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Total synthesis of cyclopentenoporphyrins of sedimentary origin: deoxophylloerythroetioporphyrin, chlorophyll c fossils and related compounds.

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Abstract: *This article describes the total synthesis of seven porphyrins, fossils of chlorophyll derivatives, isolated from sedimentary sources and possess five-membered rings fused to the porphyrin nucleus, this additional ring being placed between positions 13,15 or 15,17. This ring was built from vinyl, hydroxyethyl or isopropenyl groups under strong acidic conditions.*

The isolation, from various geological sources such as crude oils and oil shales, of porphyrins bearing a five-membered ring E demonstrated that chlorophylls must be the precursors of most of these pigments.[1-3] The structural assignments are mostly based on spectroscopic methods, in particular NMR, including the use of the nuclear Overhauser effect (Figure 1). It is, however, satisfactory to be able to compare the natural product with a synthetic reference sample and the total synthesis of cyclopentenoporphyrins has been carried out by several groups, as has been the hemisynthesis of deoxophylloerythroetioporphyrin **1** (DPEP) from natural chlorophyll *a*.[4]

In contrast to the rather straightforward synthesis of porphyrins fused to larger rings,[5-9] obtaining the corresponding five-membered homologue proved to be difficult. Schematically, two approaches have been followed: either a cyclopentenopyrrole is used as one of the building blocks of the macrocycle, or ring E is formed after the cyclization of a linear tetrapyrrole to a porphyrin. The first approach led to the successful total synthesis of DPEP by Flaugh and Rapoport[10] and was improved recently by Lash *et al.*[8-9] The second approach[11-17] is illustrated by selected synthetic routes presented in Figure 2. The most general ones, proposed by Clezy *et al*[13] and Smith *et al.*[15] still require several steps from a simple porphyrin, carrying an accessible substituent (at the monopyrrole stage) or a hydrogen at position 13.

Surprisingly, a very simple reaction, *viz.* the acid-catalyzed cyclization of a preformed vinyl group to give a five-membered ring, has been described,[18] but the article suggested the reaction to be limited to certain bacterial pheophorbides bearing a methyl substituent at C-20 (Figure 3).

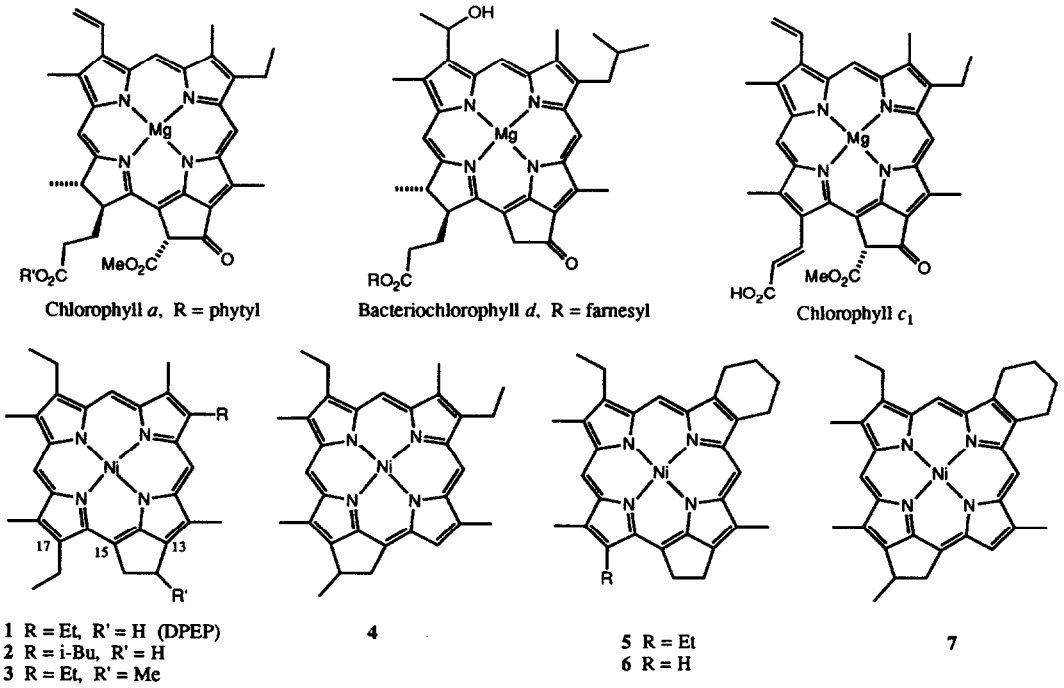


Figure 1. Biological precursors and porphyrins whose synthesis is described in this article: ubiquitous DPEP **1**, possible bacteriochlorophyll *d* fossil **2**, methylated DPEP **3** from Gilsonite, chlorophyll *c* fossil **4**, tetrahydrobenzoporphyrins **5-7**.

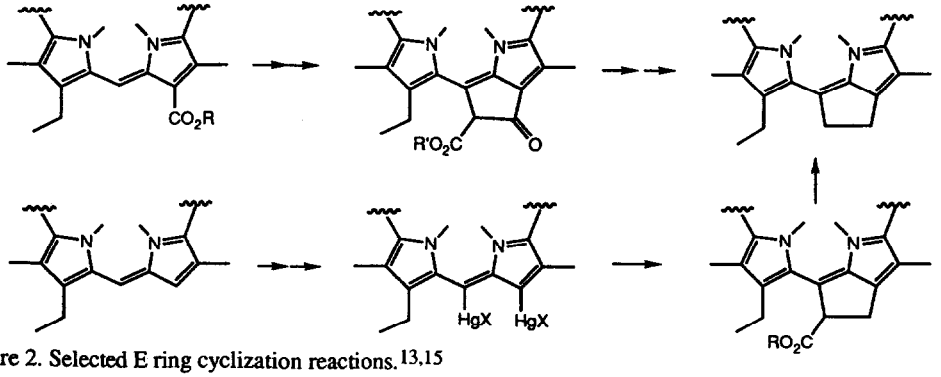


Figure 2. Selected E ring cyclization reactions.[13,15]

While preparing protoporphyrin IX by dehydration of hematoporphyrin,[19] we realized that overheating the reaction mixture (ca 160 instead of 130°C) caused the apparition of at least two minor products whose NMR data suggested the presence of an additional five-membered ring. The present article will describe the extension and optimization of this reaction, and its application to the synthesis of various porphyrins of geochemical significance.[20]

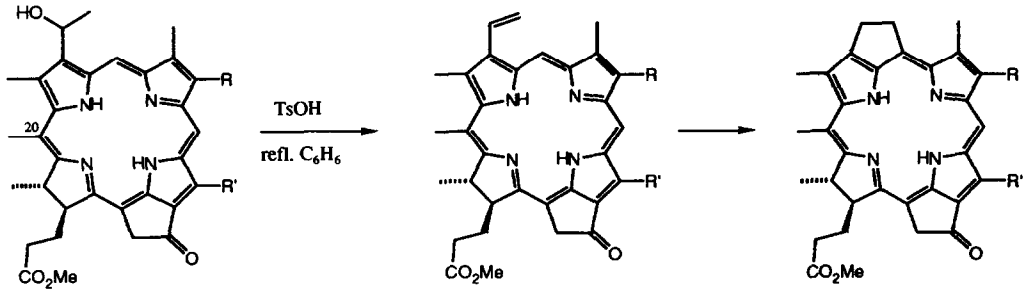


Figure 3. Cyclization of methyl bacteriopheophorbide *c*. [18]

We selected the porphyrin targets **1-6** (Figure 1), as typical chlorophyll fossils possessing a fused five-membered ring. The "classical" and ubiquitous DPEP **1**,[1-3] as well as porphyrin **2**, not yet isolated but expected to be found in the future, were synthesized first (the carboxylic acid homologue of **2** possessing a 12-ethyl substituent is known[21]). A simple methylated DPEP **3**, of unknown biological origin, isolated from Gilsonite bitumen[2] (and not from Serpiano oil shale as erroneously quoted in our preliminary communication[20b]) was also prepared. Synthesis of porphyrin **4**, a typical fossil of chlorophyll *c*,[22] required protection of the free position at C-13. The biological precursors of the last three compounds,[23,24] tetrahydrobenzoporphyrins **5-7** are still unknown, but the six-membered ring fused to porphyrin ring B suggests a diversion from the normal biosynthetic pathway of chlorophylls[23,25] while the remaining substituents suggest a chlorophyll origin, specifically a chlorophyll *c* -like origin for **6** and **7**.

Results and discussion.

Formation of the porphyrin nucleus.

We found that the route described by Smith and Craig[26] was the most suitable for the preparation of the starting porphyrins. The details of the preparation of the corresponding pyrroles, dipyrromethanes, tripyrrenes and *a,c*-biladienes, as well as the cyclization conditions and purification of the resulting porphyrins, are in the experimental section. The numbering of the porphyrins is independent of the presence of complexed metal, which is always indicated, if any.

General approach to cyclopentenoporphyrins.

The required vinylporphyrins may be obtained (Figure 4) either by base-catalyzed elimination of HCl from a preformed chloroethylporphyrin, a well documented reaction,[27] or by acid-catalyzed (TsOH) elimination of water from an α-hydroxyethylporphyrin.[19] The latter structure is accessible by reduction ($NaBH_4$) of an acetyl group, itself easily introduced by specific Friedel-Crafts acylation (Ac_2O, $SnCl_4$) of a free pyrrolic position.[28] Alternatively, Wittig methylenation of the acetyl group may produce an isopropenylporphyrin, a suitable precursor of a methylcyclopentenoporphyrin.[29] The versatile acetylporphyrin route suffers one drawback: if R = H, this position has to be protected to avoid random acylation over the two free pyrrolic positions.

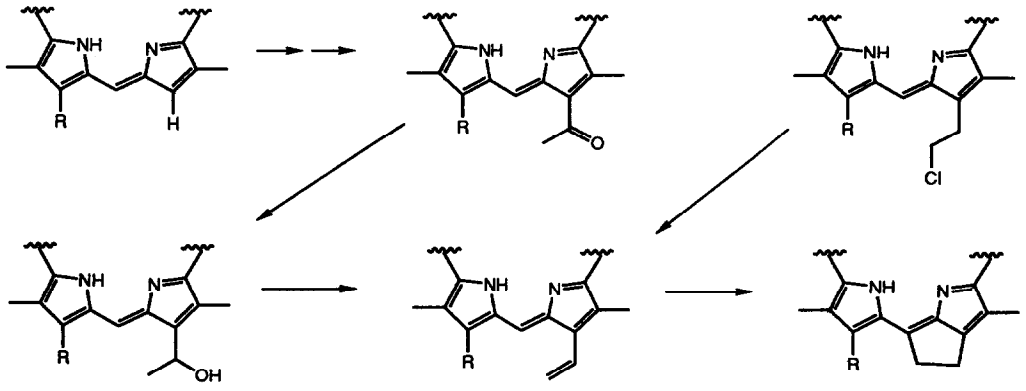
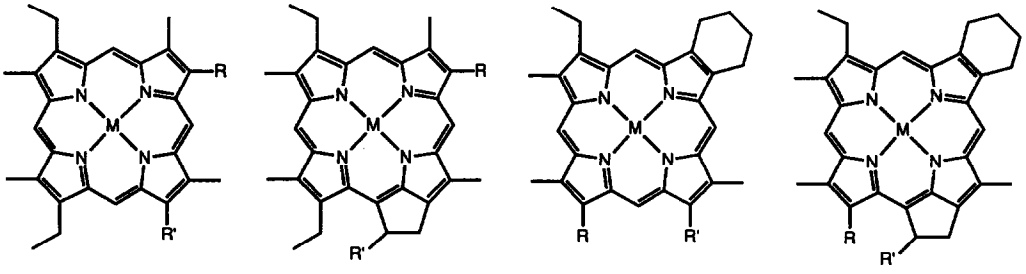


Figure 4. Synthetic routes to simple cyclopentenoporphyrins.

