Supplementary Data

Synthesis and Electrochemical Properties of Slipped-Cofacial Porphyrin Dimer of Ferrocene Functionalized Zn-Imidazolyl-Porphyrins as a Terminal Electron Donor in Photosynthetic Model

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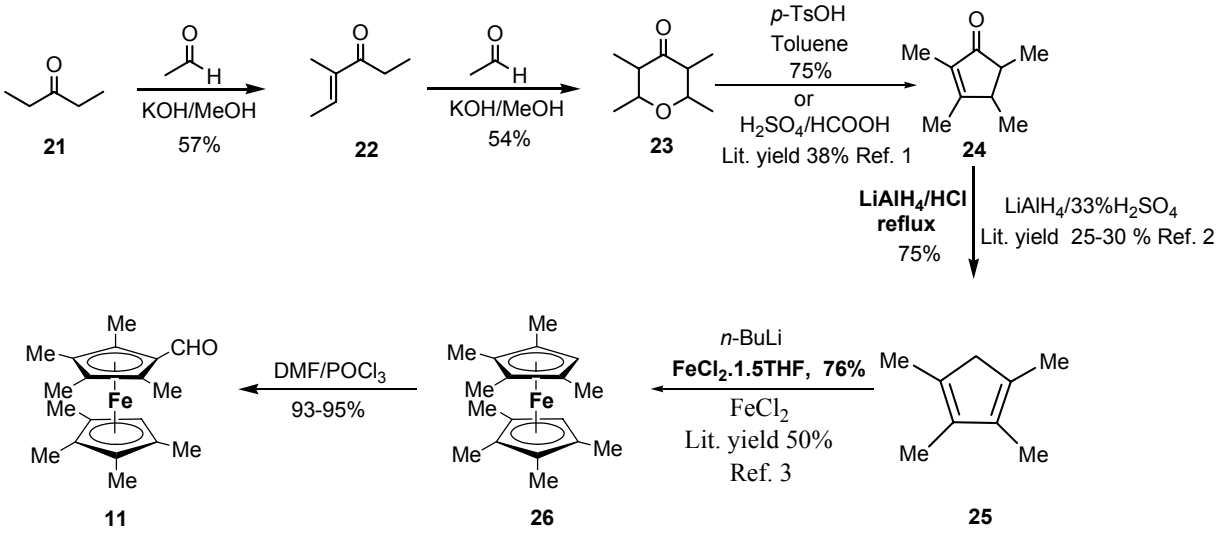
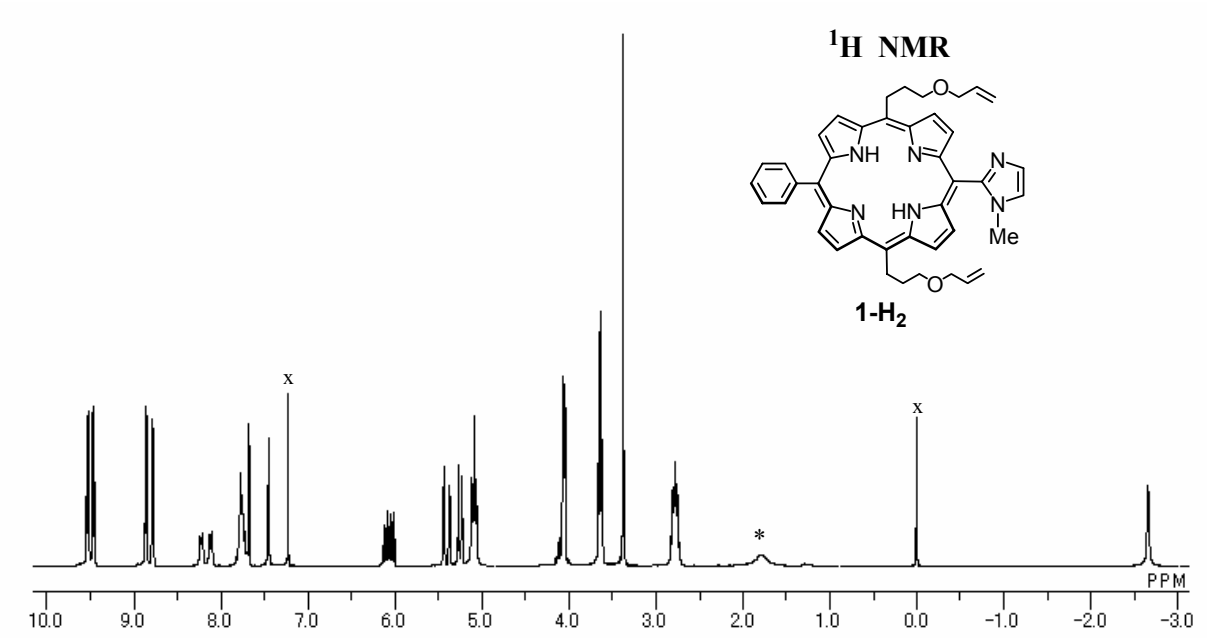
Takayama, Ikoma 630-0101, Japan

Improved synthetic route of 1-formyl-2,2′,3,3′,4,4′,5,5′-octamethyl ferrocene 11:

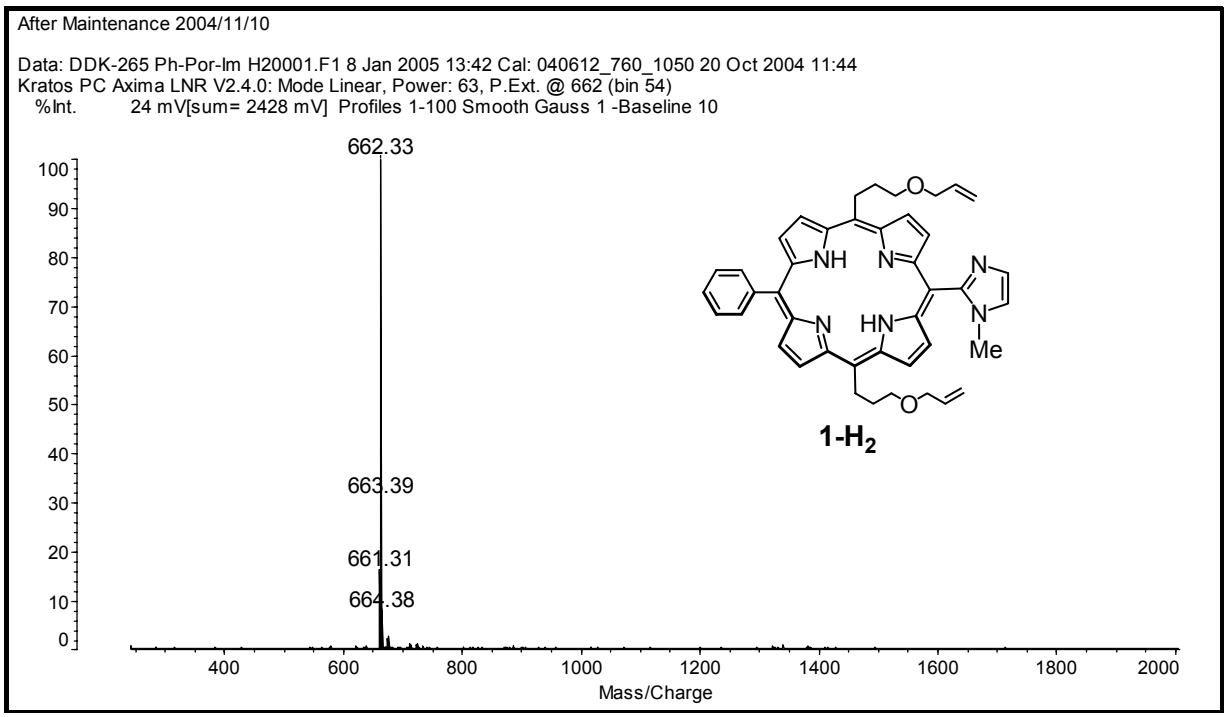


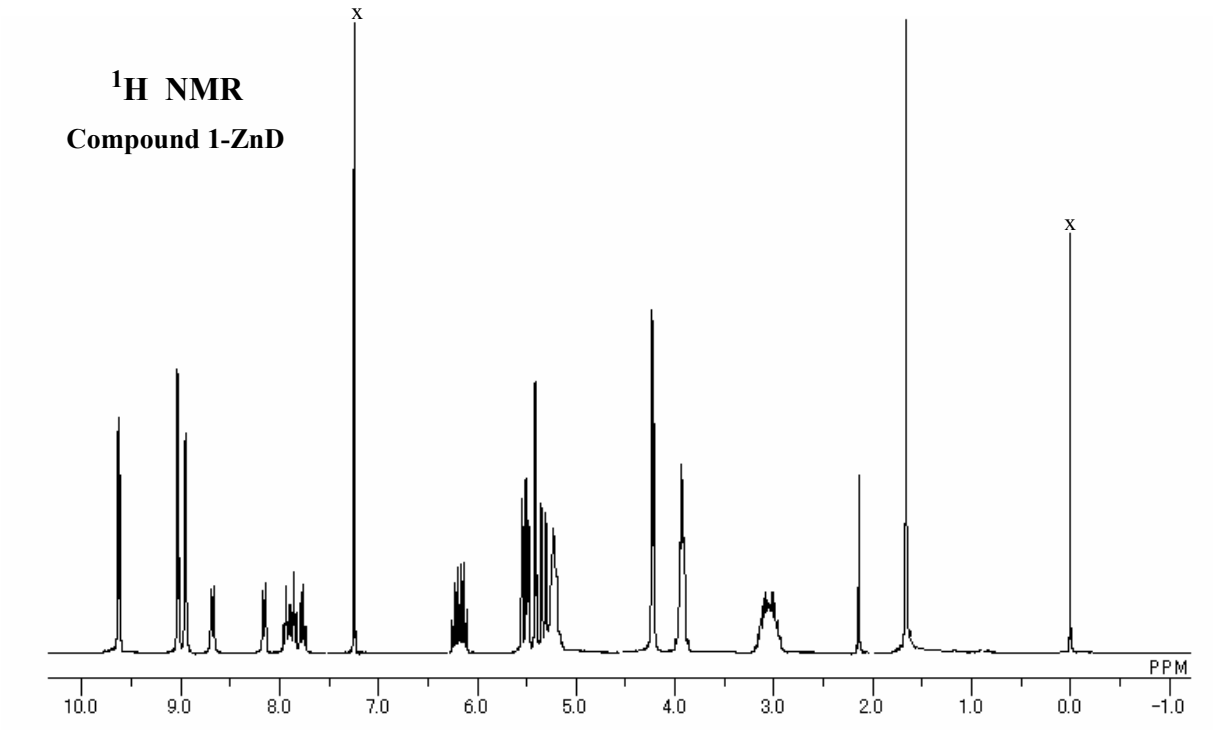
Reference:

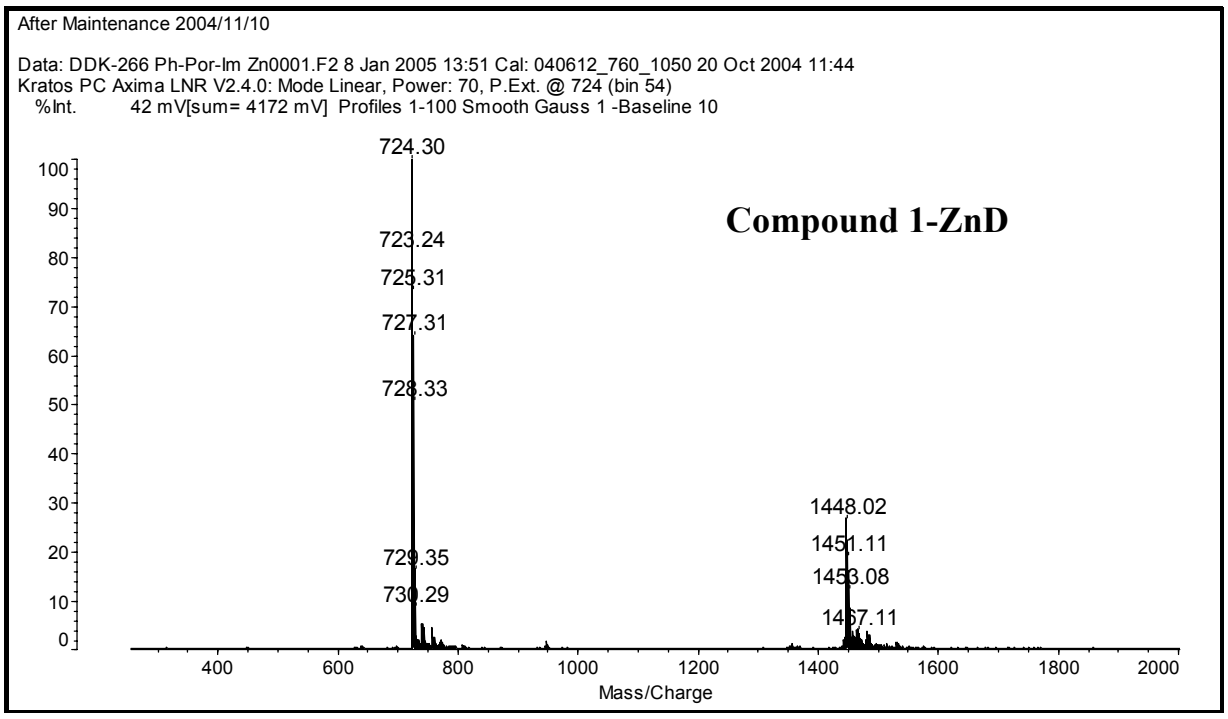
1. Whitesides, G.M. *Inorg. Chem*. **1976**, *15*, 466-469.
2. Fendric, C.M.; Schertz, L.D.; Day, V.W.; Marks, T.J. *Organometallics* **1988**, *7*, 1828-1838.
3. (a) Koeler, F.H.; Doll, K.H. *Z. Naturforsch.* **1982**, *37b*, 144-150. (b) Schmitt, V.G.; Ozman, S. *Chem. Ztg*. **1976**, *100*, 143.



