.61 3.50 3.49 3.48 3.48 3.47 2.72 2.72 2.71 2.70 2.70 2.70 2.10 2.10 2.09 1.87 1.87 1.85 1.77 1.76 1.75 1.75 1.74 1.73 1.73 1.72 1.72 1.71 1.70 1.70 1.69 1.66 1.60 1.60 1.59 1.59 1.58 1.57 1.56 1.54 1.54 1.52 1.52 1.51 1.50 1.50 1.49 1.49 1.48 1.47 1.47 1.46 1.46 1.19 1.18 1.05 0.00
^{1}H NMR (500 MHz, $CDCl_3$)
H
O
O
O
TBDPSO
3.93
5.89
1.00
2.08
1.10
2.10
1.14
2.00
0.95
11.60
3.15
9.14
.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)

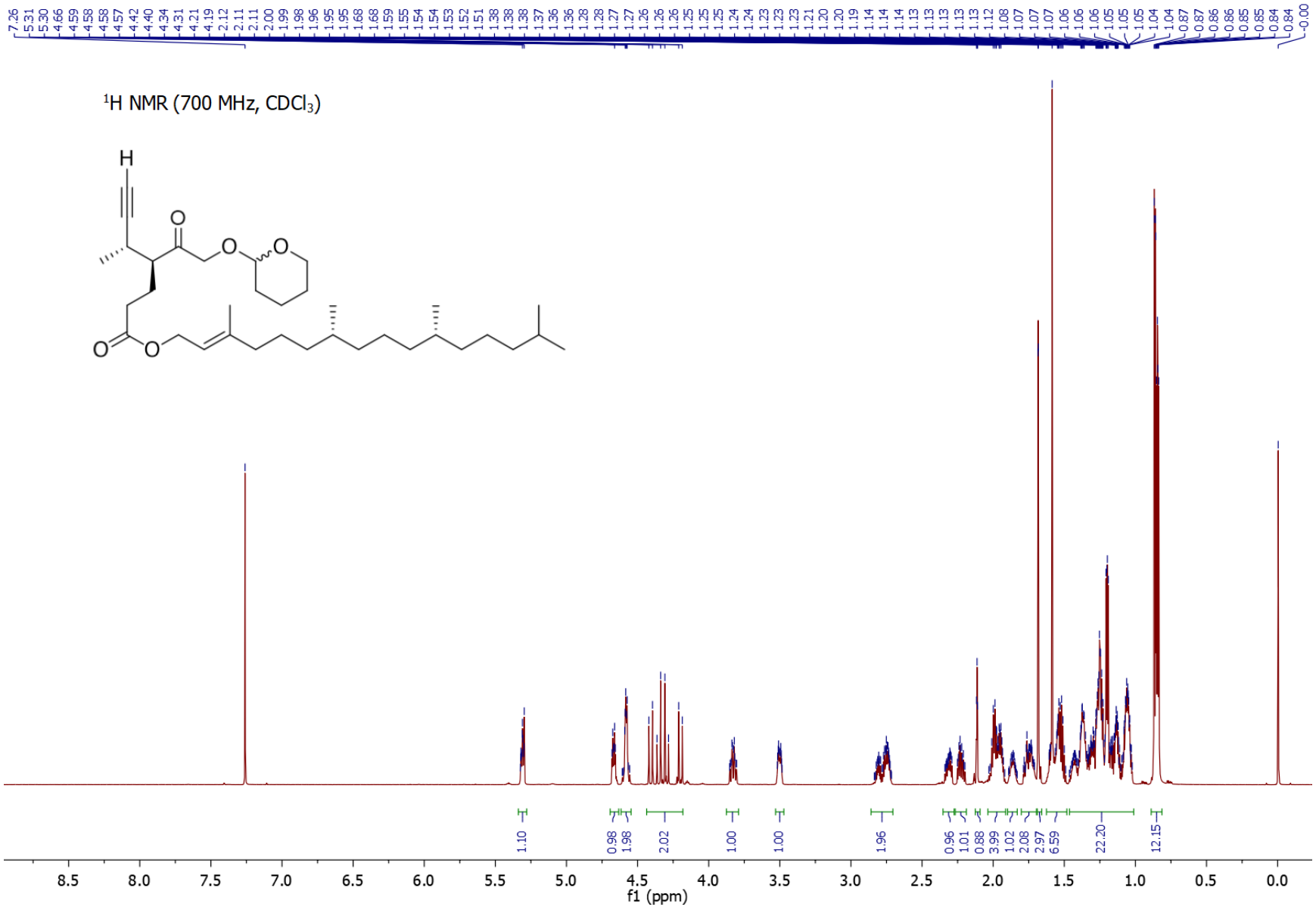

210.0
210.0
135.7
133.9
133.9
129.7
127.8
98.5
98.5
86.6
86.5
77.4
77.2
76.9
73.0
72.8
70.2
70.1
63.6
62.2
62.1
52.6
52.5
30.3
30.2
27.5
27.4
27.0
25.5
25.4
25.4
25.3
19.3
19.1
19.1
18.2
18.1
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
H
O
O
O
TBDPSO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