Synthesis of DPEP and similar porphyrins (unsubstituted five-membered ring).

Our first target, the ubiquitous DPEP **1**, required 13-vinylpyrroetioporphyrin **8** as starting material. This compound was prepared earlier[30] as an intermediate in the synthesis of pyrroetioporphyrin **9**, the vinyl group serving as a protecting group and being later cleaved in a resorcinol melt.[31] Alternatively acylation[28] of pyrroetioporphyrin **9**,[30,32] as its nickel complex, gave nickel **10** (92%). The nickel cation had to be removed prior to the reduction since attempts to demetallate the corresponding alcohol led to extensive decomposition. The demetallation (TFA, H_2SO_4) and reduction ($NaBH_4$, MeOH, CH_2Cl_2) steps gave crude alcohol **11** which could be used as such for the cyclization reaction.



8 R = Et; R' = $CH{=}CH_2$
9 R = Et; R' = H
10 R = Et; R' = $COCH_3$
11 R = Et; R' = $CHOHCH_3$
14 R = i-Bu; R' = H
15 R = i-Bu; R' = $COCH_3$
16 R = i-Bu; R' = $CHOHCH_3$

1 R = Et; R' = H
2 R = i-Bu; R' = H
12 R = Et; R' = OH
17 R = i-Bu; R' = OH

18 R = Et; R' = H
19 R = Et; R' = $COCH_3$
20 R = Et; R' = $CHOHCH_3$
22 R = CH_2CH_2Cl; R' = H
23 R = H; R' = CH_2CH_2Cl
24 R = H; R' = $CH{=}CH_2$

5 R = Et; R' = H
6 R = H; R' = H
21 R = Et; R' = OH
25 R = H; R' = OH

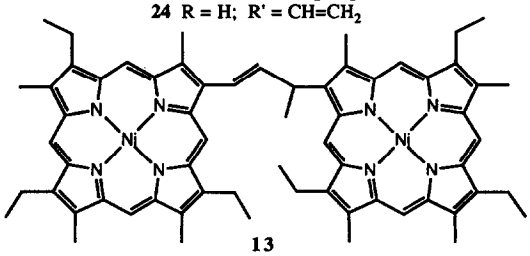


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Figure 5. Cyclopentenoporphyrins and corresponding synthetic intermediates and side-products.

The cyclization was carried out in *o*-dichlorobenzene for 8h at 150-160°C in the presence of $TsOH.H_2O$ (50 eq.) and gave three products of low polarity (whatever the starting material, vinyl- or hydroxyethylporphyrin): vinylporphyrin **8** (50%), DPEP **1** (14%) and alcohol **12** (30%). Below 140°C no appreciable reaction occurred. Alcohol **12** could be reduced quantitatively to DPEP by treatment with a large excess $NaBH_4$ in CH_2Cl_2-TFA,[33] raising the yield of DPEP **1** to 44%.

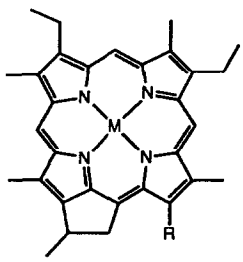
The origin of alcohol **12** is clear: the 15' position of free base **1** is highly susceptible to allylic oxidation,[34] as has been demonstrated earlier, and we always handle DPEP **1** as its stable nickel complex which we routinely use it as a geochemical standard. It is interesting to note that alcohol **12** has been described[35] as a natural product from Marl Slate, a Permian sediment from England, although the authors considered the possibility of its being an artifact. Since we suspected that the oxidation took place during the separation of the reaction products, in view of the highly variable DPEP **1** / alcohol **12** ratio, we metallated the crude mixture prior to the separation. Under these conditions the nickel complexes of vinylporphyrin **8** and DPEP **1** were produced in good yield but only traces of alcohol **12** were detected, confirming its formation during the chromatographic step. In addition we isolated a compound which we suspect, in view of its NMR data, to be dimer **13**. Under normal cyclization conditions the corresponding base is probably hidden in the polar fraction that we did not investigate. Similar dimers have been already described from the acid catalyzed oligomerization of hematoporphyrin.[36]

The above reaction sequence (acetylation route) has been applied to the synthesis of **2**, starting from porphyrin **14**. Acetylation gave **15**, which was reduced to **16**, itself cyclized to porphyrin **2** accompanied by alcohol **17**. Analogously porphyrin **5** and alcohol **21** were obtained via intermediates **18-20**. Porphyrin **5** had been obtained independently[7,37] using Smith's method,[15] but in much lower yield, via the same intermediate **18**. Porphyrin **6** was first prepared from chloroethylporphyrin **22** (following Smith's route).[15] After the introduction of ring E (4 steps), the protecting chloroethyl group was treated with base (elimination of HCl to vinyl) and the vinyl group cleaved in a resorcinol melt to furnish **6** characterized as its nickel complex (overall yield < 10% from **22**). Alternatively starting with isomeric chloroethylporphyrin **23**, whose synthesis requires the same precursors and number of steps as for **22**, a simple elimination - cyclization sequence gave **6** in fair yield (42%, including recycled 15'-alcohol **25**) and 29% recovered vinylporphyrin **24**.

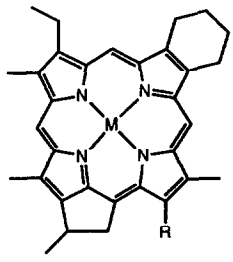
Syntheses of methylcyclopentenoporphyrins.

The simplest target is porphyrin **3**, since, in the absence of free pyrrolic positions its synthesis does not require protecting groups. Wittig methylenation of the zinc complex of acetylpyrroetioporphyrin **10** followed by a short treatment with HCl gave isopropenylporphyrin **26** (use of the nickel complex resulted in extensive decomposition during the demetallation in strong acid). Under standard conditions (see above), the cyclization gave **3** (56%) accompanied by a smaller amount of (possibly) **27**. Of importance is the fact that this cyclization also operated at a much lower temperature than that of a vinyl group: heating at 125°C during 3h gave 30% **3**, while 40% starting material **26** could be recovered.

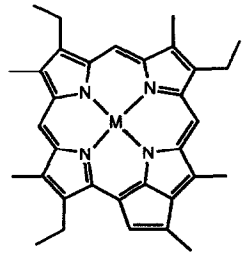
The synthesis of porphyrins **4** and **7** required the protection of the pyrrolic position at C-13. We chose the classical vinyl group as protecting function, assuming that an isopropenyl group at C-17 would cyclize under milder conditions, leaving the vinyl group intact for the subsequent cleavage in resorcinol. The intermediate target molecules must therefore have a 13-vinyl-17-isopropenylporphyrin structure in common (Figure 7).



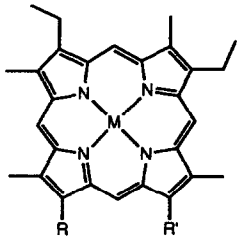
4 R = H
38 R = CH=CH$_2$



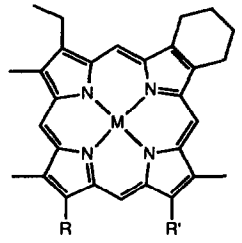
7 R = H
39 R = CH=CH$_2$



27



26 R = Et; R' = C(CH$_3$)=CH$_2$
28 R = H; R' = CH$_2$CH$_2$Cl
29 R = COCH$_3$; R' = CH$_2$CH$_2$Cl
31 R = C(OCH$_2$CH$_2$O)CH$_3$; R' = CH$_2$CH$_2$Cl
33 R = C(OCH$_2$CH$_2$O)CH$_3$; R' = CH=CH$_2$
36 R = C(CH$_3$)=CH$_2$; R' = CH=CH$_2$



30 R = COCH$_3$; R' = CH$_2$CH$_2$Cl
32 R = C(OCH$_2$CH$_2$O)CH$_3$; R' = CH$_2$CH$_2$Cl
34 R = C(OCH$_2$CH$_2$O)CH$_3$; R' = CH=CH$_2$
35 R = COCH$_3$; R' = CH=CH$_2$
37 R = C(CH$_3$)=CH$_2$; R' = CH=CH$_2$

Figure 6. Methylcyclopentenoporphyrins and corresponding synthetic intermediates and side-products.

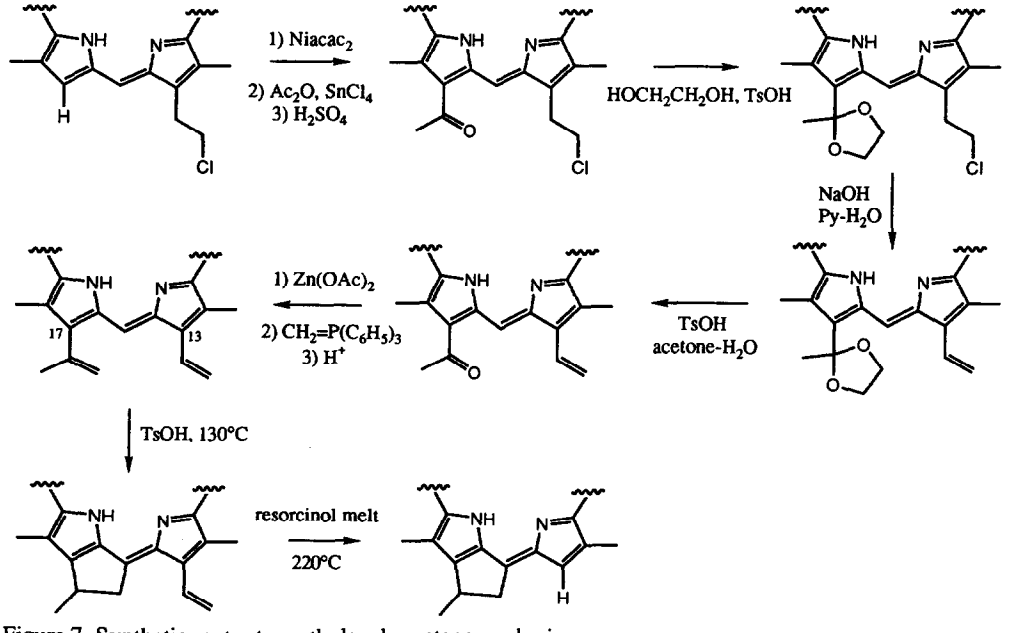


Figure 7. Synthetic routes to methylcyclopentenoporphyrins.

We used chloroethylporphyrins **28** and **23** as starting material (Figure 7 shows only the "southern halves" common to both series). Metallation with $Ni(acac)_2$, acetylation and demetallation (H_2SO_4) gave bases **29** and **30**. Protection of the acetyl group, to avoid any interference with the elimination step, was achieved quantitatively on treatment with ethylene glycol-TsOH to give ketals **31** and **32**. Elimination (NaOH in H_2O-Py) to **33** and **34** followed by regeneration of the carbonyl group gave 13-vinyl-17-acetylporphyrins (**35**, tetrahydrobenzo series; not isolated in the "normal" series). At this stage, to avoid the formation of the porphyrin dianion on treatment with the Wittig reagent, the pyrrolic nitrogen atoms were protected with zinc ($Zn(OAc)_2$ in MeOH-CH_2Cl_2). After methylenation the free bases **36** and **37** were regenerated on acid treatment (HCl) followed by neutralization. The isopropenyl group cyclized cleanly (TsOH, 130°C) in the presence of the vinyl group to give cyclopentenoporphyrins **38** and **39**. Cleavage of the protecting group in a resorcinol melt (220°C; sealed tube) gave the required porphyrins **4** ands **7**, characterized as nickel complexes which proved to be identical with the natural products (NMR, HPLC).

