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5,15-Diaryl Substituted Benzochlorins - Synthesis and Structure

Maxwell J. Gunter* and Byron C. Robinson

Department of Chemistry, The University of New England, Armidale, NSW 2351, Australia

Jacqueline M. Gulbis and Edward R.T. Tiekink

Department of Physical and Inorganic Chemistry, The University of Adelaide, Adelaide, SA 5001, Australia

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Abstract: *Nickel 5,15-Bis(p-substituted aryl)porphyrins having p-substituents CH_3, NO_2, $N(CH_3)_2$, OTosyl, were treated with 3-(dimethylamino)acrolein to produce the nickel meso-(2"-formylvinyl)porphyrins (1) - (4) These undergo cyclisation to the corresponding nickel diaryl benzochlorins (5) to (8) and thence to the corresponding free bases All these derivatives show unusual electronic spectra with strong absorptions in the visible region around 700 nm. A crystal structure of the p-dimethylamino benzochlorin (7) reveals a structure highly distorted from planarity, with the macrocycle having a distinct saddle shape The p-dimethylamino benzochlorin (7a) readily protonates in solution to a dimethylaminoquinomethene moiety An alternative route to the benzochlorins via decarboxylation of meso-acrylate derivatives and formylation of the formed vinyl compounds, produced dimeric species (15) and (16) which have been characterised by spectroscopic methods, the dimers are composed of a meso-vinyl porphyrin linked to a porphodimethene unit via an ethylenic bridge (1) - (4) under basic conditions cyclise to the corresponding 5,15-diaryl formyl purpurins*

In the burgeoning field of photodynamic therapy (PDT) for the treatment of malignant tumours, the development of new photosensitisers that show strong absorption in the red (600 - 700 nm) region of the spectrum is an important and challenging area of chemistry Representative of such molecules are the tetrapyrrolic purpurins[1], chlorins[2], phthalocyanines[3] and benzochlorins[4] It has been established that the efficiency of tumour necrosis is dependent on the functionality of the photosensitiser, as this can determine the extent of localisation at the tumour site[5] Currently the only drug being evaluated in phase III clinical trials is Photofrin II, which is a complex and poorly defined mixture of porphyrin dimers and higher oligomers This mixture displays little absorption in the red region of the visible spectrum, and has an unfortunate side effect of skin photosensitivity Thus there is a need for alternative well characterised photosensitisers whose chemical, physical, and biological properties can be rationalised In this paper, we report the synthesis of 5,15-(p-substituted)diaryl benzochlorins and related formyl substituted porphyrins which display major absorptions in the 600 - 710 nm region, that we believe may be suitable for photodynamic therapy studies Furthermore, the functionality incorporated into the p-positions of the *meso*-aryl substituents allows for flexibility of design to adjust for such properties as hydrophobicity, water solubility, and electrochemical and photophysical properties, such a capability is crucial for a systematic study of the factors influencing suitability as photodynamic therapy agents

Recently we reported the synthesis of a series of p-substituted diaryl purpurins which show major absorptions in the red (600 - 720 nm) region[6] By a similar strategy we have now developed access to a series of diaryl benzochlorins and diaryl formyl porphyrins and purpurins A recent report by Smith and coworkers[7] has described the use of 3-(dimethylamino)acrolein and $POCl_3$ to produce high yields of *meso*-(2"-

formylvinyl)porphyrins and chlorins. Strong acid treatment of the nickel derivatives under similar conditions to those used by Arnold and coworkers[8] gave the corresponding benzochlorins, benzo*iso*bacteriochlorins and benzobacteriochlorins

Thus, in this work, 5,15-*bis*(p-substituted aryl) porphyrins[6] were treated with 3-(dimethylamino)acrolein and $POCl_3$ to give the corresponding nickel *meso*-(2"-formylvinyl)porphyrins (**1**) - (**4**) in yields of 90 -100% These display unusual electronic spectra in that a single, broad Soret band at ~460 nm and one broad Q-band at ~650 nm are observed This represents a ~60 nm red shift of the Soret band from those of the corresponding nickel *meso*-(2"-formylvinyl) octaalkylporphyrins, although there is some discrepancy in the literature as to whether the octaalkyl derivatives exhibit regular or perturbed spectra Arnold and coworkers[8] report split Sorets for the nickel *meso*-(2'-formylvinyl) derivatives of octaethylporphyrin and etioporphyrin, whereas Smith[7] reports a single Soret and three distinct Q-bands for the octaethylporphyrin derivative In any case, it is clear that interruption of the porphyrin chromophore results from conjugation of the *meso*-(2'-formylvinyl) group into the porphyrin π-system in all of these derivatives, and this effect is further attenuated by the presence of the aryl groups in (**1**) - (**4**) Additionally, the electronic spectra of these derivatives show large absorption bands in the 300 - 370 nm region (ε ~16 - 23 x 10^3 $M^{-1}cm^{-1}$) The electronic spectral data is presented in Table 1 and the spectrum of (**2**) is shown in Figure 1A

Table 1 Absorption Data (nm) for Nickel *meso*-(2"-formylvinyl) Diaryl Porphyrins and Benzochlorins

Compound	Solvent	Band I(ε)[a]	Band II(ε)[a]	Band III(ε)[a]	Band IV(ε)[a]	Soret(ε)[a]
(**1**)	$CHCl_3$	637 (13705)	–	–	–	464 (93400)
(**2**)	$CHCl_3$	644 (9870)	–	–	–	466 (68220)
(**3**)	CH_2Cl_2	628 (8210)	–	–	–	457 (69400)
(**4**)	CH_2Cl_2	629 (10750)	–	–	–	459 (80460)
(**5**)	CH_2Cl_2	696 (27130)	637sh (7435)	580 (3725)	517sh (4980)	433 (67520)
(**6**)	$CHCl_3$	705 (32850)	646sh (9210)	583 (4160	522 (5820)	431 (71100)
(**7**)	CH_2Cl_2	697 (28670)	640sh (8445)	578 (4120)	522sh (5360)	434 (66325)
(**8**)	CH_2Cl_2	698 (27485)	643sh (7415)	521sh(4160)	521sh (4160)	434 (64105)
Ni(oeBC)[b]	$CHCl_3$	677 (36730)	625 (9780)	566 (4190)	500 (5020)	416 (69250)

