Supplementary Materials for:

Dihydrooxazine Byproduct of a McMurry-Melton Reaction En Route to a Synthetic Bacteriochlorin

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(1) X-ray crystal data

Table S1. Crystallographic data of **5b and 5a**

Identification code	**5a**	**5b**
CCDC number	2176728	2176729
Empirical formula	$C_{22}H_{26}N_2O_4$	$C_{22}H_{28}N_2O_6$
Formula weight	382.45	416.46
Temperature/K	100.0	100.00
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1/c$
a/Å b/Å c/Å	6.1873(4) 26.3380(17) 12.1924(8)	11.9124(9) 12.6552(9) 13.9689(10)
α/° β/° γ/°	90 102.960(3) 90	90 91.409(3) 90
Volume/Å^3	1936.3(2)	2105.2(3)
Z	4	4
ρ_{calc} g/cm^3	1.312	1.314
μ/mm^{-1}	0.091	0.096
F(000)	816.0	888.0
Crystal size/mm^3	0.48 × 0.24 × 0.12	0.22 × 0.16 × 0.12
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.618 to 54.204	4.344 to 54.968
Index ranges	$-7 \le h \le 7$, $-33 \le k \le 33$, $-15 \le l \le 15$	$-15 \le h \le 15$, $-16 \le k \le 16$, $-18 \le l \le 18$
Reflections collected	26402	62423
Independent reflections	8506 [R_{int} = 0.0423, R_{sigma} = 0.0483]	4831 [R_{int} = 0.0659, R_{sigma} = 0.0261]
Data/restraints/parameters	8506/1/521	4831/0/313
Goodness-of-fit on F^2	1.009	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0396, wR_2 = 0.0901	R_1 = 0.0439, wR_2 = 0.1112
Final R indexes [all data]	R_1 = 0.0515, wR_2 = 0.0950	R_1 = 0.0569, wR_2 = 0.1188
Largest diff. peak/hole / e Å^{-3}	0.19/–0.26	0.65/–0.33
Flack parameter	0.1(4)	–

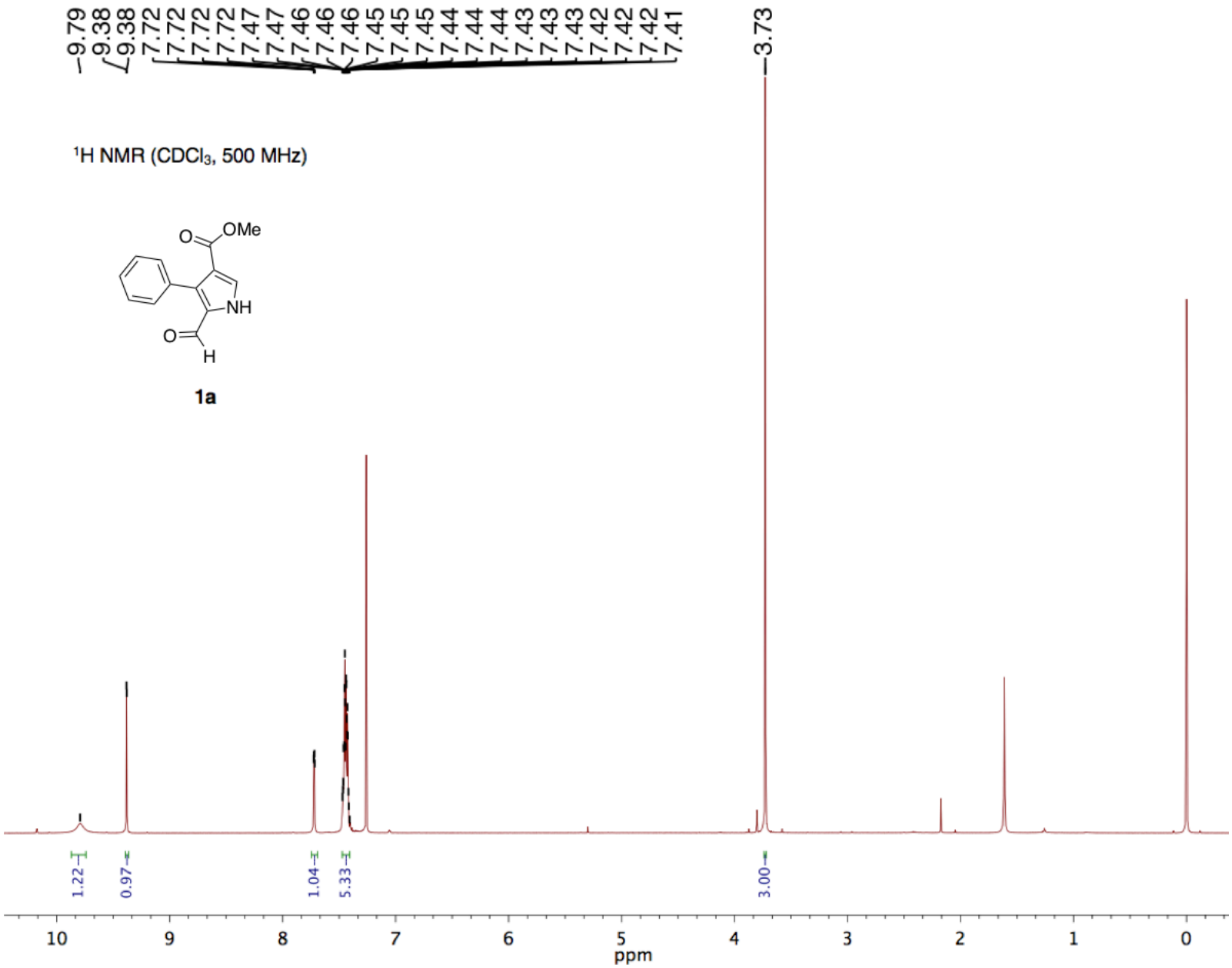
(2) pH Simulation

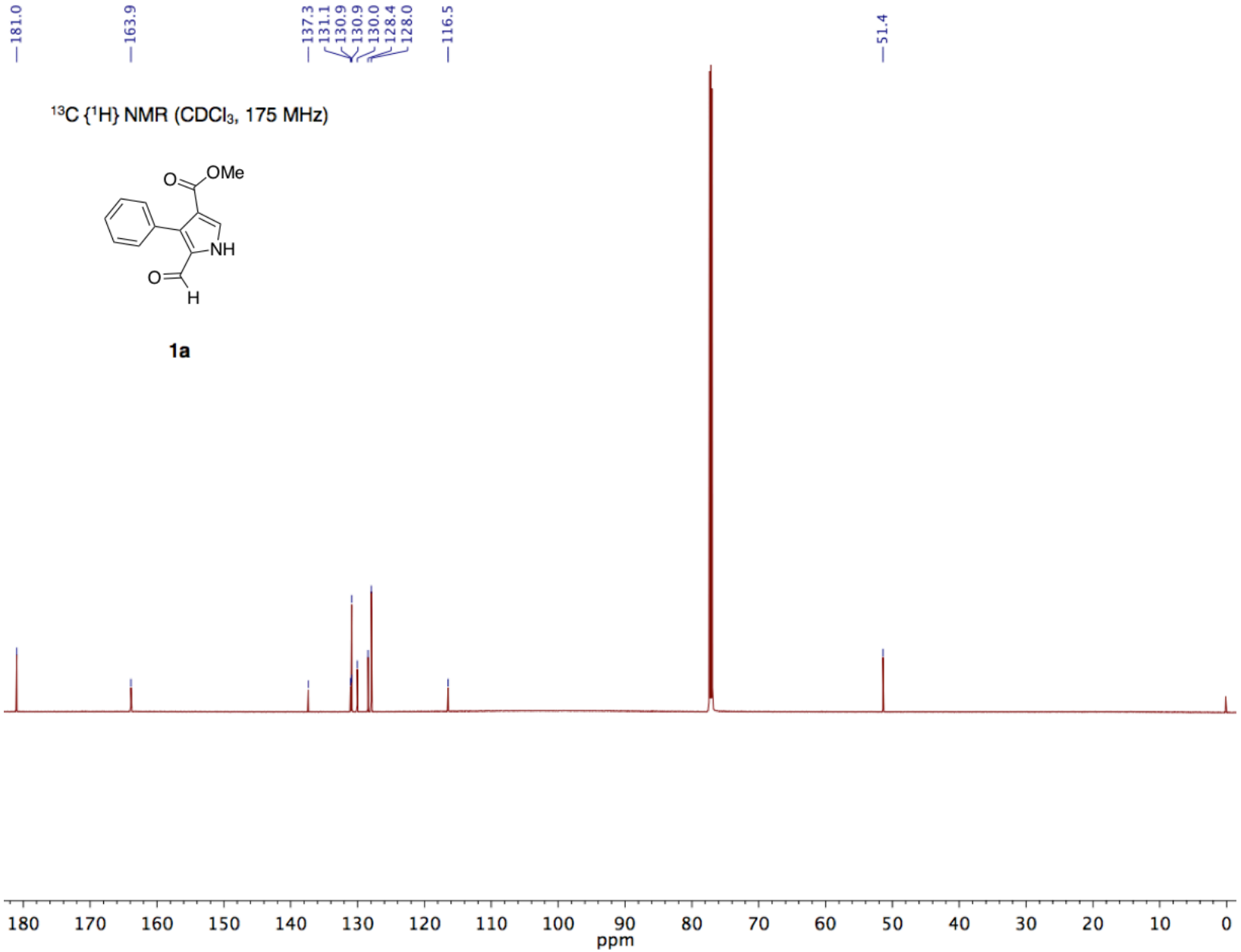
The pH simulations were computed using the following Python script:

```
import math
from scipy.optimize import fsolve
import matplotlib.pyplot as plt

pka = 9.25 # pKa of NH4
pkb = 9.25 # pKb of OAc-
kw = 1e-14 # constant
ka = 10 ** (-1 * pka) # Ka
kb = 10 ** (-1 * pkb) # Kb
equiv = 0.01  # [R-NO2] = 1 equiv =  0.01 M =  10 mM
# Assuming initial [HCl] = a M in [NH4OAc] = s M solution
# [H+] = x, [OH-] = y

def equations(p):
    x, y = p
    return (x*s/(ka + x) + x - y*s/(kb + y) - y - a, kw - x*y)

s_set = [1000, 400, 160, 64, 25.6]# [NH4OAc] (equiv)

# calculation and plot
fig, ax = plt.subplots(figsize=(6, 4))
for se in s_set:
    s = se * equiv
    pHs = []
    x, y =  1e-7, 1e-7  # initial guessing solutions
    for ae in range(120): # [HCl] (equiv)
        a = ae * equiv
        x, y  =  fsolve(equations, (x, y), factor=1, xtol=1e-24)
        pH = -1 * math.log10(x)
        pHs.append(pH)
        print(se, ae, pH, x, y, equations((x, y)))
    ax.plot(range(120), pHs, label='{} equiv'.format(se))

ax.set_ylabel('pH')
ax.set_xlabel('[HCl] equiv')
ax.minorticks_on()
ax.grid(True, which='both')
ax.legend()
```