Experimental section

General

NMR spectra were obtained in $CDCl_3$ (unless otherwise stated) on a Bruker WP-200 SY spectrometer. Chemical shifts (δ) are expressed in ppm from TMS. Mass spectra were recorded on a Finnigan TSQ 70 spectrometer, while high resolution data were measured with a Kratos MS 80 spectrometer. UV-visible spectra were obtained with a Hewlett-Packard 8451A spectrometer in CH_2Cl_2. Elemental analyses were performed by the "Service de Microanalyse de l'Institut de Chimie de Strasbourg". Chromatographic separations were obtained using Merck 60 silica gel column. HPLC analyses were run on a Waters 6000 A instrument (U6 K injector, M440 detector with a double channel detection; 405 and 546 nm filters) equipped with DU PONT 250 x 4.60 mm Zorbax ODS (RP-18) 5 µm column. Organic phases were routinely dried over anhydrous Na_2SO_4 before being evaporated under vacuum (rotary evaporator). Porphyrins were crystallized from CH_2Cl_2-MeOH, and described as bases unless otherwise stated.

Pyrroles

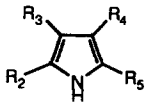
Pyrroles **40**, **41**, **44-46** were prepared according to literature procedures.[38] Pyrrole **42** was obtained from C=N-CH_2-CO_2tBu and 2-nitro-3-acetoxy-5-methylhexane.[39] Pyrrole **43** was obtained from a Kleinspehn reaction[40] of 2-formylcyclohexanone and dibenzyl oximinomalonate in the presence of zinc. This last pyrrole was also prepared in similar yield via an isonitrile, as the ethyl ester which was subsequently exchanged for benzyl.[37]

Pyrrole **42** (54 %). Mp 108°C (crystallized from MeOH-H_2O). NMR: 8.72 (broad s, 1H, NH); 6.65 (d, 1H, pyrrolic H, J = 3 Hz); 2.57 (d, 2H, i-Bu CH_2, J = 7 Hz); 2.01 (s, 3H, 4-CH_3); 1.86 (m, 1H, i-Bu CH); 1.57 (s, 9H, t-Bu); 0.91 (d, 6H, i-Bu CH_3, J = 7Hz). Anal. Calcd for $C_{14}H_{23}NO_2$: C, 70.85; H, 9.77; N, 5.90. Found: C, 71.2; H, 9.7; N, 6.0.

Pyrrole **43** (7.5 %). Mp 92°C (crystallized from MeOH-H_2O). NMR: 8.93 (broad s, 1H, NH); 7.4 (m, 5H, phenyl); 6.65 (d, 1H, pyrrolic H, J = 3 Hz); 5.31 (s, 2H, benzyl CH_2); 2.84 and 2.55 (2 broad t, 2+2H, cyclohexene α-CH_2); 1.74 (m, 4H, cyclohexene β-CH_2). Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.1; H, 6.5; N, 5.5.

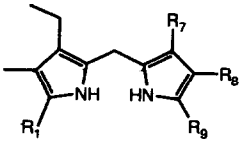
Dipyrromethanes

The coupling of pyrroles into dipyrromethanes was realized either by treatment with TsOH.H_2O in methanol (method A) or using K-10 montmorillonite in a heterogeneous reaction[41] (method B). Method B gave consistently better yields and cleaner reaction mixtures than method A. We found that the crude dipyrromethanes, usually obtained as foams, are best crystallized from



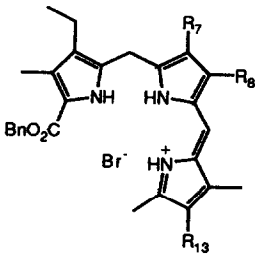
R_2, R_3, R_4, R_5

40 CO_2Bn, Me, Et, CH_2OAc
41 CO_2t-Bu, Me, Et, CH_2OAc
42 CO_2t-Bu, i-Bu, Me, H
43 CO_2Bn, $(CH_2)_4$, H
44 CHO, Me, H, Me
45 CHO, Me, Et, Me
46 CHO, Me, CH_2CH_2Cl, Me



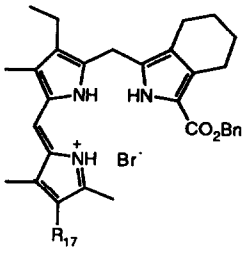
R_1, R_7, R_8, R_9

47 CO_2Bn, Me, Et, CO_2t-Bu
48 CO_2Bn, Me, i-Bu, CO_2t-Bu
49 CO_2t-Bu, $(CH_2)_4$, CO_2Bn



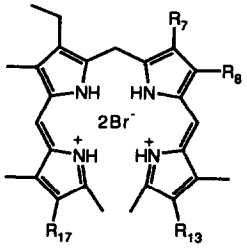
R_7, R_8, R_{13}

50 Me, i-Bu, H
53 Me, Et, CH_2CH_2Cl



R17

51 Et
52 H



R_7, R_8, R_{13}, R_{17}

54 Me, i-Bu, H, Et
55 $(CH_2)_4$, H, Et
56 $(CH_2)_4$, CH_2CH_2Cl, H
57 Me, Et, CH_2CH_2Cl, H

CH_2Cl_2-hexane (≤1:5 ratio) at -20°C, filtered and washed quickly with cold hexane. Dipyrromethane **47** is described in the literature.[42]

Dipyrromethane **48** (64%; method B). Mp 130°C. NMR: 8.66 and 8.54 (2 broad s, 1+1H, NH); 7.36 (m, 5H, phenyl); 5.27 (s, 2H, benzyl CH_2); 3.83 (s, 2H, bridge CH_2); 2.54 (d, 2H, i-Bu CH_2); 2.40 (q, 2H, ethyl CH_2); 2.30 and 1.94 (2s, 3+3H, CH_3); 1.81 (m, 1H, i-Bu CH); 1.53 (s, 9H, t-Bu); 1.03 (t, 3H, ethyl CH_3); 0.90 (d, 6H, i-Bu CH_3). Anal. Calcd for $C_{30}H_{40}N_2O_4$: C, 73.14; H, 8.18; N, 5.69. Found: C, 73.3; H, 8.1; N, 5.7.

Dipyrromethane **49** (84%; method B). Mp 115°C. NMR: 8.60 and 8.49 (2 broad s, 1+1H, NH); 7.36 (m, 5H, phenyl); 5.28 (s, 2H, benzyl CH_2); 3.80 (s, 2H, bridge CH_2); 2.76 and 2.39 (2 broad t, 2+2H, cyclohexene α-CH_2); 2.40 (q, 2H, ethyl CH_2); 2.30 (s, 3H, CH_3); 1.72 (m, 4H, cyclohexene β-CH_2); 1.53 (s, 9H, t-Bu); 1.04 (t, 3H, ethyl CH_3). Anal. Calcd for $C_{29}H_{36}N_2O_4$: C, 73.08; H, 7.61; N, 5.88. Found: C, 73.3; H, 7.6; N, 5.9.

Tripyrrenes

Condensation of dipyrromethanes with pyrrole aldehydes was done after deprotecting first the t-butyl ester in TFA. The products were treated with a little HBr in AcOH (33%) and precipitated as orange powders (hydrobromide salts) with diethylether.[26]

Tripyrrene **50** (from dipyrromethane **48** and pyrrole **44**; 76%). NMR: 10.29, 10.28 and 10.18 (3 broad s, 1+1+1H, NH); 7.5 and 7.3 (2m, 2+3H, phenyl); 7.05 (s, 1H, methine bridge); 6.18 (broad s, 1H, pyrrole H); 5.32 (s, 2H, benzyl CH_2); 4.32 (s, 2H, methylene bridge); 2.67, 2.35, 2.28 and 2.02 (4s, 3+3+3+3H, methyl); 2.50 (d, 2H, i-Bu CH_2); 2.48 (q, 2H, ethyl CH_2); 1.78 (m, 1H, i-Bu CH); 0.94 (d, 6H, i-Bu CH_3); 1.02 (t, 3H, ethyl CH_3). Vis. λ_{max} 488 nm. Anal. Calcd for $C_{32}H_{38}N_3O_2Br$: C, 66.66; H, 6.64; N, 7.29. Found: C, 64.0; H, 6.9; N, 7.9.

Tripyrrene **51** (from dipyrromethane **49** and pyrrole **45**; 67%). NMR: 10.37 and 9.60 (2 broad s, 2+1H, NH); 7.4 (m, 5H, phenyl); 7.06 (s, 1H, methine bridge); 5.30 (s, 2H, benzyl CH_2); 4.27 (s, 1H, methylene bridge); 2.78 and 2.51 (2m, 2+2H, cyclohexene α-CH_2); 2.67, 2.28 and 2.25 (3s, 3+3+3H, methyl); 2.45 (q, 4H, ethyl CH_2); 1.72 (m, 4H, cyclohexene β-CH_2); 1.04 and 1.00 (2t, 3+3H, ethyl CH_3). Vis. λ_{max} 496 nm. Anal. Calcd for $C_{33}H_{40}N_3O_2Br$: C, 67.05; H, 6.77; N, 7.11. Found: C, 66.9; H, 6.7; N, 7.0.

Tripyrrene **52** (from dipyrromethane **49** and pyrrole **43**; 81%). NMR: 10.3 (broad s, 3H, NH); 7.5 and 7.3 (2m, 2+3H, phenyl); 7.09 (s, 1H, methine bridge); 6.18 (broad s, 1H, pyrrole H); 5.30 (s, 2H, benzyl CH_2); 4.30 (s, 2H, methylene bridge); 2.78 and 2.51 (2m, 2+2H, cyclohexene α-CH_2); 2.68, 2.36 and 2.26 (3s, 3+3+3H, methyl); 2.44 (q, 2H, ethyl CH_2); 1.72 (m, 4H, cyclohexene β-CH_2); 1.00 (t, 3H, ethyl CH_3). Vis. λ_{max} 488 nm. Anal. Calcd for $C_{31}H_{36}N_3O_2Br$: C, 66.19; H, 6.44; N, 7.47. Found: C, 66.2; H, 6.5; N, 7.4.

Tripyrrene **53** (from dipyrromethane **47** and pyrrole **46**; 73%). NMR: 13.2, 13.16 and 10.49 (3 broad s, 1+1+1H, NH); 7.08 (s, 1H, methine bridge); 5.32 (s, 2H, benzyl CH_2); 4.33 (s, 2H, methylene bridge); 3.58 and 2.91 (2t, 2+2H, chloroethyl CH2); 2.69 (s, 3H, CH_3); 2.65 and 2.49 (2q, 2+2H, ethyl CH_2); 2.33, 2.28 and 2.03 (3s, 3+3+3H, CH_3); 1.16 and 1.03 (2t, 3+3H, ethyl CH_3). Vis. λ_{max} 496 nm. Anal. Calcd for $C_{32}H_{39}N_3O_2BrCl$: C, 62.70; H, 6.41; N, 6.85. Found: C, 64.0; H, 6.3; N, 7.9.

a,c-Biladienes

The benzyl esters of the tripyrrenes were cleaved in HBr-AcOH (20°C; 3h) and the biladienes obtained after addition of pyrrole aldehyde and precipitation with diethyl ether.[26] Satisfactory analytical figures could not be obtained for biladiene **54** and **57**.

Biladiene **54** (from tripyrrene **50** and pyrrole **45**; 80%). NMR: 10.34, 10.26 and 10.04 (3 broad s, 1+2+1H, NH); 7.10 and 7.09 (2s, 1+1H, methine bridges); 6.21 (braod s, 1H, pyrrole H); 5.20 (s, 2H, methylene bridge); 2.71, 2.37, 2.30, 2.25 and 1.94 (5s, 6+3+3+3+3H, methyl); 2.50 (d, 2H, i-Bu CH_2); 2.50 and 2.46 (2q, 2+2H, ethyl CH_2); 1.72 (m, 1H, i-Bu CH); 1.09 and 0.65 (2t, 3+3H, ethyl CH_3); 0.91 (d, 6H, i-Bu CH_3). Vis. λ_{max} 452 and 526 nm.