[a] Units $M^{-1}cm^{-1}$ [b] From reference 8

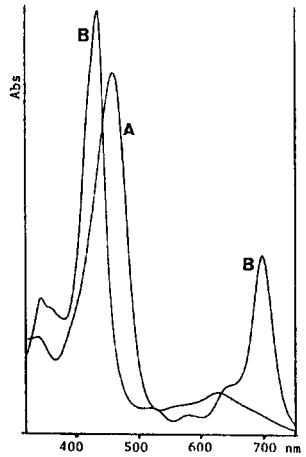
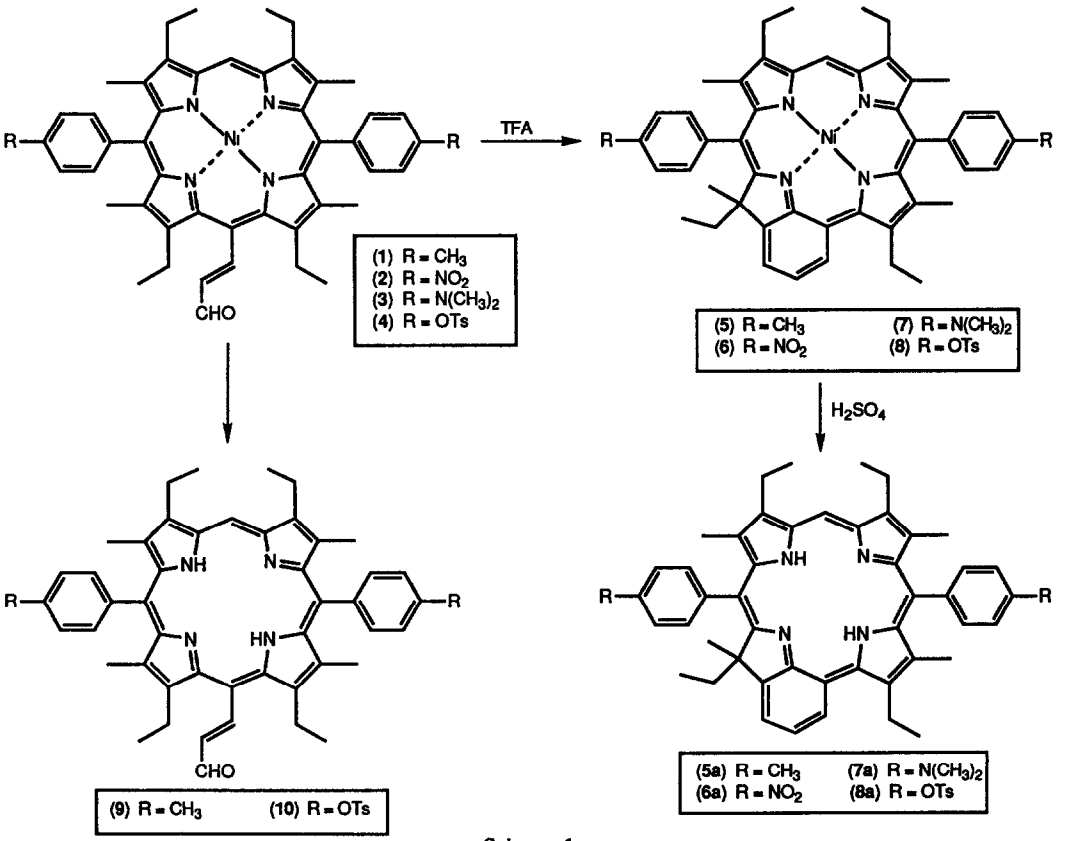


Figure 1 Absorption spectra in $CHCl_3$ of A (**2**), B (**6**)

The porphyrins (**1**) - (**4**) undergo cyclisation to the corresponding nickel diaryl benzochlorins on treatment with trifluoroacetic acid under a nitrogen atmosphere at room temperature (Scheme 1) The reaction progress is conveniently monitored by a colour change from green to brown, and is generally complete within one hour. On basic workup, the porphyrins (**1**) and (**2**) produced exclusively the nickel diaryl benzochlorins (**5**) and (**6**), while porphyrins (**3**) and (**4**) produced the corresponding free base *meso*-(2'-formylvinyl)diarylporphyrins (**9**) and (**10**) in addition to the cyclised products The free base derivatives (**9**) and (**10**) did not cyclise on further treatment with acid This substantiates the claim by Smith[7] that the central metal ion is necessary for the electrophilic attack on the porphyrin by the *meso*-group derived carbocation, metalloporphyrins that are easily

demetallated do not form good yields of the benzochlorins presumably because of the competing demetallation No benzochlorin formation was observed under less acidic conditions (e g refluxing glacial acetic acid).



Scheme 1

Crystals of the nickel diarylbenzochlorin (7) suitable for X-ray crystallographic analysis were grown from chloroform / methanol[9] The atom numbering scheme and a perspective view of the structure are shown in Figure 2

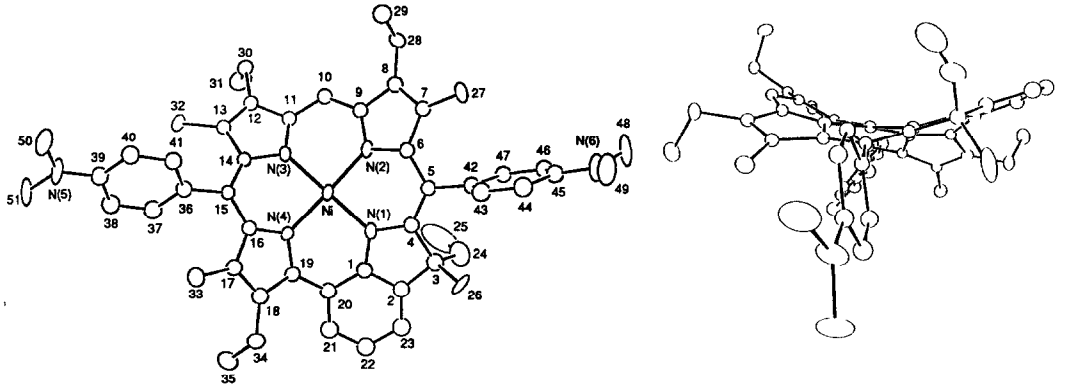


Figure 2 The atom numbering scheme and molecular structure of (2) Hydrogen atoms are not shown

A comparison between this structure and that reported by Arnold *et al*[8] for nickel octaethylbenzochlorin, Ni(oeBC), is instructive. Selected interatomic bond distances and angles are presented in Table 2, and selected interplanar dihedral angles are compared in Table 3.

Table 2. Selected Interatomic Distances(Å) and Bond Distances(Å) in the Nickel Diarylbenzochlorin (7) and Ni(oeBC)[8] Derivatives

	Ni(oeBC)	(7)		Ni(oeBC)	(7)
Atom Group	Distance	Distance	Atom Group	Distance	Distance
Ni· N1	1.930(3)	1.90(6)	N1 to N2	2 741	2.677
Ni N2	1.932(3)	1 90(0)	N1 to N4	2 729	2.756
Ni N3	1.930(3)	1 90(0)	N2 to N3	2.723	2.714
Ni N4	1 953(3)	1.92(6)	N3 to N4	2.775	2.653
Ni to C5	3 348	3 357	C6 C5	1 384(6)	1.40(1)
Ni to C10	3 381	3 292	C5 C4	1 361(6)	1.39(1)
Ni to C15	3 344	3.346	C14 C15	1 371(5)	1 37(1)
Ni to C20	3.414	3 321	C15 C16	1.364(6)	1 39(1)

Table 3. Selected Dihedral Angles Between Mean Planes for Ni(oeBC)[8] and (7)

	Ni(oeBC)				(7)		
Planes[a]	(Ø)°	Planes[a]	(Ø)°	Planes[a]	(Ø)°	Planes[a]	(Ø)°
2, 1	15.8	4, 6	27.4	2, 1	25 5	3, 2	35 3
3, 1	11.4	3, 2	19 8	3, 1	22.7	3, 5	53.9
4, 1	10 8	3, 5	31 8	4, 1	25 2	3, 6	40.0
5, 1	20.6	3, 6	24.0	5, 1	31 3	2, 5	39 6
6, 1	17.8	2, 5	28 1	6, 1	26.2	2, 6	6.9
4, 3	17.6	2, 6	5 2	4, 3	32 4	5, 6	34 1
4, 2	26 3	5, 6	25 6	4, 2	50 7	7,1	56 2
4, 5	18.0			4, 5	38 5	8,1	73 8
				4, 6	50 8		

a Plane 1 N1, N2, N3, N4 Plane 2 Pyrrole Ring N1, C1, C2, C3, C4 Plane 3 Pyrrole Ring N2, C6, C7, C8, C9 Plane 4 Pyrrole Ring N3, C11, C12, C13, C14 Plane 5. Pyrrole Ring N4, C16, C17, C18, C19 Plane 6 Benzene Ring C1, C2, C23, C22, C21, C20 Plane 7 Phenyl Ring C36, C41, C40, C39, C38, C37 Plane 8 Phenyl Ring C42, C43, C44, C45, C46, C47