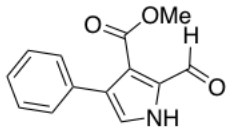
The script provides for successive iteration given an initial estimate to arrive at a calculated value. The features *factor* and *xtol* make the respective initial iteration step and error tolerance small. A root expected here is as small as 10^{-7} (pH = 7). The error was assessed by putting the calculated roots back into the acid-base equation. The maximum error was 1.78×10^{-15}. The resulting pH estimates are in excellent agreement with expected values. For example, with no HCl the calculated pH is 7.0, in agreement with expectation.

(3) NMR data

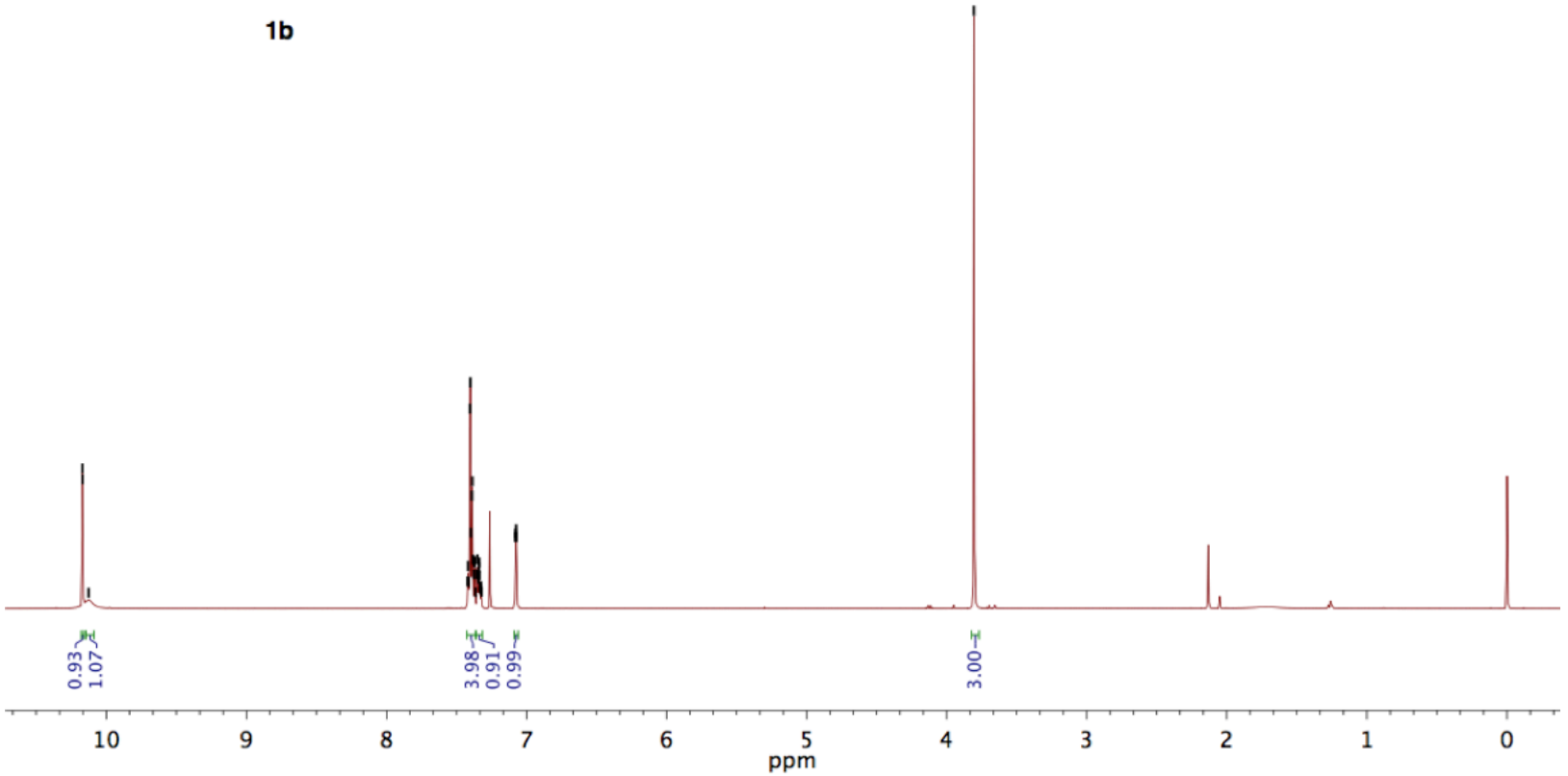

9.79
9.38
9.38
7.72
7.72
7.72
7.47
7.47
7.46
7.46
7.46
7.45
7.45
7.45
7.44
7.44
7.44
7.43
7.43
7.42
7.42
7.41
3.73
1H NMR (CDCl3, 500 MHz)
OMe
O
NH
O
H
1a
1.22
0.97
1.04
5.33
3.00
10
9
8
7
6
5
4
3
2
1
0
ppm