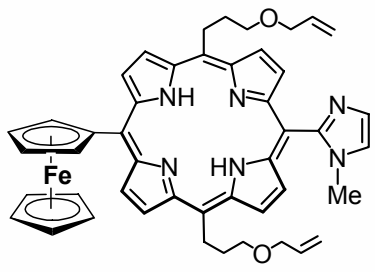
Cross (x) indicates solvent $CDCl_3$ or TMS, asterisk (*) indicates impurity.







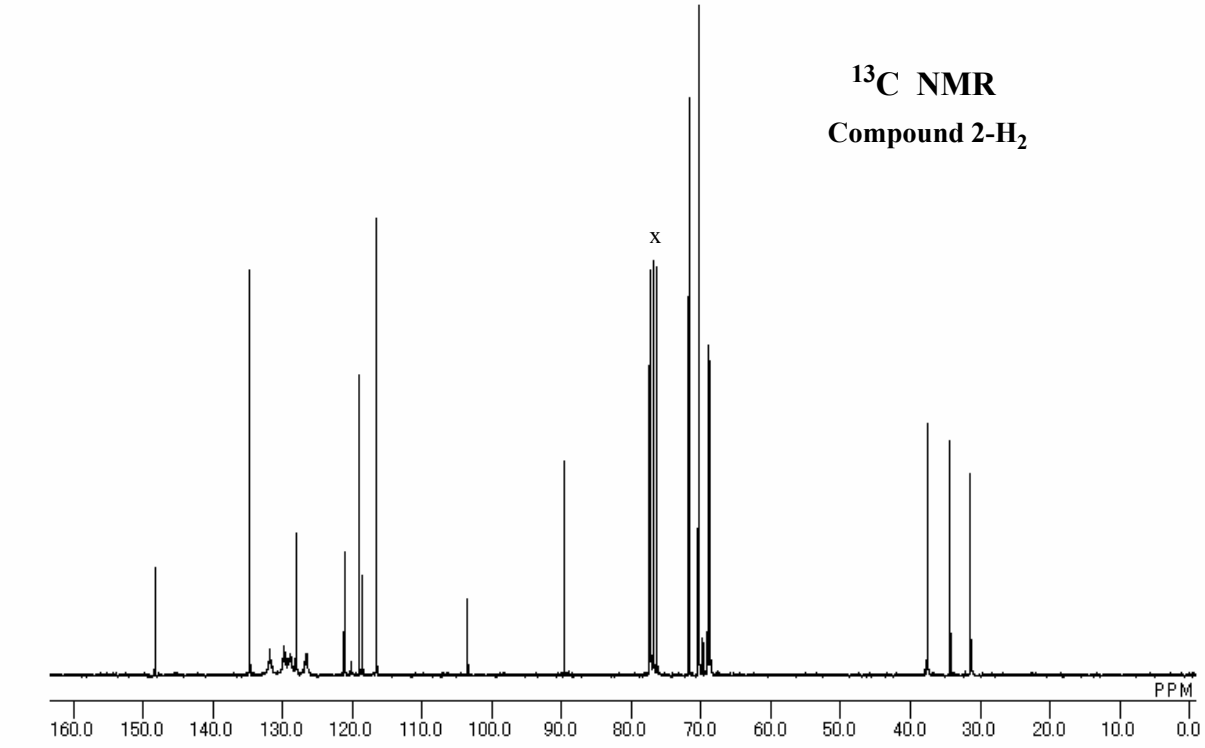
^{1}H NMR

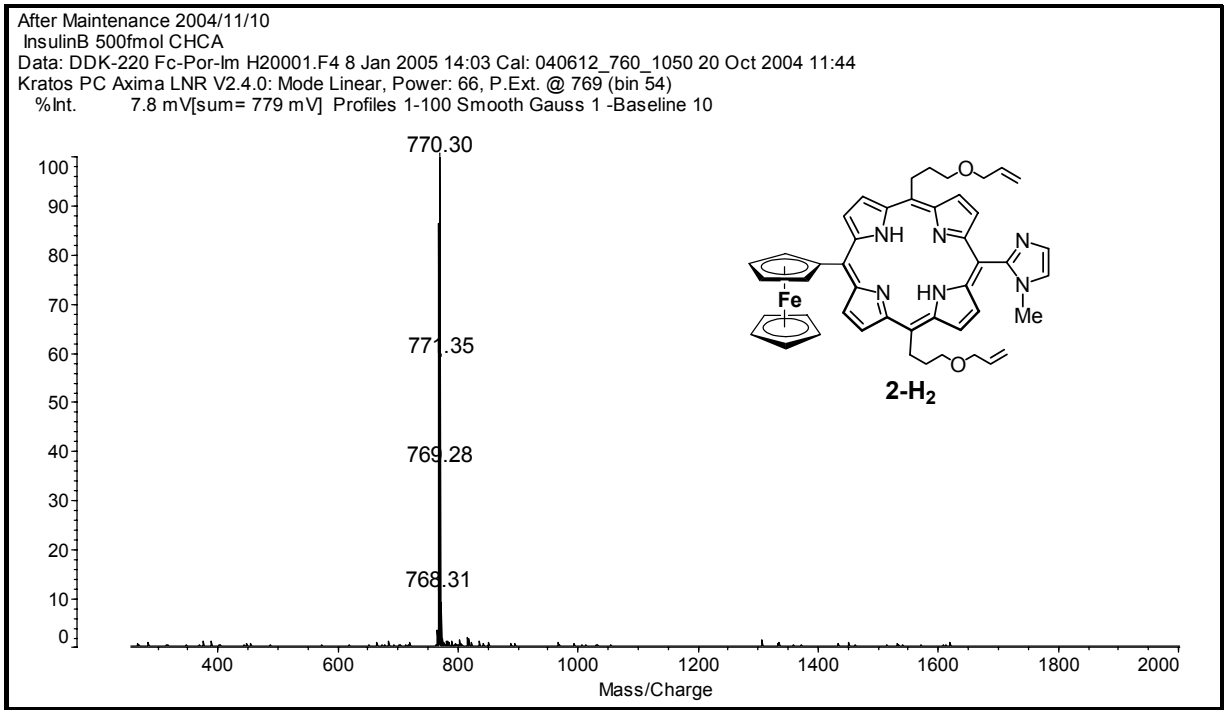


2-H_2

^{13}C NMR

Compound 2-H_2

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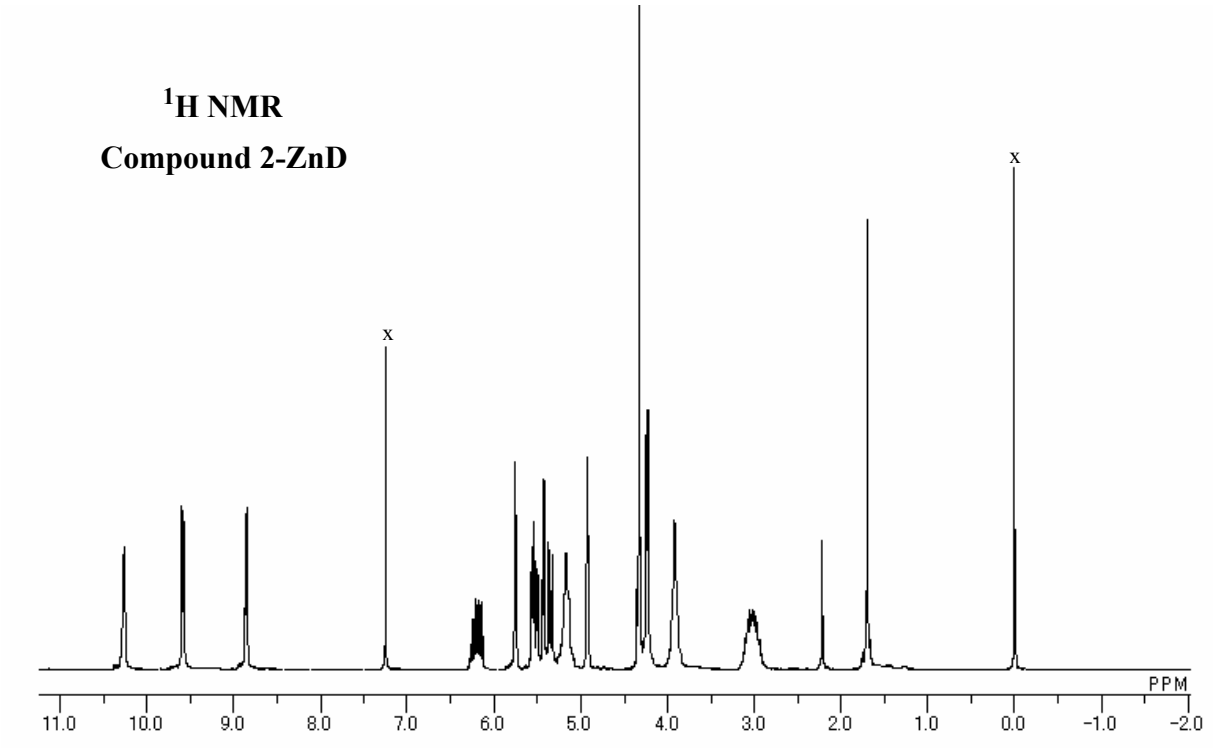
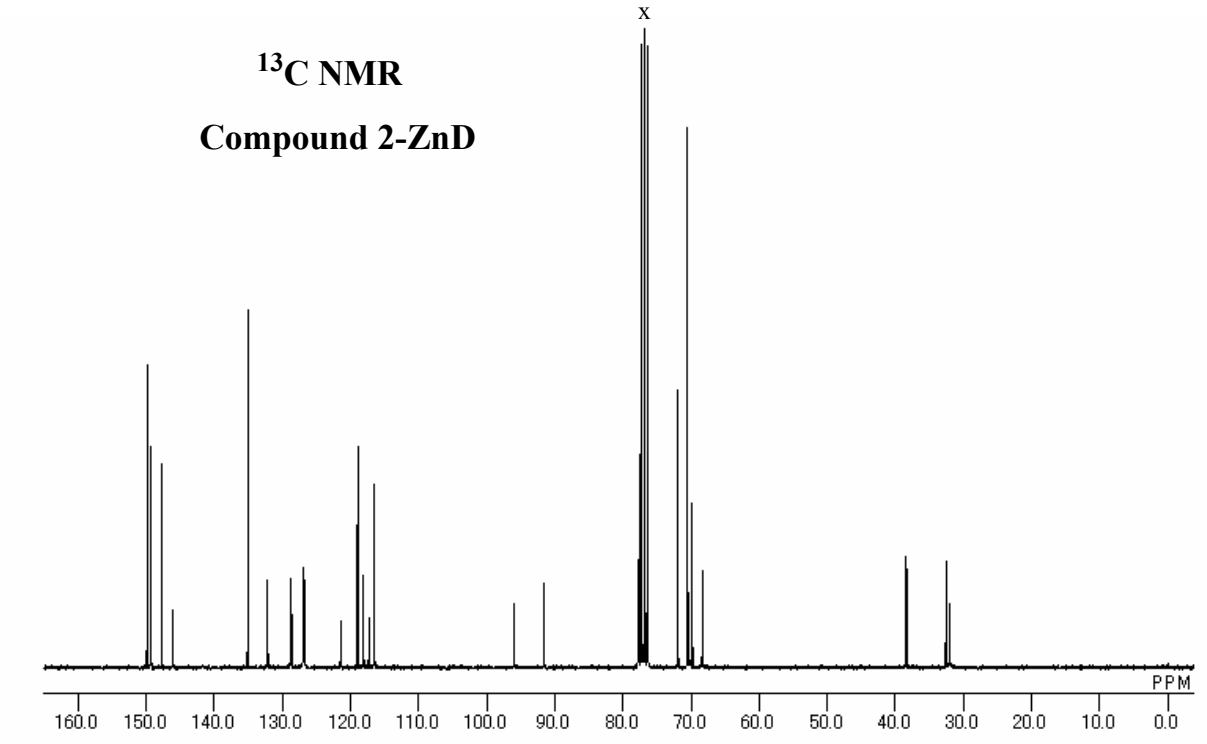
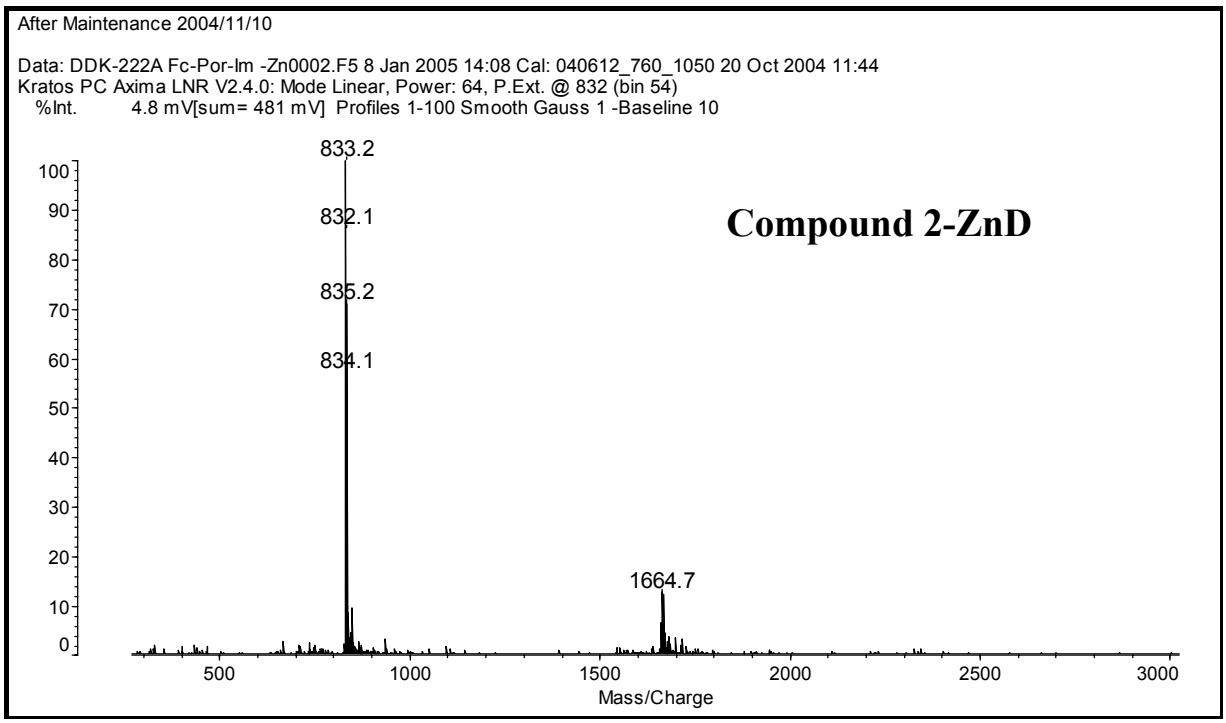
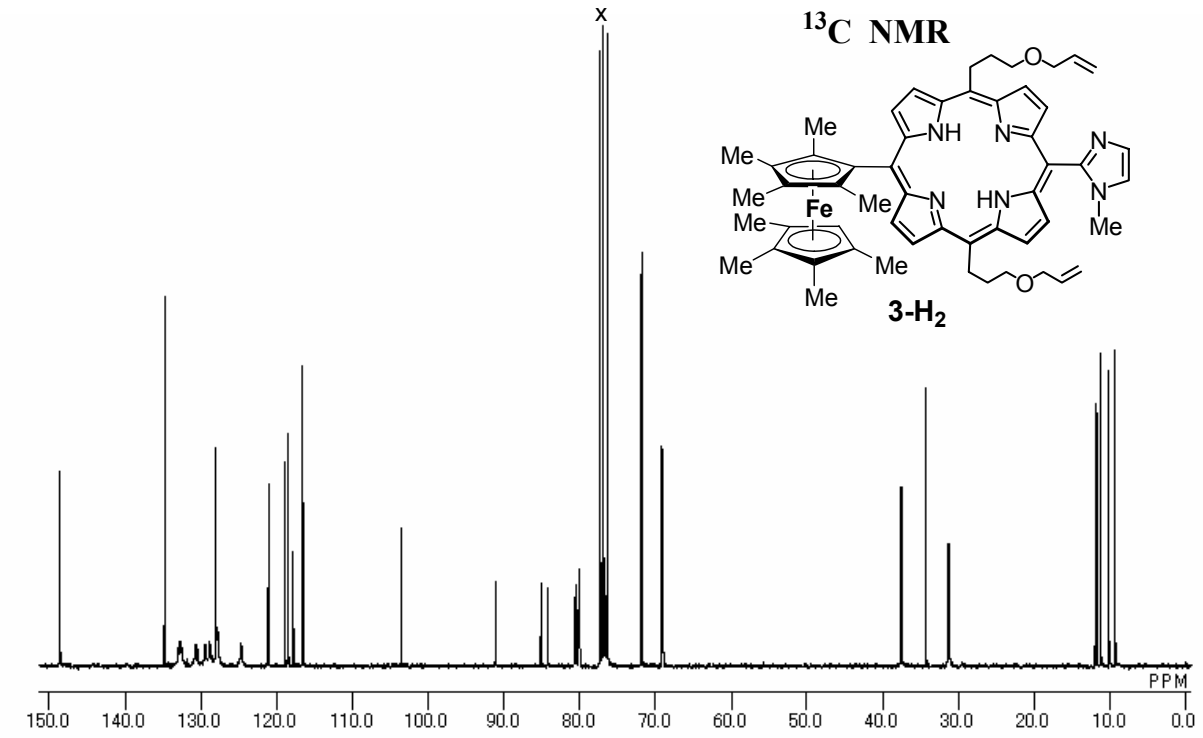
Kratos PC Axima LNR V2.4.0: Mode Linear, Power: 66, P.Ext. @ 769 (bin 54)
%Int. 7.8 mV[sum= 779 mV] Profiles 1-100 Smooth Gauss 1 -Baseline 10
