Supplementary Information for:

Synthesis of A Model Phyllobilin Bearing an Optical Marker

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(1) Single-crystal X-ray diffraction data

Single-crystal X-ray crystallography of pyrrole **2** confirmed the position of the 2,2-dicyanovinyl group at the α-position (Figure S1). Pyrrole **2** was crystallized by slow evaporation in $CDCl_3$.

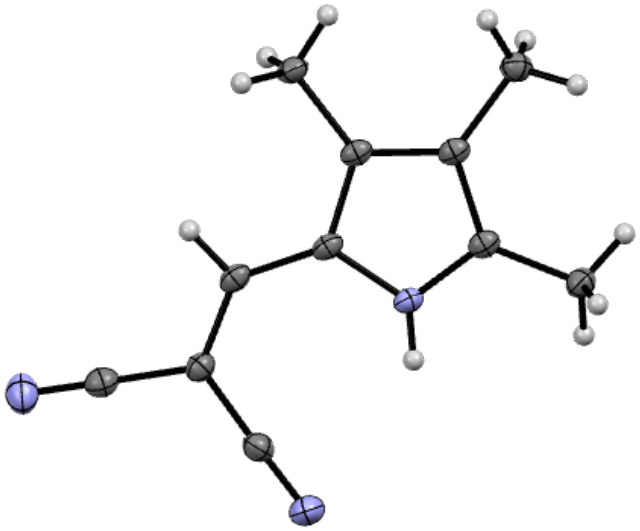


Figure S1. ORTEP diagram of pyrrole **2** with thermal ellipsoids drawn at the 50% probability level. Atom colors: C = grey, N = blue, and H = white).

Table S1. Single-crystal X-ray structure data for pyrrole **2**

CCDC registry	2341280
Chemical formula	$C_{11}H_{12}N_3$
Formula weight (g/mol)	185.23
Temperature (K)	100.0
Wavelength (Å)	0.71073
Crystal size (mm)	0.08 × 0.26 × 0.573
Crystal habit	Clear light-yellow plate
Crystal system	monoclinic
Space group	*C* 1 2 / *c* 1
Unit cell dimensions, *a* (Å)	21.710(3)
Unit cell dimensions, *b* (Å)	3.9545(4)
Unit cell dimensions, *c* (Å)	23.298(3)
α, deg	90
β, deg	92.074(5)
γ, deg	90
Volume ($Å^3$)	1998.9(4)
Z	8
Density (calculated) (g/cm^3)	1.231
Absorption coefficient (mm^{-1})	0.077
F(000)	784.0
Theta range for data collection, deg	2.520 to 26.730
Index ranges	–26<=h<=26, –5<=k<=5, -29<=l<=27
Reflections collected	2098
Independent reflections	R_{int} = 0.045
R_1	0.0449
wR_2	0.1216
R_1 (all data)	0.0517
wR_2 (all data)	0.1168
Largest diff. peak and hole ($eÅ^{-3}$)	0.348 and -0.355
R.M.S. deviation from mean ($eÅ^{-3}$)	0.047

(2) Absorption spectra

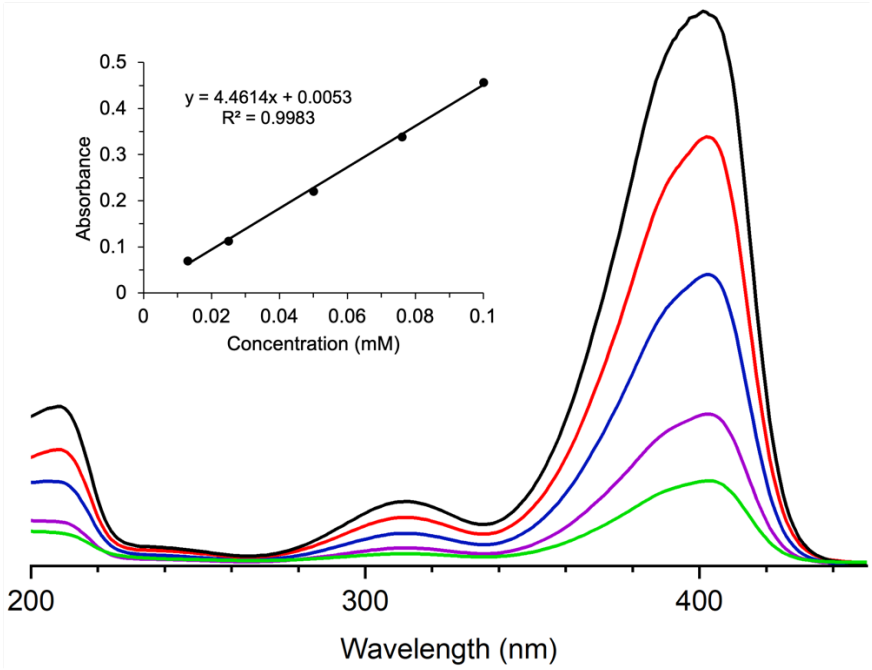


Figure S2. Absorption spectrum of **2** in acetonitrile at room temperature at different concentrations and the corresponding calibration curves for the peak at ~313 nm (ε = 4,600 $M^{-1}cm^{-1}$).

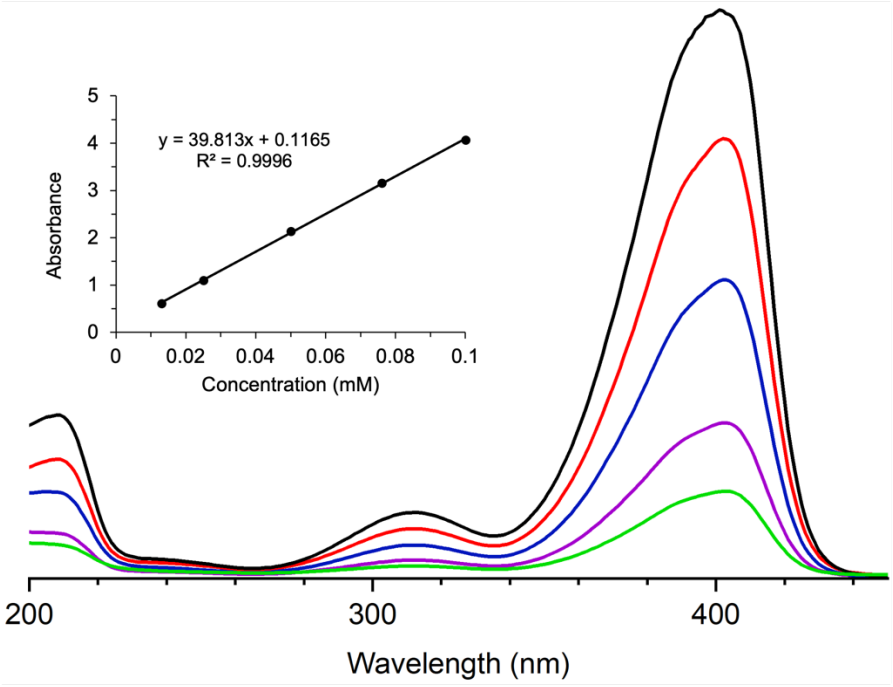


Figure S3. Absorption spectrum of **2** in acetonitrile at room temperature at different concentrations and the corresponding calibration curves for the peak at ~403 nm (ε = 43,000 $M^{-1}cm^{-1}$).

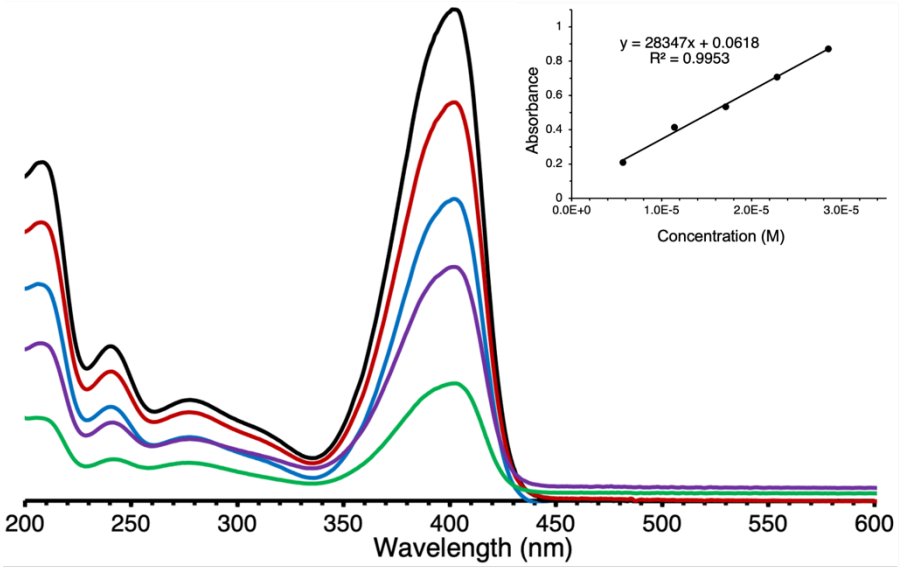


Figure S4. Absorption spectrum of **5** in acetonitrile at room temperature at different concentrations and the corresponding calibration curves for the peak at ~400 nm ($\varepsilon = 28{,}000\ M^{-1}cm^{-1}$). A separate measurement, reported in the text, gave ($\varepsilon = 34{,}000\ M^{-1}cm^{-1}$).

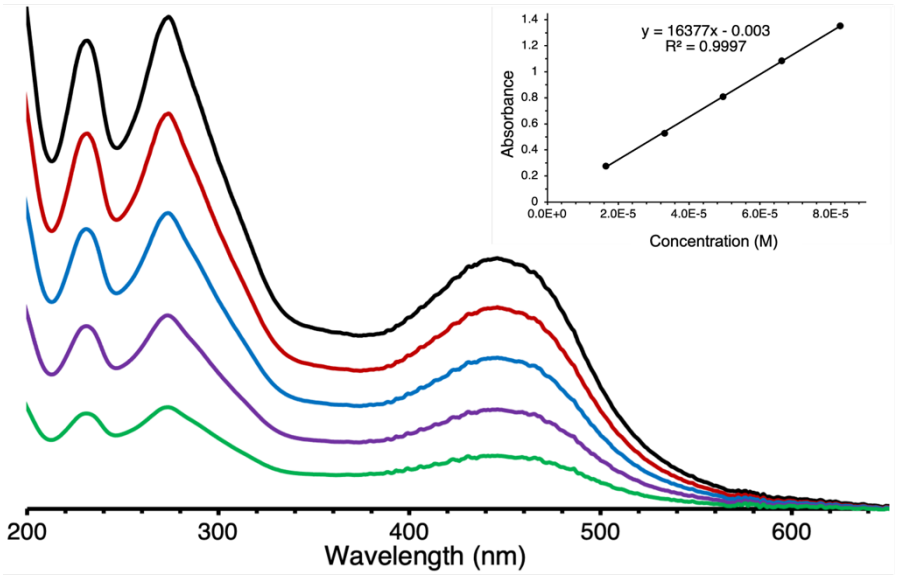


Figure S5. Absorption spectrum of **6** in acetonitrile at room temperature at different concentrations and the corresponding calibration curves for the peak at ~231 nm ($\varepsilon = 16{,}000\ M^{-1}cm^{-1}$).

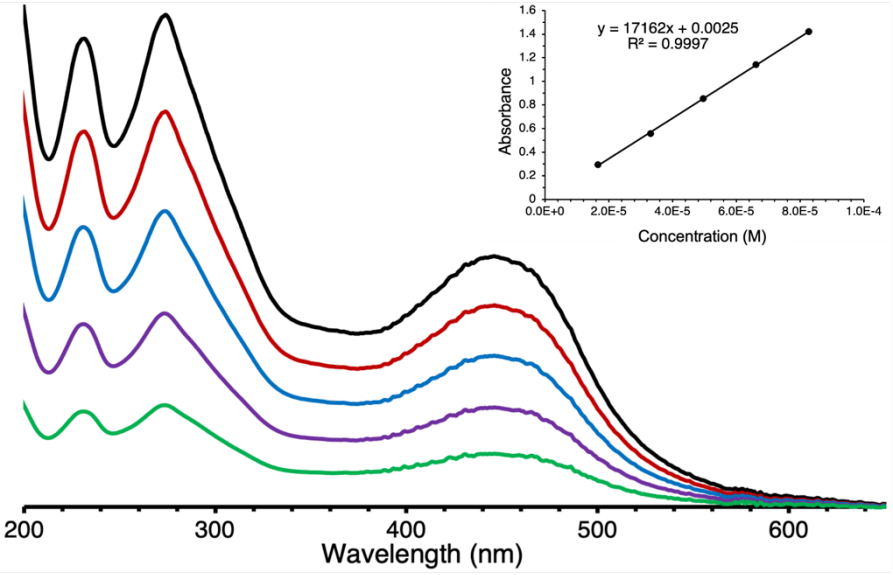


Figure S6. Absorption spectrum of **6** in acetonitrile at room temperature at different concentrations and the corresponding calibration curves for the peak at ~274 nm (ε = 17,000 $M^{-1}cm^{-1}$).