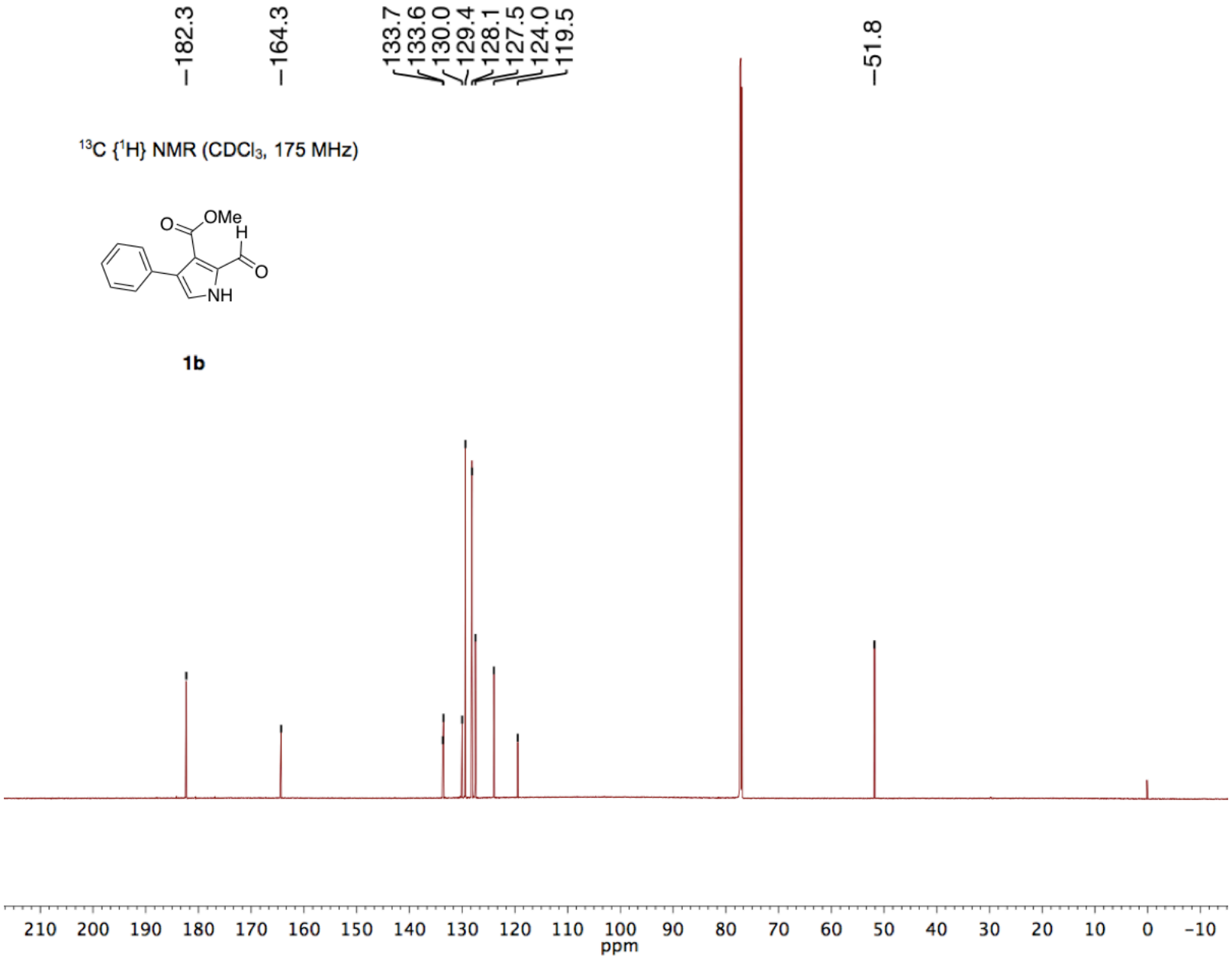

181.0
163.9
137.3
131.1
130.9
130.9
130.0
128.4
128.0
116.5
51.4
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 175 MHz)
O
OMe
NH
O
H
1a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

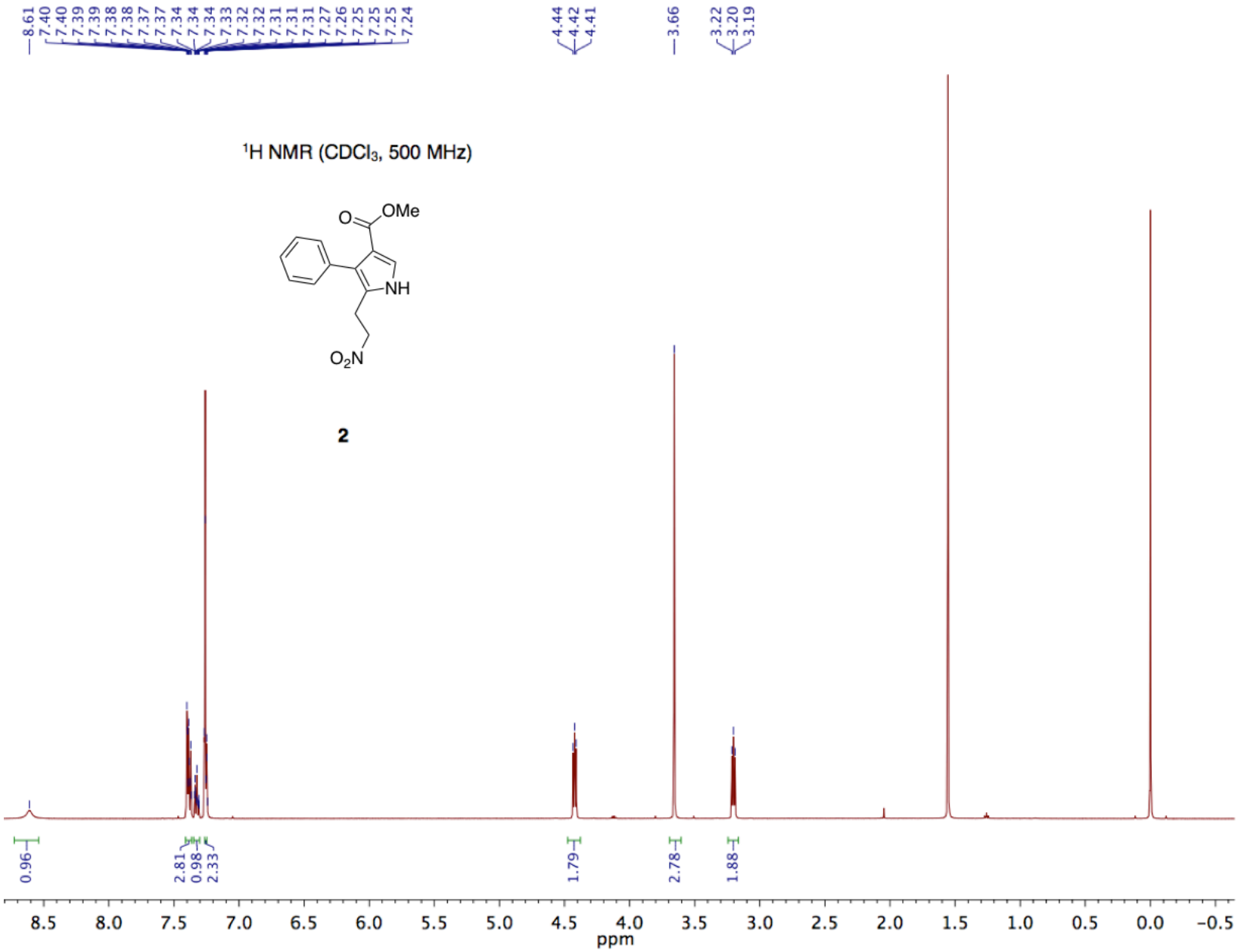
^{1}H NMR ($CDCl_3$, 500 MHz)