The perspective views of (7) show the macrocycle to be highly distorted and assuming a distinct saddle shape The coordination geometry about the nickel ion is essentially square planar in both compounds, with small deviations from an ideal square planar geometry evident in both as best seen by comparing the N1--Ni--N3 and N2--Ni--N4 bond angles (173.5° and 175 1° respectively for Ni(oeBC), compared to 173 5° and 175 1° for (7)) and the deviations of the individual nitrogen atoms from the mean plane (plane 1) of the four nitrogen atoms (Table 3) The pyrrole, annelated benzene and *meso*-phenyl rings are all essentially planar

A measure of the large distortion of the nickel diarylbenzochlorin ring system compared to that of the Ni(oeBC) is most easily seen by comparing the perspective view of (7) with that of Ni(oeBC) taken from reference 8 and shown in Figure 3, or by comparing the dihedral angles between plane (1) (defined by the four pyrrole nitrogens) and the mean planes of the pyrrole rings (planes 2 to 5), the pyrrole ring corresponding to plane 5 in the Ni(oeBC) shows the largest dihedral angle with plane 1 of 20 6° compared to 31 3° in (7) The remaining pyrrole rings in (7) also show substantially larger dihedral angles of ~10° more than the Ni(oeBC) derivative

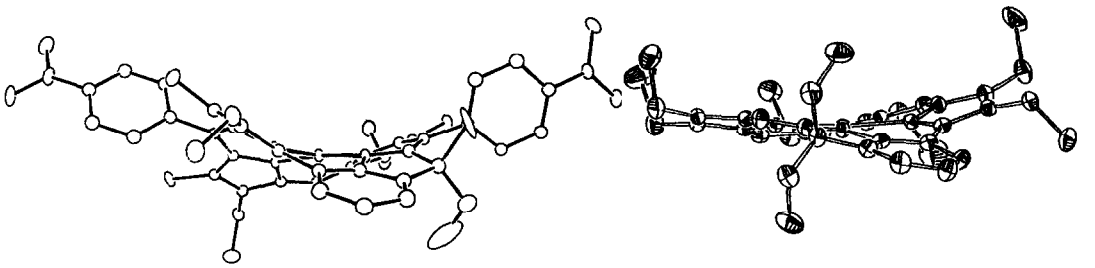


Figure 3 Perspective views of (7) (left), and nickel octaethylbenzochlorin, Ni(oeBC), (taken from reference 8)

Two of the nitrogen-nitrogen interatomic distances, N1 N4 and N2 · N3, are similar for both benzochlorins. The interatomic distances N1 · N2 and N3· N4 however are significantly shorter in (7) compared to Ni(oeBC). This results in an elongation of the nickel diarylbenzochlorin along the 5,15 axis and a reduction of the N2--Ni and N3--Ni bond lengths These bond distances (1 899Å) are remarkably short for a porphyrin-like macrocycle Similar bond distances have been reported for the highly distorted porphodimethene derivative 5,15-dimethyl-5,15-dihydro-2,3,7,8,12,13,17,18-octaethylporphinato-nickel(II)[10] (1.921, 1 904, 1 902, 1.904Å) and two homoporphyrins[11] (1 889, 1.883, 1 885, 1 961Å) Further, the phenyl substituents at C5 and C15 result in a tendency towards an increase in the carbon-carbon bond lengths around these positions compared to the Ni(oeBC) derivative. Thus the severe distortion of the nickel diarylbenzochlorin appears to be a direct consequence of these two factors

The perspective view of (7) shown in Figure 2 shows that one of the *meso*-phenyl rings is twisted considerably away from perpendicularity with the mean plane of the benzochlorin ring system This phenyl ring (plane 7) maintains a dihedral angle of 56° with plane 1 The other phenyl ring (plane 8) has a dihedral angle of 73° with plane 1 These twist angles are comparable to those observed in the highly distorted nickel homoporphyrin (46 - 78°)[10]

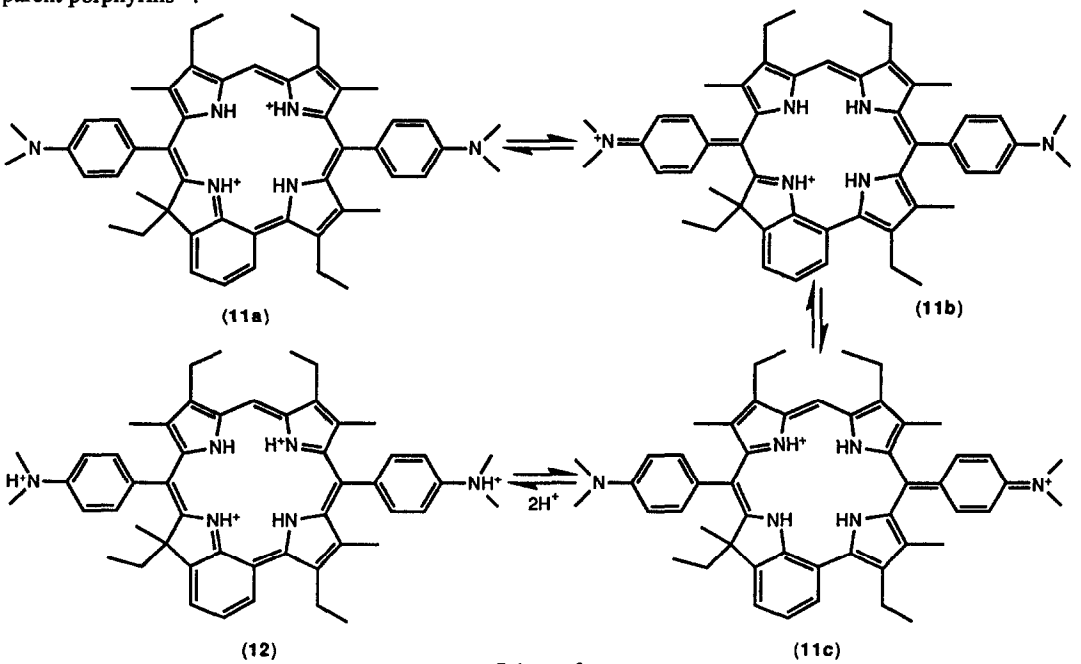
The non-reduced pyrrole rings in the two benzochlorin derivatives have bond lengths and angles similar to those found in other metalloporphyrin complexes[12] In the reduced pyrrole ring, the bond lengths of C3--C4 and C2--C3 are longer as expected

The nickel diarylbenzochlorins (5) - (8) show strong Band I absorptions at ~699 nm (ε~30000 $M^{-1}cm^{-1}$) and a low intensity Soret band at ~433 nm (ε~70000 $M^{-1}cm^{-1}$) (Figure 1 and Table 1) This represents a 20 nm red shift in both the Band I and Soret peaks compared to the Ni(oeBC) derivative reported by Arnold and coworkers[8] (however, there are inconsistencies in the wavelengths and molar extinction coefficients as reported by Smith *et al*[7] and Arnold *et al*[8]) The large red shift is a reflection of the distortion of the nickel diarylbenzochlorin macrocycles which allows twisting of one of the phenyl rings resulting in increased conjugation with the benzochlorin ring system[13] The ^1H and ^{13}C NMR data are consistent with the assigned structures and were assigned by standard techniques

The nickel benzochlorins can be efficiently demetallated with concentrated H_2SO_4 to produce the free base derivatives (**5a** - **8a**) The absorption spectra again show strong Band I absorptions at ~670 nm and broad Soret bands around 416 nm This represents a significant red shift of Band I compared to the alkyl benzochlorins, and indicates that the distortion of the diaryl benzochlorins is not relieved by removal of the central metal ion

