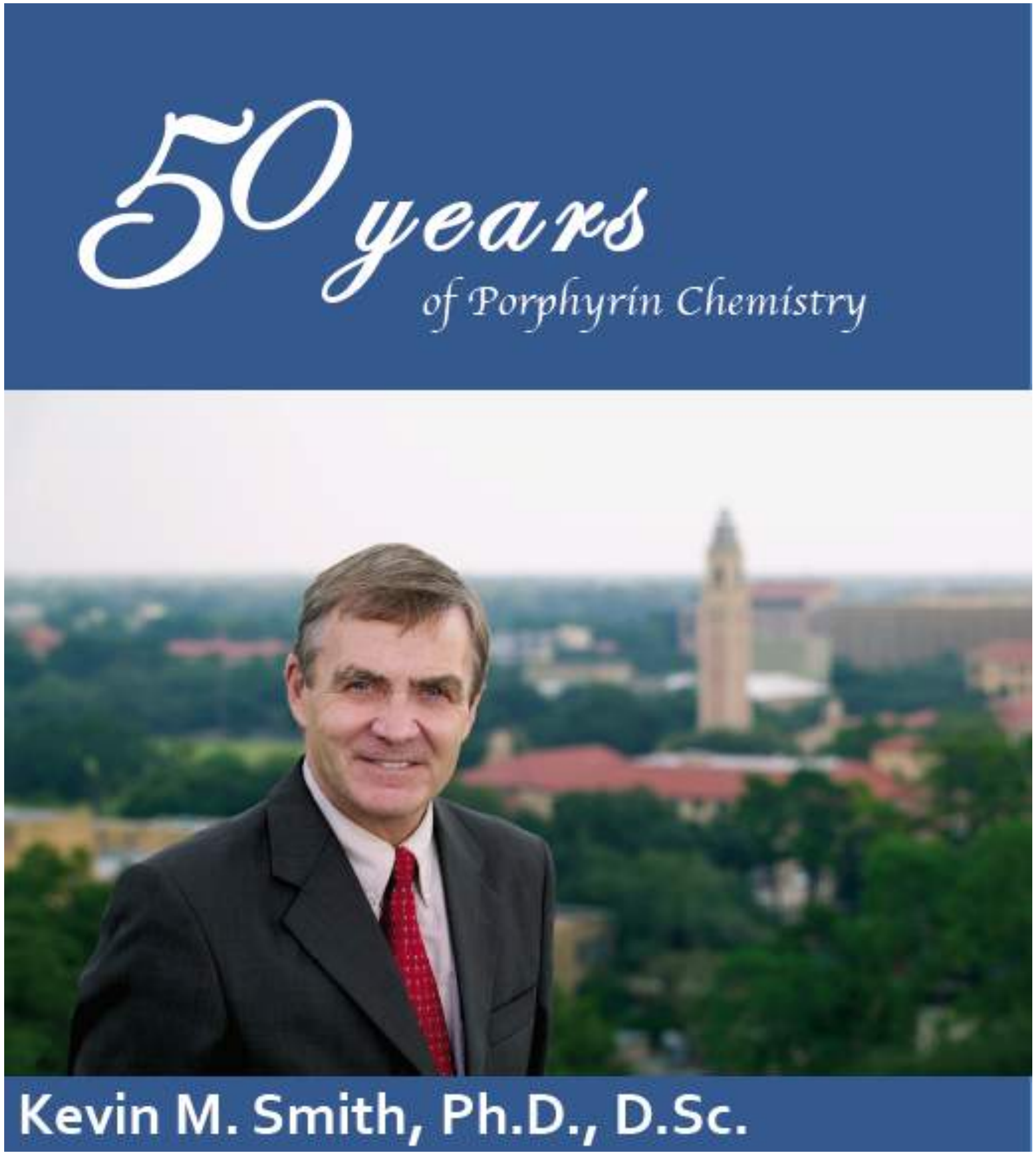
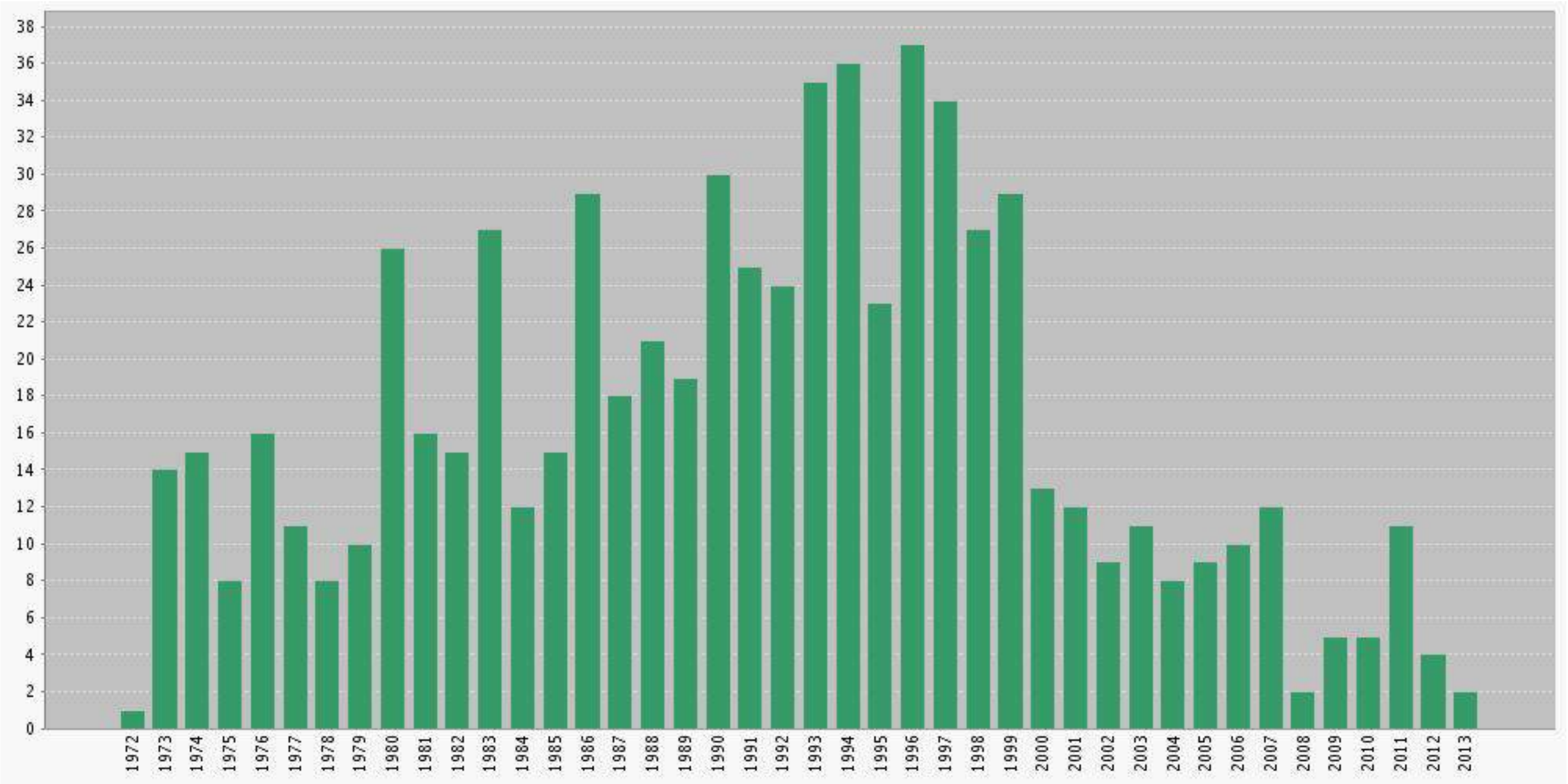


Presented by Roberto Paolesse, 6/24/2014

How to summarize the work? Just few number ....



Tetrahedron, 1965, Vol. 21, pp. 2913 to 2924. Pergamon Press Ltd. Printed in Northern Ireland

PYRROLES AND RELATED COMPOUNDS—VIII[1]

MASS SPECTROMETRY IN STRUCTURAL AND STEREOCHEMICAL PROBLEMS—LXXVI[2] THE MASS SPECTRA OF PORPHYRINS

A. H. JACKSON, G. W. KENNER and K. M. SMITH
The Robert Robinson Laboratories, University of Liverpool

and

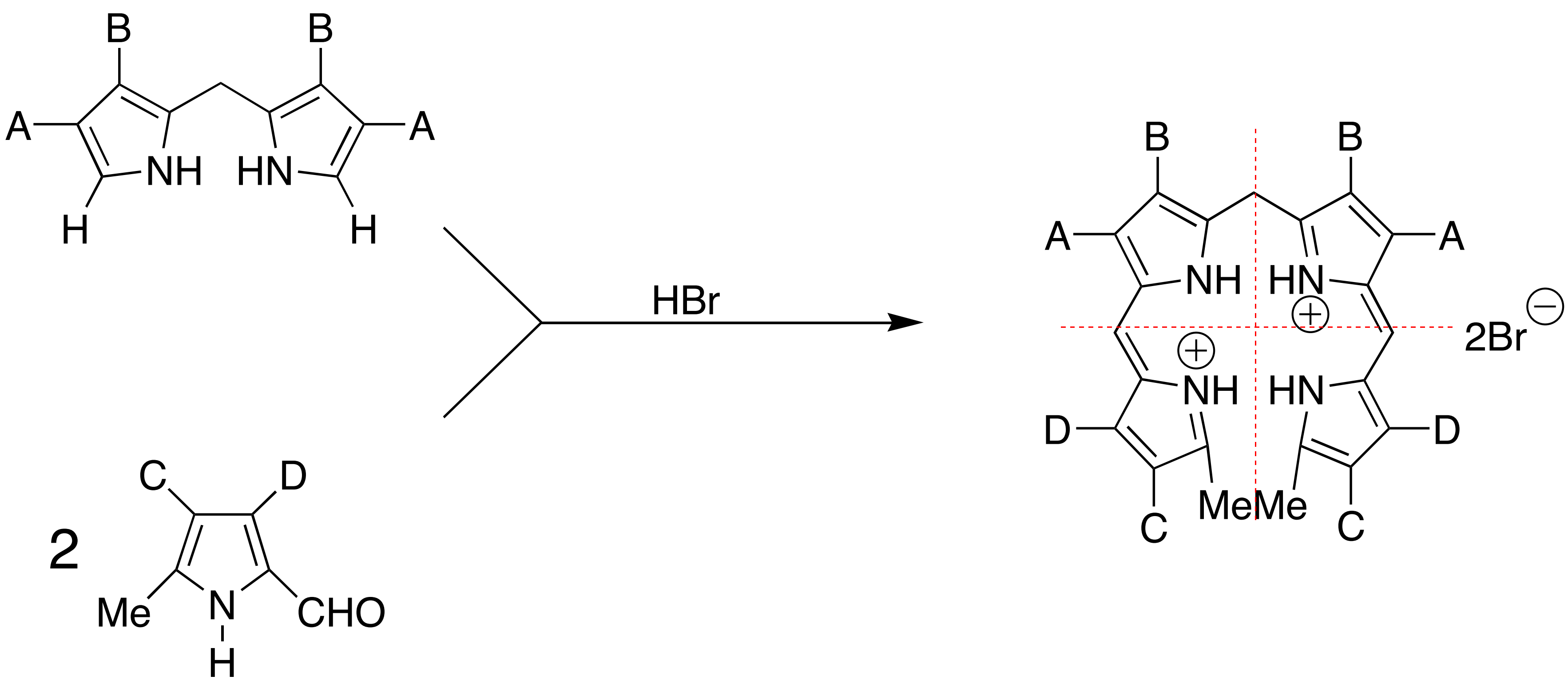
R. T. APLIN, H. BUDZIKIEWICZ and CARL DJERASSI
Department of Chemistry, Stanford University, Stanford, California

(*Received* 4 *May* 1965)

Abstract—The molecular ion nearly always produces the strongest peak in mass spectra of porphyrins. The macrocyclic nucleus is remarkably stable and fragmentation gives mainly "benzylic" ions. In derivatives of porphin this involves cleavage at the bond once removed from the macrocycle, but in chlorins the entire substituent is lost from the reduced "pyrrole" ring. Methyl esters of chlorins derived from chlorophyll lose directly 147 and 159 mass units in complex processes marked by strong metastable peaks. All the spectra contain a prominent series of peaks from doubly charged ions; a novel feature is loss of ketene from propionate side-chains.

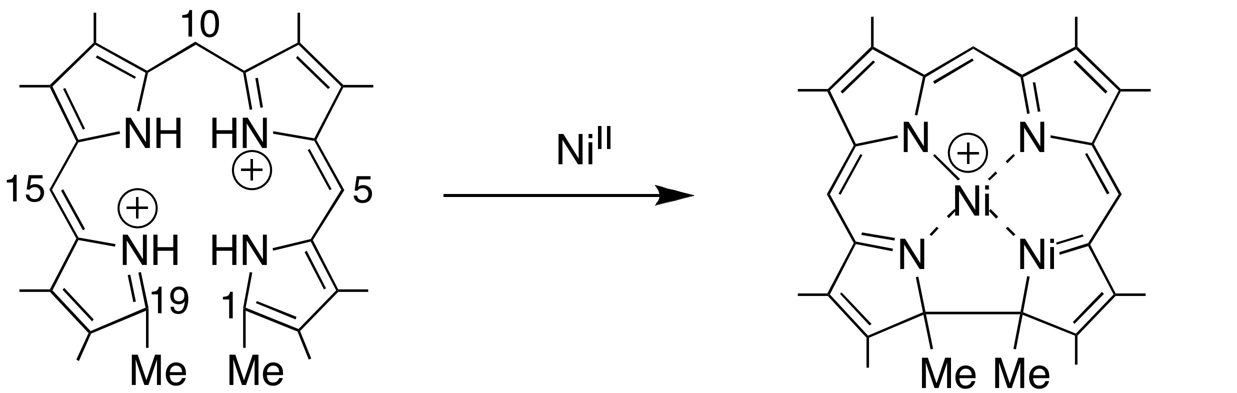
Porphyrins from a,c-biladienes

a,c-Biladiene Synthesis

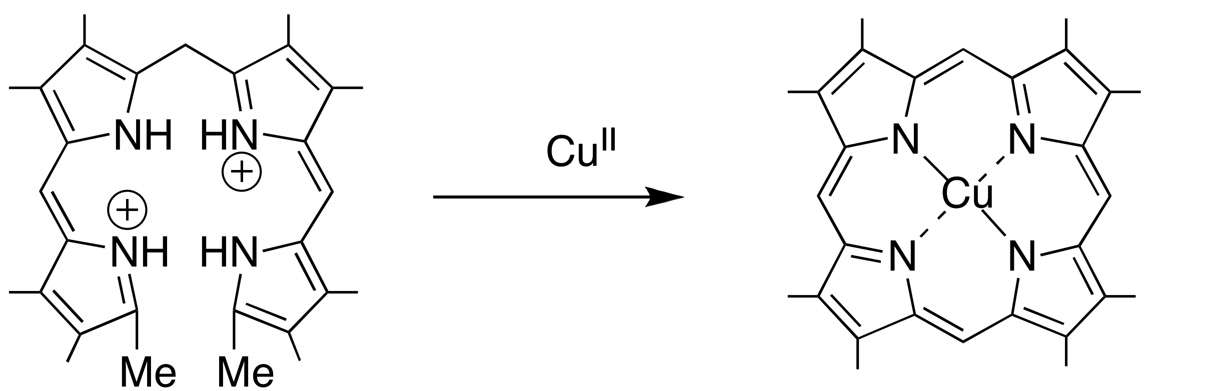


A. W. Johnson and I. T. Kay, *J. Chem. Soc. C*, **1961**, 2418.

a,c-Biladiene Oxidative Cyclization

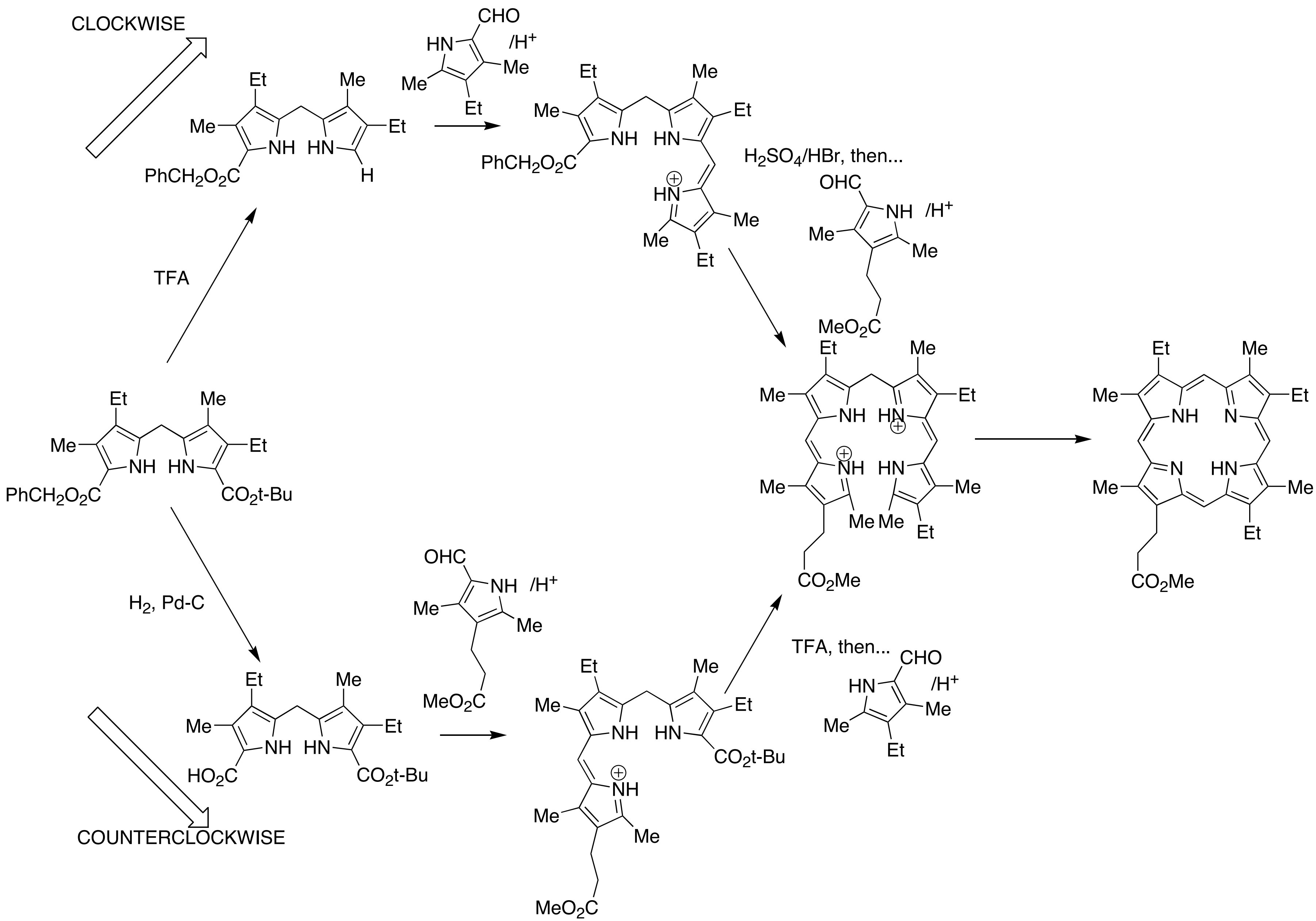


Ni (or Co) tetradehydrocorrin



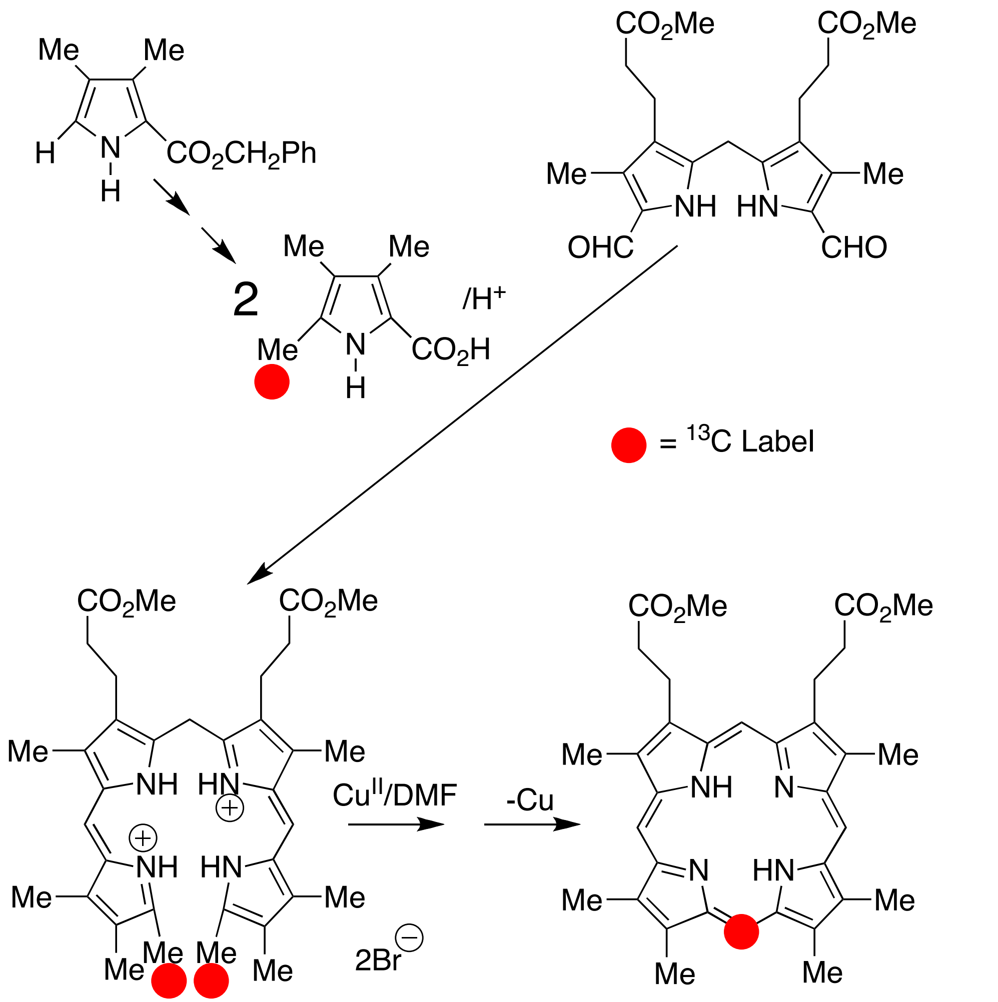
Cu porphyrin

A. W. Johnson and I. T. Kay, *J. Chem. Soc. C*, **1961**, 2418.



J. A. P. B. Almeida, G. W. Kenner, J. Rimmer and K. M. Smith, *Tetrahedron* **1976**, *32*, 1793.
K. M. Smith and G. W. Craig, *J. Org. Chem.* **1983**, *48*, 4302.

Copper(II) Cyclization Mechanism



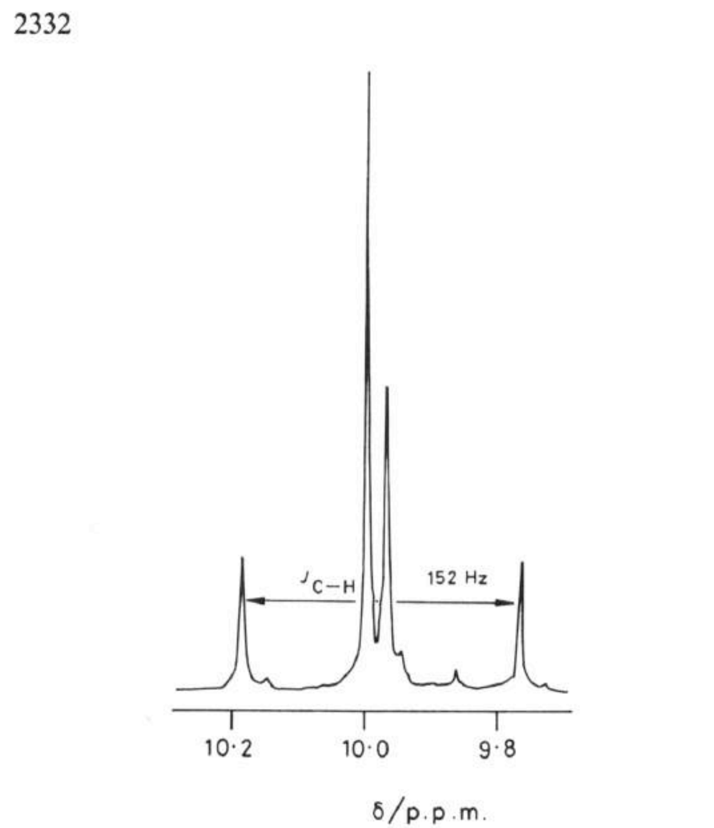
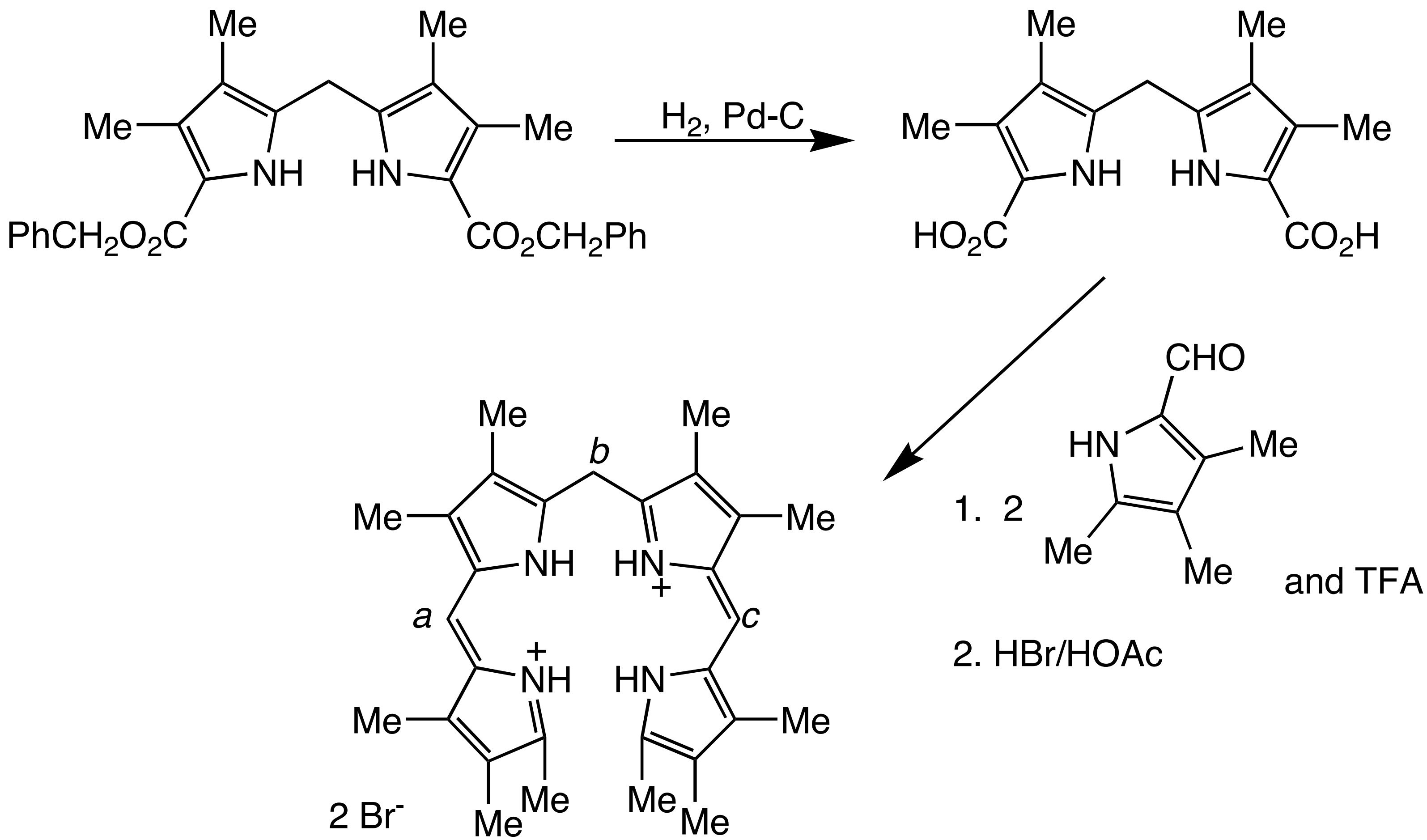


Figure. ^{1}H N.m.r. spectrum (360 MHz) of the *meso* proton region of the zinc(II) complex of the α *meso* ^{13}C labelled porphyrin (34). The solvent is $CDCl_3$ with a small amount of pyrrolidine added to ensure absence of aggregation

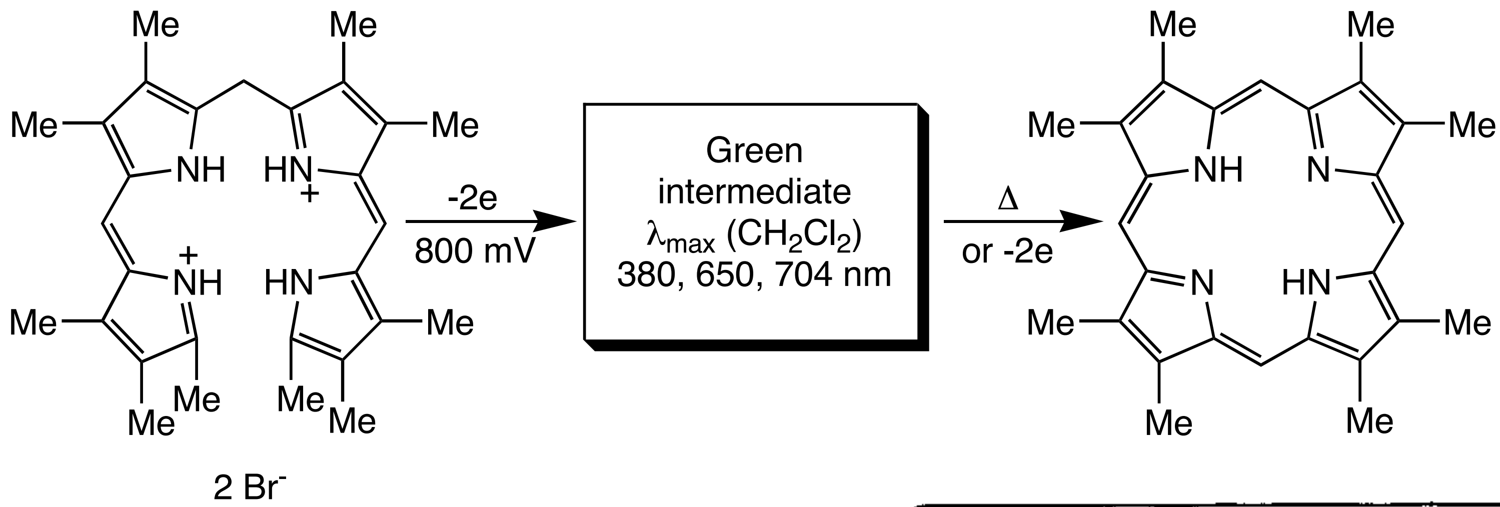
K. M. Smith and L. A. Kehres. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2329.