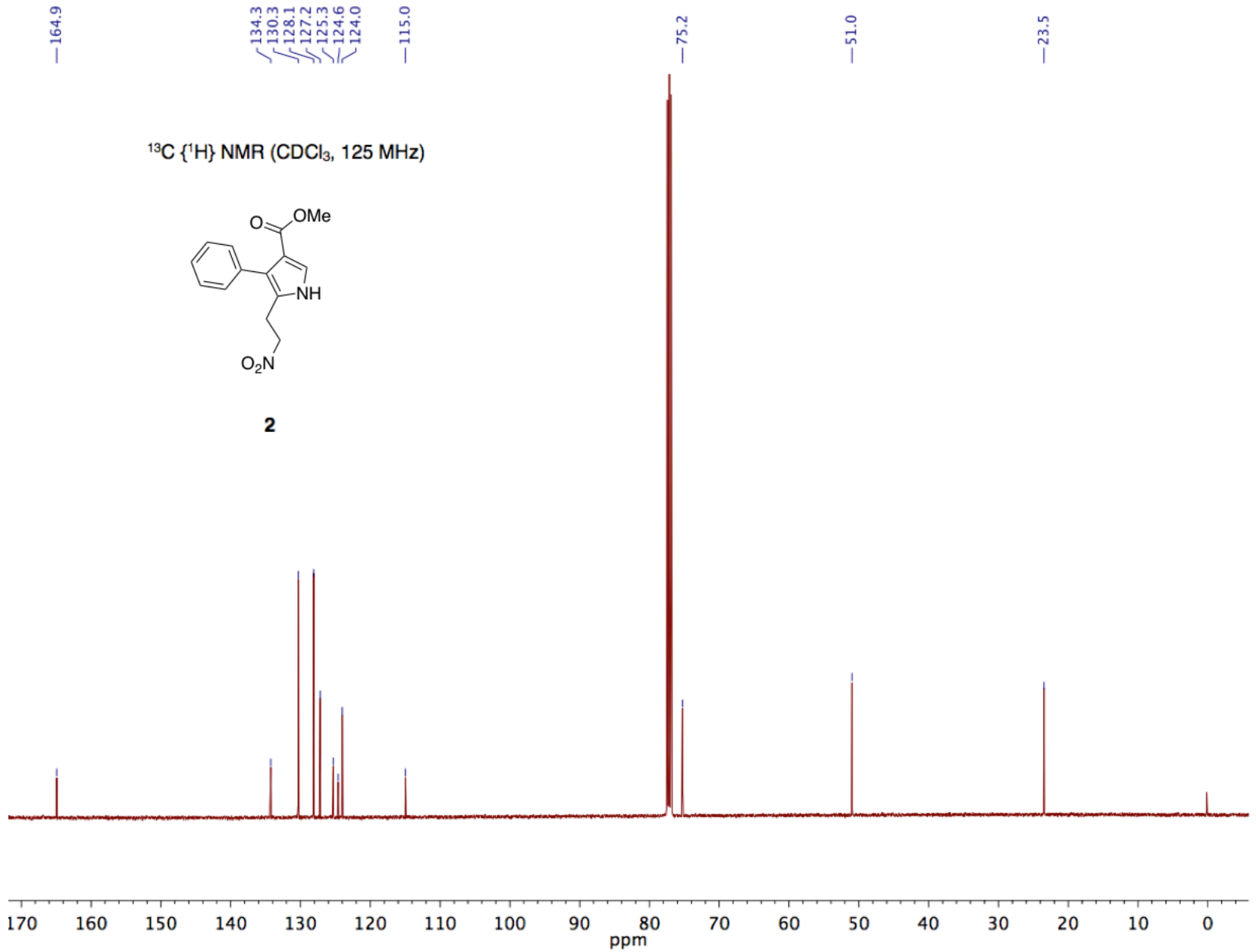


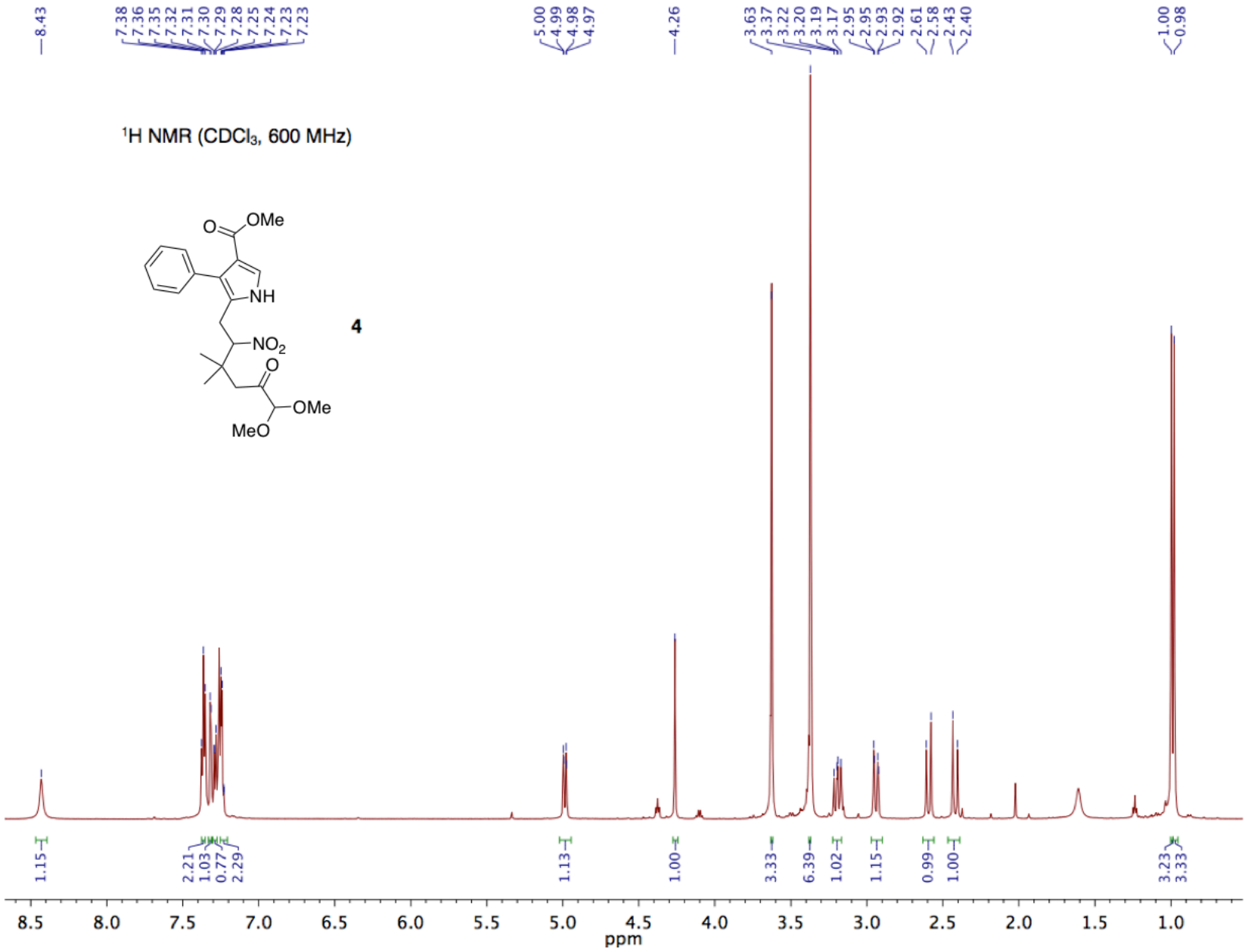
1b

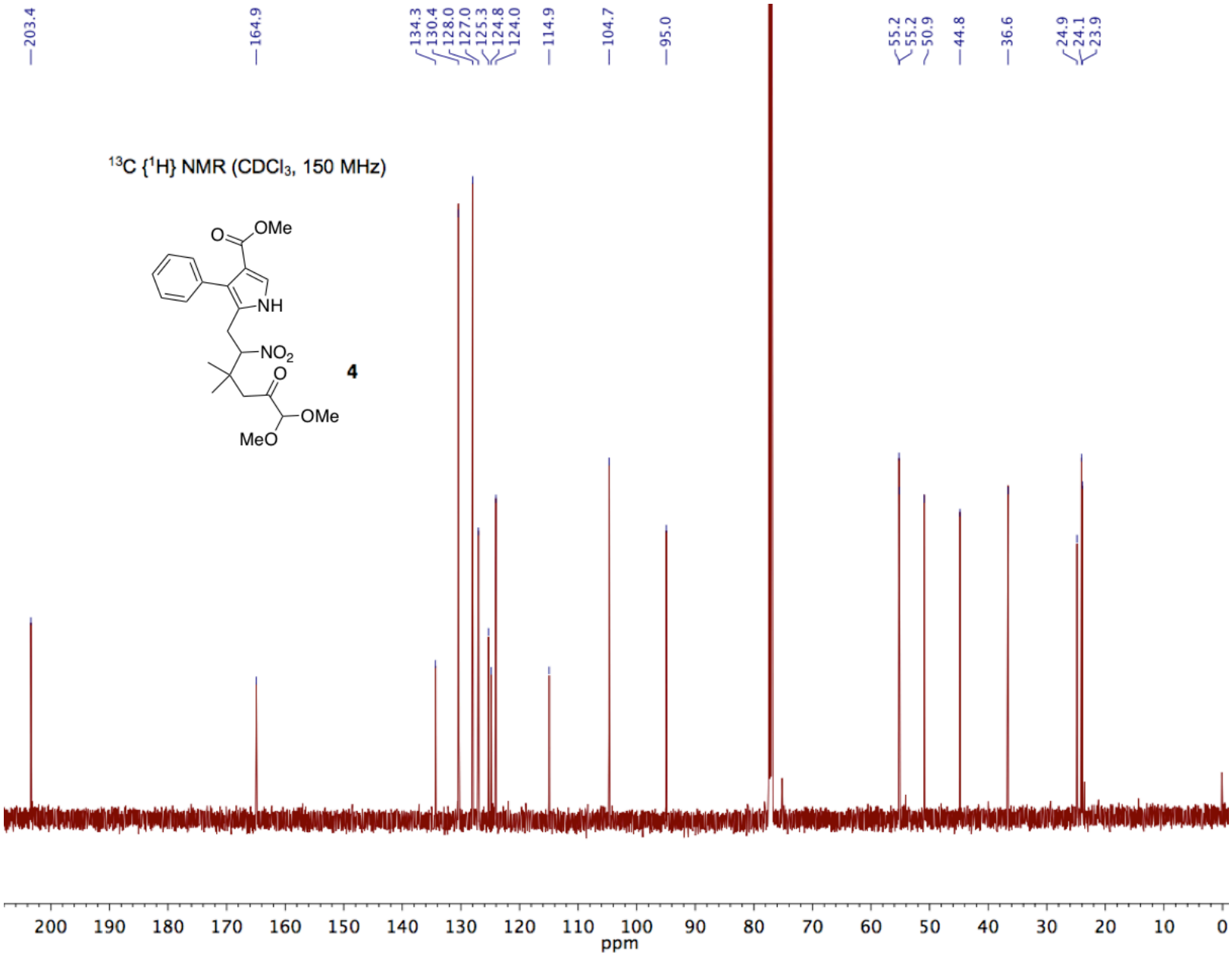


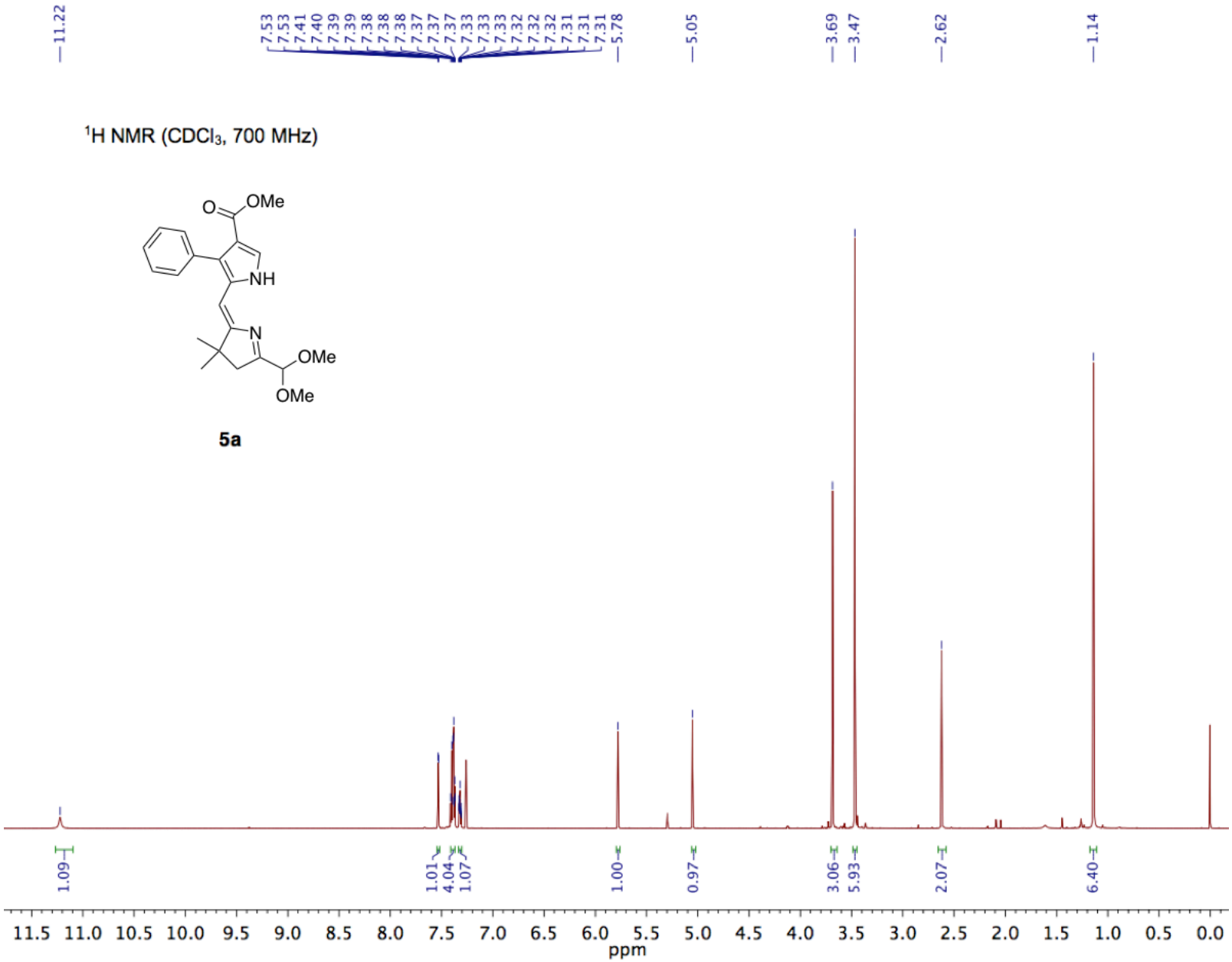

182.3
164.3
133.7
133.6
130.0
129.4
128.1
127.5
124.0
119.5
51.8
^{13}C {^{1}H} NMR (CDCl$_3$, 175 MHz)
O
OMe
H
O
NH
1b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