Biladiene **55** (from tripyrrene **51** and pyrrole **44**; 91%). NMR: 10.35, 10.32, 10.23 and 9.98 (4broad s, 1+1+1+1H, NH); 7.11 and 7.02 (2s, 1+1H, methine bridges); 6.18 (broad s, 1H, pyrrole H); 5.15 (s, 2H, methylene bridge); 2.71, 2.35, 2.30 and 2.27 (4s, 6+3+3+3H, methyl); 2.68 (m, 4H, cyclohexene α-CH_2); 2.48 and 2.46 (2q, 2+2H, ethyl CH_2); 1.65 (m, 4H, cyclohexene β-CH_2); 1.09 and 0.72 (2t, 3+3H, ethyl CH_3). Vis. λ_{max} 450 and 524 nm. Anal. Calcd for $C_{32}H_{42}N_4Br_2$: C, 59.82; H, 6.59; N, 8.72. Found: C, 59.6; H, 6.5; N, 8.5.

Biladiene **56** (from tripyrrene **52** and pyrrole **46**; 62%). NMR: 7.93, 7.73 and 7.59 (3 broad s, 2+1+1H, NH); 7.15 and 7.04 (2s, 1+1H, methine bridges); 6.23 (broad s, 1H, pyrrole H); 5.18 (s, 2H, methylene bridge); 3.58 (t, 2H, chloroethyl CH_2); 2.92 (t, 2H, chloroethyl CH_2); 2.73, 2.71, 2.39, 2.32 and 2.28 (5s, 5x3H, methyl); 2.70 and 2.36 (2m, 2+2H, cyclohexene α-CH_2); 2.47 (q, 2H, ethyl CH_2); 1.66 (m, 4H, cyclohexene β-CH_2); 0.71 (t, 3H, ethyl CH_3). Vis. λ_{max} 448 and 524 nm. Anal. Calcd for $C_{32}H_{41}N_4Br_2Cl$: C, 56.77; H, 6.10; N, 8.27. Found: C, 56.0; H, 6.2; N, 7.9.

Biladiene **57** (from tripyrrene **53** and pyrrole **44**; 79%). NMR: 13.49, 13.42, 13.31 and 13.22 (4 broad s, 1+1+1+1H, NH); 7.13 and 7.11 (2s, 1+1H, methine bridge); 6.22 (broad s, 1H, pyrrole H); 5.21 (s, 2H, methylene bridge); 3.58 and 2.92 (2t, 2+2H, chloroethyl CH_2); 2.73, 2.71, 2.38, 2.34, 2.26 and 1.94 (6s, 6x3H, CH_3); 2.62 and 2.48 (2q, 2+2H, ethyl CH_2); 1.11 and 0.64 (2t, 3+3H, ethyl CH_3). Vis. λ_{max} 447 and 522 nm.

Cyclizations to porphyrins

Biladienes were cyclized into porphyrins using 1:1 $Cu(OAc)_2$ + $Zn(OAc)_2$ in DMF, according to Smith.[32] The crude copper porphyrin was chromatographed on silica gel (eluent CH_2Cl_2) to eliminate the aldehydic side-products (in the case of free pyrrolic position next to the new bridge) and demetallated either in TFA-H_2SO_4 or in TFA-ethanedithiol,[43] followed by an additional chromatography to purify the required base from "phyllo-type" impurities. Since we characterize all porphyrins of geochemical interest as their nickel complexes, so was done with the porphyrins from the cyclizations. Nickel complexes were crystallized from CH_2Cl_2-MeOH.

Nickel porphyrin **14** (34% based on biladiene **54**). NMR: 9.80, 9.78, 9.76 and 9.72 (4s, 1+1+1+1H, meso); 8.93 (q, 1H, 13-H, J = 1 Hz); 3.92 and 3.90 (2q, 2+2H, ethyl CH_2); 3.78 (d, 2H, i-Bu CH_2); 3.60 (d, 3H, 12-CH_3, J = 1 Hz); 3.47 (s, 9H, methyl); 2.60 (m, 1H, i-Bu CH); 1.78 and 1.76 (2t, 3+3H, ethyl CH_3); 1.26 (d, 6H, i-Bu CH_3). Vis. λ_{max} 390, 514 and 550 nm (rel. int. 1, 0.058 and 0.150). Anal. Calcd for $C_{32}H_{36}N_4Ni$: C, 71.79; H, 6.78; N, 10.46. Found: C, 71.9; H, 6.7; N, 10.5.

Nickel porphyrin **18** (29% based on biladiene **55**). NMR: 9.80, 9.75, 9.74 and 9.70 (4s, 1+1+1+1H, meso); 8.92 (q, 1H, 13-H, J = 1 Hz); 4.01 (m, 4H, cyclohexene α-CH_2); 3.91 (q, 4H, ethyl CH_2); 3.59 (d, 3H, 12-CH_3, J = 1 Hz); 3.49 (s, 6H, methyl); 2.45 (m, 4H, cyclohexene β-CH_2); 1.76 (t, 6H, ethyl CH_3). Vis. λ_{max} 390, 516 and 550 nm (rel. int. 1, 0.054 and 0.145). Anal. Calcd for $C_{31}H_{32}N_4Ni$: C, 71.70; H, 6.21; N, 10.79. Found: C, 71.4; H, 7.4; N, 12.6.

Nickel porphyrin **23** (21% based on biladiene **56**). NMR: 9.80, 9.65, 9.63 and 9.58 (4s, 1+1+1+1H, meso); 8.89 (q, 1H, 17-H, J = 1Hz); 4.26 and 4.22 (2t, 2+2H, chloroethyl); 3.96 (m, 4H, cyclohexene α-CH_2); 3.88 (q, 2H, ethyl CH_2); 3.59 (d, 1H, 18-CH_3, J = 1 Hz); 3.47 and 3.44 (2s, 3+3H, methyl); 2.44 (m, 4H, cyclohexene β-CH_2); 1.76 (t, 3H, ethyl CH_3). Vis. λ_{max} 390, 516 and 550 nm (rel. int. 1, 0.054 and 0.152). Anal. Calcd for $C_{31}H_{31}N_4ClNi$: C, 67.24; H, 5.64; N, 10.12. Found: C, 67.1; H, 5.6; N, 10.1.

Nickel porphyrin **28** (16% based on biladiene **57**). NMR: 9.82, 9.78 and 9.63 (3s, 1+2+1H, meso); 8.92 (s, 1H, 17-H); 4.32 and 4.22 (2t, 2+2H, CH_2CH_2Cl, J = 7 Hz); 3.92 (q, 4H, ethyl CH_2); 3.60, 3.51 and 3.48 (3s, 3+3+6H, CH_3); 1.77 (t, 6H, ethyl CH_3). Vis. λ_{max} 392, 514 and 550 nm (rel. int. 1, 0.067 and 0.152). Acceptable analytical figures could not be obtained for this compound.

Acid-catalyzed cyclization of vinyl- and hydroxyethylporphyrins

Synthesis of DPEP 1 from vinylporphyrin 8. Porphyrin **8** (15.5 mg) and TsOH.H_2O (344 mg; 55 eq.) were dissolved in 1,2-dichlorobenzene and heated in the dark under argon at 150-160°C for 8h. The solvent was evaporated under vacuum and the residue dissolved in CH_2Cl_2, washed with water (200 ml), saturated aqueous $NaHCO_3$ (2x100 ml), water (5x200 ml) and concentrated. Chromatography (silica gel, CH_2Cl_2) gave successively unreacted starting material, DPEP **1** and a significantly more polar band of alcohol **12** (yields: 50, 14 and 30%) . This last band increases as the "separation" proceeds. DPEP **1** was immediately metallated with $Ni(acac)_2$ in refluxing benzene and the nickel complex proved to be identical (NMR, reverse phase HPLC) with reference samples from various sources (geochemical or hemisynthetic from chlorophyll *a*).

Reduction of alcohol 12. This compound has been described in the litterature as a probable extraction artifact from geological sources.[35] The nickel complex showed the following NMR data: 9.87, 9.84 and 9.82 (3s, 1+1+1H, meso); 7.56 (d, 1H, 13"-H, J = 6 Hz); 4.65 (dd, 1H, 13'-Ha, J = 18 and 6 Hz); 4.4 (m, 1H, 17-ethyl CH_2 Ha); 3.95 (m, 1H, 17-ethyl CH_2 Hb); 3.95 (q, 4H, 3,8-ethyl CH_2); 3.71 (d, 1H, 13'-Hb, J = 18 Hz); 3.58, 3.53, 3.52 and 3.50 (4s, 3+3+3+3H, methyl); 1.89 (t, 6H, 3,8-ethyl CH_3), 1.74 (t, 3H, 17-ethyl CH_3). Alcohol **12** (8 mg, free base) was dissolved in CH_2Cl_2 and cooled to 0°C. Solid $NaBH_4$ (175 mg) was added followed, dropwise (vigourous gas evolution), by TFA (7 ml). The mixture was then stirred at 20°C for 20 h, after which it was diluted with water (100 ml), neutralized (NaOH pellets until basic), diluted with CH_2Cl_2 (30 ml), washed with water (3x100 ml) and concentrated. The product (DPEP **1**) was immediately transformed into its nickel complex. The reduction yield is virtually quantitative.

Synthesis of tetrahydrobenzoporphyrin 6. Chloroethylporphyrin **23** (20.5 mg) was dissolved in pyridine (24 ml; distilled over KOH) and heated to ca 100°C. After addition of aqueous NaOH (1M; 4 ml) the mixture was kept in the dark under argon at 115°C for 3 h. The solution was cooled to 20°C and a 1:1 H_2O-AcOH solution added (20 ml). After 10 min the mixture is evaporated to dryness, the residue dissolved in CH_2Cl_2 (50 ml) and washed with water (4x200 ml). The yield is quantitative and the vinylporphyrin **24** was used as such for the cyclization. NMR: 10.17, 10.12, 10.03 and 9.98 (4s, 1+1+1+1H, meso); 9.12 (broad s, 1H, pyrrole H); 8.30 (dd, 1H, 13'-H, J = 12 and 18 Hz); 6.39 (dd, 1H, 13"-Ha, J = 18 and 2 Hz); 6.17 (dd, 1H, 13"-Hb, J = 12 and 2 Hz); 4.17 (m, 4H, cyclohexene α-CH_2); 4.07 (q, 2H, ethyl CH_2); 3.77, 3.72 and 3.63 (3s, 3+3+3H, methyl); 2.55 (m, 4H, cyclohexene β-CH_2); 1.86 (t, 3H, ethyl CH_3); -3.7 (broad s, 2H, NH). Vis. λ_{max} 402, 502, 536, 572 and 626 nm (rel. int. 1, 0.090, 0.081, 0.054 and 0.041).

Tetrahydrobenzoporphyrin 6. The cyclization procedure described above was followed to give **6** (14%), alcohol **25** (28%), recycled into **6**) and recovered **24** (29%).

Alcohol **25** was only characterized by its NMR and visible data before being reduced to **6**. NMR: 10.00, 9.92 and 9.72 (3s, 1+1+1H, meso); 8.96 (broad s, 1H, pyrrole H); 7.12 (d, 1H, 13"-H, J = 6 Hz); 4.34 (dd, 1H, 13'-Ha, J = 18 and 6 Hz); 3.94-4.2 (m, 5H, 13'-Hb + cyclohexene α-CH_2); 3.99 (q, 2H, ethyl CH_2); 3.69 and 3.40 (2 broad s, 3+3H, 12,18-CH_3); 3.54 (s, 3H, 2-CH_3); 2.56 (m, 4H, cyclohexene β-CH_2); 1.84 (t, 3H, ethyl CH_3); -3.13 (broad s, 2H, NH). Vis. λ_{max} 400, 500, 534, 564 and 616 nm (rel. int. 1, 0.077, 0.034, 0.038 and 0.037).

