Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for
An N-Heterocyclic carbene phenanthroline ligand: synthesis, multi-metal coordination and spectroscopic studies.

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Contents:

Emission Measurements and Quantum Yields

Fluorescence spectroscopy was performed with a Shimadzu RF-5301PC spectrofluorophotometer using a quartz cuvette with 1 cm path length with four polished sides, the slit widths on the spectrofluorophotometer were set to 10 nm resolution (for both excitation and emission) with an excitation λ = 436 nm with a detection range from 446 to 800 nm. All samples were dissolved in acetonitrile and spectra was acquired at 20 °C in air. The instrument was calibrated with $(Rubpy_3)$ $2Cl^-$ dissolved in a MeOH/EtOH 1:4 mixture with all sample concentrations ≤ 1.0×10^{-5} M and absorbances ≤ 0.2 at the excitation wavelength.

Time-Correlated Single Photon Counting (TCSPC) measurements were carried out in a Horiba Fluorolog TCSPC coupled to a Horiba iHR320 grating monochromator (1200 g/mm). The source of excitation was from a 452 nm LED Horiba DD-450L Delta Diode picosecond laser with detection set to $\lambda_{max,em}$. All spectra was collected on a Horiba Jobin Yvon TBX-04 photon detection system. All measurements were taken with using a quartz cuvette with a 1cm path length with four polished sides.

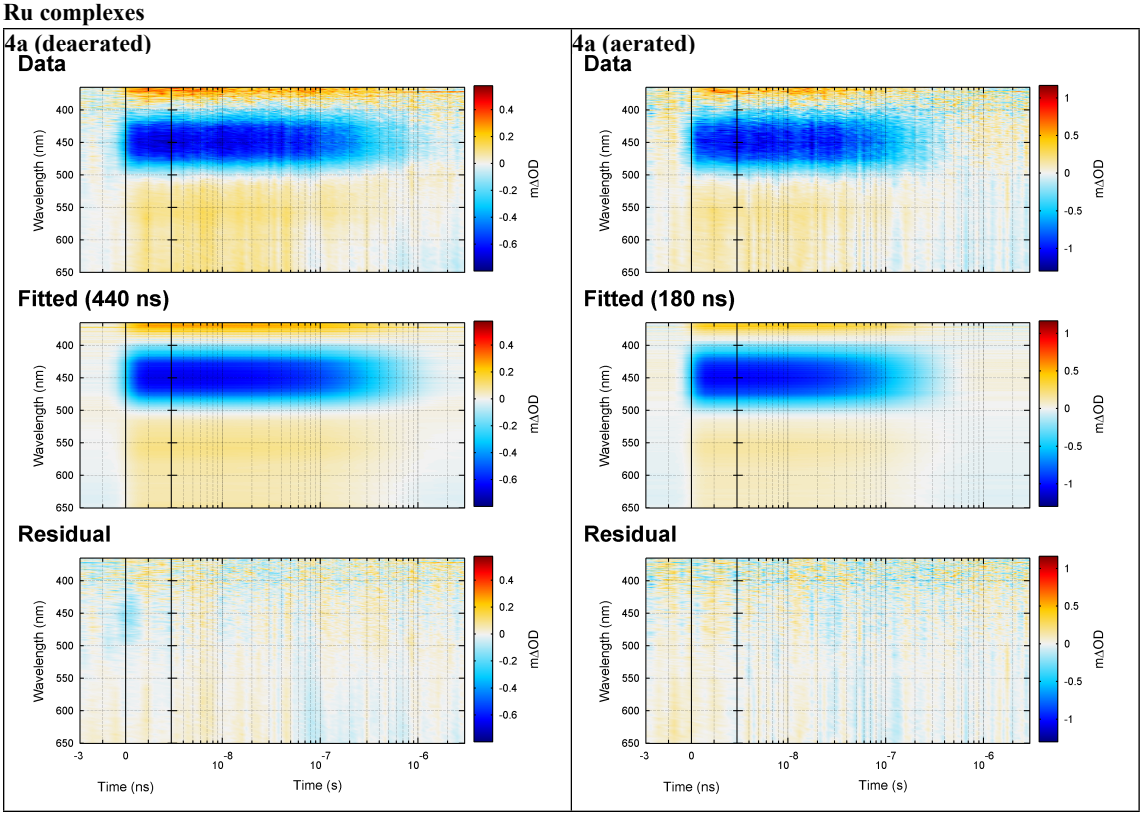
Transient Absorption Spectroscopy

TA spectroscopy was carried out using an amplified Ti:Sapphire laser (Spectra Physics, Spitfire 100 fs pulsewidth) synchronized with a Q-switched Nd:YVO_4 laser (AOT-YVO-25QSP, 700 ps pulsewidth). The 3rd harmonic 355 nm output of the Nd:YVO_4 served as the excitation beam, which was attenuated to ~100-300 μW (66-200 nJ/pulse) and focused onto the sample with a beam diameter of 170 μm. A small portion of the 800 nm Ti:Sapphire output was used to generate UV-visible continuum probe pulses by focusing in a constantly moving 3 mm CaF_2 window. The probe beam was overlapped at the magic angle polarization with the excited region of the sample and spectrally dispersed using a home-built prism based polychromator. The pump-probe delay was electronically varied by a delay generator (Stanford Systems, DG535). Probe shots were read out at the laser rep-rate of 3 KHz using a linear photodiode array (Stresing). Differential absorption spectra are obtained by comparing the transmission of sequential pairs of probe pulses with the pump beam chopped at ω/2 (1500 Hz). 200 shots where typically averaged per time point, and the series of ~100 time points (including some at negative pump-probe delay times) was then scanned ~12 times per measurement. Analysis of the TA surfaces, including global fitting, was carried out using MATLAB.

TA global fitting

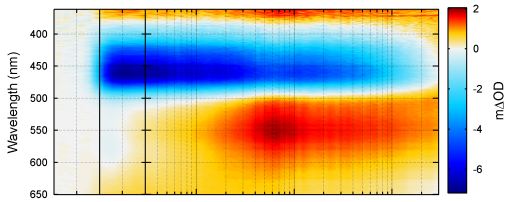
In each case, the measured TA surface is shown in the top panel, followed by the globally fitted surface with the time constants shown (and also given in the main text). The bottom panel shows the residual surface, where the dominance of random noise indicates a good fit to the data.

Ru complexes

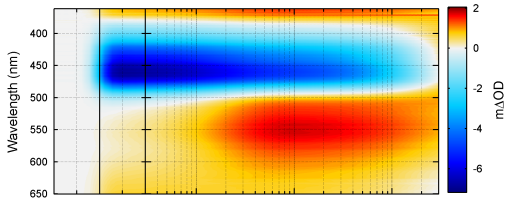


6 deaerated

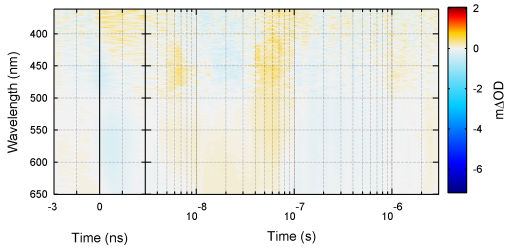
Data

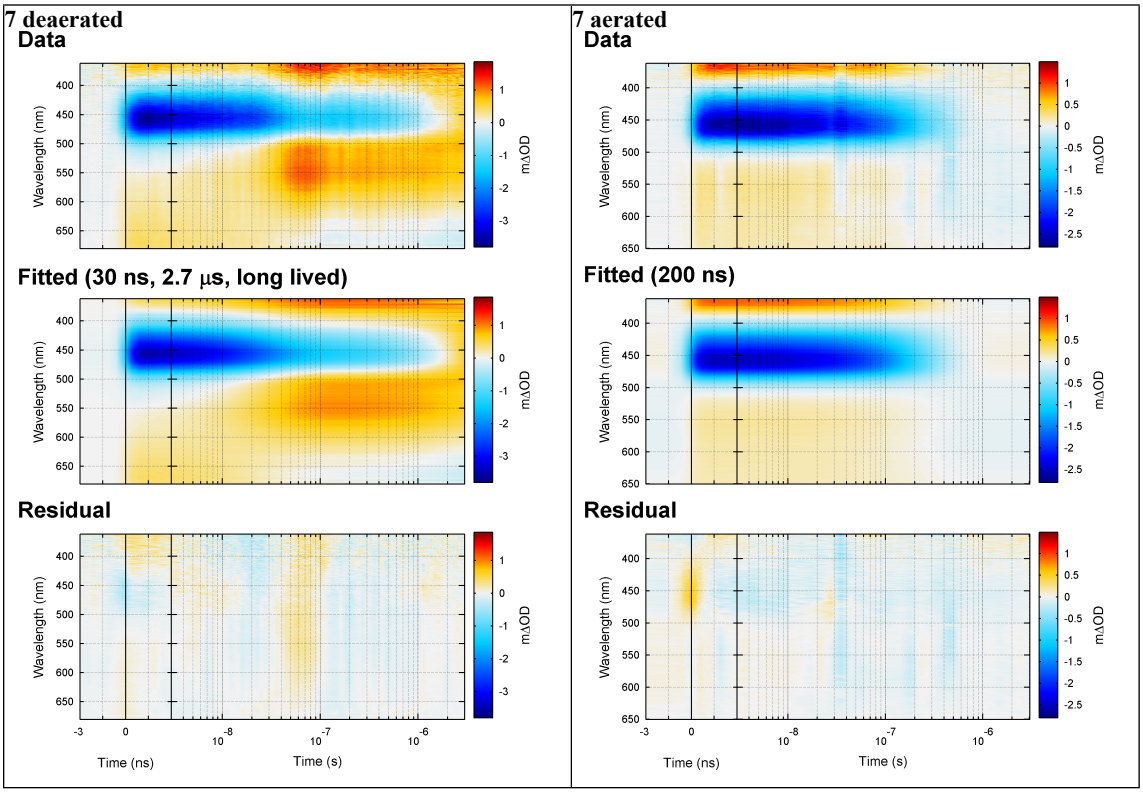


Fitted (20 ns, 1.9 μs, long lived)

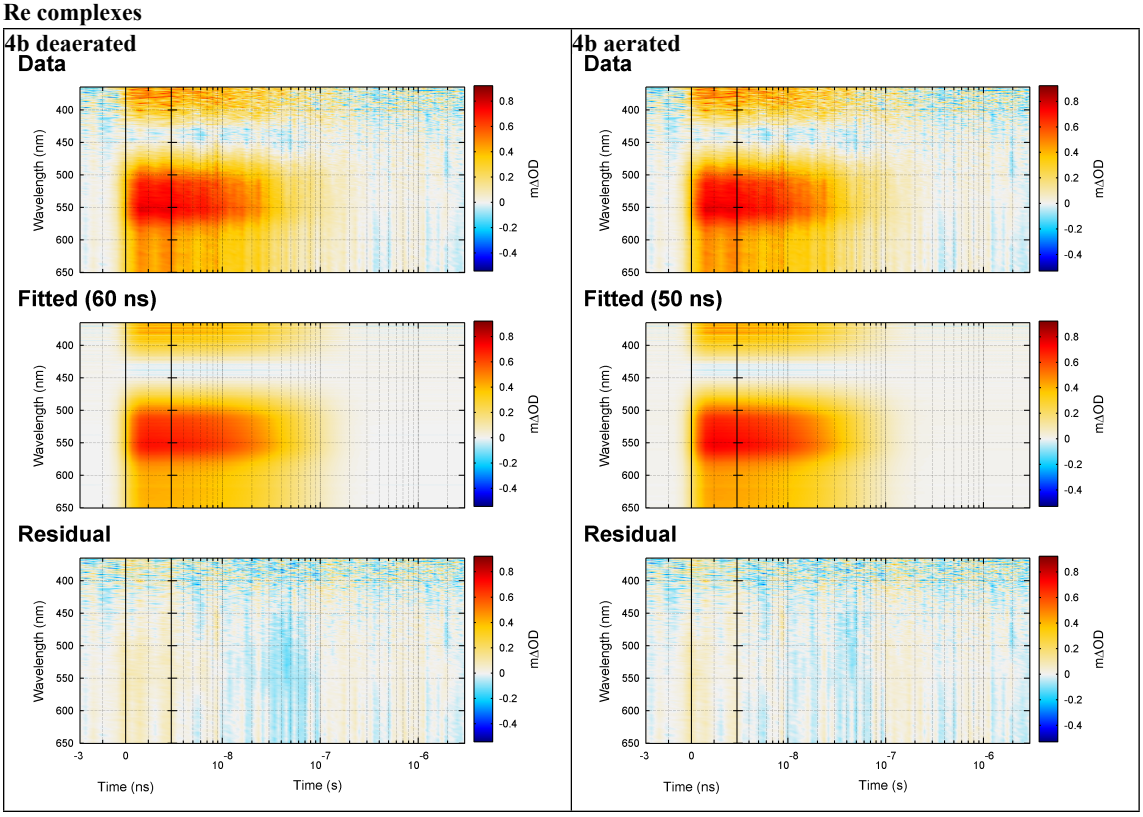


Residual

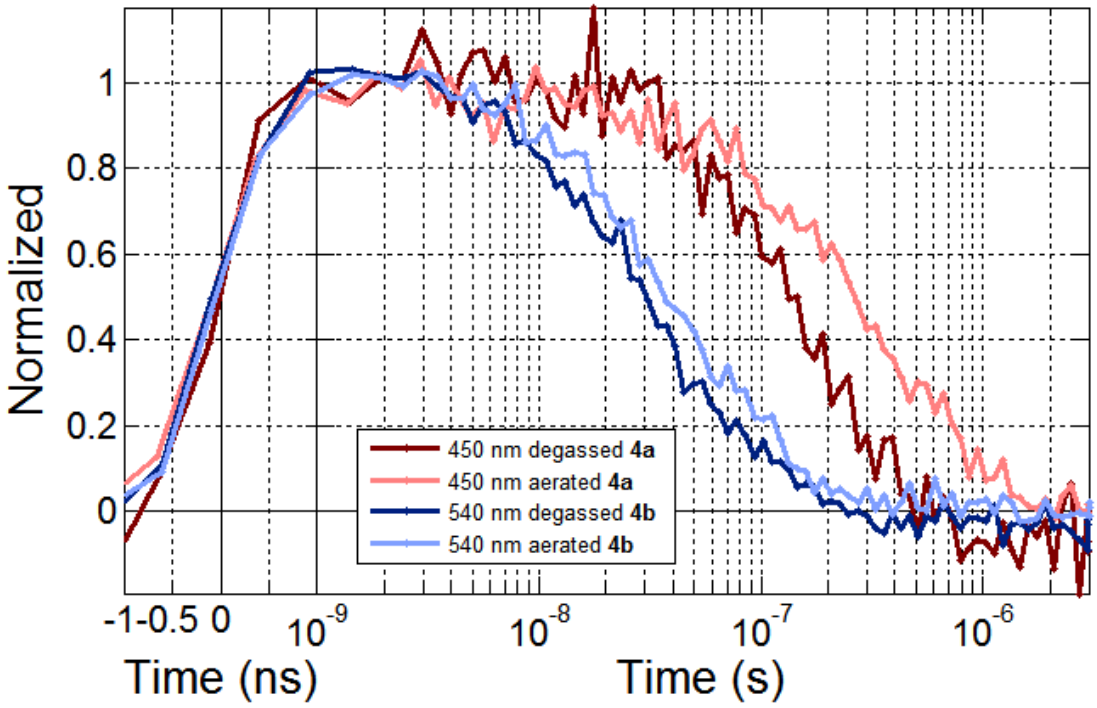


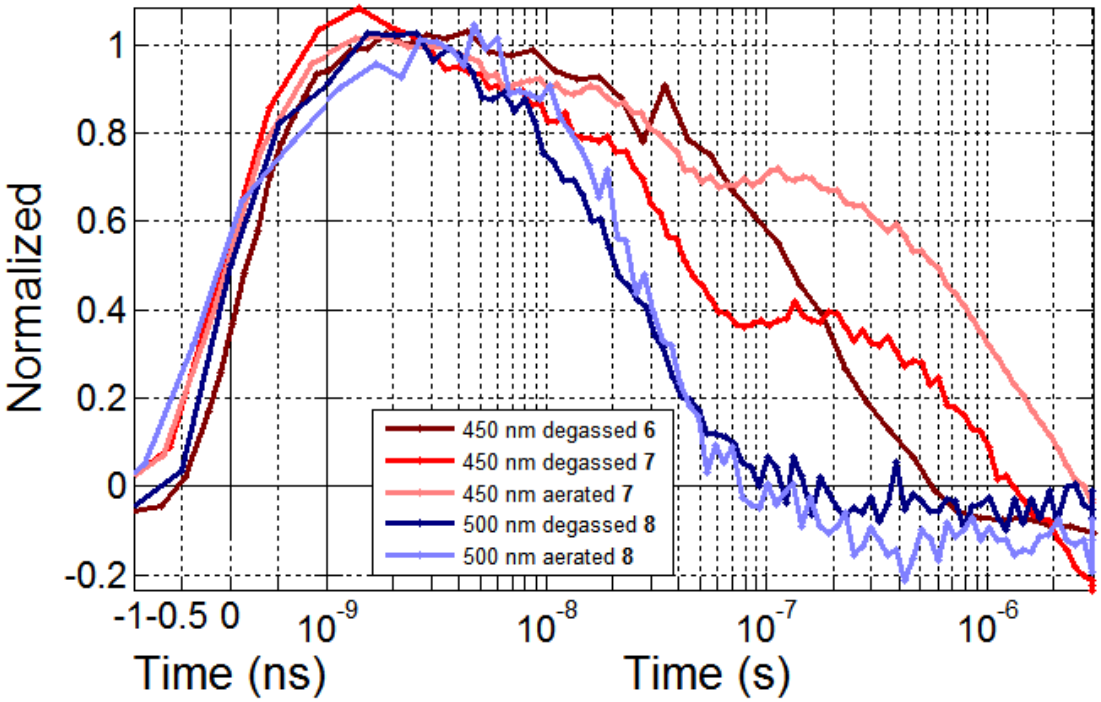

7 deaerated
Data
Fitted (30 ns, 2.7 μs, long lived)
Residual
7 aerated
Data
Fitted (200 ns)
Residual
Wavelength (nm)
mΔOD
Time (ns)
Time (s)

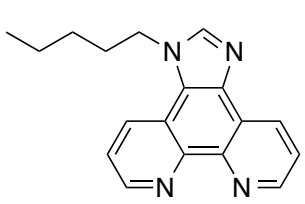
Re complexes



Decay curves





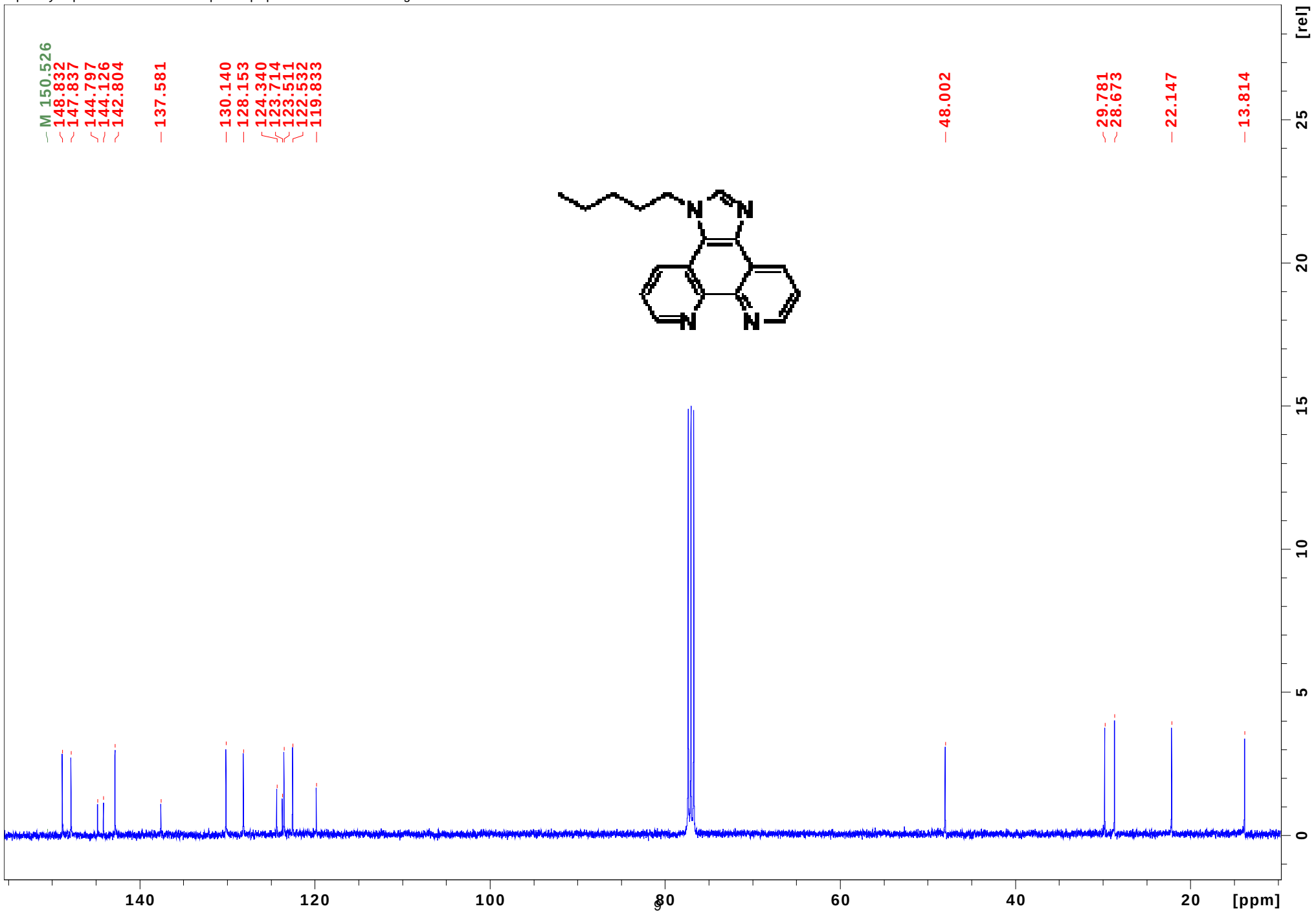


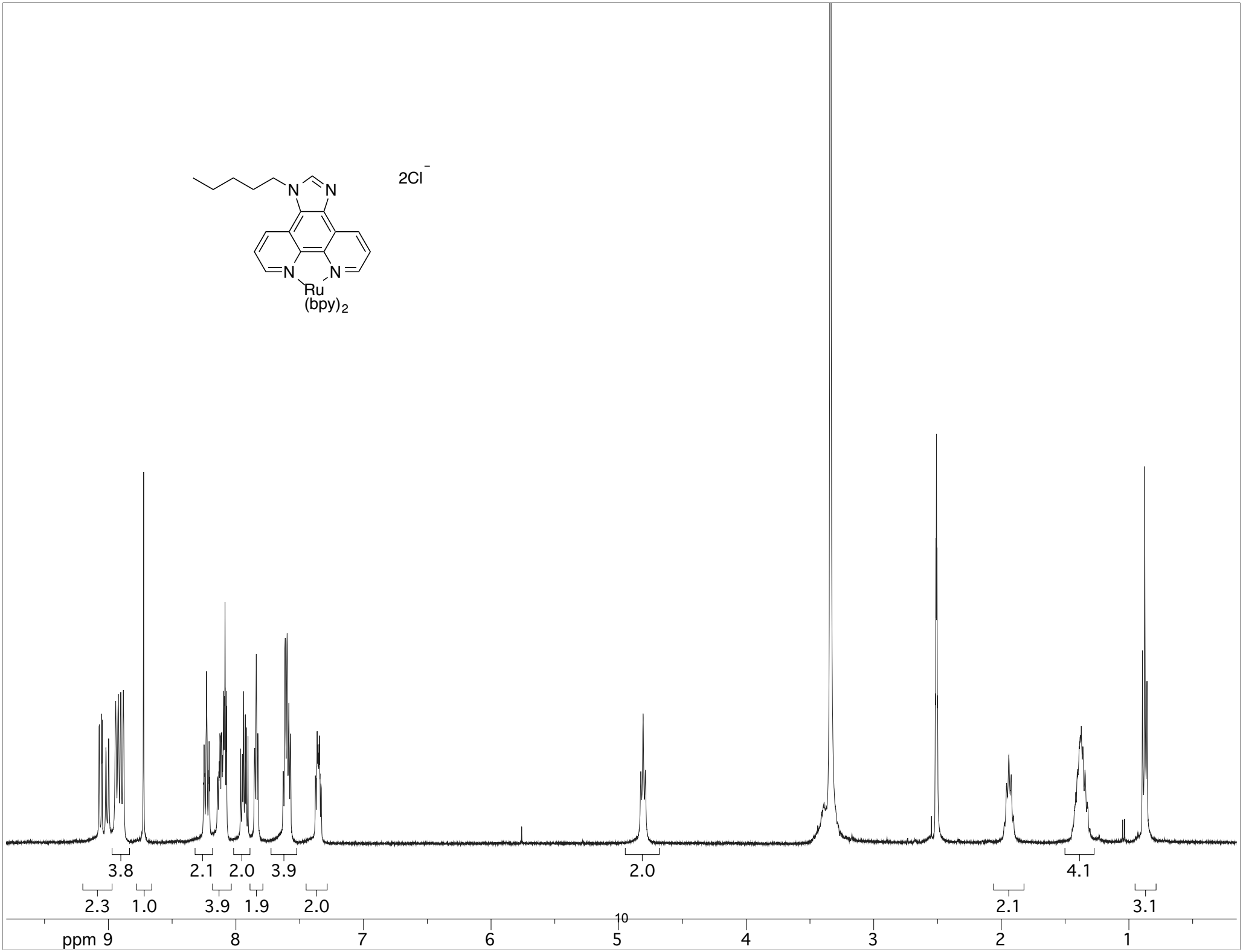
1.0 1.0 2.1 2.1 4.2

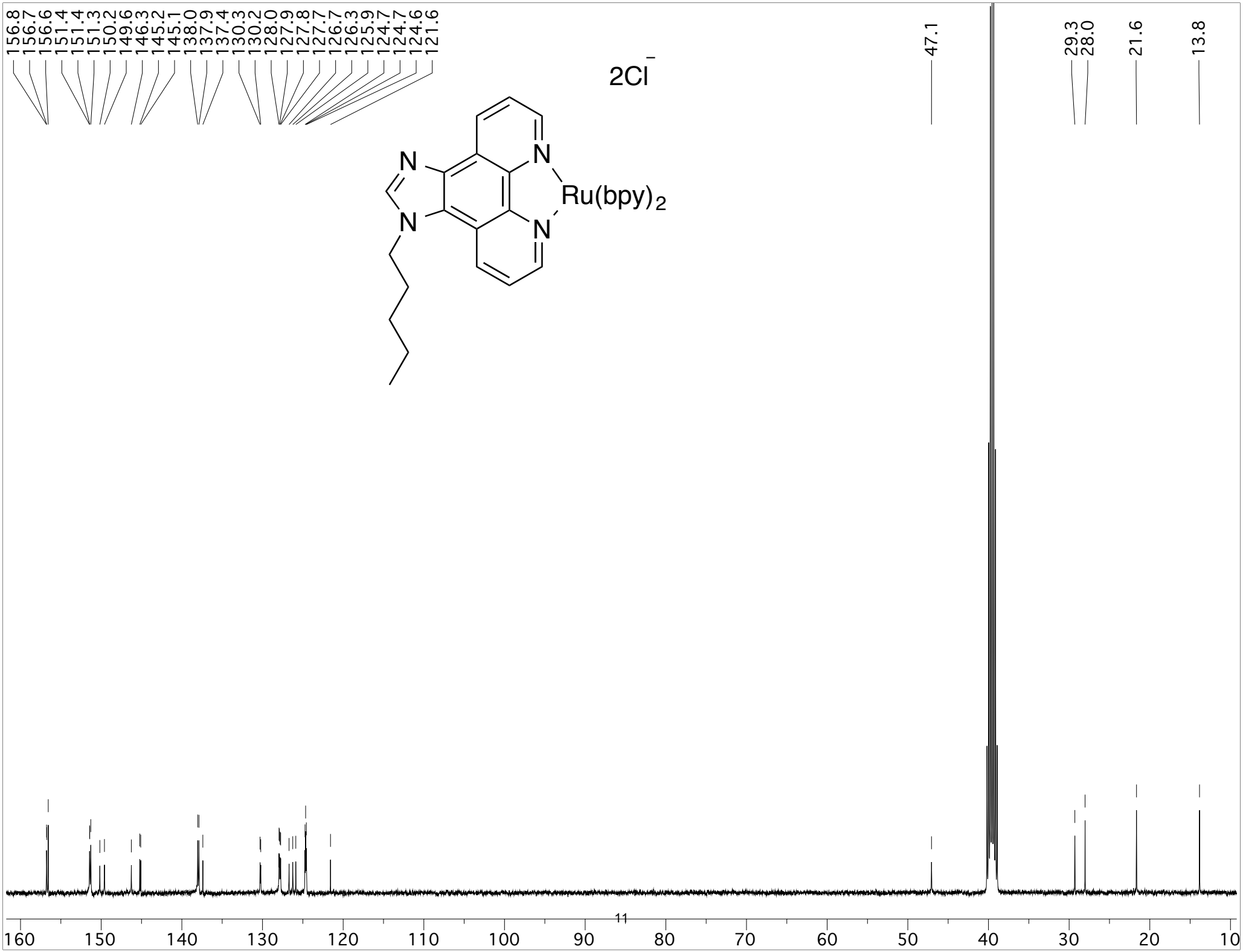
2.0 1.0 2.1 2.2 3.2

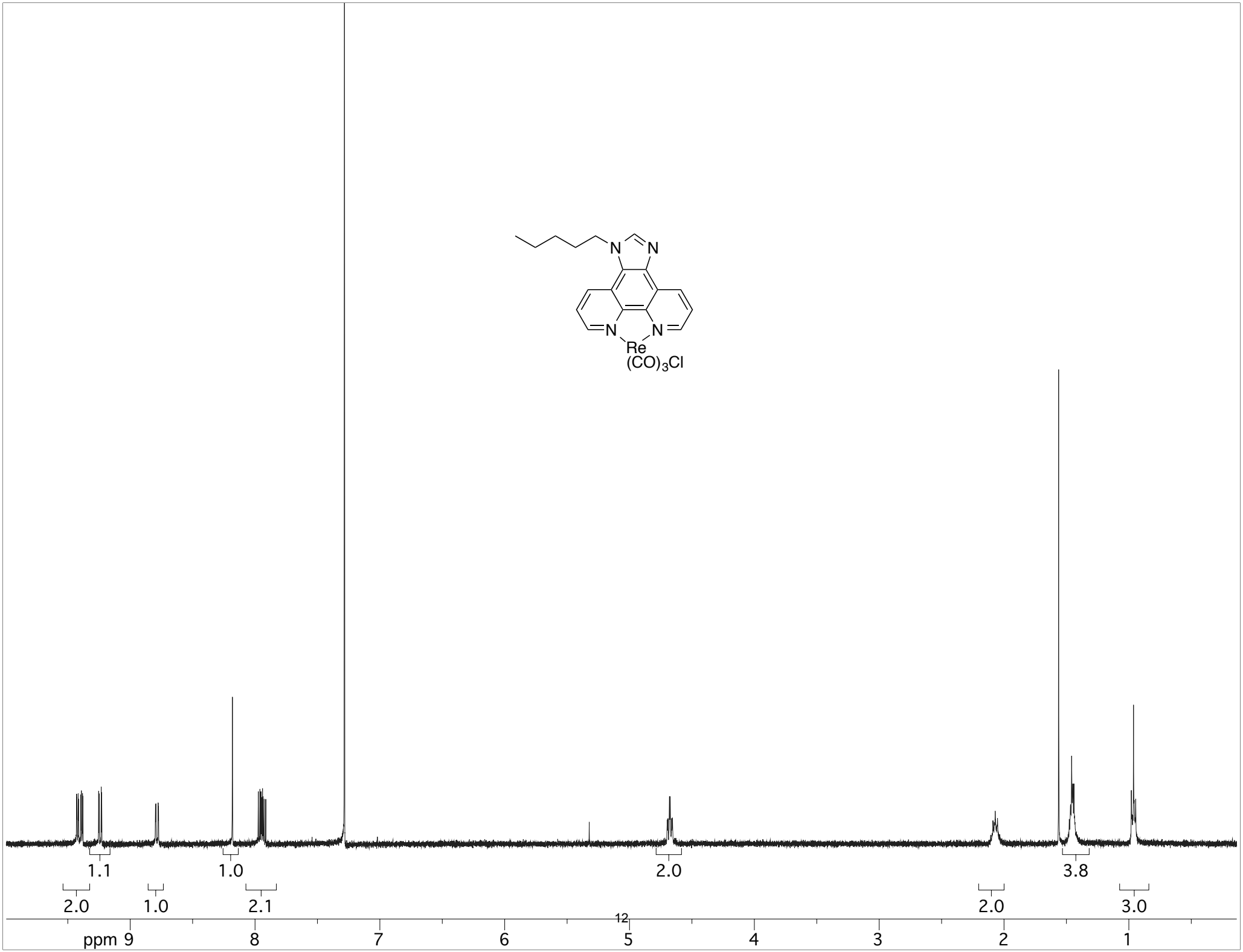
ppm 9 8 7 6 5 4 3 2 1

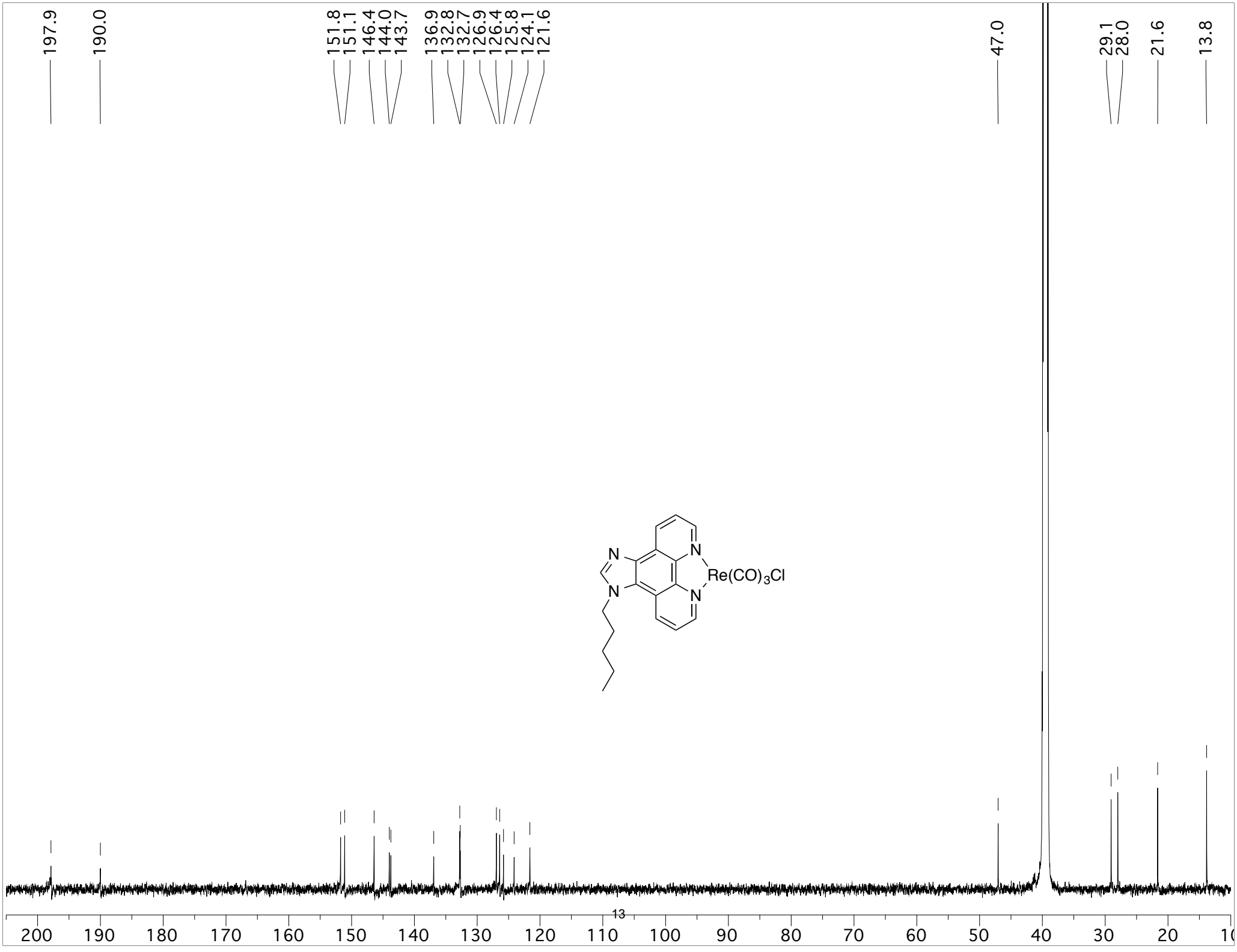
"pentyl phim C" 1 1 /opt/topspin3.0/data/hoberg

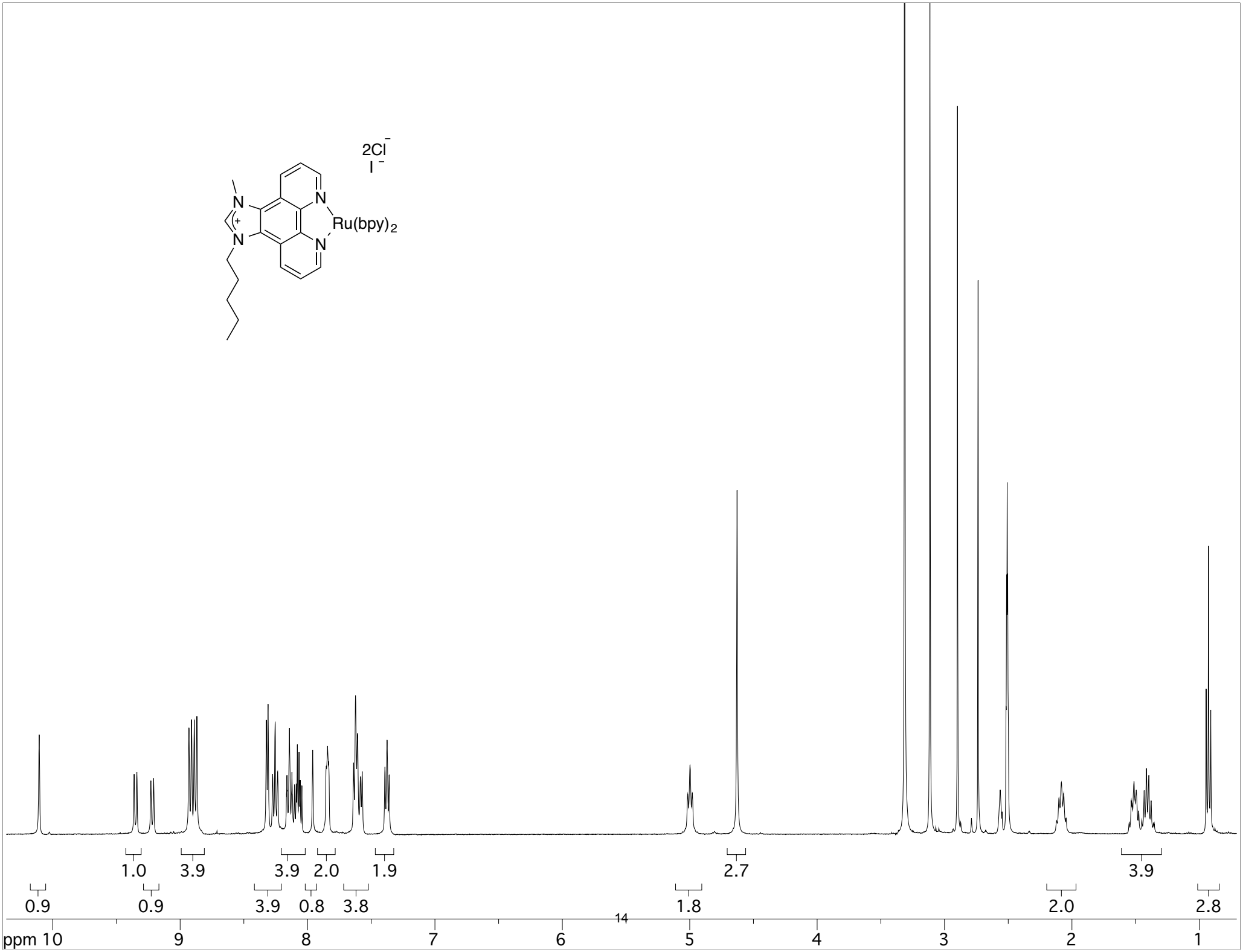


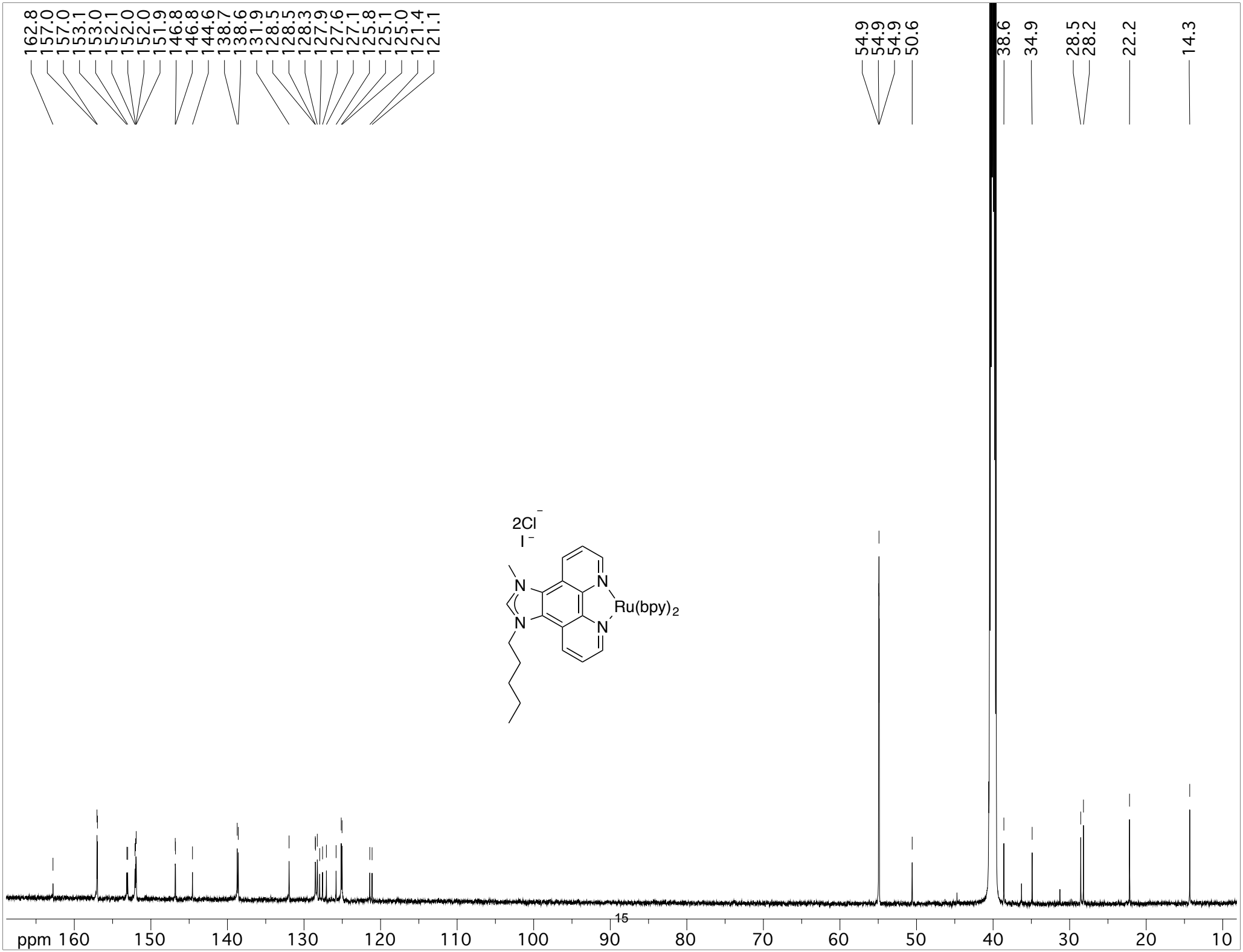

2Cl⁻
N
N
N
N
Ru
(bpy)2
3.8
2.1
2.0
3.9
2.0
4.1
2.3
1.0
3.9
1.9
2.0
2.1
3.1
ppm 9
8
7
6
5
4
3
2
1

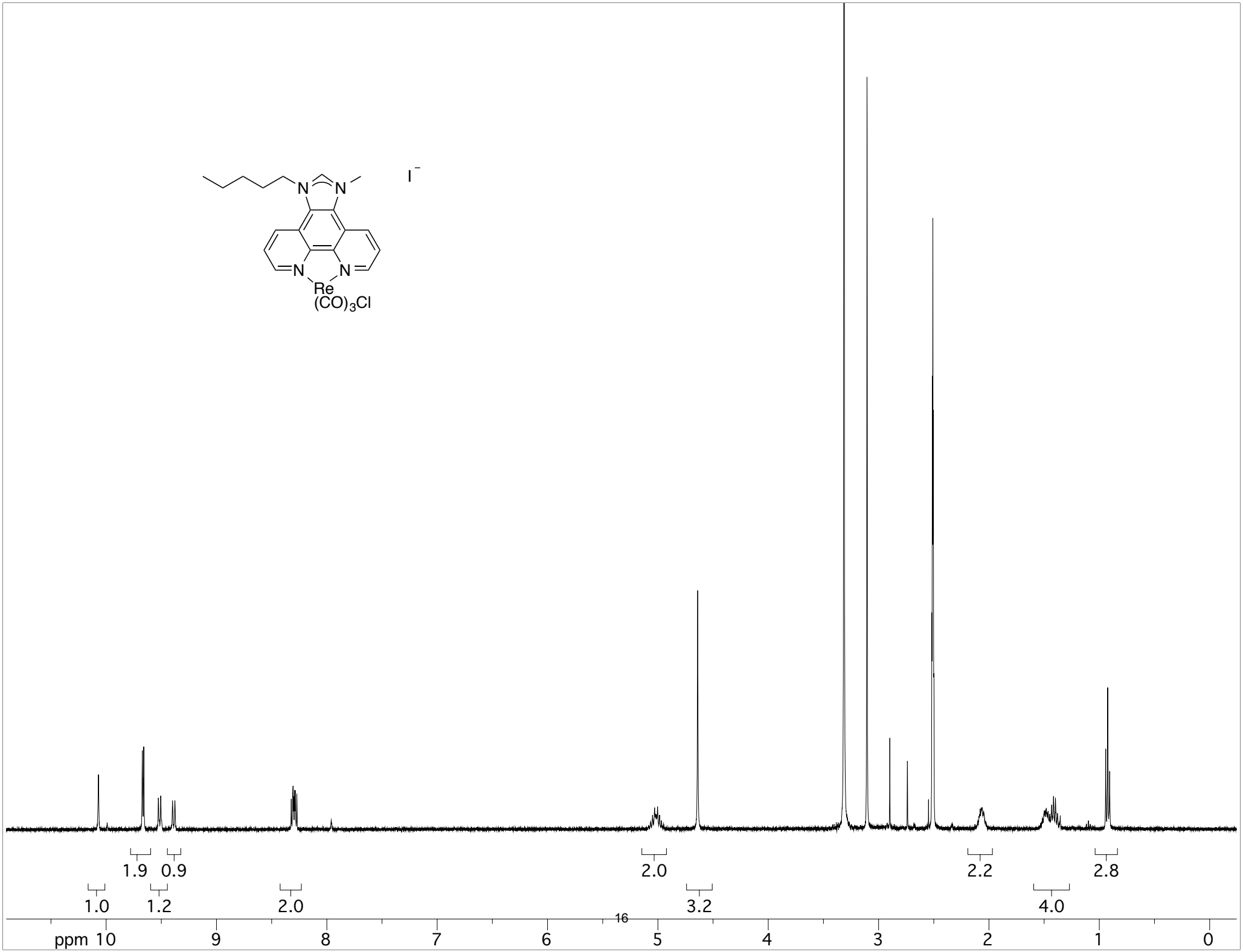

156.8
156.7
156.6
151.4
151.4
151.3
150.2
149.6
146.3
145.2
145.1
138.0
137.9
137.4
130.3
130.2
128.0
127.9
127.8
127.7
126.7
126.3
125.9
124.7
124.7
124.6
121.6
47.1
29.3
28.0
21.6
13.8
2Cl⁻
N
N
N
N
Ru(bpy)2
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

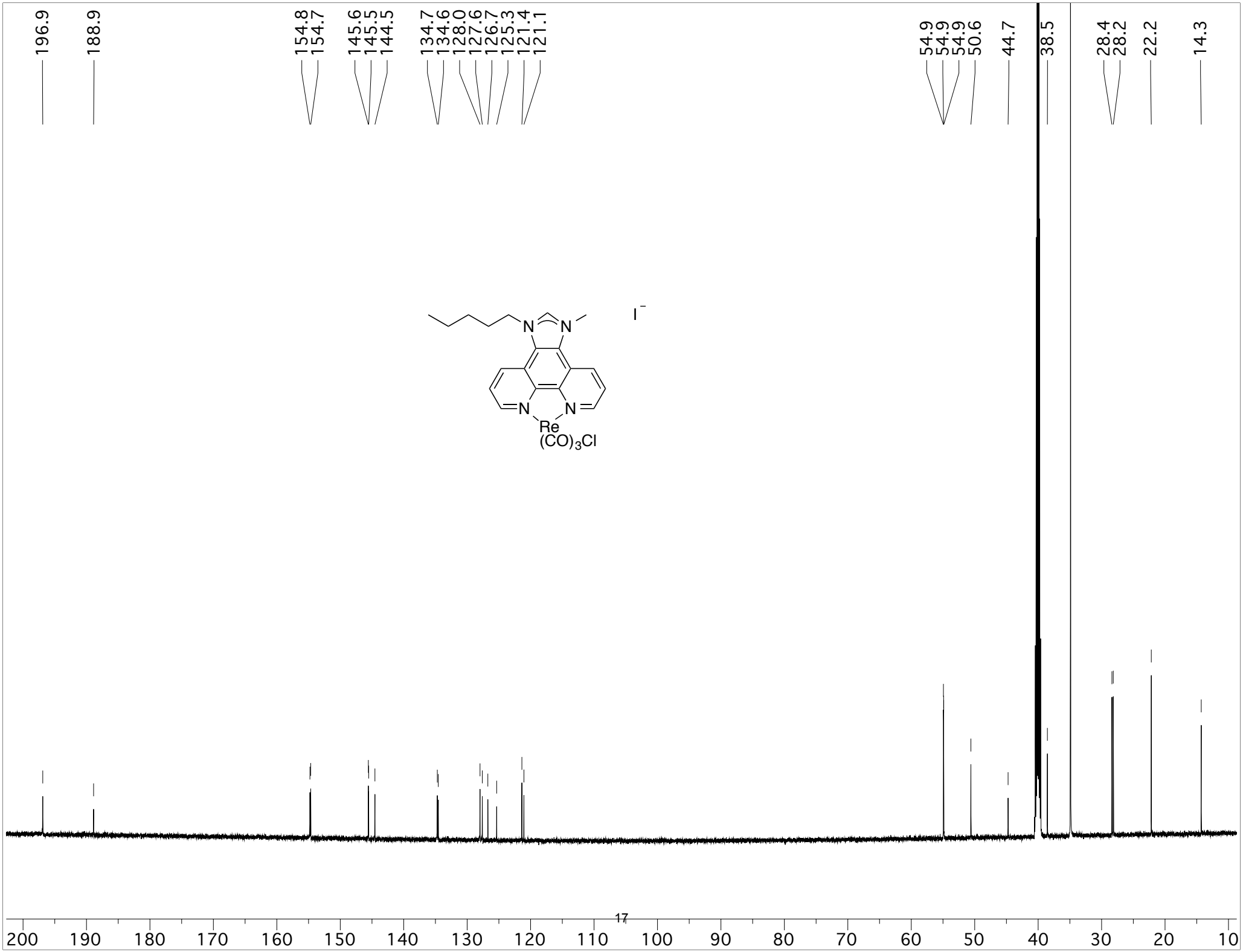

N
N
N
N
Re
(CO)3Cl
1.1
1.0
2.0
3.8
2.0
1.0
2.1
2.0
3.0
ppm 9
8
7
6
5
4
3
2
1

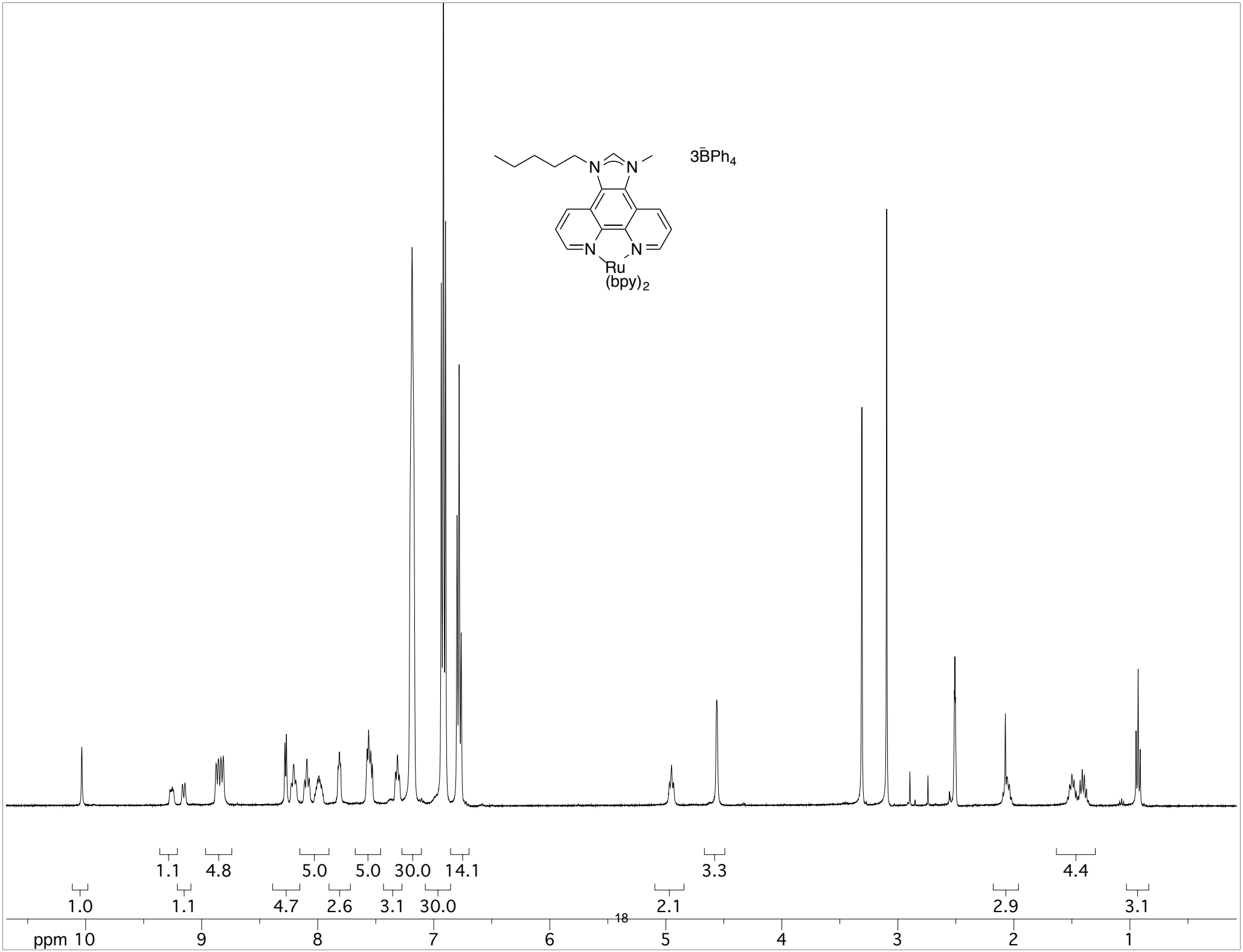

197.9
190.0
151.8
151.1
146.4
144.0
143.7
136.9
132.8
132.7
126.9
126.4
125.8
124.1
121.6
47.0
29.1
28.0
21.6
13.8
N
N
N
N
Re(CO)3Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


