Supporting Information for:

Synthesis of the Ring C Pyrrole of Native Chlorophylls and Bacteriochlorophylls

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1. Single-crystal X-ray data

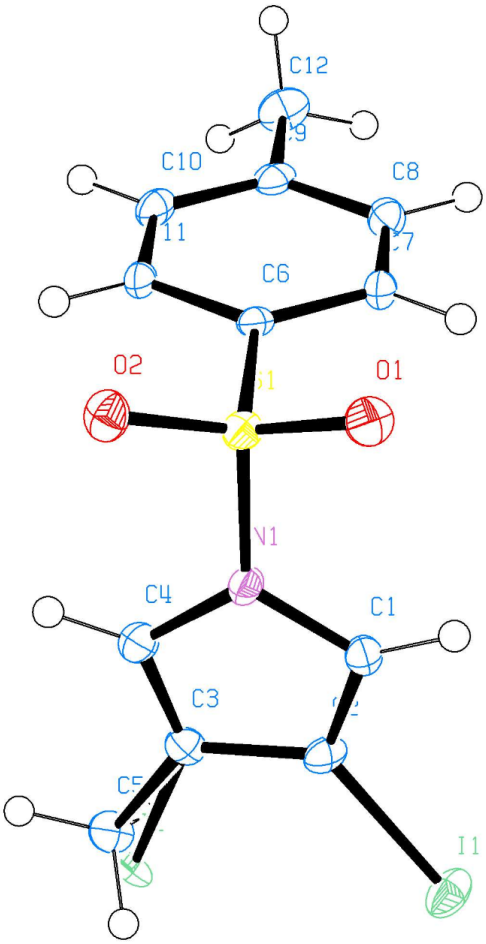


Figure S1. ORTEP diagram of compound **Ts-1-I**. with thermal ellipsoids drawn at the 50% probability level.

Table S1. Single-crystal X-ray structure data for **Ts-1-I**

CCDC registry	1934915
Chemical formula	$C_{11.99}H_{11.96}I_{1.01}NO_2S$
Formula weight (g/mol)	362.83
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal size (mm)	0.050 × 0.065 × 0.198
Crystal habit	Colorless rod
Crystal system	Orthorhombic
Space group	*P* b c a
Unit cell dimensions, *a* (Å)	6.3705(3)
Unit cell dimensions, *b* (Å)	16.0873(7)
Unit cell dimensions, *c* (Å)	25.9006(11)
α, deg	90
β, deg	90
γ, deg	90
Volume ($Å^3$)	2654.4(2)
Z	8
Density (calculated) (g/cm^3)	1.816
Absorption coefficient (mm^{-1})	2.594
F(000)	1413
Theta range for data collection, deg	2.53 to 28.27
Index ranges	-8<=h<=8, -21<=k<=21, -34<=l<=34
Reflections collected	61299
Independent reflections	3295 [R(int) = 0.0726]
R_1	0.0450
wR_2	0.0805
R_1 (all data)	0.0625
wR_2 (all data)	0.0850
Largest diff. peak and hole ($eÅ^{-3}$)	0.837 and -1.046
R.M.S. deviation from mean ($eÅ^{-3}$)	0.143

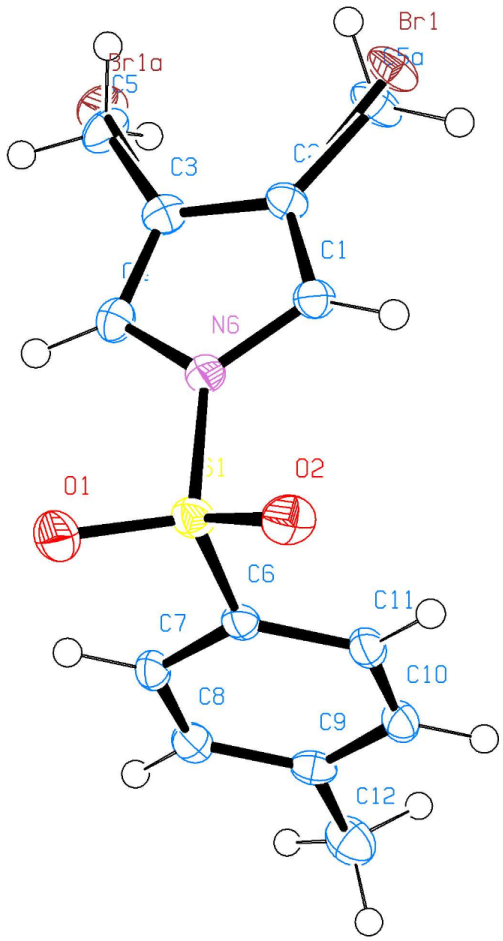
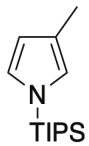


Figure S2. ORTEP diagram of compound **Ts-1-Br** with thermal ellipsoids drawn at the 50% probability level.

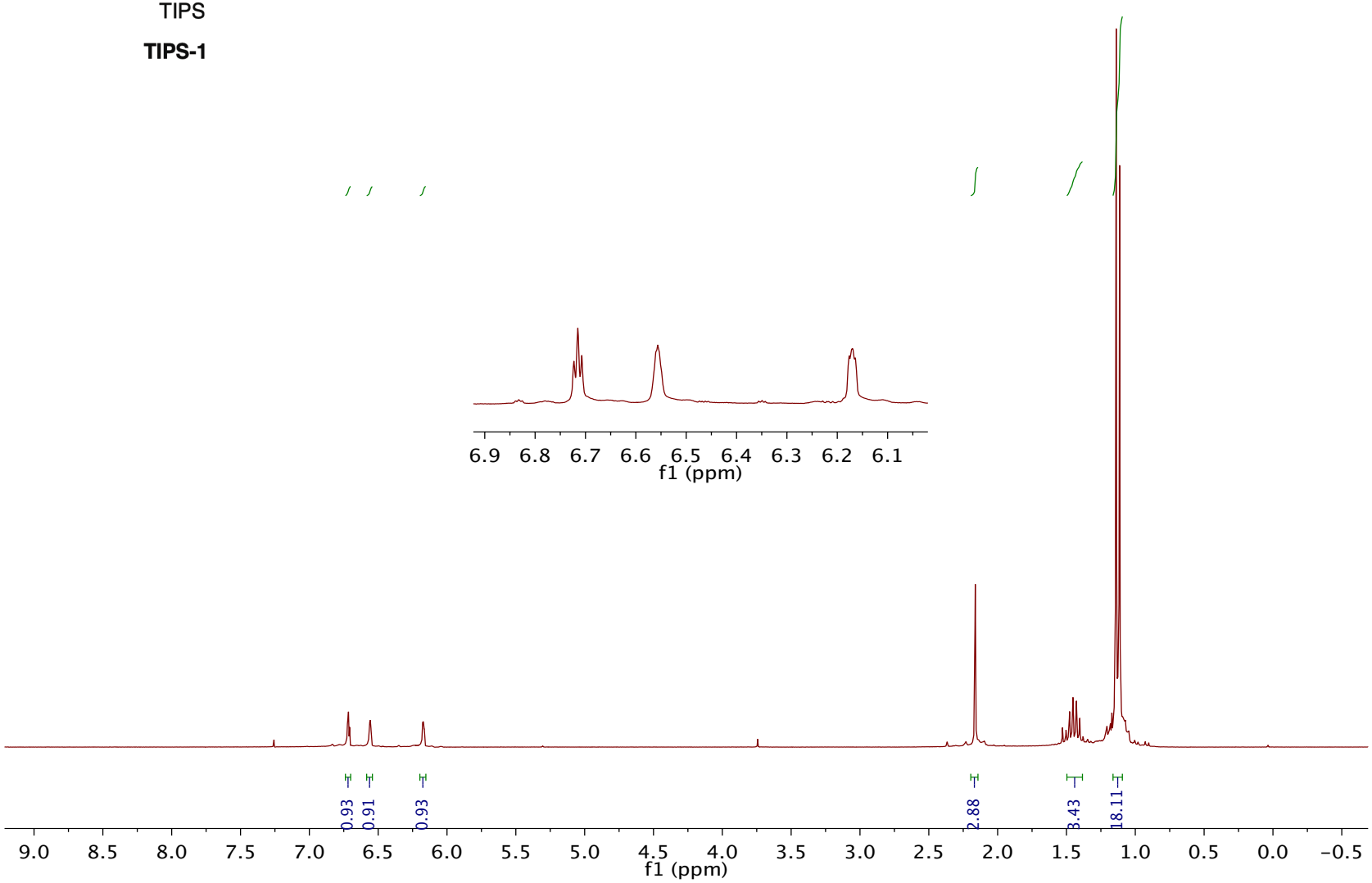
Table S2. Single-crystal X-ray structure data for **Ts-1-Br**

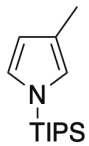
CCDC registry	1934914
Chemical formula	$C_{12}H_{12}BrNO_2S$
Formula weight (g/mol)	314.20
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal size (mm)	0.065 × 0.101 × 0.418
Crystal habit	Colorless needle
Crystal system	Monoclinic
Space group	*P*1 21/c1
Unit cell dimensions, *a* (Å)	13.1467(9)
Unit cell dimensions, *b* (Å)	6.1735(4)
Unit cell dimensions, *c* (Å)	15.7907(11)
α, deg	90
β, deg	94.671(2)
γ, deg	90
Volume ($Å^3$)	1277.33(15)
Z	4
Density (calculated) (g/cm^3)	1.634
Absorption coefficient (mm^{-1})	3.370
F(000)	632
Theta range for data collection, deg	2.59 to 28.30
Index ranges	-17<=h<=17, -8<=k<=8, -18<=l<=21
Reflections collected	12231
Independent reflections	3172 [R(int) = 0.0362]
R_1	0.0315
wR_2	0.0639
R_1 (all data)	0.0545
wR_2 (all data)	0.0707
Largest diff. peak and hole ($eÅ^{-3}$)	0.598 and -0.442
R.M.S. deviation from mean ($eÅ^{-3}$)	0.077

2. Spectra

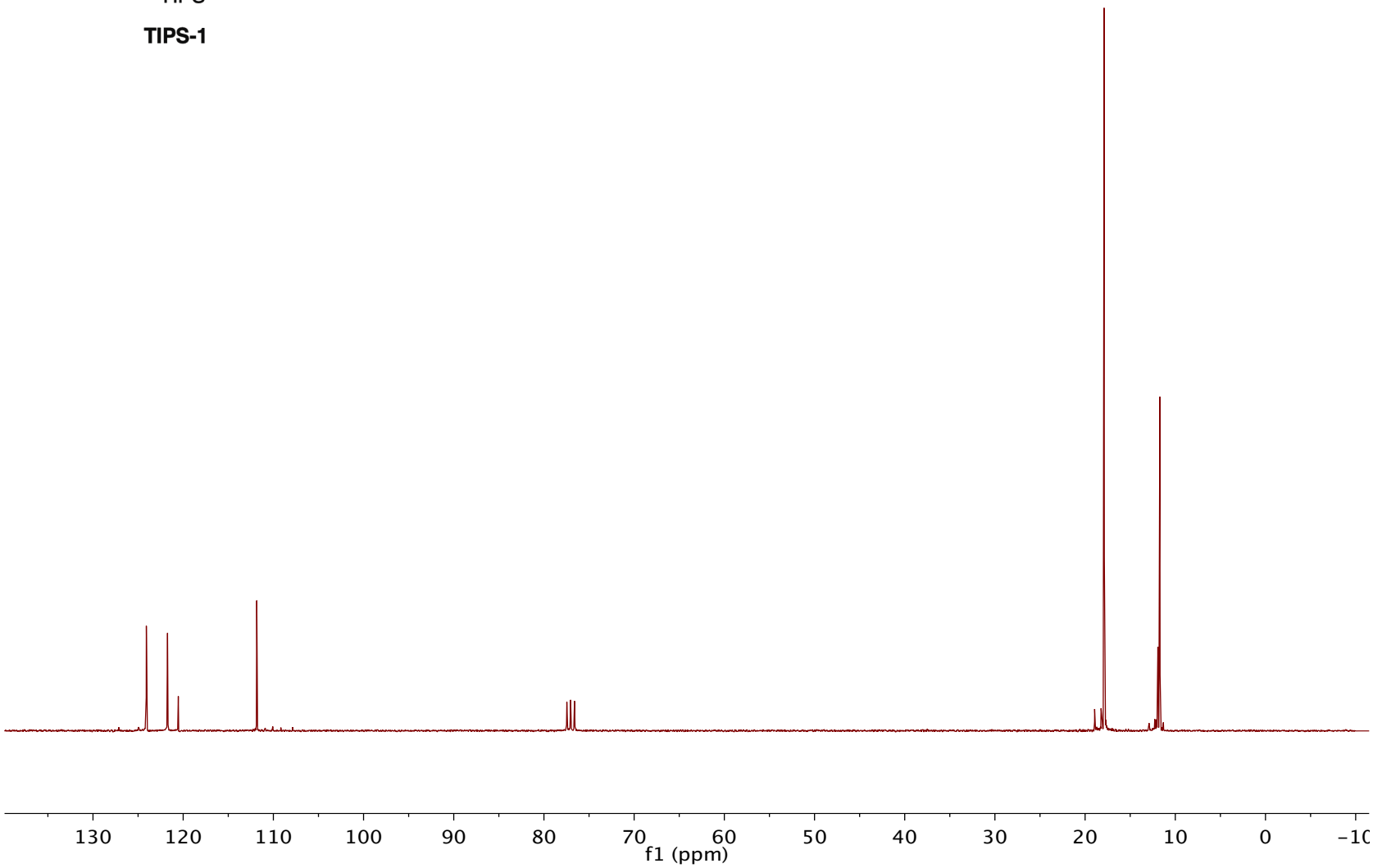

N
TIPS

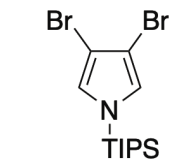
TIPS-1


0.93
0.91
0.93
2.88
3.43
18.11
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)
6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1
f1 (ppm)