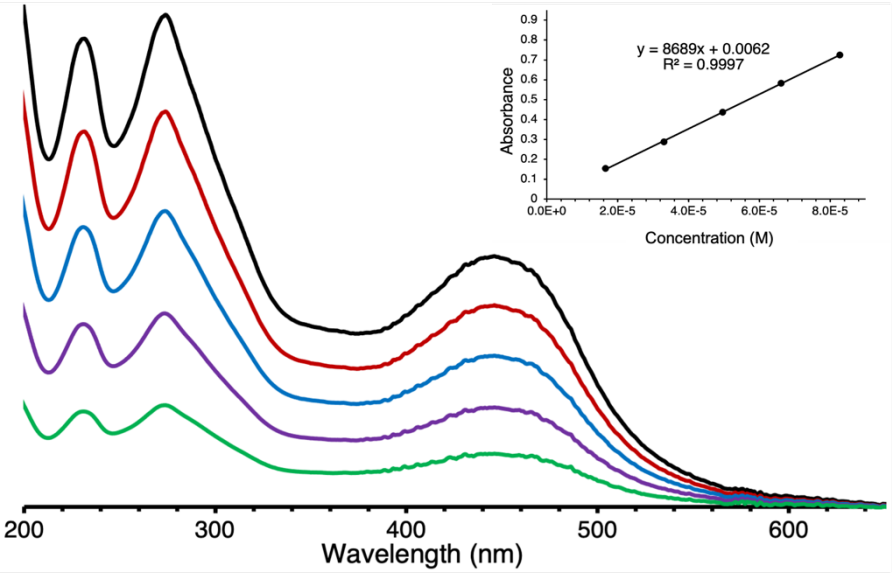


Figure S7. Absorption spectrum of **6** in acetonitrile at room temperature at different concentrations and the corresponding calibration curves for the peak at ~446 nm (ε = 8,600 $M^{-1}cm^{-1}$).

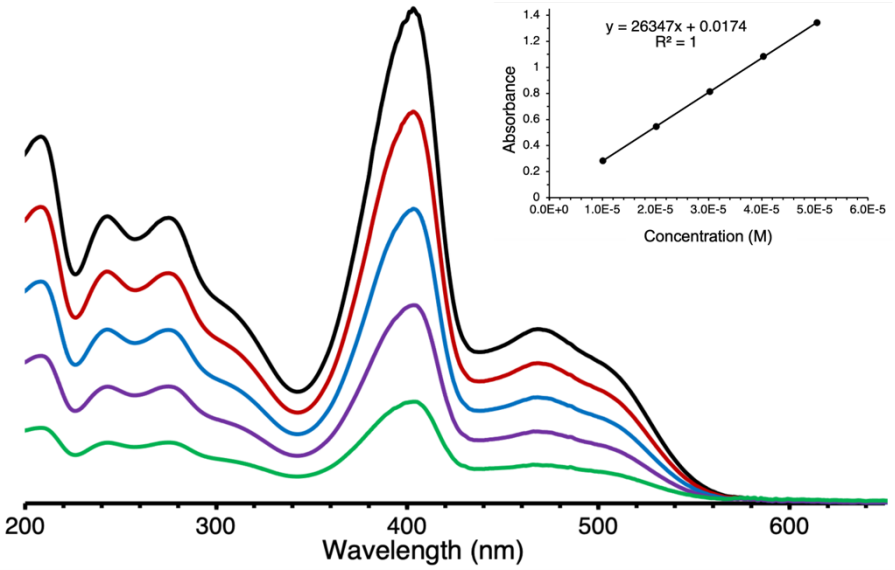


Figure S8. Absorption spectrum of **7** in acetonitrile at room temperature at different concentrations and the corresponding calibration curves for the peak at ~243 nm (ε = 26,000 $M^{-1}cm^{-1}$).

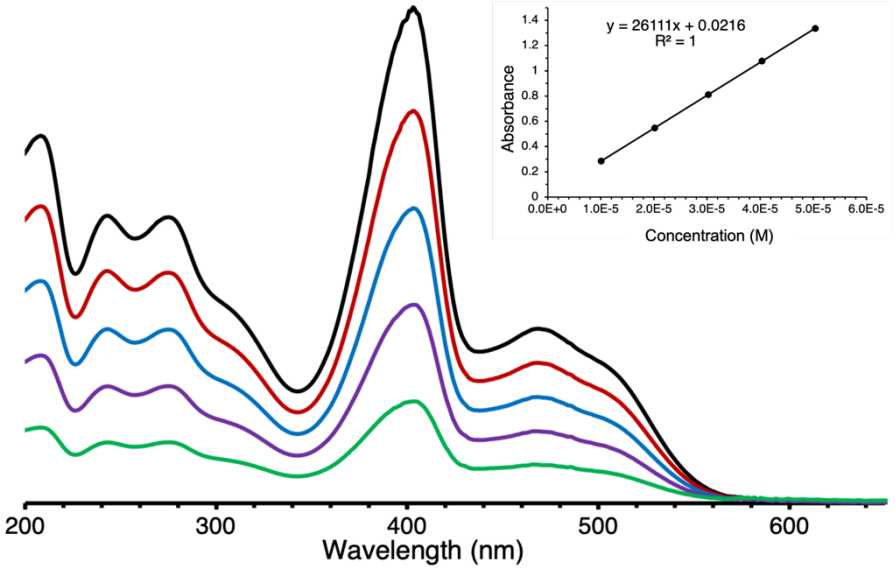


Figure S9. Absorption spectrum of **7** in acetonitrile at room temperature at different concentrations and the corresponding calibration curves for the peak at ~278 nm (ε = 22,000 $M^{-1}cm^{-1}$).

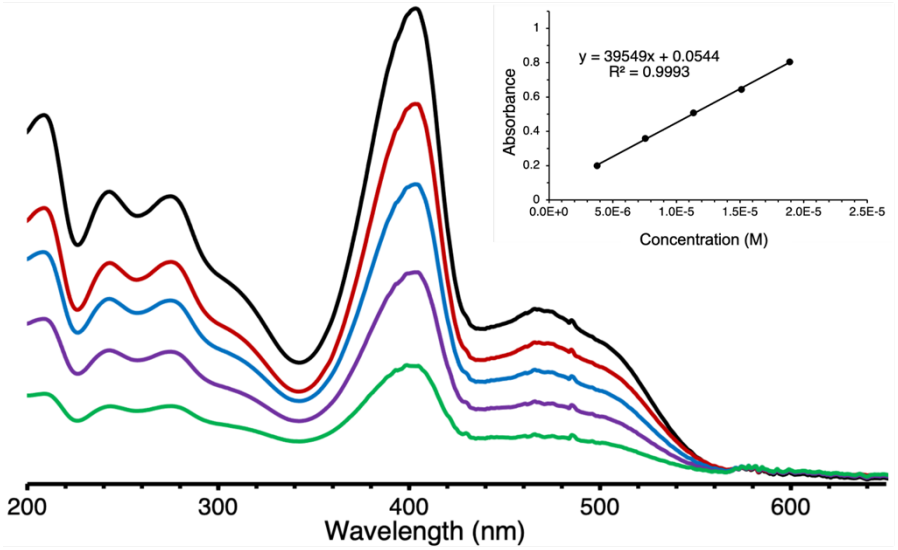


Figure S10. Absorption spectrum of **7** in acetonitrile at room temperature at different concentrations and the corresponding calibration curves for the peak at ~403 nm (ε = 34,000 $M^{-1}cm^{-1}$).

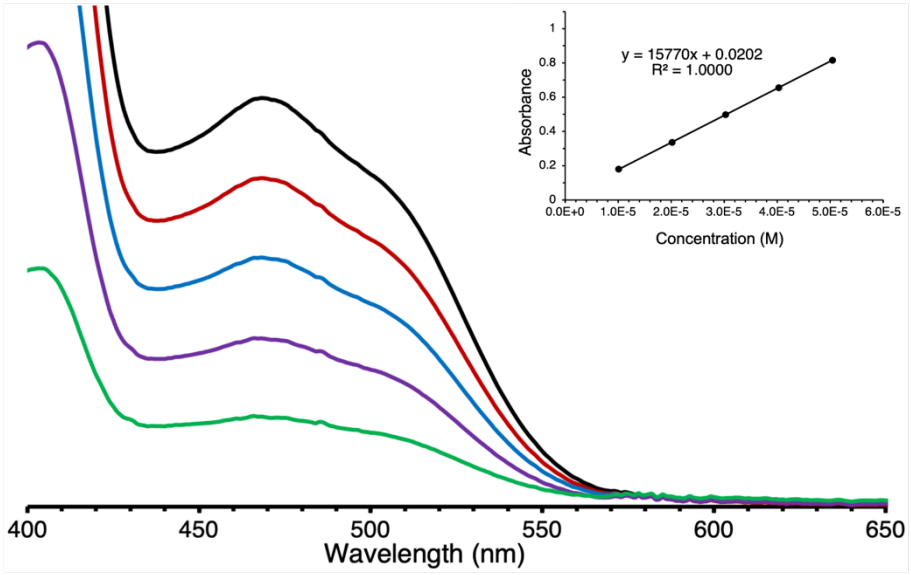


Figure S11. Absorption spectrum of **7** in acetonitrile at room temperature at different concentrations and the corresponding calibration curves for the peak at ~469 nm (ε = 12,000 $M^{-1}cm^{-1}$).

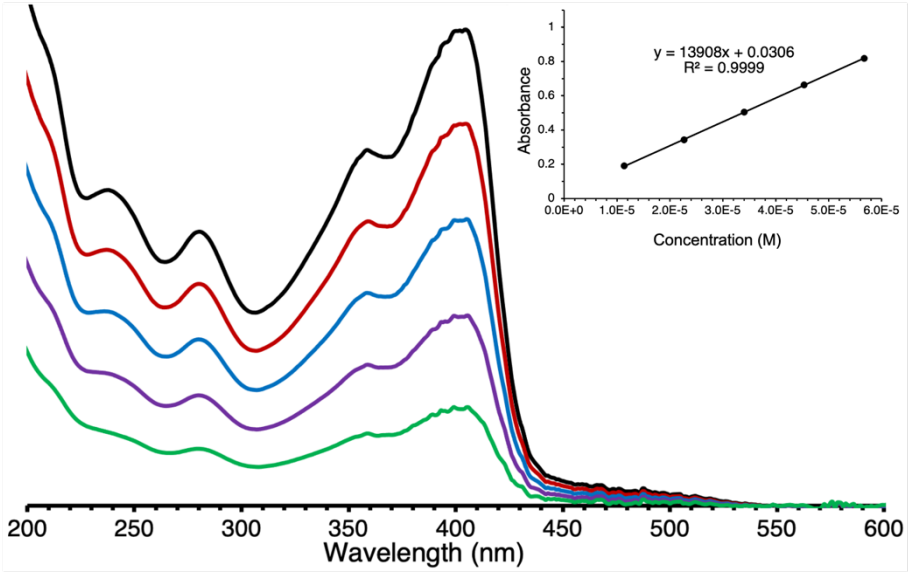


Figure S12. Absorption spectrum of **8** in acetonitrile at room temperature at different concentrations and the corresponding calibration curves for the peak at ~237 nm (ε = 14,000 $M^{-1}cm^{-1}$).