Protonation of the free base derivatives results in an even larger red shift of ~80 - 90 nm and a split Soret Also indicative of the deviation from planarity and associated decrease in aromatic ring current is the large downfield shift of the pyrrolic NH resonances in the ^{1}H NMR spectra of the free base benzochlorins, compared to other porphyrinic macrocycles. The NH protons in (**5a** - **8a**) appear as two distinct singlets at ~δ4.5 ppm, representing a downfield shift of ~6 ppm from that observed in the free base 5,15-diarylporphyrins. Additionally, significant upfield shifts of ~1 ppm are observed for the *meso*-H and methine protons of the annelated benzene ring compared to the alkyl benzochlorins reported by Smith[7] and Arnold *et al*[8], again attributable to a decreased ring current in the more distorted diaryl benzochlorins

While the free base benzochlorins and their nickel derivatives are generally stable and readily isolable, the dimethylamino-substituted benzochlorin (**7a**) is particularly difficult to work with On silica, and to varying extent depending on the purity and identity of the solvent, this compound readily protonates to form the dimethyliminoquinomethene tautomers (**11a**↔**11b**↔**11c**), (Scheme 2), and further to the fully protonated tetracation (**12**), a variable mixture of all three components is present in some solvents and solvent mixtures These changes can be demonstrated by titration of the free base in purified chloroform with trifluoroacetic acid, illustrated in Figure 4 On acidification the formation of the dimethylaminoquinomethene moeity is accompanied by a colour change from green to brown and a large increase in the intensity of the Band I absorption at 723 nm, further acidification leads to the fully protonated benzochlorin (**12**), with a red-shifted Band I at 756 nm. Similar behaviour has been reported before for the similarly substituted dimethylaminopurpurins[6b], and indeed with the parent porphyrins[14].



Scheme 2

The free base *meso*-(formylvinyl) derivatives, obtained by demetallation of the nickel complexes (**1** - **4**) can also be used for the synthesis of 22-formyl diaryl *purpurins* by refluxing their respective free bases in triethylamine / 1,2-dichloroethane in a similar manner to that described for the synthesis of 22-(methoxycarbonyl)

diaryl purpurins[6b]. This is demonstrated by the synthesis of the purpurins (13) and (14). This route provides a convenient access to variously functionalised purpurins which are also of particular interest in photodynamic therapy studies[6b].

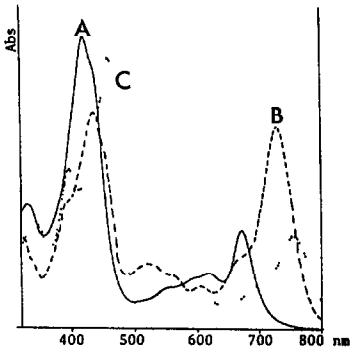
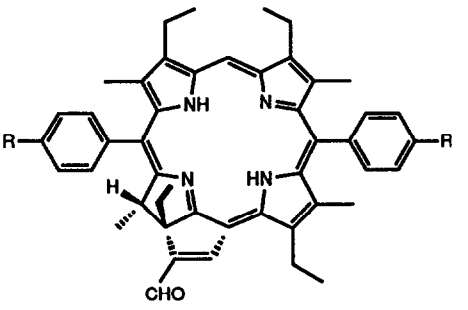
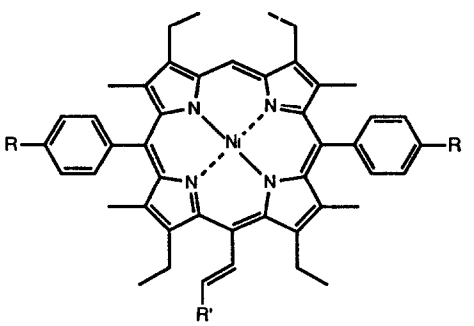


Figure 4. Absorption spectra of the free base benzochlorin (7a) **A**, in $CHCl_3$; **B**, in $CHCl_3$ containing 2 molar equivalents of TFA, i e (**11a**↔**11b**↔**11c**), **C**, in $CHCl_3$ and excess TFA, i.e. (**12**)

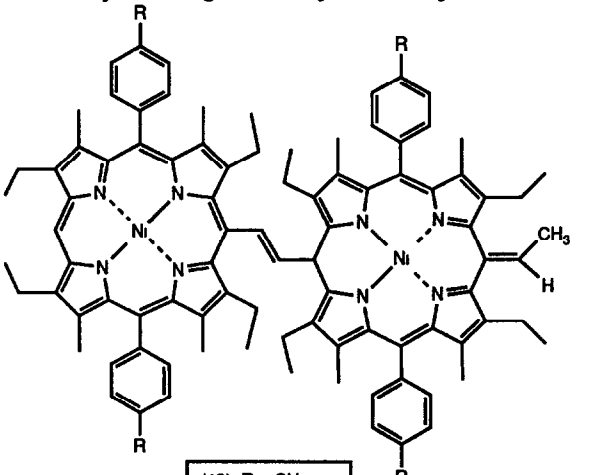


(13) R = CH_3 (14) R = OTs

As an alternative approach to these diaryl benzochlorins, it was recognised that the readily available *meso*-acrylate derivatives such as (**15**) and (**16**) might provide access to the *meso*-formylvinyl derivatives (**1**) and (**3**), respectively *via* hydrolysis, decarboxylation, and Vilsmeier formylation, porphyrins (**15**) and (**16**) have been utilised in previous studies for the synthesis of 5,15-*bis*-(p-substituted aryl) purpurins[6b] Thus, porphyrins (**15**) and (**16**) were readily hydrolysed to the acids (**15a**) and (**16a**), but on attempted decarboxylation in refluxing glacial acetic acid, a second major product was obtained in each case, in addition to the expected *meso*-vinyl derivatives (**17**) and (**18**) On the basis of extensive NMR studies, mass spectral data, and electronic spectra, these products have been assigned the dimeric structures (**19**) and (**20**), essentially comprising a *meso*-vinyl porphyrin linked to a porphodimethene-type moeity *via* an ethylenic bridge across adjacent *meso*-positions



(15) R = CH_3, R' = CO_2Me
(16) R = $N(CH_3)_2$, R' = CO_2Me
(15a) R = CH_3, R' = CO_2H
(16a) R = $N(CH_3)_2$, R' = CO_2H
(17) R = CH_3, R' = H
(18) R = $N(CH_3)_2$, R' = H



(19) R = CH_3
(20) R = $N(CH_3)_2$

The ^{1}H NMR spectrum of (**19**) is shown in Figure 5; variable temperature ^{1}H, broad band decoupled ^{13}C, DEPT, COSEY, NOESY and CH correlation techniques were used to assign the spectra and to elucidate the structures. The more significant details are as follows, for ease of explanation selected groups have been labelled as shown in the structural representation shown in Figure 5.

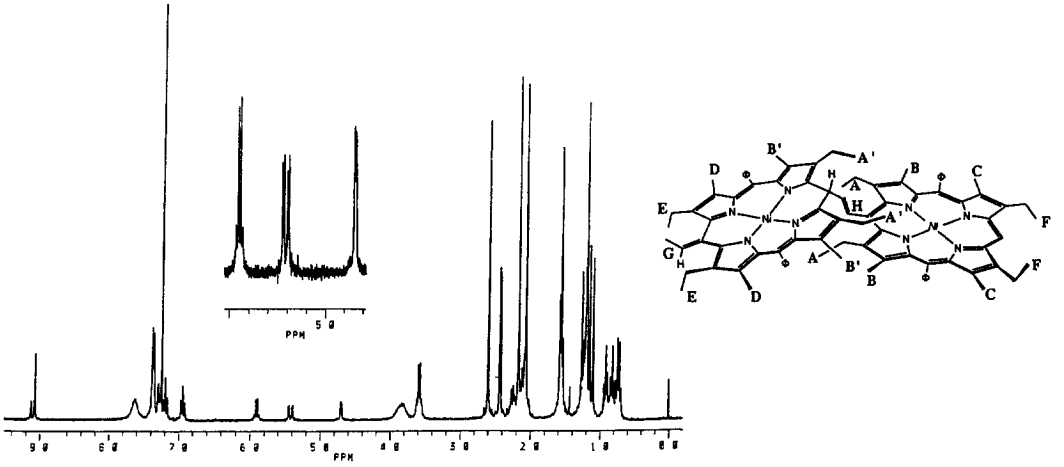


Figure 5. The ^{1}H NMR spectrum of (**19**) in $CDCl_3$ at 298K, and the lettering used for group representations discussed in the text.

