Electronic Supplementary Information for:

Synthesis of Model Southern Rim Structures of Photosynthetic Tetrapyrroles and Phyllobilins

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(1) Single-crystal X-ray diffraction data

Single-crystal X-ray crystallography of compound **4-Es** confirmed the position of the β-ketoester at C4 and the methyl ester at C2 (Fig. S1). Compound **4-Es** was crystallized by solvent diffusion with chloroform and *n*-hexane.

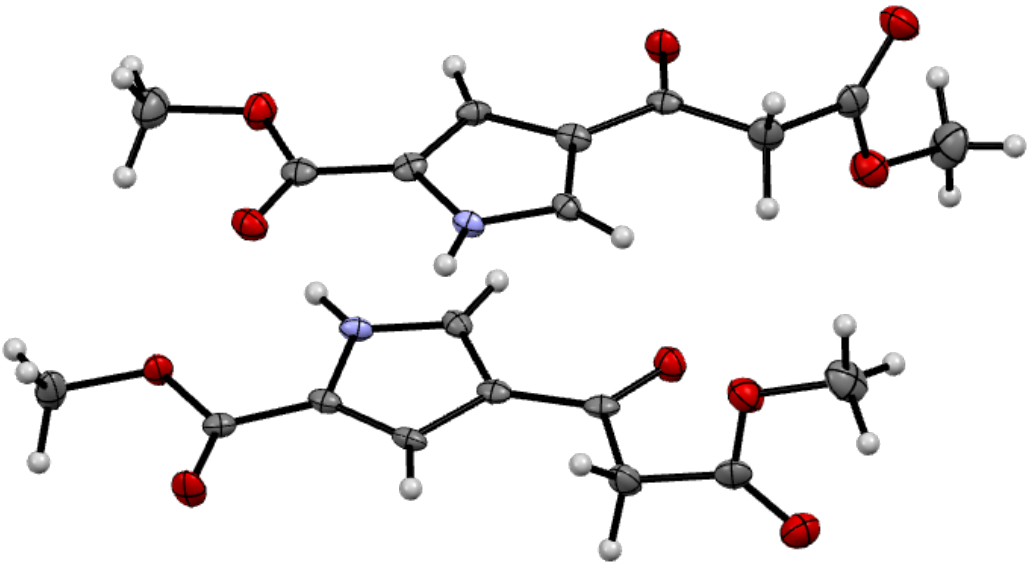


Fig. S1 ORTEP diagram of compound **4-Es** with thermal ellipsoids drawn at the 50% probability level.

Table S-1. Single-crystal X-ray structure data for **4-Es**

CCDC registry	2266091
Chemical formula	$C_{10}H_{11}NO_5$
Formula weight (g/mol)	225.20
Temperature (K)	100
Wavelength (Å)	0.71073
Crystal size (mm)	0.31 × 0.10 × 0.02
Crystal habit	Clear light colorless plate
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions, *a* (Å)	6.4414(14)
Unit cell dimensions, *b* (Å)	11.785(3)
Unit cell dimensions, *c* (Å)	13.959(3)
α, deg	92.212(7)
β, deg	96.911(8)
γ, deg	94.926(8)
Volume ($Å^3$)	1046.8(4)
Z	4
Density (calculated) (g/cm^3)	1.429
Absorption coefficient (mm^{-1})	0.116
F(000)	472.0
Theta range for data collection, deg	2.3 to 26.4
Index ranges	-8<=h<=8, -14<=k<=14, -17<=l<=17
Reflections collected	4249
Independent reflections	2731 [R(int) = 0.067]
R_1	0.0749
wR_2	0.1258
R_1 (all data)	0.1156
wR_2 (all data)	0.1391
Largest diff. peak and hole ($eÅ^{-3}$)	0.28 and -0.32
R.M.S. deviation from mean ($eÅ^{-3}$)	0.069

Table S-2. Single-crystal X-ray structure data for **6-HH**

CCDC registry	2266093
Chemical formula	$C_{13}H_{12}N_2O_3$
Formula weight (g/mol)	244.25
Temperature (K)	110(2)
Wavelength (Å)	1.54178
Crystal size (mm)	0.098 × 0.171 × 0.283
Crystal habit	Colorless block
Crystal system	monoclinic
Space group	P 2_1/c
Unit cell dimensions, *a* (Å)	11.2578(2)
Unit cell dimensions, *b* (Å)	6.8693(2)
Unit cell dimensions, *c* (Å)	14.7437(3)
α, deg	90
β, deg	98.4410(10)
γ, deg	90
Volume (Å^3)	1127.83(4)
Z	4
Density (calculated) (g/cm^3)	1.438
Absorption coefficient (mm^{-1})	0.863
F(000)	512
Theta range for data collection, deg	3.97 to 79.87
Index ranges	-14<=h<=14, -8<=k<=8, -18<=l<=18
Reflections collected	27604
Independent reflections	2446 [R(int) = 0.0243]
R_1	0.0338
wR_2	0.0882
R_1 (all data)	0.0342
wR_2 (all data)	0.0825
Largest diff. peak and hole (eÅ^{-3})	0.290 and -0.256
R.M.S. deviation from mean (eÅ^{-3})	0.049

Table S-3. Single-crystal X-ray structure data for **7** (5*R*,3^2*S* isomer)

CCDC registry	2266094
Chemical formula	$C_{15}H_{11}Cl_3N_2O_4$
Formula weight (g/mol)	389.61
Temperature (K)	100.0
Wavelength (Å)	0.71073
Crystal size (mm)	0.203 × 0.186 × 0.022
Crystal habit	Clear light colorless plate
Crystal system	monoclinic
Space group	$P2_1$
Unit cell dimensions, *a* (Å)	6.6066(2)
Unit cell dimensions, *b* (Å)	12.8897(5)
Unit cell dimensions, *c* (Å)	9.5387(4)
α, deg	90
β, deg	97.4220(10)
γ, deg	90
Volume (Å^3)	805.48(5)
Z	2
Density (calculated) (g/cm^3)	1.606
Absorption coefficient (mm^{-1})	0.592
F(000)	396.0
Theta range for data collection, deg	4.306 to 53.432
Index ranges	-7<=h<=8, -16<=k<=16, -12<=l<=12
Reflections collected	11749
Independent reflections	3398 [R_{int} = 0.0329, R_{sigma} = 0.0327]
R_1	0.0254
wR_2	0.0550
R_1 (all data)	0.0286
wR_2 (all data)	0.0566
Largest diff. peak and hole (eÅ^{-3})	0.20 and -0.18
R.M.S. deviation from mean (eÅ^{-3})	0.0327

Table S-4. Single-crystal X-ray structure data for **7** (5*S*,3²*R* isomer)

CCDC registry	2266097
Chemical formula	$C_{15}H_{11}Cl_3N_2O_4$
Formula weight (g/mol)	389.61
Temperature (K)	100.0
Wavelength (Å)	0.71073
Crystal size (mm)	0.22 × 0.072 × 0.035
Crystal habit	Clear light colorless plate
Crystal system	monoclinic
Space group	$P2_1$
Unit cell dimensions, *a* (Å)	6.5963(5)
Unit cell dimensions, *b* (Å)	12.8953(9)
Unit cell dimensions, *c* (Å)	9.5356(7)
α, deg	90
β, deg	97.461(2)
γ, deg	90
Volume (Å^3)	804.24(10)
Z	2
Density (calculated) (g/cm^3)	1.609
Absorption coefficient (mm^{-1})	0.592
F(000)	396.0
Theta range for data collection, deg	5.342 to 52.742
Index ranges	–8<=h<=8, –15<=k<=16, –10<=l<=11
Reflections collected	12227
Independent reflections	3253 [R_{int} = 0.0469, R_{sigma} = 0.0451]
R_1	0.0357
wR_2	0.0772
R_1 (all data)	0.0405
wR_2 (all data)	0.0796
Largest diff. peak and hole (eÅ^{-3})	0.26 and -0.25
R.M.S. deviation from mean (eÅ^{-3})	0.0451

2. Diastereomers confirmation via COSY for Southern rim compounds

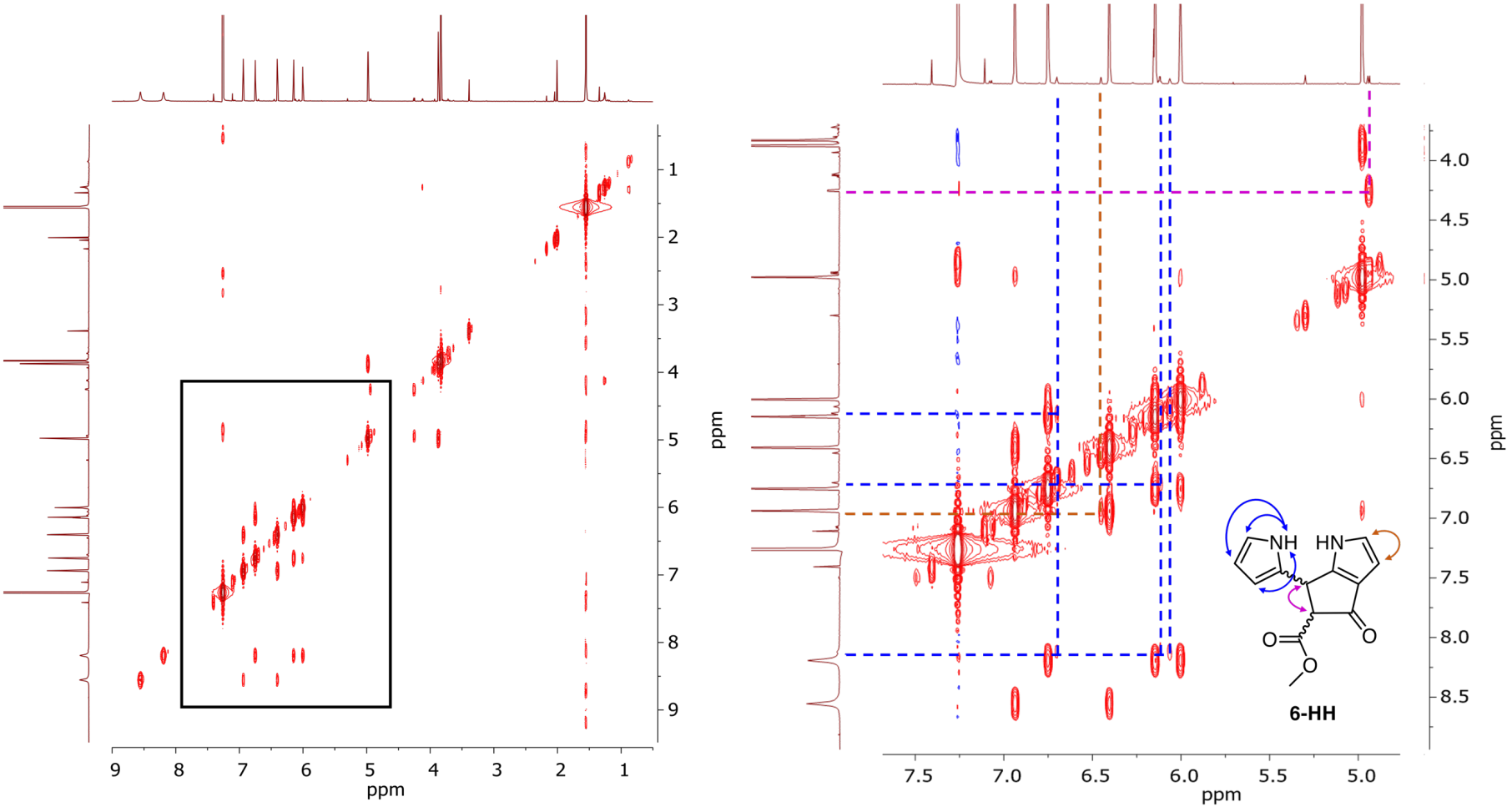


Fig. S2 Full COSY spectrum (700 MHz, $CDCl_3$) of **6-HH** (left) and enlarged region showing the correlations confirming the presence of a small quantity of the *cis* isomer (right).

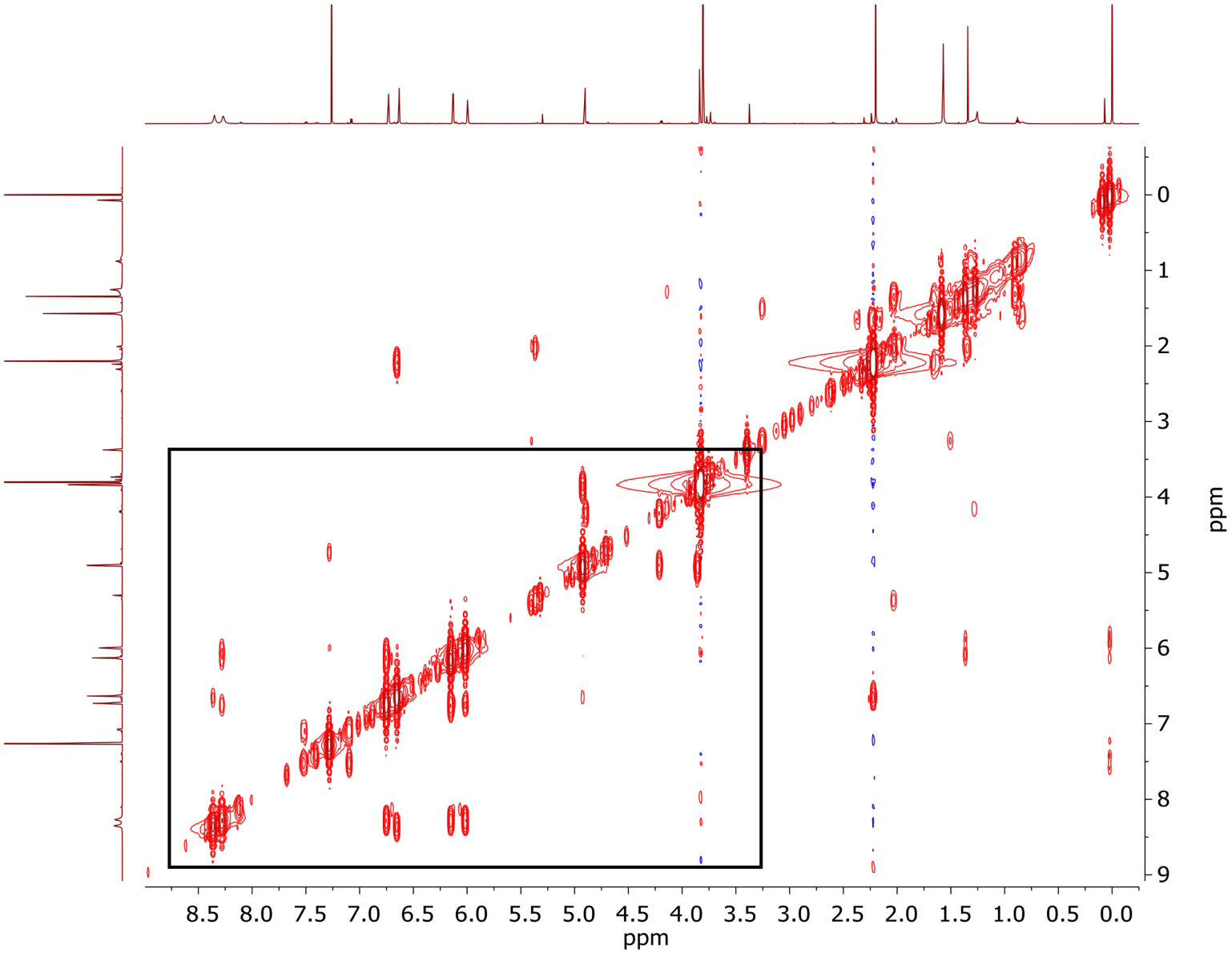


Fig. S3 Full COSY spectrum (700 MHz, $CDCl_3$) of **6-HMe** .