770.30
771.35
769.28
768.31
Mass/Charge
Fe
NH
N
HN
Me
2-H2


1H NMR
Compound 2-ZnD
x
x
PPM






x
^{13}C NMR
Me
Me
Me
Me
Fe
Me
Me
Me
Me
Me
NH
N
N
N
HN
N
Me
O
O
3-H$_2$
PPM
150.0
140.0
130.0
120.0
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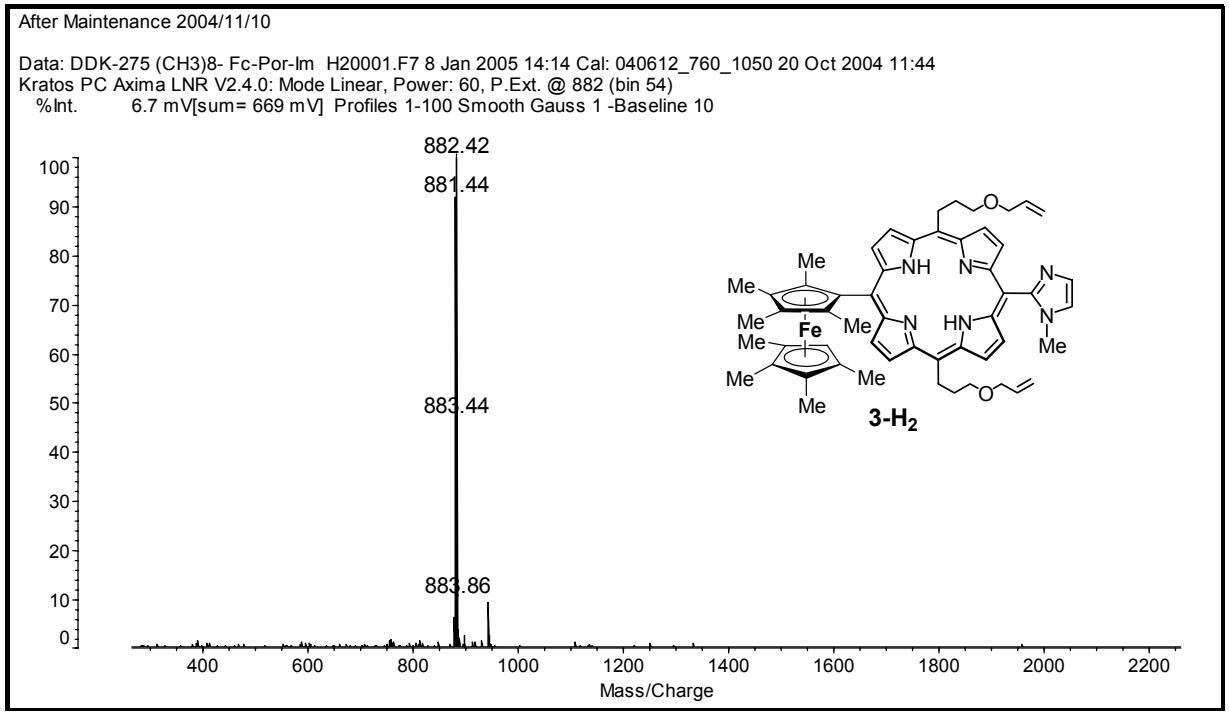
50.0
40.0
30.0
20.0
10.0
0.0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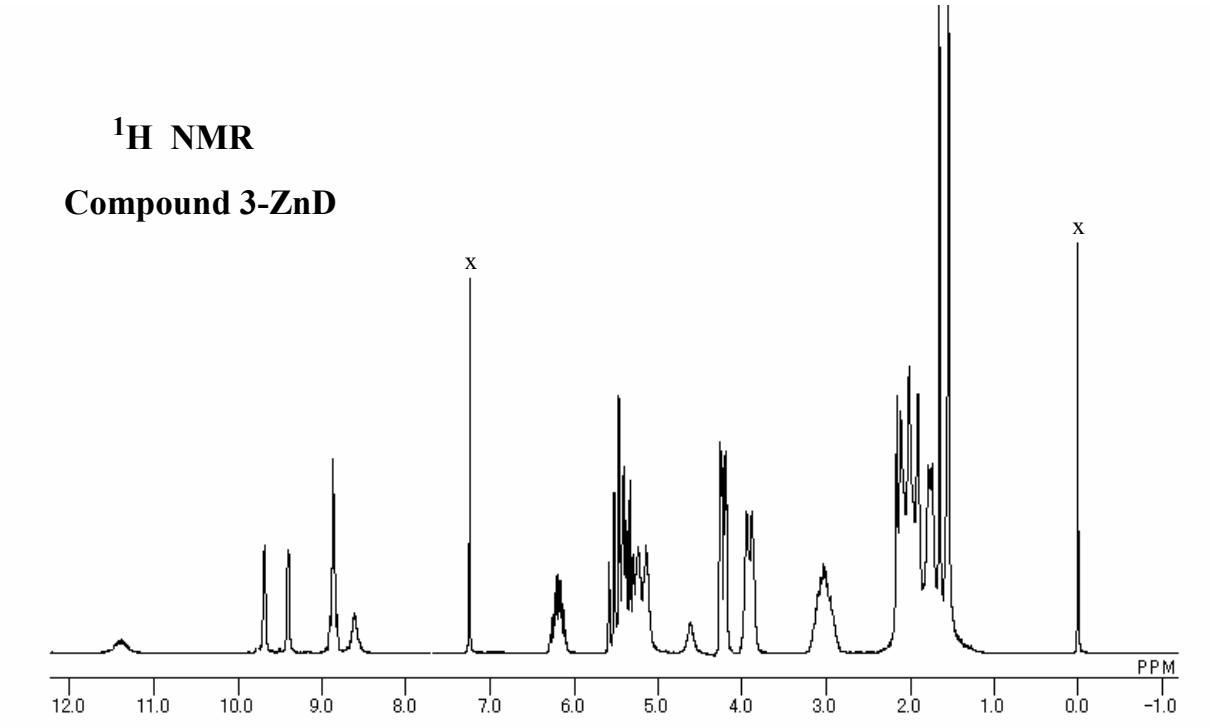
882.42
881.44
883.44
883.86
100
90
80
70
60
50
40
30
20
10
0
400
600
800
1000
1200
1400
1600
1800
2000
2200
Mass/Charge
Me
Me
Me
Me
Fe
Me
Me
Me
Me
Me
NH
N
N
N
HN
N
Me
O
O
3-H$_2$

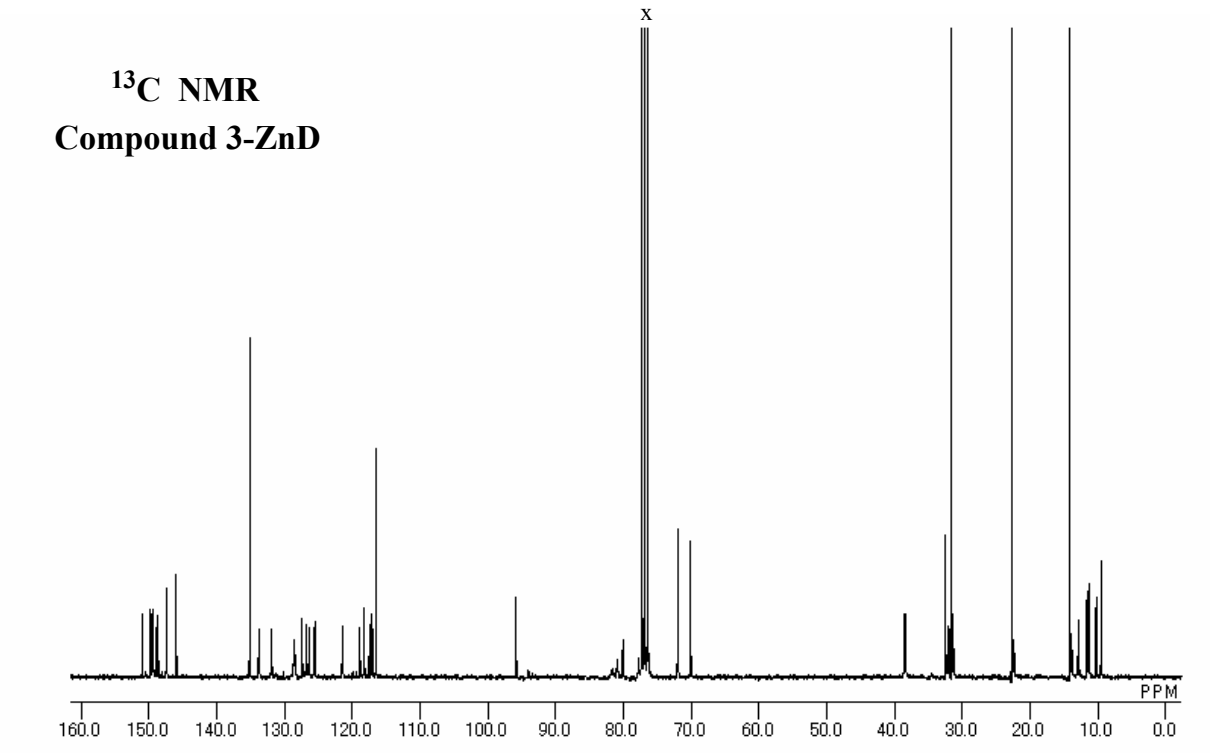
^{1}H NMR

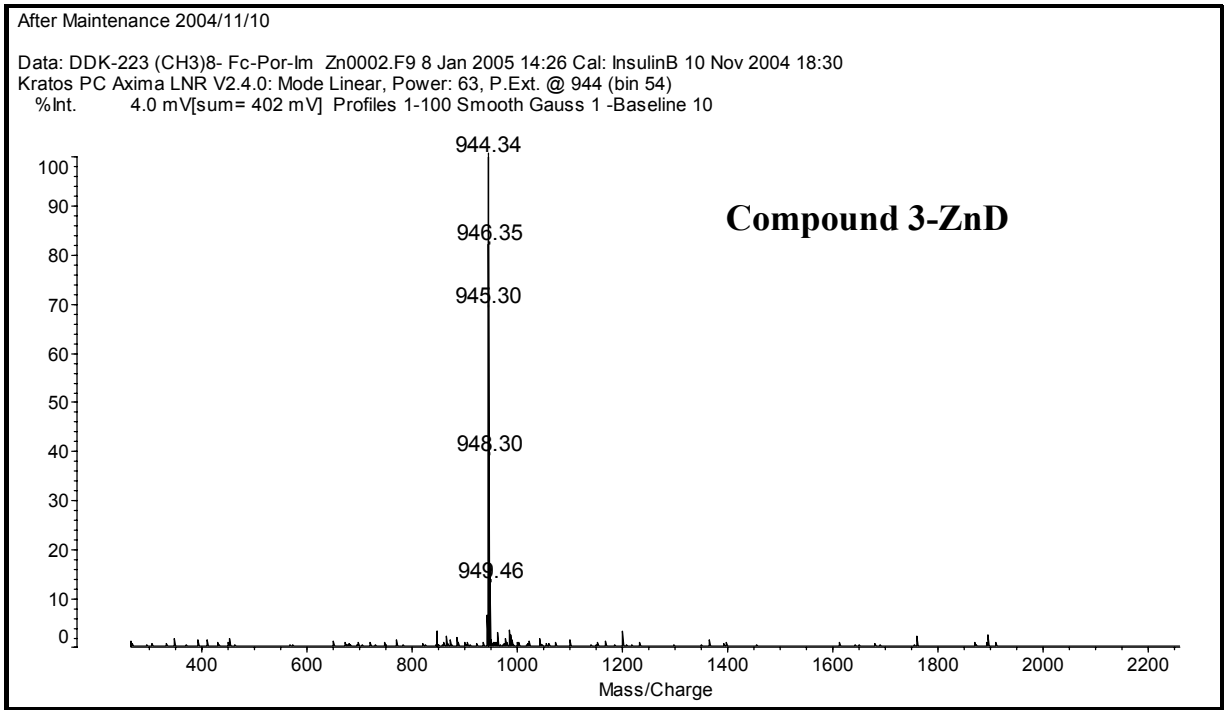
Compound 3-ZnD

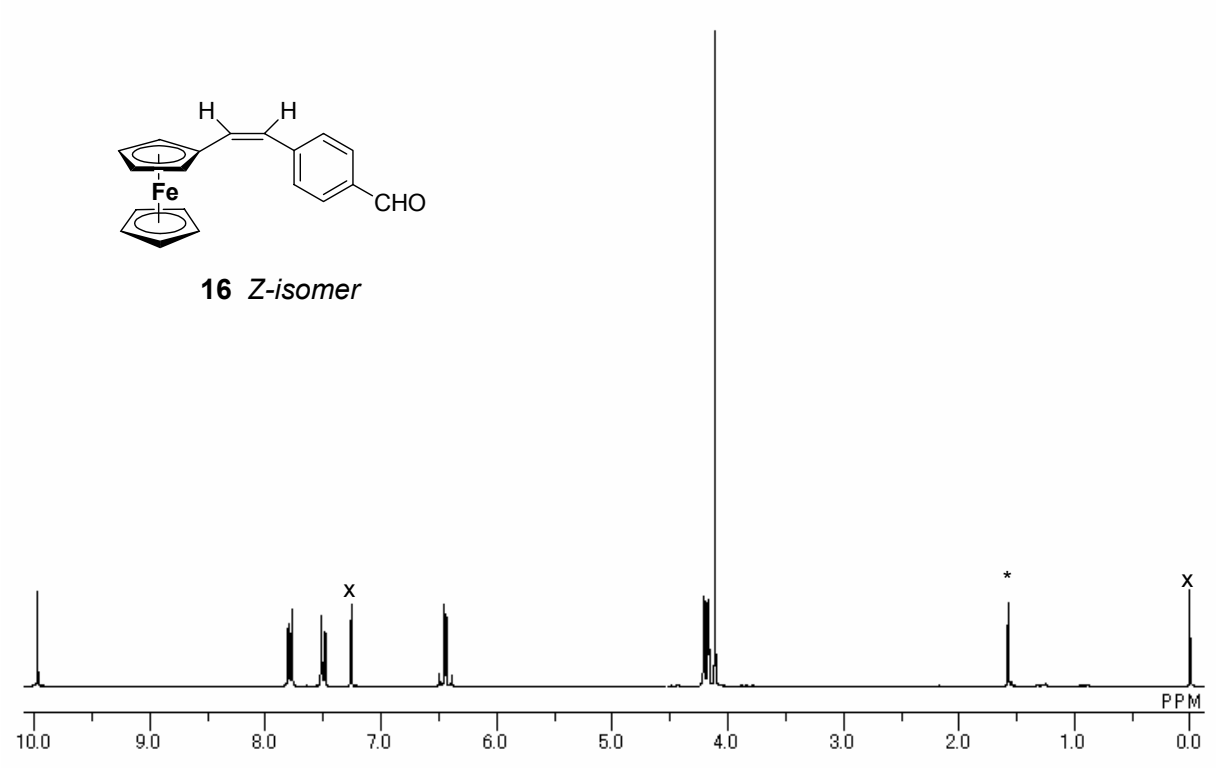


^{13}C NMR

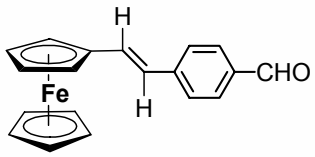
Compound 3-ZnD





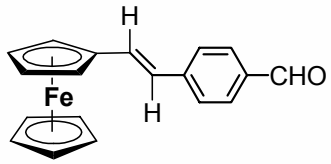


^{1}H NMR



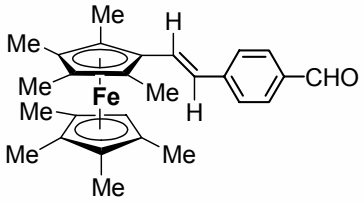
16 *E-isomer*

^{13}C NMR



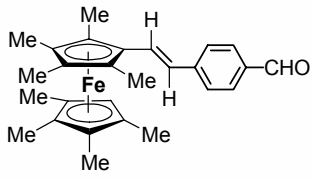
16

^{1}H NMR

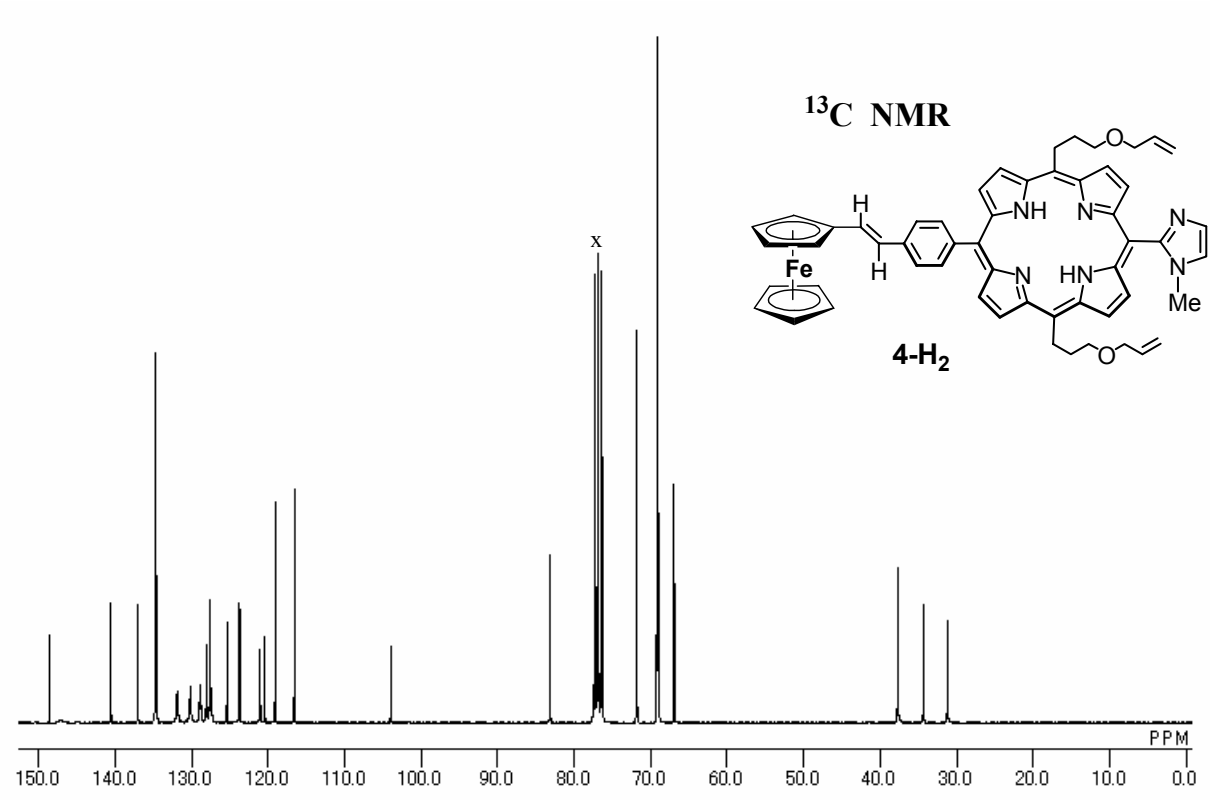


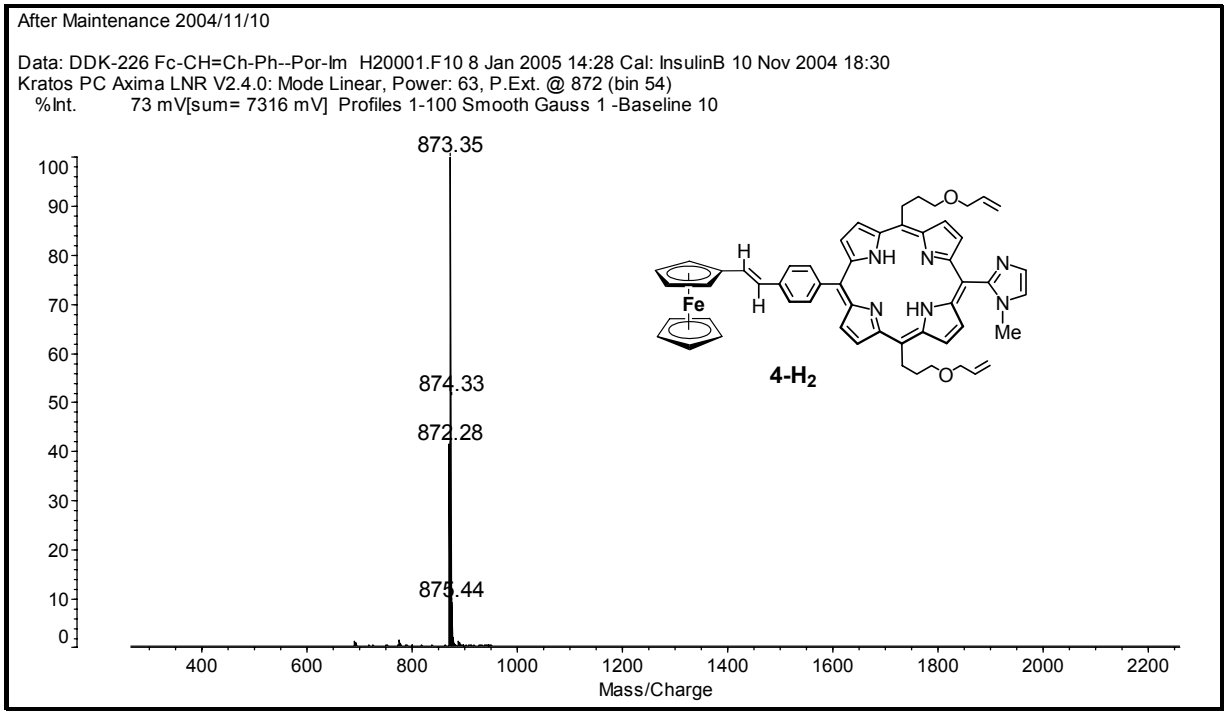
17 *E-isomer*

^{13}C NMR



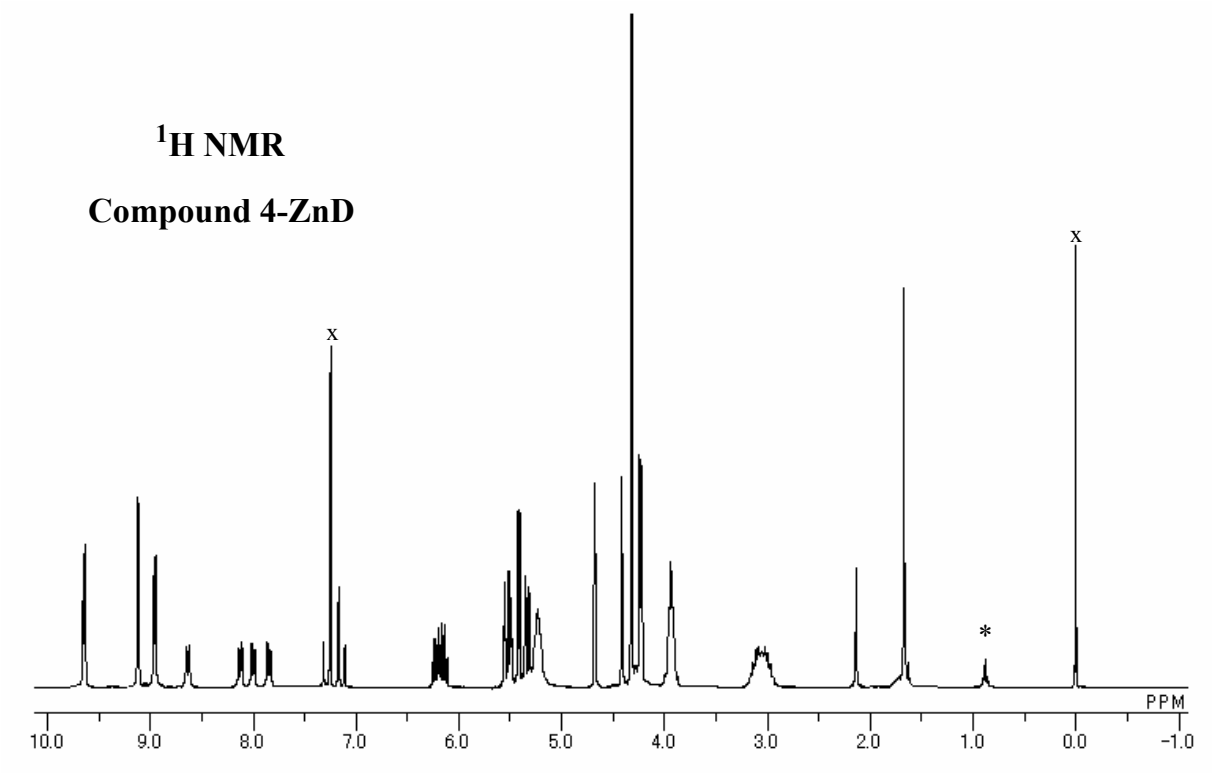
17 *E-isomer*





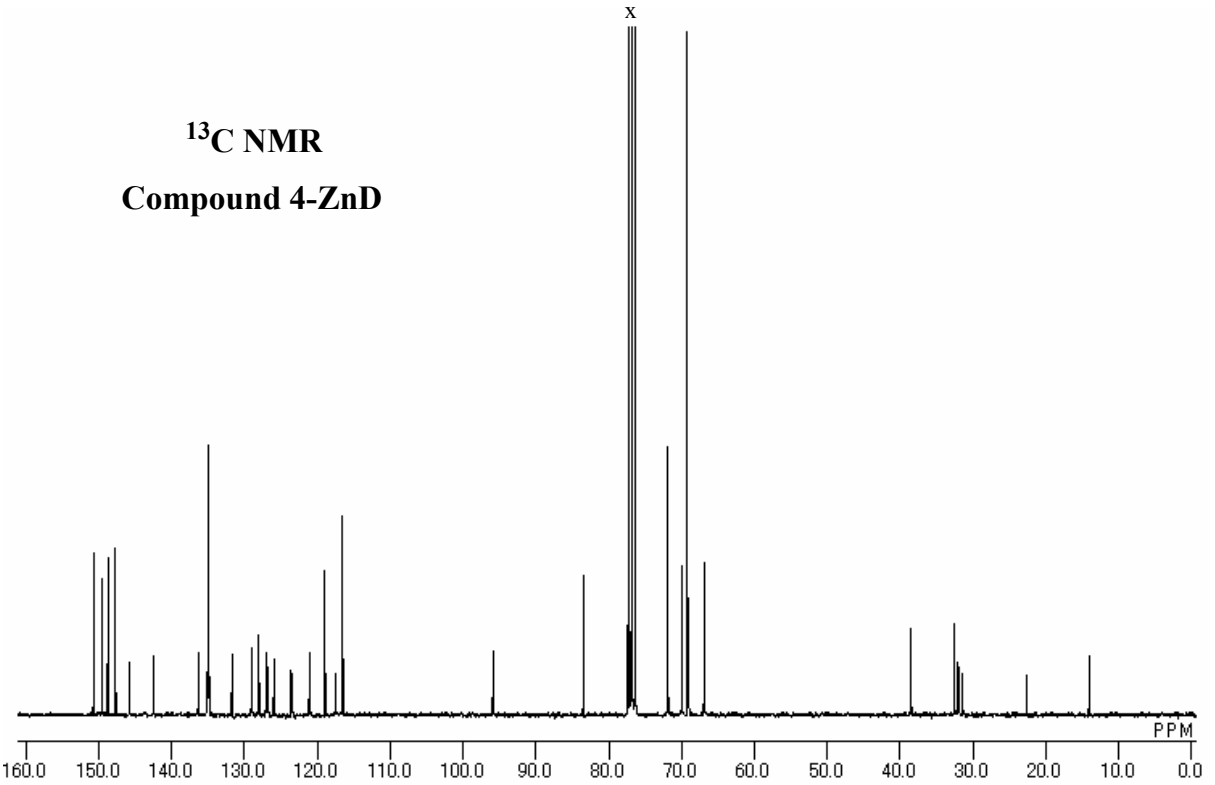
^{1}H NMR

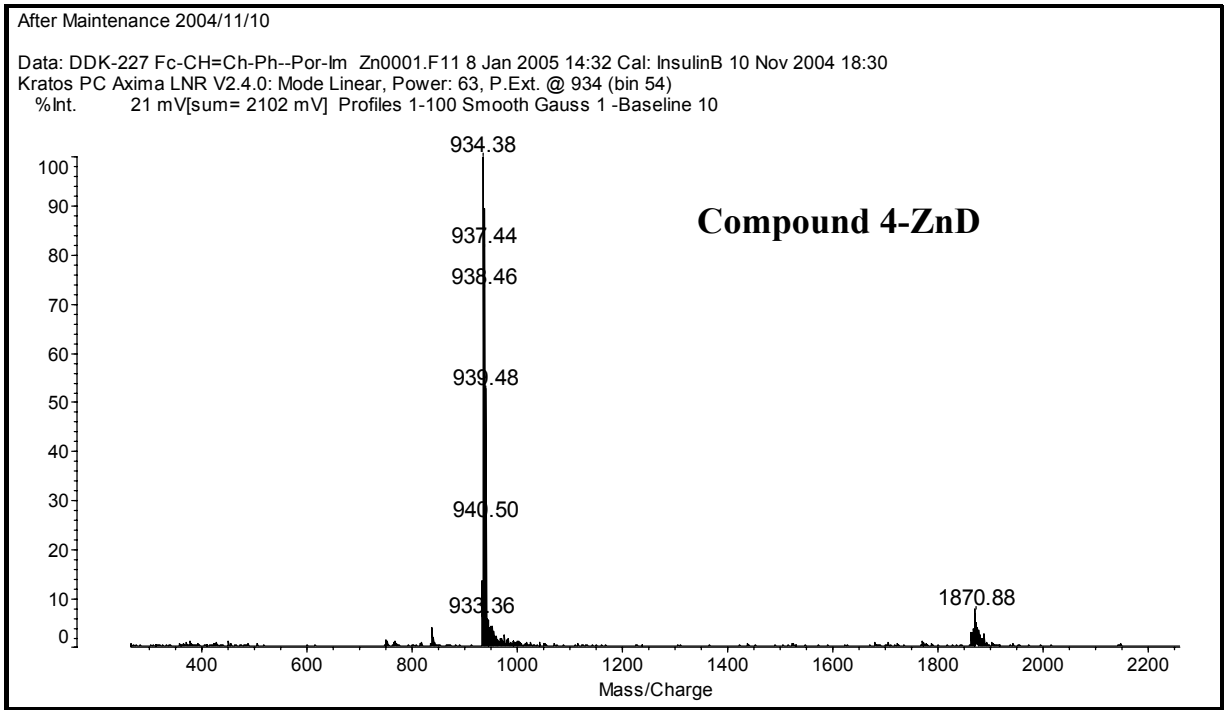
Compound 4-ZnD

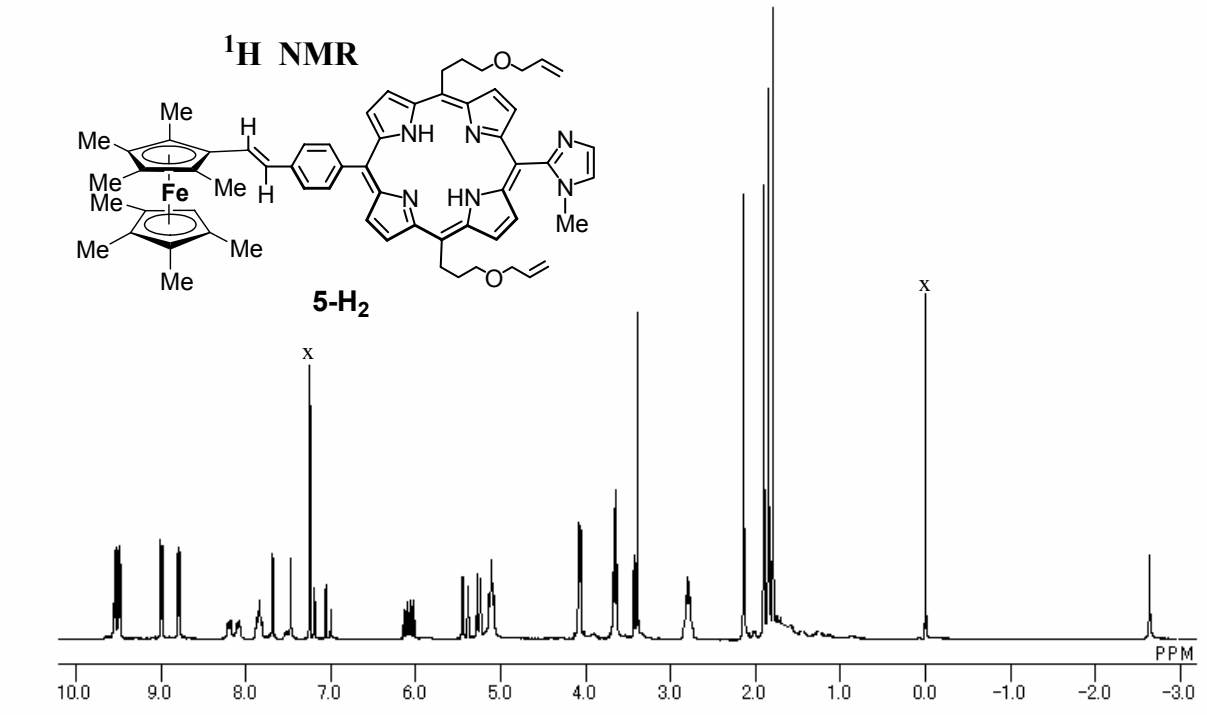


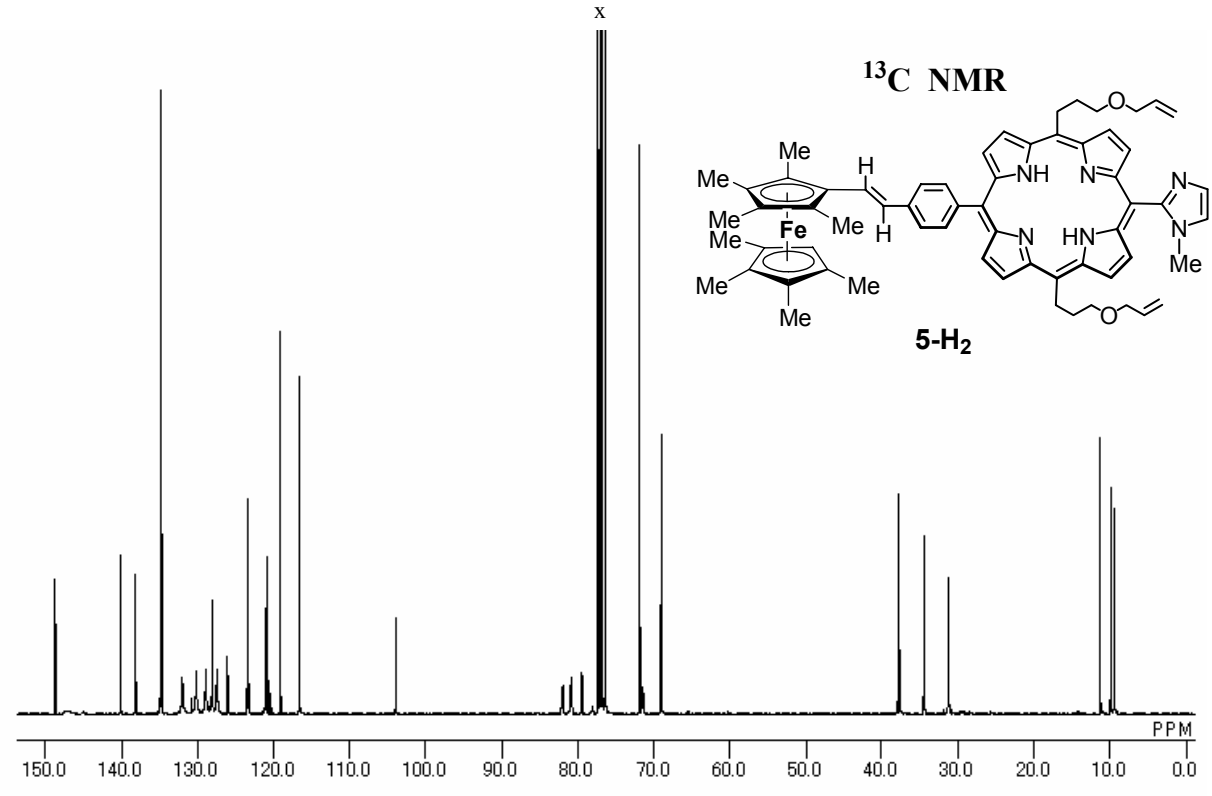
^{13}C NMR

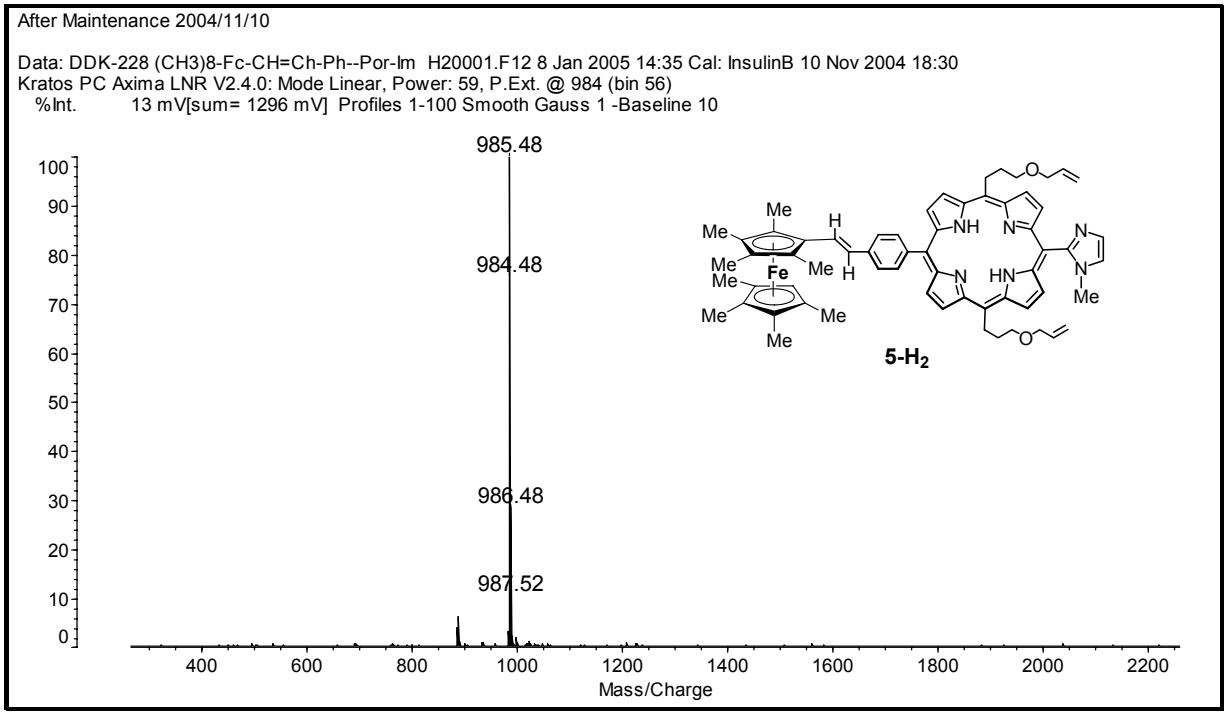
Compound 4-ZnD

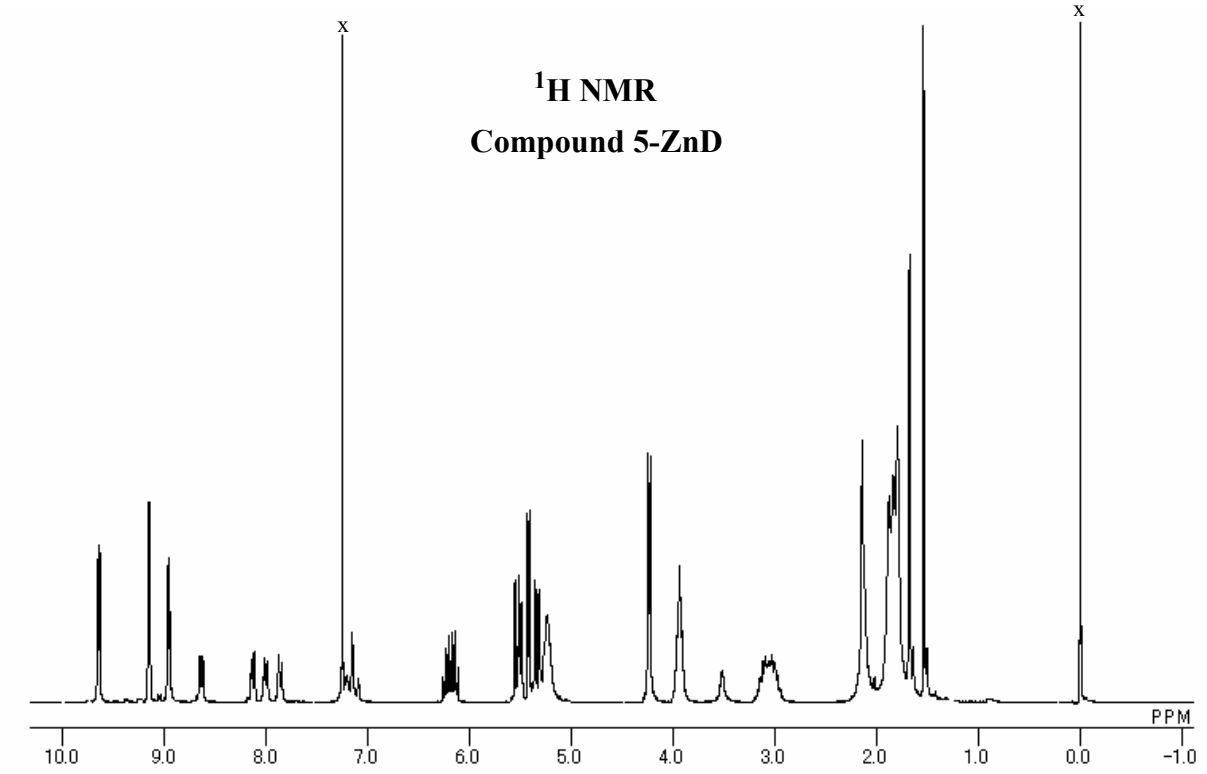






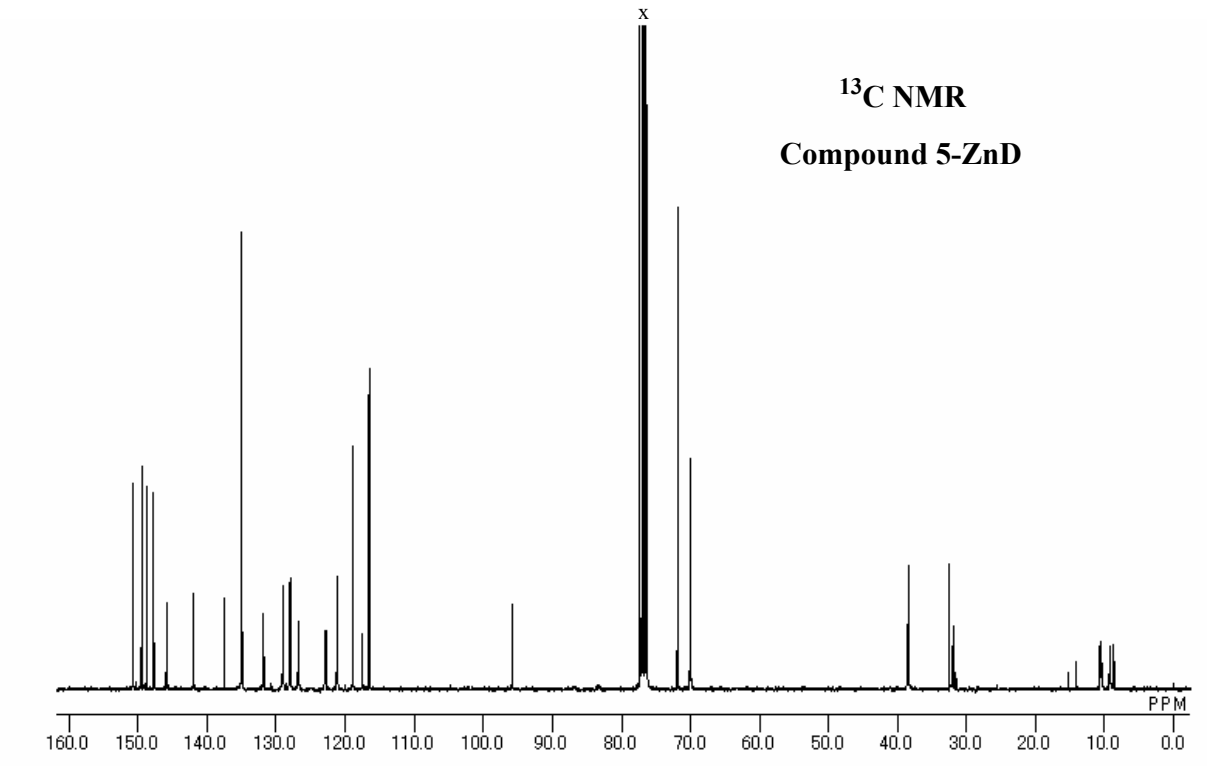






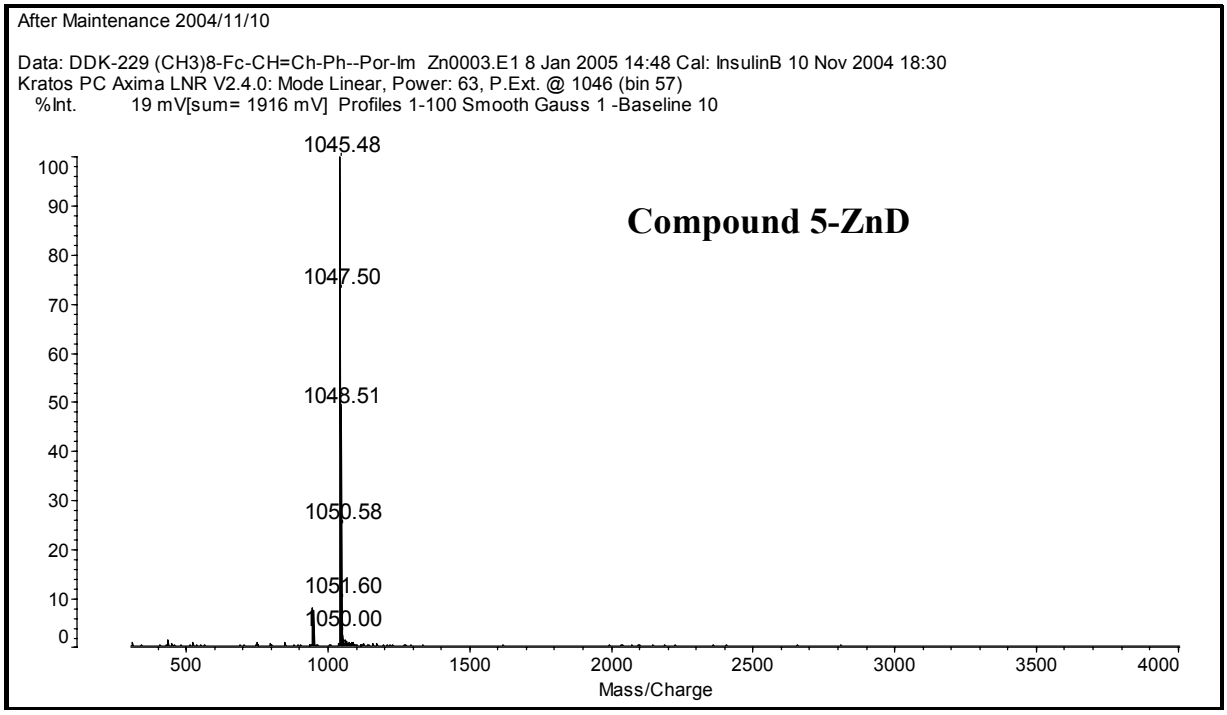
^{1}H NMR

Compound 5-ZnD



^{13}C NMR

Compound 5-ZnD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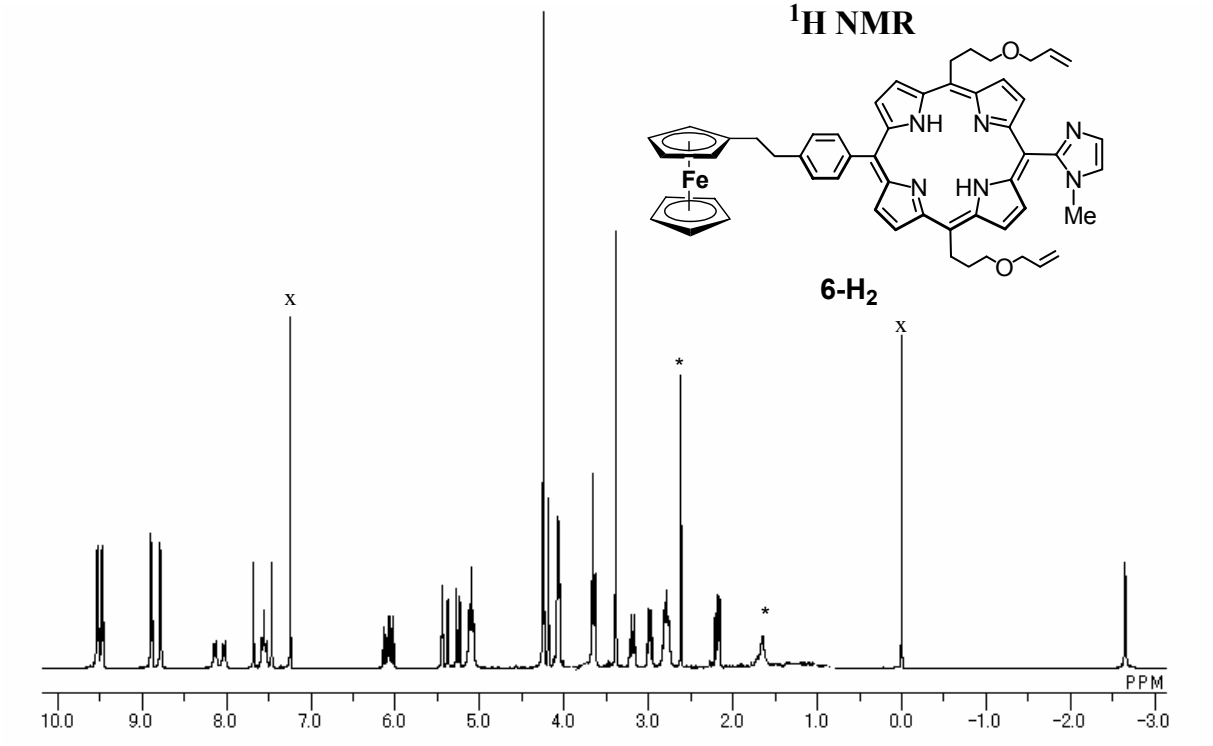
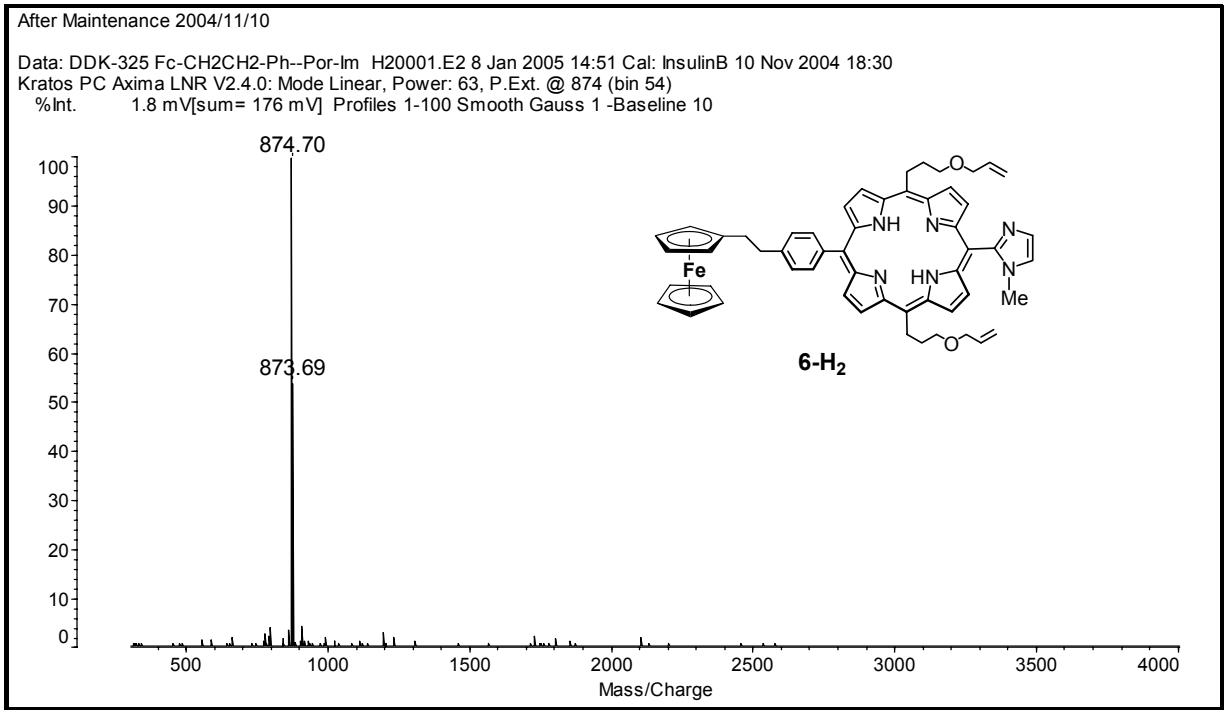
%Int. 19 mV[sum= 1916 mV] Profiles 1-100 Smooth Gauss 1 -Baseline 10
1045.48
1047.50
1048.51
1050.58
1051.60
1050.00
Compound 5-ZnD
Mass/Charge