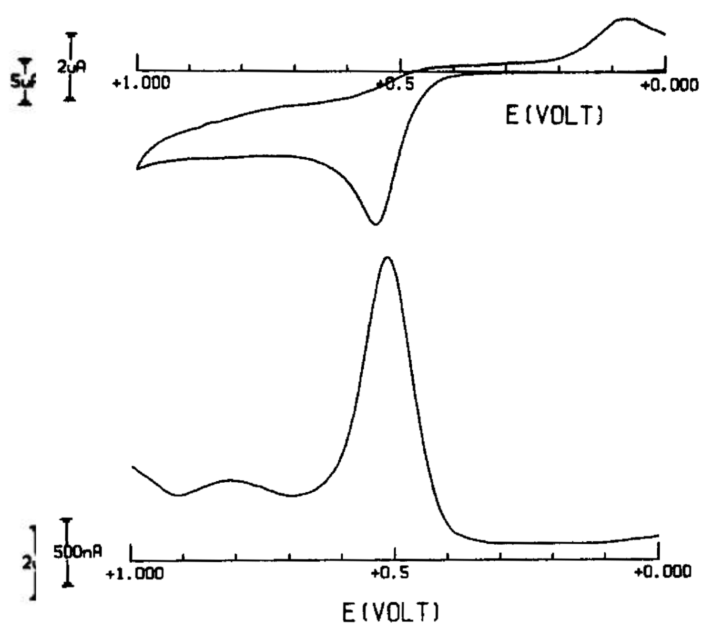
Mechanism - Use Simple Substrate and Avoid Paramagnetic Cu(II)

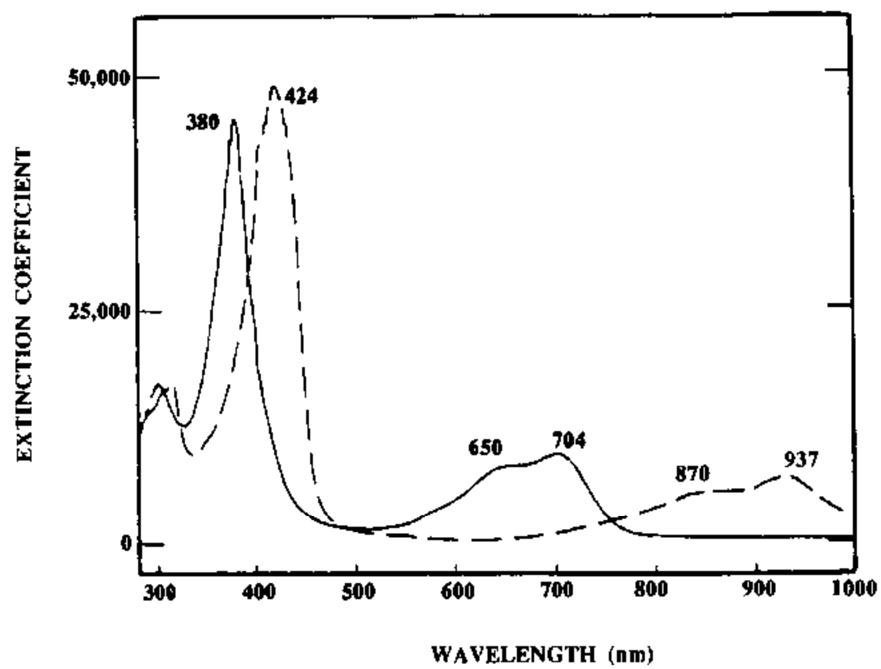


Decamethyl-
a,*c*-biladiene

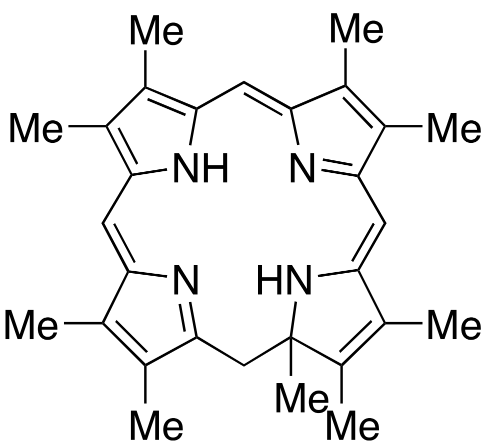
Preparative Anodic Oxidation







NMR Evidence for Intermediate



J. Am. Chem. Soc., Vol. 110, No. 25, 1988 8563

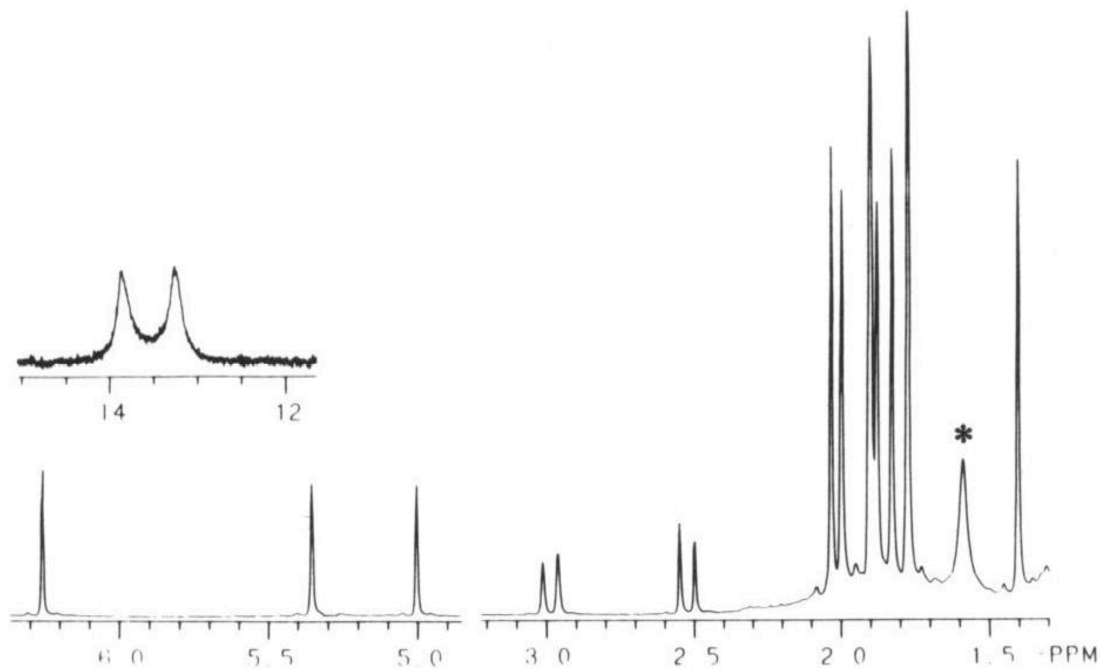
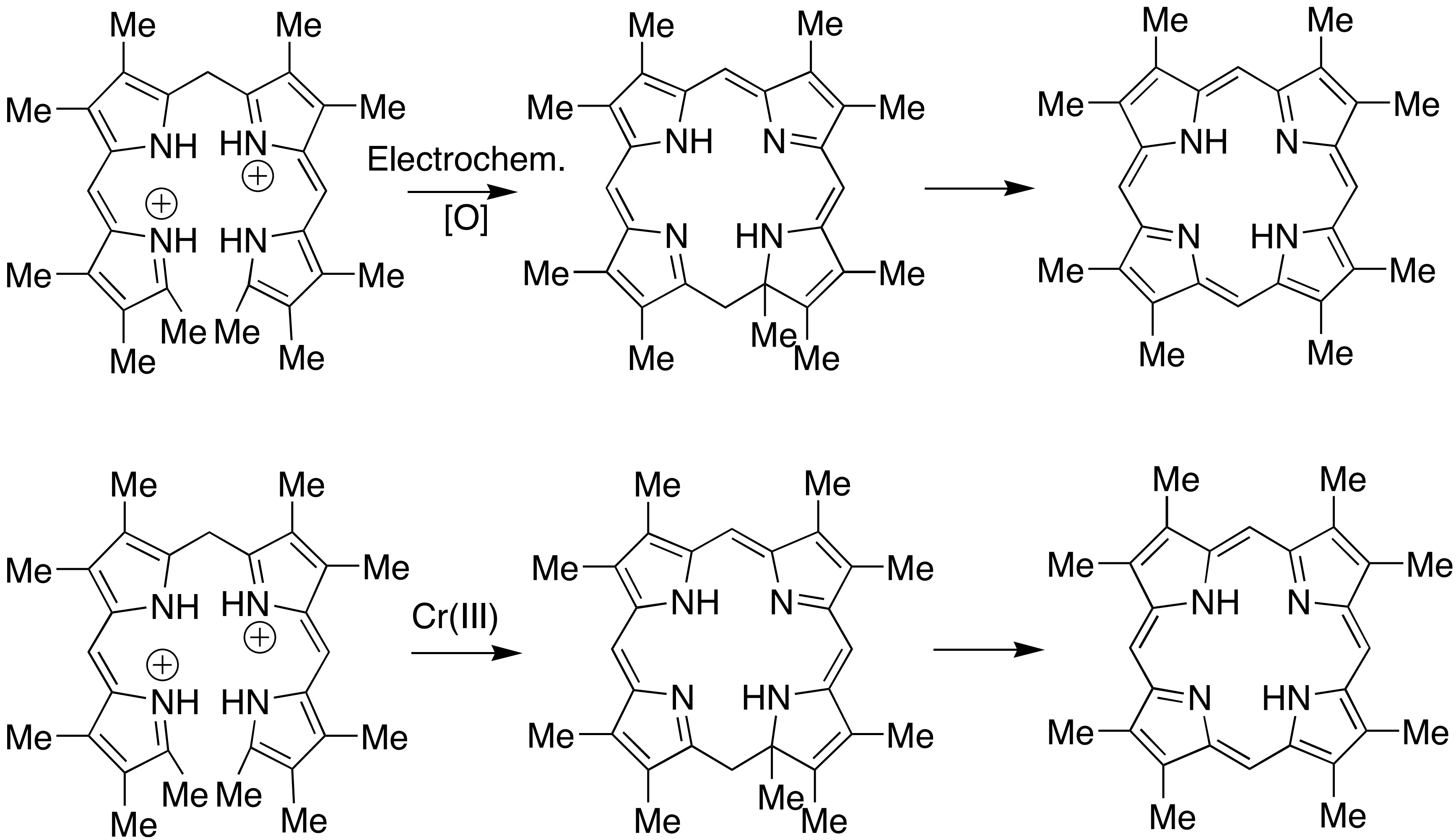


Figure 3. Proton NMR spectrum (in $CDCl_3$; 300 MHz; GE QE300 instrument) of the intermediate **6**. Vertical scale in the insert expanded. * = water.

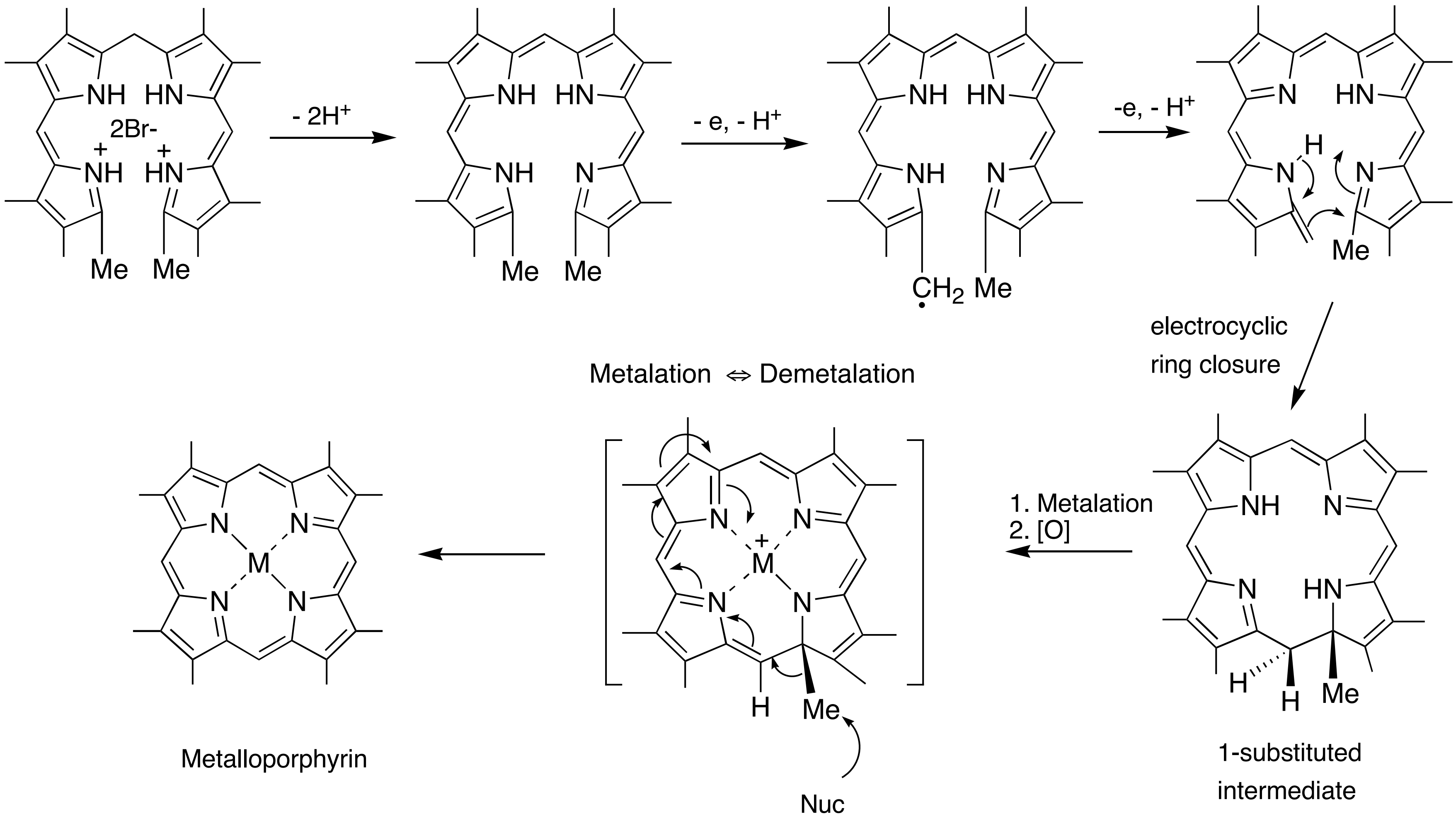
D. Jeyakumar, K. M. Snow and K. M. Smith, *J. Am. Chem. Soc.* **1988**, *110*, 8562.

a,c-Biladiene:
Electrochemical vs. Metal Cyclization



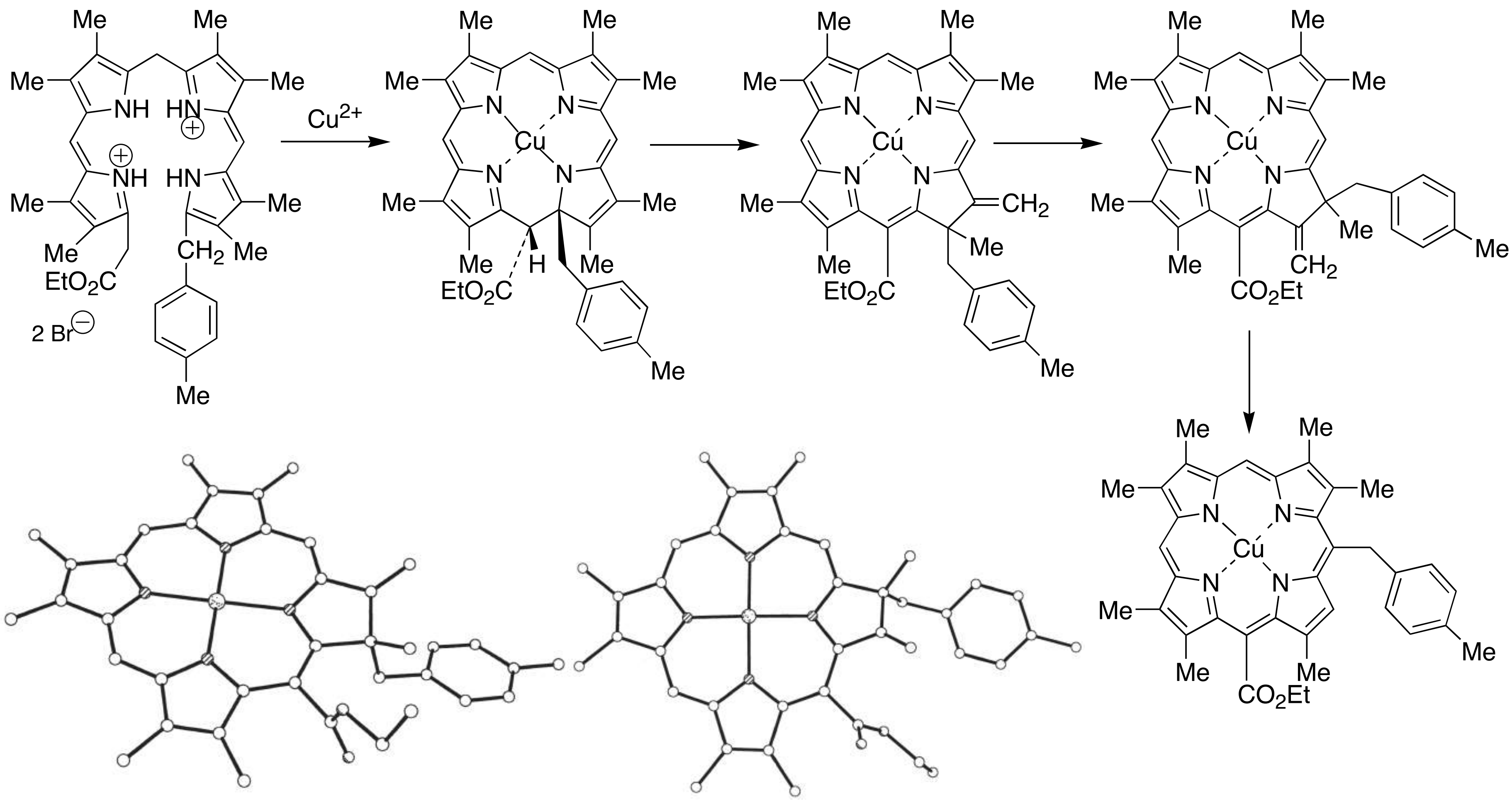
J. J. Lin, R. T. Holmes and K. M. Smith. *J. Porphyrins Phthalocyanines* **1998**, *2*, 363.

Cyclization Mechanism - Electrochemical



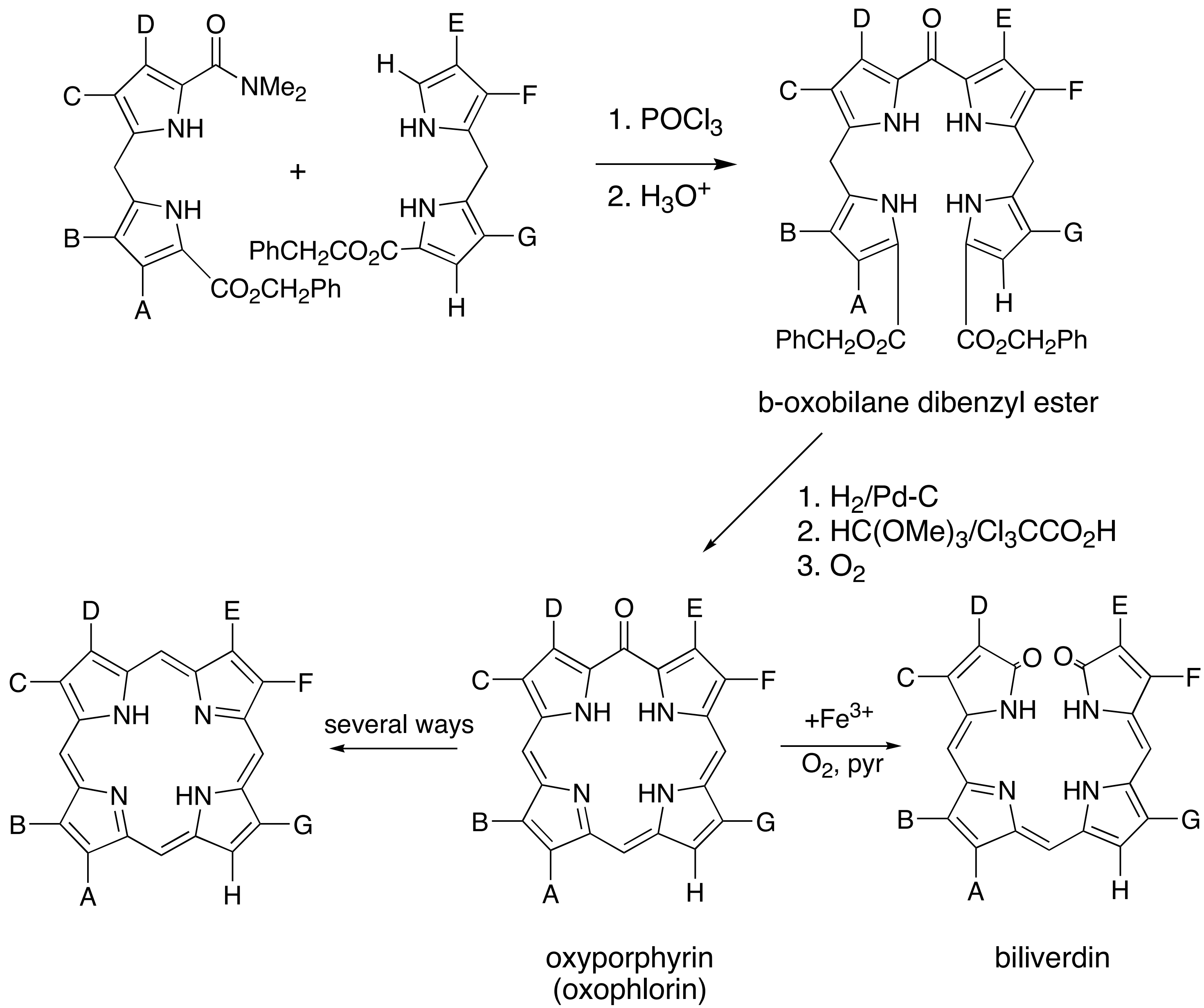
J. J. Lin, R. T. Holmes and K. M. Smith. *J. Porphyrins Phthalocyanines* **1998**, *2*, 363.

Other a,c-Biladienes

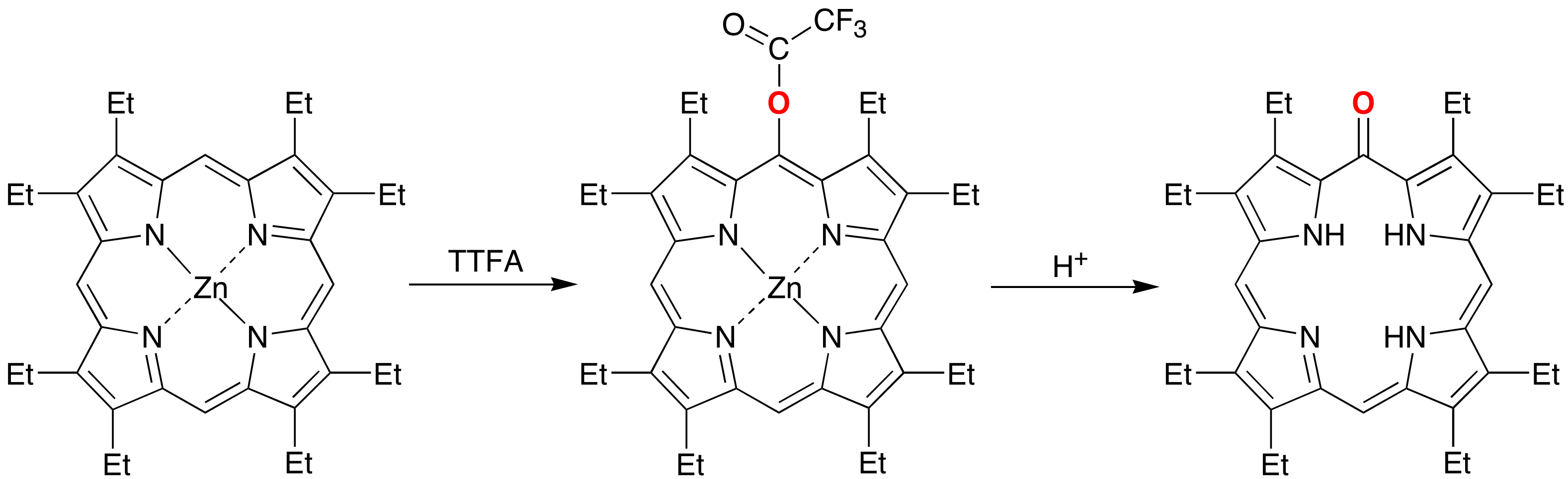


J. J. Lin, K. R. Gerzevske, P. A. Liddell, M. O. Senge, M. M. Olmstead, R. G. Khoury, B. E. Weeth, S. A. Tsao and K. M. Smith. *J. Org. Chem*. **1997**, *62*, 4266.

Oxophlorin



A. H. Jackson, G. W. Kenner, G. McGillivray and K. M. Smith, *J. Chem. Soc. C*, **1968**, 294
A. H. Jackson, G. W. Kenner and K. M. Smith, *J. Am. Chem. Soc.*, **1966**, *88*, 4539

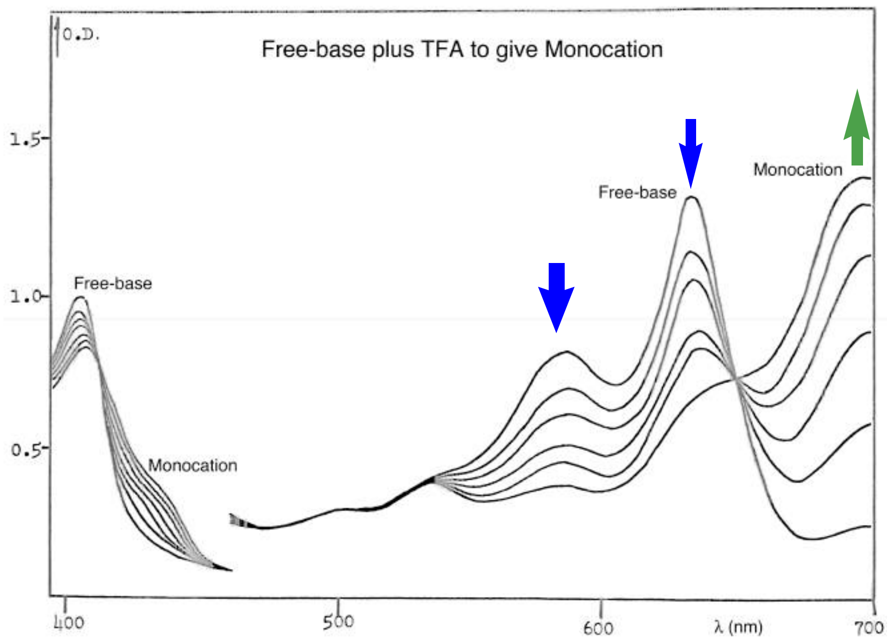


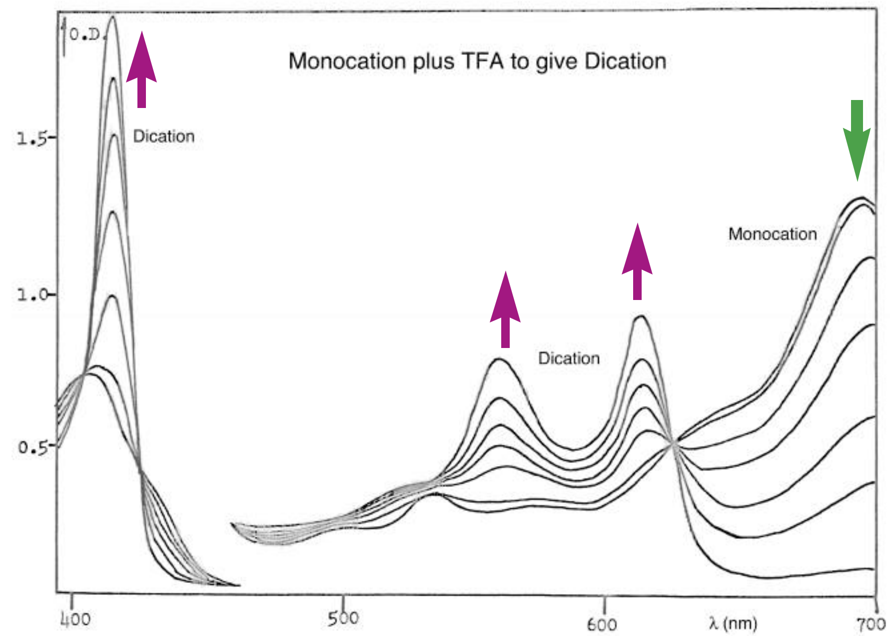
Synthesis of Oxophlorins (Oxyporphyrins) from Magnesium and Zinc Porphyrin Chelates[1]

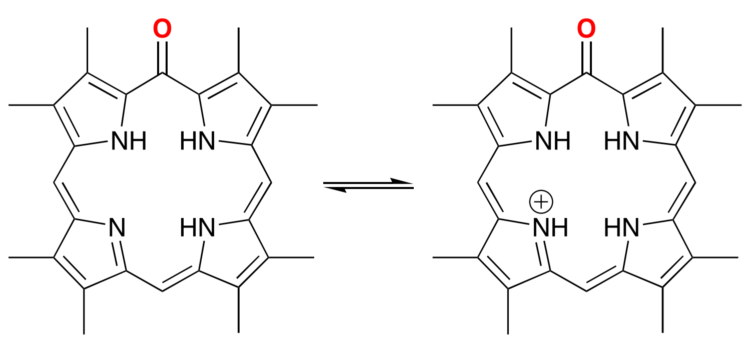
By **Graham H. Barnett, Mervyn F. Hudson, Stuart W. McCombie,** and **Kevin M. Smith,*** The Robert Robinson Laboratories, University of Liverpool, P.O. Box 147, Liverpool L69 3BX

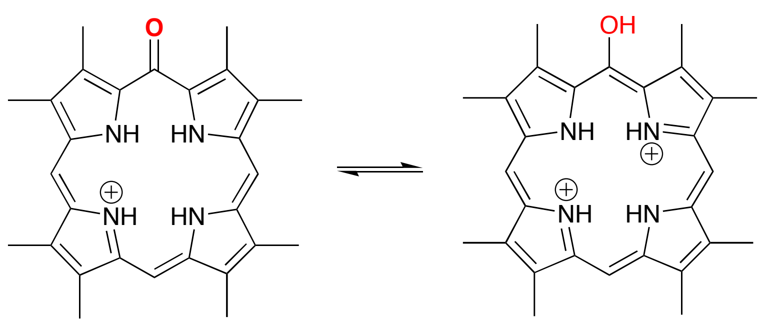
J. Chem. Soc., Perkin Trans. 1 **1973**, 691.

Titration with TFA in CH_2Cl_2

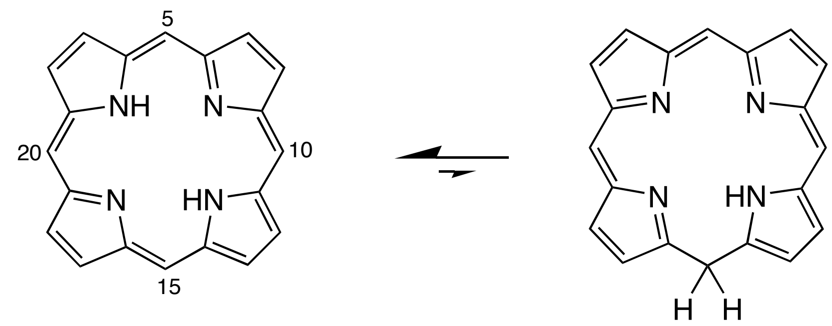






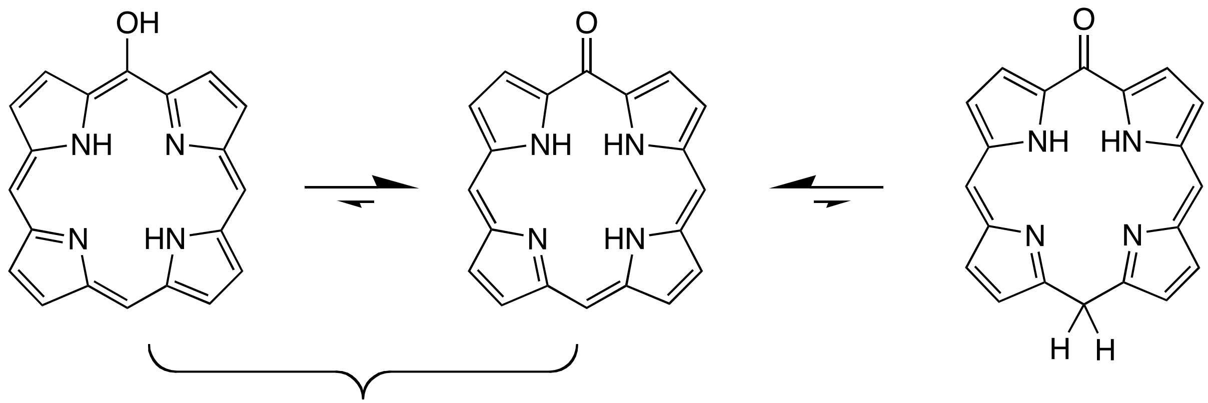


A. H. Jackson, G. W. Kenner and K. M. Smith, *J. Am. Chem. Soc.*, **1966**, *88*, 4539

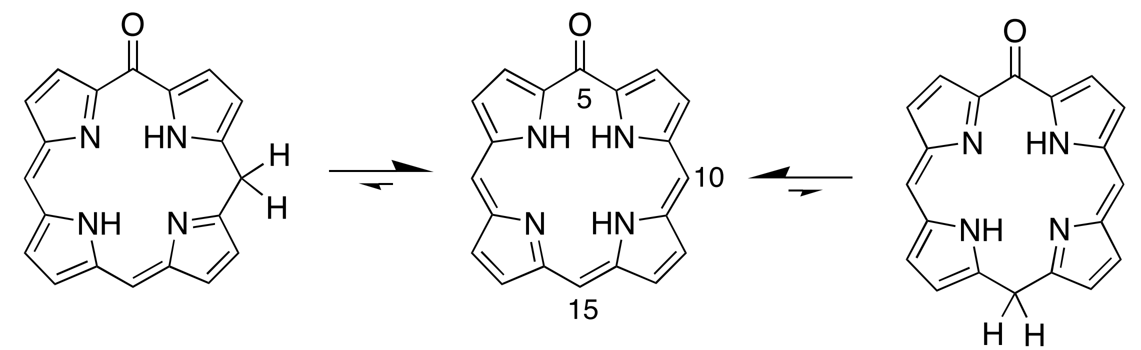


Porphyrin Isoporphyrin

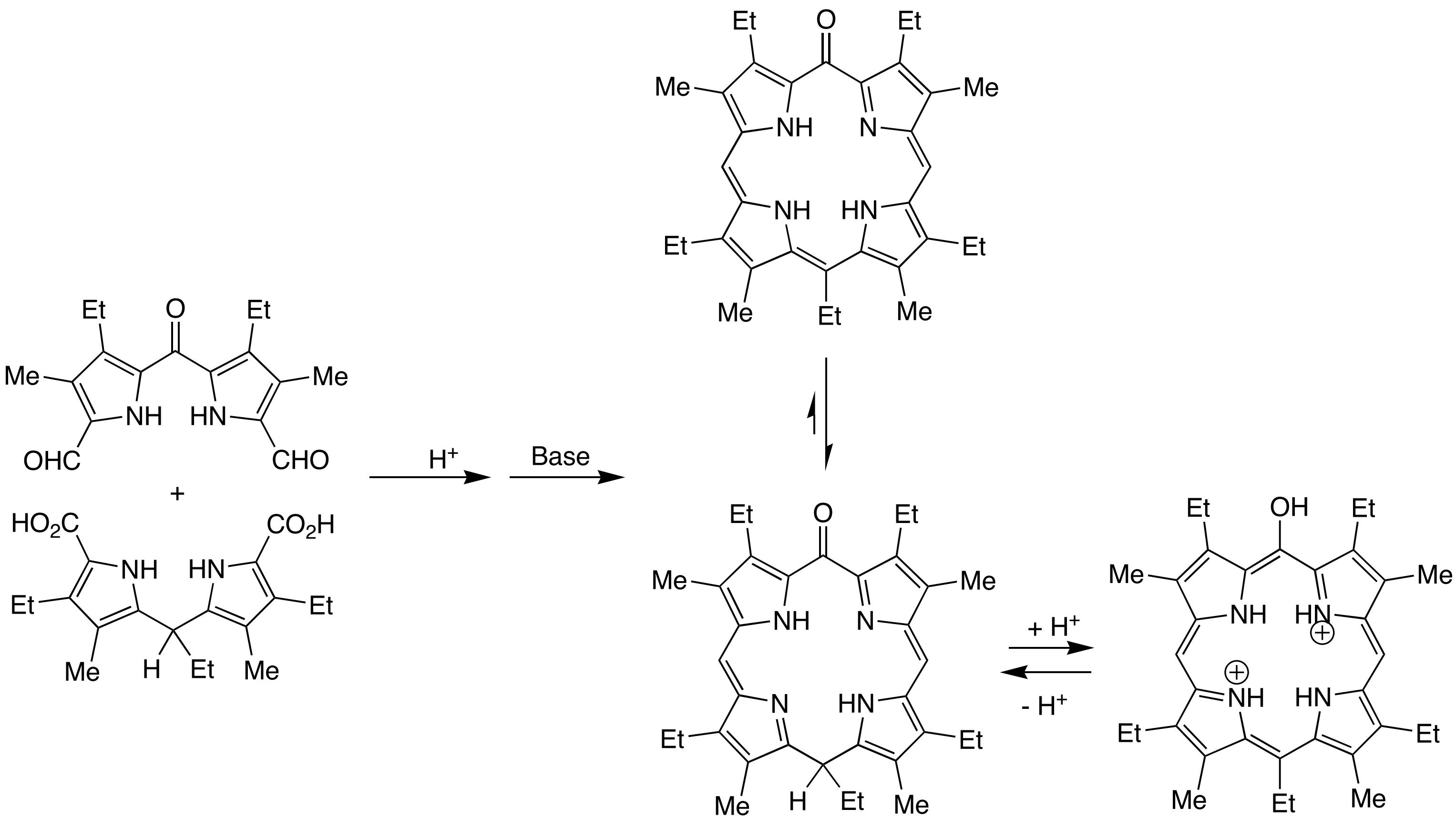
(substituents omitted)



Oxophlorin Iso-oxophlorin



10-Iso-5-oxophlorin Oxophlorin 15-Iso-5-oxophlorin



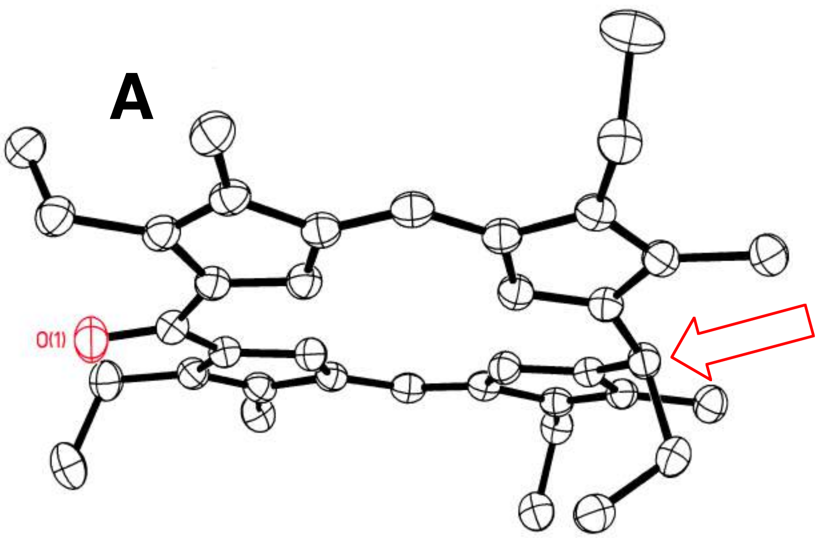
Iso-oxophlorin
(69%)

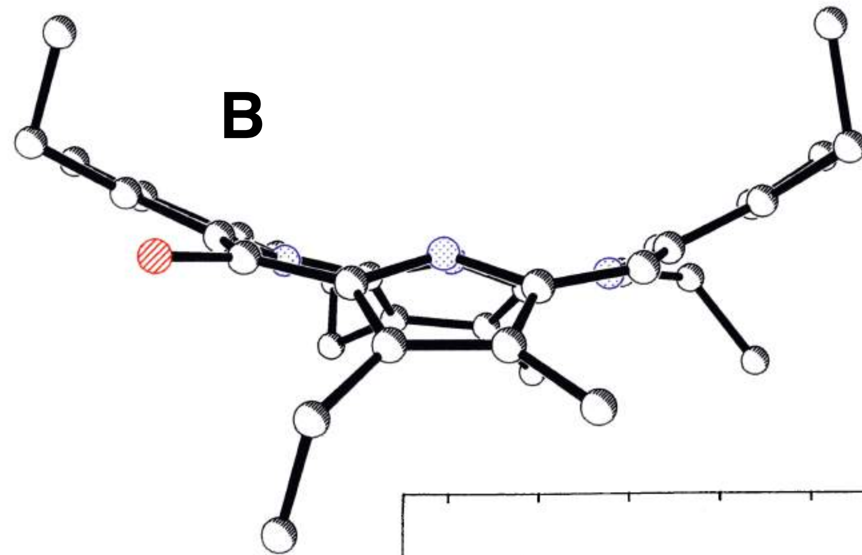
+

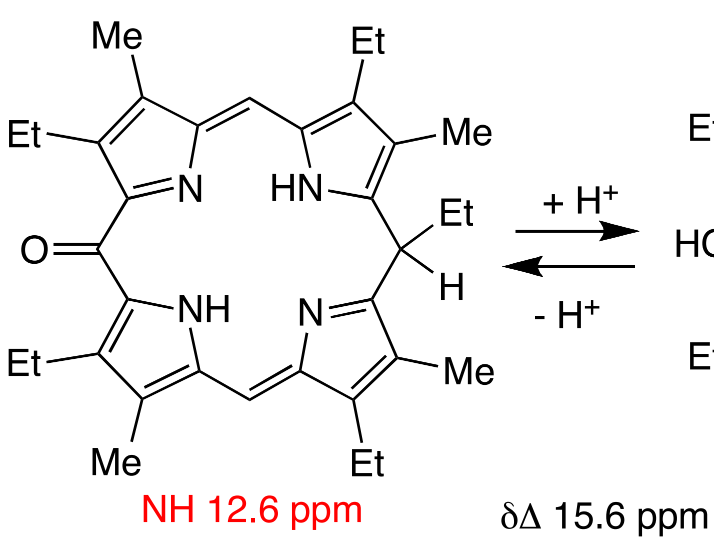
"A Dimer" (25%)
(two isomers)

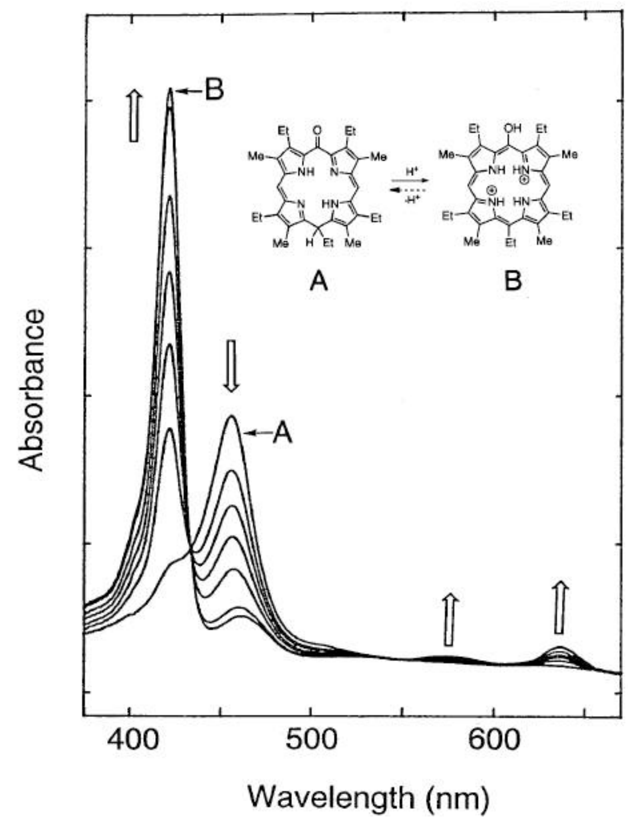
Later....

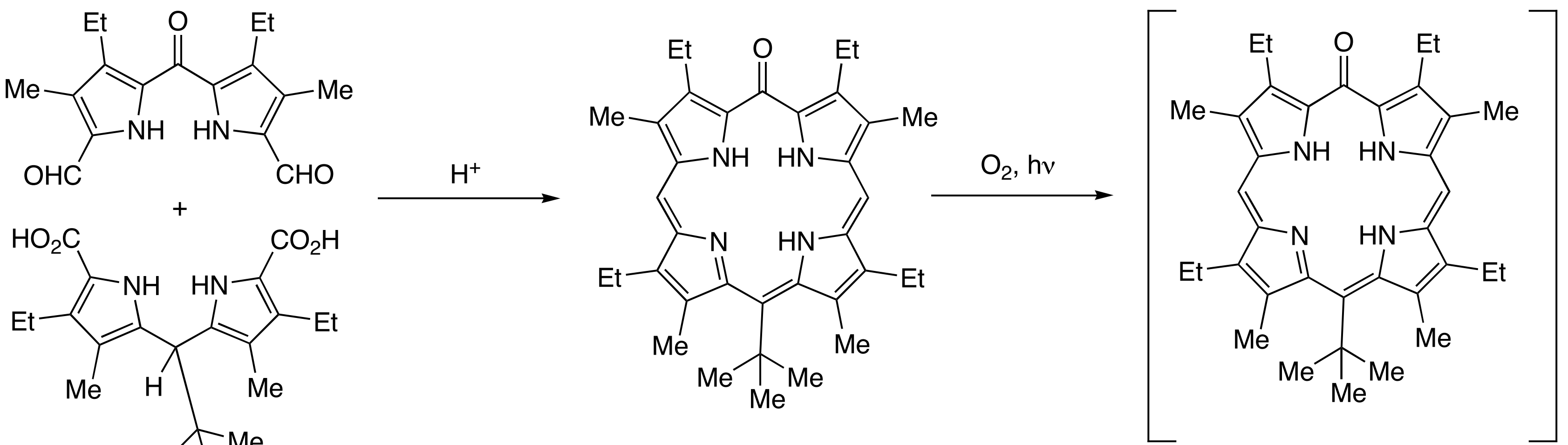
R. G. Khoury, L. Jaquinod, D. J. Nurco and K. M. Smith. *Chem. Commun*. **1996**, 1143.
R. G. Khoury, L. Jaquinod, R. Paolesse and K. M. Smith. *Tetrahedron* **1999**, *55*, 6713.


A
O(1)


B

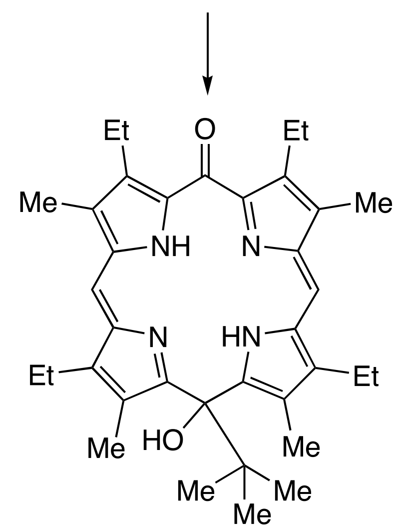

Me
Et
Et
Me
N
HN
Et
O
H
NH
N
Et
Me
Me
Et
+ H+
- H+
Me
Et
Et
Me
NH
HN
HO
Et
NH
HN
Et
Me
Me
Et
NH 12.6 ppm
δΔ 15.6 ppm
NH -3.0 ppm


B
A
Absorbance
400
500
600
Wavelength (nm)

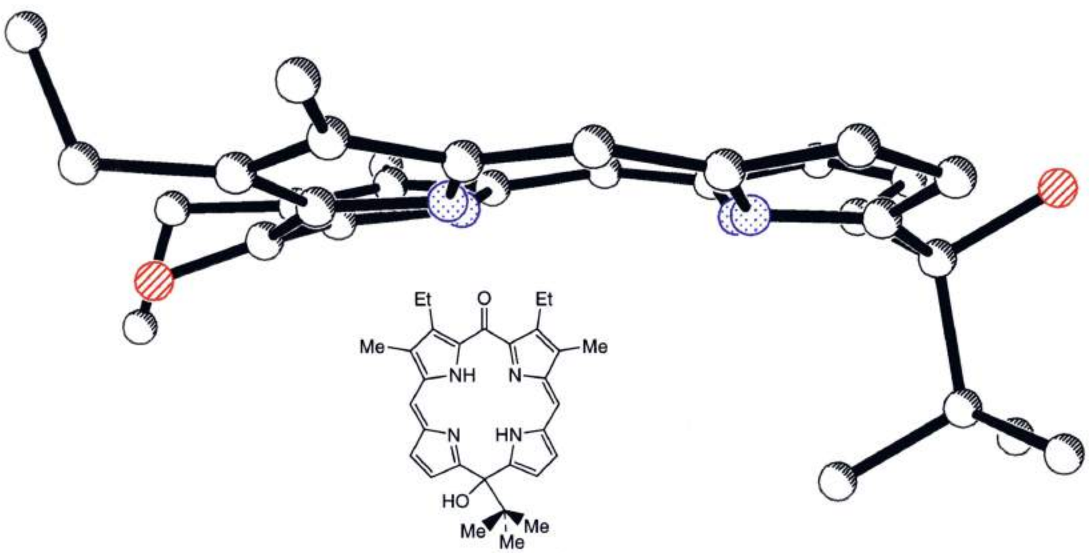


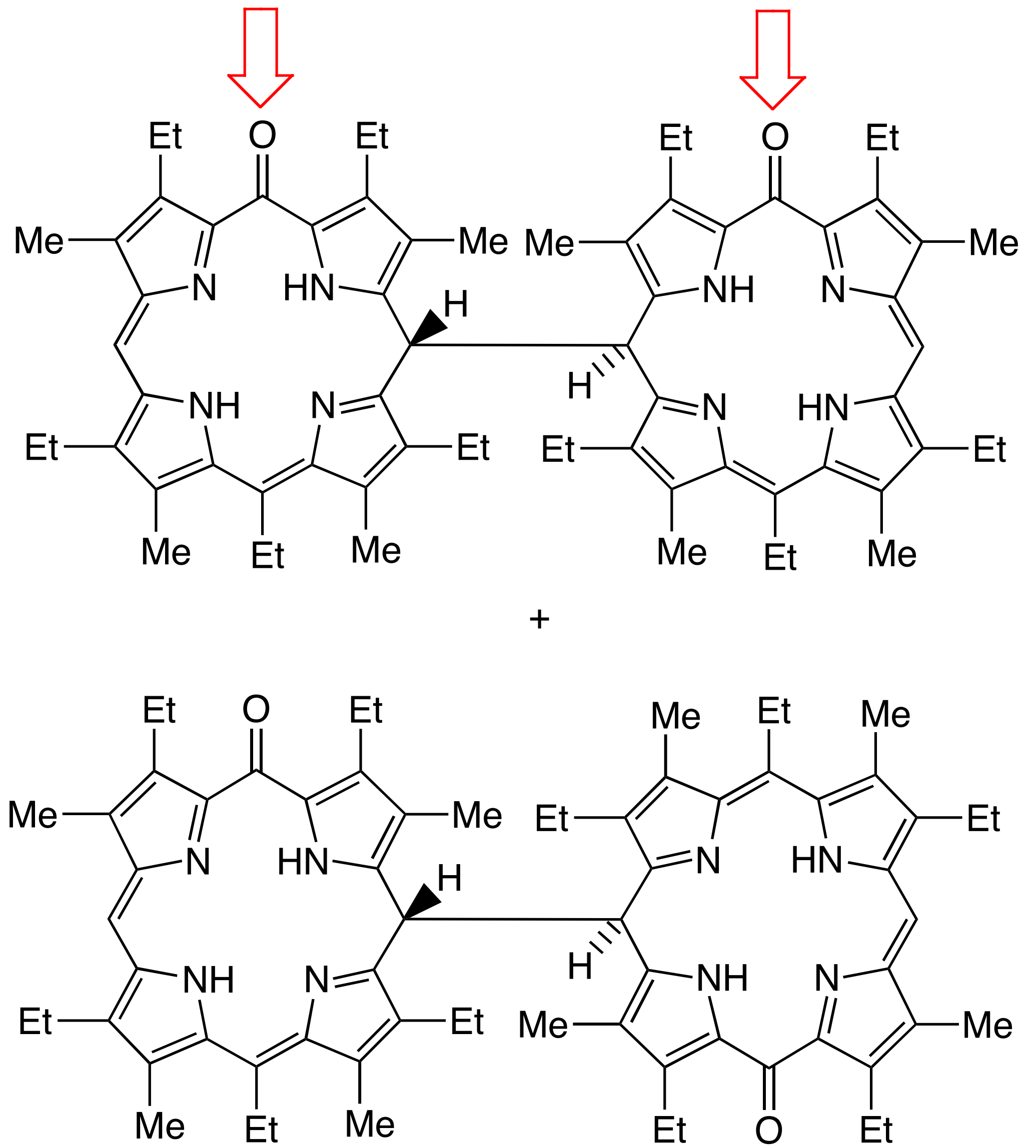
43%

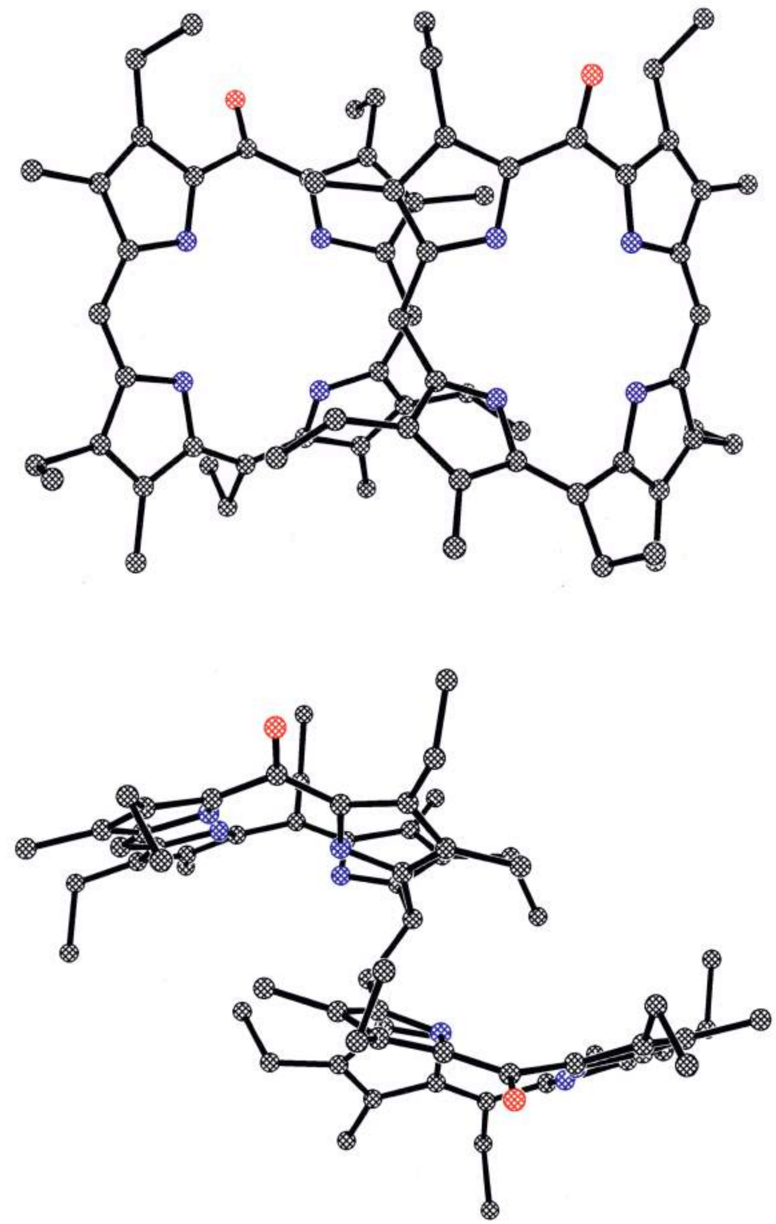
STABLE radical
90% yield
ESR 3,000G
μ_{eff} = 2.5 μ_B at 297K (Evans)
30% decomp. in soln. in presence of O_2 over 3 weeks



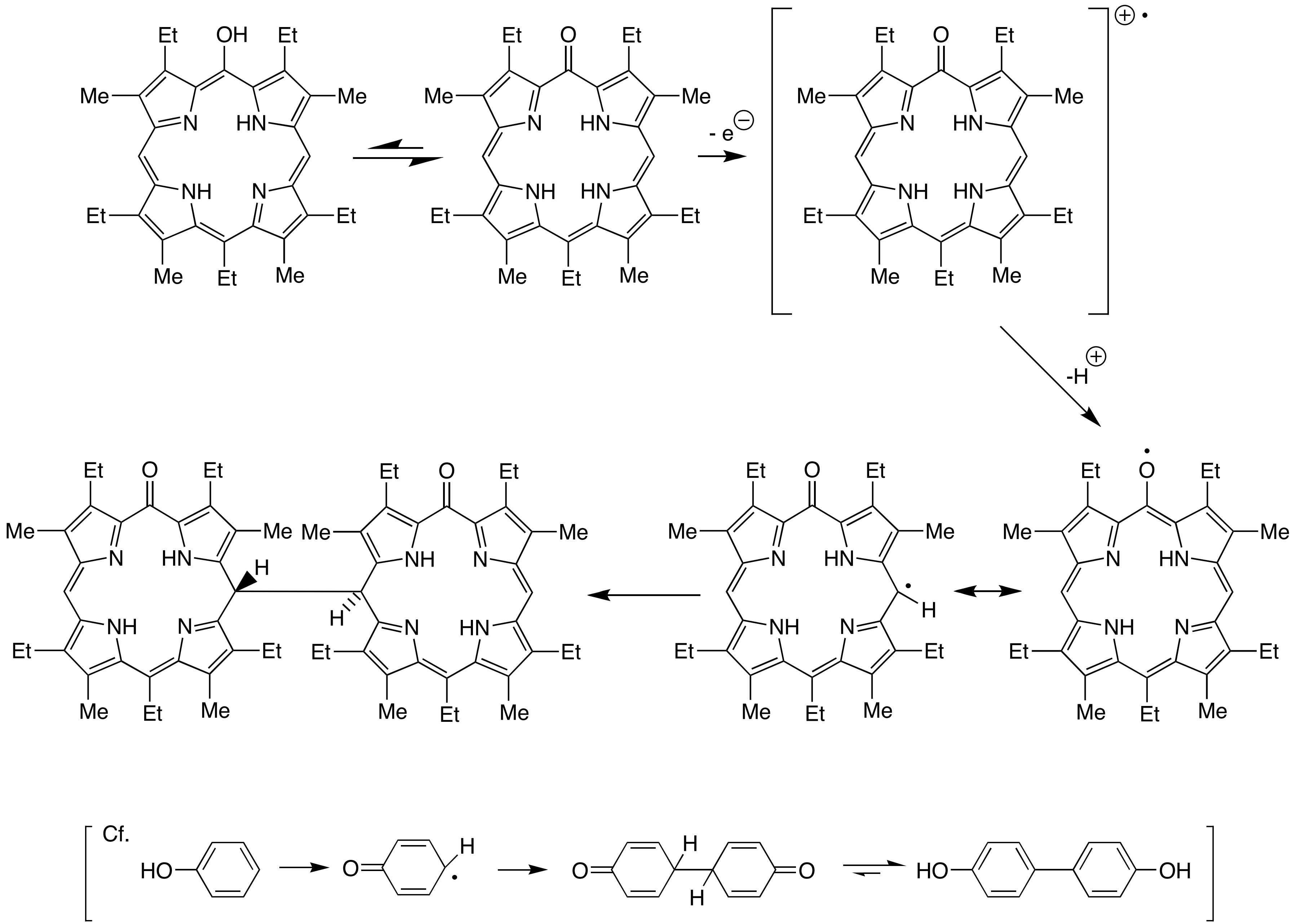
R. G. Khoury, L. Jaquinod, A. M. Shachter, N. Y. Nelson and K. M. Smith. *Chem. Commun.* **1997**, 215.



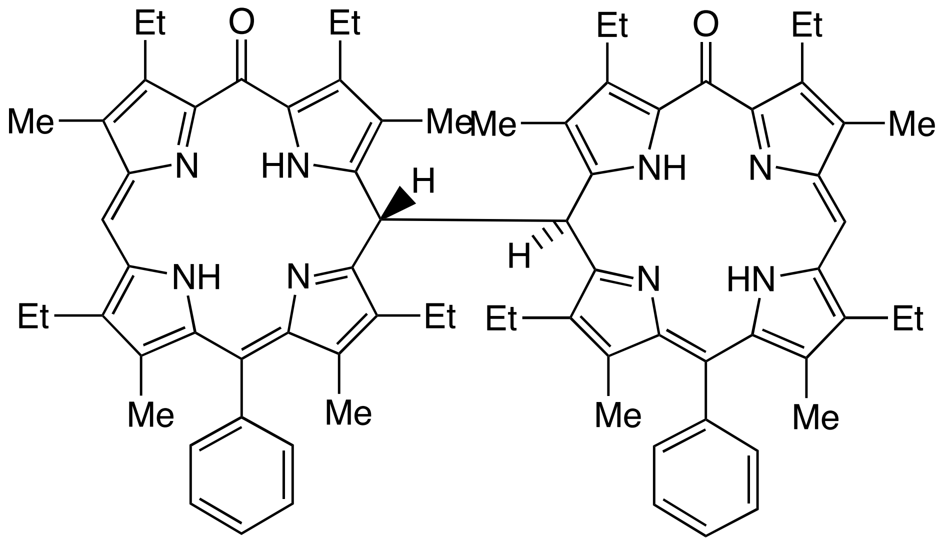




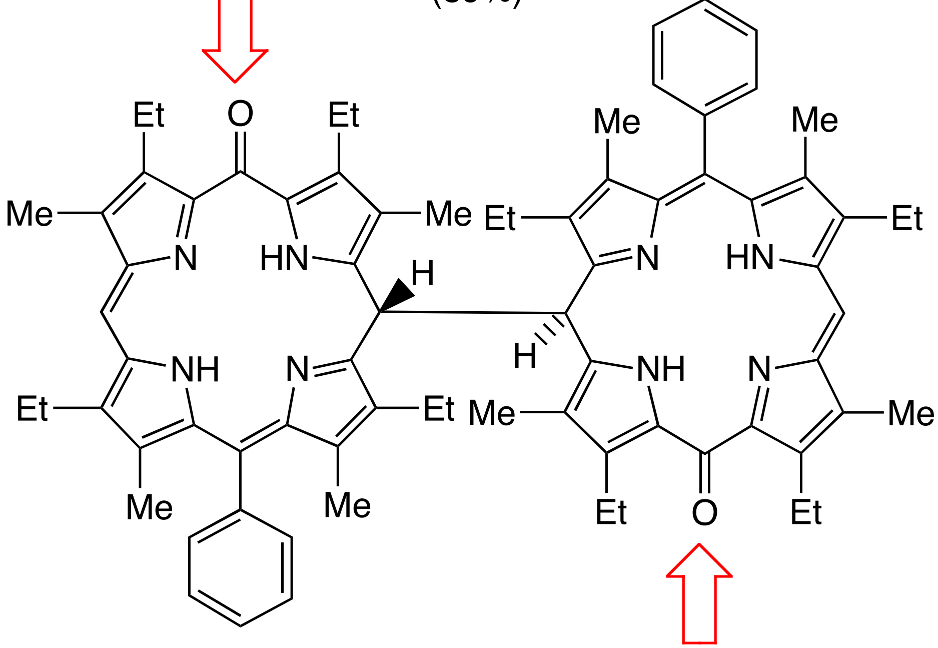
"A Dimer" (25%)

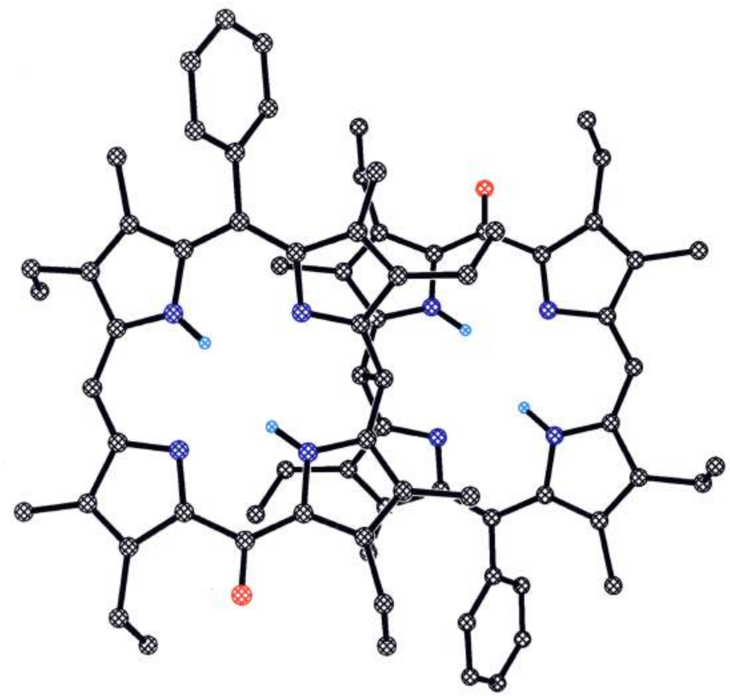


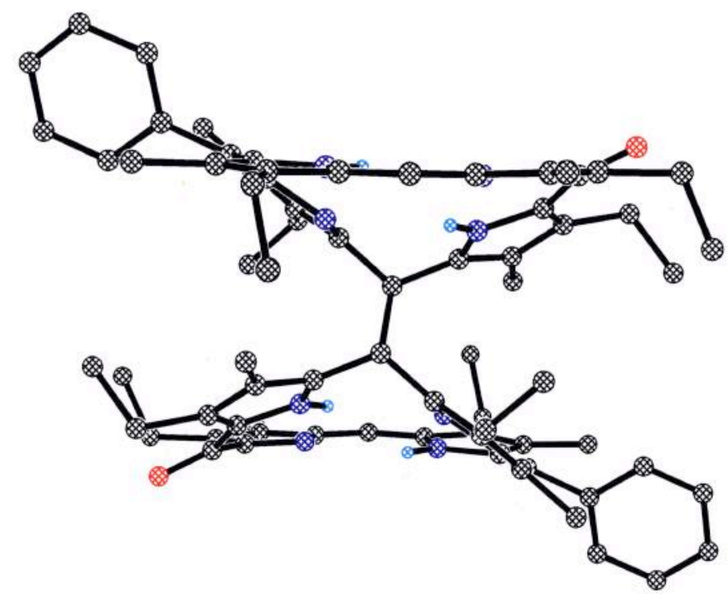
- e
-H
Cf.

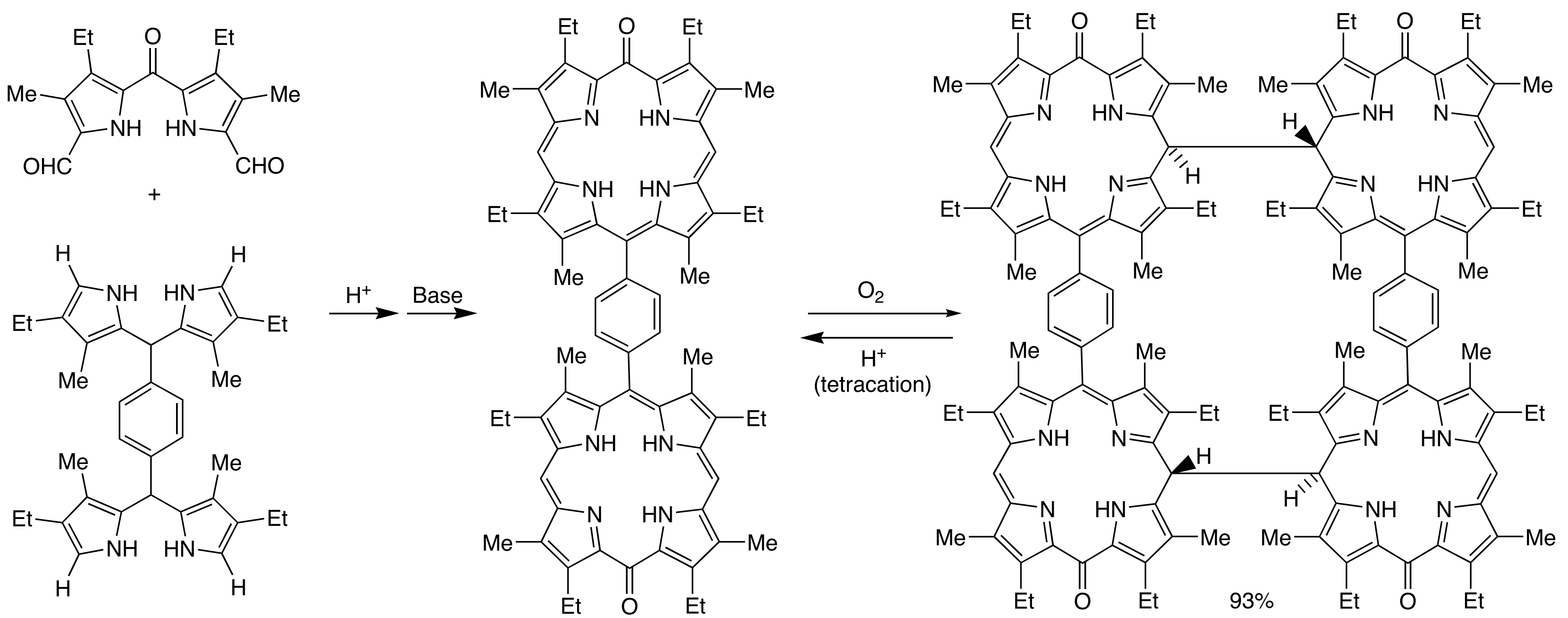


(89%)

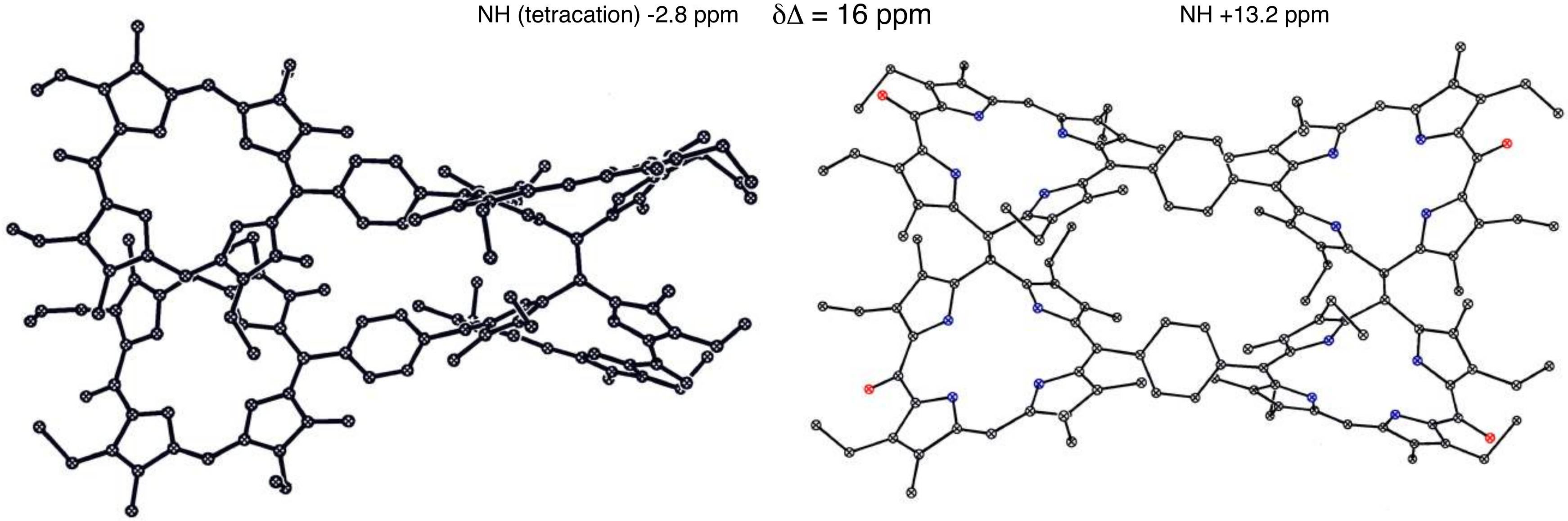






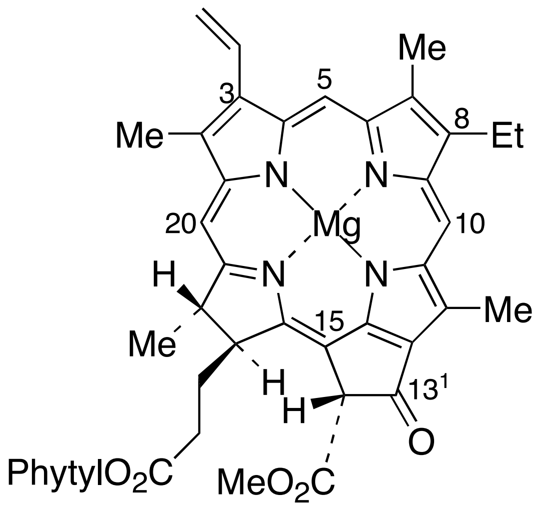


NH (tetracation) -2.8 ppm δΔ = 16 ppm NH +13.2 ppm

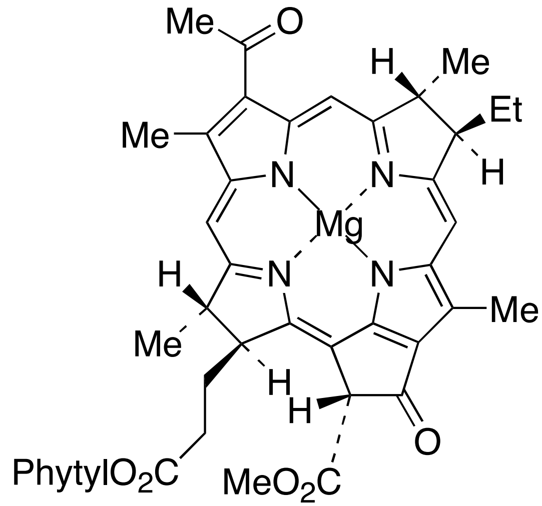


R. G. Khoury, L. Jaquinod, D. J. Nurco, R. K. Pandey and K. M. Smith. *Angew. Chem. Int. Edn Engl.* **1996**, *35*, 2496.
R. G. Khoury, L. Jaquinod, R. Paolesse and K. M. Smith. *Tetrahedron* **1999**, *55*, 6713.

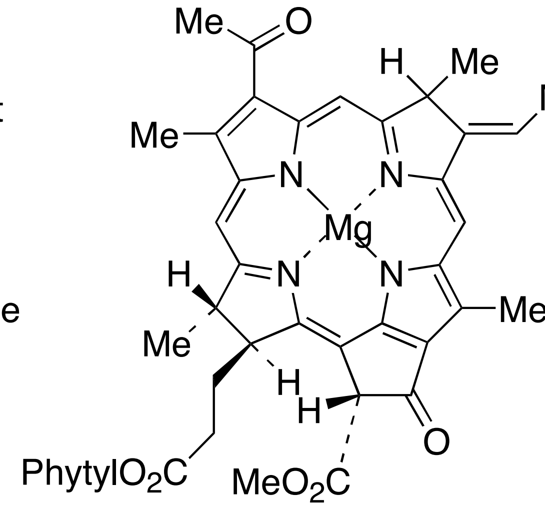
Chlorosomal Chlorophylls



Chl-a

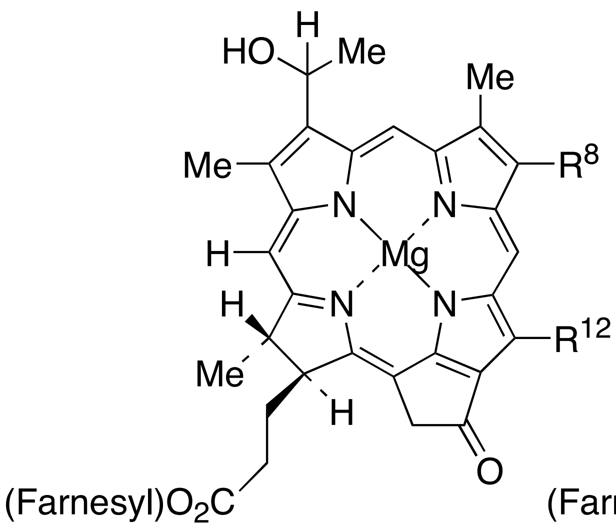


Bchl-a

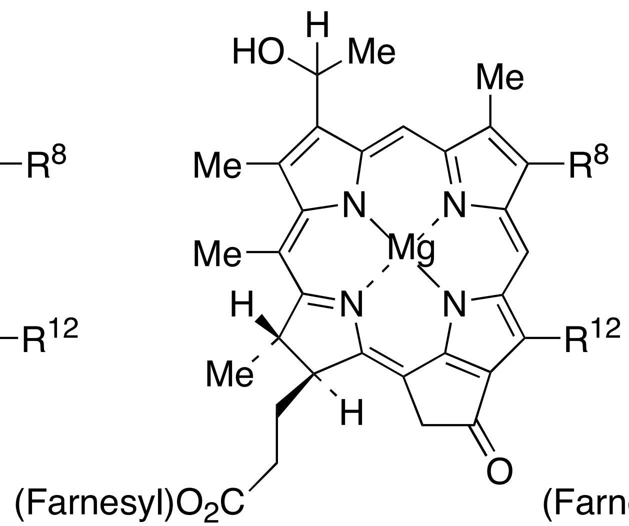


Bchl-b

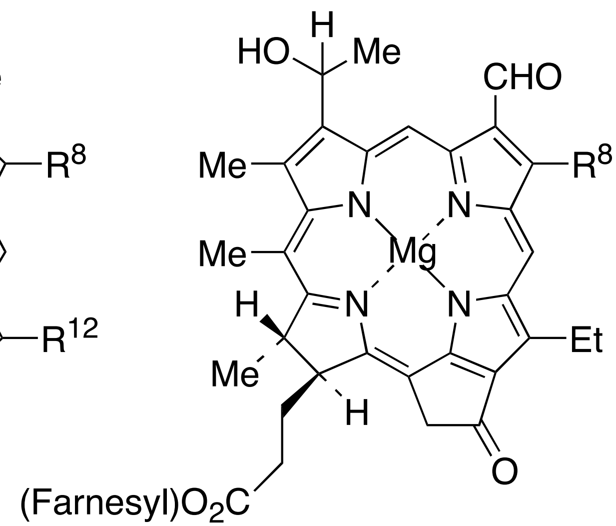
"Chlorobium" (Chlorosome) Chlorophylls:



Bchls-d



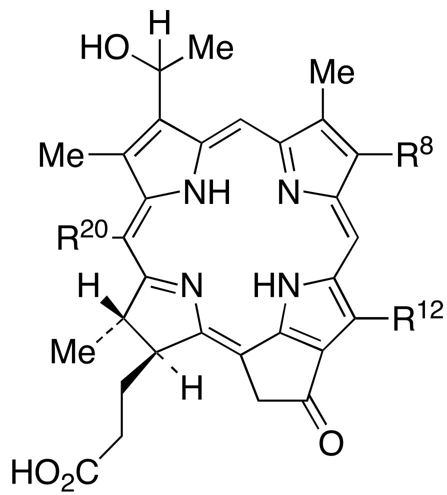
Bchls-c



Bchls-e

R^8, R^{12} = alkyl homologues, Me, Et, Pr, i-Bu, etc.

Holt's Assignments for the CbChl 650 (Bchl-d) and CbChl 660 (Bchl-c)



	"650" Series			"660" Series		
Band	R^8	R^{12}	R^{20}	R^8	R^{12}	R^{20}
1	$CH_2CH(Me)_2$	CH_2CH_3	H	$CH_2CH(Me)_2$	CH_2CH_3	CH_3
2	$CH_2CH_2CH_3$	CH_2CH_3	H	$CH_2CH(Me)_2$	CH_2CH_3	CH_2CH_3
3	$CH_2CH(Me)_2$	CH_3	H	$CH_2CH_2CH_3$	CH_2CH_3	CH_3
4	CH_2CH_3	CH_2CH_3	H	$CH_2CH_2CH_3$	CH_2CH_3	CH_2CH_3
5	$CH_2CH_2CH_3$	CH_3	H	CH_2CH_3	CH_2CH_3	CH_3
6	CH_2CH_3	CH_3	H	CH_2CH_3	CH_3	CH_3

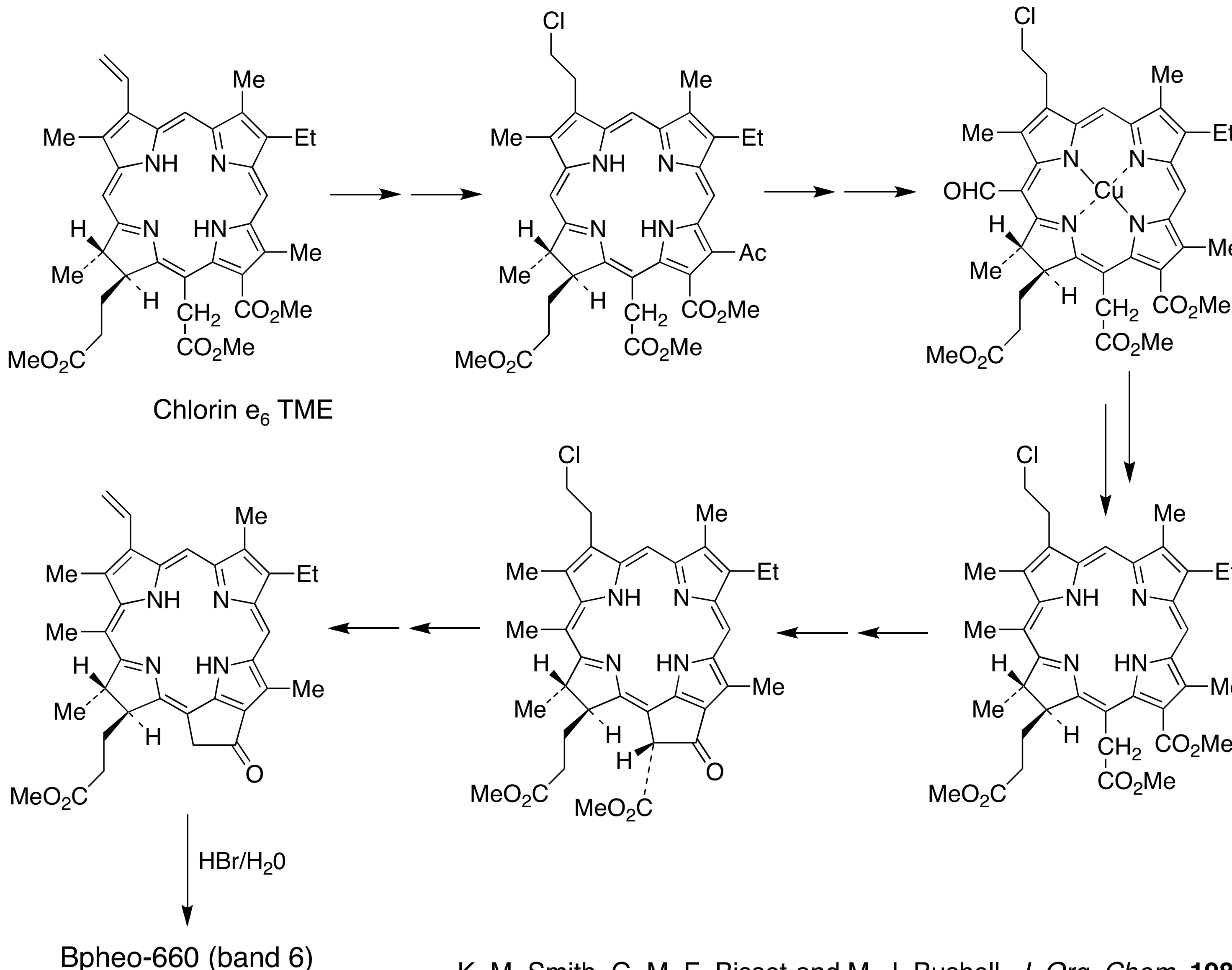
A. S. Holt, in *Chemistry and Biochemistry of Plant Pigments*, 1965, pp 3-28.

Mass Spectra of Selected Chromatographic Bands (1965)

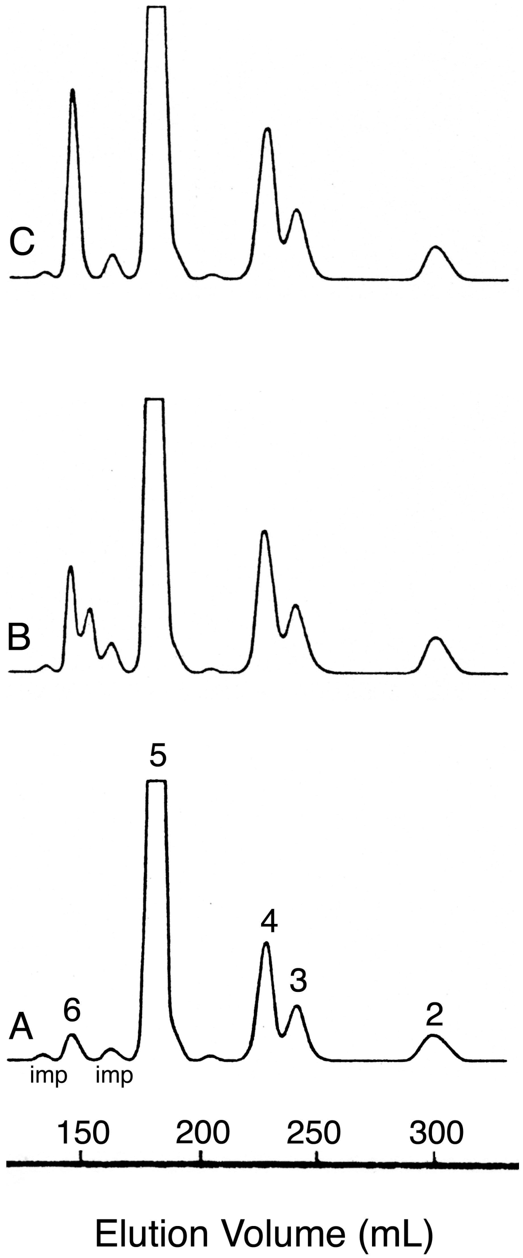
Compound	Molecular Ion (*m/e*) Proposed	Observed	Comment
"650" Series (Bchl-d)			
Band 1 methyl pheophorbide	608	608	√
Band 2 methyl pheophorbide	594	594	√
Band 3 methyl pheophorbide	594	594	√
Band 4 methyl pheophorbide	580	580	√
Band 6 methyl pheophorbide	566	566	√
"660" Series (Bchl-c)			
Band 2 methyl pheophorbide	636	622	?
Band 4 methyl pheophorbide	622	608	?
Band 5 methyl pheophorbide	594	594	√
Band 6 methyl pheophorbide	580	580	√

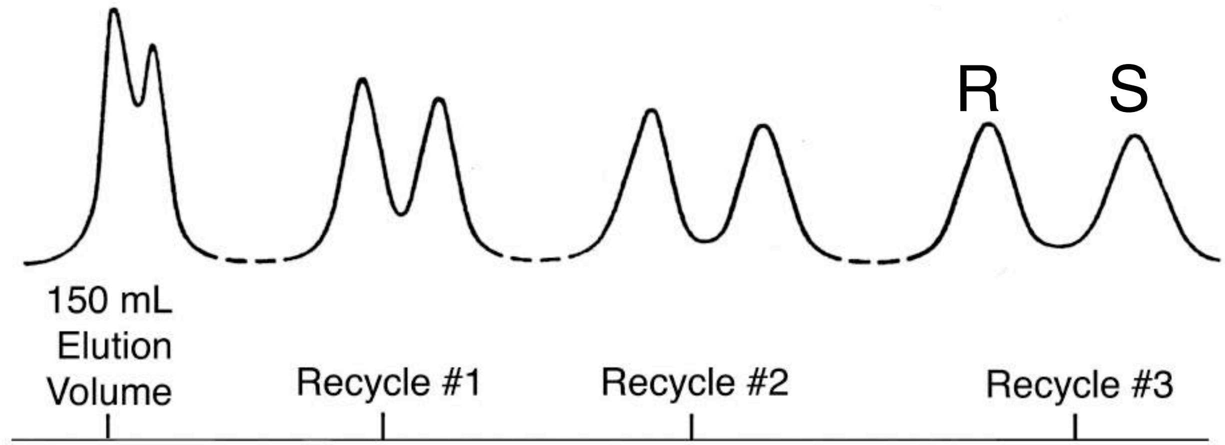
Table: Holt's Calculated and Smith's Observed Molecular Weights for Pheophorbide Degradation Products from the Chlorobium Chlorophylls "650" and "660". Note that samples from chromatographic bands 1 and 3 were "not available" according to the Ottawa group (Holt).

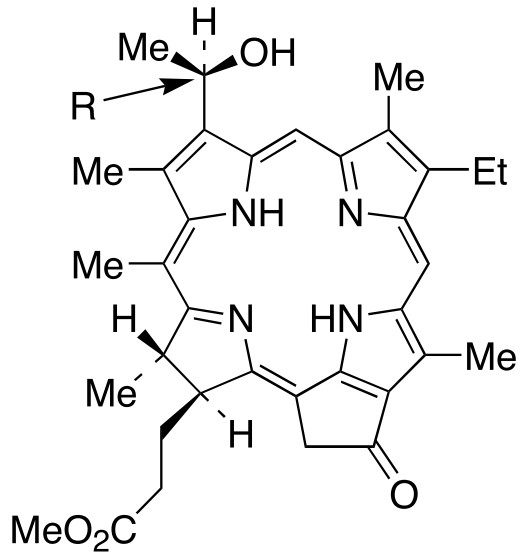
Conversion of Chl-a Series Compound into a Bchl-c Pheophorbide

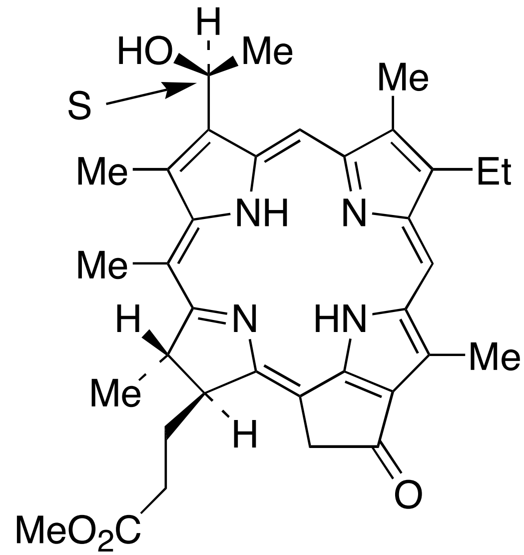


K. M. Smith, G. M. F. Bisset and M. J. Bushell. *J. Org. Chem.* **1980**, *45*, 2218.
K. M. Smith, D. A. Goff and D. J. Simpson. *J. Am. Chem. Soc.* **1985**, *107*, 4946.









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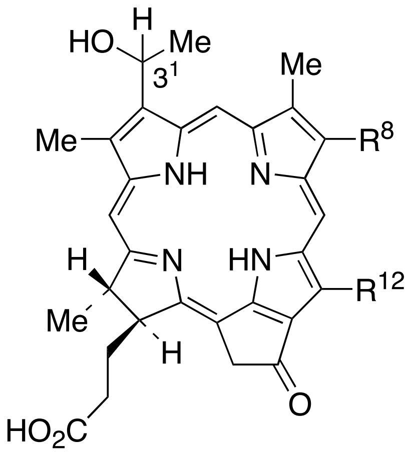
Bchl-d Series



Band	R^8	R^{12}	Config. at position-3^1
6	Et	Me	R
5	Et	Et	R
4	Pr	Me	R
3	Pr	Et	R
2	i-Bu	Me	S
1	i-Bu	Et	S
new	neo-Pn	Me	S
new	neo-Pn	Et	S

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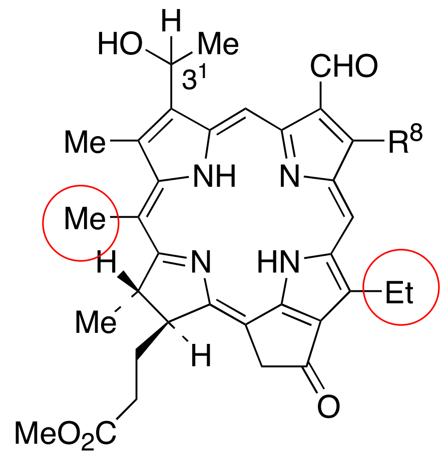
Bchl-e Series



R^8	3^1-R	3^1-S
i-Bu	2%	98%
Pr	40%	60%
Et	95%	5%

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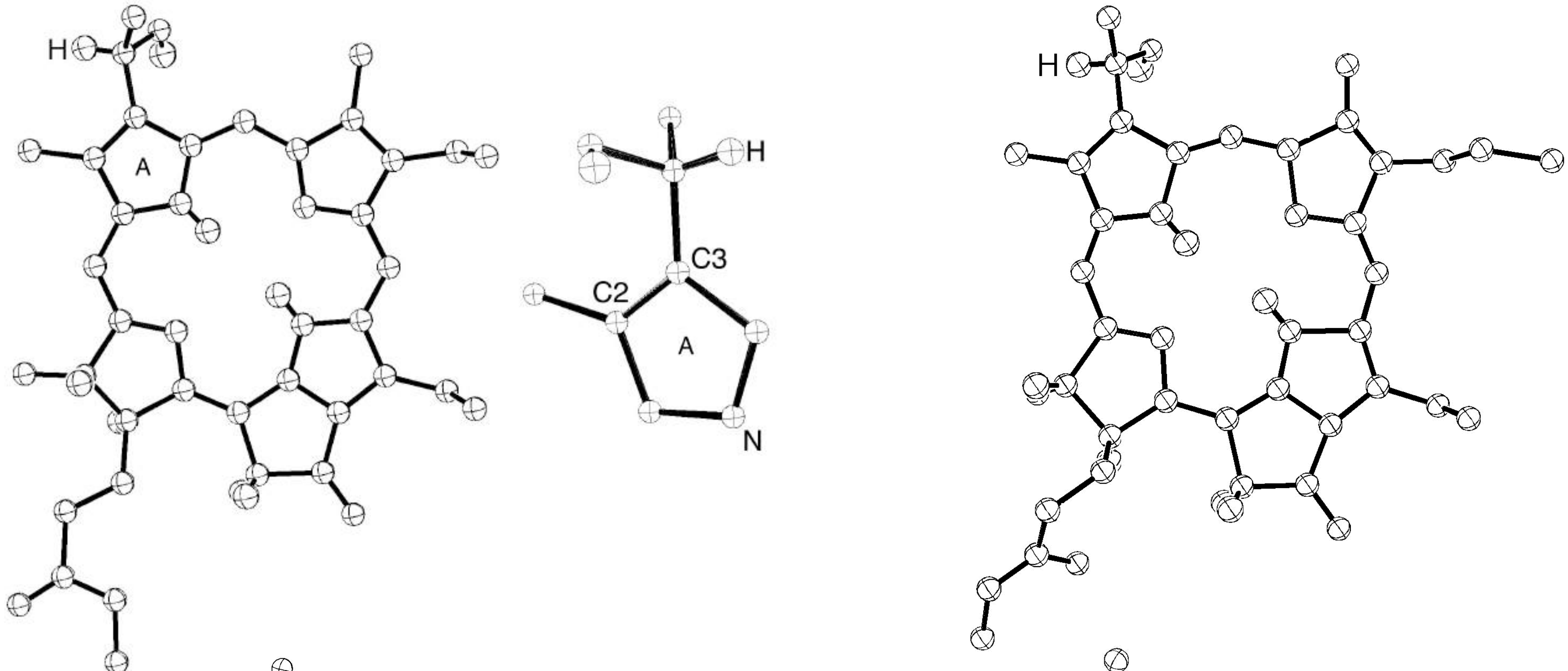

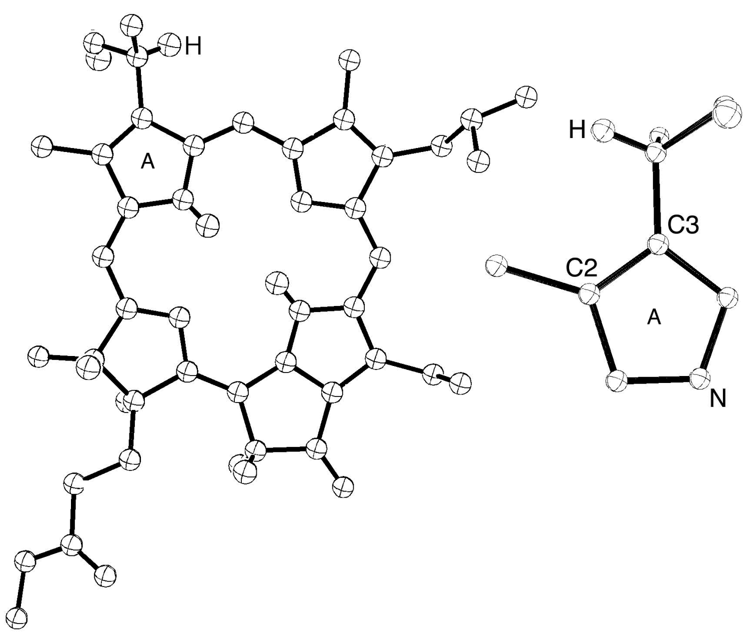

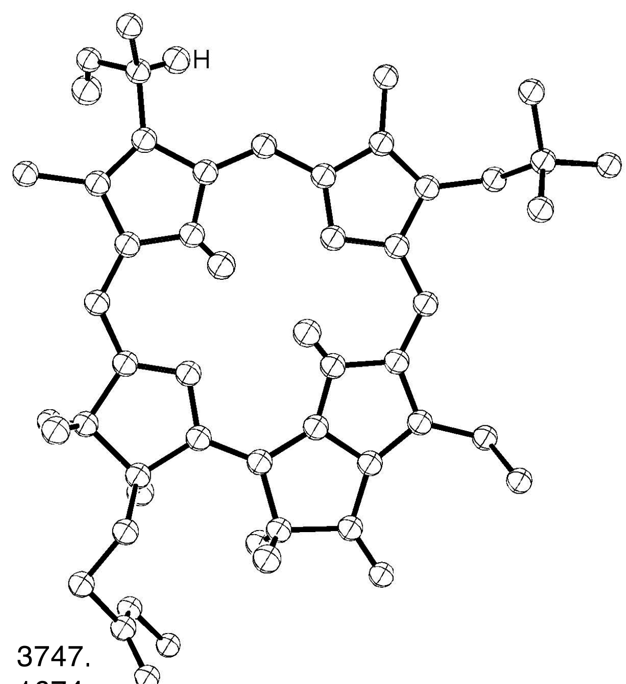

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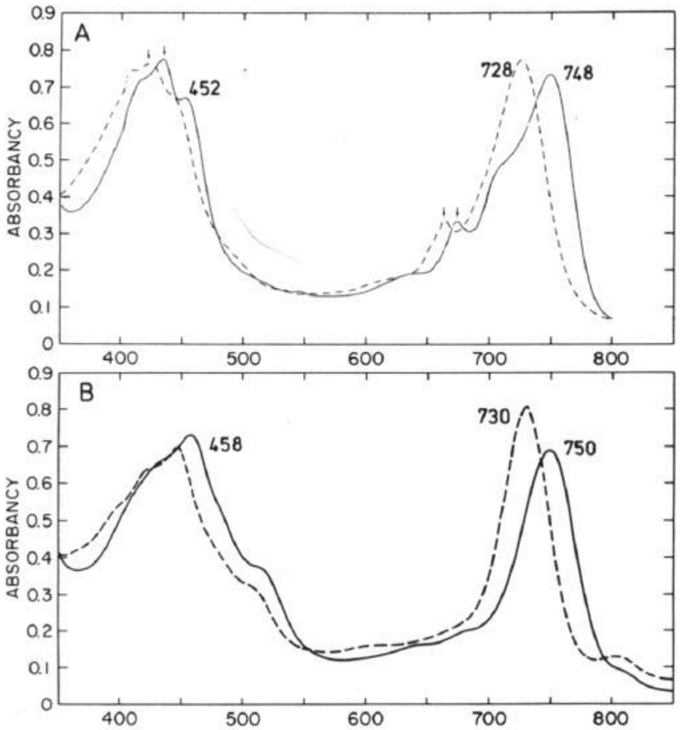
K. M. Smith, D. A. Goff, J. Fajer and K. M. Barkigia. *J. Am. Chem. Soc.* **1983**, *105*, 1674.



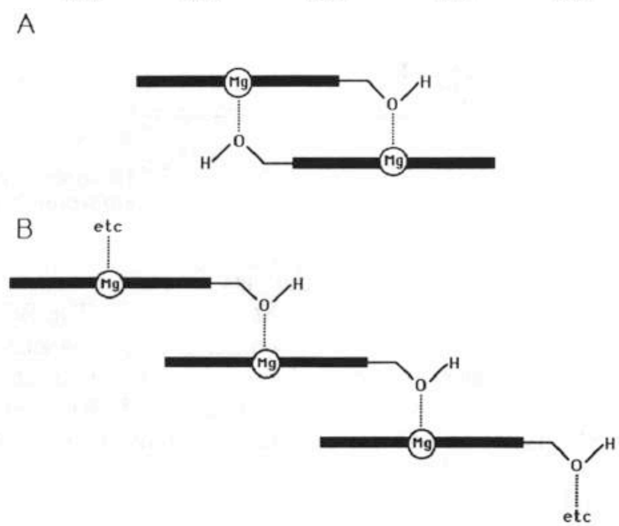


FIGURE 10: Major interactions responsible for aggregate formation in BChl-c, -d, and -e: (A) dimers; (B) higher oligomers. In (B) the opportunity is also present for the isocyclic ring carbonyl to coordinate with the magnesium in the BChl above.

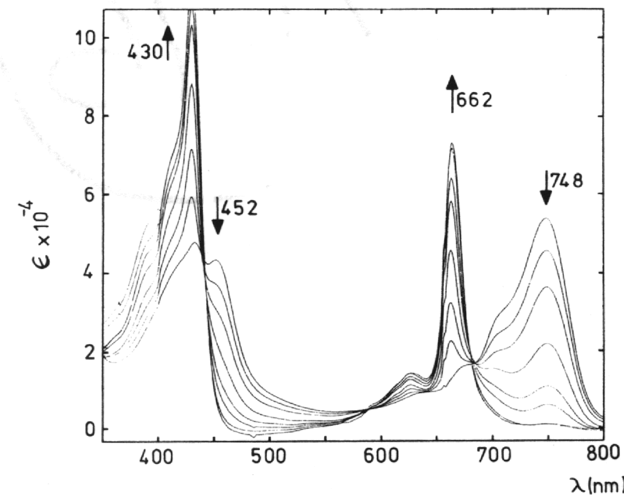


Figure 1. Spectrophotometric titration of a 1.95×10^{-5} M solution of bacteriochlorophylls *c* (**1**) in hexane–methylene chloride (200:1). During the titration, 1-μL aliquots of methanol were added to a 1-cm cell containing 4 mL of solution.

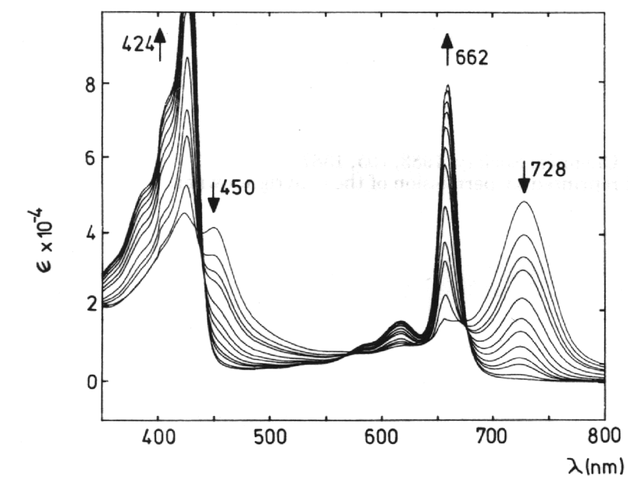


Figure 2. Spectrophotometric titration of a 1.65×10^{-5} M solution of zinc(II) methyl bacteriopheorbides *c* in hexane–methylene chloride (200:1). During the titration, 1-μL aliquots of methanol were added to a 1-cm cell containing 4 mL of solution.

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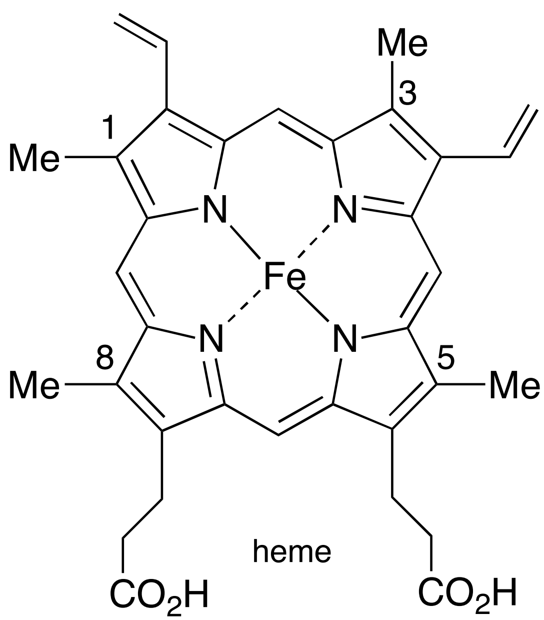
Isotope labeling of protoporphyrin IX



Fischer nomenclature

Hemoglobins
Myoglobins
Cytochromes
Catalases
Peroxidases

Smith Accounts of Chemical Research

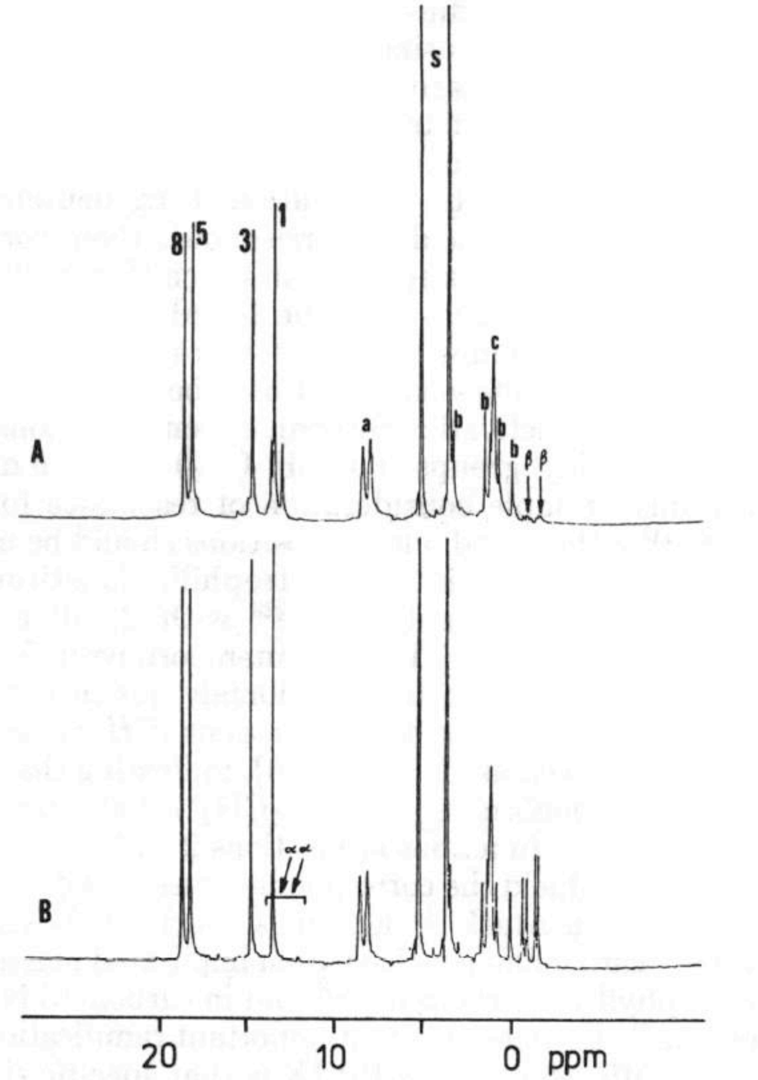
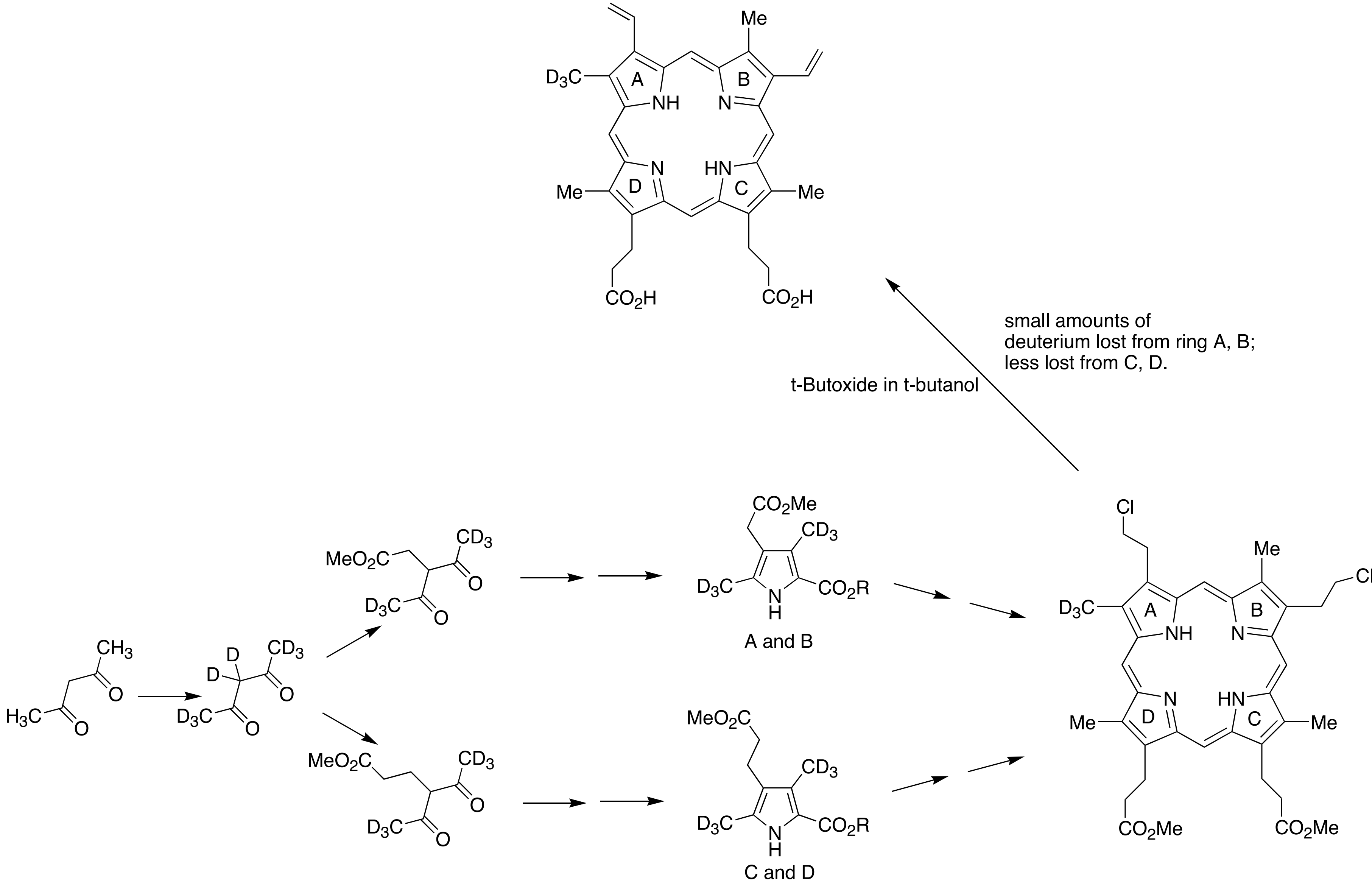


Figure 1. 100-MHz proton NMR spectra, in CD_3OD, of the dicyanoferrihemes from (A) PP-IX with vinyl H_β deuterated; (B) PP-IX with vinyl-H_α deuterated. Assignments: 8, 5, 3, 1, ring methyls; a, propionic α-CH_2; b, meso H; c, propionic β-CH_2; S solvent.



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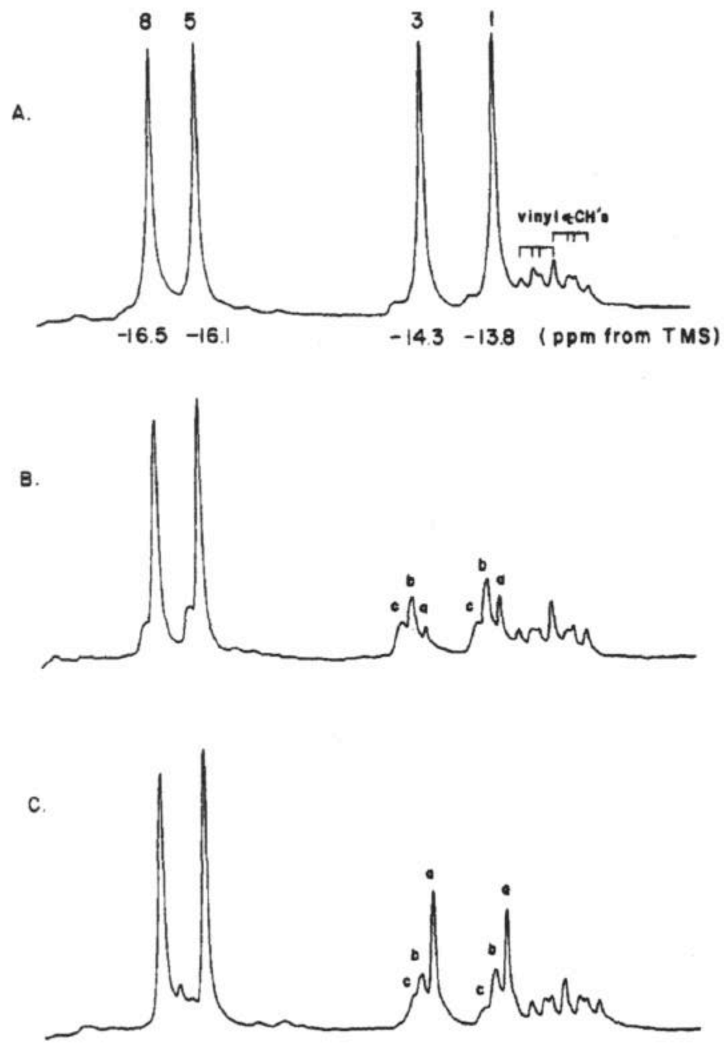
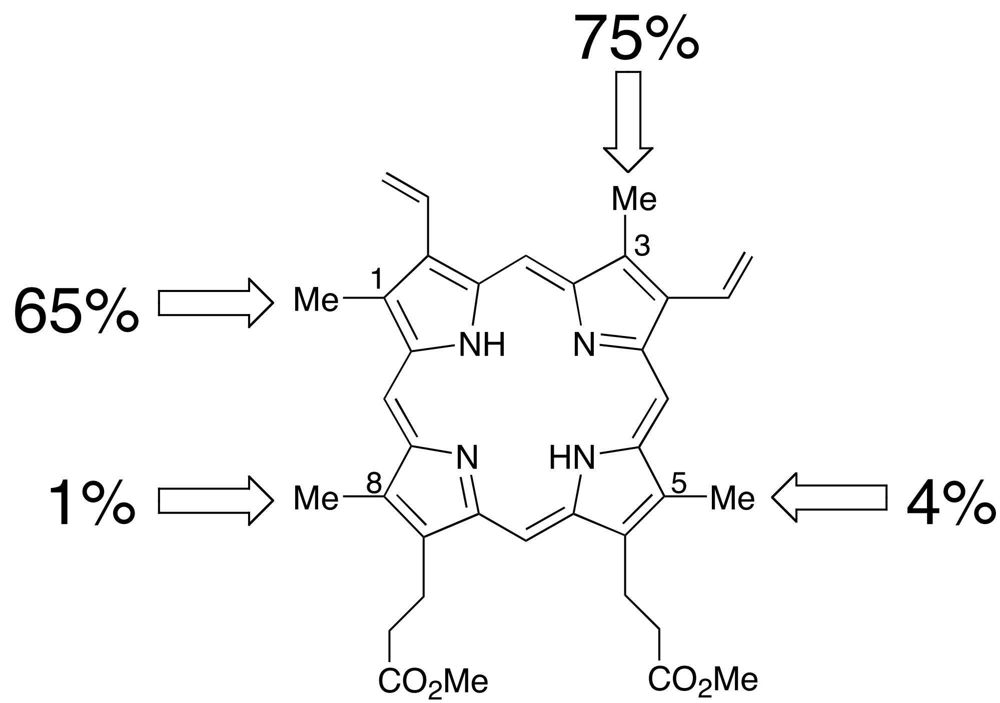


Figure 1. ^{1}H NMR traces of the ring methyl region (8–18 ppm downfield from TMS) of protoporphyrin IX iron(III) dicyanide (**4**), A; for a sample of **4** treated with CH_3ONa/CH_3OD to partially deuterate 1,3-methyls, B; and for a sample of **4** 90% deuterated at 1,3-methyls and then reprotonated via treatment with CH_3ONa/CH_3OH, C. All traces are in methanol-d_4 at 25 °C. The peaks a, b, and c for the partially deuterated methyls represent CH_3, CH_2D, and CHD_2, respectively, where the shift differences arise from isotope effects on the contact shift.[9]



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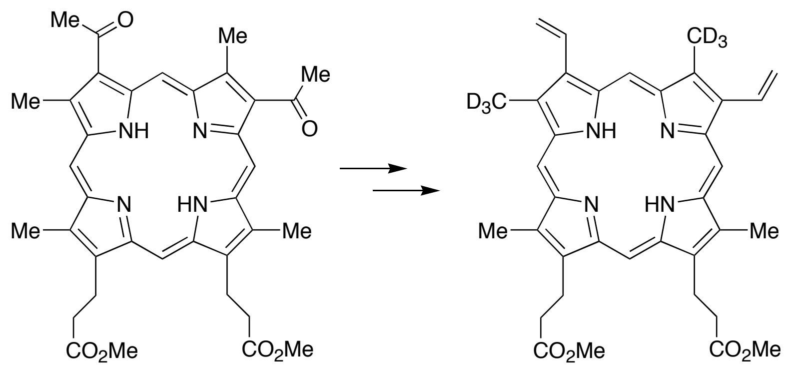

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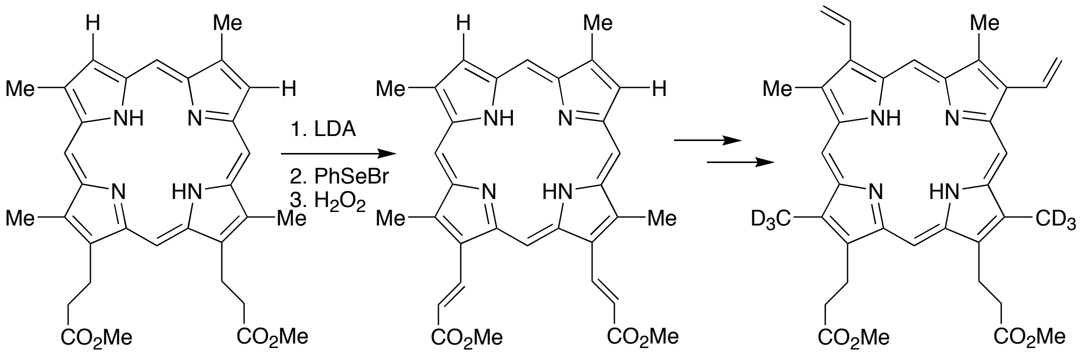

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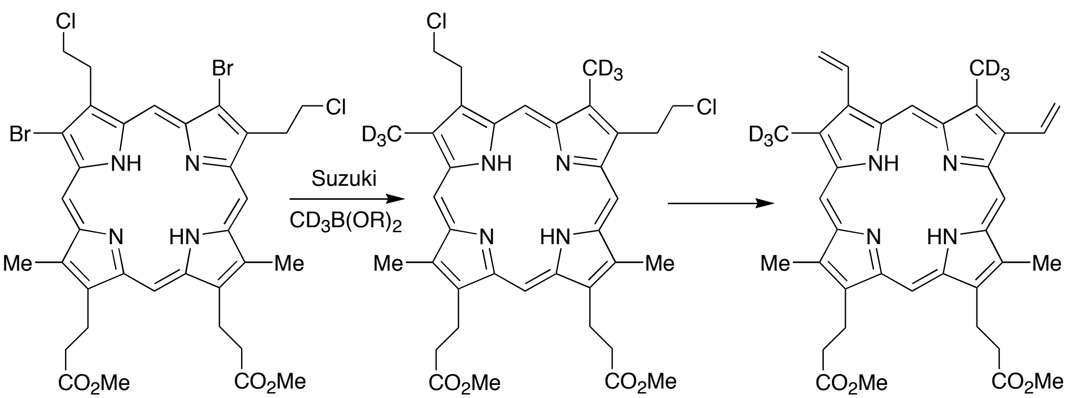

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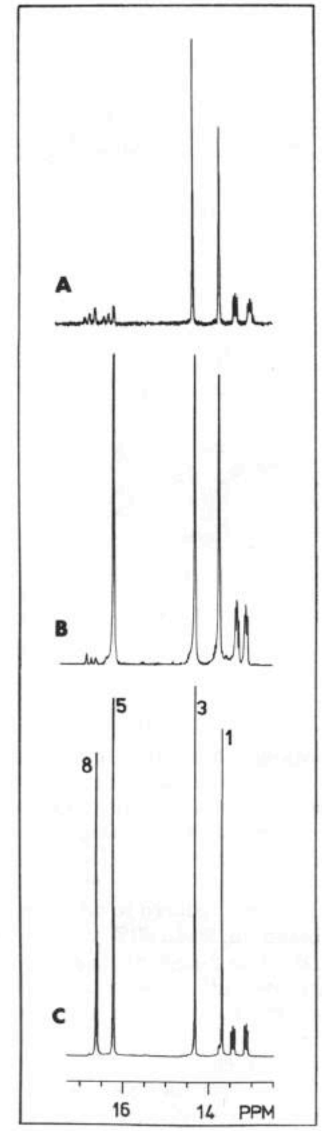

Figure 1. Proton NMR spectra (360 MHz, in methanol-d_4 containing KCN): (A) 5,8-bis(trideuteriomethyl)hemin (**13**); (B) 8-(trideuteriomethyl)hemin (**30**); (C) unlabeled protohemin IX dimethyl ester. Numbers in (C) refer to the methyl assignments;[1] also shown (ca. 13–13.5 ppm) are the vinyl α-CH resonances. Small peaks to low field of exchanged methyls are from the partially deuteriated CH_2D and CHD_2 methyls.

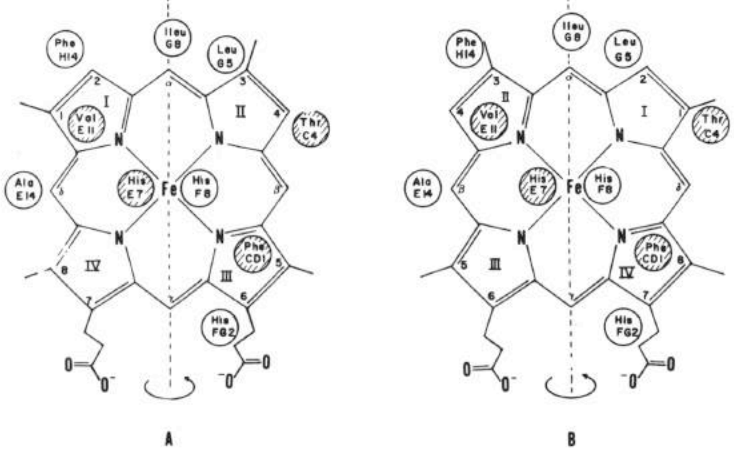

Figure 9. Heme–apoprotein contacts for protoheme in the pocket of sperm whale Mb. Open circles indicate contacts on the proximal side; shaded circles represent contacts on the distal side of the heme. Only the methyl groups and the propionic acid substituents are included to show the case for deuteroheme. (A) Normal orientations as found in the native protein. (B) Reversed orientations, with the heme rotated 180° in the heme pocket about the α,γ axis.

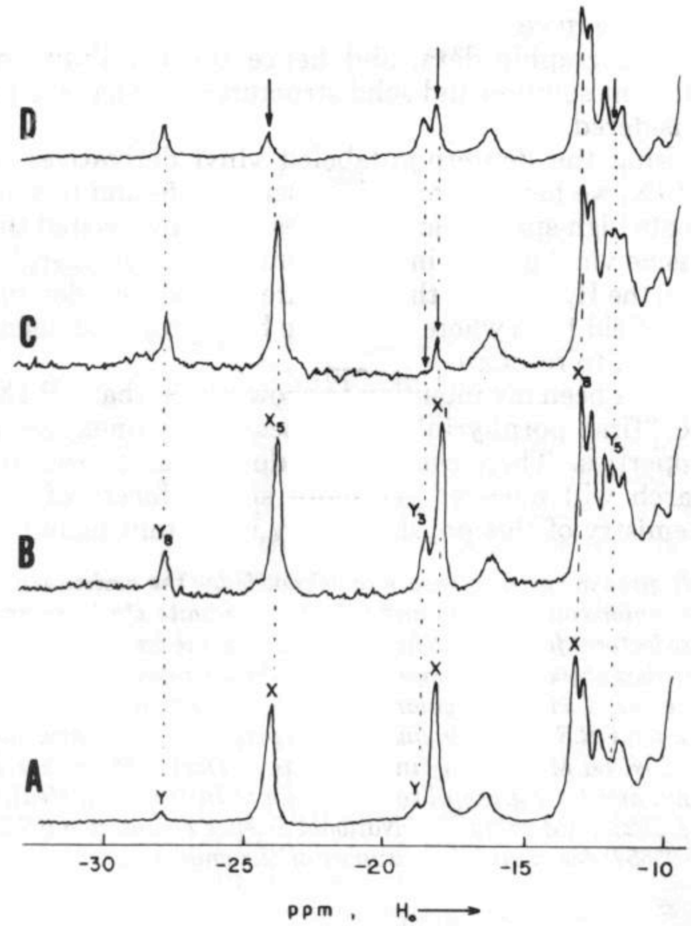

Figure 8. Proton NMR traces of deuteroporphyrin-reconstituted sperm whale metMbCN (deutero-metMbCN), at pH 8.5, 38 °C, in 0.2 M NaCl/D_2O. (A) Protein taken to pH 11.1, KCN added, pH reduced to 7, and mixture stored for several hours, and then adjusted to pH 8.5. One component dominates strongly, although minor peaks, labeled Y, are detectable. (B) Protein taken to pH 11.1, KCN added, and pH readjusted to 8.5; the minor component has increased in intensity and a third peak is evident. (C) 1,3-Deuterated deutero-metMbCN treated as in (B). (D) 1,5-Deuterated deutero-metMbCN treated as in (B). Peaks in (C) and (D) with reduced intensity due to deuterium labeling are indicated with arrows.

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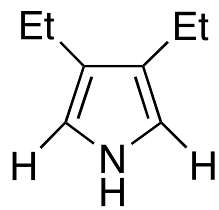
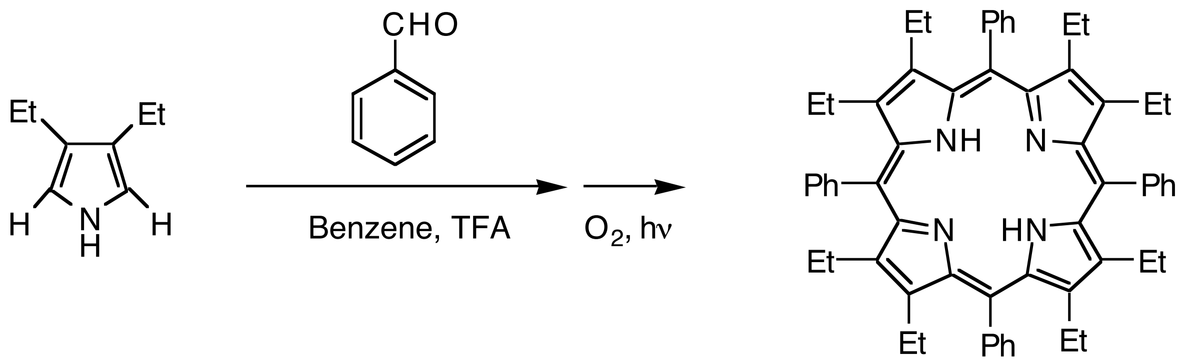
Non-planar porphyrins

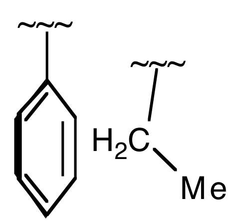




"OETPP"

OCTAETHYLTETRAPHENYLPORPHYRIN (OETPP)

- Red-shifted optical spectrum
- Very strong base (needs NaOH wash to obtain free base)
- $CH_3C\underline{H}_2$ at 0.5-0.25 ppm, i.e.:



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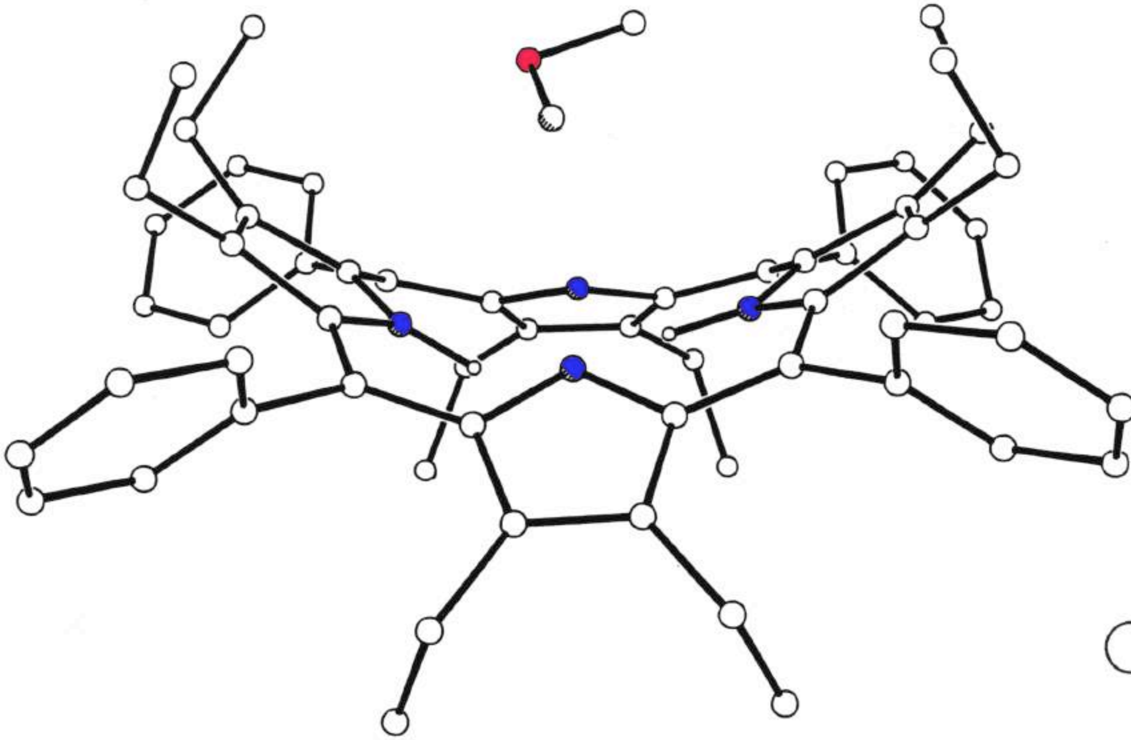

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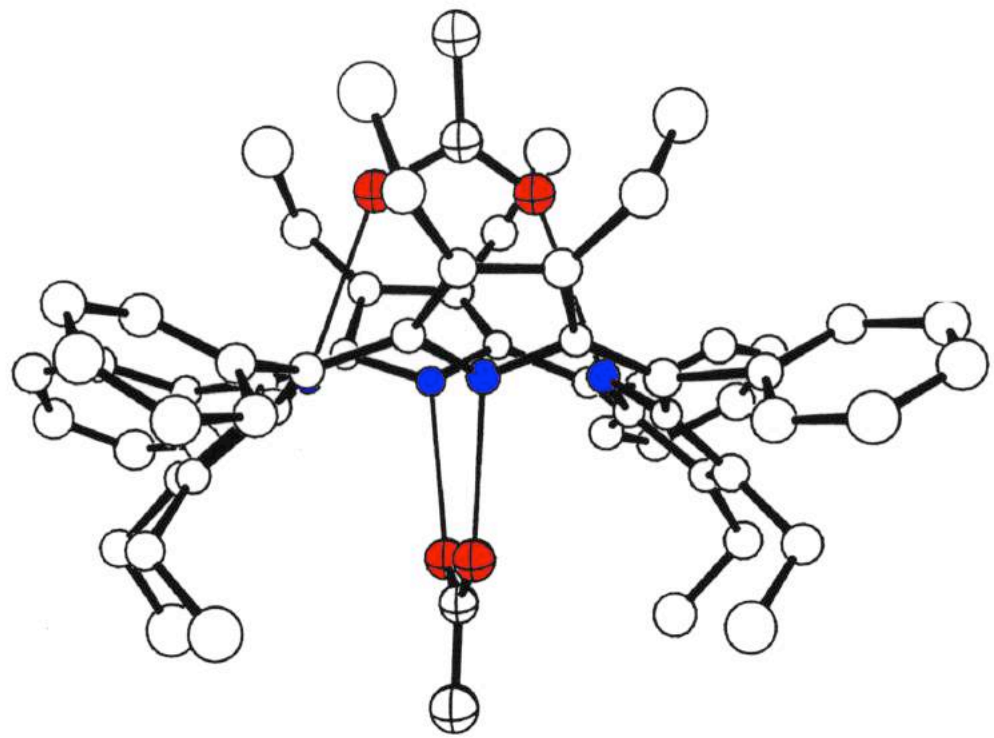

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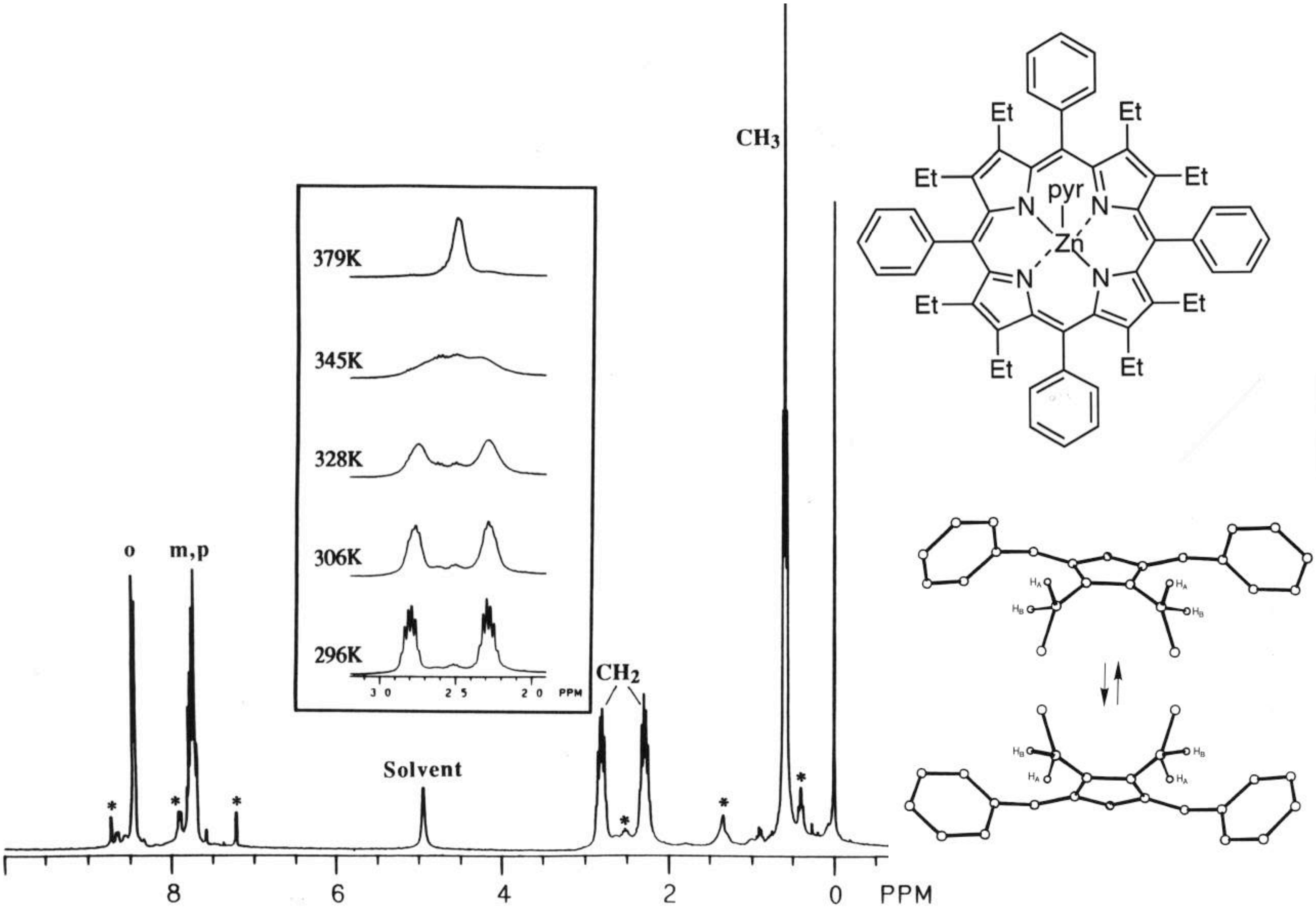

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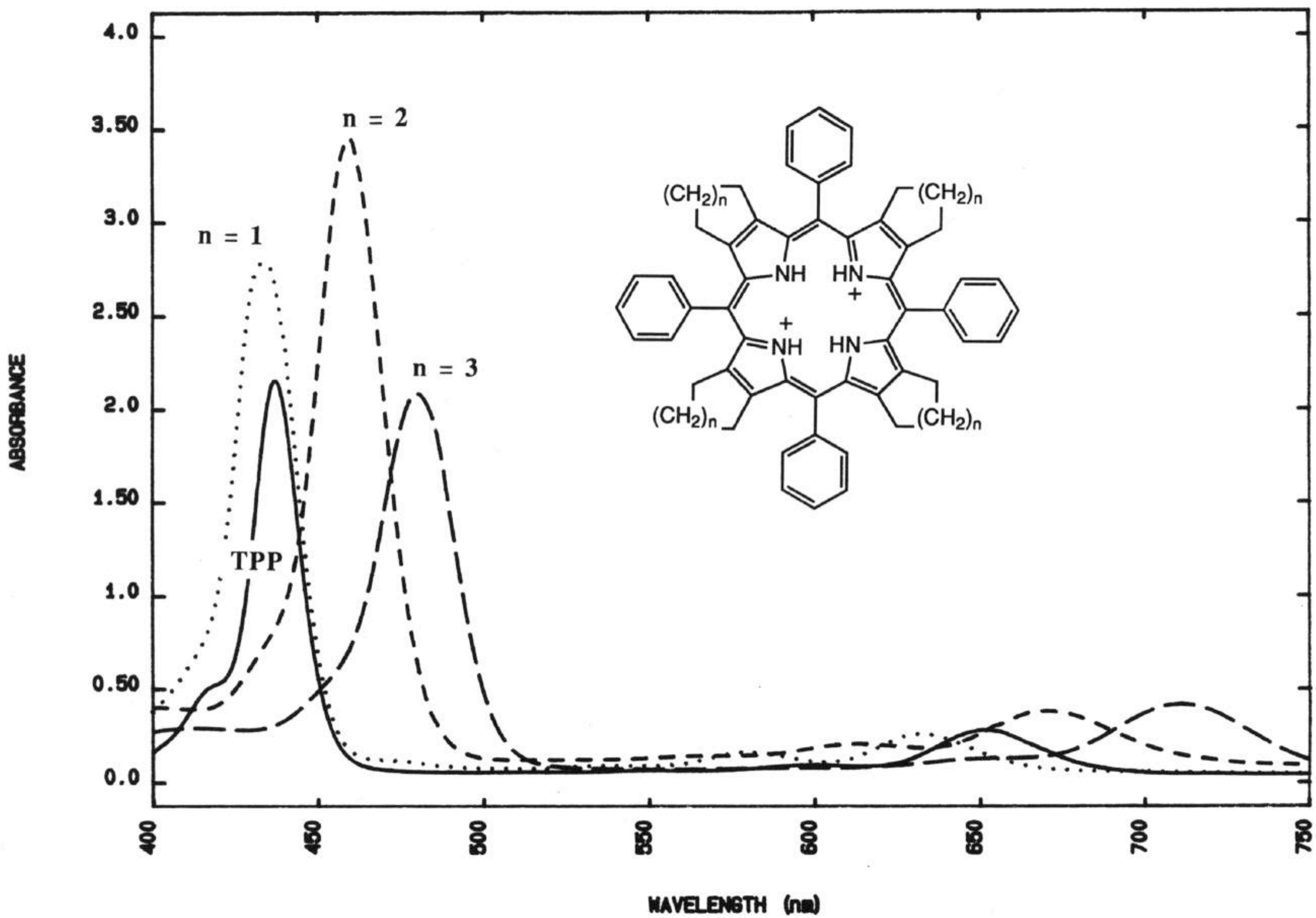

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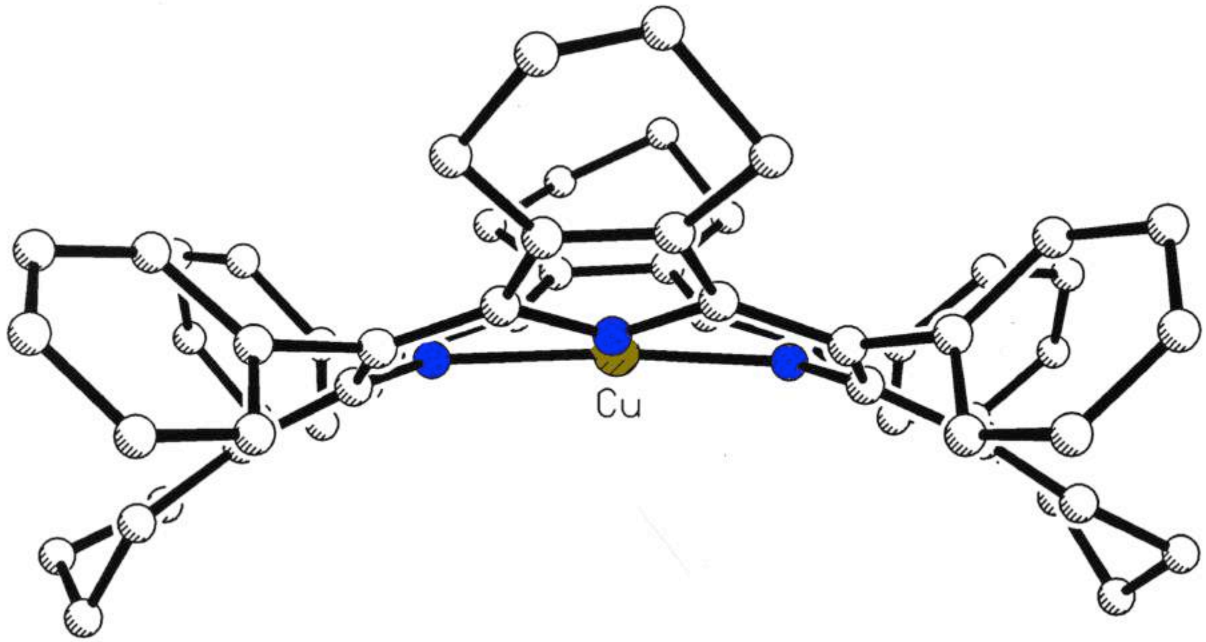

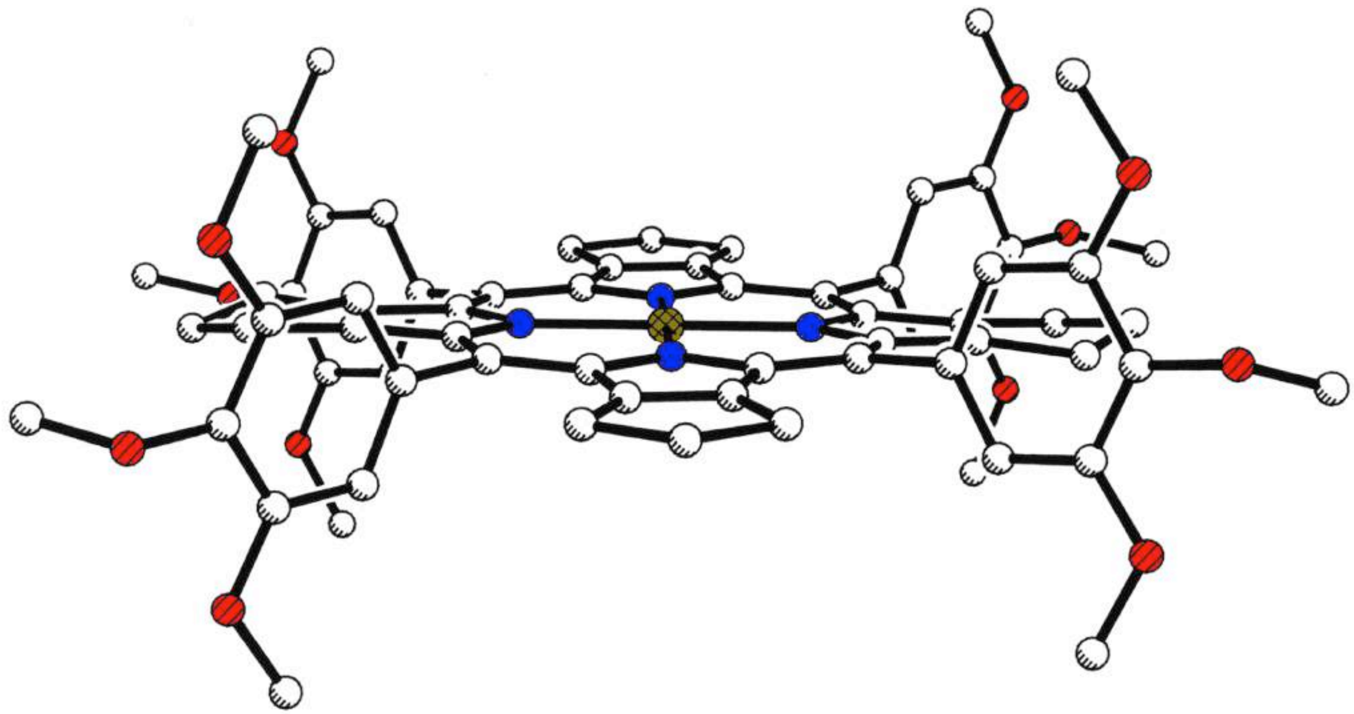

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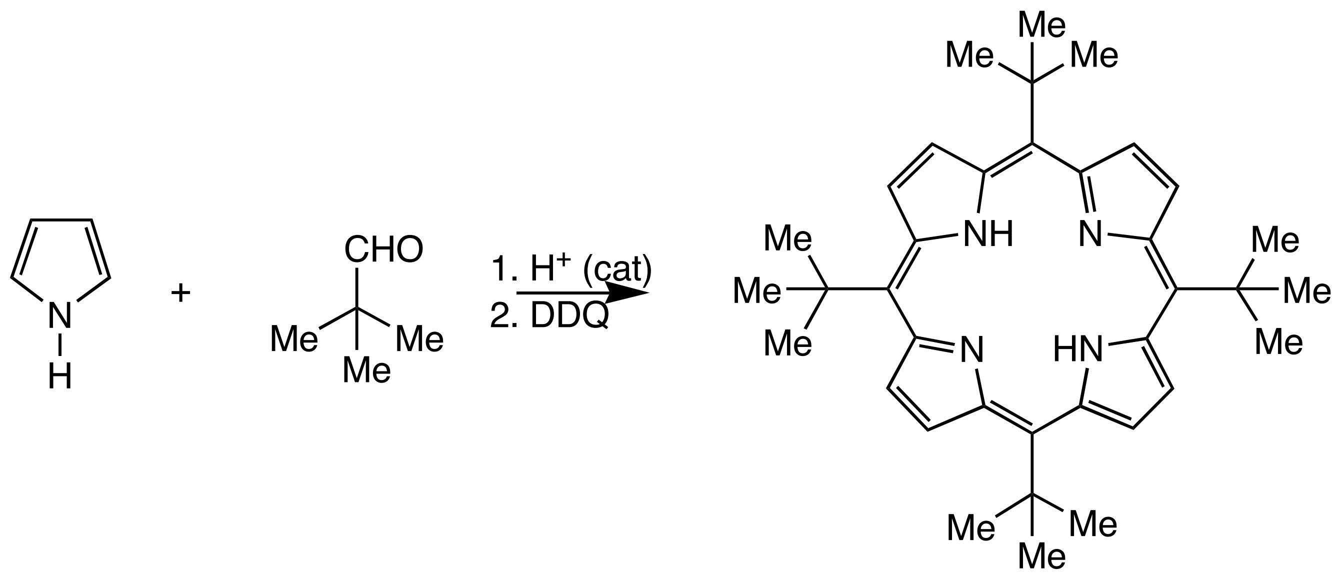
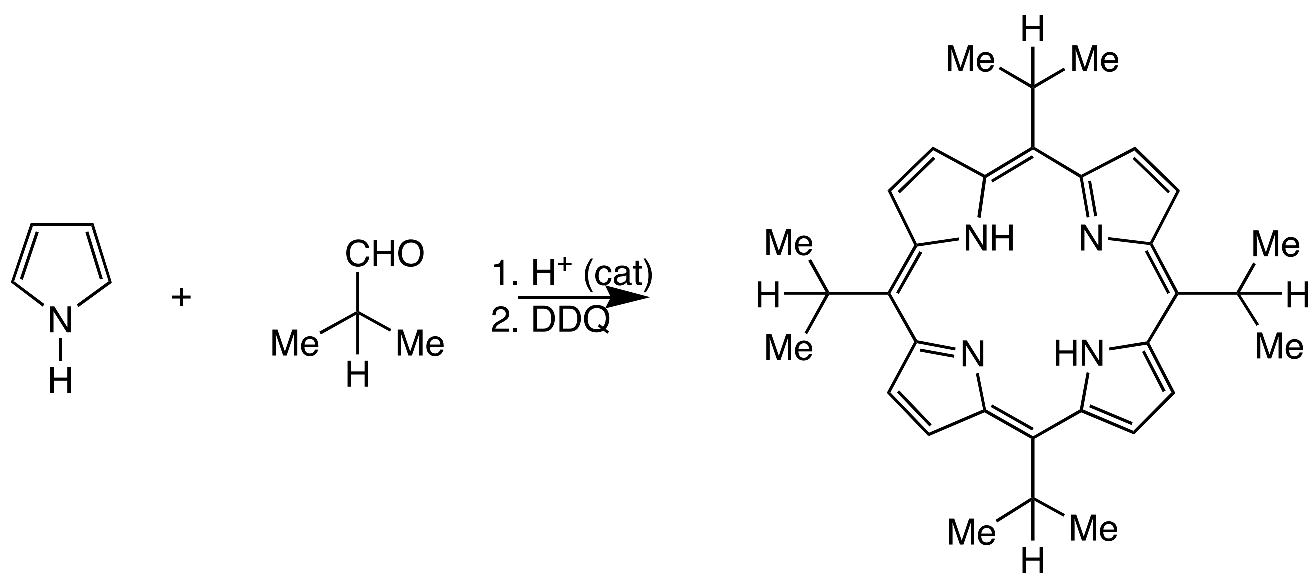


Free-base: λ_{max} 444 nm



Free-base: λ_{max} 418 nm

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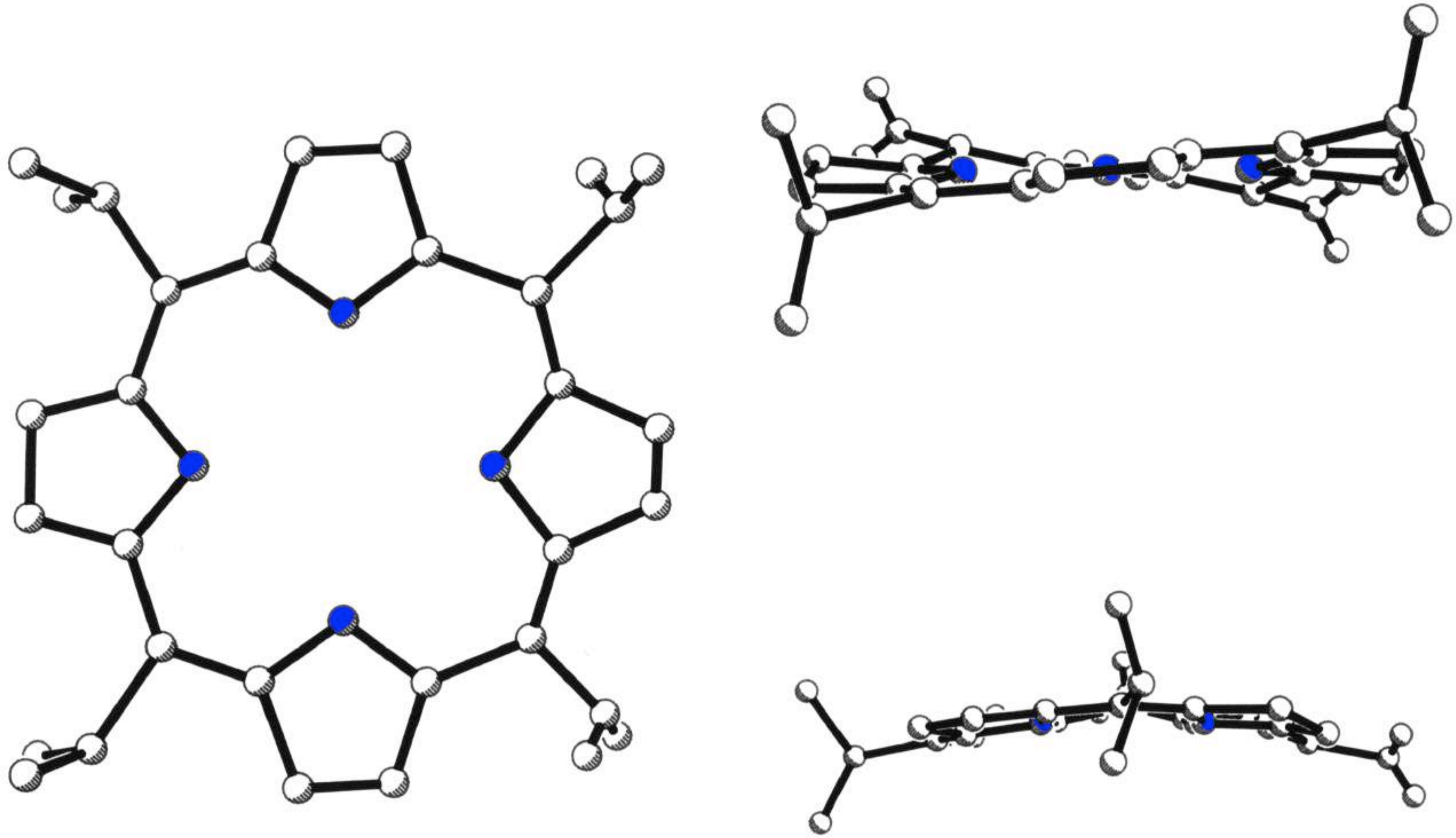

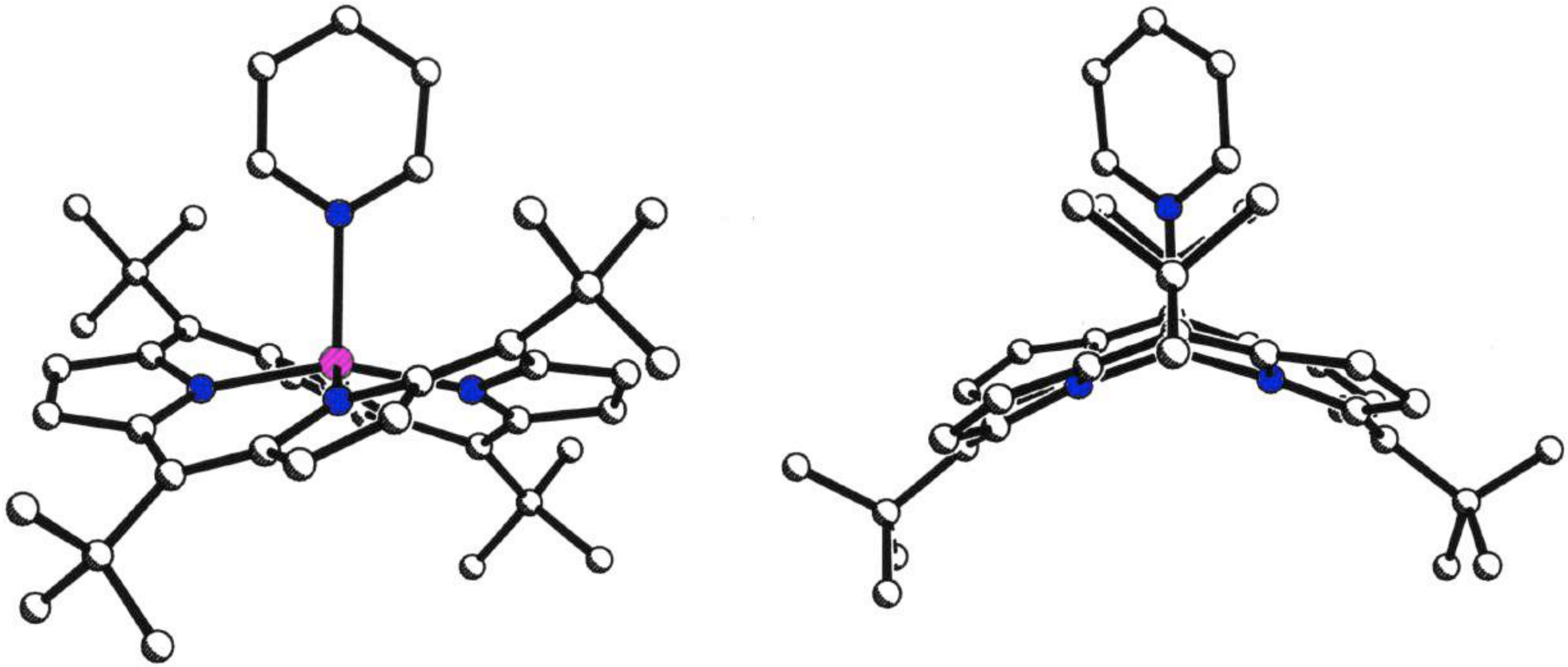

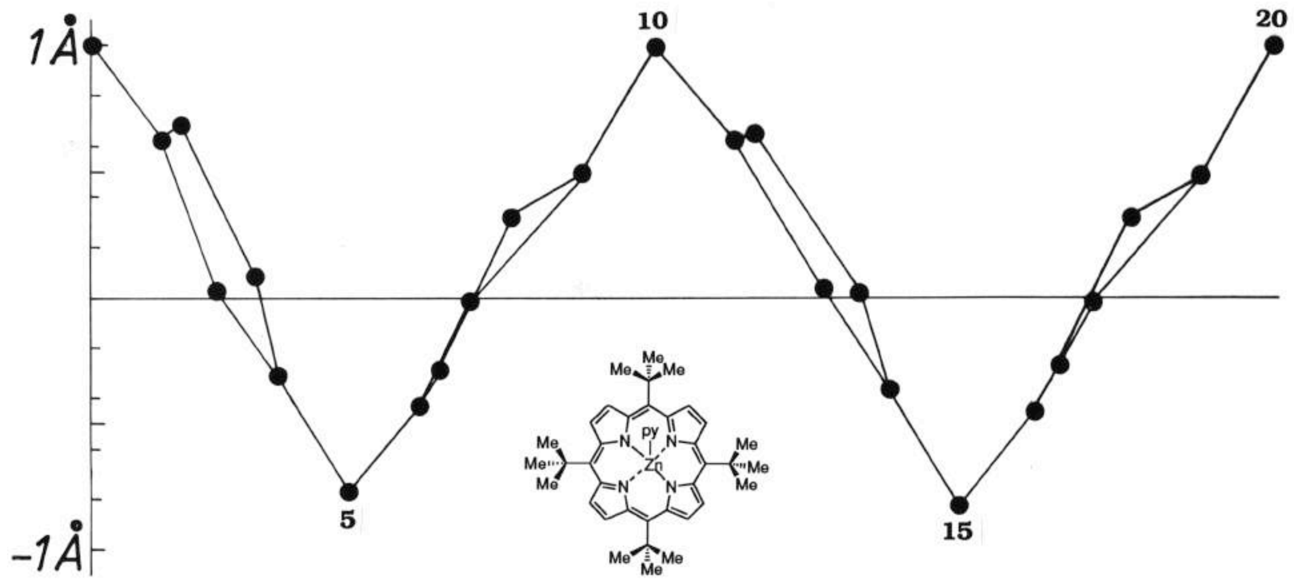

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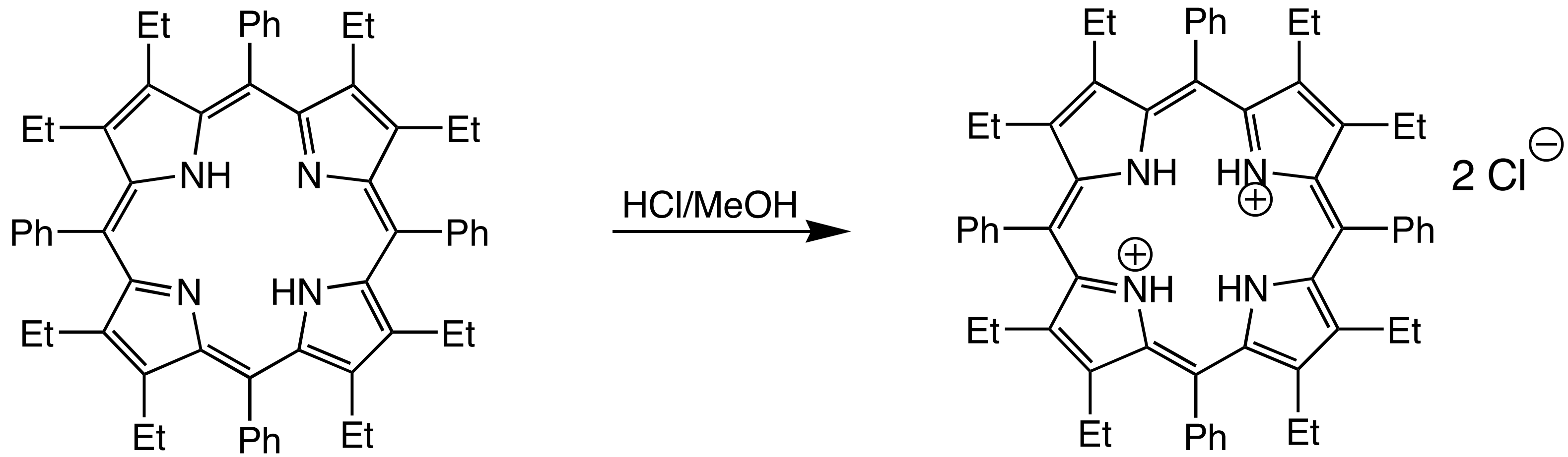
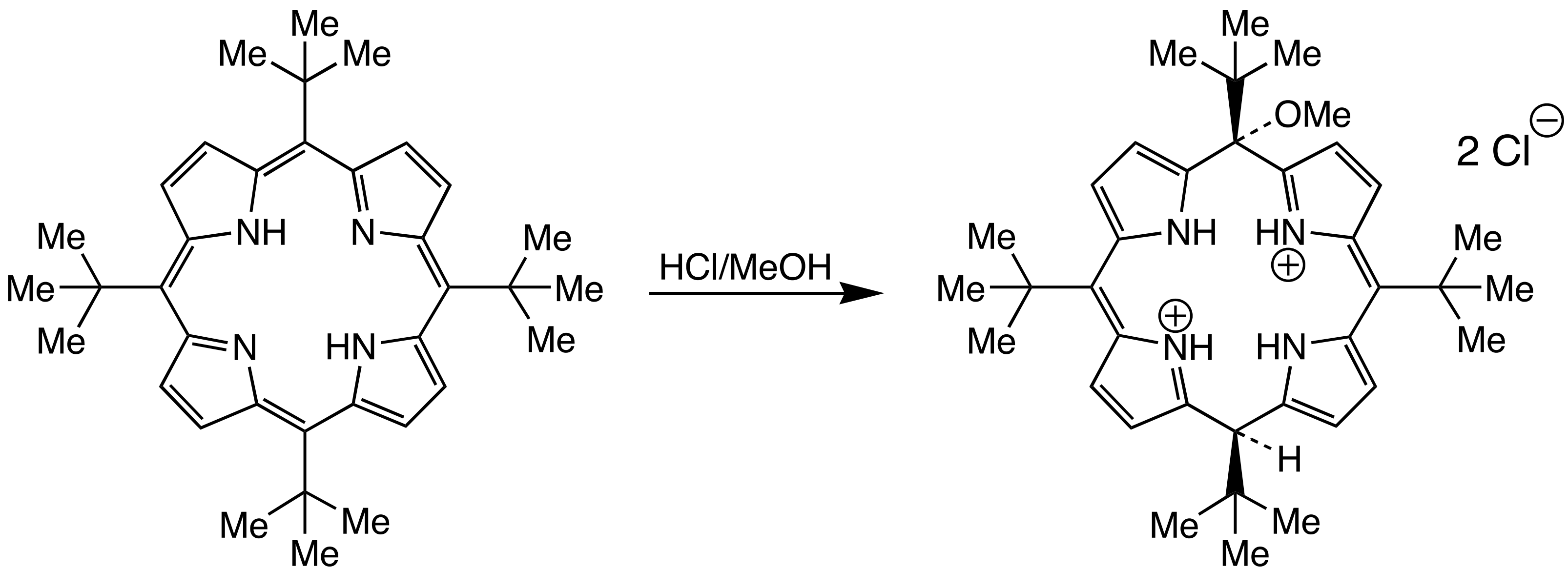
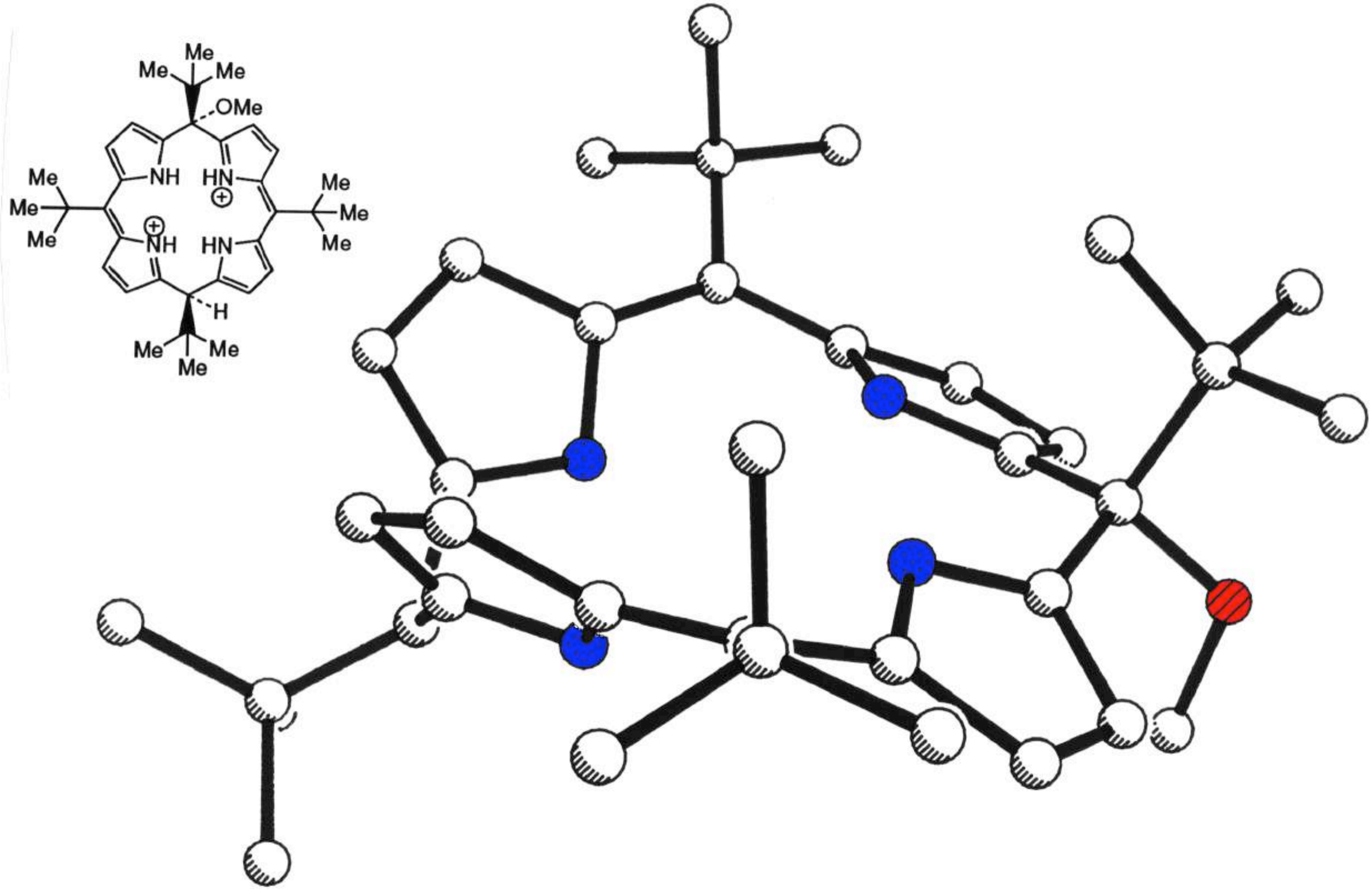


Free-base: λ_{max} 454 nm λ_{max} 476 nm



Free-base: λ_{max} 444 nm

T. Ema, M. O. Senge, N. Y. Nelson, H. Ogoshi and K. M. Smith. *Angew. Chem. Int. Edn Engl.* **1994**, *33*, 1879.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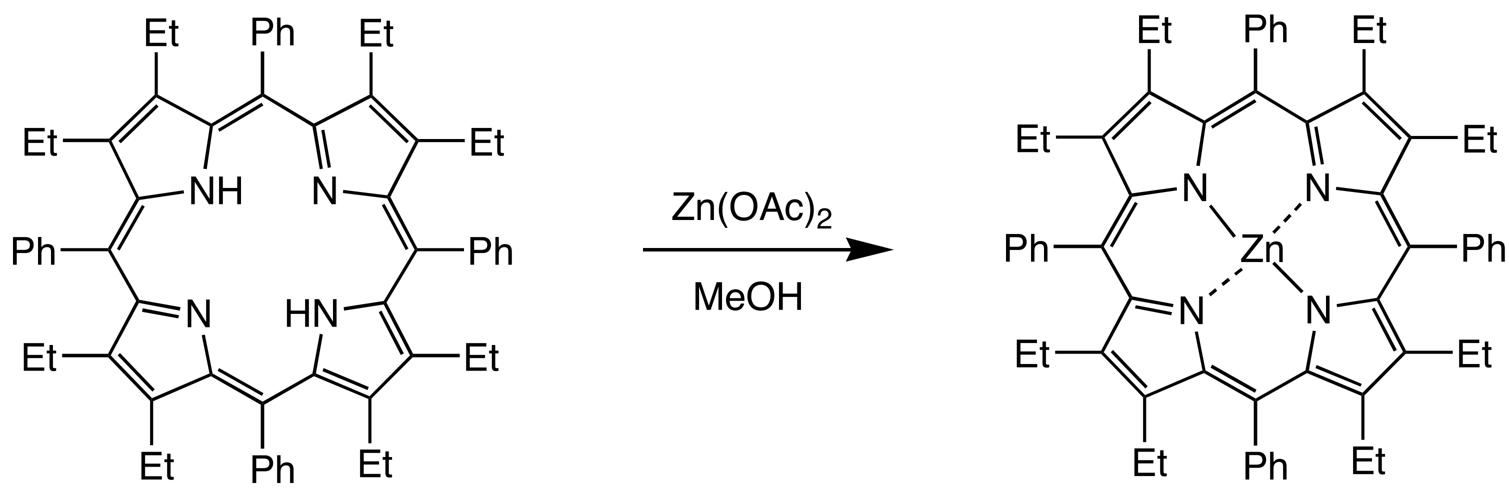