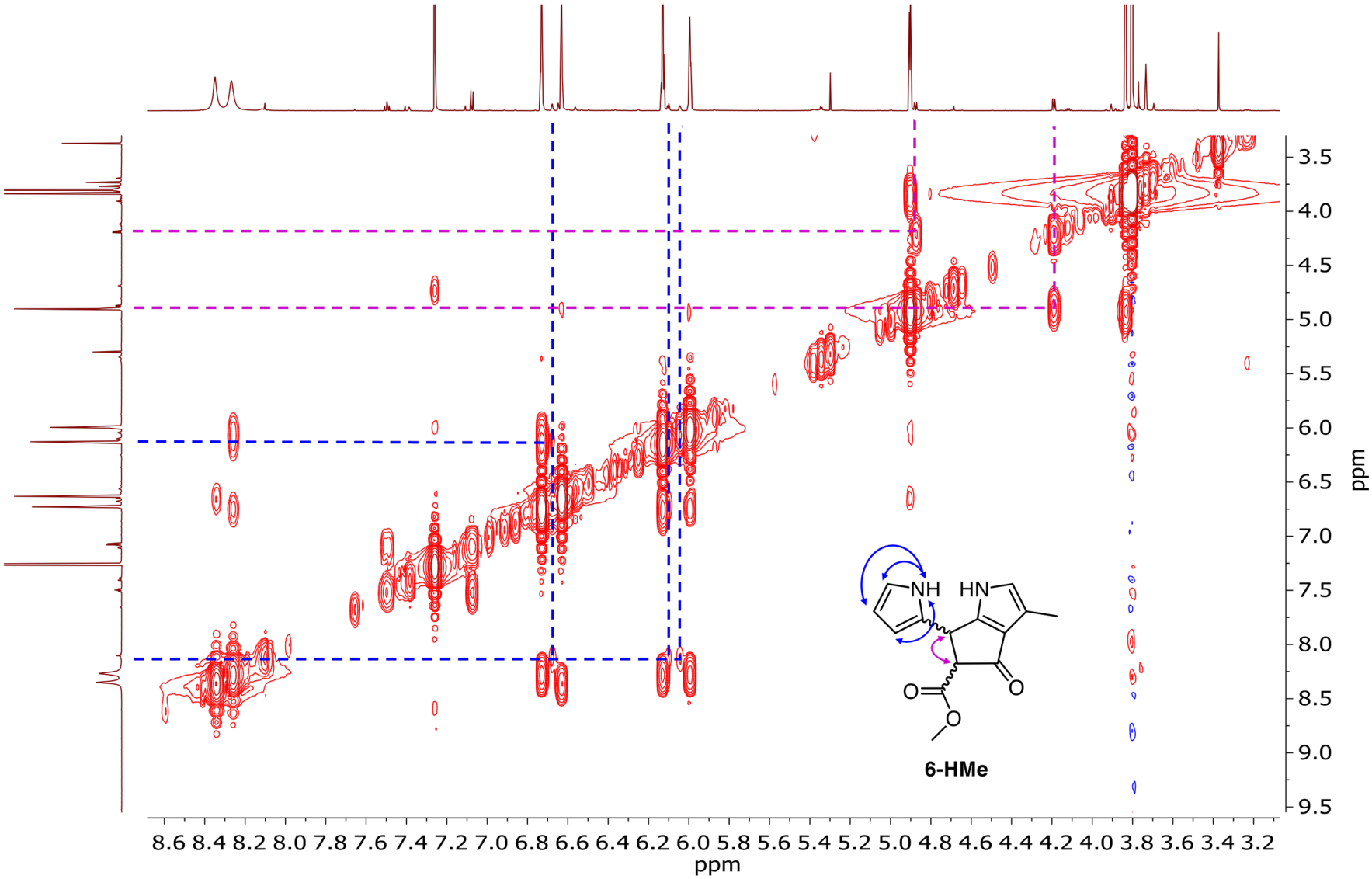


Fig. S4 An enlarged region of COSY spectrum (700 MHz, $CDCl_3$) of **6-HMe** showing the correlations confirming the presence of a small quantity of the *cis* isomer.

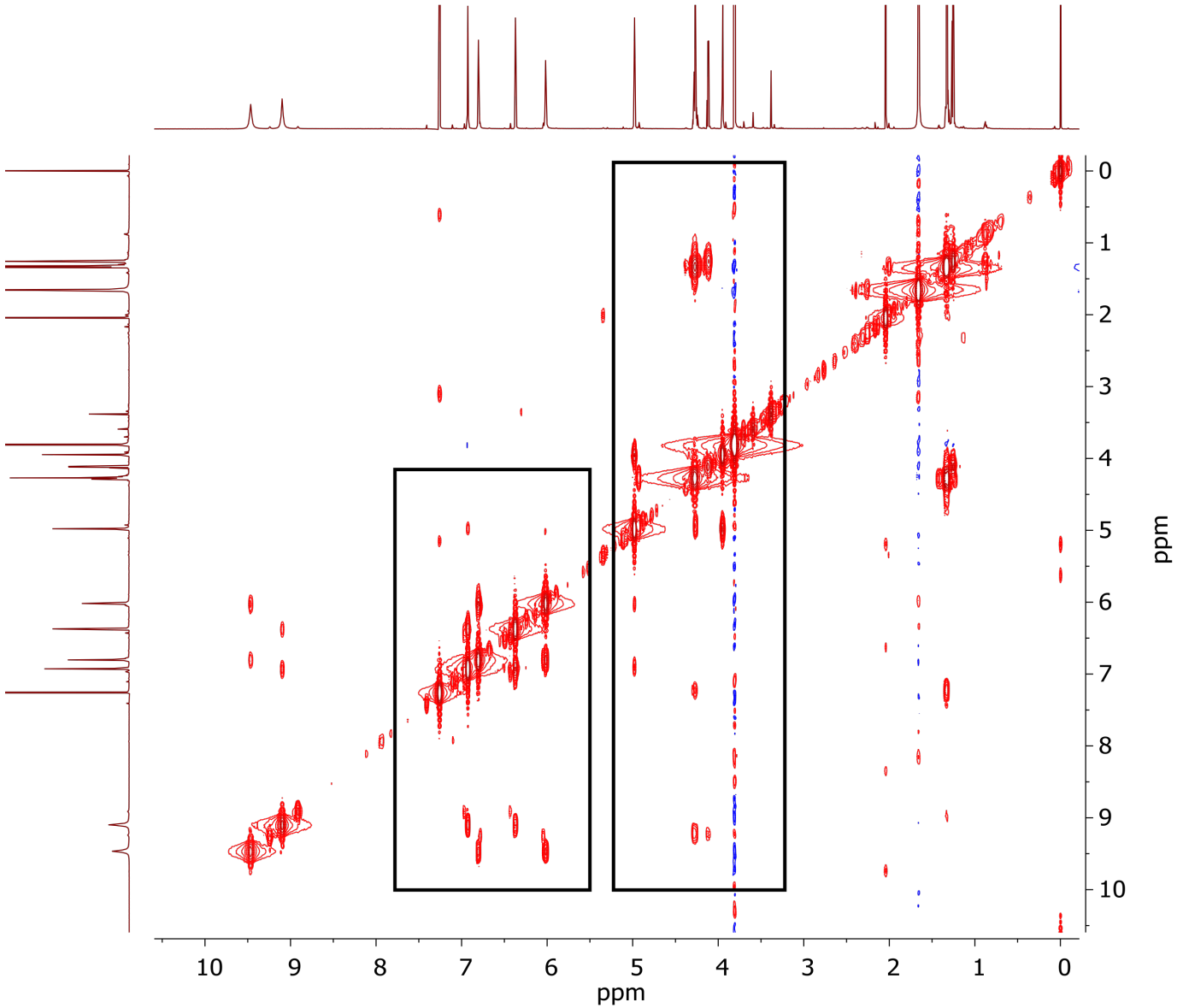


Fig. S5 Full COSY spectrum (700 MHz, $CDCl_3$) of **6-EsH**.

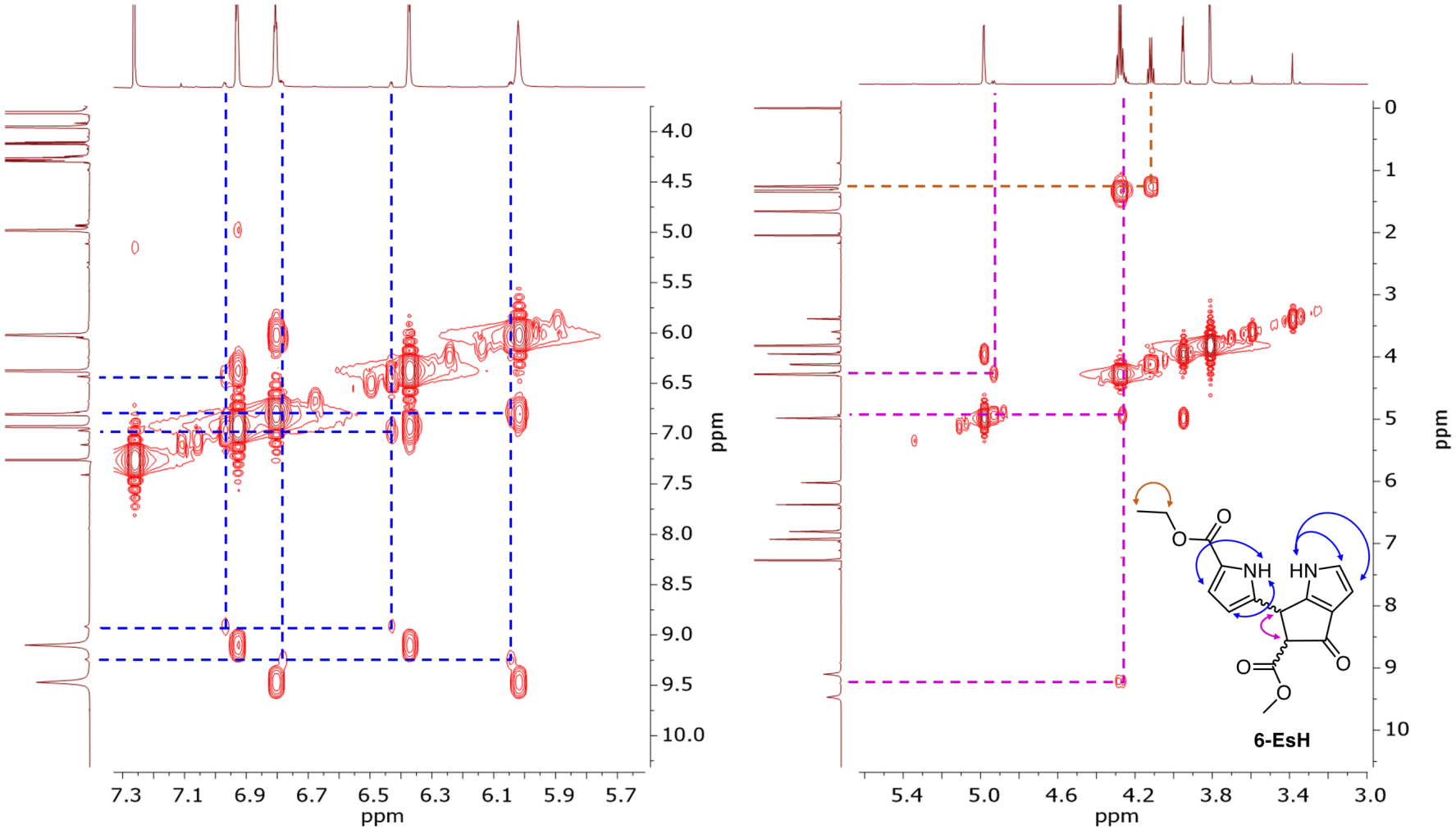
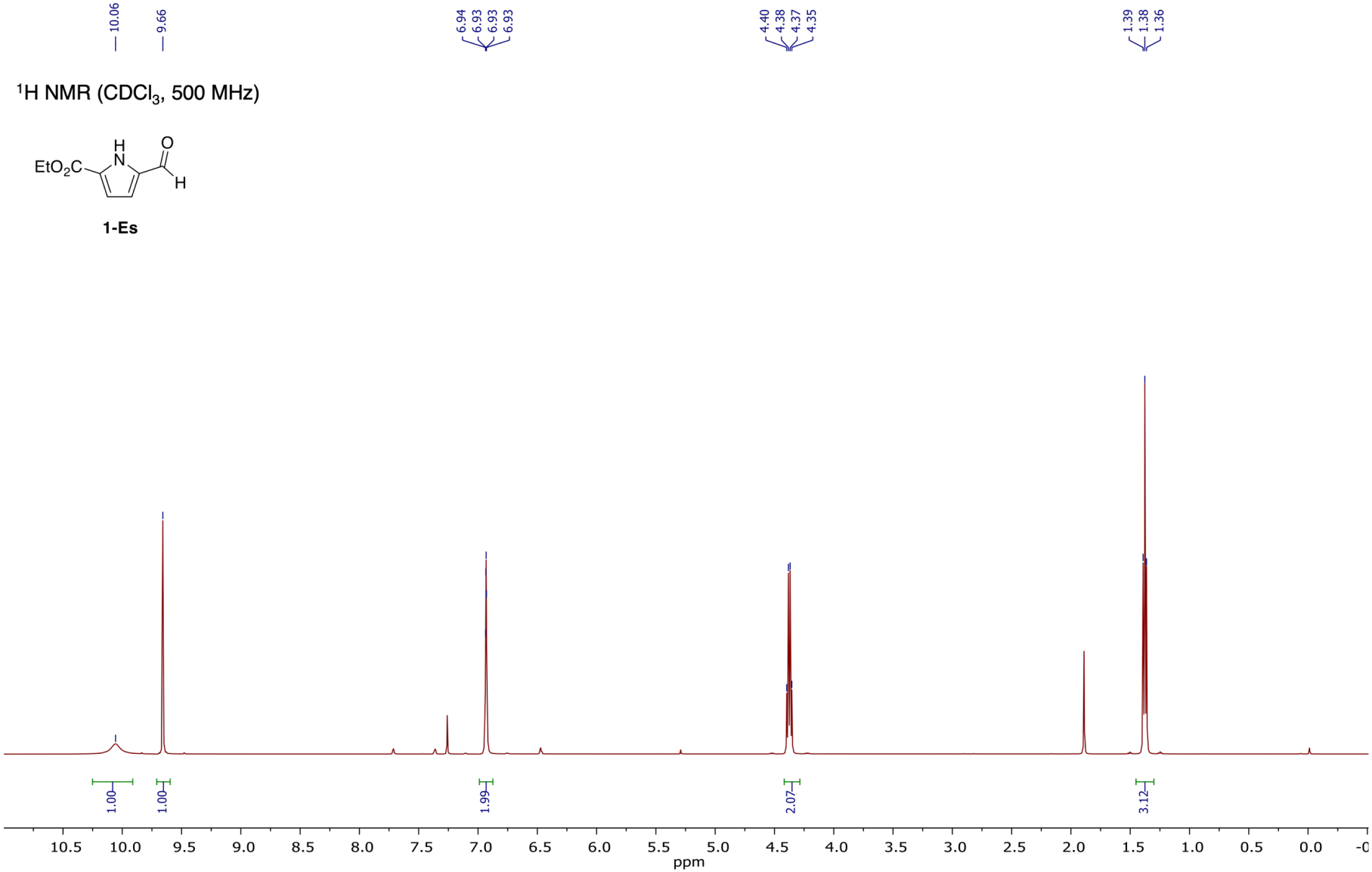


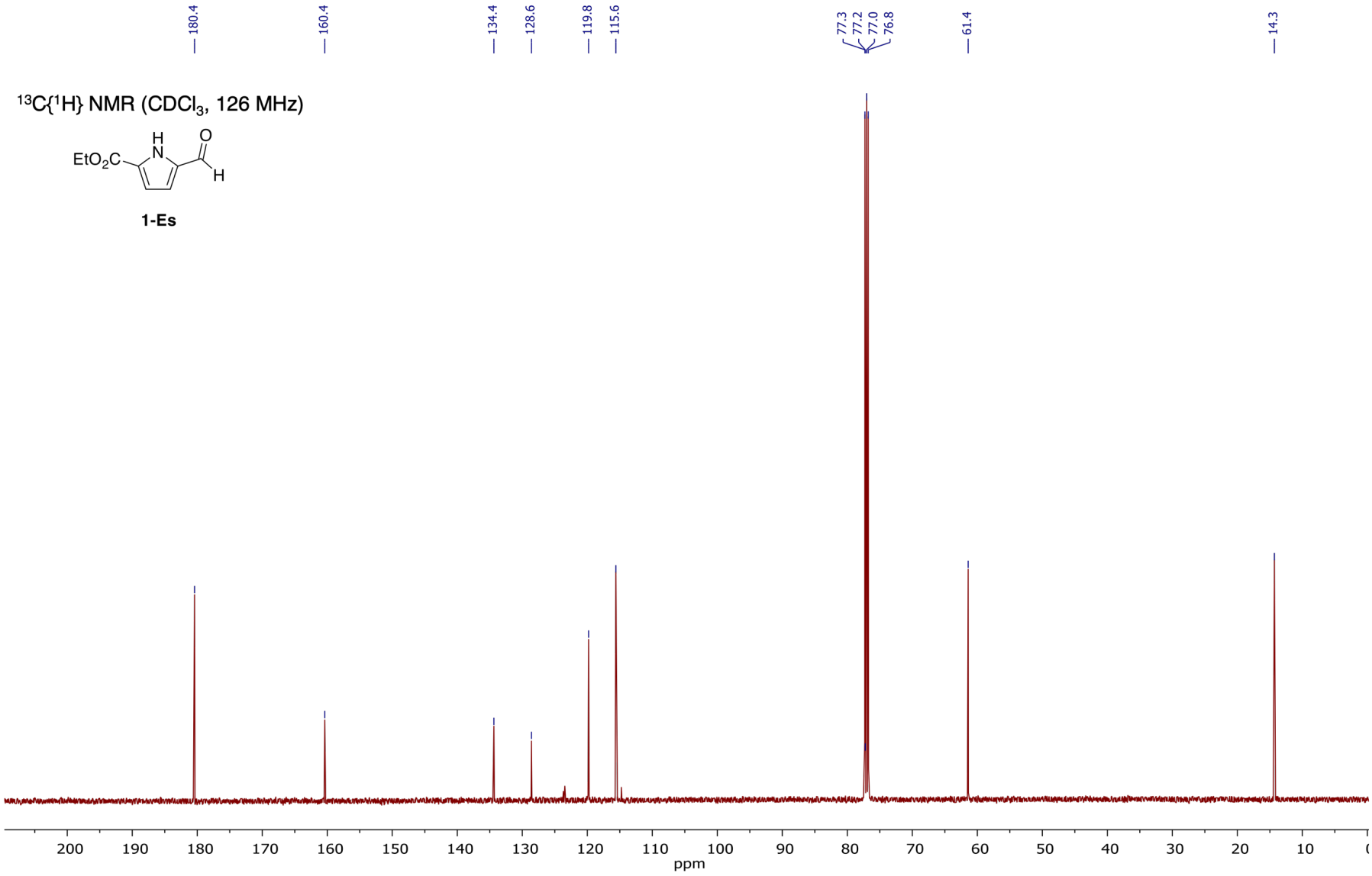
Fig. S6 An enlarged region from COSY spectrum (700 MHz, $CDCl_3$) of **6-EsH** showing the correlations confirming the presence of a small quantity of the *cis* isomer.