Tetrahydrobenzoporphyrin **6** was fully characterized as its nickel complex, but NMR data for the free base are also given below.

Nickel complex **6**. NMR (high dilution in $CDCl_3$): 9.85, 9.69 and 9.66 (3s, 1+1+1H, meso); 8.93 (q, 1H, pyrrole H, J = 1 Hz); 5.09 (m, 2H, 13"-CH_2); 4.02 (m, 4H, cyclohexene α-CH_2); 4.01 (m, 2H, 13'-CH_2); 3.92 (q, 2H, ethyl CH_2); 3.62 (d, 3H, 18-CH_3, J = 1 Hz); 3.50 (s, 3H, 2-CH_3); 3.44 (broad s, 3H, 12-CH_3); 2.46 (m, 4H, cyclohexene β-CH_2); 1.78 (t, 3H, ethyl CH_3). NMR (high dilution in C_6D_6): 9.91, 9.80 and 9.75 (3s, 1+1+1H, meso); 8.79 (q, 1H, pyrrole H, J = 1 Hz); 4.70 (m, 2H, 13"-CH_2); 3.61 (m, 2H, 13'-CH_2); 3.83 (q, 2H, ethyl CH_2); 3.78 (m, 4H, cyclohexene α-CH_2); 3.46 (d, 3H, 18-CH_3); 3.30 (s, 6H, 2,12-CH_3); 2.2 (m, 4H, cyclohexene β-CH_2); 1.75 (t, 3H, ethyl CH_3). Vis. λ_{max} 394, 514 and 552 nm (rel. int. 1, 0.06 and 0.12). HRMS calcd for $C_{31}H_{30}N_4{}^{58}Ni$: 516.1823. Found: 516.1805.

Free base **6**: 10.05, 9.88 and 9.81 (3s, 1+1+1H, meso); 9.08 (broad s, 1H, pyrrole H); 5.34 (m, 2H, 13"-CH_2); 4.18 (m, 4H, cyclohexene α CH_2); 4.06 (m, 2H, 13'-CH_2); 4.00 (q, 2H, ethyl CH_2); 3.79 (broad s, 3H, 18-CH_3); 3.56 (s, 3H, 2-CH_3); 3.54 (broad s, 3H, 12-CH_3); 2.56 (m, 4H, cyclohexene β CH_2); 1.84 (t, 3H, ethyl CH_3); -2.7 (broad s, 2H, NH). Vis. λ_{max} 400, 500, 534, 566 and 616 nm (rel. int. 1, 0.084, 0.034, 0.036 and 0.027).

Synthesis of cyclopentenoporphyrins from hydroxyethylporphyrins; general procedure.

Acetylation. To a cold (0°C) solution of a nickel porphyrin ($6.1x10^{-5}$ mole) in CH_2Cl_2 (35 ml), kept under argon, was added Ac_2O (redistilled before use; 0.6 ml; 100 eq.) followed immediately by $SnCl_4$ (0.15 ml; 20 eq.). The resulting green reaction mixture was kept at 0°C for 3 min, then quenched with ice and water (100 ml) and stirred for 30 min. To the mixture was added CH_2Cl_2 (30 ml) and the organic phase was washed with saturated aqueous $NaHCO_3$ (200 ml) and water (4x200 ml). Evaporation of the solvent gave a residue which was purified on a silica gel column (elution with CH_2Cl_2).

Demetallation and reduction. A nickel acetylporphyrin (70 mg) was demetallated in TFA-H_2SO_4 (2 + 1 ml) for 40-50 min. Dilution with water, neutralization with NaOH pellets, extraction in CH_2Cl_2 and water washing gave the crude acetylporphyrin free base. This product was dissolved under argon in CH_2Cl_2 (20 ml) and a methanol solution of $NaBH_4$ (292 mg in 8 ml) slowly added. The reaction mixture was stirred for 2 h at 20°C, then quenched by addition of AcOH (7 ml), diluted with CH_2Cl_2 (60 ml), washed with saturated aqueous $NaHCO_3$ (100 ml) and water (4x200 ml). Evaporation gave the crude alcohol which was used as such for the cyclization step. The overall yield, from a nickel acetylporphyrin to a hydroxyethylporphyrin free base, as evaluated by tlc and NMR, is in the 80-95% range. The cyclization step was run under the same conditions as for the preformed vinylporphyrins and gave identical results.

DPEP series; additional experiments. Nickel acetylporphyrin **10**[28] was demetallated and reduced according to the above procedure into the corresponding alcohol (not characterized) which was immediately subjected to the cyclization conditions described above and gave DPEP **1** and alcohol **12** in addition to vinylporphyrin **8**. In another run, before the chromatography, the crude reaction mixture was metallated with $Ni(acac)_2$ (refluxing benzene in the dark for 13 h). The products were separated (preparative silica gel tlc; eluent CH_2Cl_2-hexane 1:2), to give the nickel complex of vinylporphyrin **8** (identical to a reference sample obtained by metallation of **8** free base), the nickel complex of DPEP **1**, and an additional red band. The absence of alcohol **12** confirmed that it was formed during the separation step. The additional band was tentatively attributed to dimer **13** and showed the following NMR data: 10.37, 9.95, 9.88, 9.83, 9.81, 9.80, 9.74, 9.68 (8s, 8x1H, meso); 8.32 (d, 1H, bridge olefin H α to porphyrin, J = 16 Hz); 7.64 (dd, 1H, bridge olefin H β to porphyrin, J = 16 and 6 Hz); 3.8-4.1 (m, 12H, ethyl CH_2); 3.82, 3.60, 3.54, 3.51, 3.47, 3.44, 3.39, 3.26 (8s, 8x3H, methyl), 3.15 (m, 1H, bridge allylic H); 2.58 (d, 3H, bridge methyl, J = 7 Hz); 1.7-1.9 (m, 18H, ethyl CH_3). Vis. λ_{max} 394, 518 and 554 nm (rel. int. 1, 0.80 and 0.188).

Isobutylporphyrin 2. Acetylation of nickel porphyrin **14** gave acetylporphyrin **15** (87%) which was demetallated and reduced to alcohol **16** (90%, crude).

Nickel acetylporphyrin **15** . NMR: 10.49, 9.78 and 9.64 (3s, 1+1+2H, meso); 3.88 and 3.87 (2q, 2+2H, ethyl CH_2); 3.76, 3.42 and 3.25 (3s, 3+9+3H, CH_3); 3.72 (d, 2H, i-Bu CH_2); 2.54 (m, 1H, i-Bu CH); 1.76 and 1.75 (2t, 3+3H, ethyl CH_3); 1.24 (d, 6H, i-Bu CH_3). Vis. λ_{max} 402, 525 and 572 nm (rel. int. 1, 0.070 and 0.155). Anal. Calcd for $C_{34}H_{38}N_4NiO$ + 0.5 CH_2Cl_2: C, 66.85; H, 6.34; N, 9.04. Found: C, 66.1; H, 6.3; N, 9.0.

Alcohol **16**. NMR: 10.45, 10.07 and 10.04 (3s, 1+2+1H, meso); 6.48 (q, 1H, 13'-CH, J = 7Hz); 4.09 and 4.06 (2q,

2+2H, ethyl CH_2); 3.66, 3.65, 3.63 and 3.61 (4s, 3+3+3+3H, methyl); 3.96 (d, 2H, i-Bu CH_2); 2.71 (m, 1H, i-Bu CH); 2.25 (d, 3H, 13"-CH_3, J = 7 Hz); 1.88 and 1.86 (2t, 3+3H, ethyl CH_3); 1.31 (d, 6H, i-Bu CH_3); -3.75 (broad s, 2H, NH). Vis. λ_{max} 400, 498, 536, 564 and 620 nm (rel. int. 1, 0.090, 0.066, 0.045 and 0.033).

The cyclization of alcohol **16** gave a first fraction which was not further characterized (= corresponding vinylporphyrin according to chromatographic behavior; 26%), the required cyclopentenoporphyrin **2** (9%) followed by alcohol **17** (8%) as showed by its NMR spectra run before it was recycled into **2** itself characterized as its nickel complex.

Nickel isobutylporphyrin **2**. NMR (high dilution in $CDCl_3$): 9.81, 9.80 and 9.77 (3s, 1+1+1H, meso); 5.20 (m, 2H, 13"-CH_2); 3.9-4.0 (m, 6H, 13'-CH_2 + 2 ethyl CH_2); 3.81 (d, 2H, i-Bu CH_2); 3.50 (broad s, 12H, methyl); 2.62 (m, 1H, i-Bu CH); 1.80 and 1.67 (2t, 3+3H, ethyl CH_3); 1.27 (d, 6H, i-Bu CH_3). NMR (high dilution in C_6D_6): 9.91, 9.89 and 9.80 (3s, 1+1+1H, meso); 4.63 (m, 2H, 13'-CH_2); 3.83 and 3.56 (2q, 2+2H, ethyl CH_2); 3.75 (d, 2H, i-Bu CH_2); 3.46 (m, 2H, 13"-CH_2); 3.35 (broad s, 3H, 12-CH_3); 3.30 and 3.27 (2s, 6+3H, methyl); 2.64 (m, 1H, i-Bu CH); 1.74 and 1.51 (2t, 3+3H, ethyl CH_3); 1.24 (d, 6H, i-Bu CH_3). Vis. λ_{max} 394, 514 and 552 nm (rel. int. 1, 0.06 and 0.11). HRMS calcd for $C_{34}H_{38}N_4{}^{58}Ni$: 560.2449. Found: 560.2467.

Free base **2**. 10.06, 10.02 and 9.97 (3s, 1+1+1H, meso); 5.43 (m, 2H, 13"-CH_2); 4.1-4.0 (m, 6H, 13'-CH_2 + 2 ethyl CH_2); 4.00 (d, 2H, i-Bu CH_2); 3.70, 3.69 and 3.58 (3s, 3+3+3H, 2,7,18-CH_3); 3.60 (broad s, 3H, 12-CH_3); 2.73 (m, 1H, i-Bu CH); 1.86 and 1.78 (2t, 3+3H, ethyl CH_3); 1.30 (d, 6H, i-Bu CH_3); -2.91 (broad s, 2H, NH).

Alcohol **17**. NMR: 10.08, 10.05 and 9.92 (3s, 1+1+1H, meso); 7.51 (d, 1H, 13"-H, J = 6 Hz); 4.54 (dd, 1H, 13'-Ha, J = 18 and 6 Hz); 4.38 (m, 1H, 17-ethyl CH_2 Ha); 4.00 (q, 2H, 3-ethyl CH_2); 3.94 (d, 2H, i-Bu CH_2); 3.89 (m, 1H, 17-ethyl CH_2 Hb); 3.77 (d, 1H, 13'-Hb, J = 18 Hz); 3.66 and 3.55 (2s, 6+3H, 2,7,18-CH_3); 3.53 (broad s, 3H, 12-CH_3); 2.70 (m, 1H, i-Bu CH); 1.88 and 1.69 (2t, 3+3H, ethyl CH_3); 1.29 (d, 6H, i-Bu CH_3); -3.02 (broad s, 2H, NH). Vis. λ_{max} 400, 500, 536, 566 and 618 nm (rel. int. 1, 0.083, 0.042, 0.044 and 0.042).

Tetrahydrobenzoporphyrin 5. Acetylation of nickel porphyrin **18** gave acetylporphyrin **19** (70%) which was demetallated and reduced to alcohol **20** (91%, crude).