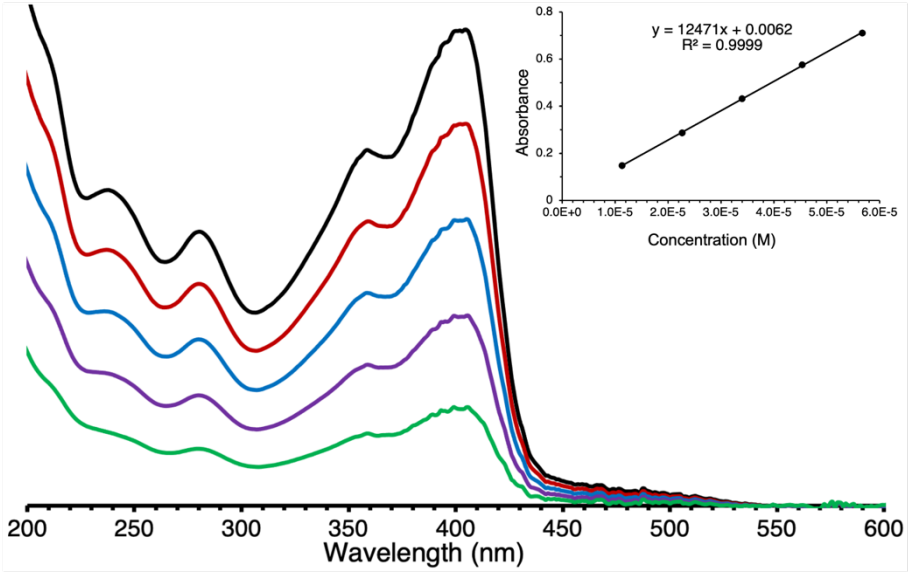


Figure S13. Absorption spectrum of **8** in acetonitrile at room temperature at different concentrations and the corresponding calibration curves for the peak at ~280 nm (ε = 15,000 $M^{-1}cm^{-1}$).

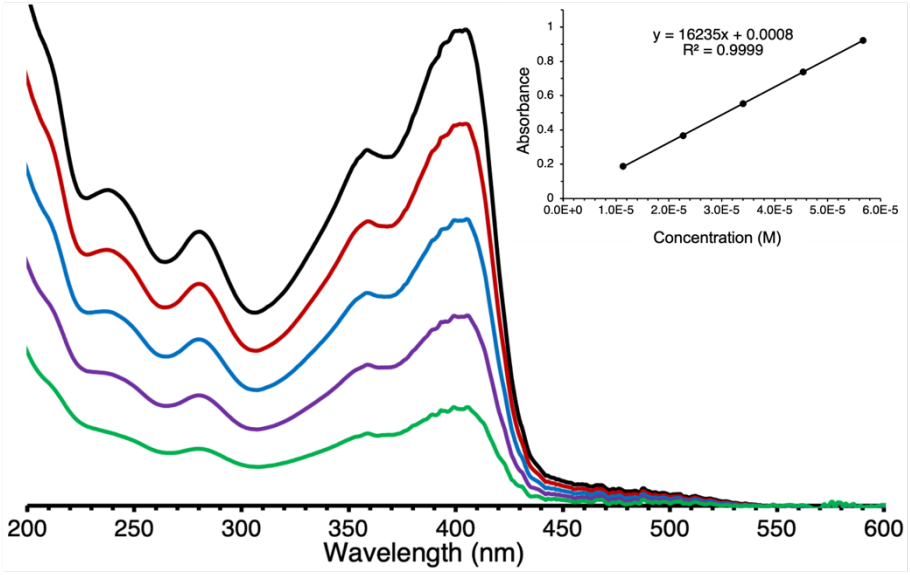


Figure S14. Absorption spectrum of **8** in acetonitrile at room temperature at different concentrations and the corresponding calibration curves for the peak at ~357 nm (ε = 20,000 $M^{-1}cm^{-1}$).

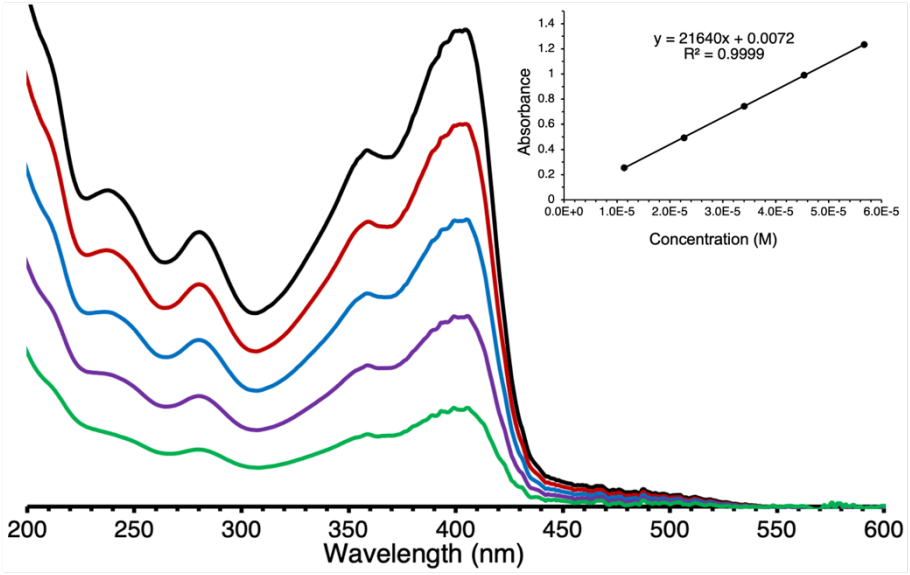


Figure S15. Absorption spectrum of **8** in acetonitrile at room temperature at different concentrations and the corresponding calibration curves for the peak at ~403 nm (ε = 26,000 $M^{-1}cm^{-1}$)

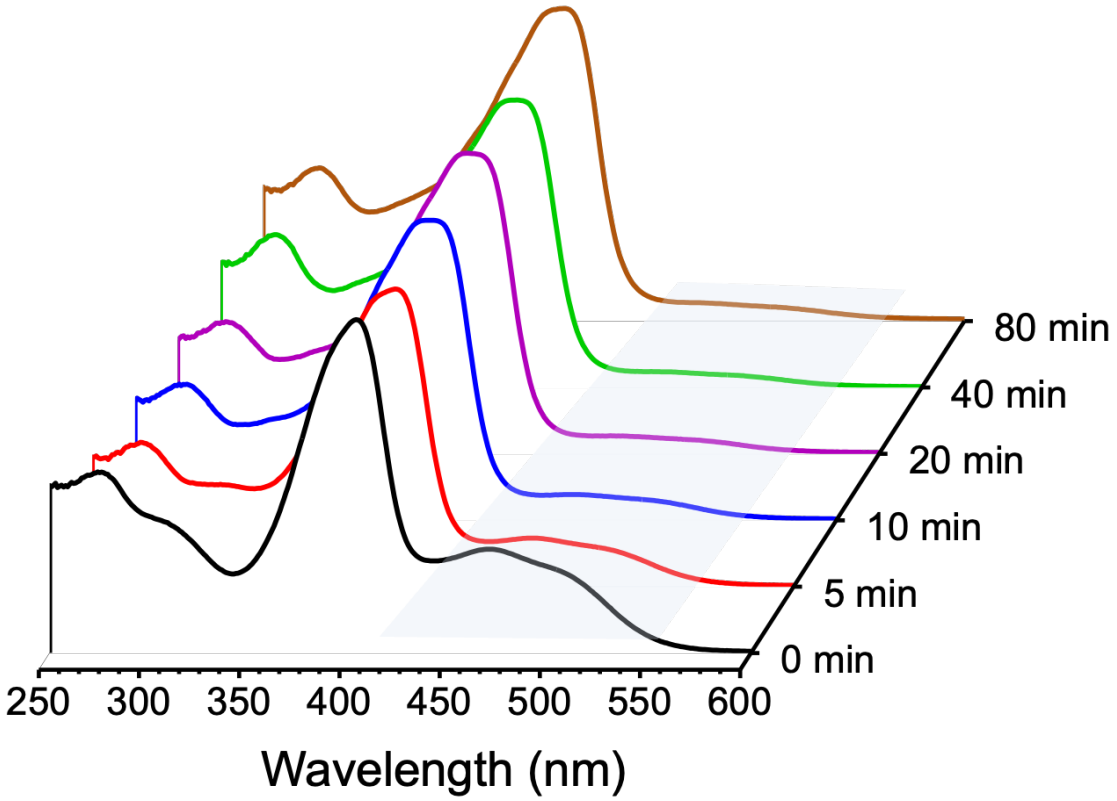


Figure S16. Time-course spectral evolution of the conversion of **7** to **8** upon treatment under the Nazarov cyclization conditions in acetonitrile. Legend: 0 min, black; 5 min, red; 10 min, blue; 20 min, magenta; 40 min, green; 80 min, brown.

(3) ^{1}H NMR assignments for model phyllobilin 8.

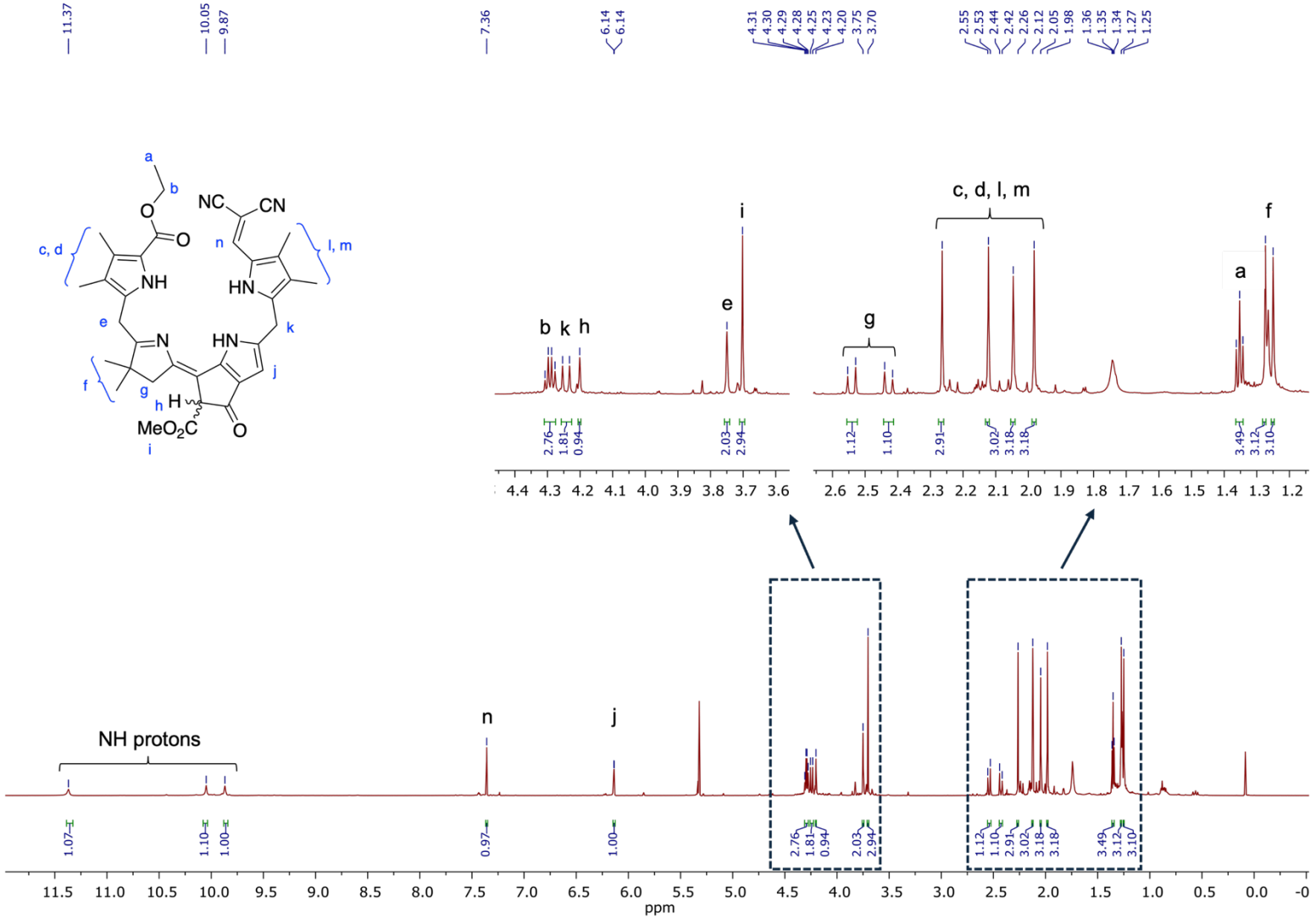


Figure S17. ^{1}H NMR (700 MHz, CD_2Cl_2) assignment of model phyllobilin **8**.