3. NMR spectra

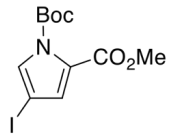
^{1}H NMR ($CDCl_3$, 500 MHz)

1-Es

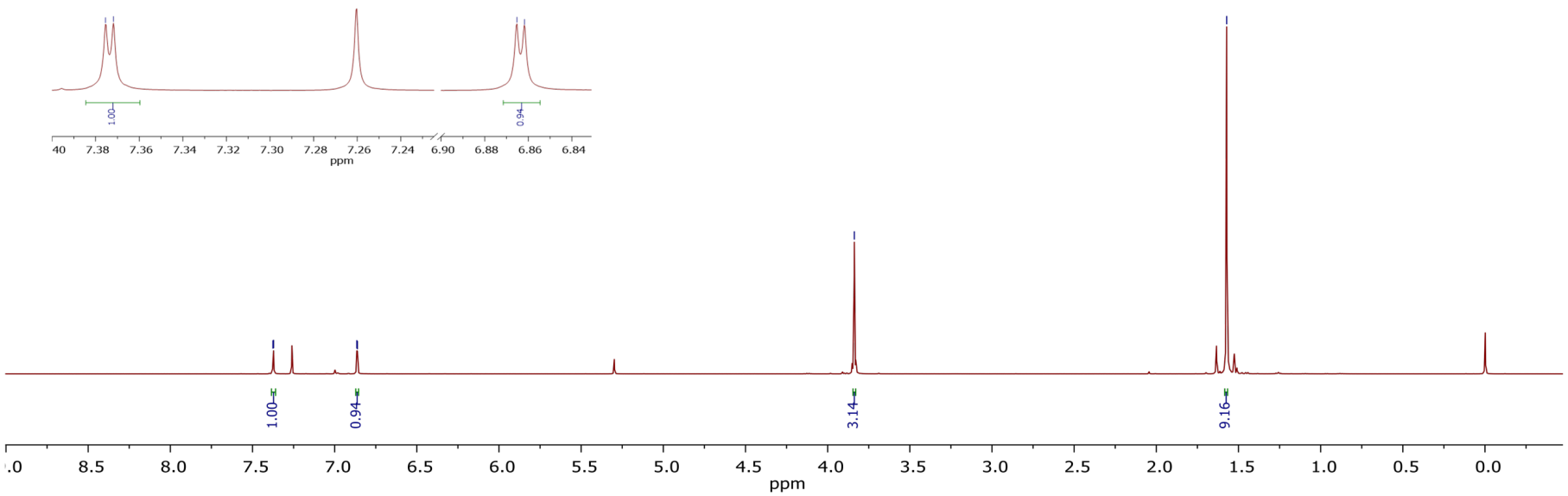



180.4
160.4
134.4
128.6
119.8
115.6
77.3
77.2
77.0
76.8
61.4
14.3
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz)
EtO_2C
H
N
O
H
1-Es
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

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

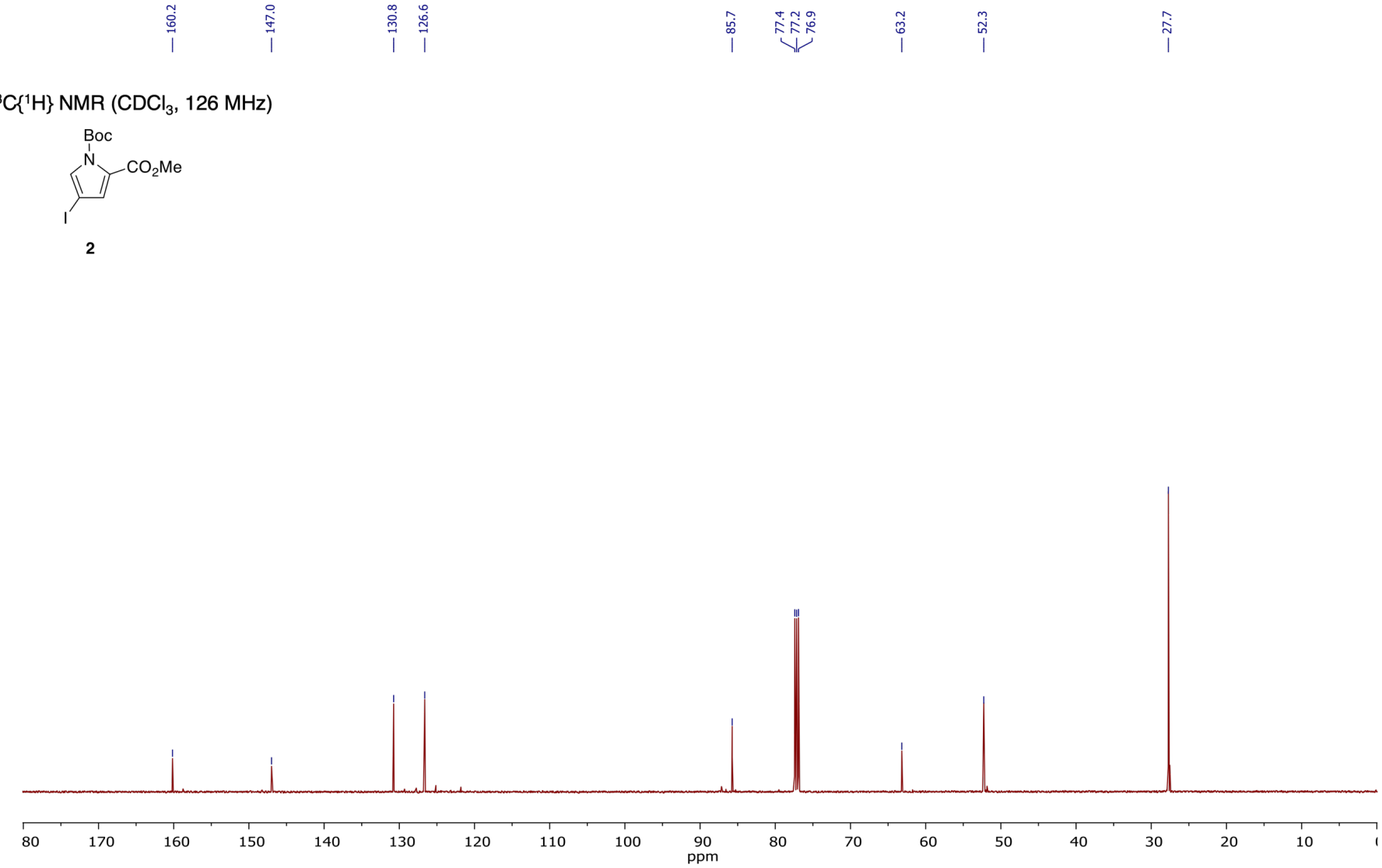


2



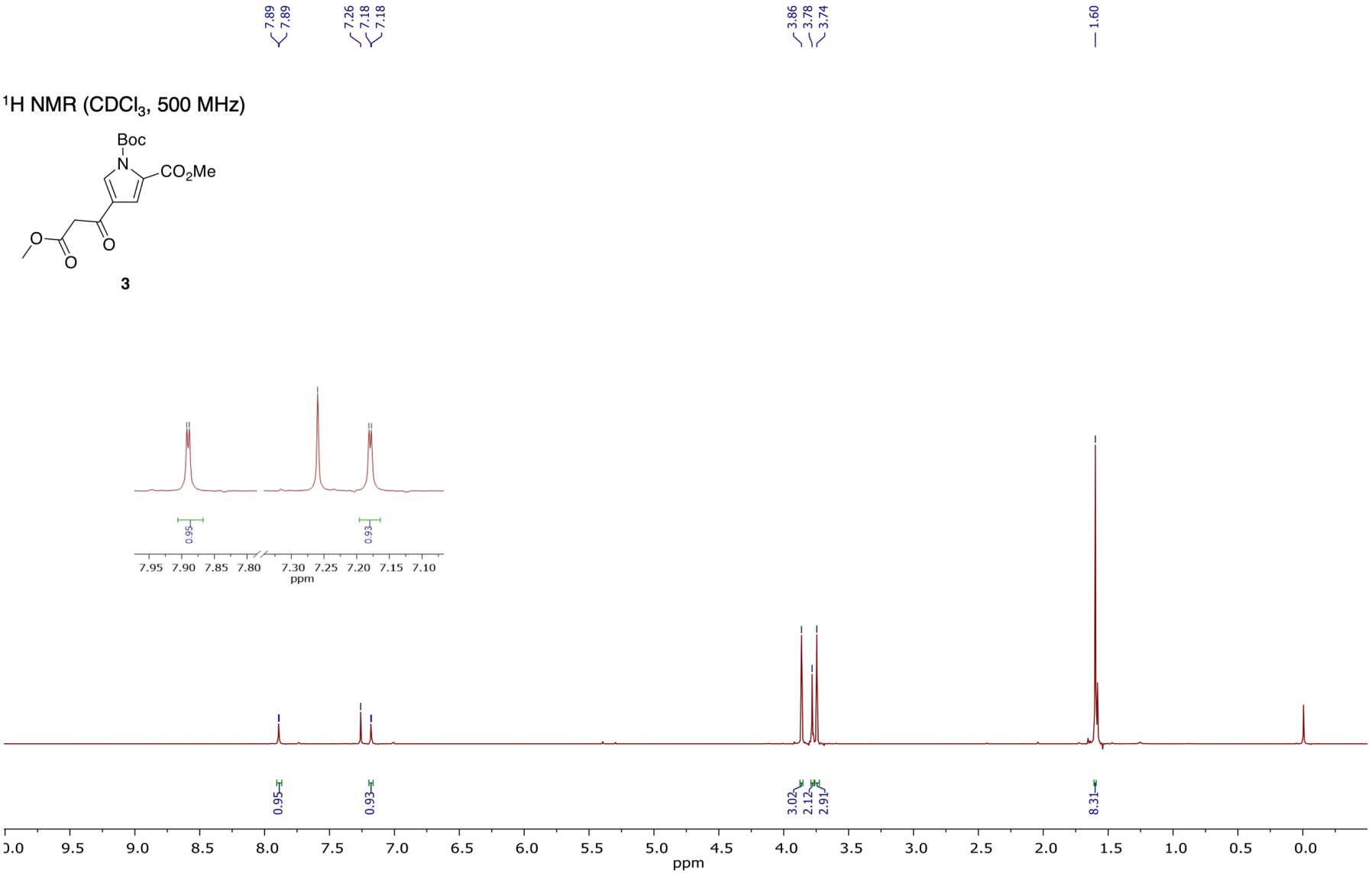
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz)

2



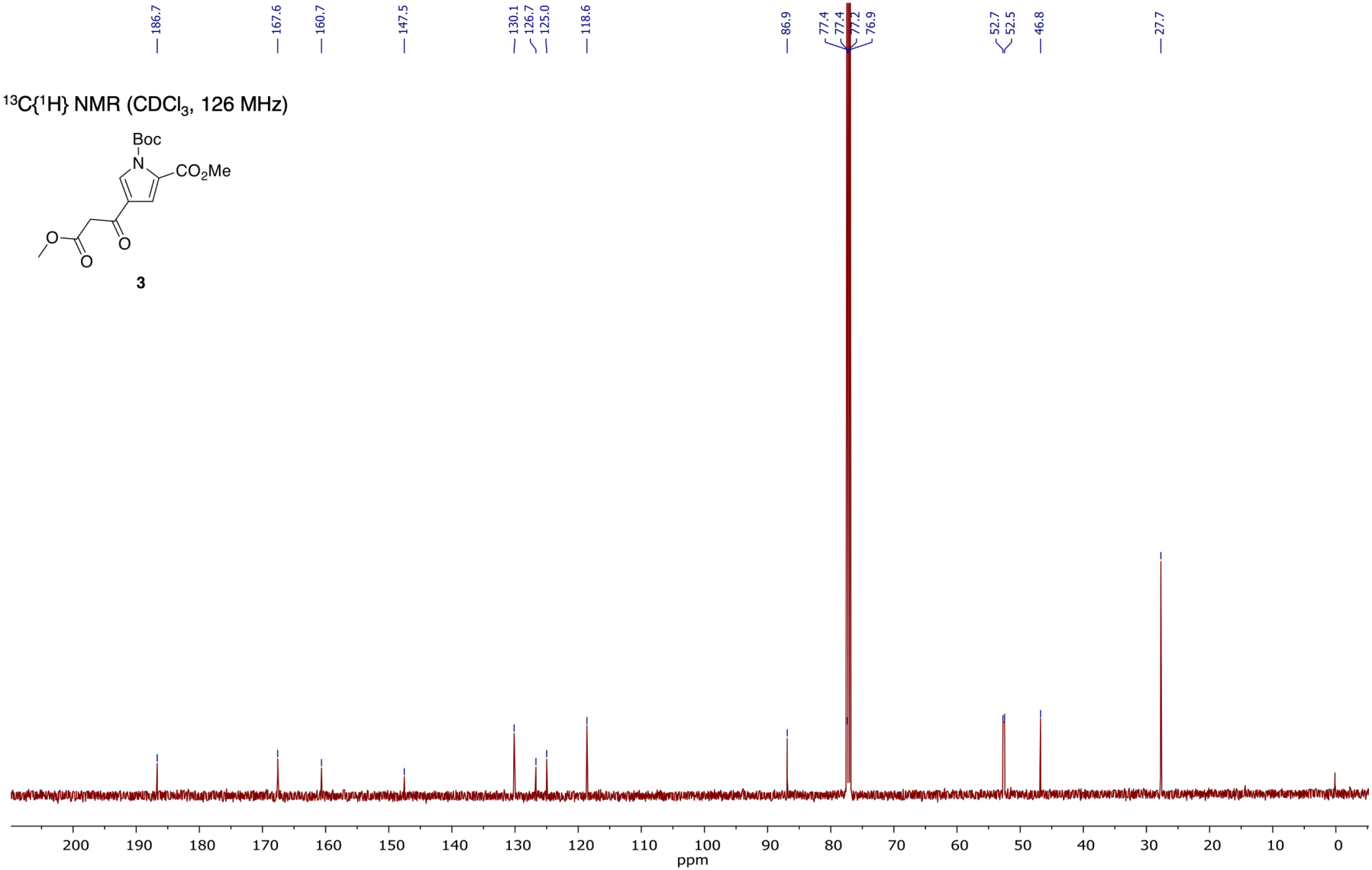
^{1}H NMR ($CDCl_3$, 500 MHz)

3



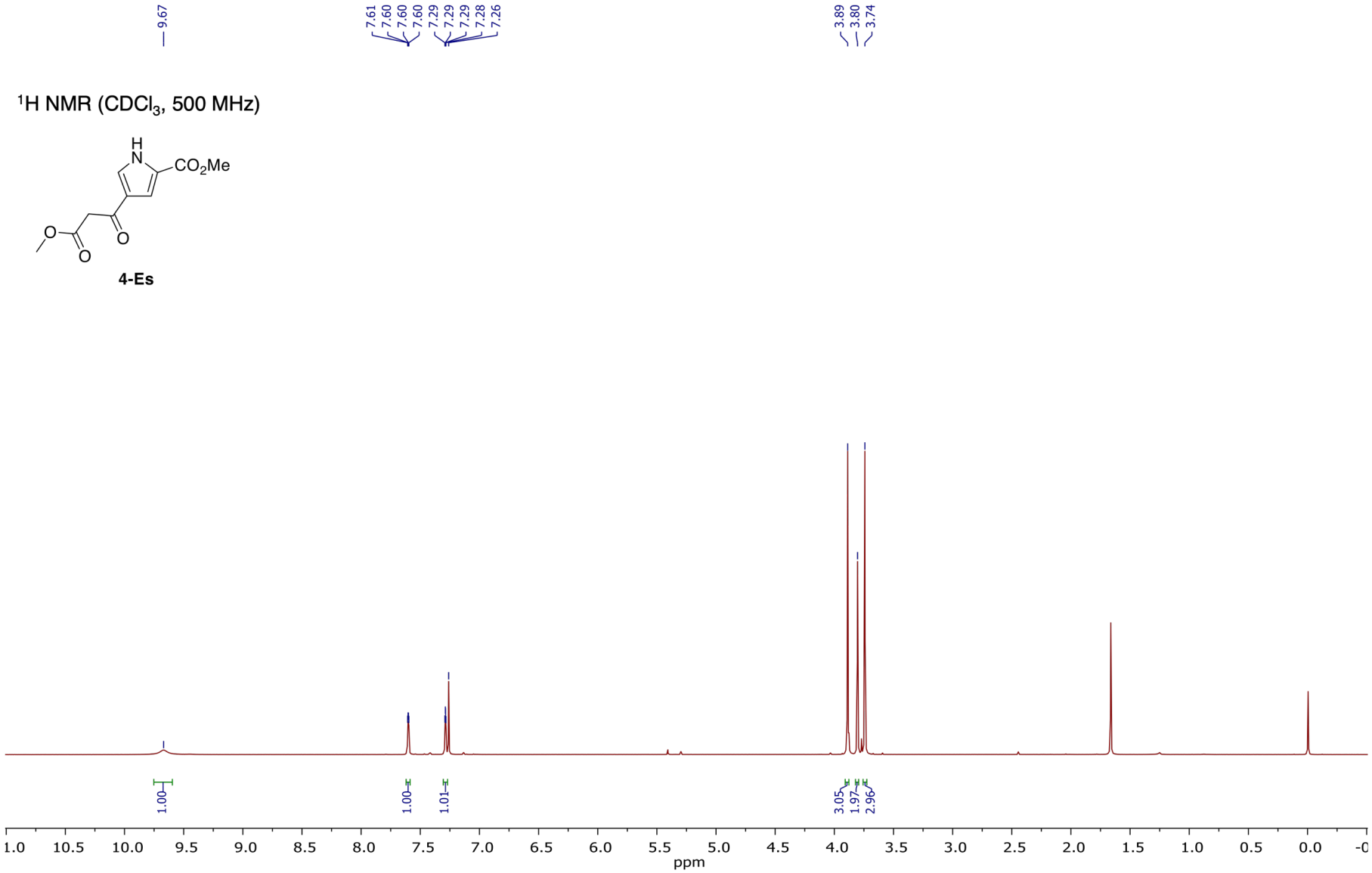
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz)