Nickel acetylporphyrin **19**. NMR: 10.53, 9.76, 9.67 and 9.57 (4s, 1+1+1+1H, meso); 3.95 (m, 4H, cyclohexene α-CH_2); 3.89 and 3.86 (2q, 2+2H, ethyl CH_2); 3.78, 3.44 and 3.43 (3s, 3+3+3H, methyl); 3.26 (s, 3H, acetyl CH_3); 2.43 (m, 4H, cyclohexene β-CH_2); 1.76 and 1.74 (2t, 3+3H, ethyl CH_3). Vis. λ_{max} 402, 530 (sh.) and 574 nm (rel. int. 1, ca 0.065 and 0.16). Anal. Calcd for $C_{33}H_{34}N_4NiO$: C, 70.61; H, 6.10; N, 9.98. Found: C, 69.5; H, 6.5; N, 9.4.

Alcohol **20**. NMR: 10.54, 10.10, 10.00 and 9.98 (4s, 1+1+1+1H), meso); 6.57 (q, 1H, 13'-H); 4.19 (m, 4H, cyclohexene α CH_2); 4.09 and 4.05 (2q, 2+2H, ethyl CH_2); 3.67 and 3.62 (2s, 6+3H, methyl); 2.56 (m, 4H, cyclohexene β CH2); 2.30 (d, 3H, 13'-CH_3); 1.87 and 1.86 (2t, 3+3H, ethyl CH_3); -3.8 (broad s, 2H, NH). Vis. λ_{max} 398, 498, 534, 566 and 620 nm (rel. int. 1, 0.080, 0.061, 0.039 and 0.022)

The cyclization of alcohol **20** gave a first fraction which was not further characterized (= corresponding vinylporphyrin according to chromatographic behavior; 26%), the required porphyrin **5** (8%) followed by alcohol **21** (23%) as showed by its NMR spectrum run before it was recycled into **5**, itself characterized as its nickel complex.

Nickel tetrahydrobenzoporphyrin **5**. NMR (high dilution in $CDCl_3$): 9.78, 9.67 and 9.65 (3s, 1+1+1H, meso); 5.12 (m, 2H, 13"-CH_2); 3.9-4.0 (m, 6H, 13'-CH_2 + cyclohexene α-CH_2); 3.91 and 3.84 (2q, 2+2H, ethyl CH_2); 3.49 and 3.48 (2s, 3+3H, 2,18-CH_3); 3.42 (broad s, 3H, 12-CH_3); 2.46 (m, 4H, cyclohexene β-CH_2); 1.77 and 1.65 (2t, 3+3H, ethyl CH_3). NMR (high dilution in C_6D_6): 9.90, 9.83 and 9.81 (3s, 1+1+1H, meso); 4.76 (m, 2H, 13"-CH_2); 3.82 (m, 4H, cyclohexene α-CH_2); 3.55 (m, 2H, 13'-CH_2); 3.84 and 3.71 (2q, 2+2H, ethyl CH_2); 3.34 and 3.33 (2s, 3+3H, 2,18-CH_3); 3.36 (broad s, 3H, 12-CH_3); 2.19 (m, 4H, cyclohexene β-CH_2); 1.75 and 1.58 (2t, 3+3H, ethyl CH_3). Vis. λ_{max} 394, 514 and 552 nm (rel. int. 1, 0.06 and 0.12). HRMS calcd for $C_{33}H_{34}N_4{}^{58}Ni$: 544.2136. Found: 544.2140.

Free base **5**. NMR: 10.04, 9.89 and 9.87 (3s, 1+1+1H, meso); 5.38 (m, 2H, 13"-CH_2); 4.19 (m, 4H, cyclohexene α-CH_2); 4.08 and 4.00 (2q, 2+2H, ethyl CH_2); 4.06 (m, 2H, 13'-CH_2); 3.67 (broad s, 3H, 12-CH_3); 3.56 (s, 6H, 2,18-CH_3); 2.57 (m, 4H, cyclohexene β-CH_2); 1.84 and 1.77 (2t, 3+3H, ethyl CH_3); -3.03 (broad s, 2H, NH).

Alcohol **21**. NMR: 10.10, 9.93 and 9.87 (3s, 1+1+1H, meso); 7.58 (d, 1H, 13"-H, J = 6 Hz); 4.59 (dd, 1H, 13'-Ha, J = 18 and 6 Hz); 4.45 (m, 1H, 17-ethyl CH_2 Ha); 4.19 (m, 4H, cyclohexene α-CH_2); 3.96 (q, 2H, 3-ethyl CH_2); 3.9 (m, 1H,

17-ethyl CH_2 Hb); 3.86 (d, 1H, 13'-Hb, J = 18 Hz); 3.68 and 3.54 (2s, 3+3H, 2,18-CH_3); 3.52 (broad s, 3H, 12-CH_3); 2.57 (m, 4H, cyclohexene β-CH_2); 1.82 and 1.73 (2t, 3+3H, ethyl CH_3); -2.85 (broad s, 2H, NH).Vis λ_{max} 400, 502, 536, 564 and 616 nm (rel. int. 1, 0.075, 0.038, 0.041 and 0.039).

Cyclization of isopropenylporphyrins

Porphyrin 3 from Gilsonite. Acetylporphyrin free base **10** in CH_2Cl_2 was treated at reflux with an excess $Zn(OAc)_2$ in MeOH. After evaporation the mixture is filtered through a short silica gel column (eluent CH_2Cl_2) to give the zinc complex used as such for the next step. Wittig reaction: to triphenylmethylphosphonium bromide (129 mg: 12 eq.) in anhydrous THF (2 ml) under argon was added n-BuLi (11 eq.; hexane solution) followed, after 15 min, by the solid acetylporphyrin zinc complex (16 mg; $2.9x10^{-5}$ mole). After 50 min at 55°C the solution was diluted with CH_2Cl_2 (50 ml), washed with water (3x100 ml) and concentrated. Isolation of the less polar red band on a short silica gel column (eluent CH_2Cl_2) followed by treatment with a few drops 6N HCl, washing with aqueous ammonium carbonate and water, gave isopropenylporphyrin free base **26** (10 mg; 70%). This product was used as such for the cyclization reaction ($TsOH.H_2O$, 52 eq.; 150°C; 8.75 h: work-up as for vinylporphyrins) and gave (silica gel column, eluent CH_2Cl_2) the required porphyrin **3** (56%), fully characterized as its nickel complex, and a minor fraction (ca 20%) which could not be freed from traces of **3**. We attribute structure **27** to this last product (see NMR data below).

Isopropenylporphyrin **26**. NMR: 10.18, 10.16 and 10.10 (3s, 1+1+2H, meso); 6.13 (broad s, 1H, 13"-Ha); 5.71 (broad s, 1H, 13"-Hb); 4.15, 4.12 and 4.08 (3q, 2+2+2H, ethyl CH_2); 3.69 (s, 6H, 2,7-CH_3); 3.67 and 3.62 (2 broad s, 3+3H, 12,18-CH_3); 2.85 (s, 3H, 13'-CH_3); 1.90 and 1.89 (2t, 3+6H, ethyl CH_3); -3.7 (broad s, 2H, NH). Vis. λ_{max} 397, 497, 533, 565 and 619 nm (rel. int. 1, 0.080, 0.061, 0.040 and 0.023).

Nickel porphyrin **3**. NMR: (high dilution in $CDCl_3$) 9.78, 9.77 and 9.76 (3s, 1+1+1H, meso); 5.58 (dd, 1H, 13"-Ha, J = 17 and 7 Hz); 4.71 (dd, 1H, 13"-Hb, J = 17 and 2 Hz); 4.49 (m, 1H, 13'-H); 3.95, 3.92 and 3.87 (3q, 2+2+2H, ethyl CH_2); 3.52 (d, 3H, 12-CH_3, J = 1 Hz); 3.50 and 3.48 (2s, 3+6H, 2,7,18-CH_3); 1.96 (d, 3H, 13'-CH_3, J = 7 Hz); 1.79, 1.78, 1.67 (3t, 3+3+3H, ethyl CH_3). NMR: (high dilution in C_6D_6) 9.93, 9.89 and 9.86 (3s, 1+1+1H, meso); 5.15 (dd, 1H, 13"-Ha, J = 17 and 7 Hz); 4.48 (dd, 1H, 13"-Hb, J = 17 and 2 Hz); 4.14 (m, 1H, 13'-H); 3.82, 3.81 and 3.70 (3q, 2+2+2H, 3,8,17-ethyl CH_2); 3.36 (d, 3H, 12-CH_3, J = 1 Hz); 3.32 and 3.29 (2s, 3+6H, 2,7,18-CH_3); 1.75 (d, 3H, 13'-CH_3, J = 7 Hz); 1.73 (t, 6H, 3,8-ethyl CH_3); 1.58 (t, 3H, 17-ethyl CH_3). Vis. λ_{max} 393, 515 and 551 nm (rel. int. 1, 0.061 and 0.112). HRMS calcd for $C_{33}H_{36}N_4{}^{58}Ni$: 546.2292. Found: 546.2295.

Free base **3**. NMR: 10.06, 10.01 and 10.00 (3s, 1+1+1H, meso); 5.76 (dd, 1H, 13"-Ha, J = 18 and 7 Hz); 4.95 (dd, 1H, 13"-Hb, J = 18 and 2 Hz); 4.60 (m, 1H, 13'-H); 4.15, 4.12 and 4.03 (3q, 2+2+2H, 3,8,17-ethyl CH_2); 3.70 (s, 6H, 2,7-CH_3); 3.64 (d, 3H, 12-CH_3, J= 1 Hz); 3.58 (s, 3H, 18-CH_3); 2.05 (d, 3H, 13'-CH_3, J = 7 Hz); 1.90, 1.86 and 1.80 (3t, 3+3+3H, 3,8,17-ethyl CH_3); -2.87 (broad s, 2H, NH).

Porphyrin **27**. NMR: 10.10, 10.05 and 9.76 (3s, 1+1+1H, meso); 8.59 (broad s, 1H, 13"-H); 4.20, 4.15 and 3.96 (3q, 2+2+2H, 3,8,17-ethyl CH_2); 3.70, 3.69, 3.65 and 3.54 (4s, 3+3+3+3H, 2,7,12,18-CH_3); 3.12 (s, 3H, 13'-CH_3); 1.92, 1.90 and 1.84 (3t, 3+3+3H, ethyl CH_3); -2.83 (broad s, 2H, NH).

Tetrahydrobenzoporphyrin 7. Along this synthesis and the following, and due to the small quantities of starting material used, the intermediate products were only analyzed by NMR, UV-visible and tlc (one clean spot on visible + UV detection) after each step.

Acetylation and demetallation (see above) of nickel porphyrin **23** gave acetylporphyrin **30** (crystallized from CH_2Cl_2-MeOH): NMR: 10.81, 10.20 and 9.92 (3s, 1+1+2H, meso); 4.59 (t, 2H, 13'-CH_2); 4.42 (t, 2H, 13"-CH_2); 4.10 (q, 2H, ethyl CH_2); 4.06 (m, 4H, cyclohexene α-CH_2); 3.94, 3.69 and 3.68 (3s, 3+3+3H, CH_3); 3.34 (s, 3H, acetyl CH_3); 2.50 (m, 4H, cyclohexene β-CH_2); 1.87 (t, 3H, ethyl CH_3); -3.5 (broad s, 2H, NH). Vis. λ_{max} 410, 510, 548, 576 and 632 nm (rel. int. 1, 0.061, 0.071, 0.048 and 0.012).

Protection of acetyl group. A solution of porphyrin **30** (28 mg), ethylene glycol (2.5 ml), $TsOH.H_2O$ (27 mg) in benzene (10 ml) was refluxed for 4 h under a Dean-Stark apparatus. Partition between CH_2Cl_2 60 ml) and water (100 ml) gave an organic phase which was washed with water (2x200 ml) and concentrated. Elution through alumina (20 ml, eluent CH_2Cl_2) and

evaporation of the solvent gave porphyrin **32** (27 mg). NMR: 10.92, 10.18, 10.00 and 9.99 (4s, 1+1+1+1H, meso); 4.60 (t, 2H, 13'-CH_2); 4.40 (t, 2H, 13"-CH_2); 4.46 and 4.15 (2t, 2+2H, OCH_2CH_2O); 4.14 (m, 4H, cyclohexene α-CH_2); 4.08 (q, 2H, ethyl CH_2); 3.84, 3.69 and 3.65 (3s, 3+3+3H, CH_3); 2.48 (s, 3H, 17" CH_3); 2.53 (m, 4H, cyclohexene β-CH_2); 1.87 (t, 3H, ethyl CH_3); -3.7 (broad s, 2H, NH). Vis. λ_{max} 400, 500, 532, 568 and 622 nm (rel. int. 1, 0.077, 0.055, 0.040 and 0.023).

Vinylporphyrin **34**. The elimination reaction from **32** was performed in pyridine (20 ml) + 1M aqueous NaOH (4 ml) at 115°C for 3 h. Dilution with 1:1 water-AcOH (20 ml), then CH_2Cl_2 (50 ml) and washings with water (4x100 ml) gave, after evaporation, porphyrin **34** (22 mg). NMR: 11.11, 10.16, 10.03 and 9.94 (4s, 1+1+1+1H, meso); 8.36 (dd, 1H, 13'-H, J = 12 and 18 Hz); 6.48 (dd, 1H, 13"-H, J = 18 and 2 Hz); 6.22 (dd, 1H, 13"-Hb, J = 12 and 2 Hz); 4.45 and 4.18 (2t, 4H, OCH_2CH_2O); 4.15 (m, 4H, cyclohexene α-CH_2); 4.07 (q, 2H, ethyl CH_2); 3.84, 3.75 and 3.64 (3s, 3+3+3H, CH_3); 2.54 (m, 4H, cyclohexene β-CH_2); 2.48 (s, 3H, 17"-CH_3); 1.86 (t, 3H, ethyl CH_3); -3.6 (broad s, 2H, NH). Vis. λ_{max} 404, 502, 536, 572 and 626 nm (rel. int. 1, 0.084, 0.065, 0.054 and 0.033).

Deprotection of the acetyl group. To a solution of porphyrin **34** (24 mg) in acetone (30 ml) and CH_2Cl_2 (6 ml) was added water (3 ml) an $TsOH.H_2O$ (70 mg). The mixture was heated at 55°C for 20 h, then diluted with CH_2Cl_2 (60 ml), and washed successively with water (200 ml), saturated aqueous $NaHCO_3$ (100 ml) and water (4x200 ml). Evaporation gave porphyrin **35** (20 mg). NMR: 10.97, 10.20, 9.96 and 9.91 (4s, 1+1+1+1H, meso); 8.34 (dd, 1H, 13'-H, J = 12 and 18 Hz); 6.52 (dd, 1H, 13"-Ha, J = 18 and 2 Hz); 6.25 (dd, 1H, 13"-Hb, J = 12 and 2 Hz); 4.09 (m, 4H, cyclohexene α-CH_2); 4.10 (q, 2H, ethyl CH_2); 3.94, 3.75 and 3.68 (3s, 3+3+3H, CH_3); 3.35 (s, 3H, acetyl CH_3); 2.50 (m, 4H, cyclohexene β-CH_2); 1.86 (t, 3H, ethyl CH_3); -2.8 (broad s, 2H, NH). Vis. λ_{max} 414, 512, 552, 582 and 656 nm (rel. int. 1, 0.065, 0.071, 0.055 and 0.015).

Wittig reaction. Porphyrin **35** was first metallated with zinc (excess $Zn(OAc)_2$ in refluxing CH_2Cl_2-MeOH), the solution evaporated and the resulting product filtered through a short silca gel column (eluent CH_2Cl_2 + 5% AcOEt). To dry (vacuum, 50°C) methyltriphenylphosphonium bromide was added successively anhydrous THF (7 ml) and n-BuLi (1.5 M; 0.35 ml). After 15 min at 20°C zinc porphyrin **35** (16 mg) was added and the solution kept at 20°C for 1 h. The solvent were then evaporated and the residue dissolved in CH_2Cl_2 (60 ml) and washed with water (4x200 ml). Chromatography on silica gel (eluent CH_2Cl_2) gave the zinc complex of porphyrin **37** (9 mg; 56 %). This complex was quantitatively demetallated with HCl (few drops added to a CH_2Cl_2 solution; then aqueous ammonium carbonate and water washings) to give free base **37**. NMR: 10.30, 10.12, 10.04 and 9.97 (4s, 1+1+1+1H, meso); 8.31 (dd, 1H, 13'-H, J = 12 and 18 Hz); 6.41 (dd, 1H, 13"-Ha, J = 18 and 2 Hz); 6.17 (dd, 1H, 13"-Hb, J = 12 and 2 Hz); 6.12 (broad s, 1H, 17"-Ha); 5.71 (broad s, 1H, 17"-Hb); 4.16 (m, 4H, cyclohexene α-CH_2); 4.07 (q, 2H, ethyl CH_2); 3.74, 3.68 and 3.64 (3s, 3+3+3H, CH_3); 2.82 (s, 3H, isopropenyl CH_3); 2.54 (m, 4H, cyclohexene β-CH_2); 1.86 (t, 3H, ethyl CH_3); -3.6 (broad s, 2H, NH). Vis. λ_{max} 404, 502, 538, 572 and 626 nm (rel. int. 1, 0.088, 0.074, 0.051 and 0.035).

Cyclization to porphyrin **39**. Free base **37** (8 mg) and $TsOH.H_2O$ (40 mg) in o-dichlorobenzene (6 ml) were heated at 125°C for 5 h. The solvent was evaporated under vacuum and the residue dissolved in CH_2Cl_2 (50 ml) and washed with saturated aqueous $NaHCO_3$ (2x200 ml) and water (4x200 ml). Pure porphyrin **39** (3 mg) was obtained after filtration through a short silica gel column (eluent CH_2Cl_2). NMR: 9.96, 9.94 and 9.87 (3s, 1+1+1H, meso); 8.36 (dd, 1H, 13'-H, J = 12 and 18 Hz); 6.19 (dd, 1H, 13"-Ha, J = 18 and 2 Hz); 6.16 (dd, 1H, 13"-Hb, J = 12 and 2 Hz); 5.64 (dd, 1H, 15'-Ha, J = 17 and 7 Hz); 4.90 (dd, 1H, 15'-Hb, J = 17 and 2 Hz); 4.55 (m, 1H, 15"-H); 4.10 (q, 2H, ethyl CH_2); 4.09 (m, 4H, cyclohexene α-CH_2); 3.78, 3.65 and 3.60 (3s, 3+3+3H, CH_3); 2.50 (m, 4H, cyclohexene β-CH_2); 2.02 (d, 3H, 15"-CH_3, J = 7 Hz); 1.86 (t, 3H, ethyl CH_3); -2.77 (broad s, 2H, NH). Vis. λ_{max} 406, 504, 538, 572 and 622 nm (rel. int. 1, 0.088, 0.027, 0.046 and 0.053).

Cleavage of vinyl group to **7**. Porphyrin **39** (3 mg) and resorcinol (240 mg) were heated in a sealed tube for 1.5 h at 220°C. The content of the tube was then extracted with acetone and diluted with CH_2Cl_2 (60 ml) and water (200 ml). The aqueous phase was extracted with CH_2Cl_2 (2x30 ml) and the combined organic phases washed with water (3x200 ml). Base **7** was purified by filtration through silica gel (eluent CH_2Cl_2). Metallation with $Ni(acac)_2$ followed by filtration on silica gel (eluent CH_2Cl_2) gave the nickel complex of **7** (2 mg).

Nickel porphyrin **7**. NMR (high dilution in C_6D_6): 9.86, 9.82 and 9.80 (3s, 1+1+1H, meso); 8.83 (s, 1H, 13-H); 5.05 (dd, 1H, 15'-Ha, J = 17 and 7 Hz); 4.36 (dd, 1H, 15'-Hb, J = 17 and 2 Hz); 4.2 (m, 1H, 15"-H); 3.76 (m, 4H, cyclohexene α-CH_2); 3.82 (q, 2H, ethyl CH_2); 3.48 (s, 3H, 12-CH_3); 3.34 (s, 3H, 18-CH_3); 3.30 (s, 3H, 2-CH_3); 2.17 (m, 4H, cyclohexene-

β CH_2); 1.74 (d, 3H, 15"-CH_3, J = 7 Hz); 1.74 (t, 3H, ethyl CH_3). NMR (high dilution in $CDCl_3$): 9.76, 9.72 and 9.67 (3s, 1+1+1H, meso); 8.91 (s, 1H, 13-H); 5.37 (dd, 1H, 15'-Ha, J = 17 and 7 Hz); 4.62 (dd, 1H, 15'-Hb, J = 17 and 2 Hz); 4.54 (m, 1H, 15"-H); 4.00 (m, 4H, cyclohexene α-CH_2); 3.92 (q, 2H, ethyl CH_2); 3.59 (s, 3H, 12-CH_3); 3.49 (s, 6H, 2,18-CH_3); 2.45 (m, 4H, cyclohexene β-CH_2); 1.96 (d, 3H, 15"-CH_3, J = 7 Hz); 1.78 (t, 3H, ethyl CH_3). Vis. λ_{max} 394, 514 and 552 nm (rel. int. 1, 0.07 and 0.12). HRMS calcd for $C_{32}H_{32}N_4{}^{58}Ni$: 530.1980. Found: 530.1954.

Free base 7. NMR: 9.95, 9.94 and 9.91 (3s, 1+1+1H, meso); 9.08 (s, 1H, 13-H); 5.64 (dd, 1H, 15'-Ha, J = 17 and 7 Hz); 4.88 (dd, 1H, 15'-Hb, J = 17 and 2 Hz); 4.61 (m, 1H, 15"-H); 4.08 (m, 4H, cyclohexene α-CH_2); 4.09 (q, 2H, ethyl CH_2); 3.78 (s, 3H, 18-CH_3); 3.65 (s, 3H, 2-CH_3); 3.61 (s, 3H, 12-CH_3); 2.49 (m, 4H, cyclohexene β-CH_2); 2.03 (d, 3H, 15"-CH_3, J = 7 Hz); 1.87 (t, 3H, ethyl CH_3); -2.72 (broad s, 2H, NH).

Porphyrin 4. The procedure employed to prepare **4** was identical to that described above for **7** and as was the yield of each step.

Acetylporphyrin **29**. NMR: 10.81, 10.17, 10.02 and 10.01 (4s, 1+1+1+1H, meso); 4.60 and 4.42 (2t, 2+2H, CH_2CH_2Cl, J = 7 Hz); 4.12 and 4.00 (2q, 2+2H, ethyl CH_2); 3.92, 3.71, 3.66, 3.56 and 3.33 (5s, 5x3H, CH_3); 1.88 and 1.85 (2t, 3+3H, ethyl CH_3); -3.58 (broad s, 2H, NH). Vis. λ_{max} 407, 509, 548, 577 and 634 nm (rel. int. 1, 0.080, 0.094, 0.064 and 0.013).

Protected acetylporphyrin **31**. NMR: 10.92, 10.18, 10.10 and 10.08 (4s, 1+1+1+1H, meso); 4.60 and 4.40 (2t, 2+2H, CH_2CH_2Cl, J = 7Hz); 4.45 (m, 2H, OCH_2); 4.05-4.18 (m, 6H, ethyl CH_2 + OCH_2); 3.84, 3.71, 3.66 and 3.64 (4s, 3+3+3+3H, CH_3); 2.48 (s, 3H, 17'-CH_3); 1.88 (t, 6H, ethyl CH_3); -3.7 (broad s, 2H, NH). Vis. λ_{max} 399, 498, 569 and 621 nm (rel. int. 1, 0.082, 0.057, 0.040 and 0.025).