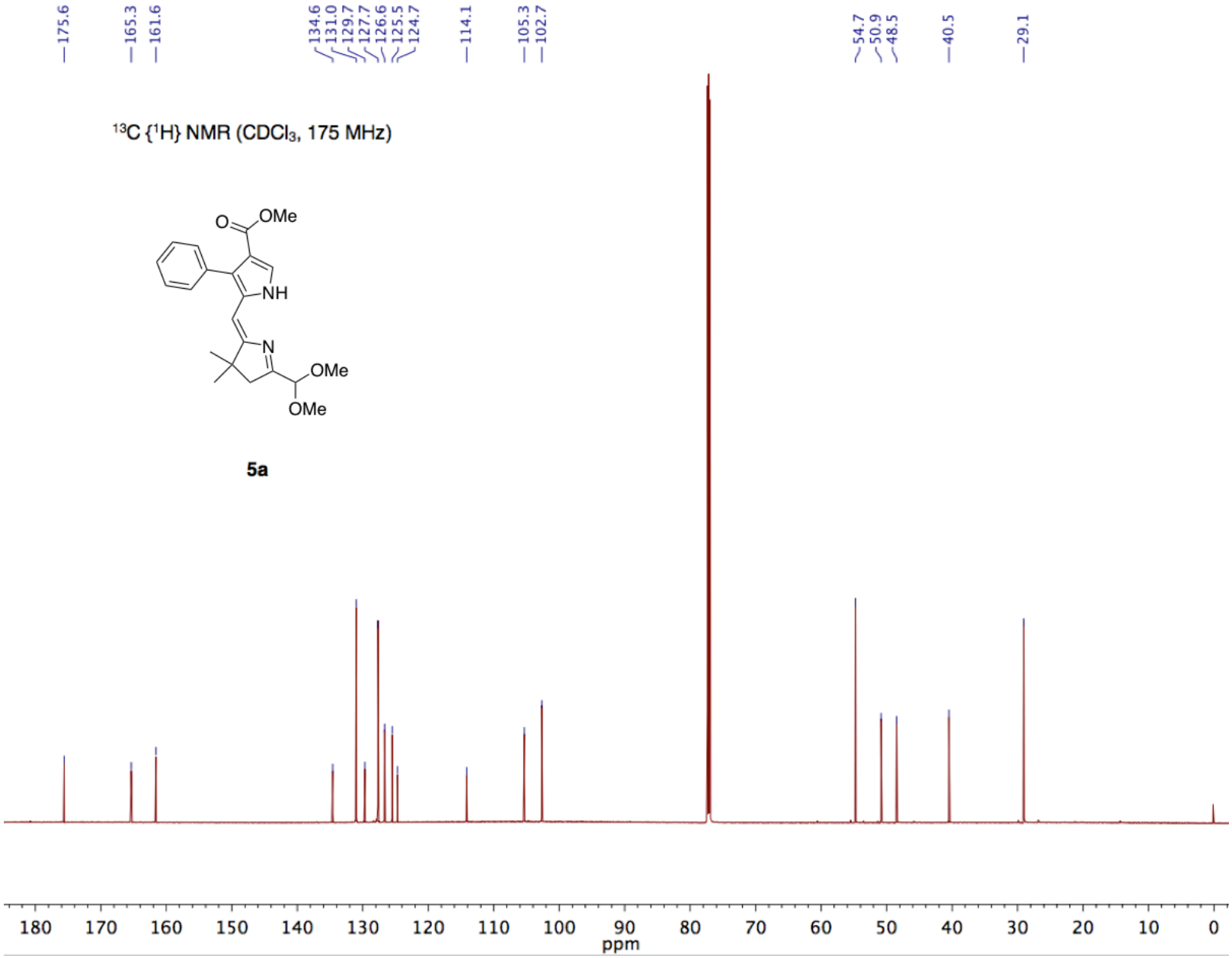

8.61
7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.34
7.34
7.34
7.33
7.32
7.32
7.31
7.31
7.31
7.27
7.26
7.25
7.25
7.25
7.24
4.44
4.42
4.41
3.66
3.22
3.20
3.19
¹H NMR (CDCl₃, 500 MHz)
O
OMe
NH
O₂N
2
0.96
2.81
0.98
2.33
1.79
2.78
1.88
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm

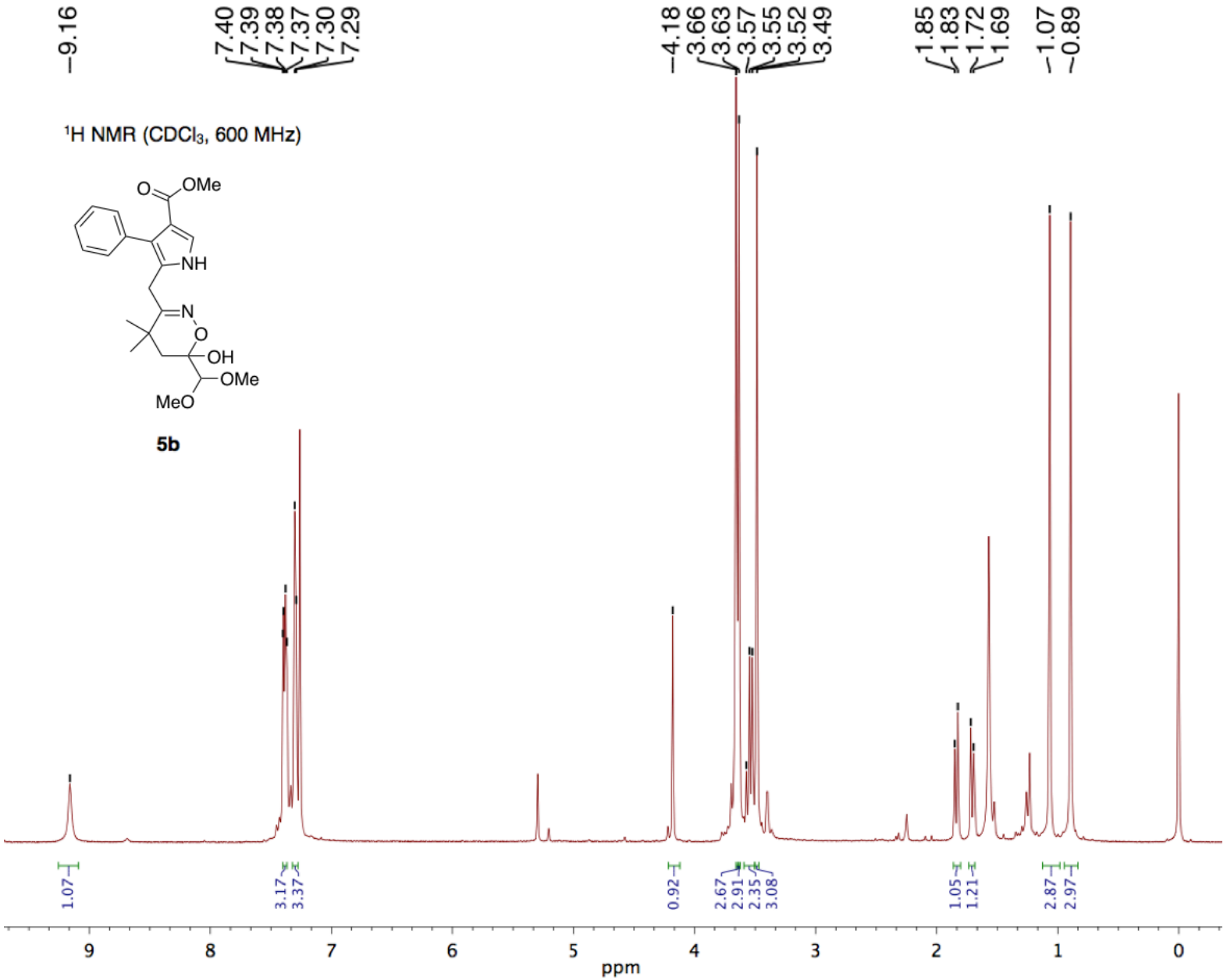

164.9
134.3
130.3
128.1
127.2
125.3
124.6
124.0
115.0
75.2
51.0
23.5
^{13}C {^{1}H} NMR ($CDCl_3$, 125 MHz)
OMe
O
NH
O_2N
2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

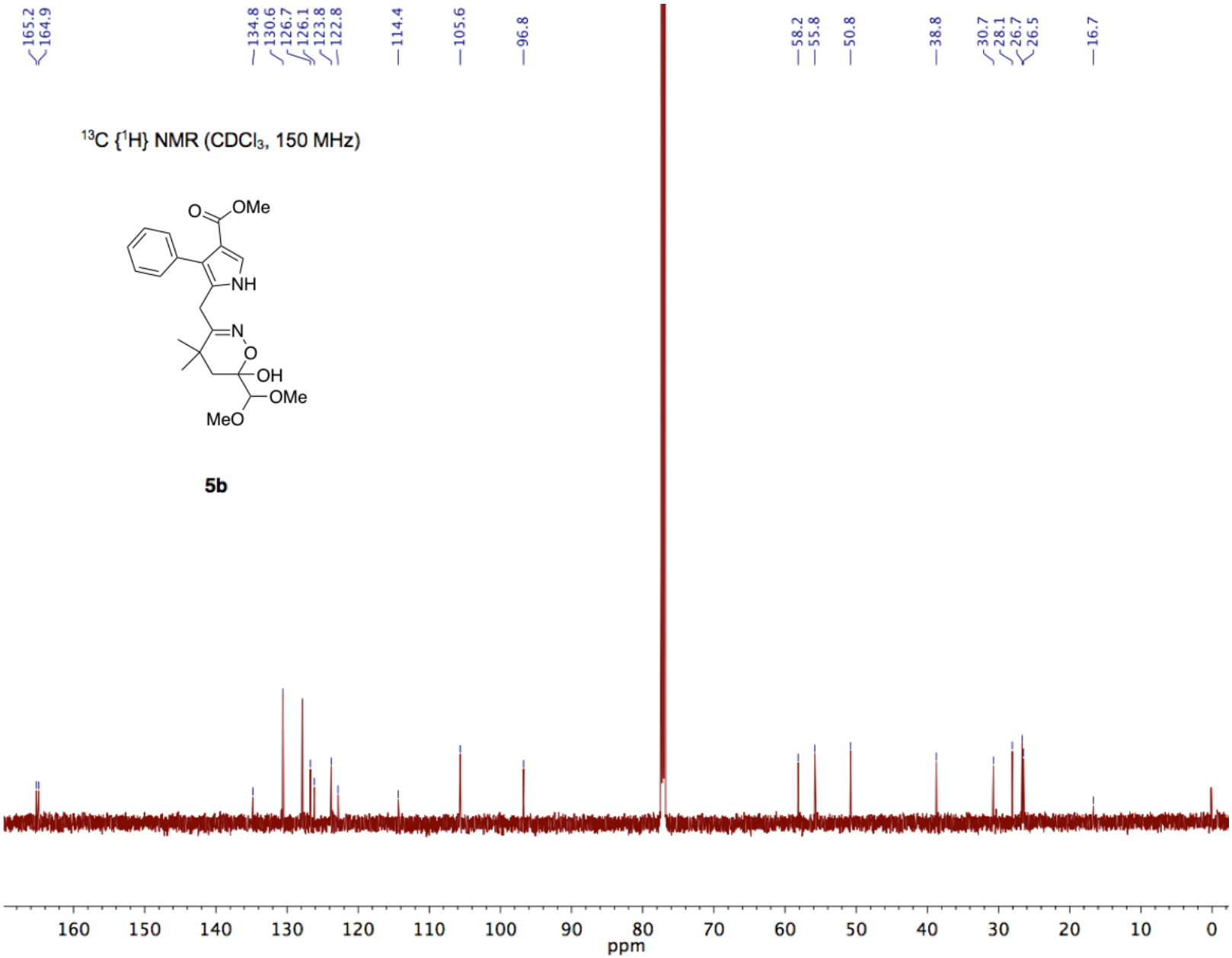

8.43
7.38
7.36
7.35
7.32
7.31
7.30
7.29
7.28
7.25
7.24
7.23
7.23
5.00
4.99
4.98
4.97
4.26
3.63
3.37
3.22
3.20
3.19
3.17
2.95
2.95
2.93
2.92
2.61
2.58
2.43
2.40
1.00
0.98
1H NMR (CDCl3, 600 MHz)
O
OMe
NH
NO2
O
OMe
MeO
4
1.15
2.21
1.03
0.77
2.29
1.13
1.00
3.33
6.39
1.02
1.15
0.99
1.00
3.23
3.33
8.5
8.0
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
ppm