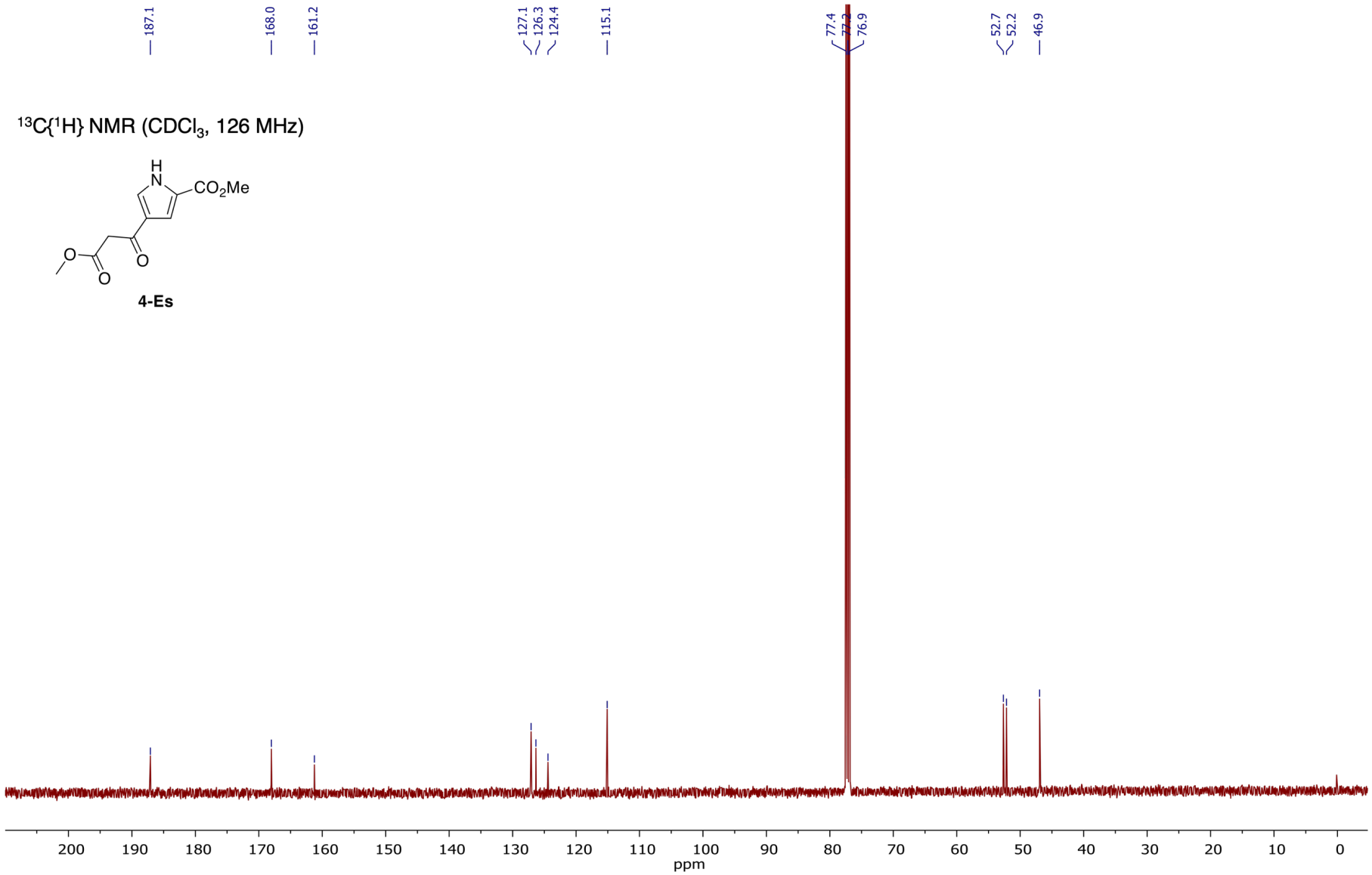
3

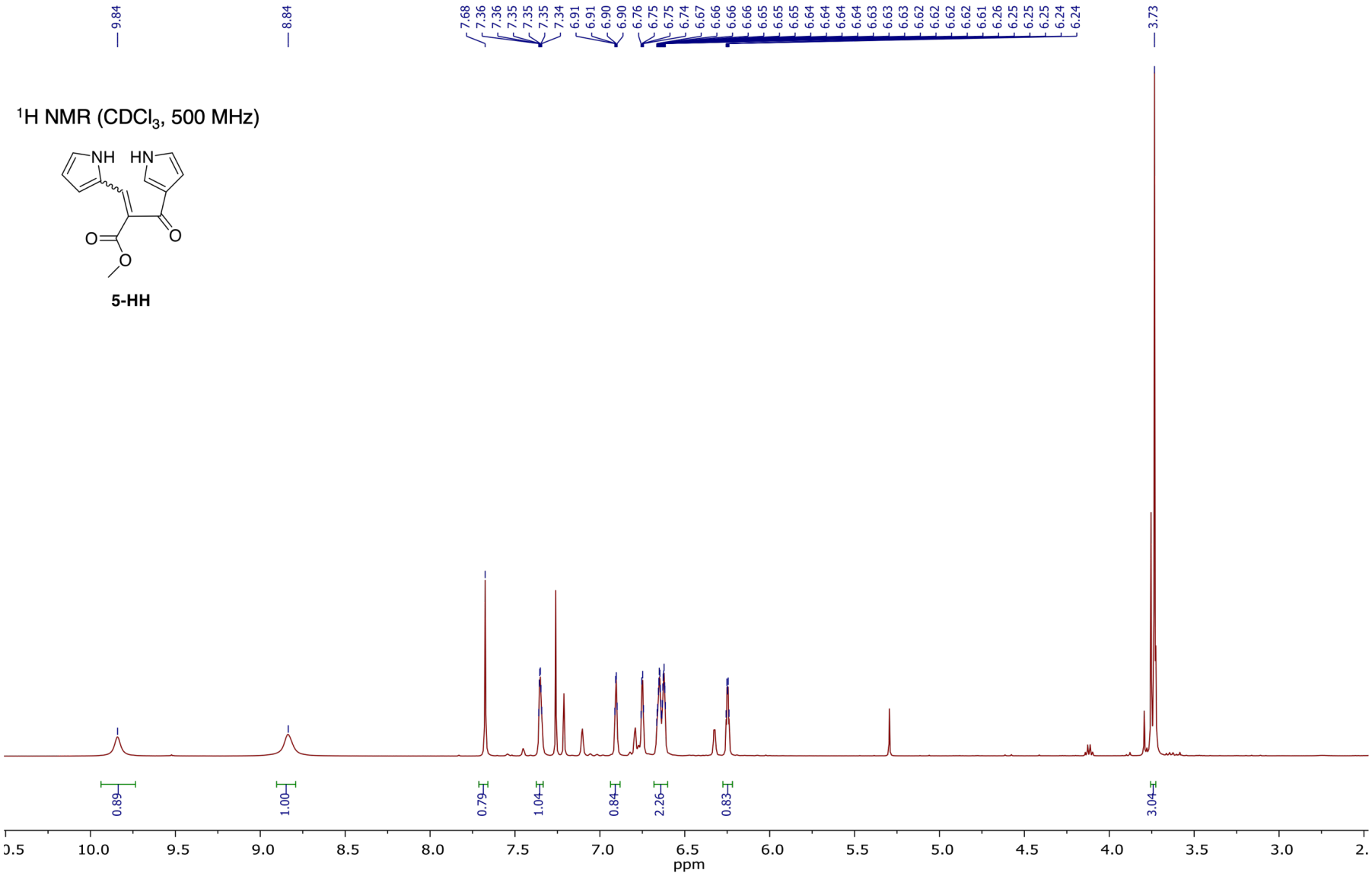


^{1}H NMR ($CDCl_3$, 500 MHz)

4-Es

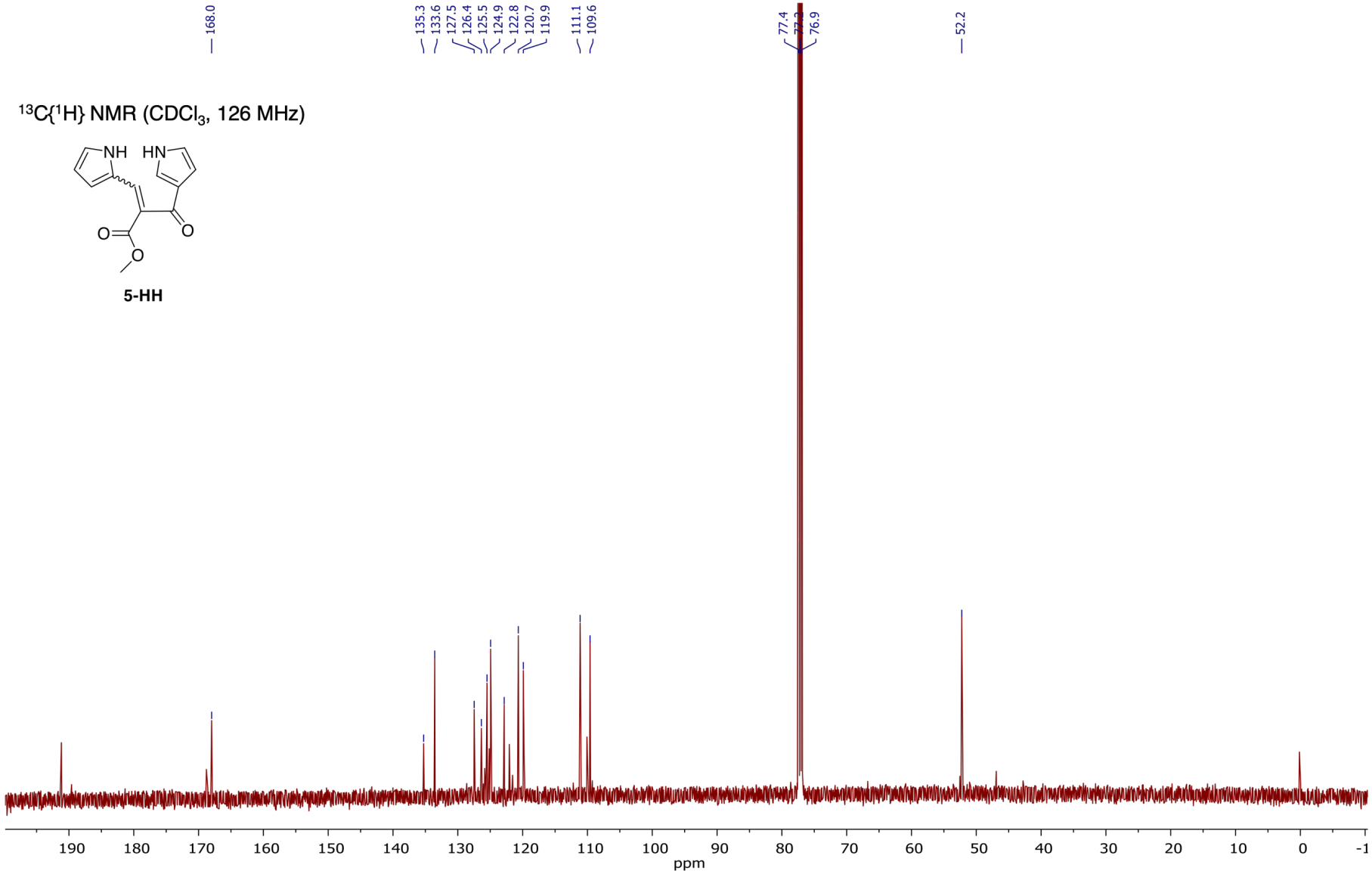


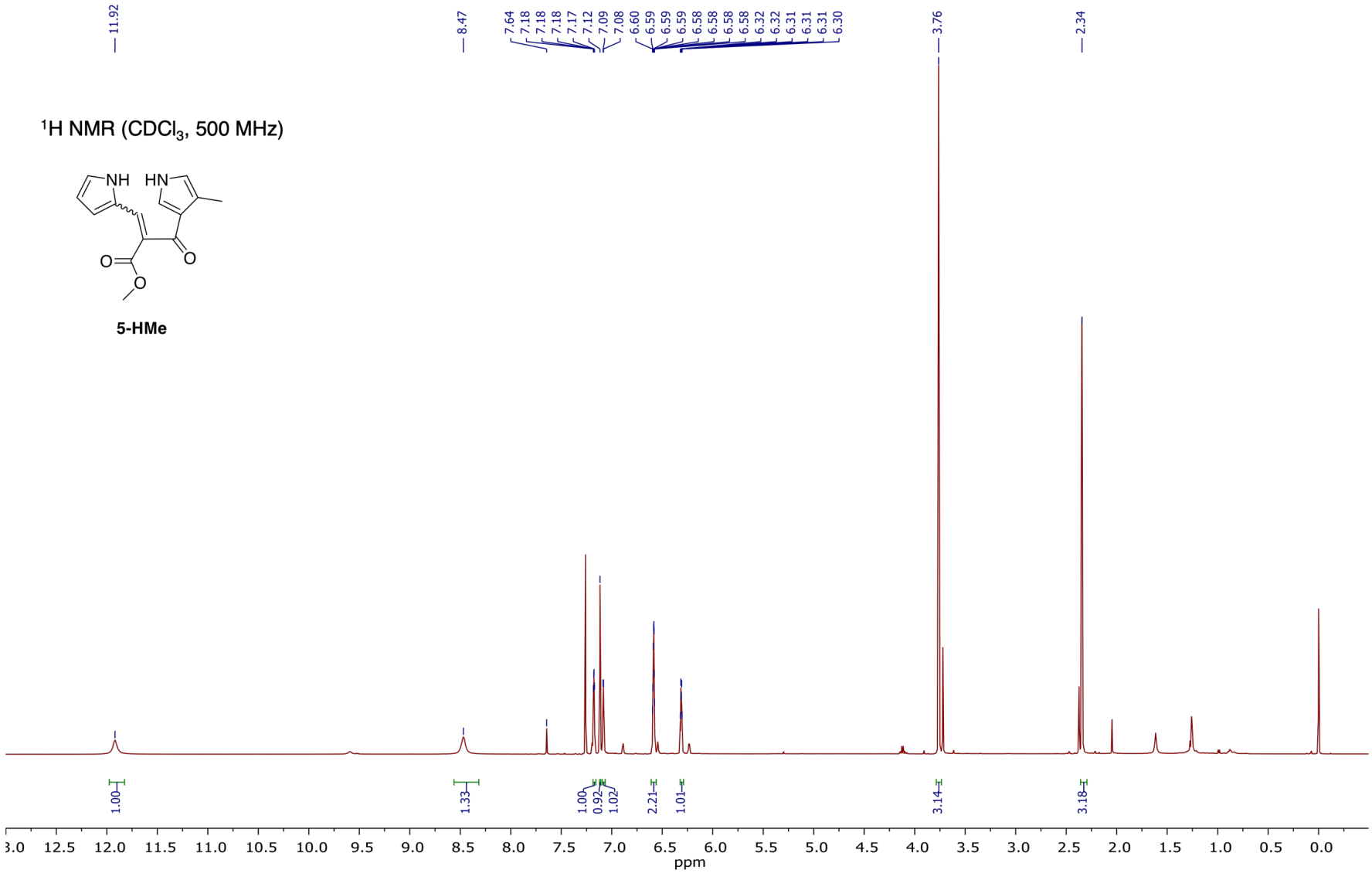

187.1
168.0
161.2
127.1
126.3
124.4
115.1
77.4
77.3
76.9
52.7
52.2
46.9
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz)
H
N
CO_2Me
O
O
O
4-Es
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


9.84
8.84
7.68
7.36
7.36
7.35
7.35
7.35
7.34
6.91
6.91
6.90
6.90
6.76
6.75
6.75
6.74
6.67
6.66
6.66
6.66
6.65
6.65
6.65
6.64
6.64
6.64
6.64
6.63
6.63
6.62
6.62
6.62
6.62
6.61
6.26
6.25
6.25
6.25
6.24
6.24
3.73
^{1}H NMR ($CDCl_3$, 500 MHz)
NH
HN
O
O
O
5-HH
0.89
1.00
0.79
1.04
0.84
2.26
0.83
3.04
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
ppm

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz)