• the most upfield shifted proton resonances in the region δ 0 76 - 0 99 ppm (12H) are those of the CH_3's of the ethyl groups A and A' which experience strong shielding because of their positions above and below the respective neighbouring porphyrin rings The inequivalence of the resonances is a reflection of the different sub-units of the dimer, and the asymmetry of the porphodimethene unit[15]. The methylene protons of these groups are partly hidden in the region δ 2 13 - 2 34 ppm;

• the four methyl resonances B and B' appear as four singlets in the region δ 1.23 - 1 41 ppm and are likewise significantly shielded,

• the methyl and ethyl proton resonances for the groups C and F are least influenced by any shielding effects of the porphodimethene ring, and hence appear close to their positions in their respective parent derivatives (**15**) and (**16**),

• the ethyl groups E are shielded by the adjacent double bond, and hence appear at δ 1 23 ppm in both dimers,

• the methyl singlets for groups D appear at δ 2 05 and δ 2 13 ppm for (**19**) and (**20**), respectively The upfield shift of this group compared to group C reflects the loss of aromaticity in the porphodimethene unit compared to the porphyrin unit,

• the methine quartets at δ 5 88 and 5 89 ppm for (**19**) and (**20**) and the methyl doublets (J = 12Hz) of group G can be deconvoluted from overlapping signals at 330K,

• the three vinyl protons of group H are clearly discernible at δ 9 08 (Hα, doublet, J_{trans}= 19Hz), δ 5 39 (Hβ, doublet of doublets) and δ 4 67 (methine, doublet) for (**19**), and likewise for (**20**).

• only one *meso*-proton is observed in a typical position at δ 9 05,

• the phenyl protons appear as two overlapping doublets. This proton splitting pattern has been observed in all non-symmetrical diaryl porphyrin derivatives such as the purpurins[6] and benzochlorins;

• methyl resonances for the p-substituent of the phenyl rings in (**19**) appear as three singlets at δ 2 58 (6H, porphyrin unit) and δ 2.41 and δ 2.43 ppm (3H each, porphodimethene unit);

• carbon resonances associated with all of the above protons are also consistent with the assigned structures

The electronic spectra exhibit strong broad Soret bands at ~434nm (ε~150000 $M^{-1}cm^{-1}$) and a single large featureless Q-band at ~561nm (ε~28000 $M^{-1}cm^{-1}$). The large Q-band absorption is characteristic of porphodimethene-type structures

The formation of these dimers may be rationalised in terms of an initial decarboxylation of the porphyrin acid with concomitant electrophilic attack at the *meso* position of a second porphyrin unit; a second decarboxylation of the formed porphodimethene produces the diaryl dimers

The *meso*-vinyl porphyrins, which are the other major products of the decarboxylation, can be cleanly formylated with dimethylformamide and $POCl_3$, thus providing an alternative route to the formylvinyl derivatives (**1**) to (**4**)

EXPERIMENTAL SECTION

General

Silica gel 60 (230 - 400 mesh, Merck) was used for column chromatography. Analytical thin-layer chromatography was performed on Merck 60 F254 silica gel (precoated sheets on aluminium) ^1H and ^{13}C NMR spectra were obtained at 300 MHz using a Brucker AC-300 spectrometer, chemical shifts of proton spectra are expressed in parts per million relative to tetramethylsilane (0 1%), while ^{13}C spectra are referenced with $CDCl_3$ = δ 77 0ppm Electronic spectra were measured on an Hitachi U3200 spectrophotometer. Electron impact (e i) mass spectra were obtained at 70eV Fast atom bombardment (FAB) mass spectra were obtained on a VG-ZAB 2F instrument, using a *p*-nitrobenzyl alcohol matrix Microanalyses were performed by the Microanalytical Unit, Research School of Chemistry, Australian National University

Synthesis of meso-(2"-formylvinyl)porphyrins. General Procedure A.

To a stirred solution of 3-(dimethylamino)acrolein (2mL) in 1,2-dichloroethane (50mL) at -19^{0}C was added dropwise $POCl_3$ (1 8mL) Solid Ni porphyrin (~0 30g) was added and the solution warmed to RT. The reaction progress was monitored closely by tlc until no more porphyrin starting material remained. Saturated sodium acetate (150mL) was added and the solution stirred vigorously until hydrolysis was complete as judged by tlc (~0 5hr) Any precipitated porphyrin was filtered off The organic layer was washed well with water, dilute HCl, with water and finally dried over sodium sulfate After filtering, the solvent was removed by rotary evaporation The remaining residue was chromatographed on silica using dichloromethane as eluent and the major green fraction collected After evaporation of solvent the porphyrin was recrystalized from dichloromethane / acetonitrile

[2,8,12,18-Tetraethyl-3,7,13,17-tetramethyl-5,15-bis(4'-methylphenyl)porphyrin-10-vinyl-2"-carbaldehydato-(2-)]nickel(II) (1)

Synthesised by method A using. porphyrin (0.32 g) Yield of (**1**) = 0 35 g, (100%)

^1H NMR ($CDCl_3$) δ 1 51 (t, 6H, 2 x CH_3), 1 55 (t, 6H, 2 x CH_3), 2 04 (s, 6H, 2 x CH_3), 2.08 (s, 6H, 2 x CH_3), 2 57 (s, 6H, $ArCH_3$), 3 46 (q, 4H, 2 x CH_2), 3 55 (q, 4H, 2 x CH_2), 5 49 (d of d, 1H, vinyl H_β), 7 36 (d, 4H, ArH), 7.50 (d, 4H, ArH), 9 00 (d, 1H, vinyl H), 9 01 (s,1H, meso H), 9 61 (d, 1H, CHO) Mass spectrum, m/z 768 (M+), requires m/z 768 (M+). Anal Calcd for $C_{49}H_{50}N_4Ni_1O$· C, 76 47 , H, 6.55 , N,7 28 Found C, 76 73, H, 6 64, N, 7 50 UV / Vis (λ_{max}, $CHCl_3$)· 323sh (20820), 344 (22180), 464 (93400), 637 (13705).

^{13}C NMR decoupled ($CDCl_3$): δ 14.42, 15 28, 16.02, 17.06, 19.26, 21.41, 21 58, 99.55 , 101 26, 119 73, 128.44, 132 10, 137.15, 138 03, 138.27, 138 30, 139 09, 141 19, 141.38, 143 78, 146.05, 146.05, 146.82, 147.19, 190 24.

2.8.12.18-Tetraethyl-3.7.13.17-tetramethyl-5.15-bis(4'-nitrophenyl)-porphyrin-10-vinyl-2"-carbaldehydato-(2⁻)]nickel(II) (2).

Synthesised by method A using porphyrin (0 25g) Yield of (2) = 0 24 g, (90%).

^{1}H NMR ($CDCl_3$). δ 1.53 (t, 6H, 2 x CH_3), 1.55 (t, 6H, 2 x CH_3), 2.01 (s, 6H, 2 x CH_3), 2.06 (s, 6H, 2 x CH_3), 3.54 (m, 8H, 4 x CH_2), 5.52 (d of d, 1H, vinyl Hβ), 7.93 (d, 4H, ArH), 8.49 (d, 4H, ArH), 9.09 (d, 1H, vinyl-H), 9.11 (s, 1H, meso-H), 9 69 (d, 1H, CHO) Anal Calcd for $C_{47}H_{44}N_6NiO_5$.· C, 67.88 , H, 5 33 , N, 10 10 . Found: C, 67 60 , H, 5 32 , N, 9 97. UV / Vis (λ_{max}, CH_2Cl_2) 338 (ε 18635), 457 (69395), 628 (8205).

^{13}C NMR decoupled ($CDCl_3$)· δ 14.86, 15.64, 15.95, 17.05, 19.29, 21.54, 99.66, 103.06, 116 54, 122 82, 133 40, 137.55, 137 66, 138 98, 139 17, 140.26, 142 38, 146.98, 147 08, 147.30, 147 83, 148.05, 190 21 (CHO)

5.15-Bis(4'-dimethylaminophenyl)-2.8.12.18-tetraethyl-3.7.13.17-tetramethylporphyrin-10-vinyl-2"-carbaldehydato(2⁻)]nickel(II) (3).

Synthesised by method A using 3-dimethylaminoacrolein (3mL), $POCl_3$ (2.8mL) , porphyrin (1.14 g). Yield of (3) = 0.62 g, (51%) ^{1}H NMR ($CDCl_3$): δ 1 51 (t, 6H, 2 x CH_3), 1 55 (t, 6H, 2 x CH_3), 2 13 (s, 6H, 2 x CH_3), 2.17 (s, 6H, 2 x CH_3), 3.13 (s, 12H, $N(CH_3)_2$), 3 52 (m, 8H, 4 x CH_2), 5 54 (d of d, 1H, vinyl Hβ), 6 92 (d, 4H, ArH), 7 51 (d, 4H, ArH), 9 00 (s,1H, meso H), 9.02 (d, 1H, vinyl H), 9.63 (d, 1H, CHO) Anal Calcd. for $C_{51}H_{56}N_6NiO$ 2 $5H_20$ C, 70 18 , H, 7 04 , N, 9 62 . Found. C, 69.86, H, 6 62, N, 9 69. FAB mass spectrum, m/z 827(M+1), requires m/z 826 (M+) UV / Vis (λ_{max}, $CHCl_3$)· 323sh , 341 (ε 16110), 466(68220), 644 (9870)

C^{13} NMR decoupled ($CDCl_3$): δ 14 51, 15 35, 15 99, 17 06, 19 25, 21 40, 40.68, 99.45, 101.28 , 111 55, 120 24, 128.15, 132 85, 138 36, 138.76, 139 15, 139 24, 140 82, 142 19, 143.95, 145 69, 146.39, 147 46, 150.47, 190.35 (CHO).

2.8.12.18-Tetraethyl-3.7.13.17-tetramethyl-5.15-bis(4'-toluenesulphonyloxyphenyl)porphyrin-10-vinyl-2"-carbaldehydato(2⁻)]nickel(II) (4).

Synthesised by method I using porphyrin (0 29 g) Yield of (4) = 0 31g, (100%).

^{1}H NMR ($CDCl_3$)· δ 1 52(t, 6H, 2 x CH_3), 1 54 (t, 6H, 2 x CH_3), 1 95 (s, 6H, 2 x CH_3), 2 01 (s, 6H, 2 x CH_3), 2 50 (s, 6H, Tosyl CH_3), 3 53 (m, 8H, 4 x CH_2), 5 46 (d of d, 1H, vinyl Hβ), 7 22 (d, 4H, ArH), 7.39 (d, 4H, ArH), 7.63 (brd, 4H, ArH), 7 84 (d, 4H, ArH), 9 03 (d, 1H, vinyl-H), 9 05 (s, 1H, meso-H), 9.64 (d, 1H, CHO) Anal Calcd for $C_{61}H_{58}N_4NiO_7S_2.0$ $5H_20$· C, 67 15 , H, 5 63 ; N, 5 13 Found· C, 67 26; H, 5 48, N, 4.82. UV / Vis (λ_{max}, CH_2Cl_2) 341(ε 21085), 459 (80460), 629(10750)

^{13}C NMR decoupled ($CDCl_3$) δ 14 57, 15 35, 15 96, 17 04, 19 23, 21 44, 21 74, 99 49, 102 04, 117 68, 121 86, 128.77, 129.80, 131 93, 133.36, 137 93, 137.99, 138 58, 139 01, 139 26, 140 84, 141 87, 142 88, 145 63, 146 55, 147 01, 147 27, 149 96 , 190 17

Synthesis of Diaryl-3H-benzo[at]porphyrins and Free Base meso-(2"-formylvinyl) Diarylporphyrins. General procedure B.

To solid *meso*-(2"-formylvinyl) diarylporphyrin (~0 2g) under a nitrogen atmosphere, was added trifluoroacetic acid (10mL) The solution was stirred vigorously for ~ 1 - 1.5hr after which the colour of the solution had changed from green to brown / orange Methylene chloride was added, followed by water and the solution neutralized by the addition of saturated sodium bicarbonate solution After stirring for 15 min, the organic layer was washed well with water and dried over sodium sulfate After filtering, the solvent was removed by rotary evaporation and the residue chromatographed on silica, using methylene chloride / petroleum spirit (69-70^{0}C) (1 1) The first major green fraction was collected and evaporated to give the benzochlorin The column was then eluted with methylene chloride followed by acetone / methylene chloride (1%) which in some cases removed a second green fraction identified as the free base *meso*-(2"-formylvinyl)porphyrin derivative The benzochlorin residue was recrystallized using methanol / chloroform and the free base porphyrin recrystallized using acetonitrile / methylene chloride

2,8,12,18-Tetraethyl-3,7,13,17-tetramethyl-5,15-bis(4'-methylphenyl)porphyrin-10-vinyl-2"-carbaldehyde (9).
Synthesised by method B using: porphyrin (1) (2.17 g). Yield of (9) = 0.98g, (49%).

^{1}H NMR ($CDCl_3$): δ -0 28 (brs, 2H, NH), 1 39 (t, 6H, 2 x CH_3), 1.52 (t, 6H, 2 x CH_3), 2 02 (s, 6H, 2 x CH_3), 2.17 (s, 6H, 2 x CH_3), 2.66 (s, 6H, $ArCH_3$), 3 45 (q, 4H, 2 x CH_2), 3 66 (q, 4H, 2 x CH_2), 6.18 (d of d, 1H, vinyl Hβ), 7.49 (d, 4H, ArH), 7.81 (d, 4H, ArH), 9.39 (s, 1H, meso H), 9.53 (d, 1H, vinyl H), 9.90 (d, 1H, CHO) Anal. Calcd. for $C_{49}H_{54}N_4O$ H_2O: C, 80 51 ; H, 7.47 ; N, 7.66. Found. C, 80.70, H, 7 75; N, 8.20 UV / Vis (λ_{max}, $CHCl_3$)· 361 (ε 24790), 462 (100110), 639 (8980)

^{13}C NMR decoupled ($CDCl_3$). δ 13 78, 13 82, 15 86, 17 11, 19 34, 21 63, 21 78, 100 45, 105 24, 121 80, 128.67, 133.20, 135.55, 137.78, 138.09, 138.23, 141 48, 141 64, 142 55, 143.25, 144 20, 145 25, 146 37, 150 08, 190.92

2,8,12,18-Tetraethyl-3,7,13,17-tetramethyl-5,15-bis(4'-toluenesulfonyloxyphenyl)porphyrin-10-vinyl-2"-carbaldehyde (10)
Synthesised by method B using porphyrin (2) (250 mg) Yield of (10) = 54mg, (21%)

^{1}H NMR ($CDCl_3$). δ -0.64 (brs, 2H, NH), 1 41 (t, 6H, 2 x CH_3), 1 54 (t, 6H, 2 x CH_3), 1.95 (s, 6H, 2 x CH_3), 2 11 (s, 6H, 2 x CH_3), 2.53 (s, 6H, $ArCH_3$), 3 46 (q, 4H, 2 x CH_2), 3 66 (q, 4H, 2 x CH_2), 6.15 (d of d, 1H, vinyl Hβ), 7 33 (d, 4H, ArH), 7 42 (d, 4H, ArH), 7 86 (d, 4H, ArH), 7 89 (d, 4H, ArH), 9.45 (s, 1H, meso H), 9 57 (d, 1H, vinyl H), 9 93 (d, 1H, CHO) Anal. Calcd. for $C_{61}H_{60}N_4O_7S_2$: C, 71.46 ; H, 5 90 ; N, 5 46 Found C, 71.19 , H, 6 01 ; N, 5 13 UV / Vis (λ_{max}, CH_2Cl_2): 351 (ε 27865), 455 (118970), 629 (10060), 698 (6610).