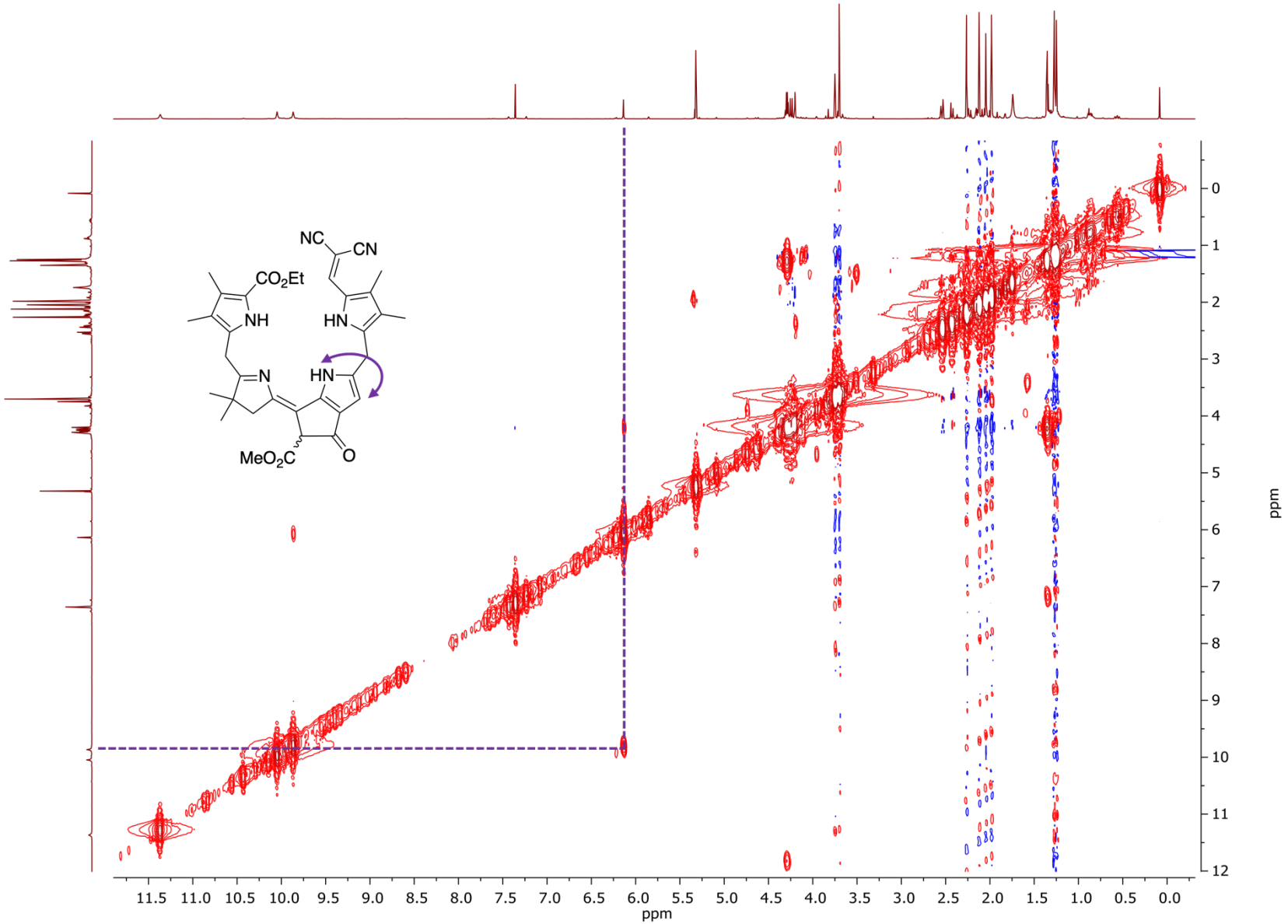


Figure S18. Full COSY spectrum (700 MHz, CD_2Cl_2) of model phyllobilin **8**.

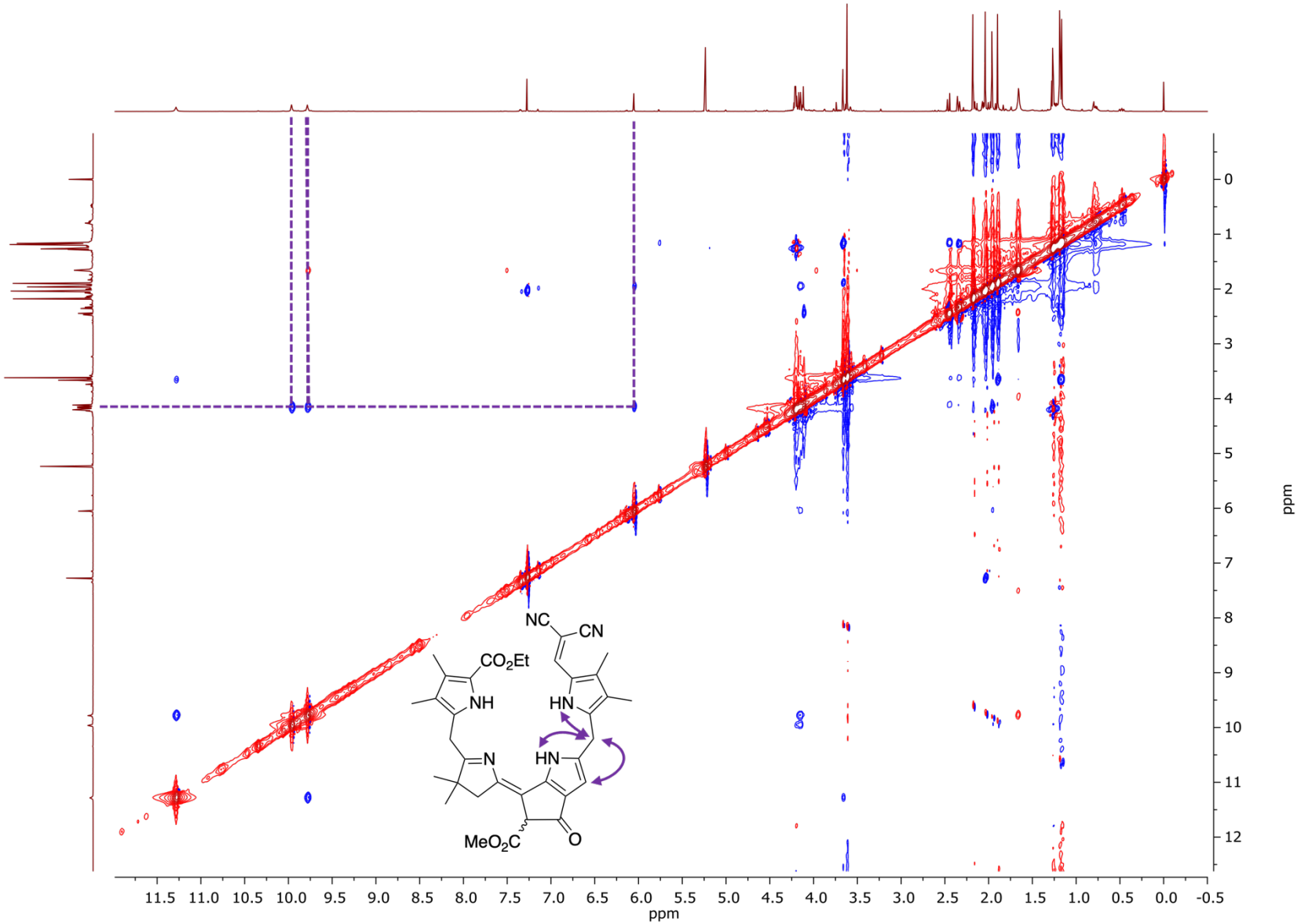


Figure S19. Full NOESY spectrum (700 MHz, CD_2Cl_2) of model phyllobilin **8**.

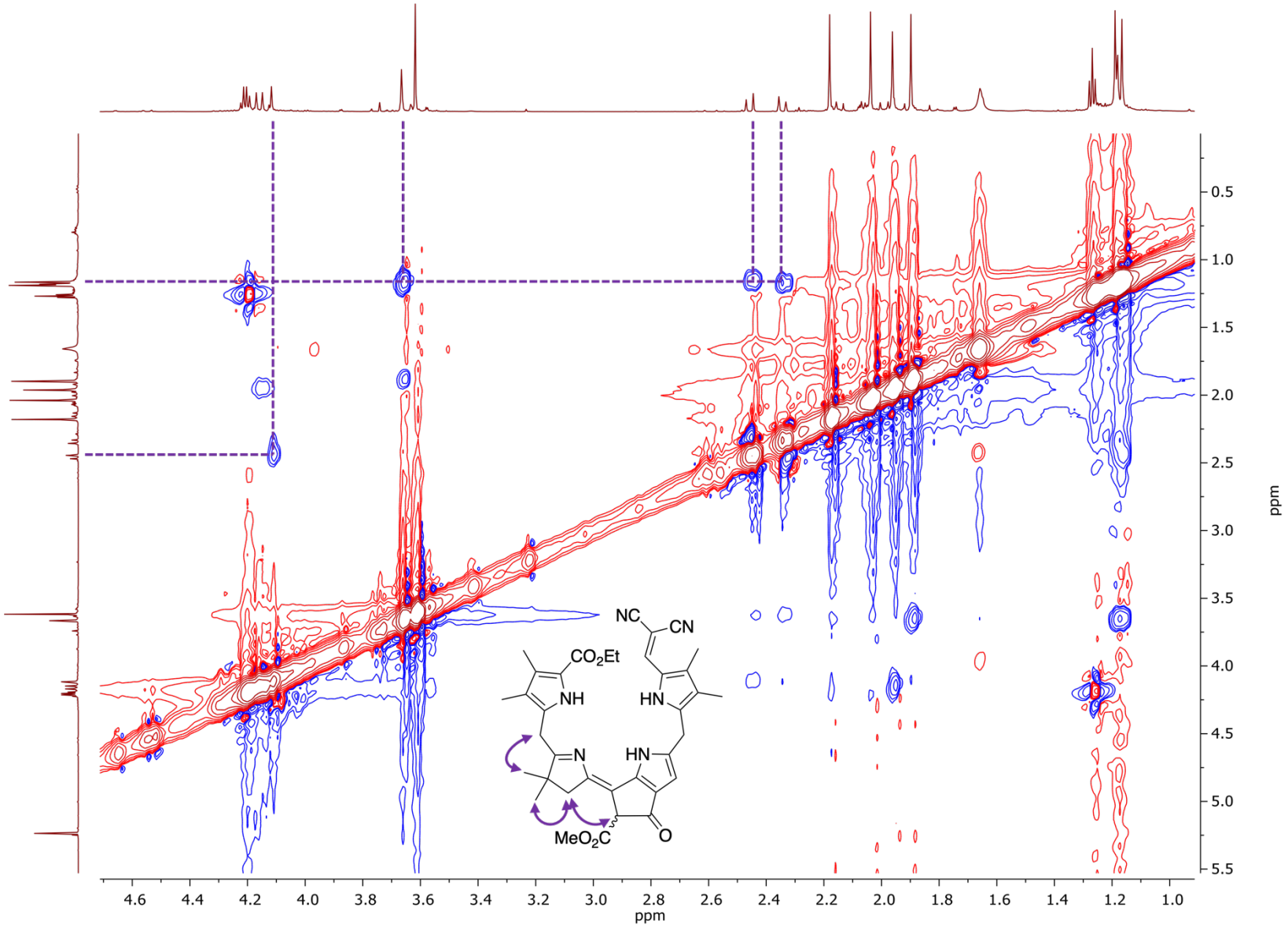


Figure S20. Enlarged NOESY spectrum (700 MHz, CD_2Cl_2) of model phyllobilin **8**.