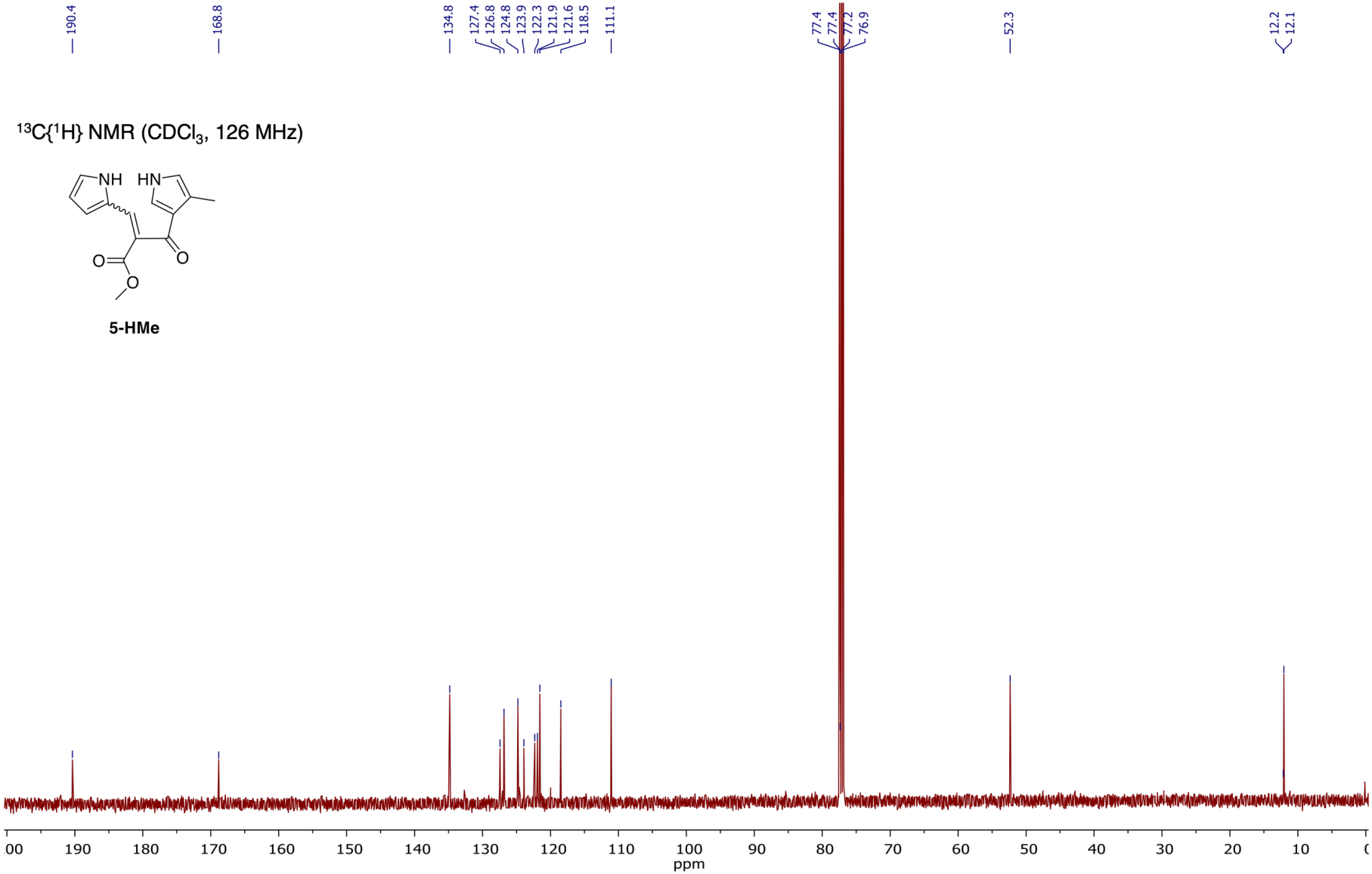
5-HH

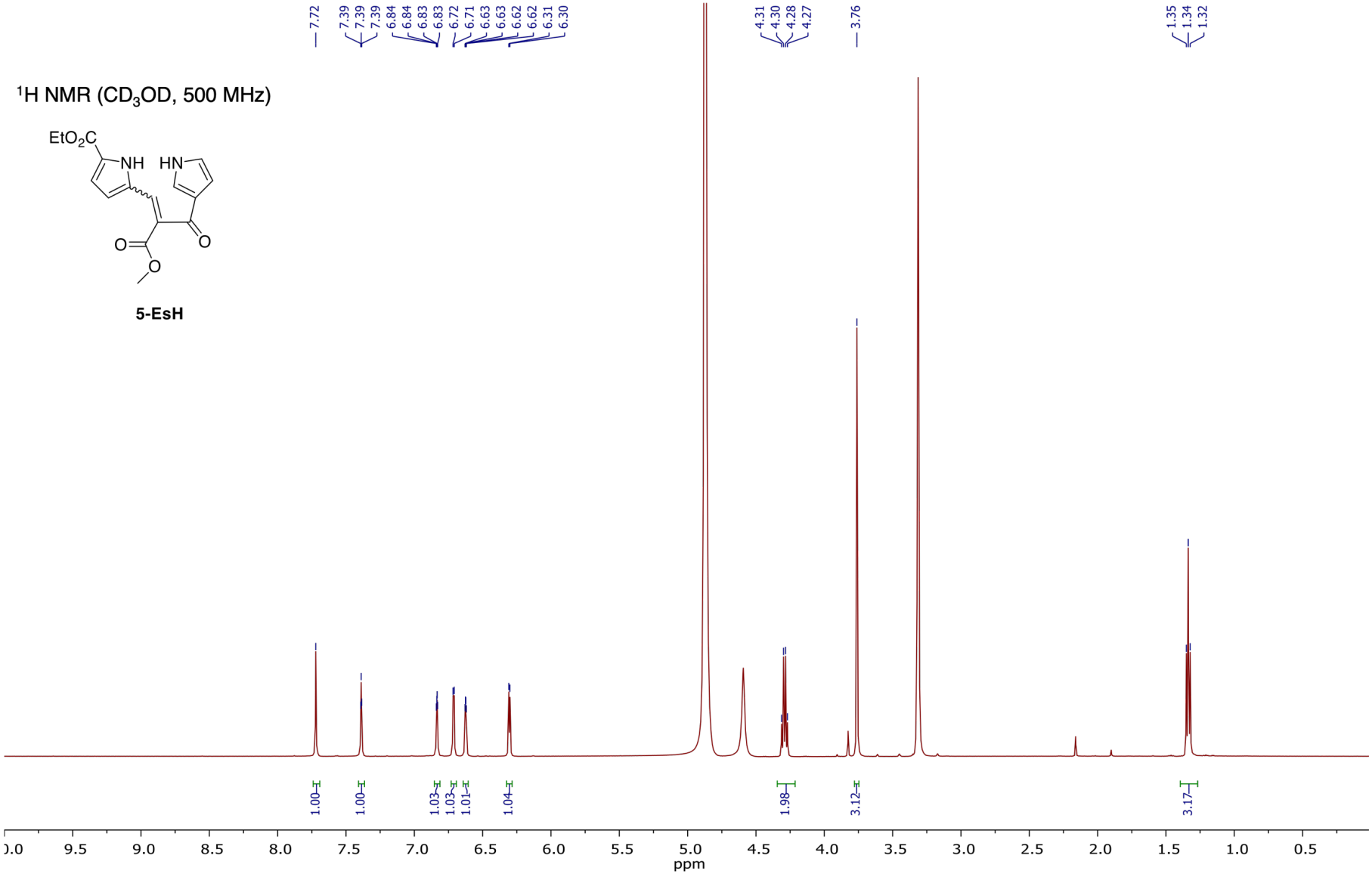



11.92
8.47
7.64
7.18
7.18
7.18
7.17
7.12
7.09
7.08
6.60
6.59
6.59
6.59
6.58
6.58
6.58
6.58
6.32
6.32
6.31
6.31
6.30
3.76
2.34
1H NMR (CDCl3, 500 MHz)
NH
HN
O
O
O
5-HMe
1.00
1.33
1.00
0.92
1.02
2.21
1.01
3.14
3.18
ppm

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz)

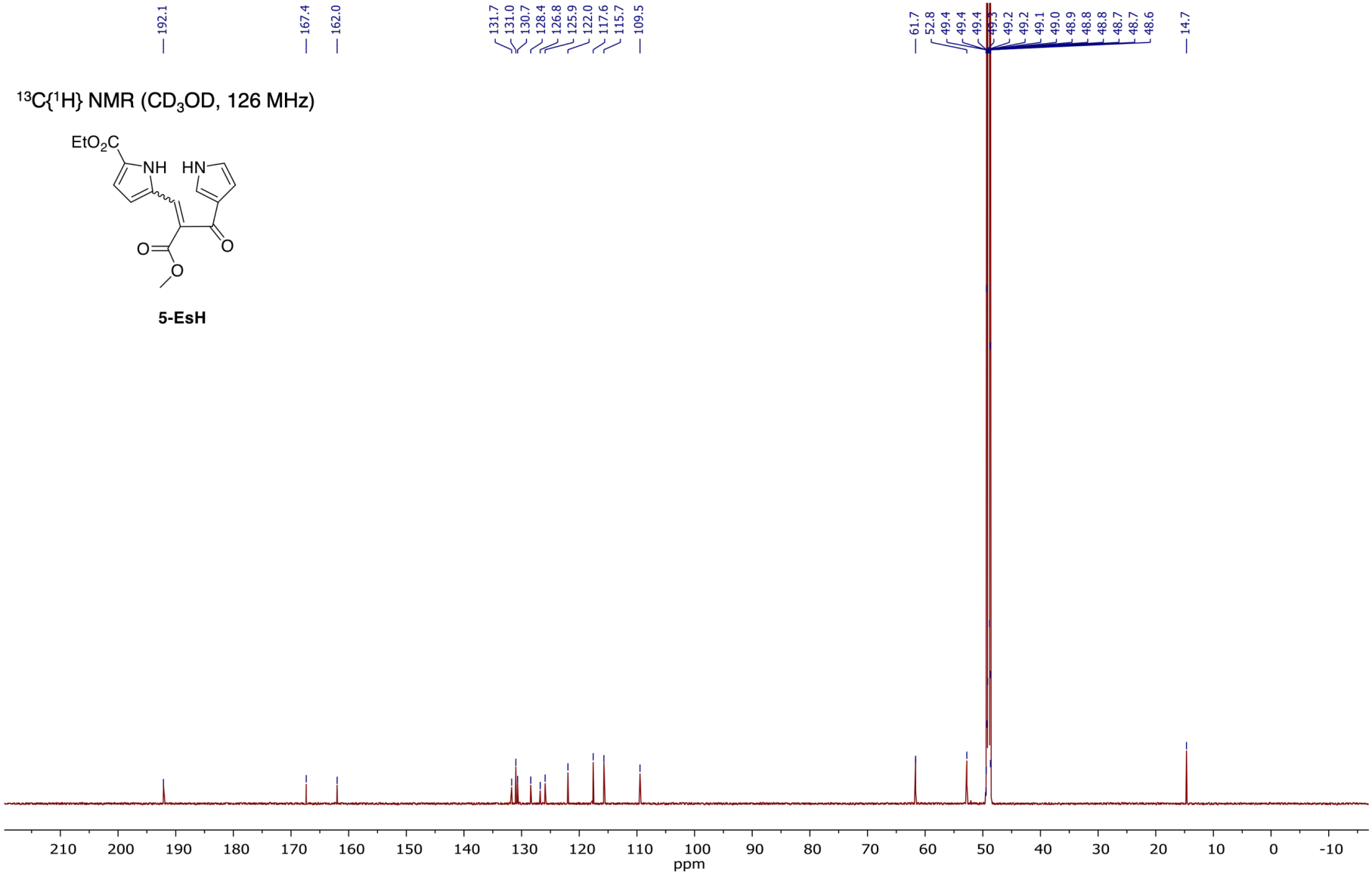
5-HMe





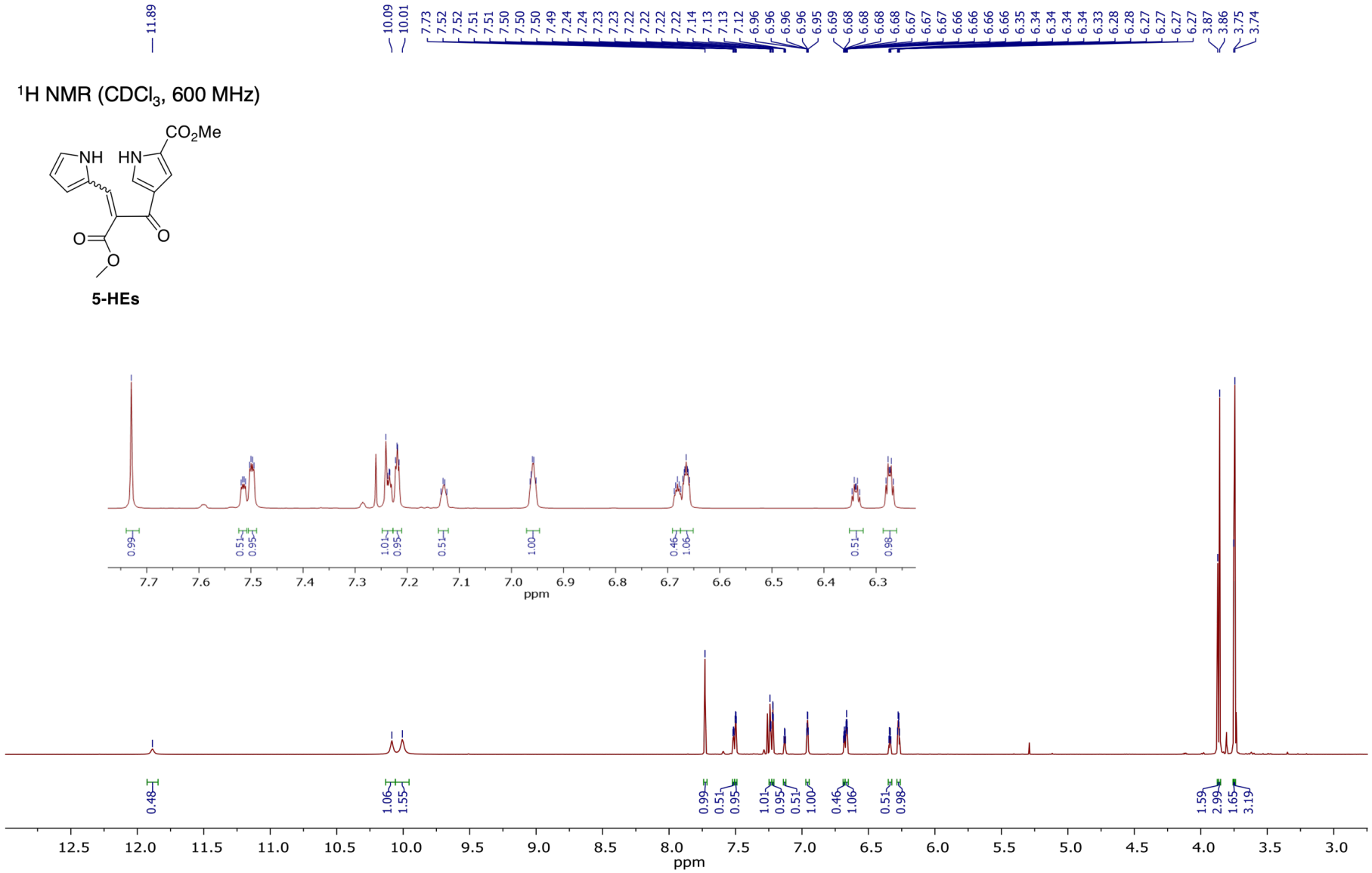
^{1}H NMR (CD_3OD, 500 MHz)