^{13}C NMR decoupled ($CDCl_3$). δ 14 01, 15.84, 17 11, 19 36, 21 83, 100 24, 106.14, 119 63, 122 10, 128.88, 129.88, 132 06, 134 44, 135 16, 137 18, 140 14, 142 02, 143 01, 143 34, 144 78, 145.71, 145 75, 149 85, 150 19, 190 90

[3,8,12,18-Tetraethyl-3,7,11,17-tetramethyl-5,15-bis-(4'-methylphenyl)-3H-benzo[at]porphyrin-(2-)] nickel(II) (5).

Sythesised by general procedure B using porphyrin (1) (217mg) Yield of (5) = 61mg, (29%).

^{1}H NMR ($CDCl_3$) δ -0 05 (t, 3H, CH_3 of 3-ethyl), 1 29 (t, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.43 (t, 3H, CH_3), 1.52 (t, 3H, CH_3), 1.73 (s, 3H, CH_3), 1.81 (m, 1H, CH_2 of 3-ethyl) 1.83 (s, 3H, CH_3), 1.89 (s, 3H, CH_3), 2 06 (m, 1H, CH_2 of 3-ethyl), 2 50 (s, 3H, $ArCH_3$), 2 54 (s, 3H, $ArCH_3$), 3 19 (m, 6H, CH_2), 7.23 (brs, 2H, ArH), 7.34 (d, 2H, ArH), 7.43-7 52(m, 6H, ArH and 2xbenzoH), 8 22 (s, 1H, meso-H), 8.44 (d, 1H, benzoH). Anal Calc for $C_{49}H_{50}N_4Ni$ 0 5$CHCl_3$: C, 73.09 , H, 6 25 , N, 6 88. Found C, 73 23, H, 6.44, N, 6 67. UV / Vis (λ_{max}, $CHCl_3$) 344 (ε 22190), 362sh (19860), 433 (67515), 517sh (4980), 580 (3725), 637sh (7435), 696 (27125)

^{13}C NMR decoupled ($CDCl_3$) δ 8 78, 13 49, 14 30, 14 67, 15 54, 16 43, 16 57, 18 75, 18 99, 20 18, 21 47, 21 56, 28 15, 29 69, 34 75, 56.59, 97 14, 107 80, 112 11, 116 30, 119 69, 123.23, 127.16, 127.28, 128 51, 131 73, 133 52, 134 61, 134 80, 136 34, 137 64, 137 69, 137 77, 138 96, 139.70, 140.55, 141 28, 142 14, 146.00, 148 70, 164 53

3,8,12,18-Tetraethyl-3,7,11,17-tetramethyl-5,15-bis(4'-nitrophenyl)-3H-benzo[at]porphyrin (2-)]nickel(II) (6).

Sythesised by general procedure B using porphyrin (2) (94mg) Yield of (6) = 59mg, (64%).

^{1}H NMR ($CDCl_3$) δ -0 05 (t, 3H, CH_3 of 3-ethyl), 1 31 (t, 3H, CH_3), 1 41 (s, 3H, CH_3), 1.43 (t, 3H, CH_3), 1 49 (t, 3H, CH_3), 1 70 (s, 3H, CH_3), 1 77 (s, 3H, CH_3), 1 83 (s, 3H, CH_3), 1.86 (m, 2H, CH_2 of 3-ethyl), 3 18 (m, 6H, CH_2), 7 51 (d, 1H, benzo-H), 7 61 (t, 1H, benzo-H), 7 85 (brs, 4H, ArH), 8.29 (s, 1H, meso-H), 8 33 (d, 2H, ArH), 8 45(m, 3H, ArH and benzoH). UV / Vis (λ_{max}, $CHCl_3$) 345 (ε 26900), 359sh (25325), 431 (71100), 522 (5830), 583 (4160), 646sh (9210), 705 (32850)

^{13}C NMR decoupled ($CDCl_3$) δ 8 63, 13 86, 14 80, 15 07, 15 44 , 16 46, 16 55, 18 72, 19.01, 20 15, 28 17, 34 87, 56 56, 98 30, 105 68, 111 91, 117 02, 120 43, 121.66, 123 02, 123 51, 124.79, 132 94, 134 84, 135 38, 136 66, 137 26, 137 54, 139 06, 139.25, 141 44, 141 58, 141.75, 142 29, 145.08, 145.54, 147.25, 147 48, 147 69, 147 81, 147 84, 163 55

[3,8,12,18-Tetraethyl-3,7,11,17-tetramethyl-5,15-bis(4'-dimethylaminophenyl)-3H-benzo[at]porphyrin(2-)] nickel(II) (7).

Sythesised by general procedure B using porphyrin (3) (200mg). Yield of (7) = 116mg, (59%).

^{1}H NMR ($CDCl_3$). δ -0.04 (t, 3H, CH_3 of 3-ethyl), 1.30 (t, 3H, CH_3), 1.43 (t, 3H, CH_3), 1.47 (s, 3H, CH_3), 1.51 (t, 3H, CH_3), 1.79 (s, 3H, CH_3), 1.81 (m, 1H, CH_2 of 3-ethyl) 1.91 (s, 3H, CH_3), 1.98 (s, 3H, CH_3), 2.16 (m, 1H, CH_2 of 3-ethyl), 3.07 (s, 6H, $N(CH_3)_2$), 3.10 (s, 3H, $N(CH_3)_2$), 3.22 (m, 6H, CH_2), 6.79 (d, 2H, ArH), 6.90 (d, 2H, ArH), 7.38 (d 1H, benzoH), 7 45 (d, 4H, ArH), 7.55 (t, 1H, benzoH), 8.21 (s, 1H, meso-H), 8.44 (d, 1H, benzoH). Anal. Calc. for $C_{51}H_{56}N_6Ni$. H_2O: C, 73.82 ; H, 7.04 ; N, 10.12. Found C, 73.56; H, 7.05; N, 9.72. UV / Vis (λ_{max}, CH_2Cl_2). 341 (ε 22870), 434 (66325), 522sh (5355), 578 (4115), 640sh (8445), 697 (28670).

^{13}C NMR decoupled ($CDCl_3$): δ 8.84, 13.55, 14.36, 14.80, 15.59, 16.45, 16.58, 18.76, 18.99, 20.17, 28.19, 34 67, 40.62, 40.68, 56 67, 96 90, 108.06, 110.21, 110.33, 111.71, 112.29, 116.13, 119 51, 121.96, 123.16, 125.60, 128.30, 128.98, 132.59, 134.18, 135.48, 135.98, 136.56, 136.73, 138.01, 138.96, 139.03, 139.72, 140.20, 141.31, 142.25, 142.34, 144.62, 145.61, 149.44, 150.14, 150.34, 165.24.

[3,8,12,18-Tetraethyl-3,7,11,17-tetramethyl-5,15-bis(4'-toluenesulfonyloxyphenyl)-3H-benzo[at]porphyrin-(2-)]nickel(II) (8).