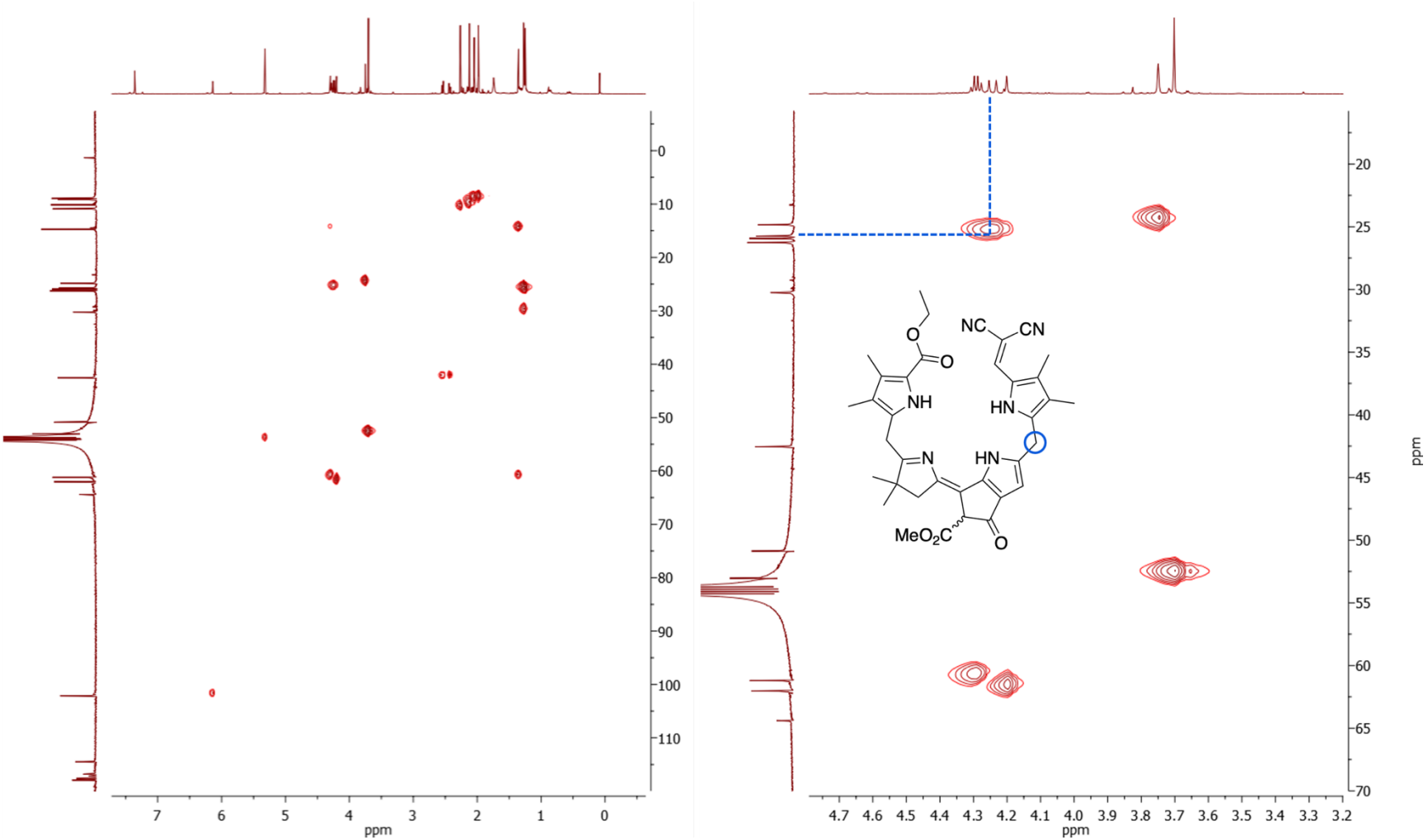
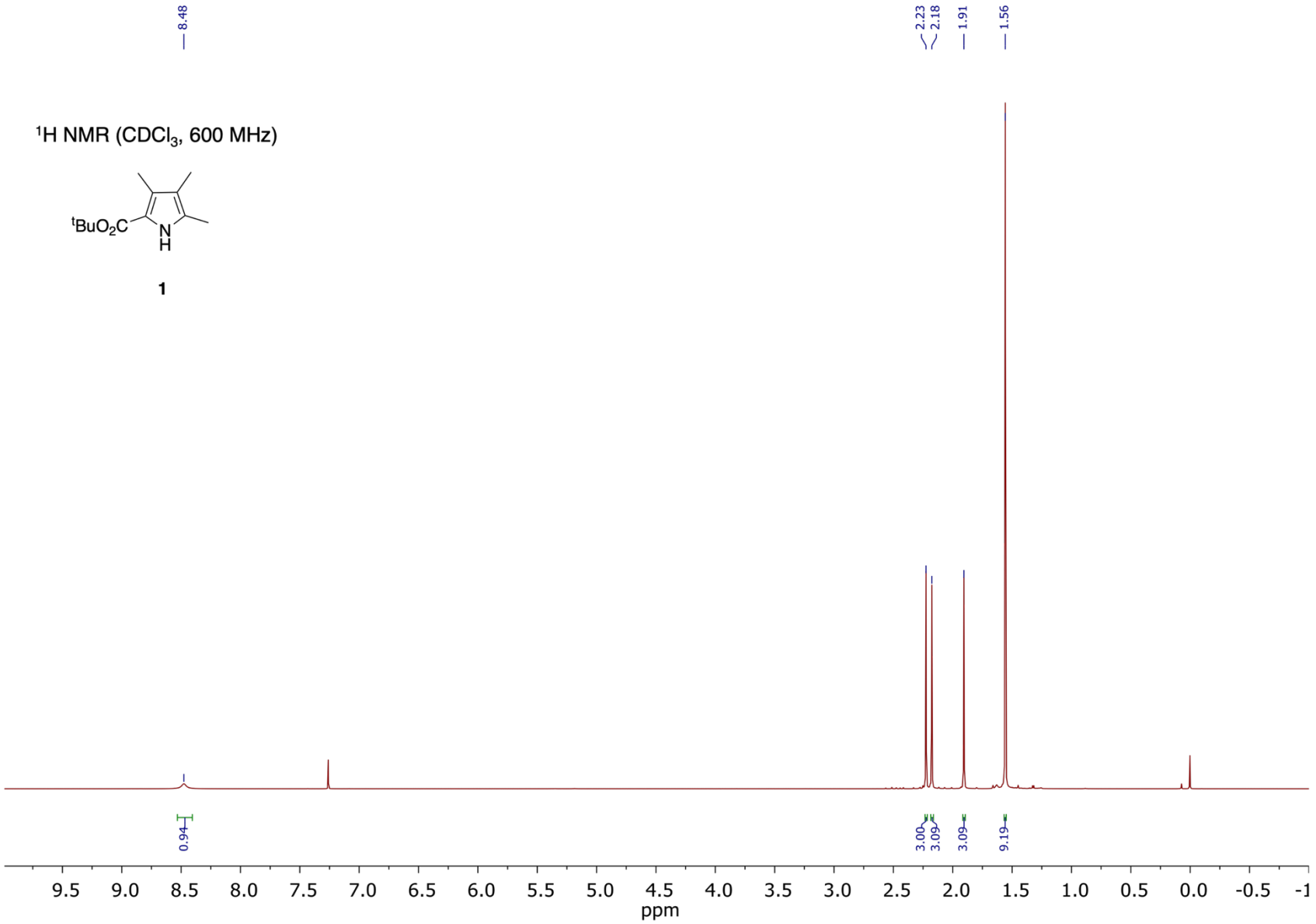
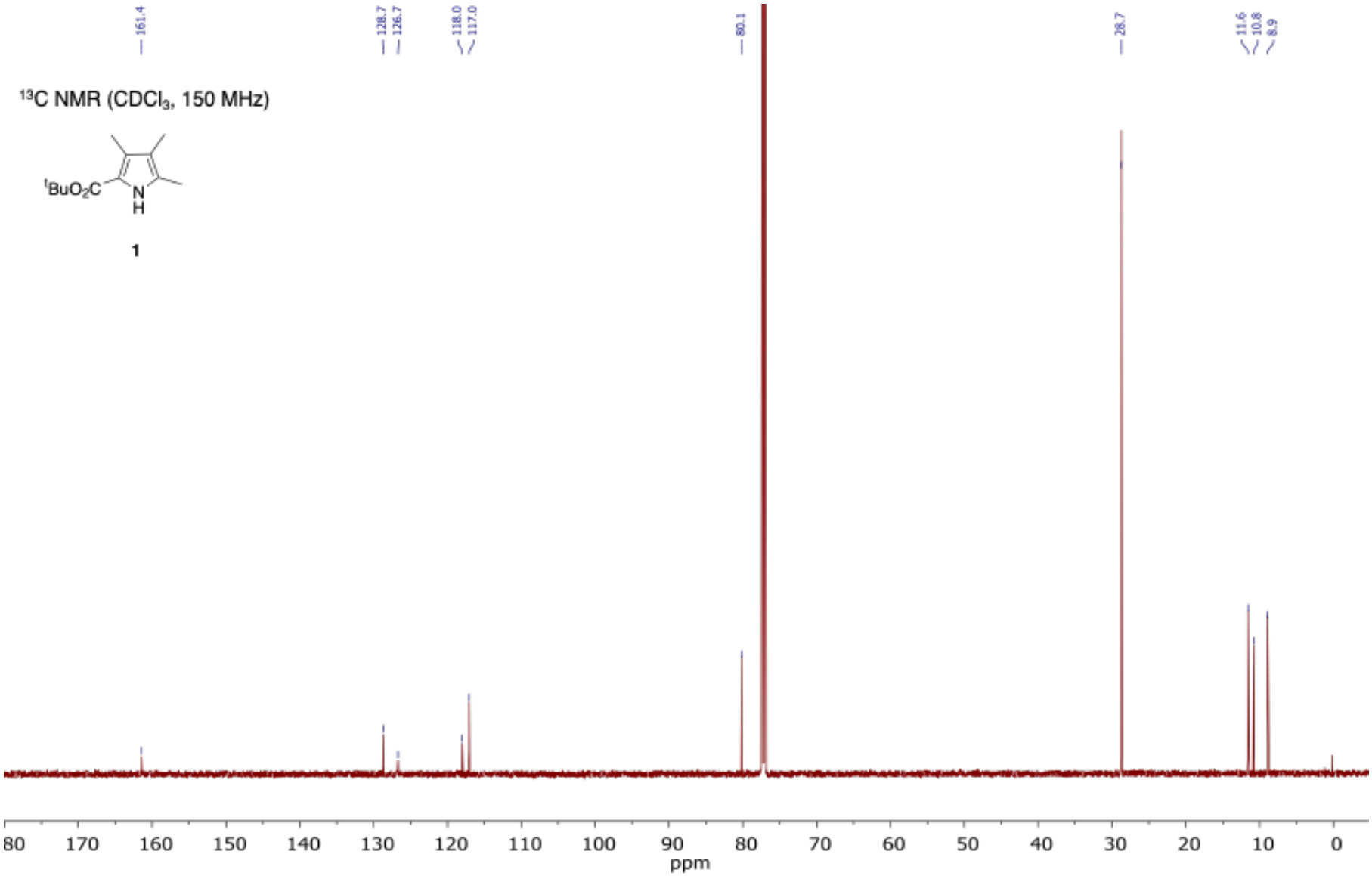
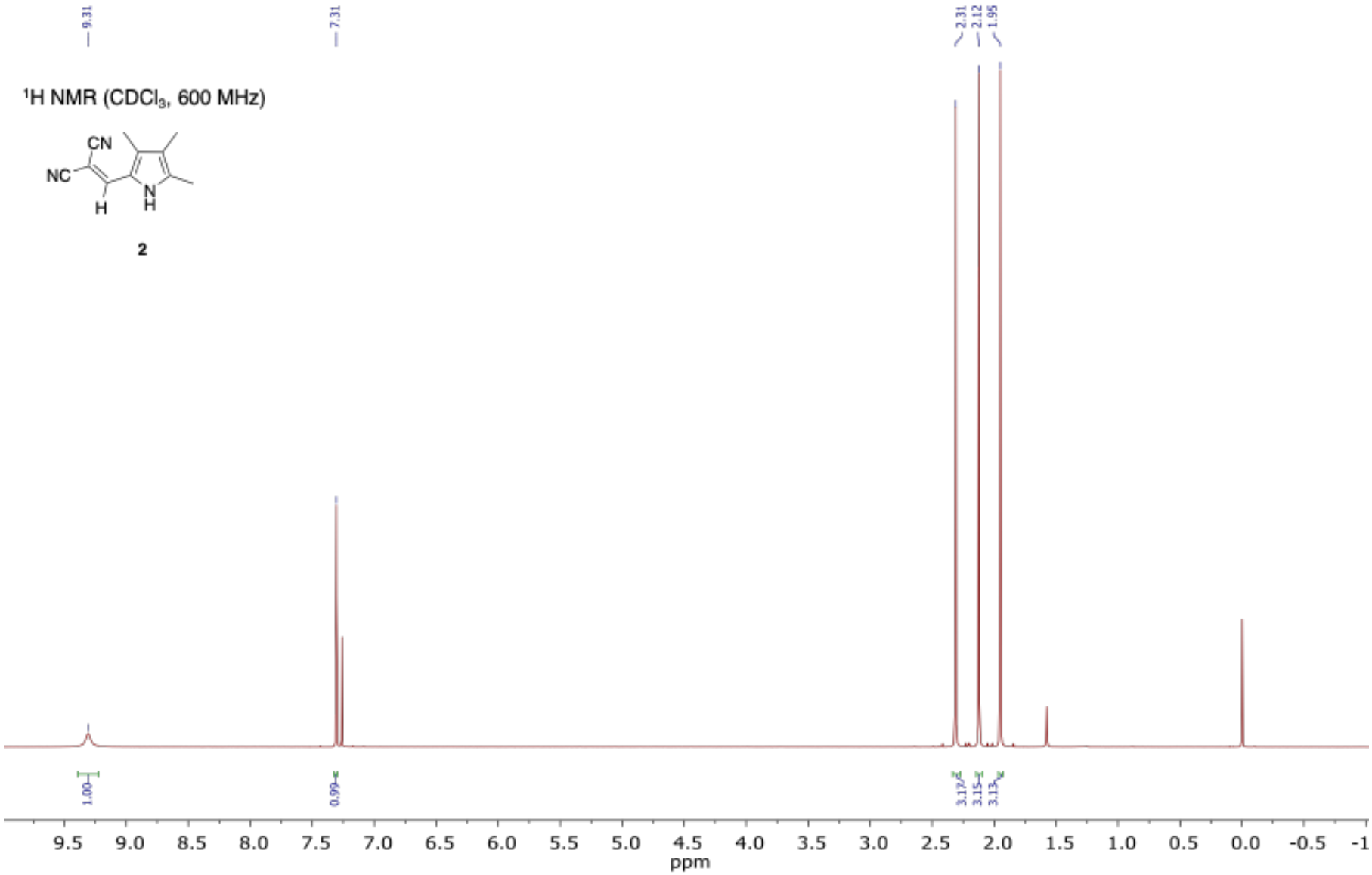