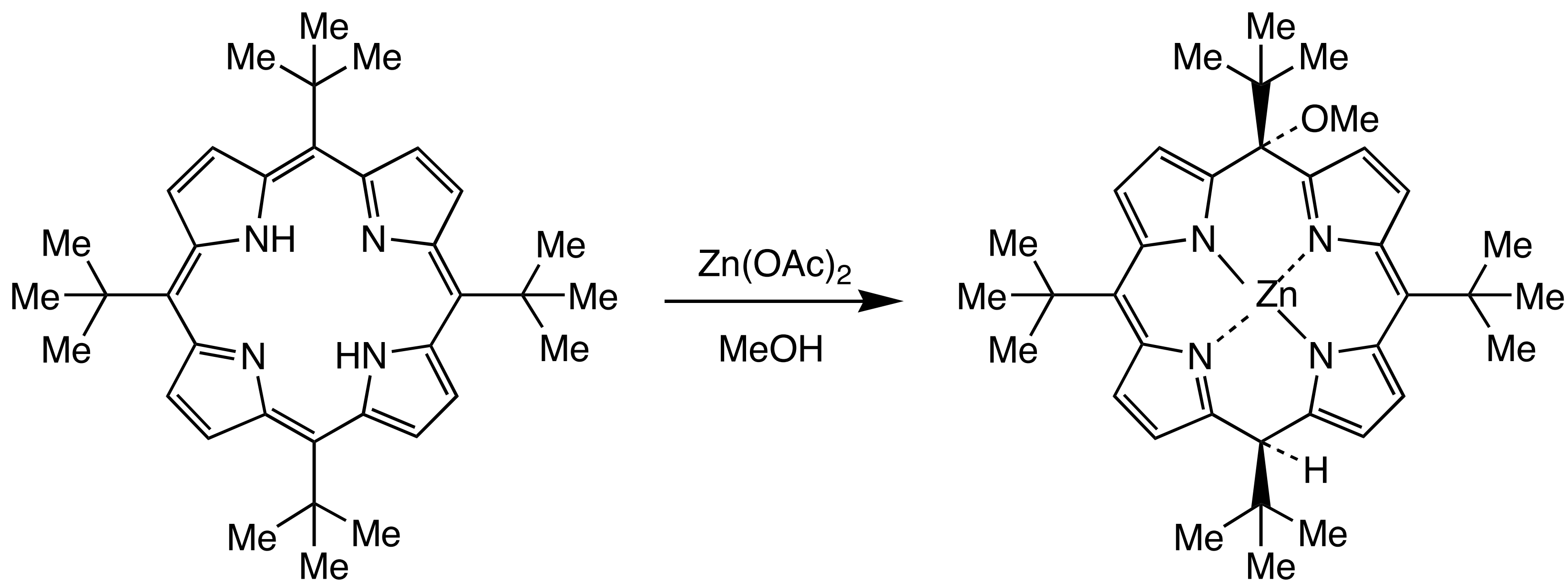

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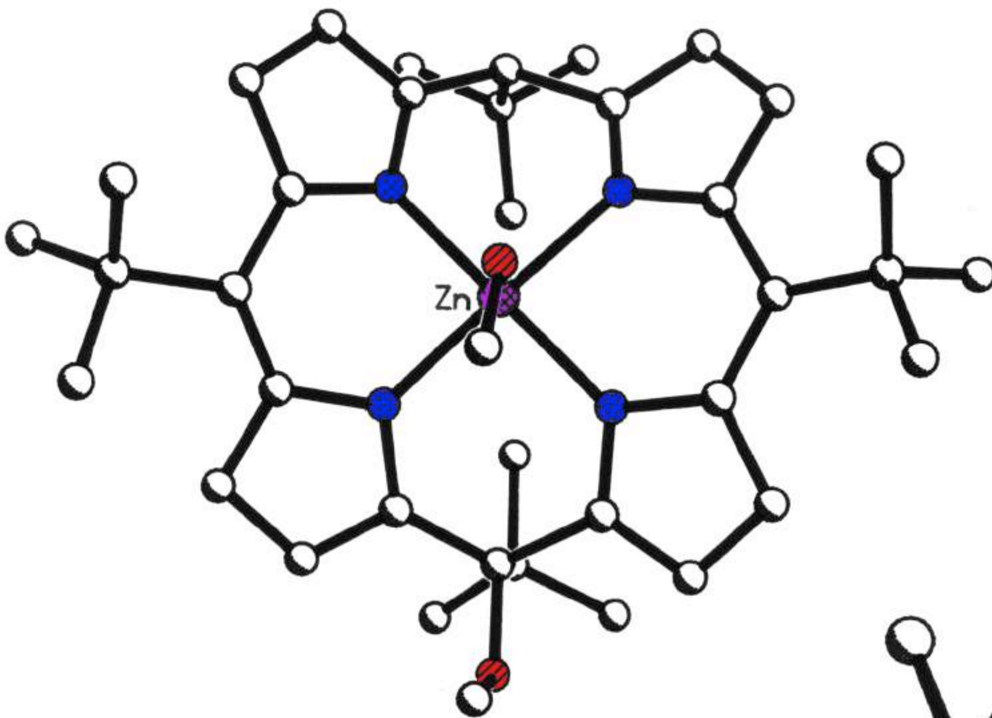
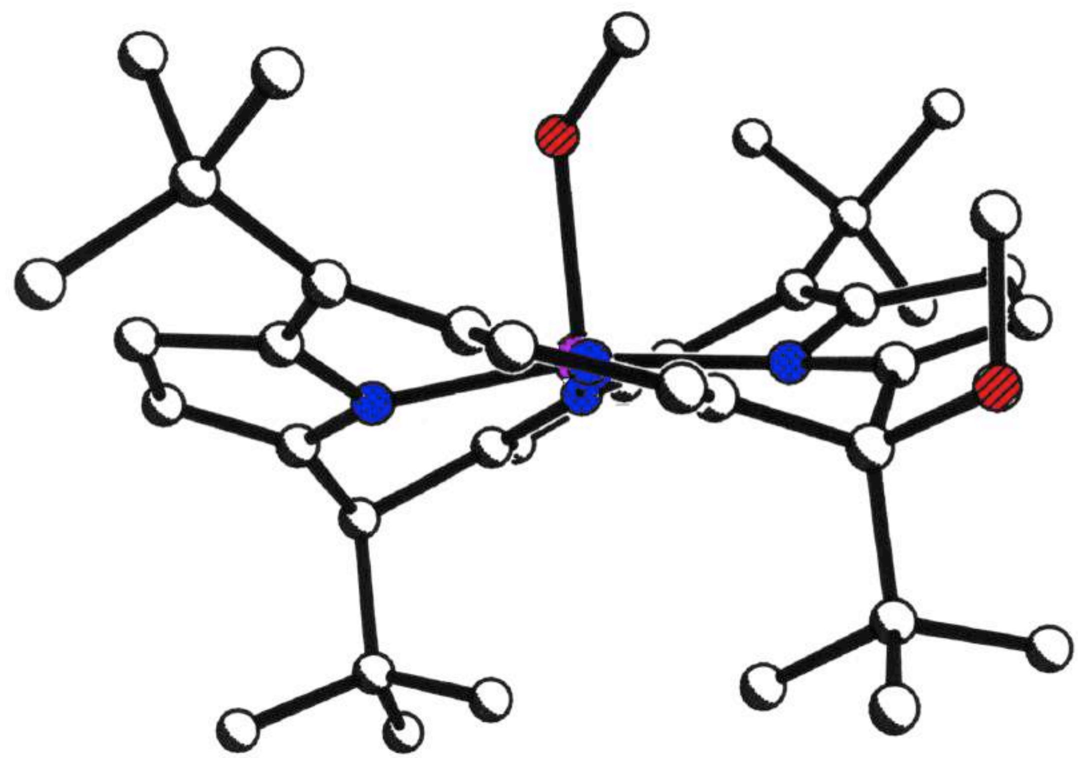
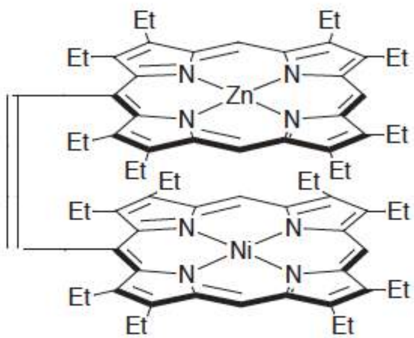

Zn



Porphyrin arrays



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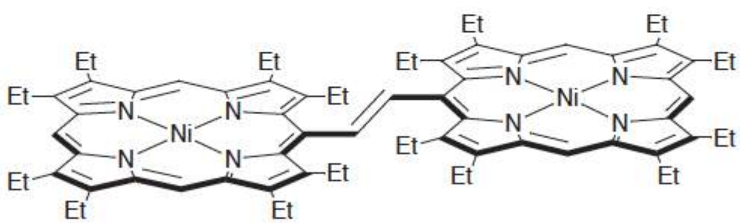

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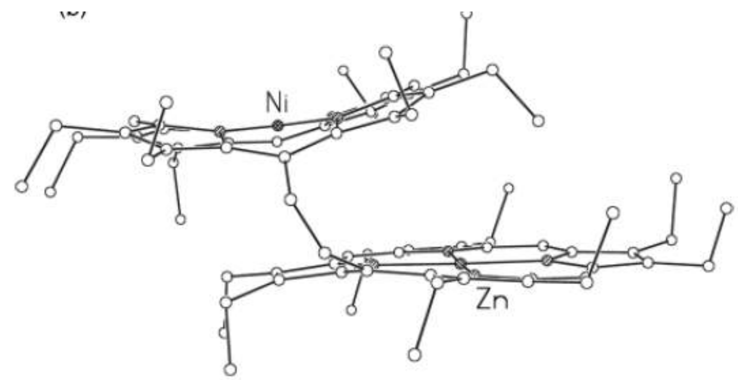

Fig. 1 Molecular structure of heterobimetallic [Ni^{II}][Zn^{II}] *cis*-ethene dimer **1** (hydrogen atoms not shown); (*a*) top view, (*b*) side view.

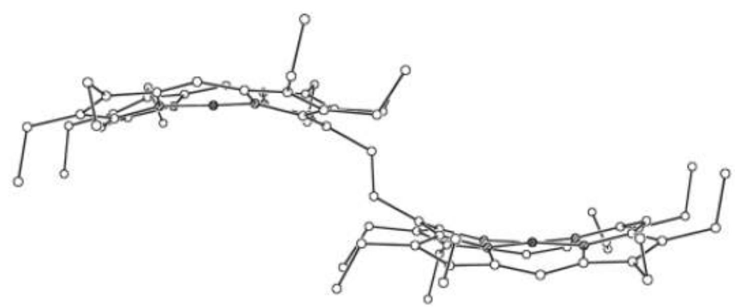

Fig. 2 Molecular structure of bis-Ni^{II} *trans*-ethene dimer **2** (hydrogen atoms not shown).

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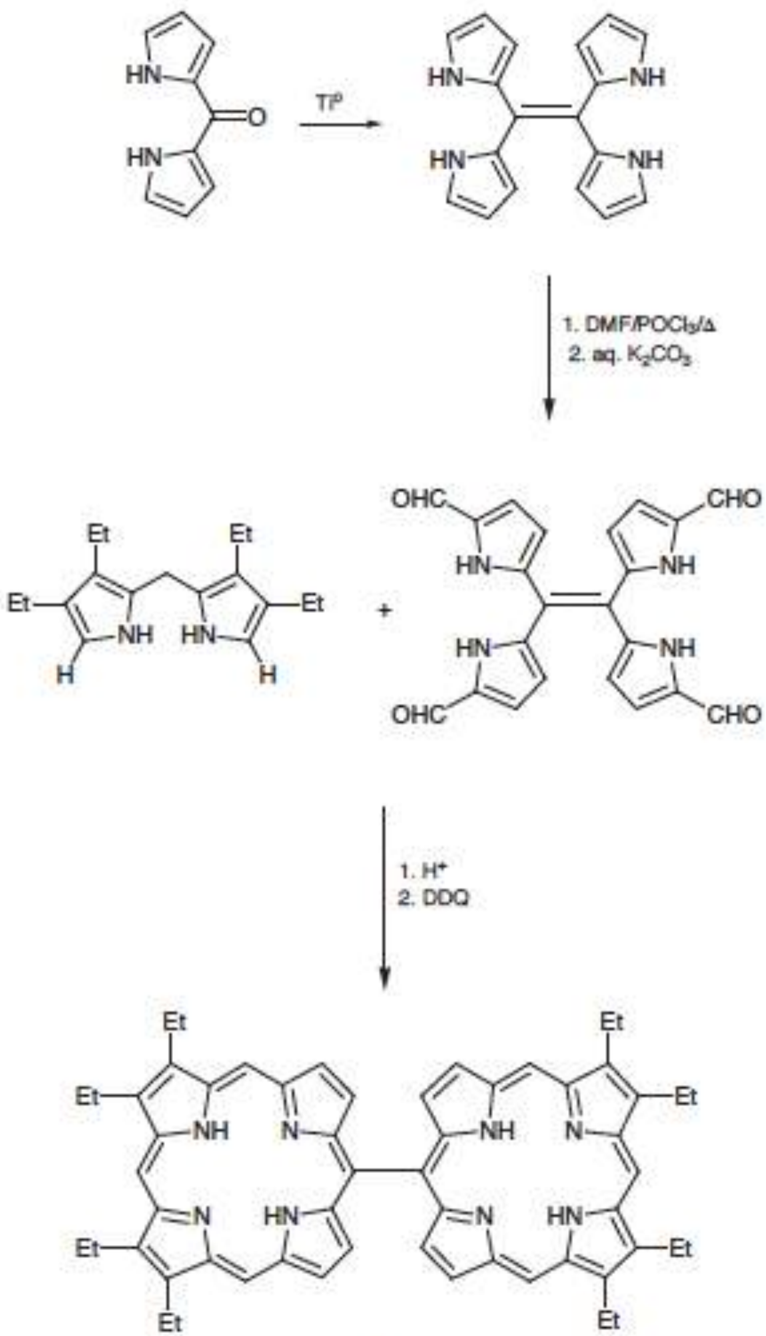

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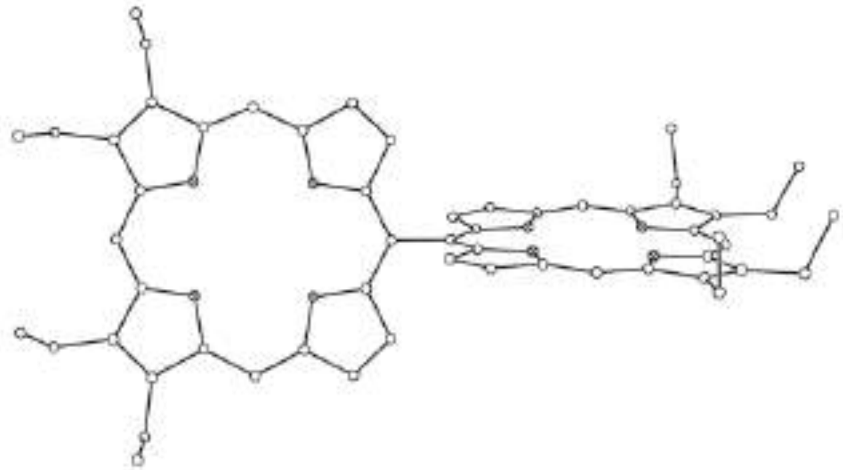

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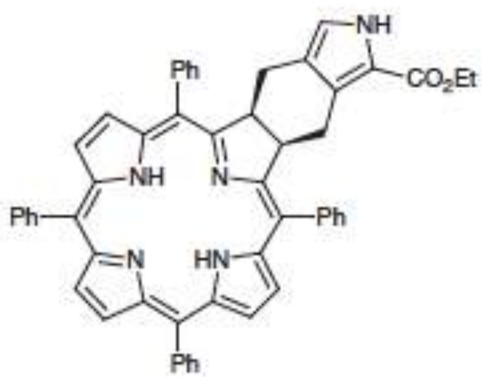

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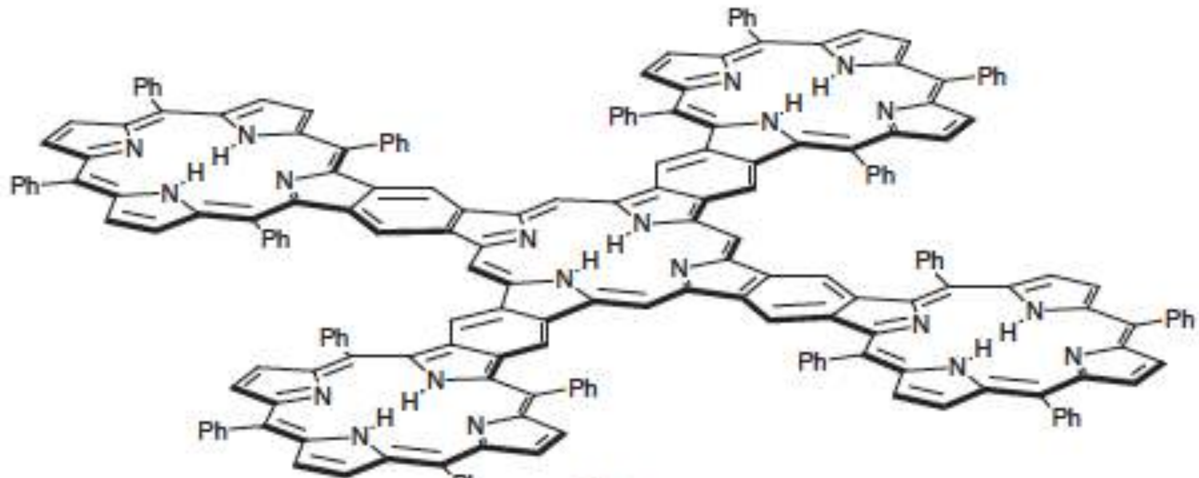

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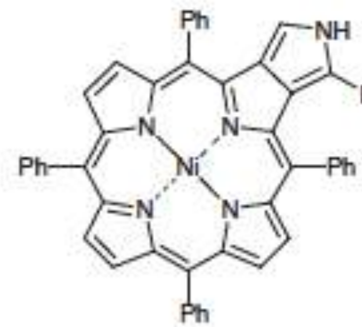
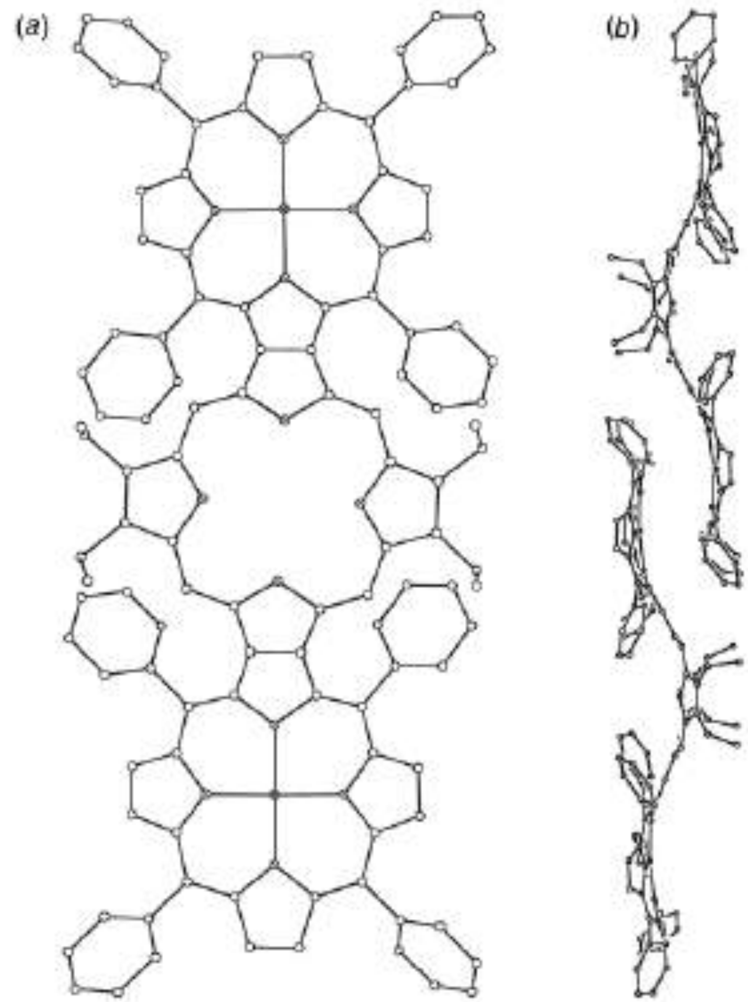


15 R = CO_2Pr^i
16 R = CO_2Bz
20 R = H



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β-Fused Oligoporphyrins: A Novel Approach to a New Type of Extended Aromatic System

Roberto Paolesse,[*,†] Laurent Jaquinod,[‡] Fabio Della Sala,[§] Daniel J. Nurco,[‡] Luca Prodi,[⊥] Marco Montalti,[⊥] Corrado Di Natale,[§] Arnaldo D'Amico,[§] Aldo Di Carlo,[§] Paolo Lugli,[§] and Kevin M. Smith[*,‡]

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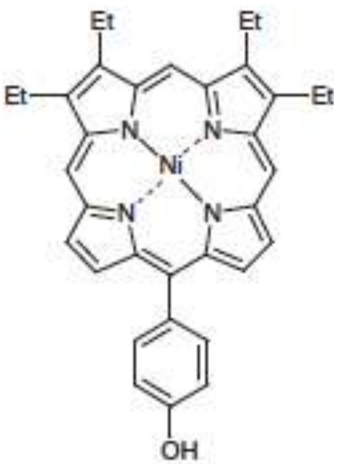
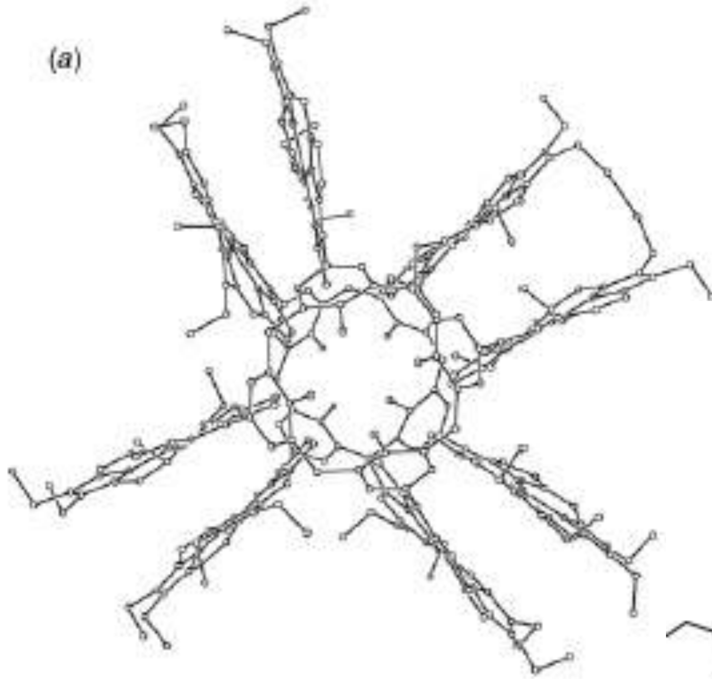


(*a*)



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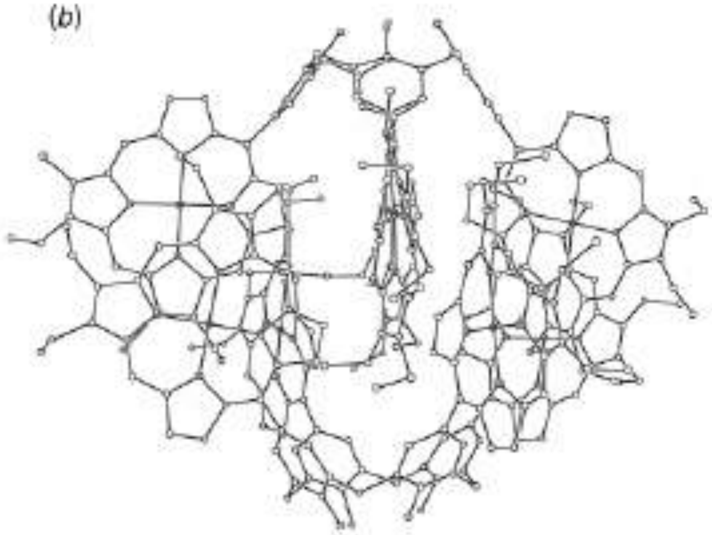

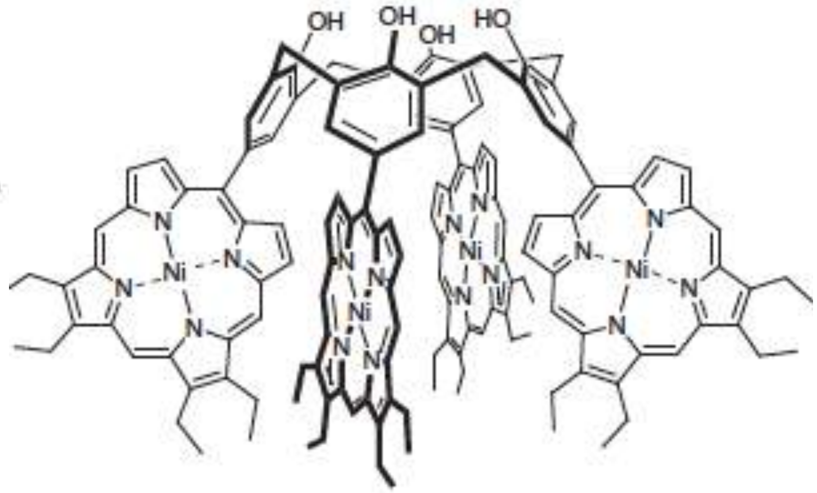

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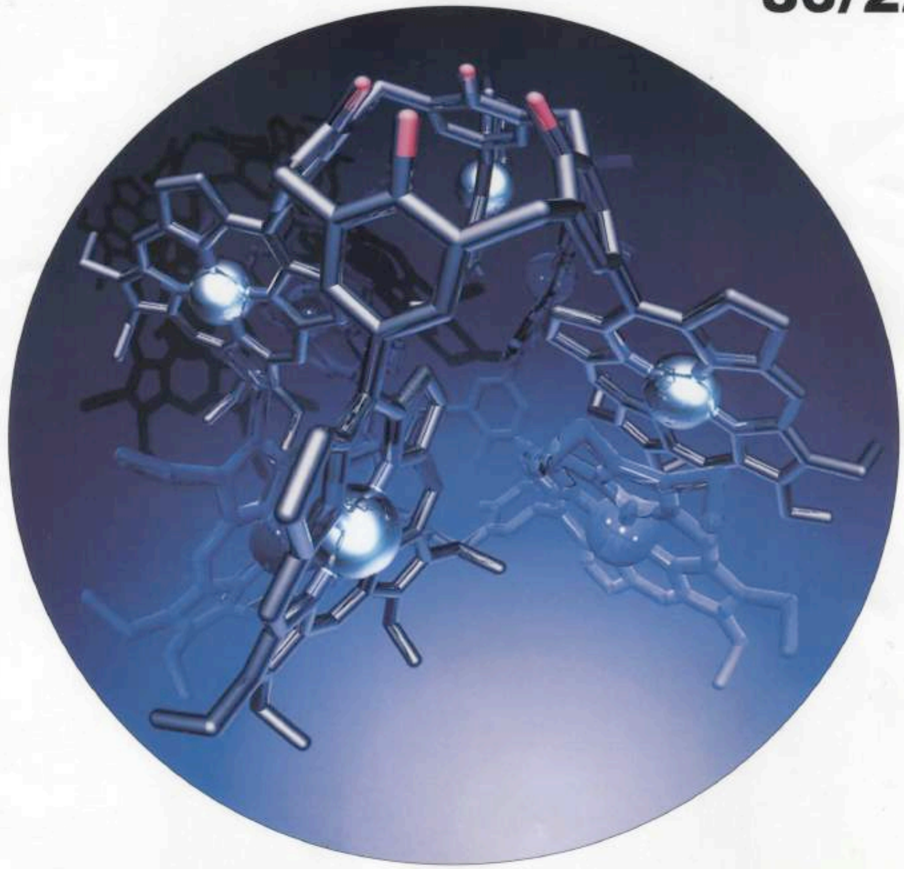

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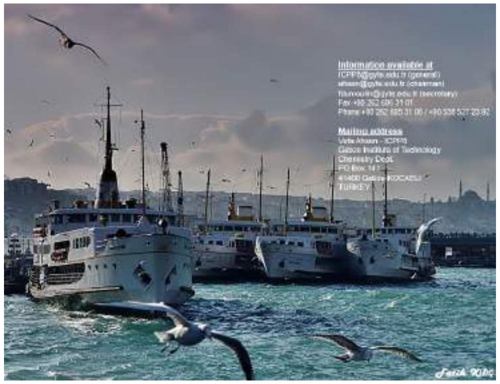

CORROLE AND MORE: THE ROMAN CONNECTION

Roberto Paolesse

Department of Chemical Science and Technologies University of Rome Tor Vergata; Italy
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