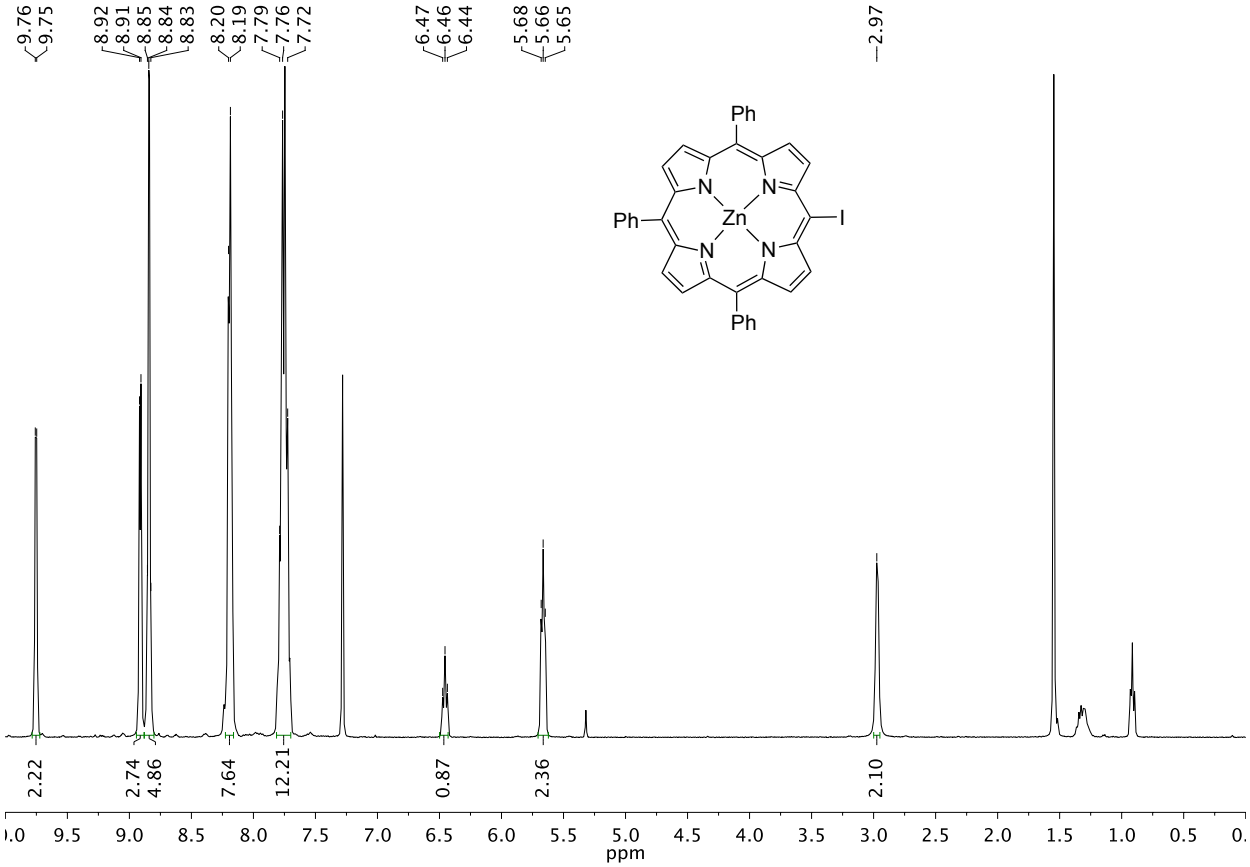
Eur. J. Org. Chem. **2015** · ISSN 1099–0682

SUPPORTING INFORMATION

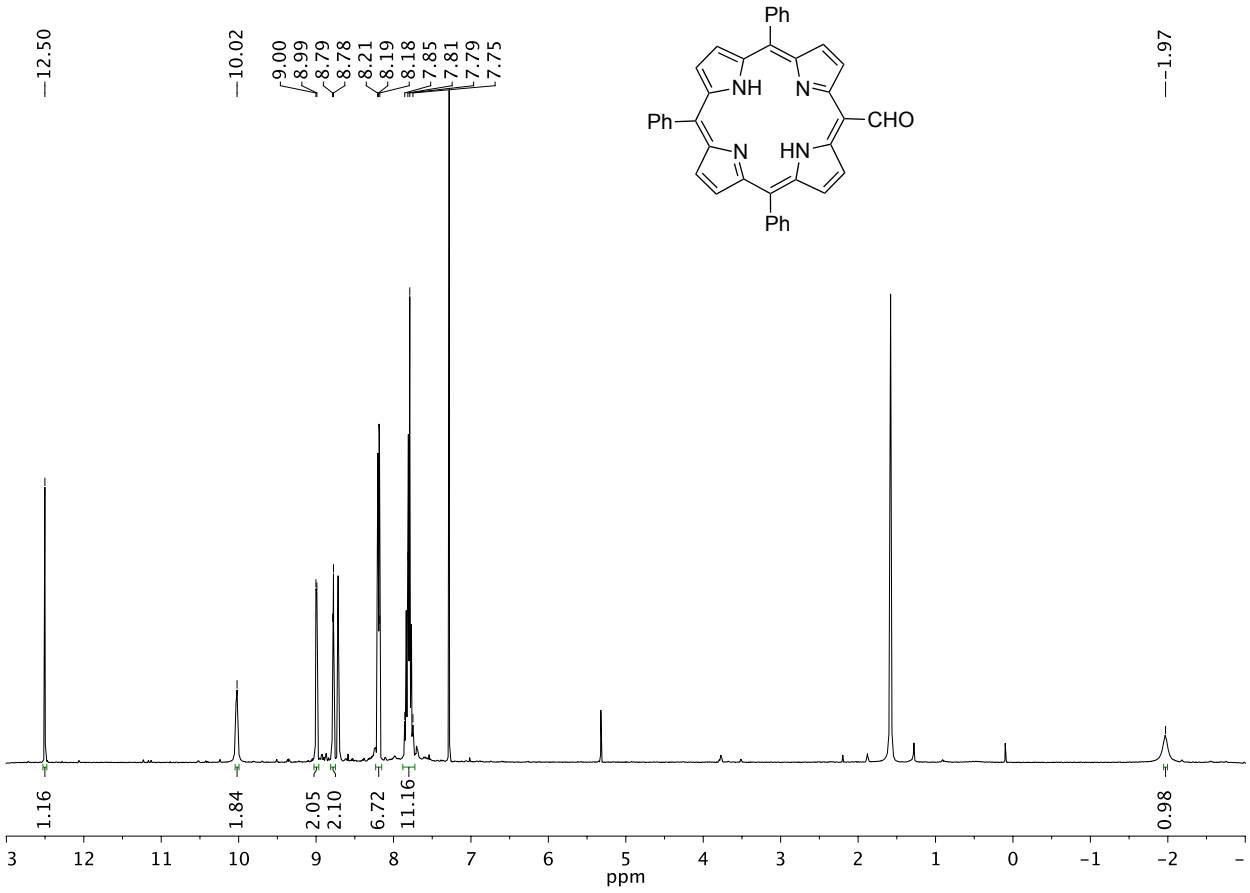
DOI: 10.1002/ejoc.201500183
Title: Synthetic, Structural, and Spectroscopic Studies of Bis(porphyrinzinc) Complexes Linked by Two-Atom Conjugating Bridges
Author(s): Shannon R. Harper, Michael C. Pfrunder, Louisa J. Esdaile, Paul Jensen, John C. McMurtrie, Dennis P. Arnold*