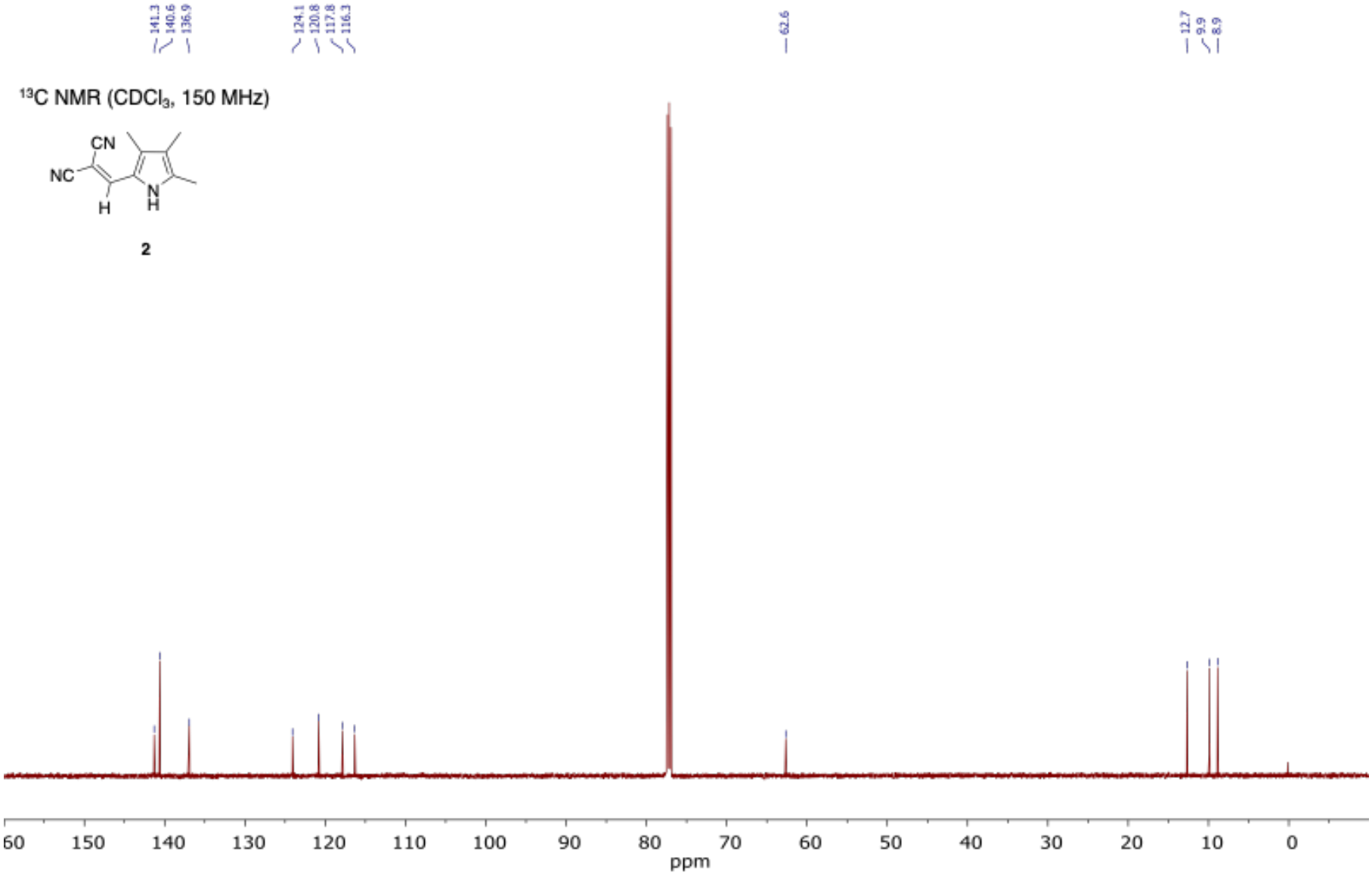
Figure S21. Full HSQC spectrum (700 MHz, CD_2Cl_2) of model phyllobilin **8** (left) and enlarged region showing the correlations of the methylene protons and those at position 5.

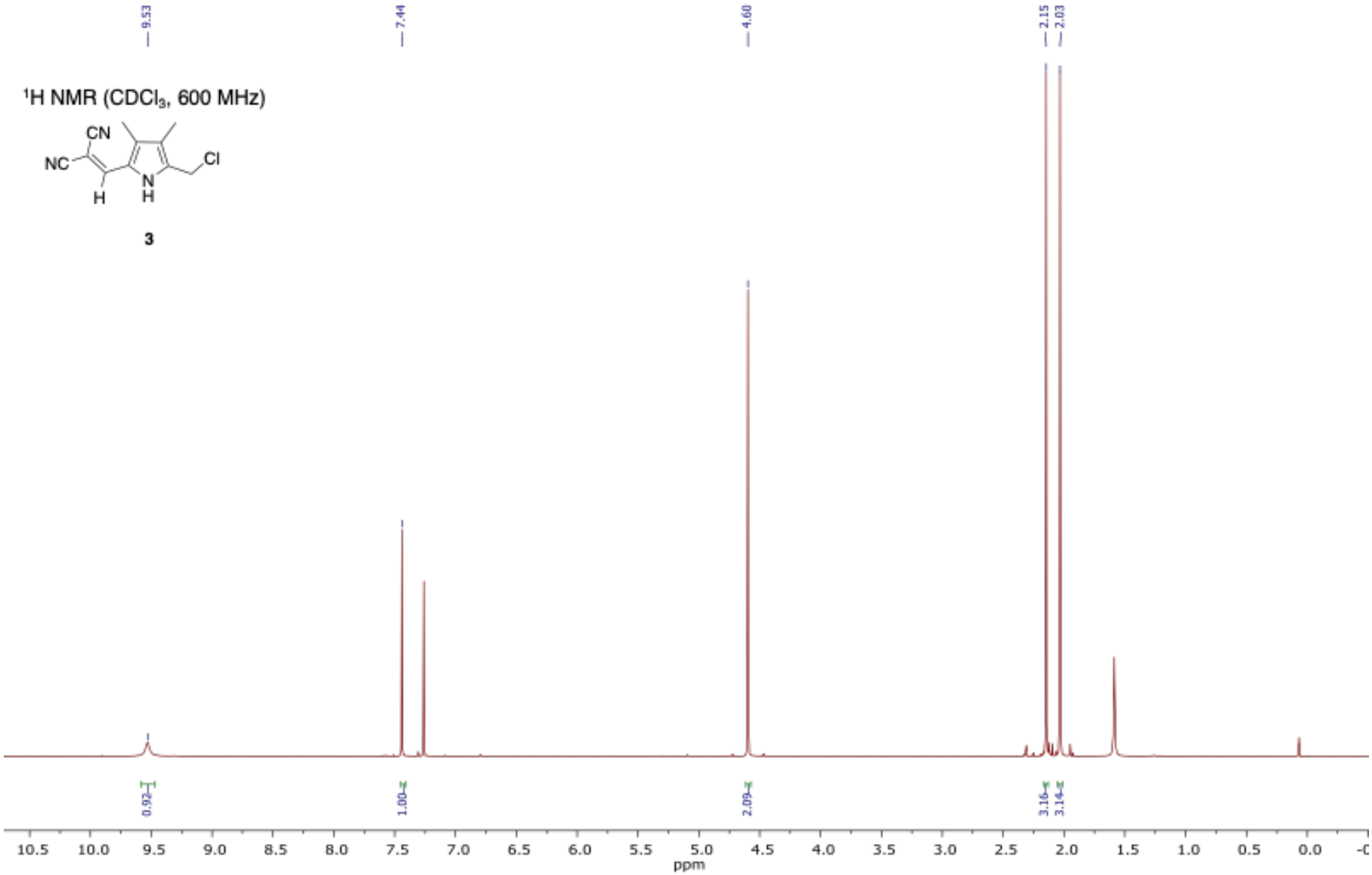
(4) Spectral data.