Vinylporphyrin **33**. NMR: 11.10, 10.16, 10.13 and 10.06 (4s, 1+1+1+1H, meso); 8.36 (dd, 1H, 13'-H, J = 18 and 12 Hz); 6.47 (dd, 1H, 13"-Ha, J = 18 and 2 Hz); 6.22 (dd, 1H, 13"-Hb, J = 12 and 2 Hz); 4.45 (m, 2H, CH_2O); 4.07 -4.18 (m, 6H, ethyl CH_2 + CH_2O); 3.85, 3.77 and 3.64 (3s, 3+3+6H, CH_3); 2.48 (s, 3H, 17"-CH_3); -3.62 (broad s, 2H, NH). Vis. λ_{max} 401, 502, 536, 571 and 625 nm (rel. int. 1, 0.096, 0.068, 0.044 and 0.024). In this series, deprotection of the acetyl group, metallation of the resulting product by zinc, Wittig reaction, and removal of zinc were carried out without isolation of any intermediate.

Porphyrin **36**. NMR: 10.30, 1015, 10.13 and 10.09 (4s, 1+1+1+1H, meso); 8.31 (dd, 1H, 13'-H, J = 18 and 12 Hz); 6.42 (dd, 1H, 13"-Ha, J = 18 and 2 Hz); 6.18 (dd, 1H, 13"-Hb, J = 12 and 2 Hz); 6.13 and 5.70 (2d, 1+1H, 17"-CH_2, J = 2 Hz); 4.12 and 4.11 (2q, 2+2H, ethyl CH_2); 3.77, 3.68 and 3.65 (3s, 3+3+6H, CH_3); 2.82 (s, 3H, 17'-CH_3); 1.89 (t, 6H, ethyl CH_3); -3.65 (broad s, 2H, NH). Vis. λ_{max} 402, 501, 536, 570 and 625 nm (rel. int. 1, 0.093, 0.073, 0.047 and 0.028).

Cyclopentenoporphyrin **38**. NMR: 10.12, 10.04 and 9.91 (3s, 1+1+1H, meso); 8.30 (dd, 1H, 13'-H, J = 18 and 12 Hz); 6.17 (dd, 1H, 13"-Ha, J = 18 and 2 Hz); 6.15 (dd, 1H, 13"-Hb, J = 12 and 2 Hz); 5.61 (dd, 1H, 15'-Ha, J = 17 and 7 Hz); 4.85 (dd, 1H, 15'-Hb, J = 17 and 2 Hz); 4.49 (m, 1H, 15"-H); 4.12 and 4.02 (2q, 2+2H, ethyl CH_2); 3.79, 3.64, 3.59 and 3.58 (4s, 3+3+3+3H, CH_3); 2.00 (d, 3H, 15"-CH_3, J = 7 Hz); 1.88 and 1.86 (2t, 3+3H, ethyl CH_3); -2.8 (broad s, 2H, NH). Vis. λ_{max} 404, 503, 538, 570 and 622 nm (rel. int. 1, 0.094, 0.025, 0.031 and 0.034).

Nickel porphyrin **4**. NMR (high dilution in C_6D_6): 9.97, 9.89 and 9.83 (3s, 1+1+1H); 8.81 (broad s, 1H, 13-H); 5.03 (dd, 1H, 15'-Ha, J = 17 and 7 Hz); 4.35 (dd, 1H, 15'-Hb, J = 17 and 2 Hz); 4.17 (m, 1H, 15"-H); 3.81 (q, 4H, ethyl CH_2); 3.47, 3.33, 3.28 and 3.27 (4s, 3+3+3+3H, CH_3); 1.73 and 1.70 (2q, 3+3H, ethyl CH_3); 1.72 (d, 3H, 15"-CH_3). NMR (high dilution in $CDCl_3$): 9.85 and 9.80 (2s, 1+2H, meso); 8.93 (broad s, 1H, 13-H); 5.40 (dd, 1H, 15'-Ha, J = 17 and 7 Hz); 4.64 (dd, 1H, 15'-Hb, J = 17 and 2 Hz); 4.56 (m, 1H, 15"-H); 3.95 (q, 4H, ethyl CH_2); 3.63, 3.51 and 3.50 (3s, 3+3+6H, CH_3); 1.83 (d, 3H, 15"-CH_3); 1.79 (t, 6H, ethyl CH_3). Vis. λ_{max} 396, 514 and 552 nm (rel. int. 1, 0.07, 0.12). HRMS calcd for $C_{31}H_{32}N_4{}^{58}Ni$: 518.1980. Found: 518.1948.

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References.

1. Callot, H.J.; Ocampo, R.; Albrecht P. *Energy and Fuels*, **1990**, *4*, 635-639.
2. Chicarelli, M.M.; Kaur, S.; Maxwell J.R. *A.C.S. Symposium Series*, **1987**, *344*, 40-67.
3. Ocampo, R.; Callot, H.J.; Albrecht P. *A.C.S. Symposium Series*, **1987**, *344*, 68-73.
4. Baker, E.W.; Corwin, A.H.; Klesper, E.; Wei, P.E. *J. Org. Chem.* **1968**, *33*, 3144-3148.
5. Clezy, P.S.; Prashar J.K. *Austr. J. Chem.* **1990**, *43*, 825-837.
6. Clezy, P.S.; Jenie, U.; Prashar, J.K. *Austr. J. Chem.* **1990**, *43*, 839-856.
7. Verne-Mismer, J.; Ocampo, R.; Callot, H.J.; Albrecht P. *J. Chem. Soc., Chem. Commun.* **1987**, 1581-1583.
8. Lash, T.D.; Balasubramaniam, R.P.; Catarello, J.J.; Johnson, M.C.; May, D.A. Jr; Bladel, K.A.; Feely, J.M.; Hoehner M.C.; Marron, T.G.; Nguyen, T.H.; Perun, T.J. Jr; Quinzon, D.M.; Shiner, C.M.; Watson, A. *Energy & Fuels*, **1990**, *4*, 668-674.
9. Lash, T.D.; Balasubramaniam, R.P. *Tetrahedron Lett.* **1990**, *31*, 7545-7548.
10. Flaugh, M.E.; Rapoport, H. *J. Am. Chem. Soc.* **1968**, *90*, 6877-6879.
11. Chaudry, I.A.; Clezy, P.S.; Mirza, A.H. *Austr. J. Chem.* **1980**, *33*, 1095-1104.
12. Clezy, P.S.; Phuc, L.V.; Prashar, J.K. *Aust. J. Chem.* **1991**, *44*, 1061-1075.
13. Clezy, P. S. *Aust. J. Chem.* **1991**, *44*, 1163-1193.
14. Clezy, P.S.; Mirza, A.H.; Prashar, J.K. *Austr. J. Chem.* **1990**, *43*, 857-866.
15. Smith, K.M.; Langry, K.C.; Minnetian, O.M. *J. Org. Chem.* **1984**, *49*, 4602-4609.
16. Evstigneeva, R.P. *Pure Appl. Chem.* **1981**, *53*, 1129-1140.
17. Ponomarev, G.V.; Shul'ga, A.M. *Khim. Geterotsikl. Seodin.* **1984**, 479-484.
18. Kenner, G.W.; Rimmer, J.; Smith, K.M.; Unsworth, J.F. *Phil. Trans. R. Soc. London B*, **1976**, *273*, 255-276; *J. Chem. Soc. Perkin Trans. 1*, **1978**, 845-852.
19. Carr, R.P.; Jackson, A.H.; Kenner, G.W.; Sach, G.S. *J. Chem. Soc.* (C) **1971**, 487-502
20. Preliminary accounts of this work: a) Bauder, C.; Ocampo, R.; Callot, H.J. *Synlett*, **1990**, 335-337; b) Bauder, C.; Ocampo, R.; Callot, H.J. *Tetrahedron Lett.* **1991**, *32*, 2537-2540.
21. Ocampo, R.; Callot, H.J.; Albrecht, P. *J. Chem. Soc. Chem. Comm.* **1985**, 200-201.
22. Ocampo, R.; Callot, H.J.; Albrecht, P.; Kintzinger, J.P. *Tetrahedron Lett.* **1984**, *25*, 2589-2592.
23. Verne-Mismer, J.; Ocampo, R.; Callot, H.J.; Albrecht, P. *J. Chem. Soc. Chem. Comm.* **1987**, 1581-1583.
24. Verne-Mismer, J.; Ocampo, R.; Bauder, C.; Callot, H.J.; Albrecht, P. *Energy & Fuels*, **1990**, *4*, 639-643.
25. Clezy, P.S.; Mirza, A.H. *Austr. J. Chem.* **1982**, *35*, 197-209.
26. Smith, K.M.; Craig, G.W. *J. Org. Chem.* **1983**, *48*, 4302-4306.
27. Smith, K.M.; Goff, D.A. *J. Org. Chem.* **1986**, *51*, 657-666. Jackson, A.H.; Pandey, R.K.; Smith, K.M. *J. Chem. Soc. Perkin Trans. 1*, **1987**, 299-305.
28. Jeandon, C.; Bauder, C.; Callot, H.J. *Energy & Fuels*, **1990**, *4*, 665-667.
29. An alternative route to isopropenylporphyrins, via palladium mediated coupling of 3-chloro-2-methylpropene has been proposed recently: see Morris, I.K.; Snow, K.M.; Smith, N.W.; Smith, K.M. *J. Org. Chem.* **1990**, *55*, 1231-1236.
30. Clewlow, P.J.; Jackson, A.H. *J. Chem. Soc. Perkin Trans. 1*, **1990**, 1925-1936.
31. Bonnett, R.; Campion-Smith, I.H.; Page, A.J. *J. Chem. Soc. Perkin Trans. 1*, **1977**, 68-71. DiNello, R.K.; Dolphin, D. *J. Org. Chem.* **1981**, *46*, 3498-3502.
32. Smith, K.M.; Minnetian, O.M. *J. Chem. Soc. Perkin 1*, **1986**, 277-280. See also ref. 15 and 26.
33. Gribble, G.W.; Leese, R.M.; Evans, B.E. *Synthesis*, **1977**, 172-176. This method was used independently to reduce a 13' carbonyl group in the pheophorbide series: Smith, N.W.; Smith, KM. *Energy & Fuels*, **1990**, *4*, 675-688.
34. Ponomarev, G.V.; Shulga, A.M. *Khim. Geterotsikl. Soedin.* **1984**, *4*, 485-489. This instability of DPEP and related compounds has been confirmed by Clezy and col.: see ref. 12 above.
35. Krane, J.; Skjetne, T.; Telnaes, N.; Bjorøy, M.; Schou, L.; Solli, H. *Org. Geochem.* 1984, *6*, 193-201.
36. Byrne, C.J.; Ward, A.D. *Tetrahedron Lett.*, **1989**, *30*, 6211-6214. Pandey, R.K.; Shiau, F.-Y.; Medforth, C.J.; Dougherty, T.J.; Smith K.M. *Tetrahedron Lett.* **1990**, *31*, 789-792.
37. Bauder, C. Thèse de Doctorat de l'Université Louis Pasteur, Strasbourg, 1990, and unpublished results.
38. Paine, J.B. III, in "The porphyrins", D. Dolphin ed. Academic Press, 1978, vol. 1, ch. 4.
39. Barton, D.H.R.; Kervagoret, J.; Zard, S.Z. *Tetrahedron*, **1990**, *46*, 7587-7598.
40. Kleinspehn, G.G. *J. Am. Chem. Soc.* **1955**, *77*, 1546-1548. See also ref. 8.
41. Jackson A.H., Pandey R.K., Rao K.R.N., Roberts E. *Tetrahedron Lett.* **1985**, *26*, 793-796.
42. See ref. 30 and articles cited therein.
43. Battersby, A.R.; Jones, K.; Snow, R.J. *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 734-735.