Table of Contents

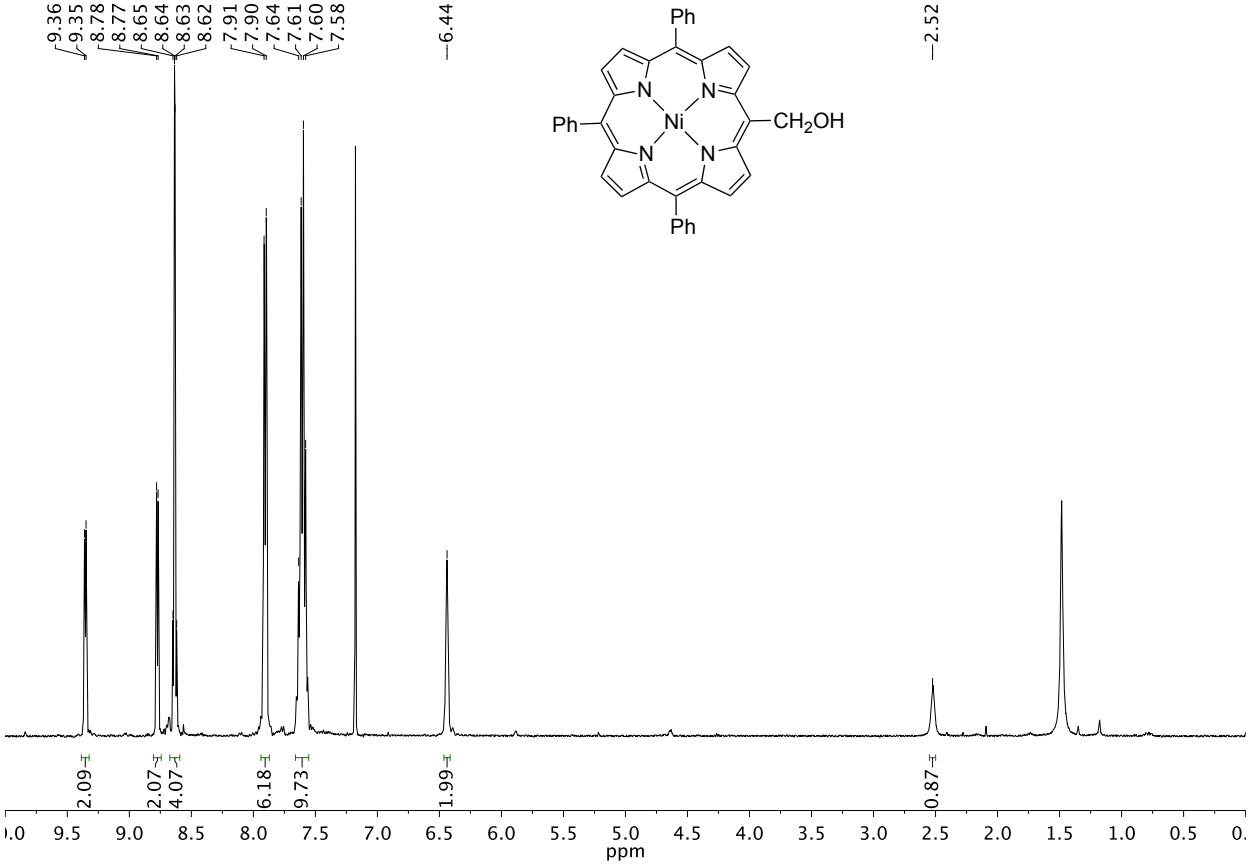
ZnTriPPI 24

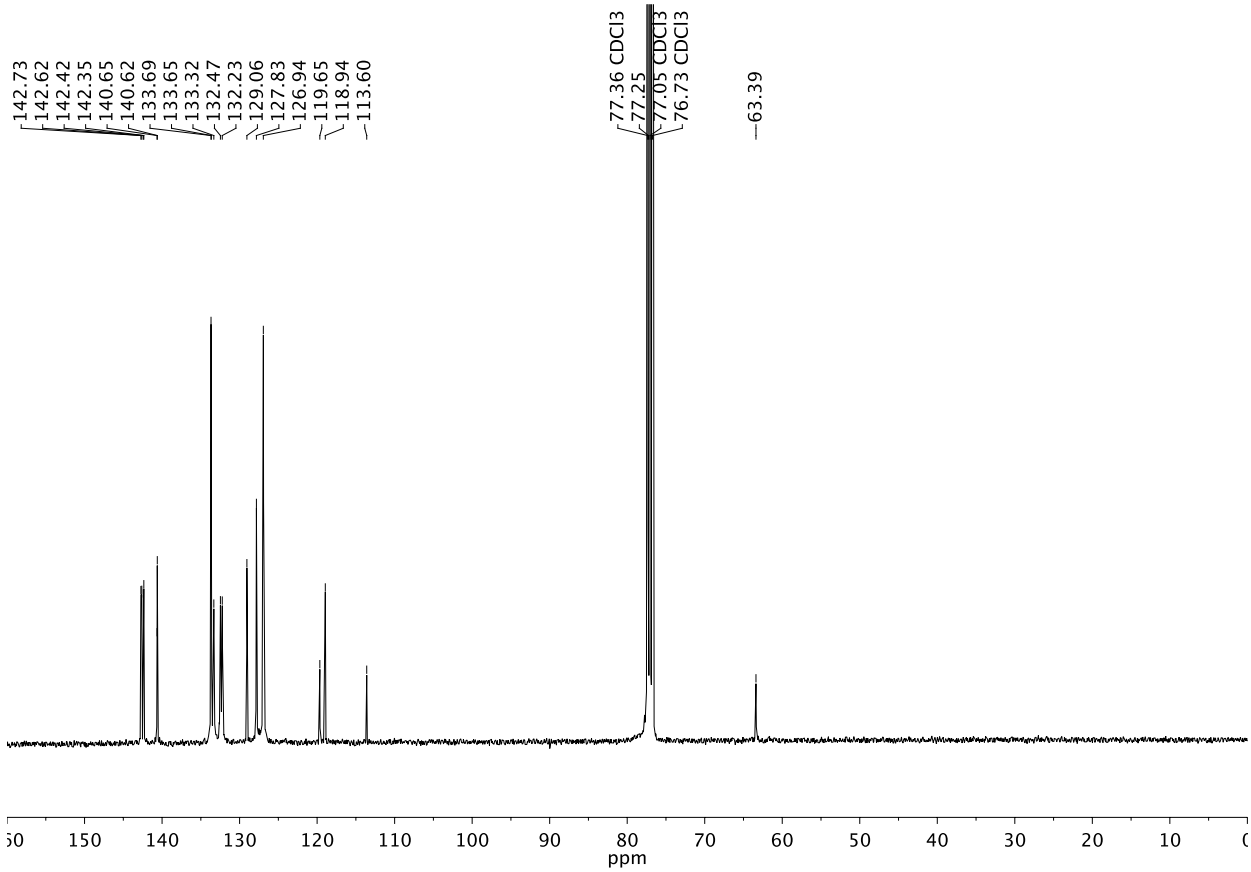


H_2TriPPCHO 33

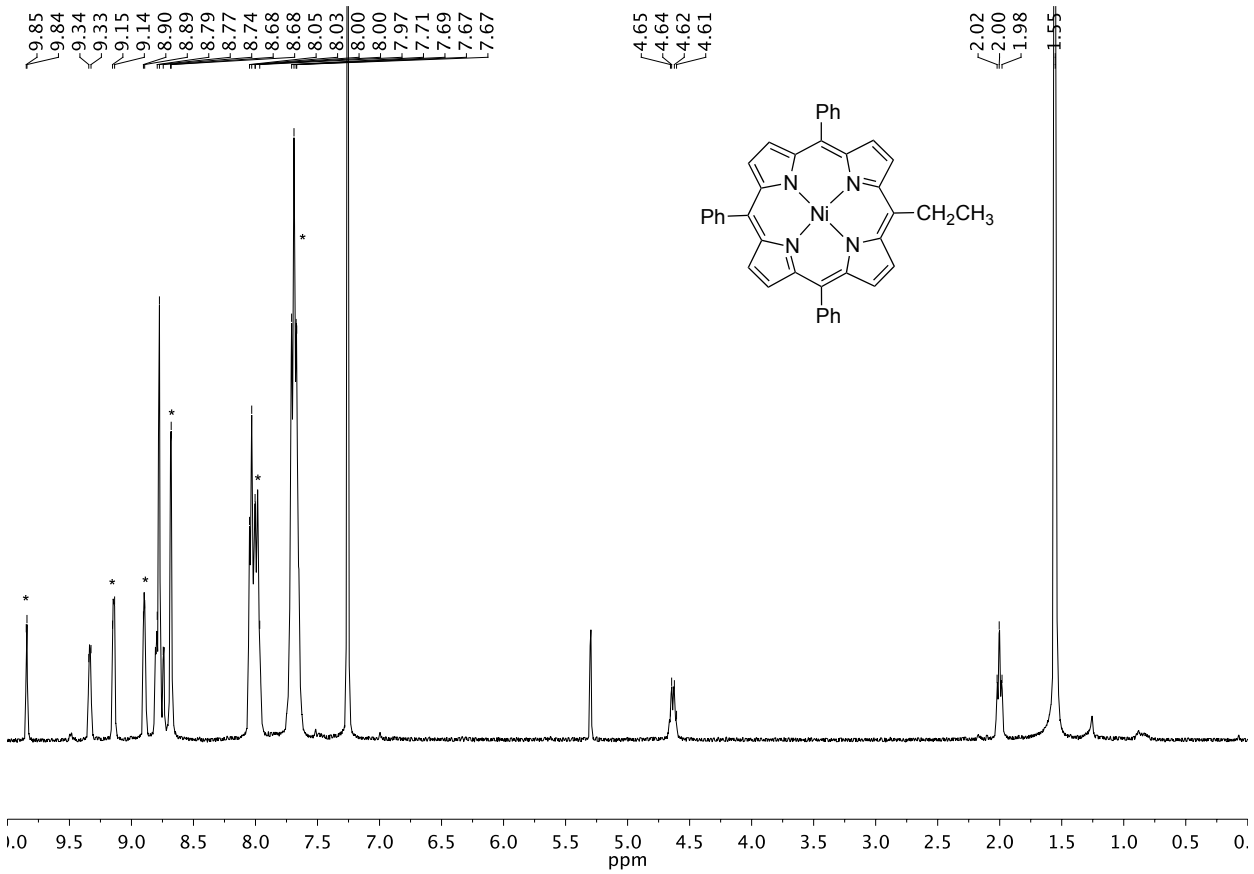


NiTriPPCH$_2$OH 8

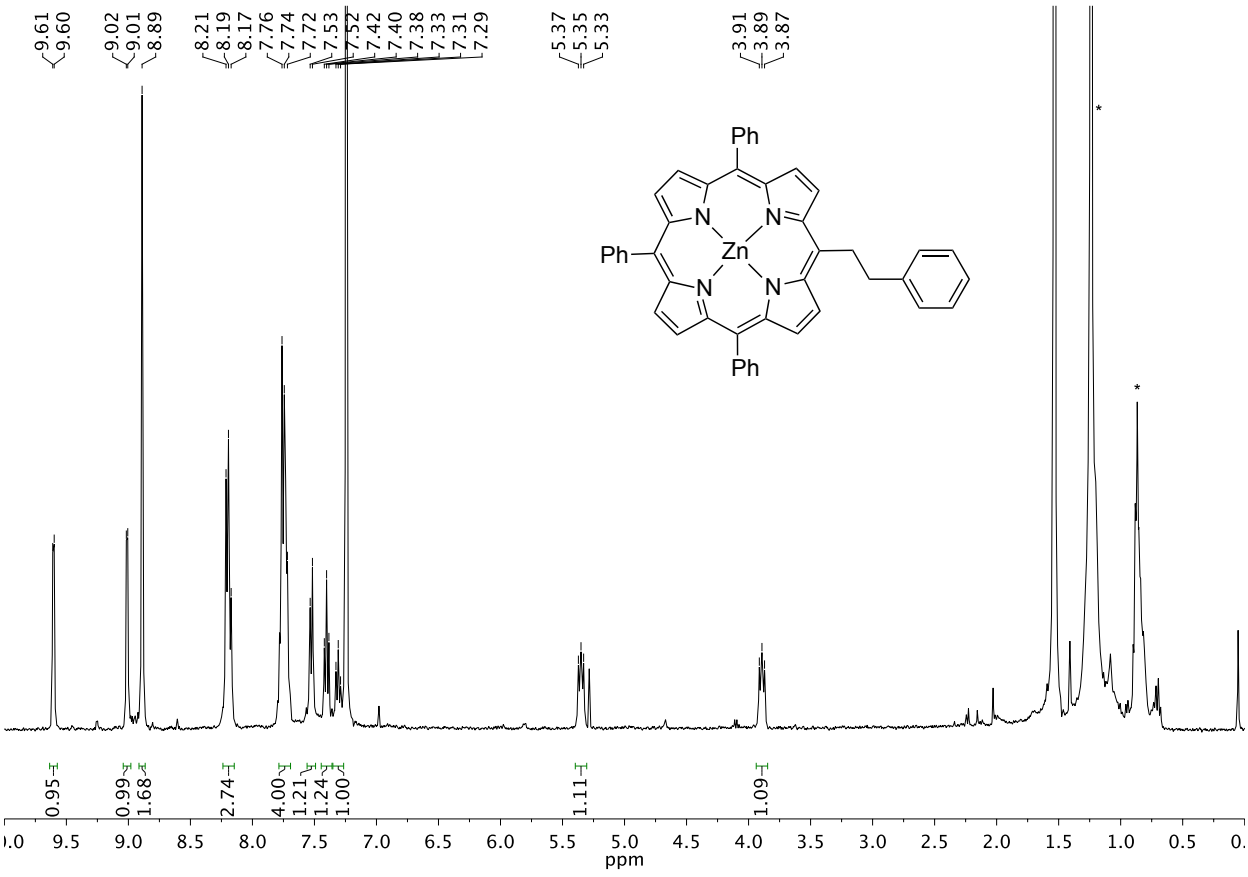




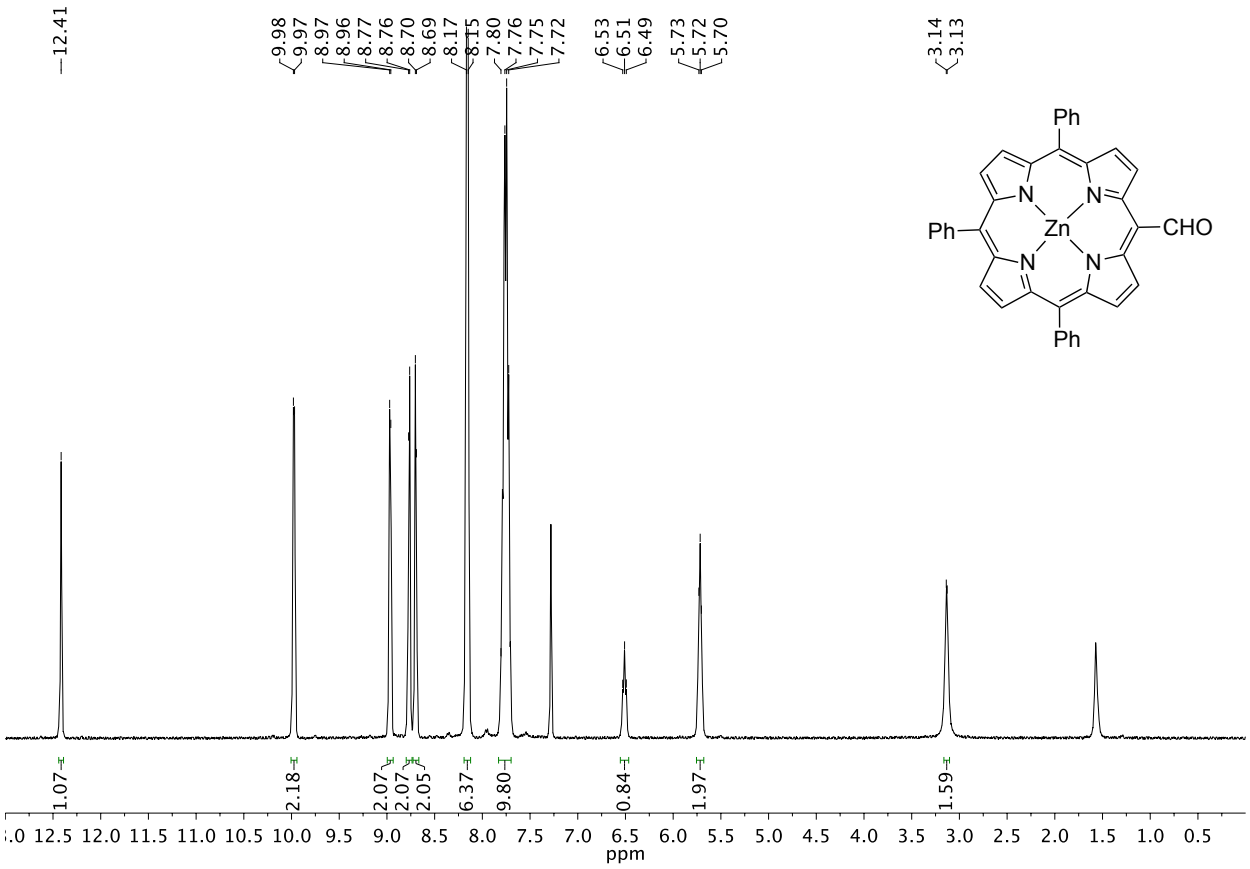
NiTriPPCH$_2$CH$_3$ 17 (* = NiTriPP **6**)

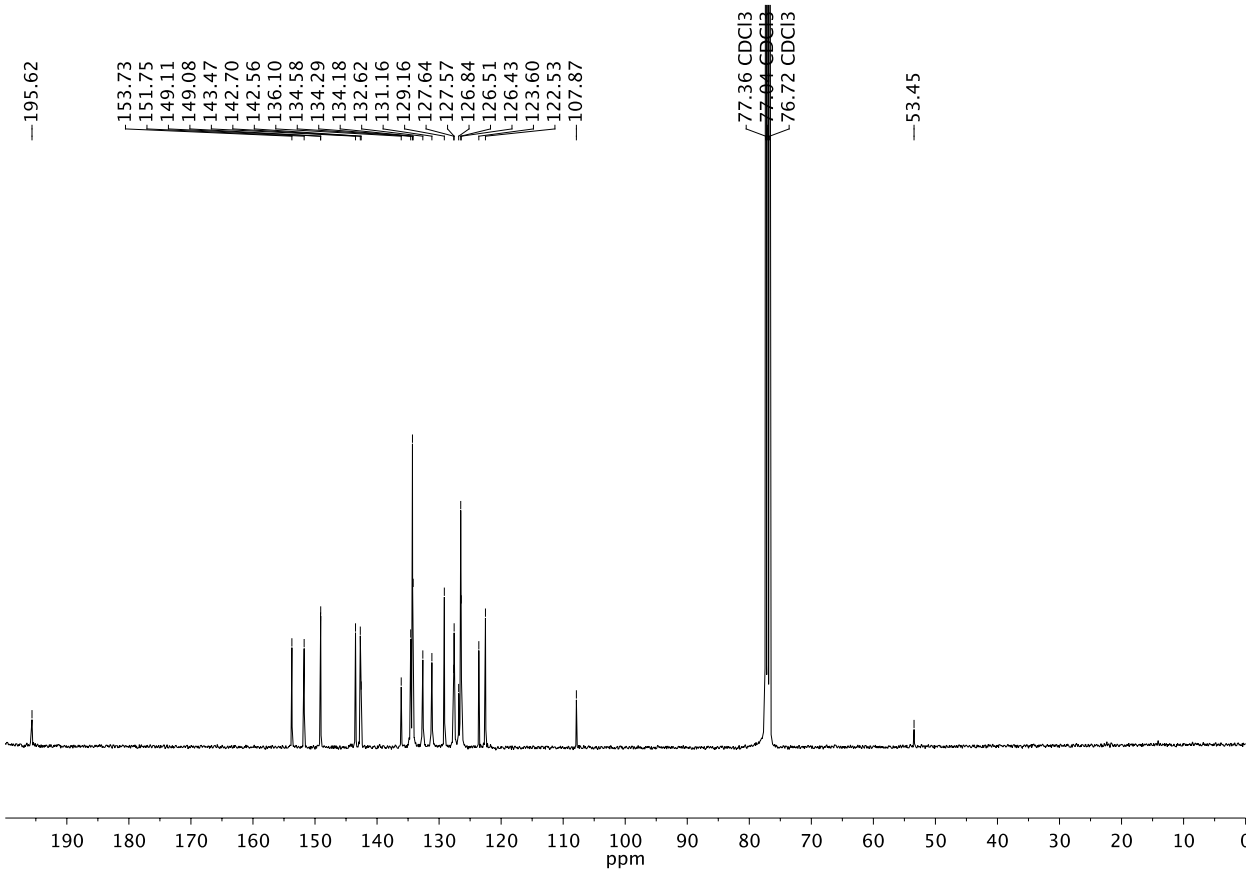


ZnTriPPCH$_2$CH$_2$Ph 18 (* = aliphatic hydrocarbon residues)

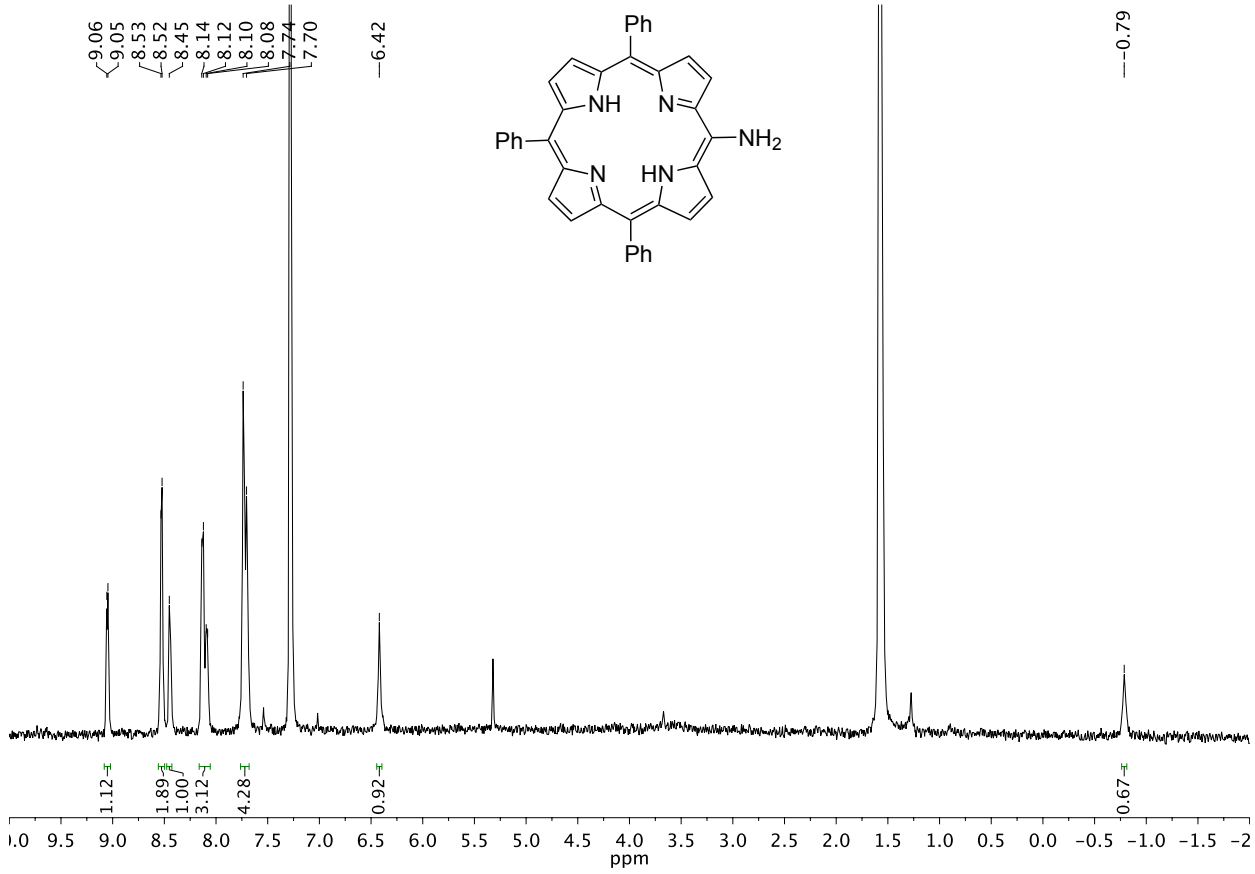


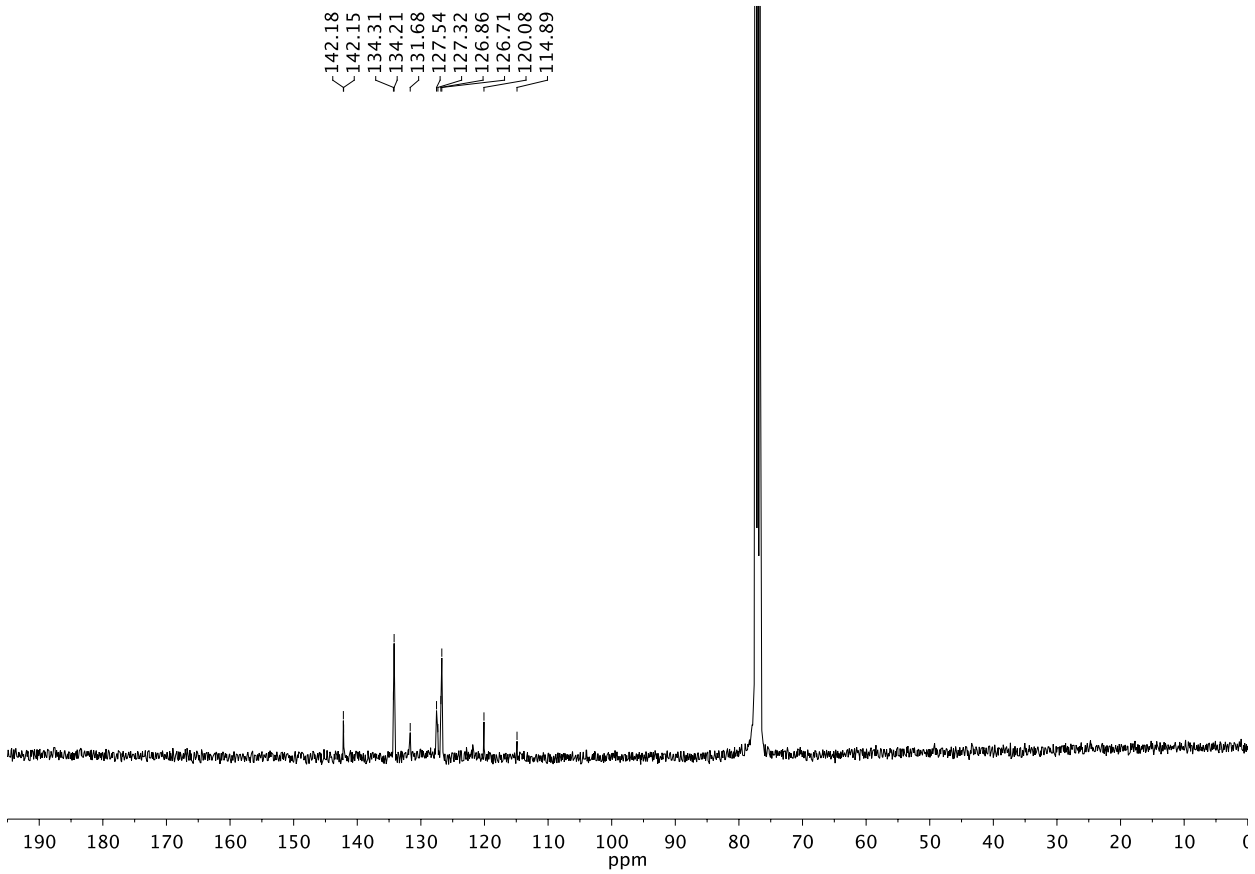
ZnTriPPCHO 23 (pyridine coordinated)



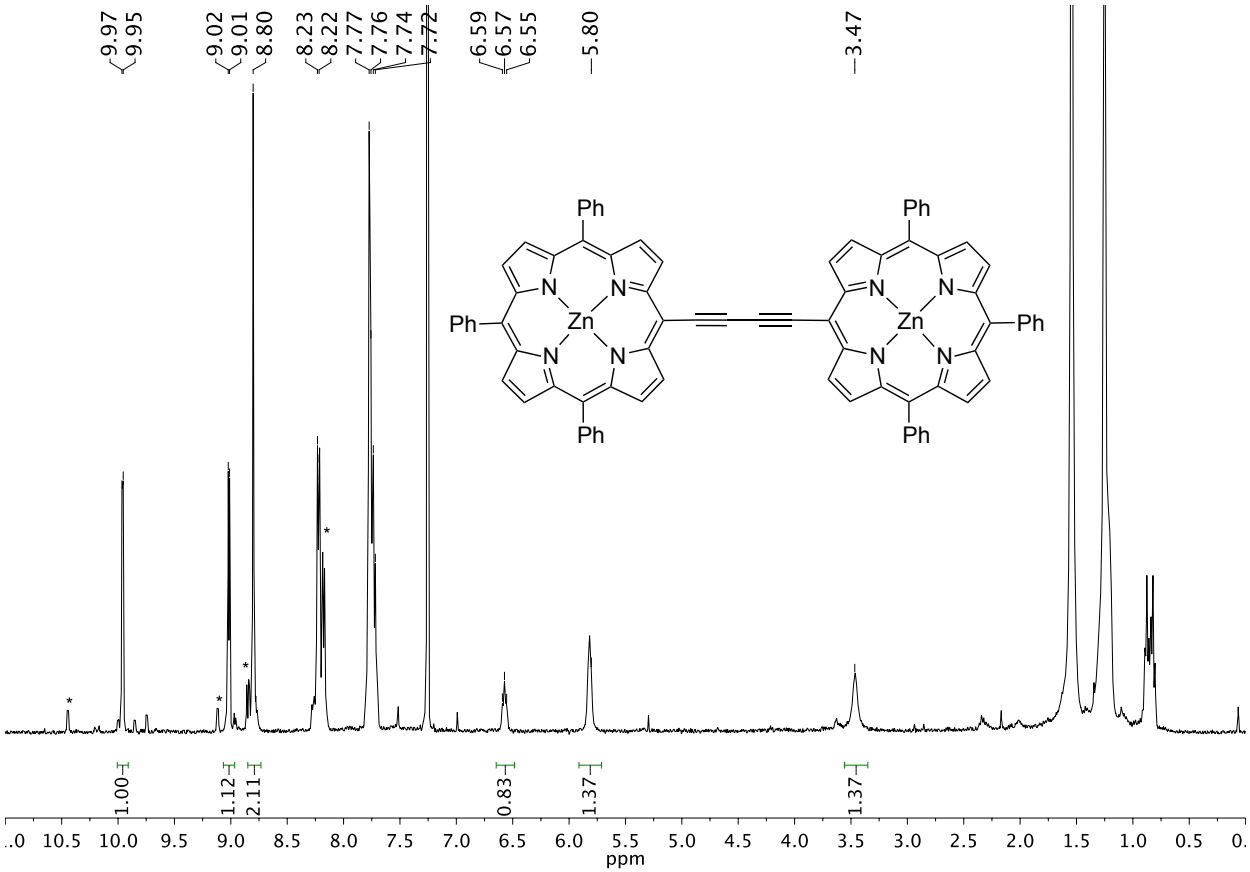


H_2TriPPNH_2 30

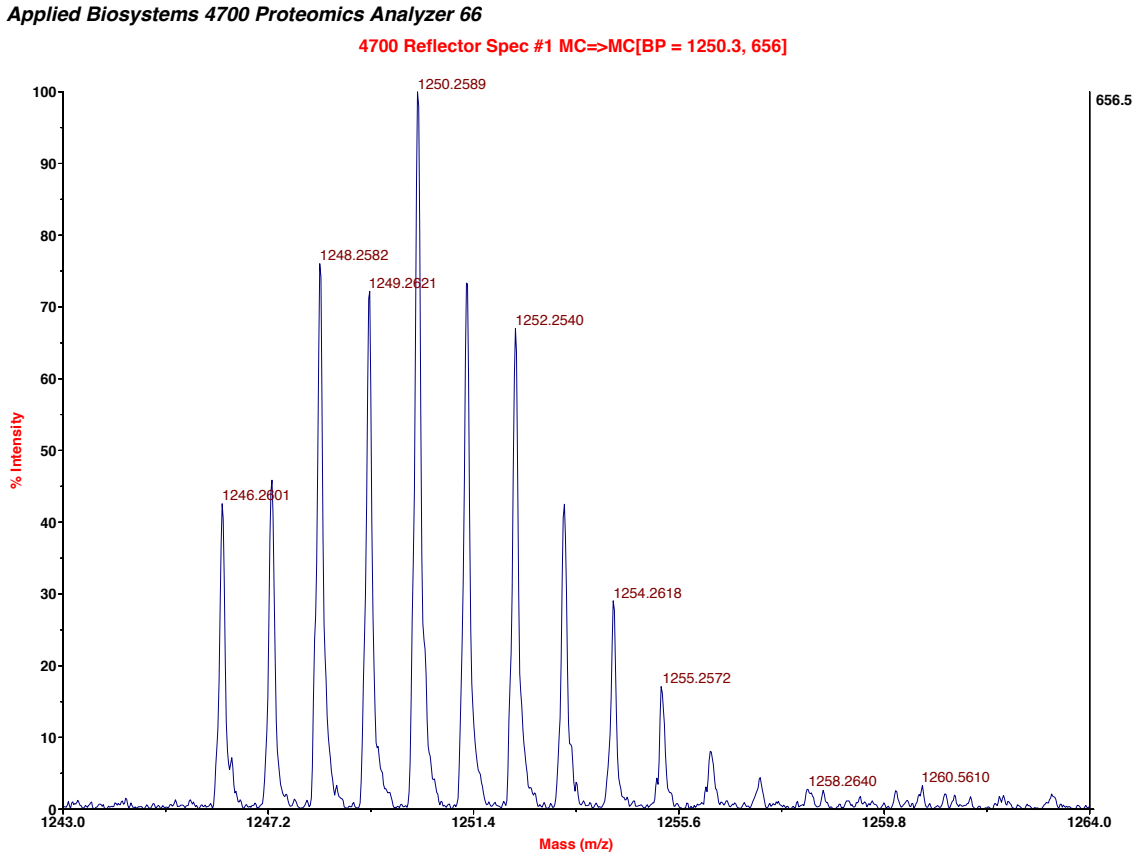




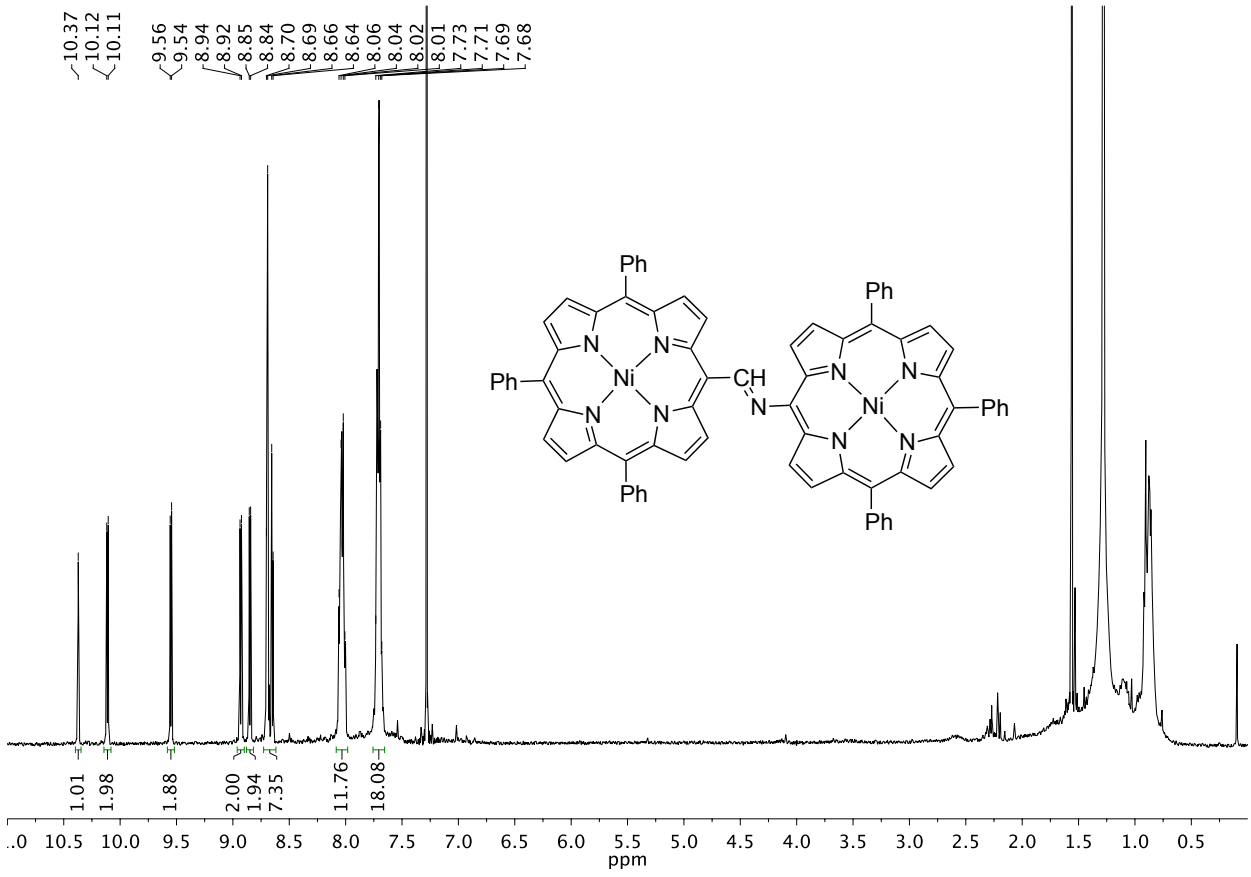
ZnTriPP–C_4–ZnTriPP 26 (pyridine coordinated; * = ZnTriPP–C_2–ZnTriPP **3**; aliphatic hydrocarbon residues present)

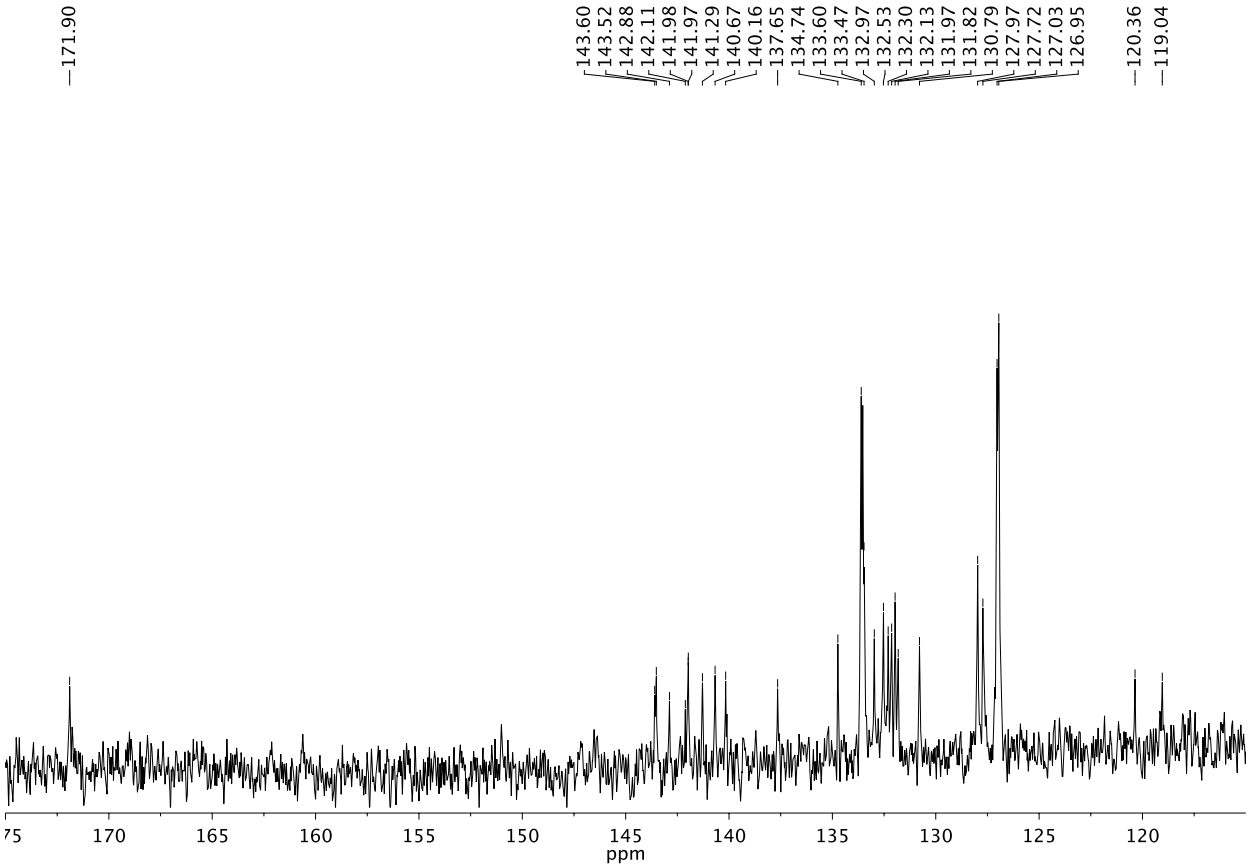


HRMS (MALDI)

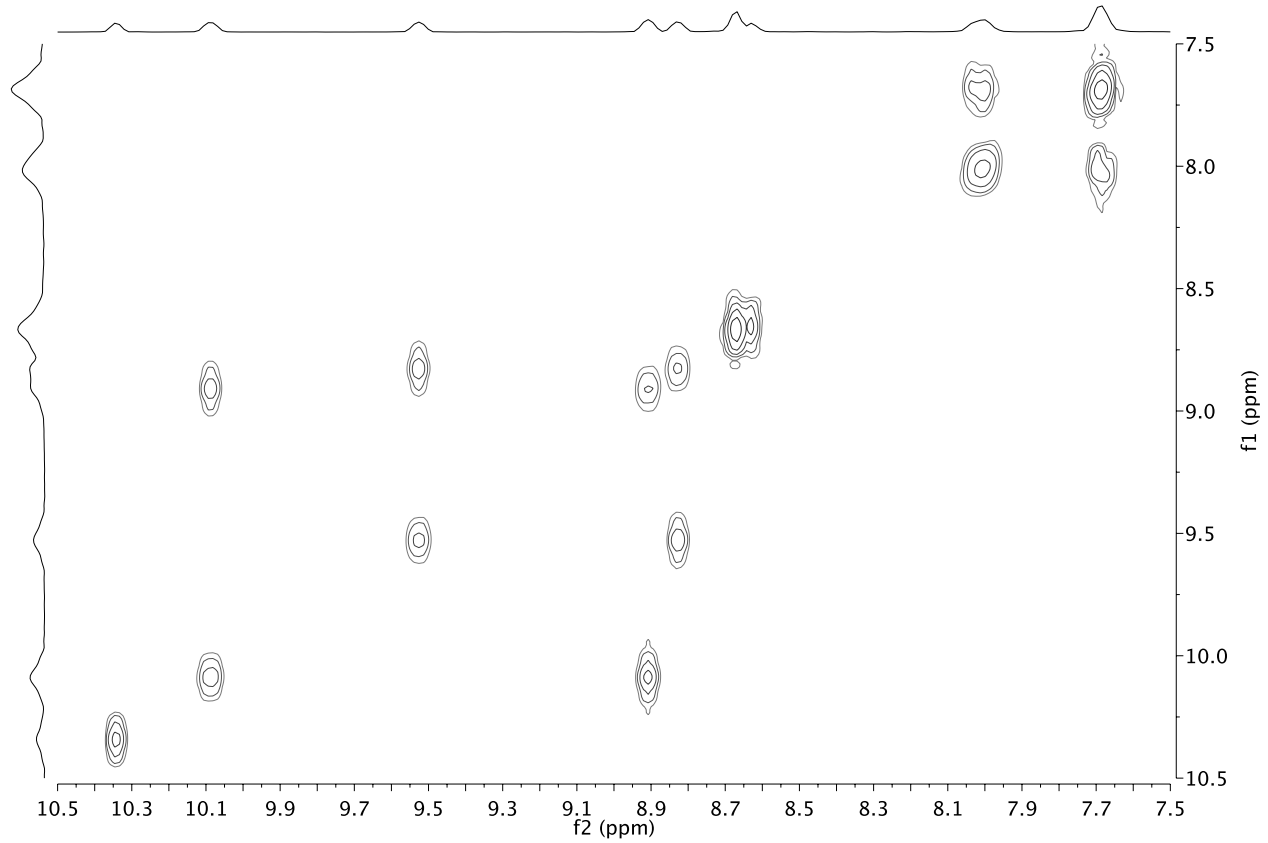


NiTriPP–CH=N–NiTriPP 29 (aliphatic hydrocarbon residues present)

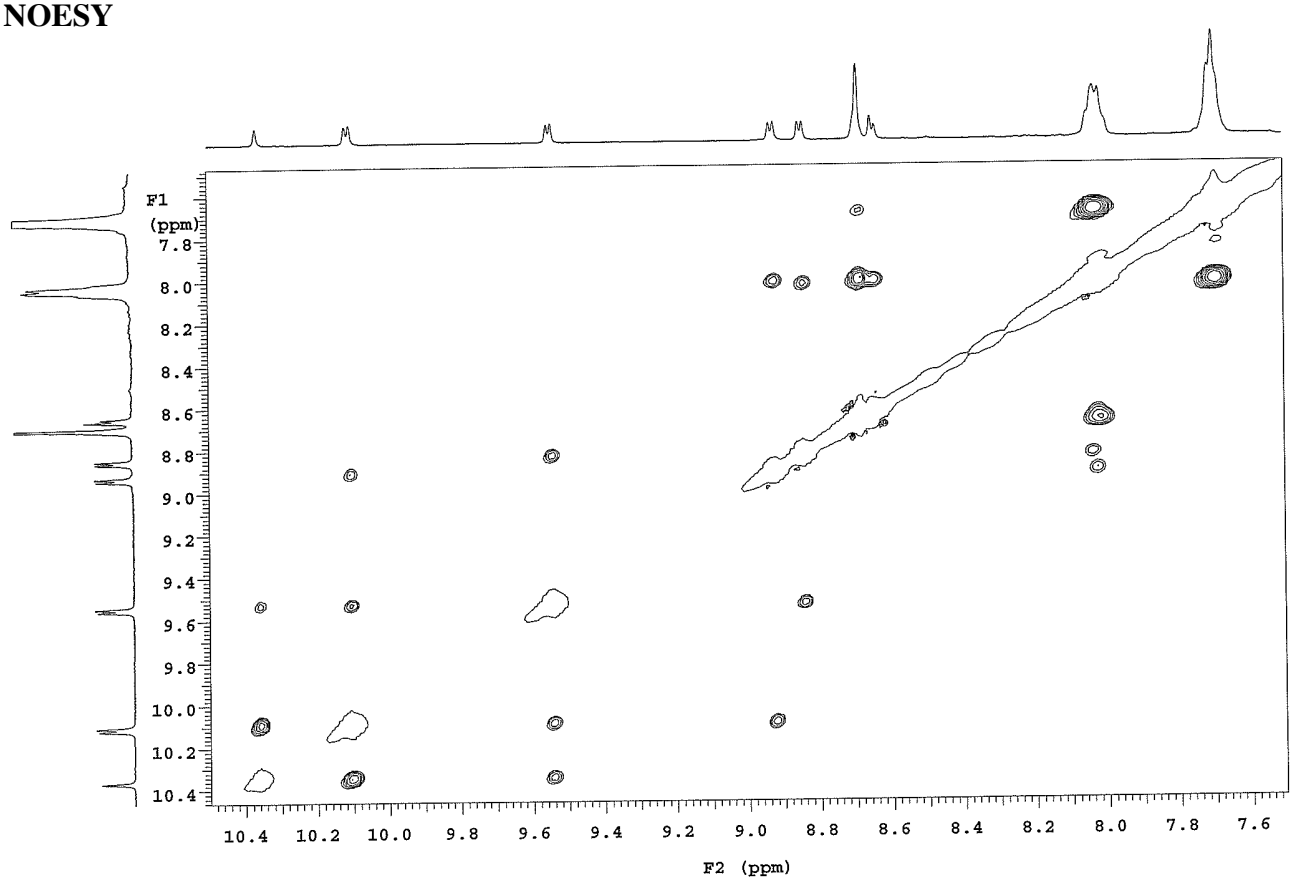




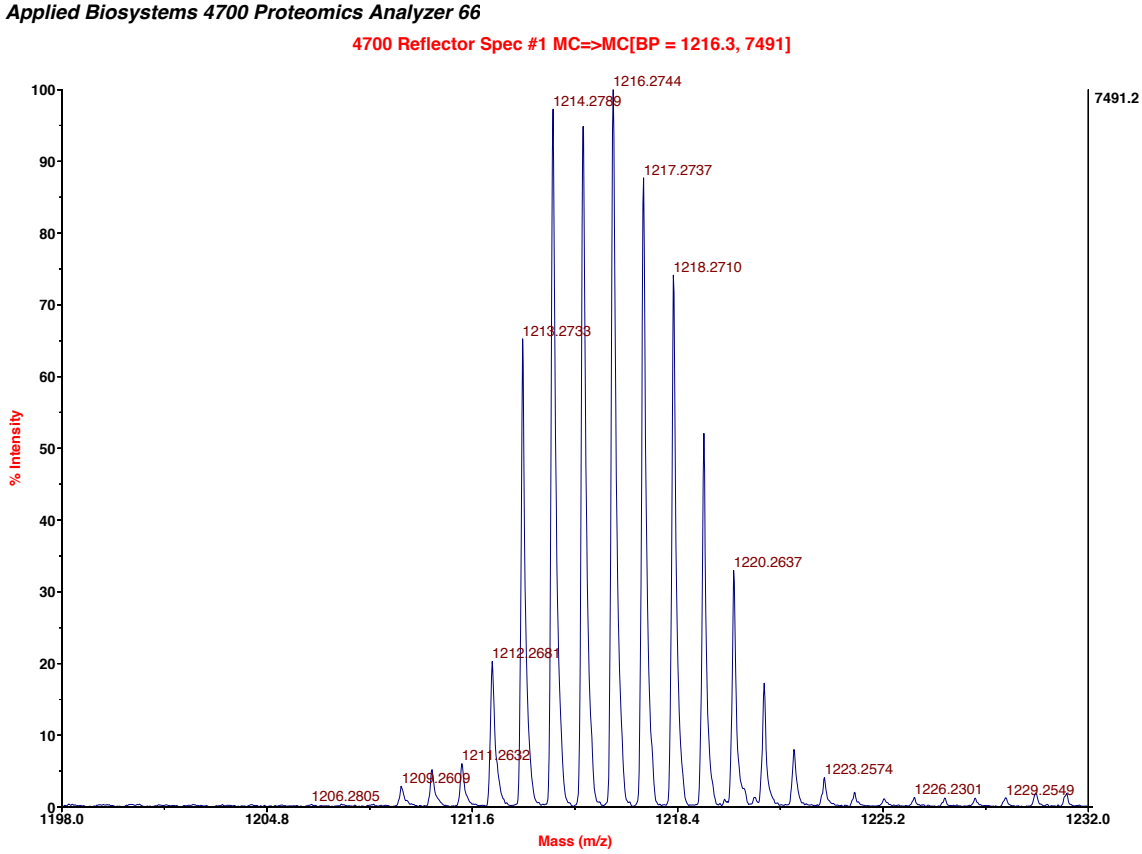
COSY


7.5
8.0
8.5
9.0
9.5
10.0
10.5
f1 (ppm)
10.5 10.3 10.1 9.9 9.7 9.5 9.3 9.1 8.9 8.7 8.5 8.3 8.1 7.9 7.7 7.5
f2 (ppm)

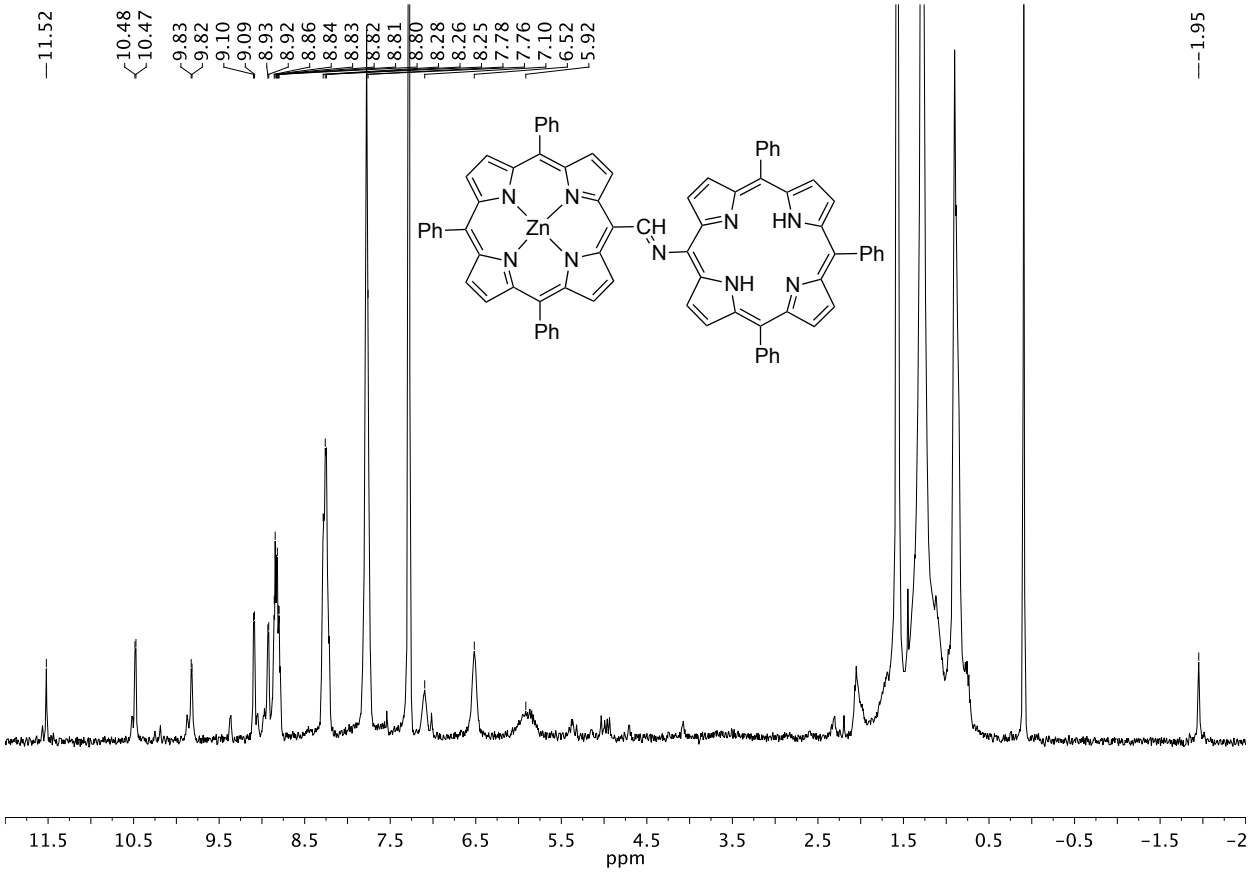
NOESY


F1
(ppm)
7.8
8.0
8.2
8.4
8.6
8.8
9.0
9.2
9.4
9.6
9.8
10.0
10.2
10.4
10.4 10.2 10.0 9.8 9.6 9.4 9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6
F2 (ppm)

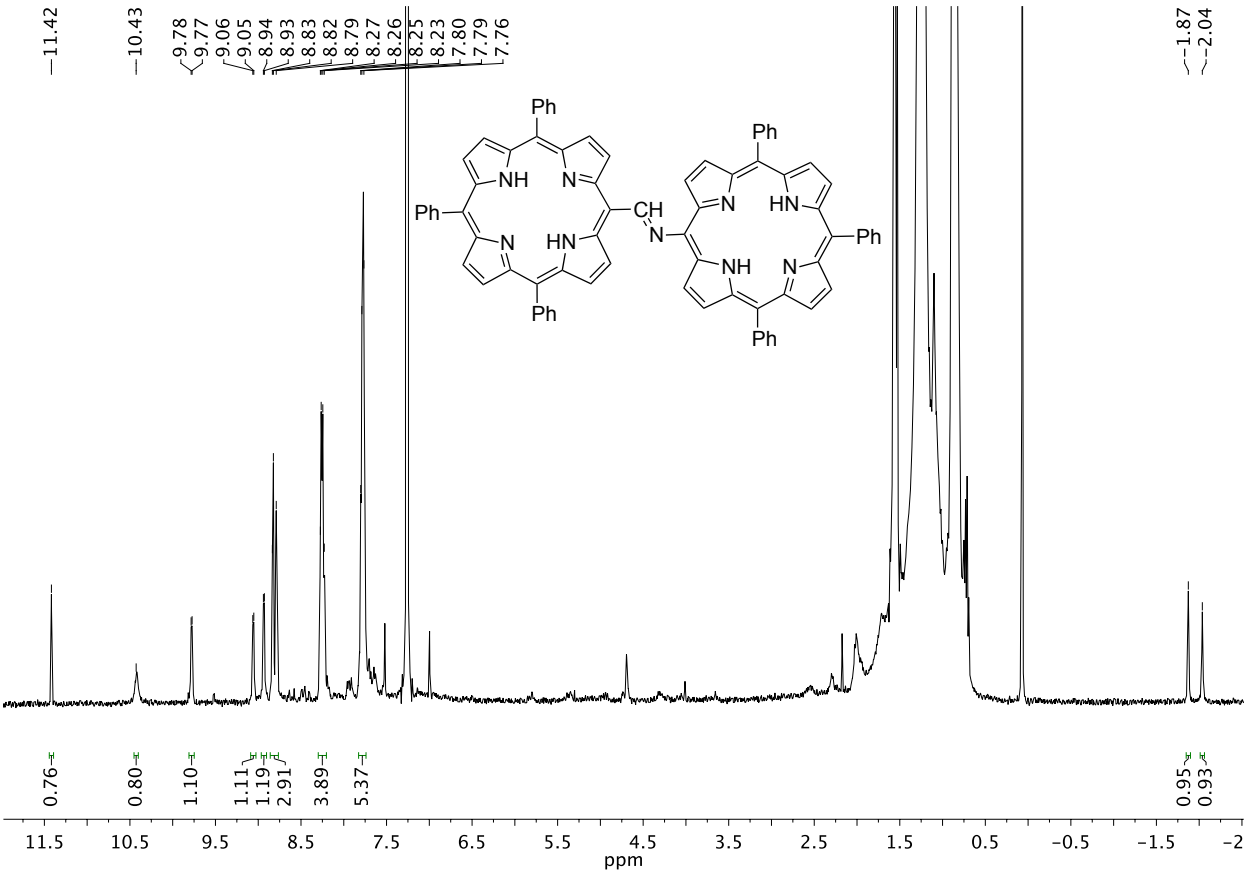
HRMS (MALDI)


Applied Biosystems 4700 Proteomics Analyzer 66
4700 Reflector Spec #1 MC=>MC[BP = 1216.3, 7491]
1216.2744
1214.2789
1217.2737
1218.2710
1213.2733
1220.2637
1212.2681
1211.2632
1209.2609
1206.2805
1223.2574
1226.2301
1229.2549
7491.2
% Intensity
Mass (m/z)
100
90
80
70
60
50
40
30
20
10
0
1198.0
1204.8
1211.6
1218.4
1225.2
1232.0

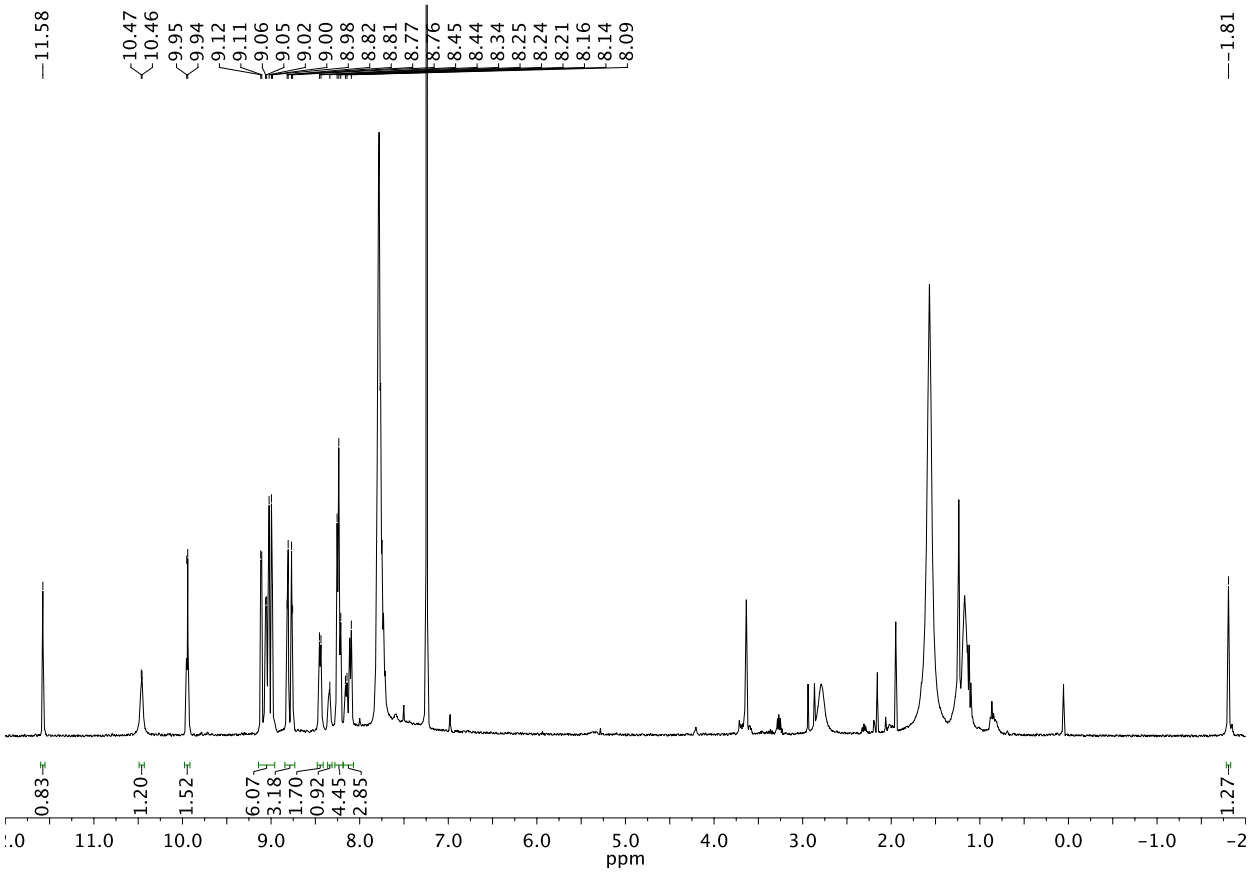
ZnTriPP–CH=N–H_2TriPP 31 (minor porphyrin impurities, some coordinated pyridine and aliphatic hydrocarbon and other residues present)



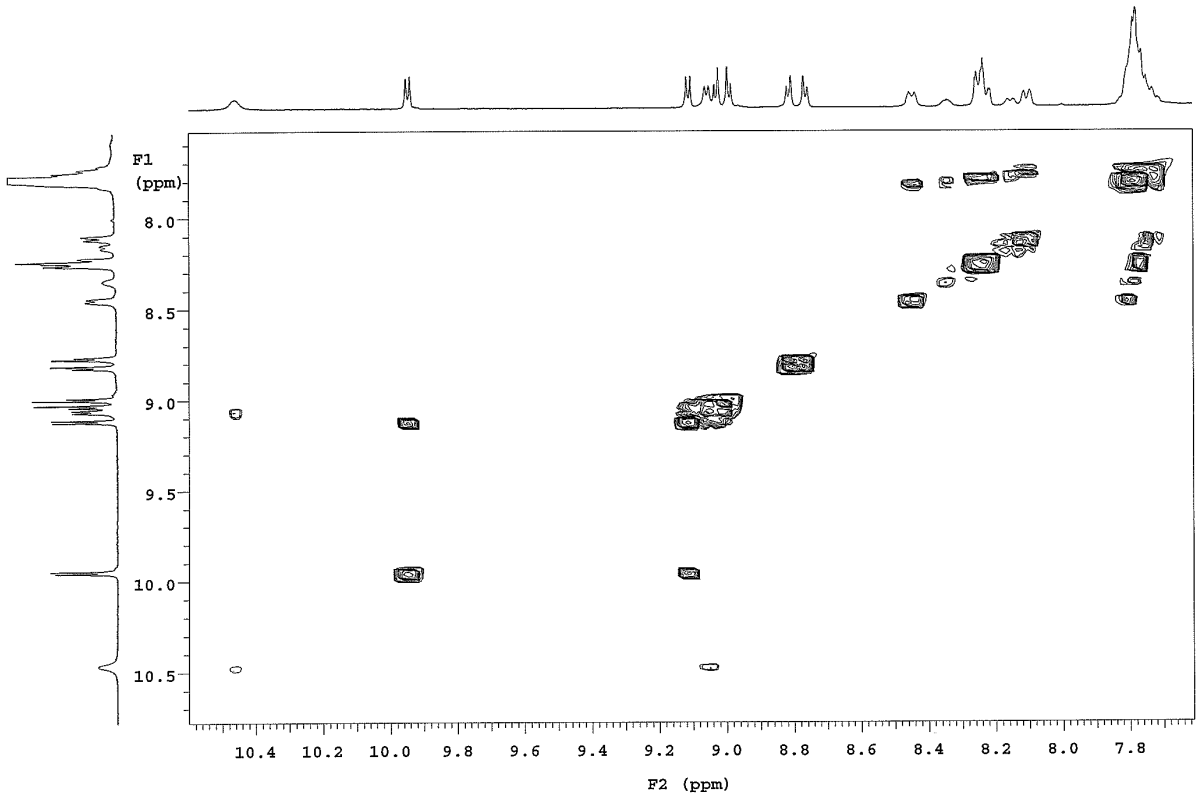
H_2TriPP–CH=N–H_2TriPP 32 (aliphatic hydrocarbon and other residues present)



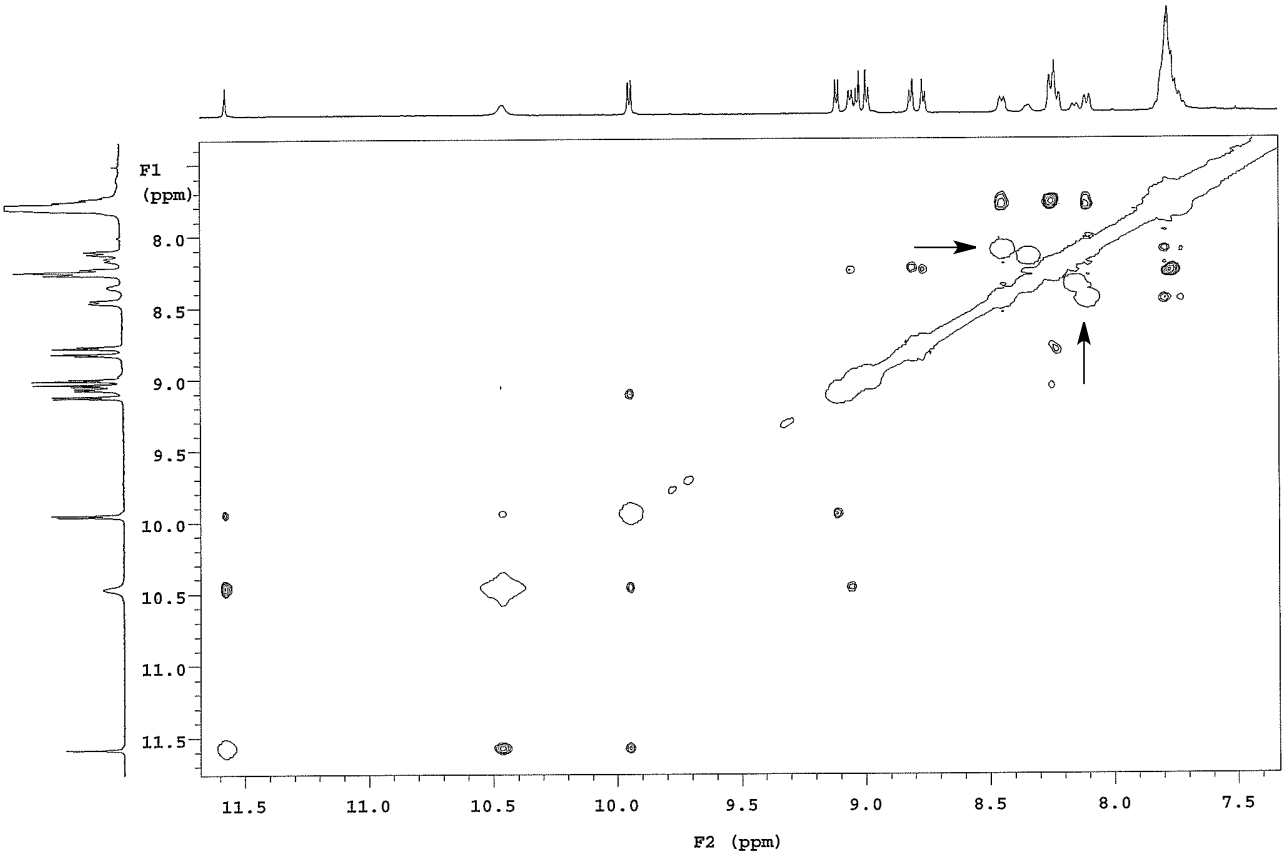
InXTriPP–CH=N–H_2TriPP 35 (aliphatic hydrocarbon and other residues present)



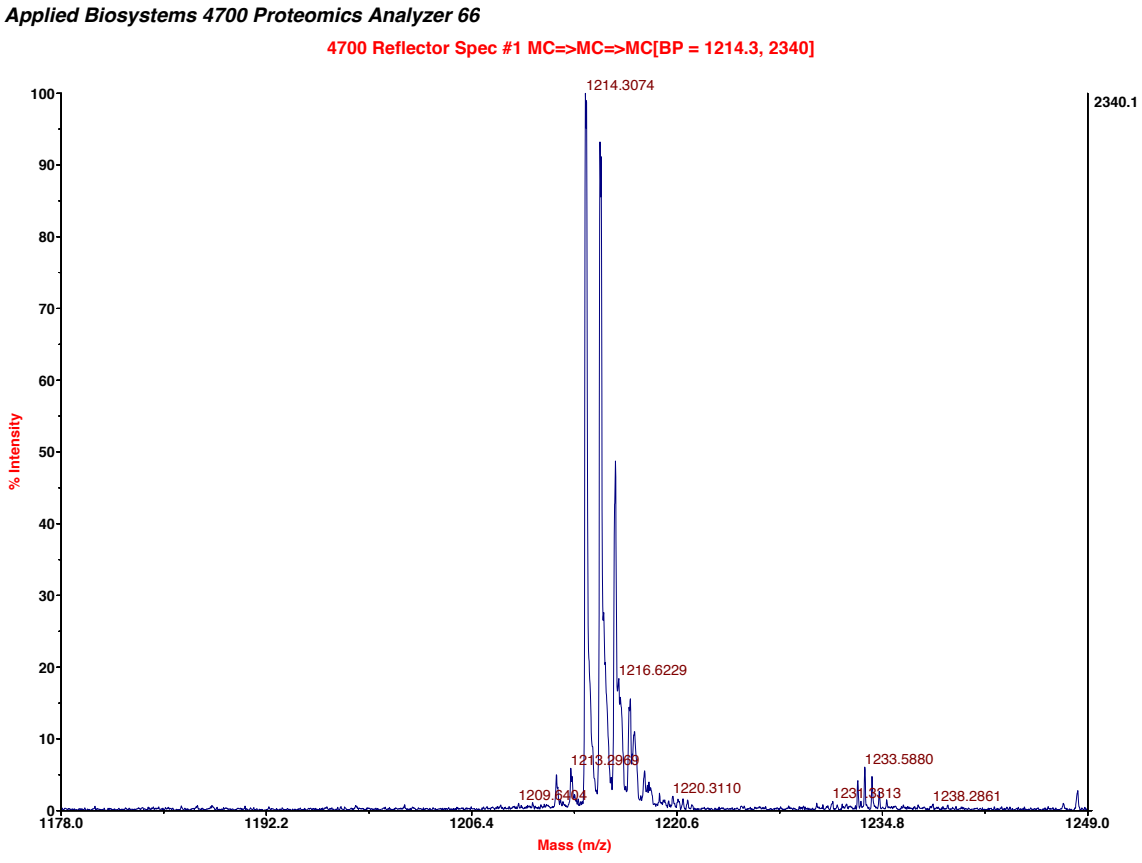
COSY



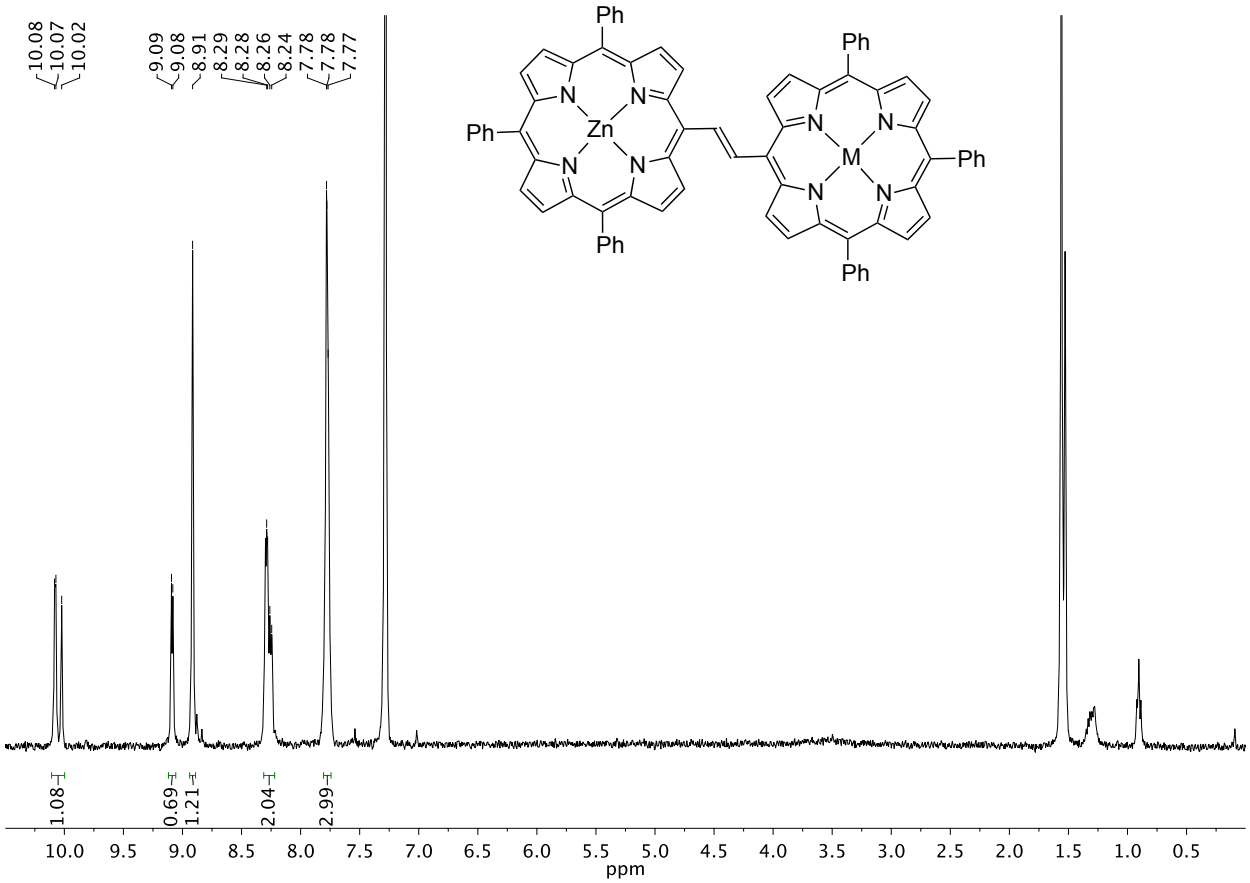
NOESY (the peaks marked with arrows are positive contours, i.e. EXSY cross-peaks showing exchange between *ortho*-phenyl protons on the lateral phenyl groups on the indium(III) ring)



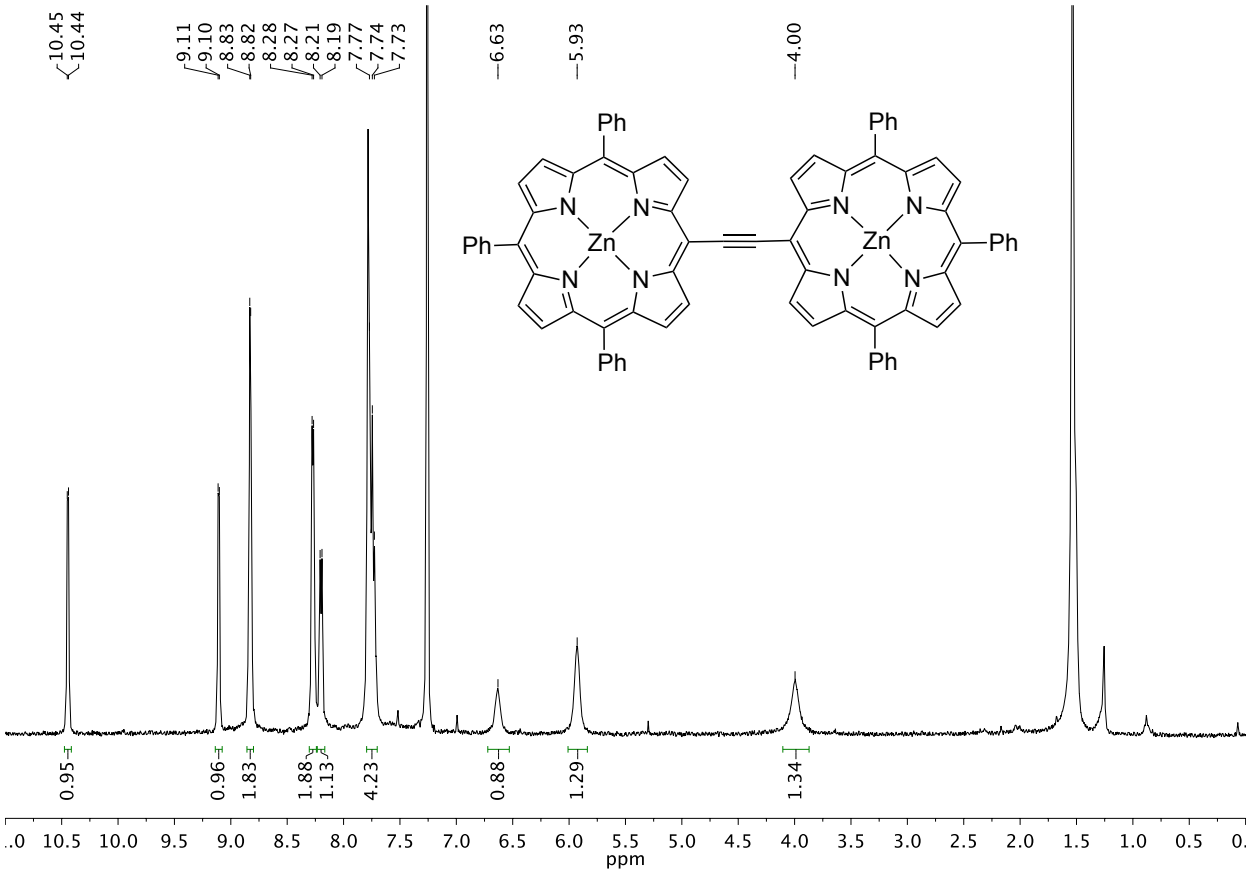
HRMS (MALDI)



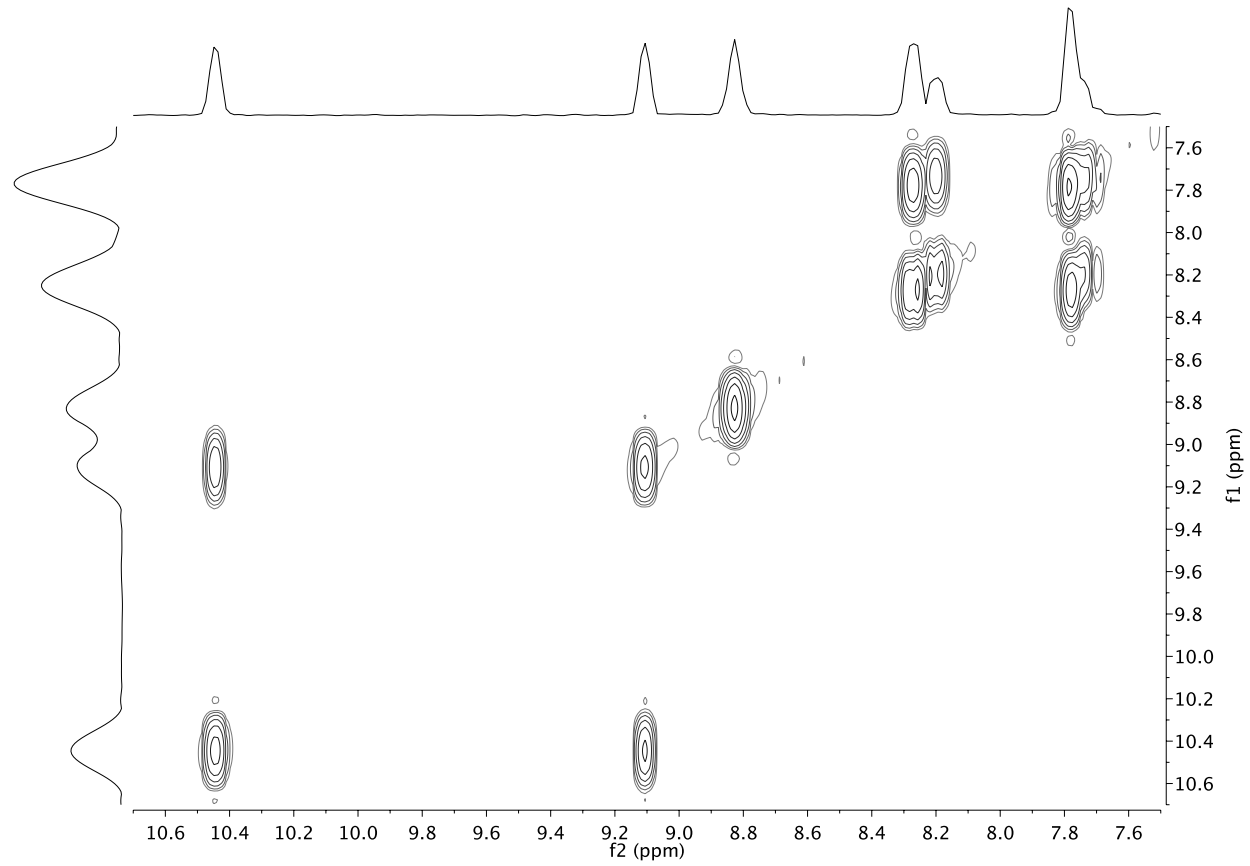
ZnTriPP–CH=CH–ZnTriPP 2



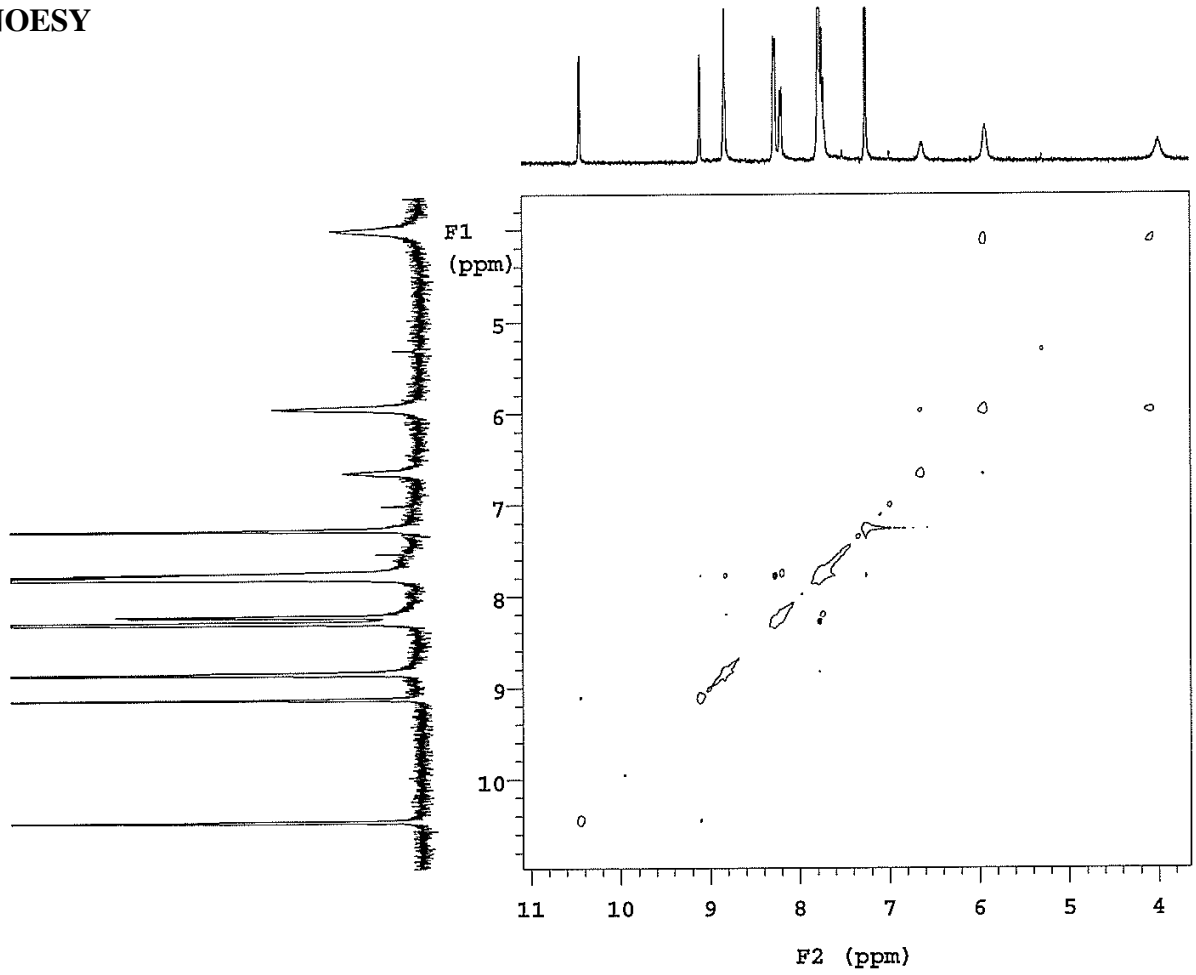
ZnTriPP–C_2–ZnTriPP 3 (pyridine coordinated)



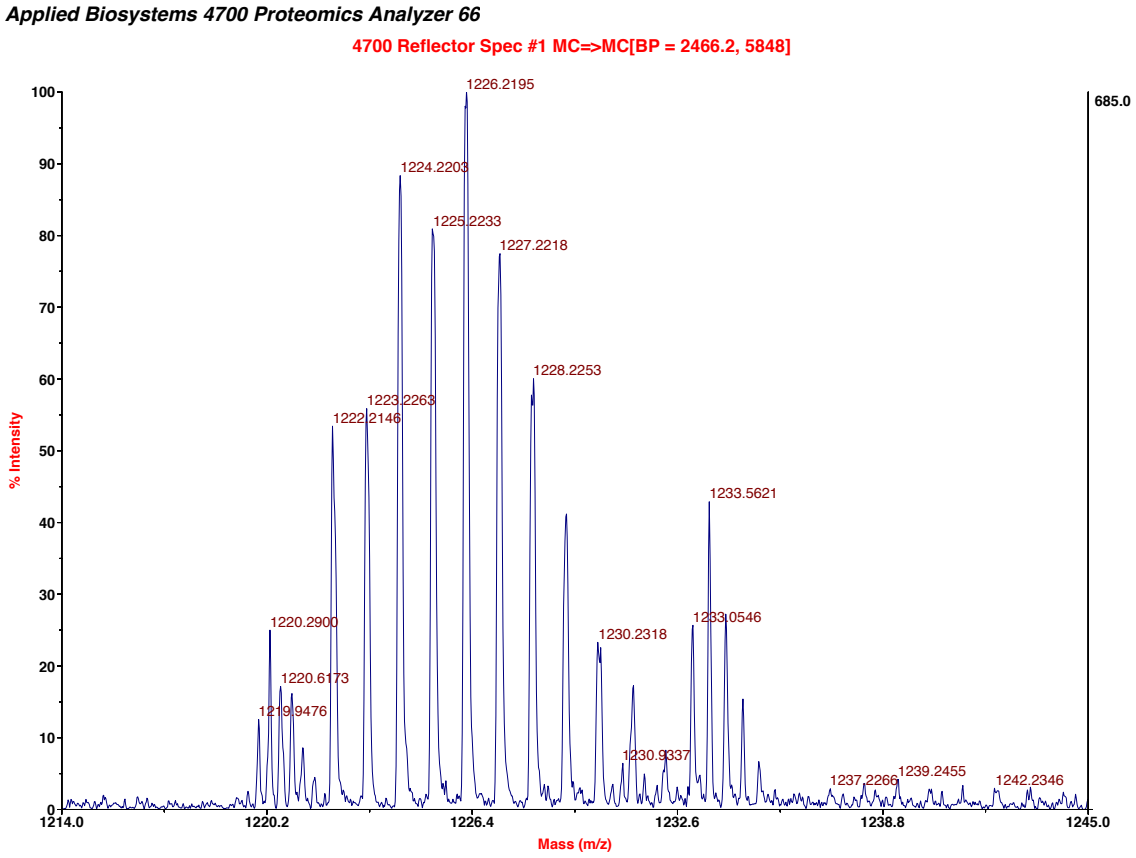
COSY



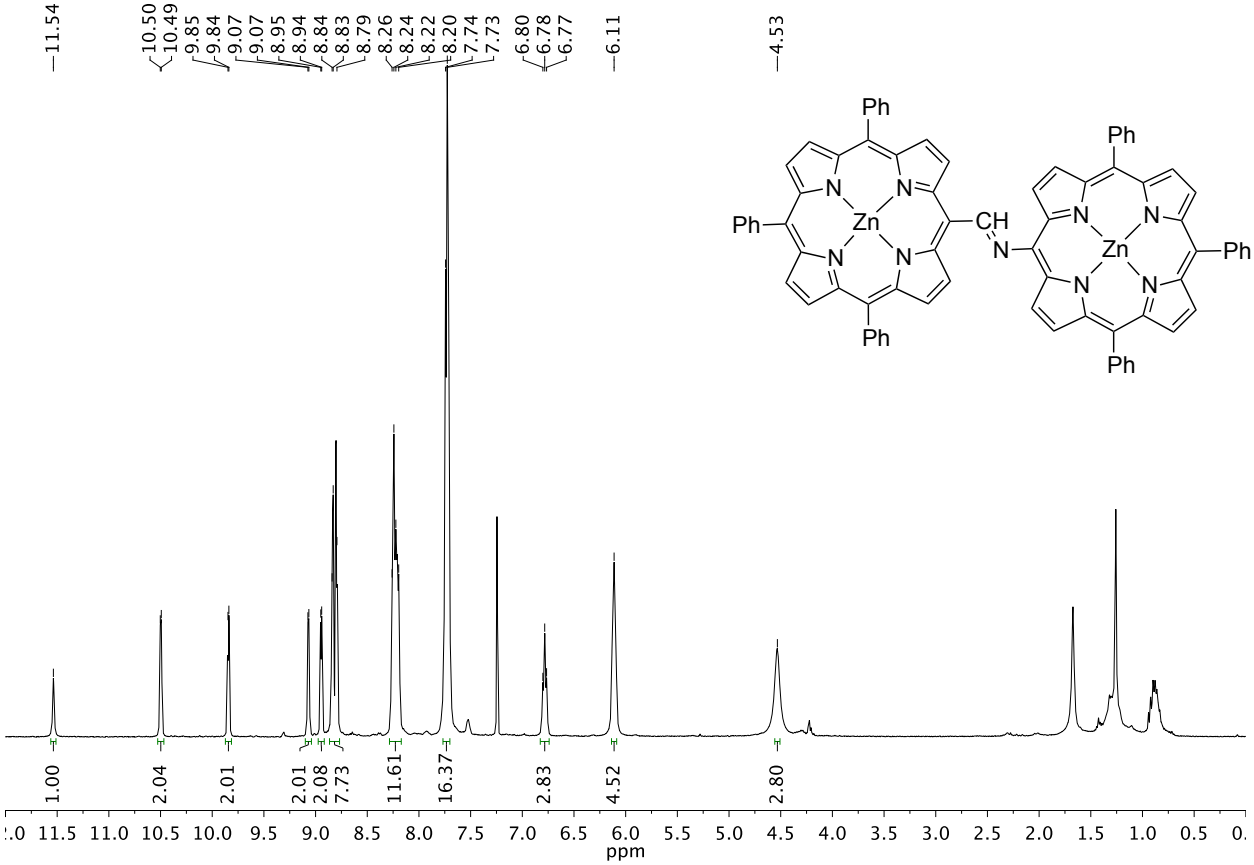
NOESY

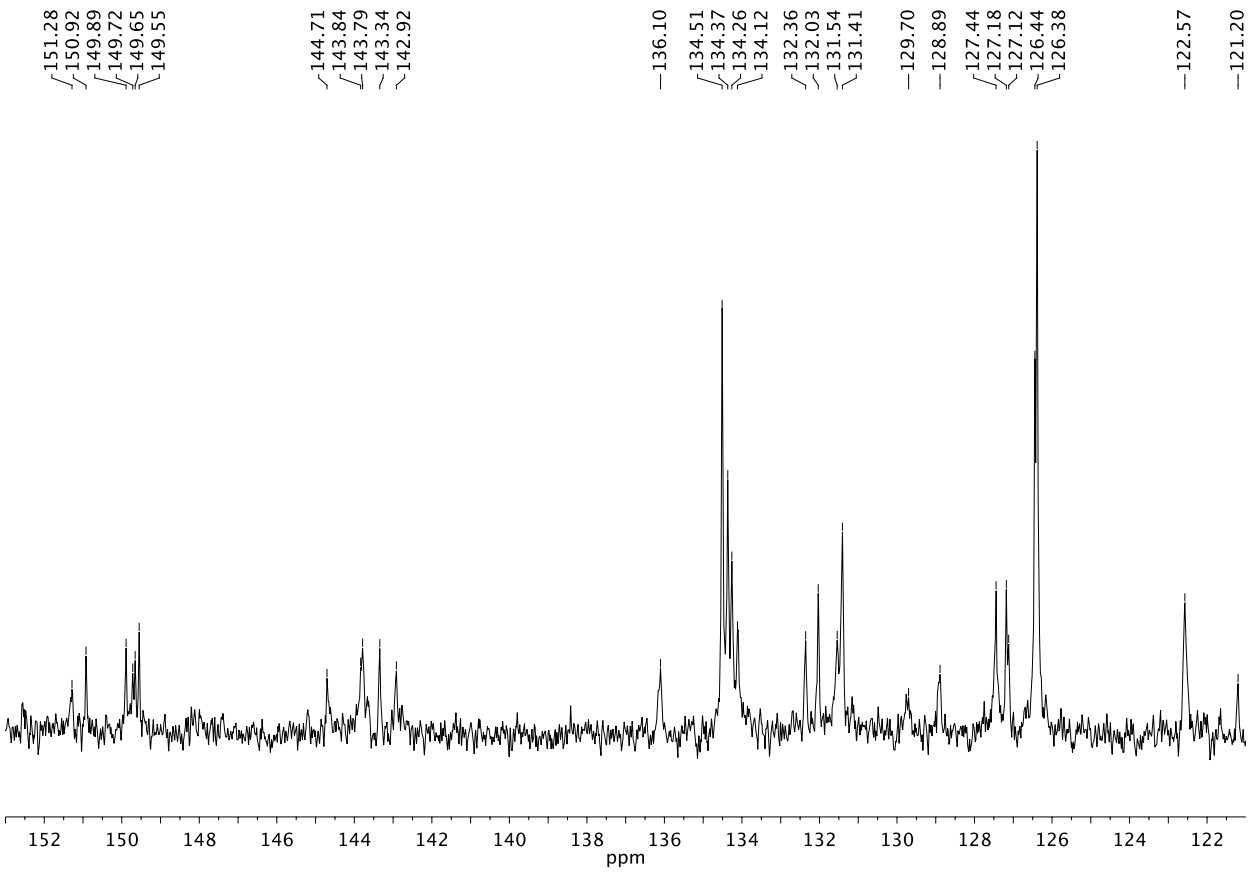


HRMS (MALDI)

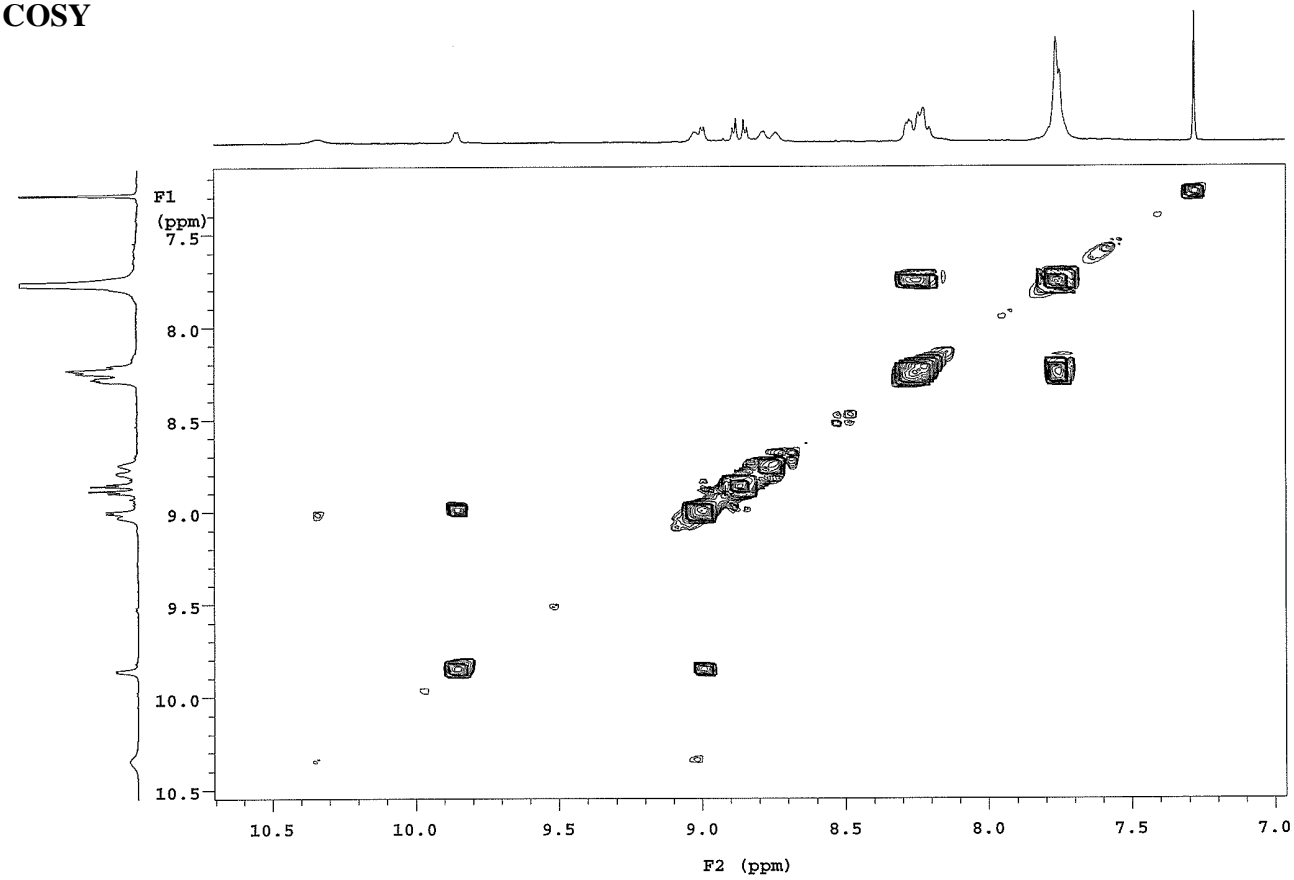


ZnTriPP–CH=N–ZnTriPP 4 (pyridine coordinated)

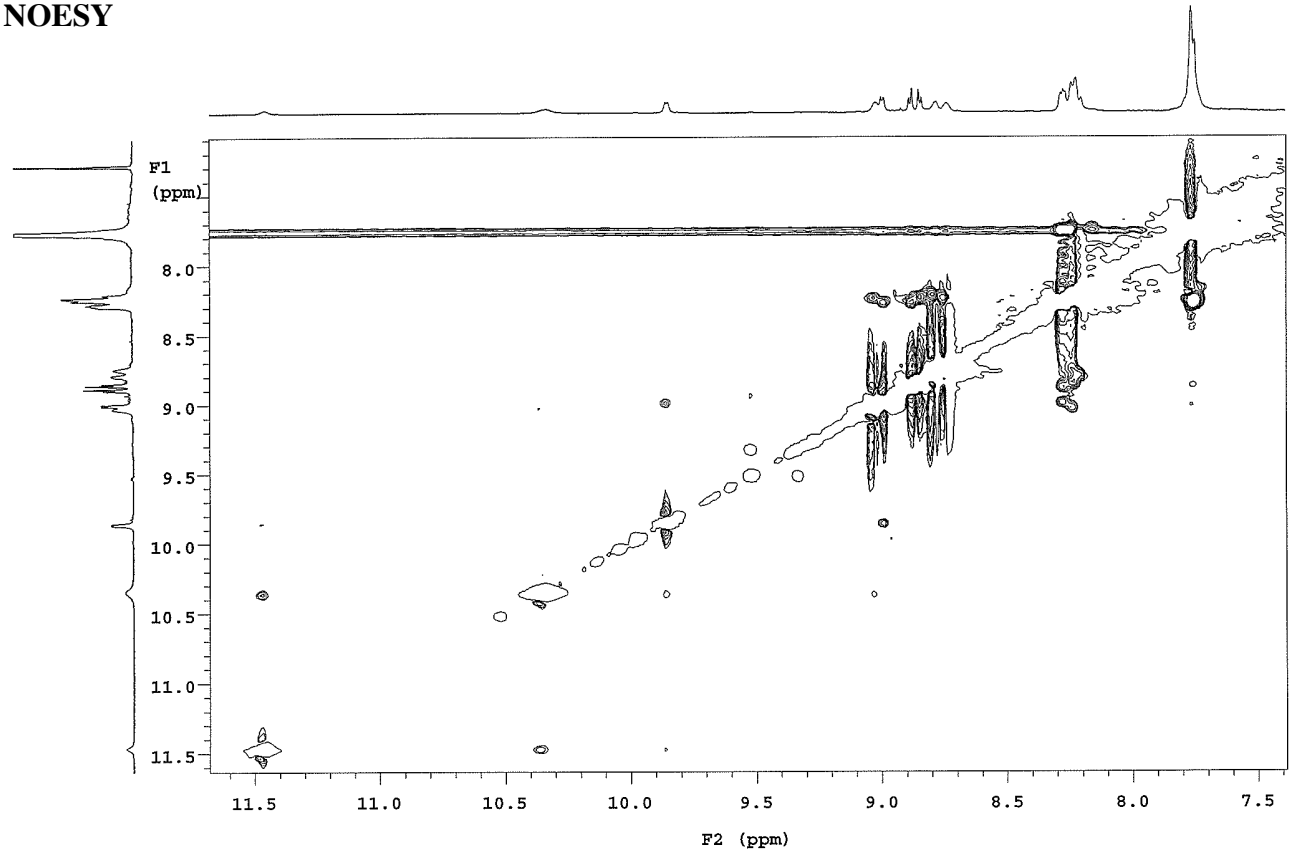




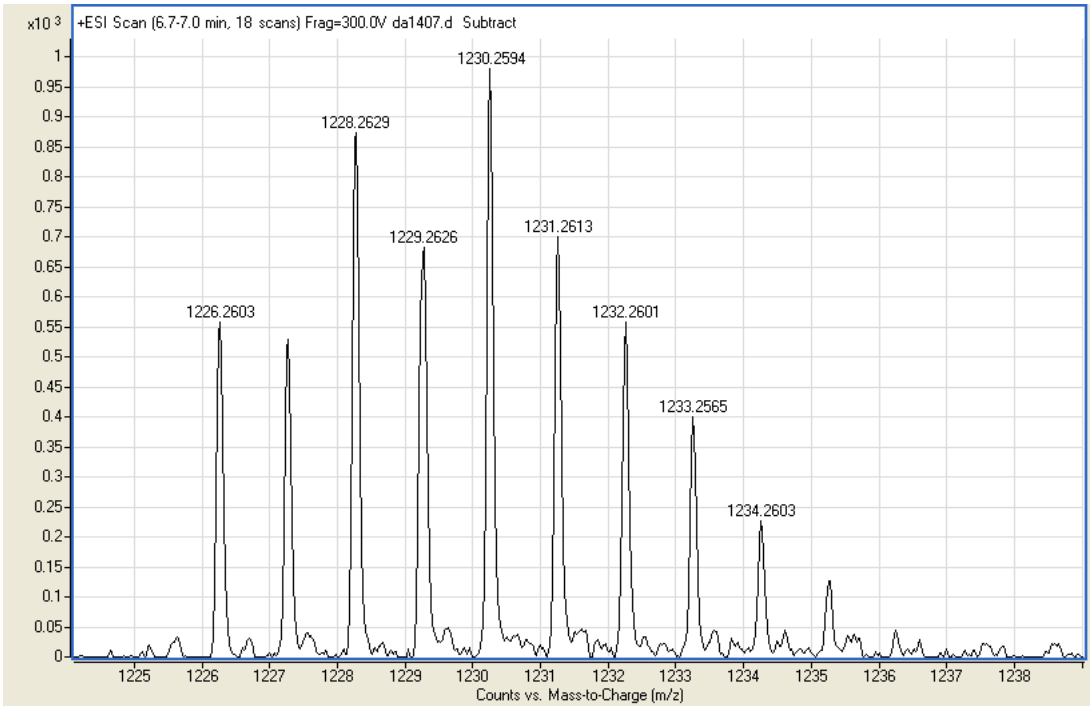
COSY


F1
(ppm)
7.5
8.0
8.5
9.0
9.5
10.0
10.5
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
F2 (ppm)

NOESY


F1
(ppm)
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
F2 (ppm)

HRMS (ESI)



ZnTriPP–N=N–ZnTriPP 5 (in $CDCl_3$ + C_5D_5N; * = water in exchange with pyridine)

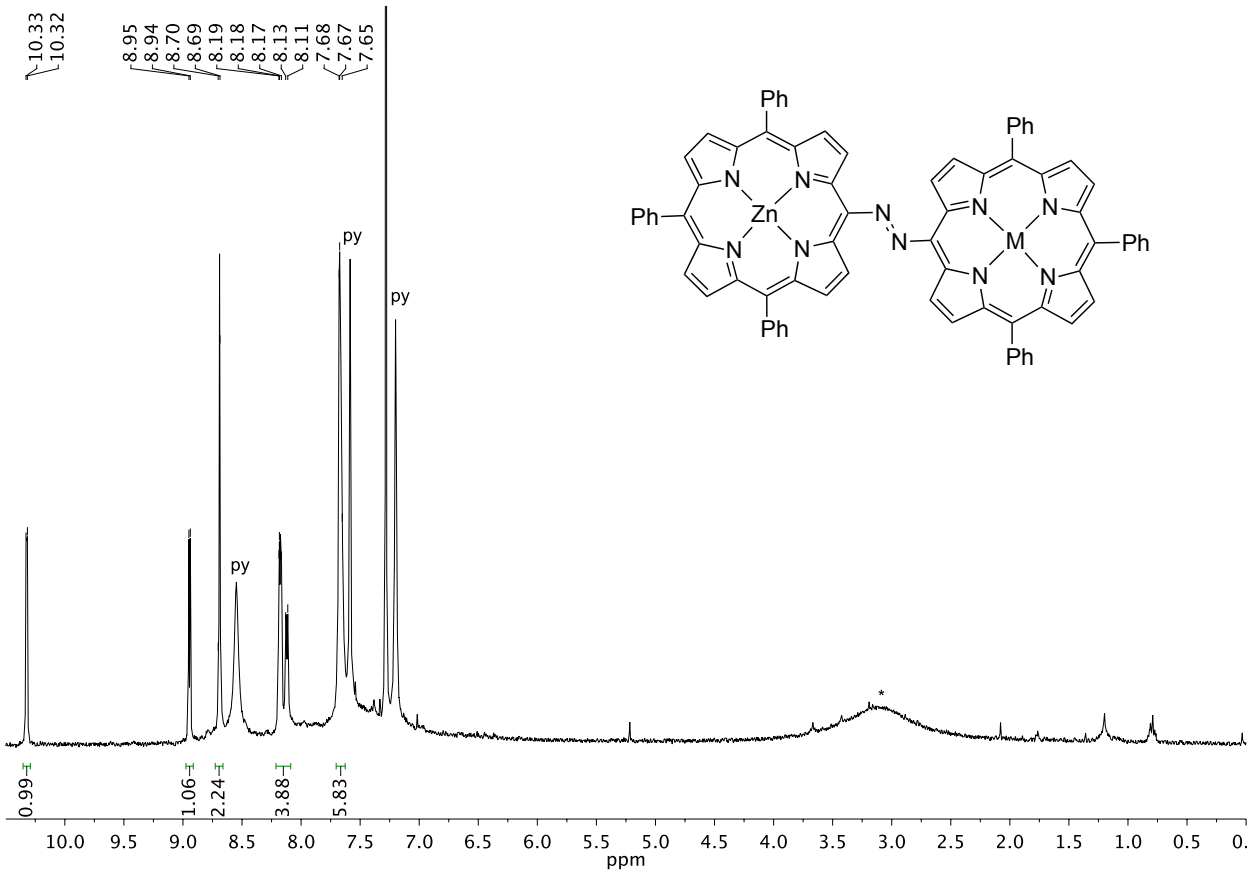


Figure S1. The hydrogen bonded cyclic hexamer in the crystal structure of the zinc formylporphyrin **23**.

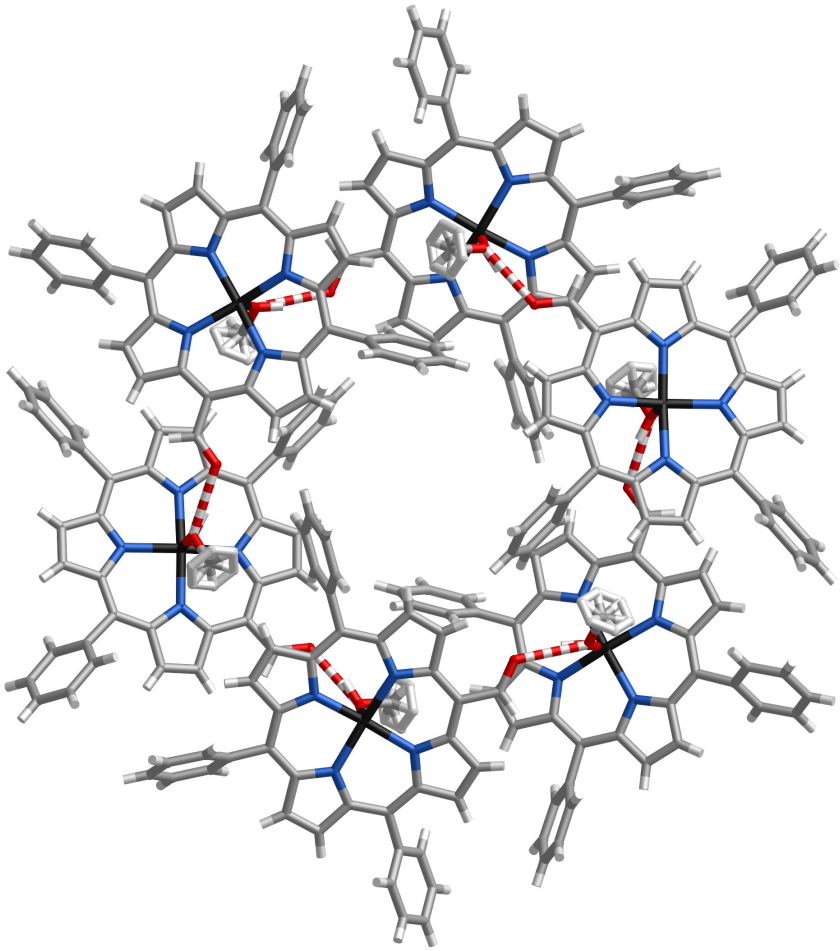
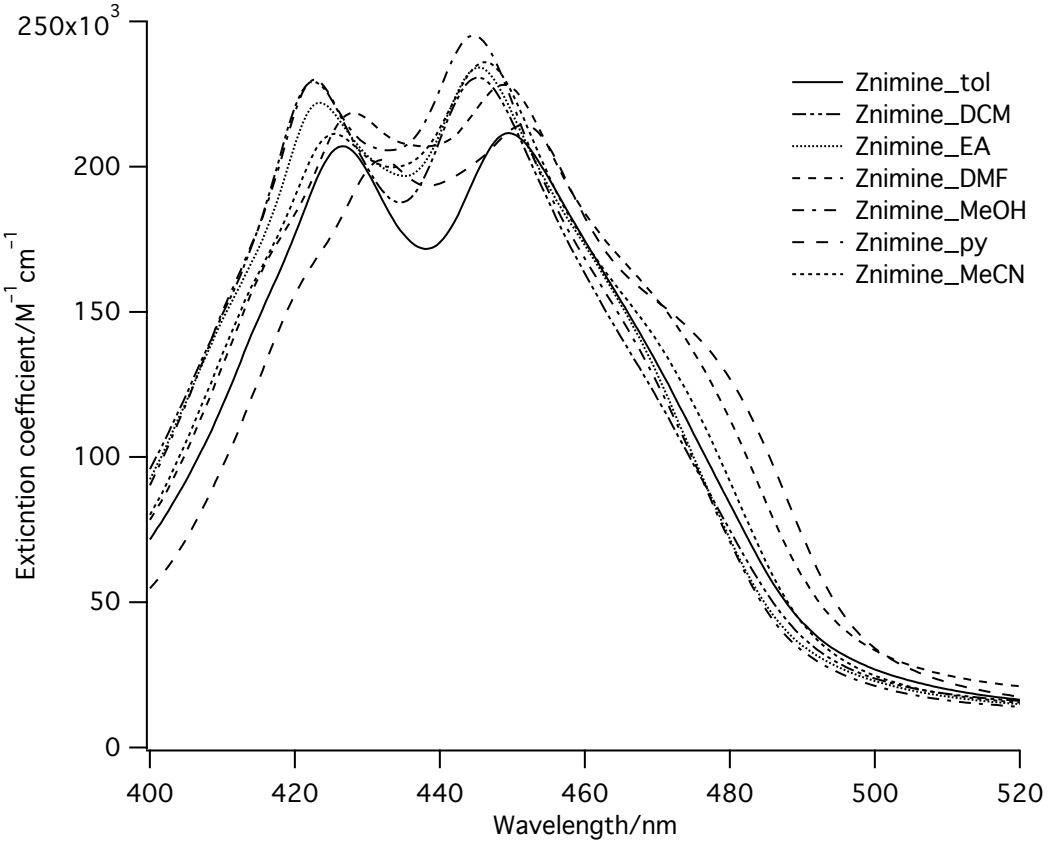


Figure S2. Effects of solvents on the Soret band region of the electronic absorption spectrum of imine diporphyrin **4**: (a) the Soret band region; (b) the Q band region.

(a)



(b)

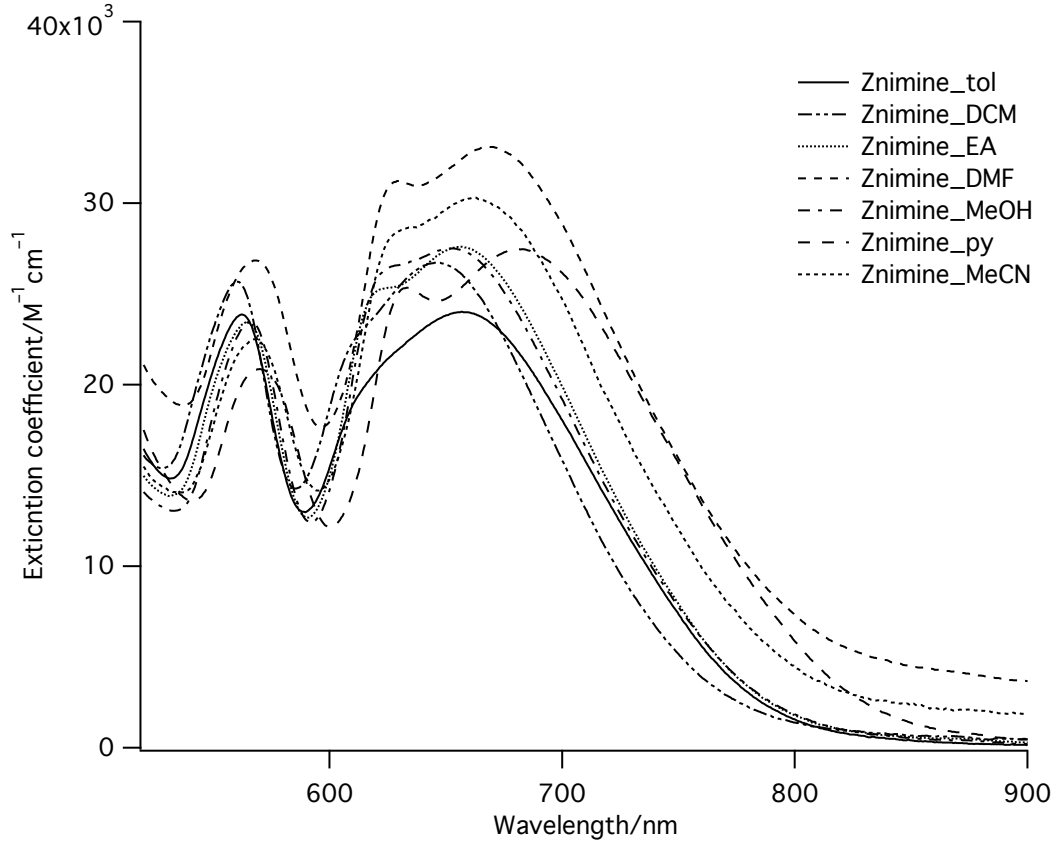
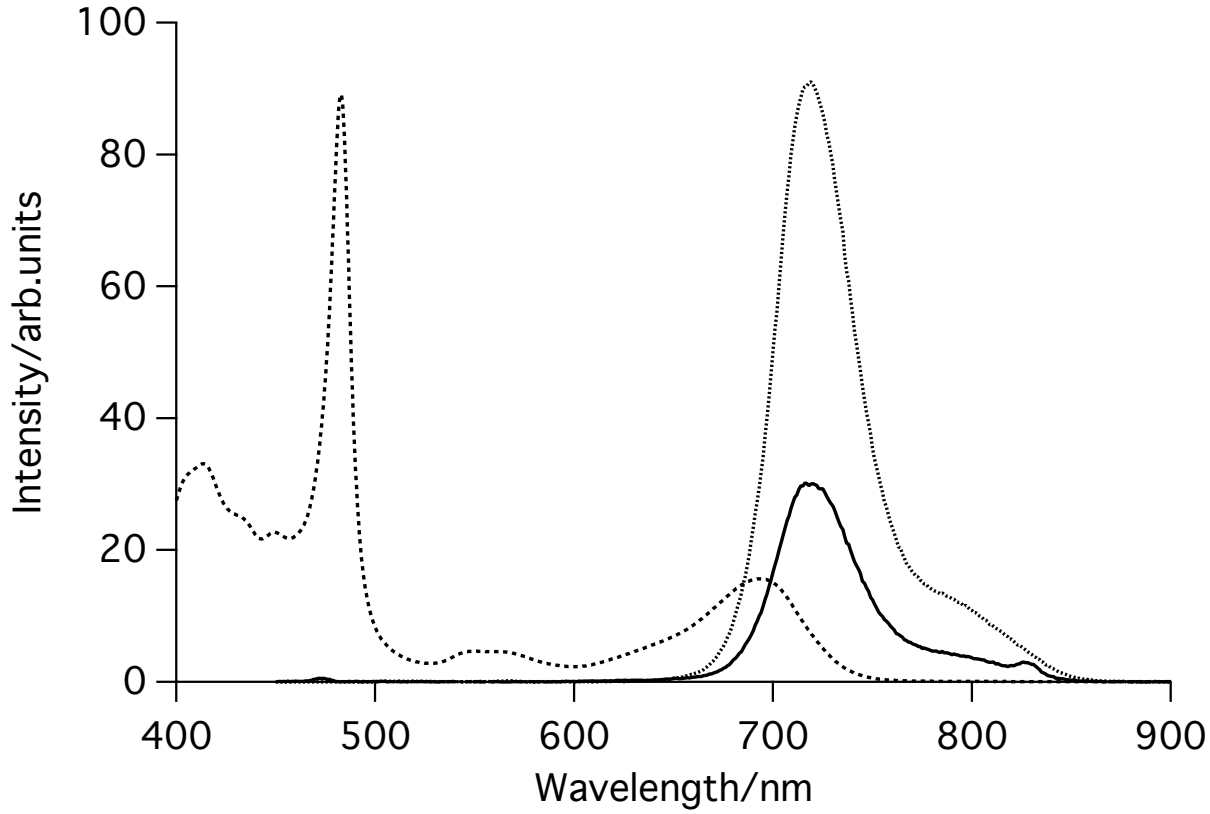


Figure S3. Fluorescence emission spectra in toluene: (a) ethyne **3** excited at 414 nm (solid), 482 nm (dots), and absorption spectrum scaled for convenience (dashes); (b) imine **4** excited at 427 nm (solid), 449 nm (dots), and absorption spectrum scaled for convenience (dashes).

(a)



(b)