^{1}H NMR
Fe
NH
N
HN
Me
O
6-H$_2$
x
x
*
*
PPM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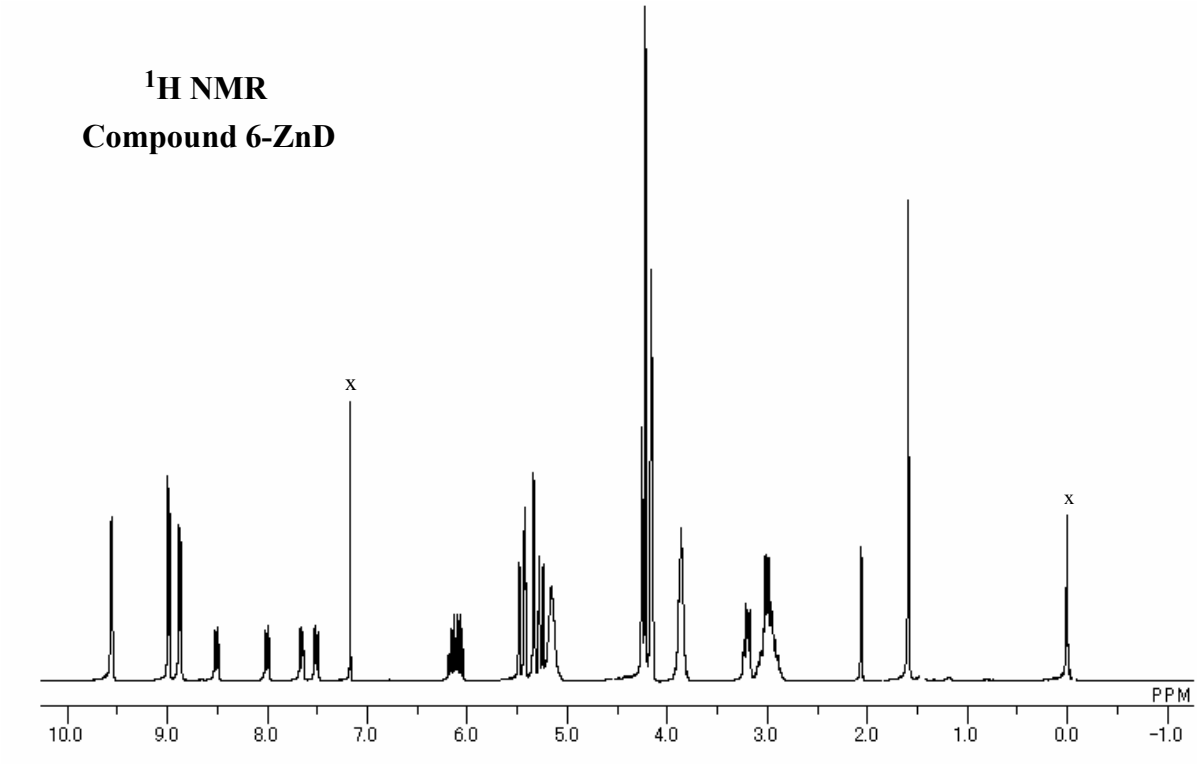
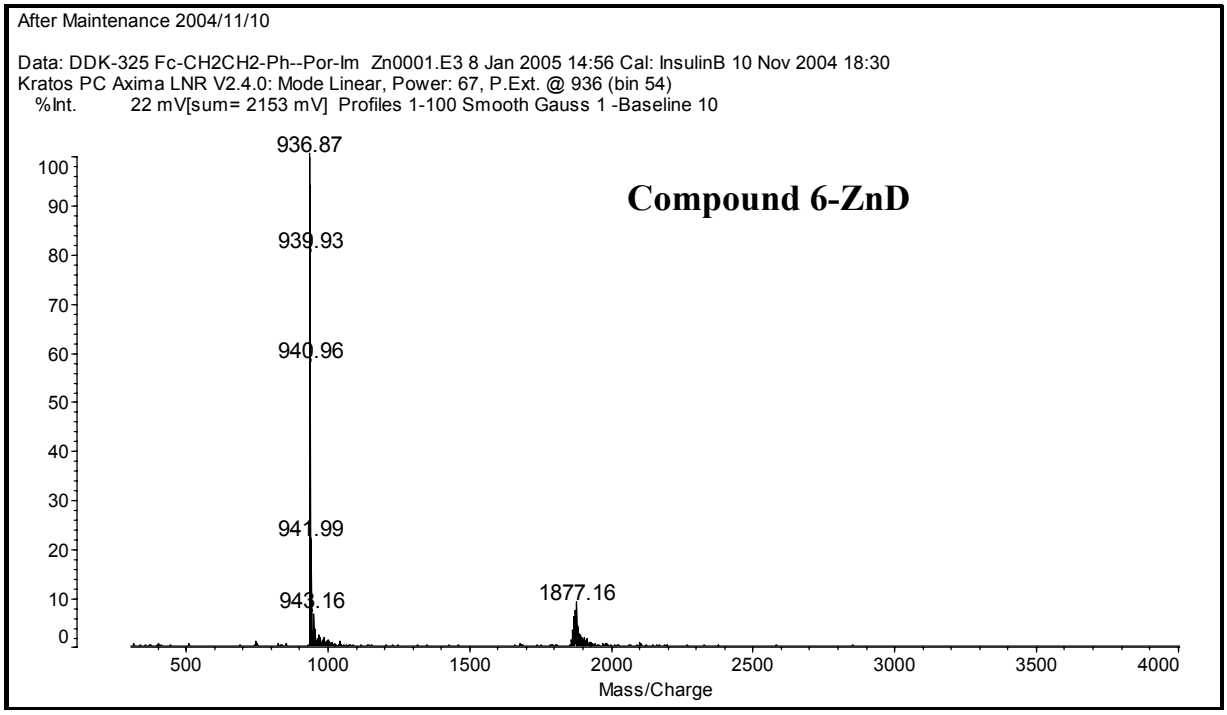
%Int. 1.8 mV[sum= 176 mV] Profiles 1-100 Smooth Gauss 1 -Baseline 10
874.70
873.69
Mass/Charge
Fe
NH
HN
N
Me
6-H2


1H NMR
Compound 6-ZnD
x
x
PPM



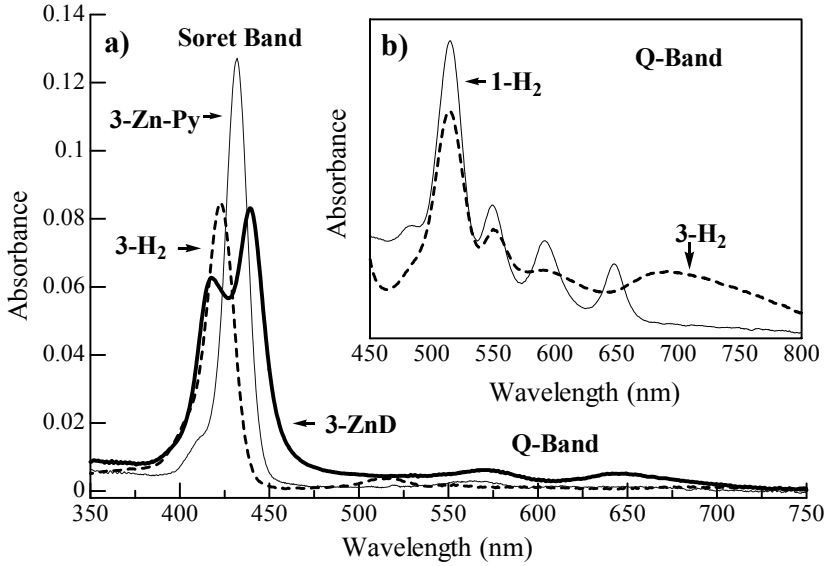


Figure S1. UV-visible absorption spectra of a) free base porphyrin **3-H_2** (bold broken line), Zn-dimer **3-ZnD** (bold solid line) and compound **3-ZnD** in pyridine, **3-Zn-Py** (thin line) b) inset Q-band region of the reference free base sample **1-H_2** (thin line) and **3-H_2** (bold broken line) in CH_2Cl_2 at rt.

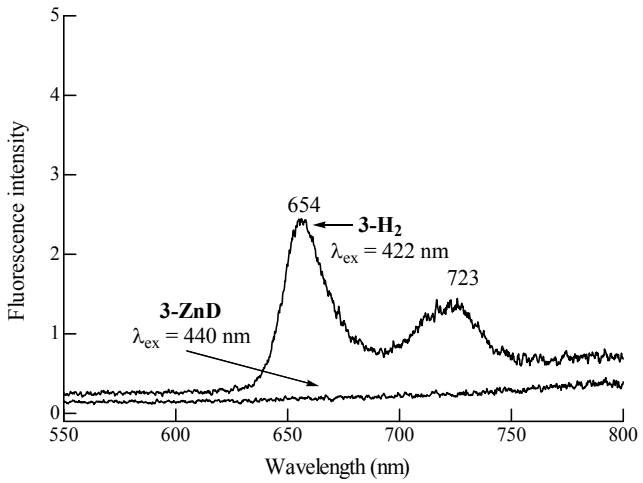


Figure S2. Steady state fluorescence spectra of compound **3-H_2** and **3-ZnD** in CH_2Cl_2 at 25 ^oC, with excitation of the Soret band in each case.

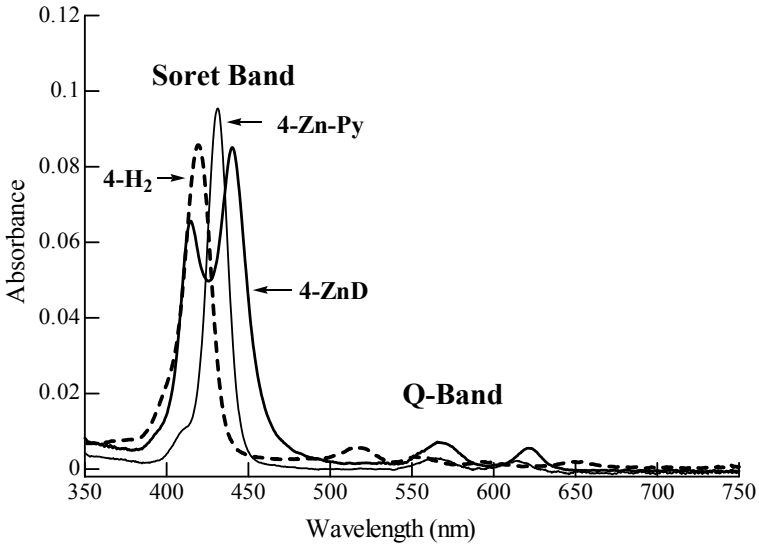


Figure S3. UV-visible absorption spectra of free base porphyrin **4-H_2** (bold broken line), Zn-dimer **4-ZnD** (bold solid line) and compound **4-ZnD** in pyridine, **4-Zn-Py** (thin line) in CH_2Cl_2 at rt.

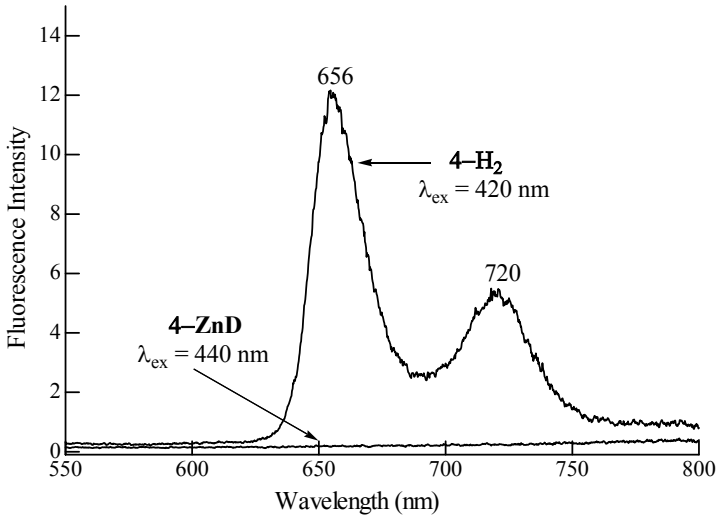


Figure S4. Steady state fluorescence spectra of compound **4-H_2** and **4-ZnD** in CH_2Cl_2 at 25 ^oC, with excitation of the Soret band in each case.

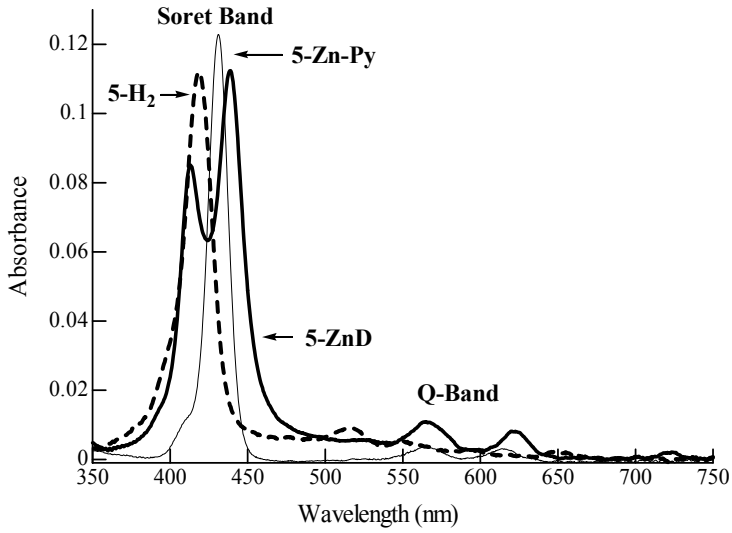


Figure S5. UV-visible absorption spectra of free base porphyrin **5-H_2** (bold broken line), Zn-dimer **5-ZnD** (bold solid line) and compound **5-ZnD** in pyridine, **5-Zn-Py** (thin line) in CH_2Cl_2 at rt.

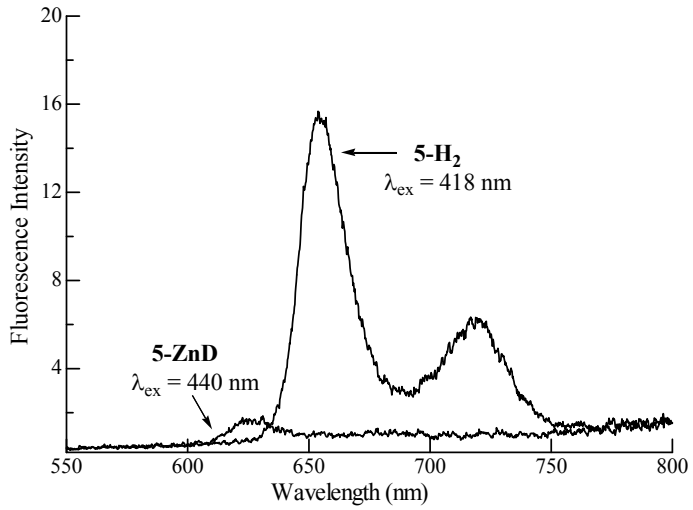


Figure S6. Steady state fluorescence spectra of compound **5-H_2** and **5-ZnD** in CH_2Cl_2 at 25 ^oC, with excitation of the Soret band in each case.