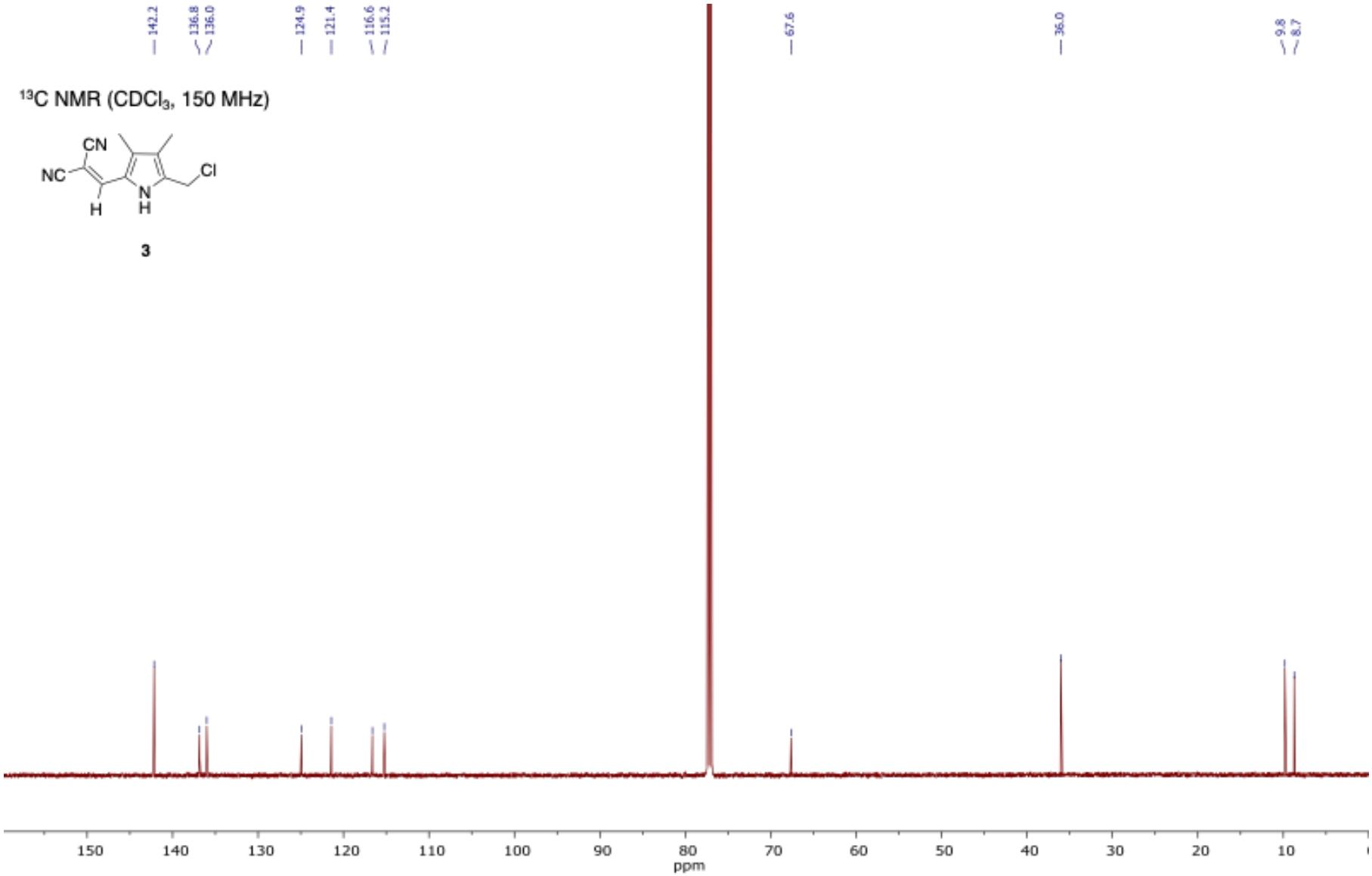


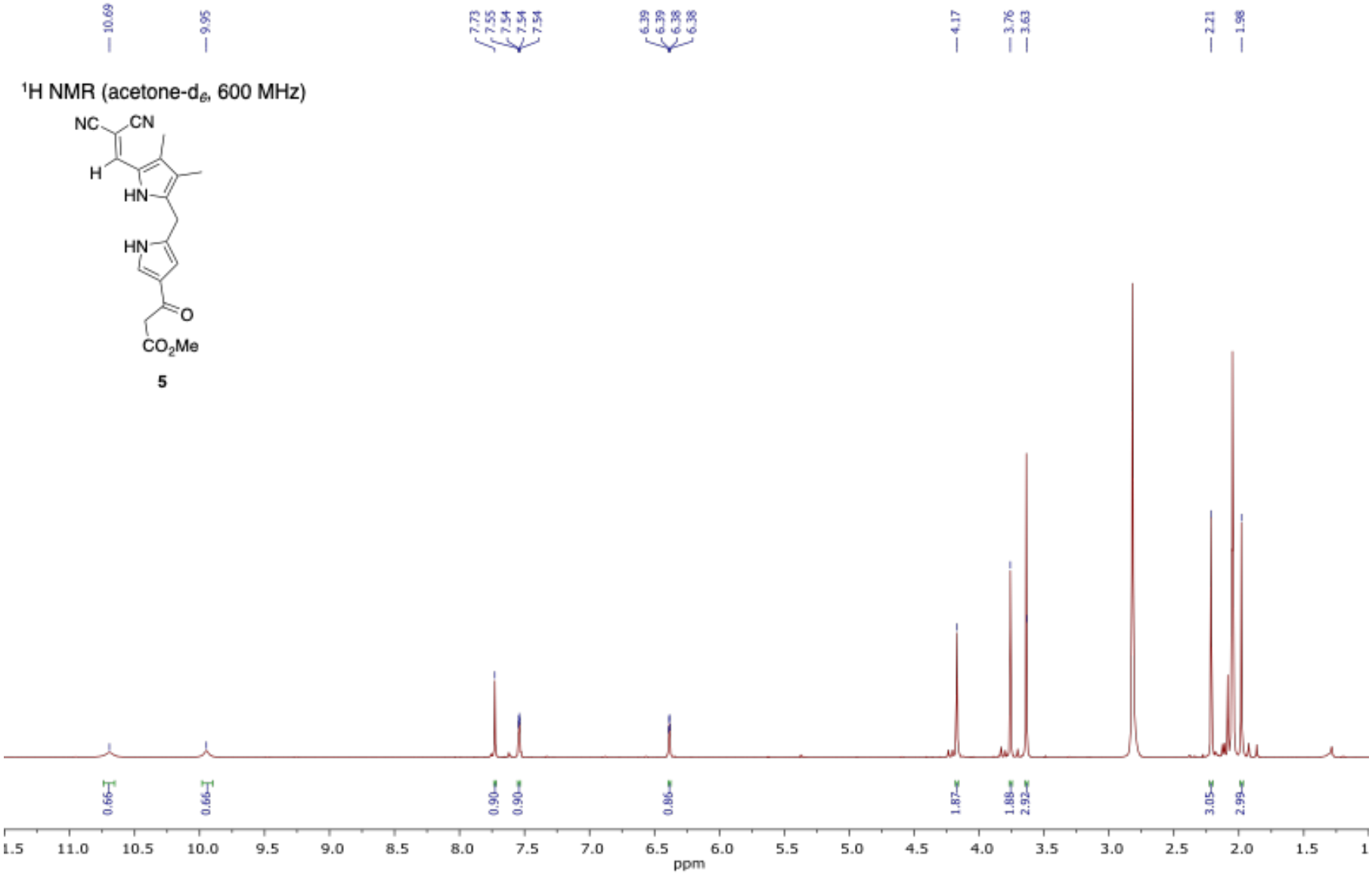

161.4
128.7
126.7
118.0
117.0
80.1
28.7
11.6
10.8
8.9
^{13}C NMR ($CDCl_3$, 150 MHz)
$^tBuO_2C$
N
H
1
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

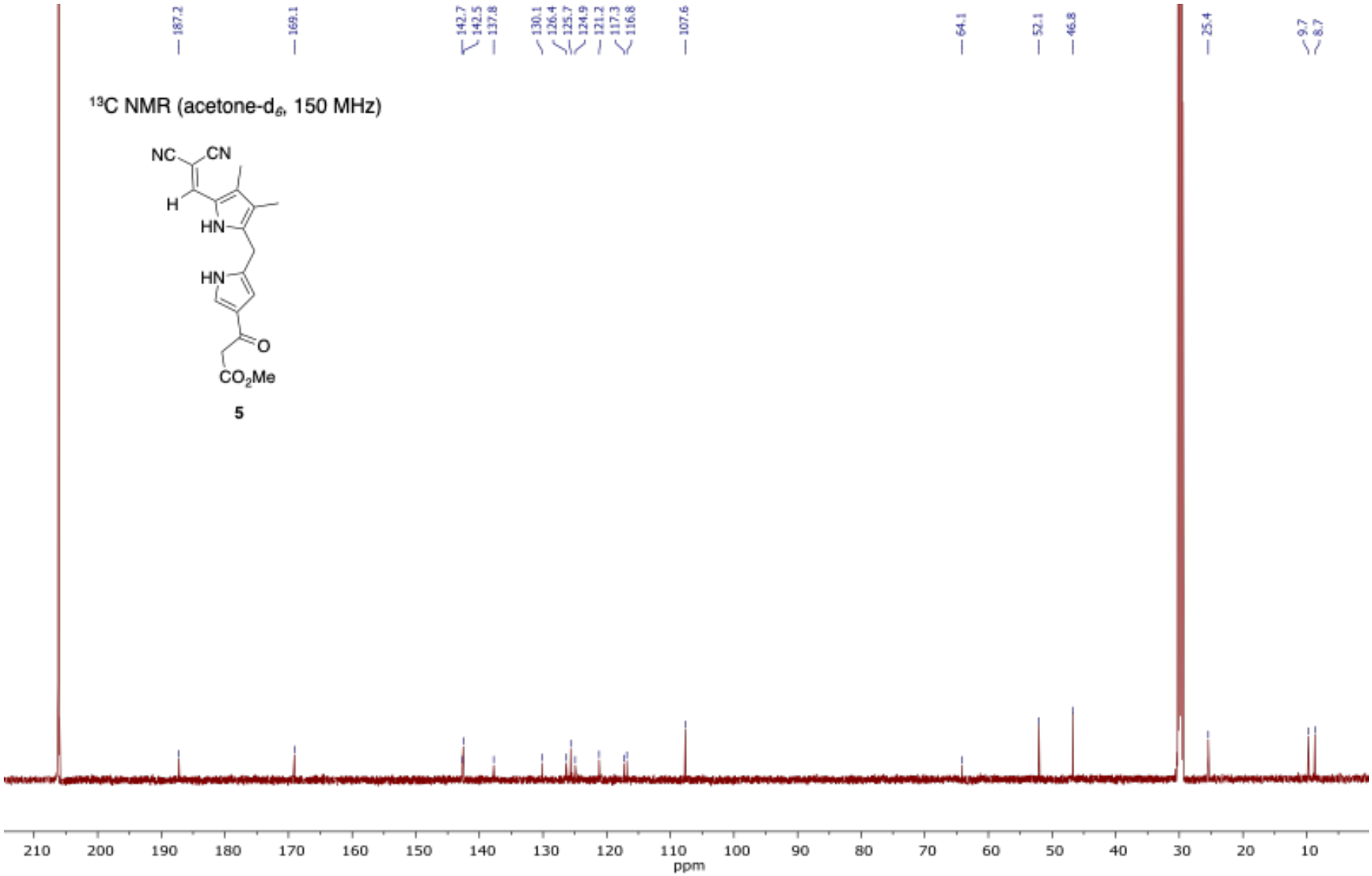

9.31
7.31
2.31
2.12
1.95
¹H NMR (CDCl₃, 600 MHz)
CN
NC
H
N
H
2
1.00
0.99
3.17
3.15
3.13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
ppm


141.3
140.6
136.9
124.1
120.8
117.8
116.3
62.6
12.7
9.9
8.9
^{13}C NMR ($CDCl_3$, 150 MHz)
CN
NC
H
N
H
2
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

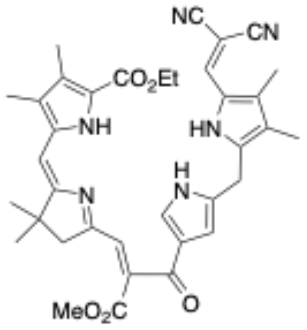

9.53
7.44
4.60
2.15
2.03
^{1}H NMR ($CDCl_3$, 600 MHz)
CN
NC
H
N
H
Cl
3
0.92
1.00
2.09
3.16
3.14
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


142.2
136.8
136.0
124.9
121.4
116.6
115.2
67.6
36.0
9.8
8.7
13C NMR (CDCl3, 150 MHz)
CN
NC
H
N
H
Cl
3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