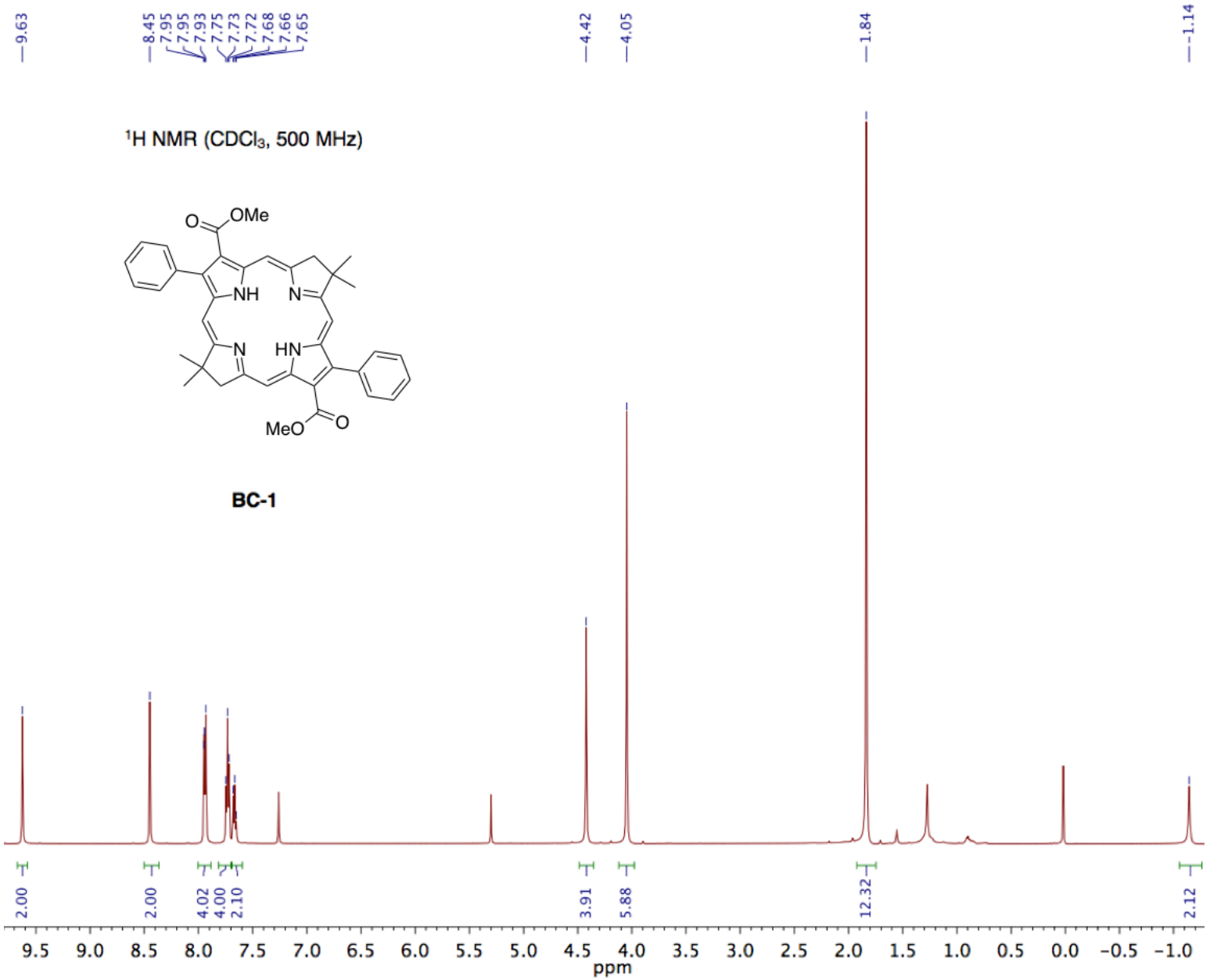

203.4
164.9
134.3
130.4
128.0
127.0
125.3
124.8
124.0
114.9
104.7
95.0
55.2
55.2
50.9
44.8
36.6
24.9
24.1
23.9
13C {1H} NMR (CDCl3, 150 MHz)
OMe
O
NH
NO2
O
OMe
MeO
4
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

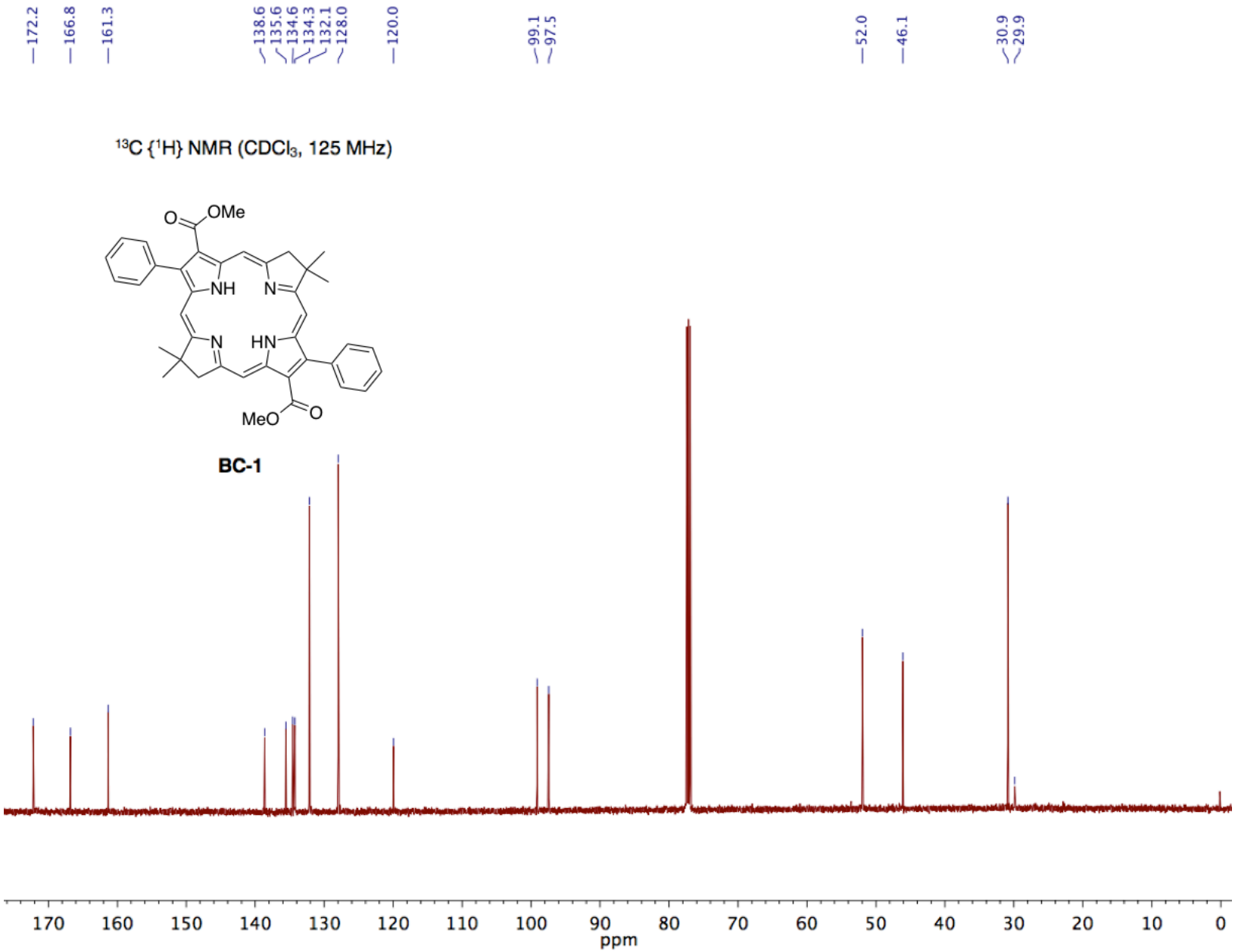

11.22
7.53
7.53
7.41
7.40
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.37
7.33
7.33
7.33
7.32
7.32
7.32
7.31
7.31
7.31
5.78
5.05
3.69
3.47
2.62
1.14
1H NMR (CDCl3, 700 MHz)
O
OMe
NH
N
OMe
OMe
5a
1.09
1.01
4.04
1.07
1.00
0.97
3.06
5.93
2.07
6.40
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

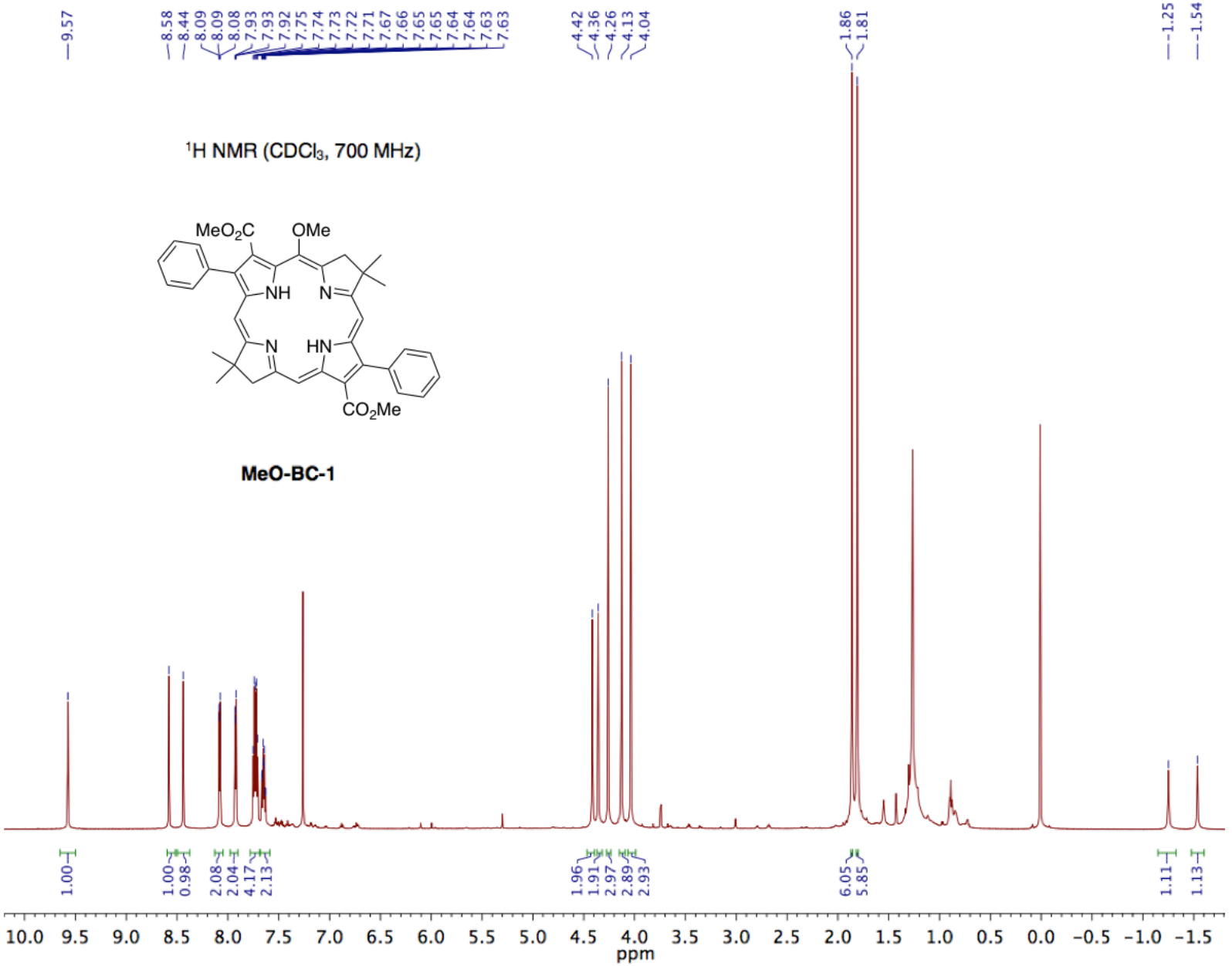

175.6
165.3
161.6
134.6
131.0
129.7
127.7
126.6
125.5
124.7
114.1
105.3
102.7
54.7
50.9
48.5
40.5
29.1
13C {1H} NMR (CDCl3, 175 MHz)
O
OMe
NH
N
OMe
OMe
5a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

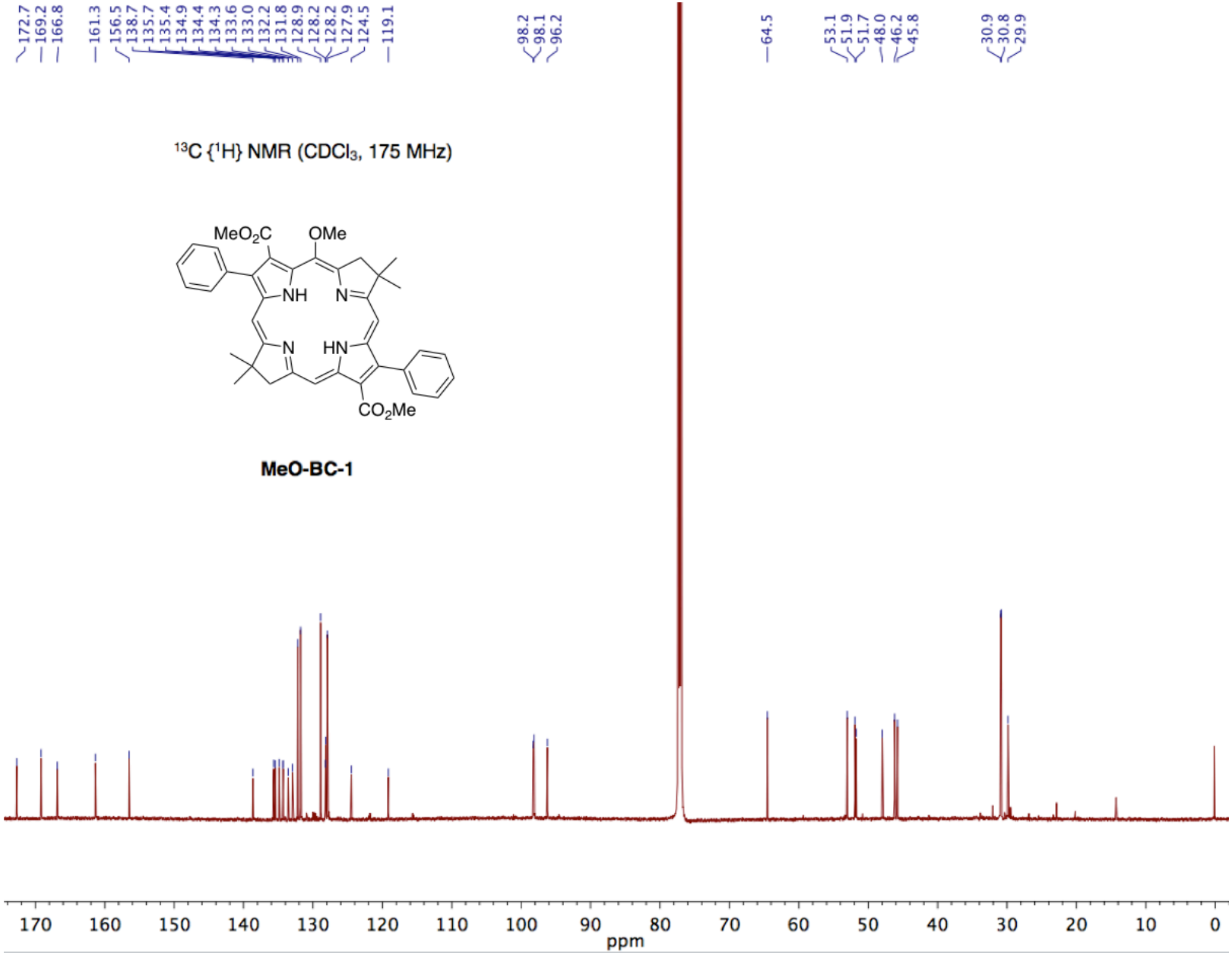

9.16
7.40
7.39
7.38
7.37
7.30
7.29
4.18
3.66
3.63
3.57
3.55
3.52
3.49
1.85
1.83
1.72
1.69
1.07
0.89
1H NMR (CDCl3, 600 MHz)
O
OMe
NH
N
O
OH
OMe
MeO
5b
1.07
3.17
3.37
0.92
2.67
2.91
2.35
3.08
1.05
1.21
2.87
2.97
9
8
7
6
5
4
3
2
1
0
ppm


165.2
164.9
134.8
130.6
126.7
126.1
123.8
122.8
114.4
105.6
96.8
58.2
55.8
50.8
38.8
30.7
28.1
26.7
26.5
16.7
^{13}C {^{1}H} NMR (CDCl$_3$, 150 MHz)
O
OMe
NH
N
O
OH
OMe
MeO
5b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


9.63
8.45
7.95
7.95
7.93
7.75
7.73
7.72
7.68
7.66
7.65
4.42
4.05
1.84
-1.14
1H NMR (CDCl3, 500 MHz)
O
OMe
NH
N
N
HN
MeO
O
BC-1
2.00
2.00
4.02
4.00
2.10
3.91
5.88
12.32
2.12
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
ppm


172.2
166.8
161.3
138.6
135.6
134.6
134.3
132.1
128.0
120.0
99.1
97.5
52.0
46.1
30.9
29.9
13C {1H} NMR (CDCl3, 125 MHz)
O
OMe
NH
N
N
HN
MeO
O
BC-1
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


9.57
8.58
8.44
8.09
8.09
8.08
7.93
7.93
7.92
7.75
7.74
7.73
7.72
7.71
7.67
7.66
7.65
7.65
7.64
7.64
7.63
7.63
4.42
4.36
4.26
4.13
4.04
1.86
1.81
1.25
1.54
1H NMR (CDCl3, 700 MHz)
MeO2C
OMe
NH
N
N
HN
CO2Me
MeO-BC-1
1.00
1.00
0.98
2.08
2.04
4.17
2.13
1.96
1.91
2.97
2.89
2.93
6.05
5.85
1.11
1.13
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 -1.5
ppm


172.7
169.2
166.8
161.3
156.5
138.7
135.7
135.4
134.9
134.4
134.3
133.6
133.0
132.2
131.8
128.9
128.2
128.2
127.9
124.5
119.1
98.2
98.1
96.2
64.5
53.1
51.9
51.7
48.0
46.2
45.8
30.9
30.8
29.9
^{13}C {^{1}H} NMR ($CDCl_3$, 175 MHz)
MeO_2C
OMe
NH
N
N
HN
CO_2Me
MeO-BC-1
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm