Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Electronic Supporting Information for:

Copper(I)-Induced Amplification of a [2]catenane in a Virtual Dynamic Library of Macrocyclic Alkenes

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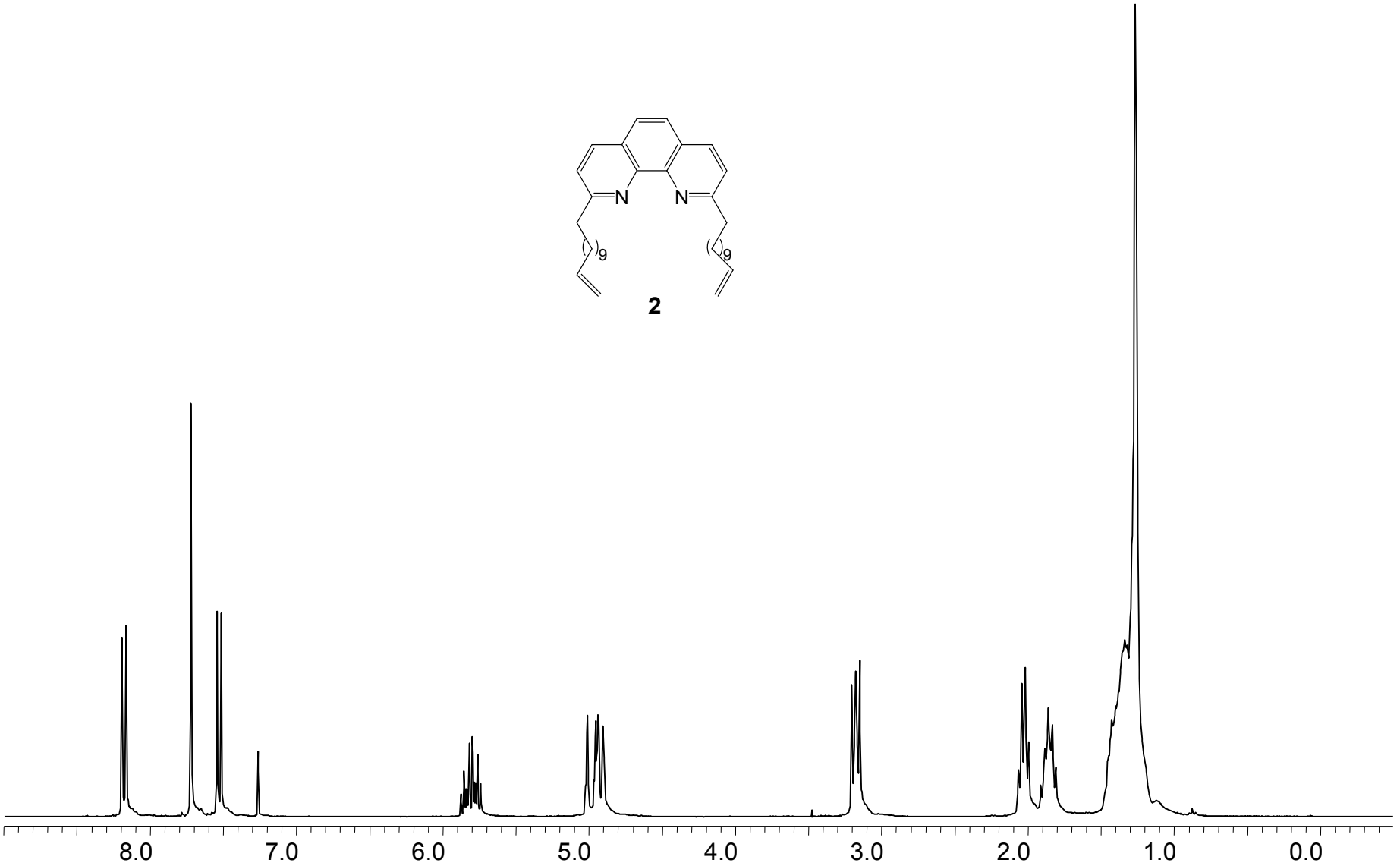

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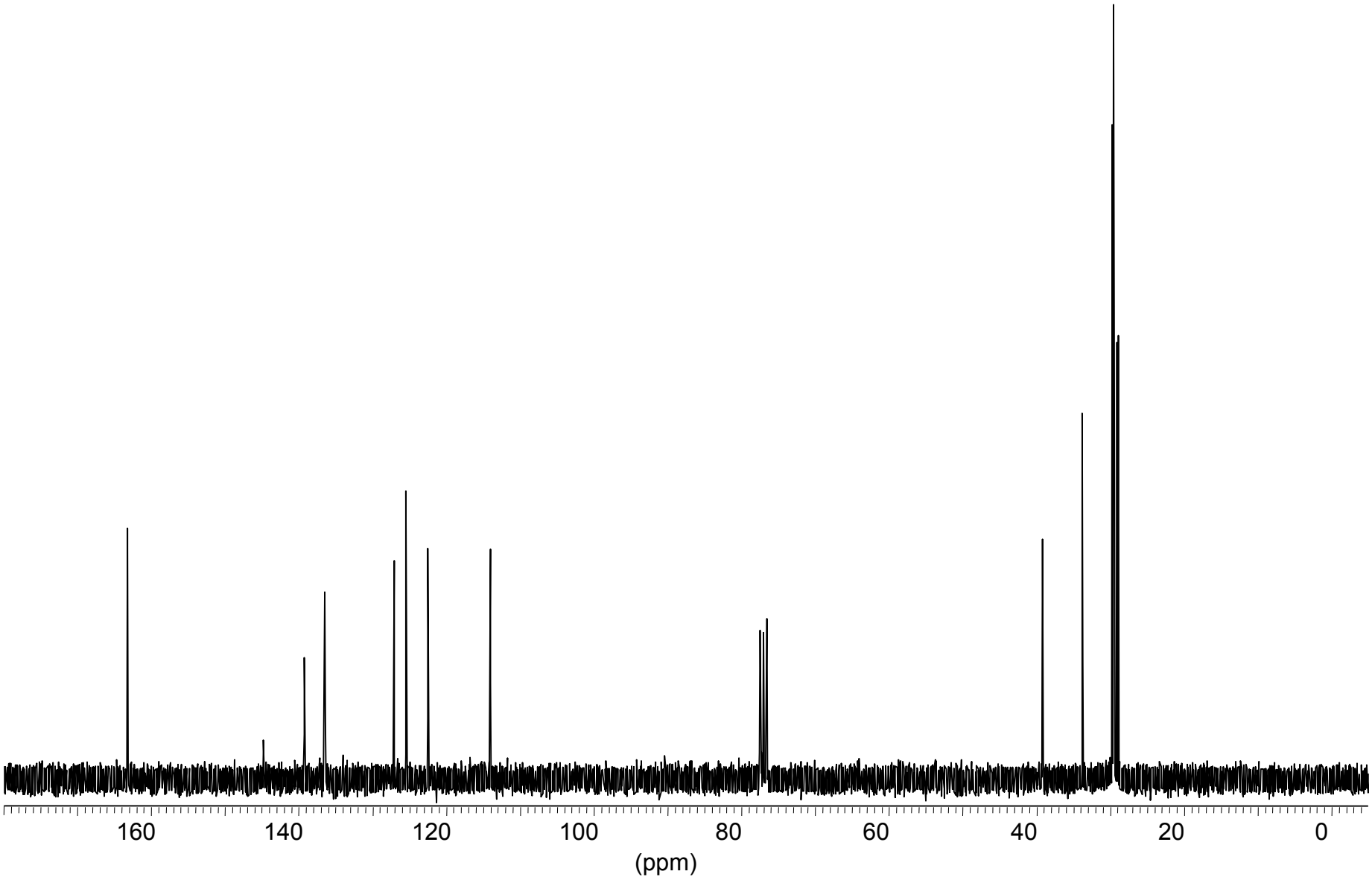
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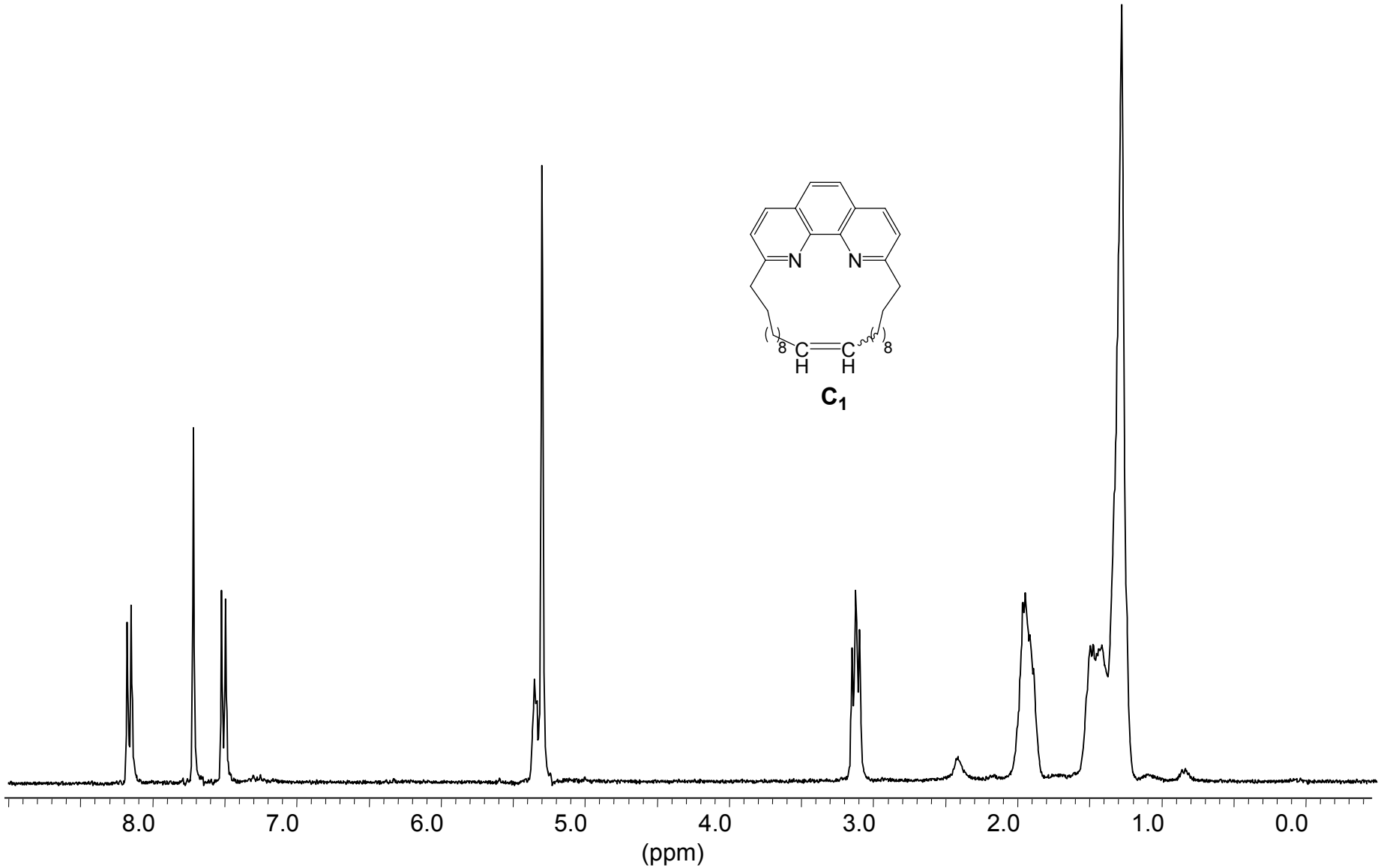
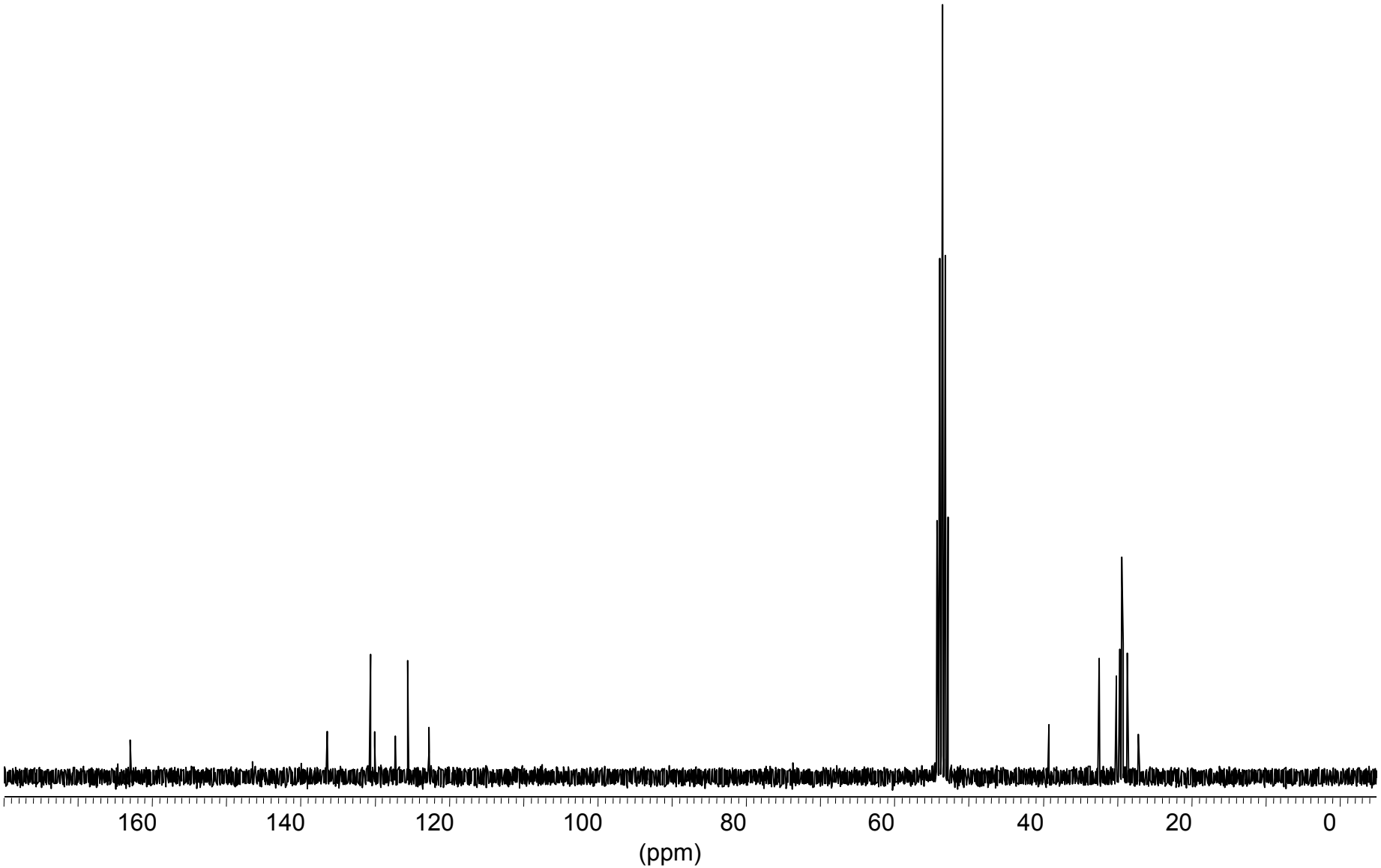


C$_1$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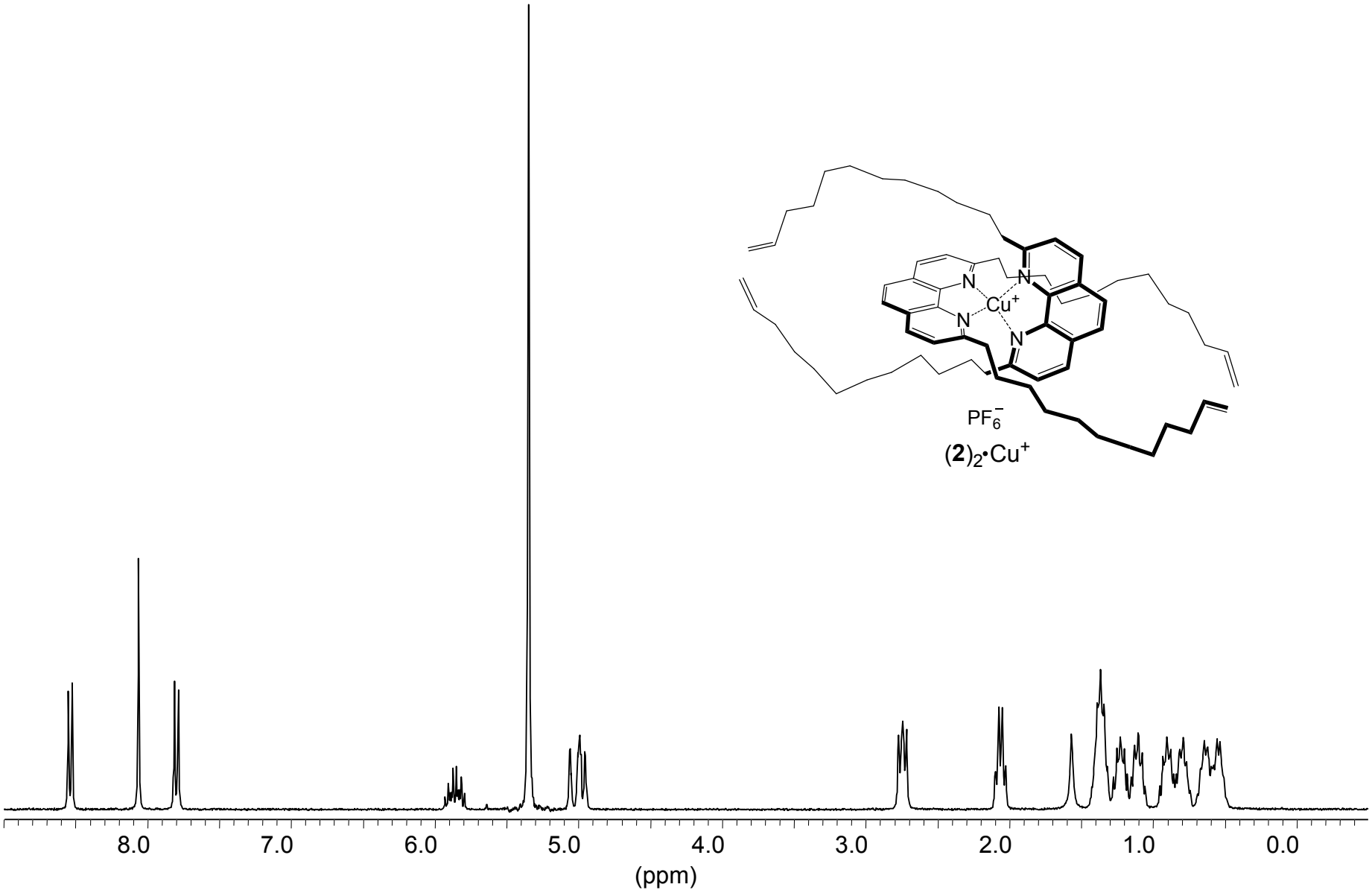
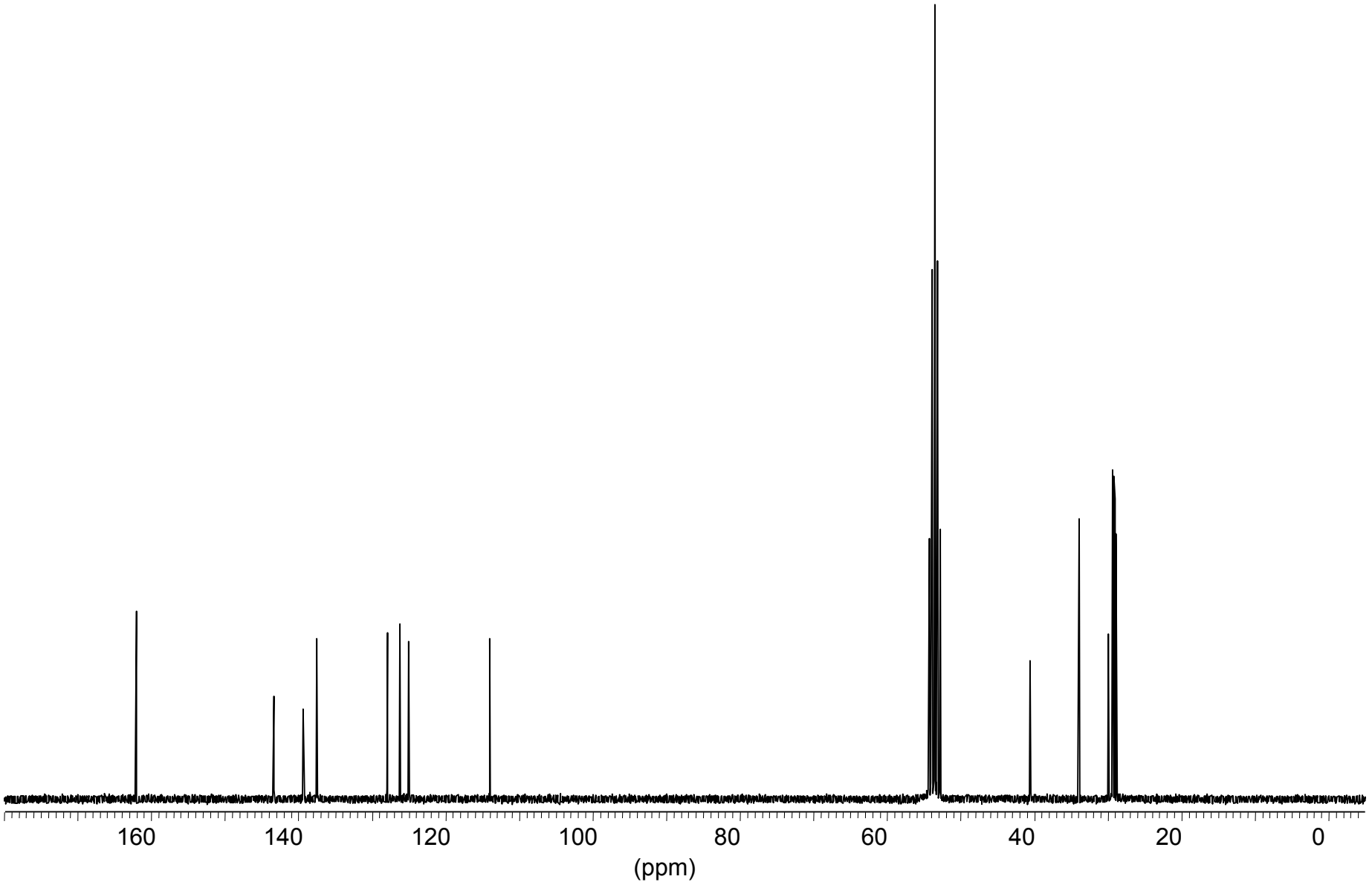

N
N
Cu+
N
N
PF6−
(2)2•Cu+
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)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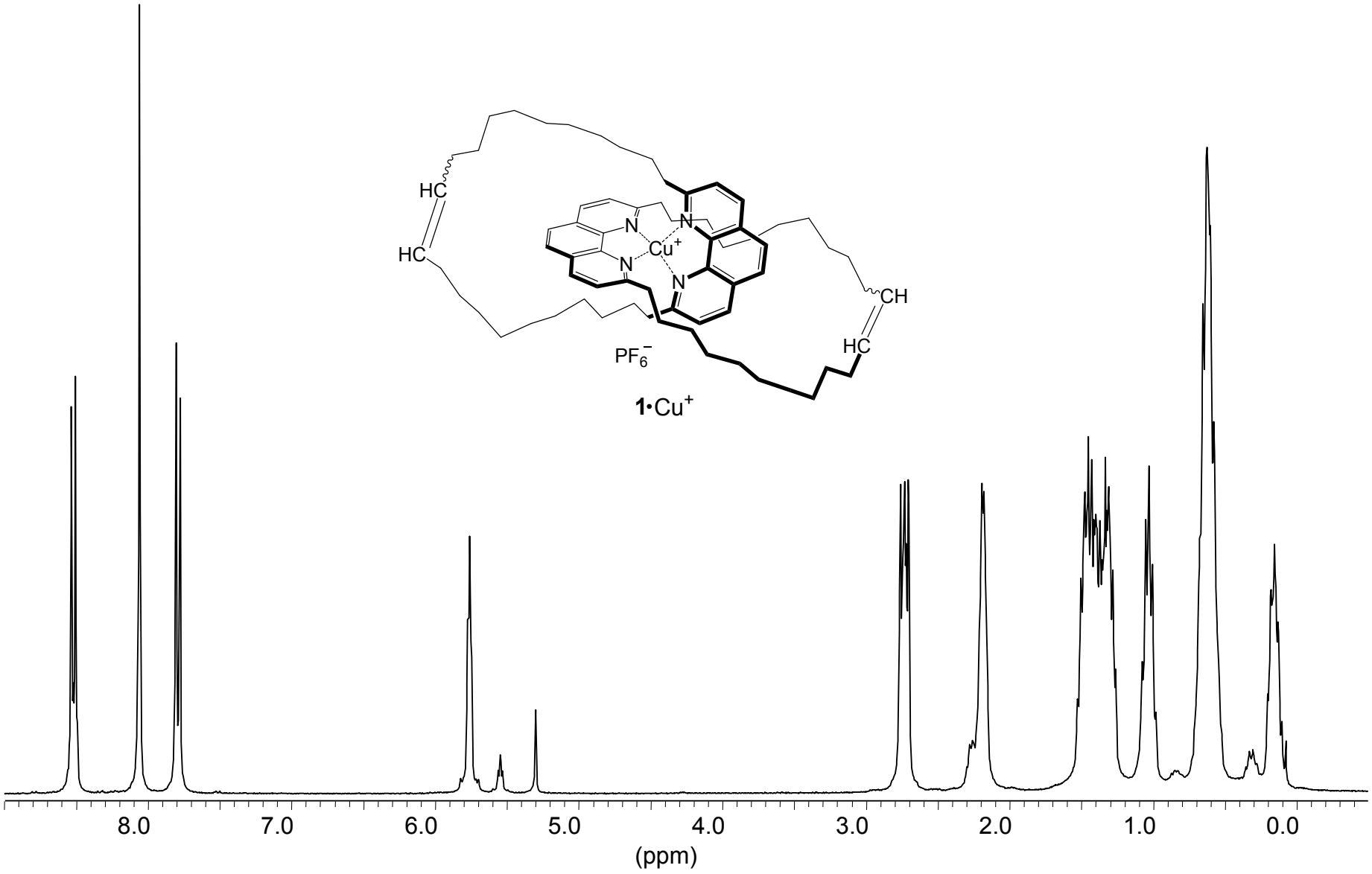
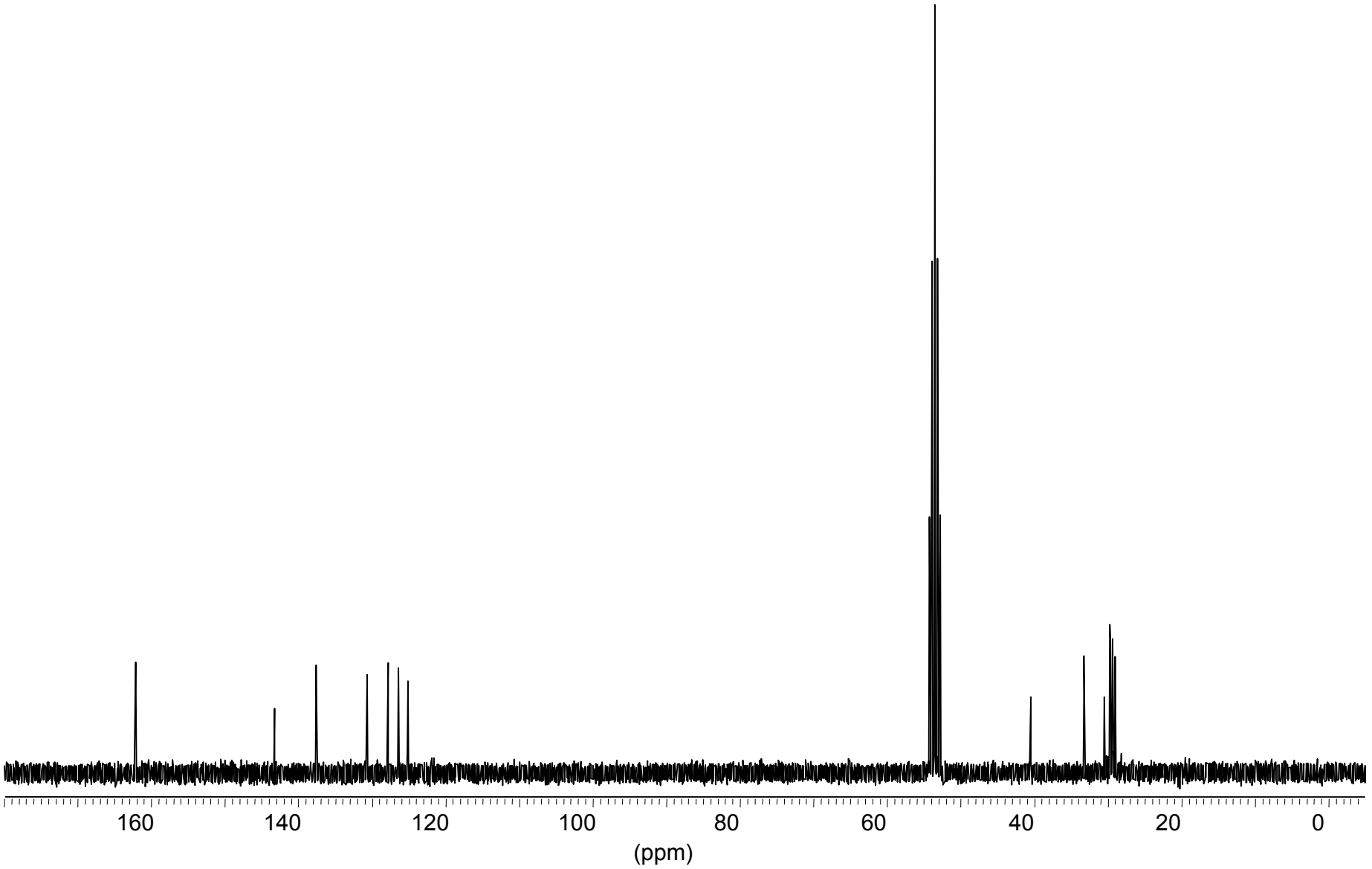


1•Cu^{+}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60
40
20
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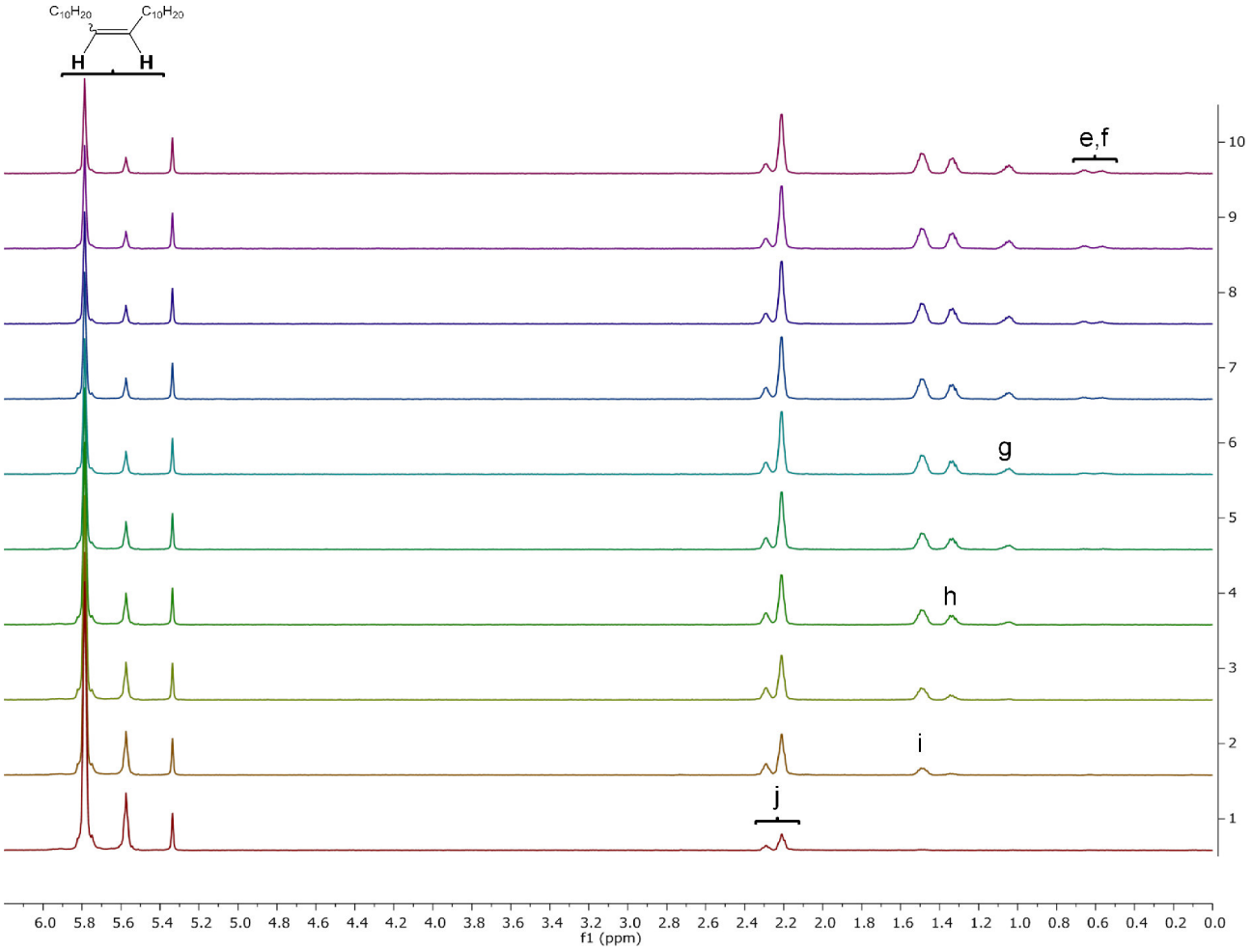
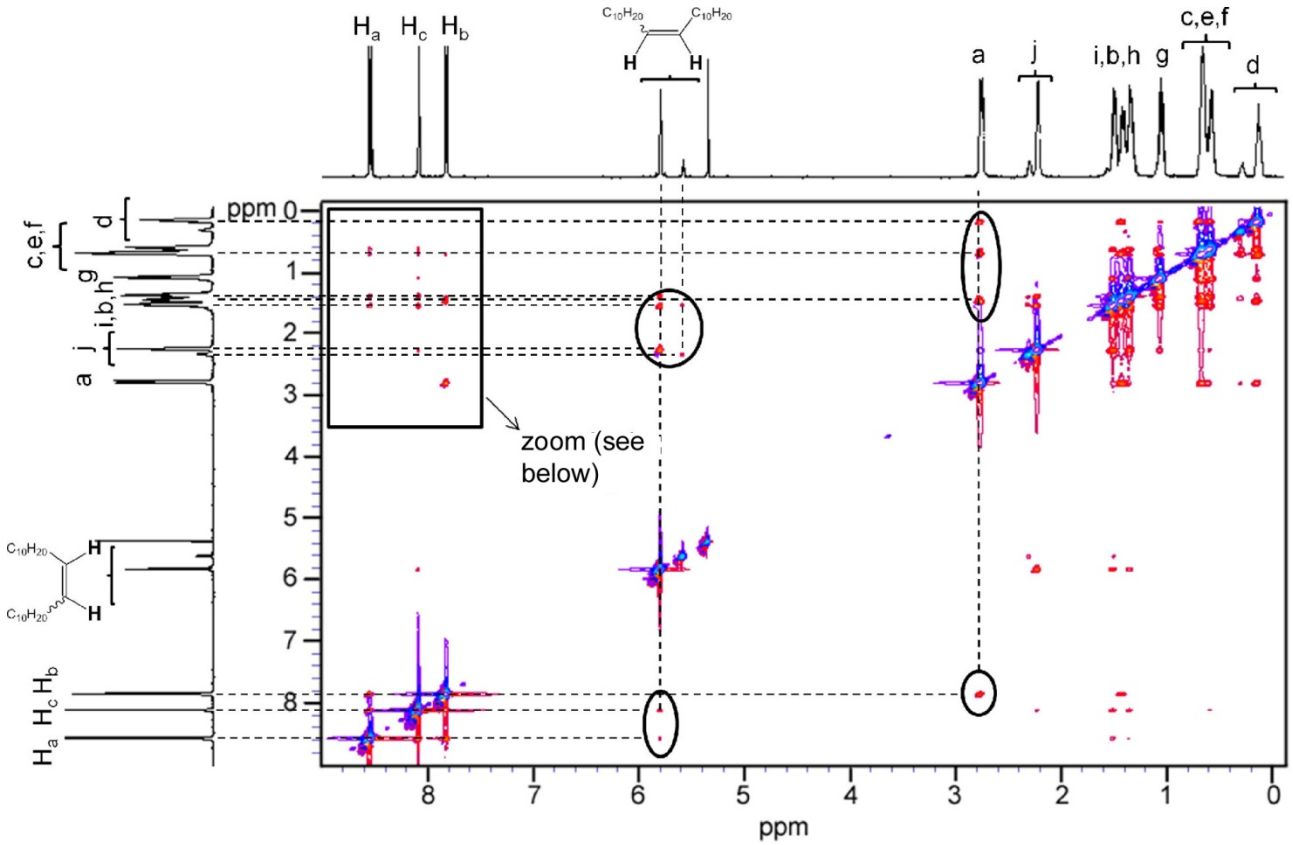
(ppm)

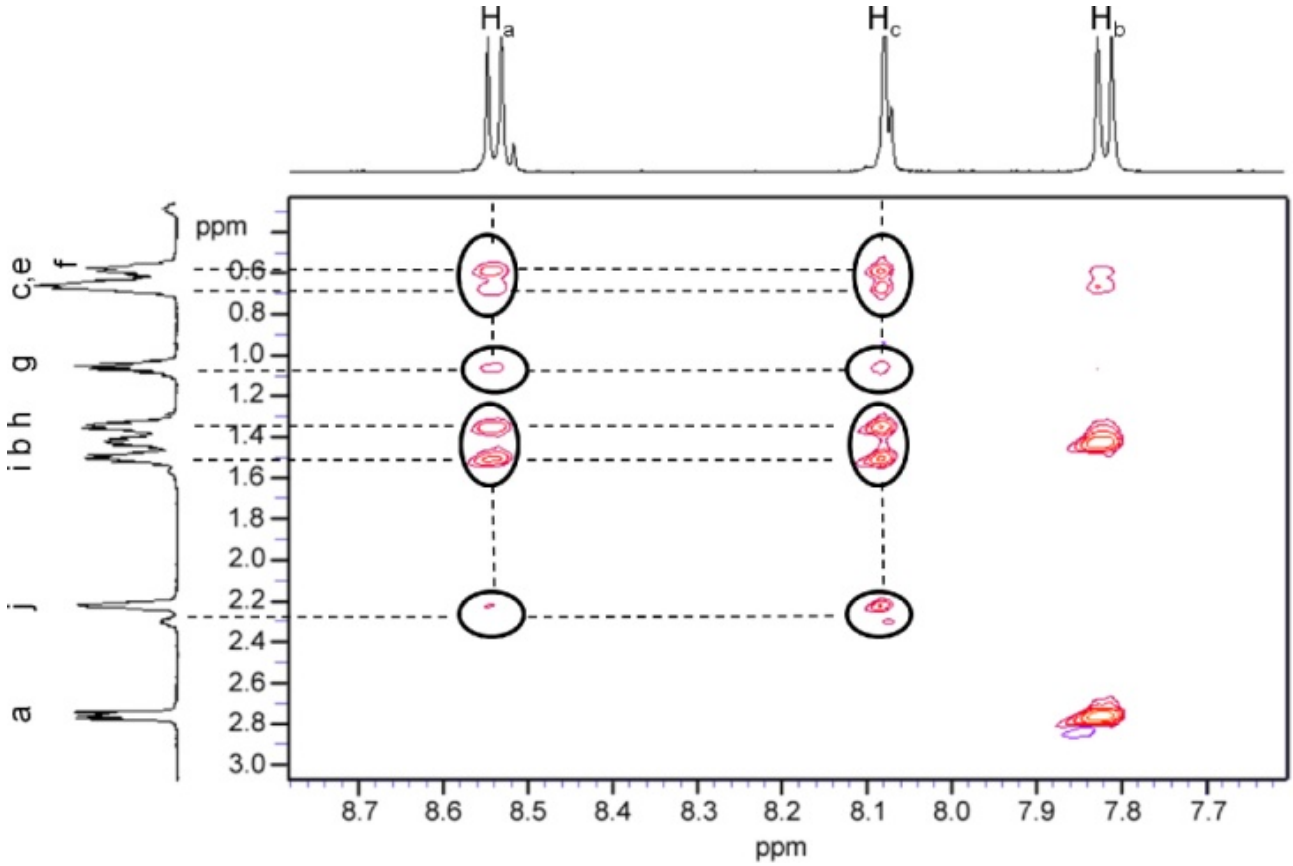
1D TOCSY



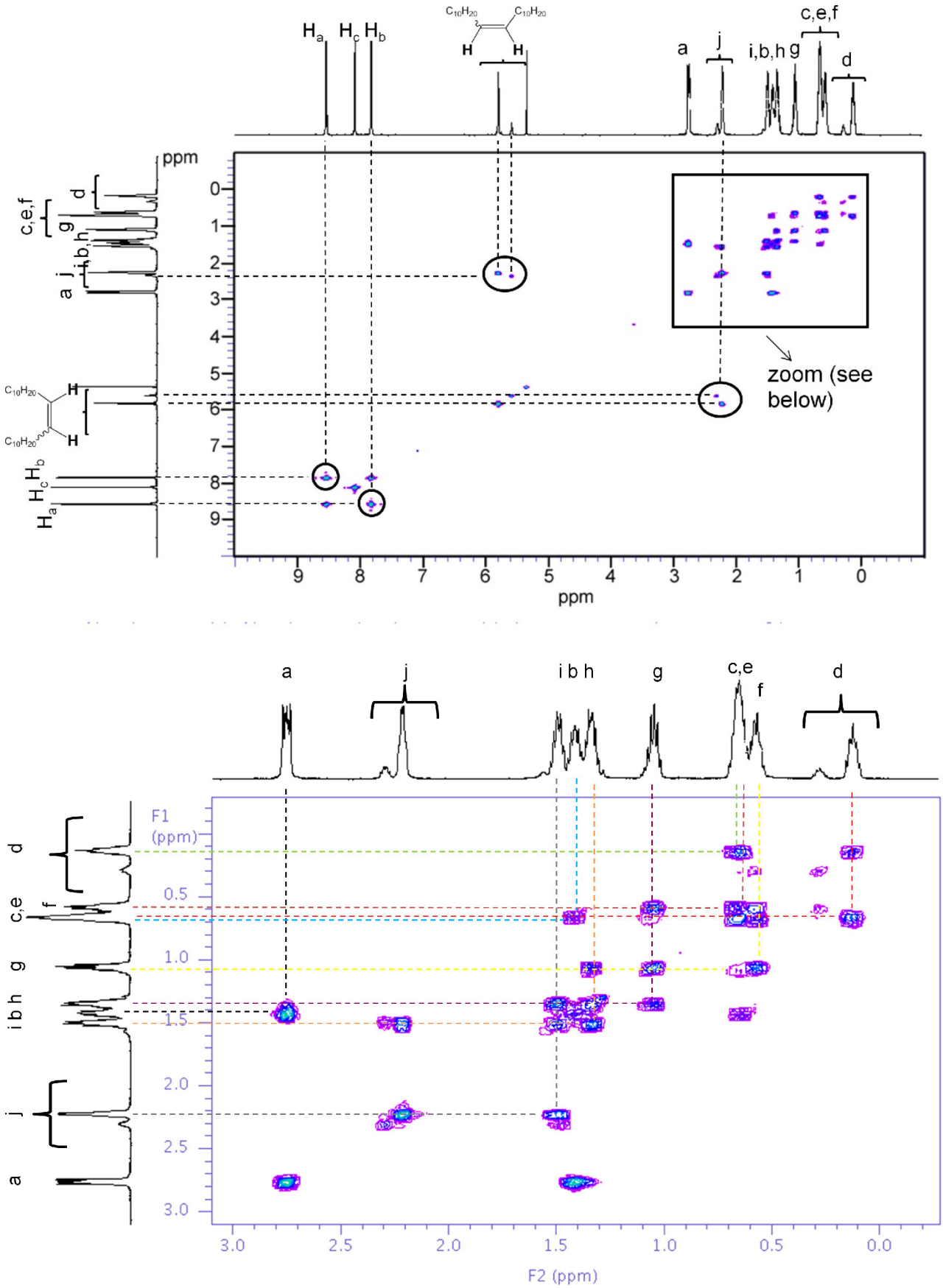
Protons **j**, **i**, **e**, **h**, **e** and **f** were assigned through the 1D TOCSY spectra reported in this page. The remaining protons were assigned through the 2D ROESY and 2D COSY spectra reported in the two following pages.

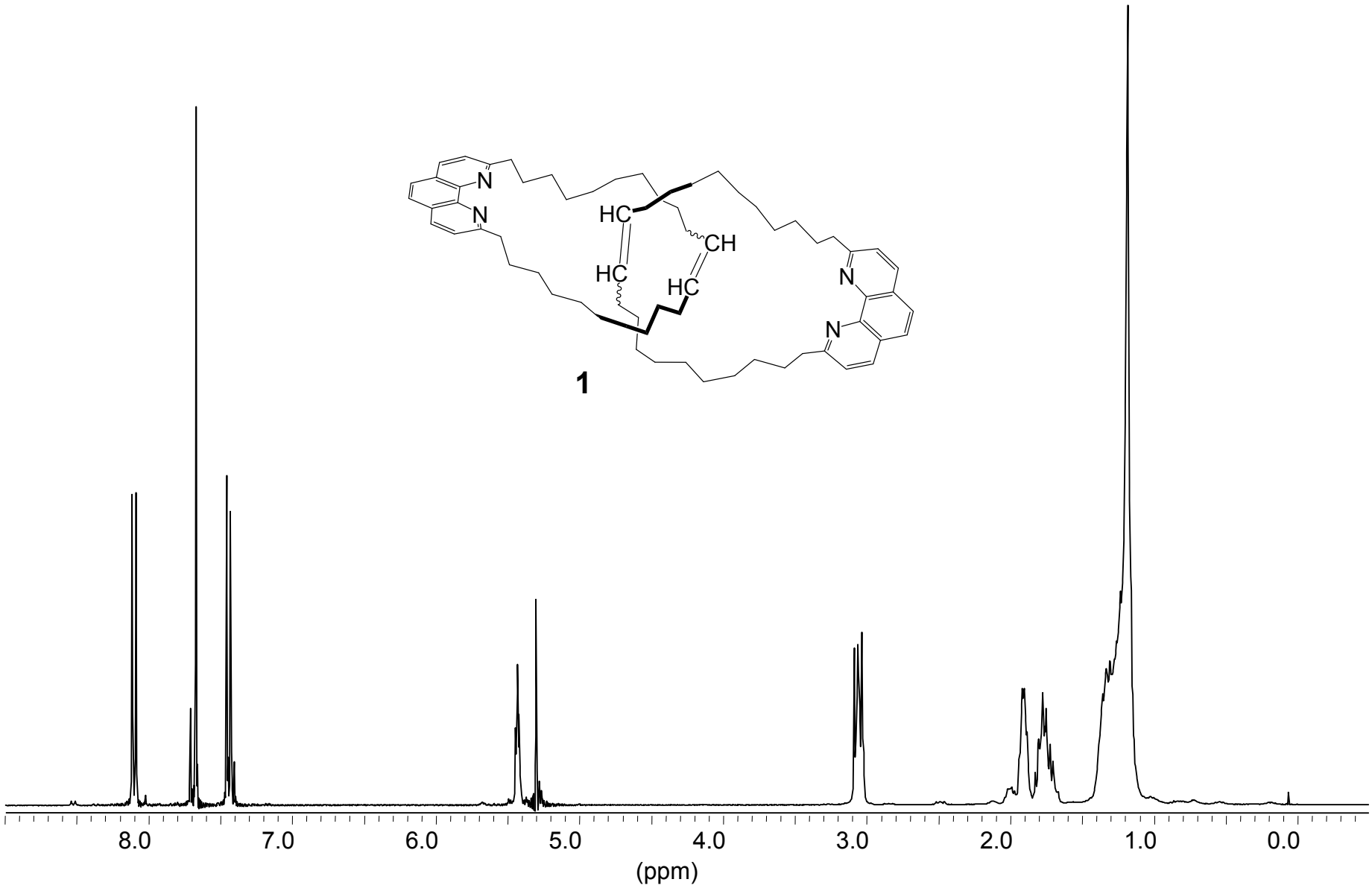
2D ROESY


Ha Hc Hb
a
j
i,b,h
g
c,e,f
d
ppm
zoom (see below)
ppm

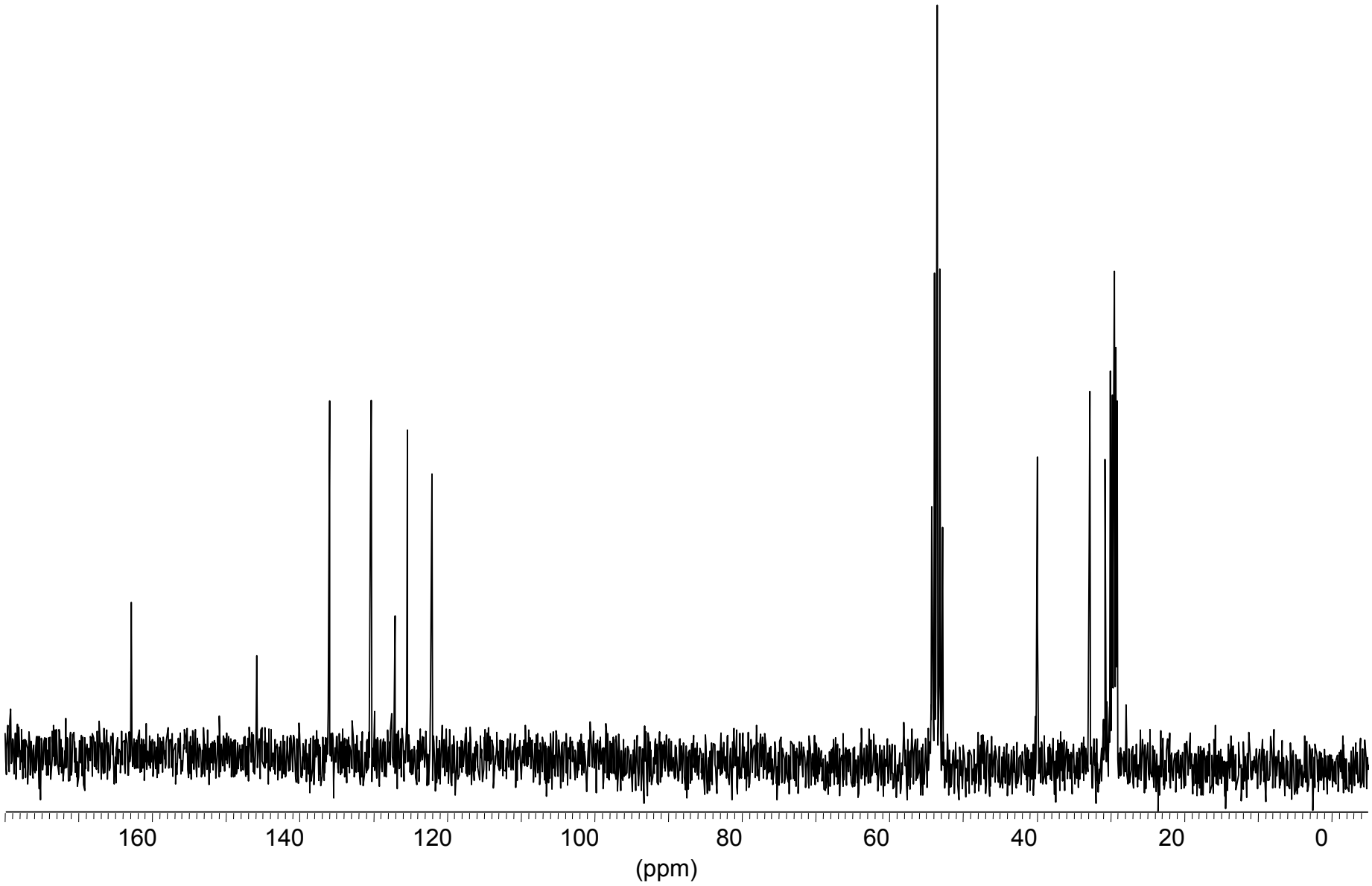

Ha
Hc
Hb
ppm
c,e
f
g
i b h
j
a
ppm

2D COSY

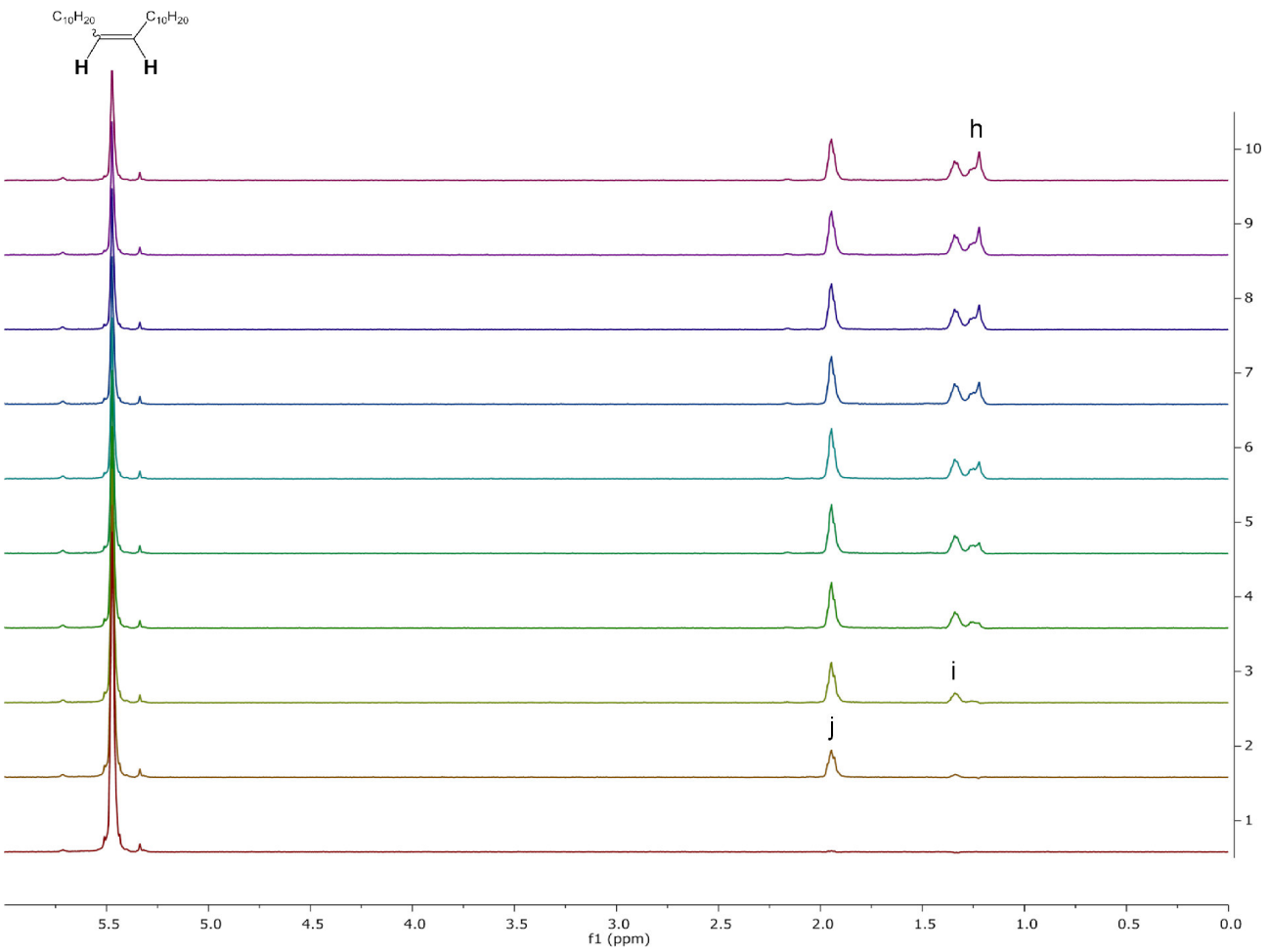

Ha Hc Hb
C10H20 C10H20
H H
a j i,b,h g c,e,f d
ppm
zoom (see below)
F1 (ppm)
F2 (ppm)



1


160
140
120
100
80
60
40
20
0
(ppm)

1D TOCSY

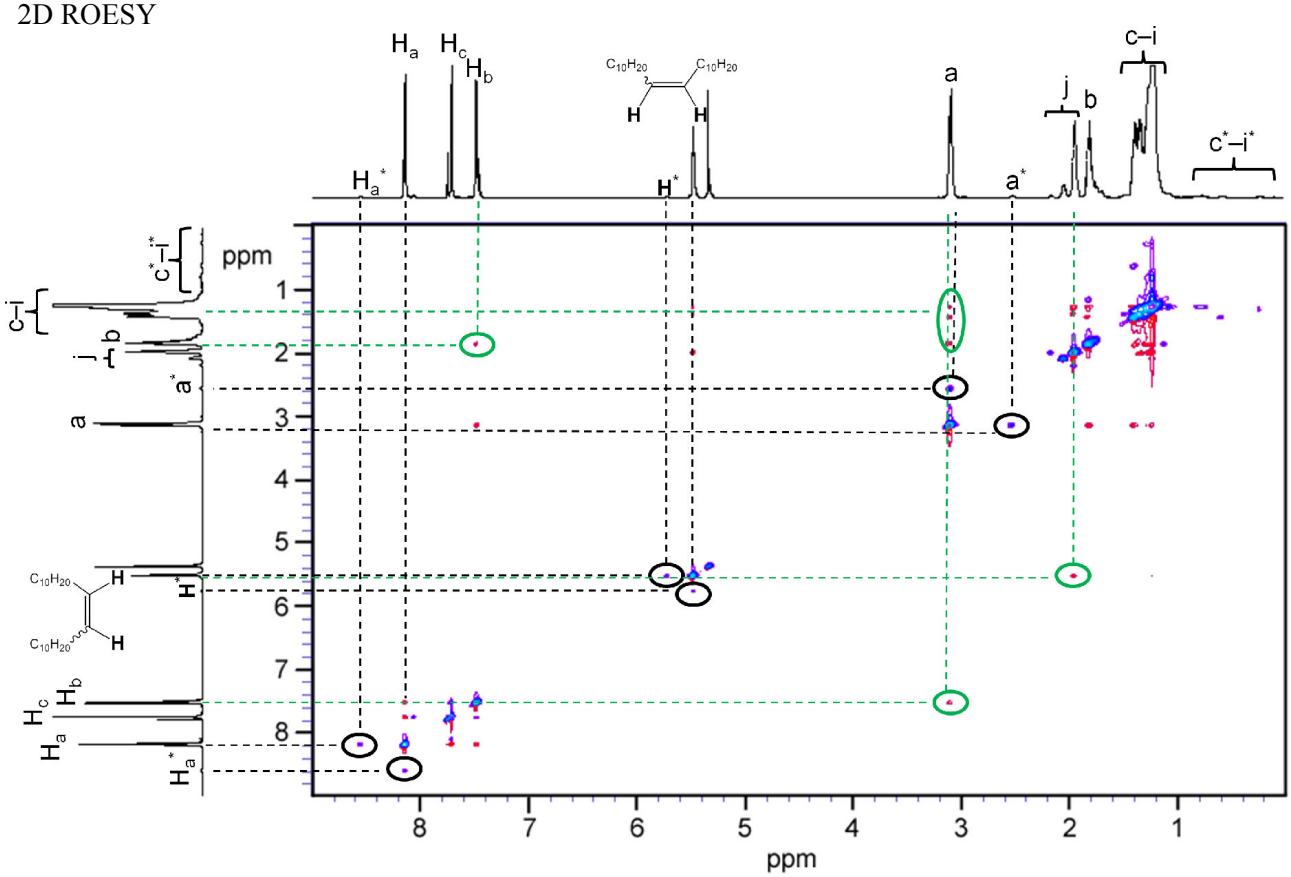


Protons **j**, **i**, **h** were assigned through the 1D TOCSY spectra reported in this page. The assignment of the other protons was obtained through the 2D ROESY and 2D COSY spectra reported in the following page.

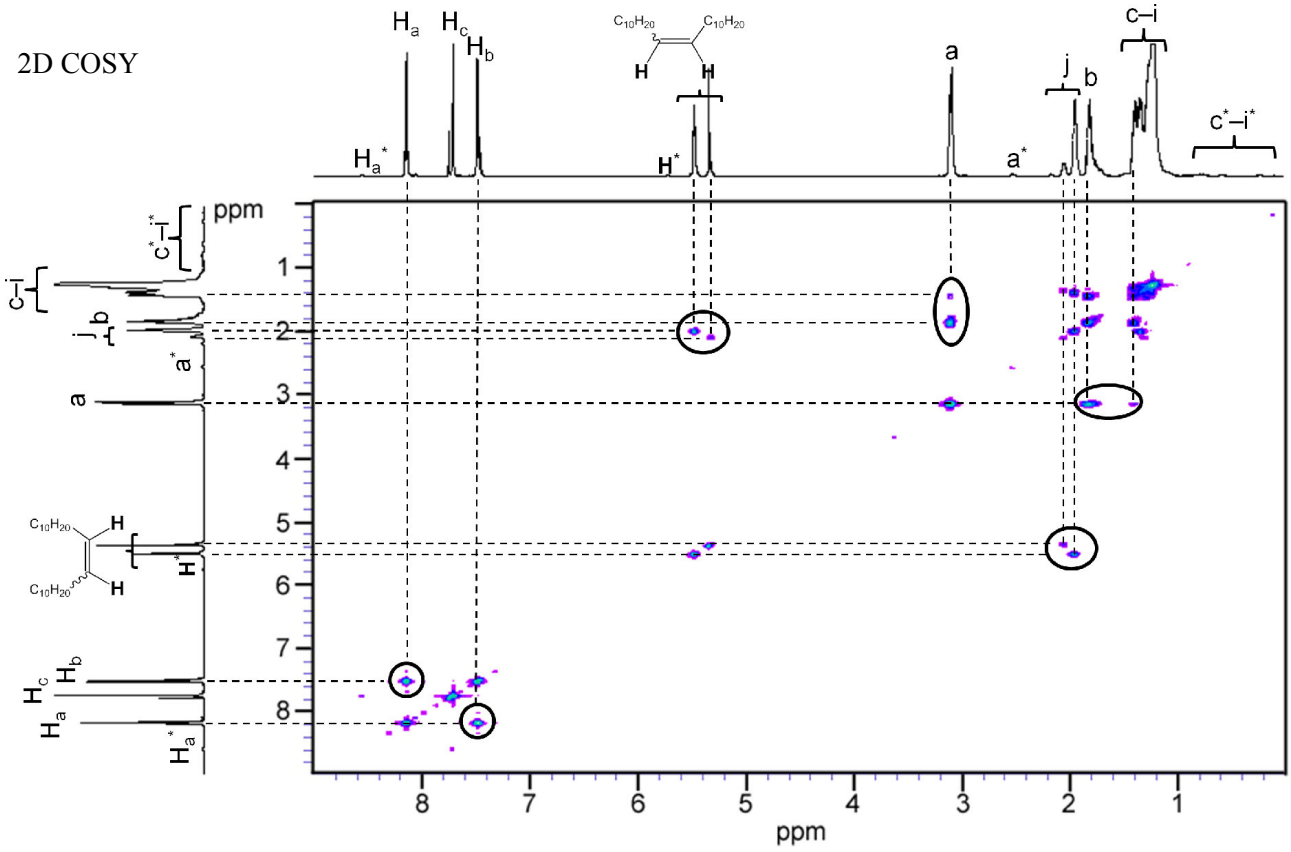
In particular the 2D ROESY spectrum of catenand **1** (see page ESI 17) clearly shows the existence of a proton exchange which is slow in the ^{1}H NMR time scale at room temperature. Signals marked with asterisks are related to the protonated catenand. Protonation of **1** is not larger than 1% and likely occurs in the deuterated solvent.