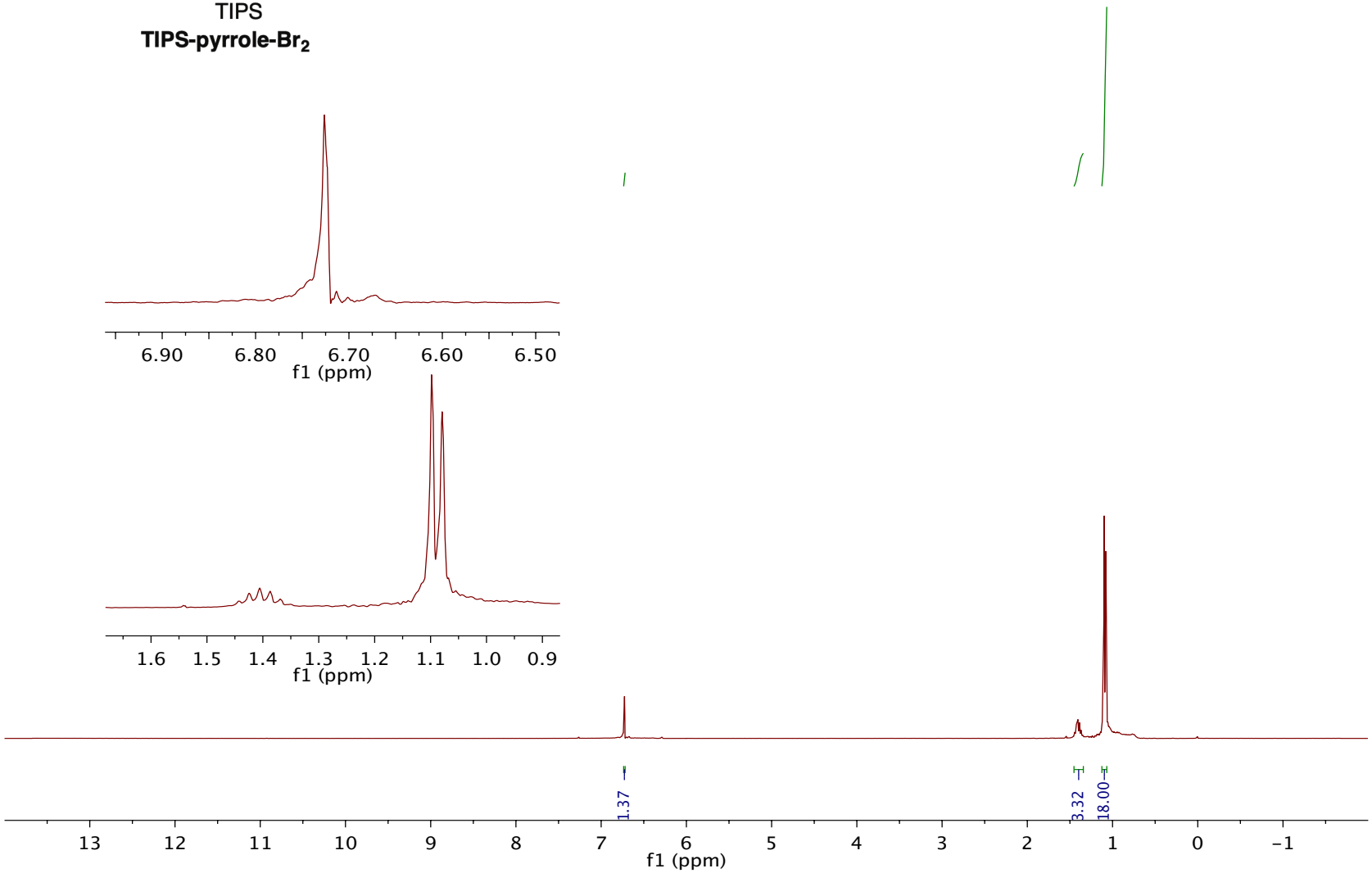


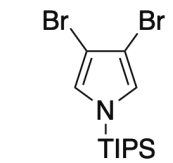
TIPS-1



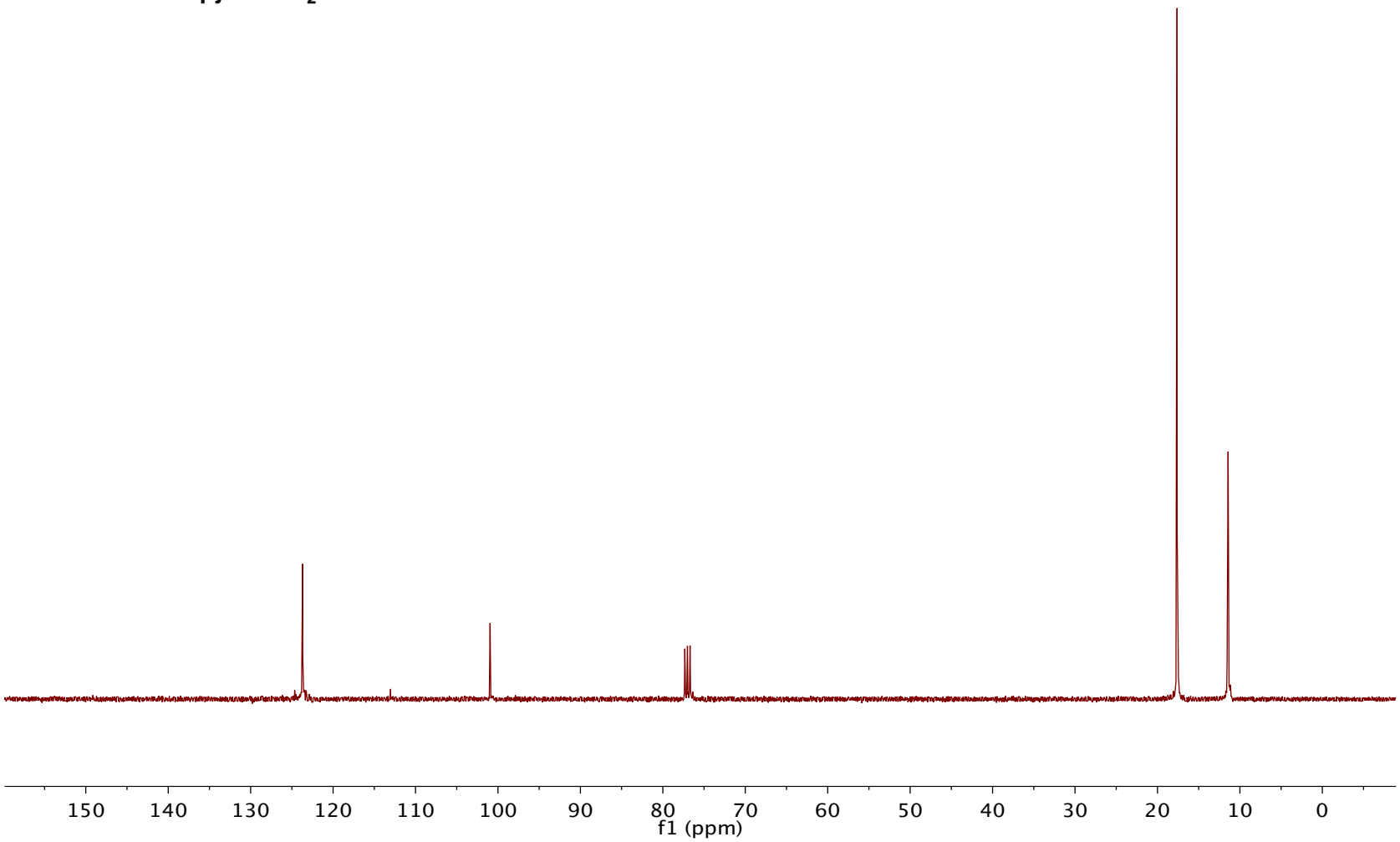


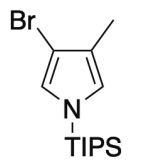
TIPS-pyrrole-Br_2



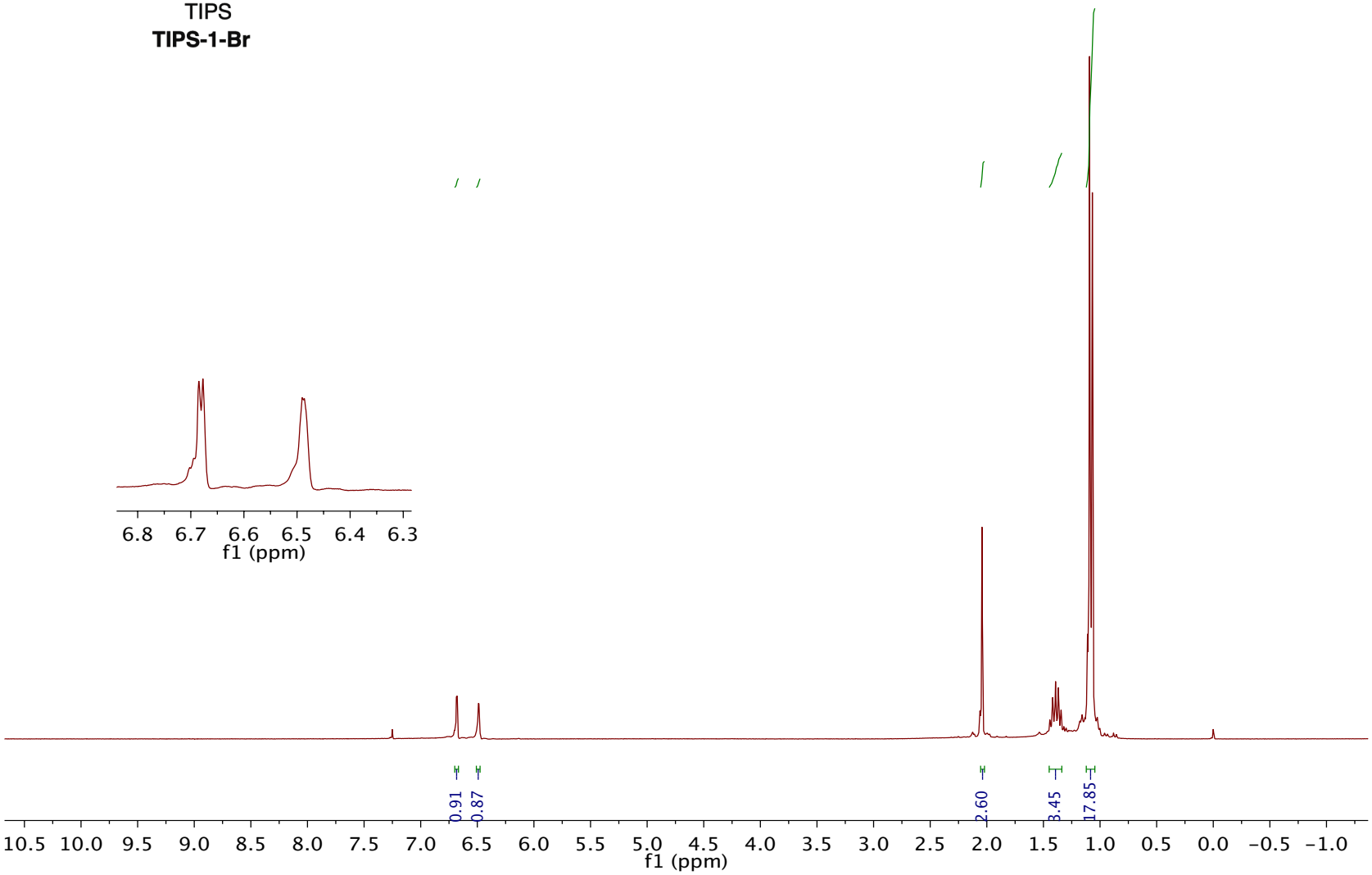


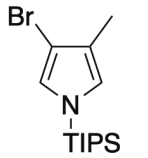
TIPS-pyrrole-Br_2



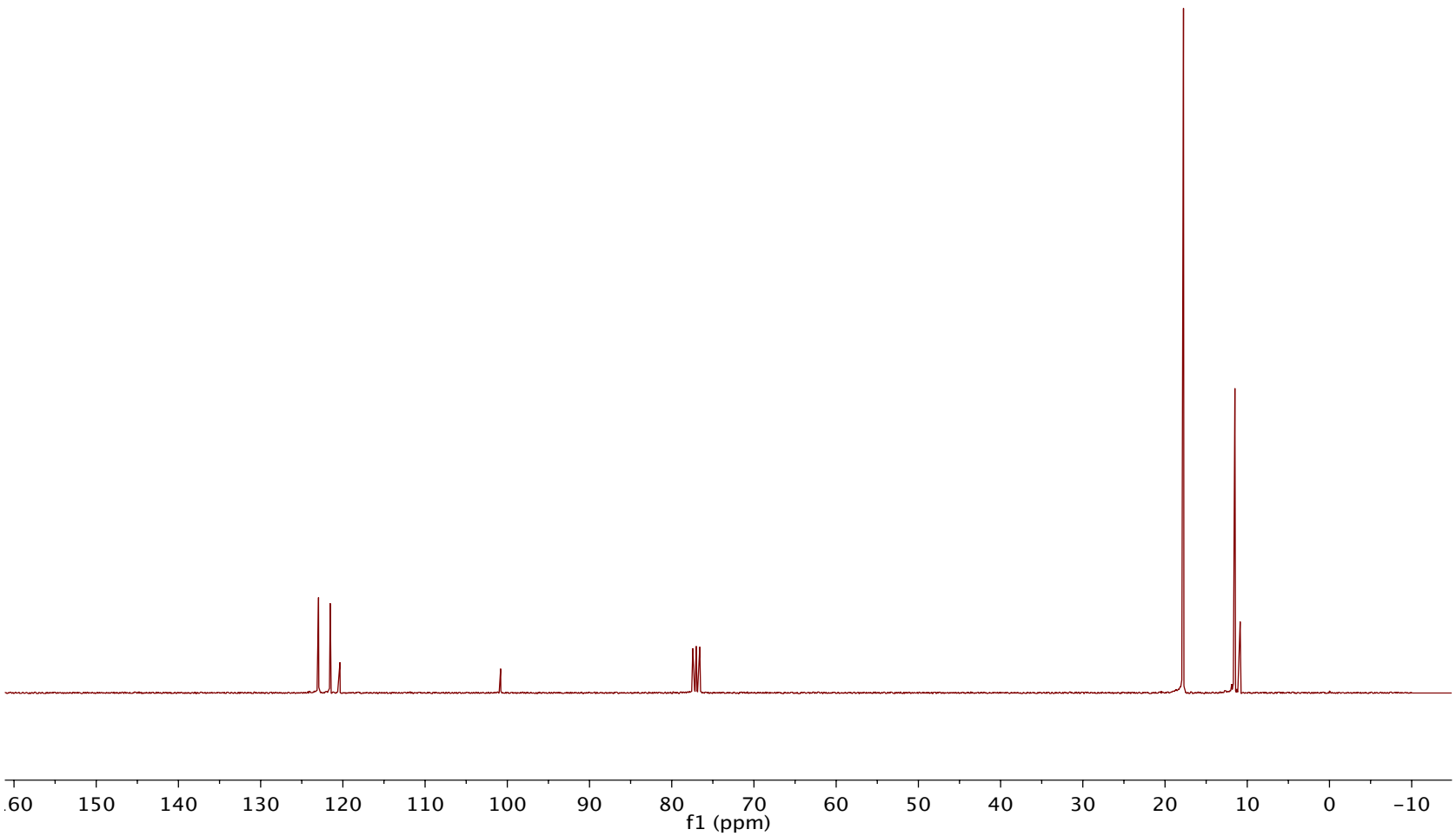

Br
N
TIPS

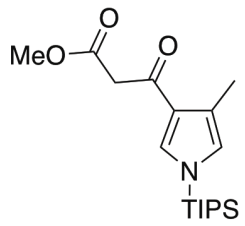
TIPS-1-Br


6.8 6.7 6.6 6.5 6.4 6.3
f1 (ppm)
0.91
0.87
2.60
3.45
17.85
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)