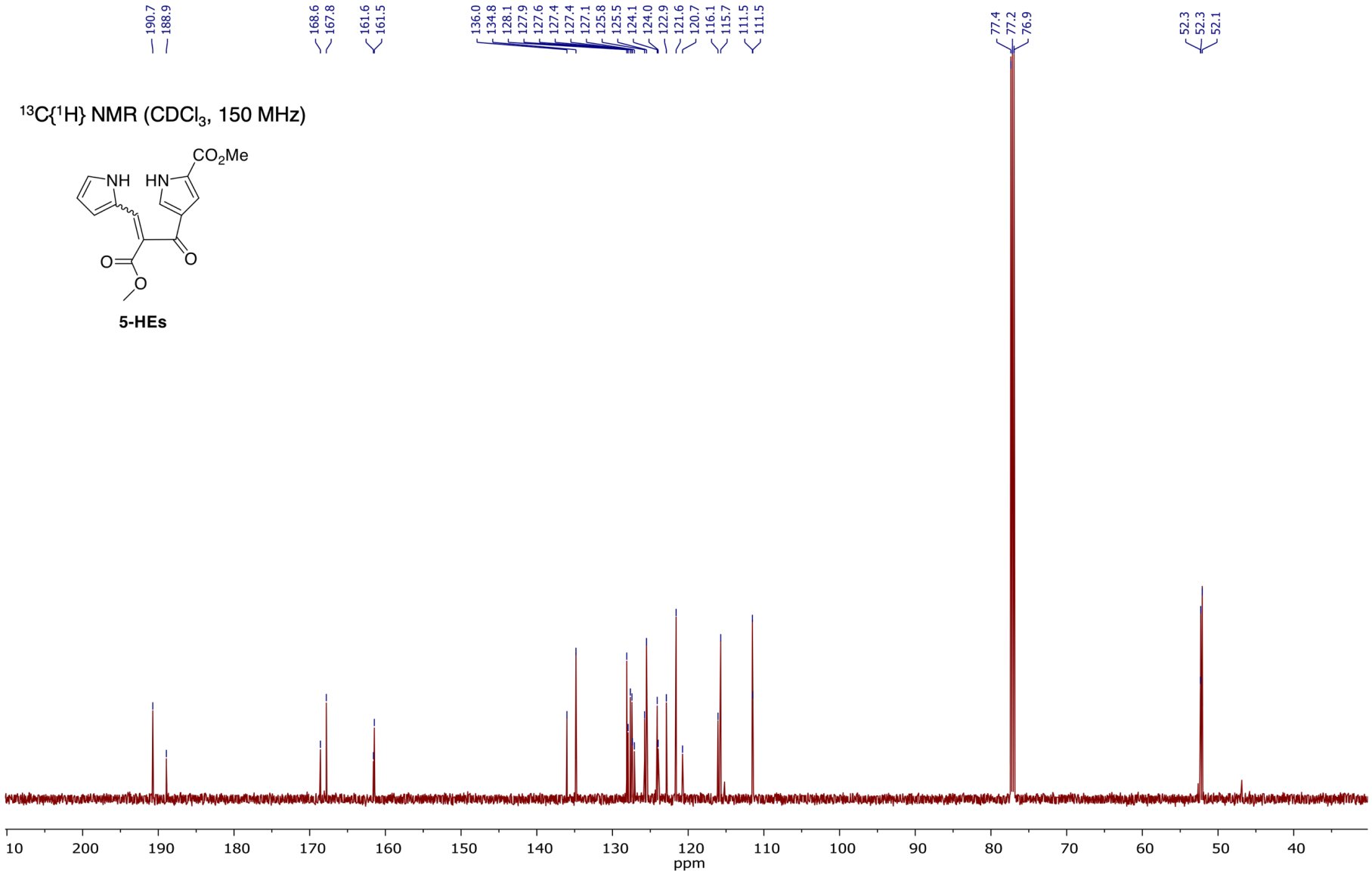
5-EsH

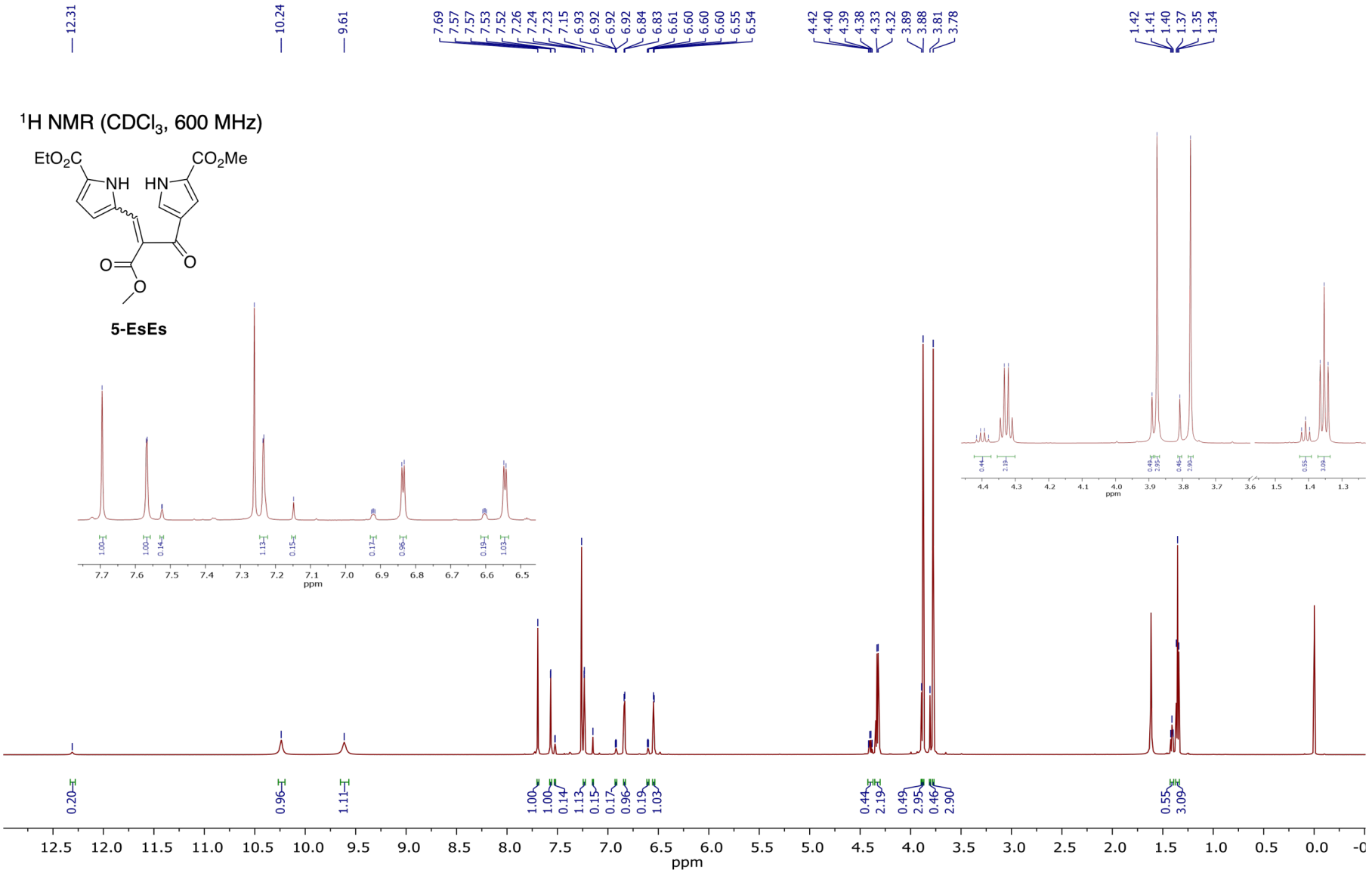

192.1
167.4
162.0
131.7
131.0
130.7
128.4
126.8
125.9
122.0
117.6
115.7
109.5
61.7
52.8
49.4
49.4
49.4
49.3
49.2
49.2
49.1
49.0
48.9
48.8
48.8
48.7
48.7
48.6
14.7
13C{1H} NMR (CD3OD, 126 MHz)
EtO2C
NH
HN
O
O
O
5-EsH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

^{1}H NMR ($CDCl_3$, 600 MHz)

5-HEs

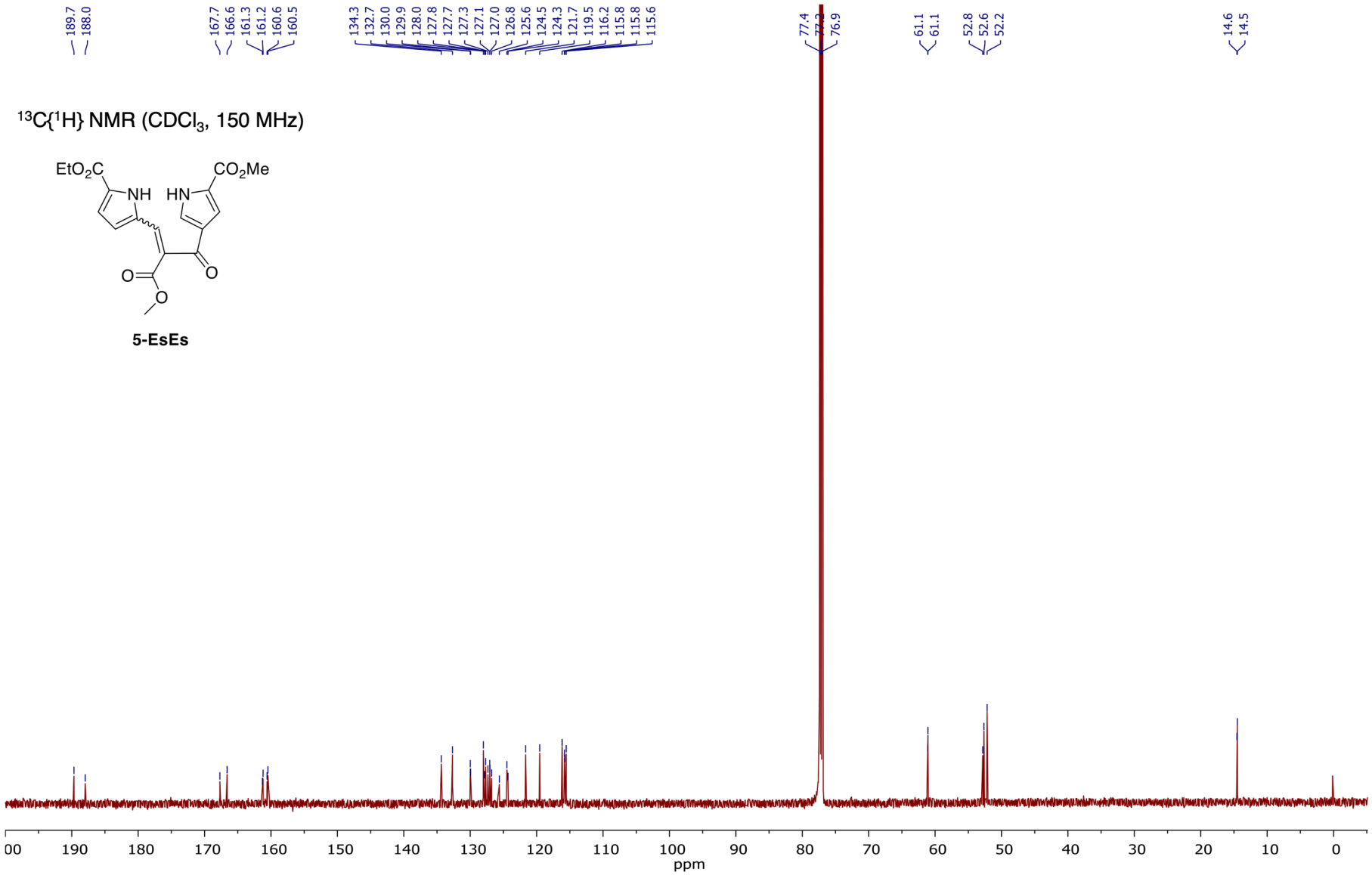


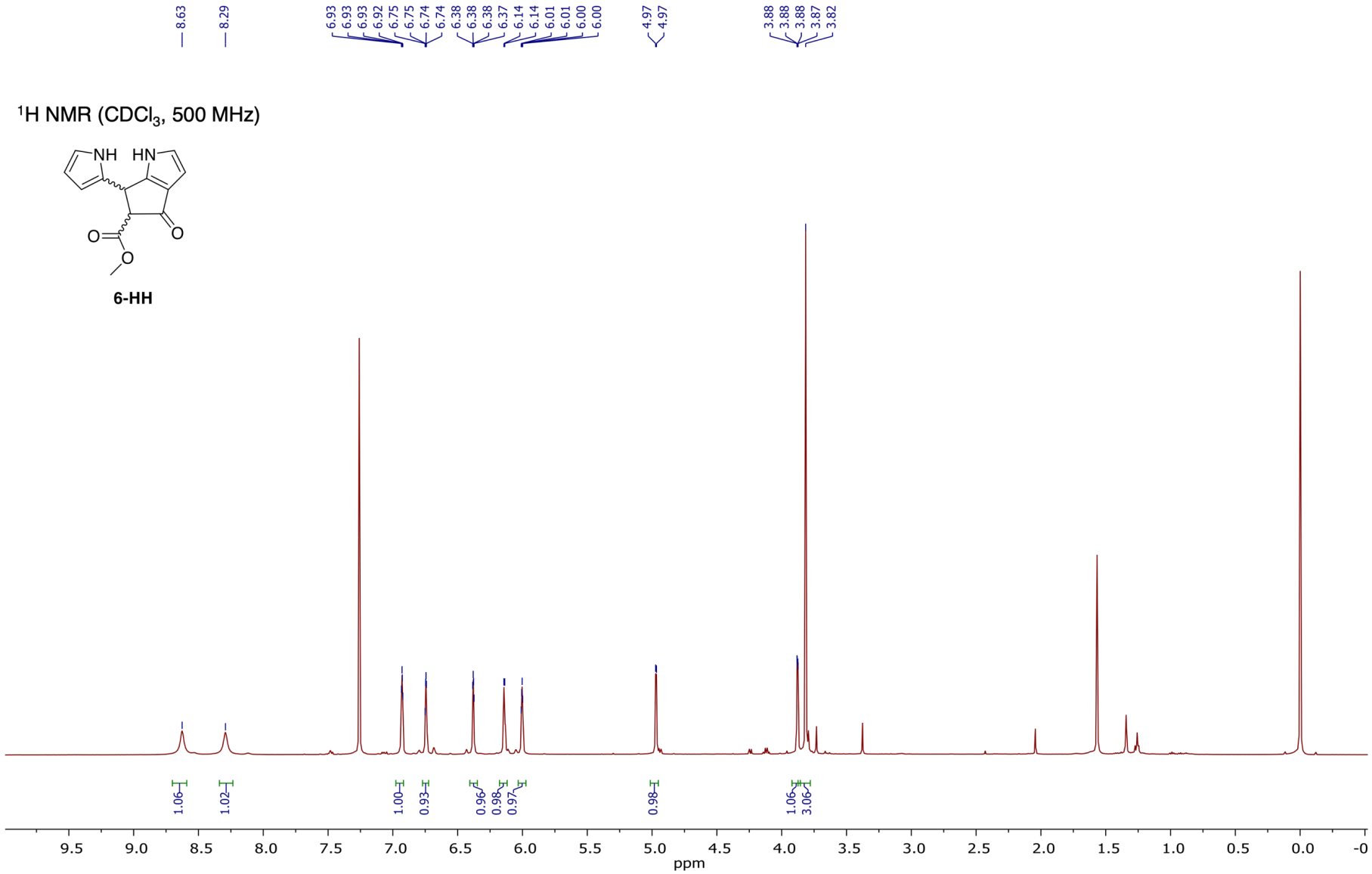

190.7
188.9
168.6
167.8
161.6
161.5
136.0
134.8
128.1
127.9
127.6
127.4
127.4
127.1
125.8
125.5
124.1
124.0
122.9
121.6
120.7
116.1
115.7
111.5
111.5
77.4
77.2
76.9
52.3
52.3
52.1
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz)
CO_2Me
NH
HN
O
O
O
5-HEs
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

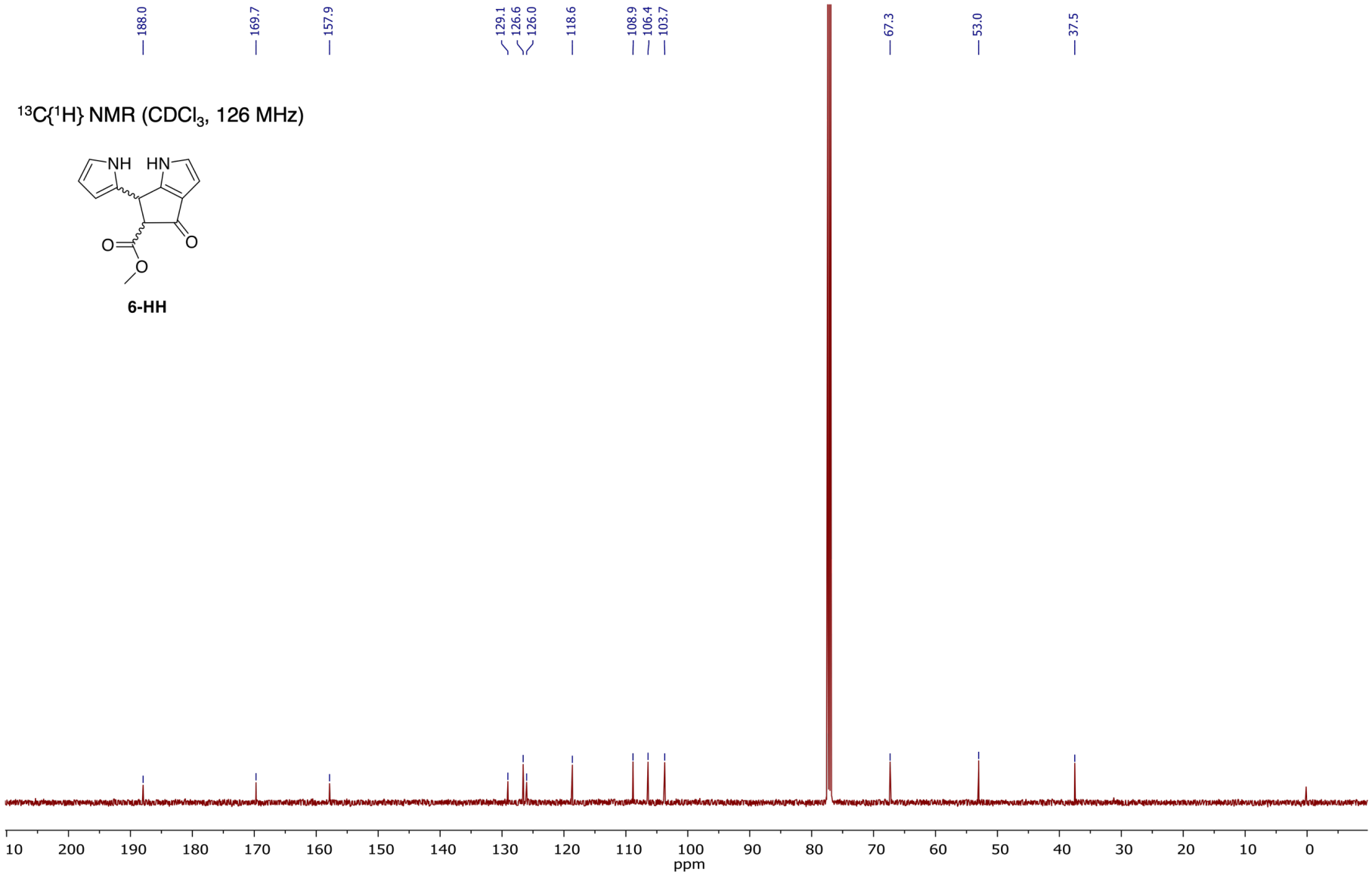

12.31
10.24
9.61
7.69
7.57
7.57
7.53
7.52
7.26
7.24
7.23
7.15
6.93
6.92
6.92
6.92
6.84
6.83
6.61
6.60
6.60
6.60
6.55
6.54
4.42
4.40
4.39
4.38
4.33
4.32
3.89
3.88
3.81
3.78
1.42
1.41
1.40
1.37
1.35
1.34
¹H NMR (CDCl₃, 600 MHz)
EtO2C
NH
HN
CO2Me
O
O
O
O
5-EsEs
0.20
0.96
1.11
1.00
1.00
0.14
1.13
0.15
0.17
0.96
0.19
1.03
0.44
2.19
0.49
2.95
0.46
2.90
0.55
3.09
ppm