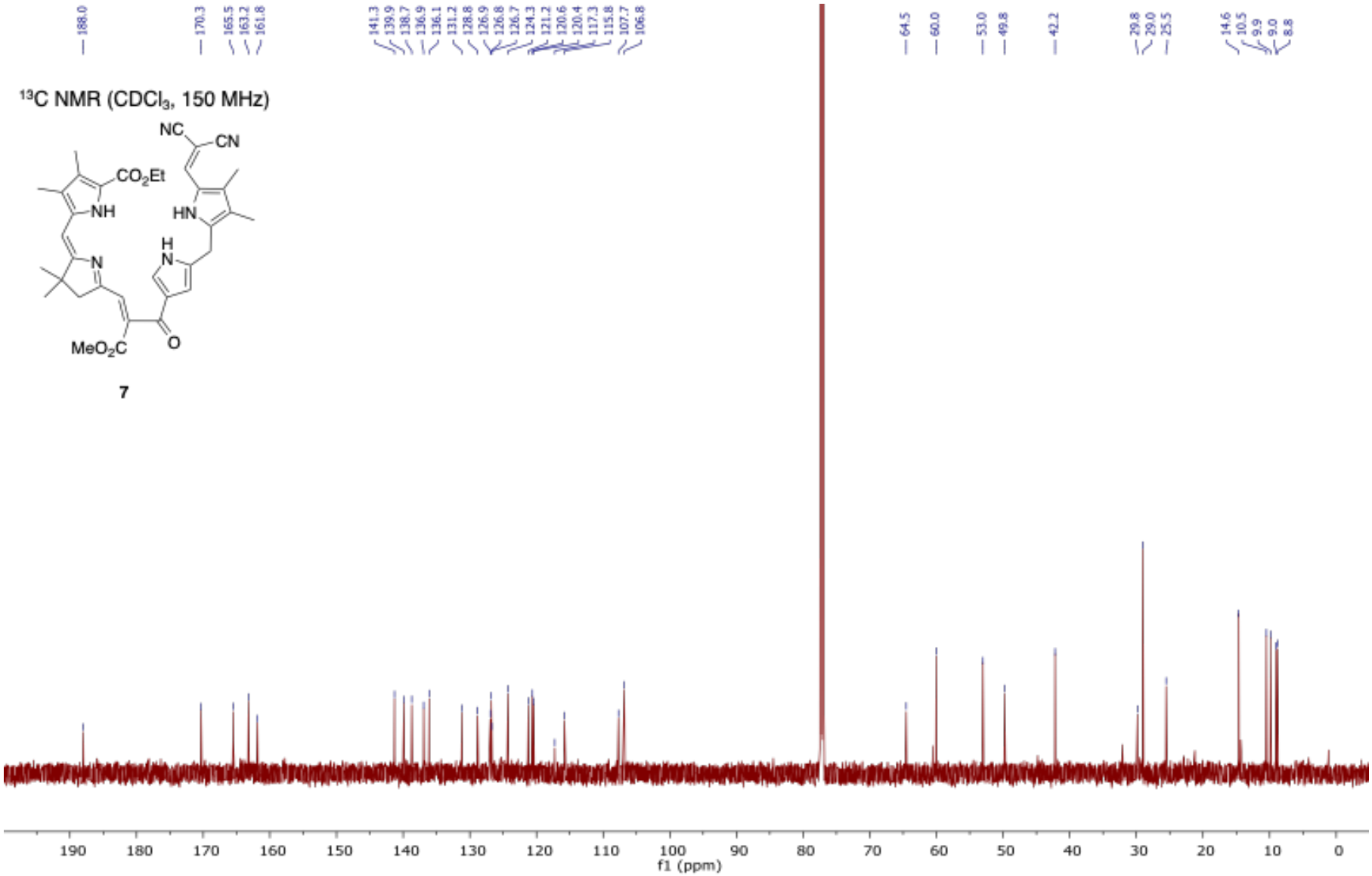

10.69
9.95
7.73
7.55
7.54
7.54
7.54
6.39
6.39
6.38
6.38
4.17
3.76
3.63
2.21
1.98
¹H NMR (acetone-d6, 600 MHz)
NC
CN
H
HN
HN
O
CO2Me
5
0.66
0.66
0.90
0.90
0.86
1.87
1.88
2.92
3.05
2.99
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1
ppm

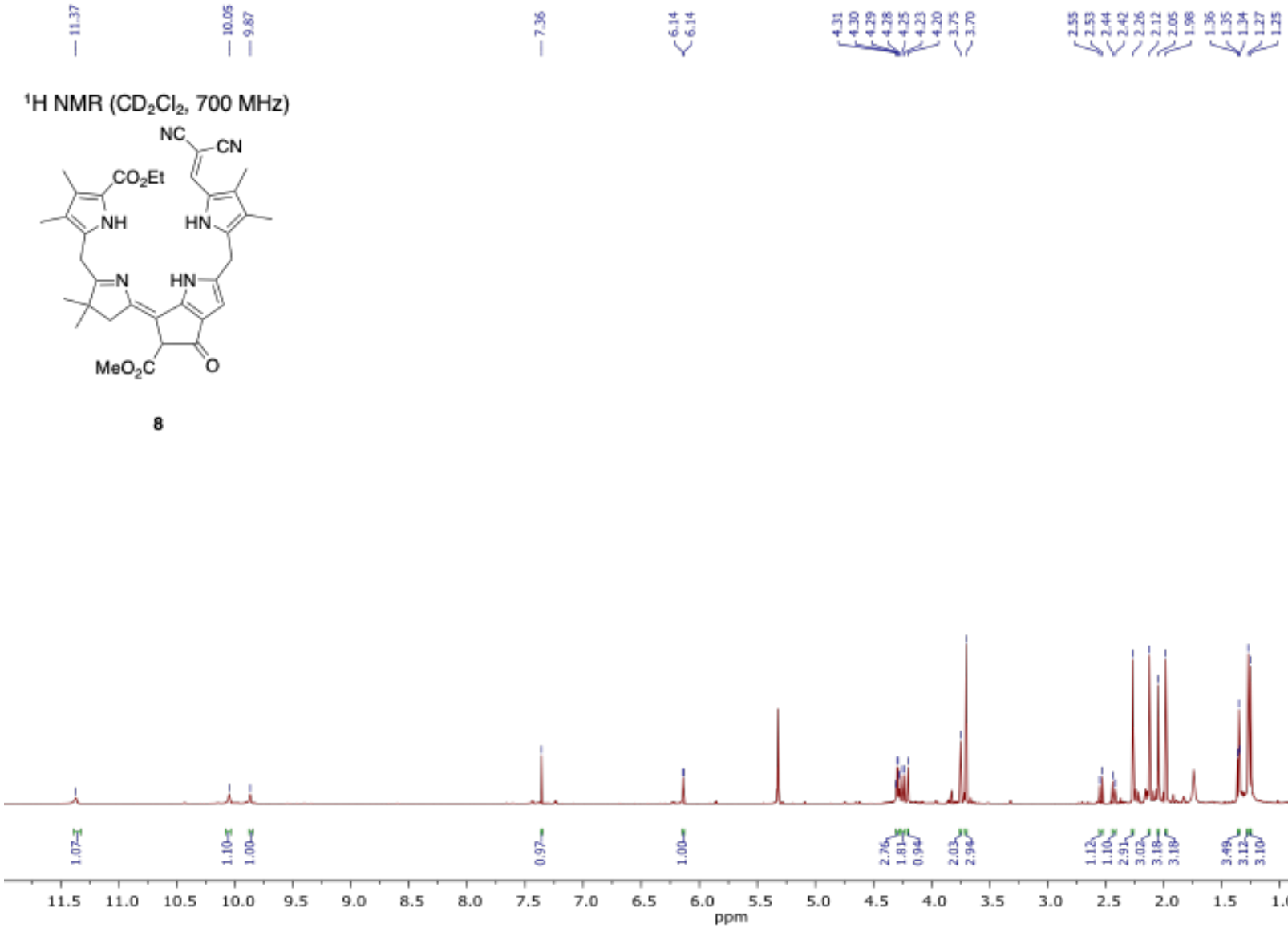

187.2
169.1
142.7
142.5
137.8
130.1
126.4
125.7
124.9
121.2
117.3
116.8
107.6
64.1
52.1
46.8
25.4
9.7
8.7
13C NMR (acetone-d6, 150 MHz)
NC
CN
H
HN
HN
O
CO2Me
5
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

^{1}H NMR (CD_2Cl_2, 700 MHz)



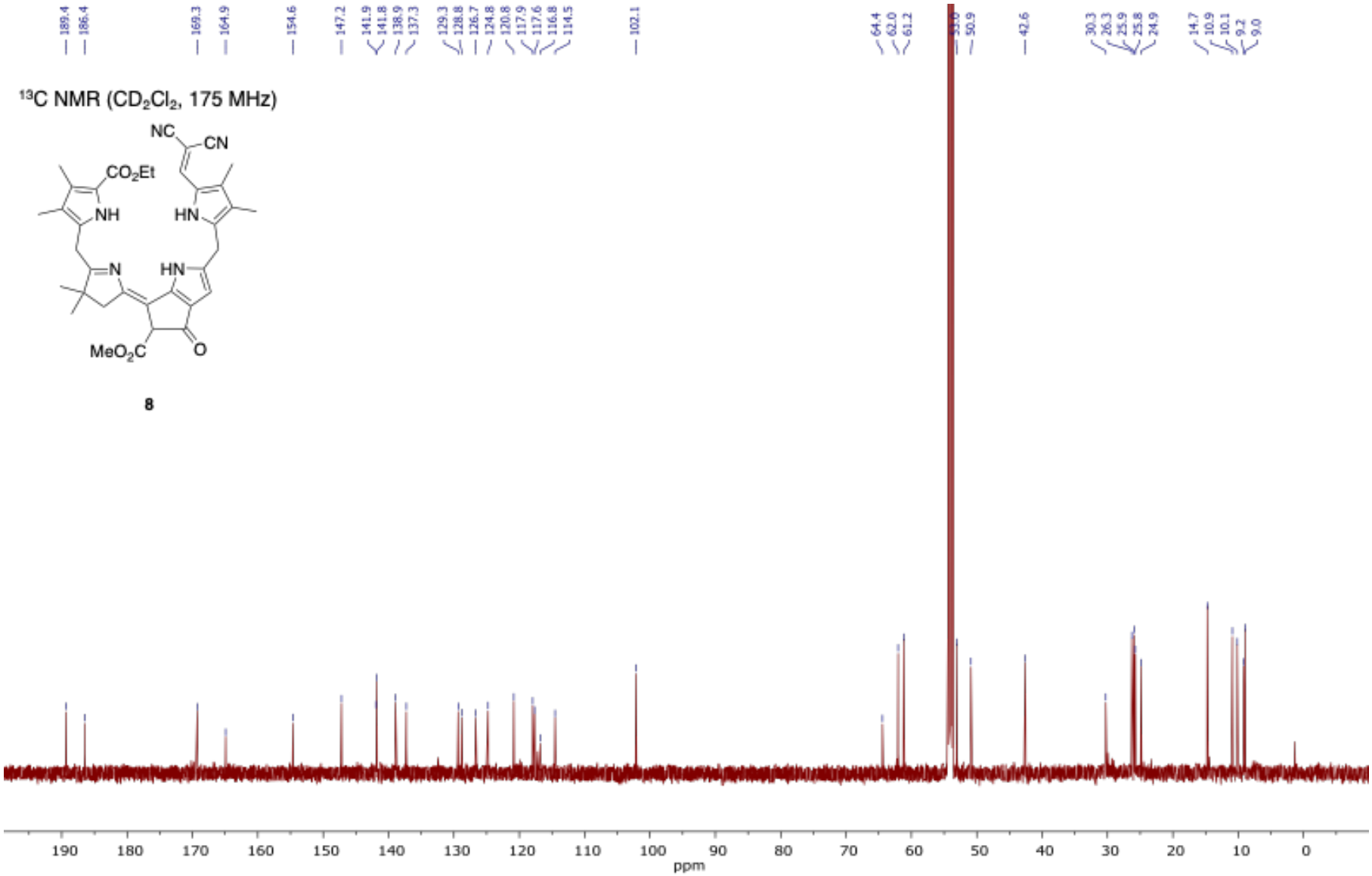
7


188.0
170.3
165.5
163.2
161.8
141.3
139.9
138.7
136.9
136.1
131.2
128.8
126.9
126.8
126.7
124.3
121.2
120.6
120.4
117.3
115.8
107.7
106.8
64.5
60.0
53.0
49.8
42.2
29.8
29.0
25.5
14.6
10.5
9.9
9.0
8.8
13C NMR (CDCl3, 150 MHz)
NC
CN
CO2Et
NH
HN
H
N
N
MeO2C
O
7
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 (CD_2Cl_2, 700 MHz)

8


189.4
186.4
169.3
164.9
154.6
147.2
141.9
141.8
138.9
137.3
129.3
128.8
126.7
124.8
120.8
117.9
117.6
116.8
114.5
102.1
64.4
62.0
61.2
53.0
50.9
42.6
30.3
26.3
25.9
25.8
24.9
14.7
10.9
10.1
9.2
9.0
13C NMR (CD2Cl2, 175 MHz)
NC
CN
CO2Et
NH
HN
N
HN
MeO2C
O
8
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm