Digital Appendix

NMR Spectra

This chapter consists of research previously published under the following titles:

"Photocatalytic Hydrogen Evolution Driven by a Heteroleptic Ruthenium(II) Bis(terpyridine) Complex" in *Inorganic Chemistry*.

Reproduced with permission of American Chemical Society from *Inorganic Chemistry*, **2019**, *58*, 9127-9134.

"Electrochemical and photophysical study of homoleptic and heteroleptic methylated ruthenium(II) bis-terpyridine complexes" in *European Journal of Inorganic Chemistry*.

Reproduced with permission of Wiley-VCH, from *Electrochemical and photophysical study of homoleptic and heteroleptic methylated ruthenium(II) bis-terpyridine complexes*, Mira T. Rupp, Thomas Auvray, Garry S. Hanan, Dirk G. Kurth, *European Journal of Inorganic Chemistry* **2021**.

"Substituted 2,4-Di(pyridin-2-yl)pyrimidine-Based Ruthenium Photosensitizers for Hydrogen Photoevolution under Red Light" in *Inorganic Chemistry*.

Reproduced with permission of American Chemical Society from *Inorganic Chemistry*, **2021**, *60*, 292-302.

CCDC 2090569: Experimental Crystal Structure Determination, **2021**

and

submitted to *Dalton Transactions* as a full paper under the title

"Dinuclear 2,4-di(pyridin-2-yl)-pyrimidine based ruthenium photosensitizers for hydrogen photo-evolution under red light."

Figure IX-1

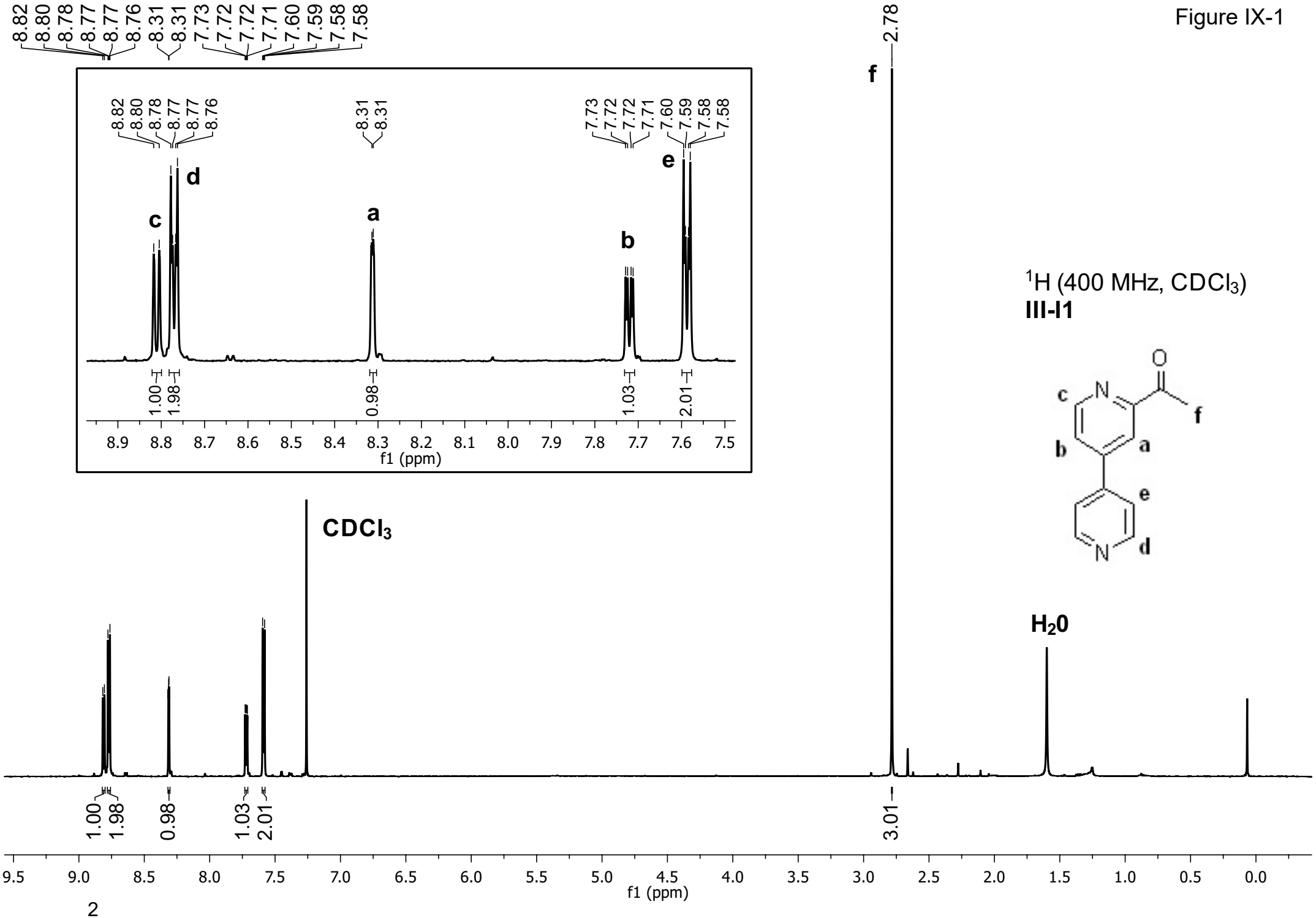

8.82
8.80
8.78
8.77
8.77
8.76
8.31
8.31
7.73
7.72
7.72
7.71
7.60
7.59
7.58
7.58
2.78
f
c
d
a
b
e
1.00
1.98
0.98
1.03
2.01
3.01
CDCl3
H20
f1 (ppm)
1H (400 MHz, CDCl3)
III-I1
O
N
N
c
b
a
f
e
d

Figure IX-2

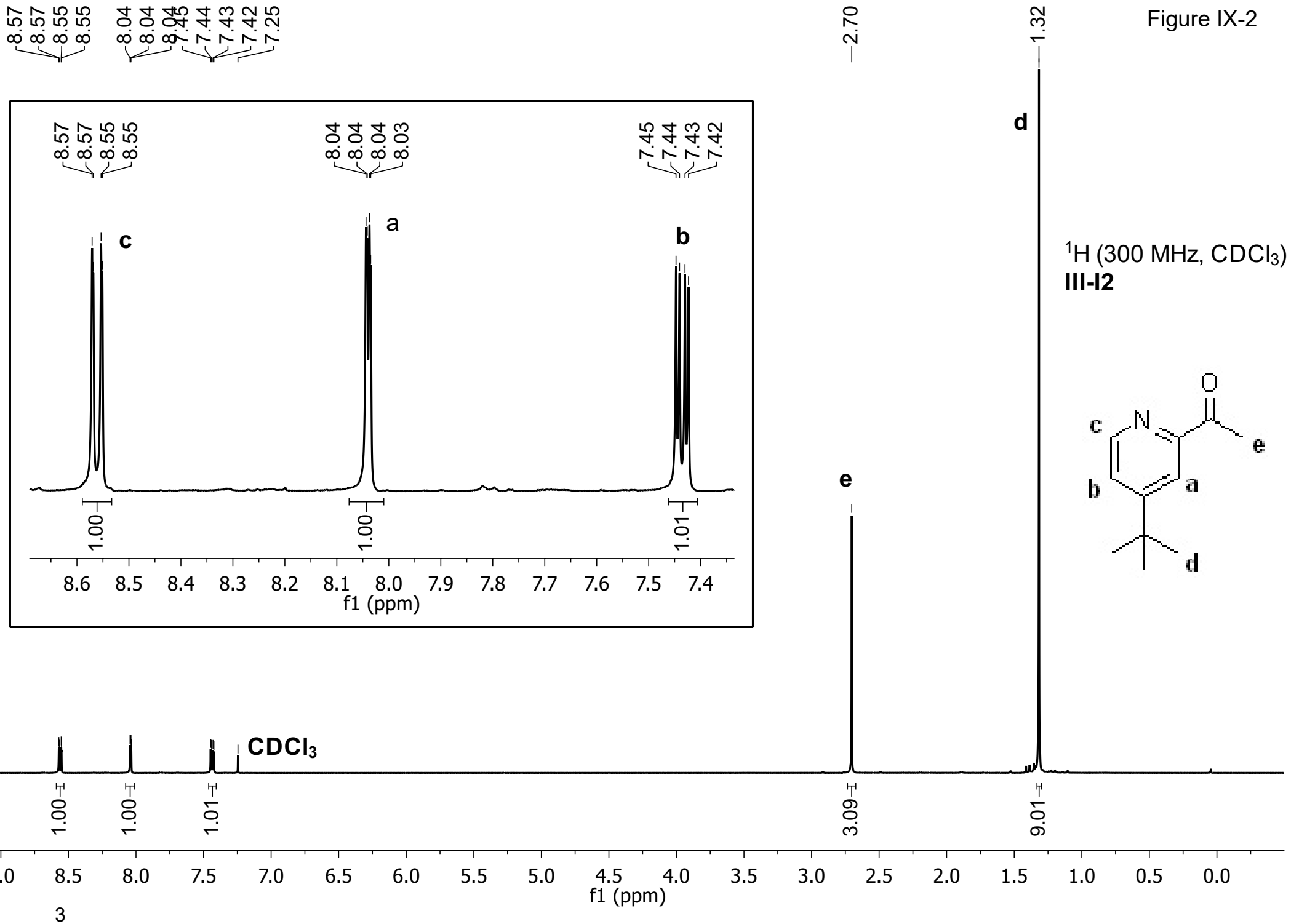

8.57
8.57
8.55
8.55
8.04
8.04
8.04
7.45
7.44
7.43
7.42
7.25
2.70
1.32
c
a
b
d
e
1.00
1.00
1.01
3.09
9.01
CDCl3
f1 (ppm)
1H (300 MHz, CDCl3)
III-I2

Figure IX-3

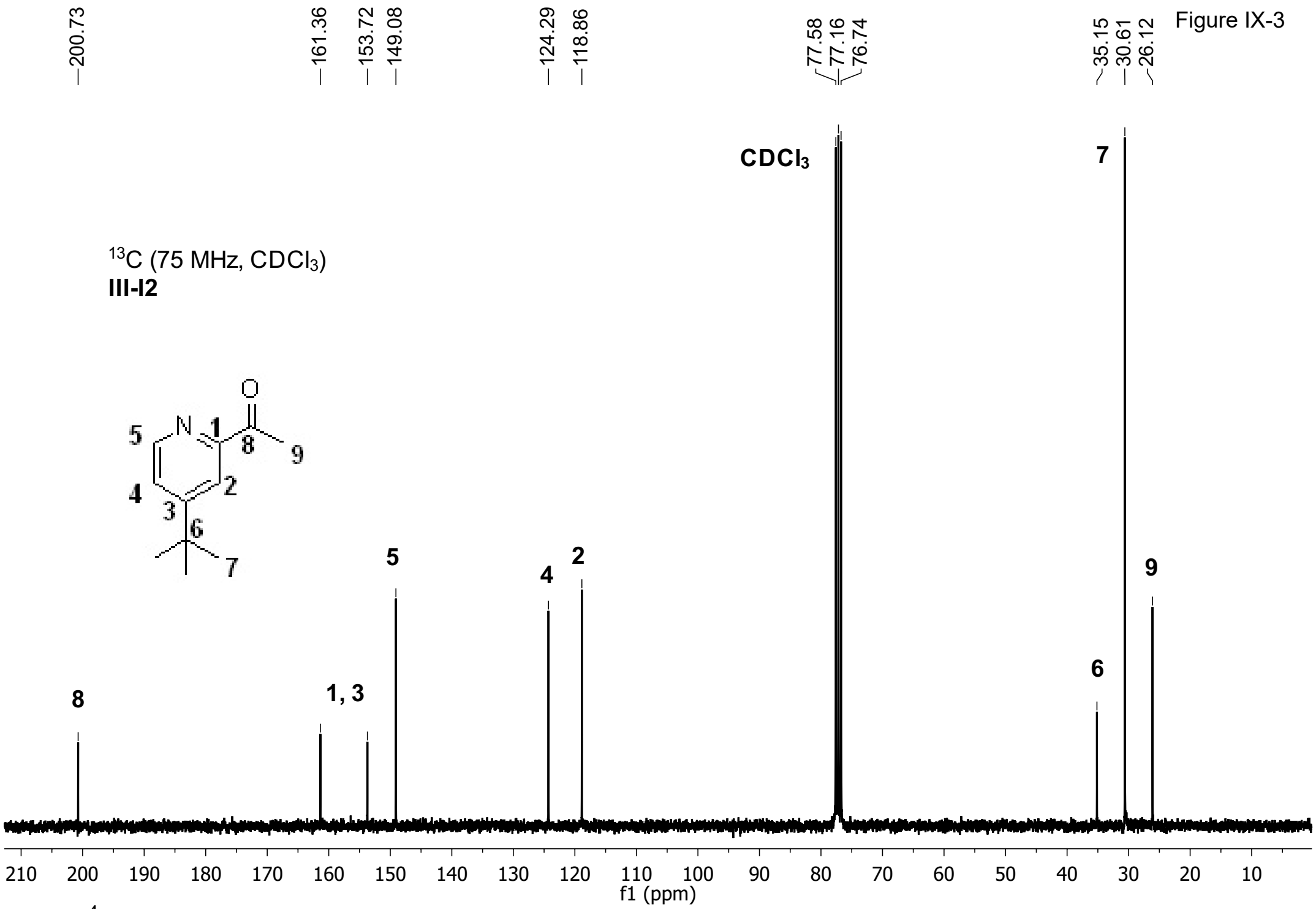
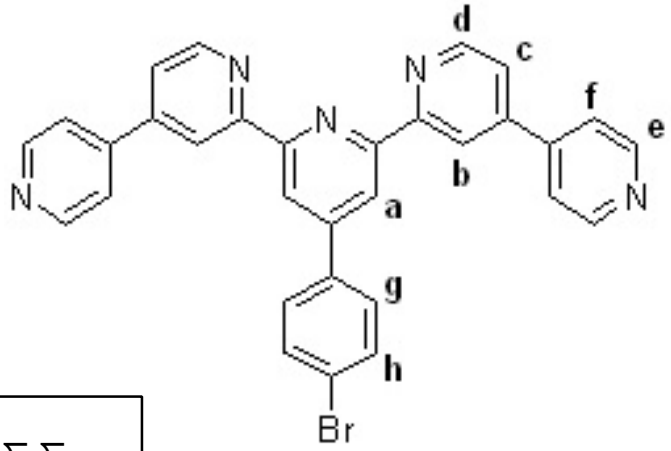

200.73
161.36
153.72
149.08
124.29
118.86
77.58
77.16
76.74
35.15
30.61
26.12
^{13}C (75 MHz, $CDCl_3$)
III-I2
$CDCl_3$
7
5
4
2
9
8
1, 3
6
f1 (ppm)

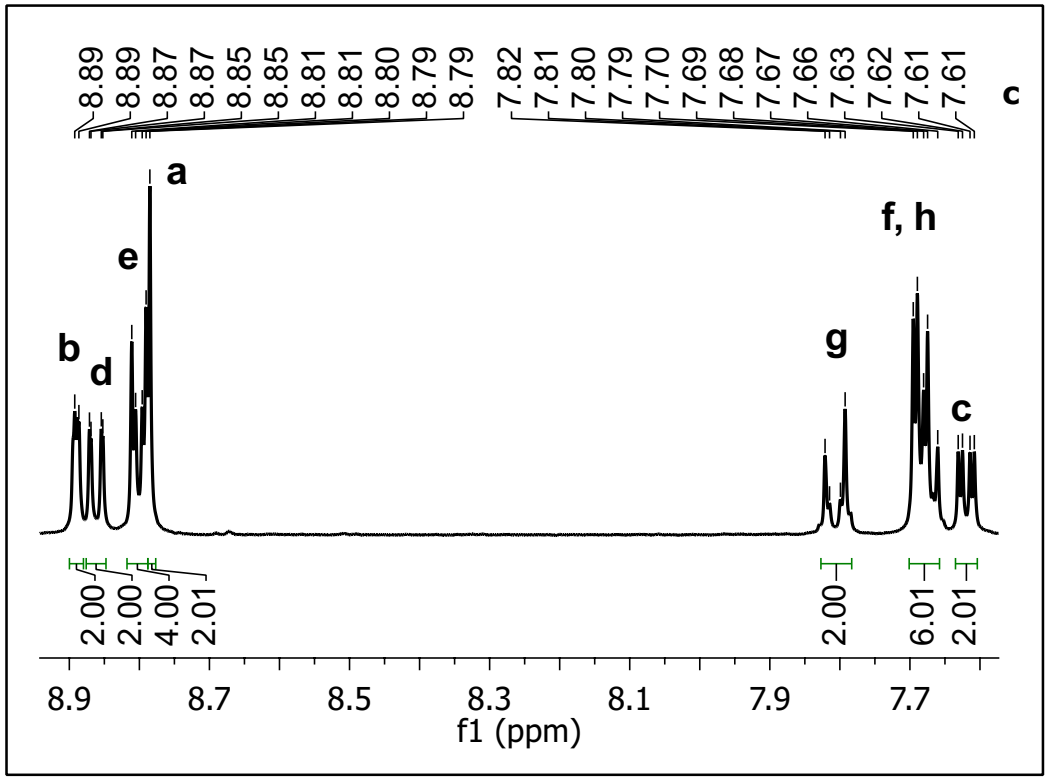
Figure IX-4



^{1}H (400 MHz, $CDCl_3$)
III-L1

$CDCl_3$

H_2O



2.00 2.00 4.00 2.01 2.00 6.01 2.01

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

f1 (ppm)

Figure IX-5

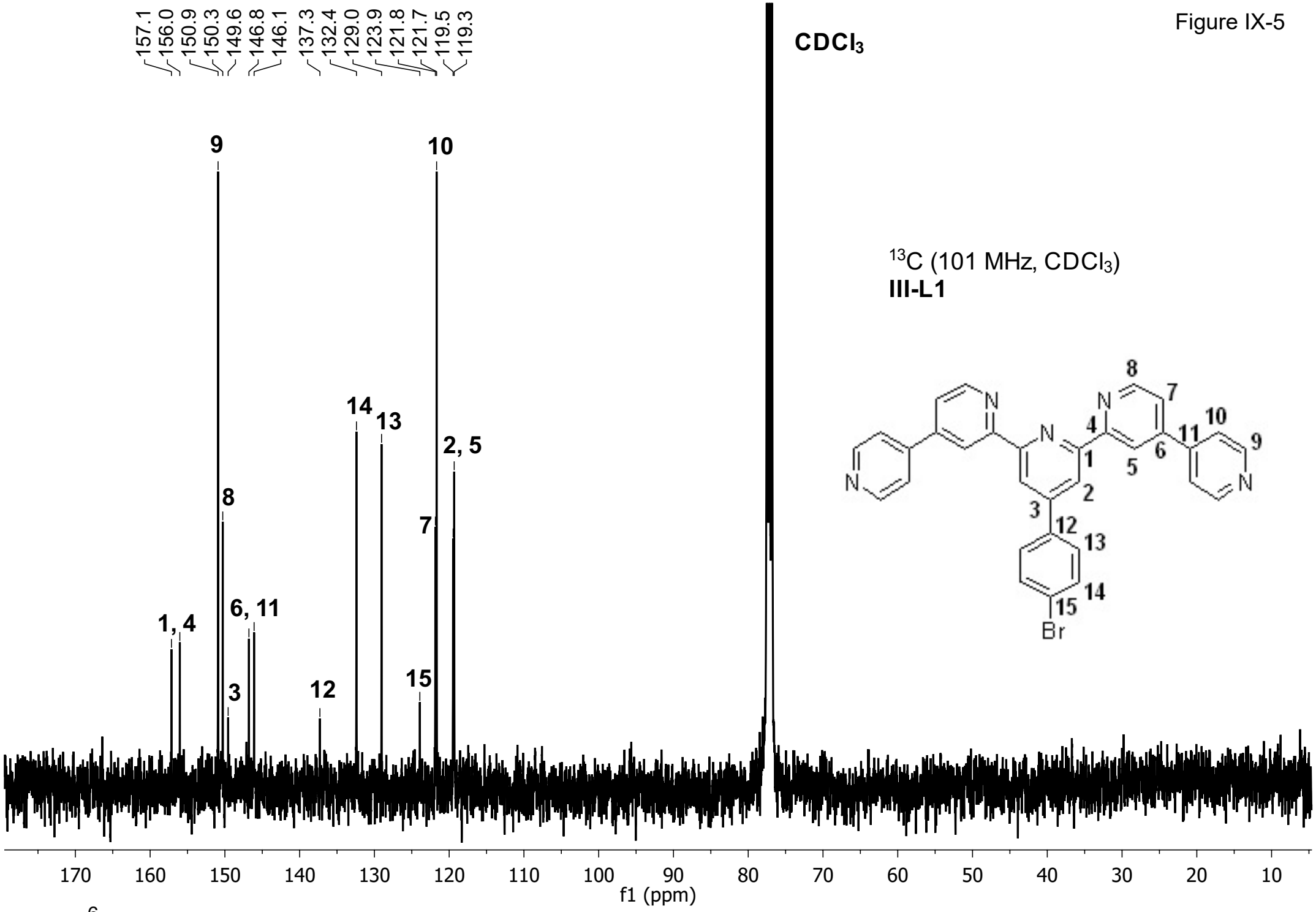
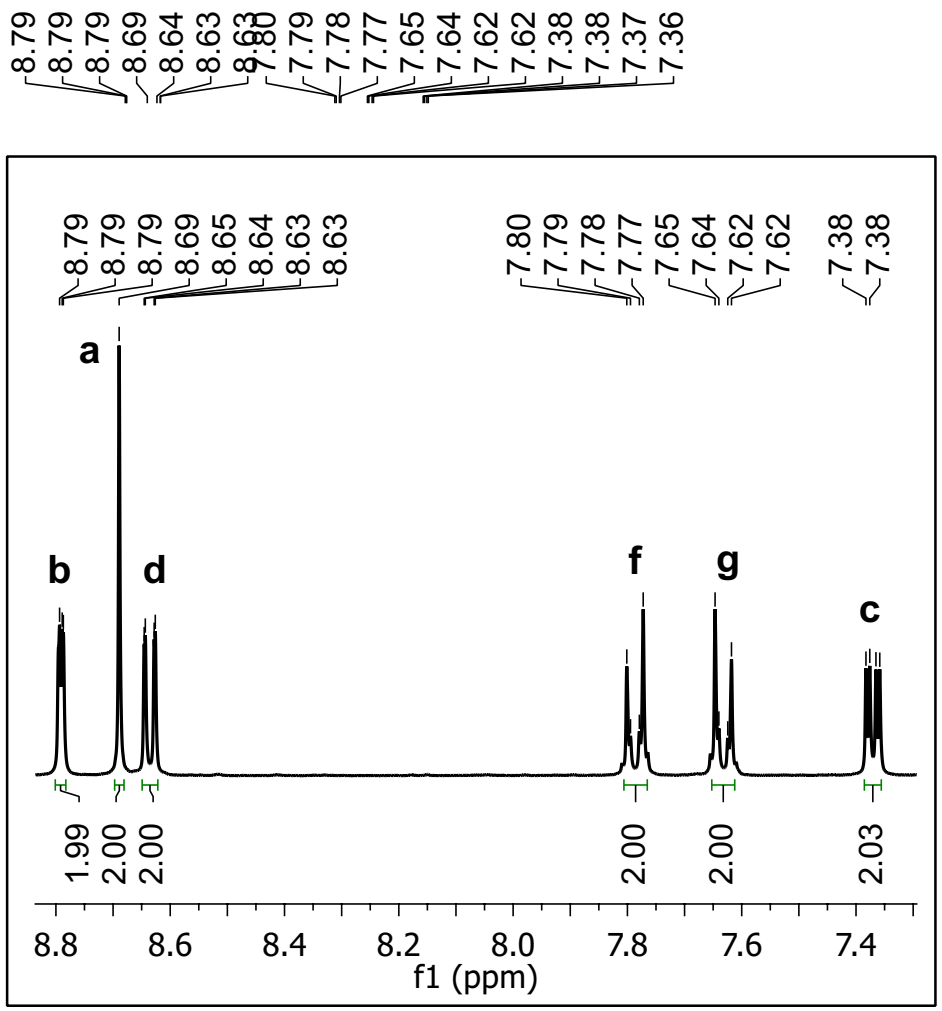

157.1
156.0
150.9
150.3
149.6
146.8
146.1
137.3
132.4
129.0
123.9
121.8
121.7
119.5
119.3
CDCl3
9
10
8
14
13
2, 5
7
6, 11
1, 4
3
12
15
13C (101 MHz, CDCl3)
III-L1
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Figure IX-6



^{1}H (300 MHz, $CDCl_3$)
III-L2

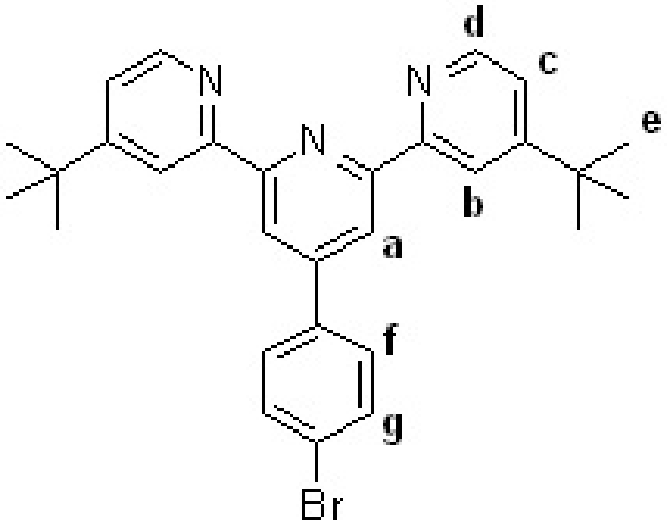


Figure IX-7

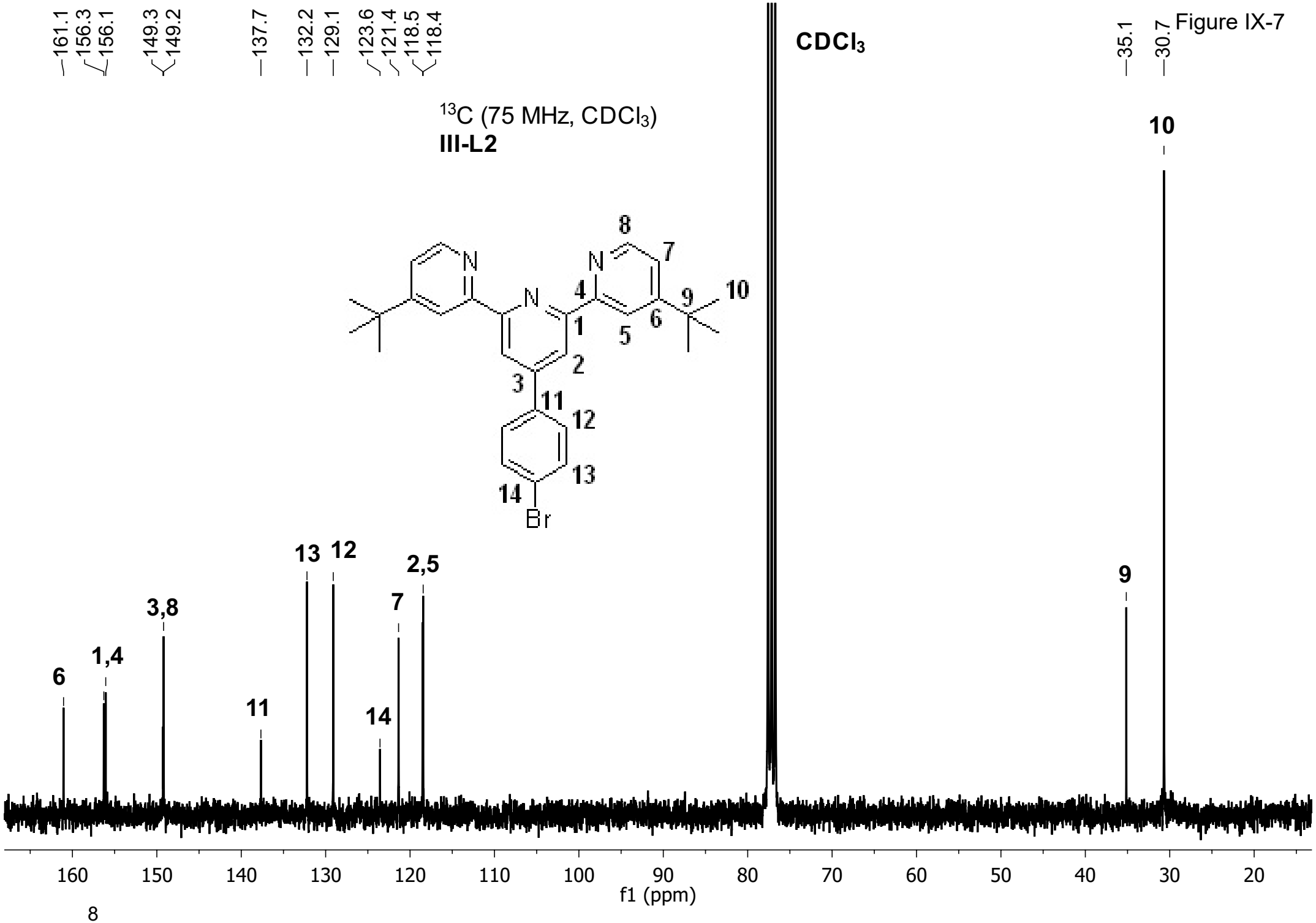

161.1
156.3
156.1
149.3
149.2
137.7
132.2
129.1
123.6
121.4
118.5
118.4
CDCl3
35.1
30.7
13C (75 MHz, CDCl3)
III-L2
10
9
13
12
2,5
7
3,8
1,4
6
11
14
Br
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

Figure IX-8

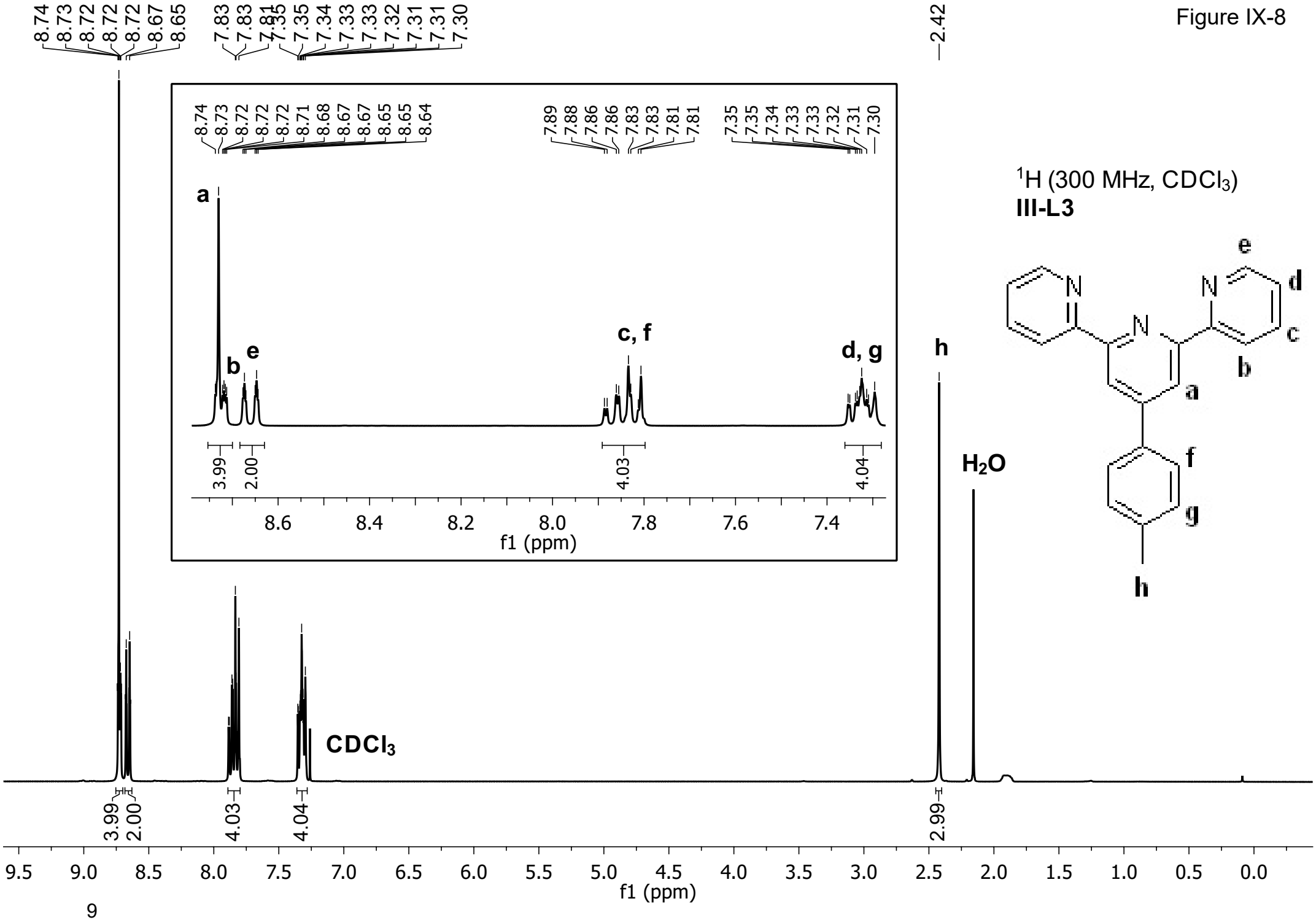


Figure IX-9

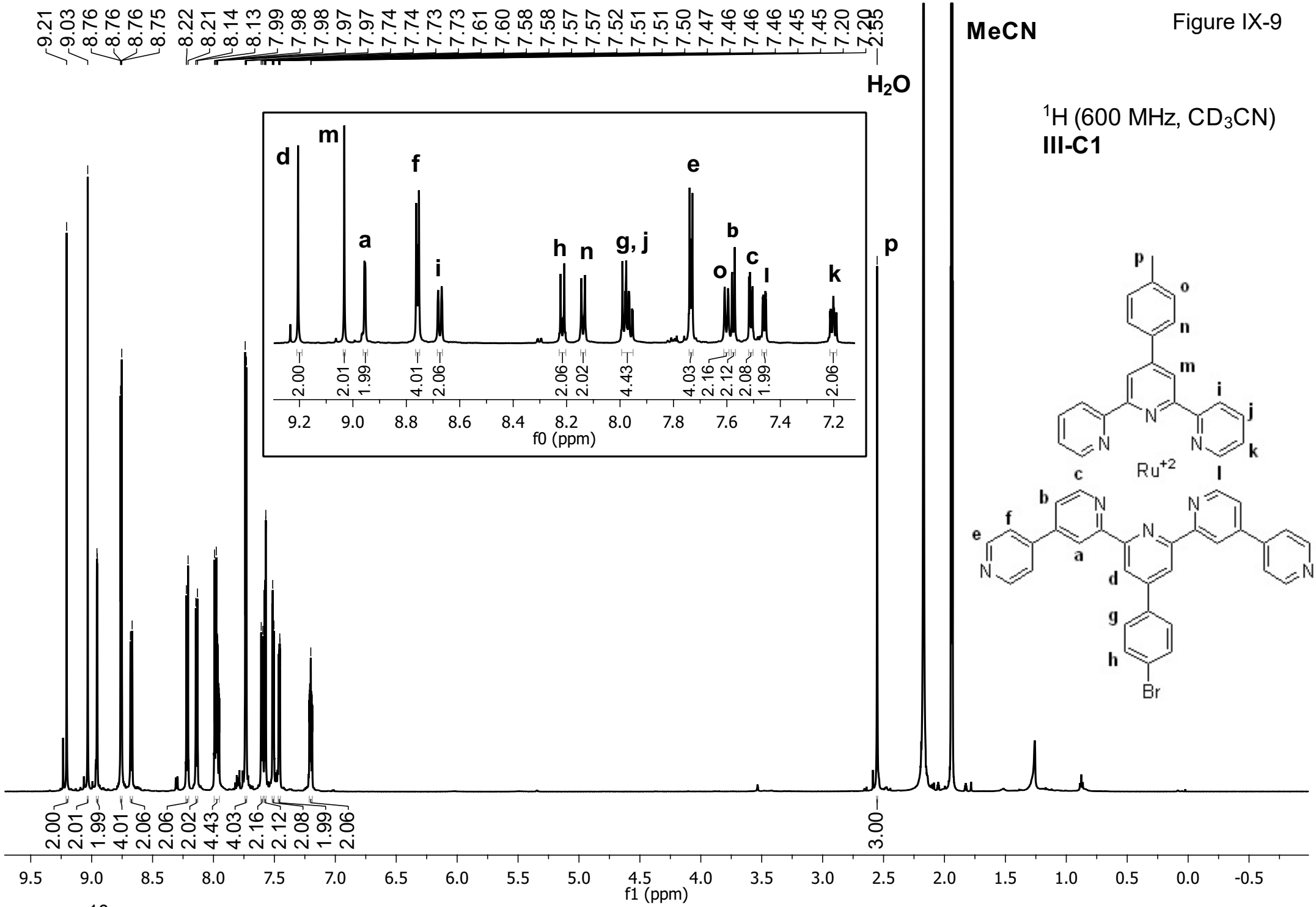
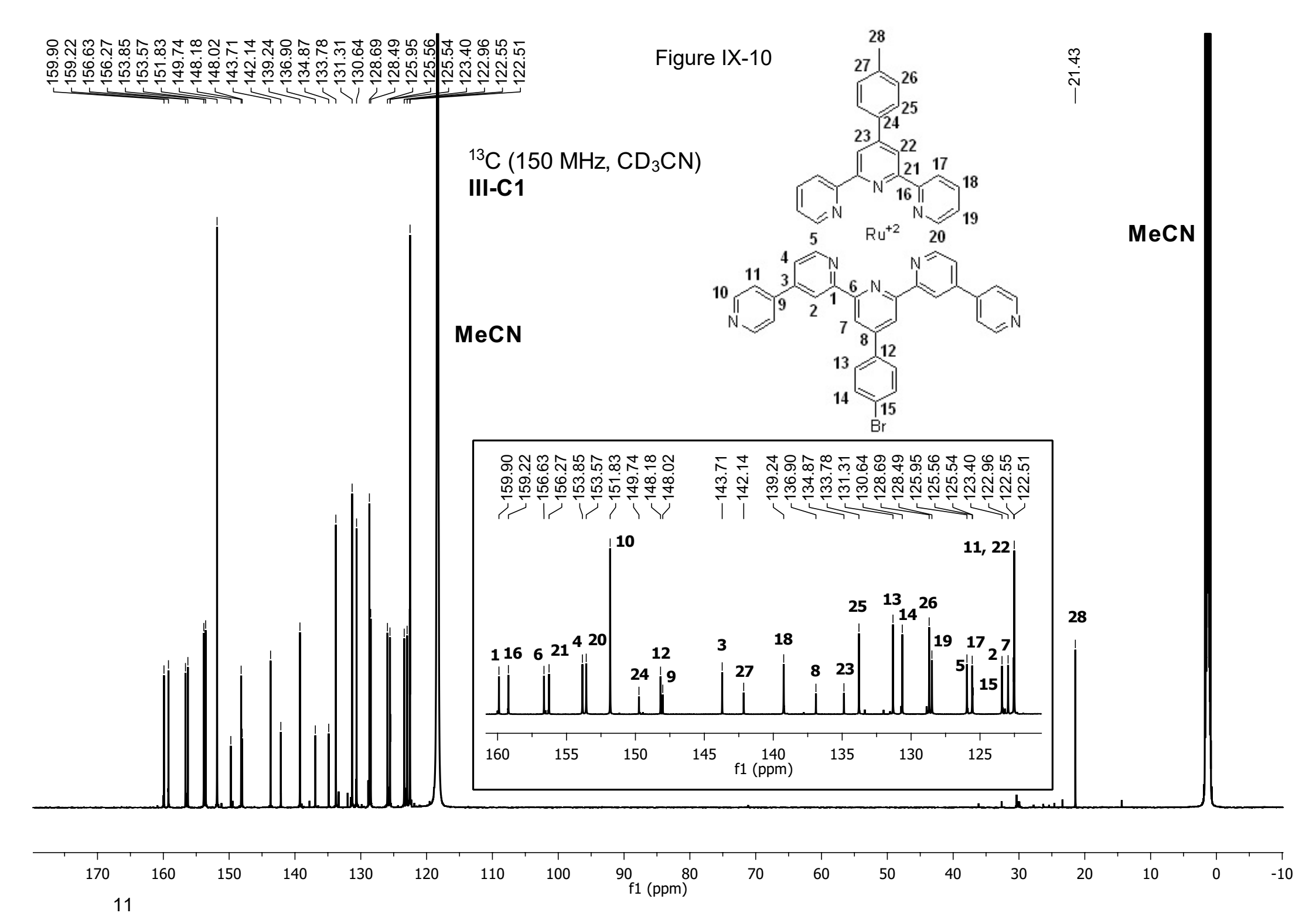

MeCN
H2O
1H (600 MHz, CD3CN)
III-C1
d
m
f
a
i
h
n
g, j
e
o
b
c
l
k
p
Ru+2
f1 (ppm)
f0 (ppm)

Figure IX-10



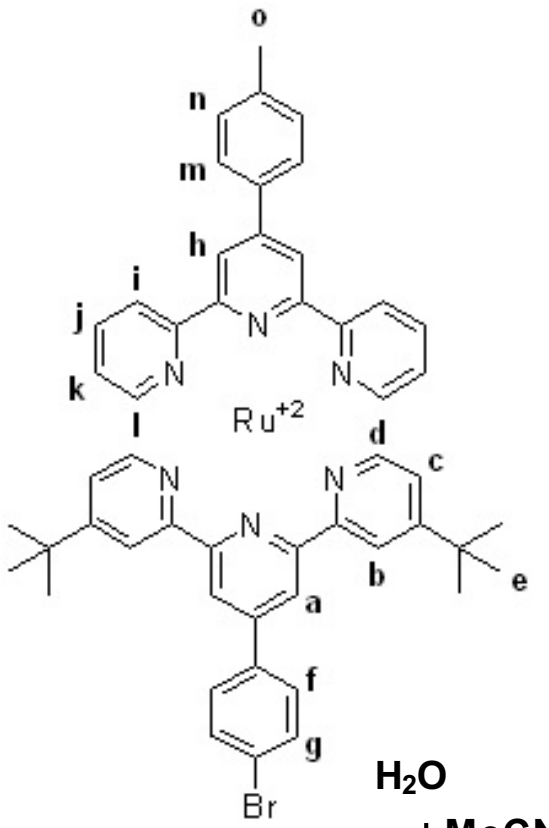
^{13}C (150 MHz, CD_3CN)

III-C1

Figure IX-11

^{1}H (300 MHz, CD_3CN)

III-C2



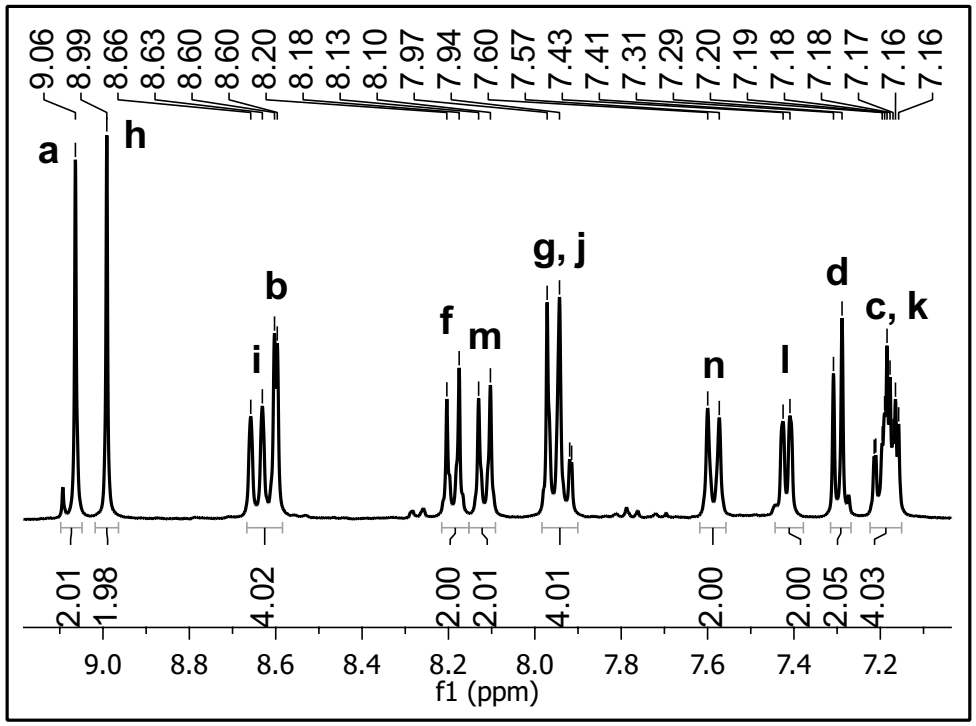


Figure IX-12

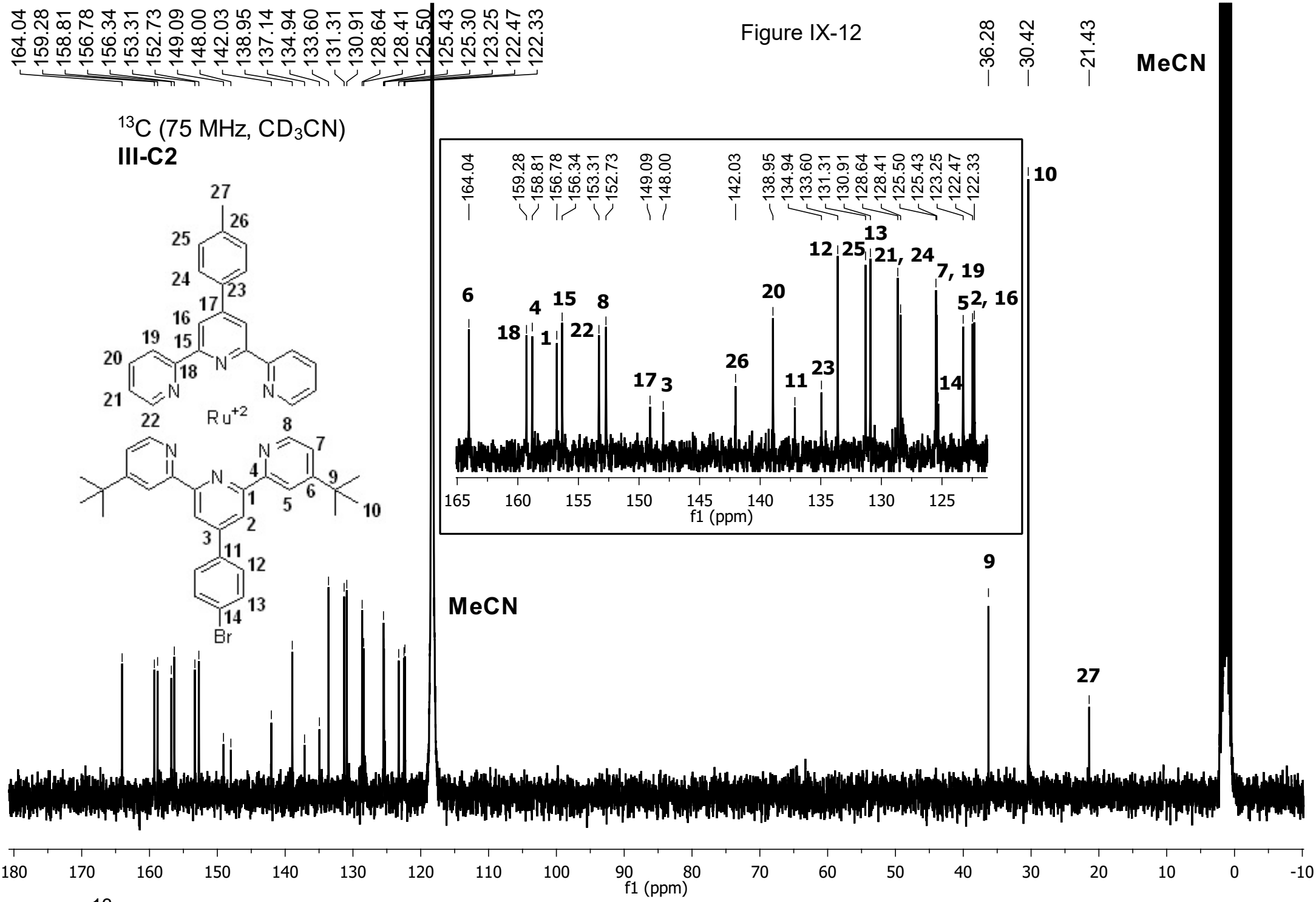

164.04
159.28
158.81
156.78
156.34
153.31
152.73
149.09
148.00
142.03
138.95
137.14
134.94
133.60
131.31
130.91
128.64
128.41
125.50
125.43
125.30
123.25
122.47
122.33
36.28
30.42
21.43
MeCN
13C (75 MHz, CD3CN)
III-C2
Ru+2
Br
MeCN
f1 (ppm)

Figure IX-13

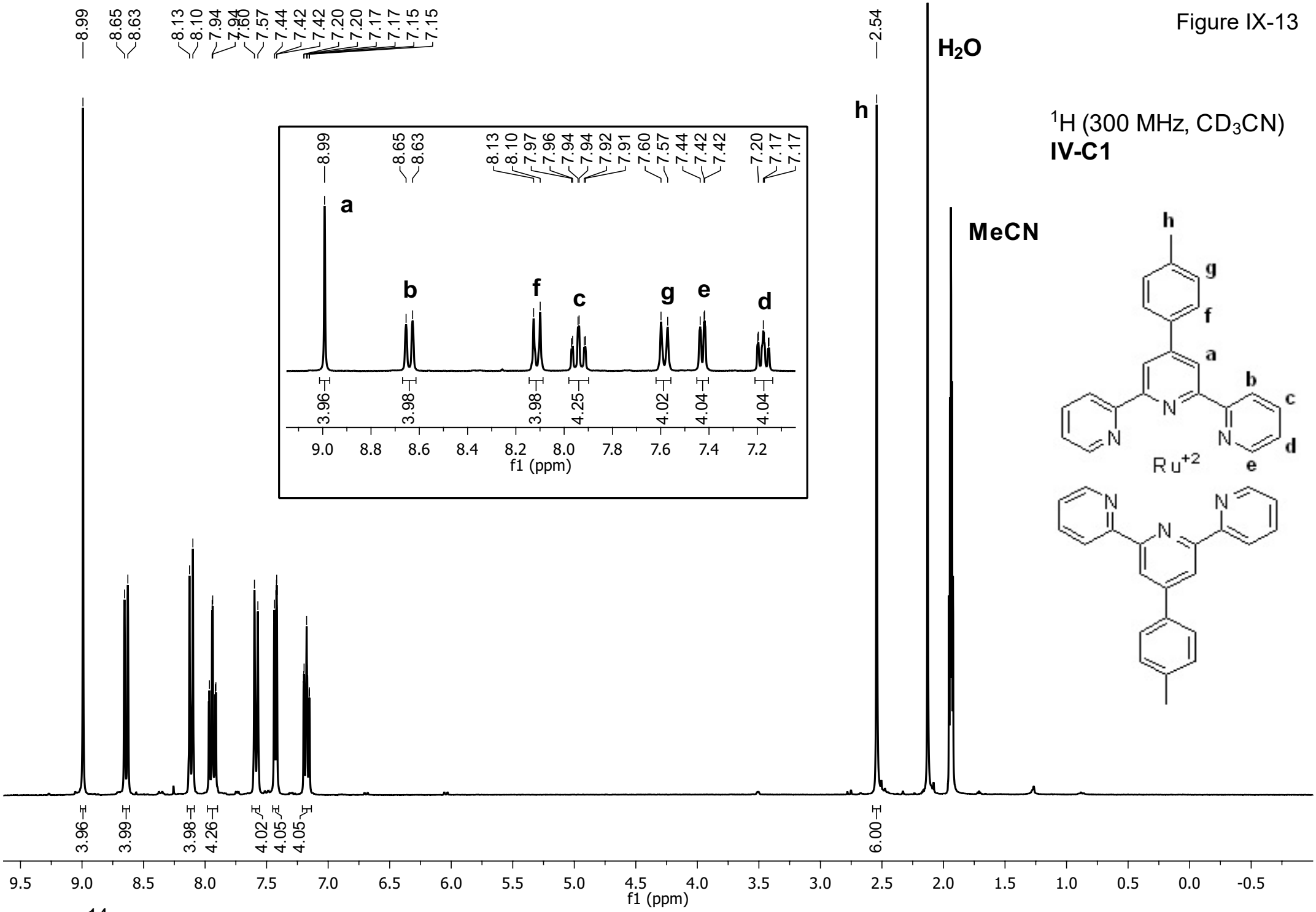

8.99
8.65
8.63
8.13
8.10
7.94
7.60
7.57
7.44
7.42
7.42
7.20
7.20
7.17
7.17
7.15
7.15
2.54
H2O
h
MeCN
1H (300 MHz, CD3CN)
IV-C1
a
b
f
c
g
e
d
3.96
3.99
3.98
4.26
4.02
4.05
4.05
6.00
f1 (ppm)
Ru+2

Figure IX-14

^{13}C (75 MHz, CD_3CN)

IV-C1

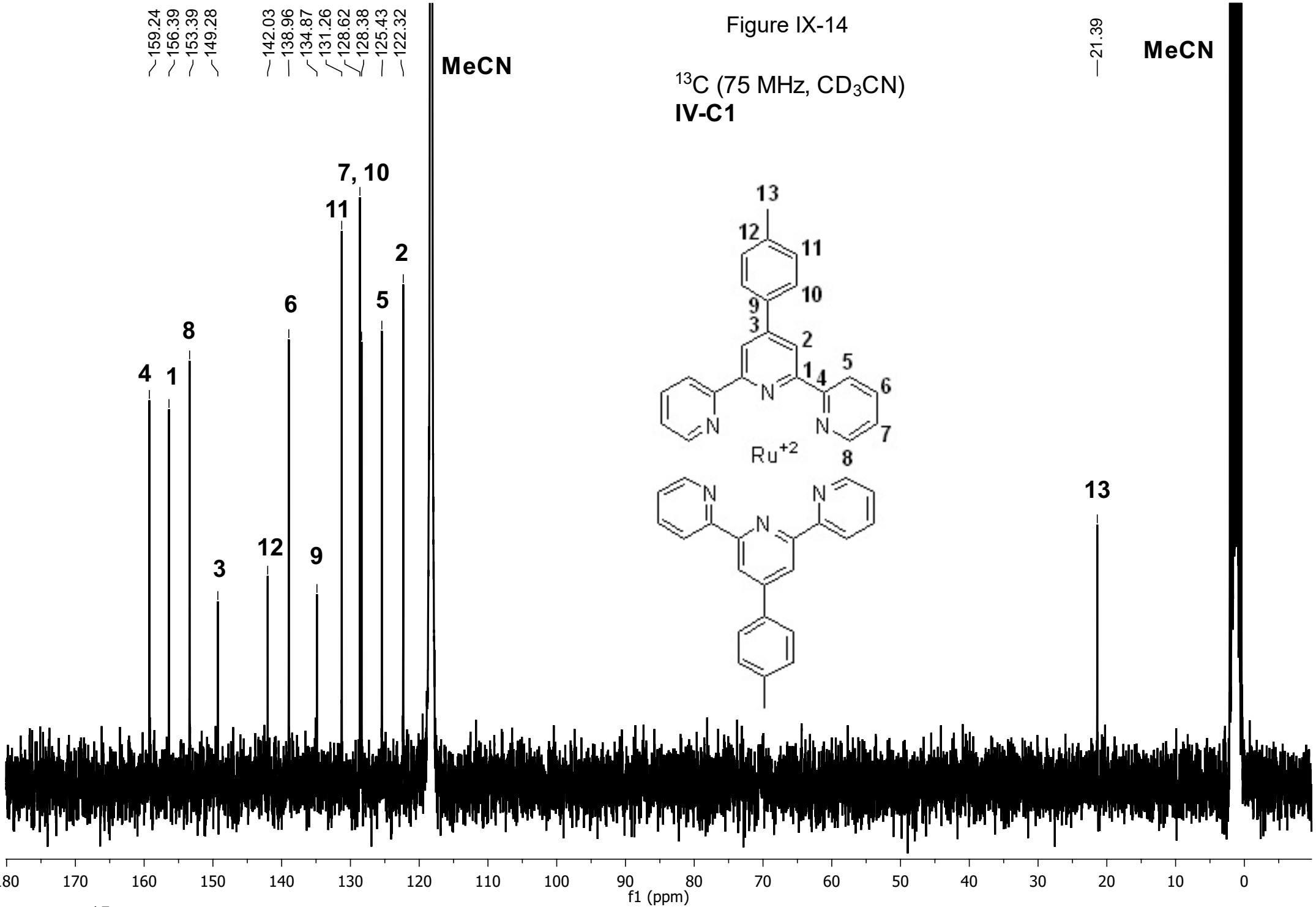


Figure IX-15

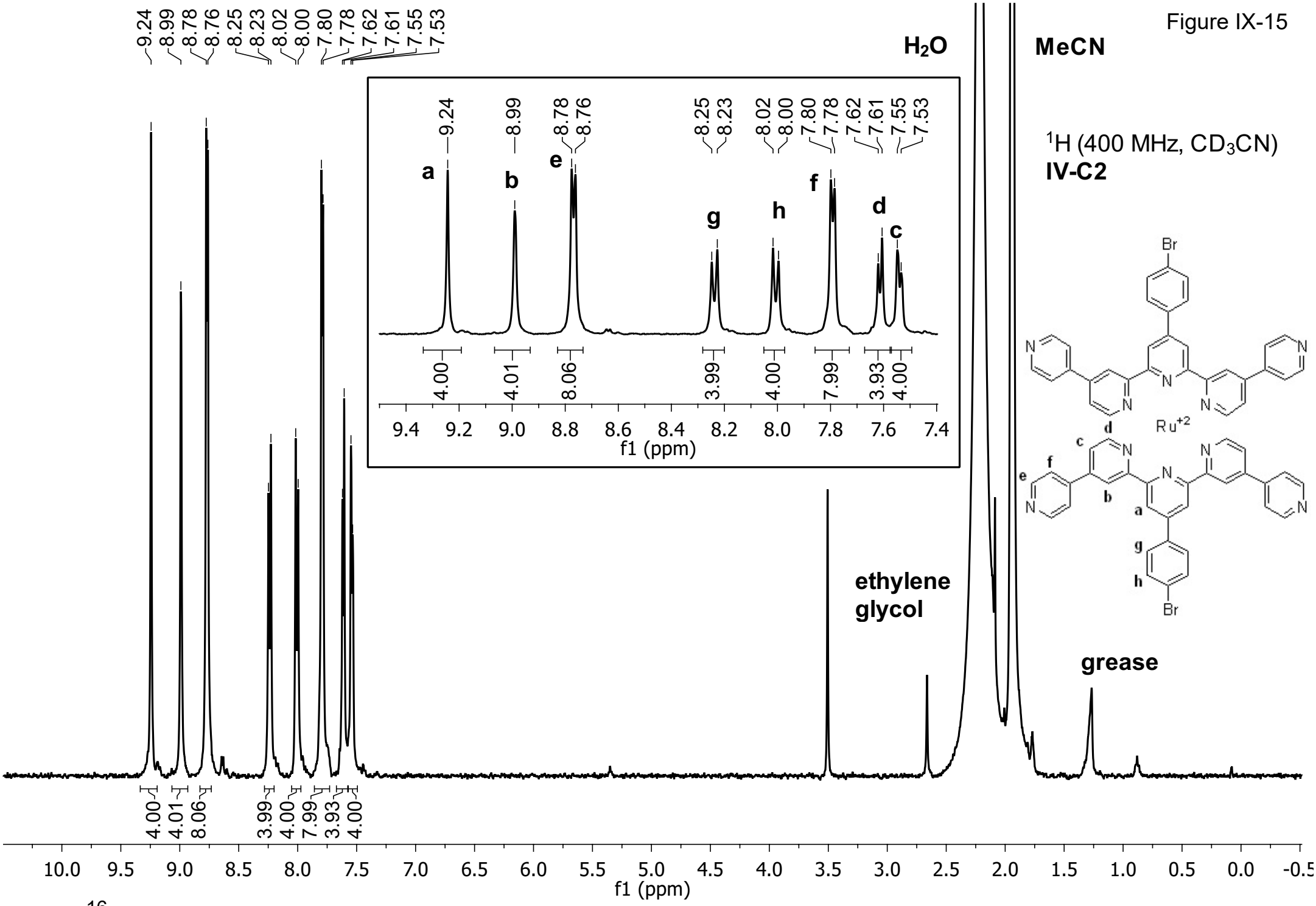

9.24
8.99
8.78
8.76
8.25
8.23
8.02
8.00
7.80
7.78
7.62
7.61
7.55
7.53
H2O
MeCN
1H (400 MHz, CD3CN)
IV-C2
a
b
e
g
h
f
d
c
4.00
4.01
8.06
3.99
4.00
7.99
3.93
4.00
f1 (ppm)
ethylene glycol
grease
Br
Ru+2

Figure IX-16

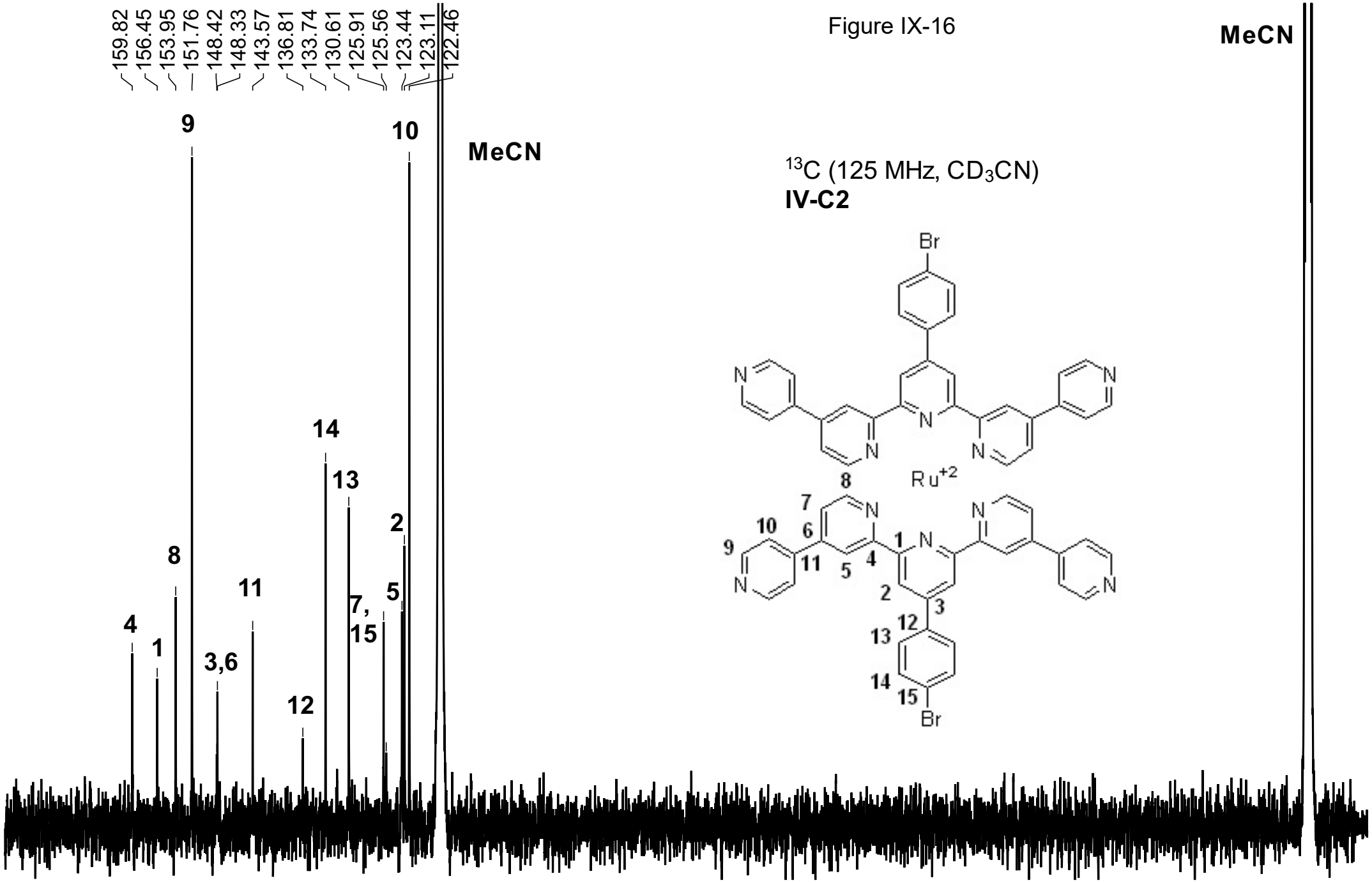

159.82
156.45
153.95
151.76
148.42
148.33
143.57
136.81
133.74
130.61
125.91
125.56
123.44
123.11
122.46
MeCN
MeCN
9
10
14
13
2
8
11
4
1
3,6
7,
15
5
12
^{13}C (125 MHz, CD_3CN)
IV-C2
Br
Ru+2
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Figure IX-17

^{1}H (300 MHz, CD_3CN)
V-C1

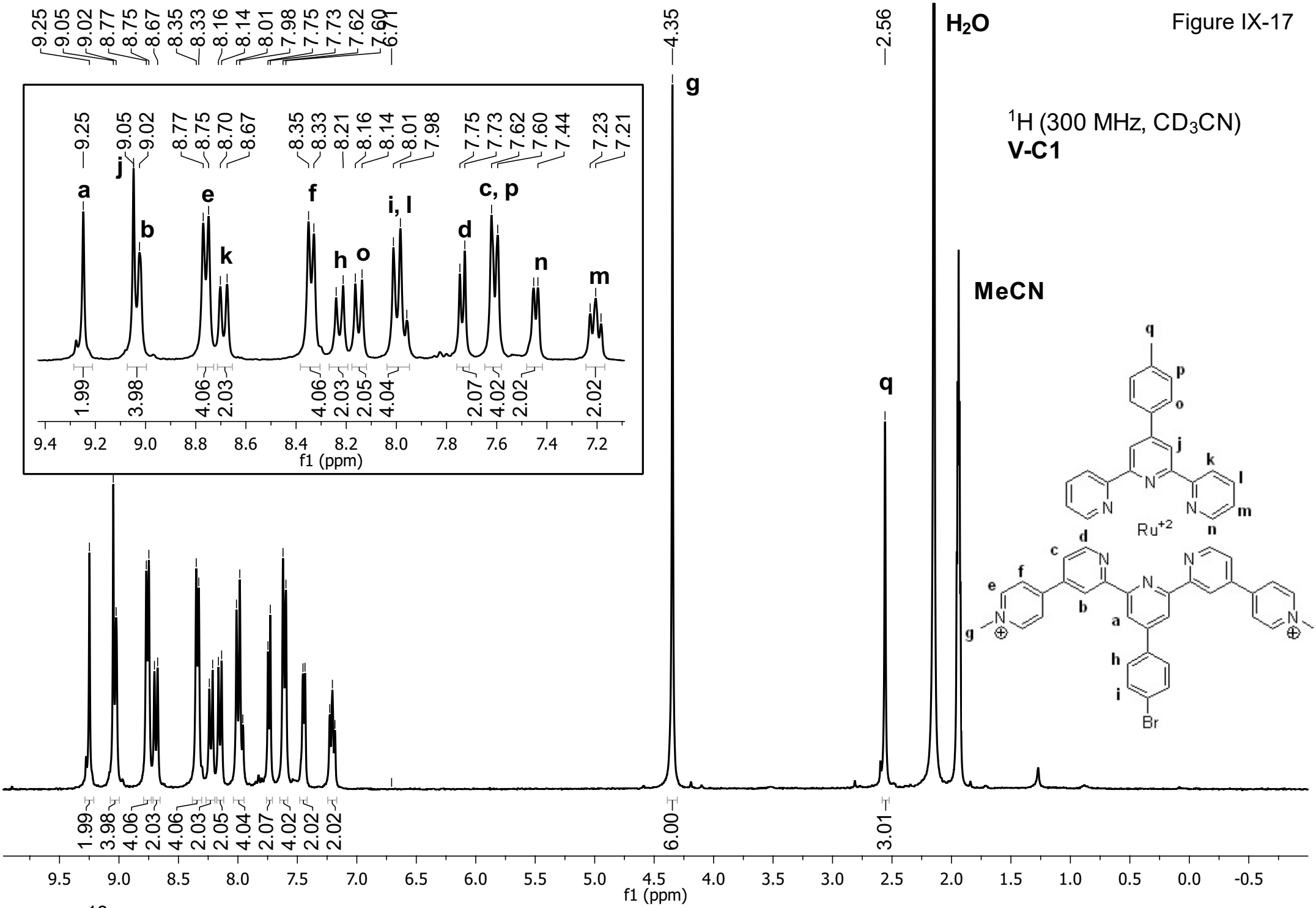


Figure IX-18

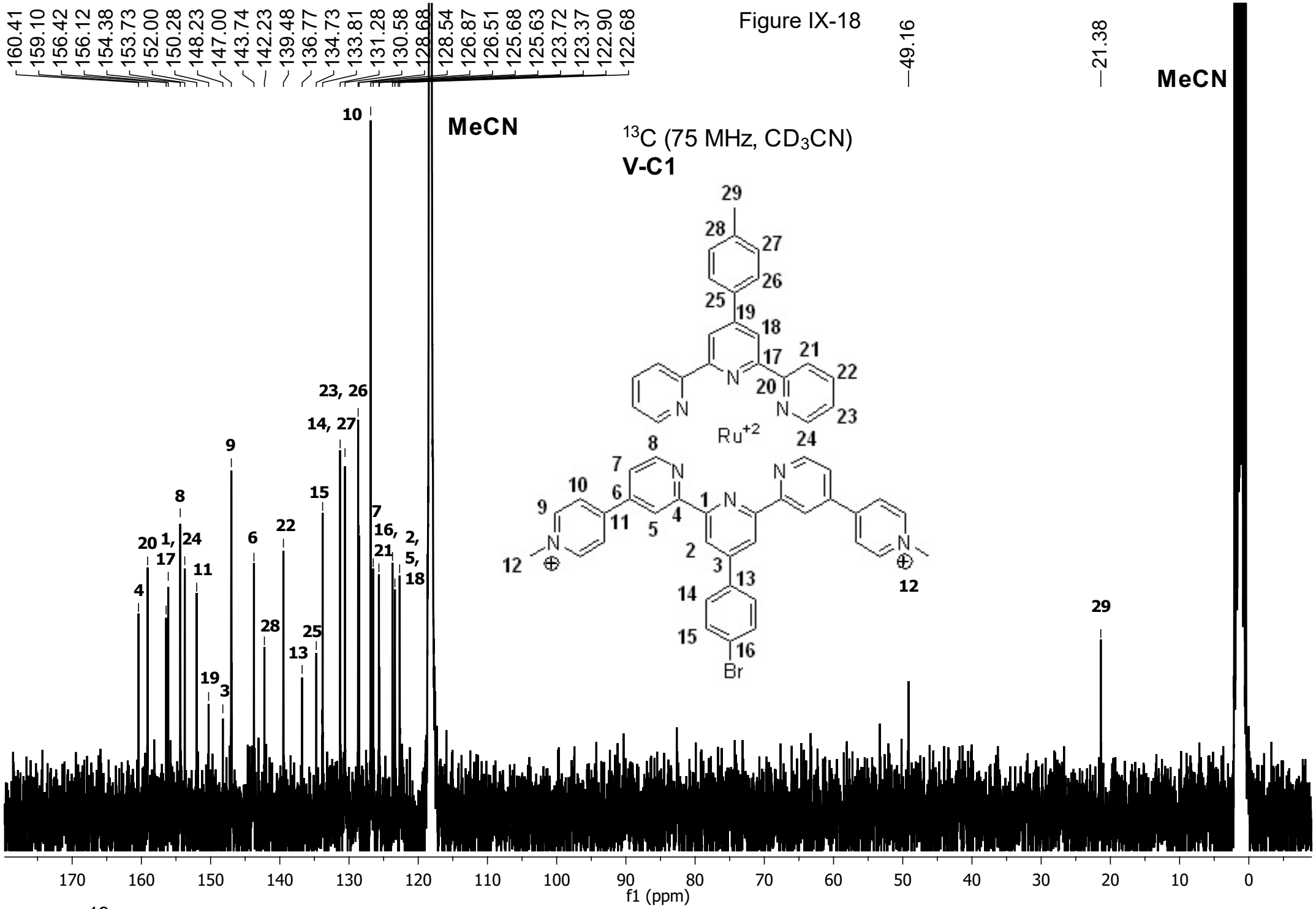

160.41
159.10
156.42
156.12
154.38
153.73
152.00
150.28
148.23
147.00
143.74
142.23
139.48
136.77
134.73
133.81
131.28
130.58
128.68
128.54
126.87
126.51
125.68
125.63
123.72
123.37
122.90
122.68
49.16
21.38
MeCN
MeCN
^{13}C (75 MHz, CD_3CN)
V-C1
Ru+2
Br
f1 (ppm)

Figure IX-19

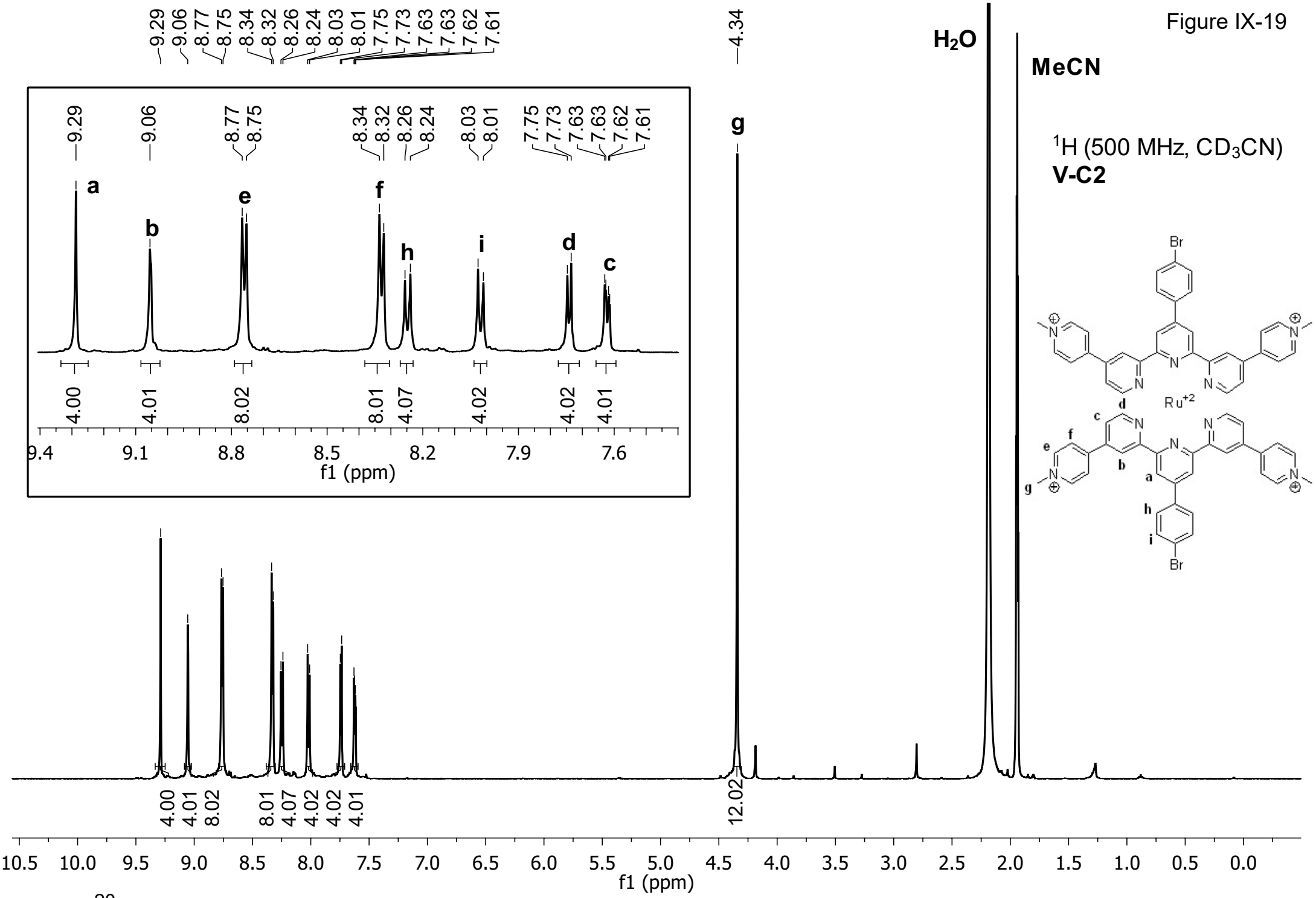

9.29
9.06
8.77
8.75
8.34
8.32
8.26
8.24
8.03
8.01
7.75
7.73
7.63
7.63
7.62
7.61
4.34
H2O
MeCN
g
a
b
e
f
h
i
d
c
4.00
4.01
8.02
8.01
4.07
4.02
4.02
4.01
12.02
f1 (ppm)
1H (500 MHz, CD3CN)
V-C2
Br
Ru+2
Br

Figure IX-20

^{13}C (125 MHz, CD_3CN)

V-C2

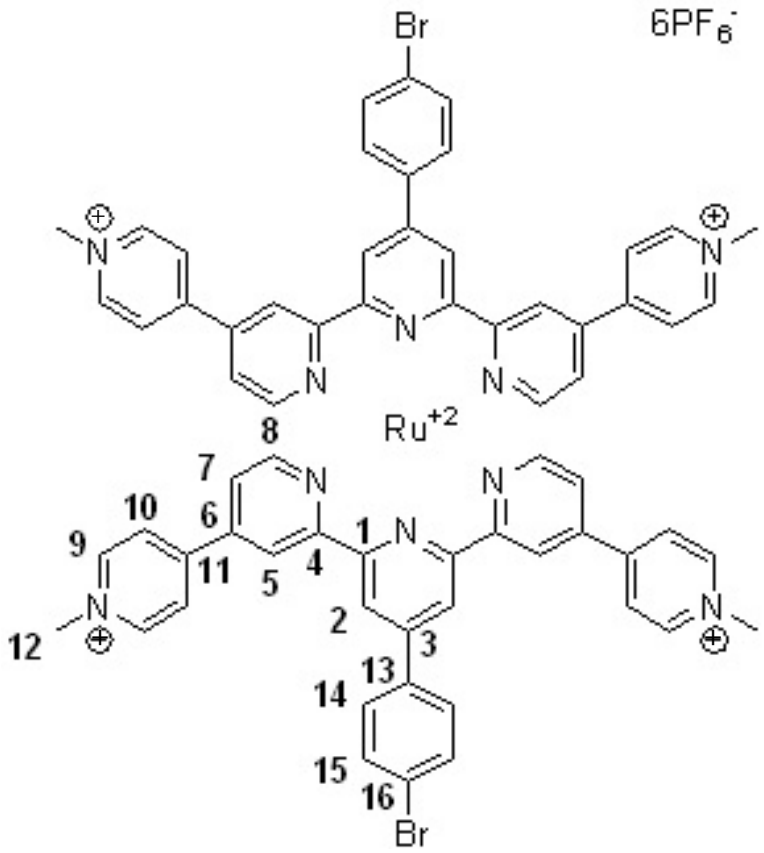
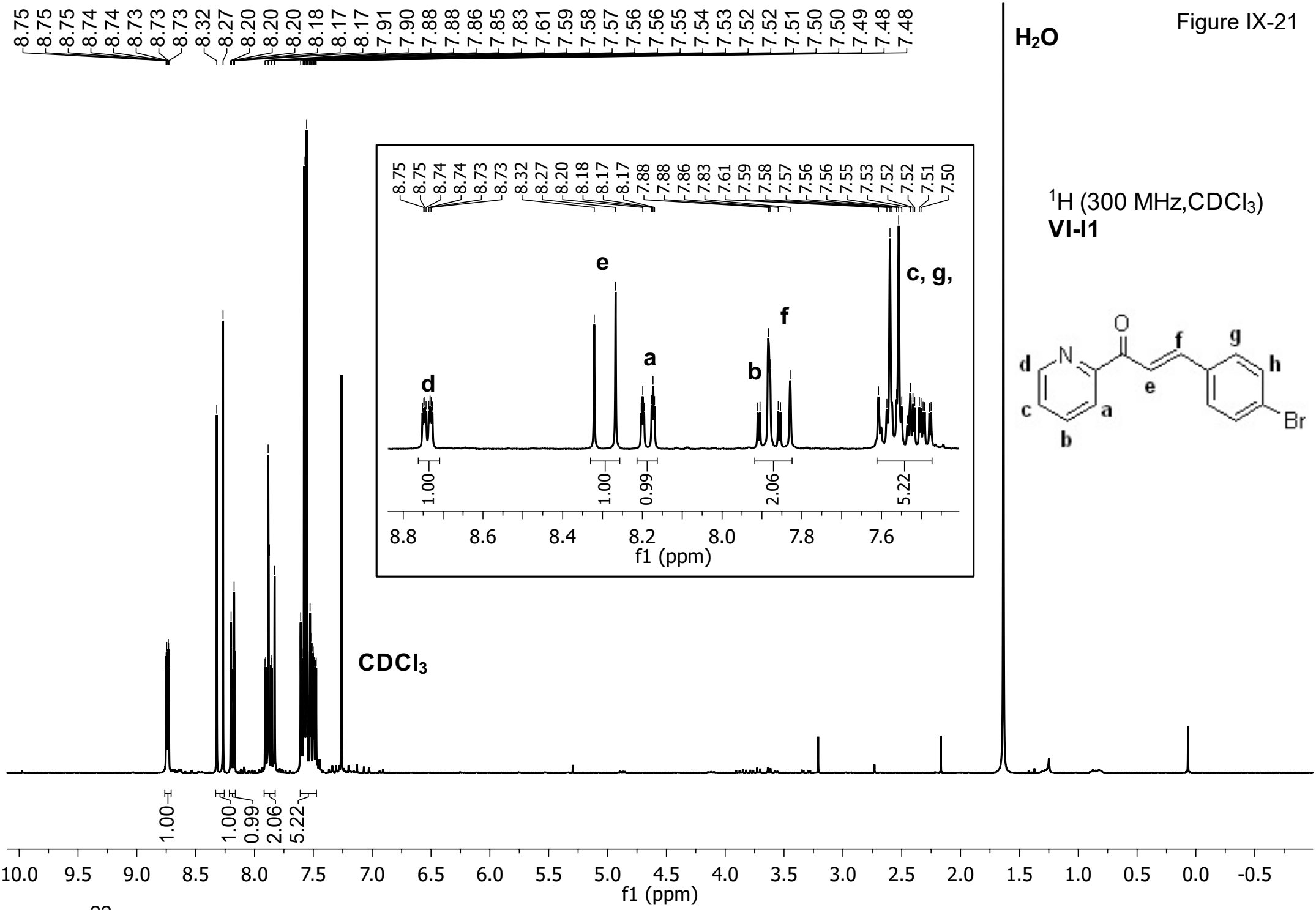


Figure IX-21



^{1}H (300 MHz,$CDCl_3$)

VI-I1

Figure IX-22

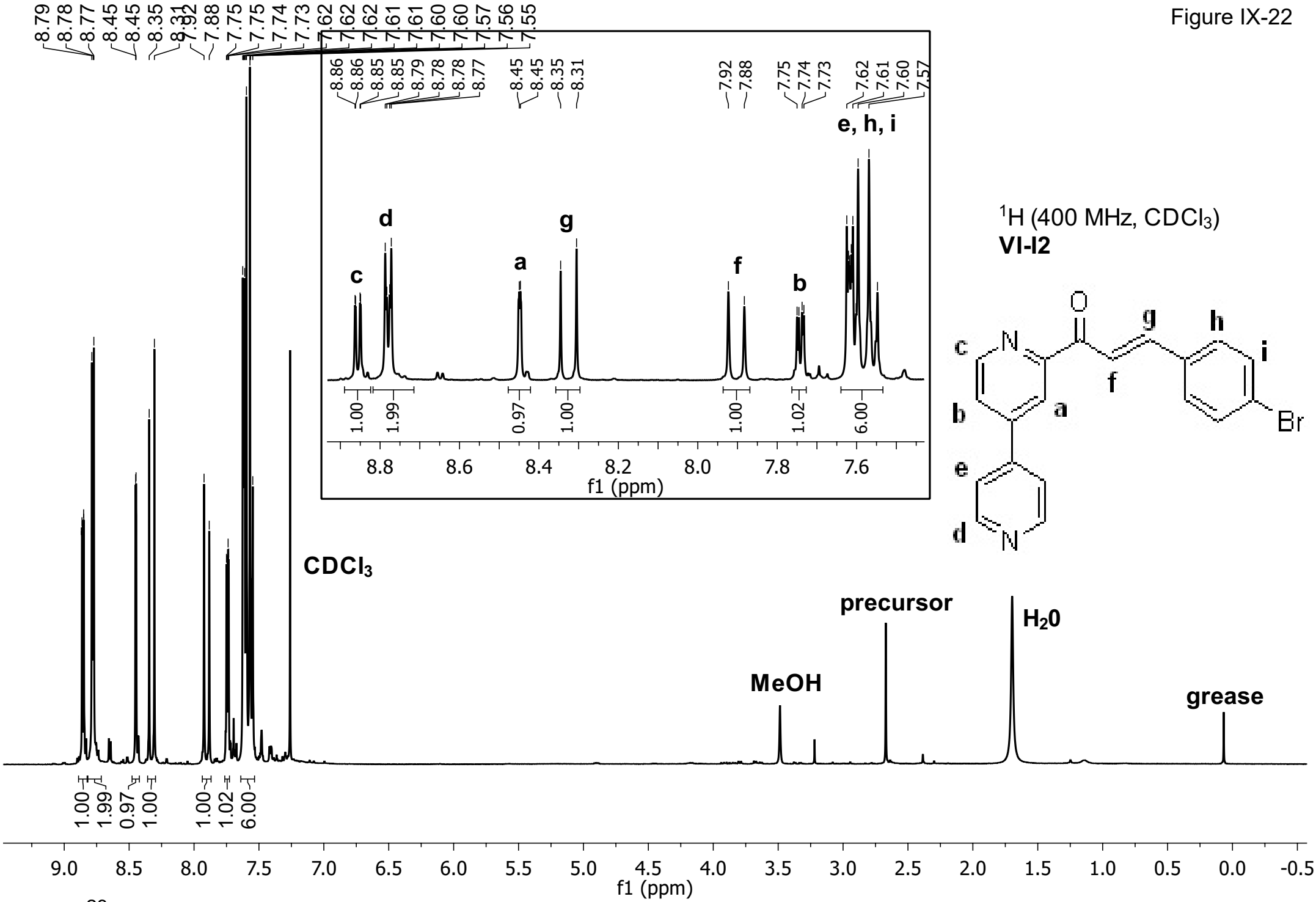

8.79 8.78 8.77 8.45 8.45 8.35 8.31 7.92 7.88 7.75 7.75 7.74 7.73 7.62 7.62 7.62 7.61 7.61 7.60 7.60 7.57 7.56 7.55
8.86 8.86 8.85 8.85 8.79 8.78 8.78 8.77 8.45 8.45 8.35 8.31 7.92 7.88 7.75 7.74 7.73 7.62 7.61 7.60 7.57
c
d
a
g
f
b
e, h, i
1.00 1.99 0.97 1.00 1.02 6.00
8.8 8.6 8.4 8.2 8.0 7.8 7.6
f1 (ppm)
^{1}H (400 MHz, $CDCl_3$)
VI-I2
c N O g h i
b a f Br
e
d N
$CDCl_3$
precursor
H_20
MeOH
grease
1.00 1.99 0.97 1.00 1.00 1.02 6.00
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)

Figure IX-23

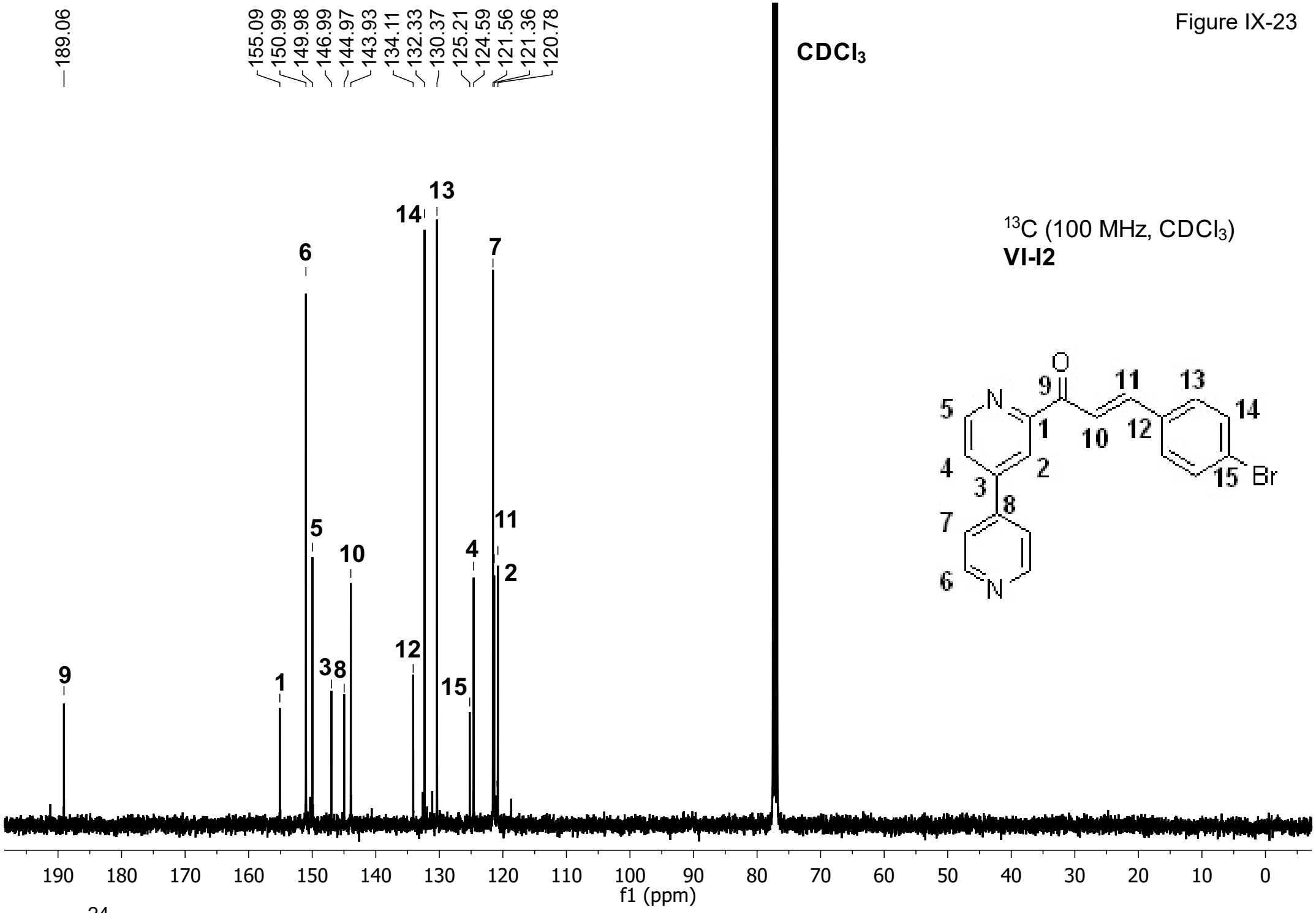

189.06
155.09
150.99
149.98
146.99
144.97
143.93
134.11
132.33
130.37
125.21
124.59
121.56
121.36
120.78
CDCl3
13
14
6
7
5
10
4
11
2
12
9
1
3
8
15
13C (100 MHz, CDCl3)
VI-I2
O
N
Br
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Figure IX-24

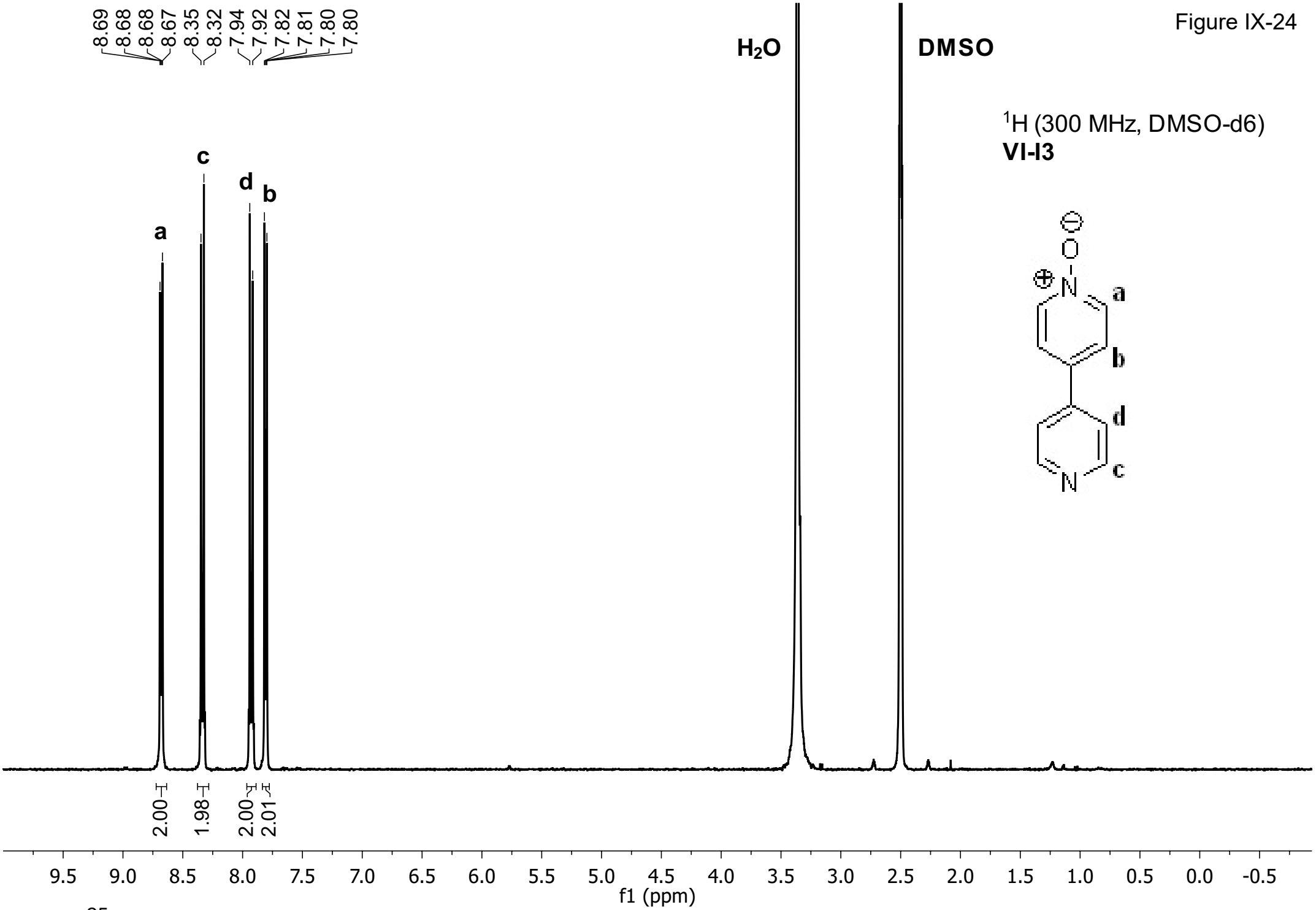

8.69
8.68
8.68
8.67
8.35
8.32
7.94
7.92
7.82
7.81
7.80
7.80
H2O
DMSO
1H (300 MHz, DMSO-d6)
VI-I3
a
c
d
b
2.00
1.98
2.00
2.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

Figure IX-25

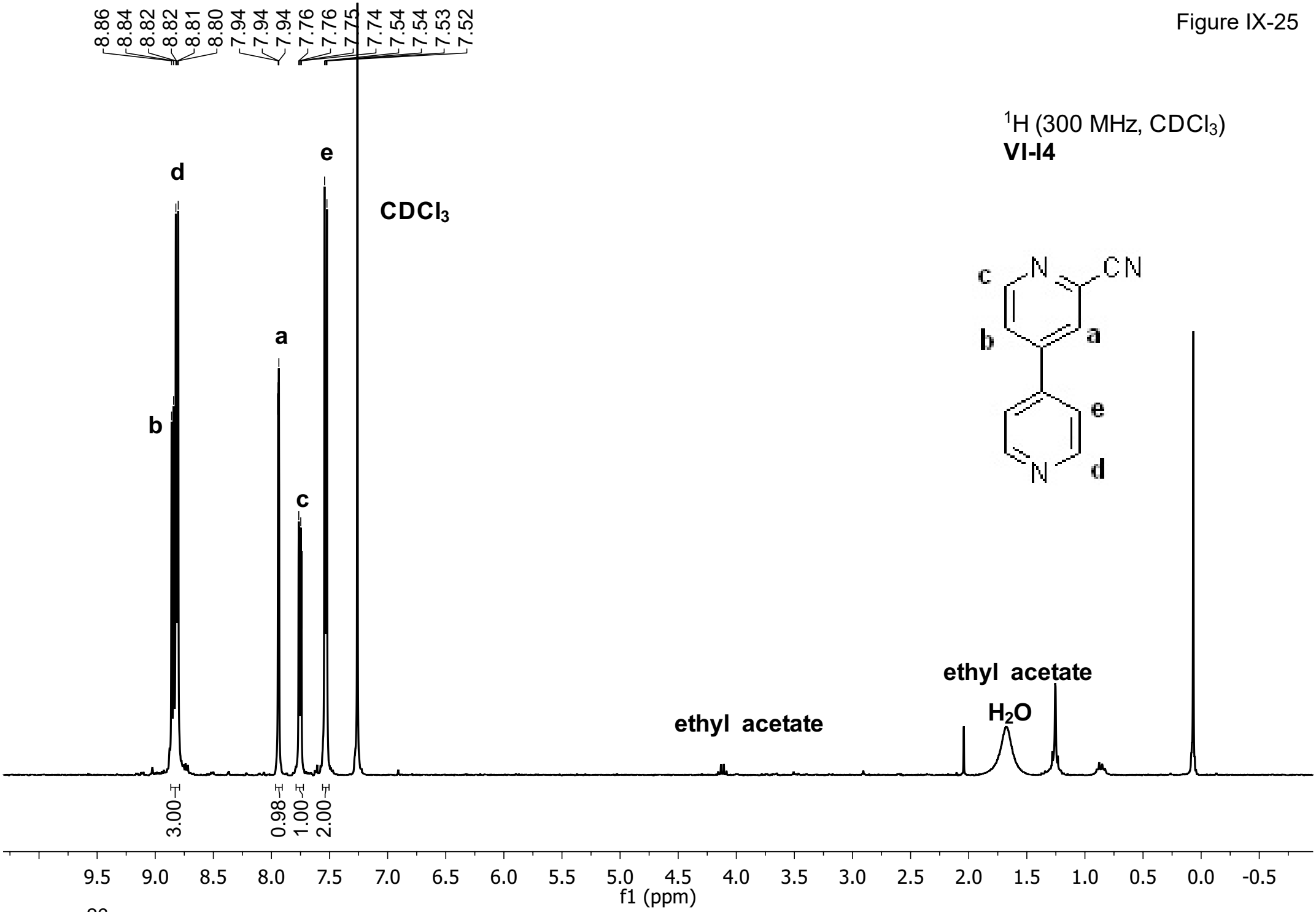

8.86
8.84
8.82
8.82
8.81
8.80
7.94
7.94
7.94
7.76
7.76
7.75
7.74
7.54
7.54
7.53
7.52
^{1}H (300 MHz, $CDCl_3$)
VI-I4
d
e
$CDCl_3$
a
b
c
N
CN
c
b
a
e
d
N
ethyl acetate
ethyl acetate
H_2O
3.00
0.98
1.00
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

Figure IX-26

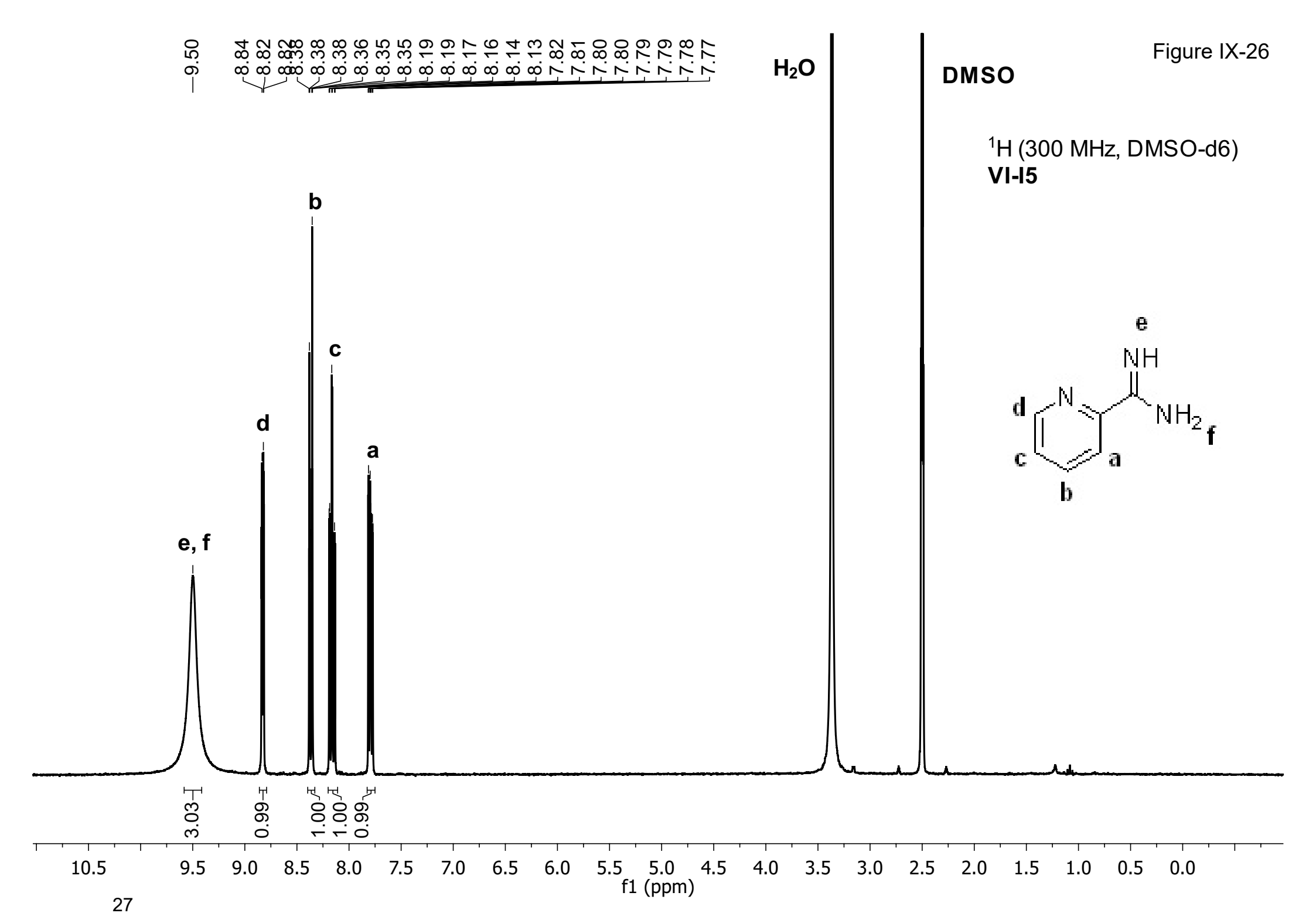

9.50
8.84
8.82
8.38
8.38
8.36
8.35
8.35
8.19
8.19
8.17
8.16
8.14
8.13
7.82
7.81
7.80
7.80
7.79
7.79
7.78
7.77
H2O
DMSO
1H (300 MHz, DMSO-d6)
VI-I5
e, f
d
b
c
a
3.03
0.99
1.00
1.00
0.99
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

Figure IX-27

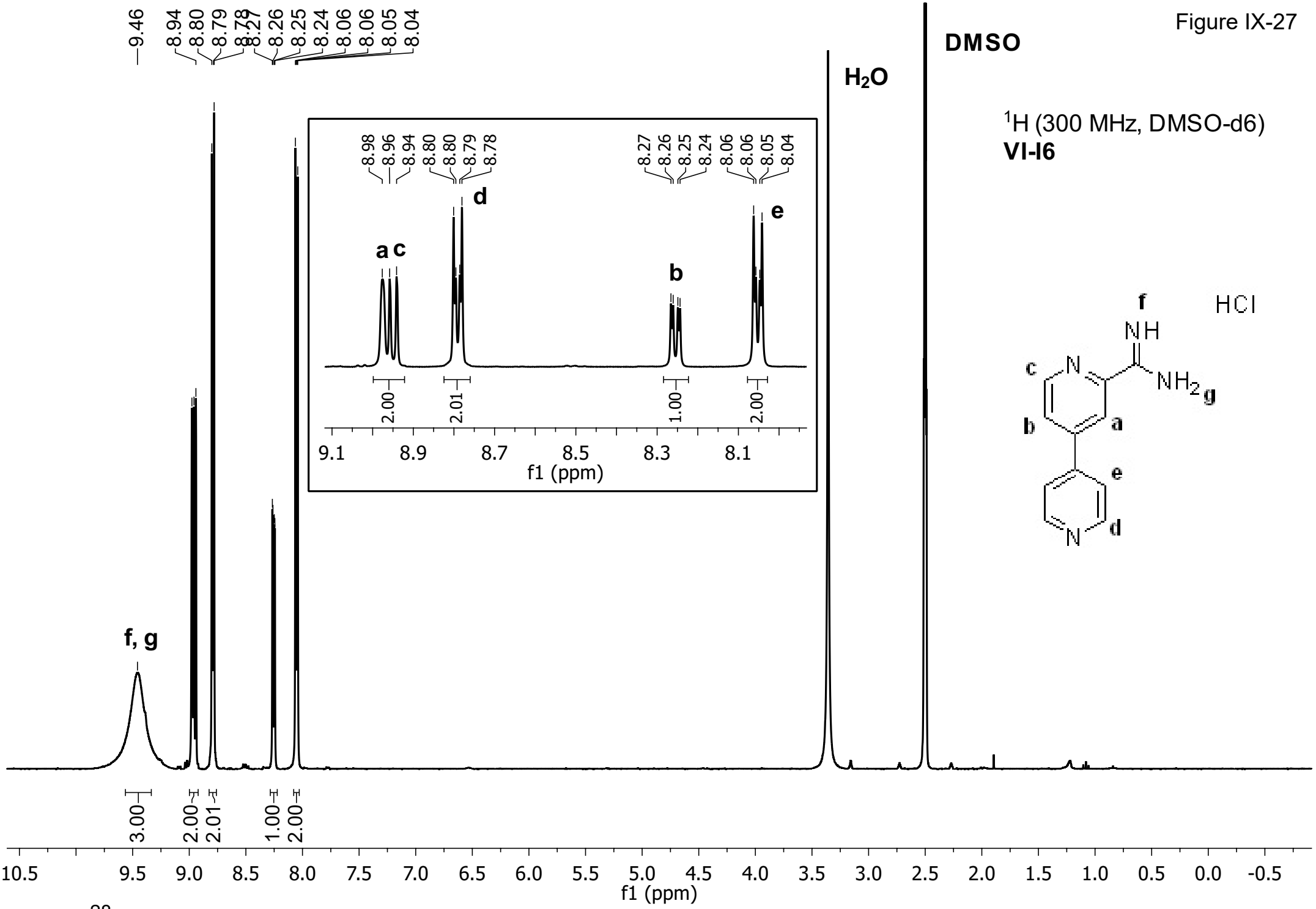

DMSO
H2O
1H (300 MHz, DMSO-d6)
VI-I6
HCl
f, g
a c
b
d
e
9.46
8.94
8.80
8.79
8.78
8.27
8.26
8.25
8.24
8.06
8.06
8.05
8.04
3.00
2.00
2.01
1.00
2.00
f1 (ppm)

Figure IX-28

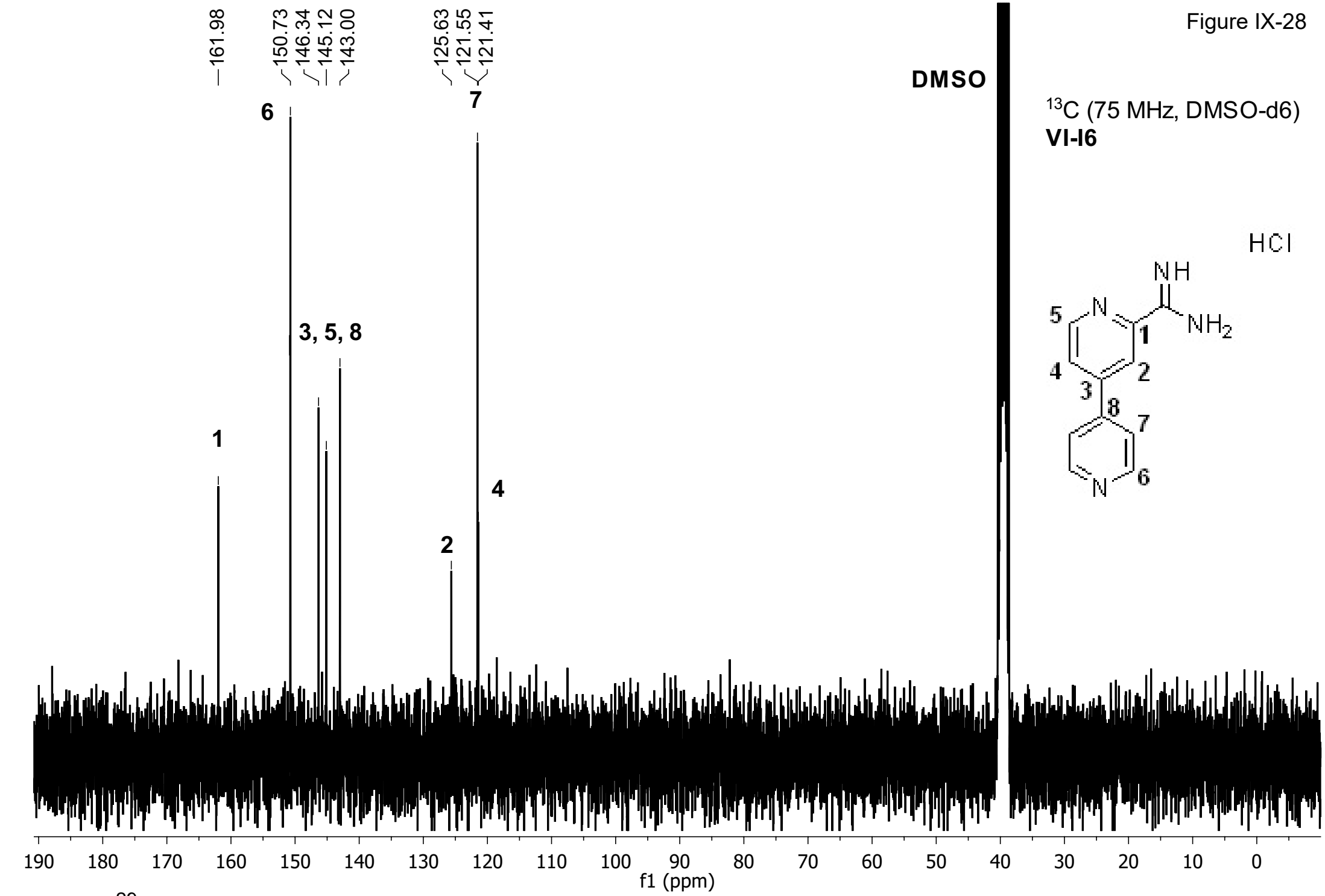

161.98
150.73
146.34
145.12
143.00
125.63
121.55
121.41
DMSO
6
7
3, 5, 8
1
4
2
^{13}C (75 MHz, DMSO-d6)
VI-I6
HCl
NH
NH_2
N
N
1
2
3
4
5
6
7
8
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Figure IX-29

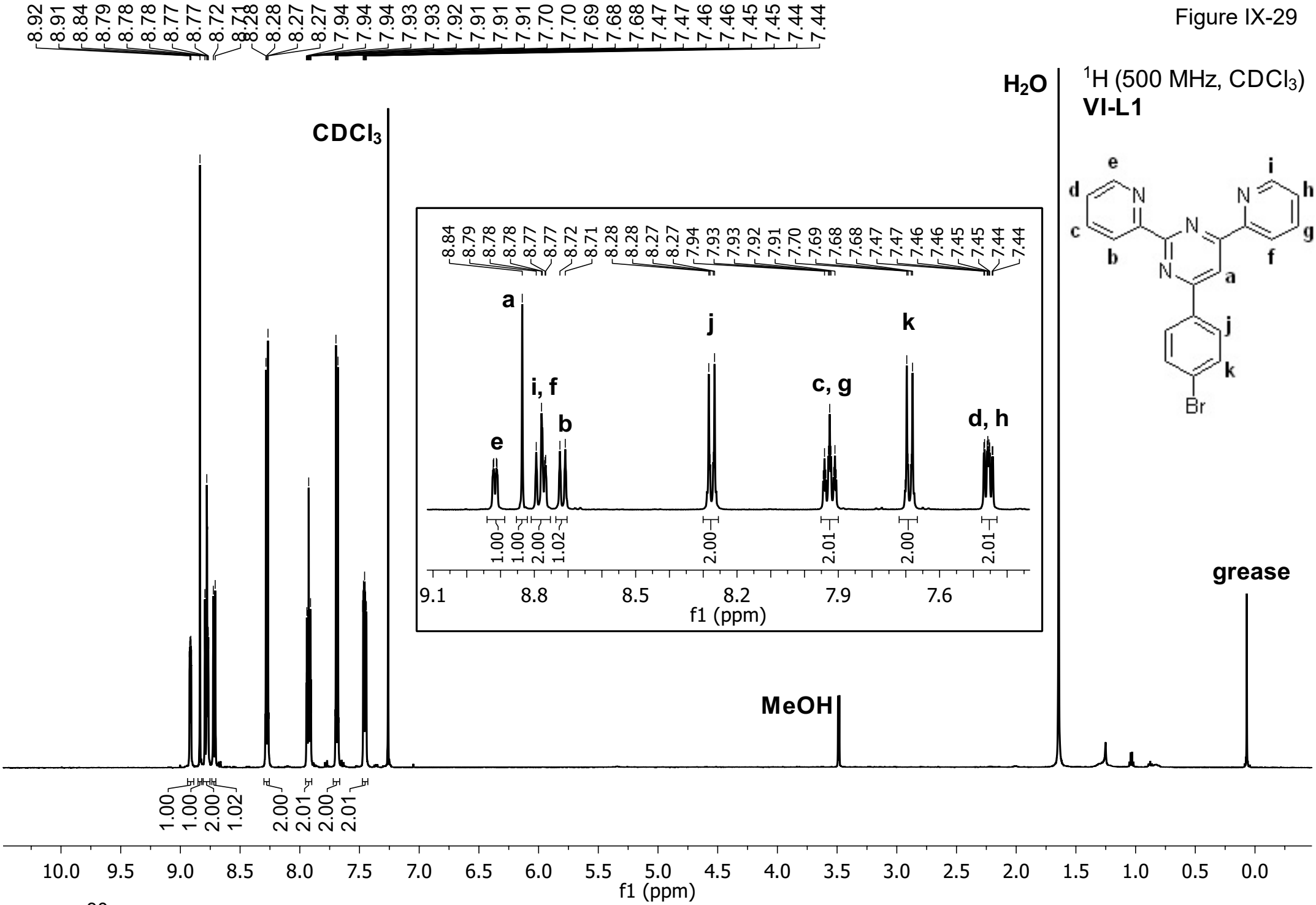


Figure IX-30

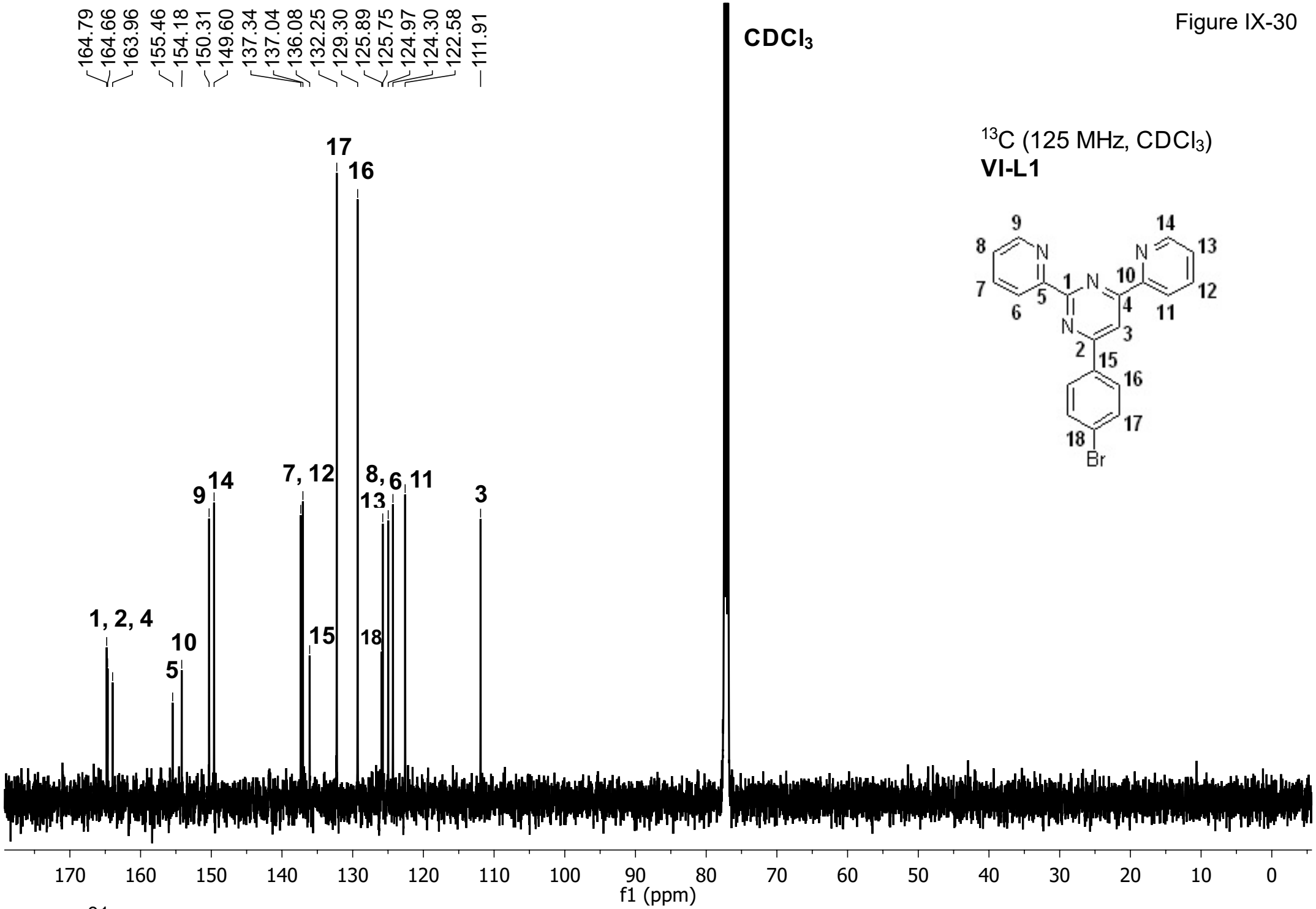

164.79
164.66
163.96
155.46
154.18
150.31
149.60
137.34
137.04
136.08
132.25
129.30
125.89
125.75
124.97
124.30
122.58
111.91
CDCl3
13C (125 MHz, CDCl3)
VI-L1
17
16
9
14
7, 12
8,
13
6
11
3
1, 2, 4
10
5
15
18
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Figure IX-31

^{1}H (500 MHz, $CDCl_3$)
VI-L2

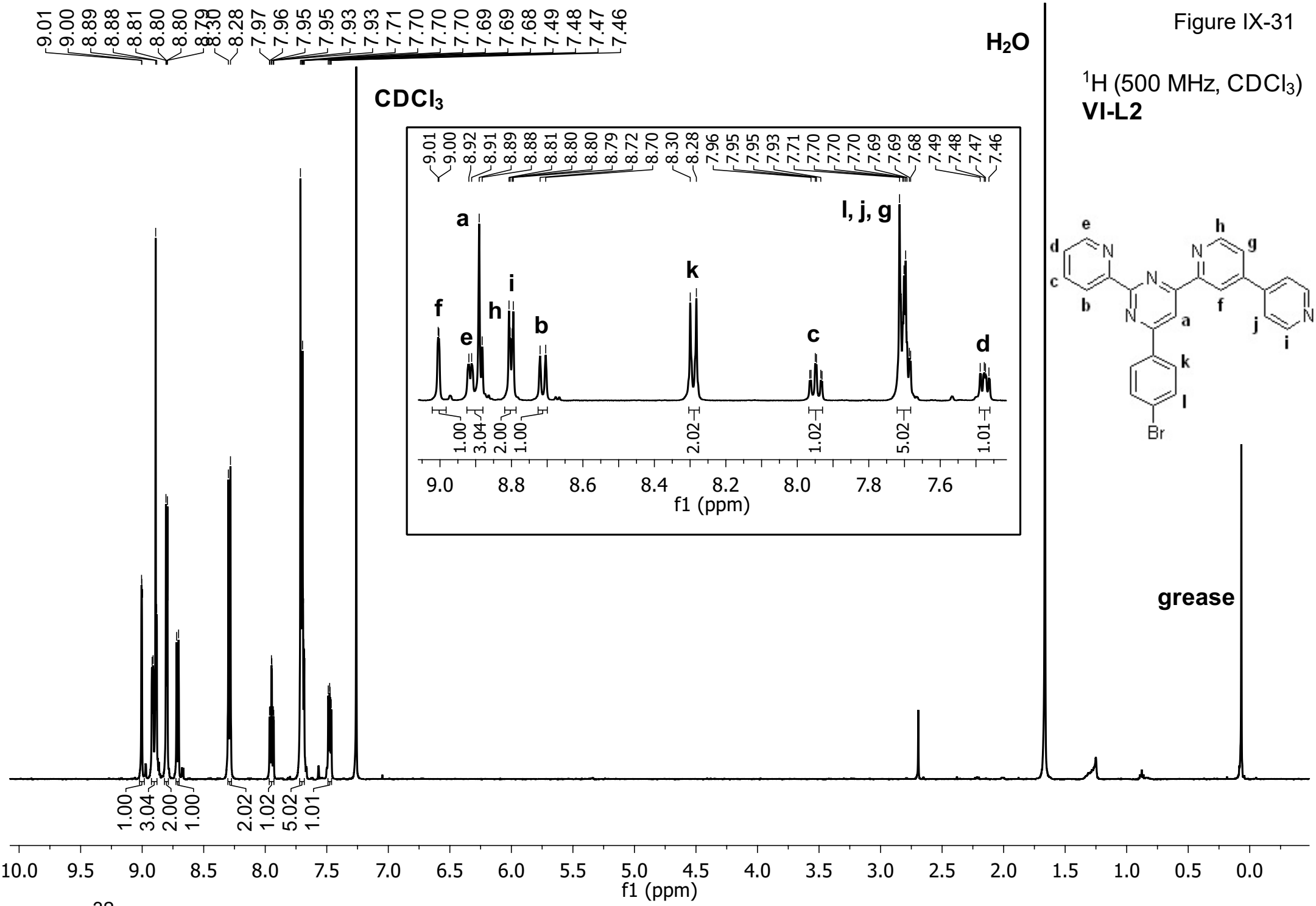
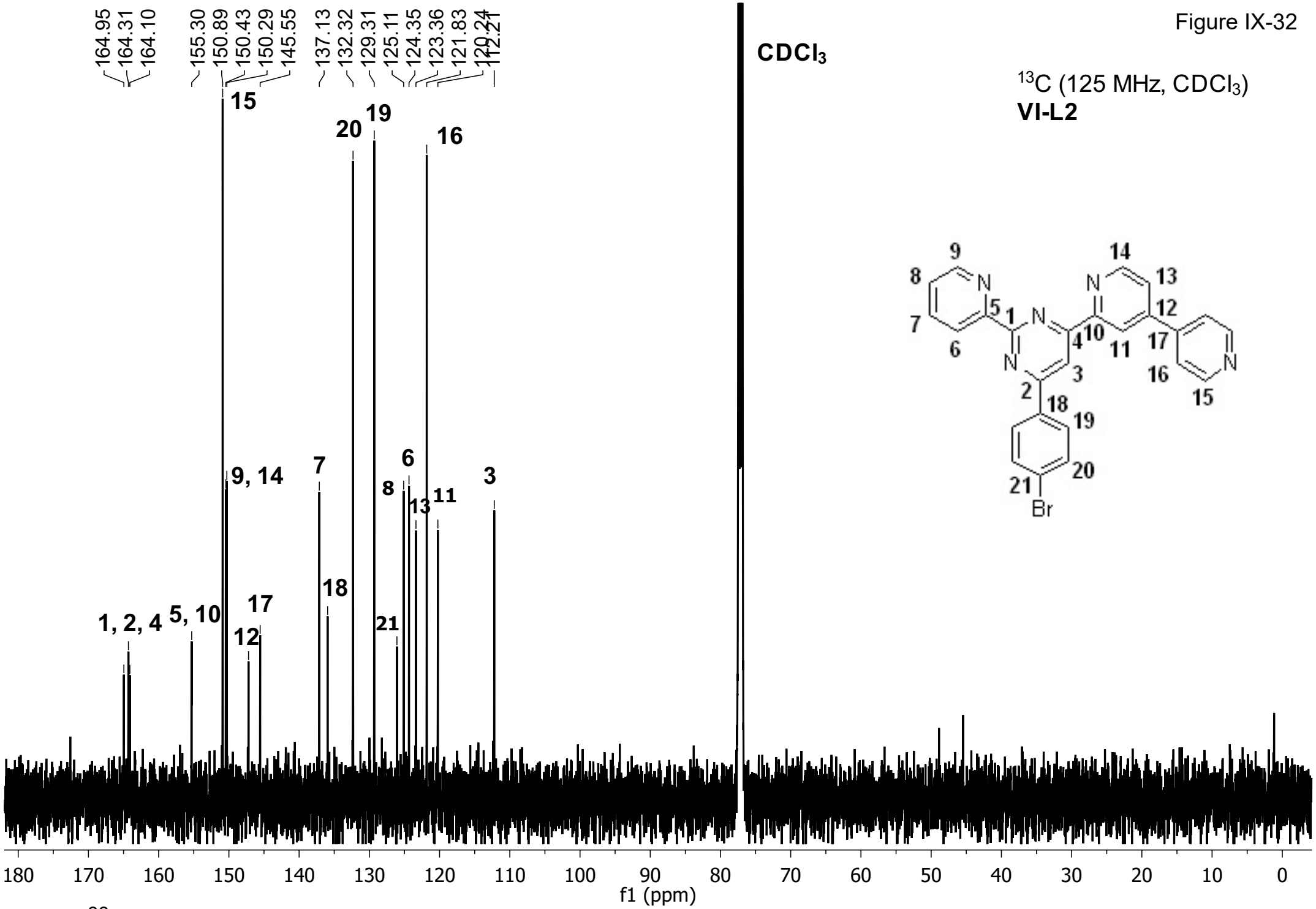


Figure IX-32



^{13}C (125 MHz, $CDCl_3$)

VI-L2

Figure IX-33

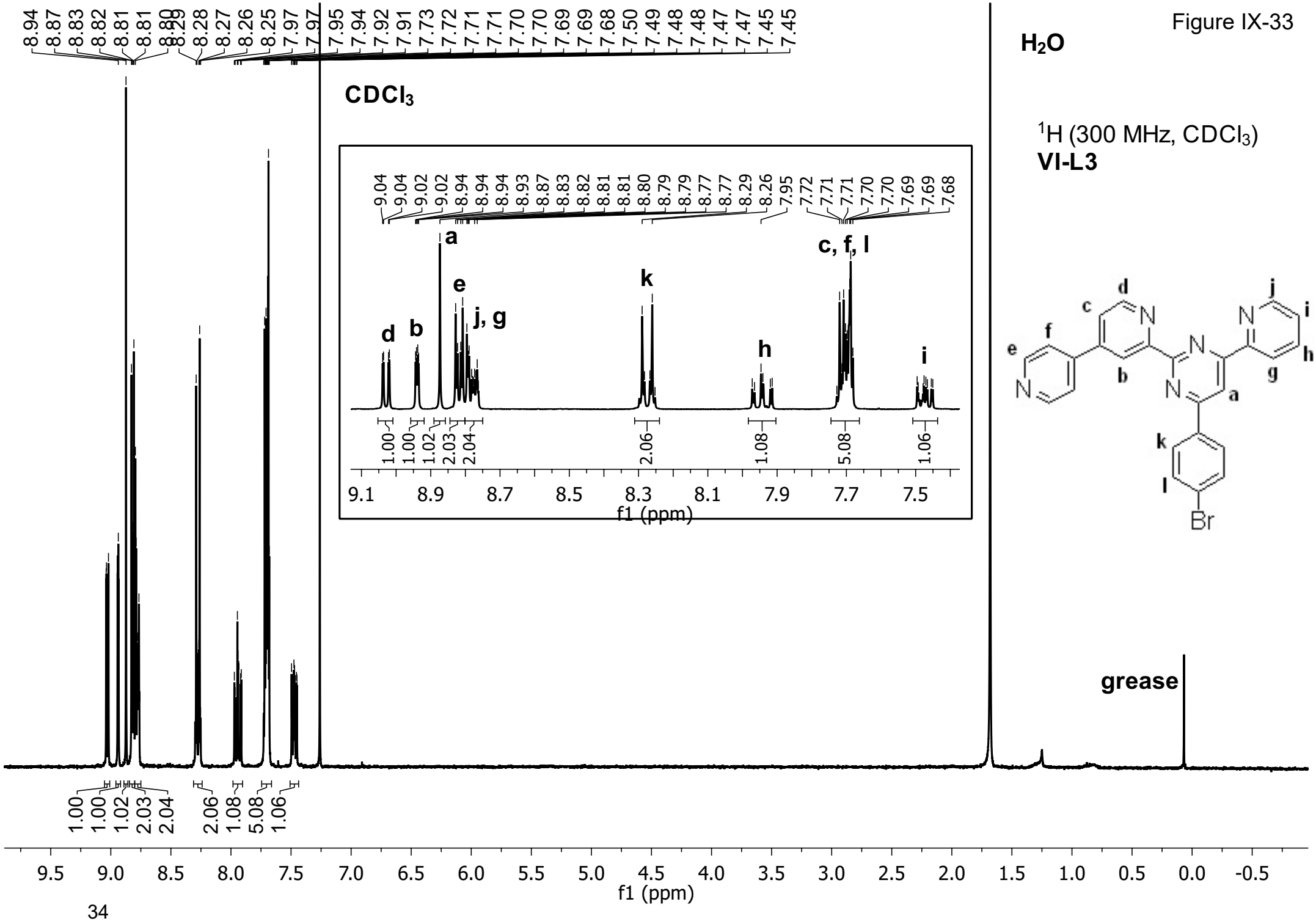


Figure IX-34

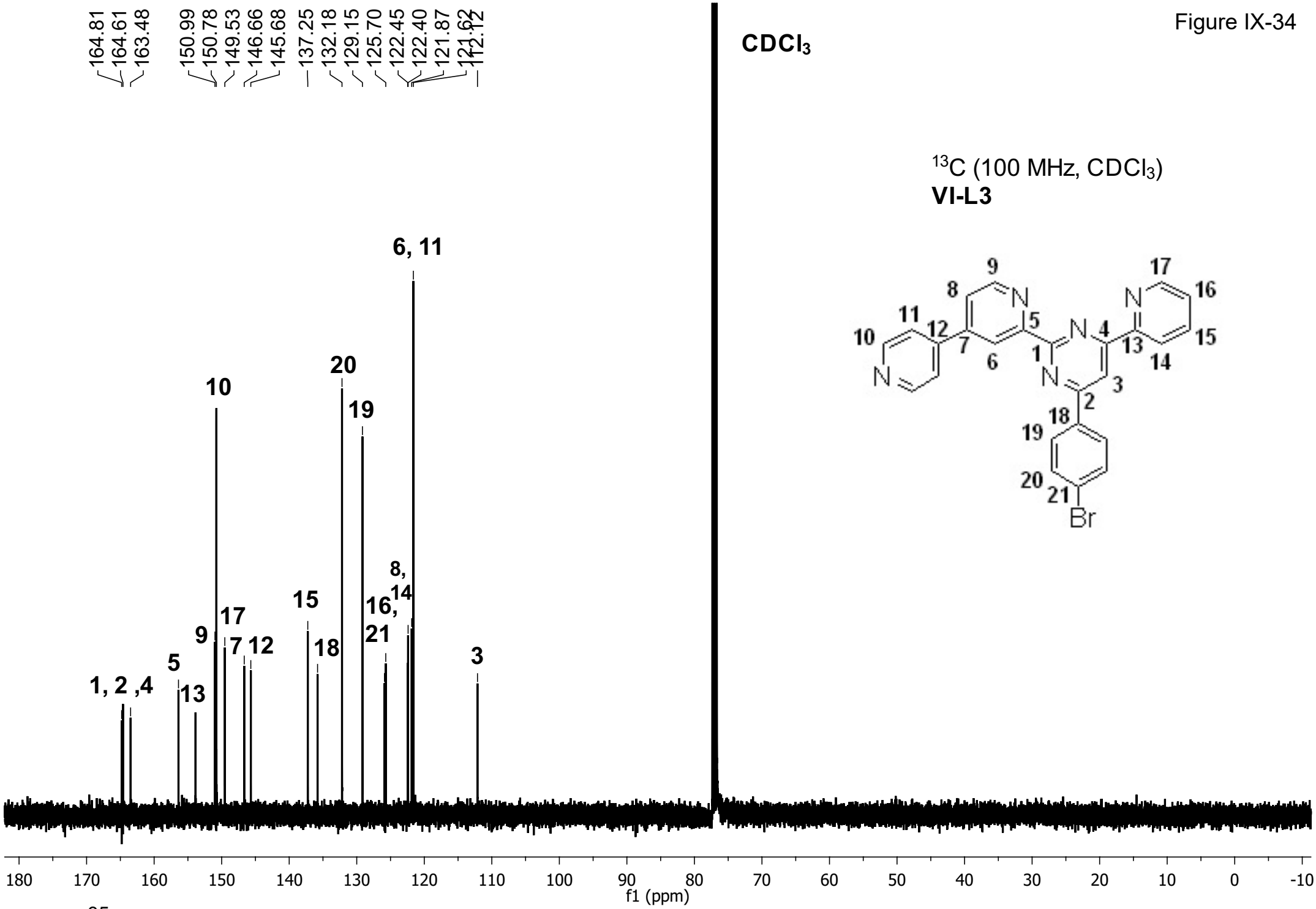
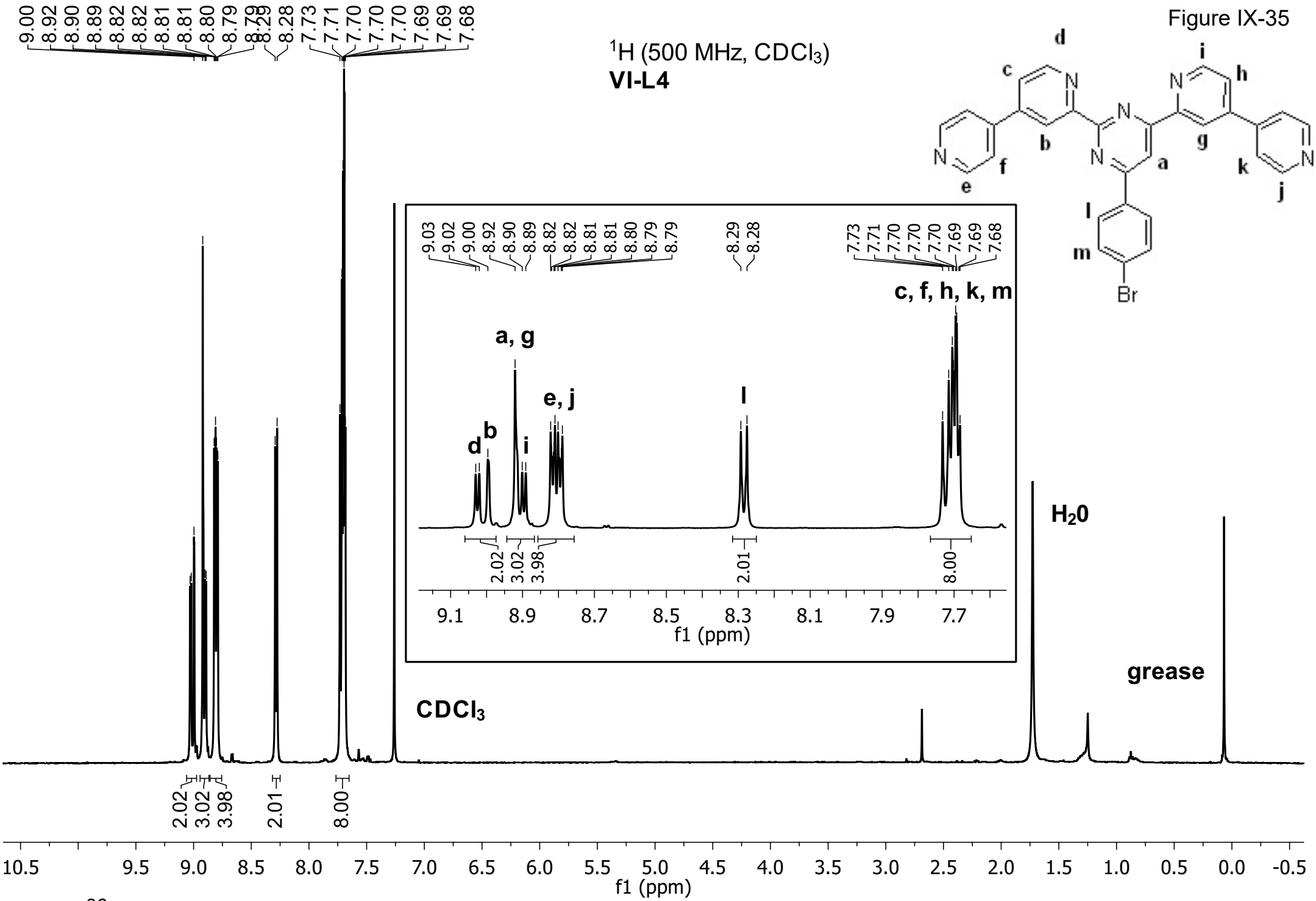
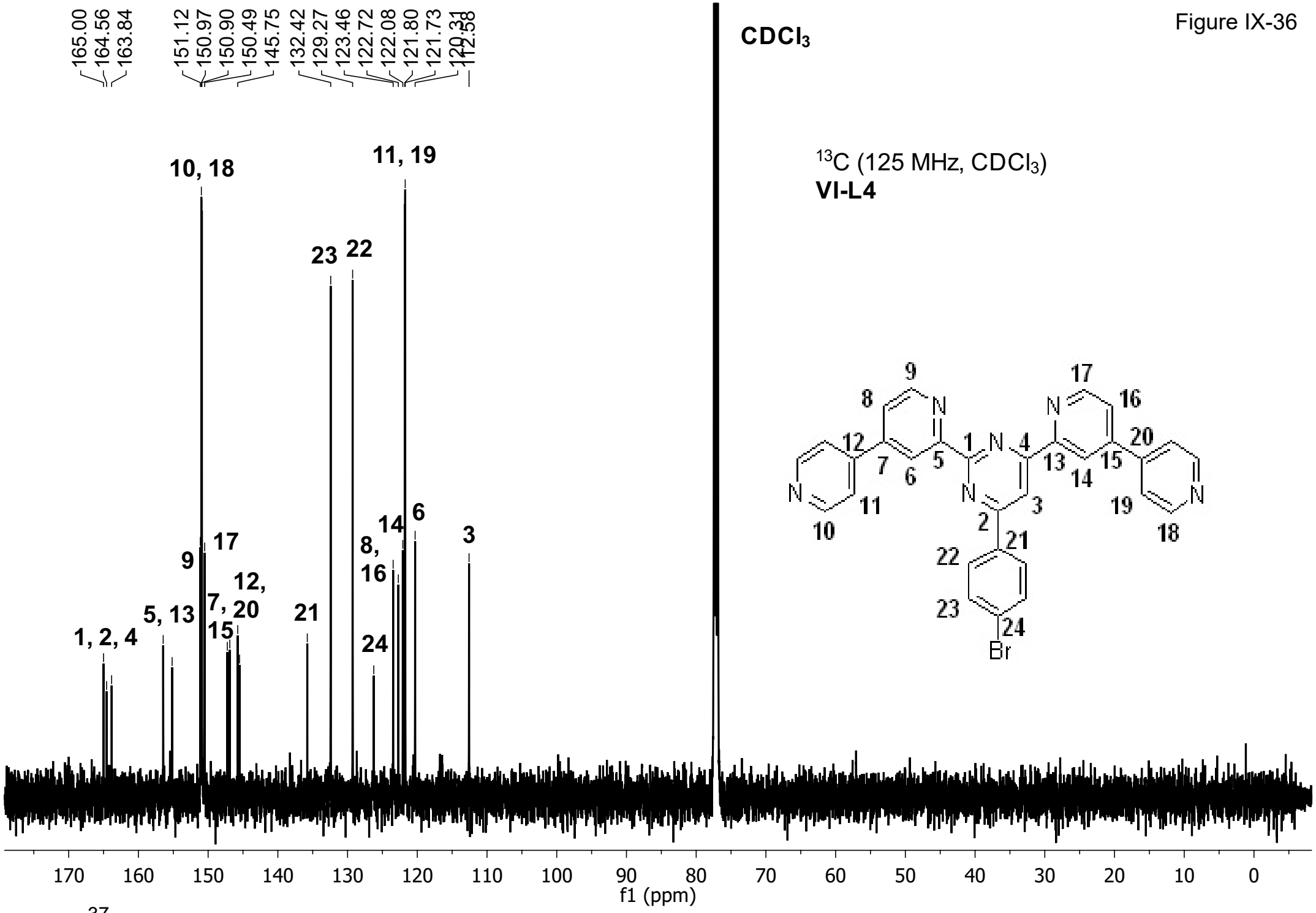

164.81
164.61
163.48
150.99
150.78
149.53
146.66
145.68
137.25
132.18
129.15
125.70
122.45
122.40
121.87
121.62
112.12
CDCl3
13C (100 MHz, CDCl3)
VI-L3
6, 11
10
20
19
15
17
9
7
12
18
5
13
1, 2 ,4
16,
21
8,
14
3
N
Br
f1 (ppm)

Figure IX-35


^{1}H (500 MHz, $CDCl_3$)
VI-L4
9.00 8.92 8.90 8.89 8.82 8.82 8.81 8.81 8.80 8.79 8.29 8.28 7.73 7.71 7.70 7.70 7.70 7.69 7.69 7.68
d
c
i
h
b
g
f
a
k
e
j
l
m
Br
c, f, h, k, m
a, g
e, j
l
d
b
i
2.02
3.02
3.98
2.01
8.00
f1 (ppm)
H_20
grease
$CDCl_3$
2.02
3.02
3.98
2.01
8.00
10.5 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)


165.00
164.56
163.84
151.12
150.97
150.90
150.49
145.75
132.42
129.27
123.46
122.72
122.08
121.80
121.73
120.31
112.58
CDCl3
13C (125 MHz, CDCl3)
VI-L4
10, 18
11, 19
23
22
1, 2, 4
5, 13
9
17
7, 15
12, 20
21
8, 16
24
14
6
3
f1 (ppm)

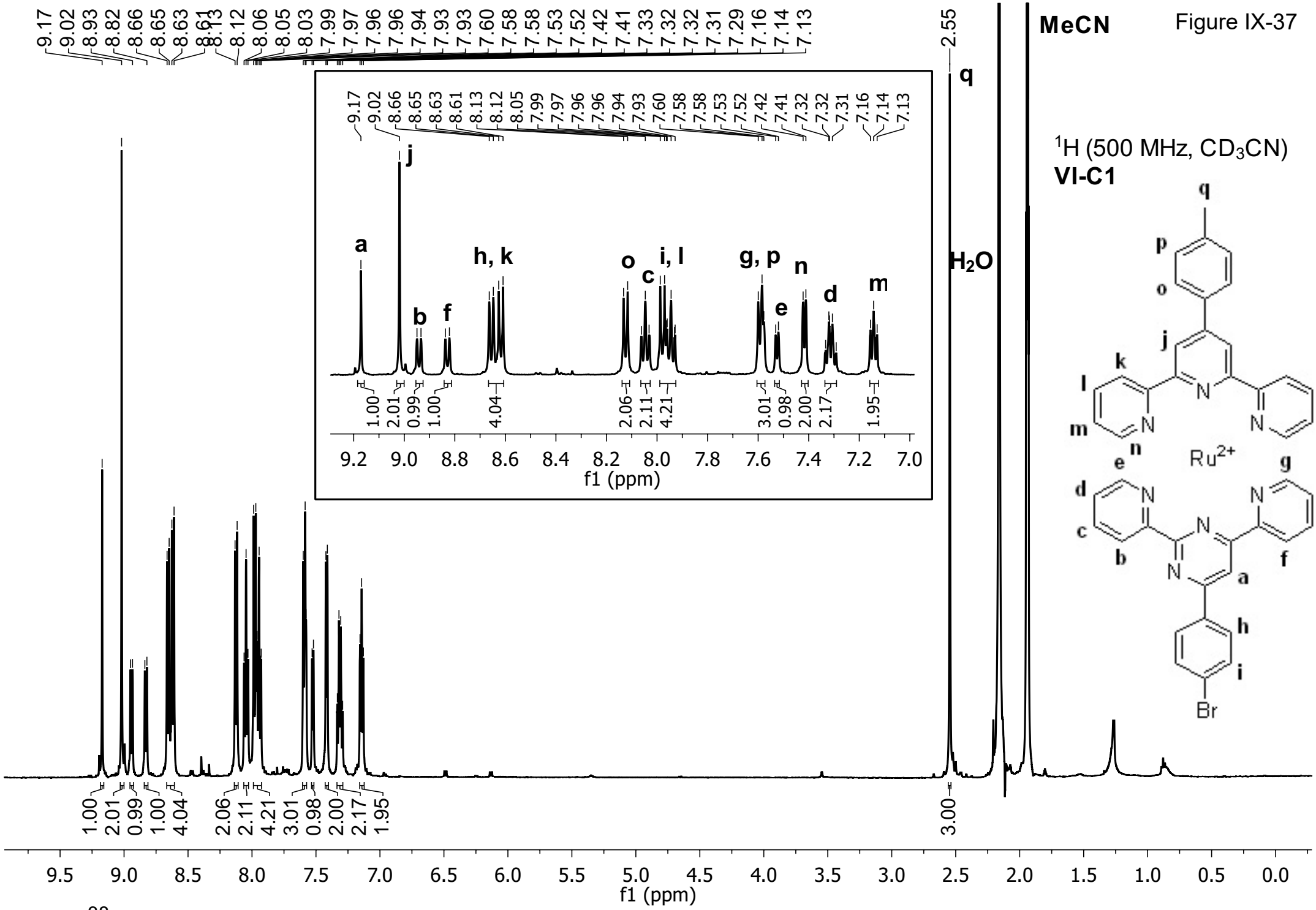

MeCN
Figure IX-37
^{1}H (500 MHz, CD_3CN)
VI-C1
H_2O
q
j
a
b
f
h, k
o
c
i, l
g, p
e
n
d
m
Ru^{2+}
f1 (ppm)

Figure IX-38

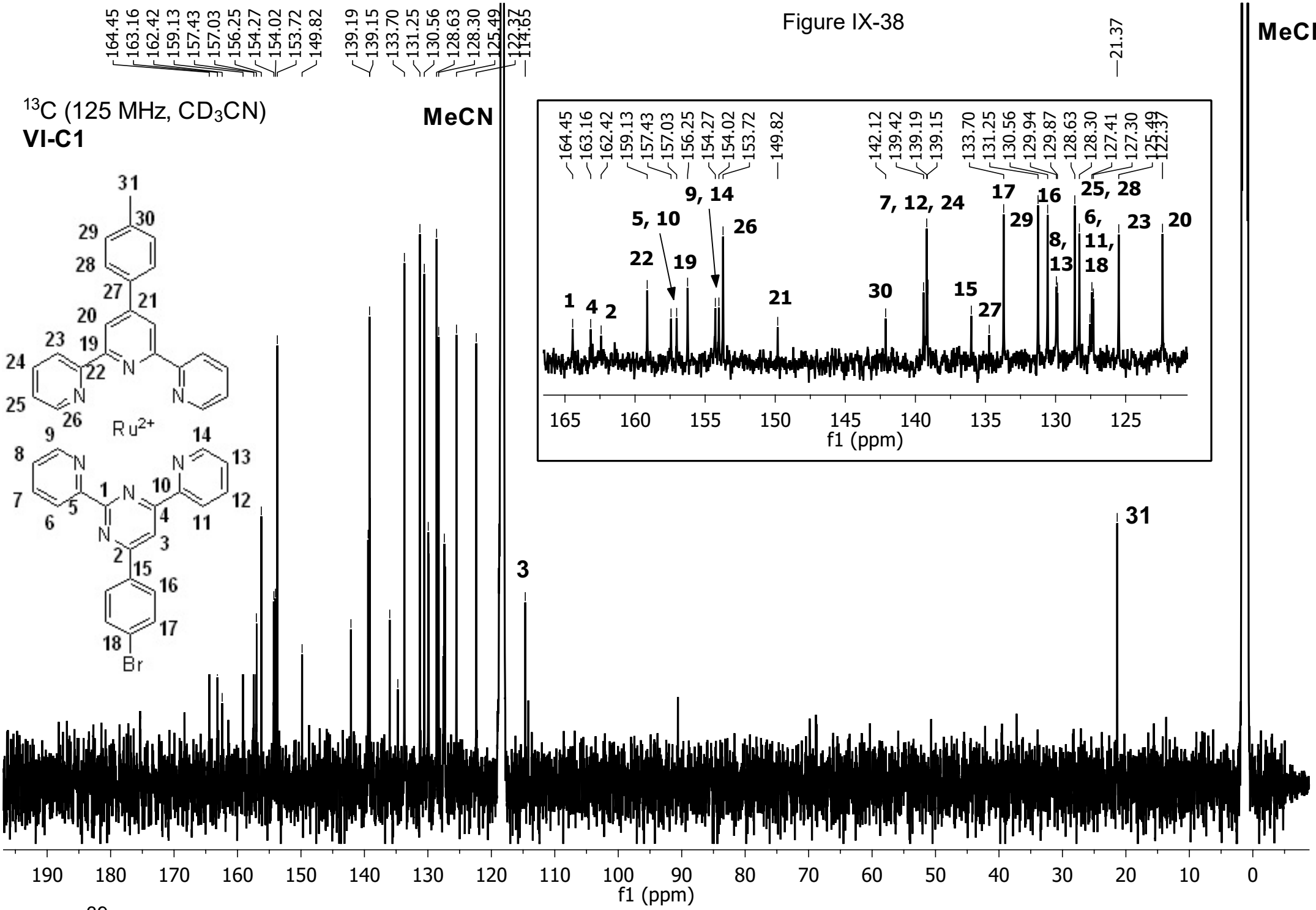
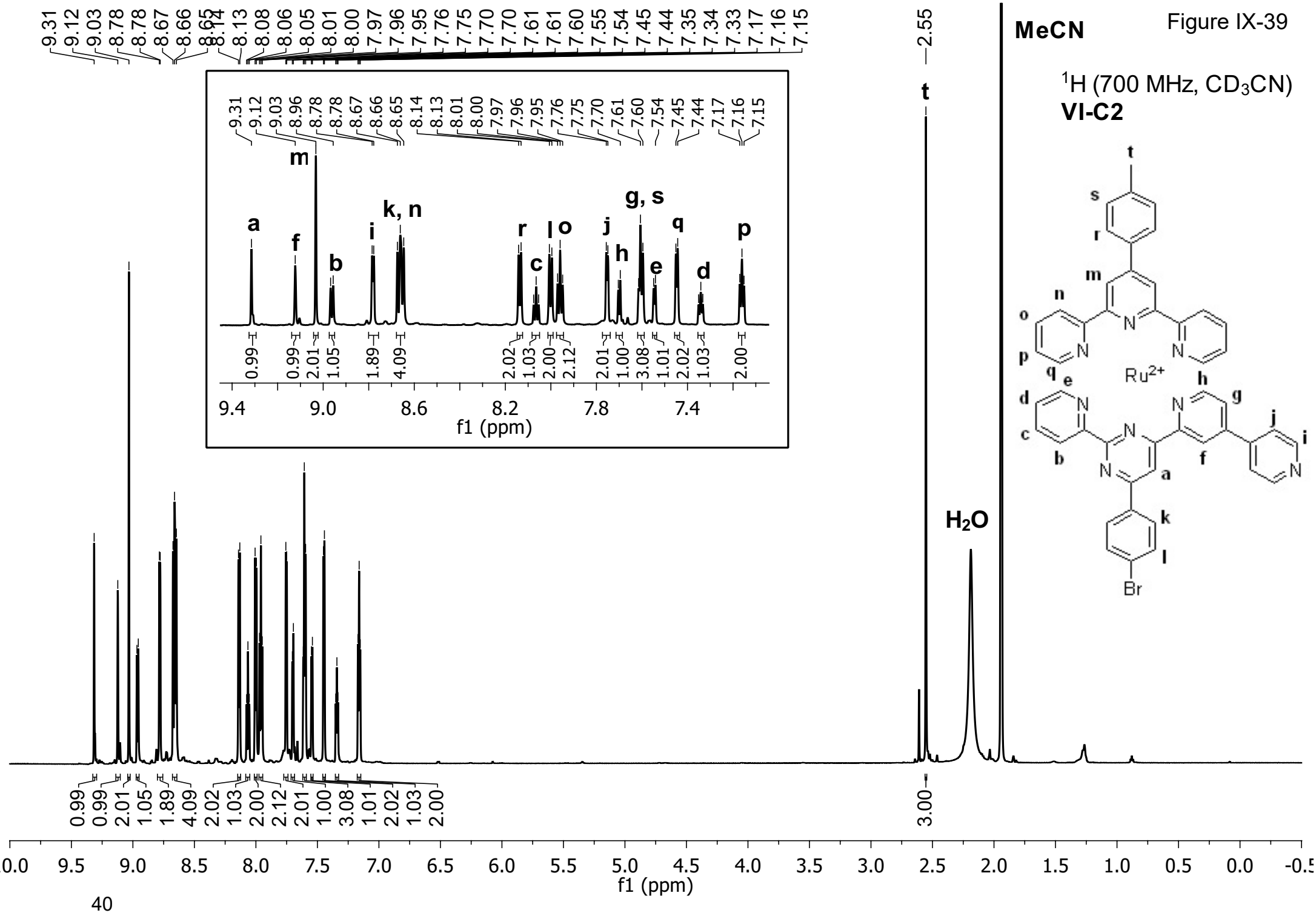

^{13}C (125 MHz, CD_3CN)
VI-C1
MeCN
MeCN
164.45 163.16 162.42 159.13 157.43 157.03 156.25 154.27 154.02 153.72 149.82 139.19 139.15 133.70 131.25 130.56 128.63 128.30 125.49 122.37 114.65
21.37
31
30
29
28
27
21
20
19
23
24
22
N
25
26
Ru2+
9
14
8
N
13
7
1
N
10
12
5
4
6
11
N
3
2
15
16
17
18
Br
1 4 2 22 5, 10 19 9, 14 26 21 30 7, 12, 24 15 27 17 29 16 8, 13 25, 28 6, 11, 18 23 20
f1 (ppm)
3
31
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

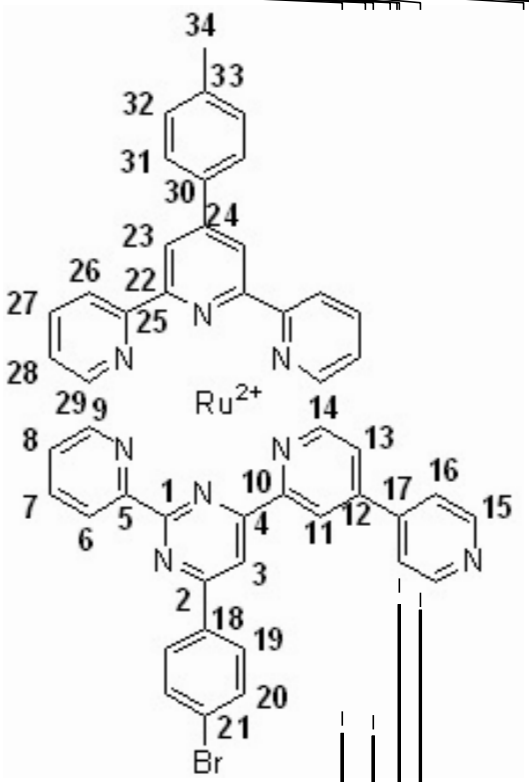
Figure IX-39



^{13}C (176 MHz, CD_3CN)

VI-C2

Figure IX-40



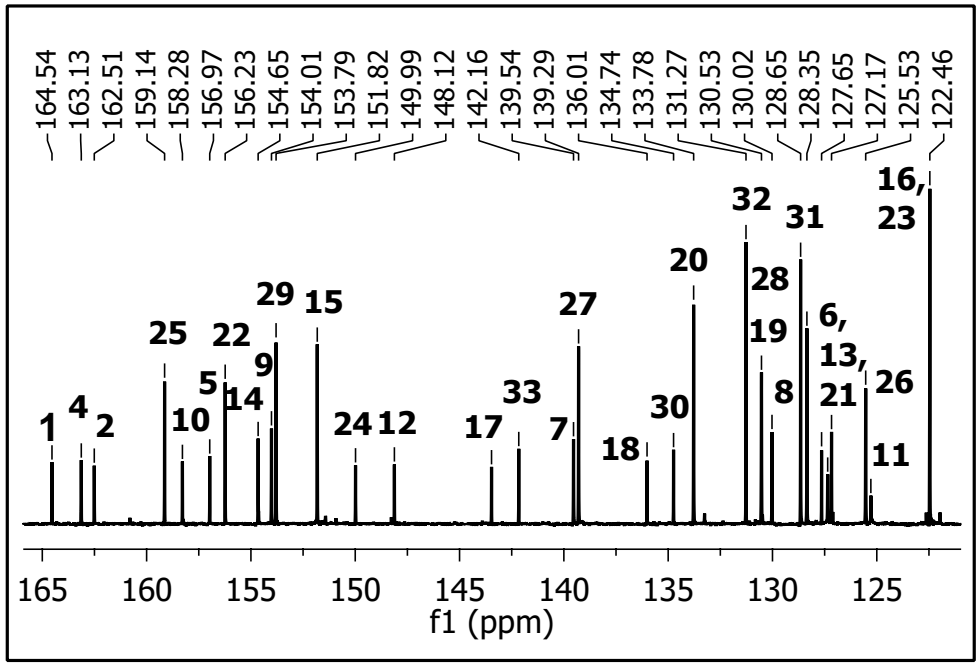


Figure IX-41

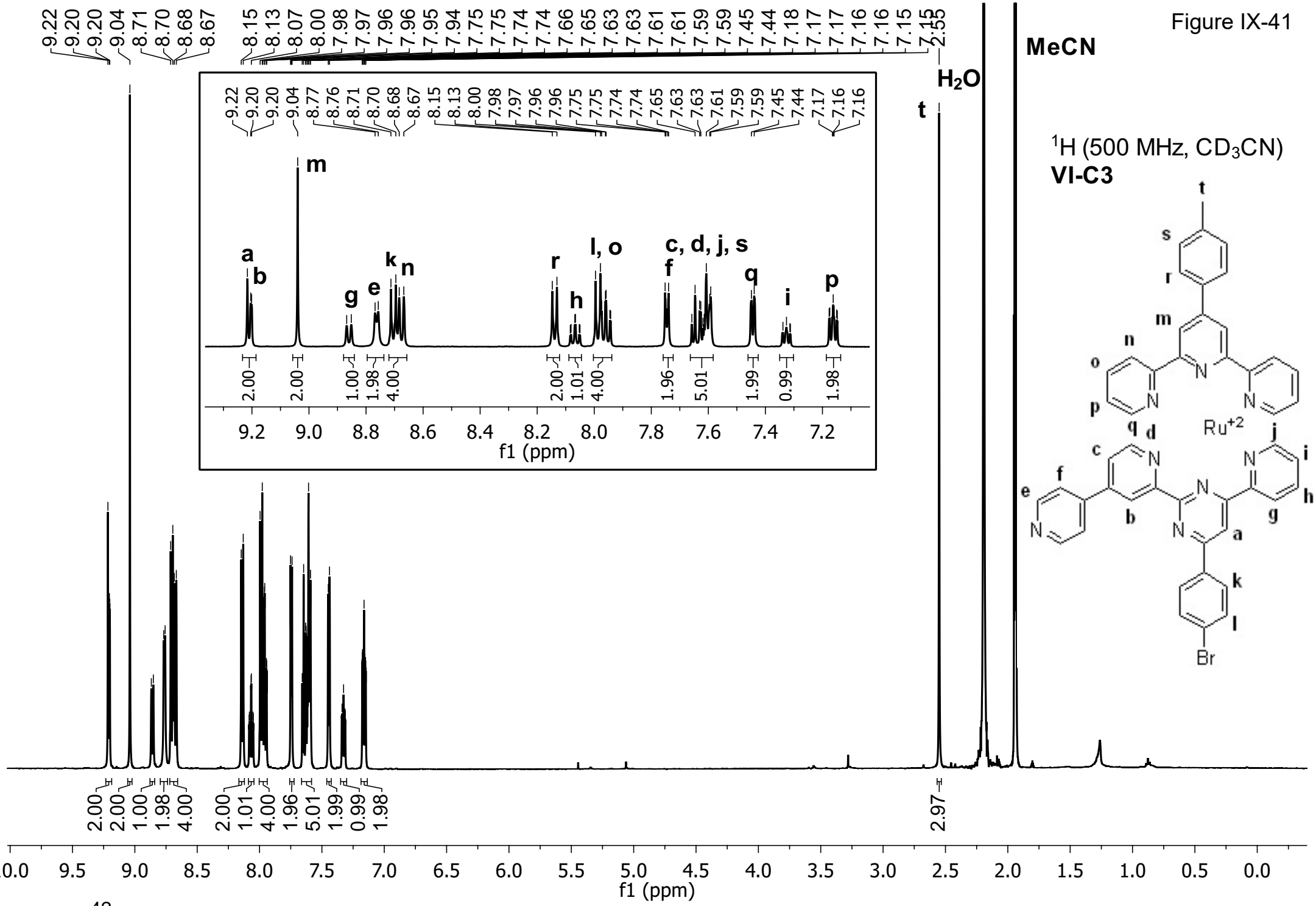

MeCN
H2O
t
1H (500 MHz, CD3CN)
VI-C3
a
b
m
g
e
k
n
r
h
l, o
f
c, d, j, s
q
i
p
Ru+2
f1 (ppm)

Figure IX-42 ^{13}C (125 MHz, CD_3CN)

VI-C3

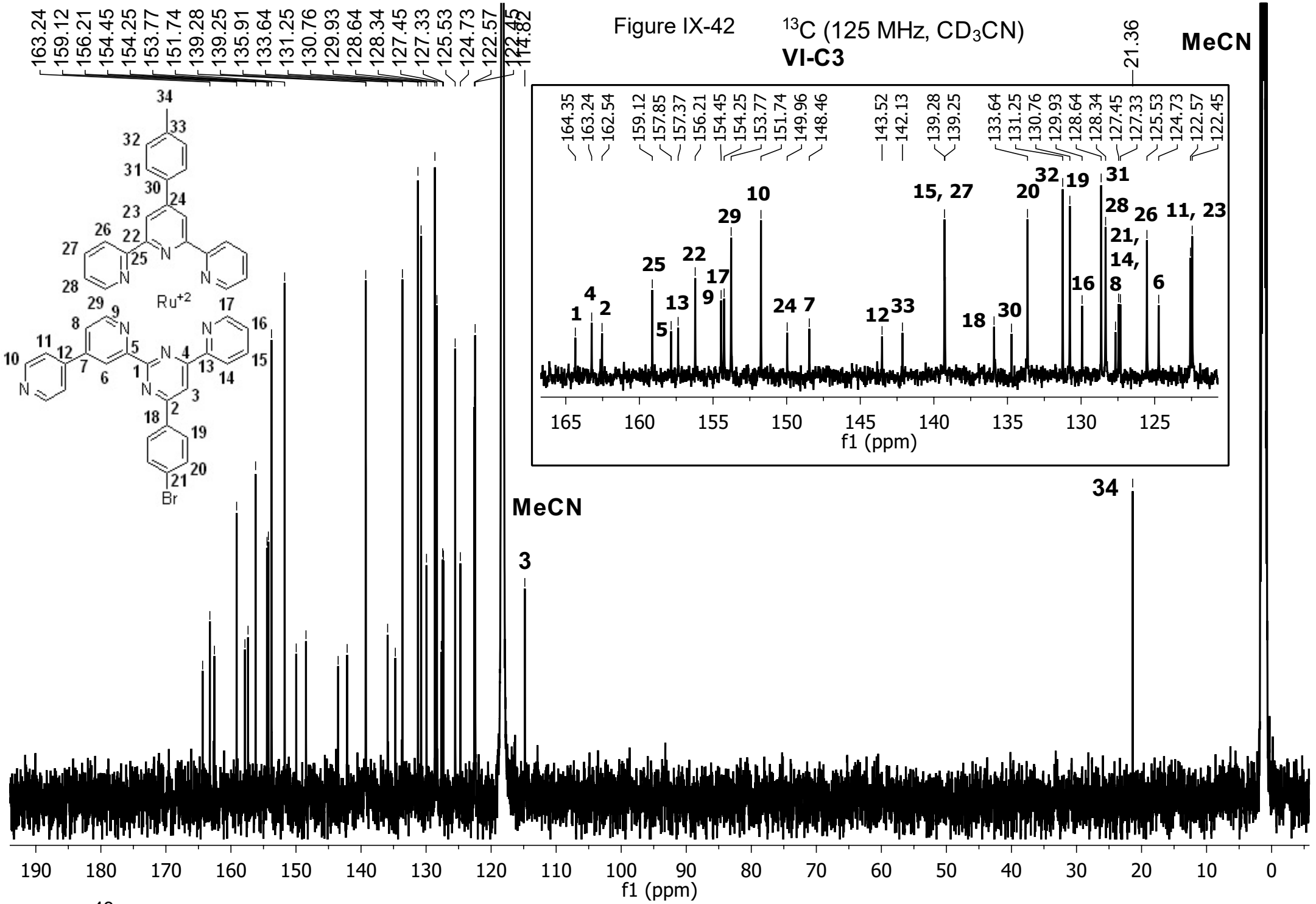
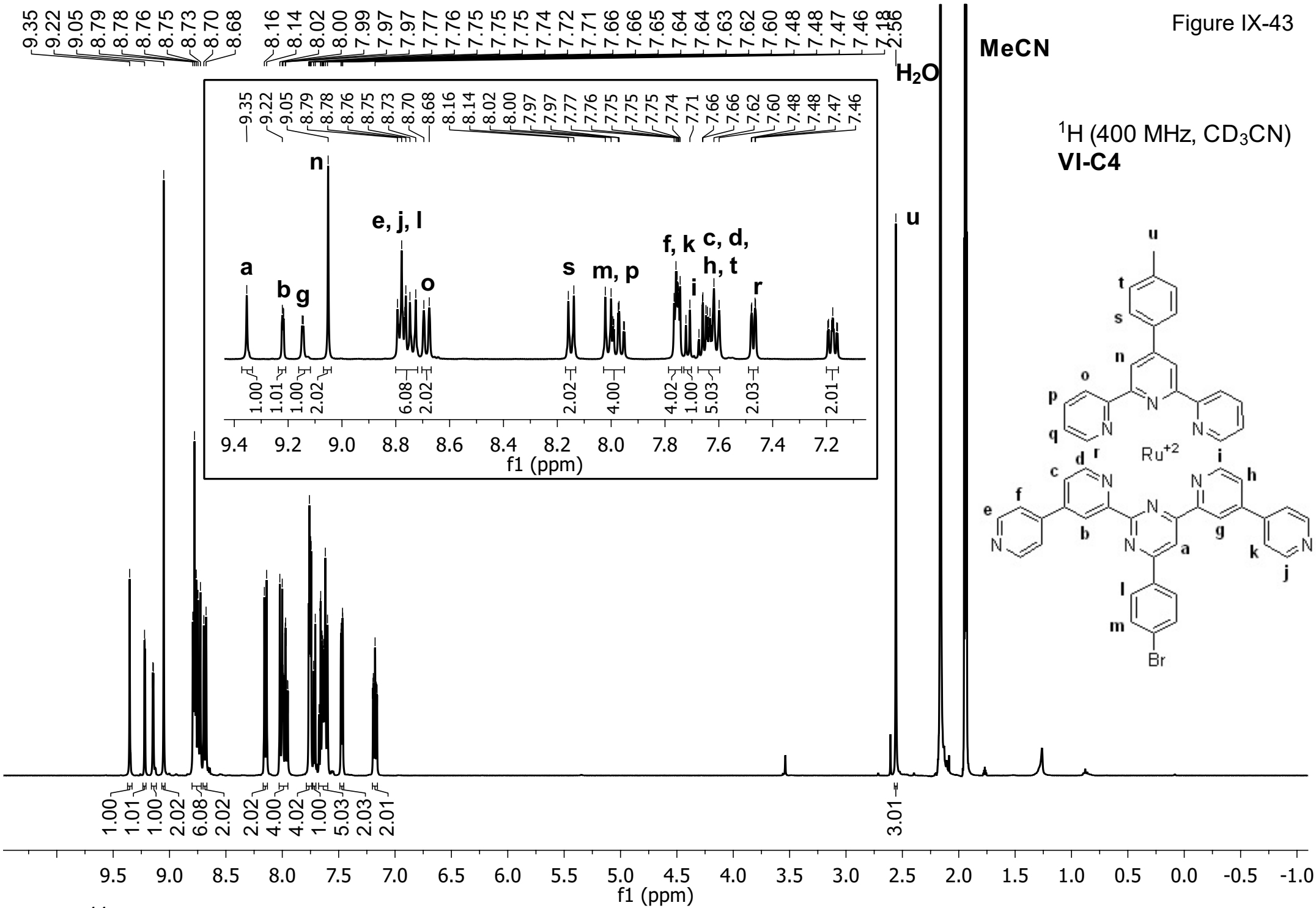


Figure IX-43


MeCN
H2O
1H (400 MHz, CD3CN)
VI-C4
a
b g
n
e, j, l
o
s
m, p
f, k
i
c, d,
h, t
r
u
Ru+2
Br
f1 (ppm)

^{13}C (100 MHz, CD_3CN) Figure IX-44

VI-C4

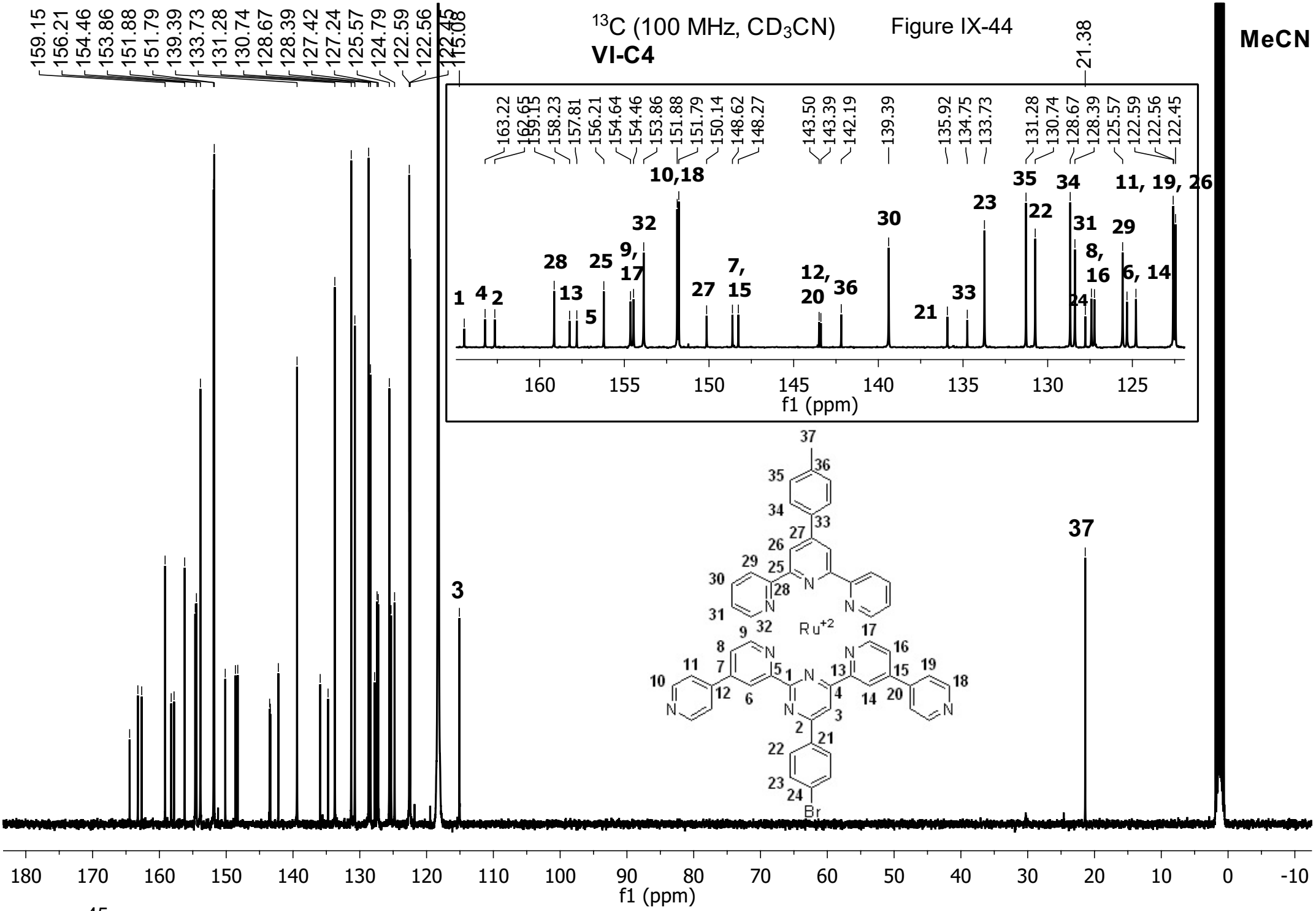
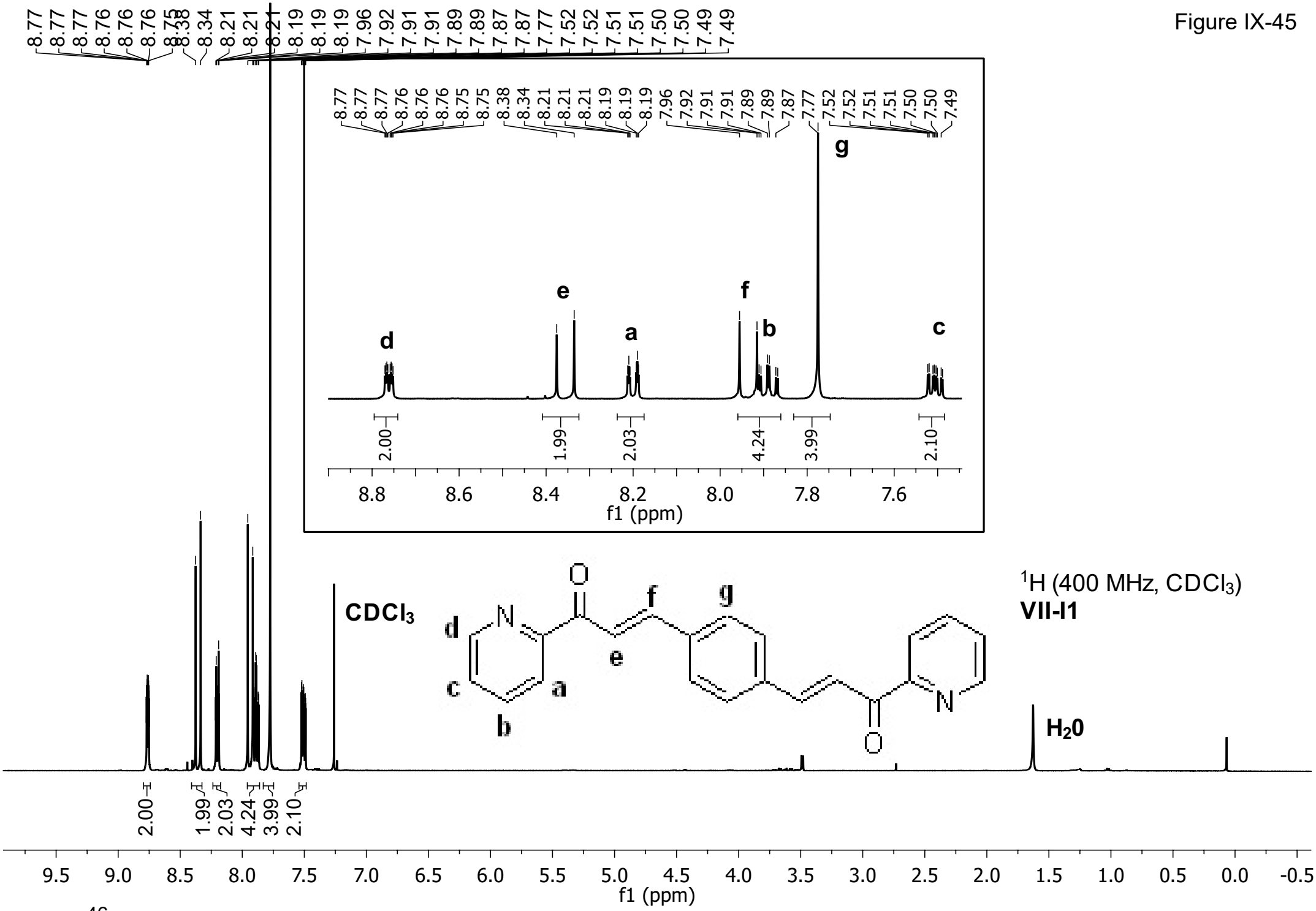


Figure IX-45



^{1}H (400 MHz, $CDCl_3$)
VII-I1

Figure IX-46

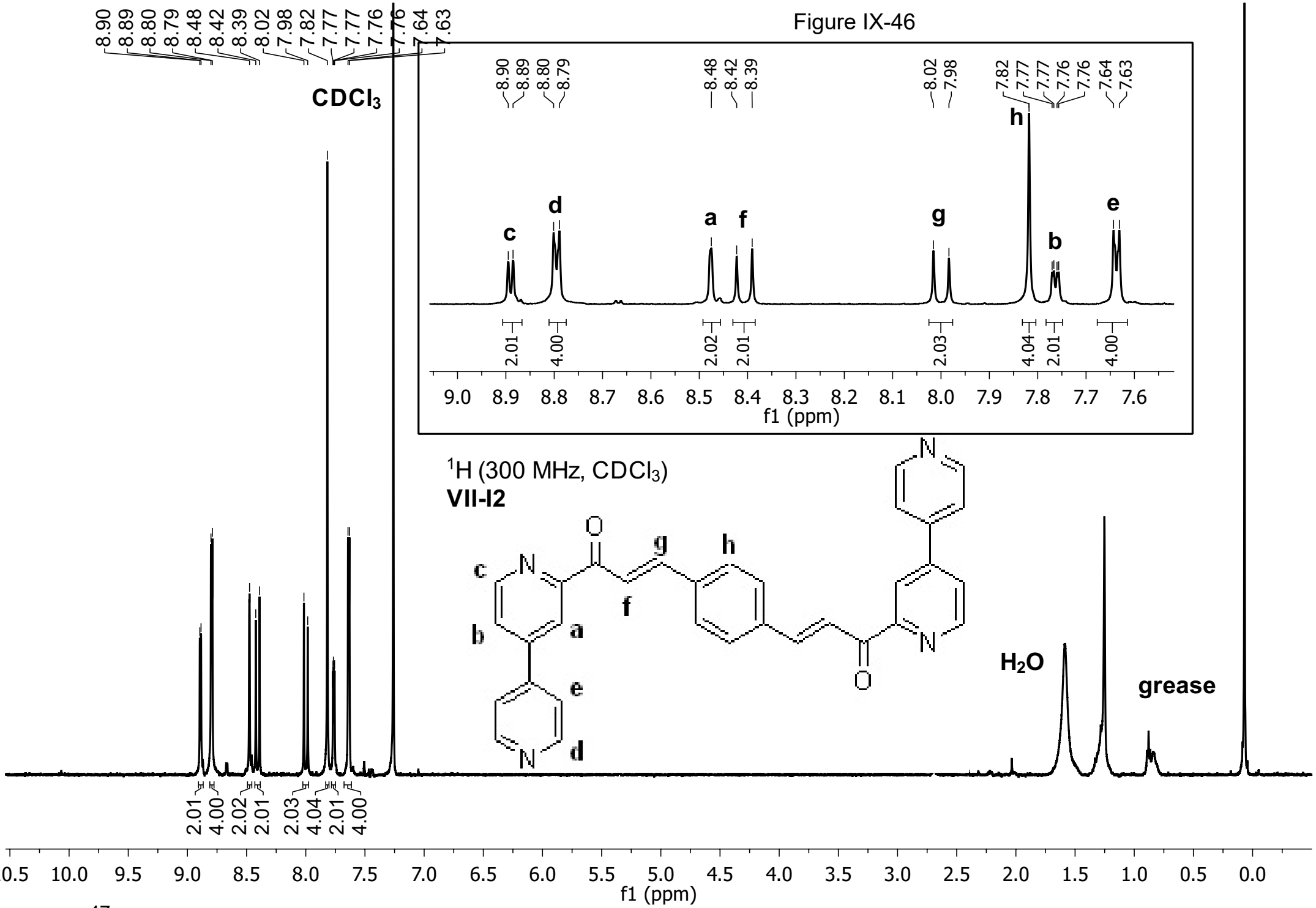

8.90
8.89
8.80
8.79
8.48
8.42
8.39
8.02
7.98
7.82
7.77
7.77
7.76
7.76
7.64
7.63
CDCl3
c
d
a
f
g
h
b
e
2.01
4.00
2.02
2.01
2.03
4.04
2.01
4.00
f1 (ppm)
1H (300 MHz, CDCl3)
VII-I2
H2O
grease

Figure IX-47

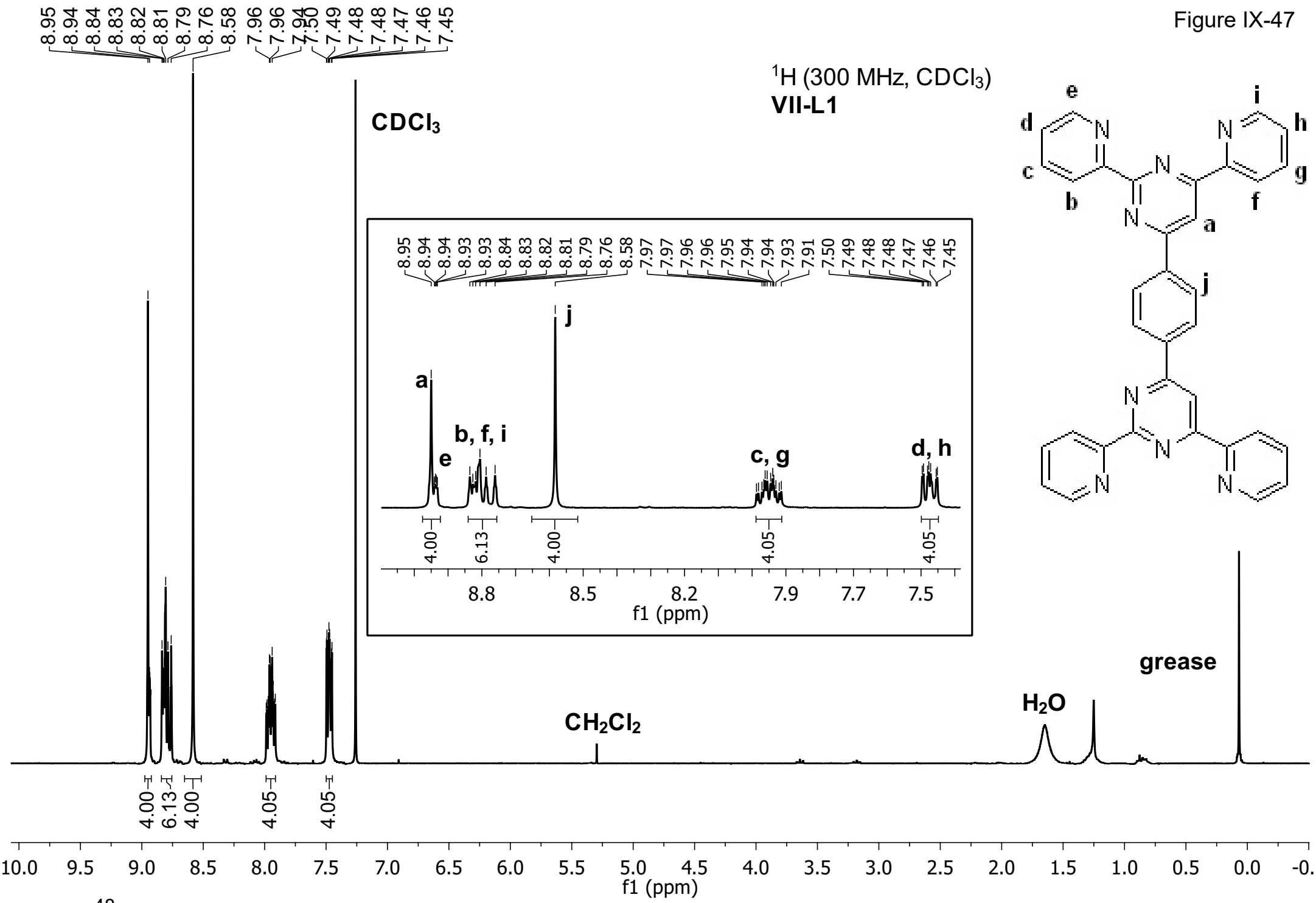
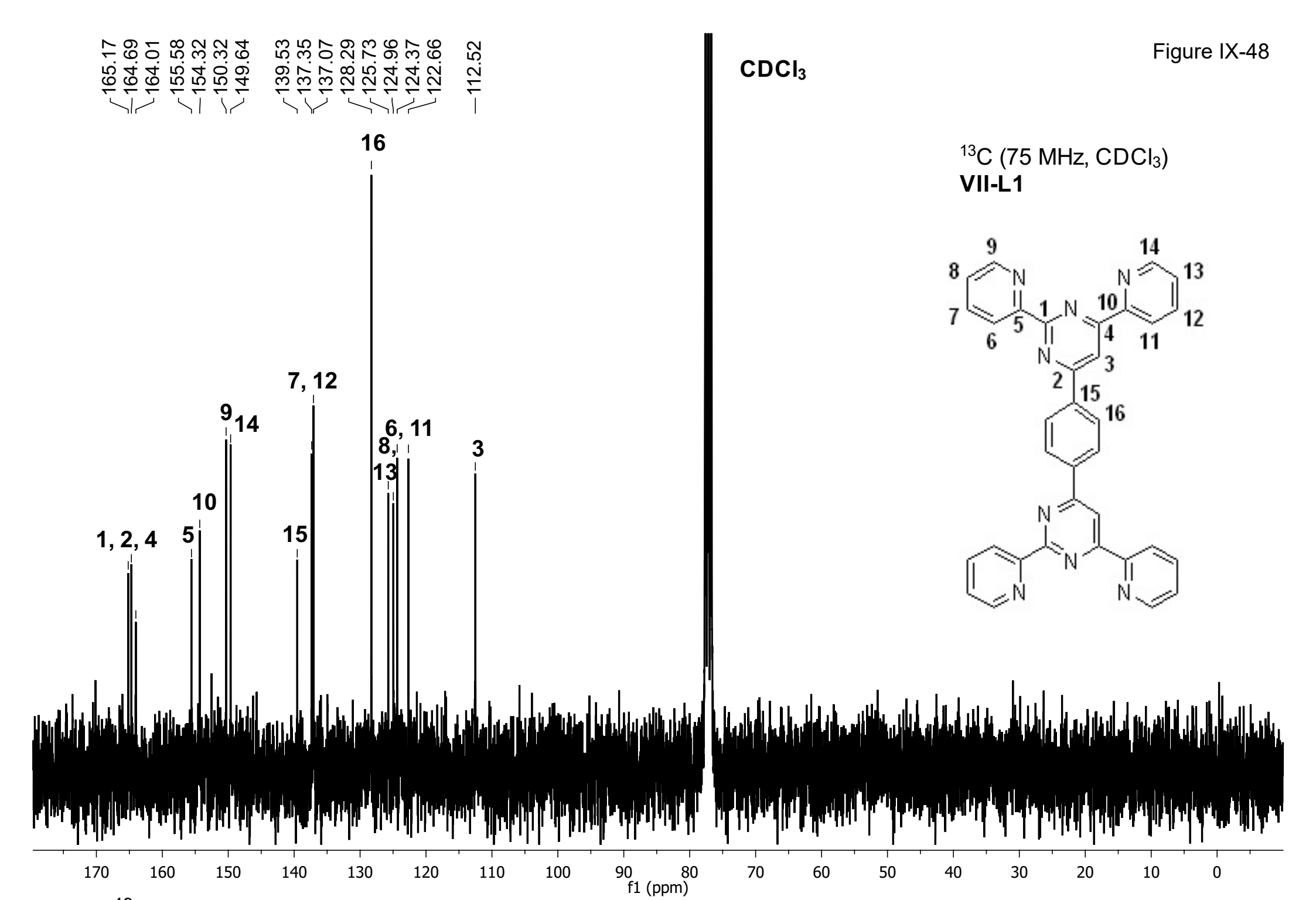

^{1}H (300 MHz, $CDCl_3$)
VII-L1
$CDCl_3$
CH_2Cl_2
H_2O
grease
a
e
b, f, i
j
c, g
d, h
4.00
6.13
4.00
4.05
4.05
f1 (ppm)

Figure IX-48


165.17
164.69
164.01
155.58
154.32
150.32
149.64
139.53
137.35
137.07
128.29
125.73
124.96
124.37
122.66
112.52
CDCl3
16
7, 12
9
14
6, 11
8,
13
10
5
1, 2, 4
15
3
13C (75 MHz, CDCl3)
VII-L1
f1 (ppm)

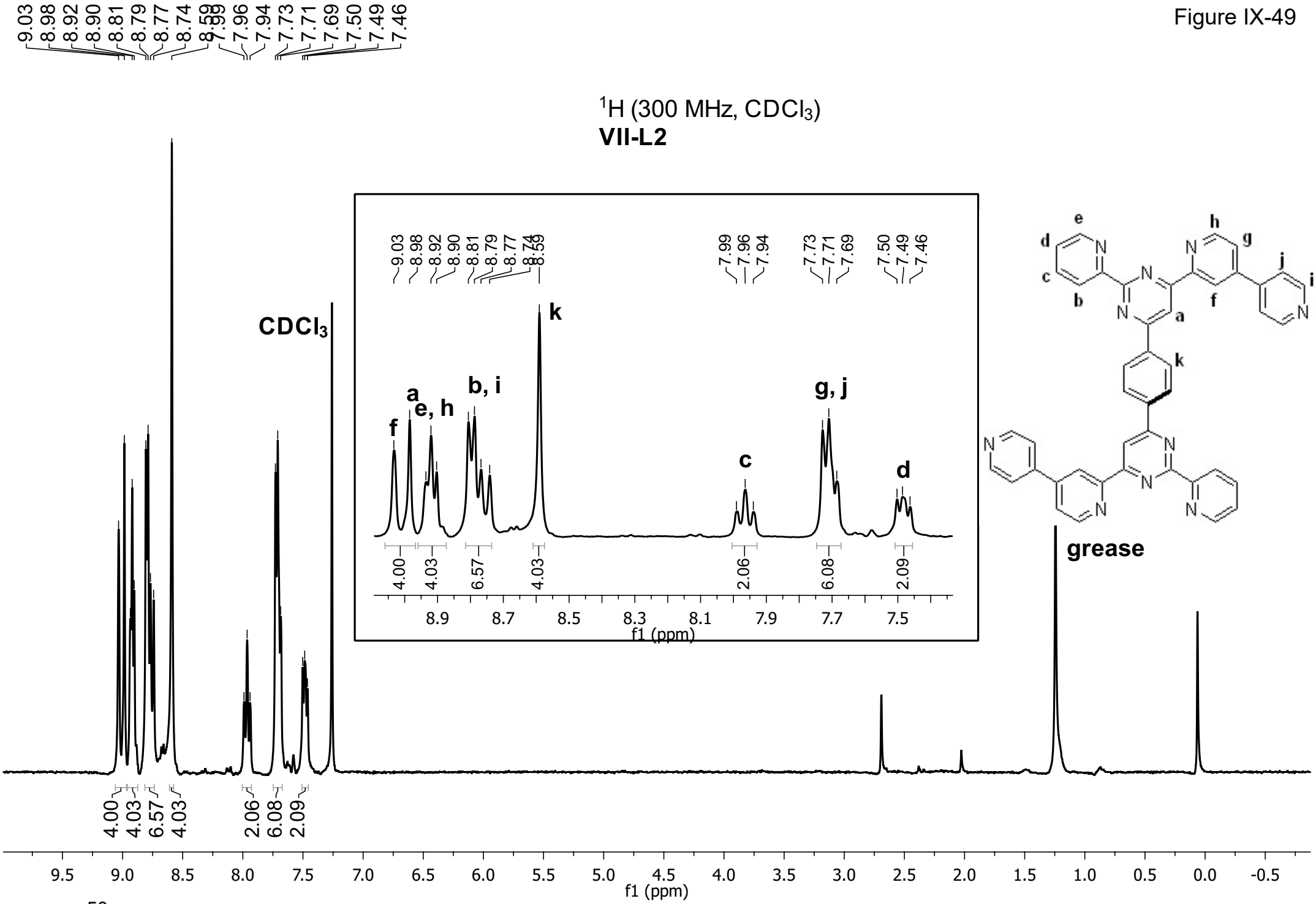

9.03
8.98
8.92
8.90
8.81
8.79
8.77
8.74
8.59
7.99
7.96
7.94
7.73
7.71
7.69
7.50
7.49
7.46
^{1}H (300 MHz, $CDCl_3$)
VII-L2
$CDCl_3$
grease
a
b, i
c
d
e, h
f
g, j
k
4.00
4.03
6.57
4.03
2.06
6.08
2.09
f1 (ppm)

Figure IX-50

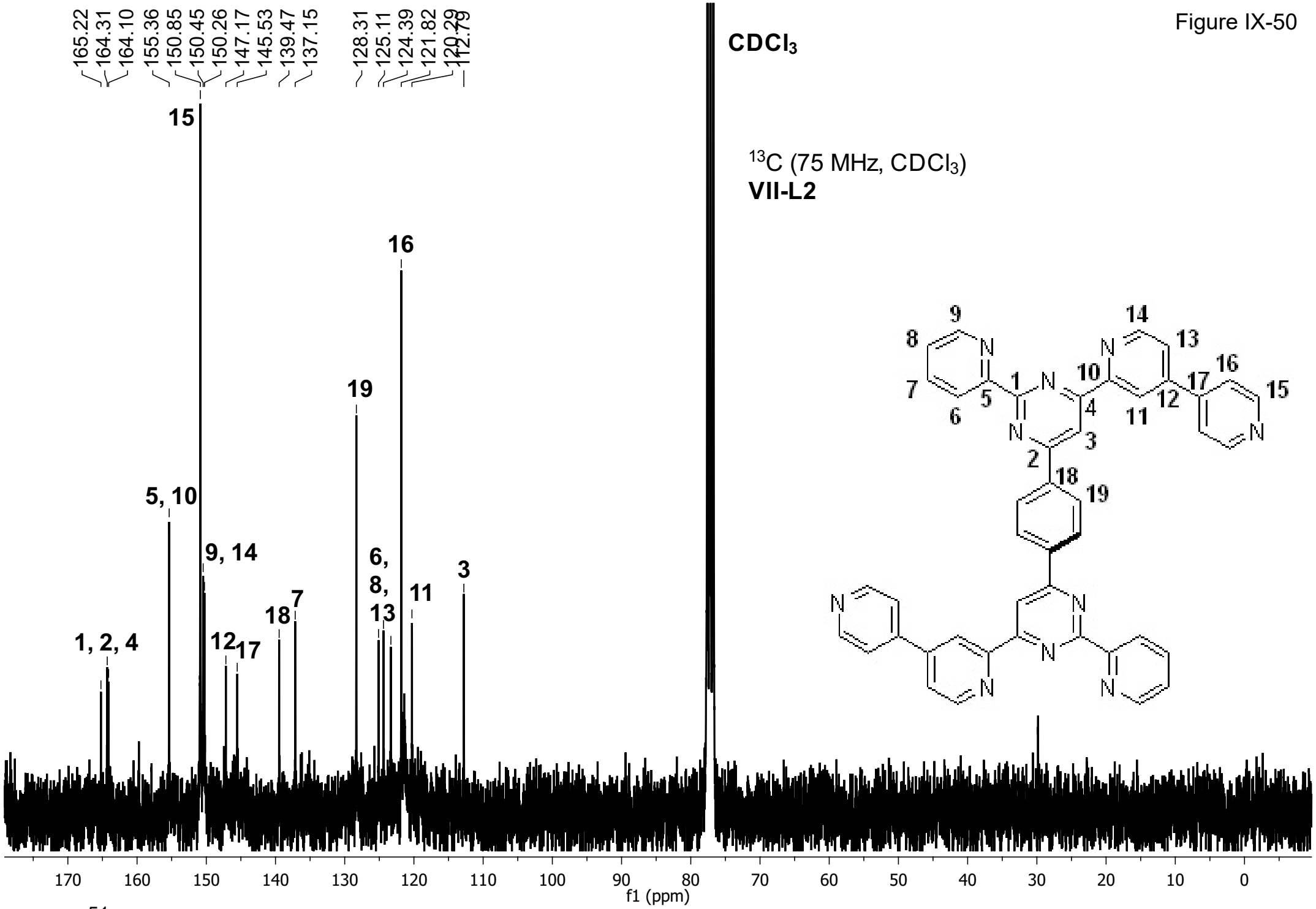

165.22
164.31
164.10
155.36
150.85
150.45
150.26
147.17
145.53
139.47
137.15
128.31
125.11
124.39
121.82
120.29
112.79
CDCl3
15
16
19
5, 10
9, 14
6,
8,
13
11
3
18
7
12
17
1, 2, 4
13C (75 MHz, CDCl3)
VII-L2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Figure IX-51

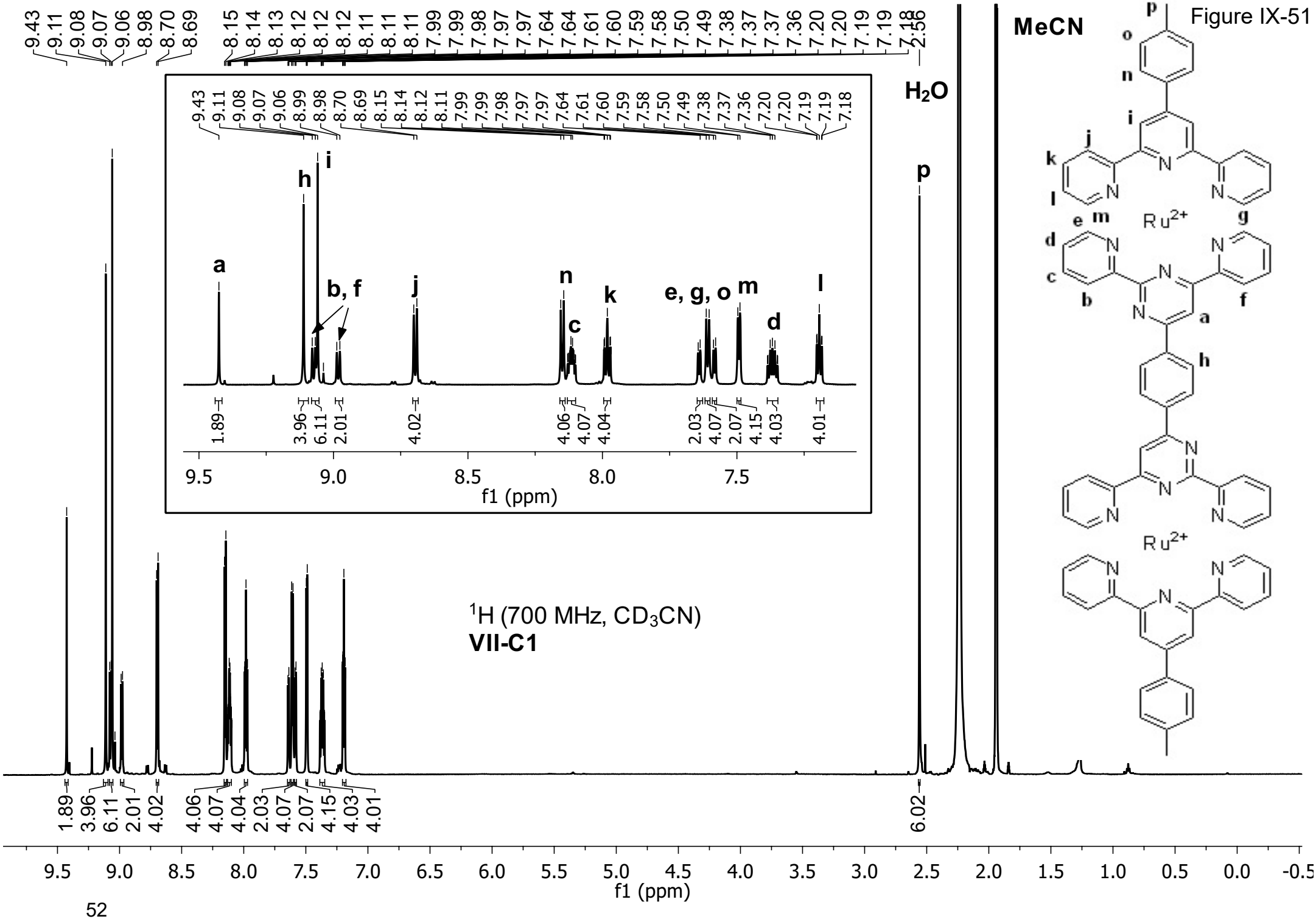
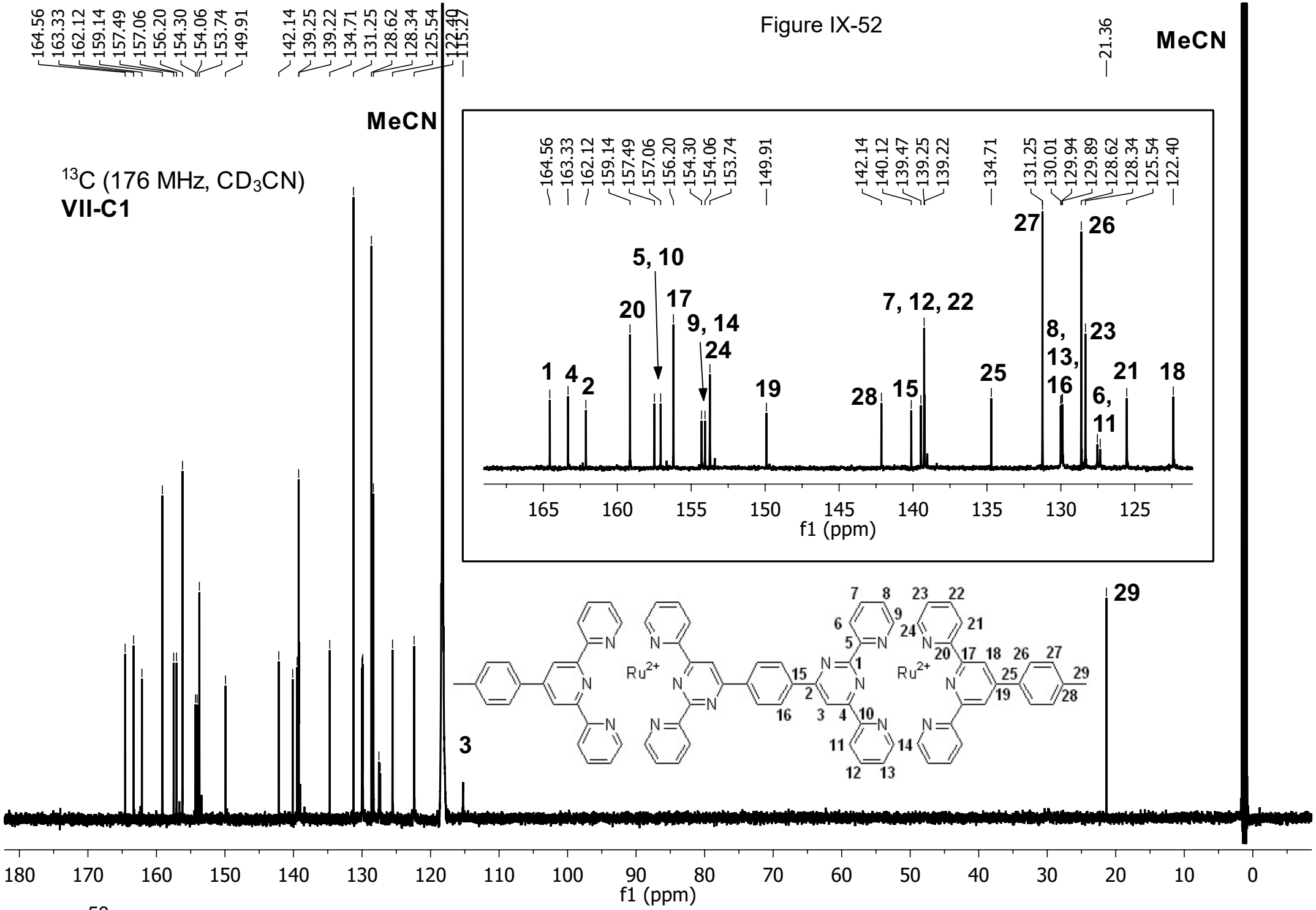

MeCN
H2O
p
a
h
i
b, f
j
n
c
k
e, g, o
m
d
l
1.89
3.96
6.11
2.01
4.02
4.06
4.07
4.04
2.03
4.07
2.07
4.15
4.03
4.01
6.02
f1 (ppm)
[1]H (700 MHz, CD3CN)
VII-C1
Ru2+

Figure IX-52


^{13}C (176 MHz, CD_3CN)
VII-C1
MeCN
MeCN
164.56
163.33
162.12
159.14
157.49
157.06
156.20
154.30
154.06
153.74
149.91
142.14
139.25
139.22
134.71
131.25
128.62
128.34
125.54
122.40
115.27
21.36
1
4
2
20
5, 10
17
9, 14
24
19
28
15
7, 12, 22
25
27
8,
13,
16
26
23
6,
11
21
18
29
3
Ru2+
Ru2+
f1 (ppm)
f1 (ppm)

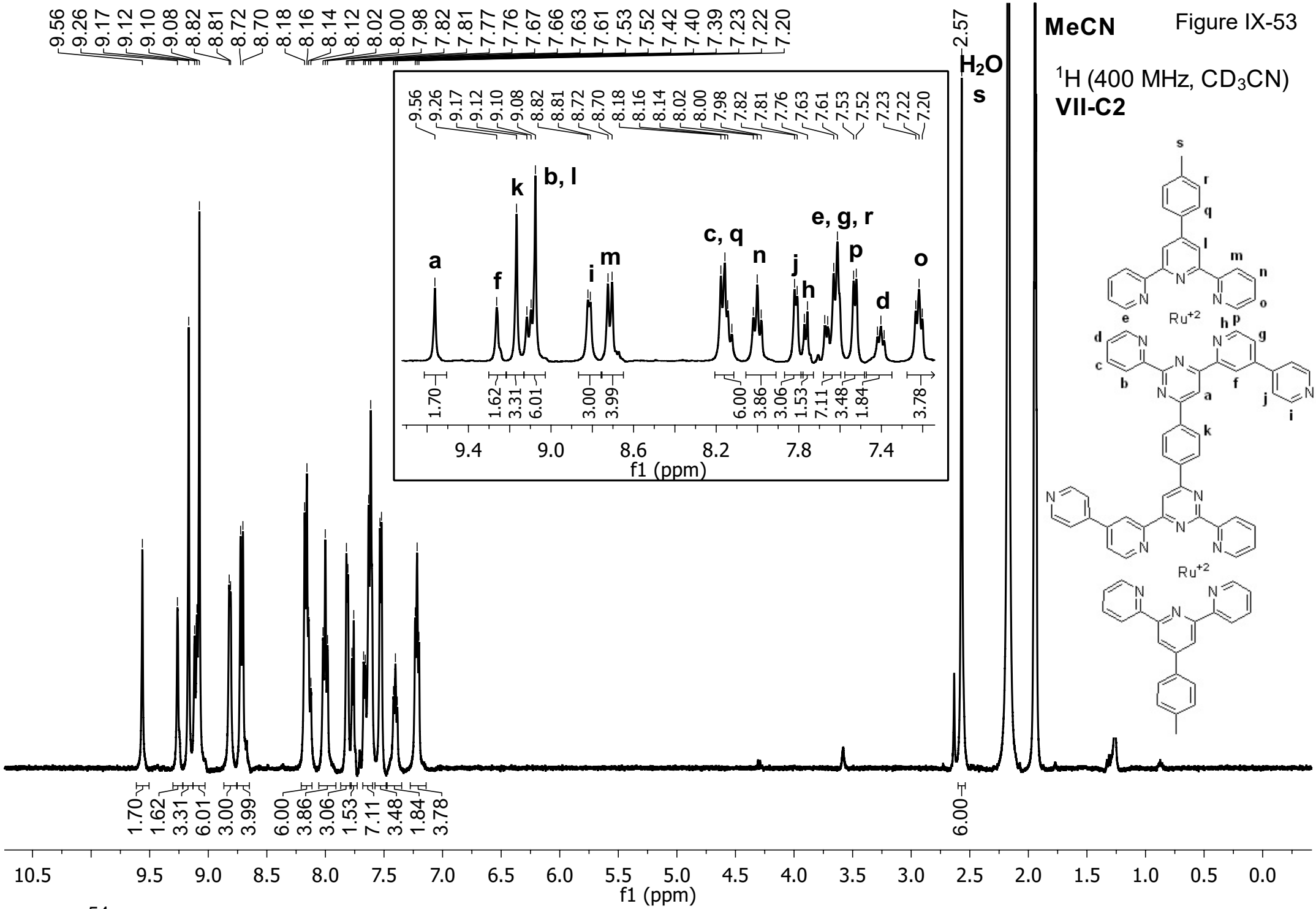
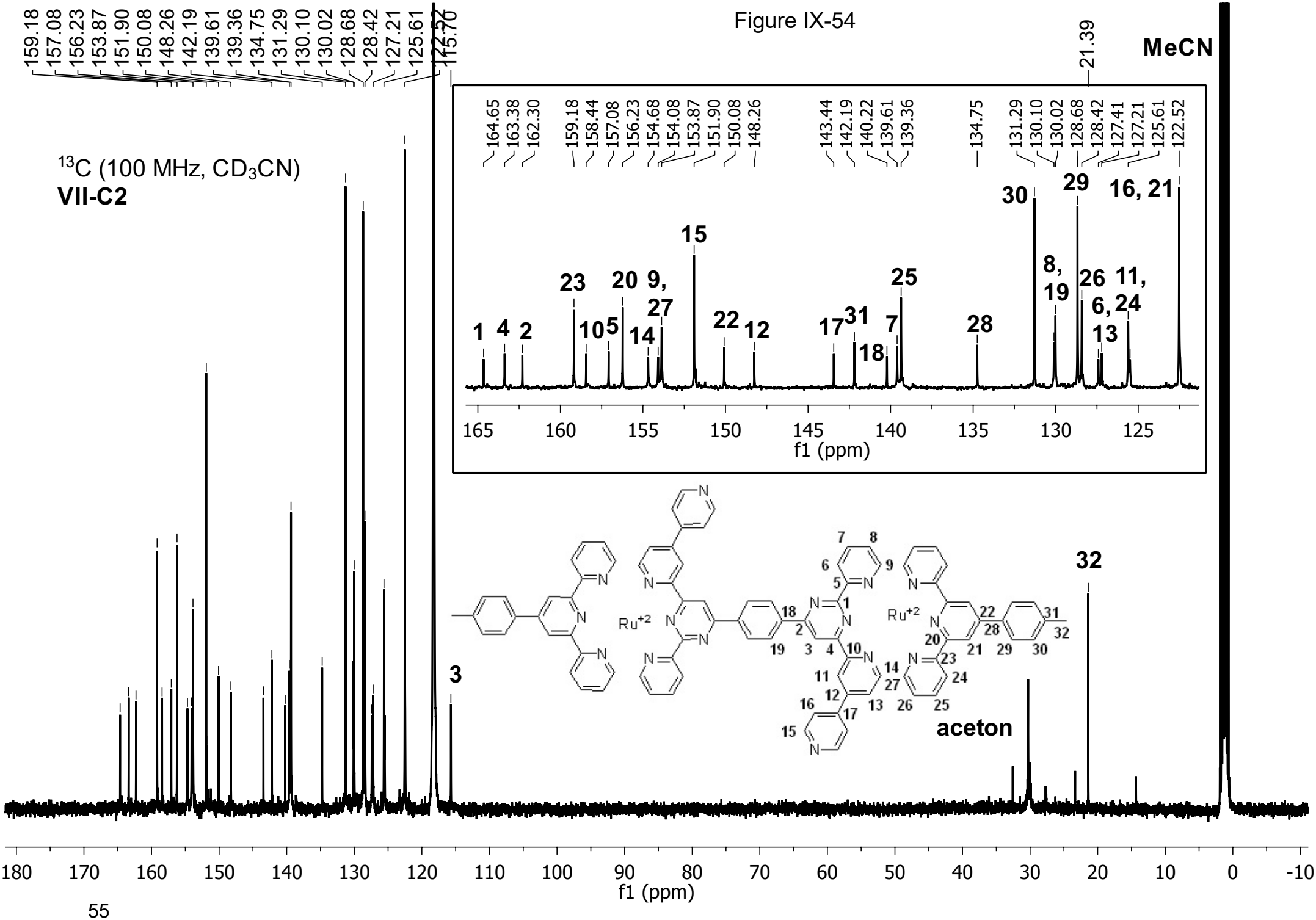

MeCN
Figure IX-53
^{1}H (400 MHz, CD_3CN)
VII-C2
H_2O
s
a
f
k
b, l
i
m
c, q
n
j
h
e, g, r
p
d
o
Ru+2
f1 (ppm)

Figure IX-54


159.18
157.08
156.23
153.87
151.90
150.08
148.26
142.19
139.61
139.36
134.75
131.29
130.10
130.02
128.68
128.42
127.21
125.61
122.52
115.70
21.39
MeCN
^{13}C (100 MHz, CD_3CN)
VII-C2
164.65
163.38
162.30
159.18
158.44
157.08
156.23
154.68
154.08
153.87
151.90
150.08
148.26
143.44
142.19
140.22
139.61
139.36
134.75
131.29
130.10
130.02
128.68
128.42
127.41
127.21
125.61
122.52
1
4
2
23
10
5
20
14
9,
27
15
22
12
17
31
18
7
25
28
30
8,
19
29
26
16, 21
11,
6,
24
13
165
160
155
150
145
140
135
130
125
f1 (ppm)
3
32
aceton
Ru+2
Ru+2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)