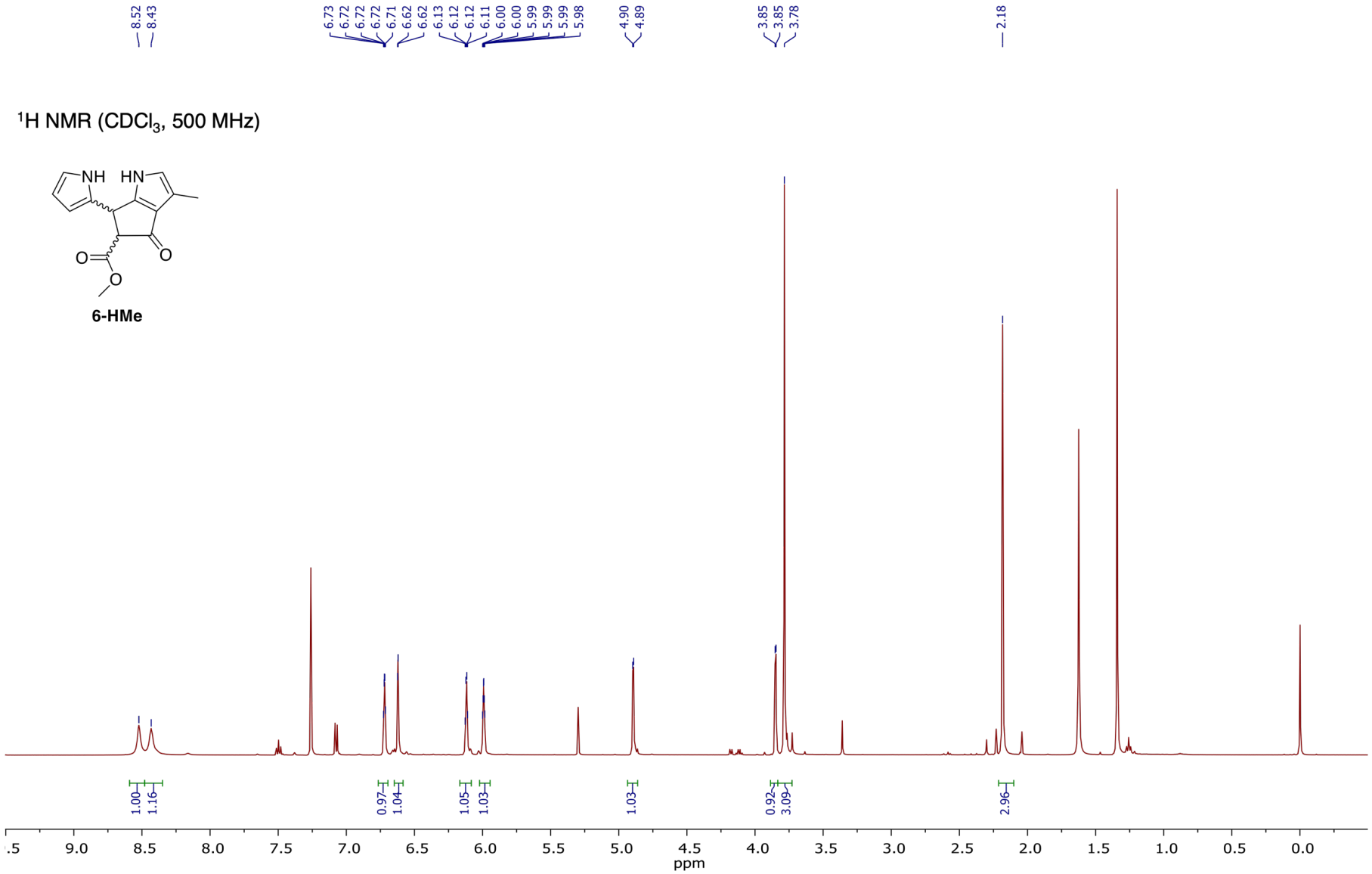
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz)

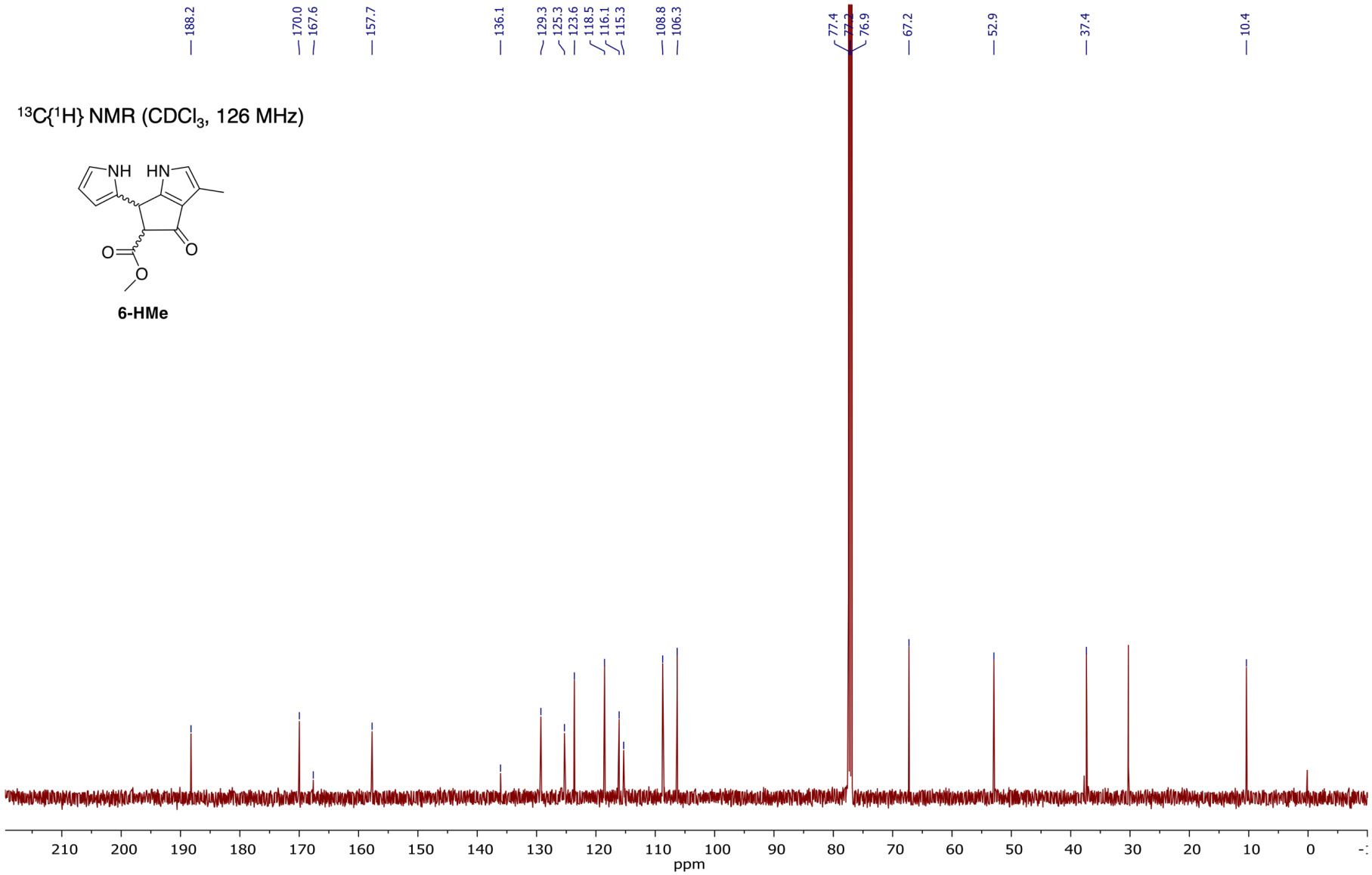
5-EsEs

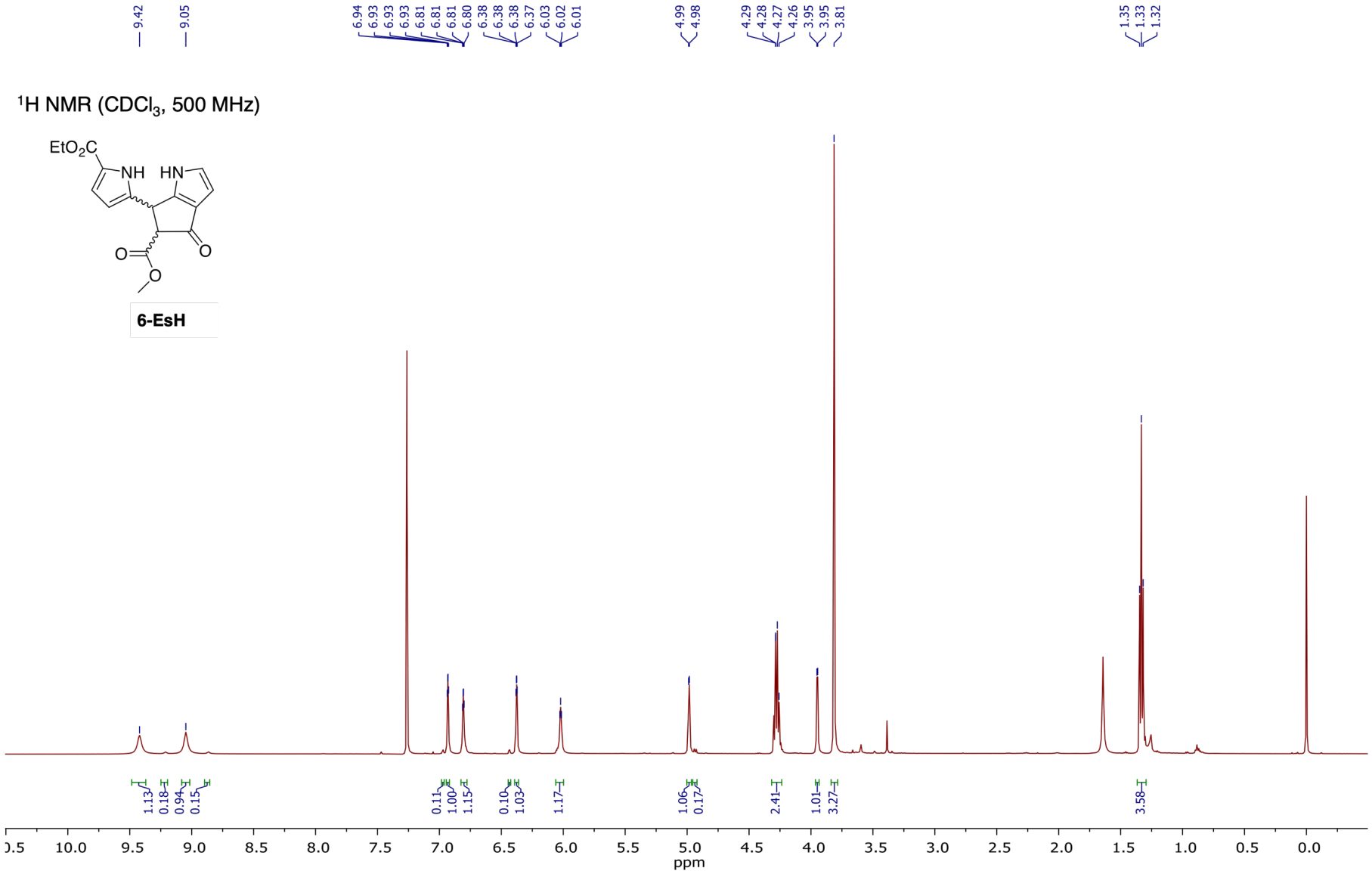



8.63
8.29
6.93
6.93
6.93
6.92
6.75
6.75
6.74
6.74
6.38
6.38
6.38
6.37
6.14
6.14
6.01
6.01
6.00
6.00
4.97
4.97
3.88
3.88
3.88
3.87
3.82
1H NMR (CDCl3, 500 MHz)
NH
HN
O
O
O
O
6-HH
1.06
1.02
1.00
0.93
0.96
0.98
0.97
0.98
1.06
3.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
ppm


188.0
169.7
157.9
129.1
126.6
126.0
118.6
108.9
106.4
103.7
67.3
53.0
37.5
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz)
NH
HN
O
O
O
6-HH
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

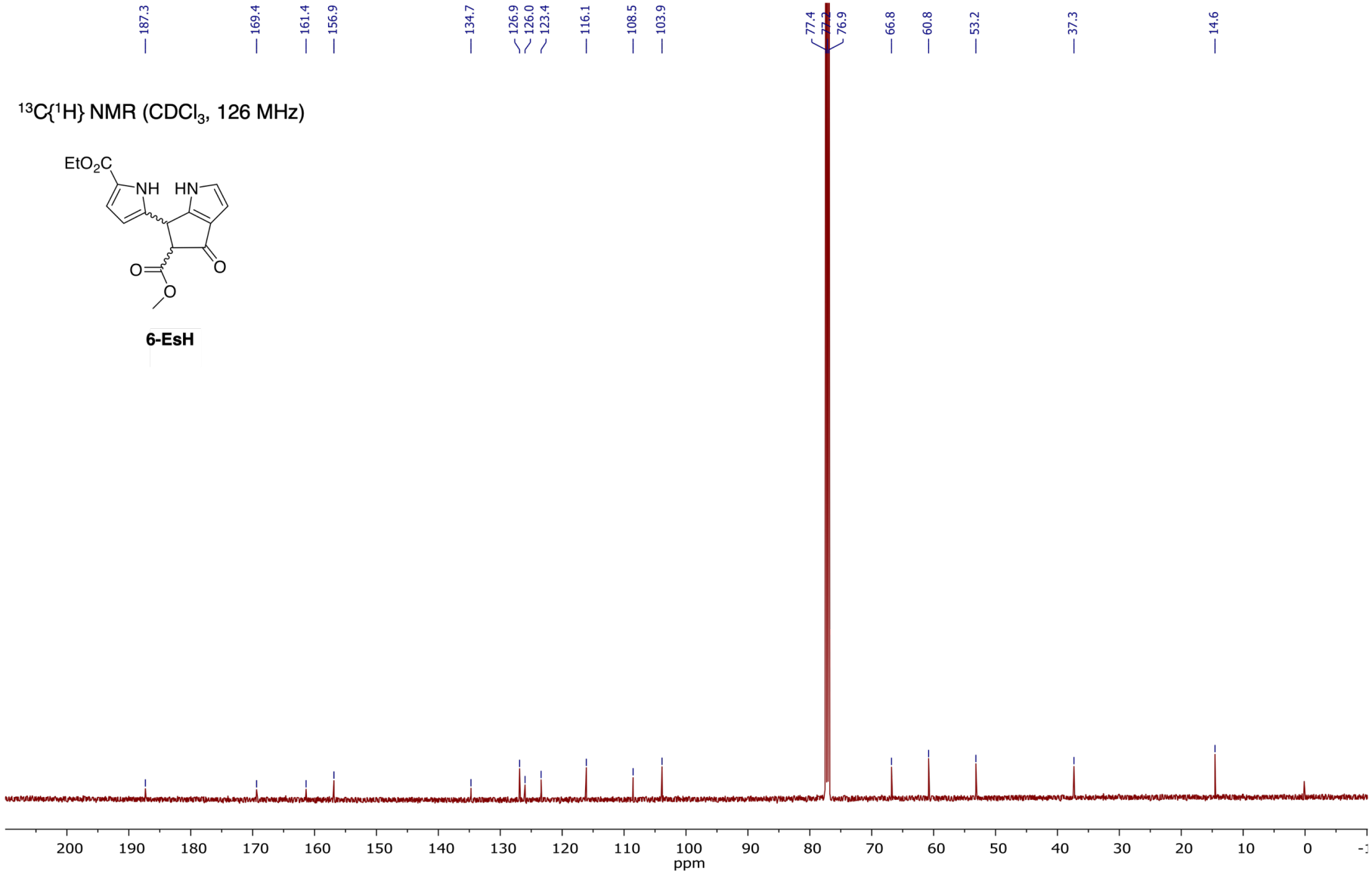

8.52
8.43
6.73
6.72
6.72
6.72
6.71
6.62
6.62
6.13
6.12
6.12
6.11
6.00
6.00
5.99
5.99
5.99
5.98
4.90
4.89
3.85
3.85
3.78
2.18
1H NMR (CDCl3, 500 MHz)
NH
HN
O
O
O
O
6-HMe
1.00
1.16
0.97
1.04
1.05
1.03
1.03
0.92
3.09
2.96
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

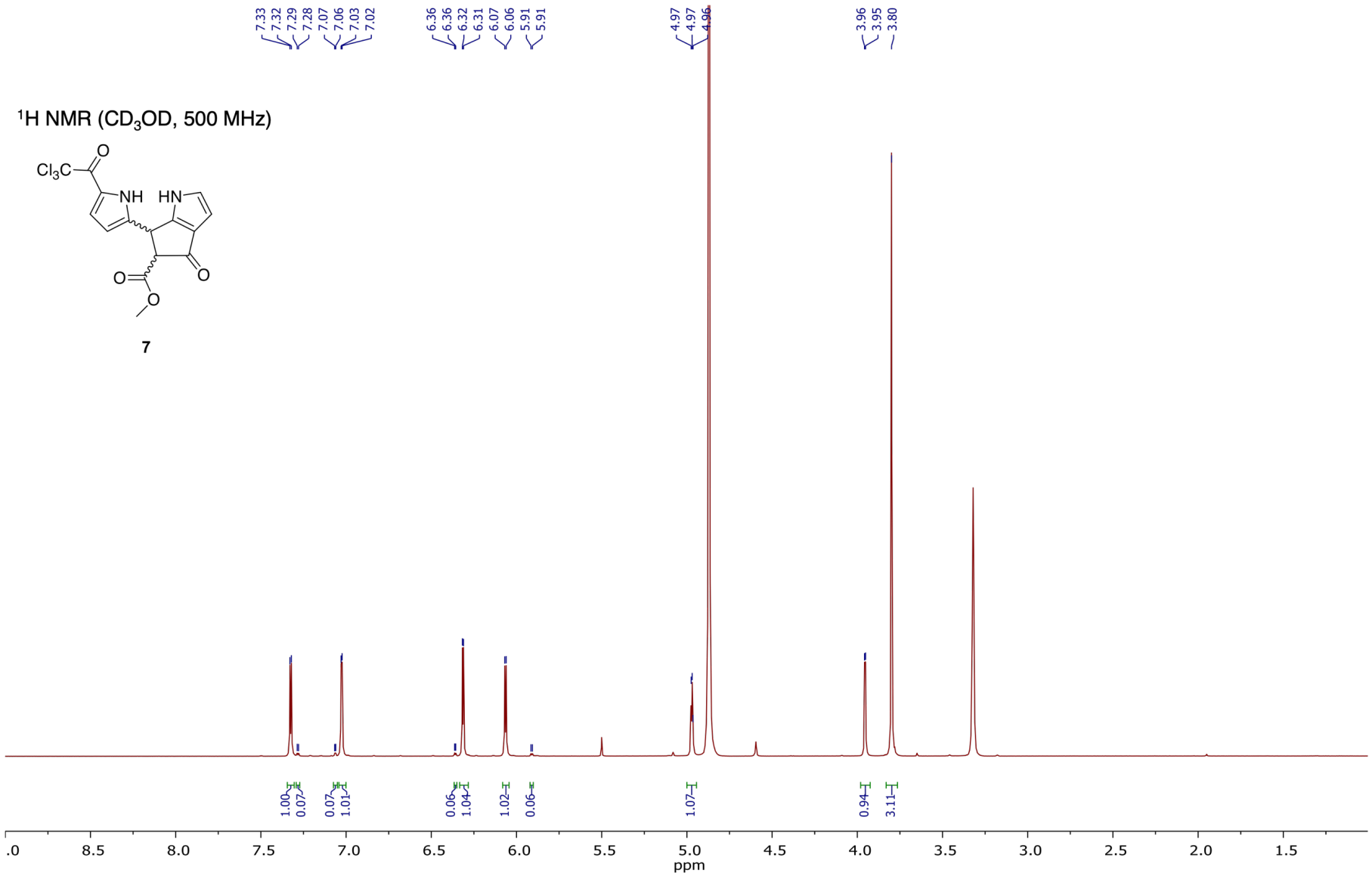

188.2
170.0
167.6
157.7
136.1
129.3
125.3
123.6
118.5
116.1
115.3
108.8
106.3
77.4
77.2
76.9
67.2
52.9
37.4
10.4
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz)
NH
HN
O
O
O
6-HMe
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


9.42
9.05
6.94
6.93
6.93
6.93
6.81
6.81
6.81
6.80
6.38
6.38
6.38
6.37
6.03
6.02
6.01
4.99
4.98
4.29
4.28
4.27
4.26
3.95
3.95
3.81
1.35
1.33
1.32
1H NMR (CDCl3, 500 MHz)
EtO2C
NH
HN
O
O
O
6-EsH
1.13
0.18
0.94
0.15
0.11
1.00
1.15
0.10
1.03
1.17
1.06
0.17
2.41
1.01
3.27
3.58
ppm

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz)

6-EsH



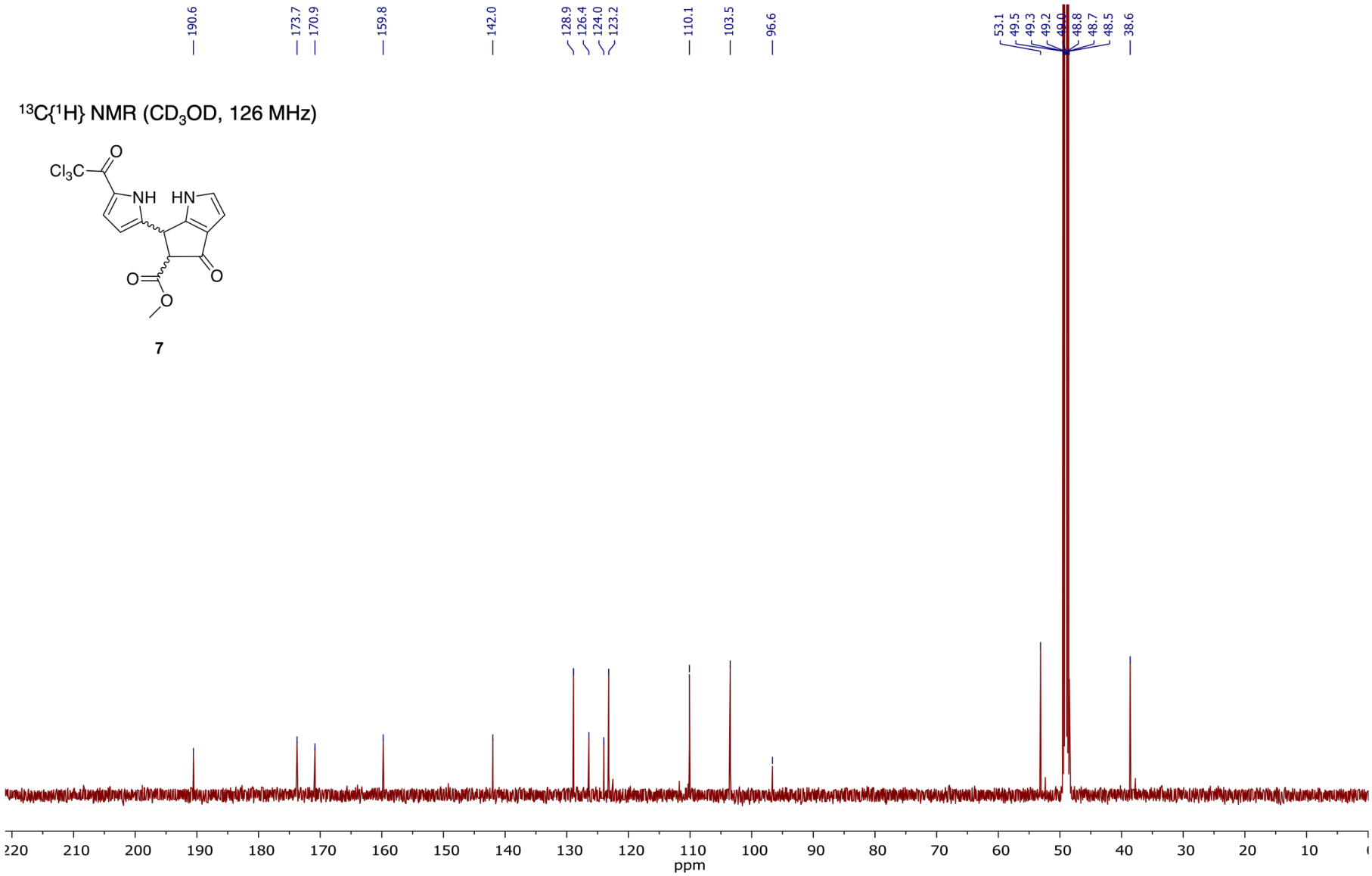


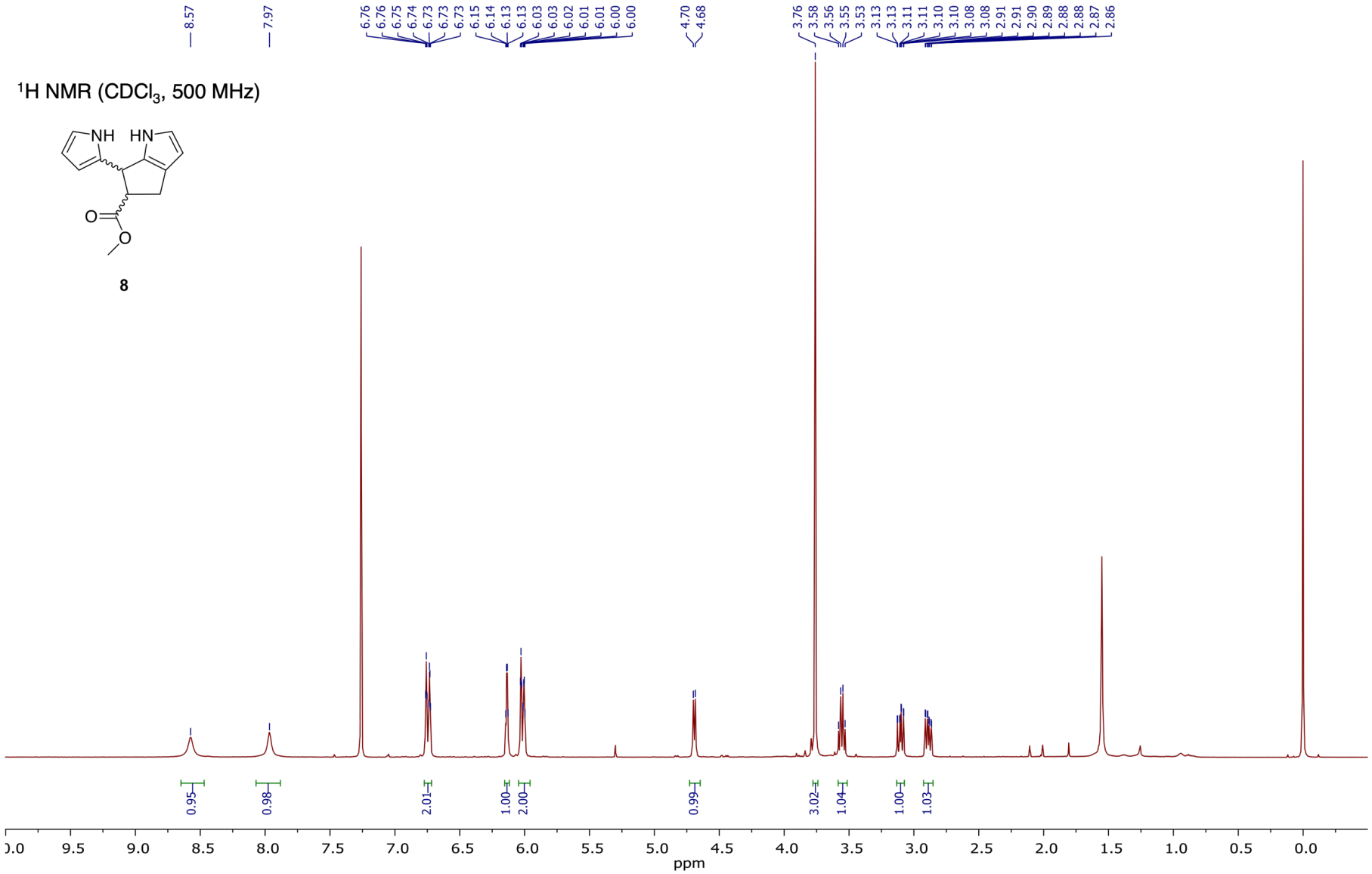
^{1}H NMR (CD_3OD, 500 MHz)

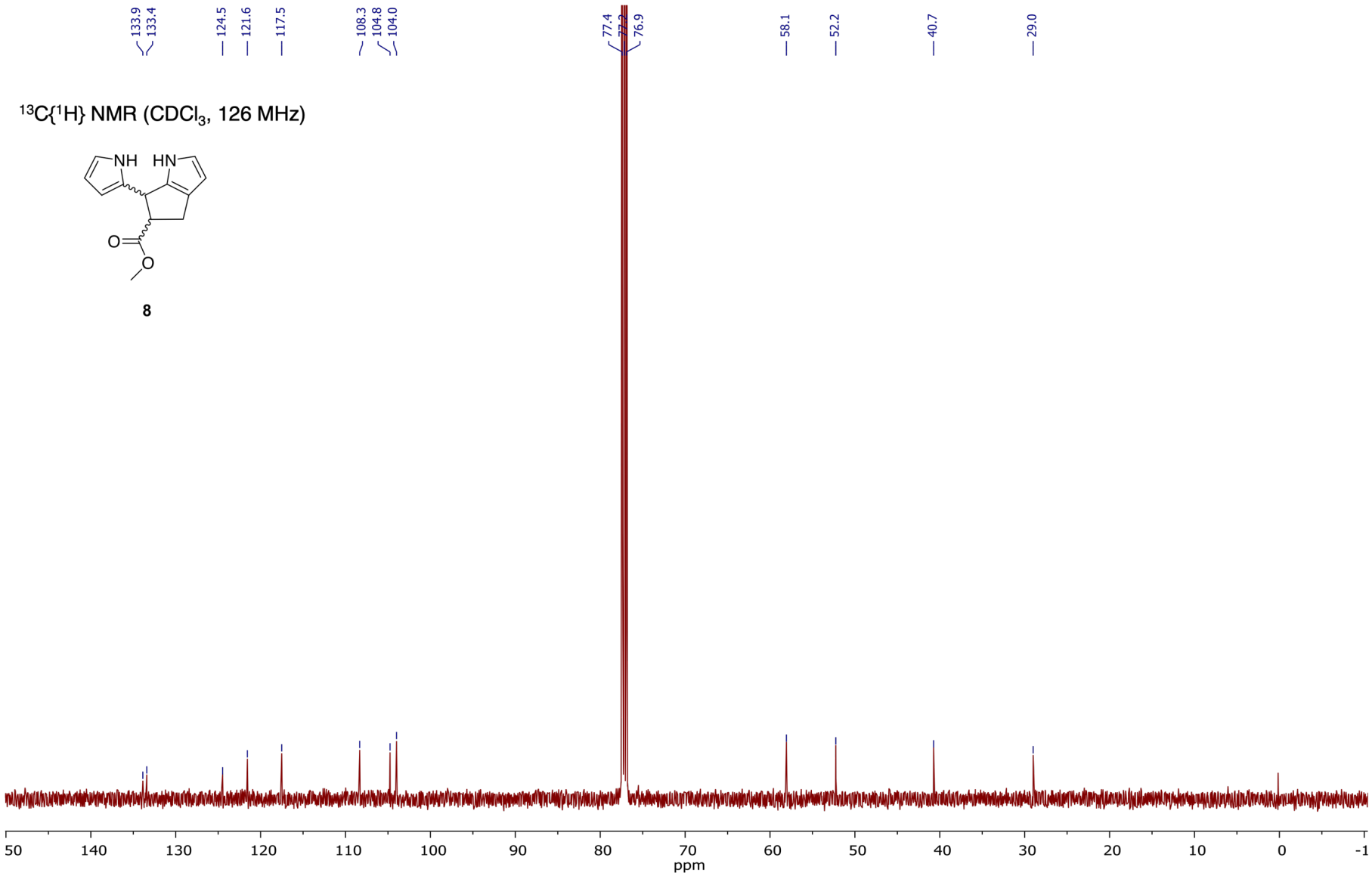
7

$^{13}C\{^{1}H\}$ NMR (CD_3OD, 126 MHz)

7




8.57
7.97
6.76
6.76
6.75
6.74
6.73
6.73
6.73
6.15
6.14
6.13
6.13
6.03
6.03
6.02
6.01
6.01
6.00
6.00
4.70
4.68
3.76
3.58
3.56
3.55
3.53
3.13
3.13
3.11
3.11
3.10
3.10
3.08
3.08
2.91
2.91
2.90
2.89
2.88
2.88
2.87
2.86
^{1}H NMR ($CDCl_3$, 500 MHz)
NH
HN
O
O
8
0.95
0.98
2.01
1.00
2.00
0.99
3.02
1.04
1.00
1.03
ppm


133.9
133.4
124.5
121.6
117.5
108.3
104.8
104.0
77.4
77.2
76.9
58.1
52.2
40.7
29.0
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz)
NH
HN
O
O
8
50
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
ppm