Br
N
TIPS

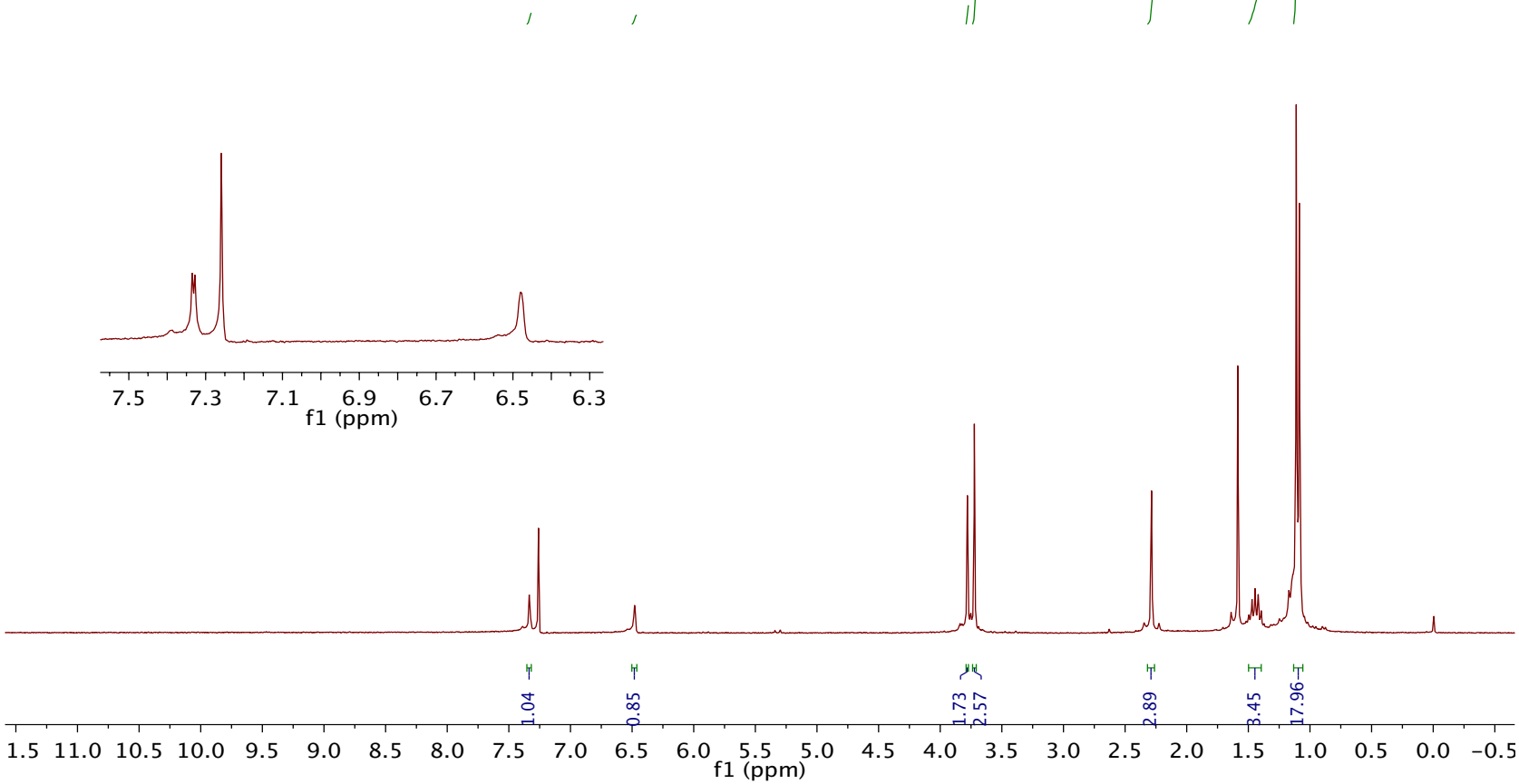
TIPS-1-Br

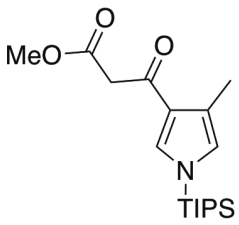

.60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



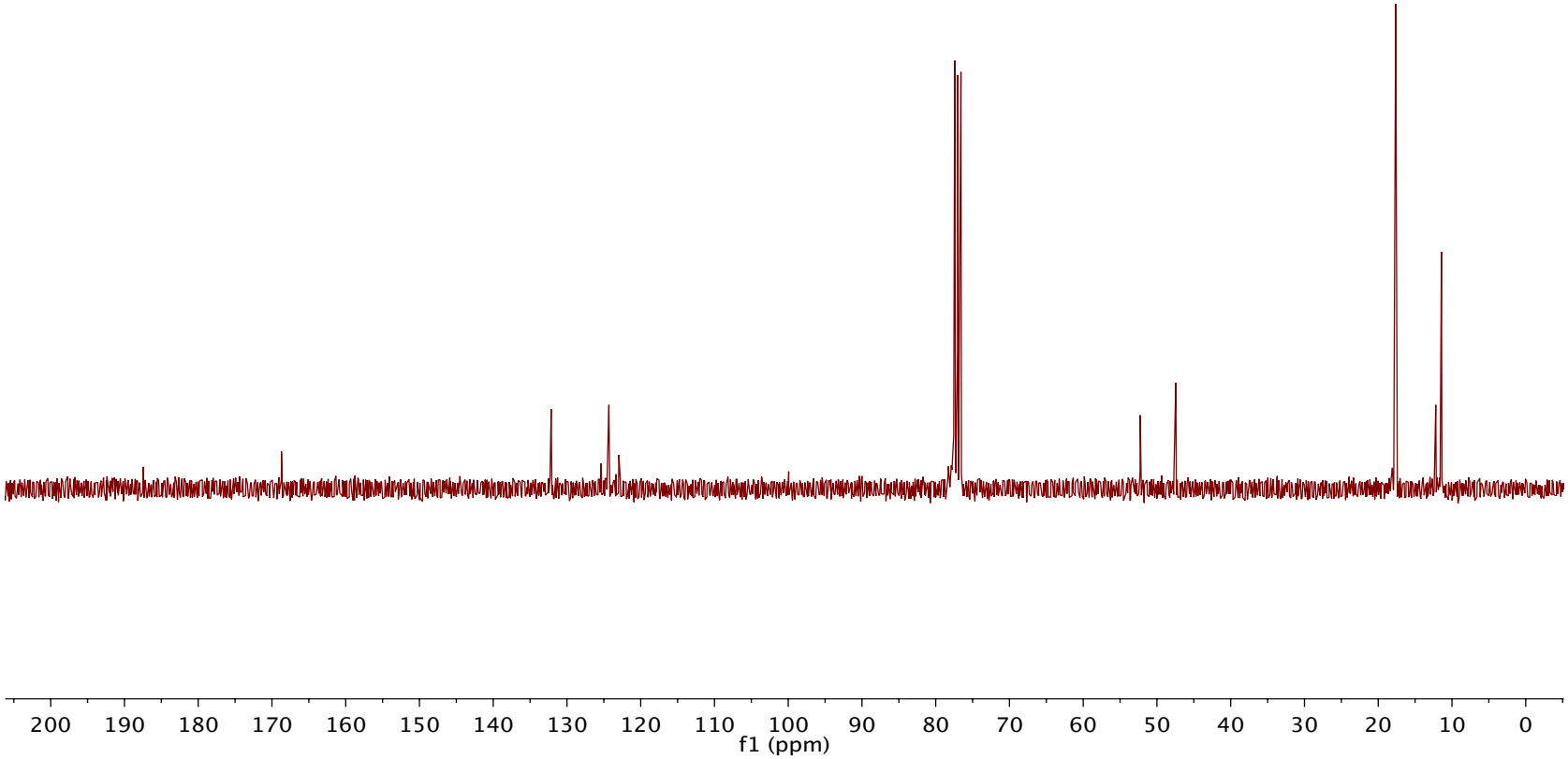
TIPS-2

From **TIPS-1-Br**




MeO
O
O
N
TIPS

TIPS-2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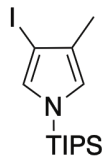
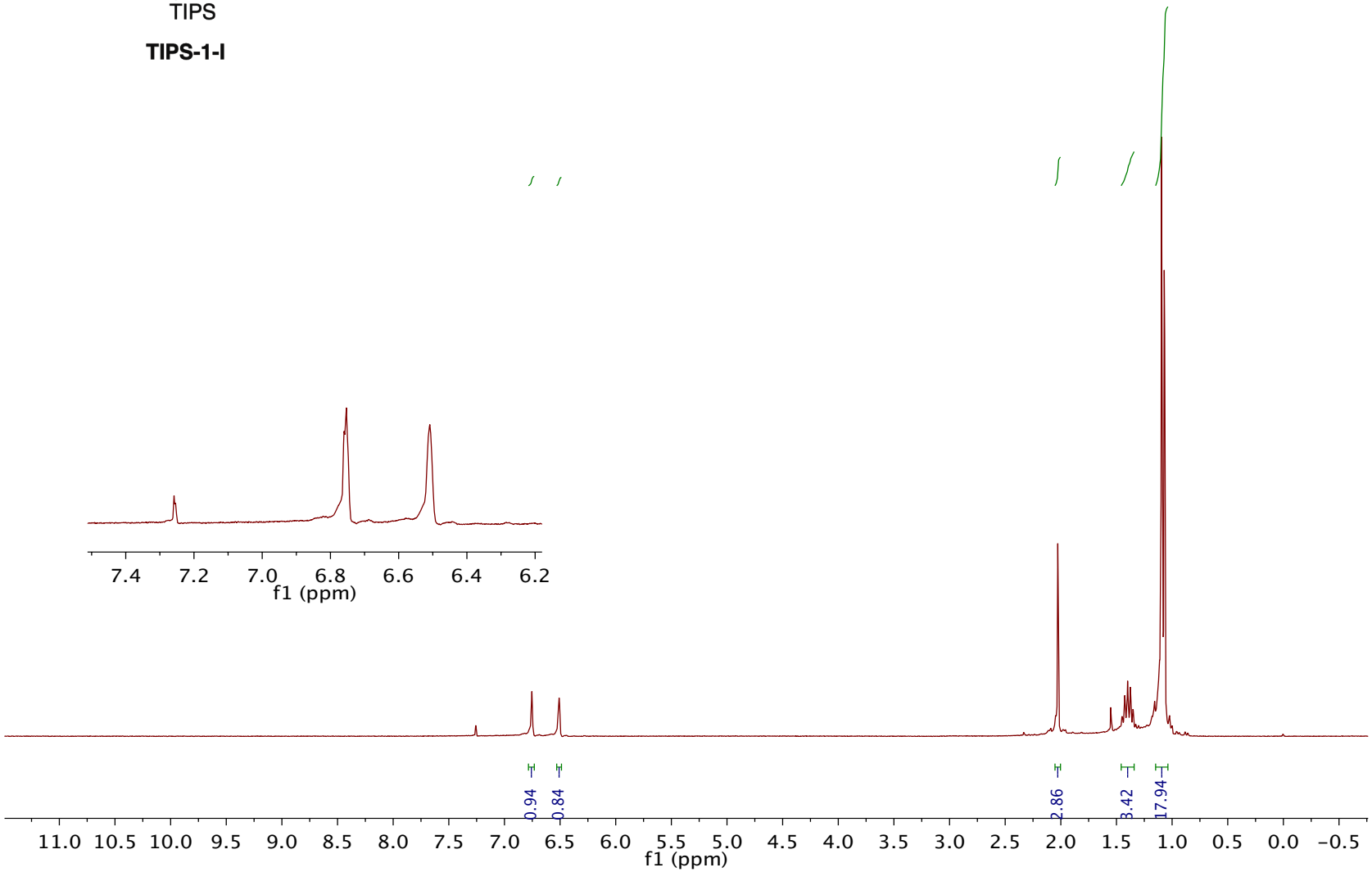
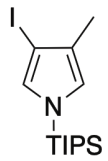
f1 (ppm)

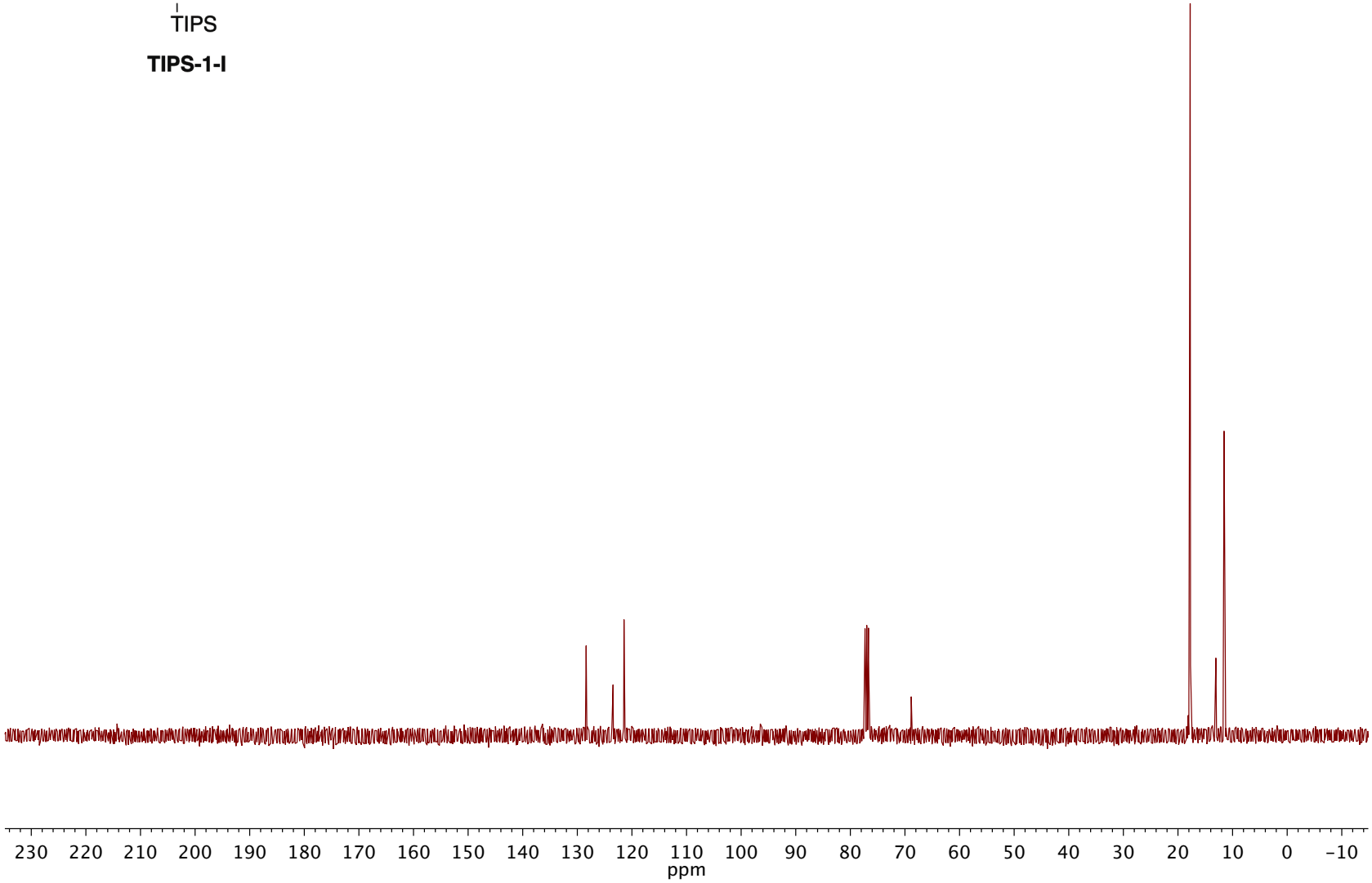

I
N
TIPS

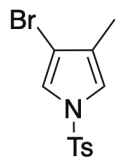
TIPS-1-I


7.4 7.2 7.0 6.8 6.6 6.4 6.2
f1 (ppm)
0.94
0.84
2.86
3.42
17.94
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

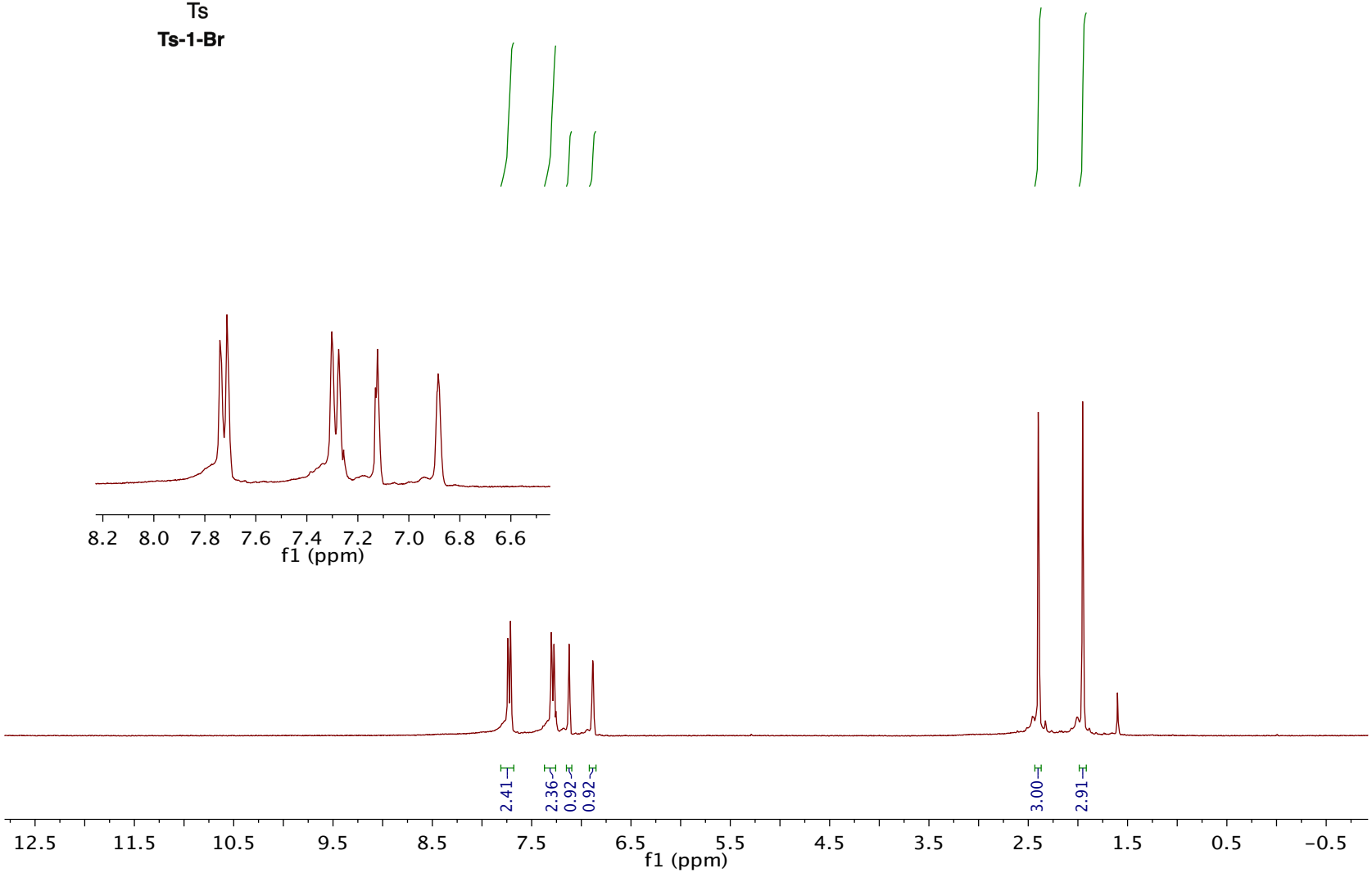

I
N
TIPS

TIPS-1-I


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
ppm


Br
N
Ts

Ts-1-Br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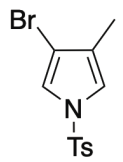
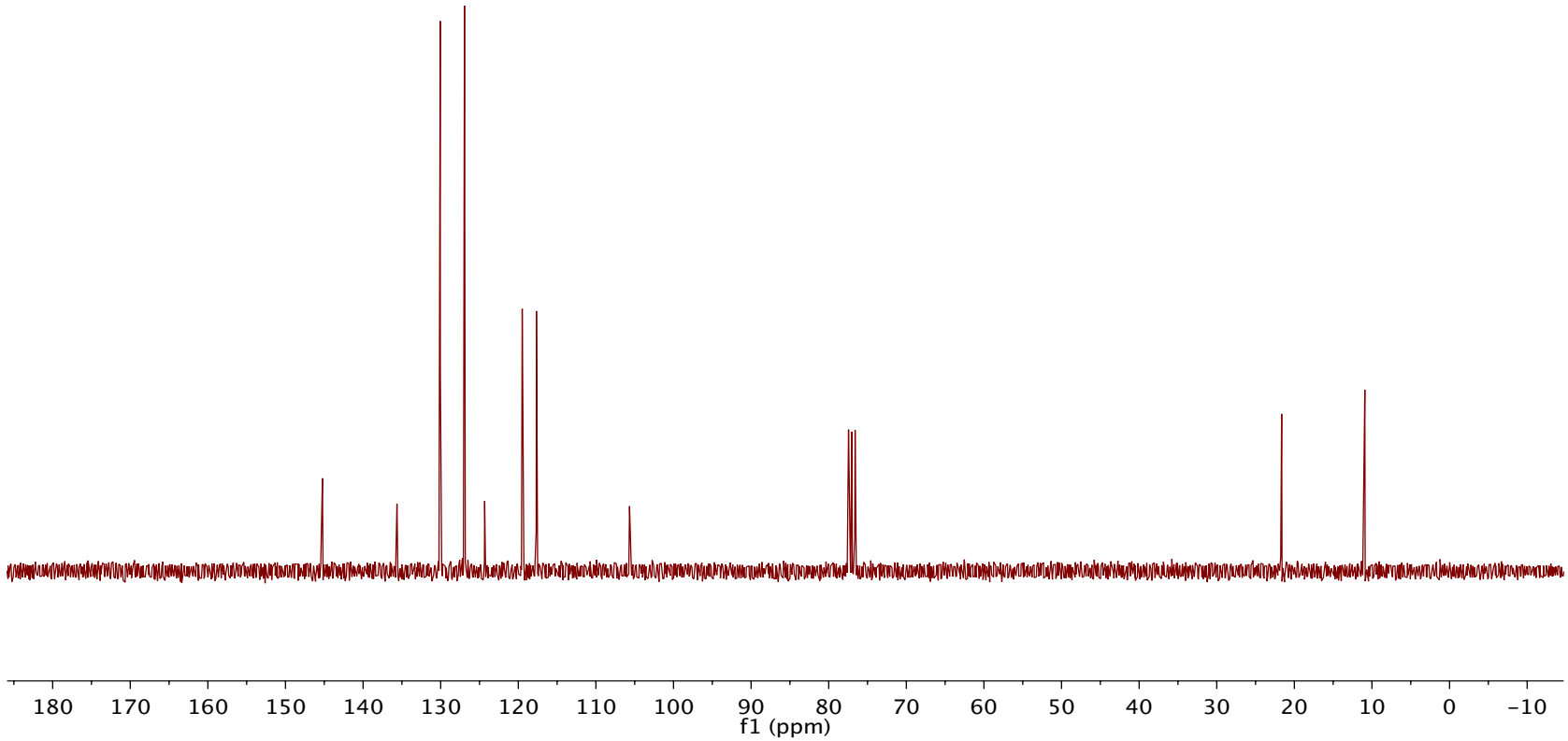
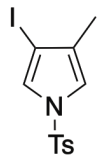
f1 (ppm)
2.41
2.36
0.92
0.92
3.00
2.91
12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 −0.5
f1 (ppm)

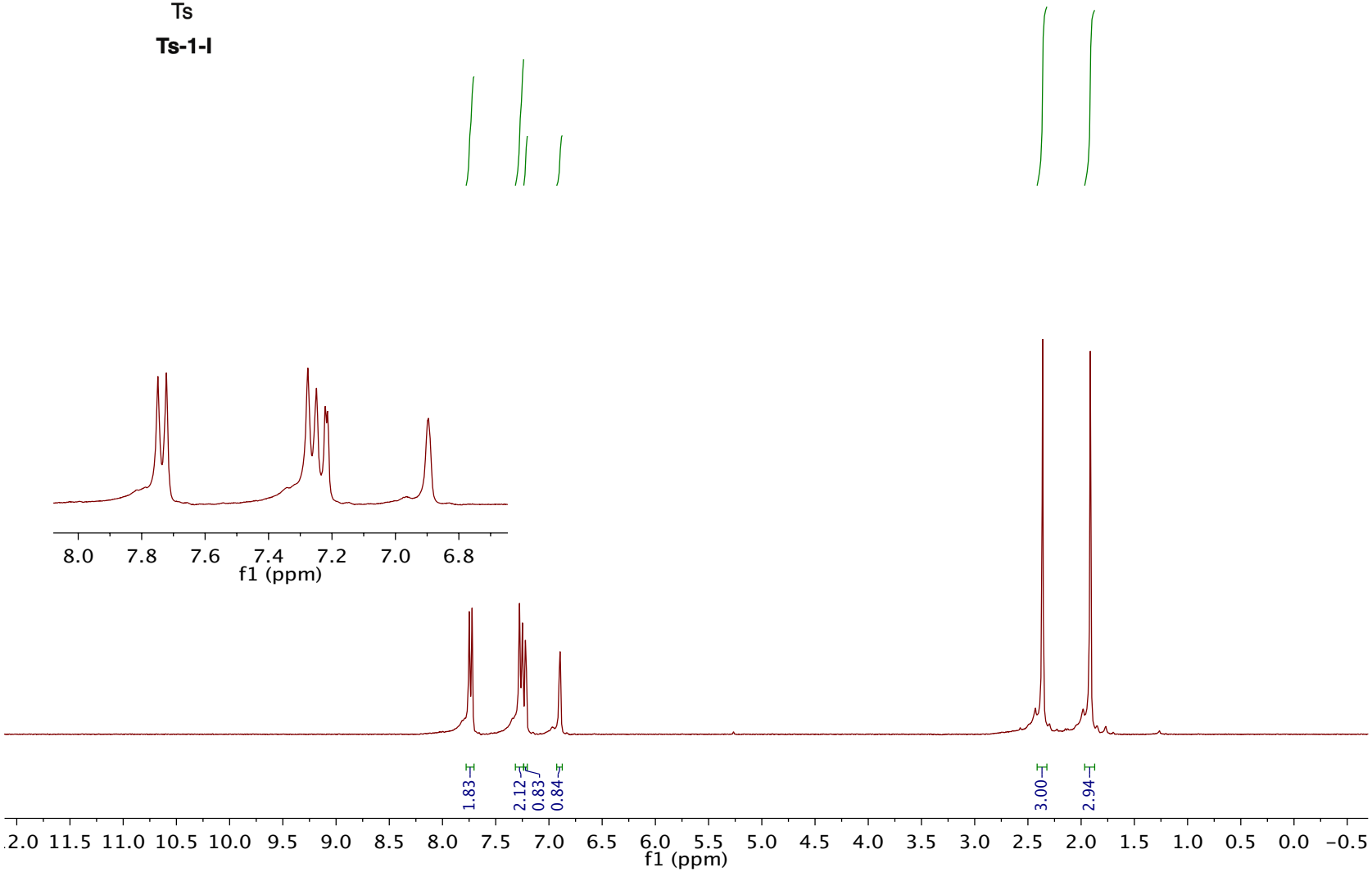

Br
N
Ts

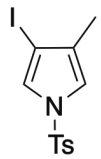
Ts-1-Br


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

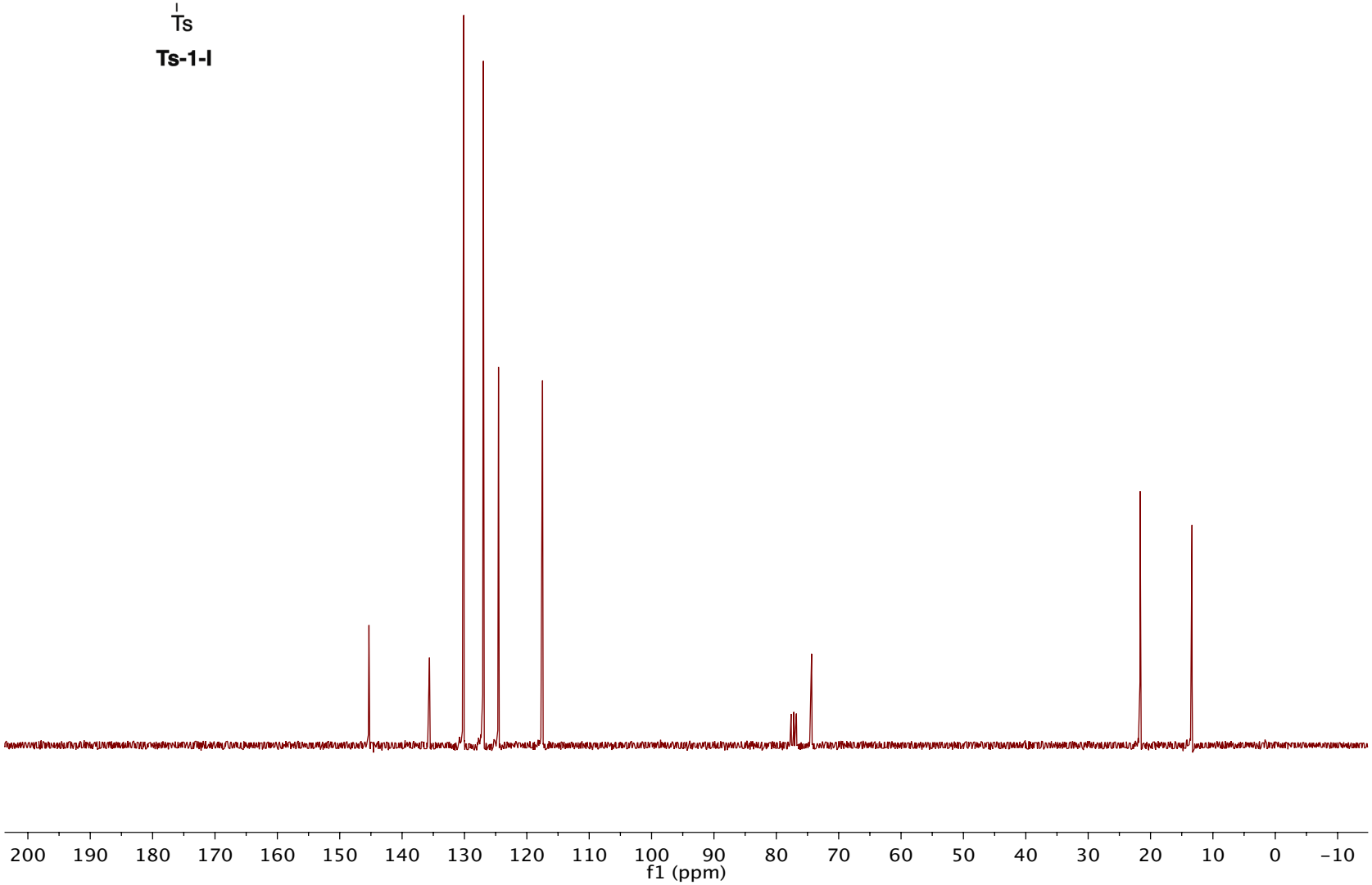

I
N
Ts

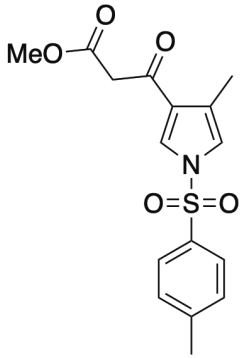
Ts-1-I


8.0 7.8 7.6 7.4 7.2 7.0 6.8
f1 (ppm)
1.83
2.12
0.83
0.84
3.00
2.94
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

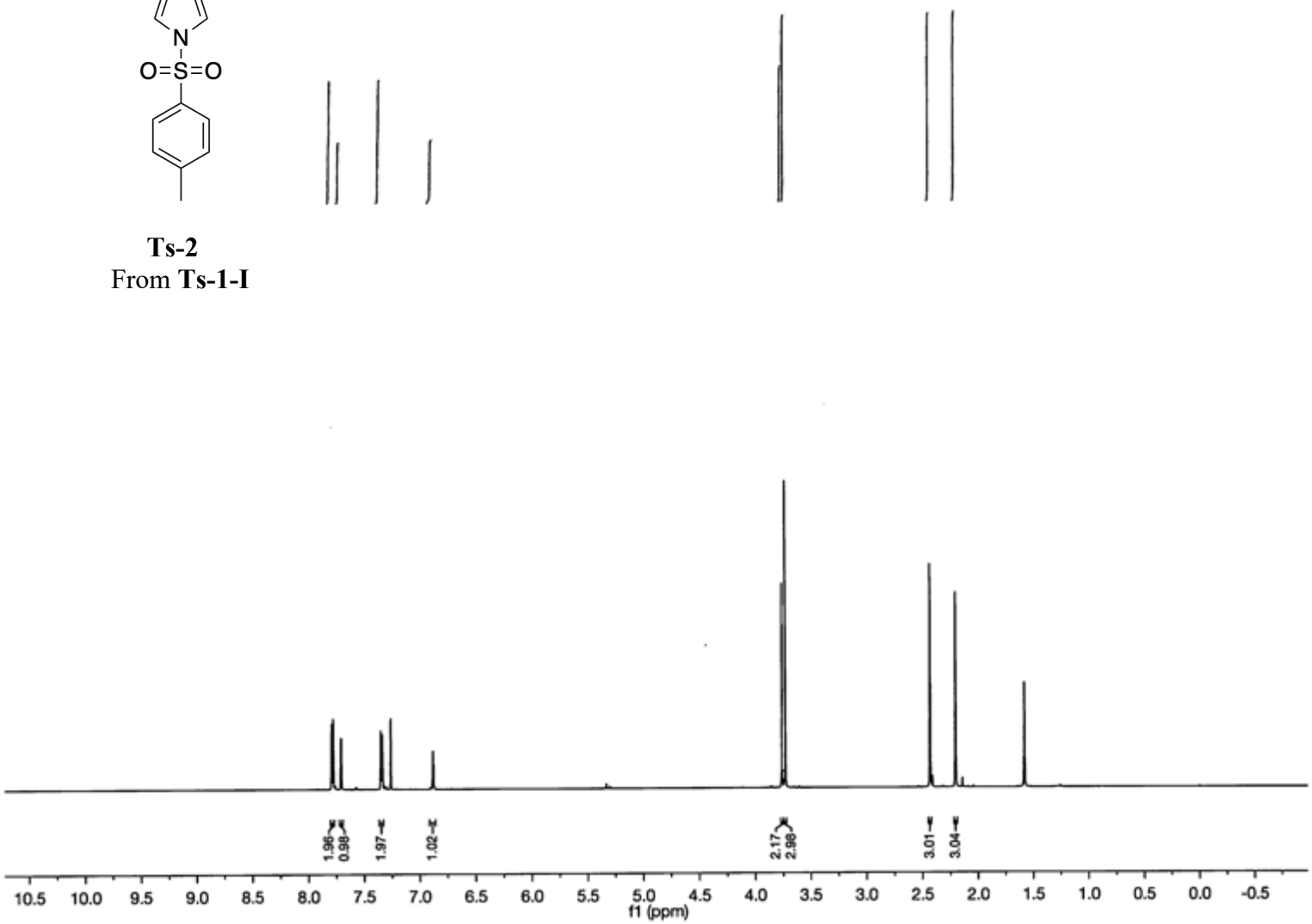

I
N
Ts

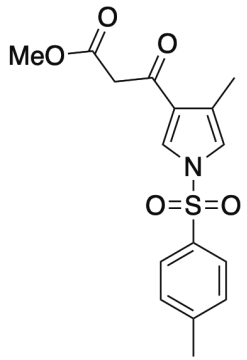
Ts-1-I


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

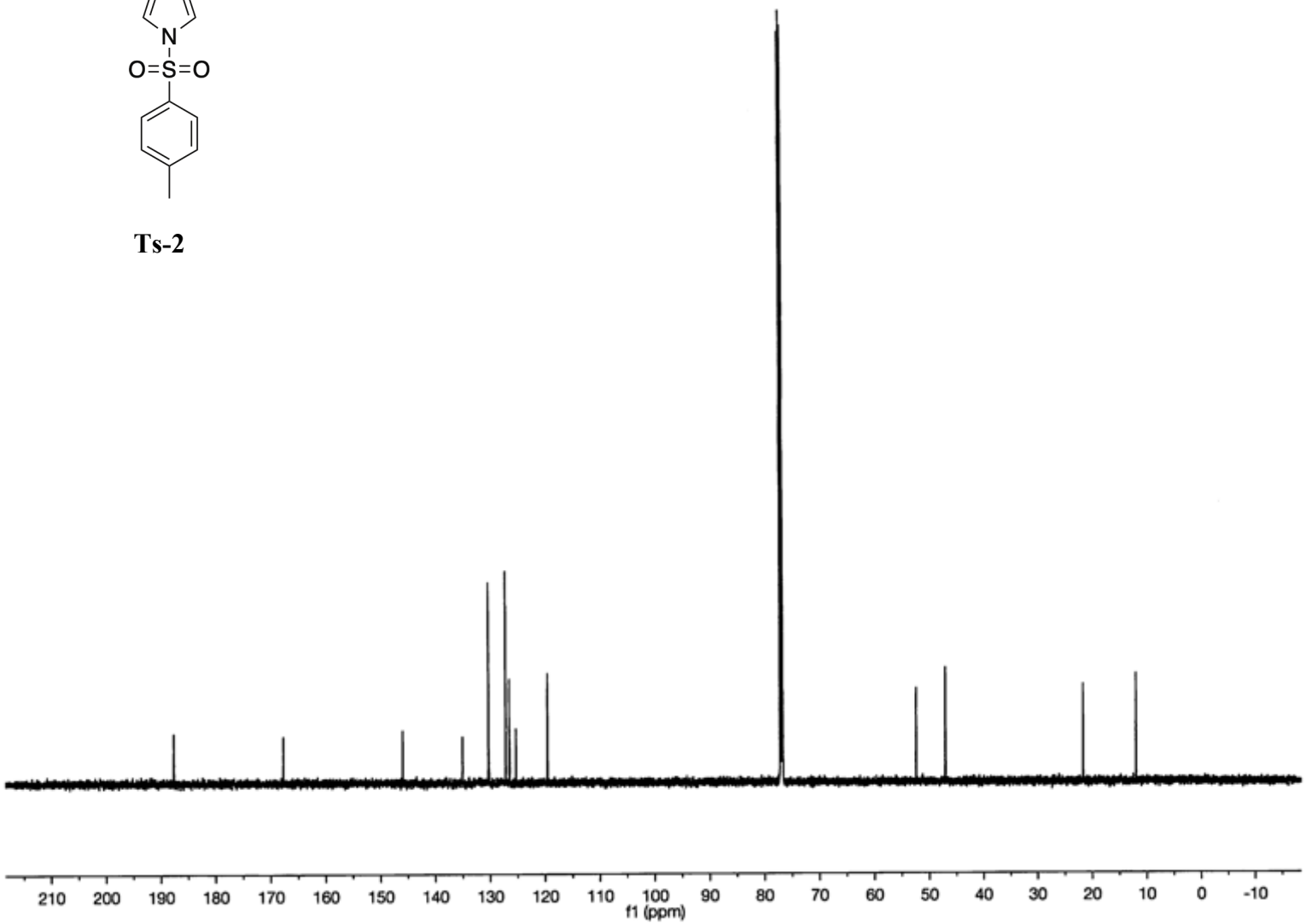


Ts-2
From **Ts-1-I**




MeO
O
O
N
O=S=O

Ts-2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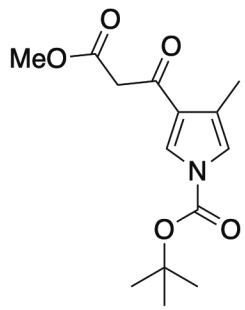
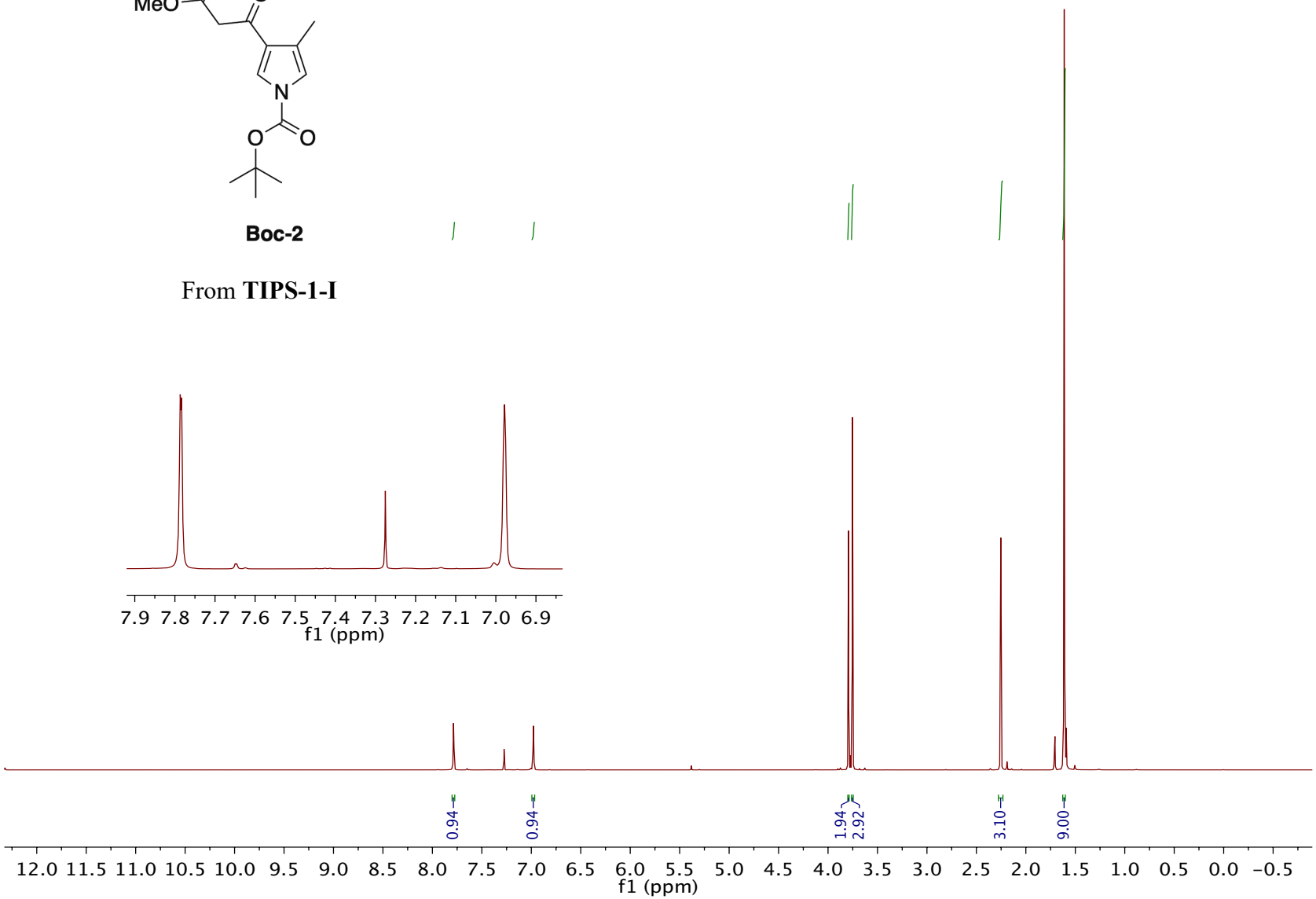
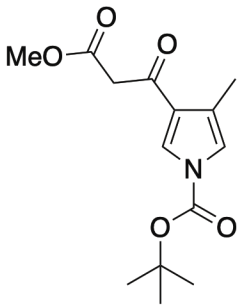
f1 (ppm)



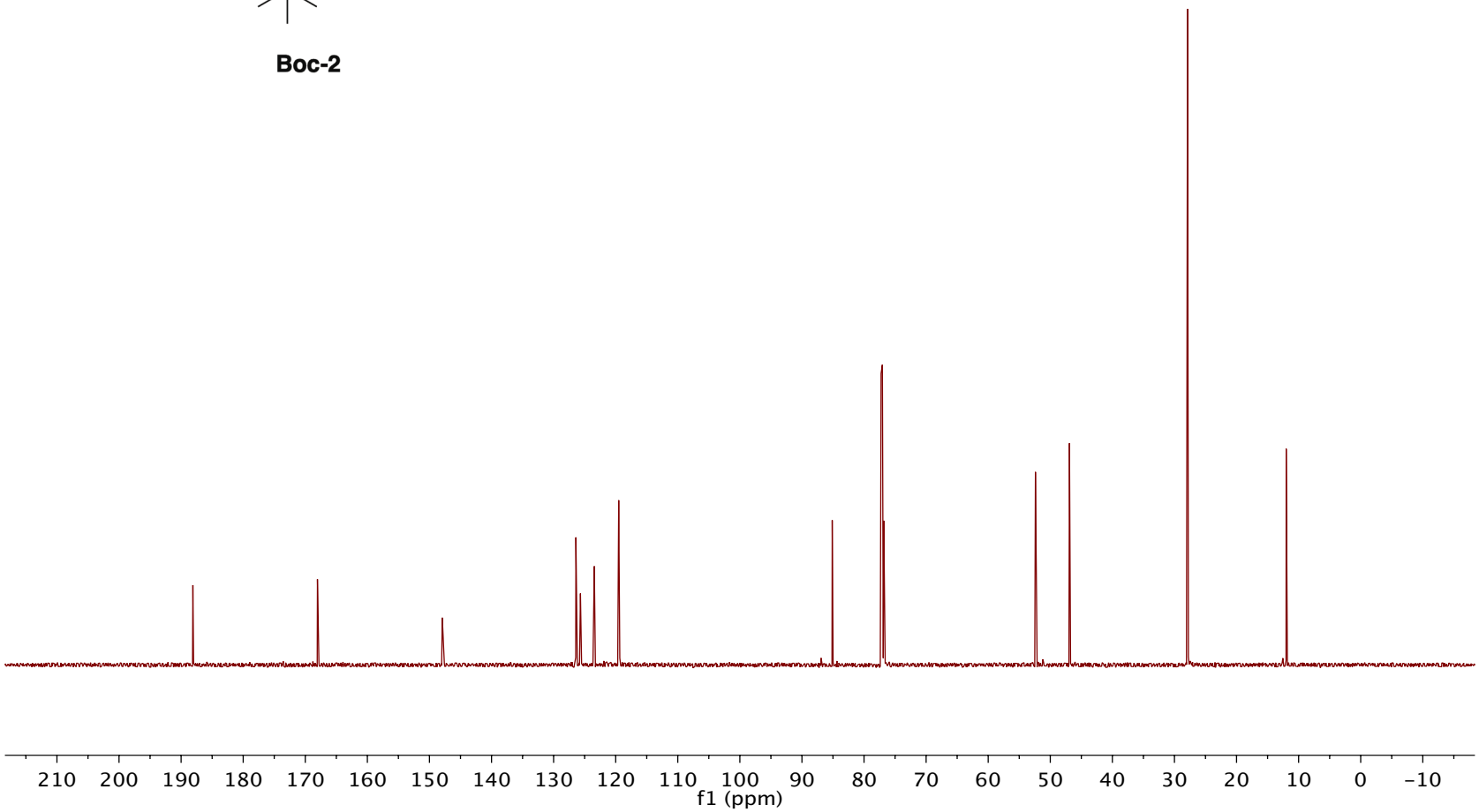
Boc-2

From **TIPS-1-I**




MeO
O
O
N
O
O

Boc-2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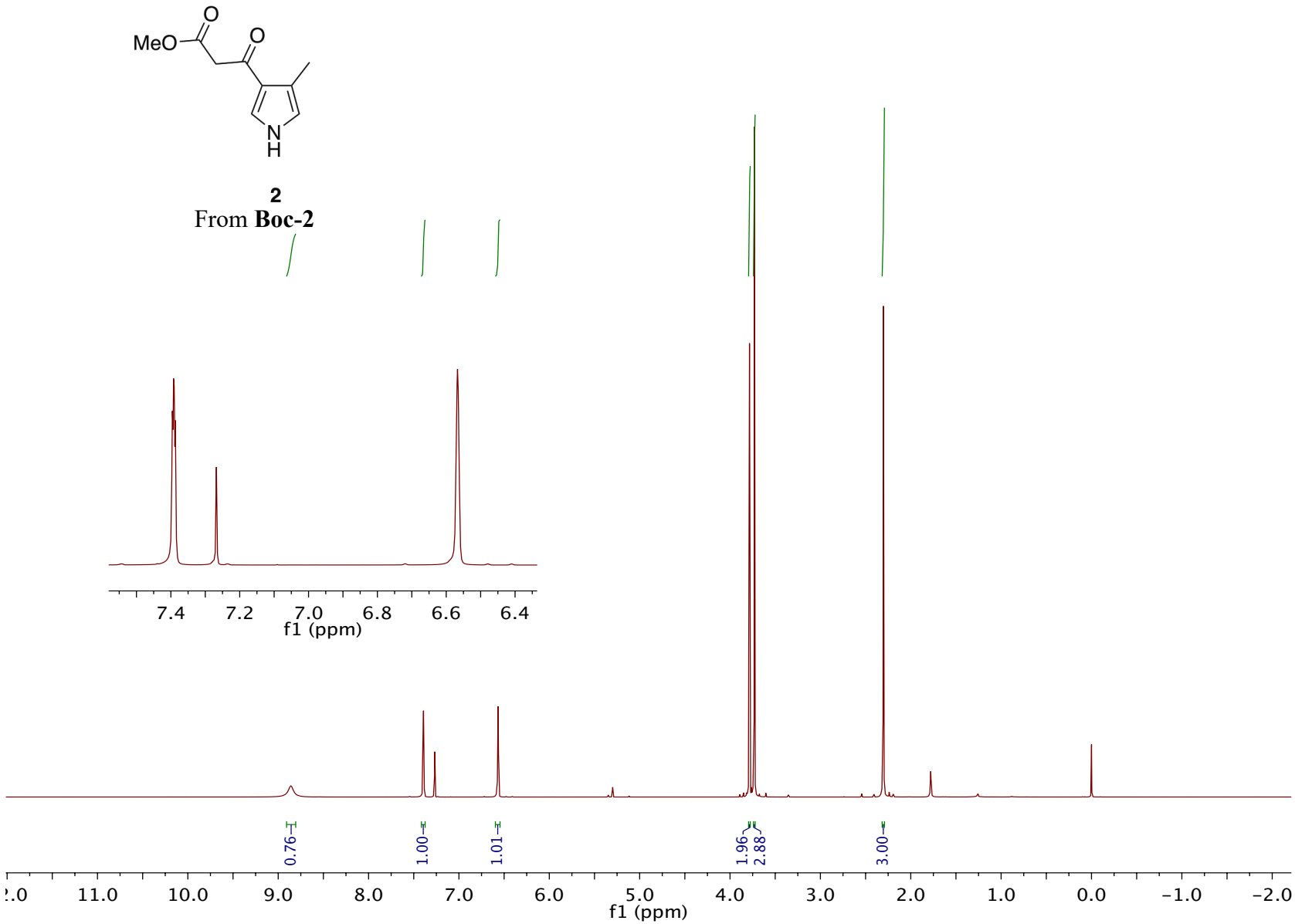
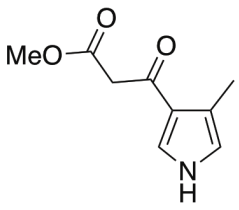
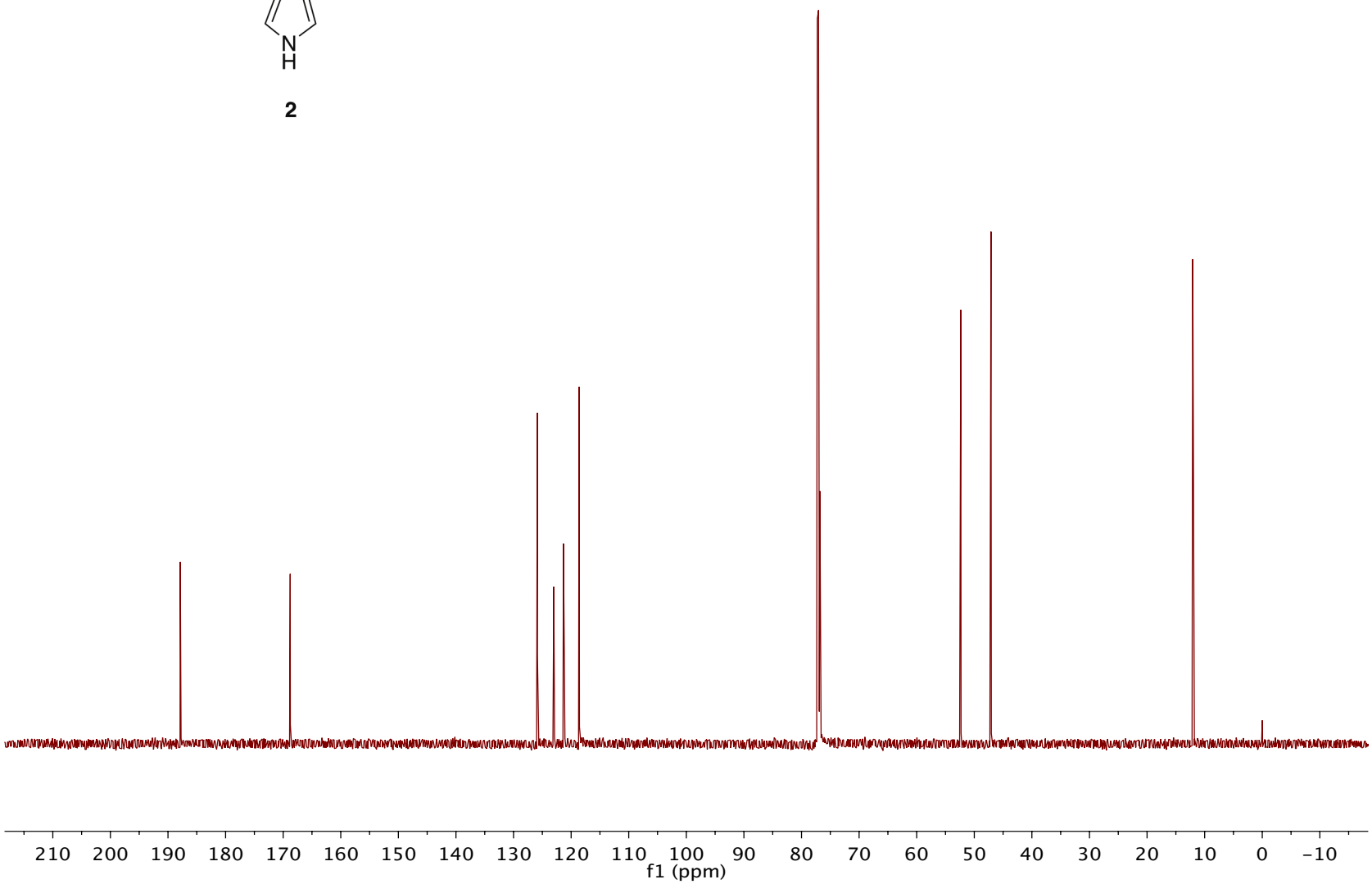
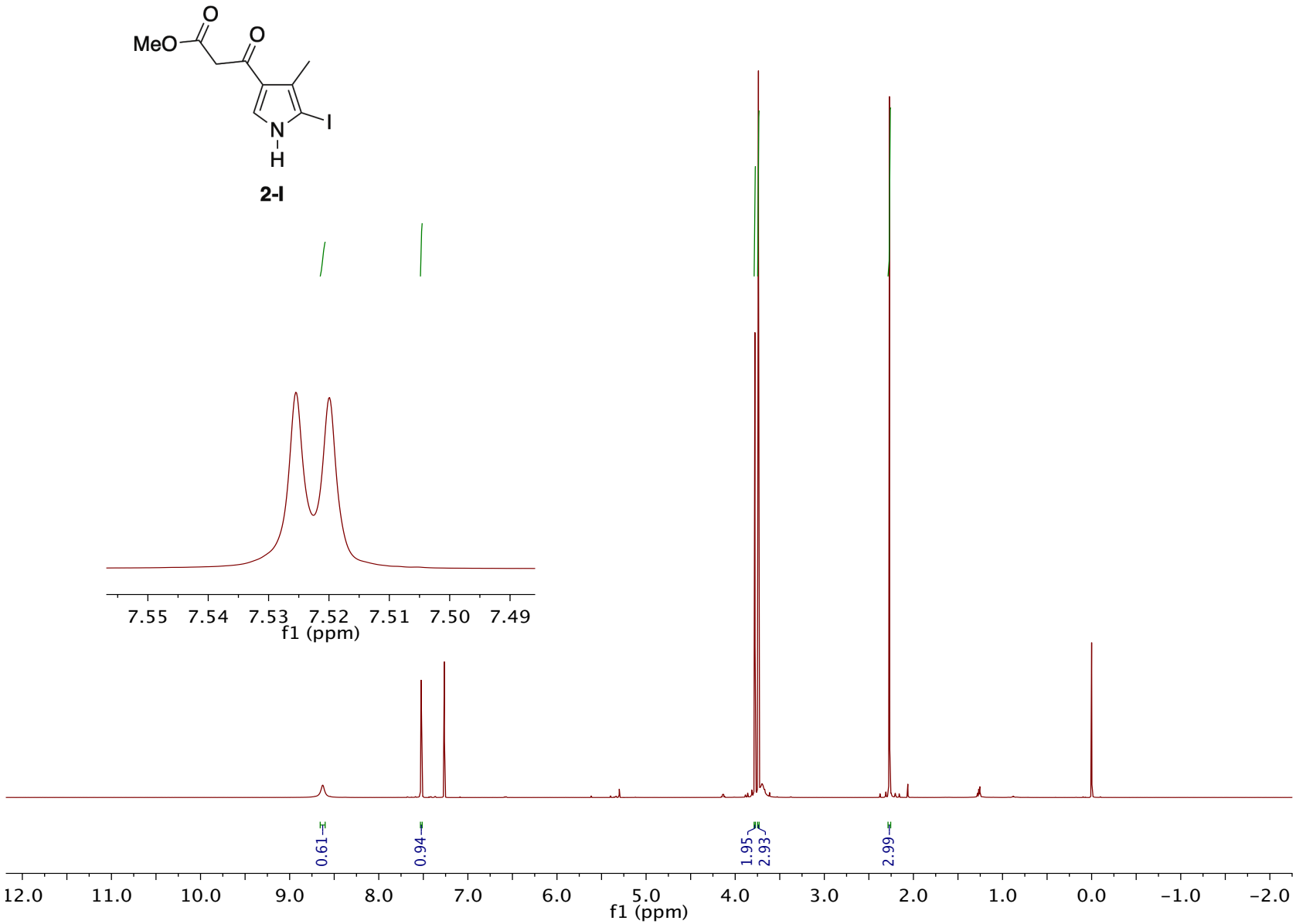
f1 (ppm)

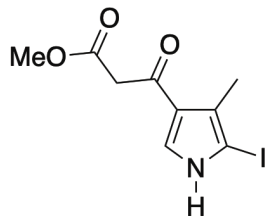

MeO
O
O
N
H
2
From Boc-2
7.4
7.2
7.0
6.8
6.6
6.4
f1 (ppm)
0.76
1.00
1.01
1.96
2.88
3.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1.0
−2.0
f1 (ppm)


MeO
O
O
N
H

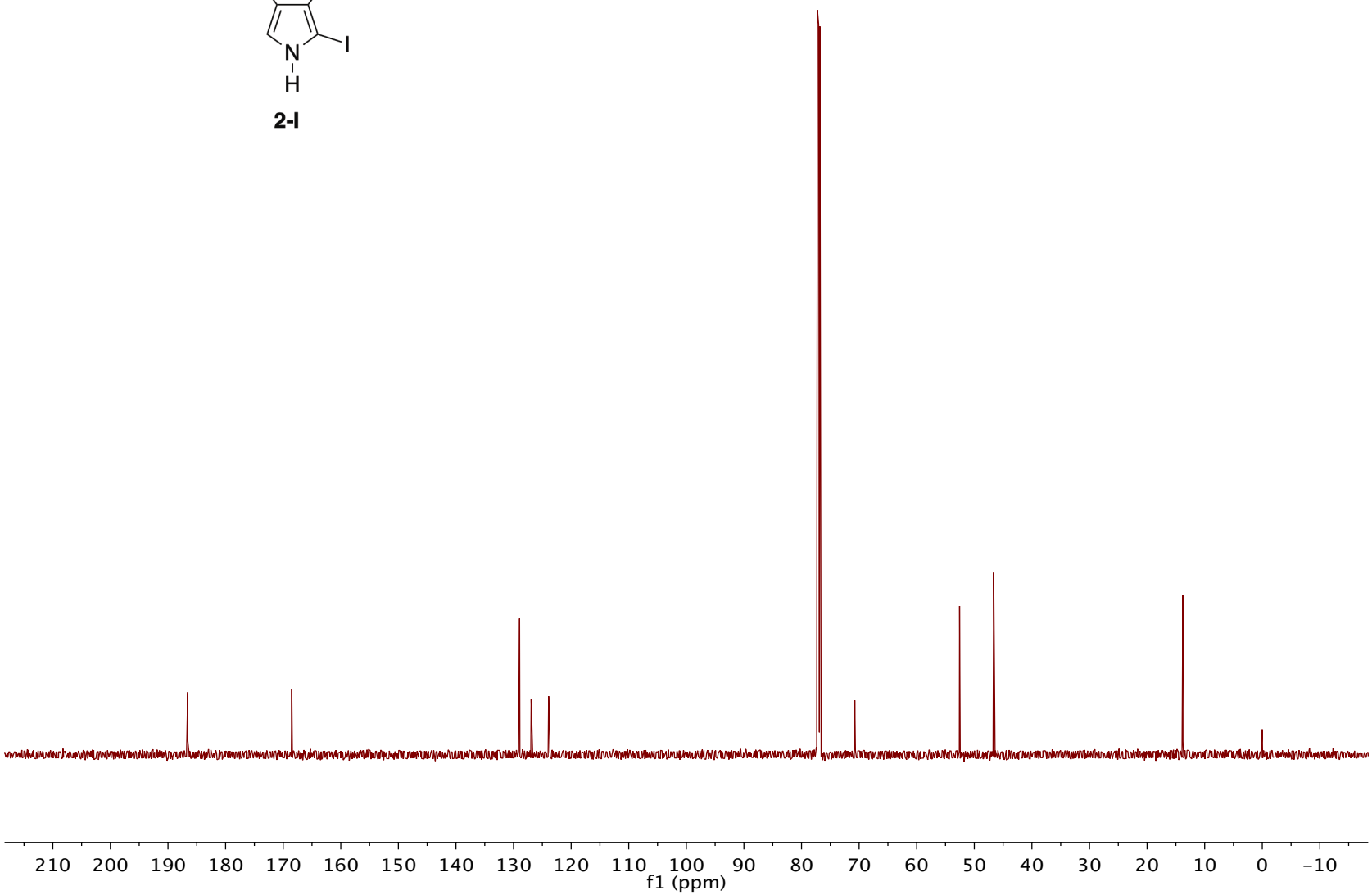
2

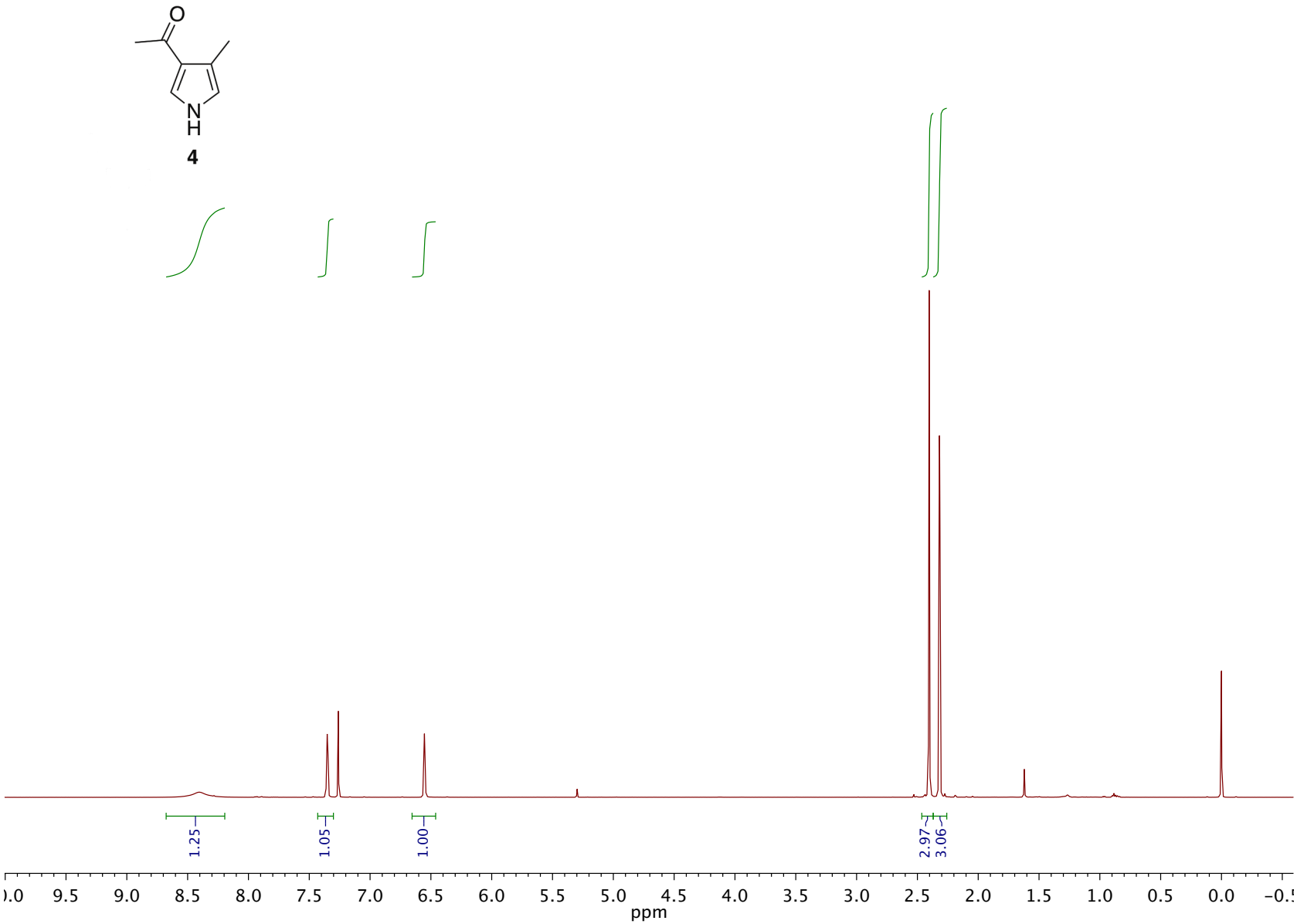

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

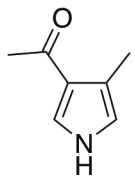

MeO
O
O
N
H
I
2-I
7.55 7.54 7.53 7.52 7.51 7.50 7.49
f1 (ppm)
0.61
0.94
1.95
2.93
2.99
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 −1.0 −2.0
f1 (ppm)


MeO
O
O
N
H
I

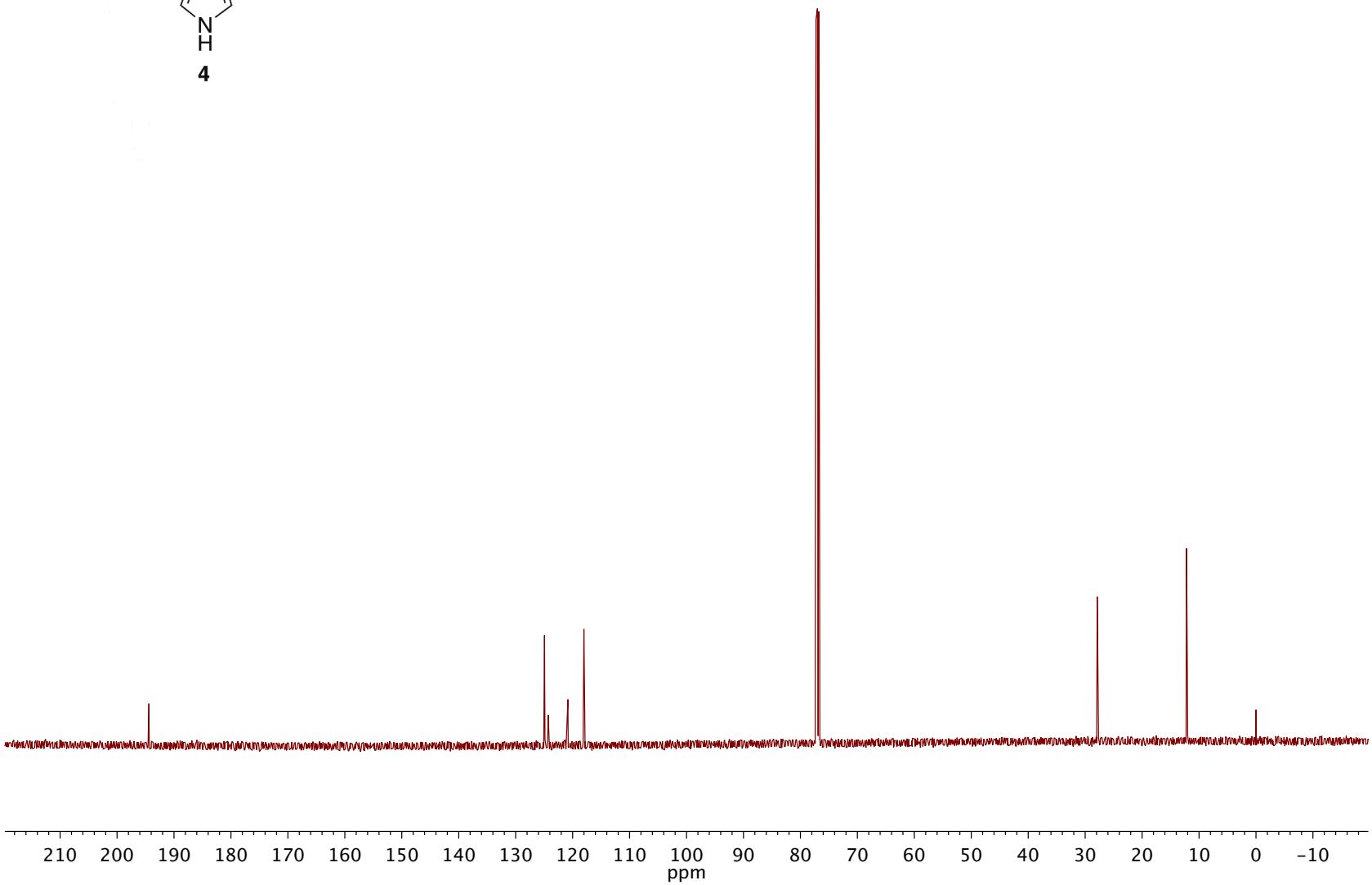
2-I

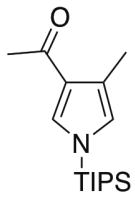

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


O
N
H
4
1.25
1.05
1.00
2.97
3.06
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
ppm

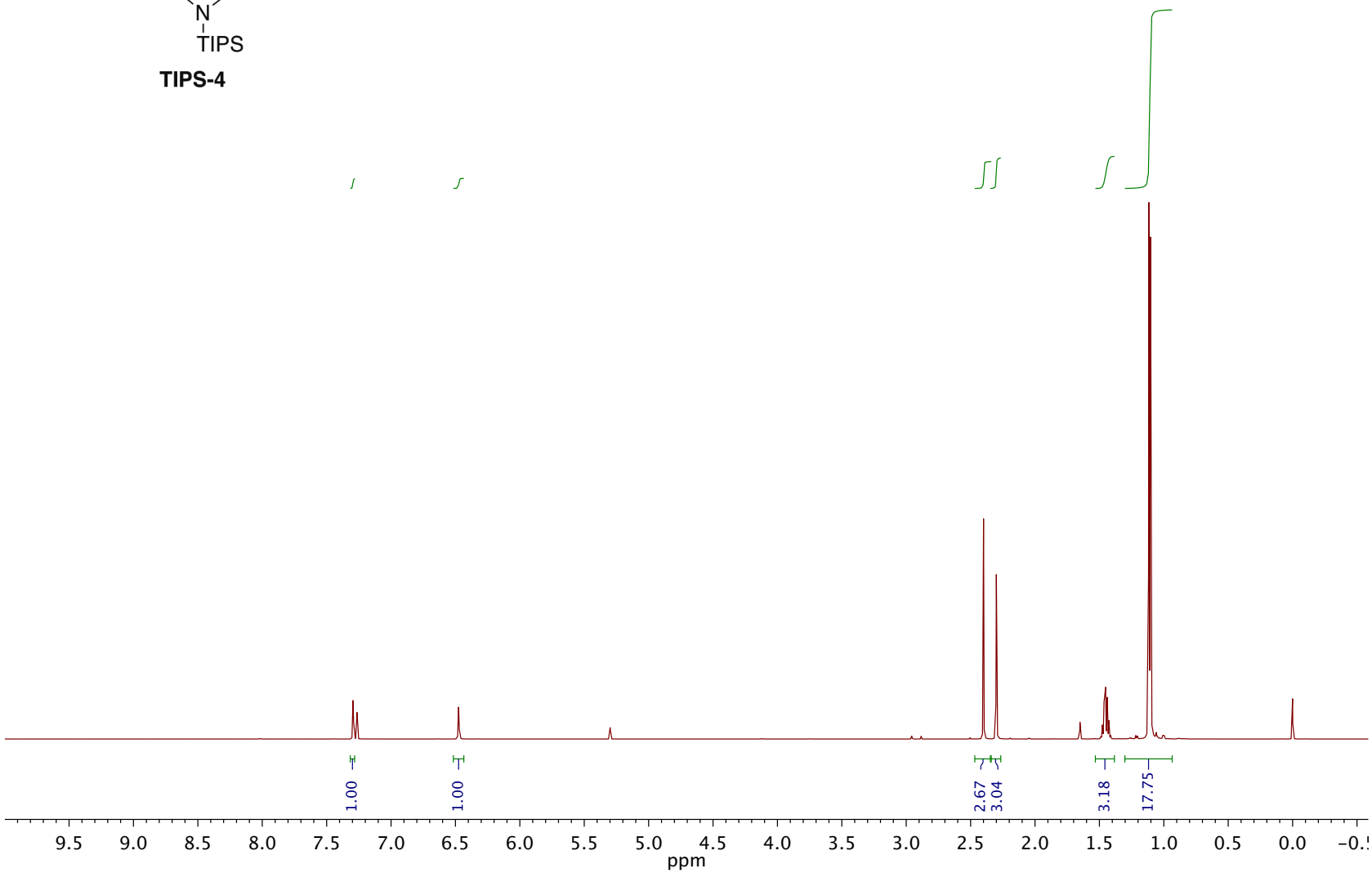


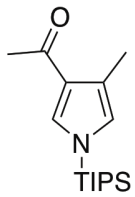
4


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
ppm

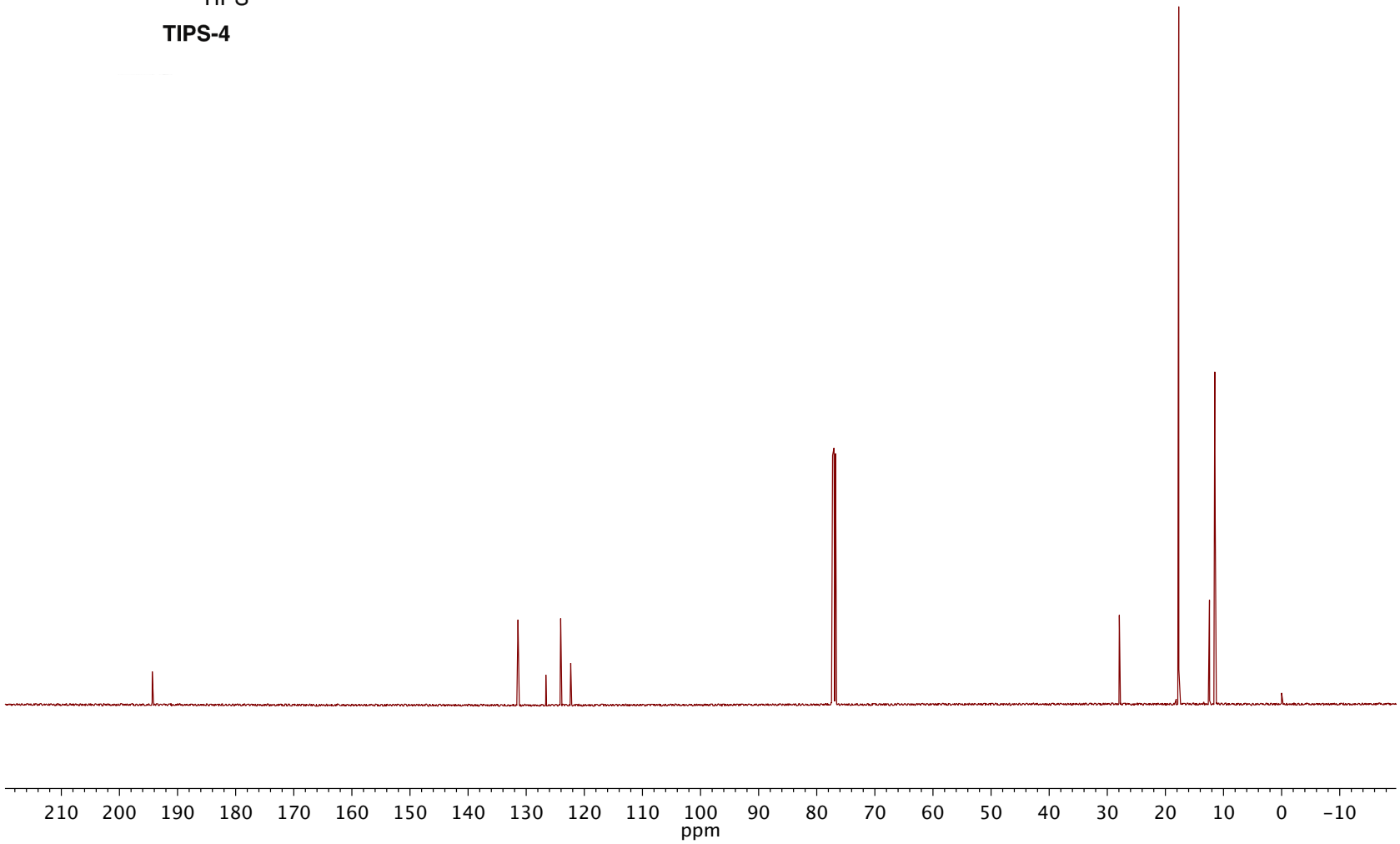

O
N
TIPS

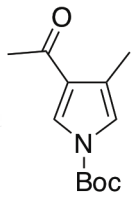
TIPS-4


1.00
1.00
2.67
3.04
3.18
17.75
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
ppm


O
N
TIPS

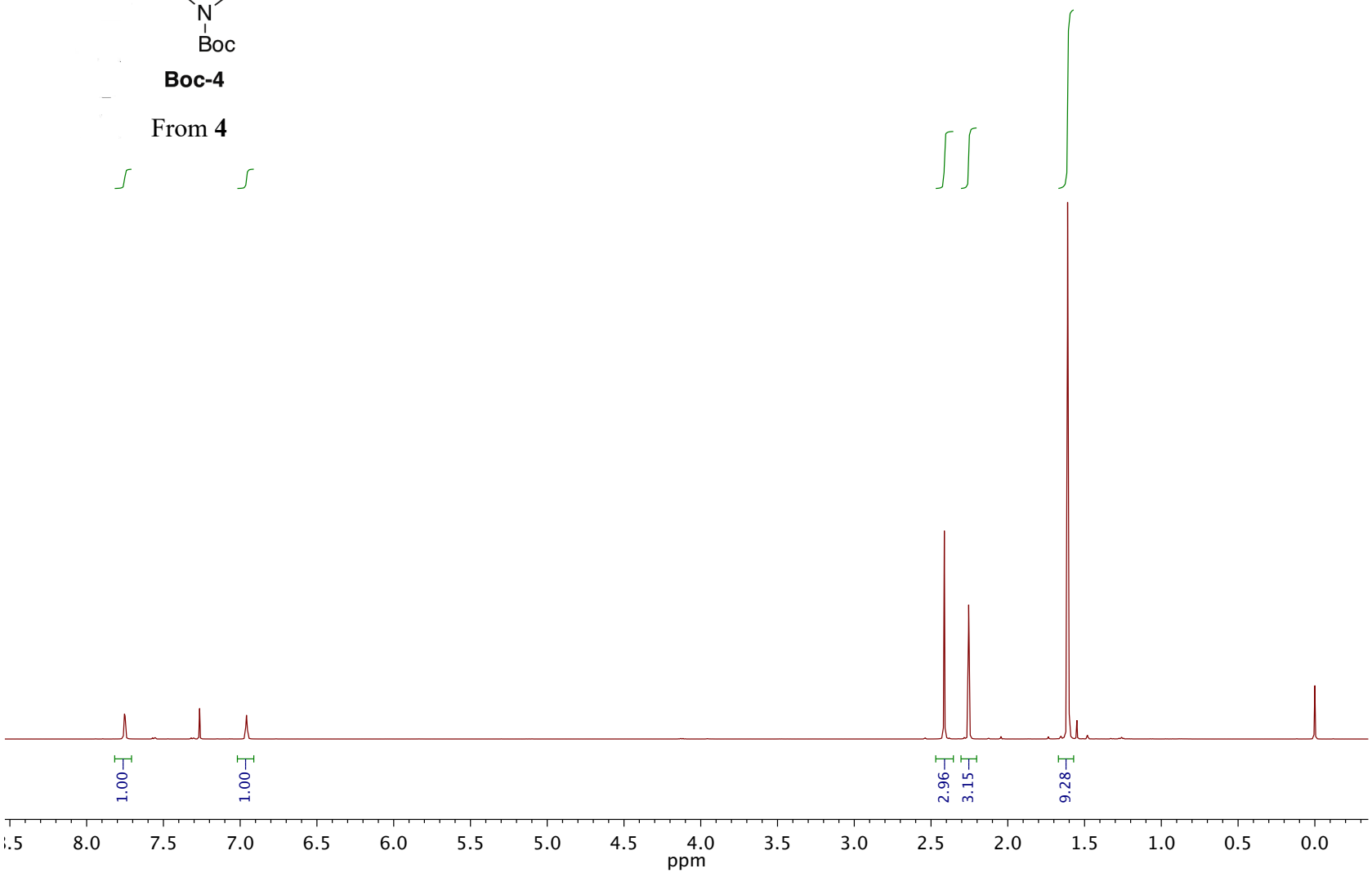
TIPS-4

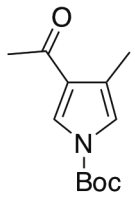

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
ppm


O
N
Boc

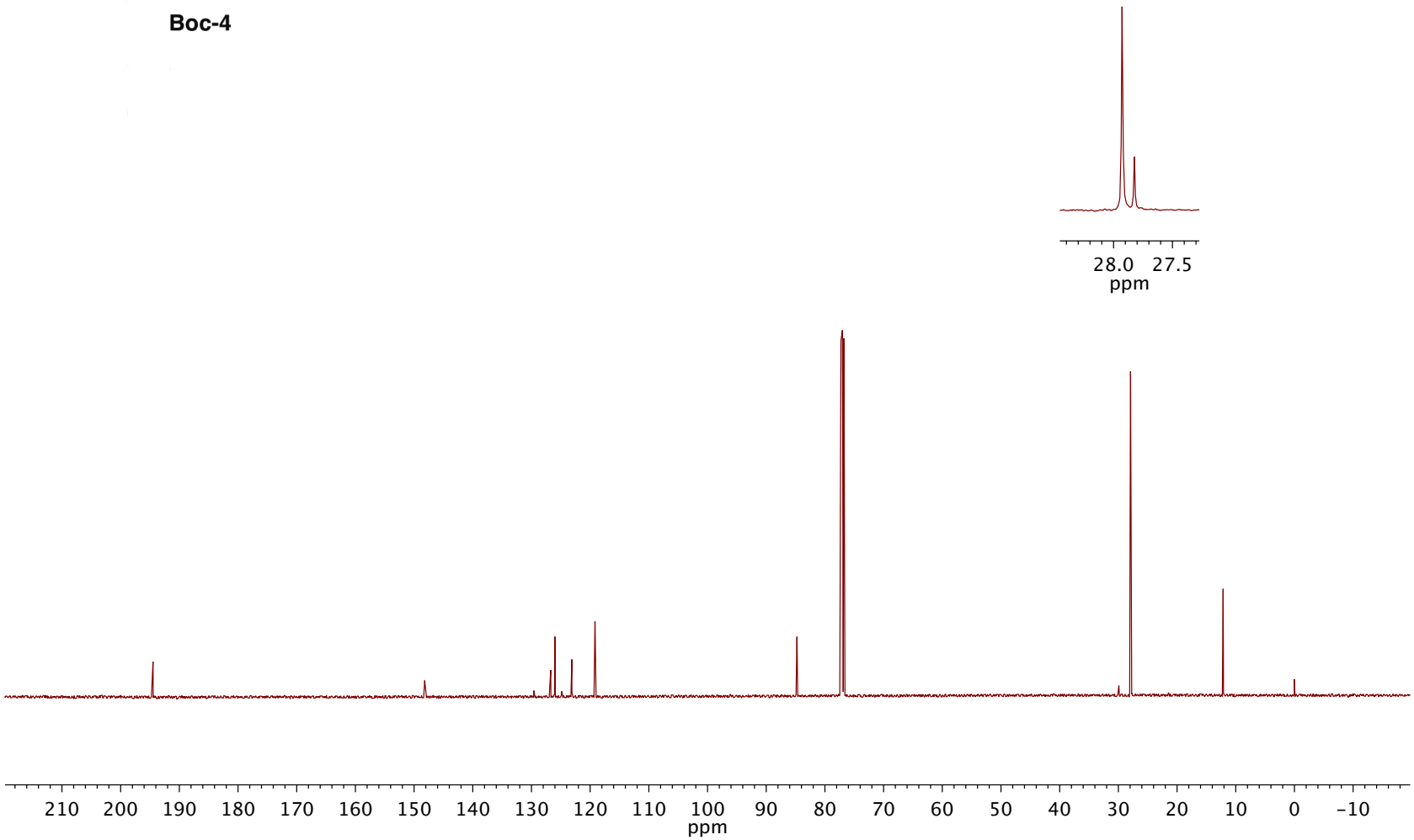
Boc-4

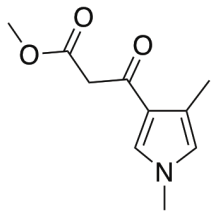
From **4**


1.00
1.00
2.96
3.15
9.28
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
ppm

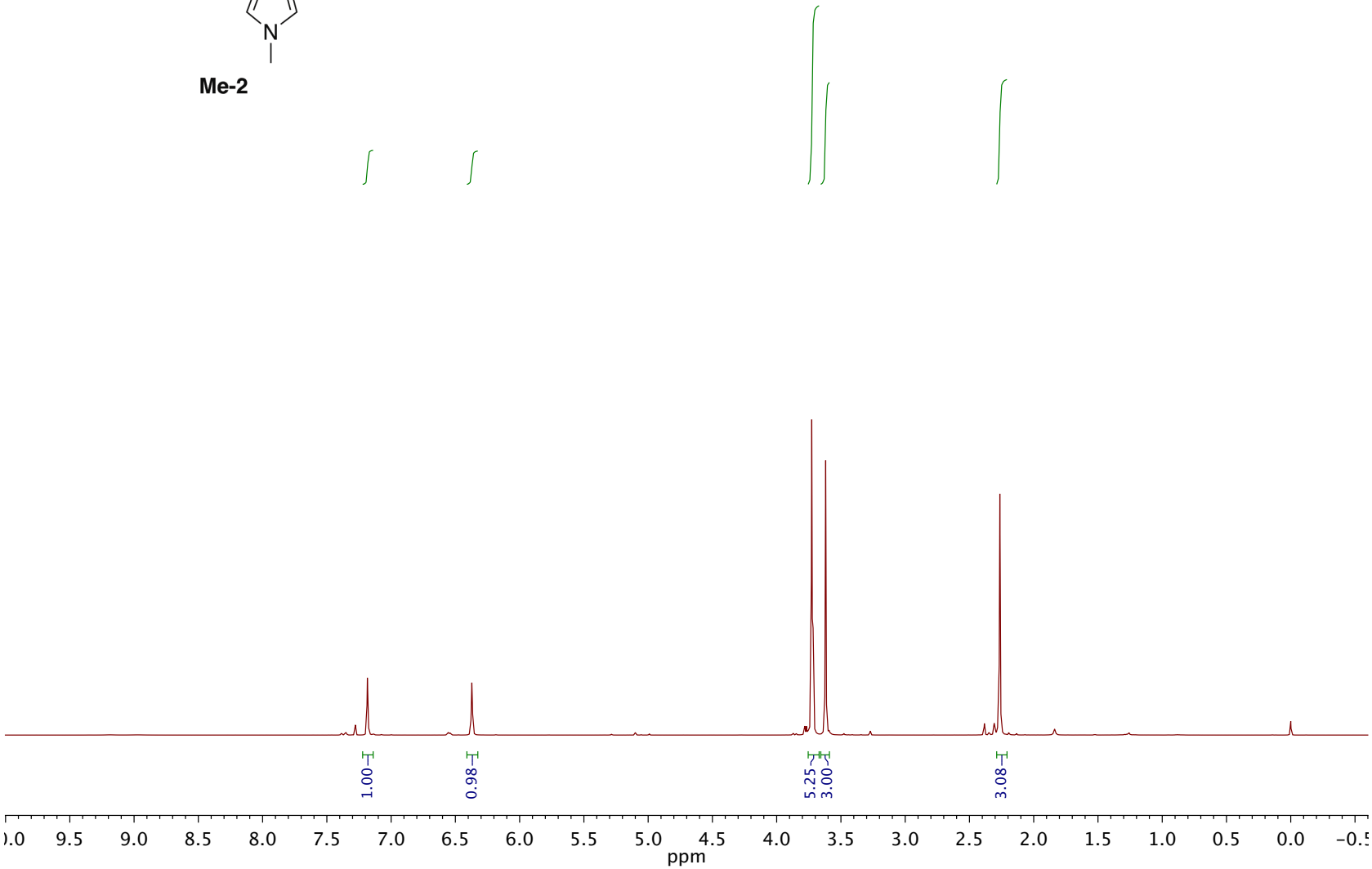

O
N
Boc

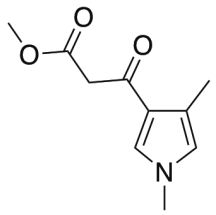
Boc-4


28.0 27.5
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
ppm

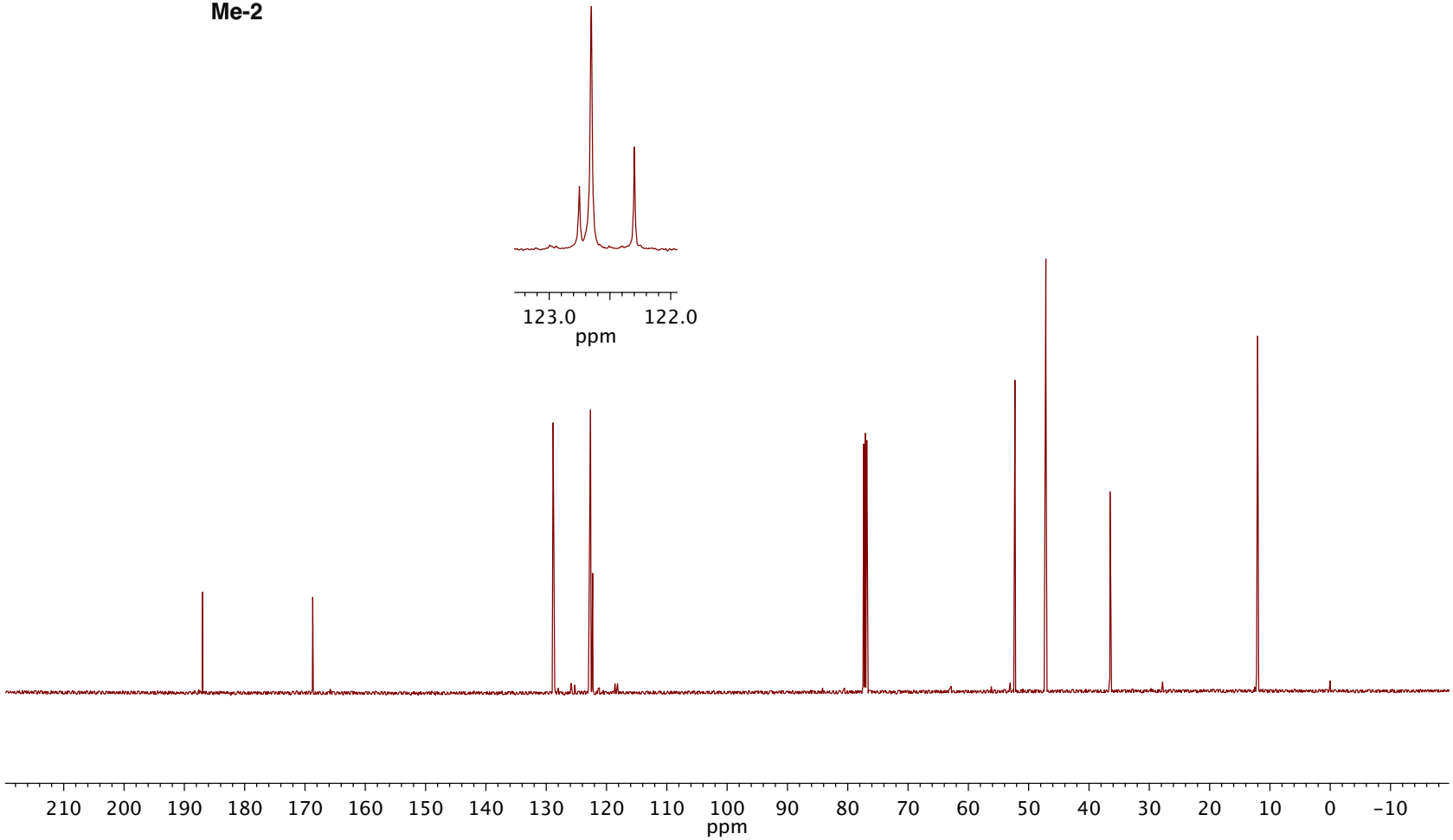


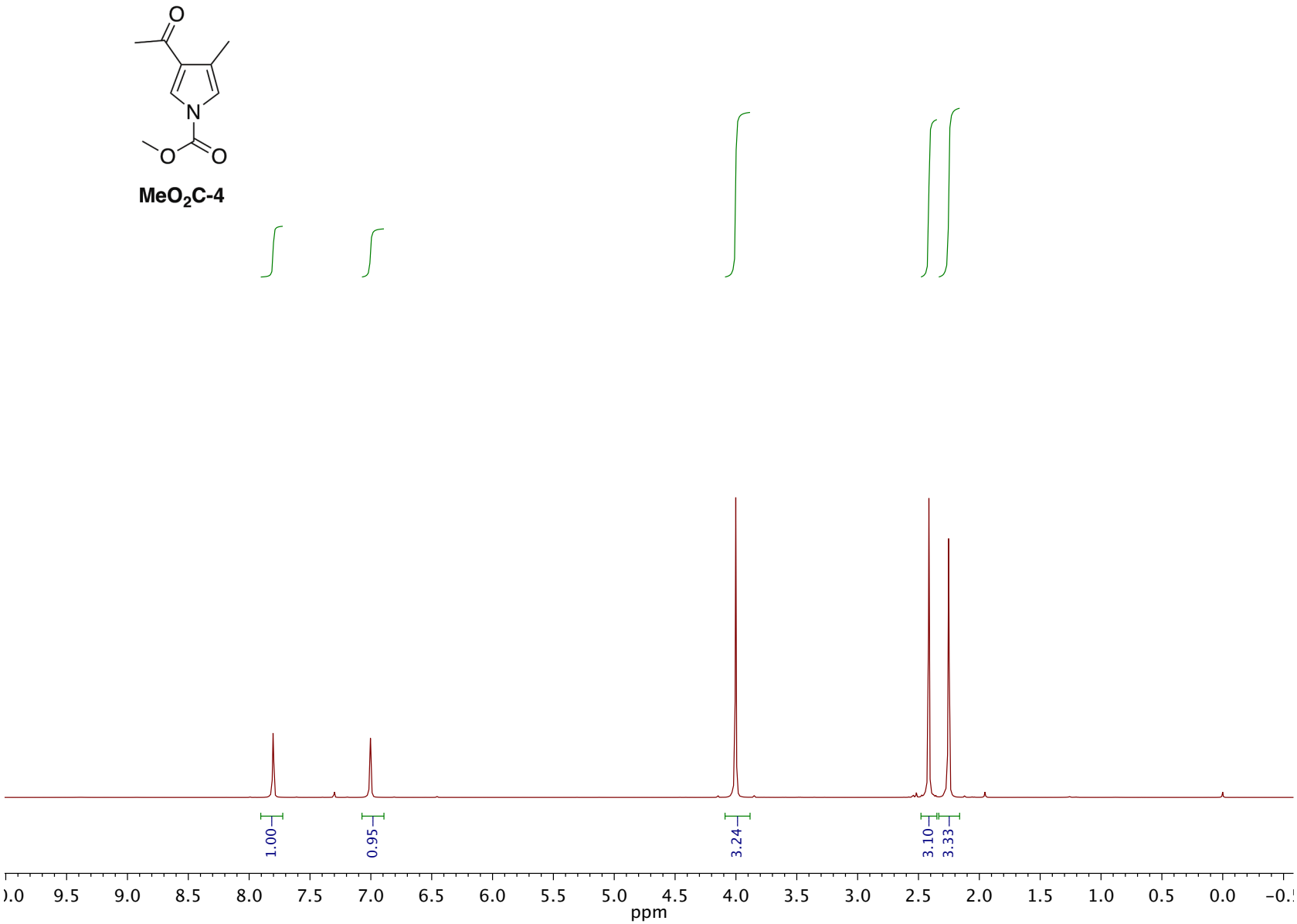
Me-2

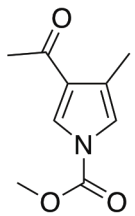

1.00
0.98
5.25
3.00
3.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm



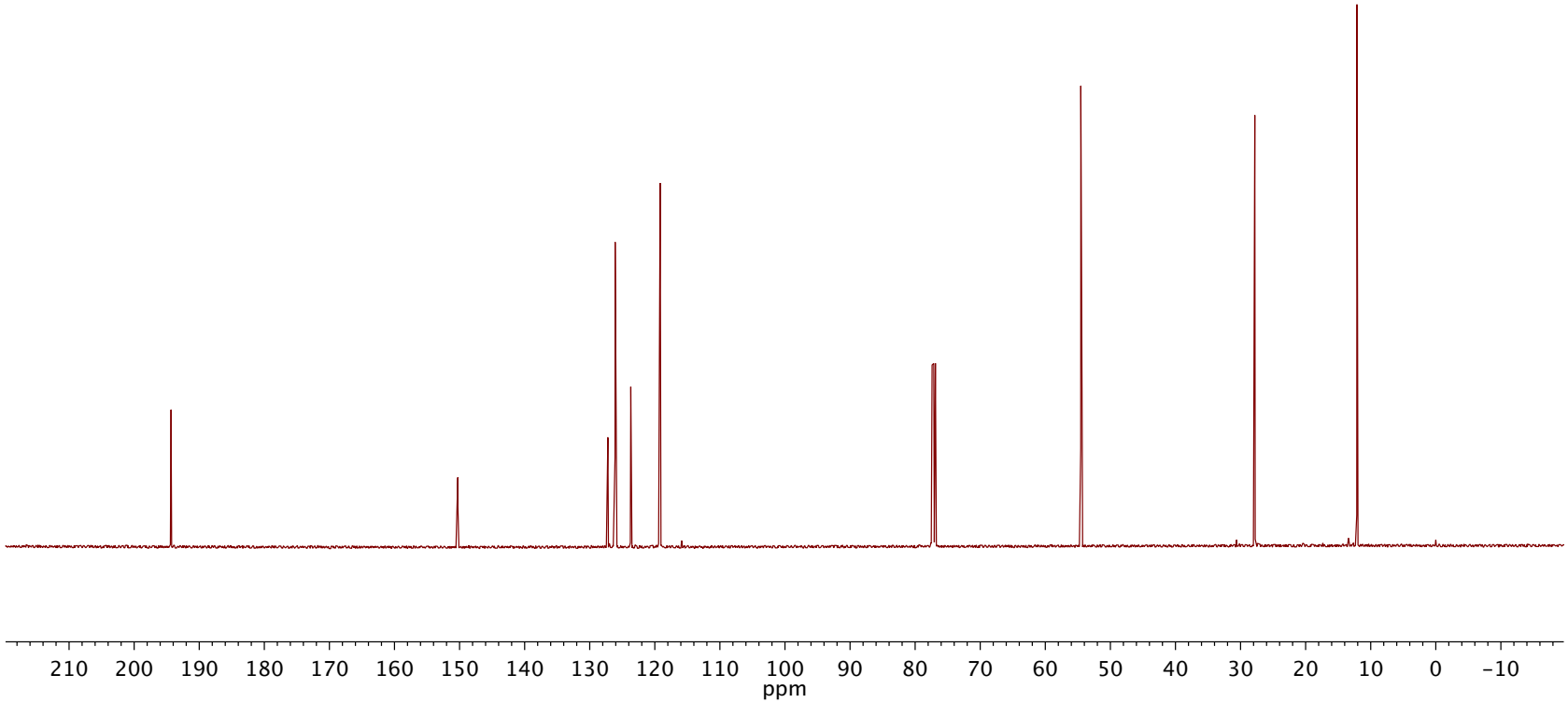
Me-2

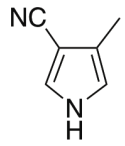

123.0
122.0
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
ppm


O
N
O
O
MeO2C-4
1.00
0.95
3.24
3.10
3.33
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

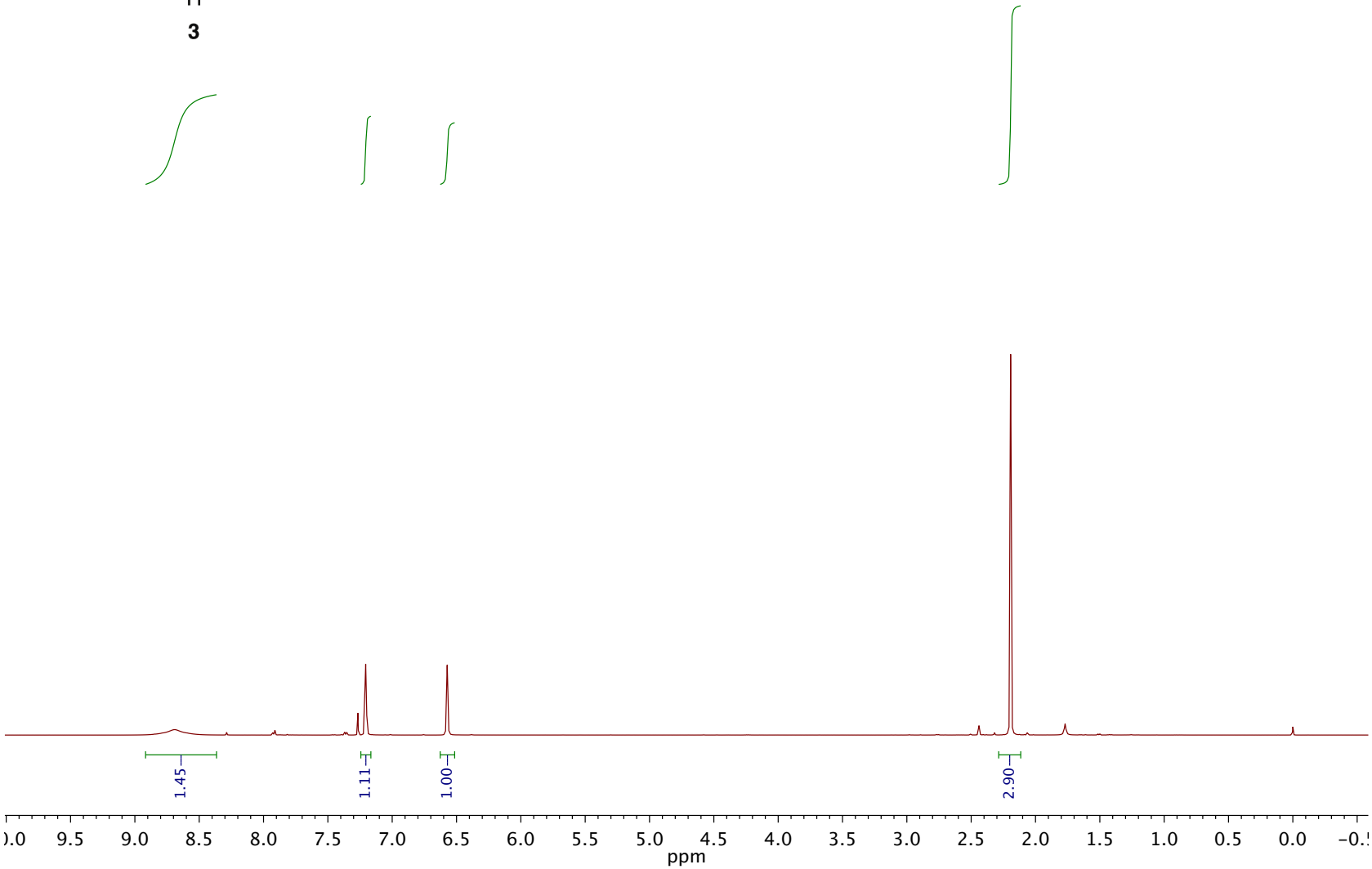


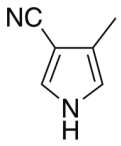
MeO_2C-4


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
ppm

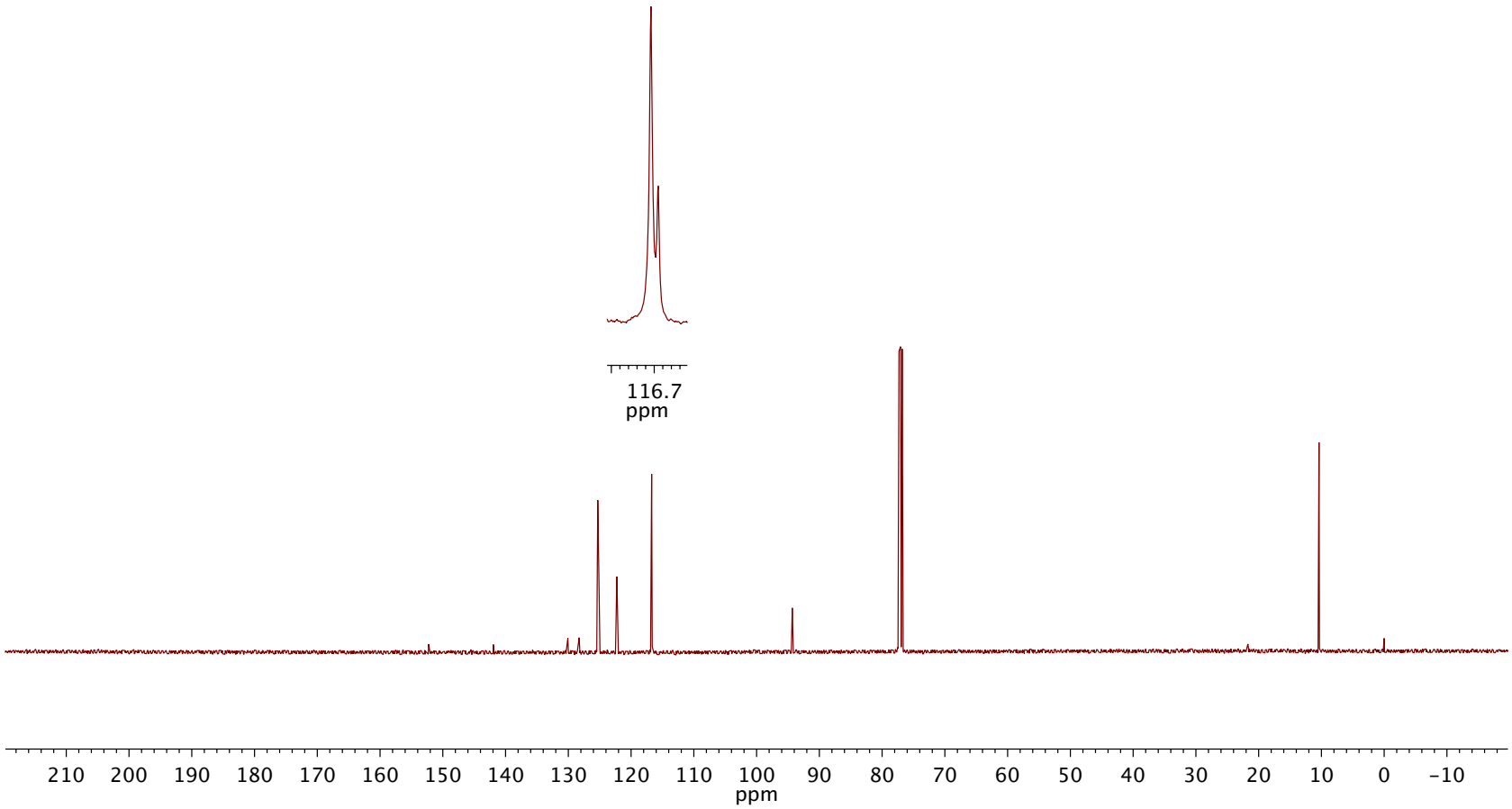

NC
N
H

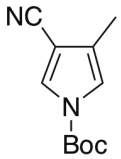
3


1.45
1.11
1.00
2.90
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
ppm


NC
N
H

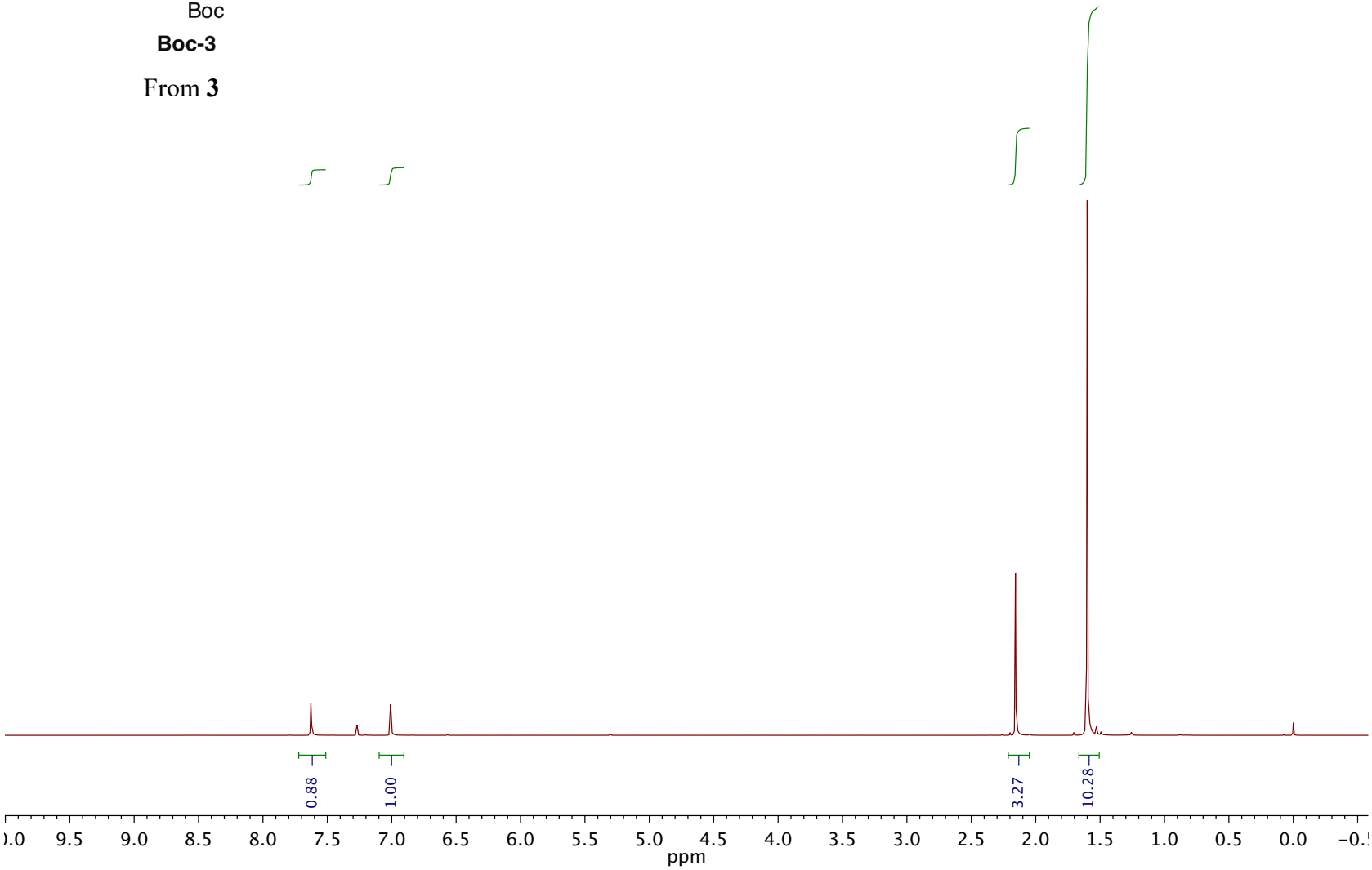
3

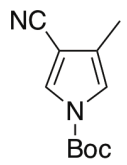

116.7
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
ppm


NC
N
Boc

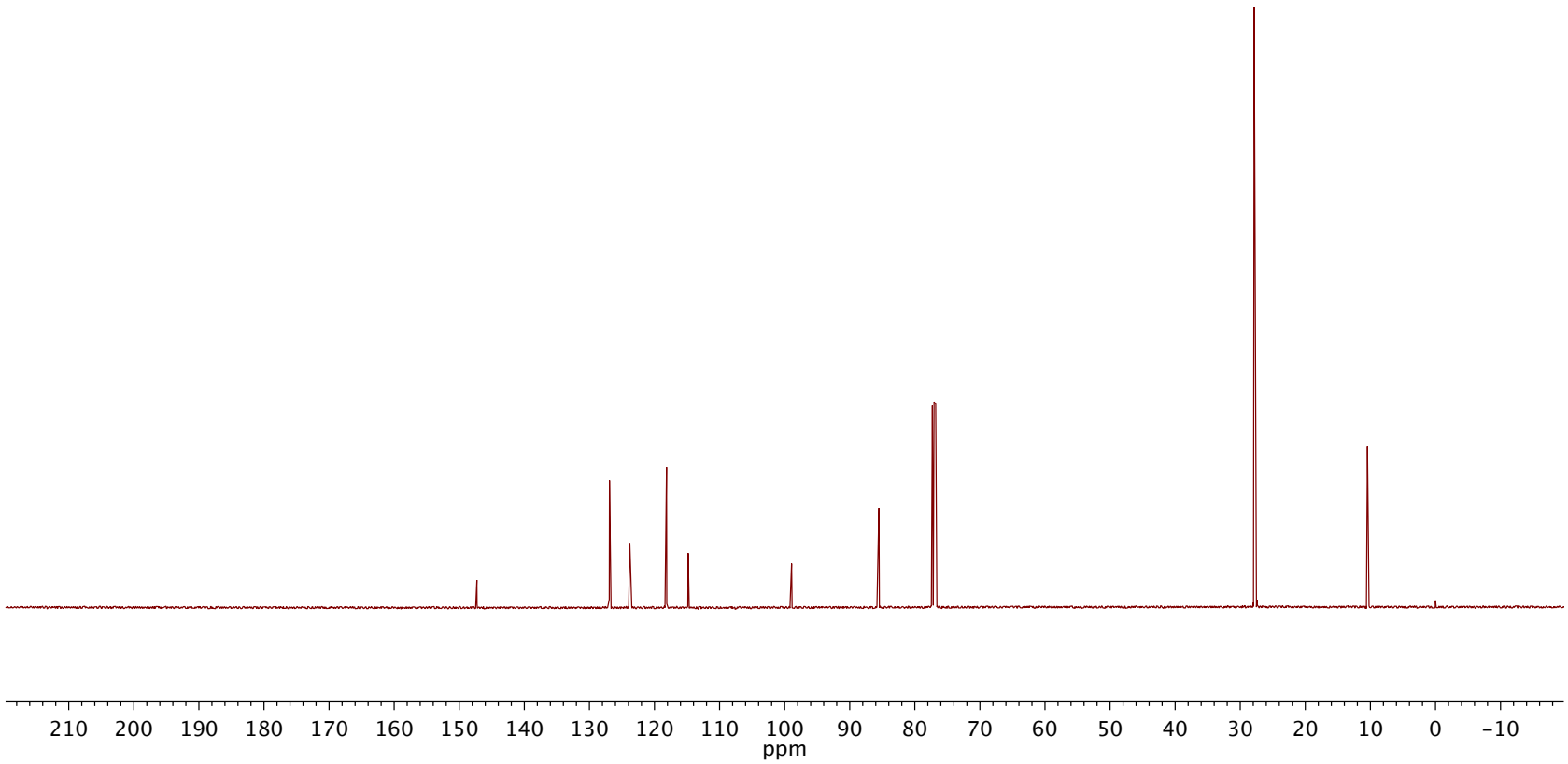
Boc-3

From **3**


0.88
1.00
3.27
10.28
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
ppm


NC
N
Boc

Boc-3


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
ppm