Preparative Scale Synthesis of Vedejs Chiral DMAP Catalysts

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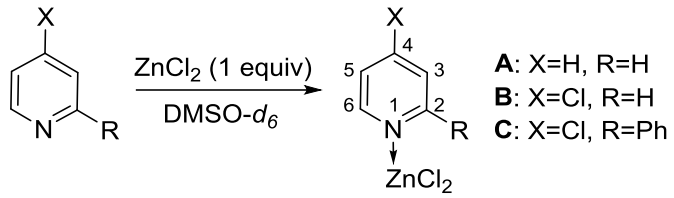
CONTENTS

NMR studies of complexes between $ZnCl_2$ and pyridines

Table S1. Change (in percents) of ^{13}C and ^{15}N chemical shifts[a] and spin-lattice relaxation time T_1.[b]



Atom	**A**[c]		**B**		**C**[d]	
	Δδ (%)	ΔT1 (%)	Δδ (%)	ΔT1 (%)	Δδ (%)	ΔT1 (%)
C2	0.51	-74.2	0.30	-39.1	0.18	-15.7
C3	-1.03	-75.0	-0.38	-43.1	0.21	-15.0
C4	-2.06	-87.7	-0.72	-61.9	0.19	-10.6
C5	-1.03	-75.0	-0.38	-43.1	0.22	-11.6
C6	0.51	-74.2	0.30	-39.1	0.16	-13.4
N1	10.5	-	4.14	-	0.05	-

[a] For chemical shift values see SI. Negative values represent downfield shift and positive values – upfield shift of NMR signals. [b] Negative ΔT1 values represent decrease of relaxation time. [c] A 1:1 mixture of 4-chloropyridine hydrochloride and DIPEA was used. [d] Determined in DMF–d_7.

Table S2. ^{13}C and ^{15}N chemical shift values and spin-lattice relaxation time T_1 of zinc-pyridine complexes.

Atom	0 equiv		1 equiv		2 equiv	
	δ, ppm	T1, sec	δ, ppm	T1, sec	δ, ppm	T1, sec
A						
C2, C6	149.6	7.57	148.8	1.95	148.6	1.36
C3, C5	123.9	7.36	125.1	1.84	125.6	1.26
C4	136.1	7.52	138.9	0.93	139.9	0.62
N1	317.7	-	284.3	-	273.8	-
B						
C2, C6	151.6	3.40	151.1	2.07	150.9	1.61
C3, C5	124.5	3.76	125.0	2.14	125.3	1.61
C4	143.3	12.57	144.3	4.79	144.9	3.16
N1	312.7	-	299.8	-	293.0	-
C						
C2	159.5	6.38	159.2	5.38	159.0	4.74
C3	123.7	2.86	123.4	2.43	123.2	2.13
C4	145.5	8.72	145.2	7.80	145.0	6.98
C5	121.4	1.55	121.2	1.37	121.0	1.16
C6	152.1	2.61	151.9	2.26	151.7	1.93
N1	304.8	-	304.6	-	304.5	-

Kinetic study of the amination reaction

Kinetic studies were carried out to establish the kinetic order of Zn(II)-mediated amination of 4-chloropyridine in each reaction component. The reactions were monitored by NMR spectroscopy, and the reaction order in zinc(II) complex **7d** and 4-chloropyridine was determined by plotting the reaction half-time vs. natural logarithm of reactants concentration (Noyes plot). The amination of 4-chloropyridine in DMF at 40 °C was found to be second-order in zinc(II) complex **7d** (Figure S1) and first-order in 4-chloropyridine (Figure S2). These data indicate that two equivalents of Zn(II) complex **7d** are involved in a rate-determining step of the amination.

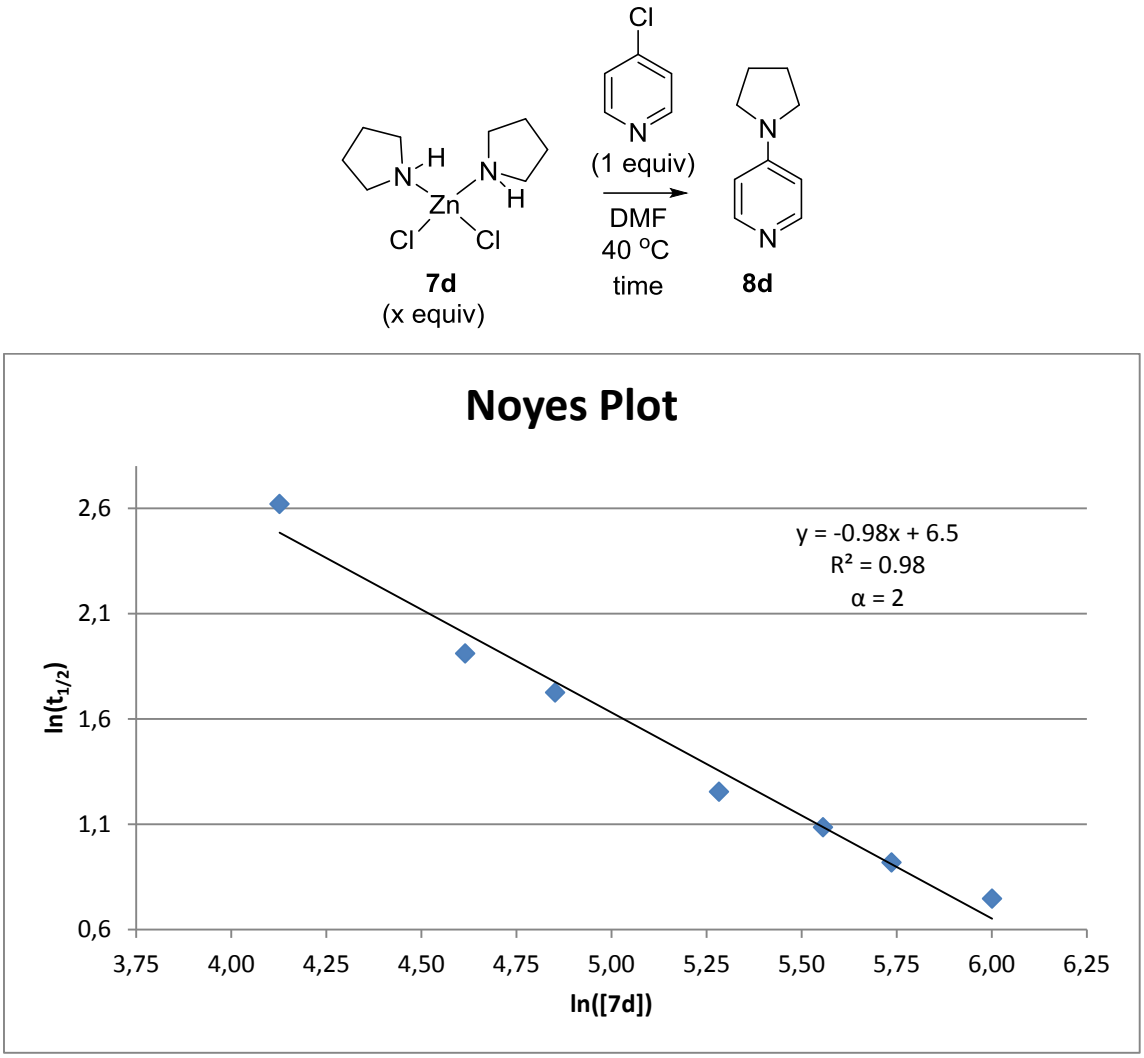


Figure S1. Determination of chlorine-amine exchange reaction order in zinc amine complex **7d**.

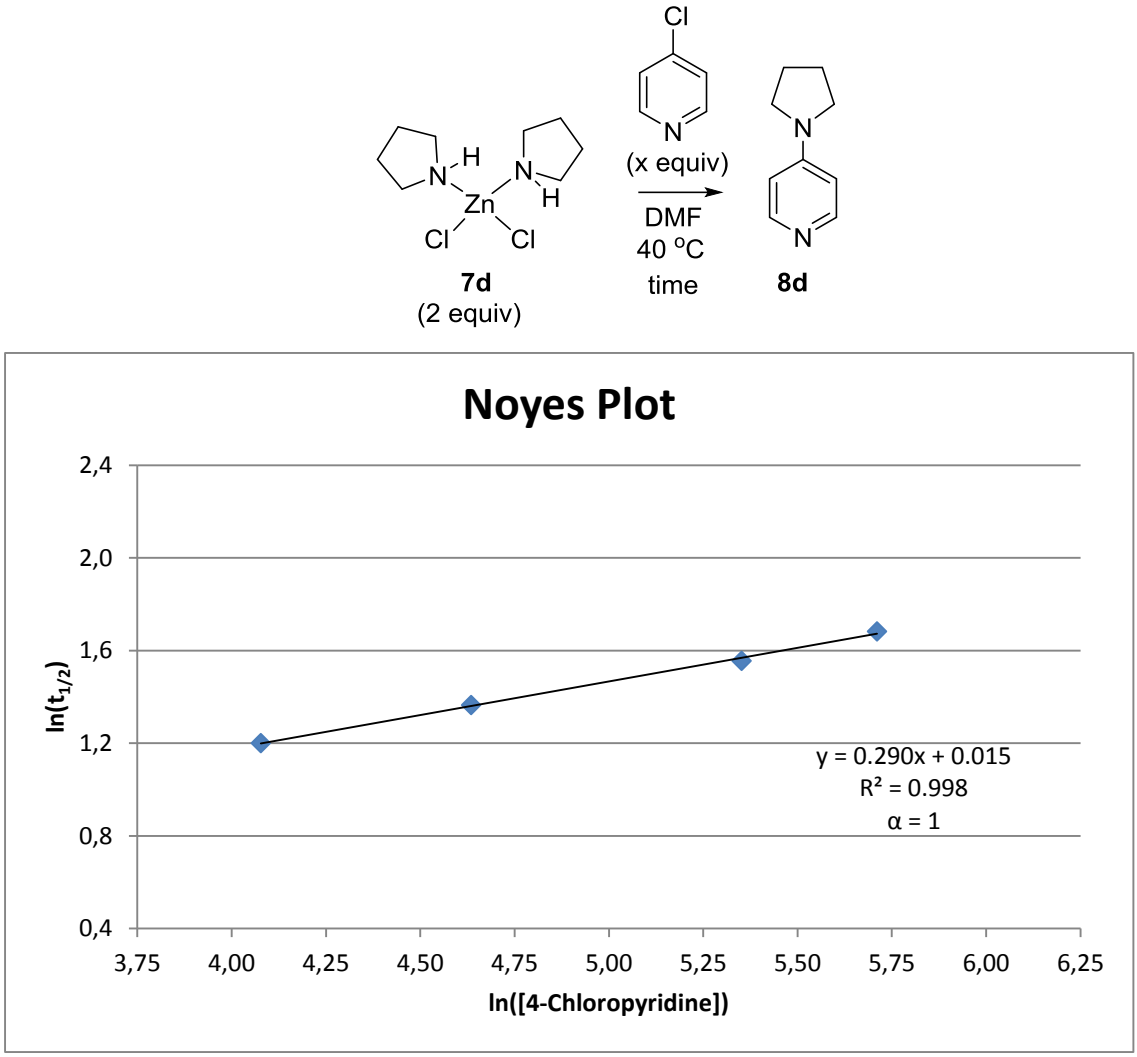


Figure S2. Determination of chlorine-amine exchange reaction order in 4-chloropyridine.

X-Ray Structure, Crystal Data and Structure Refinements for 6

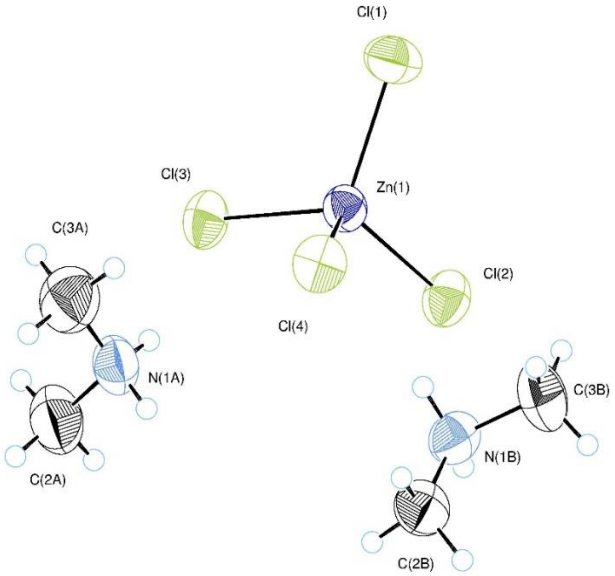


Figure S3. X-ray crystal structure of **6** (ellipsoids at 50% probability with hydrogen atoms omitted for clarity)

Identification code	sb_54
Empirical formula	C4 H16 Cl4 N2 Zn
Formula weight	299.36
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/n
Unit cell dimensions	a = 8.5348(5) A alpha = 90.000(3) deg.
	b = 11.4450(6) A beta = 89.932(3) deg.
	c = 13.2997(8) A gamma = 90.000(2) deg.
Volume	1299.12(13) A^3
Z, Calculated density	4, 1.531 Mg/m^3
Absorption coefficient	2.669 mm^-1
F(000)	608
Crystal size	0.14 x 0.12 x 0.01 mm
Two-theta max. for data	55.0 deg.
Limiting indices	-11<=h<=11, -14<=k<=14, -17<=l<=17
Reflections collected / unique	7948 / 2980 [R(int) = 0.1377]
Completeness to theta = 27.58	99%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2980 / 0 / 100
Goodness-of-fit on F^2	1.047
Final R indices [I>2sigma(I)]	R1 = 0.0654, wR2 = 0.1478
R indices (all data)	R1 = 0.1022, wR2 = 0.1683
Largest diff. peak and hole	0.876 and -0.713 e.A^-3

X-Ray Structure, Crystal Data and Structure Refinements for 7d

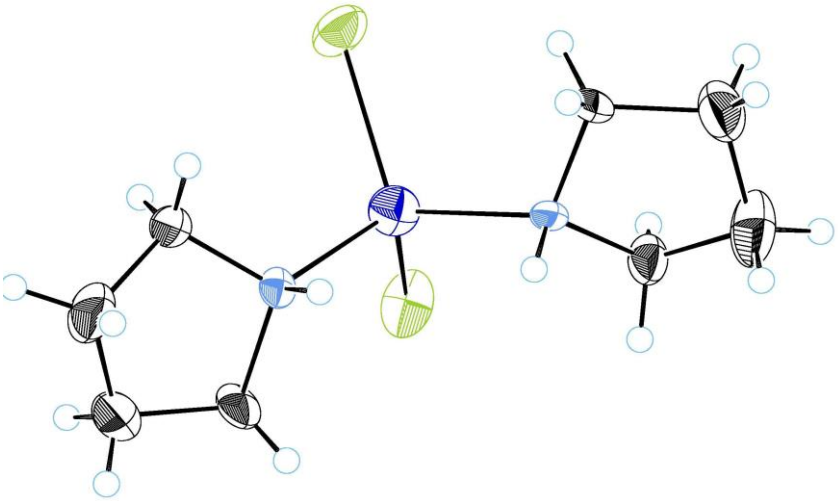


Figure S4. X-ray crystal structure of **7d** (ellipsoids at 50% probability with hydrogen atoms omitted for clarity)

Empirical formula	C8 H18 Cl2 N2 Zn
Formula weight	278.51
Temperature	193(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P c n b
Unit cell dimensions	a = 6.9308(1) A alpha = 90 deg.
	b = 17.2694(4) A beta = 90 deg.
	c = 20.0339(3) A gamma = 90 deg.
Volume	2397.87(7) A^3
Z, Calculated density	8, 1.543 Mg/m^3
Absorption coefficient	2.455 mm^-1
F(000)	1152
Crystal size	0.29 x 0.11 x 0.08 mm
Two-theta max. for data	60.0 deg.
Limiting indices	-9<=h<=9, -24<=k<=24, -28<=l<=28
Reflections collected	/ unique 6038 / 3429 [R(int) = 0.0236]
Completeness to theta= 30.0	98 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3429 / 0 / 115
Goodness-of-fit on F^2	4.89
Final R indices [I>2sigma(I)]	R1 = 0.1388, wR2 = 0.4910
R indices (all data)	R1 = 0.1504, wR2 = 0.4934
Largest diff. peak and hole	2.525 and -6.567 e.A^-3

X-Ray Structure, Crystal Data and Structure Refinements for 7f

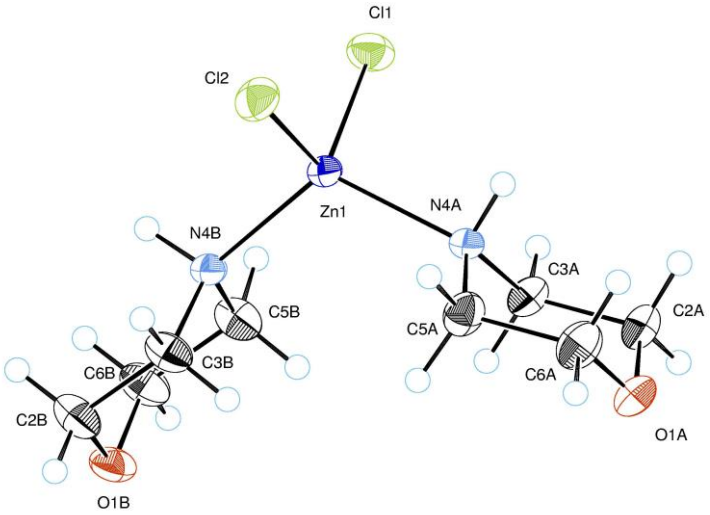


Figure S5. X-ray crystal structure of **7f** (ellipsoids at 50% probability with hydrogen atoms omitted for clarity).

Identification code	AK_371
Empirical formula	C8 H18 Cl2 N2 O2 Zn
Formula weight	310.51
Temperature	163(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 8.3177(3) A alpha = 90.660(2) deg.
	b = 8.3401(4) A beta = 103.5388(18) deg.
	c = 9.5390(4) A gamma = 100.646(2) deg.
Volume	631.22(5) A^3
Z, Calculated density	2, 1.634 Mg/m^3
Absorption coefficient	2.352 mm^-1
F(000)	320
Crystal size	0.23 x 0.14 x 0.12 mm
Two-theta max. for data	56.0 deg.
Limiting indices	-10<=h<=10, -10<=k<=10, -12<=l<=12
Reflections collected / unique	4290 / 2979 [R(int) = 0.0204]
Completeness to theta = 28.0	98%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2979 / 0 / 144
Goodness-of-fit on F^2	0.991
Final R indices [I>2sigma(I)]	R1 = 0.0265, wR2 = 0.0601
R indices (all data)	R1 = 0.0298, wR2 = 0.0633
Largest diff. peak and hole	0.381 and -0.459 e.A^-3

X-Ray Structure, Crystal Data and Structure Refinements for 7h

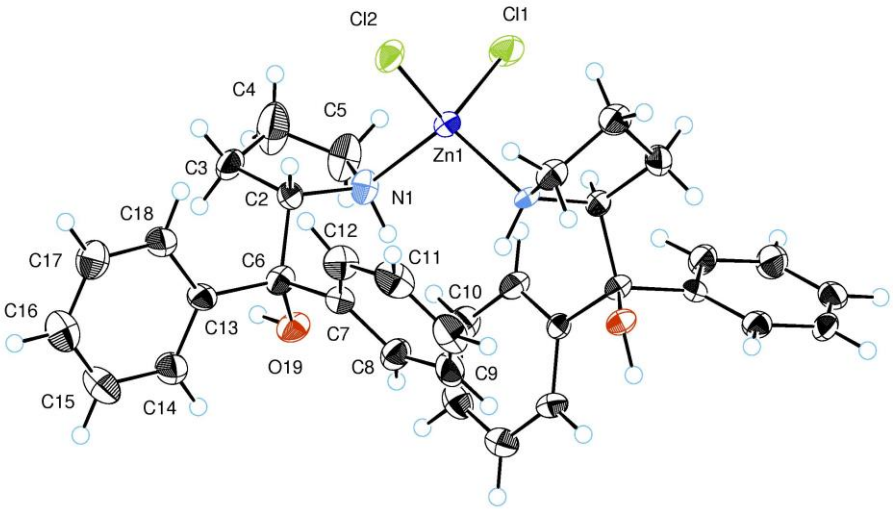


Figure S6. X-ray crystal structure of **7h** (ellipsoids at 50% probability with hydrogen atoms omitted for clarity).

Identification code	AK_409
Empirical formula	C34 H38 Cl2 N2 O2 Zn
Formula weight	642.93
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21
Unit cell dimensions	a = 8.8724(3) A alpha = 90 deg.
	b = 15.4191(5) A beta = 101.7616(16) deg.
	c = 11.6823(3) A gamma = 90 deg.
Volume	1564.63(8) A^3
Z, Calculated density	2, 1.365 Mg/m^3
Absorption coefficient	0.989 mm^-1
F(000)	672
Crystal size	0.23 x 0.17 x 0.12 mm
Two-theta max. for data	58.0 deg.
Limiting indices	-11<=h<=11, -18<=k<=20, -15<=l<=15
Reflections collected / unique	6932 / 6922 [R(int) = 0.0431]
Completeness to theta = 29.0	98%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6922 / 1 / 394
Goodness-of-fit on F^2	1.062
Final R indices [I>2sigma(I)]	R1 = 0.0506, wR2 = 0.0844
R indices (all data)	R1 = 0.0777, wR2 = 0.0947
Absolute structure parameter	-0.012(11)
Largest diff. peak and hole	0.399 and -0.426 e.A^-3

X-Ray Structure, Crystal Data and Structure Refinements for 7j

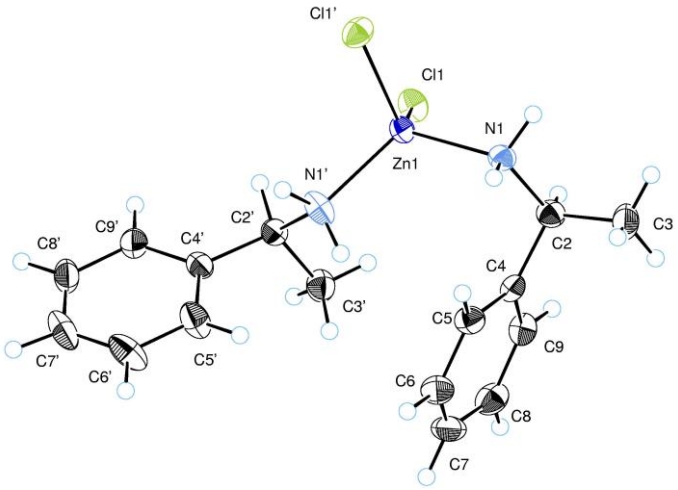
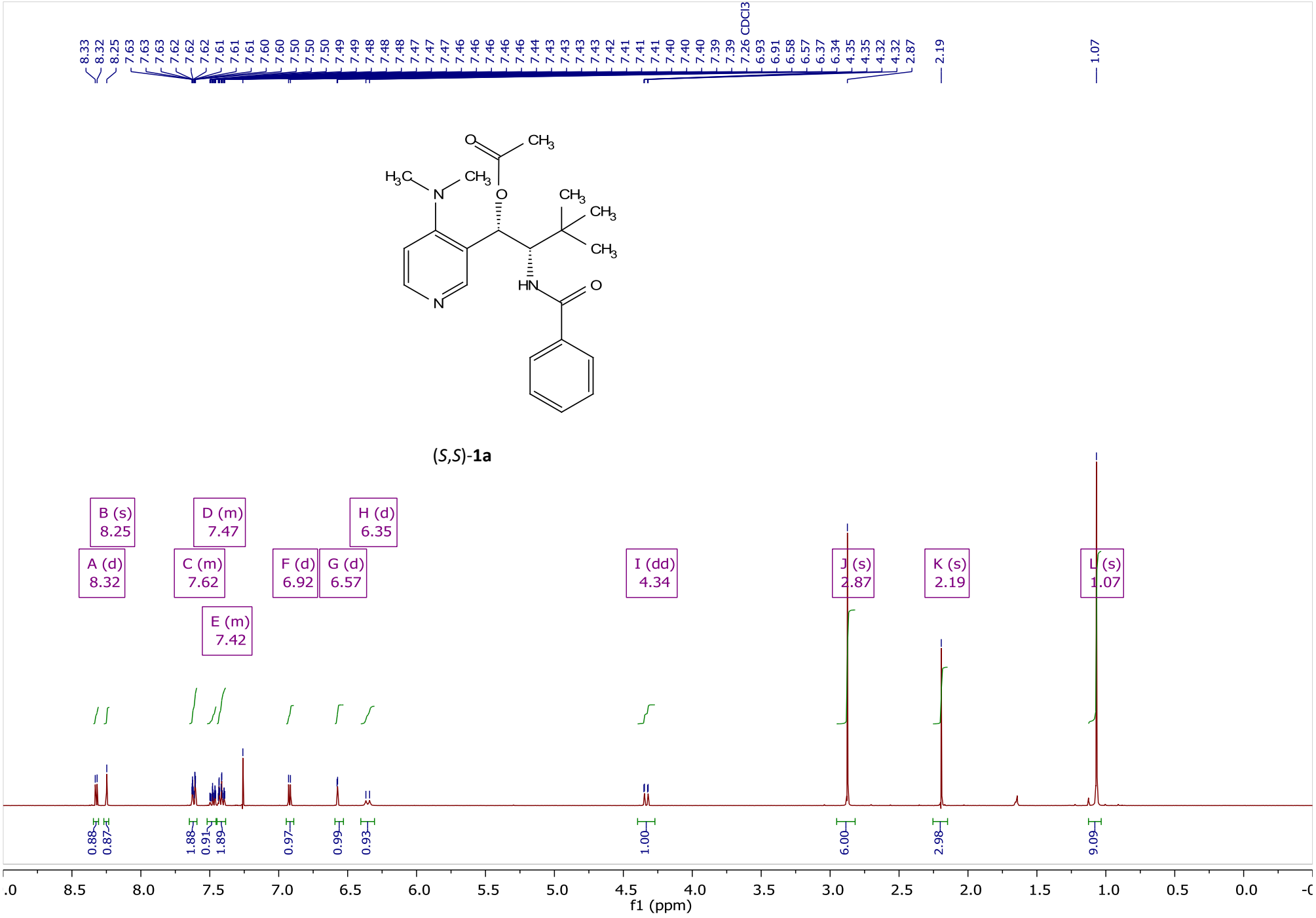


Figure S7. X-ray crystal structure of **7j** (ellipsoids at 50% probability with hydrogen atoms omitted for clarity).

Identification code	ak_393
Empirical formula	C16 H22 Cl2 N2 Zn
Formula weight	378.63
Temperature	163(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 5.98160(10) A alpha = 90 deg.
	b = 13.6923(3) A beta = 90 deg.
	c = 21.4173(5) A gamma = 90 deg.
Volume	1754.12(6) A^3
Z, Calculated density	4, 1.434 Mg/m^3
Absorption coefficient	1.700 mm^-1
F(000)	784
Crystal size	0.26 x 0.11 x 0.10 mm
Two-theta max. for data	58.0 deg.
Limiting indices	-8<=h<=8, -18<=k<=17, -29<=l<=27
Reflections collected / unique	12944 / 4715 [R(int) = 0.0564]
Completeness to theta = 29.0	99%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4715 / 0 / 206
Goodness-of-fit on F^2	1.001
Final R indices [I>2sigma(I)]	R1 = 0.0386, wR2 = 0.0702
R indices (all data)	R1 = 0.0562, wR2 = 0.0755
Absolute structure parameter	0.010(12)
Largest diff. peak and hole	0.567 and -0.353 e.A^-3

Spectroscopic Data


8.33 8.32 8.25 7.63 7.63 7.63 7.62 7.62 7.62 7.61 7.61 7.61 7.60 7.60 7.60 7.50 7.50 7.50 7.49 7.49 7.48 7.48 7.48 7.47 7.47 7.47 7.46 7.46 7.46 7.46 7.46 7.44 7.43 7.43 7.43 7.43 7.42 7.41 7.41 7.41 7.40 7.40 7.40 7.39 7.39 7.26 CDCl3 6.93 6.91 6.58 6.57 6.37 6.34 4.35 4.35 4.32 4.32 2.87 2.19 1.07
(S,S)-1a
B (s) 8.25
D (m) 7.47
H (d) 6.35
A (d) 8.32
C (m) 7.62
F (d) 6.92
G (d) 6.57
I (dd) 4.34
J (s) 2.87
K (s) 2.19
L (s) 1.07
E (m) 7.42
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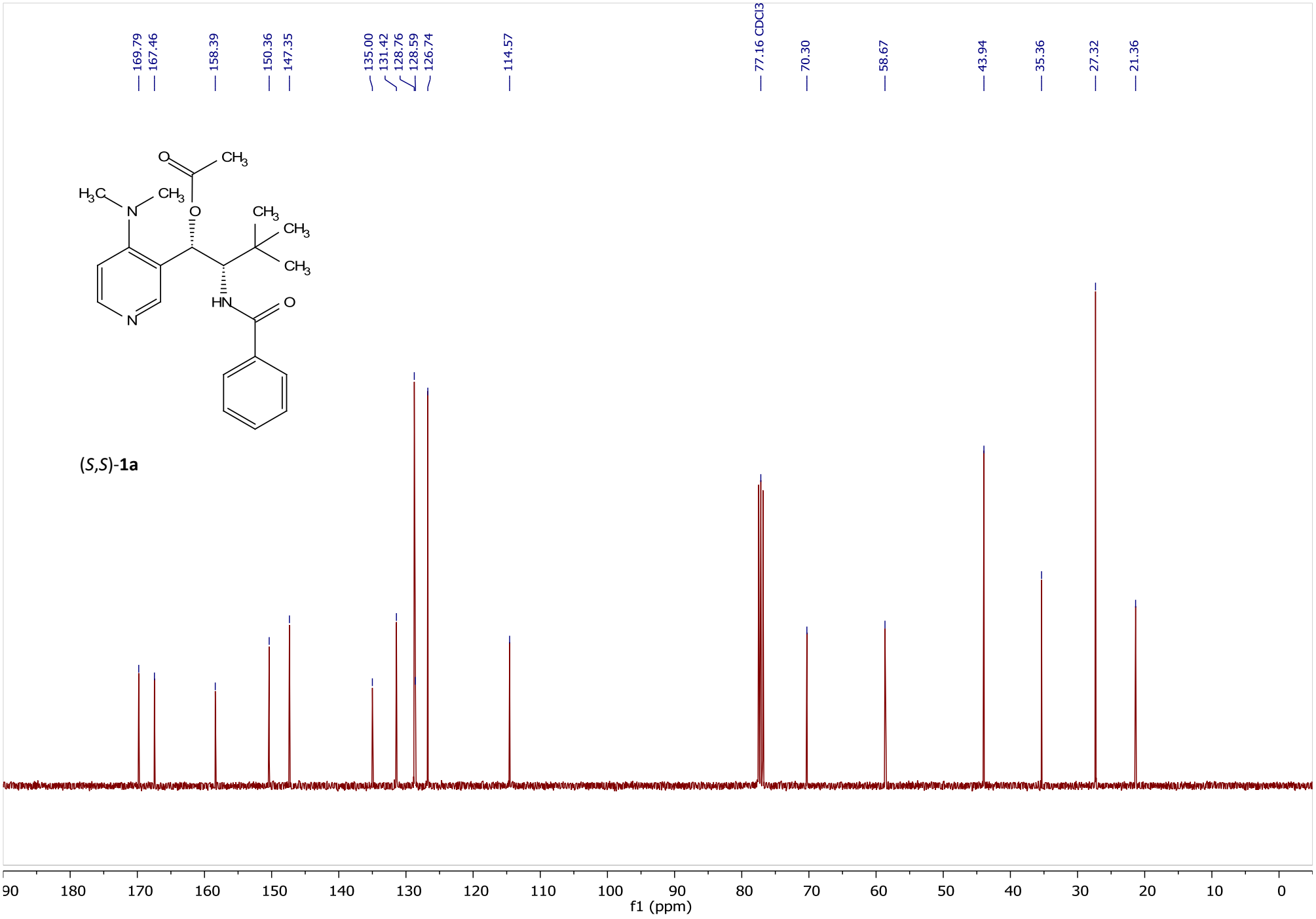
f1 (ppm)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147.35
135.00
131.42
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126.74
114.57
77.16 CDCl3
70.30
58.67
43.94
35.36
27.32
21.36
O
CH3
H3C
CH3
N
O
CH3
CH3
CH3
HN
O
N
(S,S)-1a
90
180
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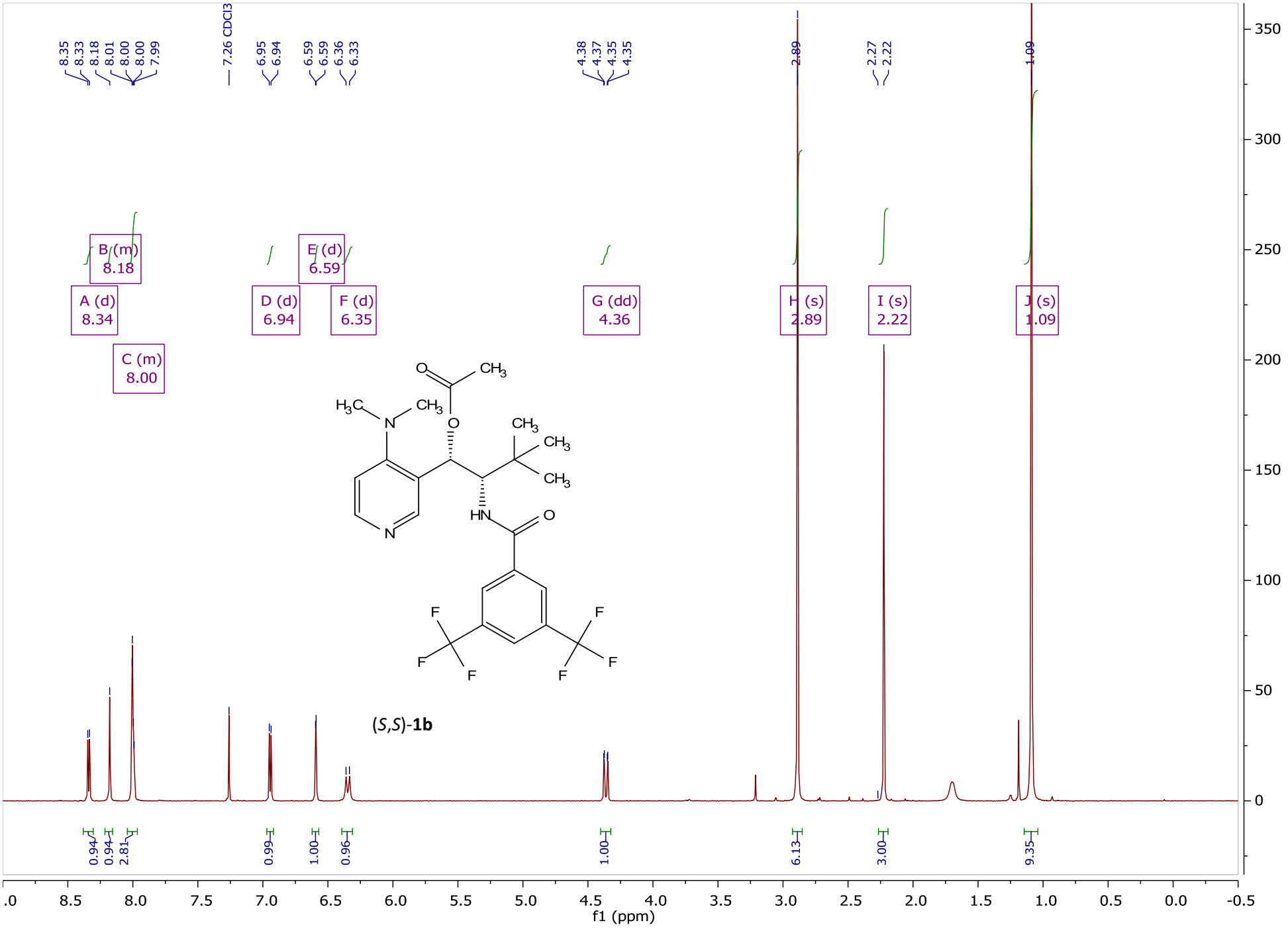
f1 (ppm)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8.00
8.00
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6.94
6.59
6.59
6.36
6.33
4.38
4.37
4.35
4.35
2.89
2.27
2.22
1.09
B (m) 8.18
E (d) 6.59
A (d) 8.34
D (d) 6.94
F (d) 6.35
G (dd) 4.36
H (s) 2.89
I (s) 2.22
J (s) 1.09
C (m) 8.00
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1.00
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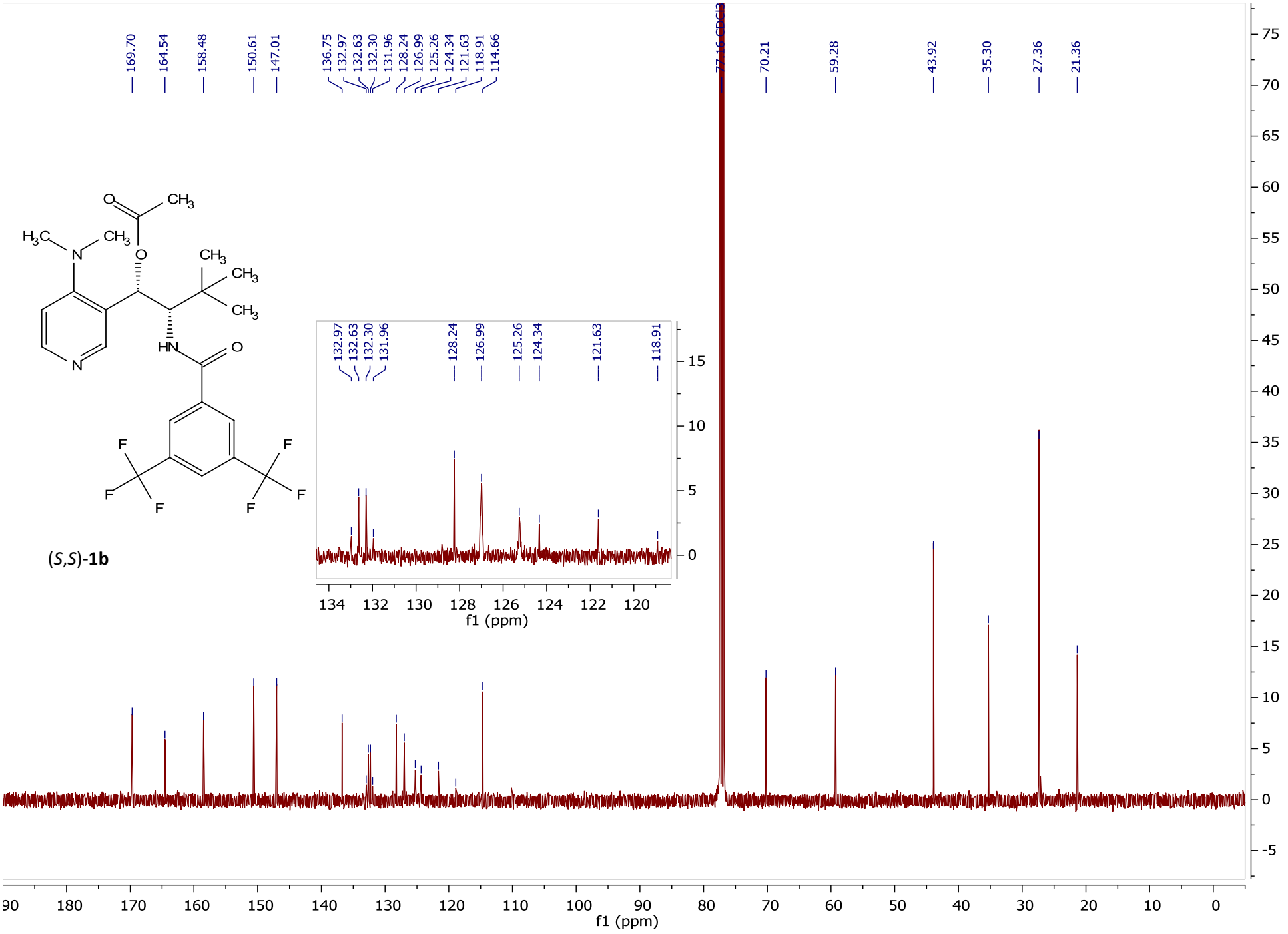
1.00
6.13
3.00
9.35
f1 (ppm)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125.26
124.34
121.63
118.91
114.66
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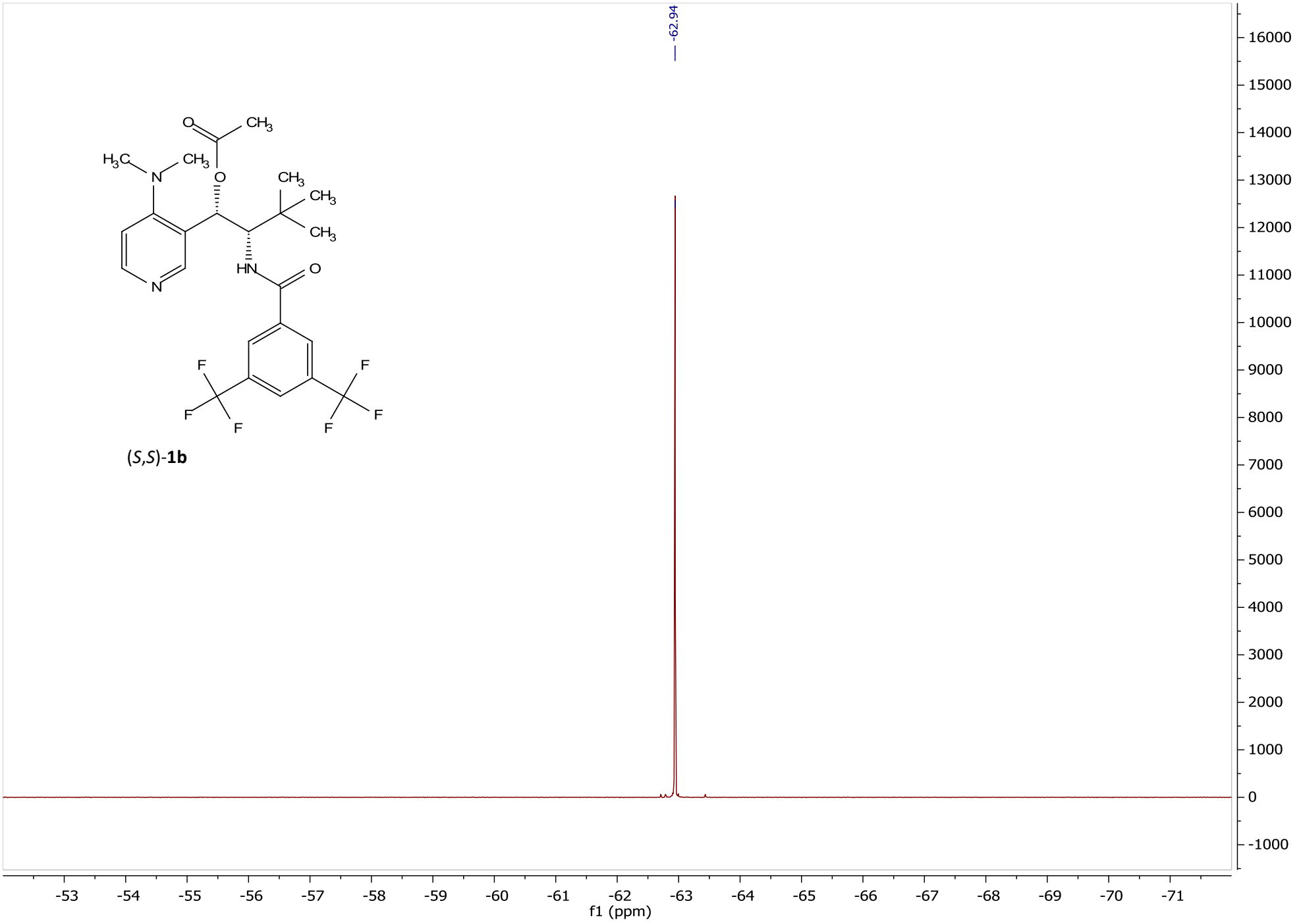
21.36
(S,S)-1b
f1 (ppm)
f1 (ppm)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15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-53
-54
-55
-56
-57
-58
-59
-60
-61
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-63
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-65
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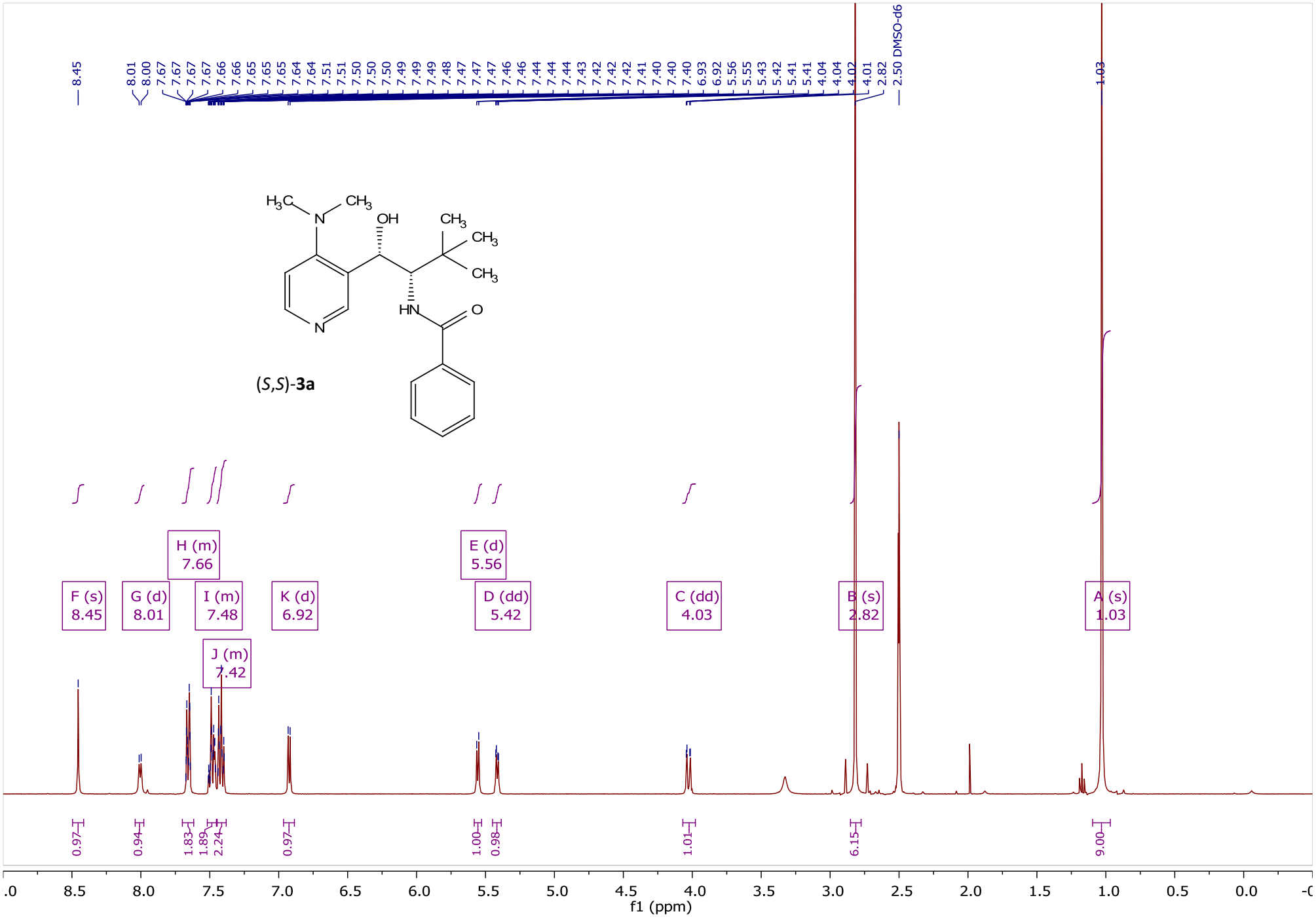
f1 (ppm)

(*S*,*S*)-**1b**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7.67
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7.43
7.42
7.42
7.42
7.41
7.40
7.40
7.40
6.93
6.92
5.56
5.55
5.43
5.42
5.41
5.41
4.04
4.04
4.02
4.01
2.82
2.50 DMSO-d6
1.03
H3C
CH3
N
OH
CH3
CH3
CH3
HN
O
N
(S,S)-3a
H (m) 7.66
E (d) 5.56
F (s) 8.45
G (d) 8.01
I (m) 7.48
K (d) 6.92
D (dd) 5.42
C (dd) 4.03
B (s) 2.82
A (s) 1.03
J (m) 7.42
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1.89
2.24
0.97
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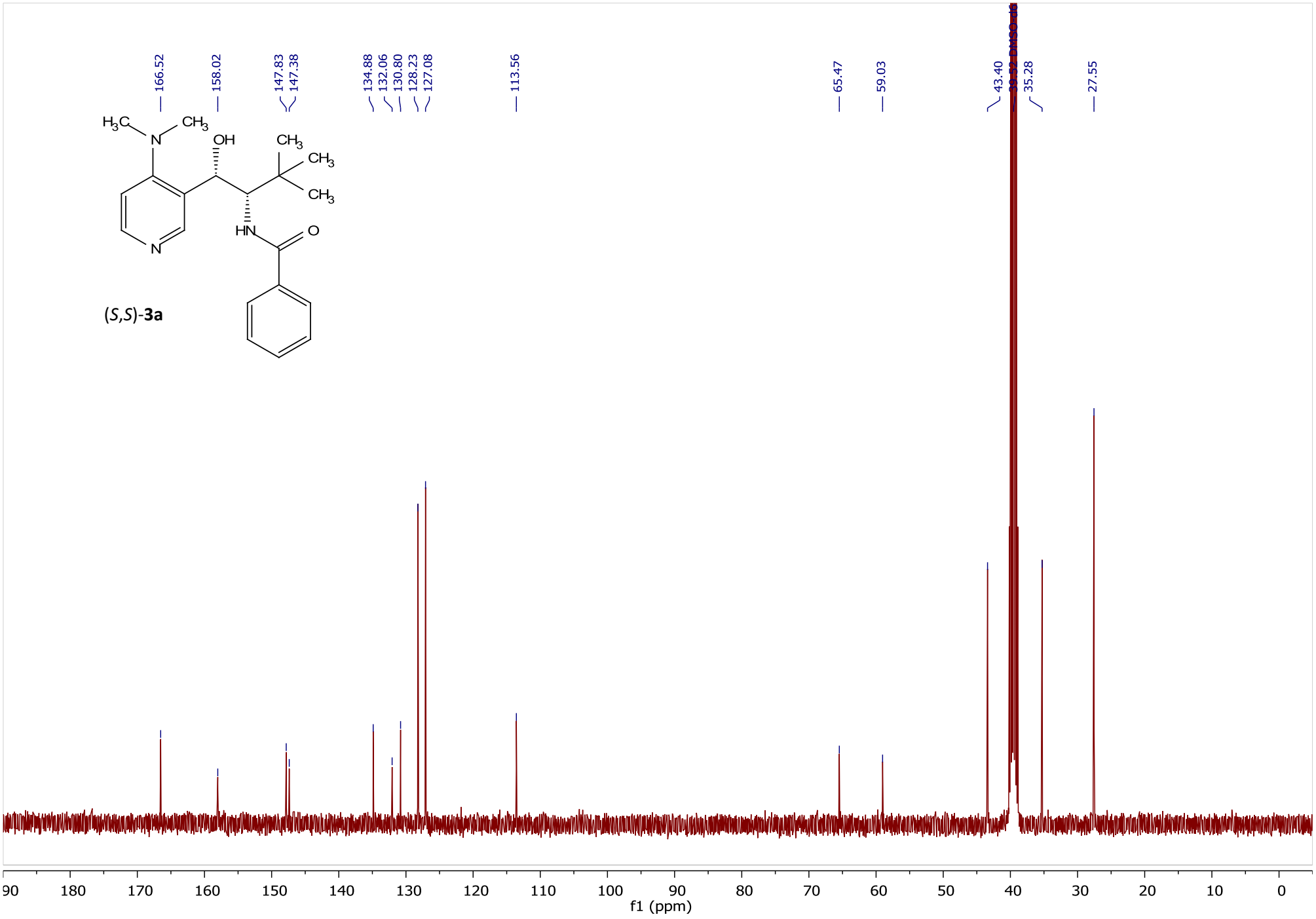
1.01
6.15
9.00
f1 (ppm)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158.02
147.83
147.38
134.88
132.06
130.80
128.23
127.08
113.56
65.47
59.03
43.40
39.52 DMSO-d6
35.28
27.55
H3C
CH3
N
OH
CH3
CH3
CH3
HN
O
N
(S,S)-3a
90
180
170
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150
140
130
120
110
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40
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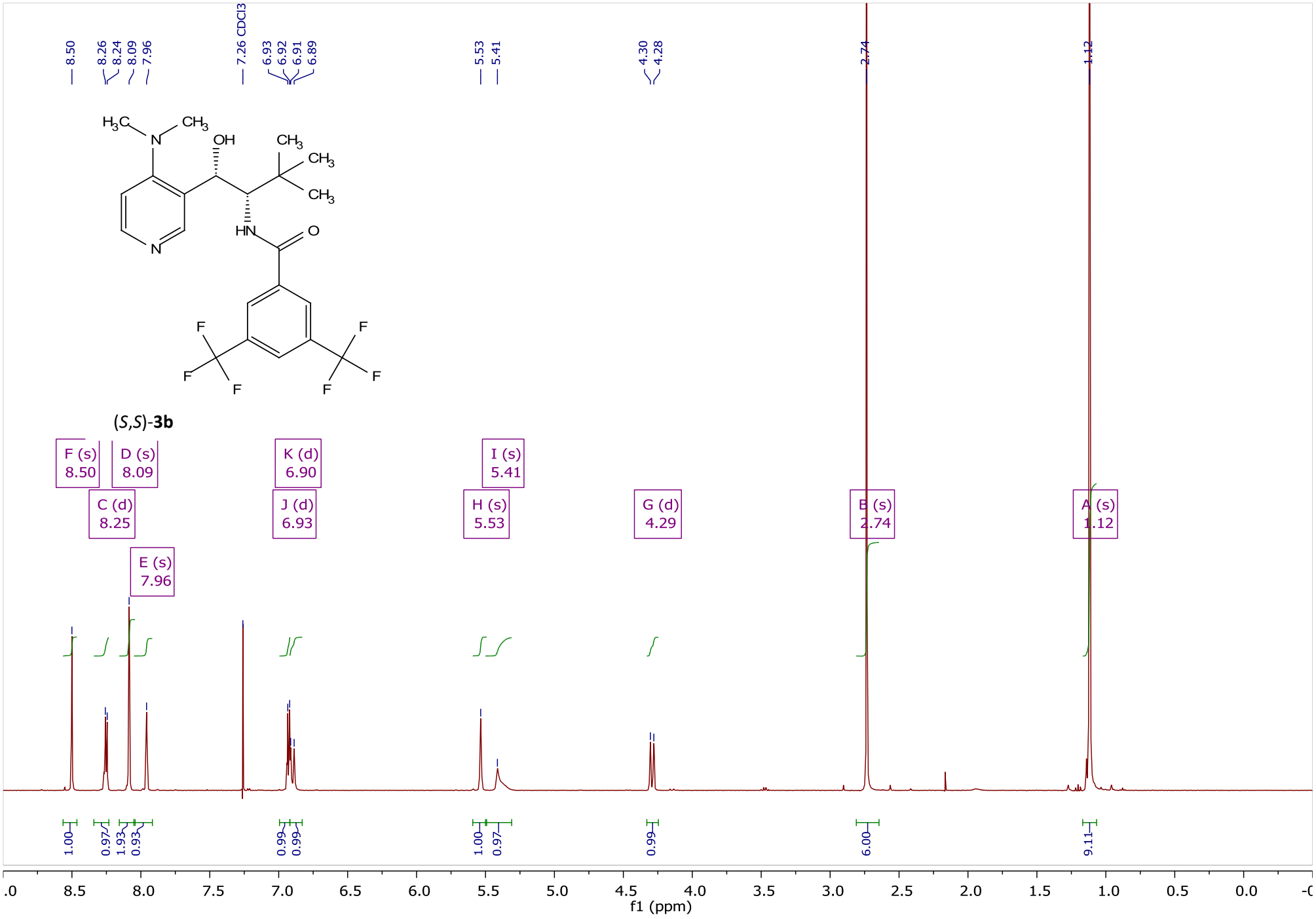
20
10
0
f1 (ppm)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8.24
8.09
7.96
7.26 CDCl3
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6.91
6.89
5.53
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4.30
4.28
2.74
1.12
H3C
N
CH3
OH
CH3
CH3
CH3
HN
O
N
F
F
F
F
F
(S,S)-3b
F (s) 8.50
D (s) 8.09
K (d) 6.90
I (s) 5.41
C (d) 8.25
J (d) 6.93
H (s) 5.53
G (d) 4.29
B (s) 2.74
A (s) 1.12
E (s) 7.96
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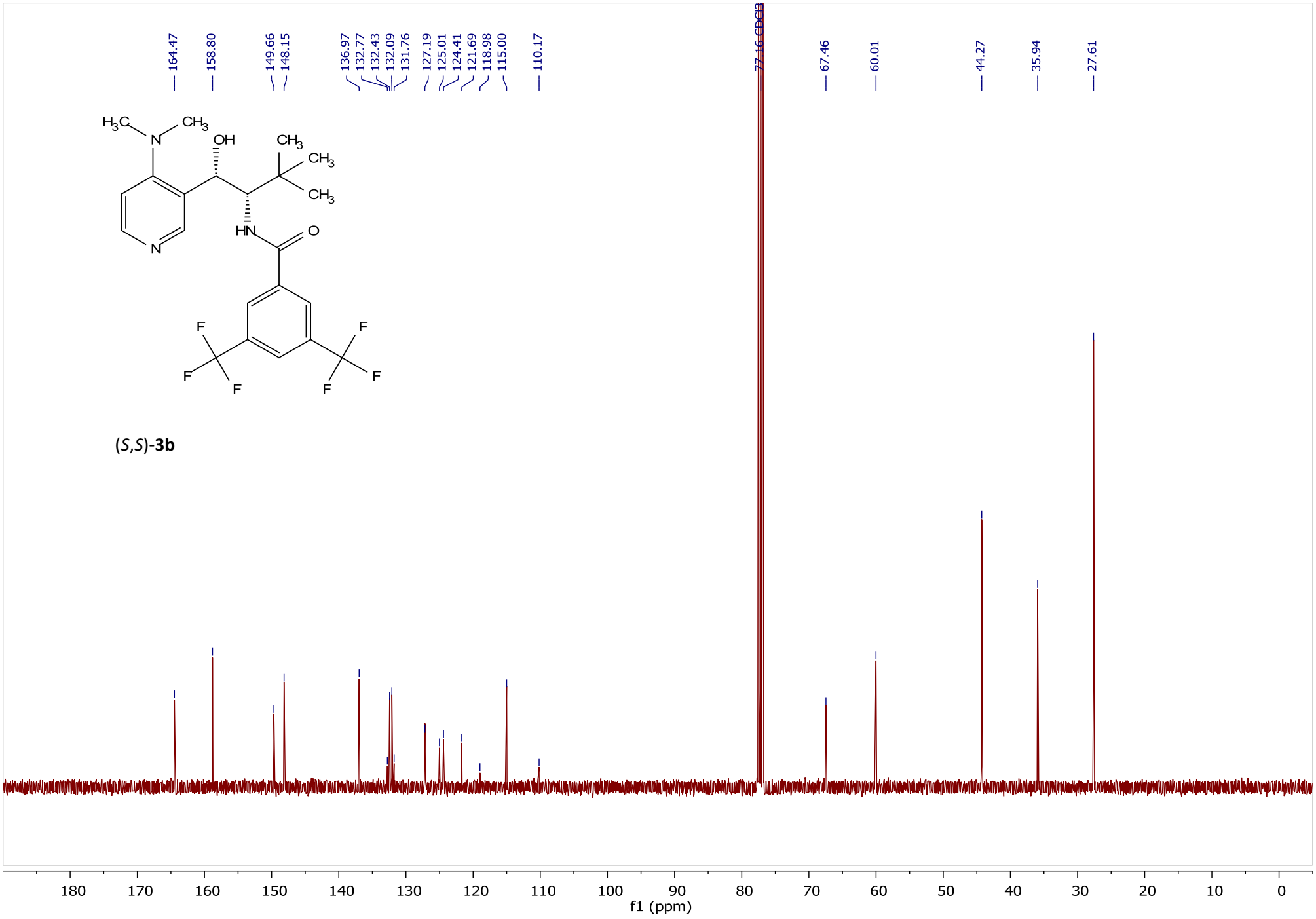
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149.66
148.15
136.97
132.77
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127.19
125.01
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118.98
115.00
110.17
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60.01
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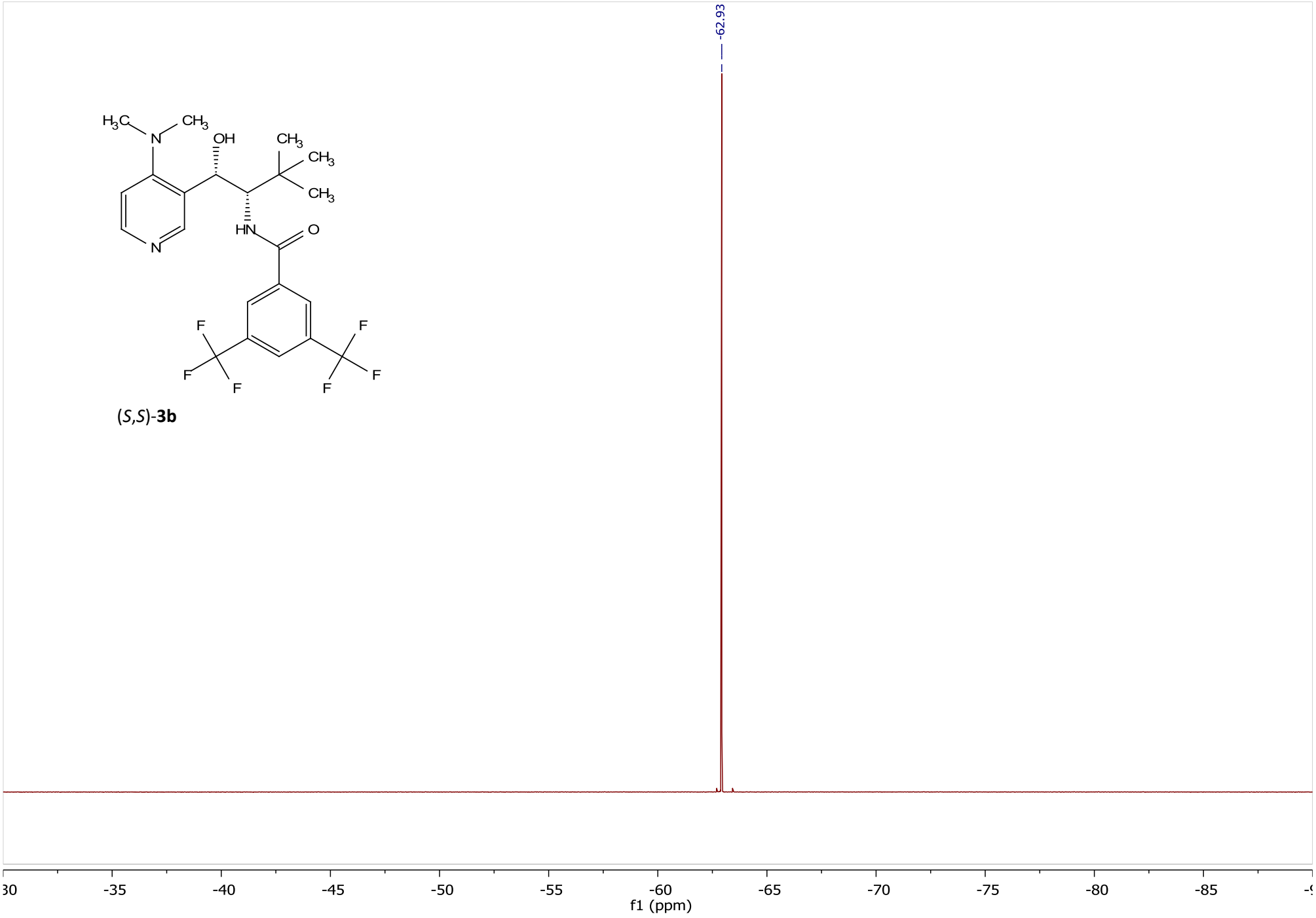
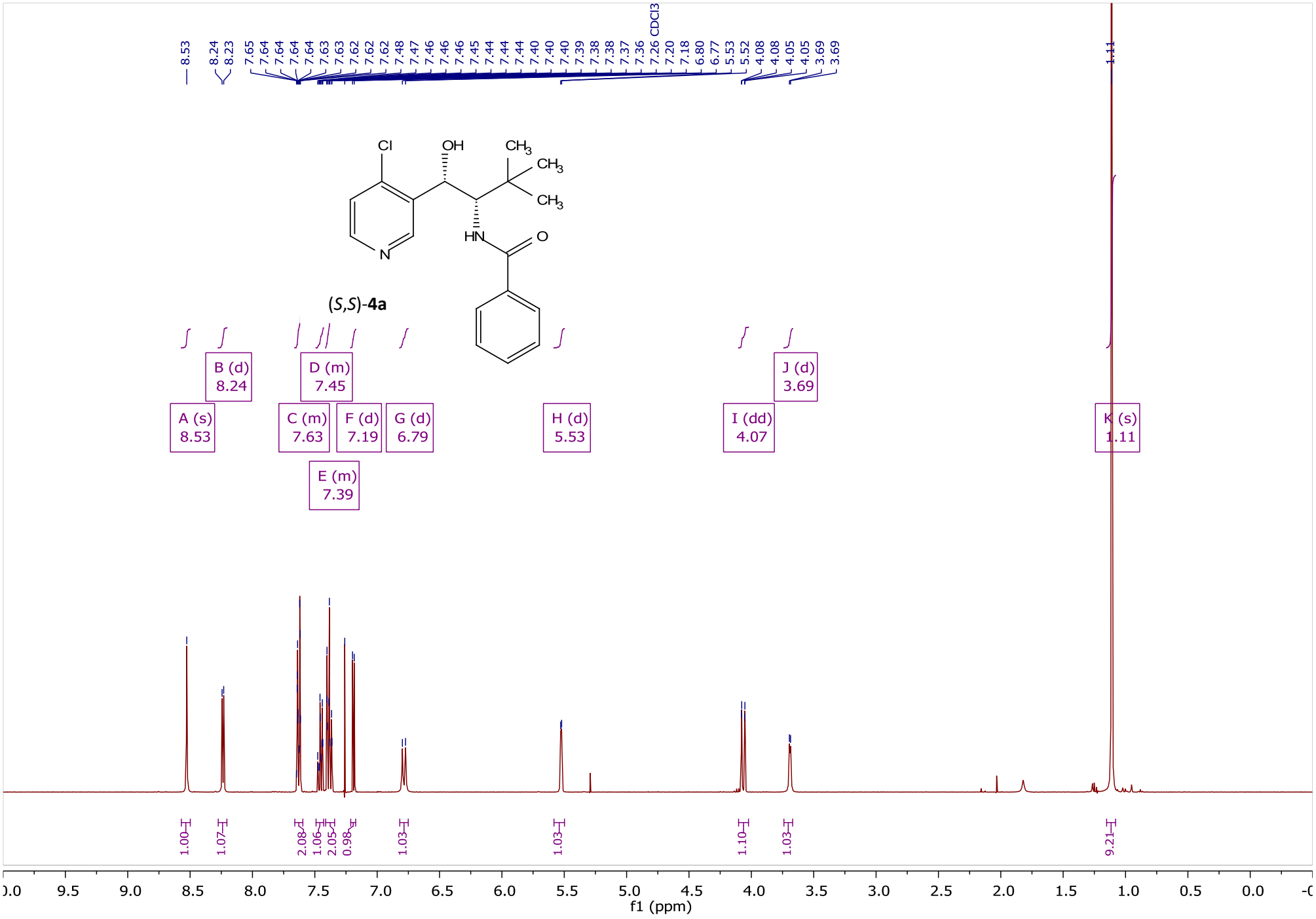
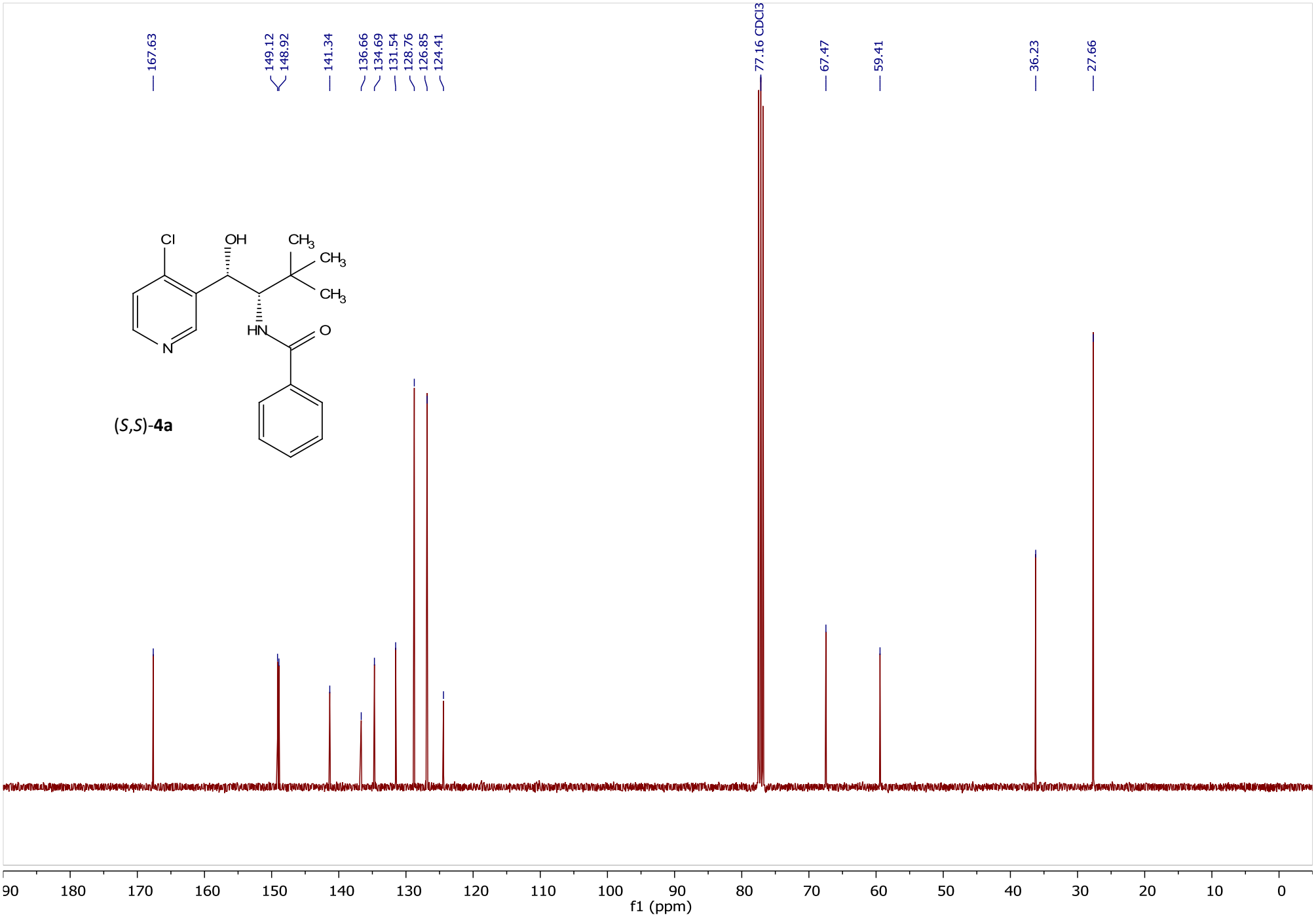
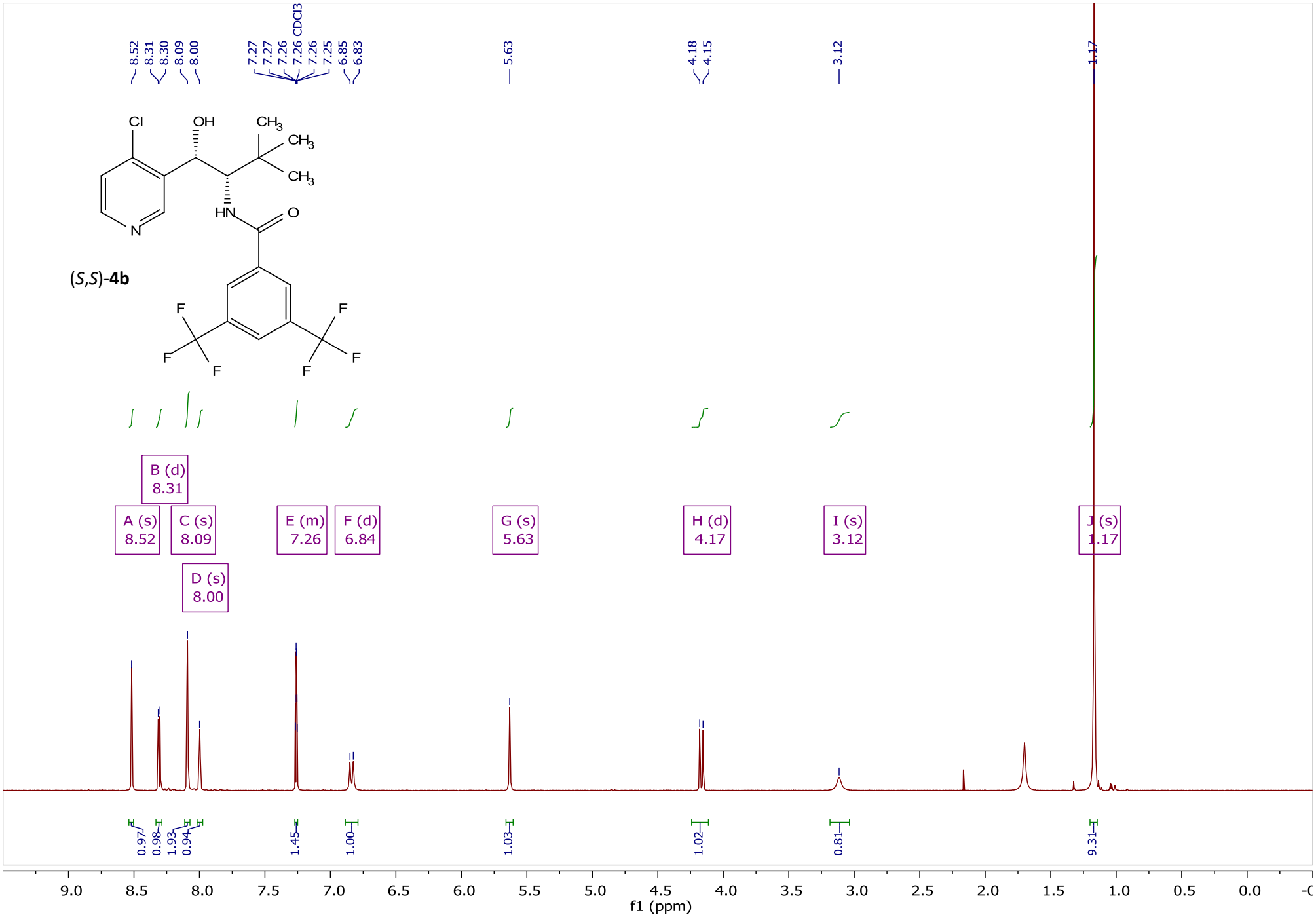
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

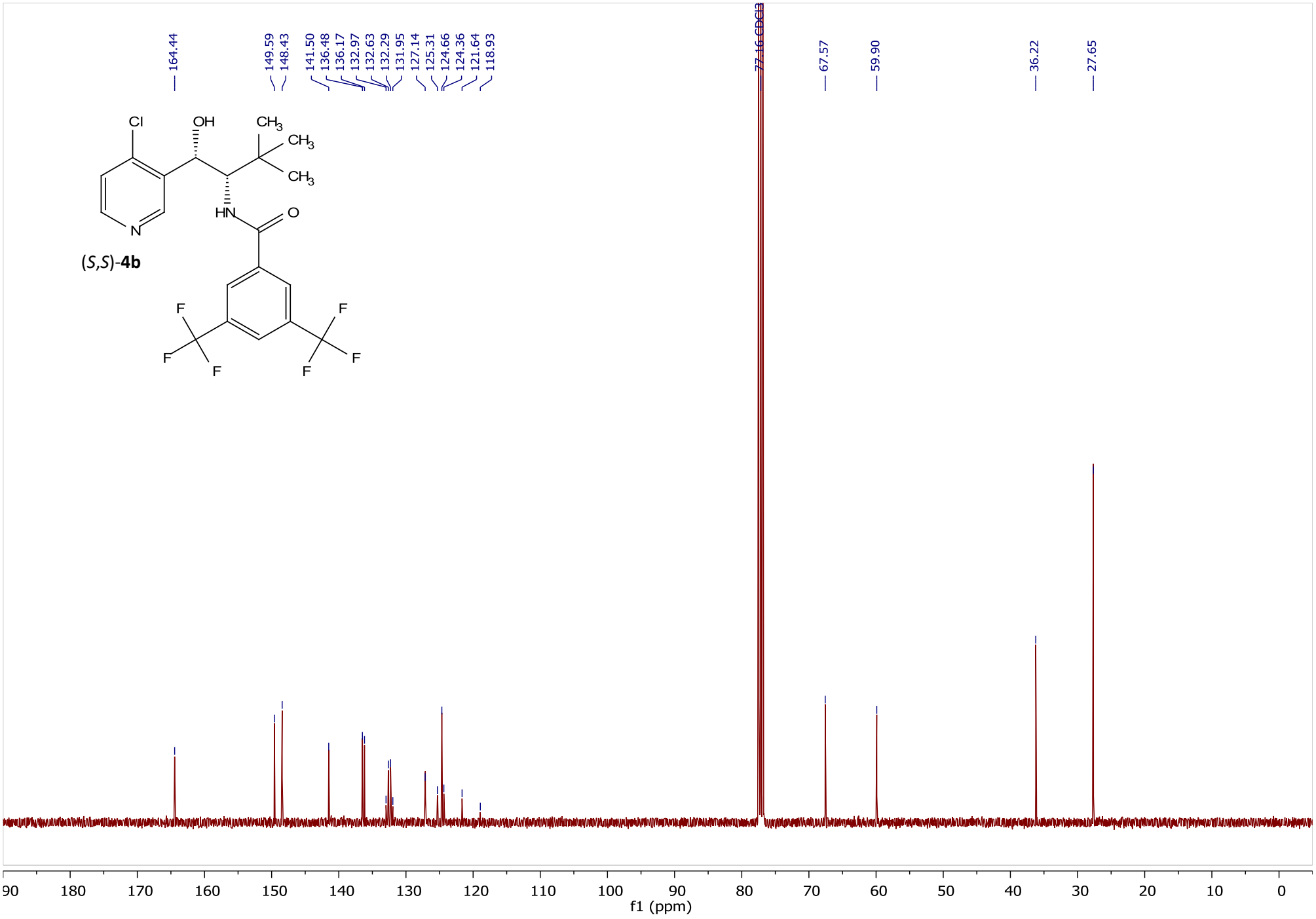


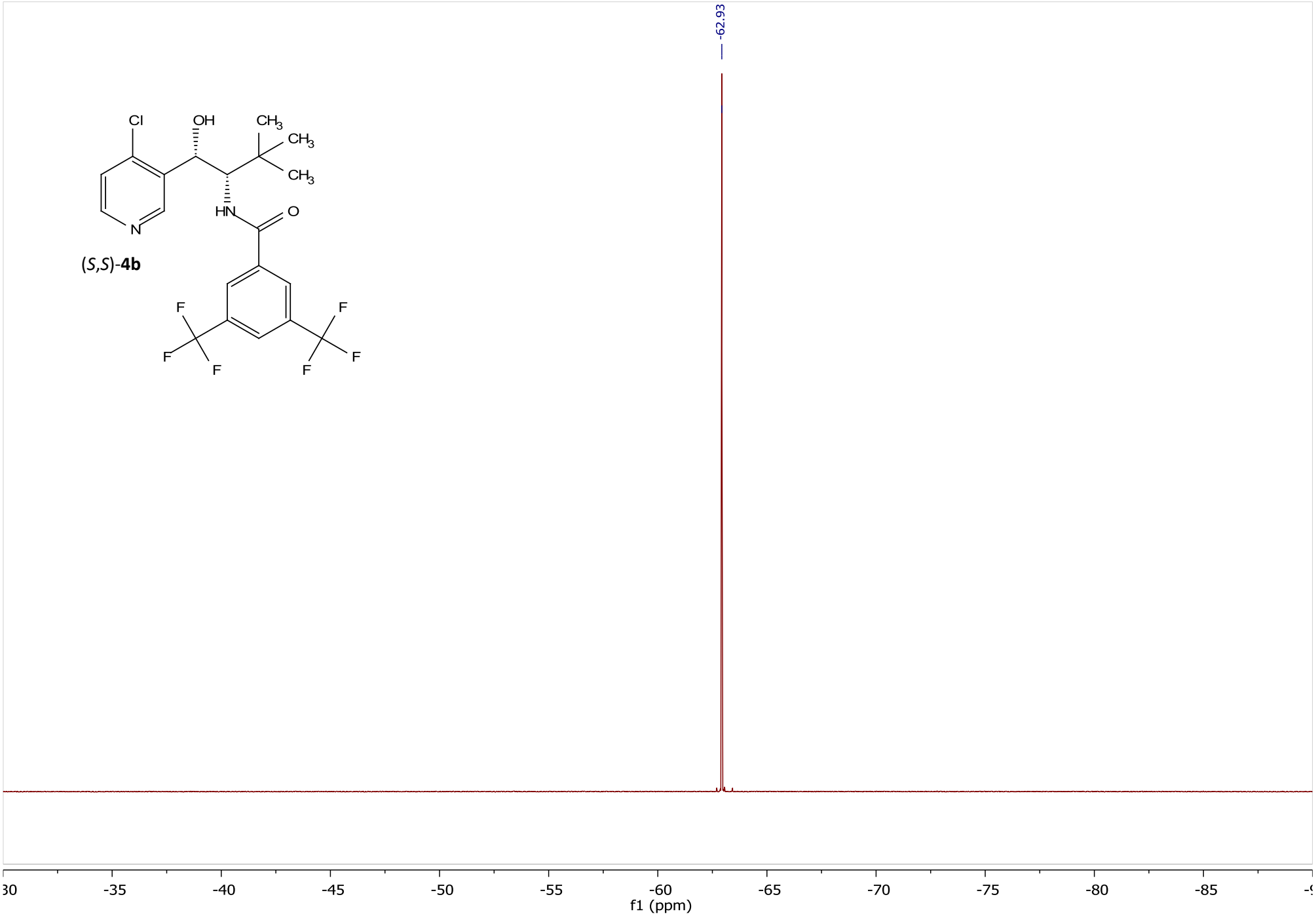
(*S*,*S*)-**3b**


8.53
8.24
8.23
7.65
7.64
7.64
7.64
7.64
7.63
7.63
7.62
7.62
7.62
7.48
7.47
7.46
7.46
7.46
7.45
7.44
7.44
7.44
7.40
7.40
7.40
7.39
7.38
7.38
7.37
7.36
7.26 CDCl3
7.20
7.18
6.80
6.77
5.53
5.52
4.08
4.08
4.05
4.05
3.69
3.69
1.11
Cl
OH
CH3
CH3
CH3
HN
O
N
(S,S)-4a
A (s) 8.53
B (d) 8.24
C (m) 7.63
D (m) 7.45
E (m) 7.39
F (d) 7.19
G (d) 6.79
H (d) 5.53
I (dd) 4.07
J (d) 3.69
K (s) 1.11
1.00
1.07
2.08
1.06
2.05
0.98
1.03
1.03
1.10
1.03
9.21
f1 (ppm)

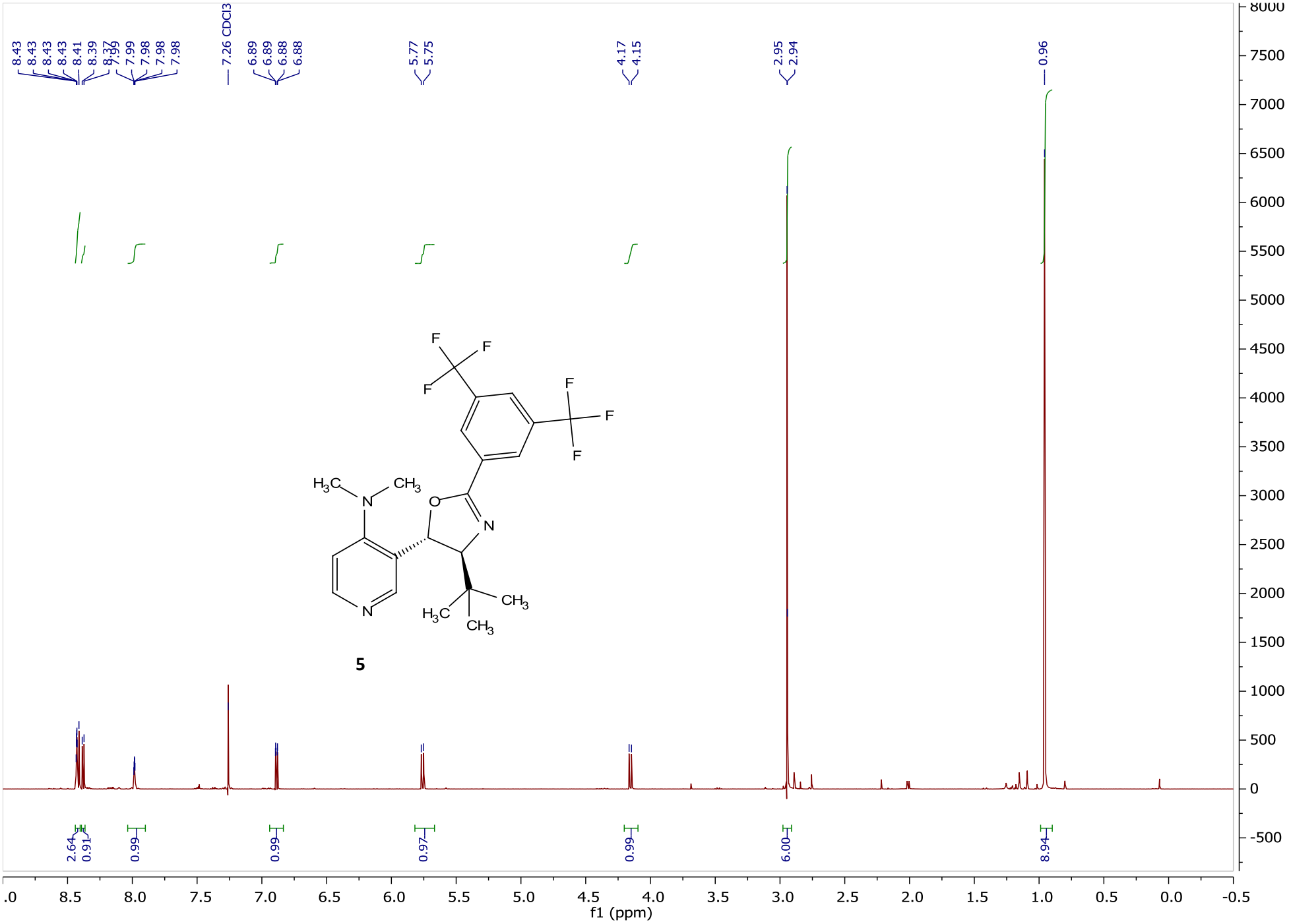

167.63
149.12
148.92
141.34
136.66
134.69
131.54
128.76
126.85
124.41
77.16 CDCl3
67.47
59.41
36.23
27.66
Cl
OH
CH3
CH3
CH3
HN
O
N
(S,S)-4a
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

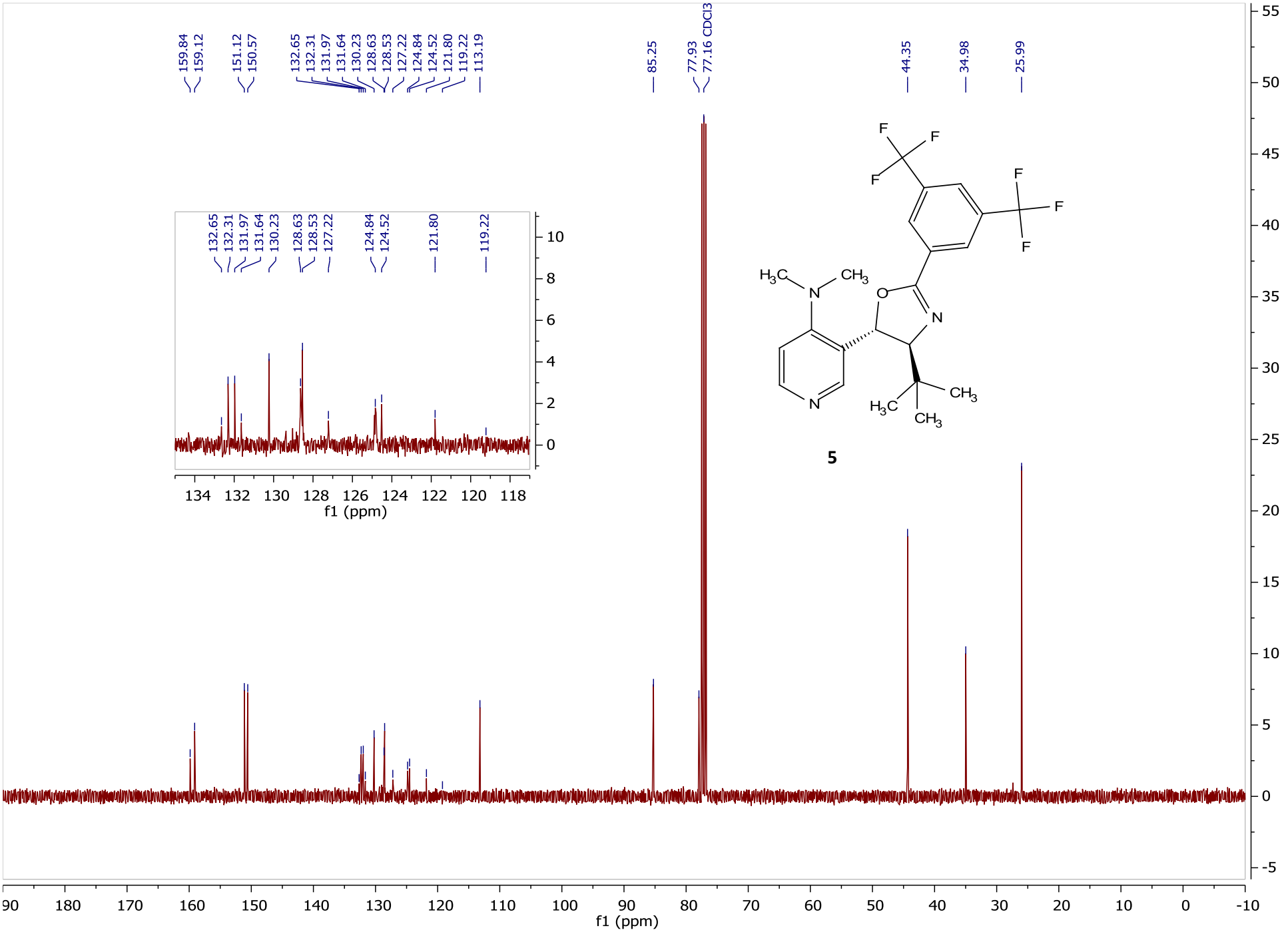

8.52
8.31
8.30
8.09
8.00
7.27
7.27
7.26
7.26 CDCl3
7.26
7.25
6.85
6.83
5.63
4.18
4.15
3.12
1.17
Cl
OH
CH3
CH3
CH3
HN
O
N
F
F
F
F
F
F
(S,S)-4b
B (d) 8.31
A (s) 8.52
C (s) 8.09
D (s) 8.00
E (m) 7.26
F (d) 6.84
G (s) 5.63
H (d) 4.17
I (s) 3.12
J (s) 1.17
0.97
0.98
1.93
0.94
1.45
1.00
1.03
1.02
0.81
9.31
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)

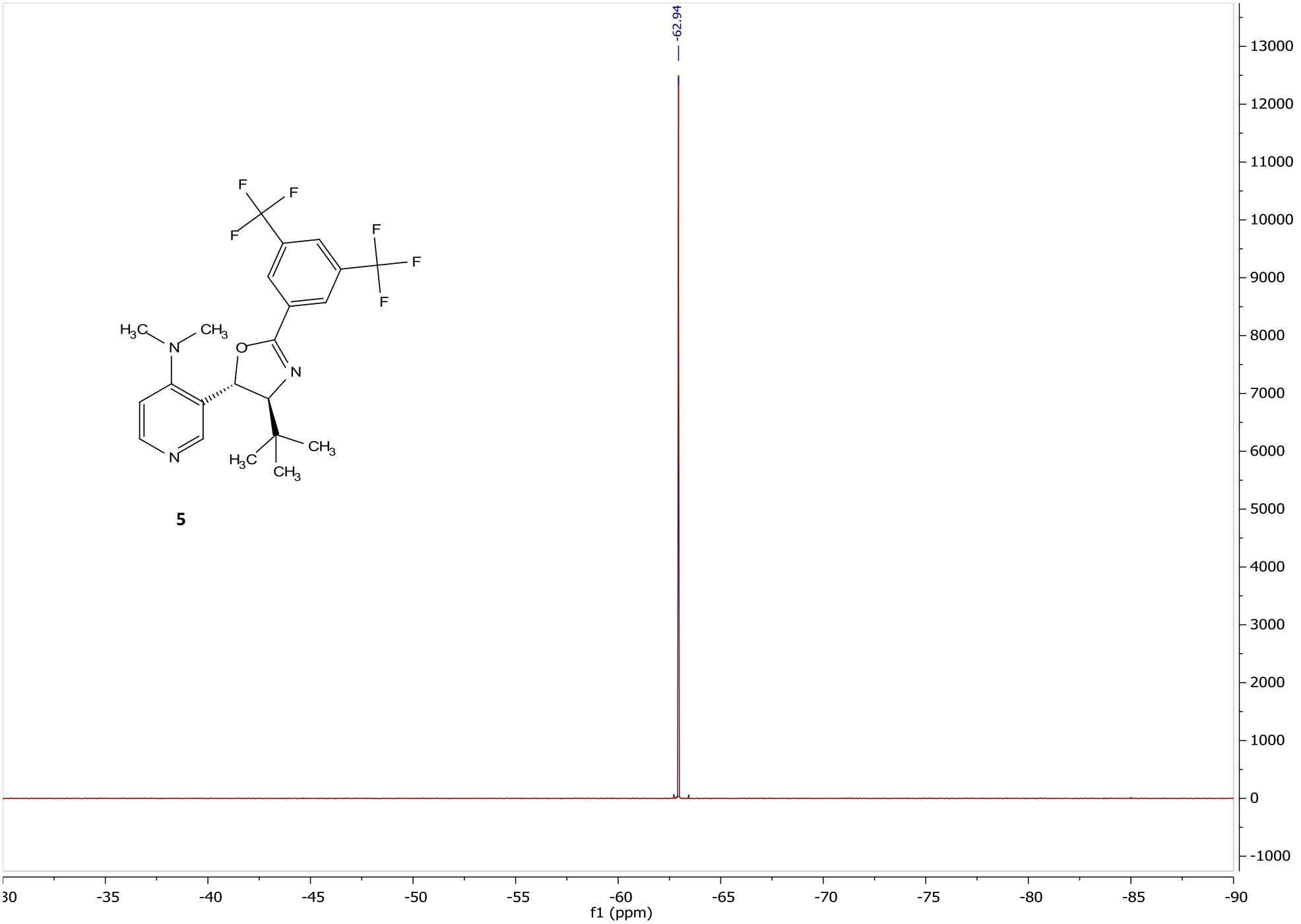

164.44
149.59
148.43
141.50
136.48
136.17
132.97
132.63
132.29
131.95
127.14
125.31
124.66
124.36
121.64
118.93
77.16 CDCl3
67.57
59.90
36.22
27.65
Cl
OH
CH3
CH3
CH3
HN
O
N
F
F
F
F
F
F
(S,S)-4b
f1 (ppm)


-62.93
Cl
OH
CH3
CH3
CH3
HN
O
N
F
F
F
F
F
F
30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
f1 (ppm)

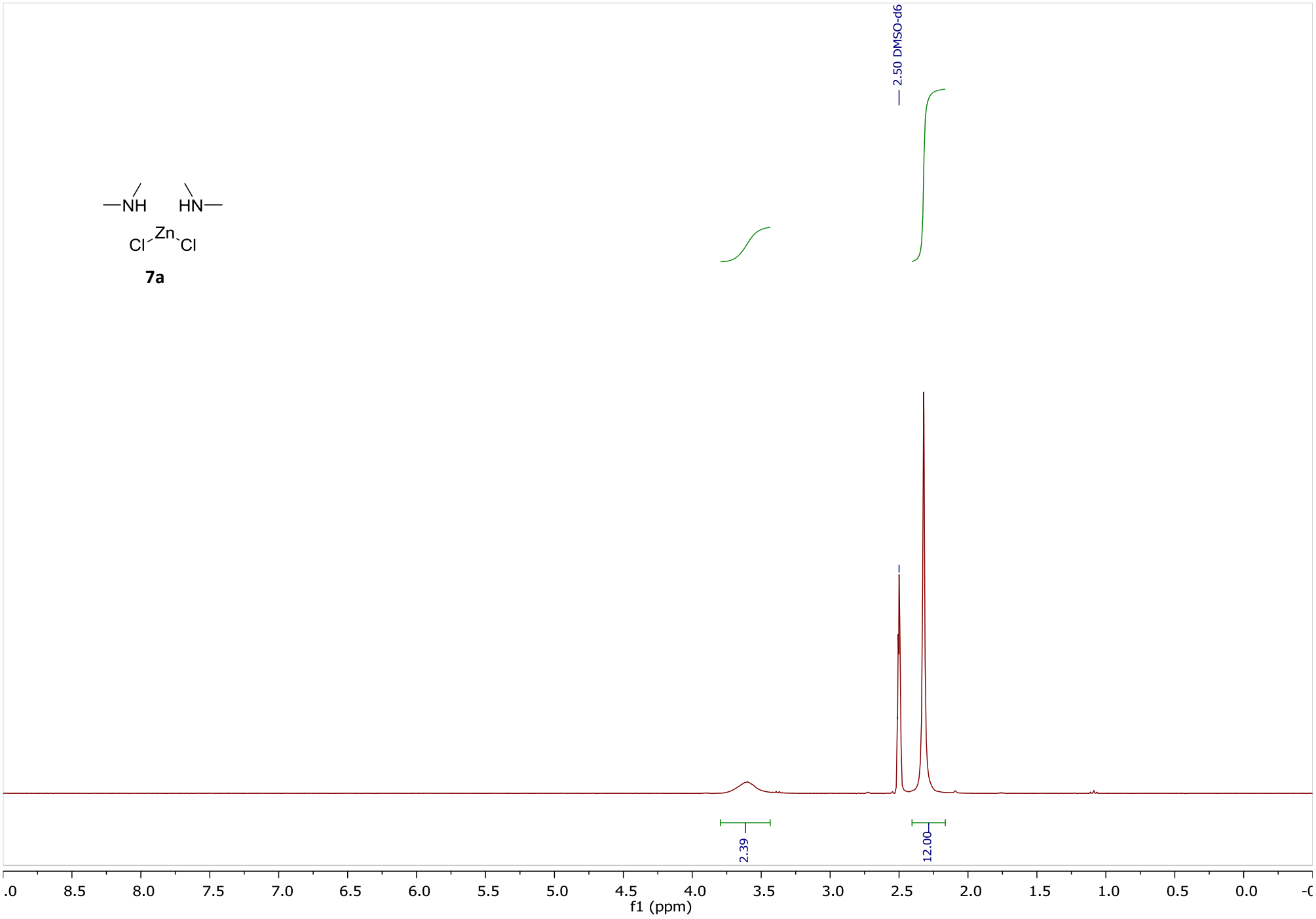
(*S*,*S*)-**4b**


8.43
8.43
8.43
8.43
8.41
8.39
8.37
7.99
7.99
7.98
7.98
7.98
7.26 CDCl3
6.89
6.89
6.88
6.88
5.77
5.75
4.17
4.15
2.95
2.94
0.96
F
F
F
F
F
F
H3C
CH3
N
O
N
N
CH3
H3C
CH3
5
2.64
0.91
0.99
0.99
0.97
0.99
6.00
8.94
f1 (ppm)

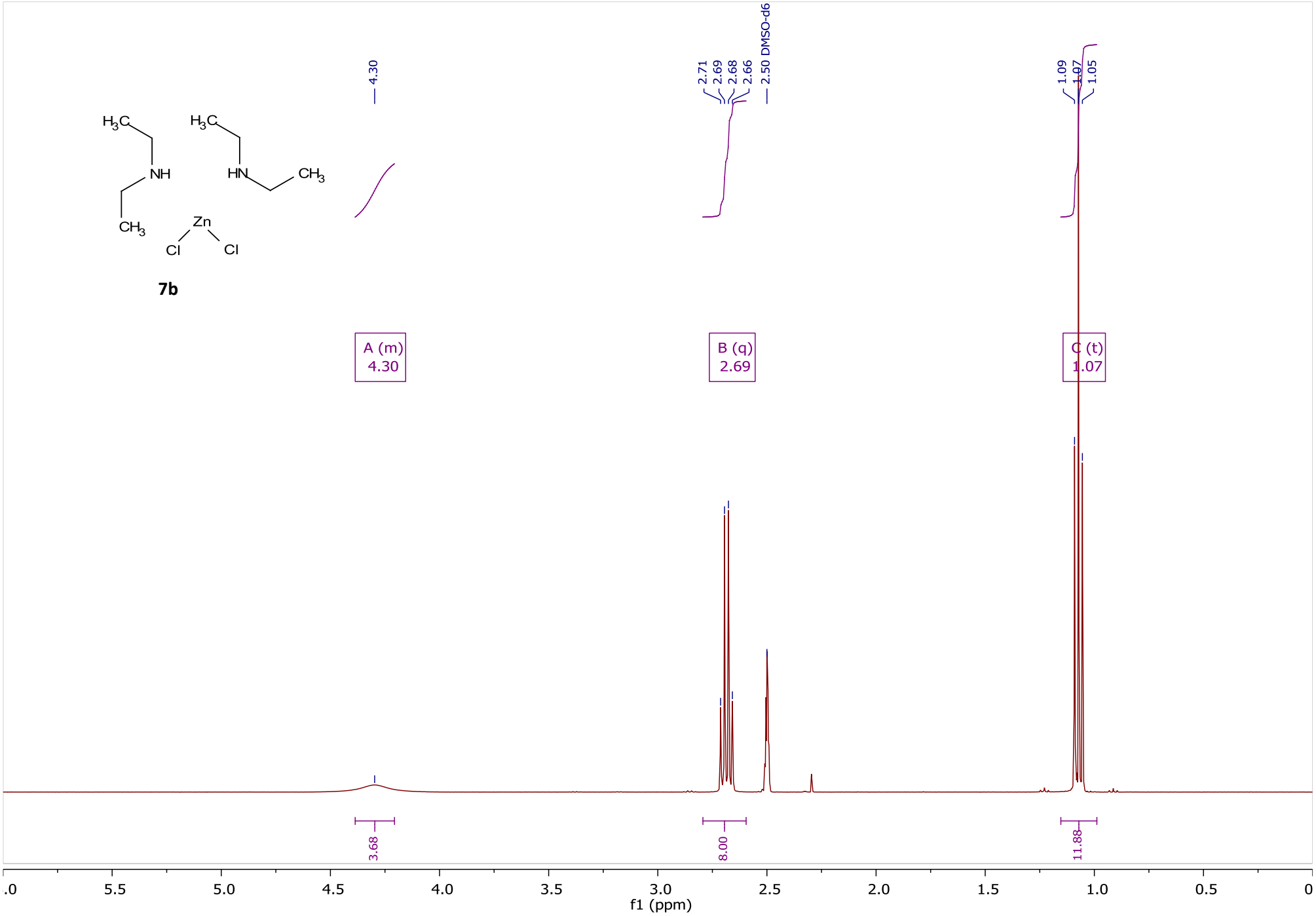

159.84
159.12
151.12
150.57
132.65
132.31
131.97
131.64
130.23
128.63
128.53
127.22
124.84
124.52
121.80
119.22
113.19
85.25
77.93
77.16 CDCl3
44.35
34.98
25.99
f1 (ppm)
5


-62.94
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
f1 (ppm)
F
F
F
F
F
F
H3C
CH3
N
O
N
N
H3C
CH3
CH3

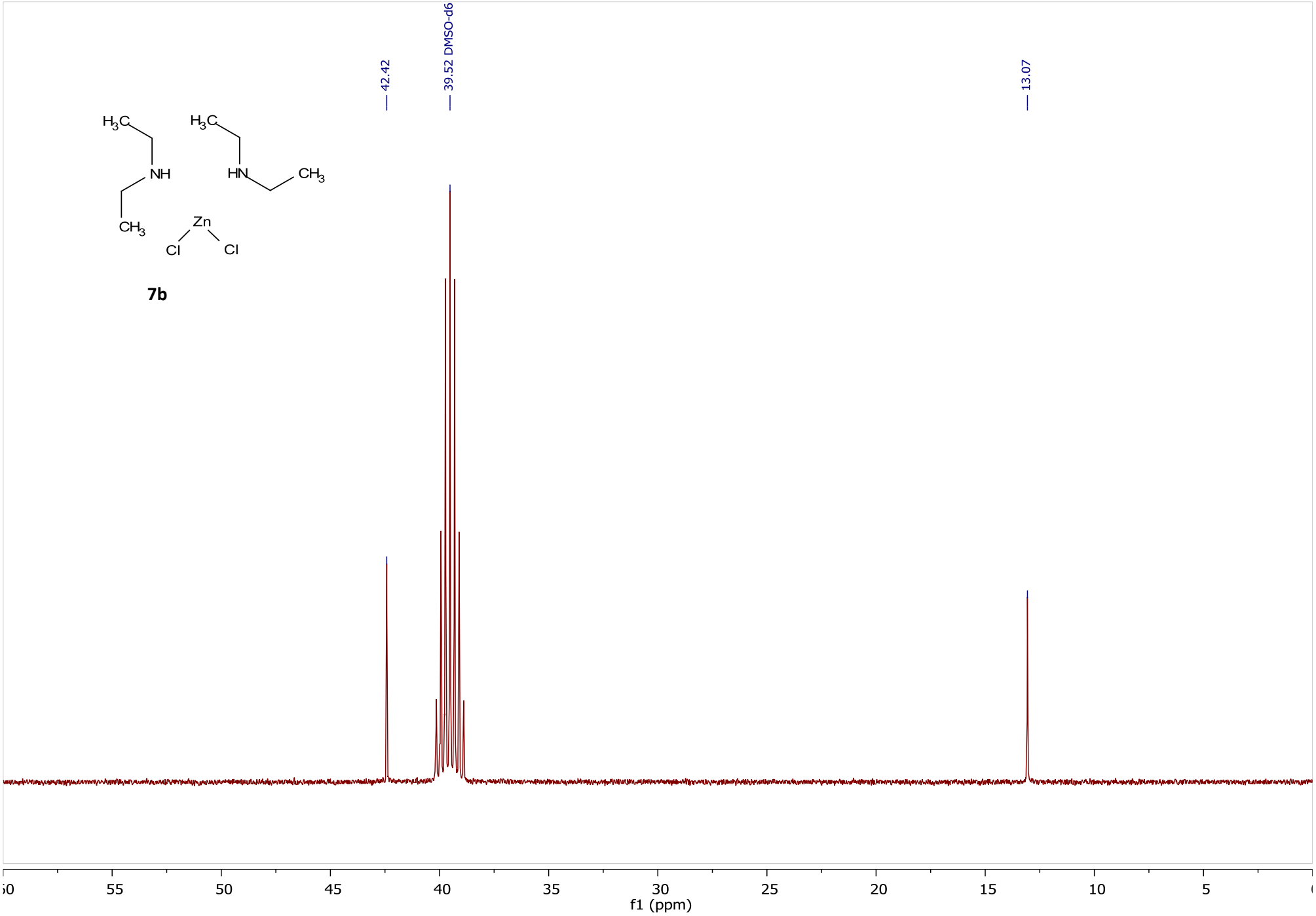
5

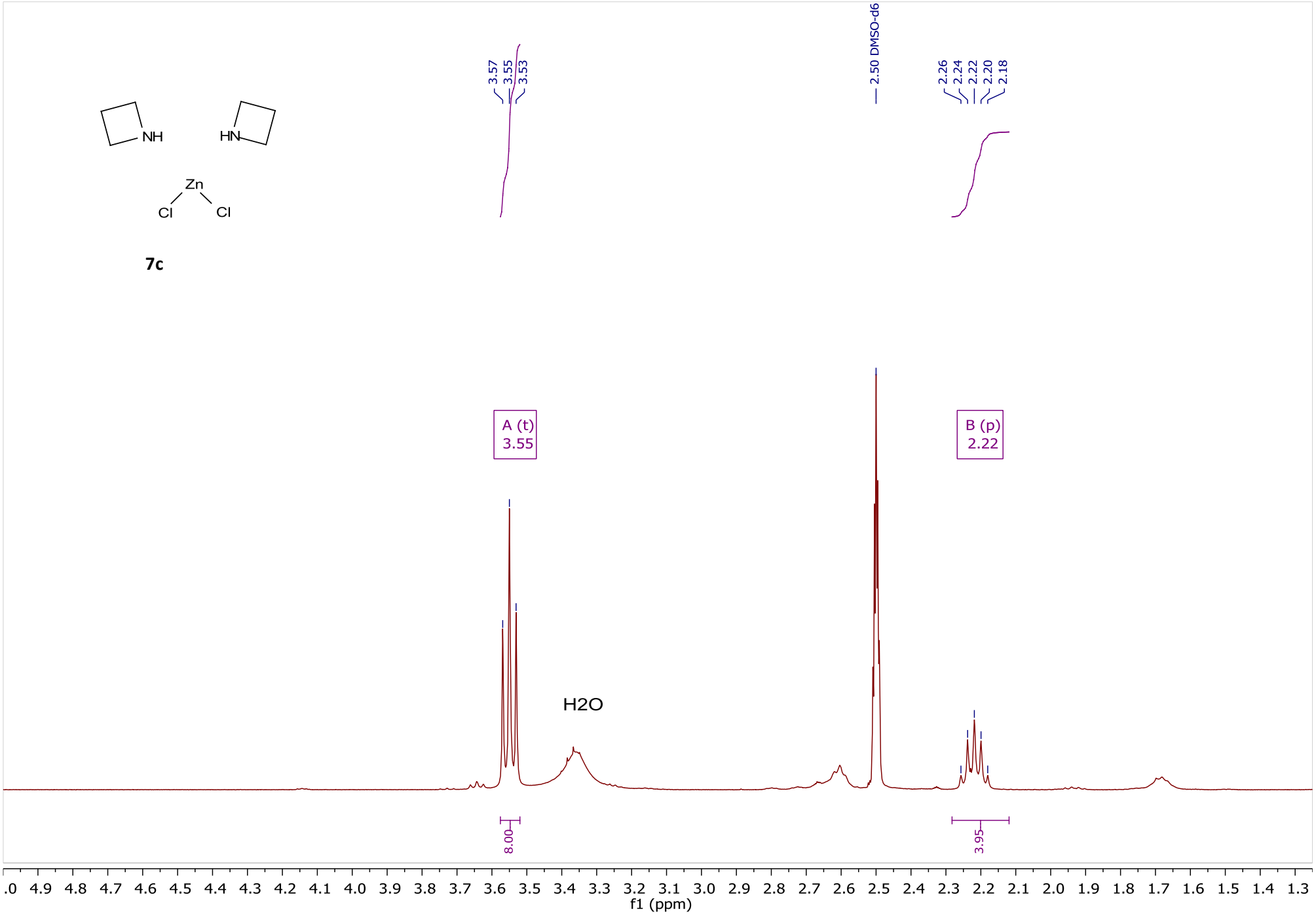


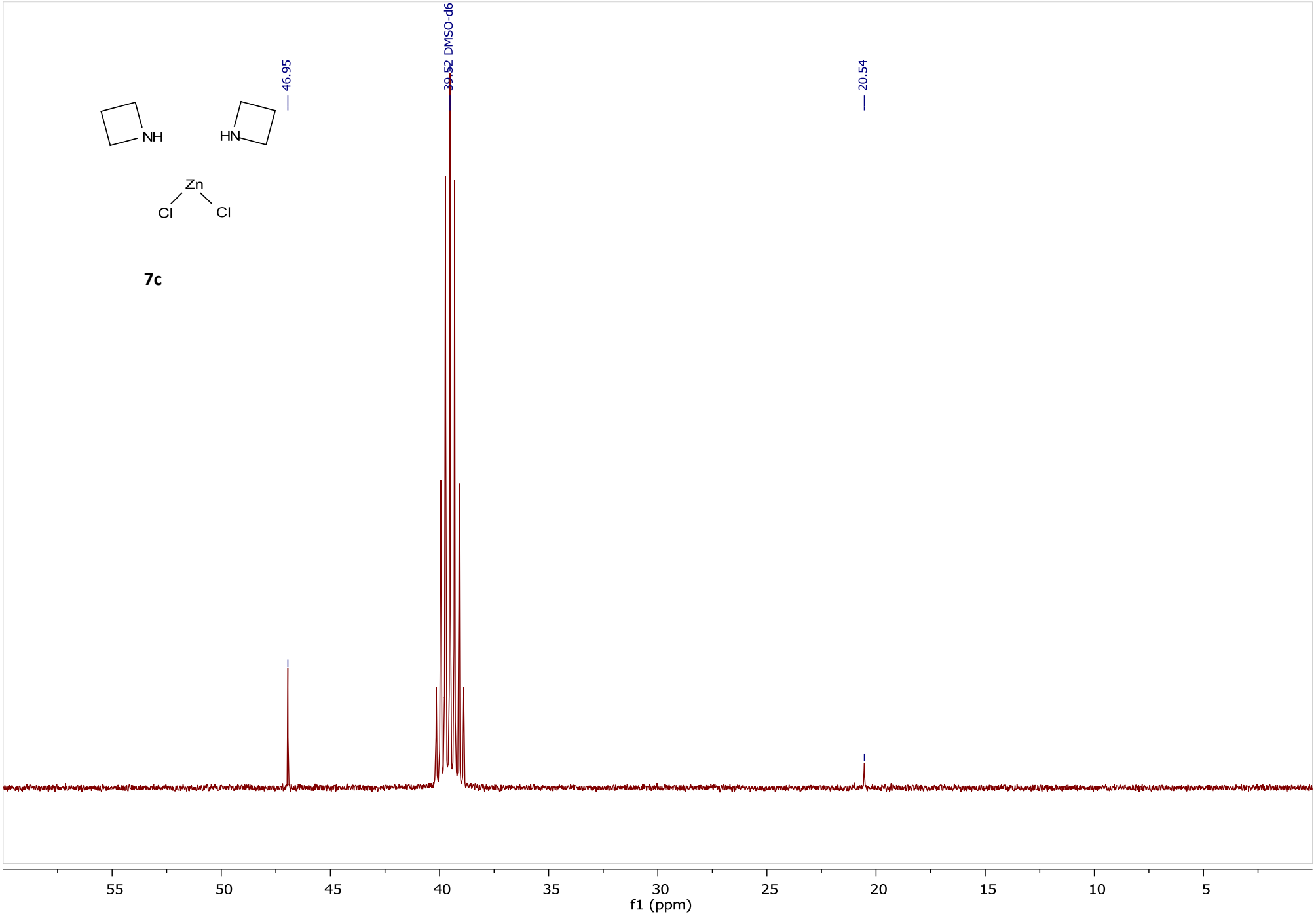
7a

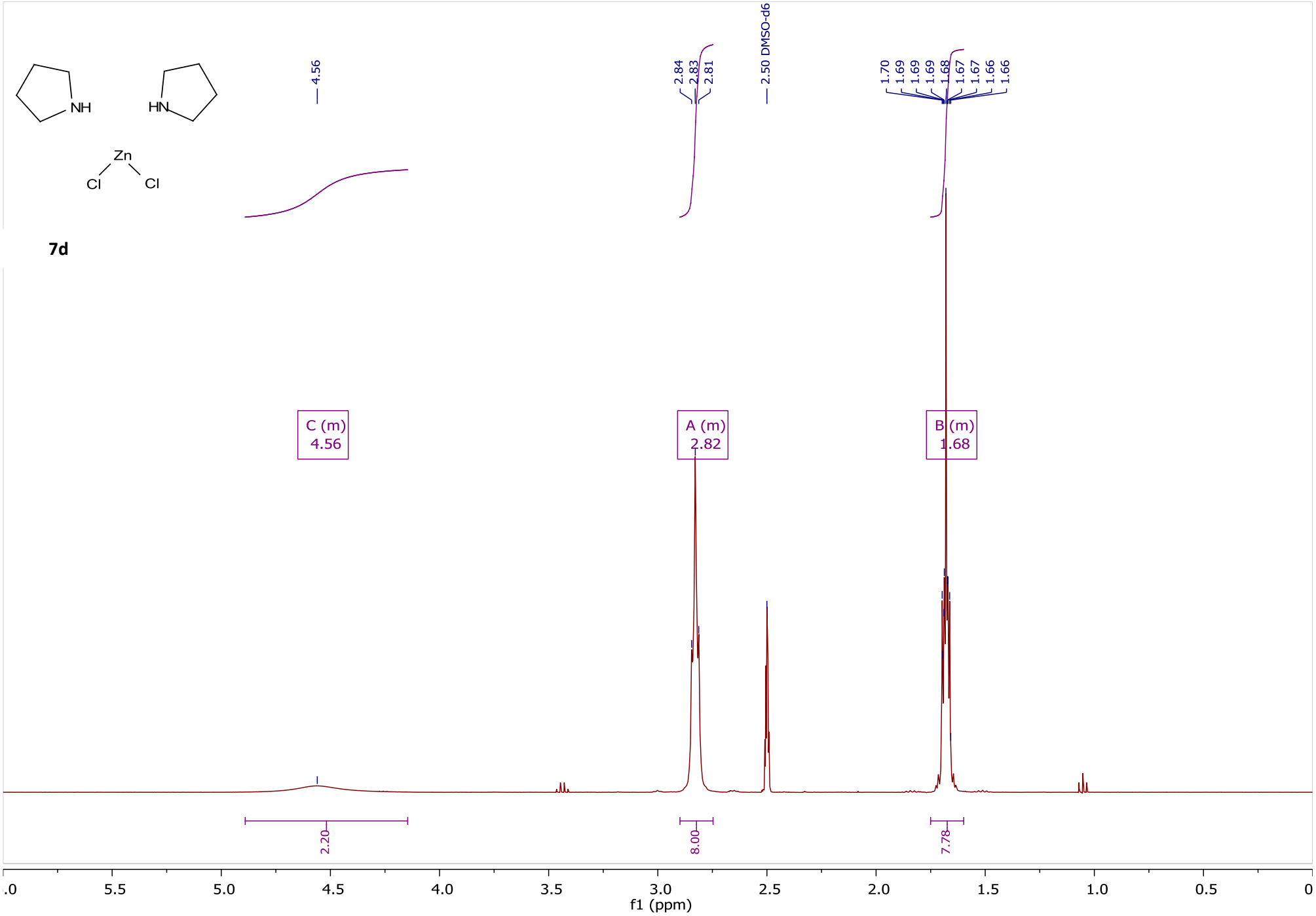

4.30
2.71
2.69
2.68
2.66
2.50 DMSO-d6
1.09
1.07
1.05
A (m)
4.30
B (q)
2.69
C (t)
1.07
3.68
8.00
11.88
f1 (ppm)

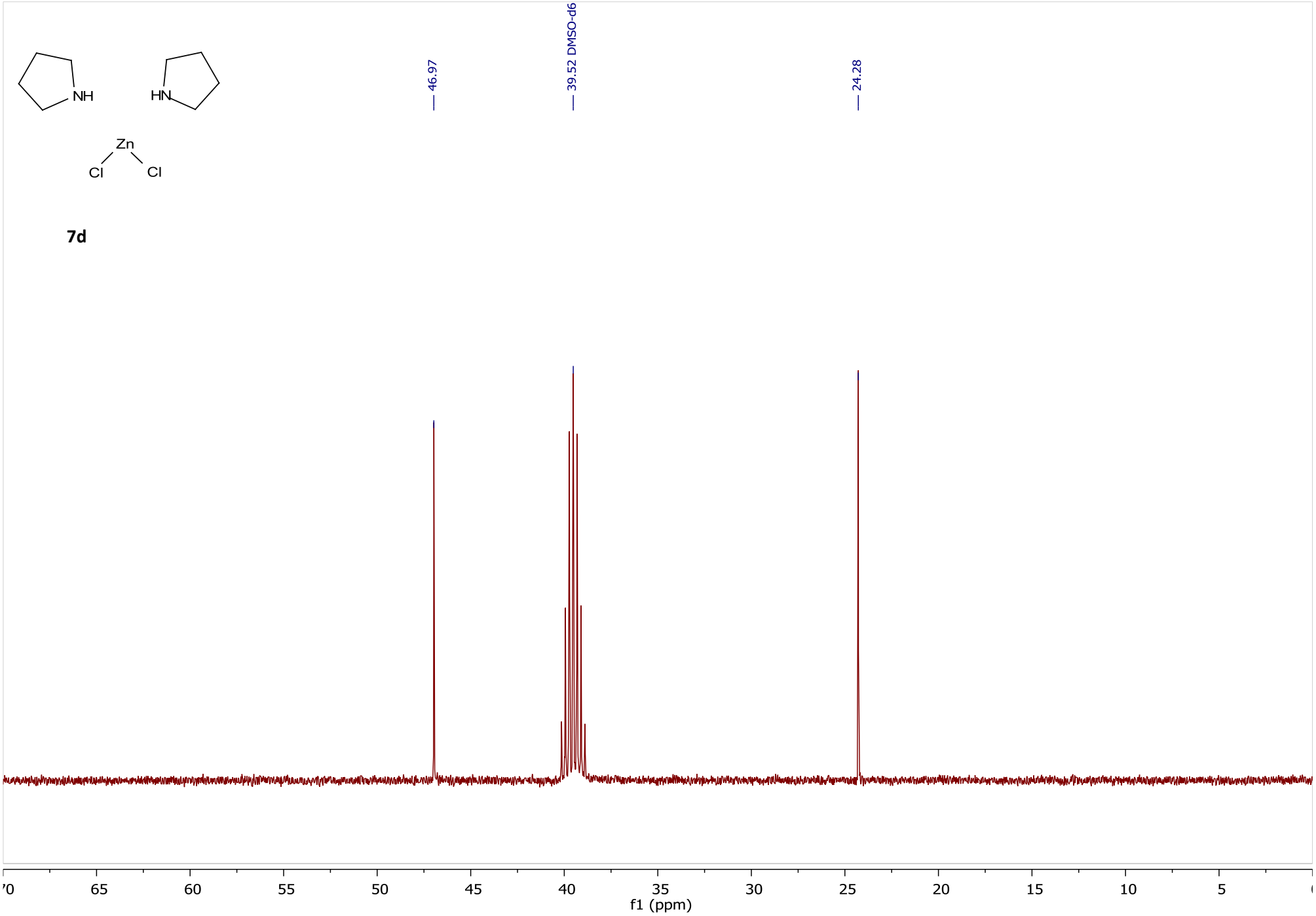
7b

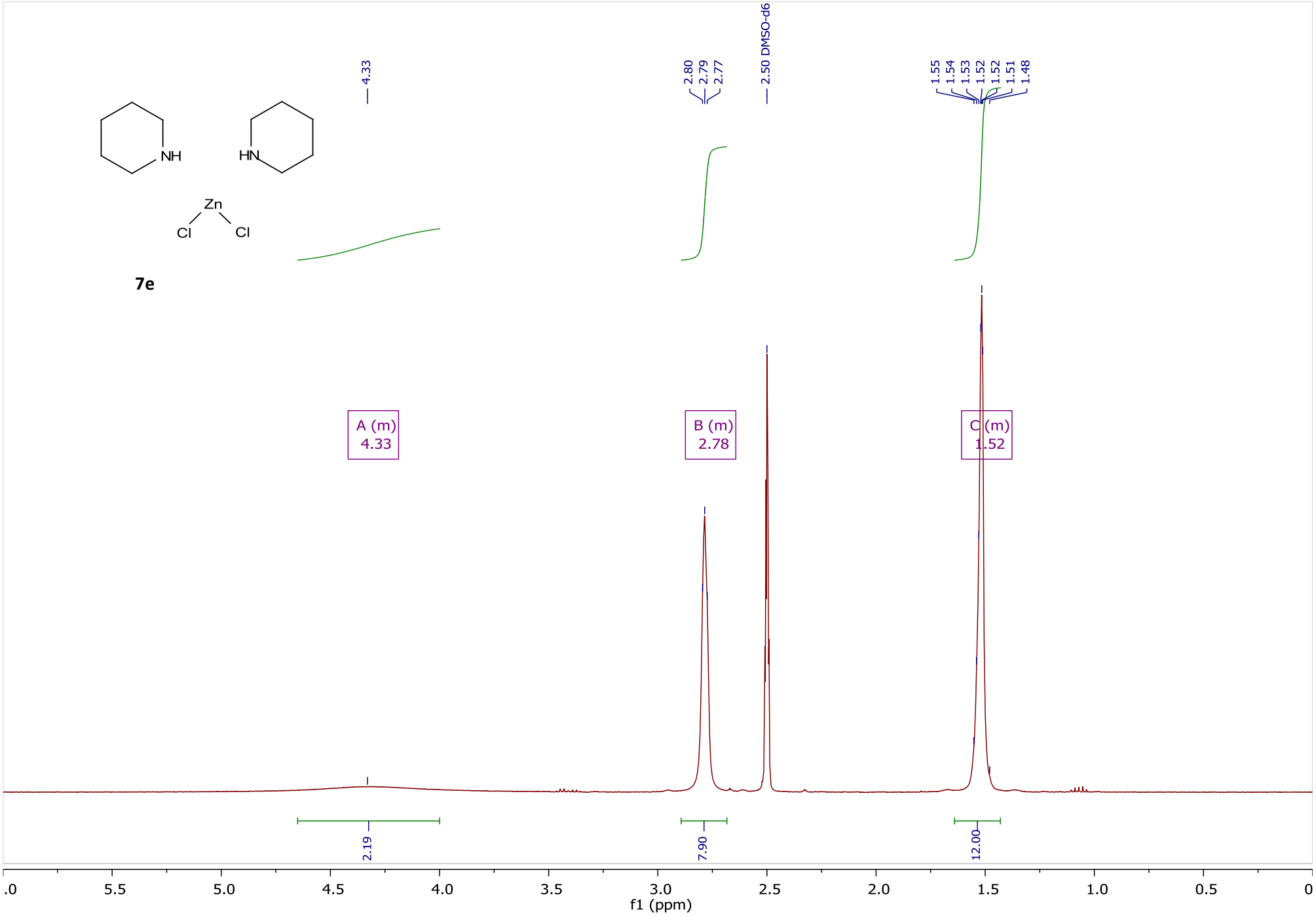

42.42
39.52 DMSO-d6
13.07
H3C
NH
CH3
H3C
HN
CH3
Zn
Cl
Cl
7b
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)

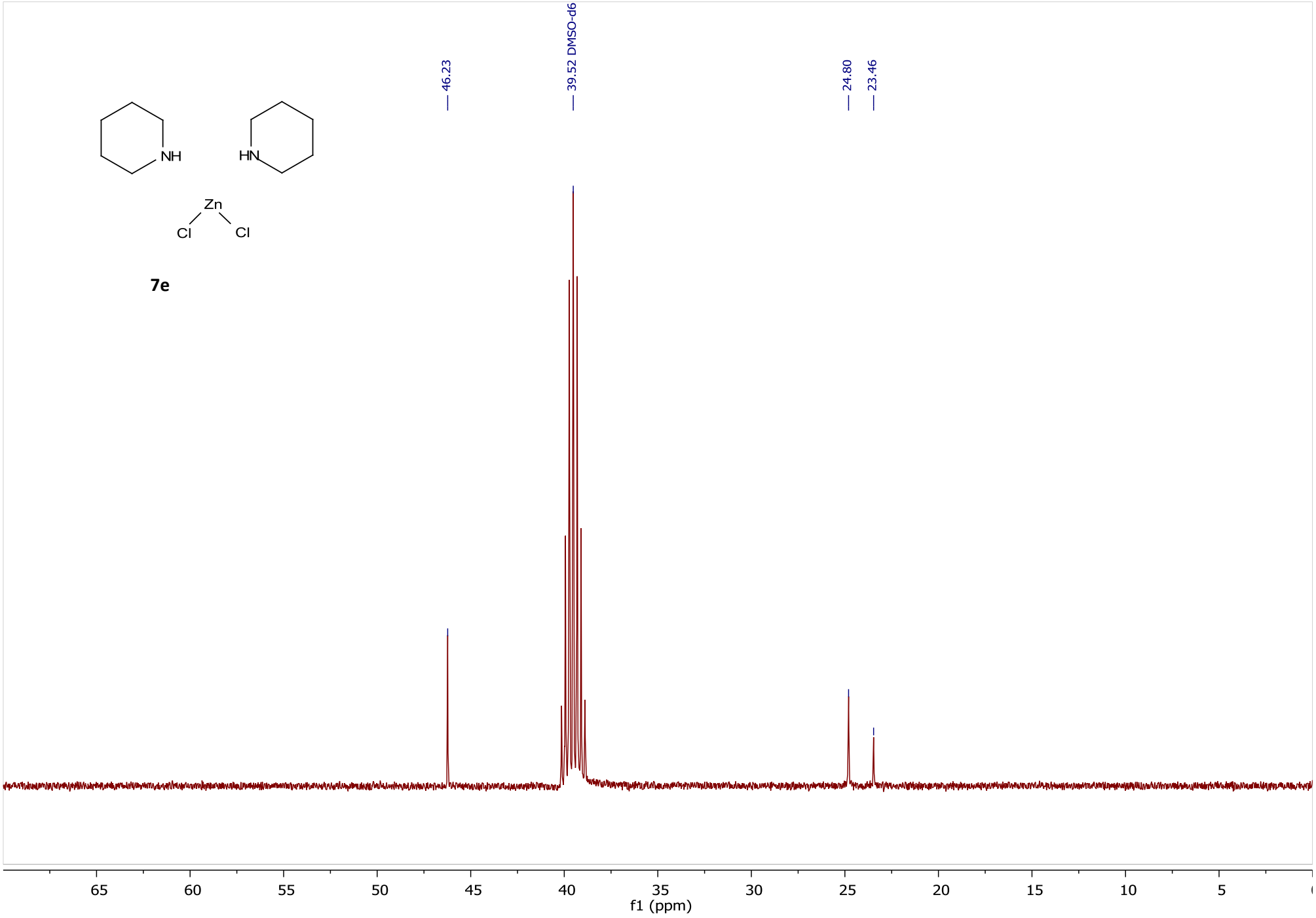

NH
HN
Zn
Cl
Cl
7c
3.57
3.55
3.53
2.50 DMSO-d6
2.26
2.24
2.22
2.20
2.18
A (t)
3.55
B (p)
2.22
H2O
8.00
3.95
f1 (ppm)

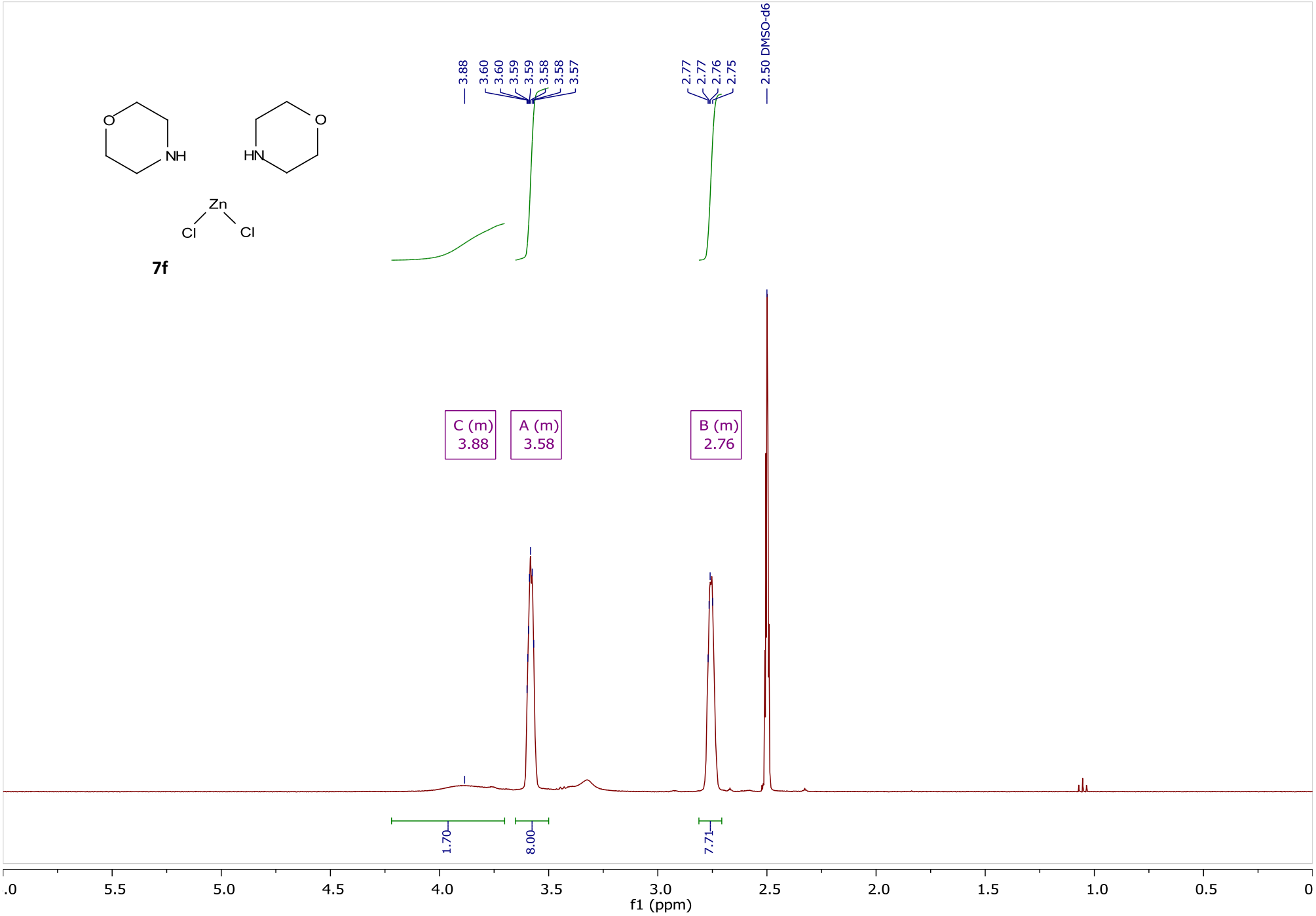

46.95
39.52 DMSO-d6
20.54
NH
HN
Zn
Cl
Cl
7c
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)

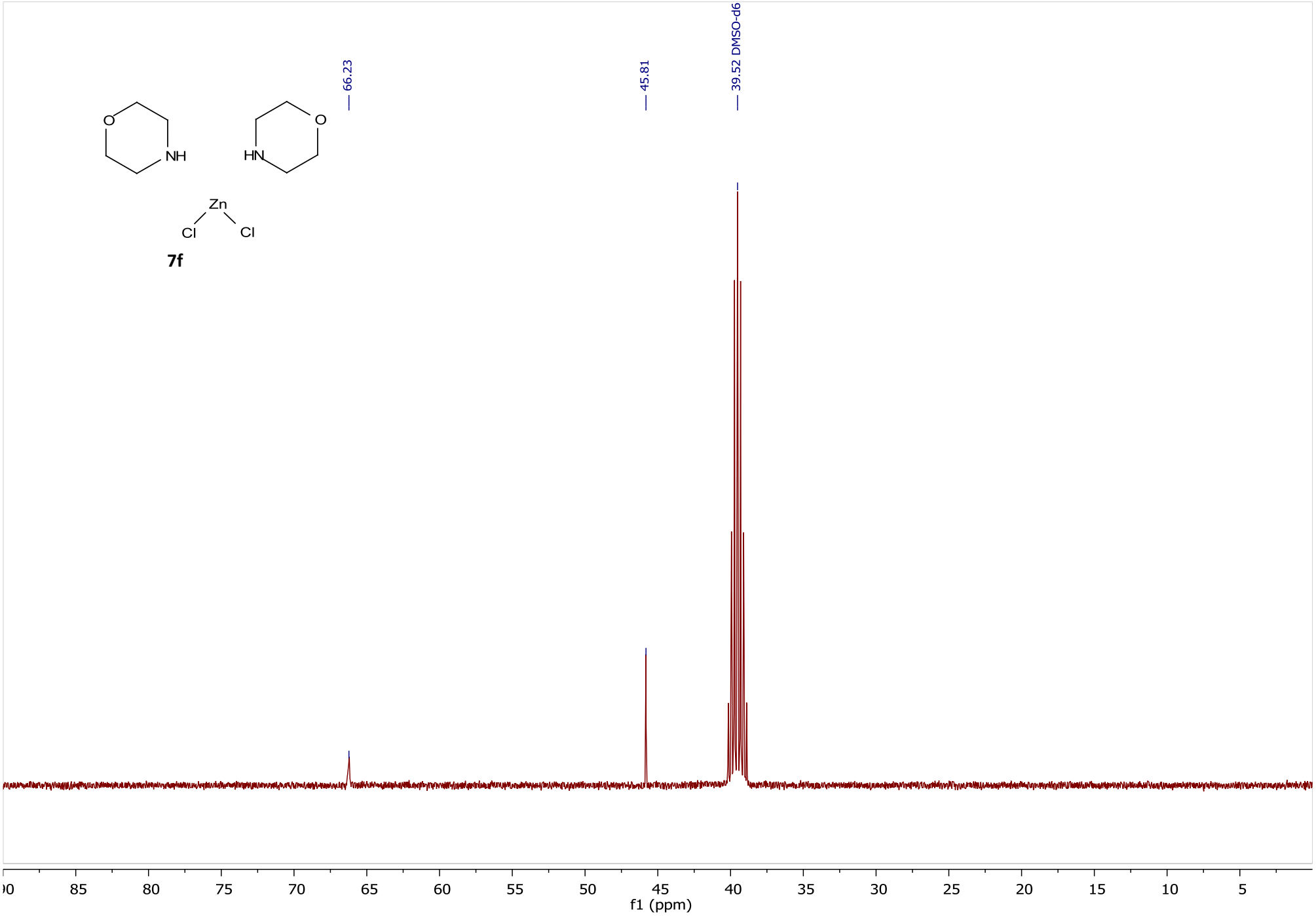

NH
HN
Zn
Cl
Cl
4.56
2.84
2.83
2.81
2.50 DMSO-d6
1.70
1.69
1.69
1.69
1.68
1.67
1.67
1.66
1.66
7d
C (m)
4.56
A (m)
2.82
B (m)
1.68
2.20
8.00
7.78
.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

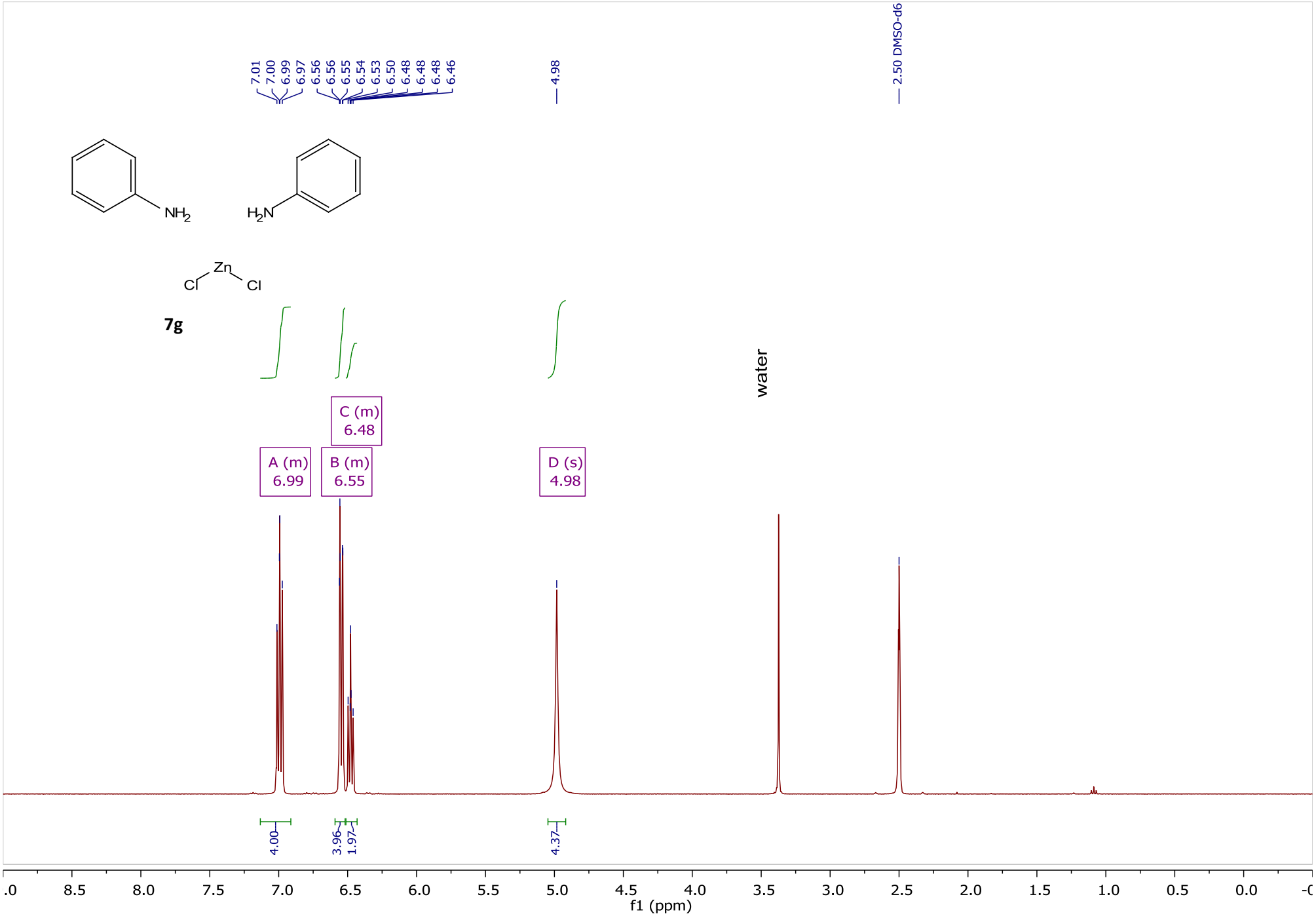

NH
HN
Zn
Cl
Cl
46.97
39.52 DMSO-d6
24.28
7d
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)

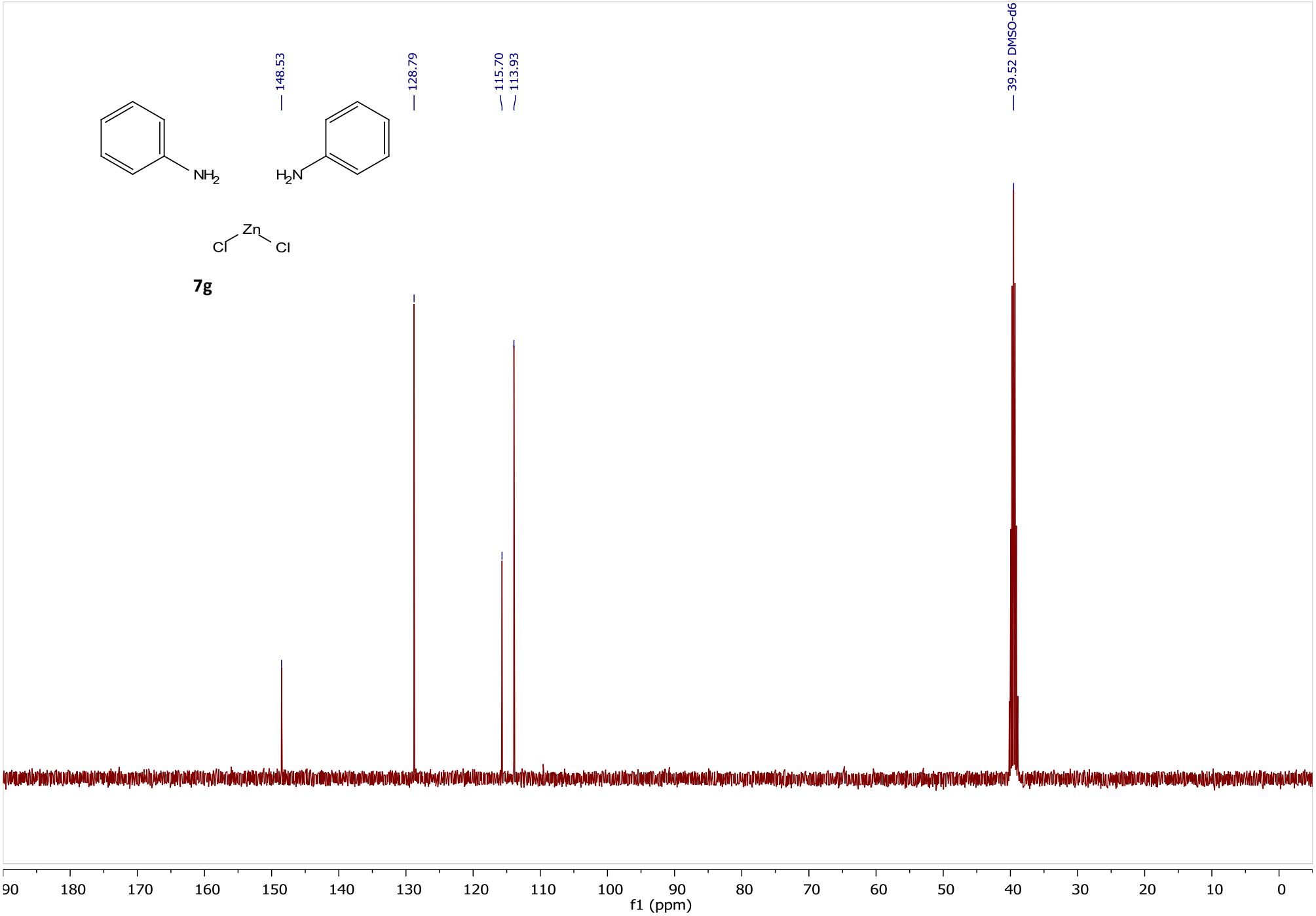

4.33
2.80
2.79
2.77
2.50 DMSO-d6
1.55
1.54
1.53
1.52
1.52
1.51
1.48
NH
HN
Zn
Cl
Cl
7e
A (m)
4.33
B (m)
2.78
C (m)
1.52
2.19
7.90
12.00
.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

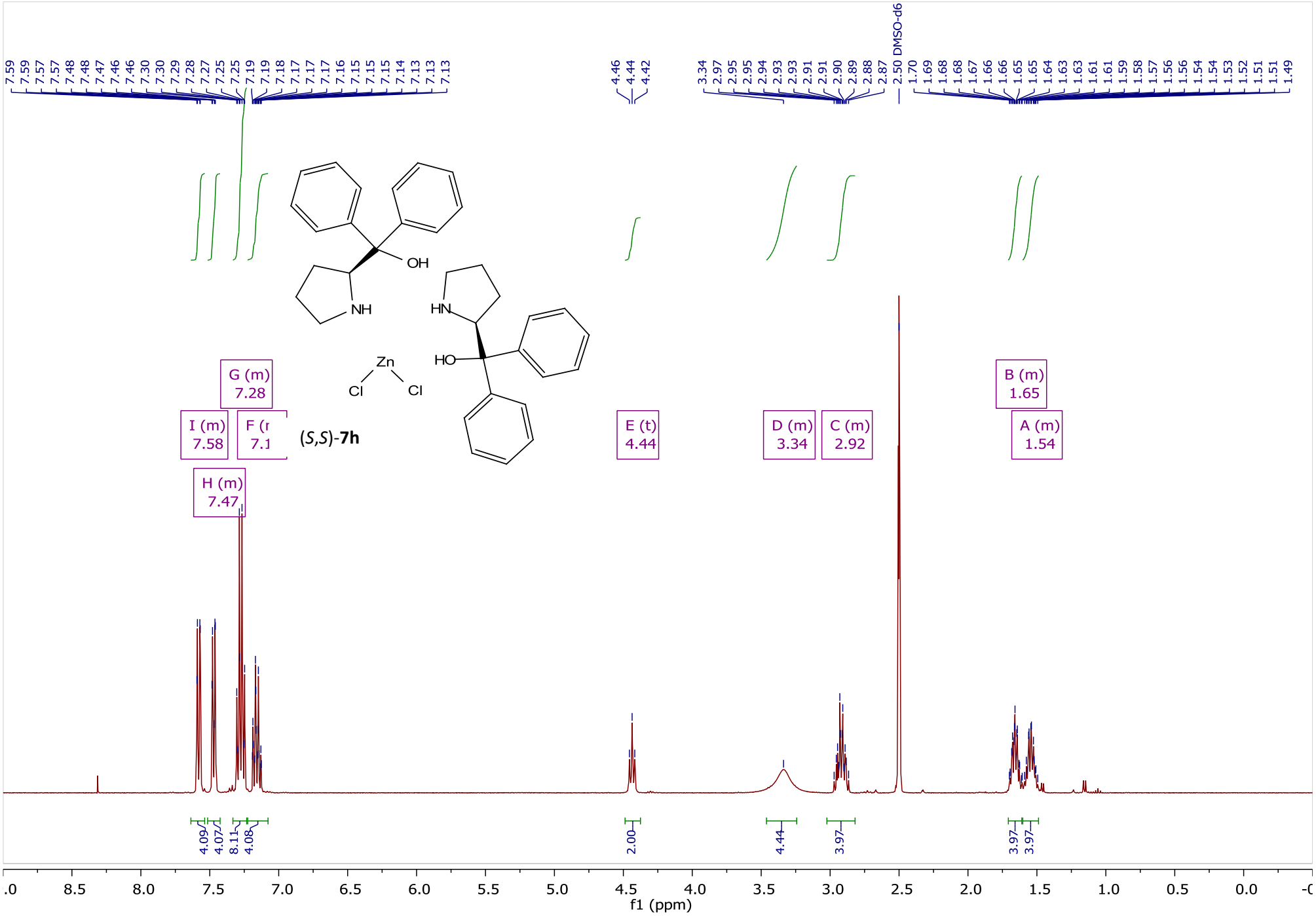

46.23
39.52 DMSO-d6
24.80
23.46
NH
HN
Zn
Cl
Cl
7e
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)

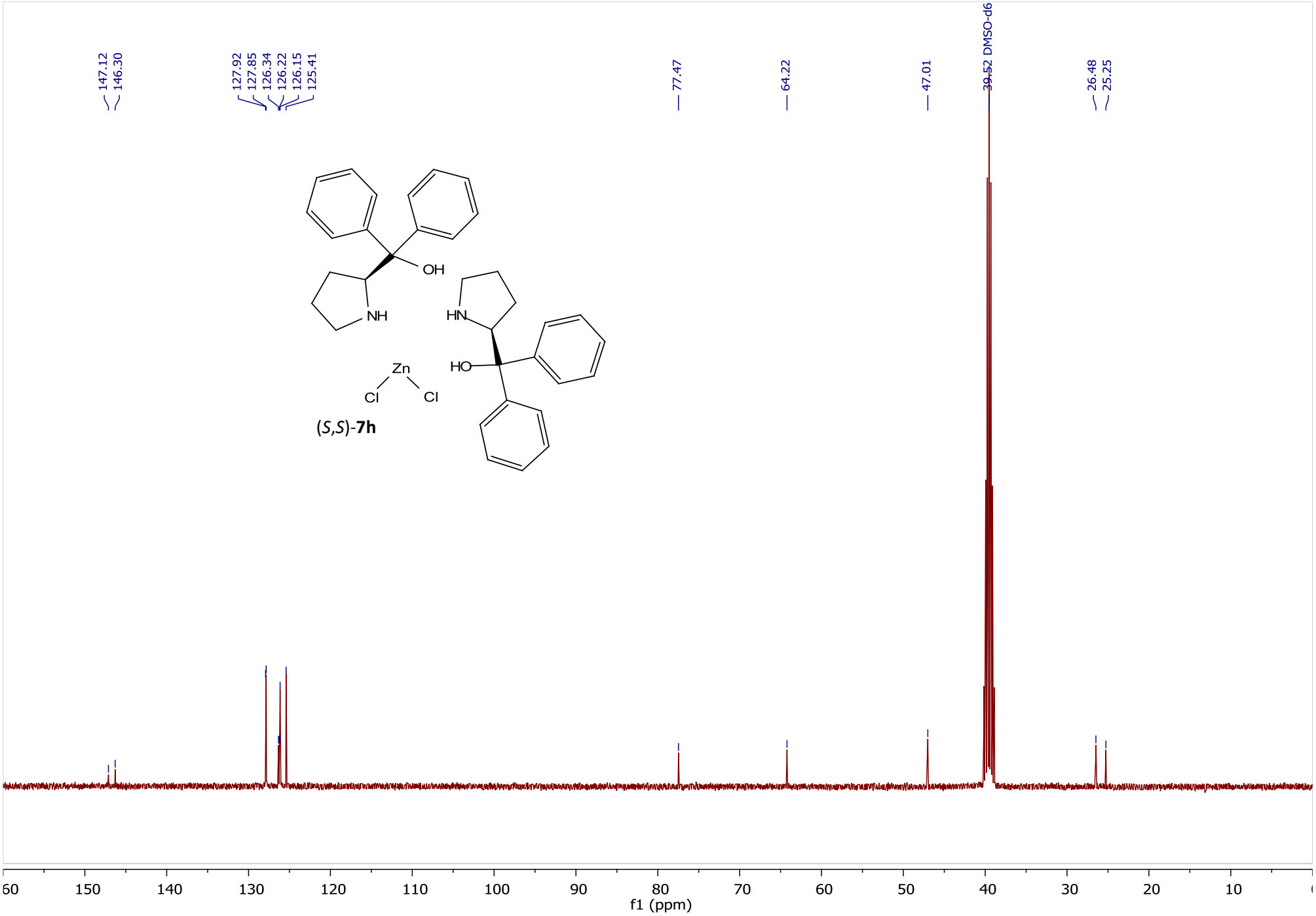

O
NH
HN
O
Zn
Cl
Cl
7f
3.88
3.60
3.60
3.59
3.59
3.58
3.58
3.57
2.77
2.77
2.76
2.75
2.50 DMSO-d6
C (m)
3.88
A (m)
3.58
B (m)
2.76
1.70
8.00
7.71
.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

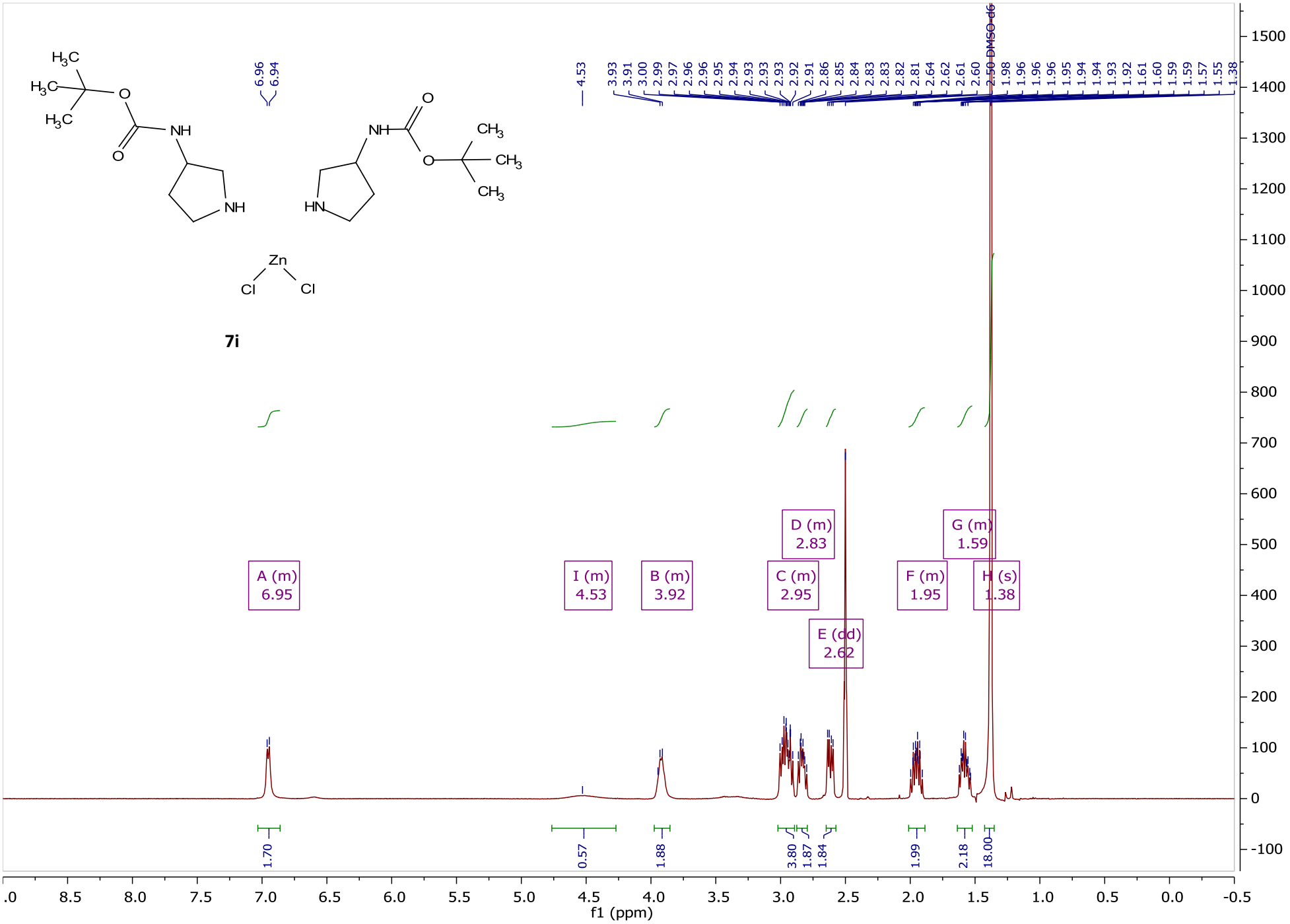

66.23
45.81
39.52 DMSO-d6
O
NH
HN
O
Zn
Cl
Cl
7f
f1 (ppm)

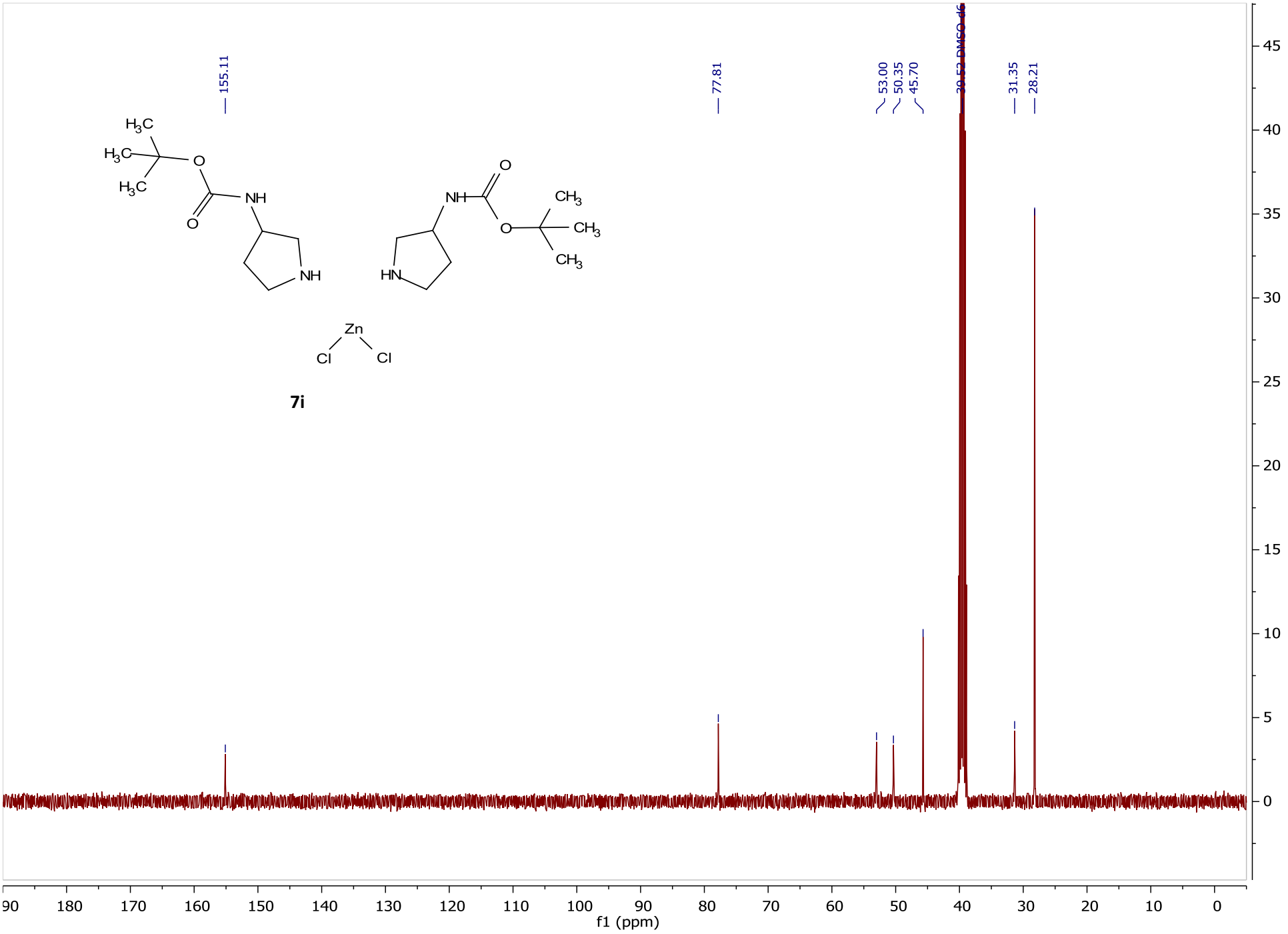

7.01
7.00
6.99
6.97
6.56
6.56
6.55
6.54
6.53
6.50
6.48
6.48
6.48
6.46
4.98
2.50 DMSO-d6
NH2
H2N
Zn
Cl
Cl
7g
water
C (m)
6.48
A (m)
6.99
B (m)
6.55
D (s)
4.98
4.00
3.96
1.97
4.37
f1 (ppm)

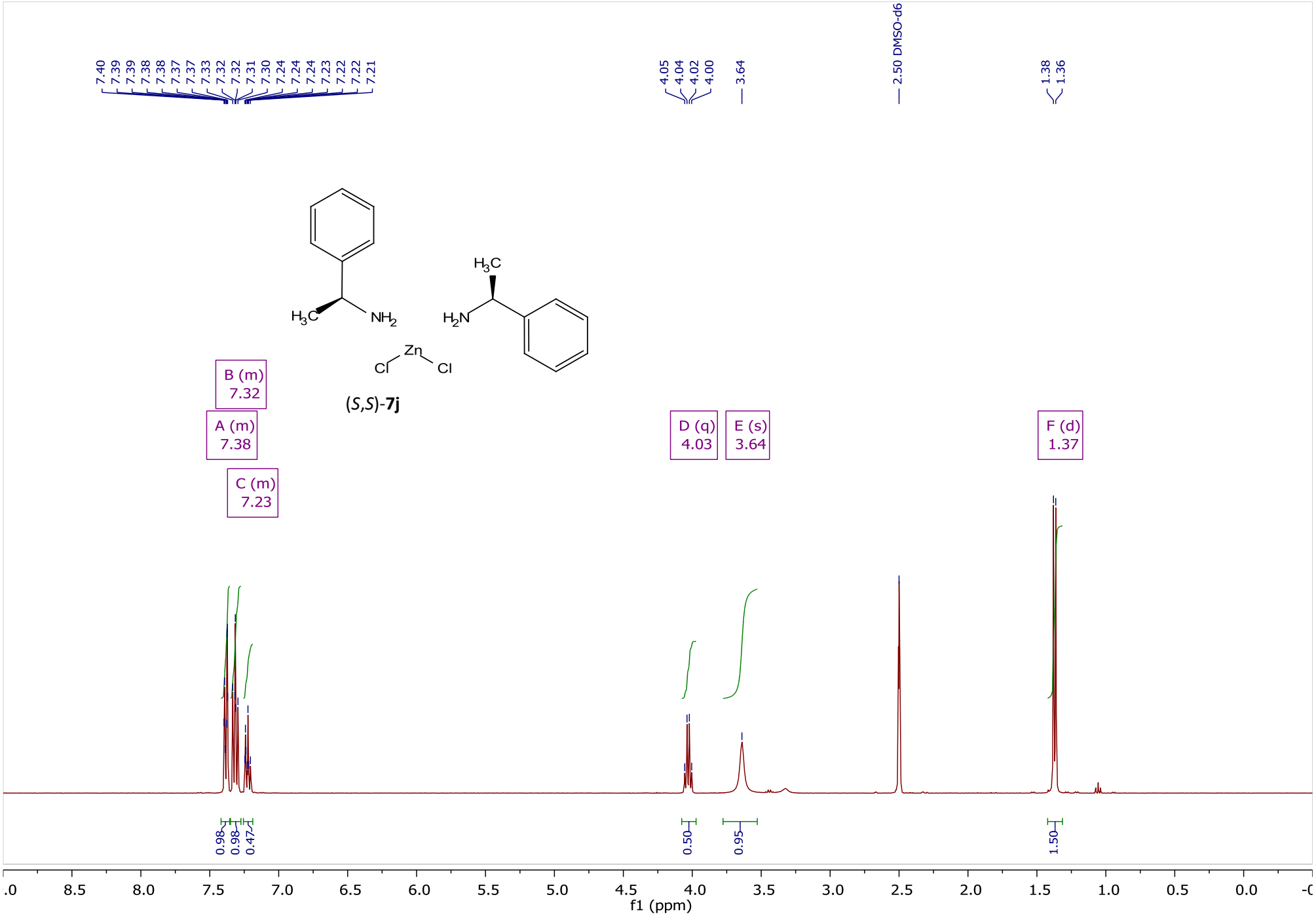

148.53
128.79
115.70
113.93
39.52 DMSO-d6
NH2
H2N
Zn
Cl
Cl
7g
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

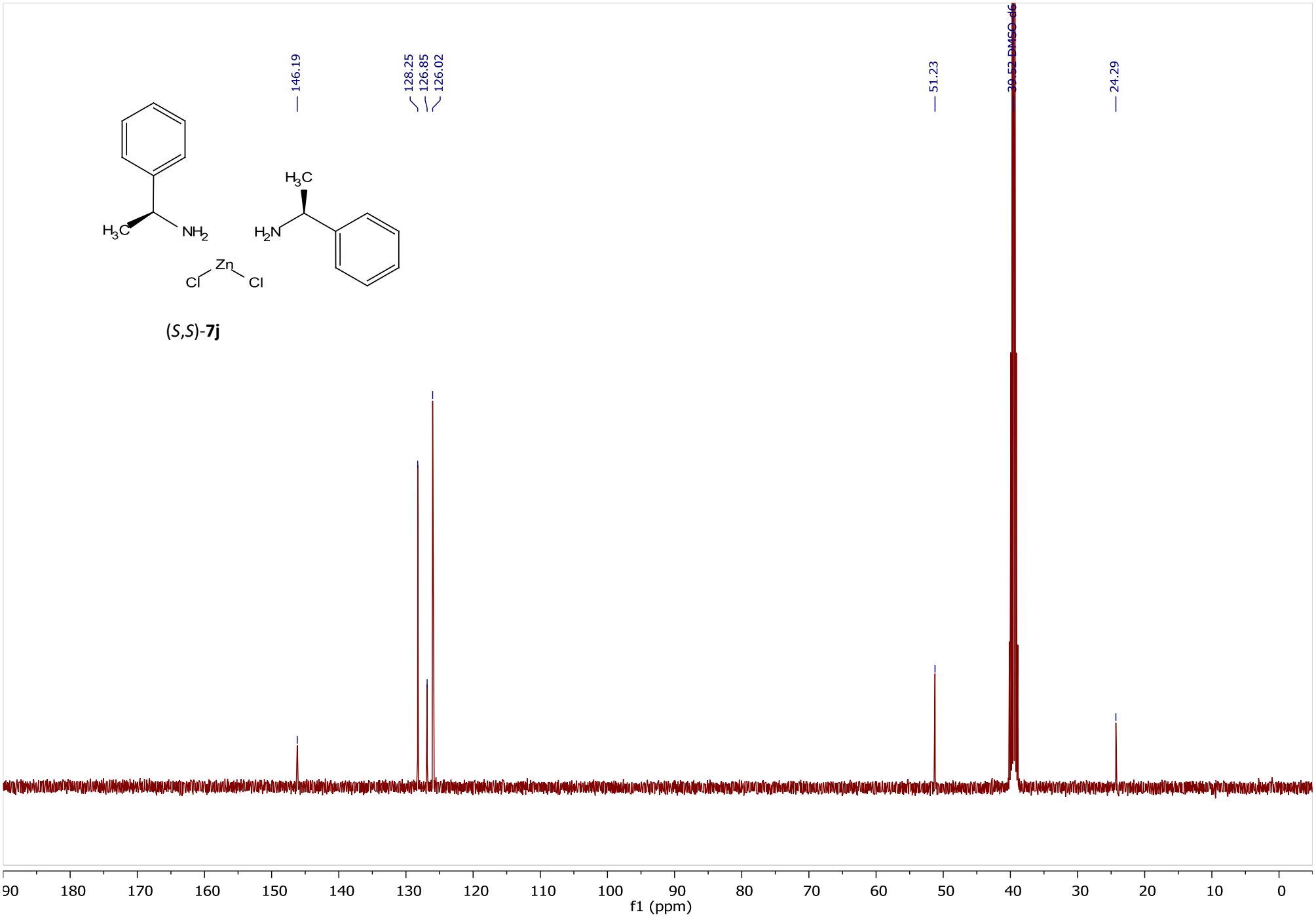

DMSO-d6
OH
NH
HN
HO
Zn
Cl
Cl
(S,S)-7h
G (m) 7.28
I (m) 7.58
F (r 7.1
H (m) 7.47
E (t) 4.44
D (m) 3.34
C (m) 2.92
B (m) 1.65
A (m) 1.54
4.09
4.07
8.11
4.08
2.00
4.44
3.97
3.97
3.97
f1 (ppm)

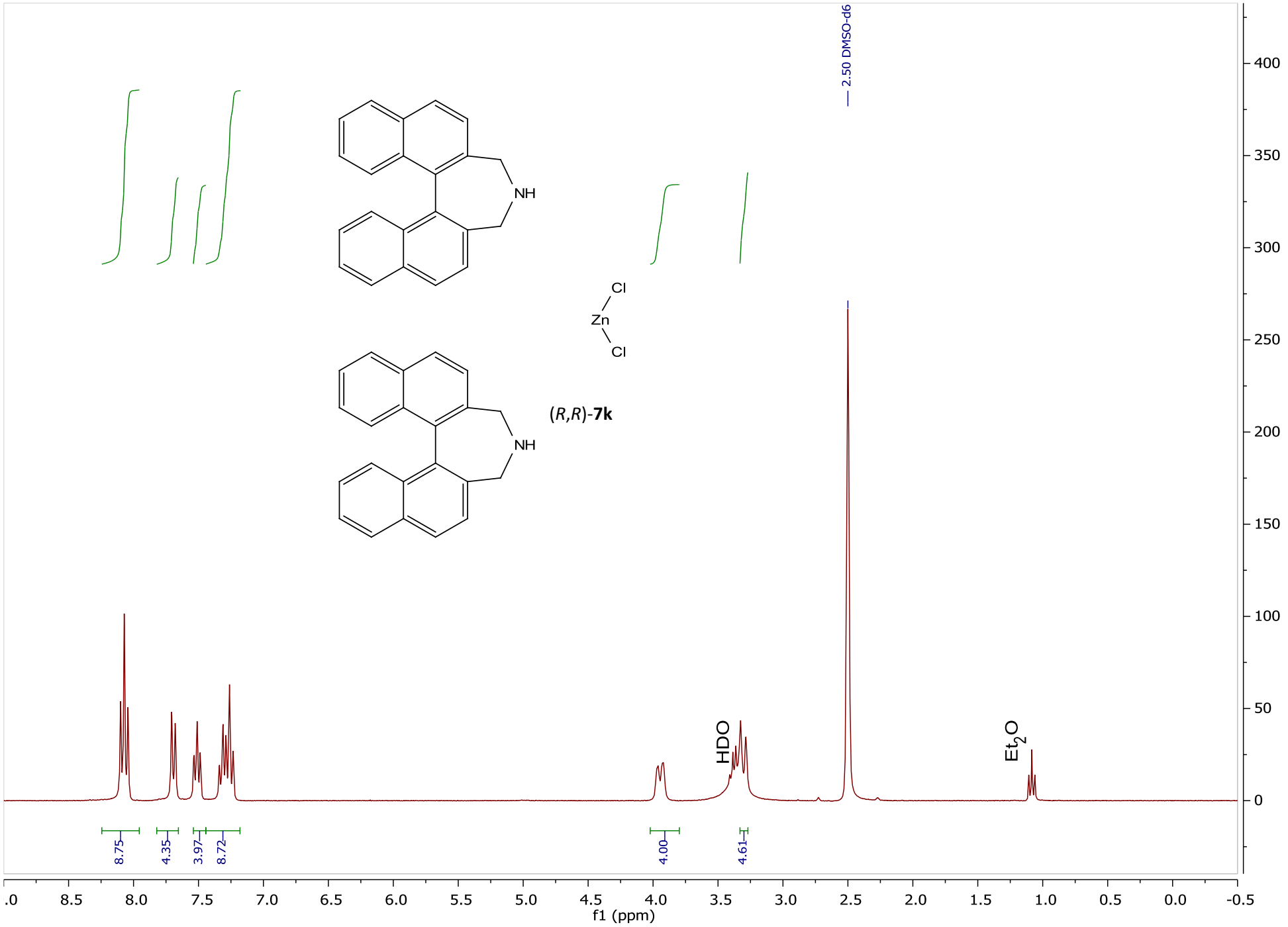

147.12
146.30
127.92
127.85
126.34
126.22
126.15
125.41
77.47
64.22
47.01
39.52 DMSO-d6
26.48
25.25
OH
NH
HN
HO
Zn
Cl
Cl
(S,S)-7h
f1 (ppm)

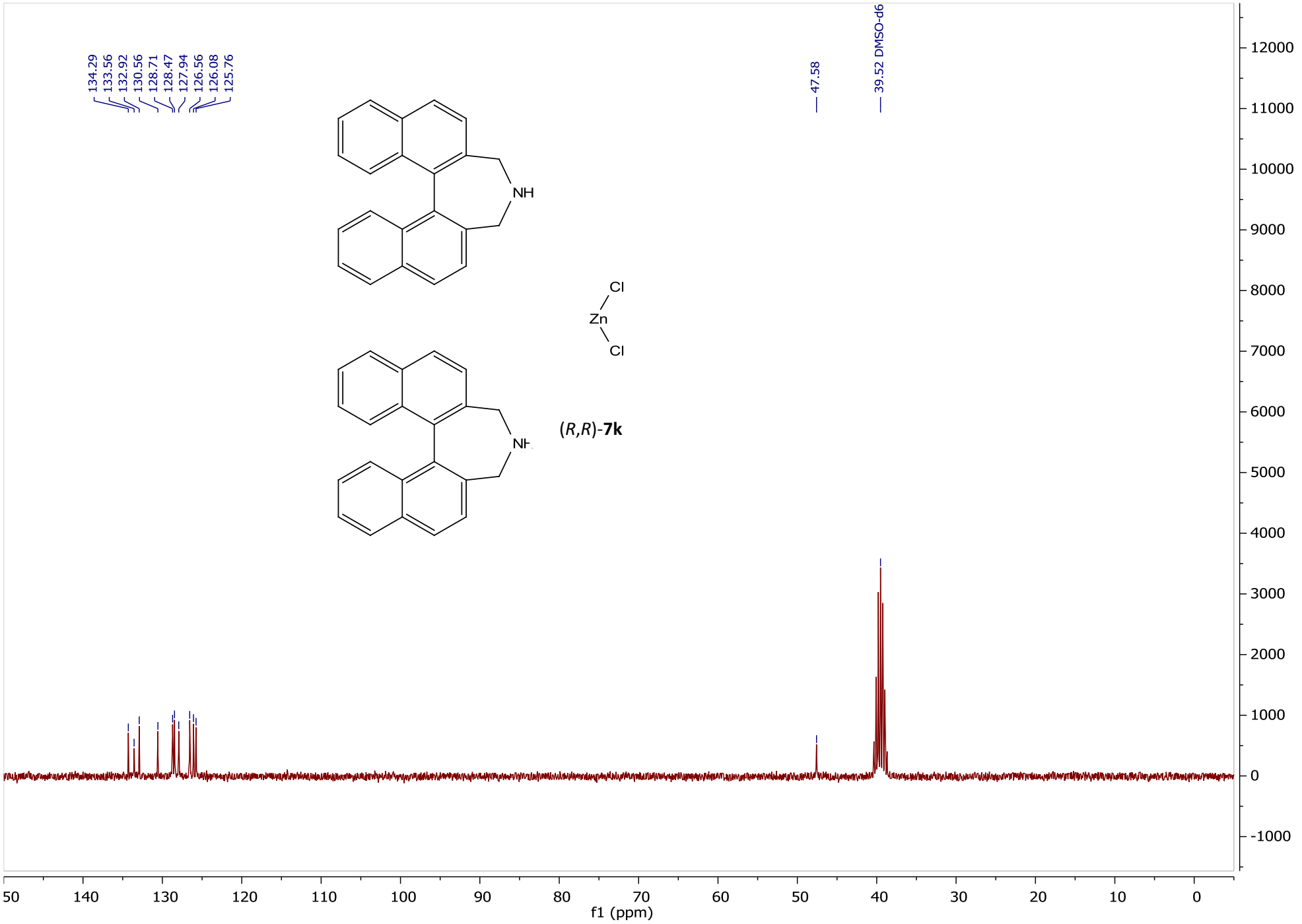

7i
A (m) 6.95
I (m) 4.53
B (m) 3.92
C (m) 2.95
D (m) 2.83
E (dd) 2.62
F (m) 1.95
G (m) 1.59
H (s) 1.38
f1 (ppm)

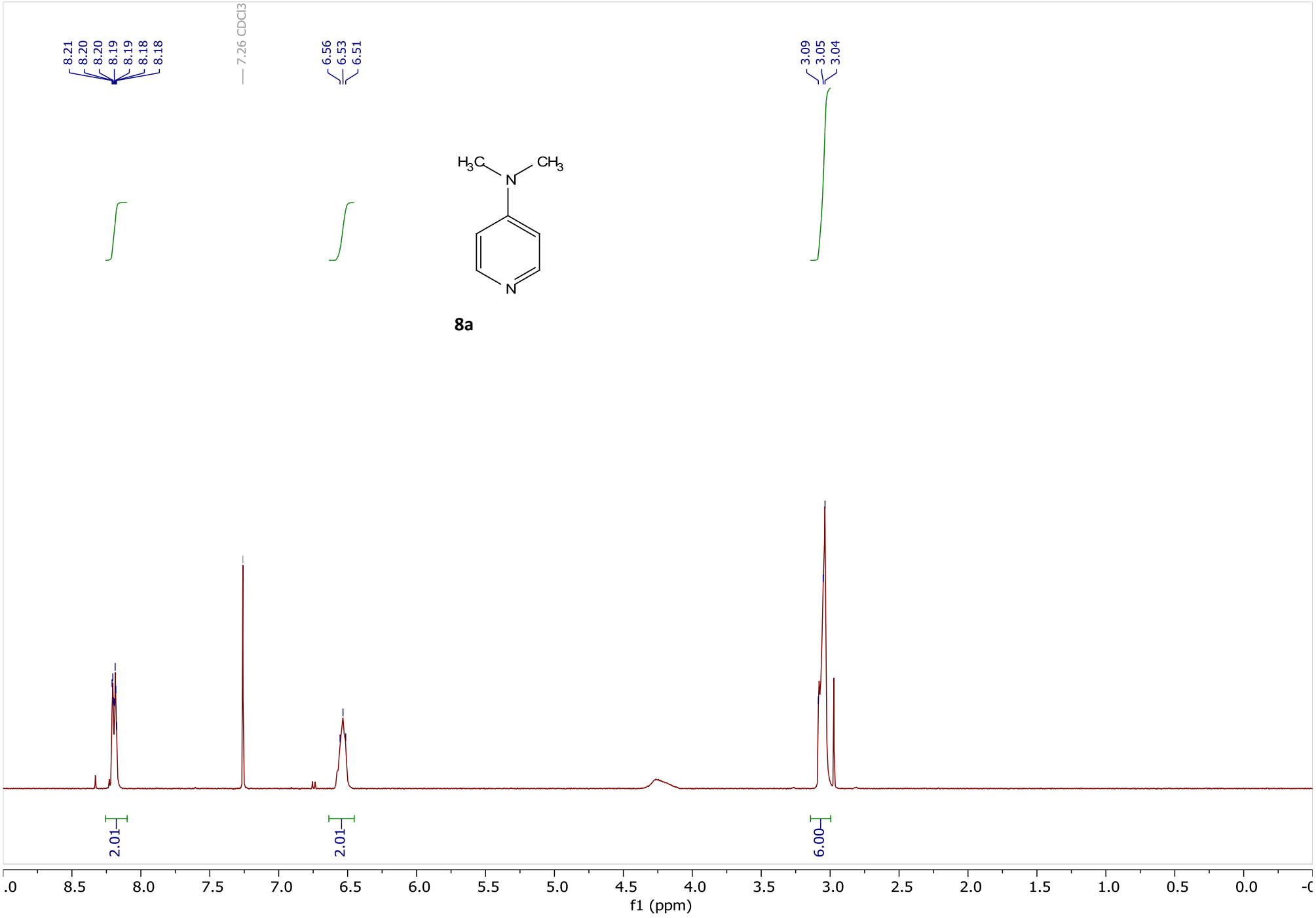

155.11
77.81
53.00
50.35
45.70
39.52 DMSO-d6
31.35
28.21
H3C
H3C
H3C
O
O
NH
NH
HN
O
O
CH3
CH3
CH3
Zn
Cl
Cl
7i
f1 (ppm)


7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.33
7.32
7.32
7.31
7.30
7.24
7.24
7.24
7.23
7.22
7.22
7.21
4.05
4.04
4.02
4.00
3.64
2.50 DMSO-d6
1.38
1.36
H3C
NH2
H2N
CH3
Zn
Cl
Cl
(S,S)-7j
B (m)
7.32
A (m)
7.38
C (m)
7.23
D (q)
4.03
E (s)
3.64
F (d)
1.37
0.98
0.98
0.47
0.50
0.95
1.50
f1 (ppm)

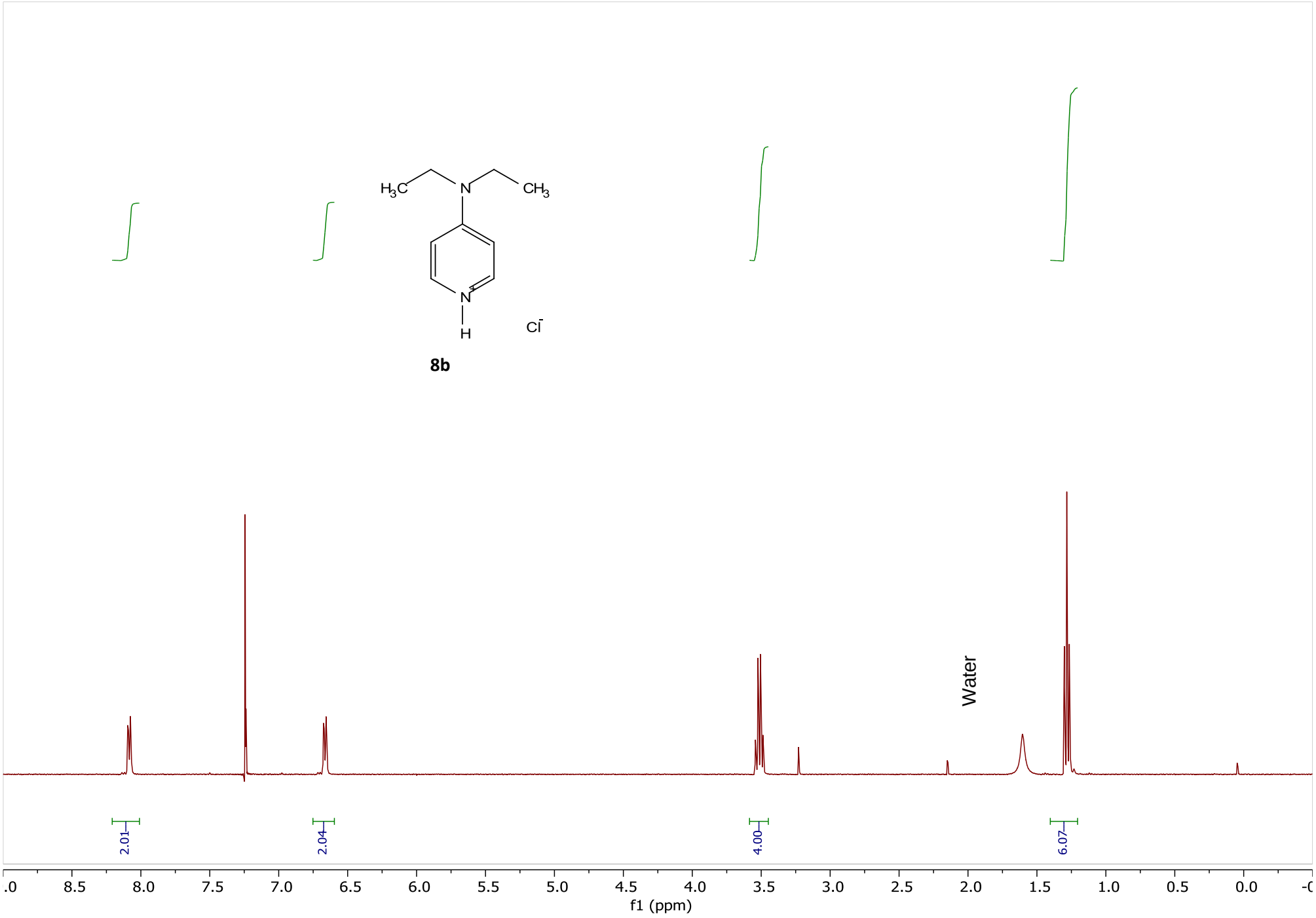

146.19
128.25
126.85
126.02
51.23
39.52 DMSO-d6
24.29
H3C
NH2
H3C
H2N
Zn
Cl
Cl
(S,S)-7j
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

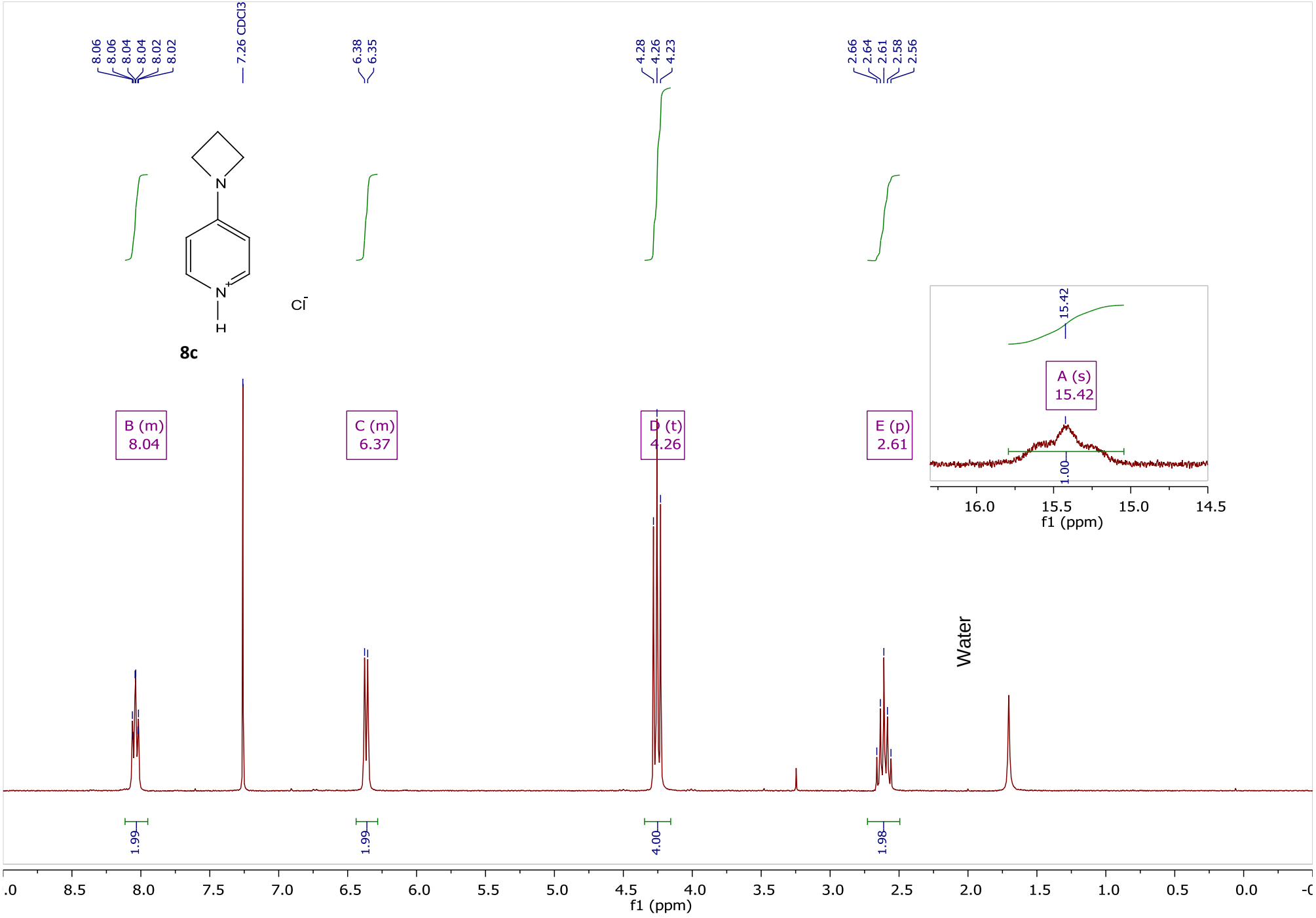

2.50 DMSO-d6
NH
Cl
Zn
Cl
NH
(*R*,*R*)-**7k**
HDO
Et_2O
8.75
4.35
3.97
8.72
4.00
4.61
f1 (ppm)

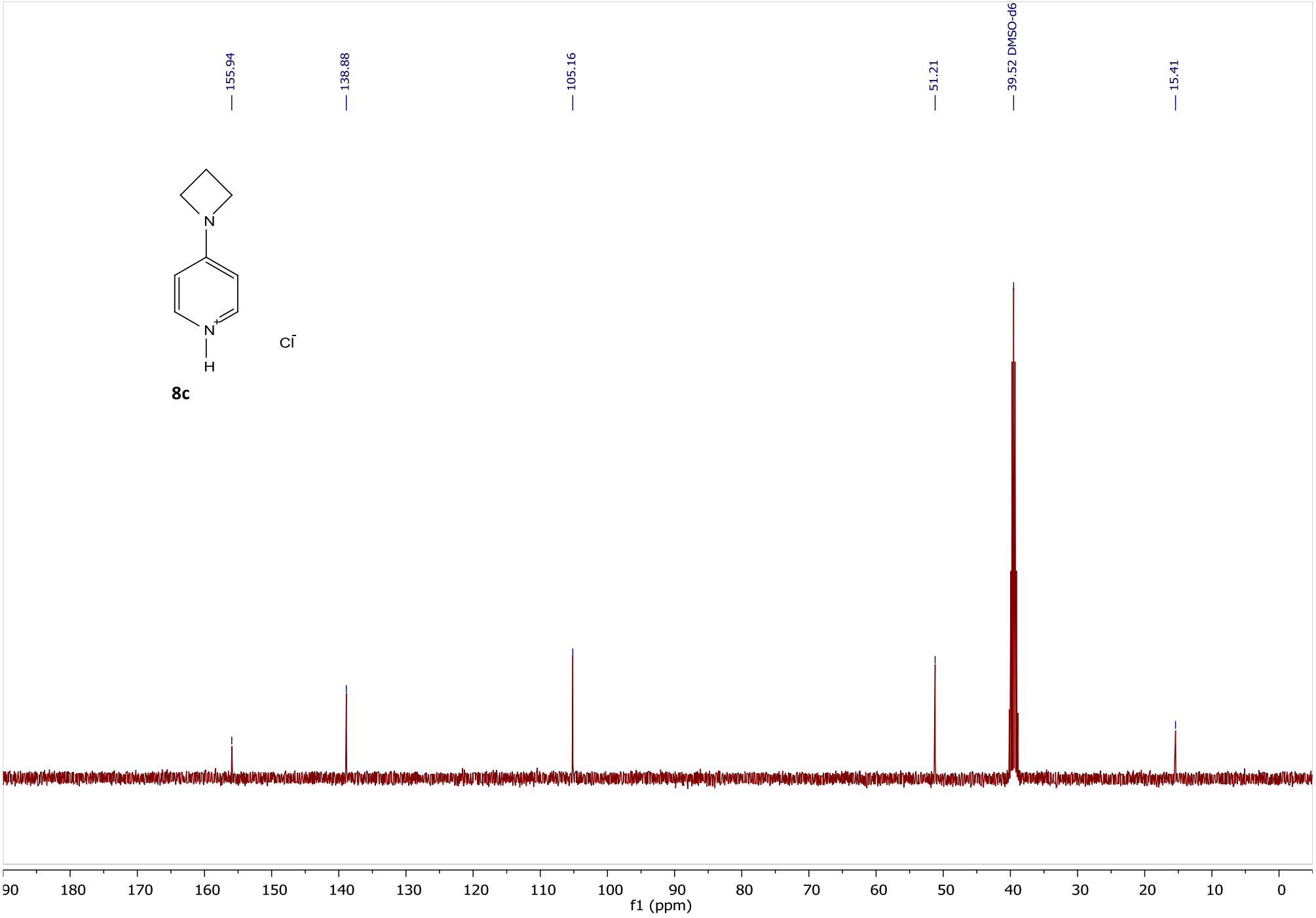

134.29
133.56
132.92
130.56
128.71
128.47
127.94
126.56
126.08
125.76
47.58
39.52 DMSO-d6
NH
Cl
Zn
Cl
NH
(R,R)-7k
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
50
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

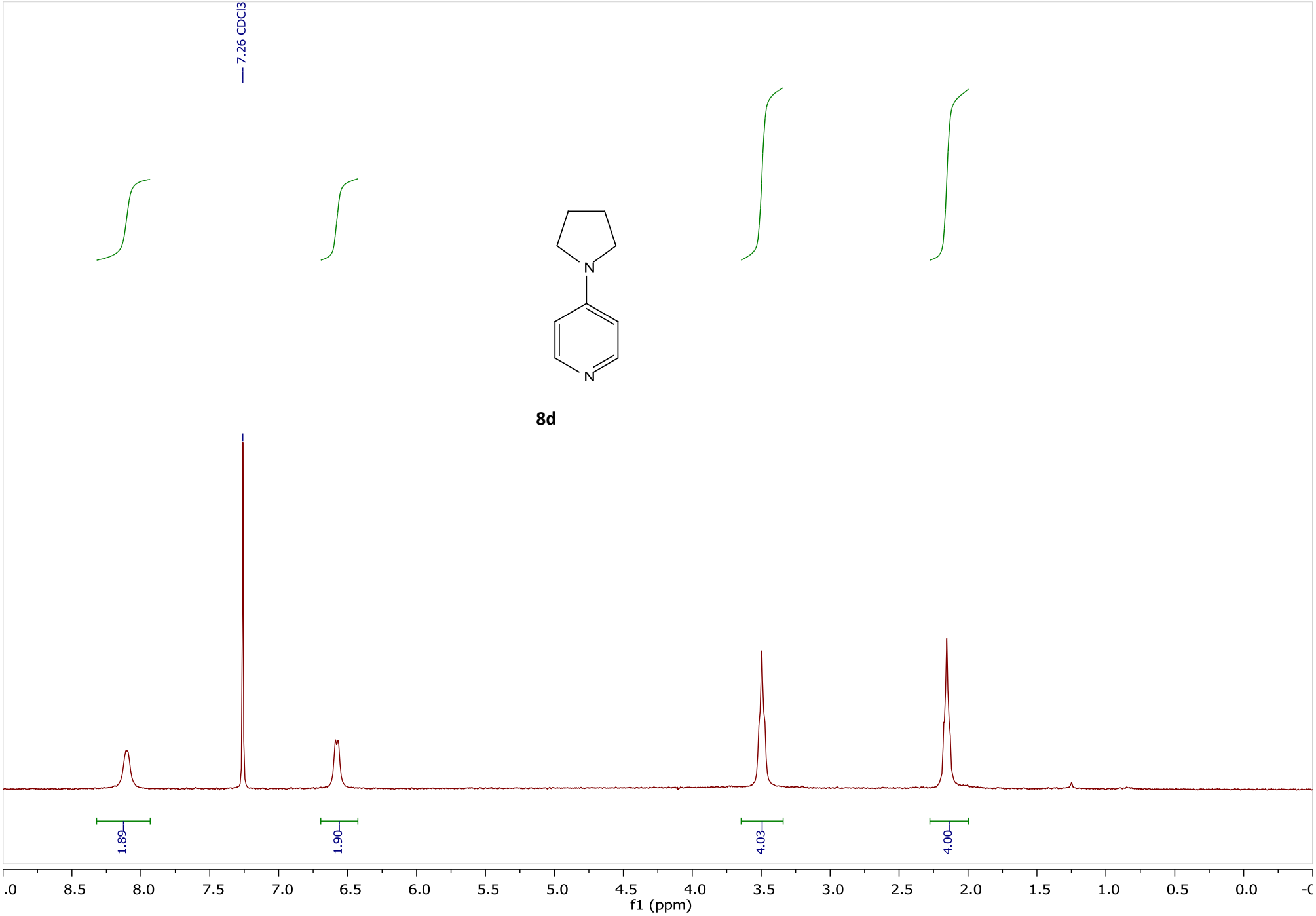

8.21
8.20
8.20
8.19
8.19
8.18
8.18
7.26 CDCl3
6.56
6.53
6.51
3.09
3.05
3.04
H3C
N
CH3
N
2.01
2.01
6.00
f1 (ppm)

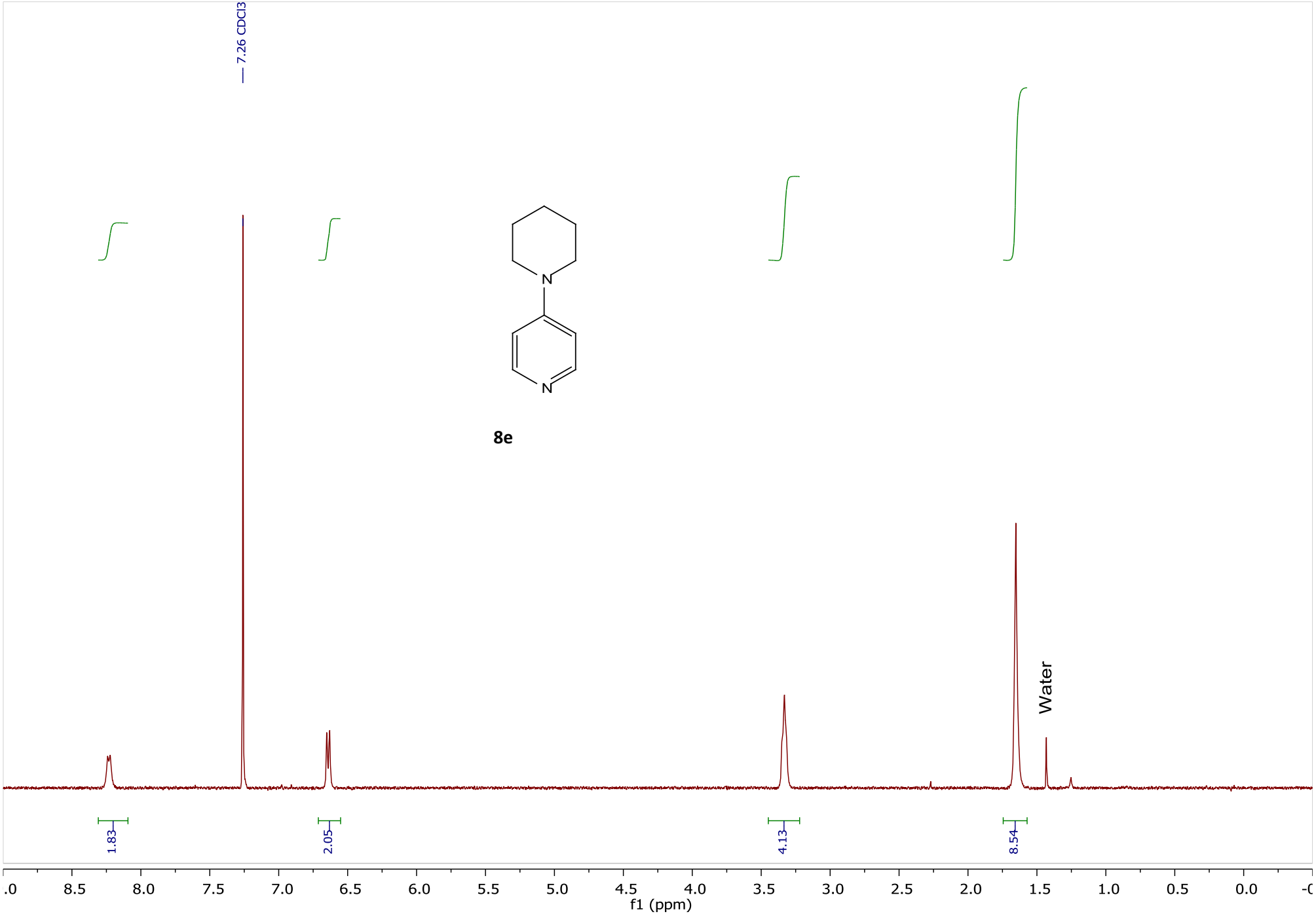
8a

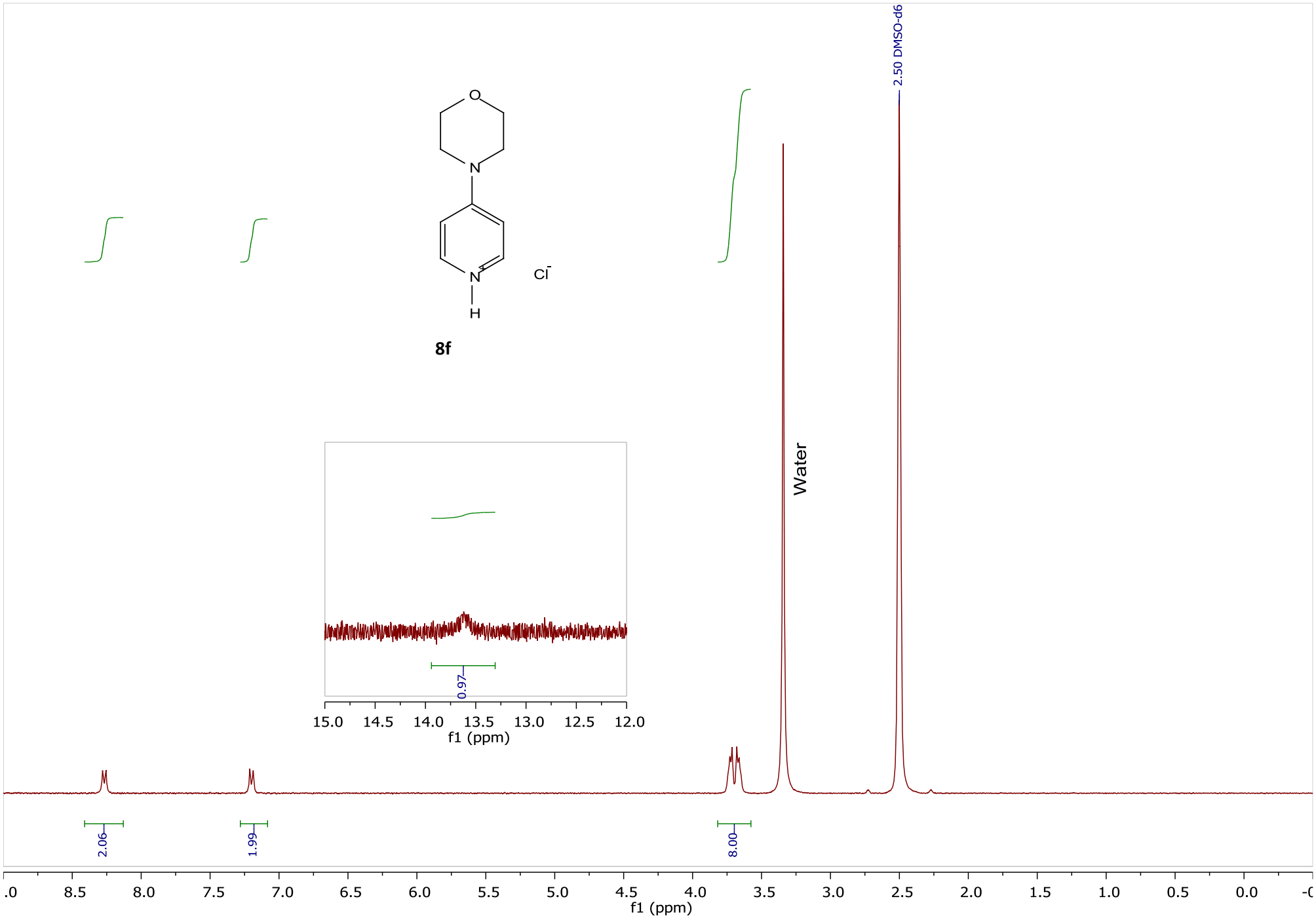

H3C
N
CH3
N
H
Cl-
8b
Water
2.01
2.04
4.00
6.07
f1 (ppm)

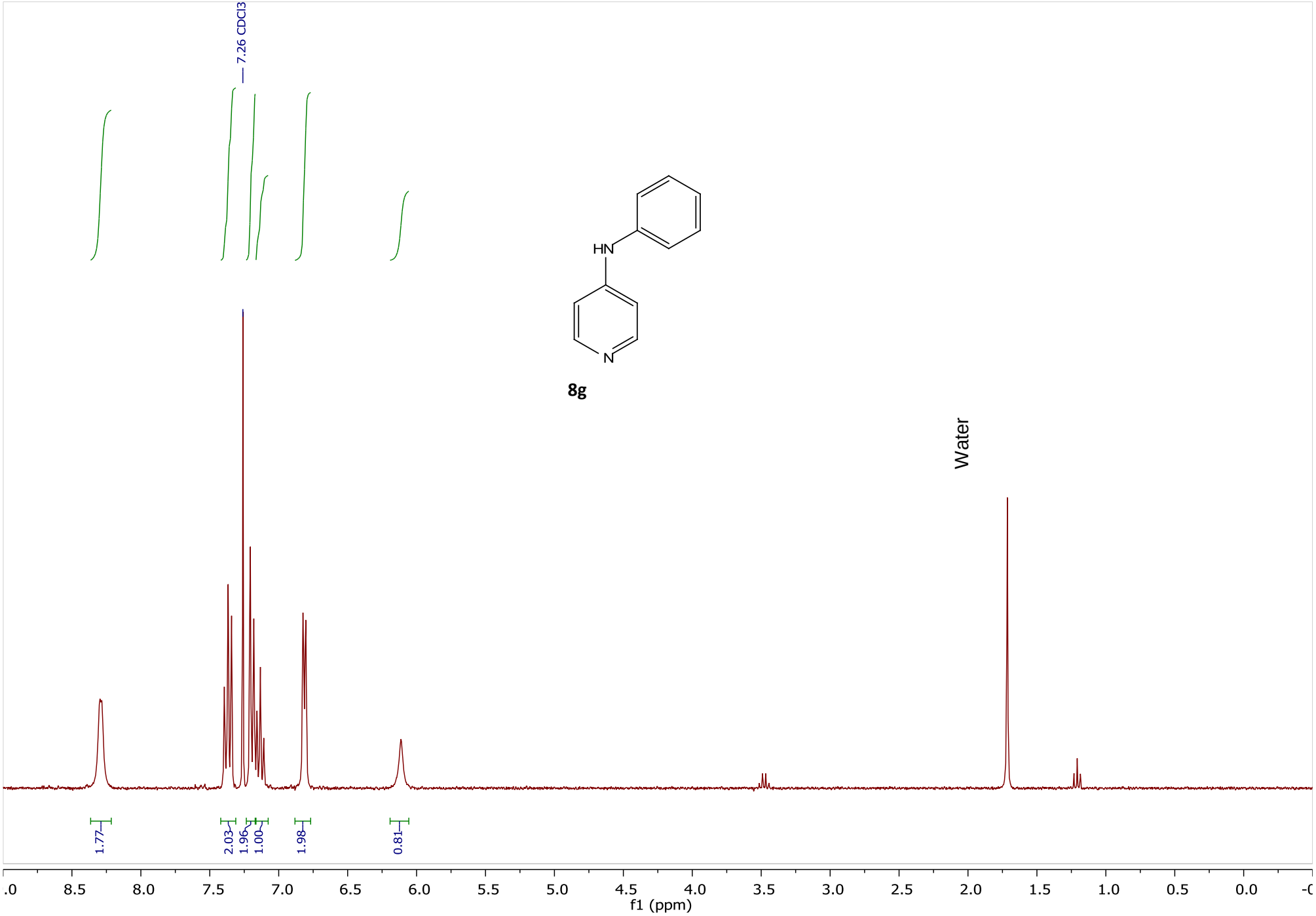

8.06
8.06
8.04
8.04
8.02
8.02
7.26 CDCl3
6.38
6.35
4.28
4.26
4.23
2.66
2.64
2.61
2.58
2.56
Cl⁻
8c
B (m)
8.04
C (m)
6.37
D (t)
4.26
E (p)
2.61
A (s)
15.42
15.42
1.00
16.0
15.5
15.0
14.5
f1 (ppm)
Water
1.99
1.99
4.00
1.98
f1 (ppm)

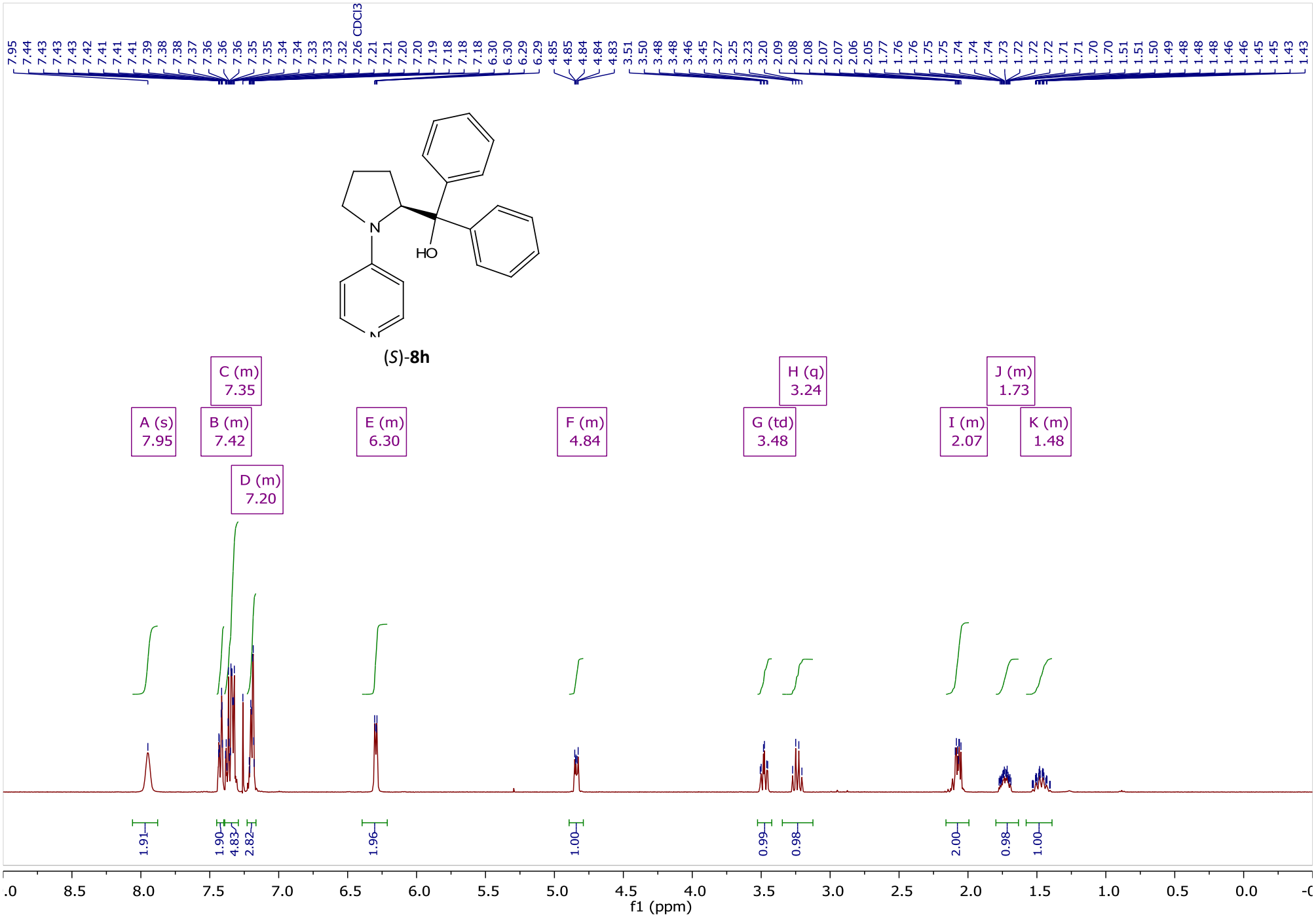

155.94
138.88
105.16
51.21
39.52 DMSO-d6
15.41
N
N+
H
Cl-
8c
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

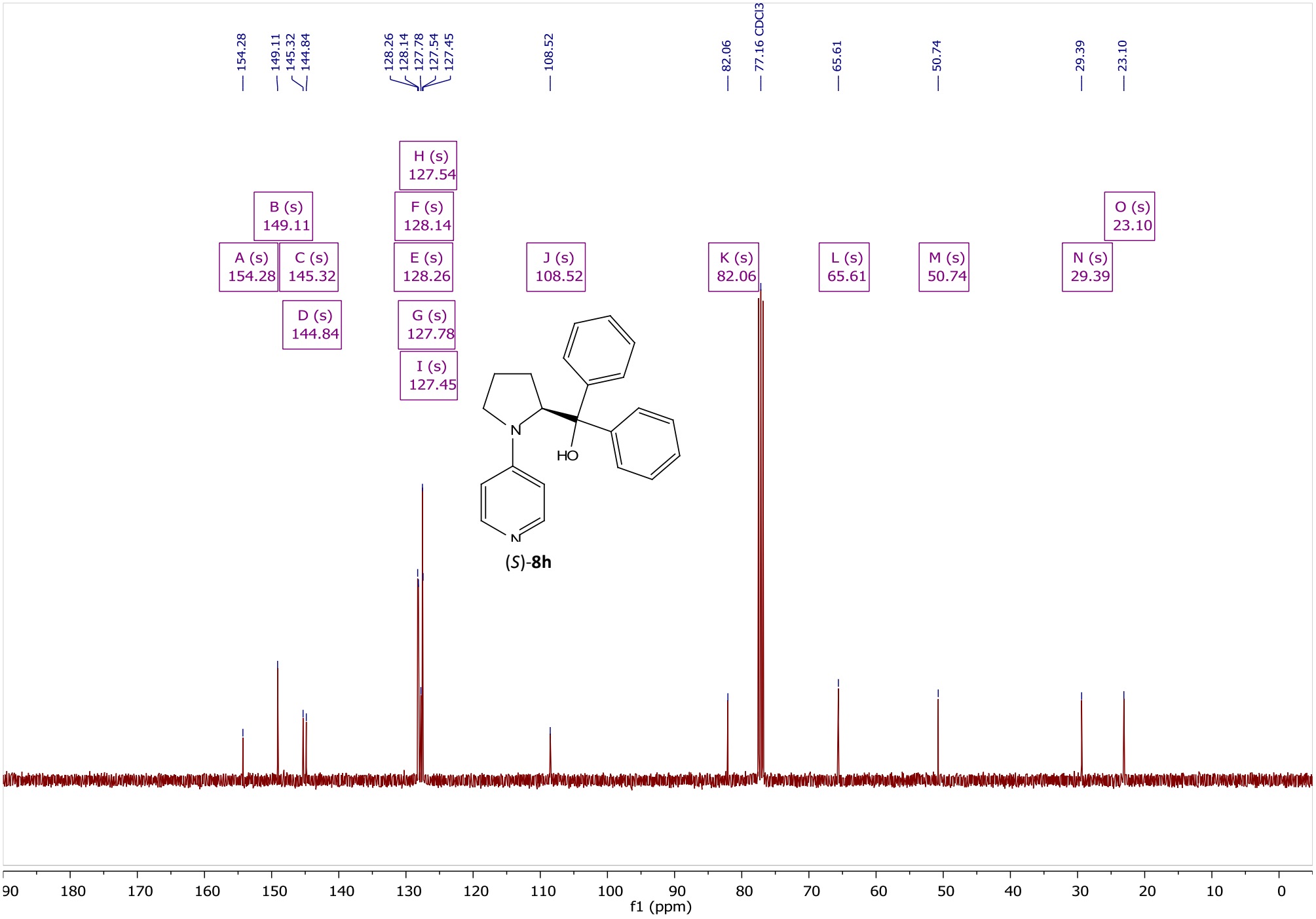

7.26 CDCl3
N
N
8d
1.89
1.90
4.03
4.00
f1 (ppm)

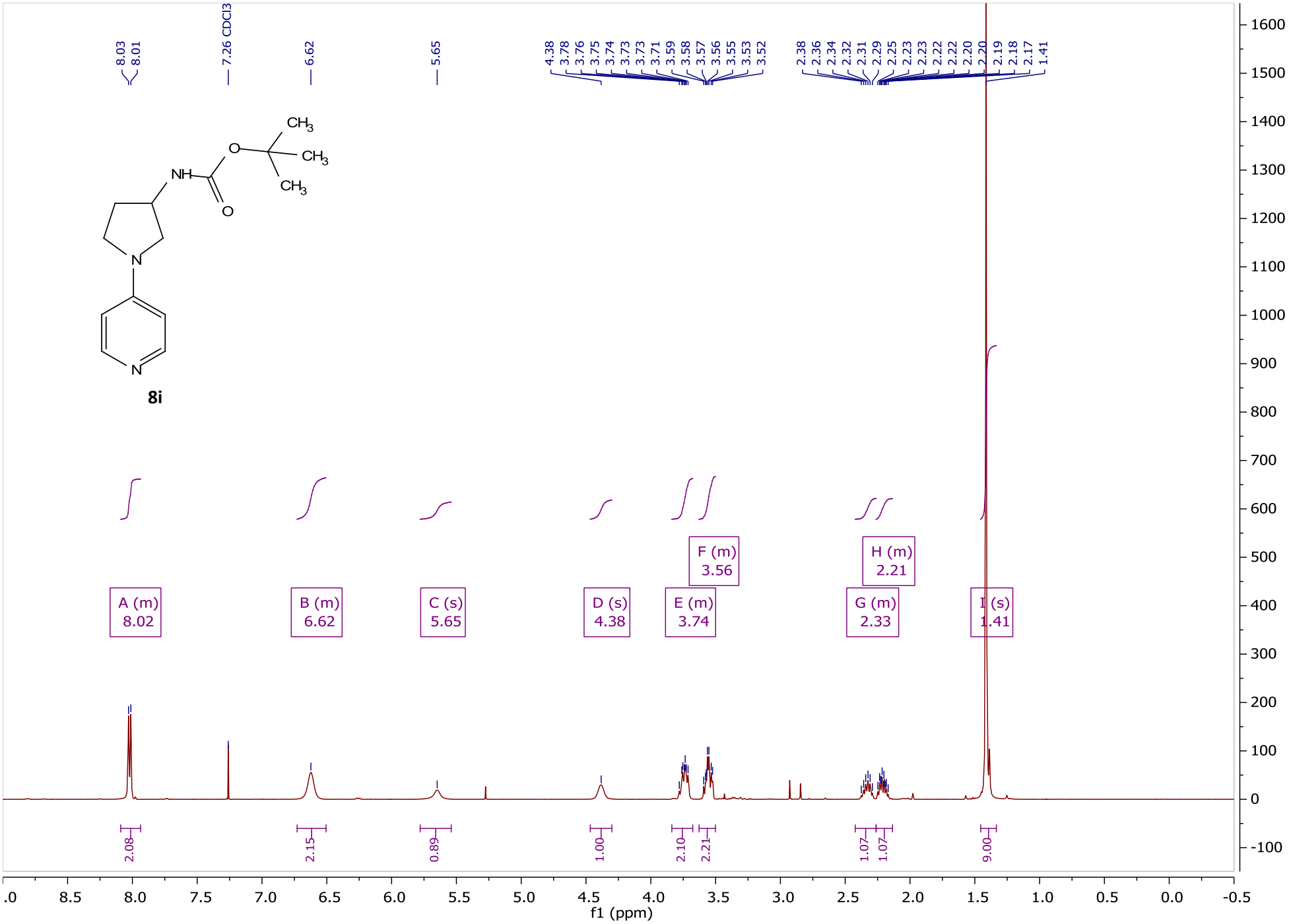

7.26 CDCl3
N
N
8e
Water
1.83
2.05
4.13
8.54
f1 (ppm)

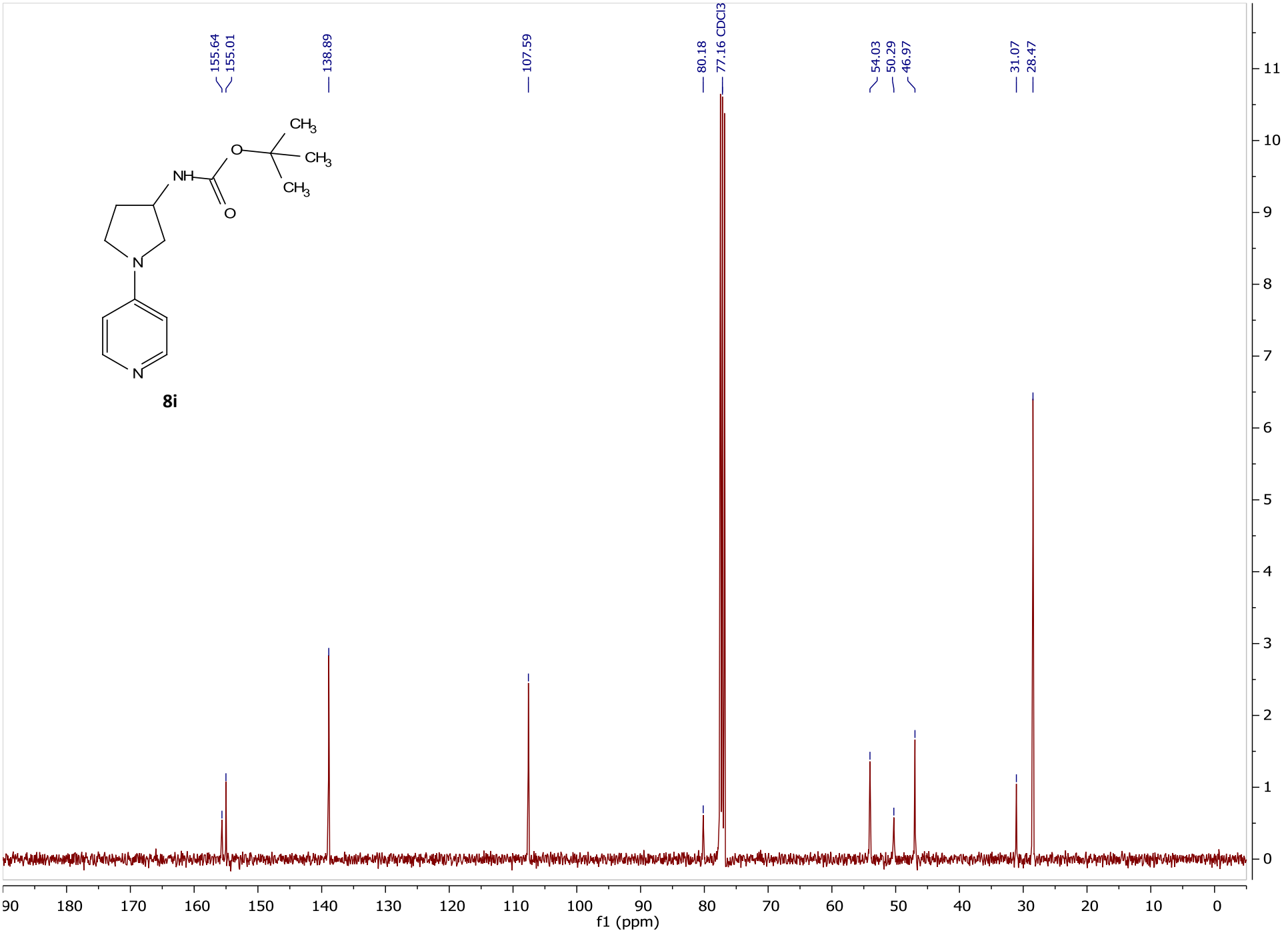

2.50 DMSO-d6
Water
O
N
N
H
Cl⁻
8f
0.97
15.0 14.5 14.0 13.5 13.0 12.5 12.0
f1 (ppm)
2.06
1.99
8.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


7.26 CDCl3
HN
N
8g
Water
1.77
2.03
1.96
1.00
1.98
0.81
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)

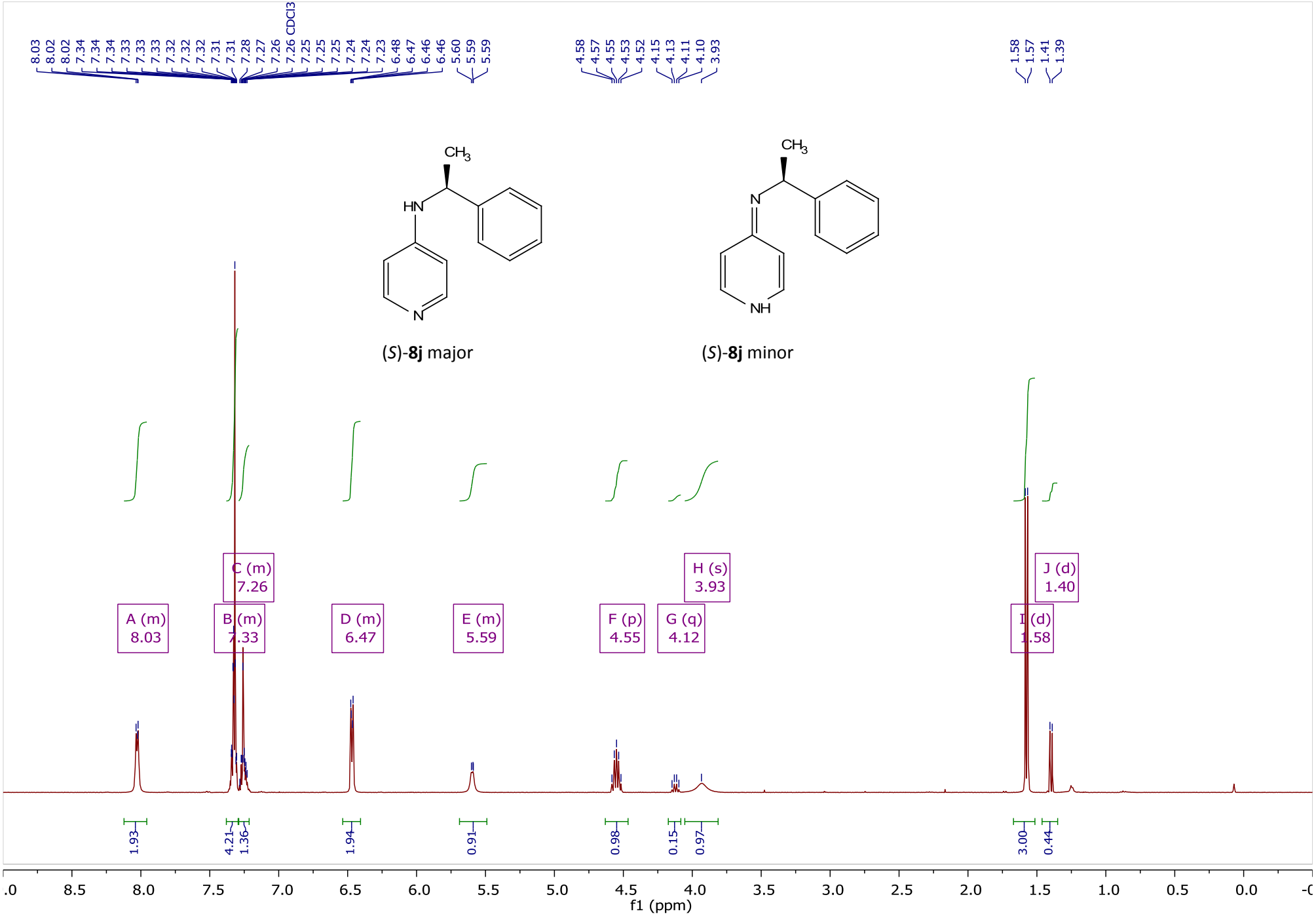

CDCl3
HO
N
(S)-8h
A (s) 7.95
B (m) 7.42
C (m) 7.35
D (m) 7.20
E (m) 6.30
F (m) 4.84
G (td) 3.48
H (q) 3.24
I (m) 2.07
J (m) 1.73
K (m) 1.48
1.91
1.90
4.83
2.82
1.96
1.00
0.99
0.98
2.00
0.98
1.00
f1 (ppm)

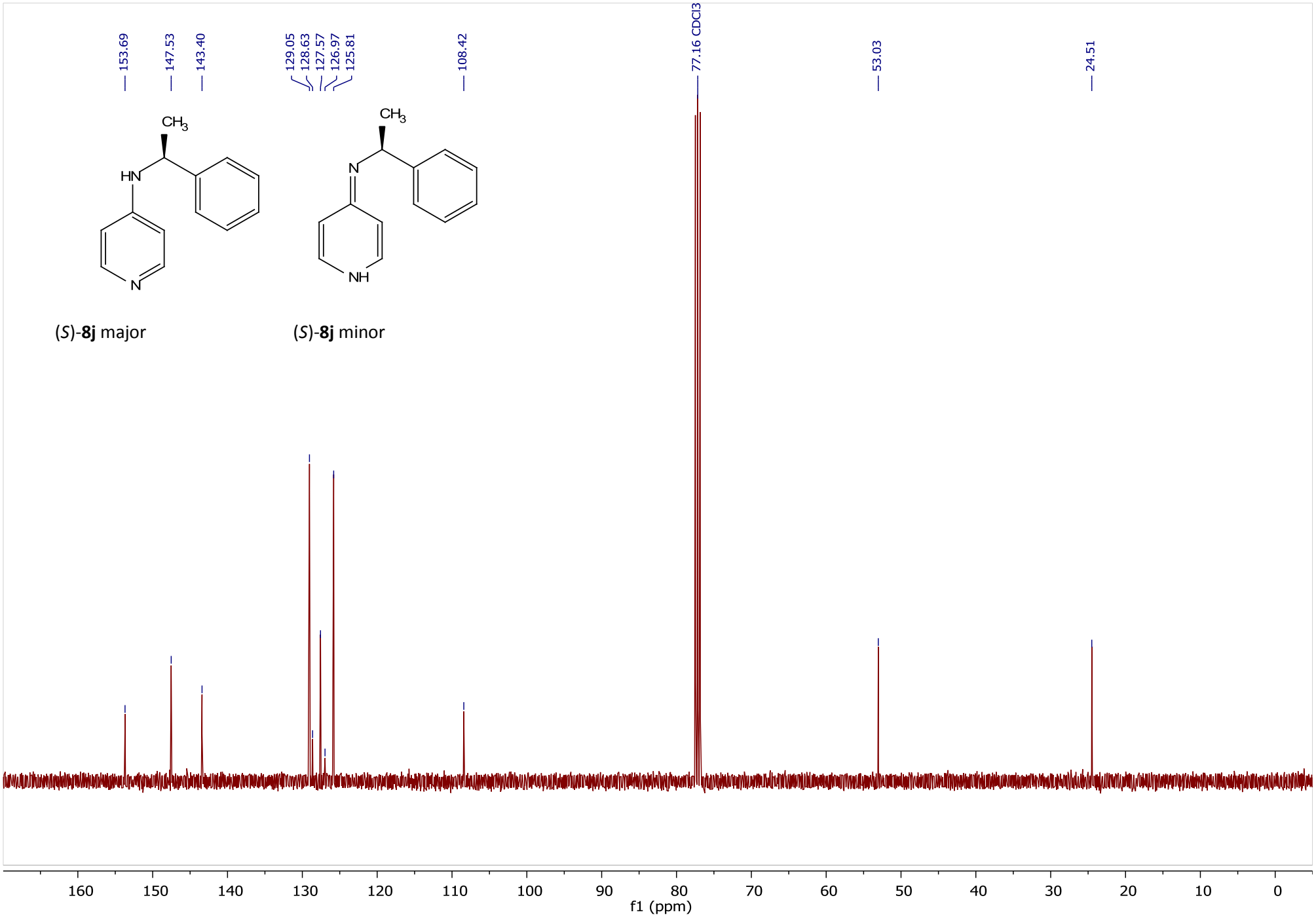

154.28
149.11
145.32
144.84
128.26
128.14
127.78
127.54
127.45
108.52
82.06
77.16 CDCl3
65.61
50.74
29.39
23.10
H (s) 127.54
B (s) 149.11
F (s) 128.14
O (s) 23.10
A (s) 154.28
C (s) 145.32
E (s) 128.26
J (s) 108.52
K (s) 82.06
L (s) 65.61
M (s) 50.74
N (s) 29.39
D (s) 144.84
G (s) 127.78
I (s) 127.45
N
HO
N
(S)-8h
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.03
8.01
7.26 CDCl3
6.62
5.65
4.38
3.78
3.76
3.75
3.74
3.73
3.73
3.71
3.59
3.58
3.57
3.56
3.55
3.53
3.52
2.38
2.36
2.34
2.32
2.31
2.29
2.25
2.23
2.23
2.22
2.22
2.20
2.20
2.19
2.18
2.17
1.41
CH3
CH3
CH3
O
NH
O
N
N
8i
A (m) 8.02
B (m) 6.62
C (s) 5.65
D (s) 4.38
E (m) 3.74
F (m) 3.56
G (m) 2.33
H (m) 2.21
I (s) 1.41
2.08
2.15
0.89
1.00
2.10
2.21
1.07
1.07
9.00
f1 (ppm)


155.64
155.01
138.89
107.59
80.18
77.16 CDCl3
54.03
50.29
46.97
31.07
28.47
CH3
CH3
CH3
O
NH
O
N
N
f1 (ppm)

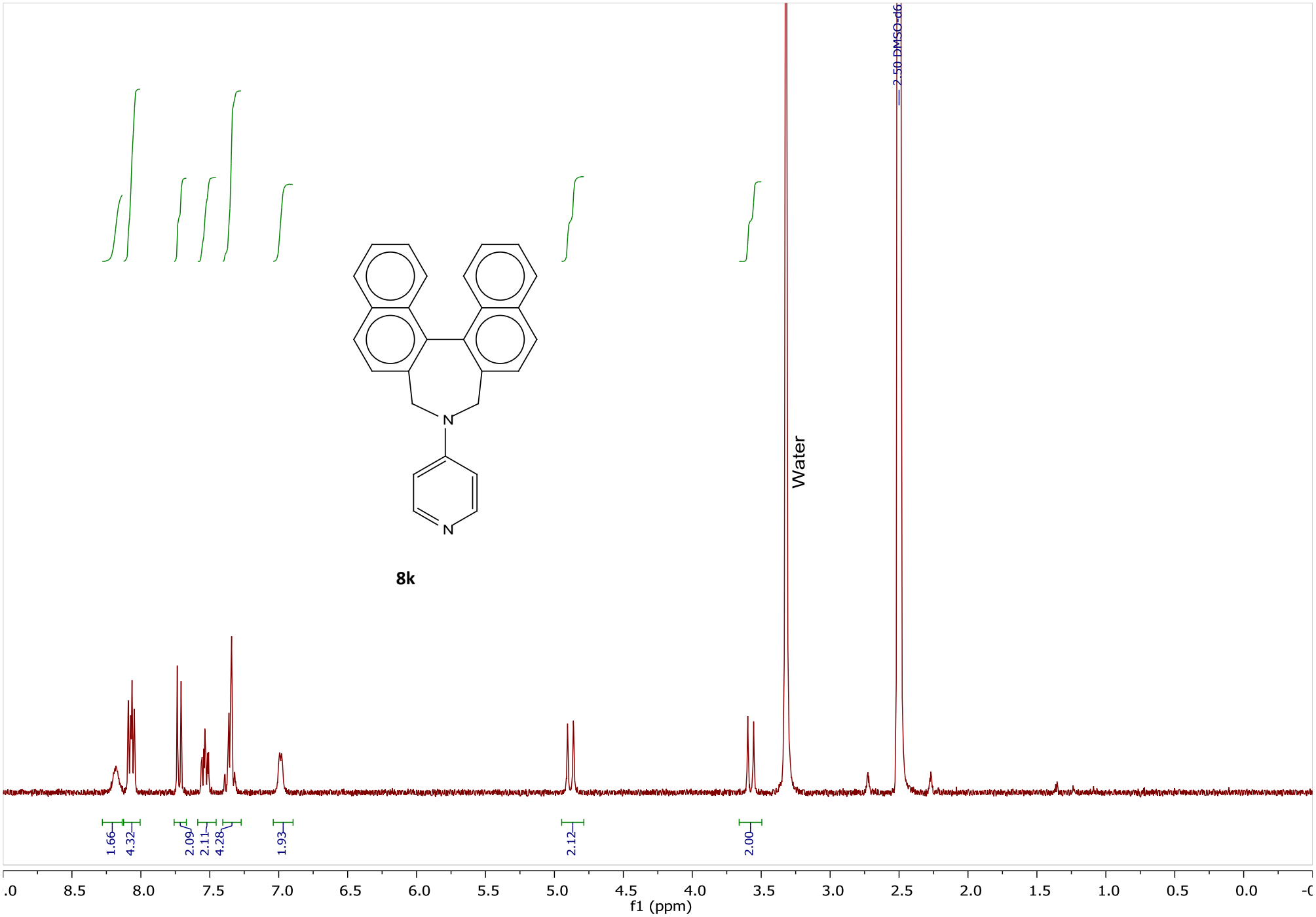
8i

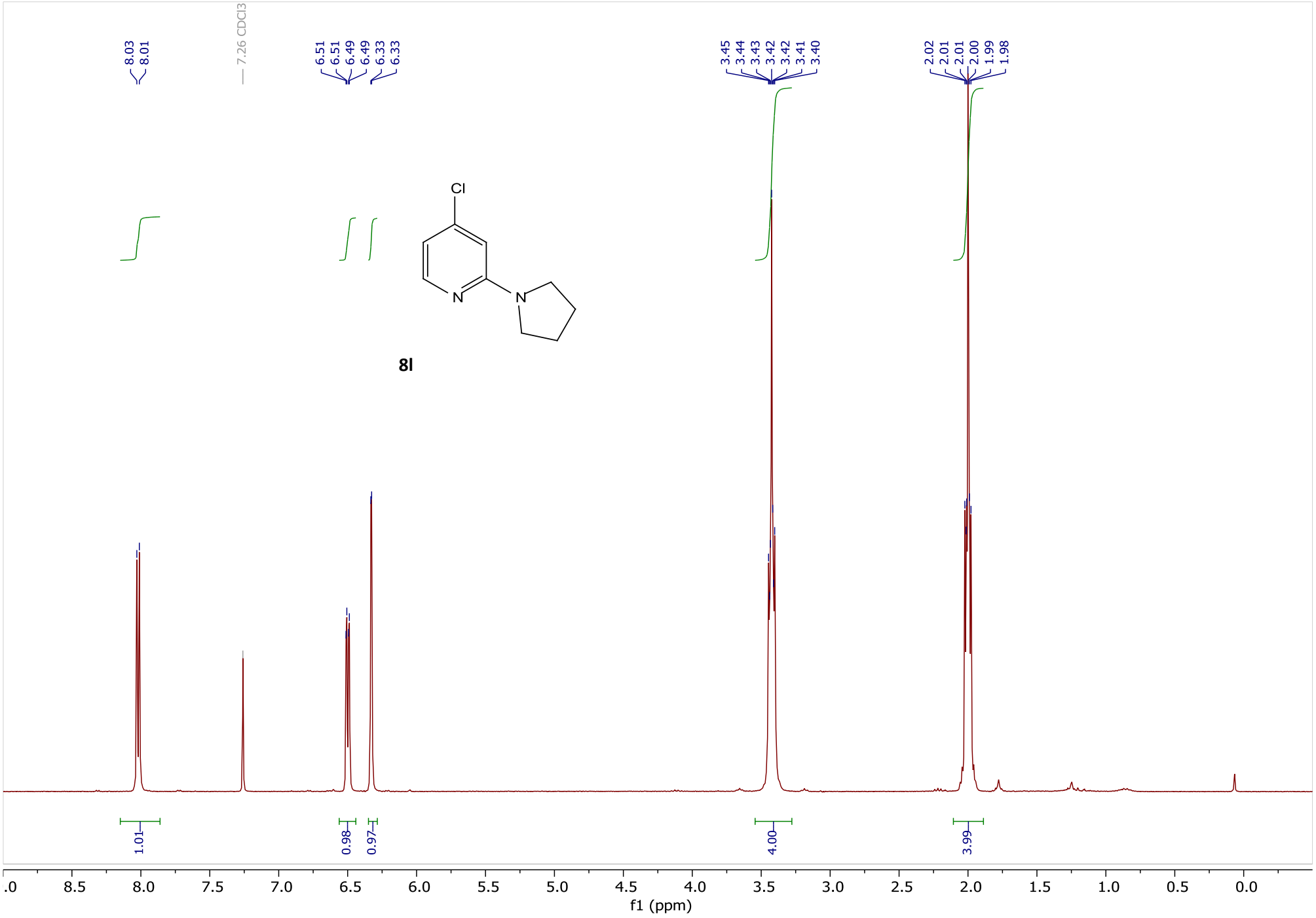

8.03 8.02 8.02 7.34 7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.32 7.31 7.31 7.28 7.27 7.26 CDCl3 7.26 7.25 7.25 7.25 7.24 7.24 7.23 6.48 6.47 6.46 6.46 5.60 5.59 5.59
4.58 4.57 4.55 4.53 4.52 4.15 4.13 4.11 4.10 3.93
1.58 1.57 1.41 1.39
CH3
HN
N
(S)-8j major
CH3
N
NH
(S)-8j minor
A (m) 8.03
B (m) 7.33
C (m) 7.26
D (m) 6.47
E (m) 5.59
F (p) 4.55
G (q) 4.12
H (s) 3.93
I (d) 1.58
J (d) 1.40
1.93
4.21
1.36
1.94
0.91
0.98
0.15
0.97
3.00
0.44
f1 (ppm)

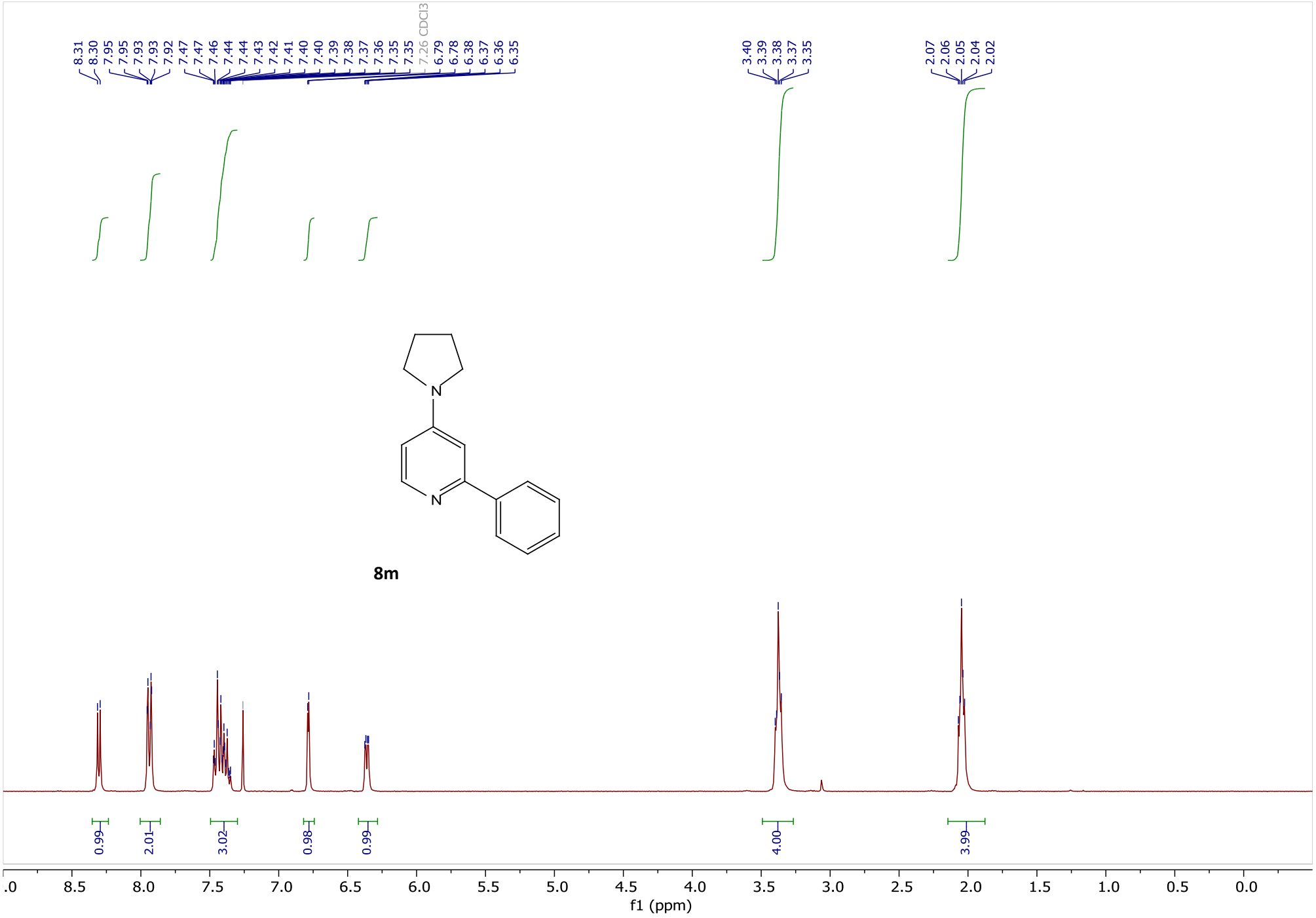


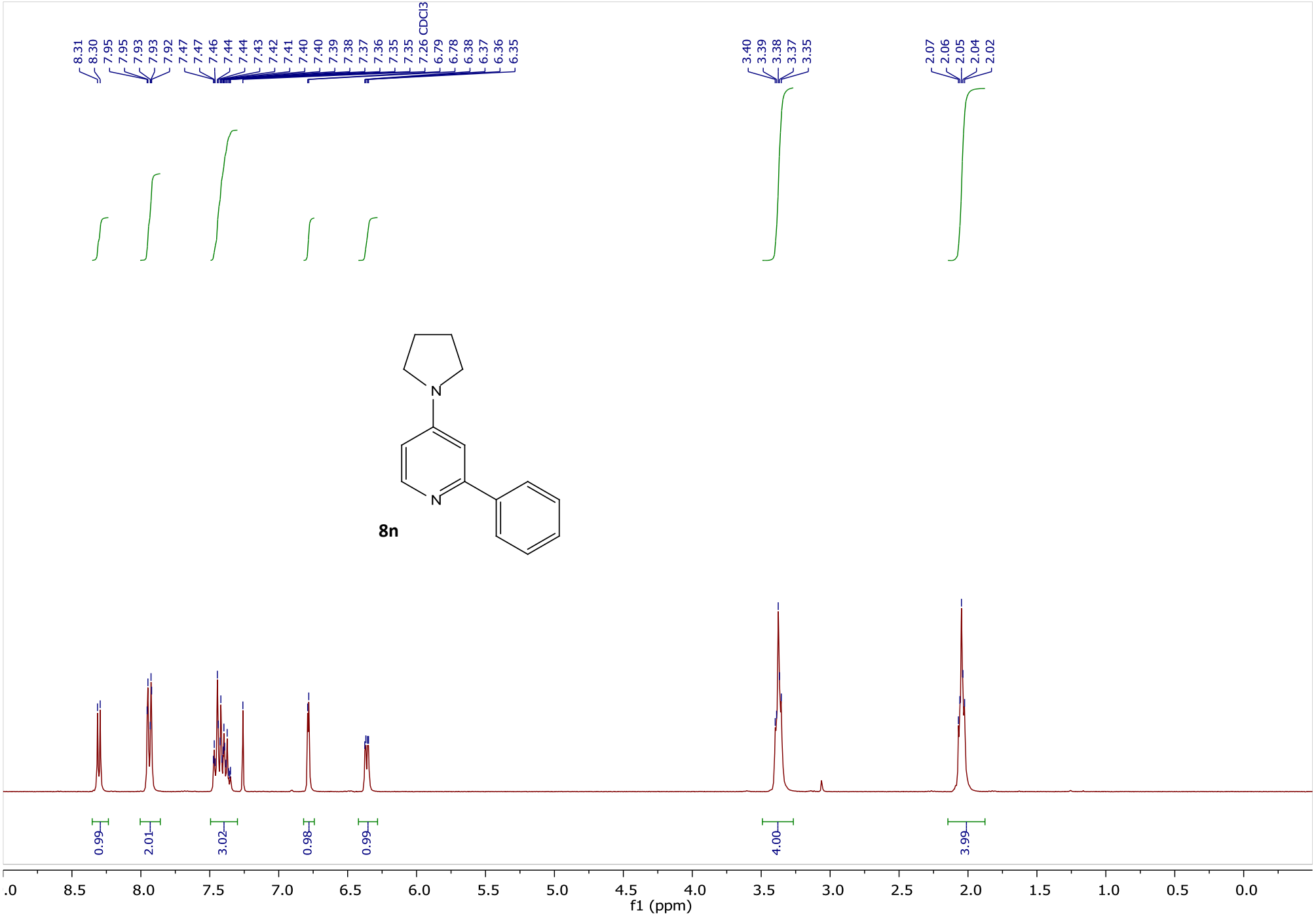
(*S*)-**8j** major

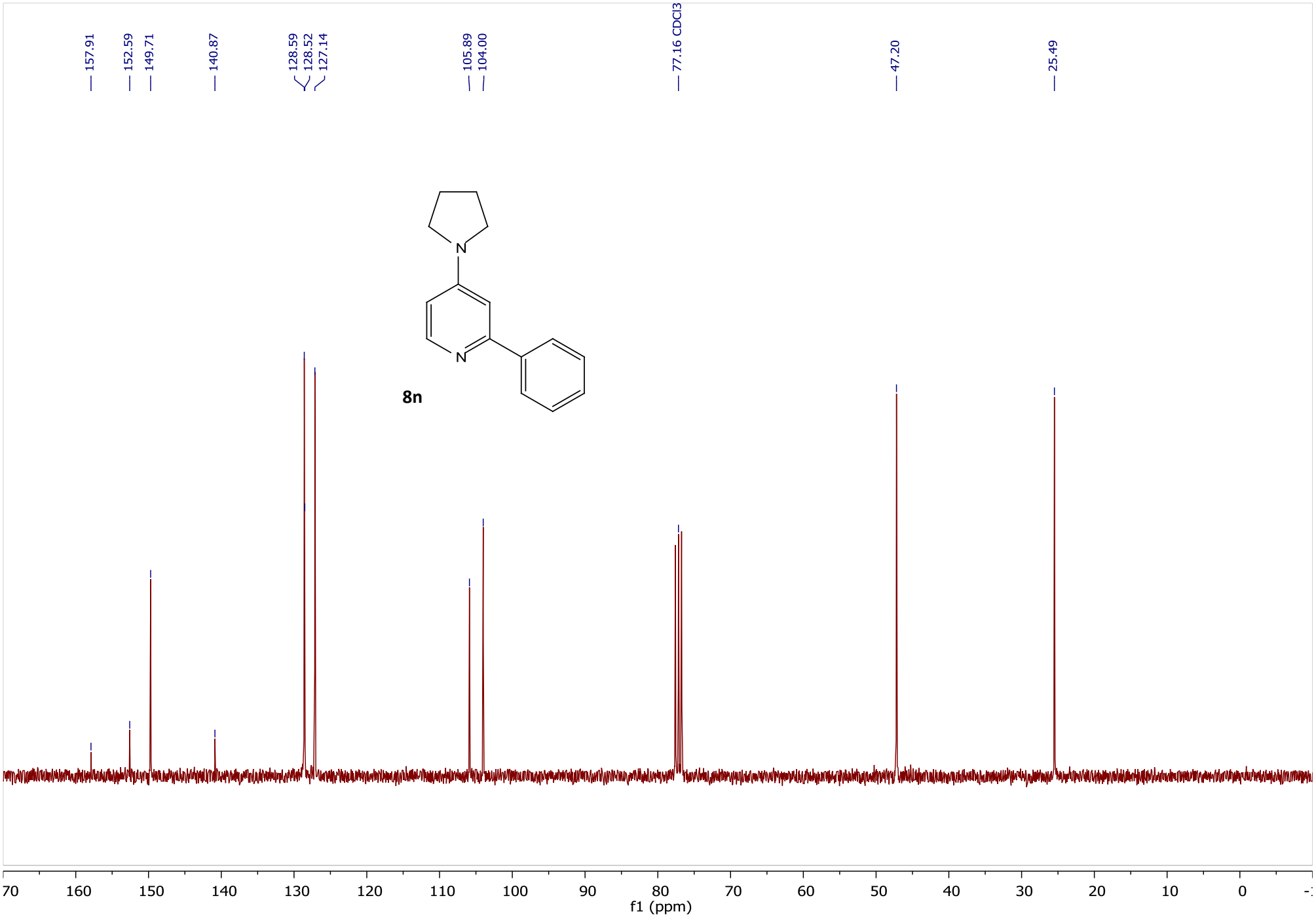
(*S*)-**8j** minor

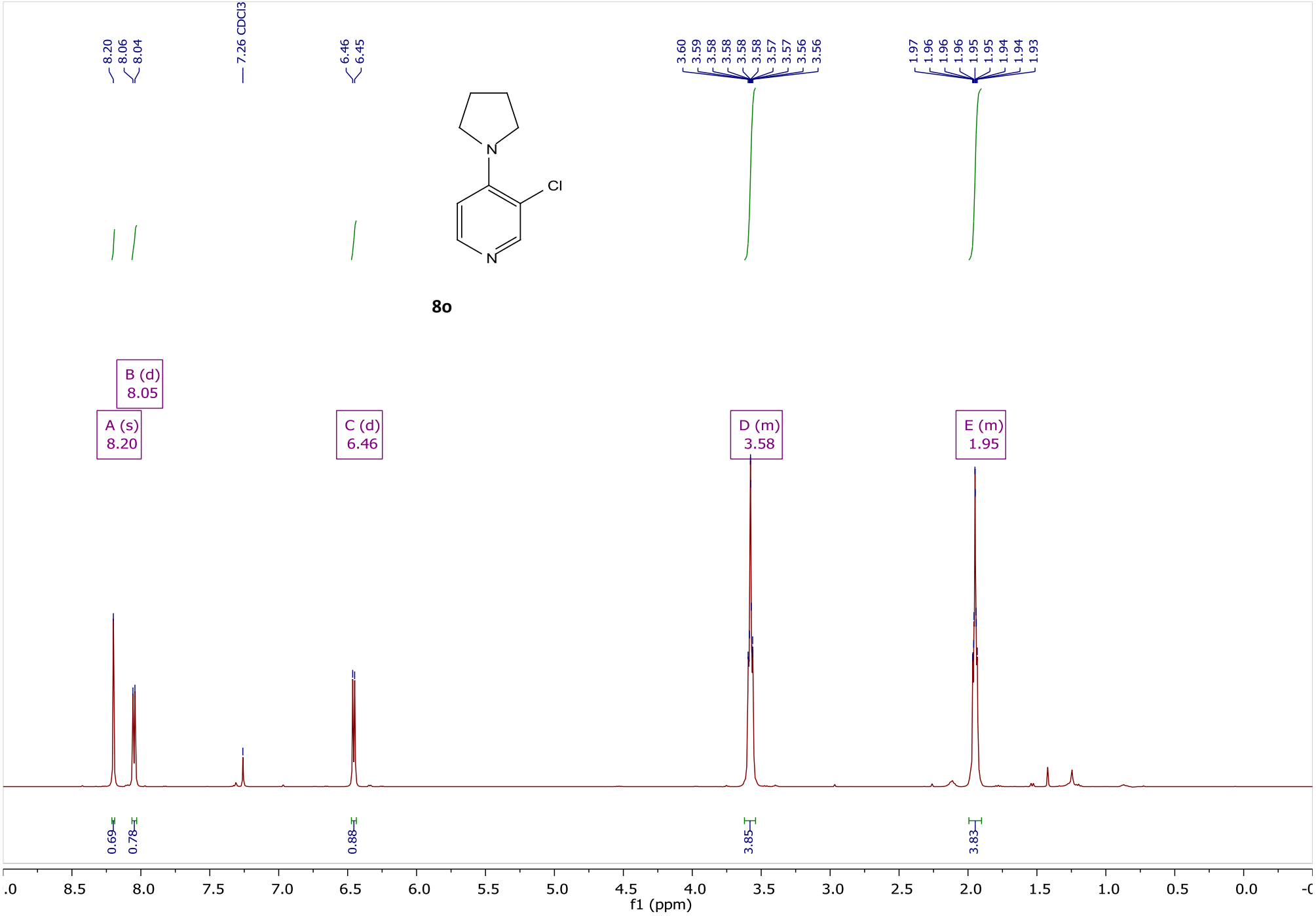

2.50 DMSO-d6
Water
N
N
8k
1.66
4.32
2.09
2.11
4.28
1.93
2.12
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

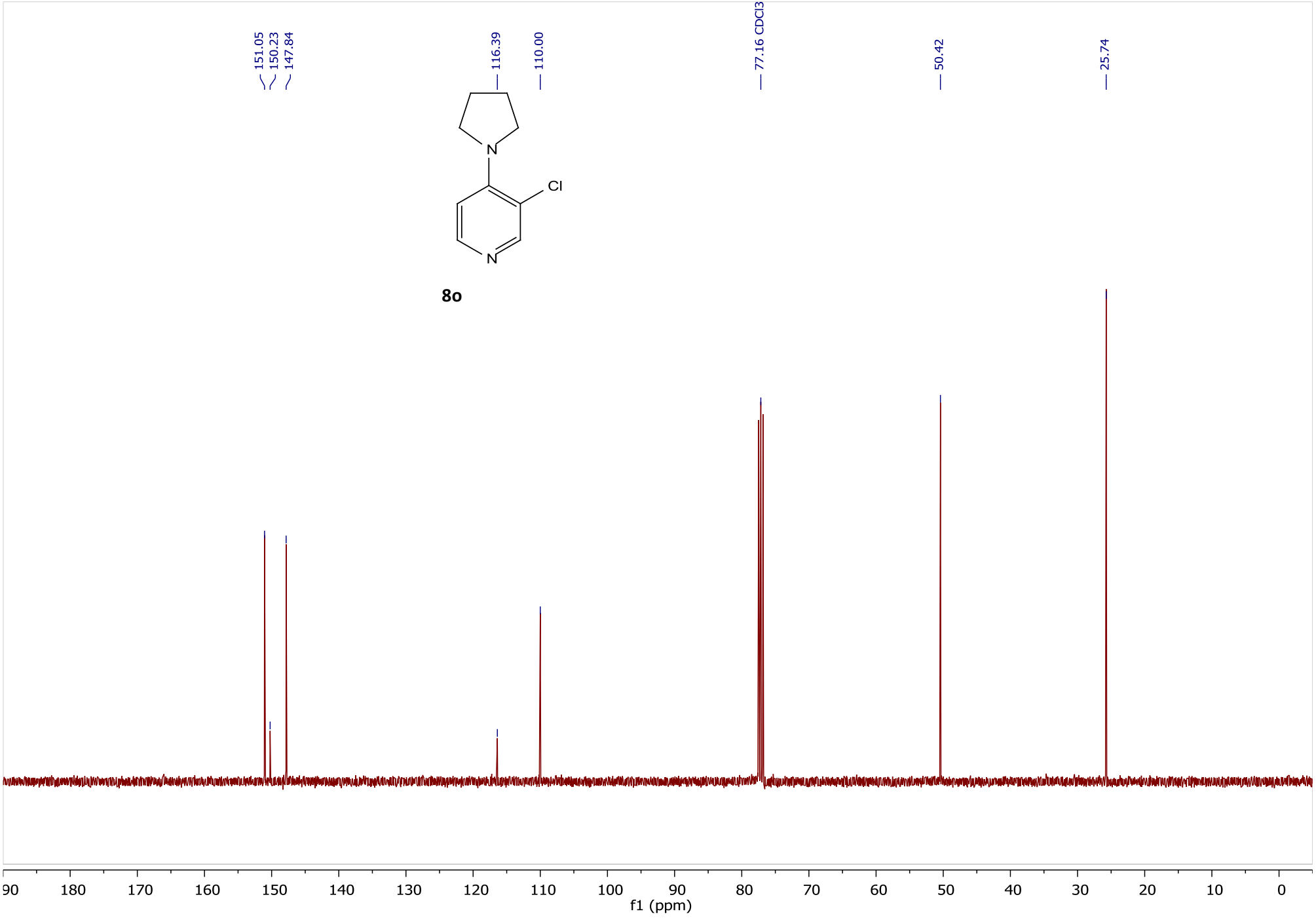

8.03
8.01
7.26 CDCl3
6.51
6.51
6.49
6.49
6.33
6.33
3.45
3.44
3.43
3.42
3.42
3.41
3.40
2.02
2.01
2.01
2.00
1.99
1.98
Cl
N
N
8l
1.01
0.98
0.97
4.00
3.99
f1 (ppm)

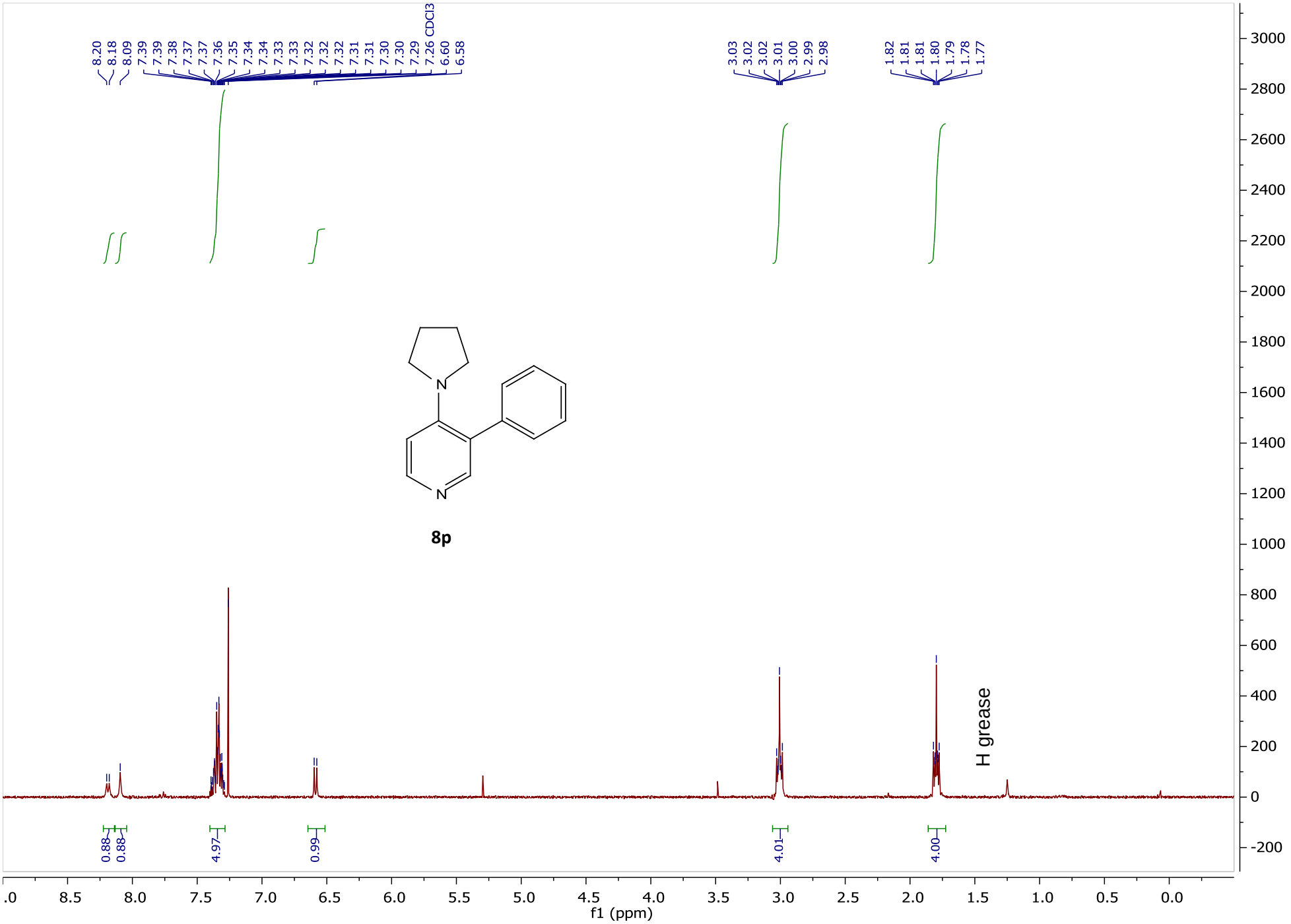

8.31
8.30
7.95
7.95
7.93
7.93
7.92
7.47
7.47
7.46
7.44
7.44
7.43
7.42
7.41
7.40
7.40
7.39
7.38
7.37
7.36
7.35
7.35
7.26 CDCl3
6.79
6.78
6.38
6.37
6.36
6.35
3.40
3.39
3.38
3.37
3.35
2.07
2.06
2.05
2.04
2.02
N
N
8m
0.99
2.01
3.02
0.98
0.99
4.00
3.99
f1 (ppm)

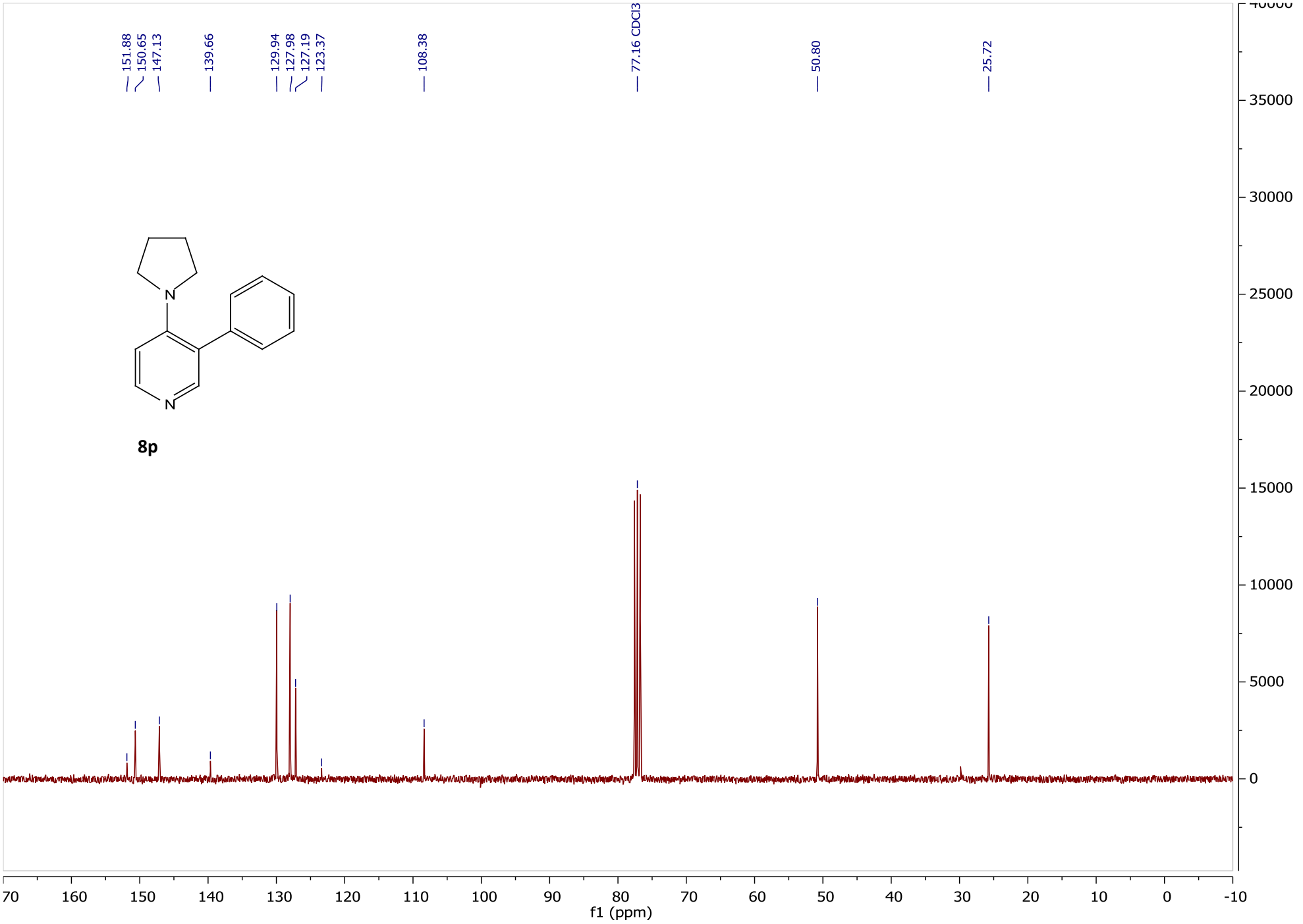

8.31
8.30
7.95
7.95
7.93
7.93
7.92
7.47
7.47
7.46
7.44
7.44
7.43
7.42
7.41
7.40
7.40
7.39
7.38
7.37
7.36
7.35
7.35
7.26 CDCl3
6.79
6.78
6.38
6.37
6.36
6.35
3.40
3.39
3.38
3.37
3.35
2.07
2.06
2.05
2.04
2.02
N
N
8n
0.99
2.01
3.02
0.98
0.99
4.00
3.99
f1 (ppm)

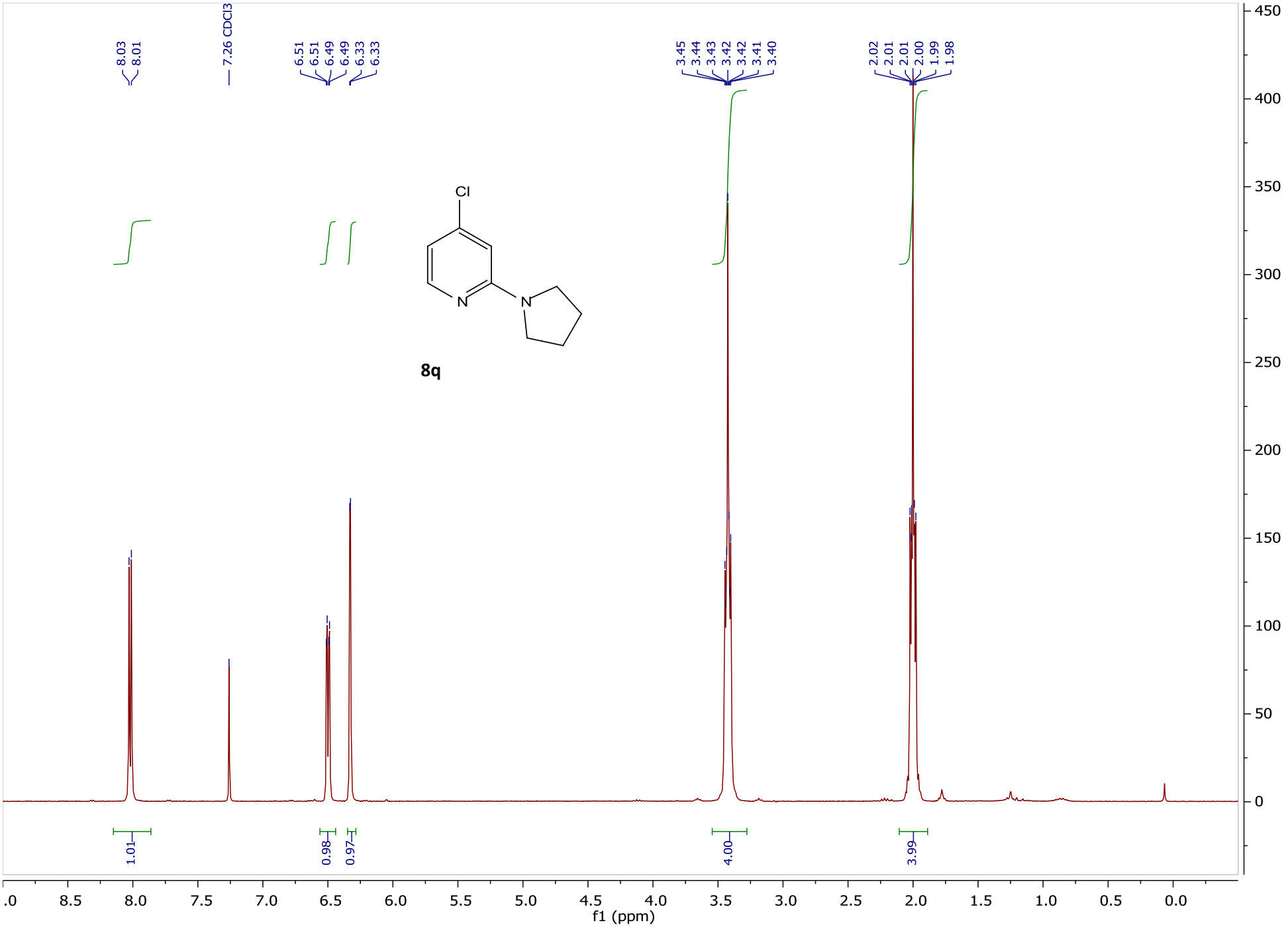

157.91
152.59
149.71
140.87
128.59
128.52
127.14
105.89
104.00
77.16 CDCl3
47.20
25.49
N
N
8n
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

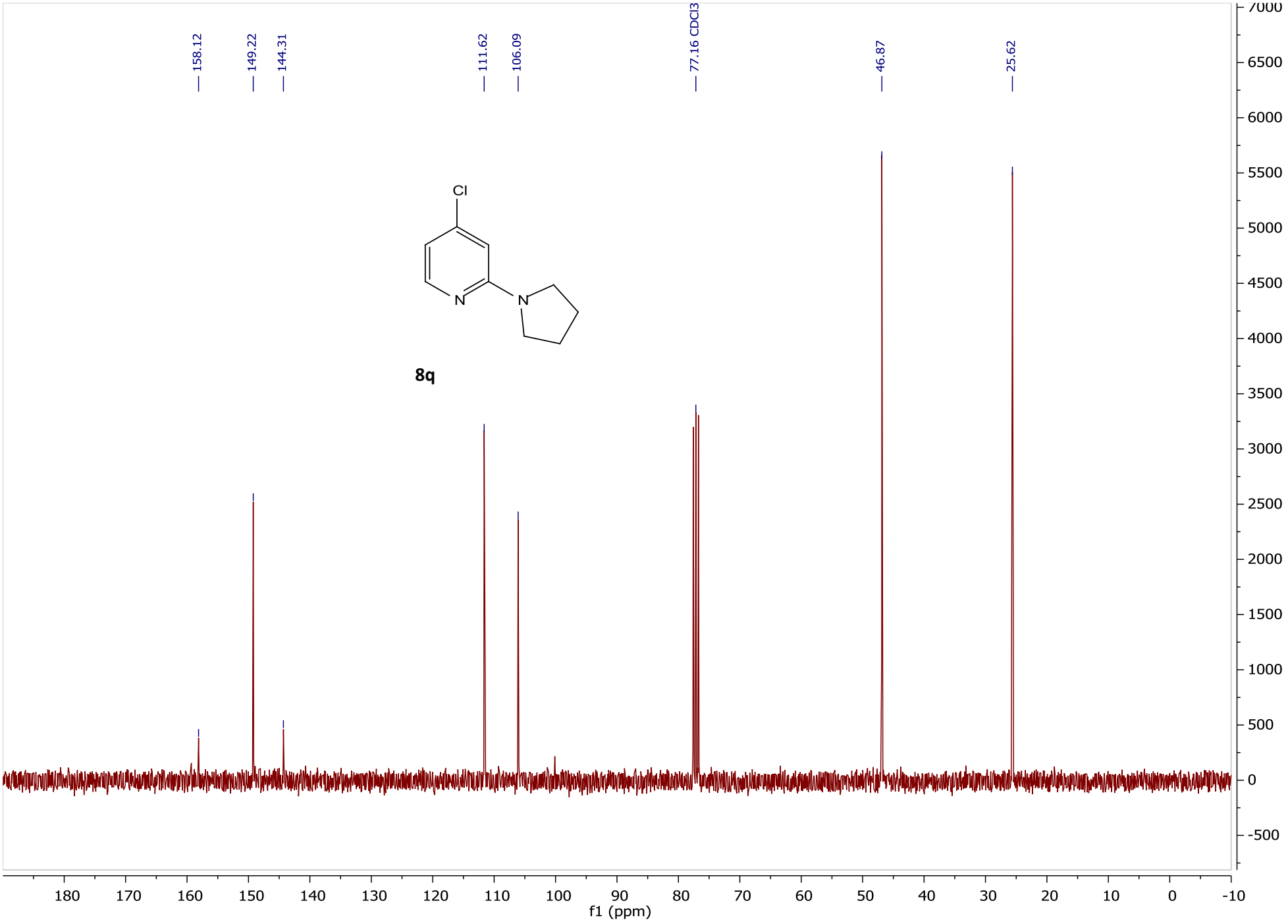

8.20
8.06
8.04
7.26 CDCl3
6.46
6.45
3.60
3.59
3.58
3.58
3.58
3.58
3.57
3.57
3.56
3.56
1.97
1.96
1.96
1.96
1.95
1.95
1.94
1.94
1.93
N
Cl
N
8o
B (d)
8.05
A (s)
8.20
C (d)
6.46
D (m)
3.58
E (m)
1.95
0.69
0.78
0.88
3.85
3.83
f1 (ppm)

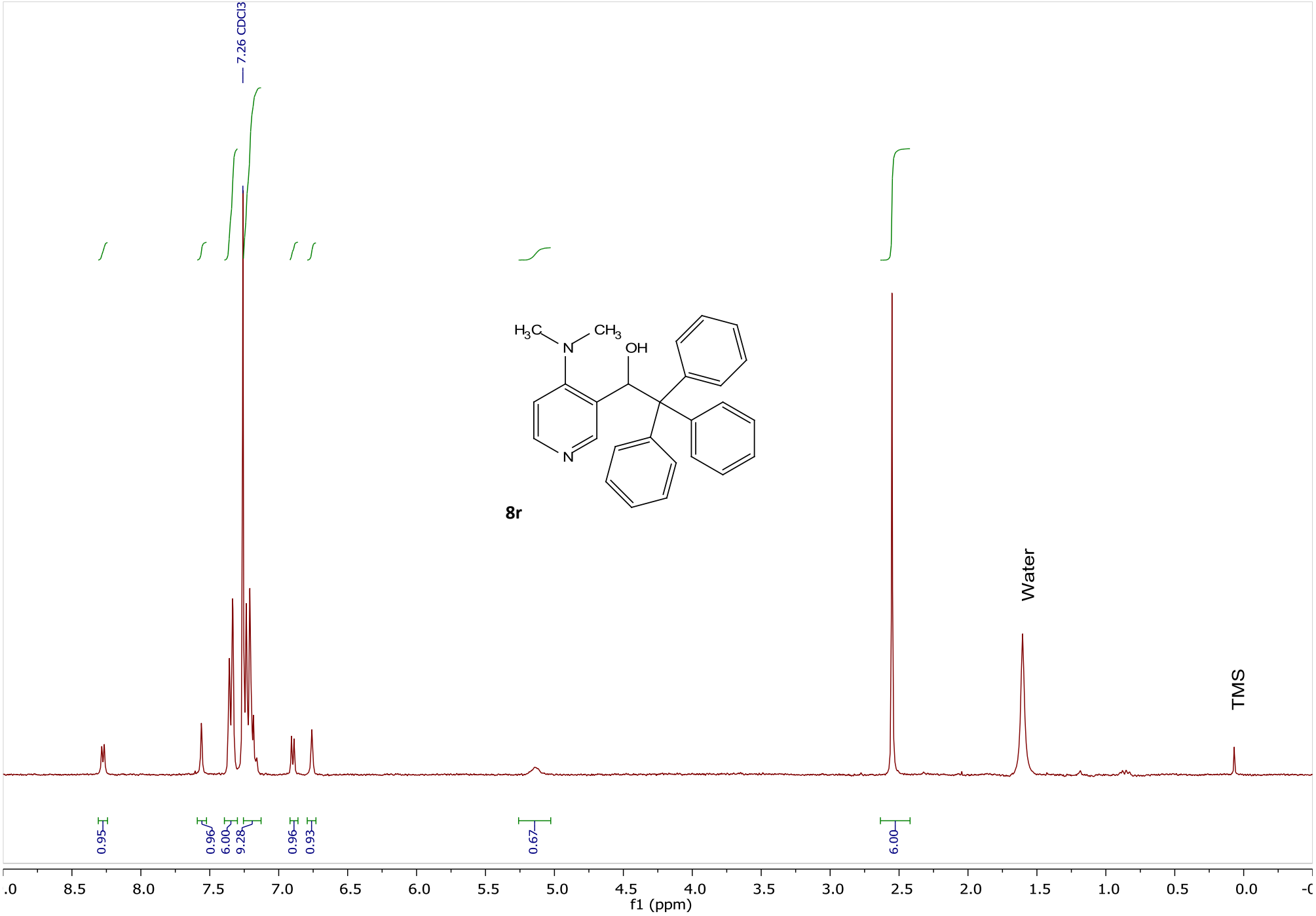

151.05
150.23
147.84
116.39
110.00
77.16 CDCl3
50.42
25.74
N
Cl
N
8o
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

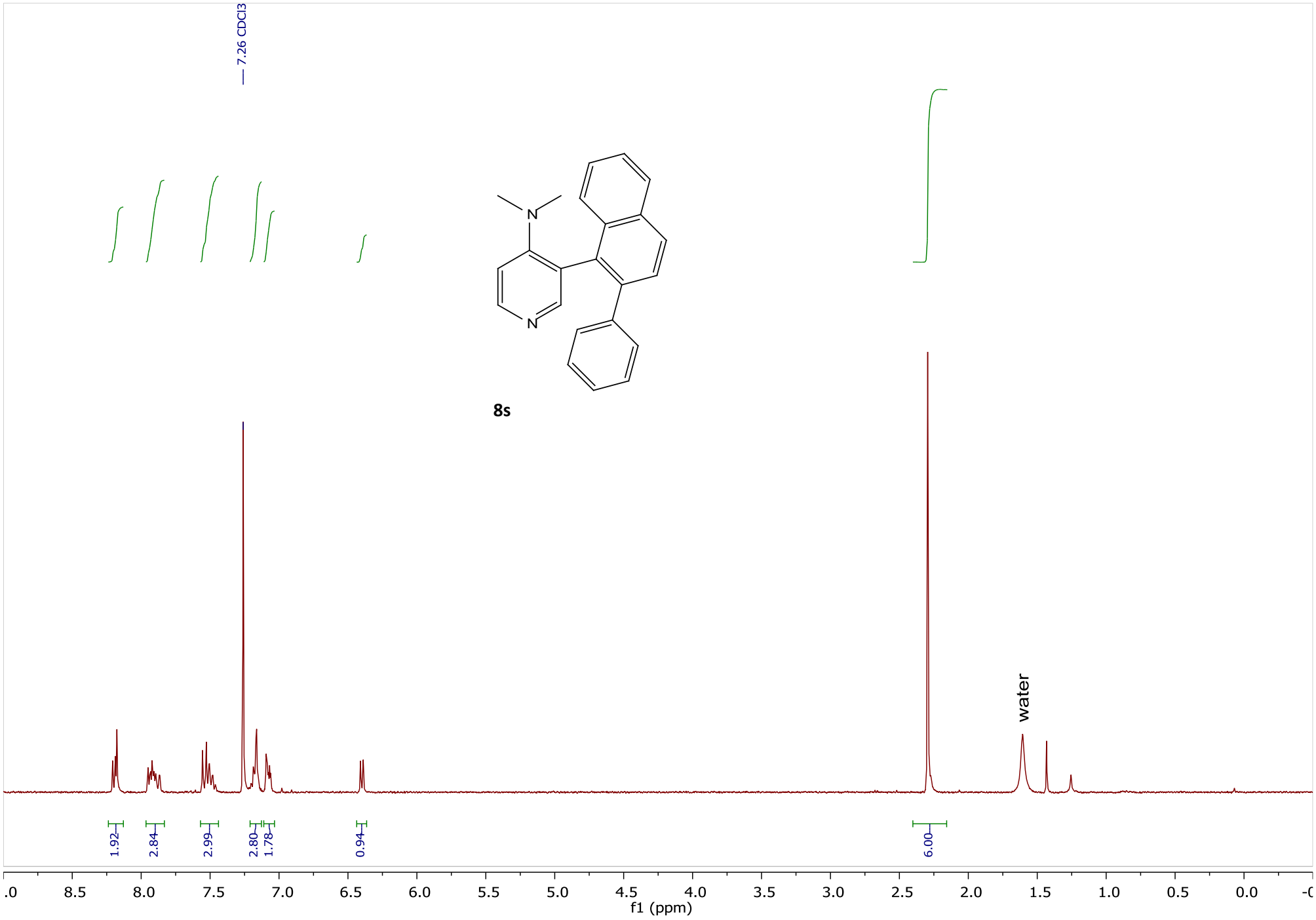

8.20
8.18
8.09
7.39
7.39
7.38
7.37
7.37
7.36
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.26 CDCl3
6.60
6.58
3.03
3.02
3.02
3.01
3.00
2.99
2.98
1.82
1.81
1.81
1.80
1.79
1.78
1.77
N
N
8p
H grease
0.88
0.88
4.97
0.99
4.01
4.00
f1 (ppm)

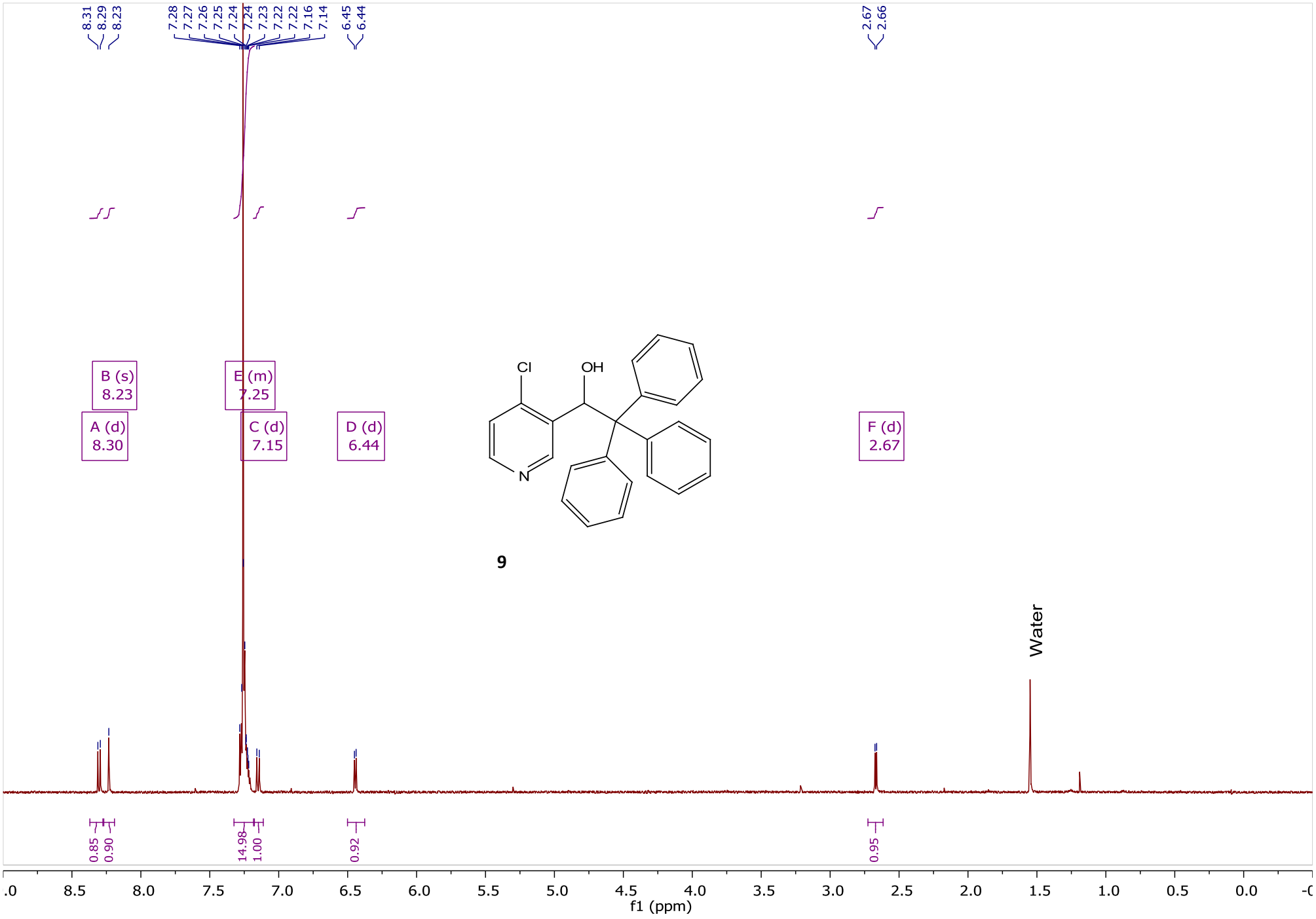

151.88
150.65
147.13
139.66
129.94
127.98
127.19
123.37
108.38
77.16 CDCl3
50.80
25.72
N
N
8p
40000
35000
30000
25000
20000
15000
10000
5000
0
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

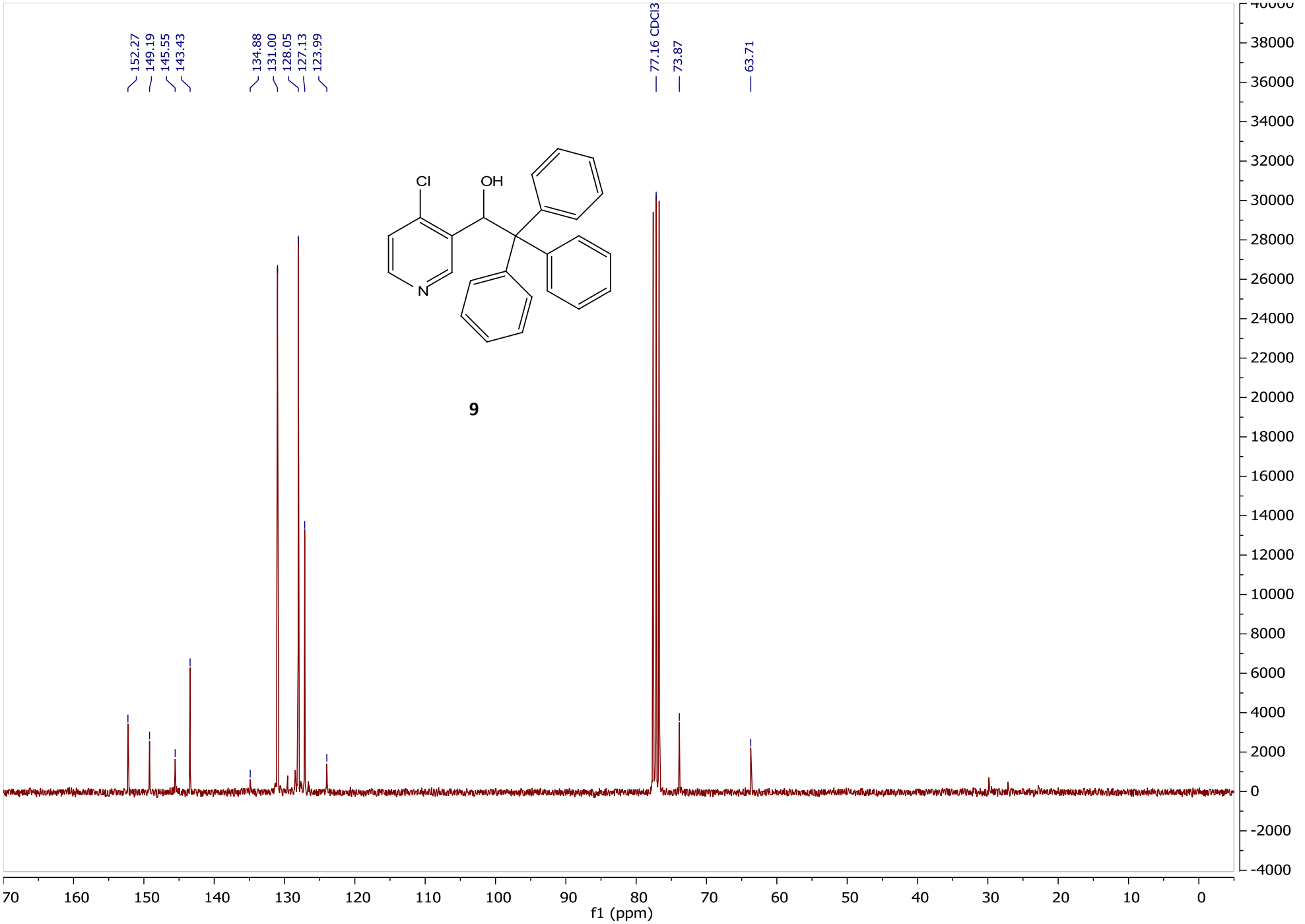

8.03
8.01
7.26 CDCl3
6.51
6.51
6.49
6.49
6.33
6.33
3.45
3.44
3.43
3.42
3.42
3.41
3.40
2.02
2.01
2.01
2.00
1.99
1.98
Cl
N
N
8q
1.01
0.98
0.97
4.00
3.99
f1 (ppm)

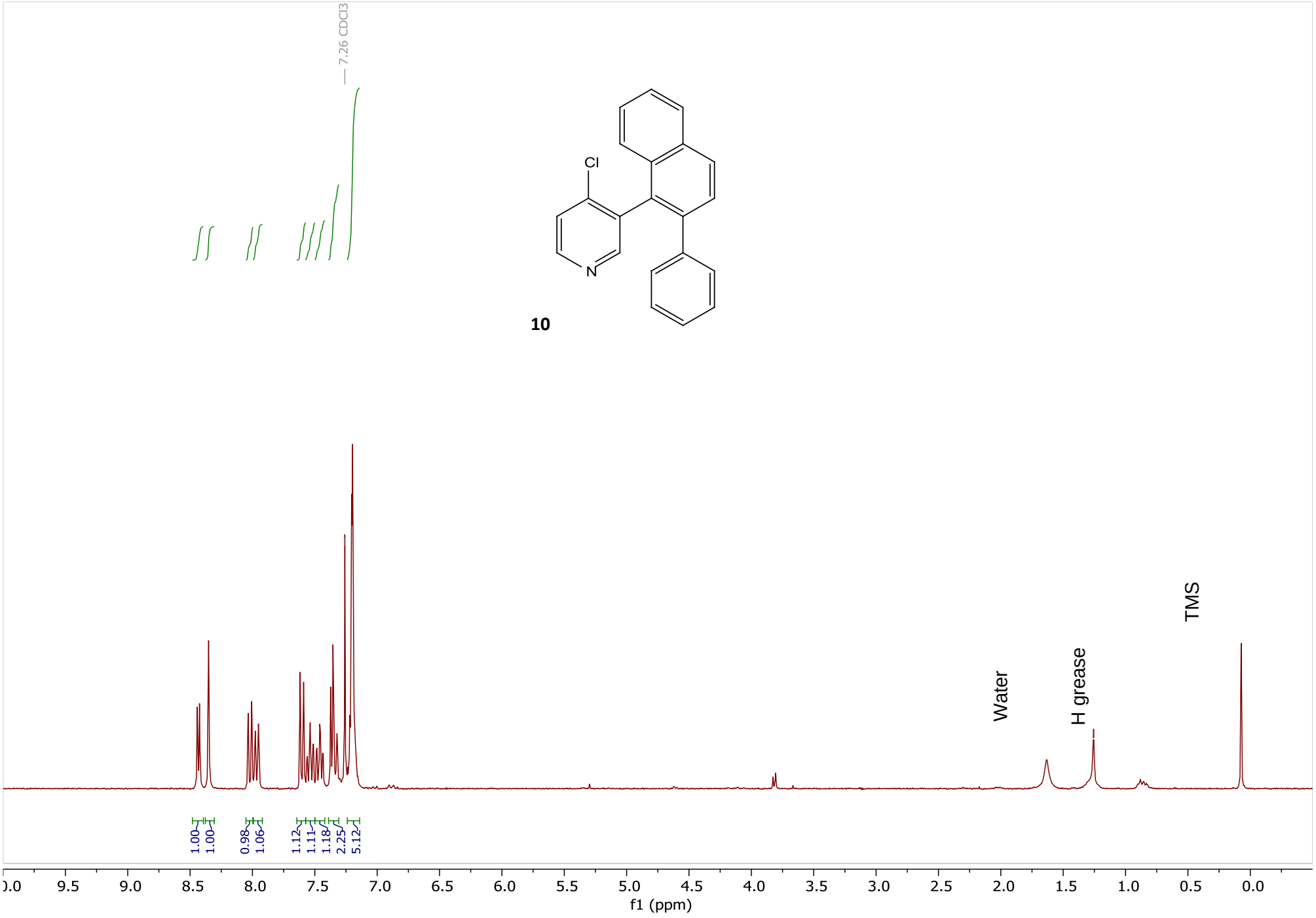

158.12
149.22
144.31
111.62
106.09
77.16 CDCl3
46.87
25.62
Cl
N
N
8q
f1 (ppm)

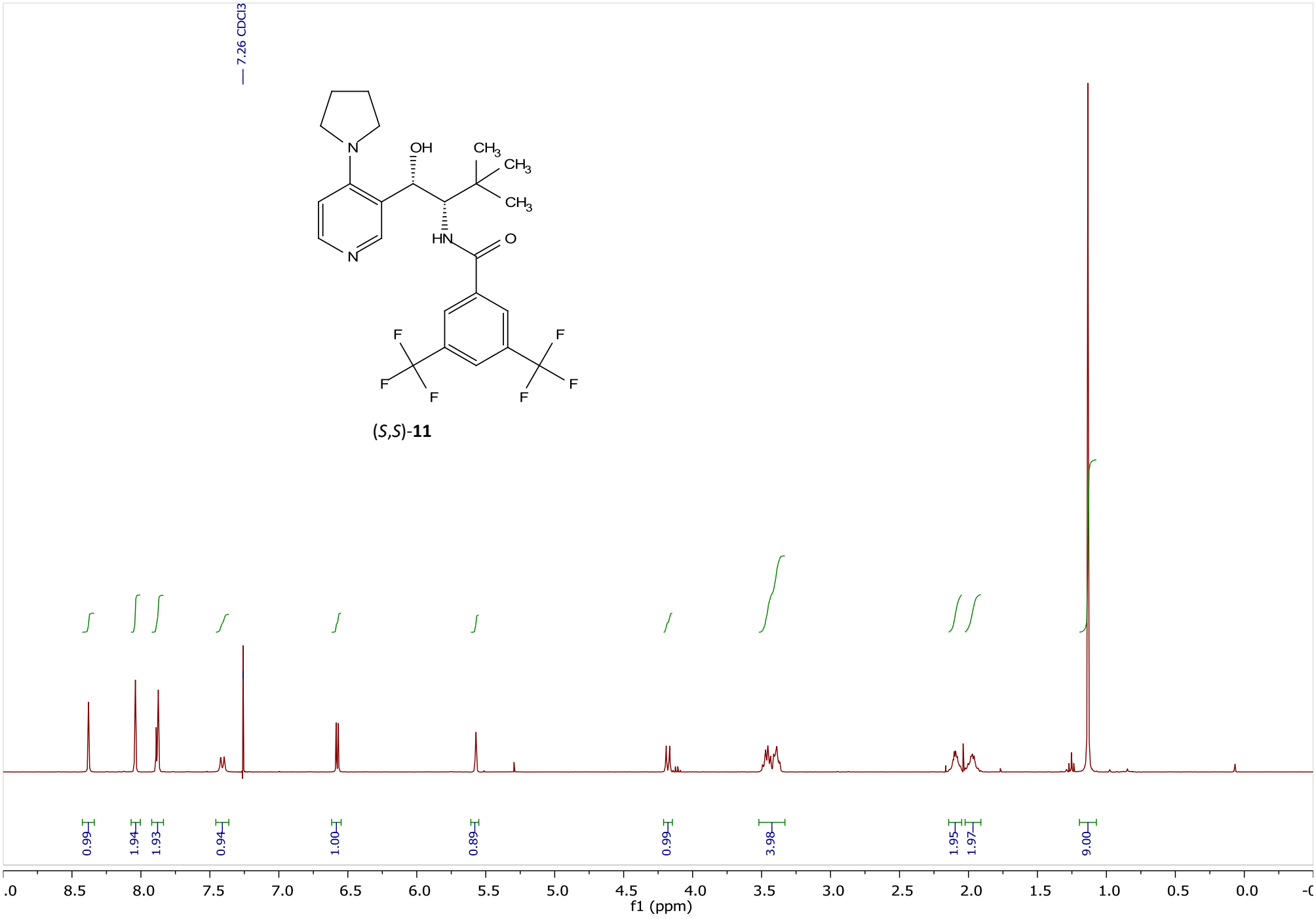

7.26 CDCl3
H3C
CH3
N
OH
N
8r
Water
TMS
0.95
0.96
6.00
9.28
0.96
0.93
0.67
6.00
f1 (ppm)


7.26 CDCl3
N
N
8s
water
1.92
2.84
2.99
2.80
1.78
0.94
6.00
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)

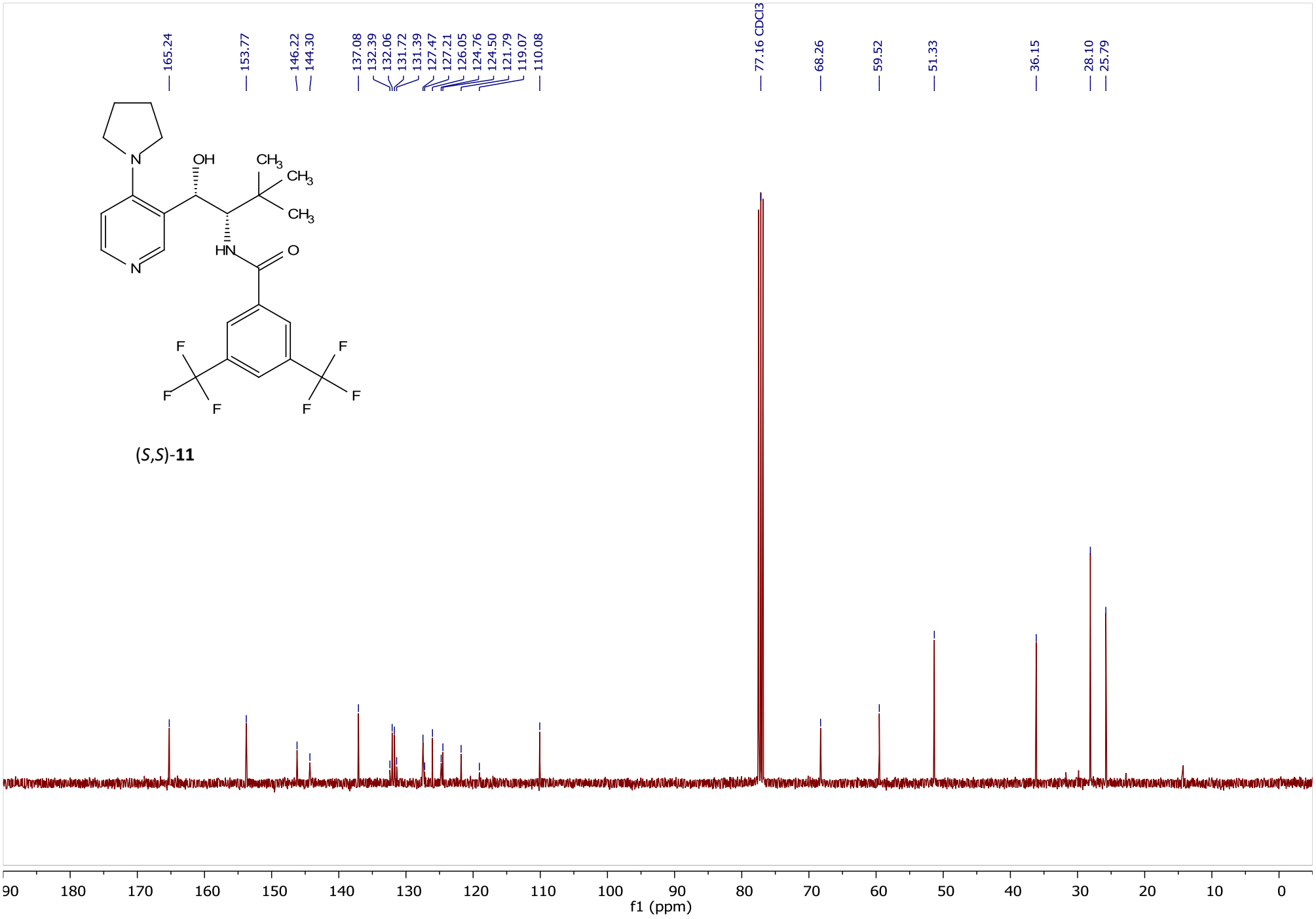

8.31
8.29
8.23
7.28
7.27
7.26
7.25
7.24
7.24
7.23
7.22
7.22
7.16
7.14
6.45
6.44
2.67
2.66
B (s)
8.23
E (m)
7.25
A (d)
8.30
C (d)
7.15
D (d)
6.44
F (d)
2.67
Cl
OH
N
9
Water
0.85
0.90
14.98
1.00
0.92
0.95
f1 (ppm)


152.27
149.19
145.55
143.43
134.88
131.00
128.05
127.13
123.99
77.16 CDCl3
73.87
63.71
Cl
OH
N
9
f1 (ppm)

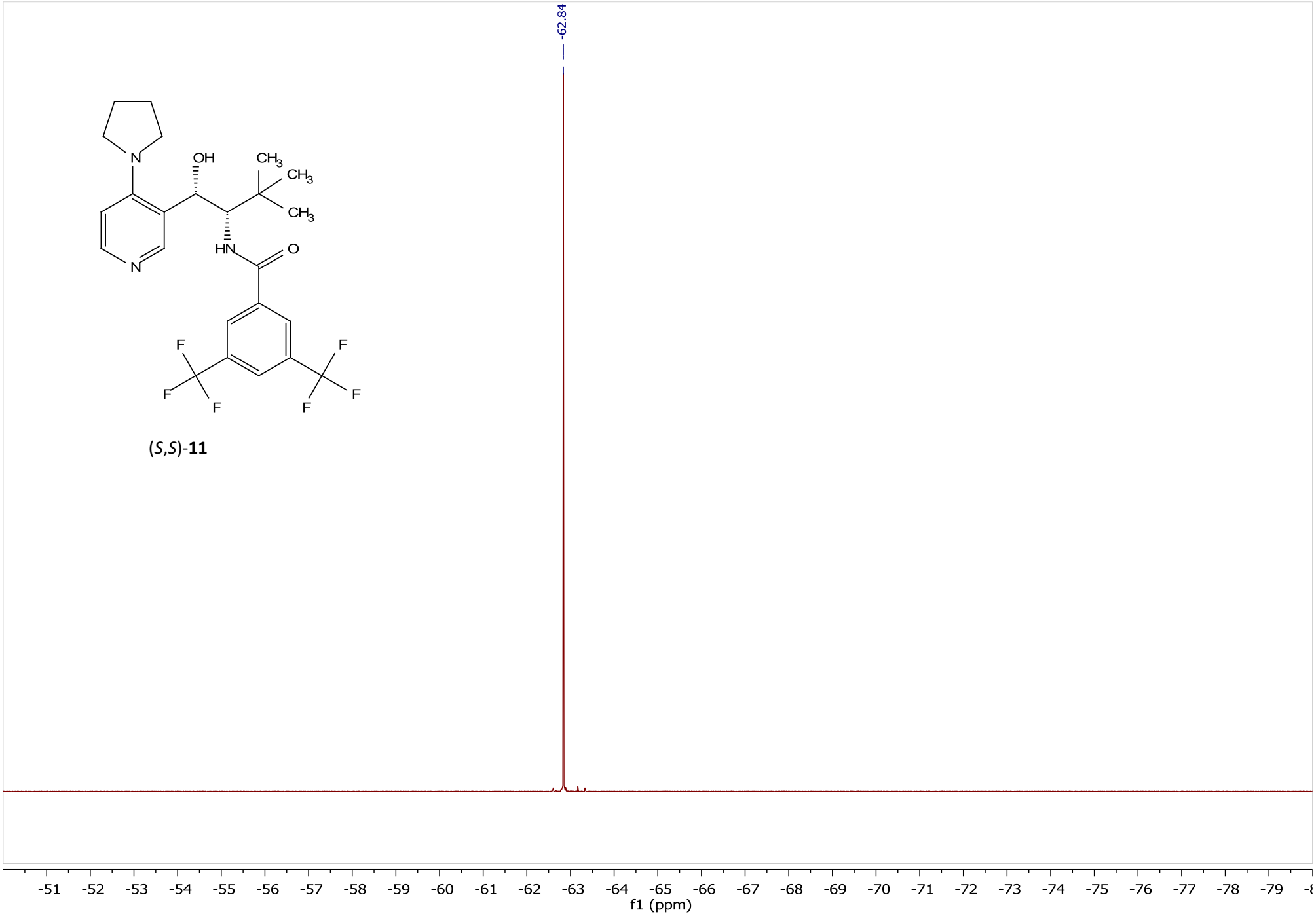

7.26 CDCl3
Cl
N
10
Water
H grease
TMS
1.00
1.00
0.98
1.06
1.12
1.11
1.18
2.25
5.12
f1 (ppm)


7.26 CDCl3
N
OH
CH3
CH3
CH3
HN
O
N
F
F
F
F
F
F
0.99
1.94
1.93
0.94
1.00
0.89
0.99
3.98
1.95
1.97
9.00
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)

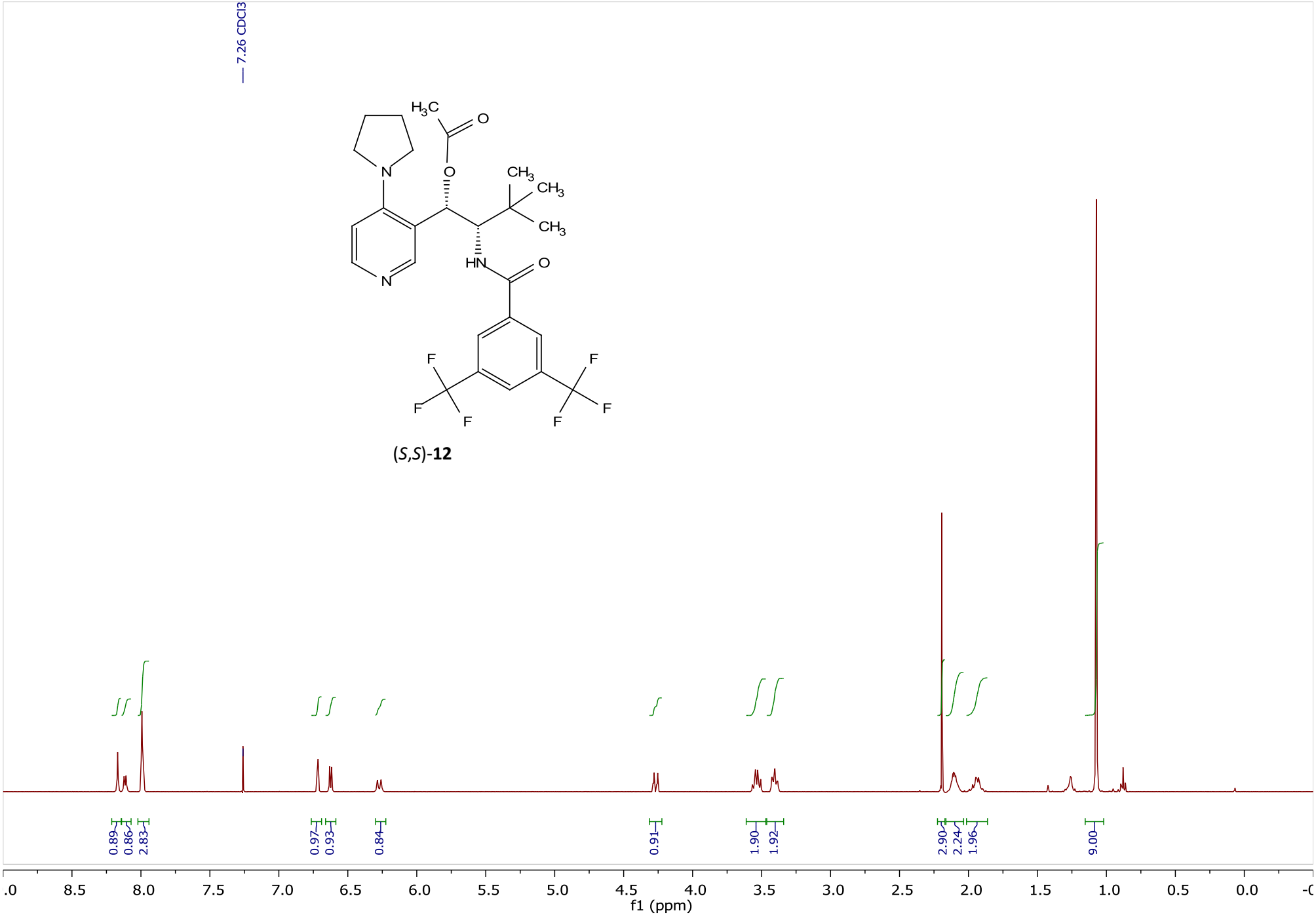
(*S*,*S*)-**11**


165.24
153.77
146.22
144.30
137.08
132.39
132.06
131.72
131.39
127.47
127.21
126.05
124.76
124.50
121.79
119.07
110.08
77.16 CDCl3
68.26
59.52
51.33
36.15
28.10
25.79
OH
CH3
CH3
CH3
HN
O
N
N
F
F
F
F
F
F
f1 (ppm)

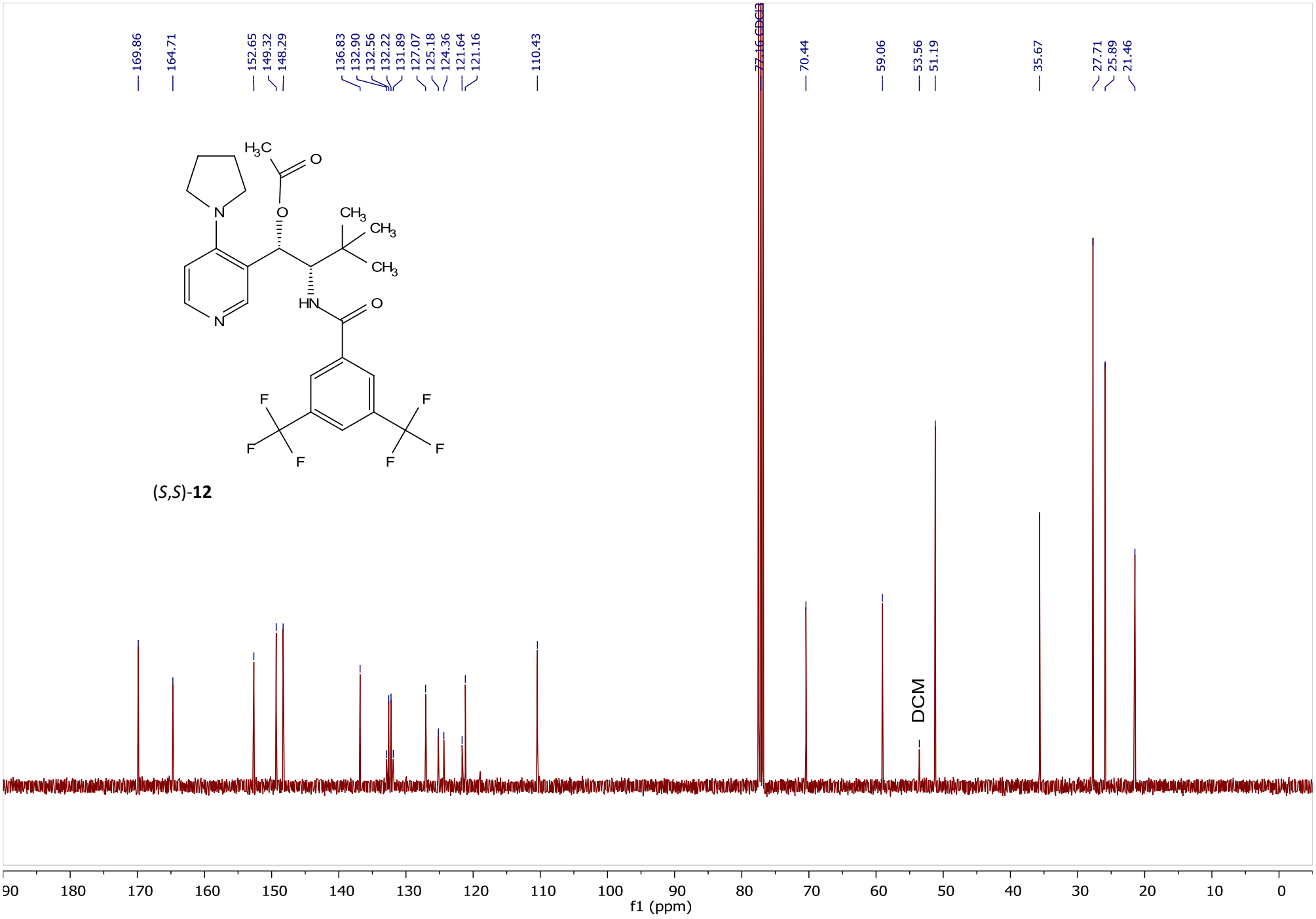
(*S*,*S*)-**11**


-62.84
N
OH
CH3
CH3
CH3
HN
O
N
F
F
F
F
F
F
-51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77 -78 -79
f1 (ppm)

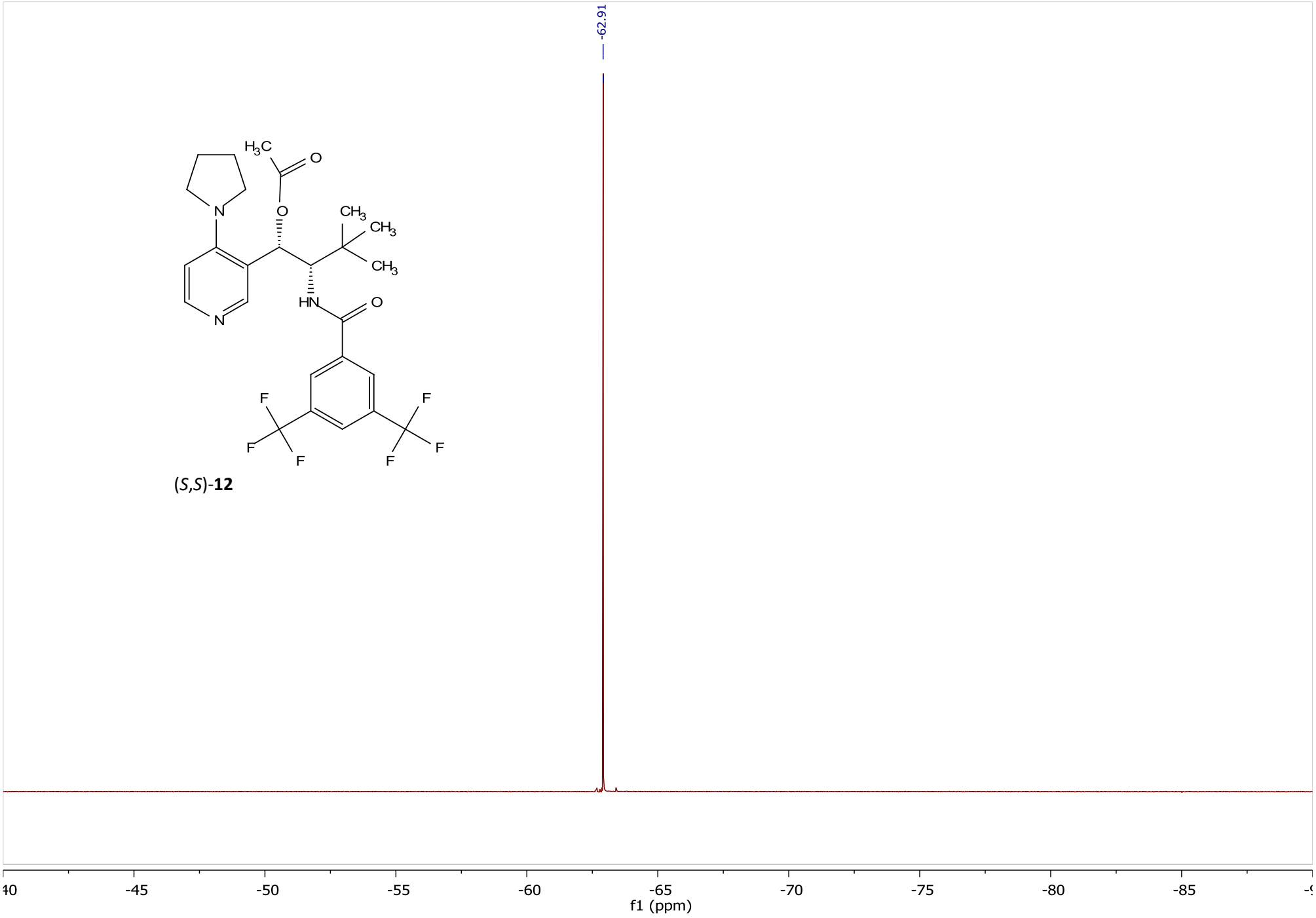
(*S*,*S*)-**11**


7.26 CDCl3
H3C
O
N
O
CH3
CH3
CH3
HN
O
N
F
F
F
F
F
F
0.89
0.86
2.83
0.97
0.93
0.84
0.91
1.90
1.92
2.90
2.24
1.96
9.00
f1 (ppm)

(*S*,*S*)-**12**

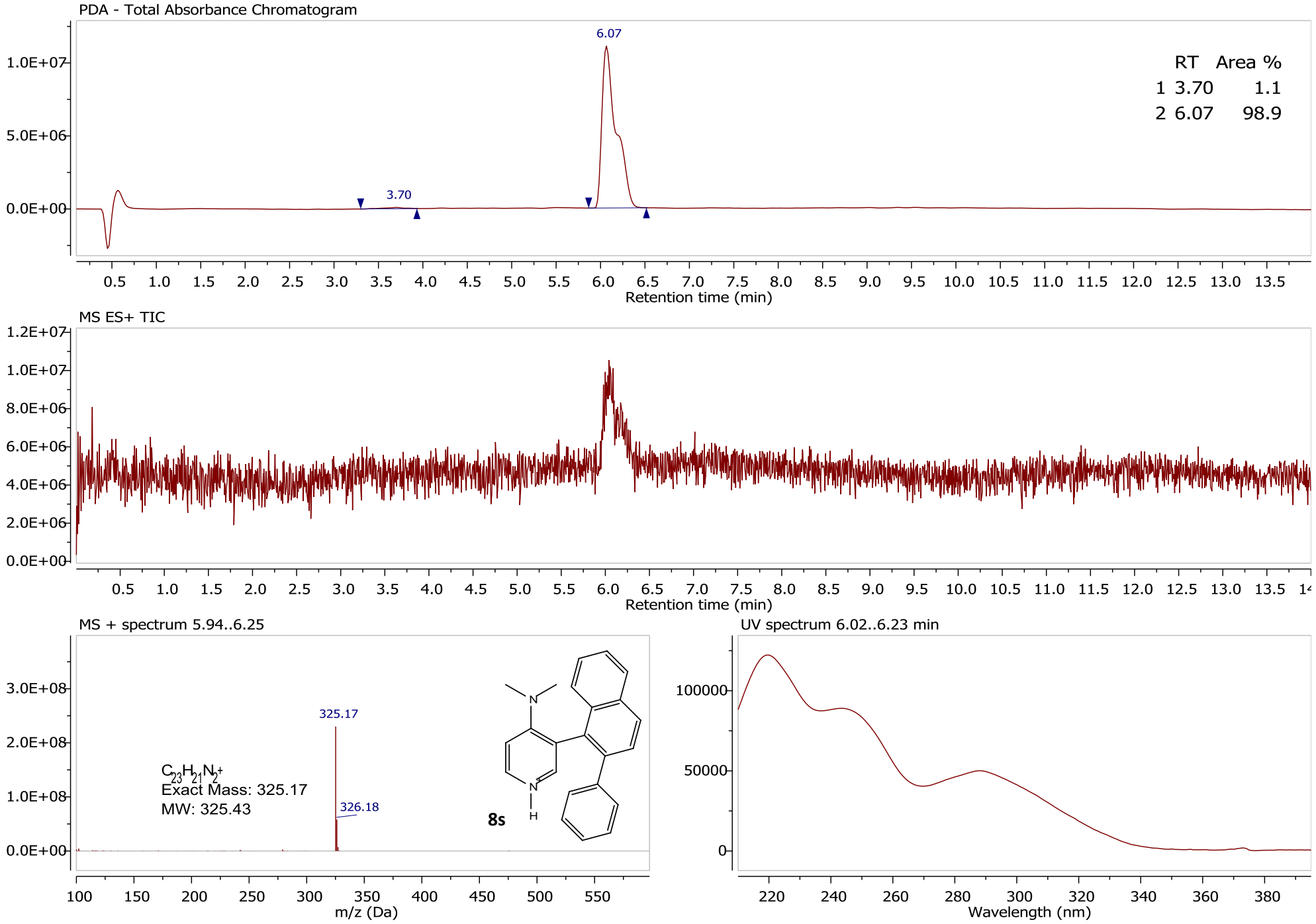

169.86
164.71
152.65
149.32
148.29
136.83
132.90
132.56
132.22
131.89
127.07
125.18
124.36
121.64
121.16
110.43
77.16
70.44
59.06
53.56
51.19
35.67
27.71
25.89
21.46
DCM
f1 (ppm)

(*S*,*S*)-**12**

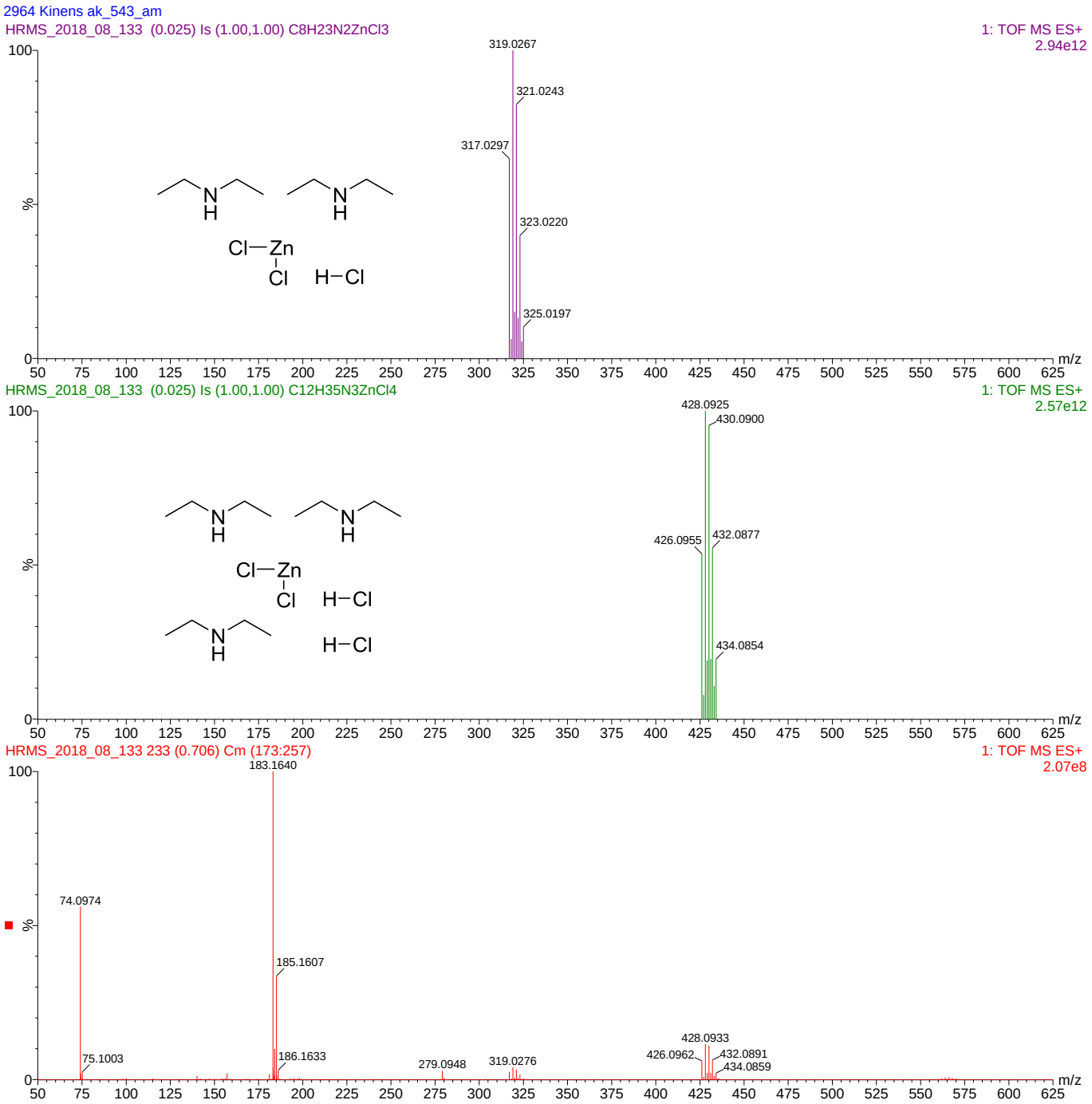

-62.91
H3C
O
N
O
CH3
CH3
CH3
HN
O
N
F
F
F
F
F
F
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
f1 (ppm)

(*S*,*S*)-**12**

Chromatographic Data


PDA - Total Absorbance Chromatogram
6.07
3.70
RT Area %
1 3.70 1.1
2 6.07 98.9
Retention time (min)
MS ES+ TIC
Retention time (min)
MS + spectrum 5.94..6.25
325.17
326.18
C23H21N2+
Exact Mass: 325.17
MW: 325.43
8s
m/z (Da)
UV spectrum 6.02..6.23 min
Wavelength (nm)

HRMS of Zn complex 7b



HRMS of Zn complex 7d