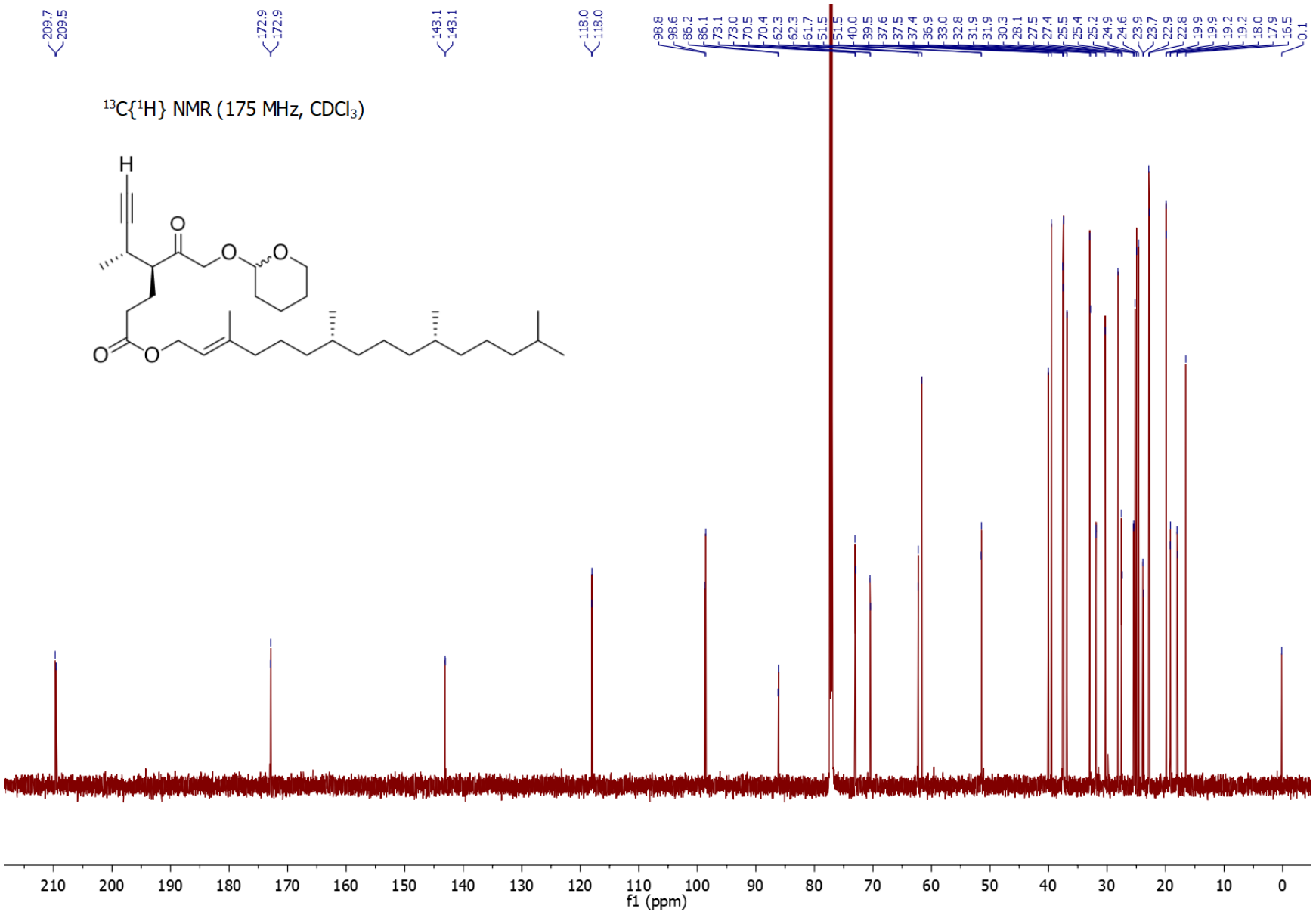

9.73
7.26
4.66
4.66
4.65
4.65
4.64
4.38
4.36
4.32
4.30
4.28
4.26
4.17
4.15
3.83
3.83
3.81
3.81
3.51
3.51
3.51
3.51
3.50
3.50
3.49
3.49
2.87
2.86
2.80
2.79
2.79
2.78
2.78
2.77
2.77
2.77
2.77
2.76
2.45
2.44
2.41
2.41
2.40
2.40
2.13
2.12
2.12
2.12
1.98
1.96
1.95
1.94
1.86
1.85
1.85
1.84
1.76
1.76
1.75
1.75
1.72
1.72
1.71
1.71
1.71
1.70
1.60
1.59
1.59
1.58
1.58
1.57
1.56
1.56
1.56
1.55
1.55
1.54
1.54
1.54
1.53
1.53
1.20
1.19
1.18
-0.01
^{1}H NMR (700 MHz, $CDCl_3$)
H
O
O
O
CHO
0.87
1.00
2.15
1.04
1.04
1.99
2.00
0.88
1.91
1.17
1.15
1.17
3.36
2.86
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


209.7
209.7
201.3
201.2
99.0
98.7
86.1
86.0
77.3
77.2
77.0
73.0
73.0
70.6
70.5
62.5
62.4
51.4
51.3
41.4
30.3
30.3
27.5
27.4
25.4
25.4
20.7
20.5
19.3
19.2
17.8
17.7
0.1
13C{1H} NMR (175 MHz, CDCl3)
H
O
O
O
CHO
30.3
30.3
27.5
27.4
25.4
25.4
20.7
20.5
19.3
19.2
17.8
17.7
30 29 28 27 26 25 24 23 22 21 20 19 18
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


^{1}H NMR (700 MHz, $CDCl_3$)
H
O
O
O
CO_2H
f1 (ppm)


209.7
209.6
177.9
177.9
98.9
98.6
86.1
86.0
77.3
77.2
77.0
73.1
73.0
70.6
70.5
62.4
62.3
51.3
51.3
31.5
31.5
30.3
30.3
27.5
27.4
25.4
25.4
23.4
23.3
19.2
19.1
17.9
17.8
2.0
0.1
13C{1H} NMR (175 MHz, CDCl3)
H
O
O
O
CO2H
f1 (ppm)
f1 (ppm)


^{1}H NMR (700 MHz, $CDCl_3$)
f1 (ppm)


209.7
209.5
172.9
172.9
143.1
143.1
118.0
118.0
98.8
98.6
86.2
86.1
73.1
73.0
70.5
70.4
62.3
62.3
61.7
51.5
51.5
40.0
39.5
37.6
37.5
37.4
36.9
33.0
32.8
31.9
31.9
30.3
28.1
27.5
27.4
25.5
25.4
25.2
24.9
24.6
23.9
23.7
22.9
22.8
19.9
19.9
19.2
19.2
18.0
17.9
16.5
0.1
$^{13}C\{^{1}H\}$ NMR (175 MHz, $CDCl_3$)
H
O
O
O
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)