2Cl⁻
I⁻
N
N
N
N
Ru(bpy)2
1.0
3.9
3.9
2.0
1.9
2.7
3.9
0.9
0.9
3.9
0.8
3.8
1.8
2.0
2.8
ppm 10
9
8
7
6
5
4
3
2
1


162.8
157.0
157.0
153.1
153.0
152.1
152.0
152.0
151.9
146.8
146.8
144.6
138.7
138.6
131.9
128.5
128.5
128.3
127.9
127.6
127.1
125.8
125.1
125.0
121.4
121.1
54.9
54.9
54.9
50.6
38.6
34.9
28.5
28.2
22.2
14.3
2Cl⁻
I⁻
N
N
N
N
Ru(bpy)2
ppm 160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


N
N
I⁻
N
N
Re
(CO)3Cl
1.9
0.9
2.0
2.2
2.8
1.0
1.2
2.0
3.2
4.0
ppm 10
9
8
7
6
5
4
3
2
1
0


196.9
188.9
154.8
154.7
145.6
145.5
144.5
134.7
134.6
128.0
127.6
126.7
125.3
121.4
121.1
54.9
54.9
54.9
50.6
44.7
38.5
28.4
28.2
22.2
14.3
I⁻
N
N
N
N
Re
(CO)3Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


3B̄Ph4
N
N
N
N
Ru
(bpy)2
1.1
4.8
5.0
5.0
30.0
14.1
3.3
4.4
1.0
1.1
4.7
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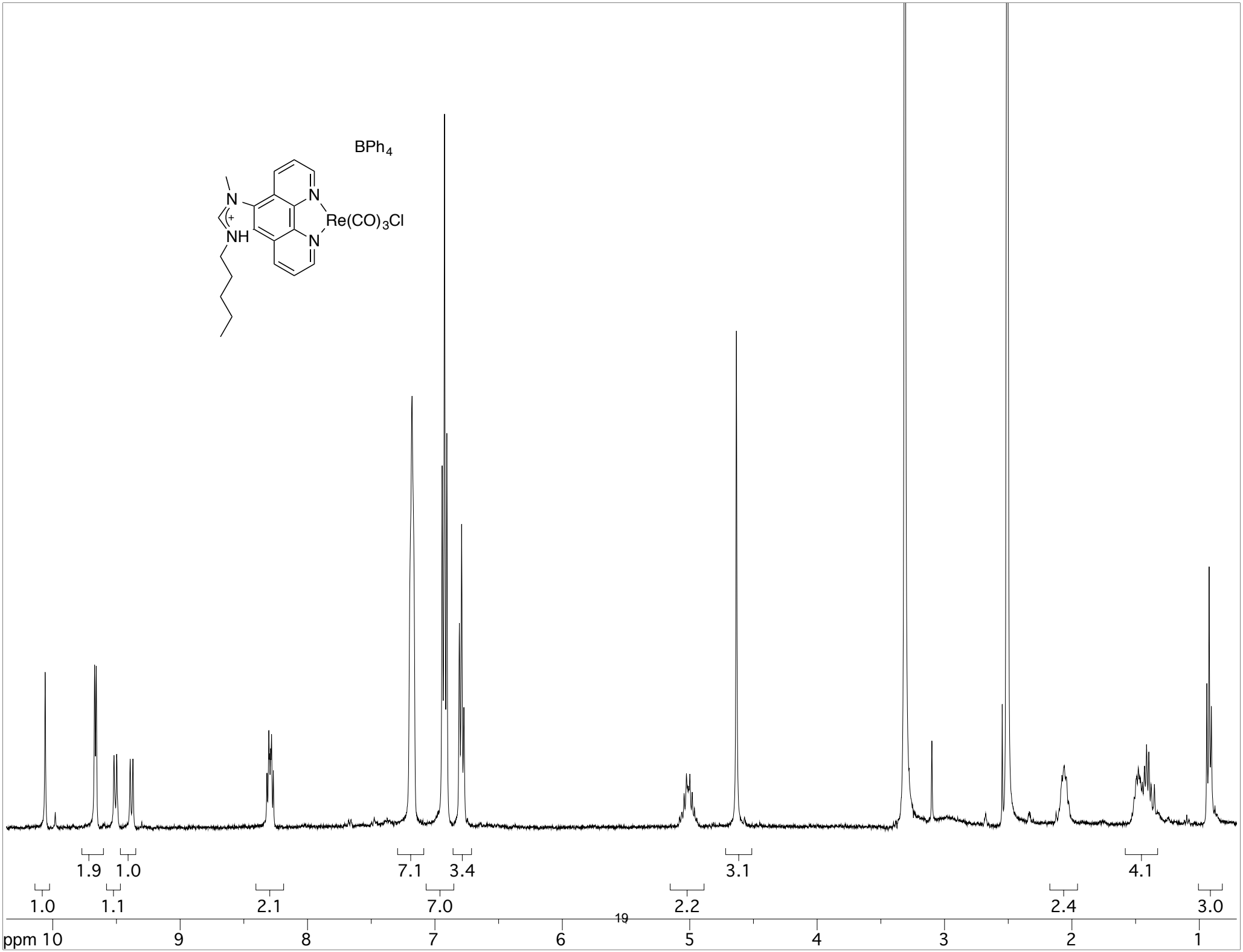
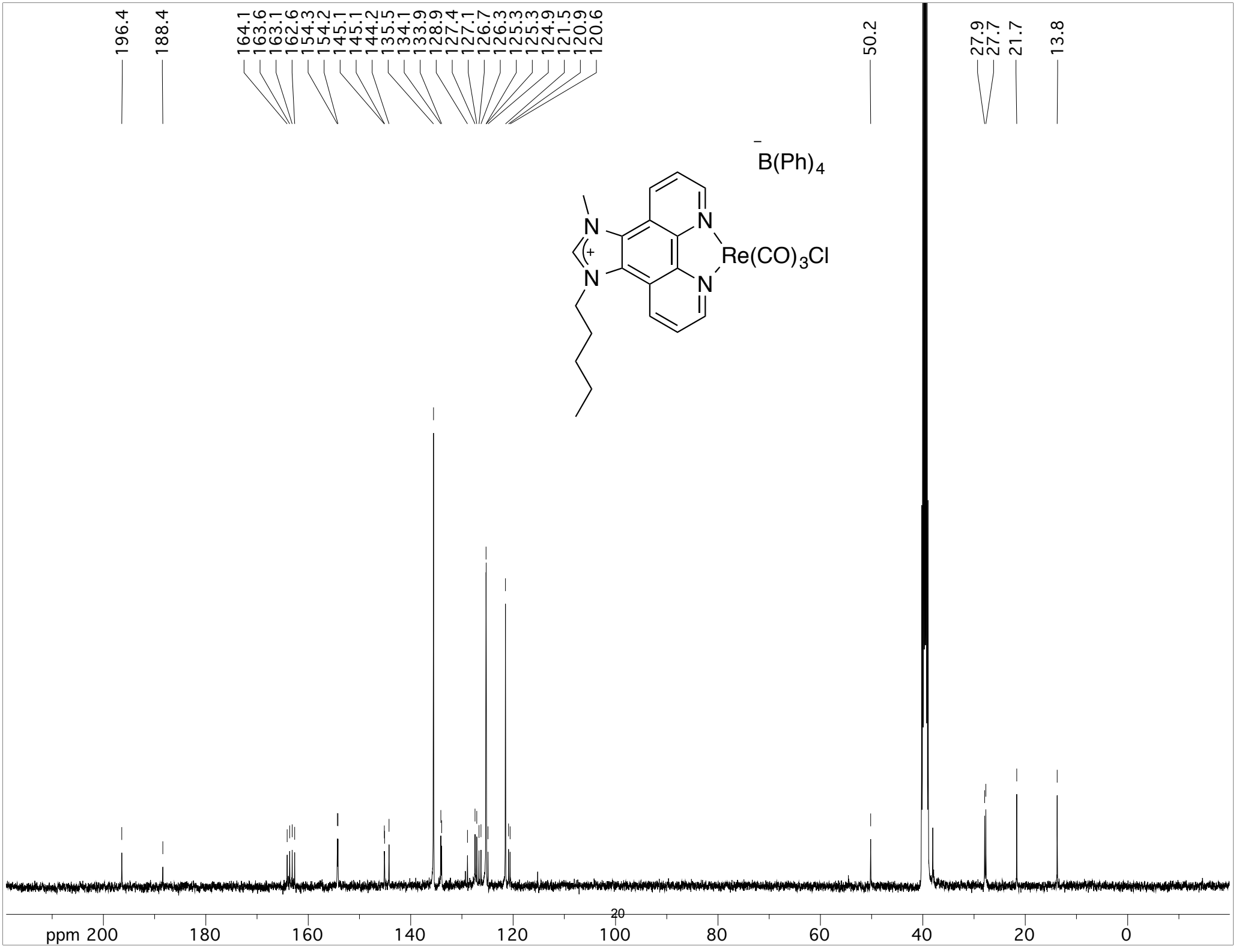
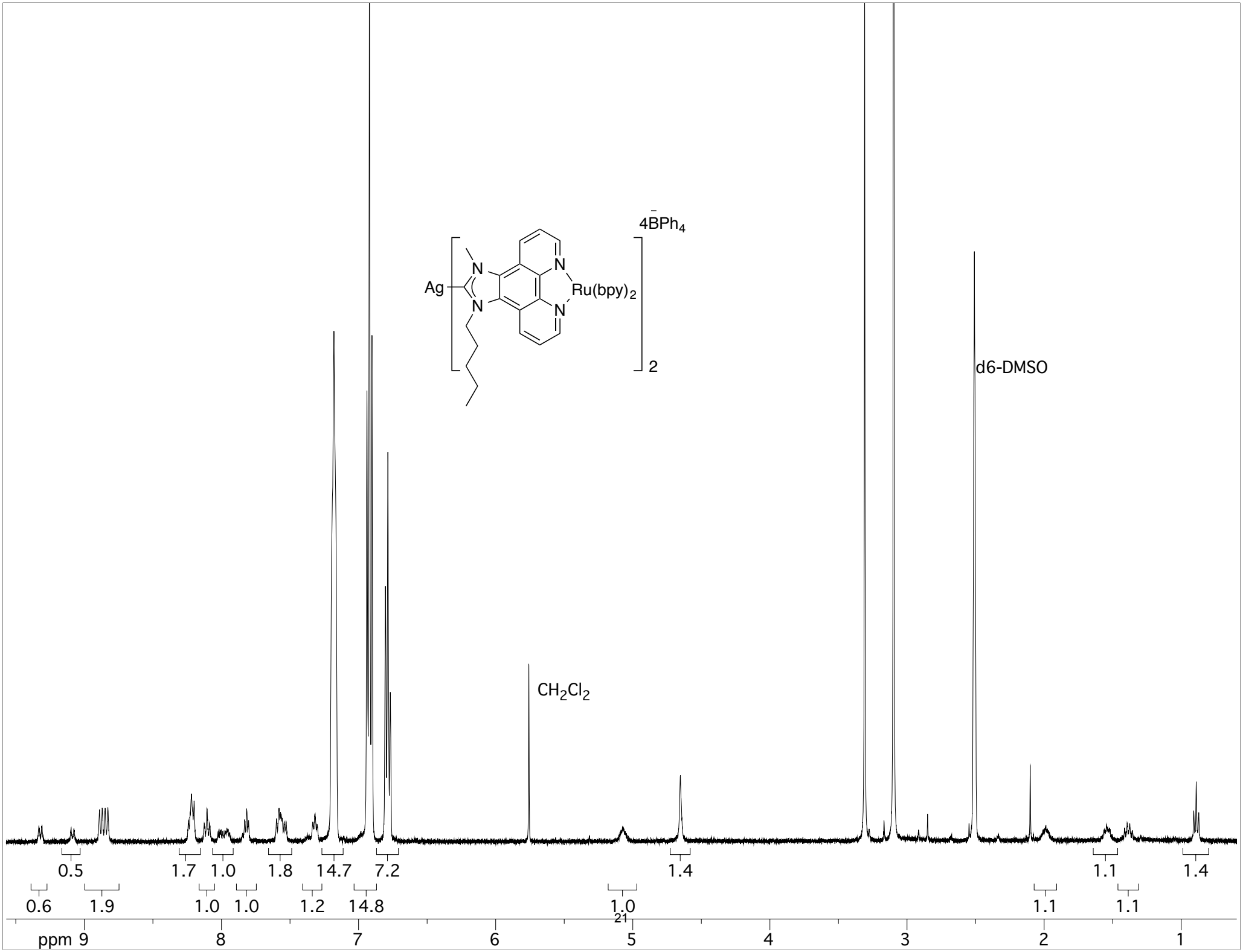
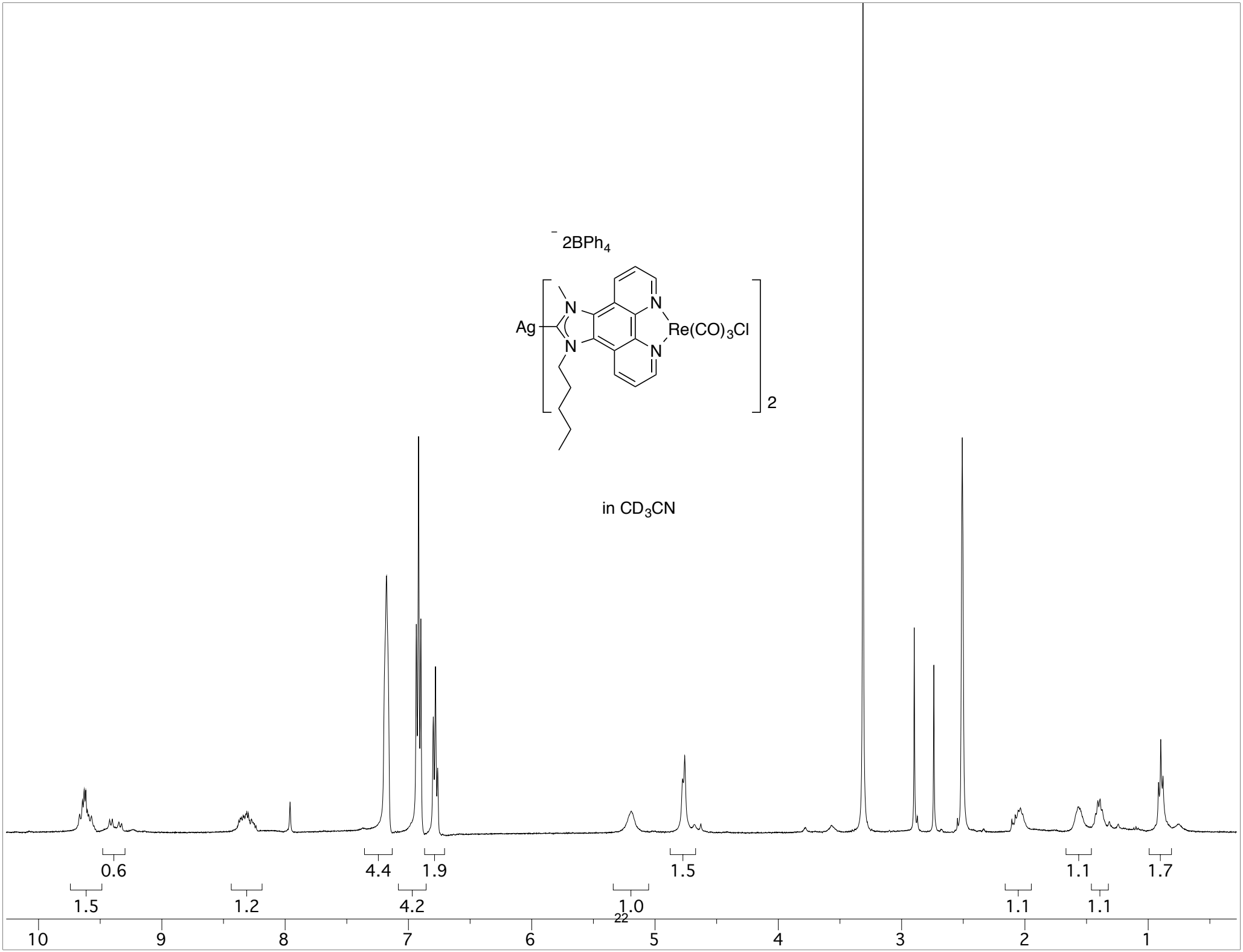
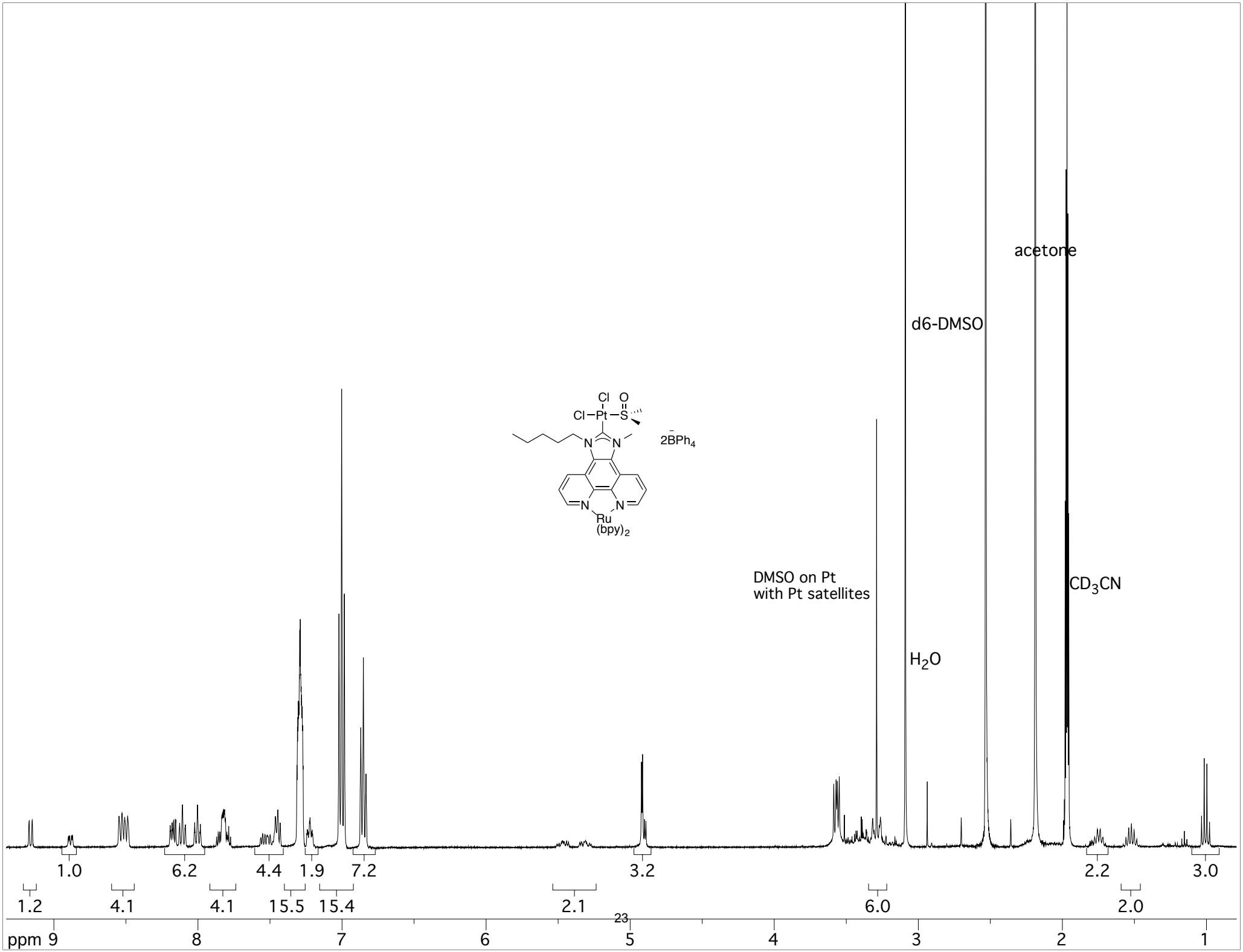
ppm 10
9
8
7
6
5
4
3
2
1

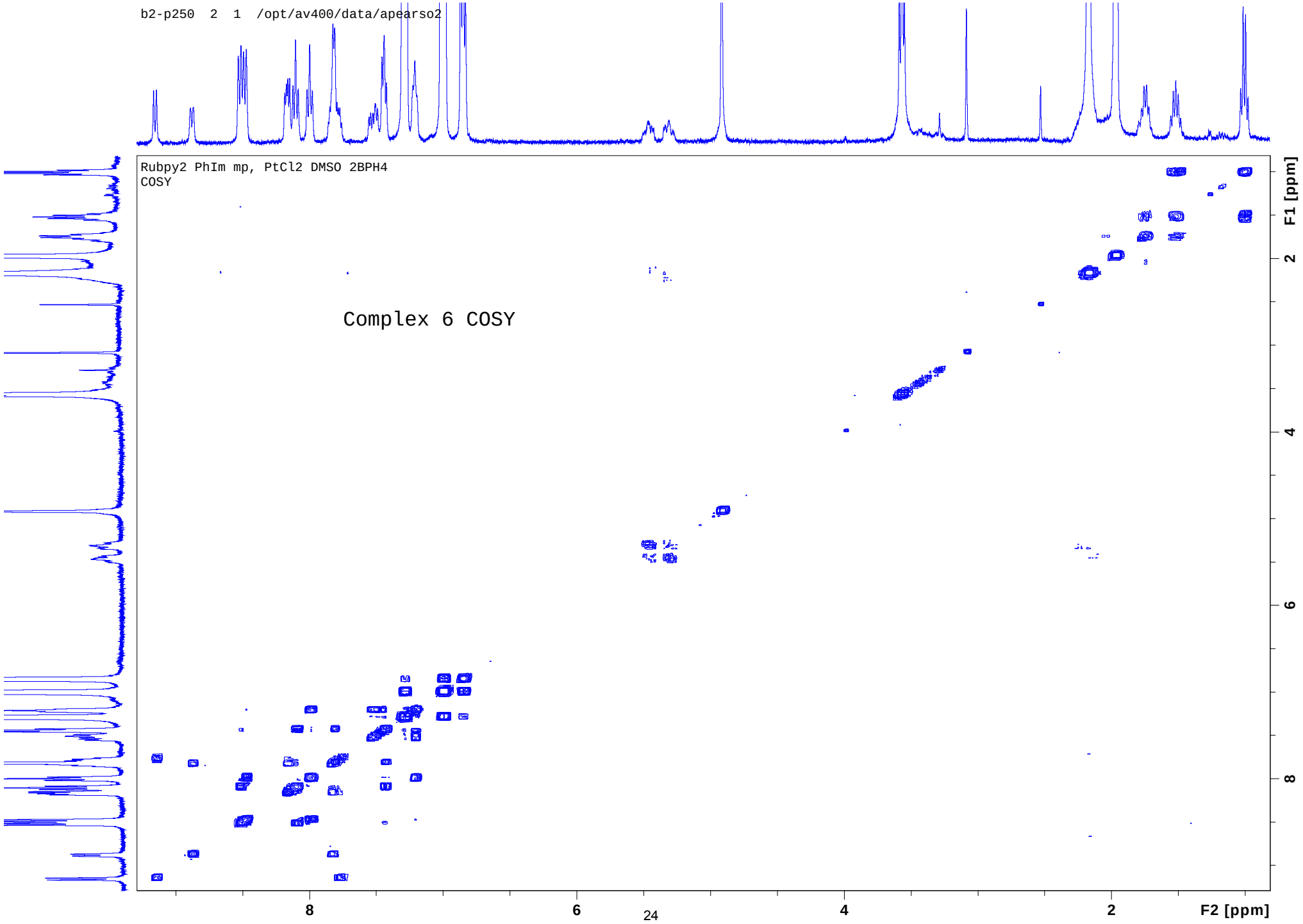

BPh4
N
N
Re(CO)3Cl
NH
N
1.9
1.0
7.1
3.4
3.1
4.1
1.0
1.1
2.1
7.0
2.2
2.4
3.0
ppm 10
9
8
7
6
5
4
3
2
1

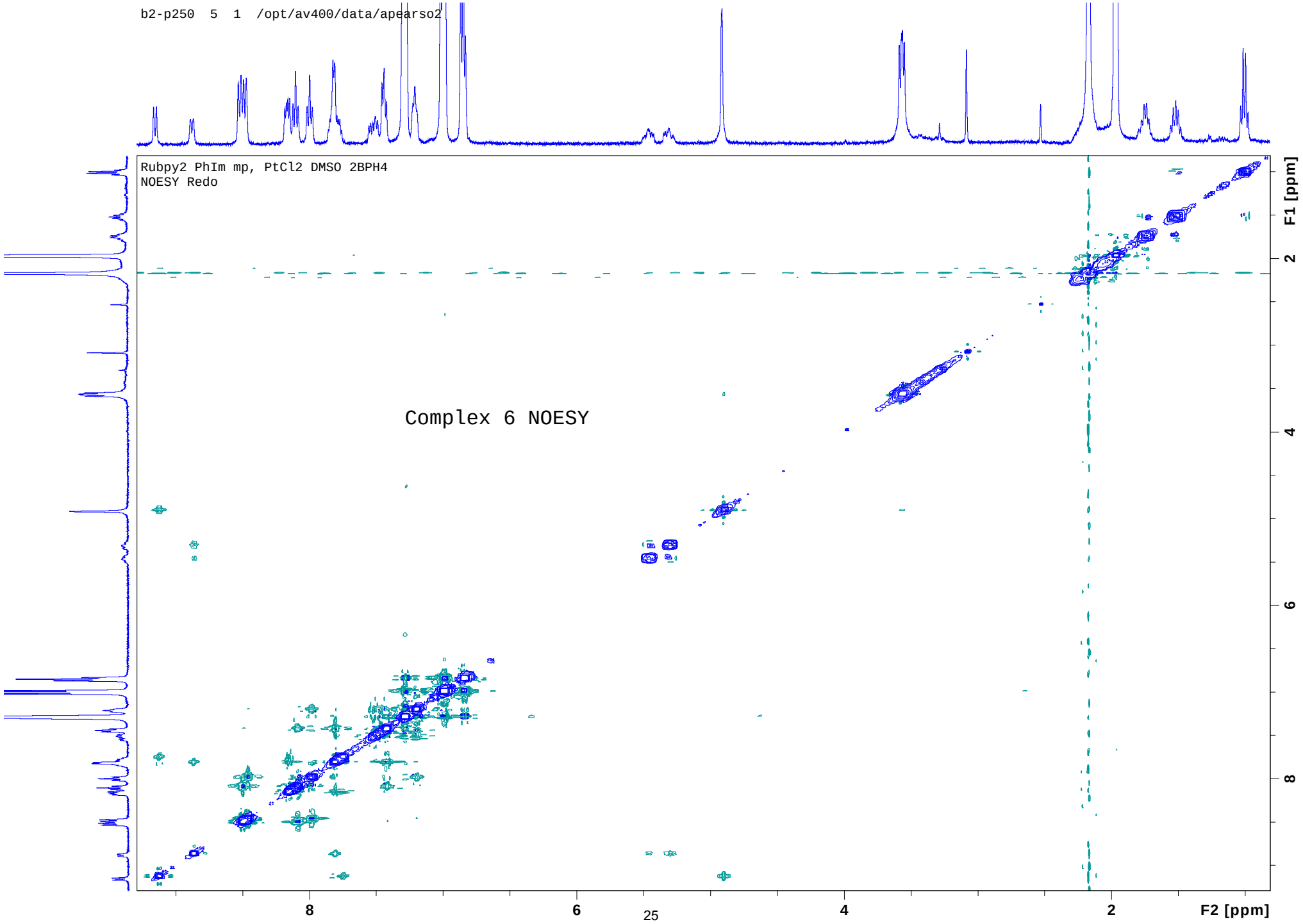

196.4
188.4
164.1
163.6
163.1
162.6
154.3
154.2
145.1
145.1
144.2
135.5
134.1
133.9
128.9
127.4
127.1
126.7
126.3
125.3
125.3
124.9
121.5
120.9
120.6
50.2
27.9
27.7
21.7
13.8
B(Ph)4
N
N
N
N
Re(CO)3Cl
ppm 200
180
160
140
120
100
80
60
40
20
0

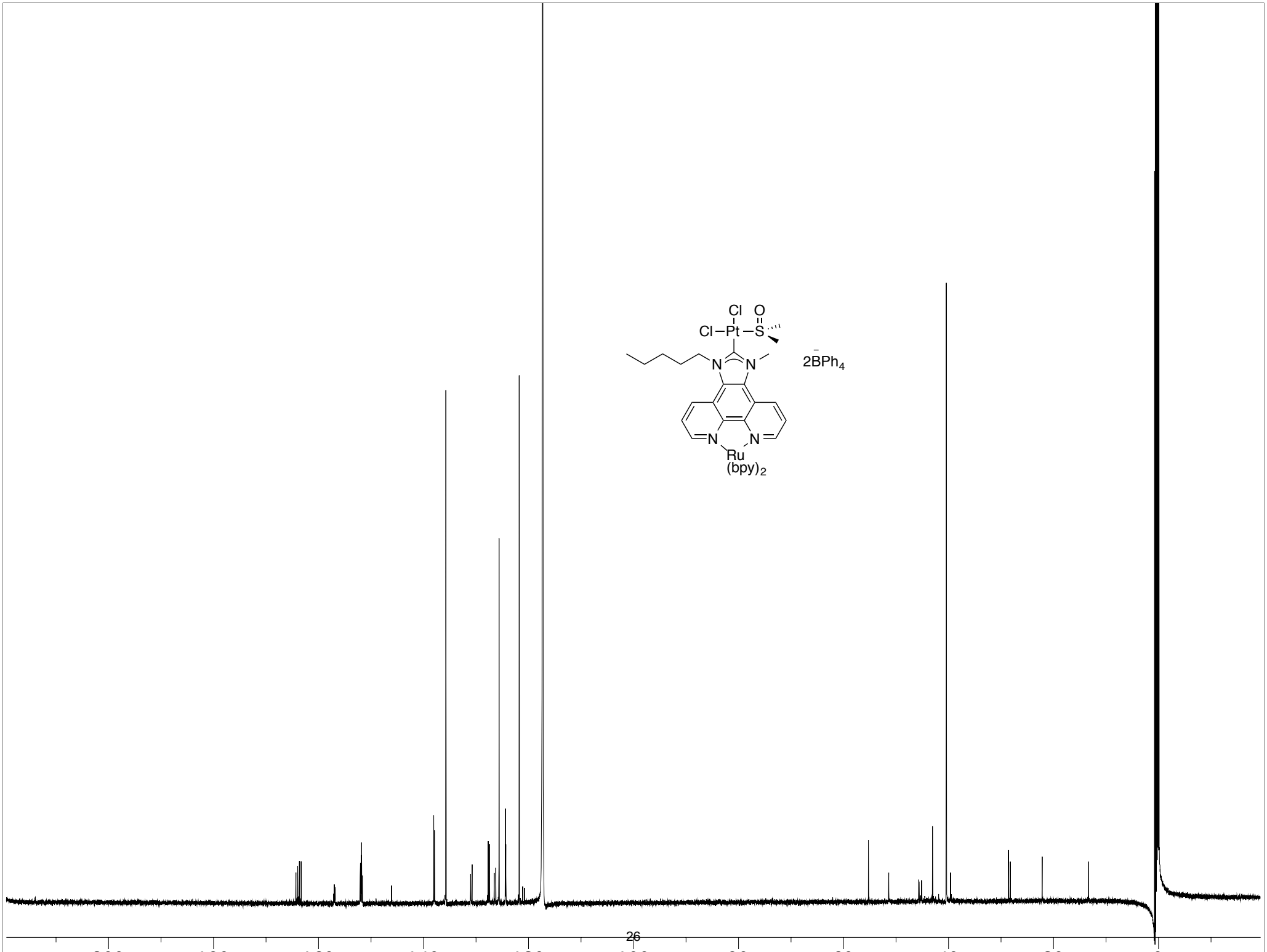

4BPh4
Ag
N
N
N
N
Ru(bpy)2
2
d6-DMSO
CH2Cl2
0.5
1.7
1.0
1.8
14.7
7.2
1.4
1.1
1.4
0.6
1.9
1.0
1.0
1.2
14.8
1.0
1.1
1.1
ppm 9
8
7
6
5
4
3
2
1

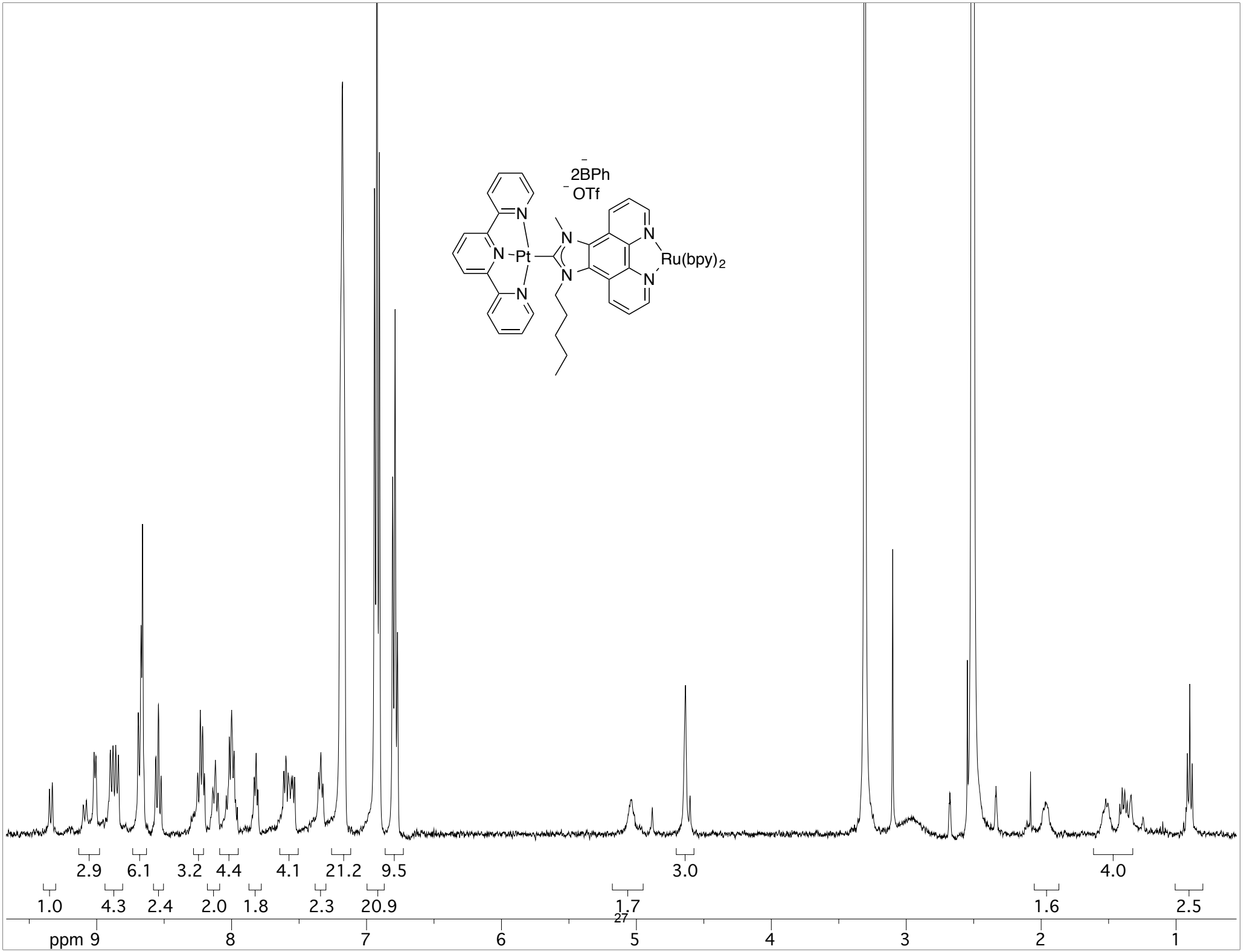

2BPh4
Ag
N
N
N
N
Re(CO)3Cl
2
in CD3CN
0.6
4.4
1.9
1.5
1.1
1.7
1.5
1.2
4.2
1.0
1.1
1.1
10
9
8
7
6
5
4
3
2
1

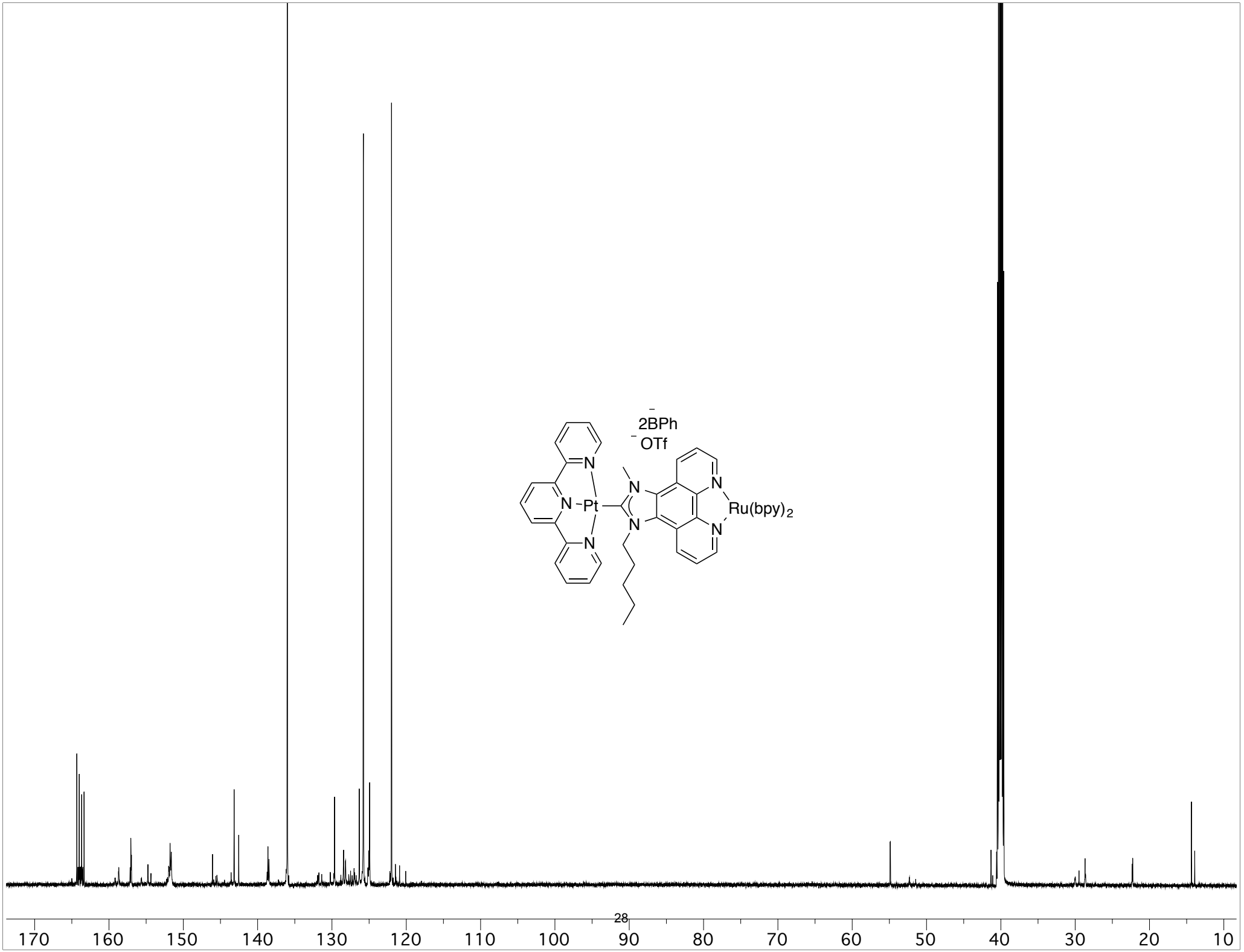

acetone
d6-DMSO
DMSO on Pt
with Pt satellites
CD_3CN
H_2O
$2\bar{B}Ph_4$
1.0
6.2
4.4
1.9
7.2
3.2
2.2
3.0
1.2
4.1
4.1
15.5
15.4
2.1
6.0
2.0
ppm 9
8
7
6
5
4
3
2
1

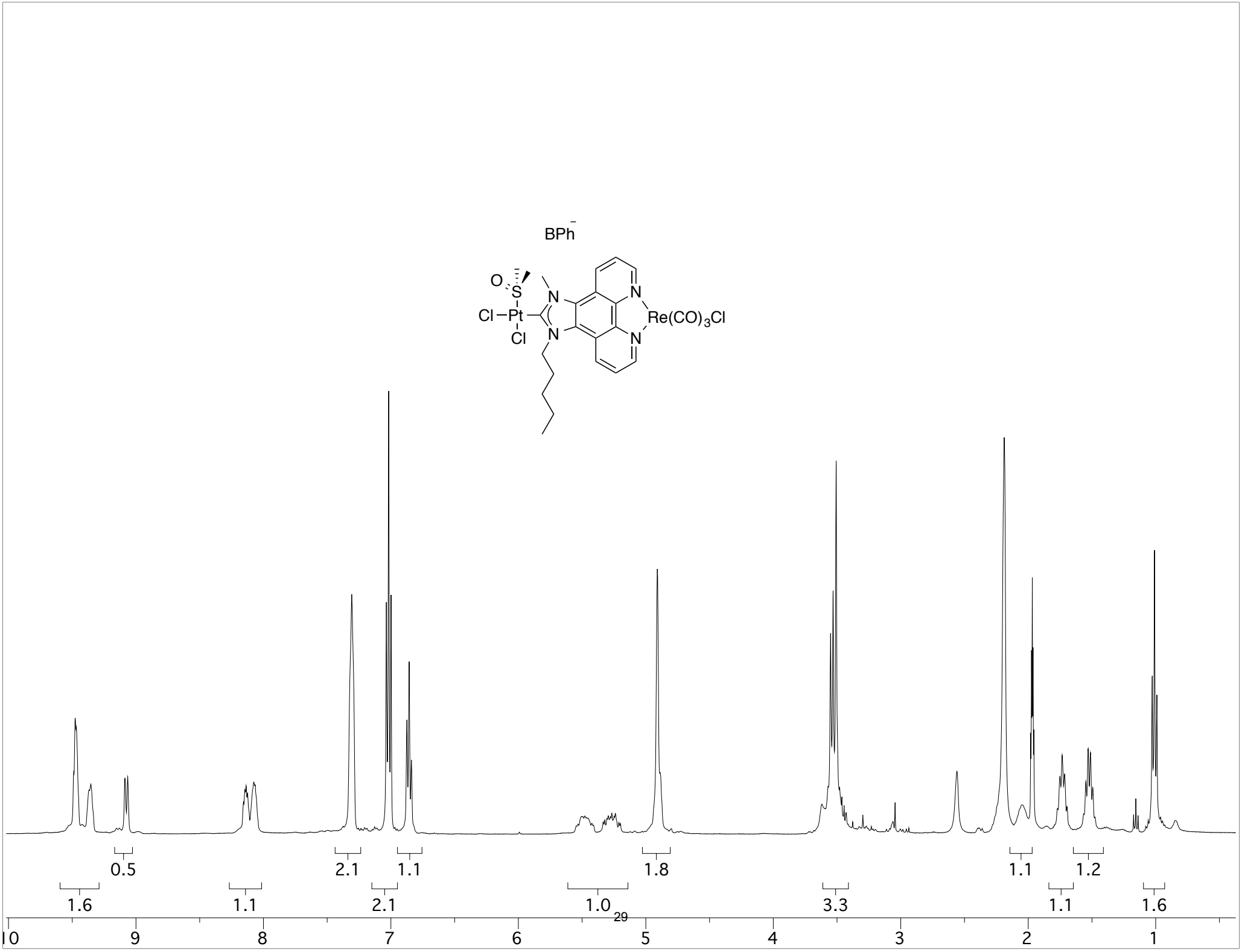

b2-p250 2 1 /opt/av400/data/apearso2
Rubpy2 PhIm mp, PtCl2 DMSO 2BPH4
COSY
Complex 6 COSY
F1 [ppm]
F2 [ppm]
2
4
6
8
8
6
4
2

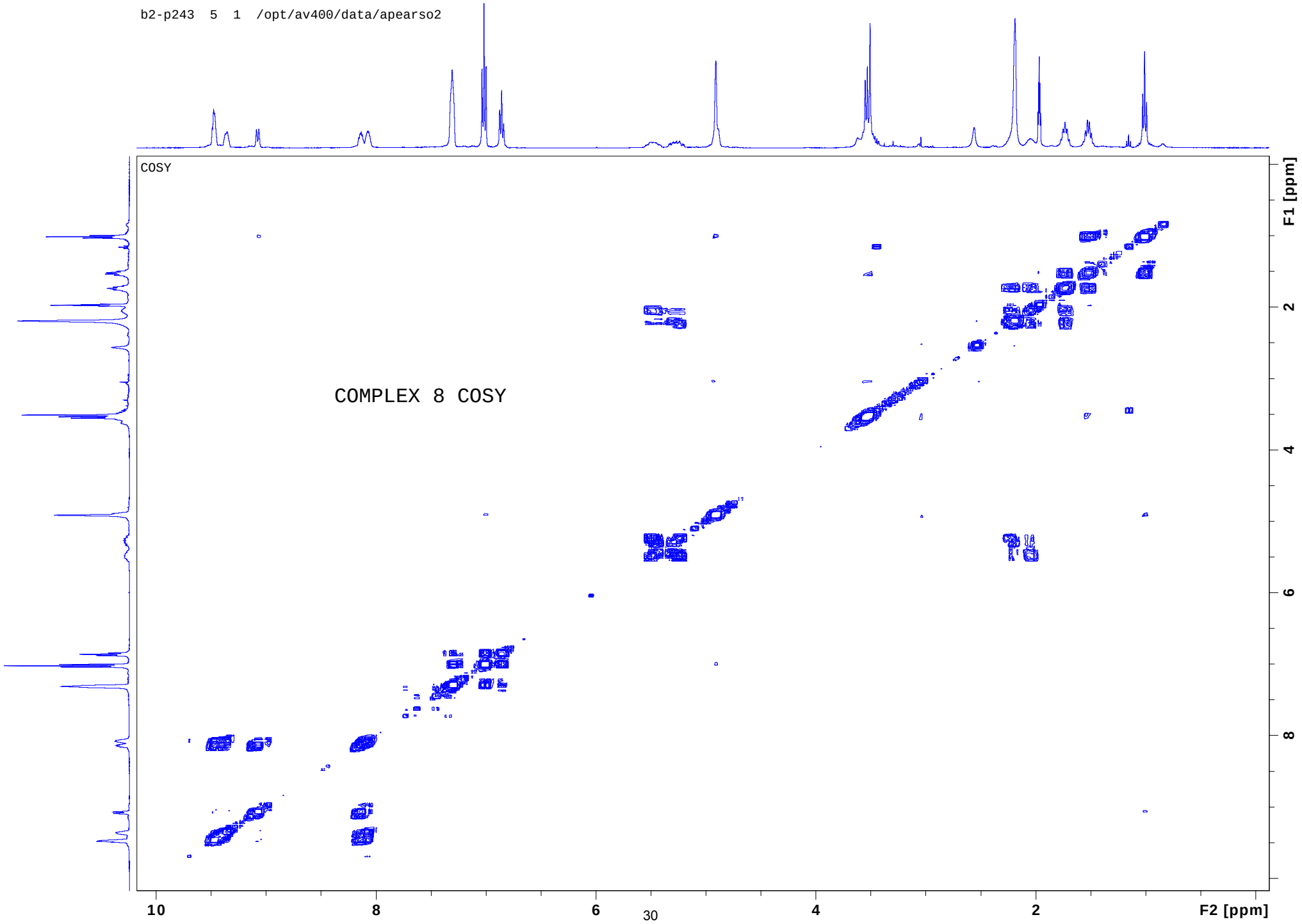

b2-p250 5 1 /opt/av400/data/apearso2
Rubpy2 PhIm mp, PtCl2 DMSO 2BPH4
NOESY Redo
Complex 6 NOESY
F1 [ppm]
F2 [ppm]
2
4
6
8
8
6
4
2

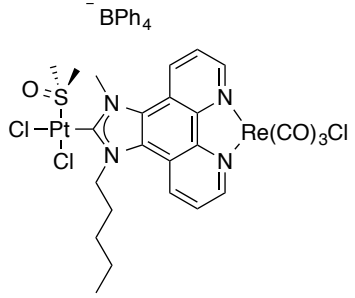

Cl
O
Cl–Pt–S
N
N
2BPh4
N
N
Ru
(bpy)2
ppm 200
180
160
140
120
100
80
60
40
20
0


2BPh
OTf
N
N
Pt
N
N
N
N
N
Ru(bpy)2
2.9
6.1
3.2
4.4
4.1
21.2
9.5
3.0
4.0
1.0
4.3
2.4
2.0
1.8
2.3
20.9
1.7
1.6
2.5
ppm 9
8
7
6
5
4
3
2
1

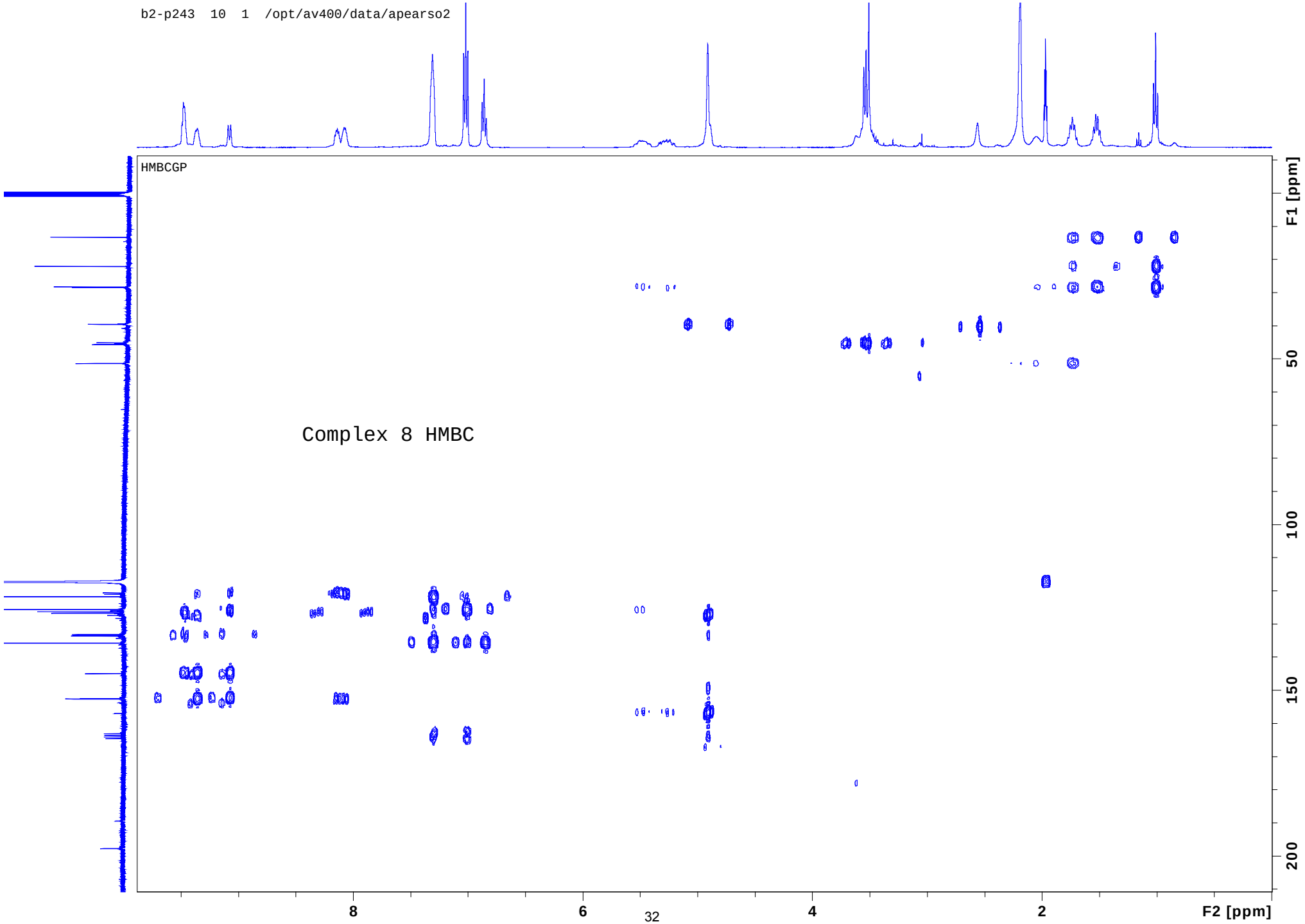

2BPh
OTf
N
N
Pt
N
N
N
N
N
Ru(bpy)2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


BPh⁻
O
S
Cl–Pt
Cl
N
N
N
N
Re(CO)3Cl
0.5
2.1
1.1
1.8
1.1
1.2
1.6
1.1
2.1
1.0
29
3.3
1.1
1.6
10
9
8
7
6
5
4
3
2
1


b2-p243 5 1 /opt/av400/data/apearso2
COSY
COMPLEX 8 COSY
F1 [ppm]
F2 [ppm]
10
8
6
4
2
30



in CD_3CN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