Protonation of catenand **1** is indeed strongly favored by the topological enhancement of basicity that phenanthroline ligands experience when they are forced into an interlocked topology (see M. Cesario, C. O. Dietrich, A. Edel, J. Guilhem, J.-P. Kintzinger, C. Pascard and J.-P. Sauvage, *J. Am. Chem. Soc.* 1986, **108**, 6250-6254).

2D ROESY



2D COSY



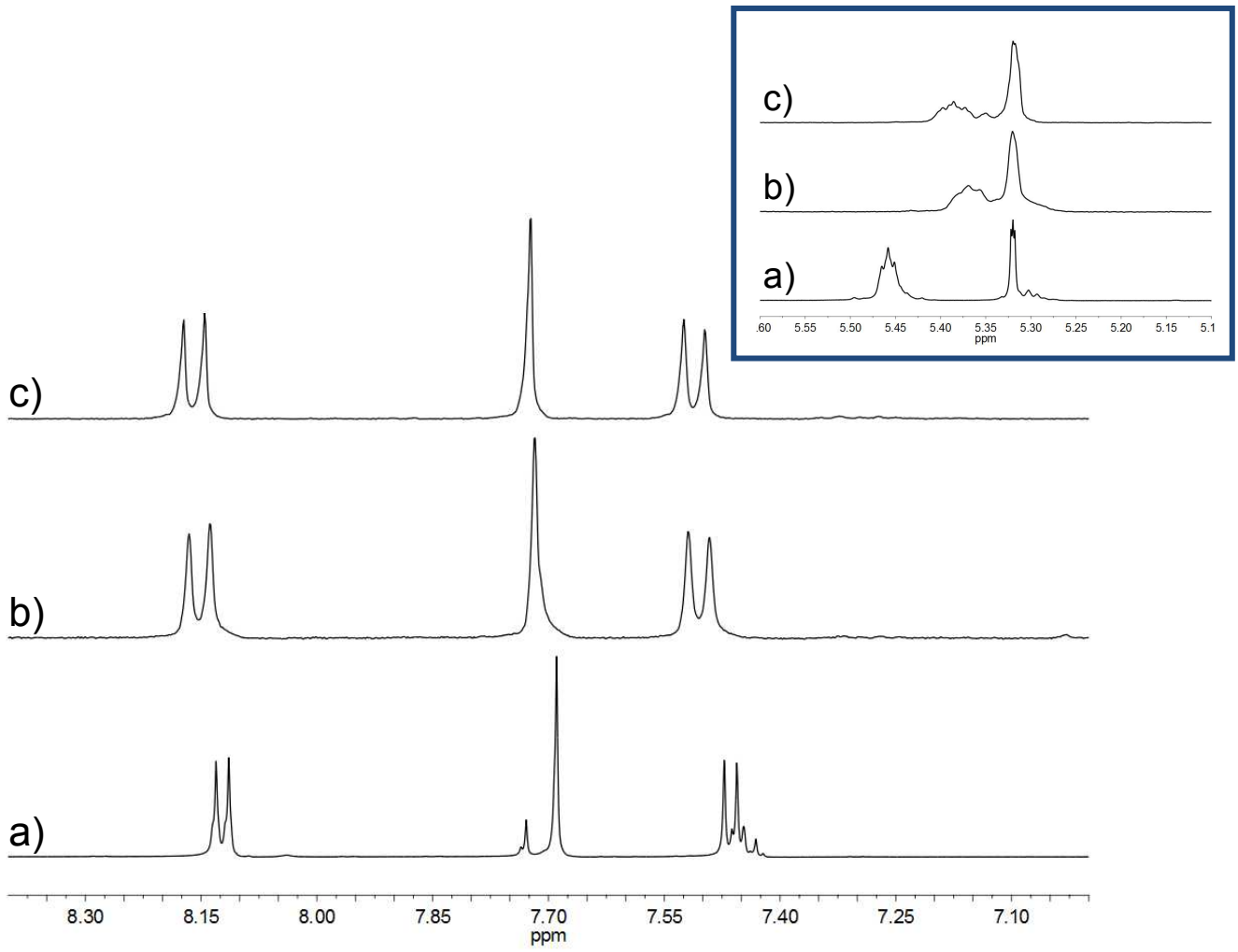


Fig. ESI 1. Partial ^{1}H-NMR spectra of (*a*) catenand **1**, (*b*) reaction product of olefin cross-metathesis of 2.5 mM catenand **1** and (*c*) $\mathbf{C_1}$. In the blue section regions of the double bonds are shown.

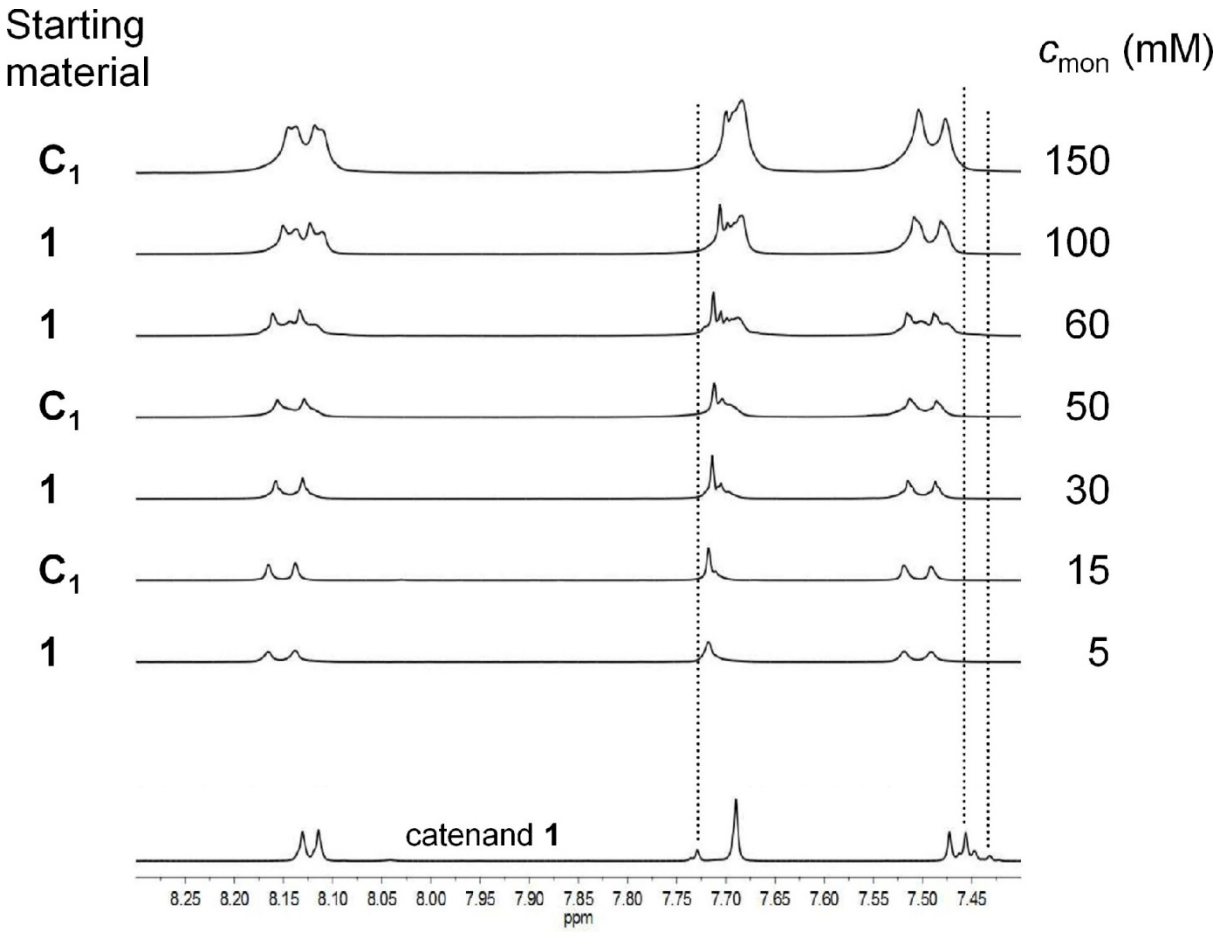


Fig. ESI 2. Partial ^{1}H-NMR spectra (aromatic region, CD_2Cl_2, 303 K) of equilibrated reaction mixtures at different c_{mon}. For comparison the spectrum of catenand **1** is also reported.