Sythesised by general procedure B using porphyrin (4) (0.25g). Yield of (8) = 115mg, (45%).

^{1}H NMR ($CDCl_3$): δ -0.10 (t, 3H, CH_3 of 3-ethyl), 1.28 (t, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.46 (t, 3H, CH_3), 1.51 (t, 3H, CH_3), 1.65 (s, 3H, CH_3), 1.78 (s, 3H, CH_3), 1.81 (s, 3H, CH_3), 1.84 (m, 2H, CH_2 of 3-ethyl), 2.45 (s, 3H, TosylCH_3), 2.46 (s, 3H, TosylCH_3), 3.19 (m, 6H, CH_2), 7.09 (d, 2H, ArH), 7 20 (d, 2H, ArH), 7.35 (m, 4H, ArH), 7.54 (m, 6H, ArH and 2xbenzoH), 7.79 (m, 4H, ArH), 8.24 (s, 1H, meso-H), 8.44 (d, 1H, benzoH). Anal Calcd. for $C_{61}H_{58}NiN_4O_6S_2$. $3H_2O$. C, 65.41 ; H, 5.76 ; N, 5.00. Found: C, 65.14 ; H, 5 21 ; N, 4 93 FAB mass spectrum, m/z 1064 (M+1), requires 1063(M+). UV / Vis (λ_{max}, CH_2Cl_2): 345 (ε 20715), 357sh (19305), 434 (64105), 521sh (4160), 643sh (7415), 698 (27485).

^{13}C NMR decoupled ($CDCl_3$). δ 8.65, 13.65, 14.47, 14.77, 15.44, 16.42, 16.54, 18 73, 18.98, 20.14, 21.73, 28 13, 34.74, 56.48, 97.66, 106.34, 111.93, 116.64, 120.09, 120.57, 120 69, 122.00, 123.37, 125 84, 128.79, 128 82, 129.75, 131.92, 132.96, 134.64, 135.46, 135.74, 135.92, 136.83, 136.89, 137.06, 137.79, 138.97, 139.32, 139.65, 141.14, 141.39, 141 68, 142.18, 145.00, 145 55, 147.63, 148.29, 149.70, 149.78, 164 09

Synthesis of Free Base 3H-Benzo[at]porphyrins. General Procedure C.

Nickel benzochlorin (~60mg) was dissolved in H_2SO_4 (conc, 5mL) and the solution stirred at room temperature for 1-2hrs. Methylene chloride (50mL) and water (50mL) were added and the solution neutralized with saturated hydrogen carbonate solution. The organic layer was washed well with water and dried over sodium sulfate After evaporation of the filtered solvent, the residue was chromatographed on silica using methylene chloride which removed a minor green band and the major green band was eluted with methylene chloride / acetone (1%). The benzochlorin was recrystallized from methylene chloride / methonol to give a dark green powder.

3,8,12,18-Tetraethyl-3,7,11,17-tetramethyl-5,15-bis(4'-methylphenyl)-3H-benzo[at]porphyrin (5a).

Sythesised by general procedure C using benzochlorin (5) (55mg) Yield of (5a) = 45mg, (89%).

^{1}H NMR ($CDCl_3$): δ -0.03 (t, 3H, CH_3 of 3-ethyl), 1.32 (t, 3H, CH_3), 1.40 (t, 3H, CH_3), 1 41 (s, 3H, CH_3), 1.48 (t, 3H, CH_3), 1.76 (s, 3H, CH_3), 1 78 (s, 3H, CH_3), 1.82 (s, 3H, CH_3), 1.88 (m, 1H, CH of 3-ethyl), 2 03 (m, 1H, CH of 3-ethyl), 2 55 (s, 3H, $ArCH_3$), 2 58 (s, 3H, $ArCH_3$), 3 02 - 3.23 (m, 6H, CH_2), 4.48 (brs, 1H, NH), 4.67 (brs,1H, NH), 7.61 (t, 1H, benzoH), 7.40 (d, 2H, ArH), 7.53-7.65 (m, 7H, ArH and benzoH), 7.80 (s, 1H, meso-H), 8 62 (d, 1H, benzoH). Anal Calc for $C_{49}H_{52}N_4$. $2\,5H_2O$· C, 79 31 , H, 7 74 ; N, 7 54 Found C, 79 47; H, 7 36, N, 7.13 UV / Vis (λ_{max}, Benzene)· 418(ε 80300), 618 (14470), 670 (32000).

^{13}C NMR decoupled ($CDCl_3$) δ 8 62, 12 35, 13 32, 13 69, 15.67, 15.86, 16.29, 18 62, 18.88, 19.72, 21 51, 21 59, 26.87, 33.21, 58.17, 93 88, 108 52, 114 90, 117.11, 120 45, 127 39, 127.49, 128 24, 128.75, 128 98, 130.54, 131.74, 132.25, 132.41, 133 21, 133 56, 134.93, 135 12, 135 29, 137.80, 137.92, 138.27, 138.42, 138 56, 142 96, 144.53, 149 14, 149 76, 156.51, 178 27

3,8,12,18-Tetraethyl-3,7,11,17-tetramethyl-5,15-bis(4'-nitrophenyl)-3H-benzo[at]porphyrin (6a).

Sythesised by general procedure C using benzochlorin (6) (62mg) Yield of (6a) = 46mg, (80%).

^{1}H NMR ($CDCl_3$). δ -0 02 (t, 3H, CH_3 of 3-ethyl), 1 33 (t, 3H, CH_3), 1.39 (s, 3H, CH_3), 1 42 (t, 3H, CH_3), 1 48 (t, 3H, CH_3), 1 75 (s, 6H, 2xCH_3), 1 77 (s, 3H, CH_3), 1 92 (m, 2H, CH_2 of 3-ethyl), 3.04-3 23 (m,

6H, CH_2), 4.45 (brs, 1H, NH), 4.58 (brs,1H, NH), 7.61 (d, 1H, benzoH), 7.69 (t, 1H, benzoH), 7.88 (s, 1H, meso-H), 7 89-8.02 (m, 4H, ArH), 8.39-8 53 (m, 4H, ArH), 8 64 (d, 1H, benzoH). Anal. Calc. for $C_{47}H_{46}N_6O_4$: C, 74.38 ; H, 6.11 , N, 11 06 . Found C, 74.35, H, 6.33; N, 10.76. UV / Vis (λ_{max}, CH_2Cl_2): 334 (ε 27180), 414 (55810), 621 (12710), 674 (24200).

^{13}C NMR decoupled ($CDCl_3$): δ 8.52 , 12.78, 13.86, 14 09, 15 64, 15.88, 16.22, 18.65, 18 85 19.65, 26 89, 33.36, 58.16, 95.02, 106.37, 114.79, 117.65, 121.22, 121.88, 123 18, 128.46, 128.58, 129.05 , 132.21, 133.35, 133.51, 134.68, 135 74, 135 94, 137.74, 138 46, 143 68, 143 84, 144 25, 144 94, 145 81, 147 90, 148.69, 149.78, 157.33, 176.83.

5,15-Bis(4'-dimethylaminophenyl)-3,8,12,18-tetraethyl-3,7,11,17-tetramethyl-3H-benzo[at]porphyrin (7a).
Sythesised by general procedure C using benzochlorin (7) (92mg) Yield of (**7a**) = 77mg, (90%)

^1H NMR ($CDCl_3$). δ -0.04 (t, 3H, CH_3 of 3-ethyl), 1 30 (t, 3H, CH_3), 1.41 (t, 3H, CH_3), 1.46 (t and s, 6H, 2xCH_3), 1 81 (s, 3H, CH_3), 1 82 (s, 3H, CH_3), 1 86 (m, 2H, CH of 3-ethyl), 1.87 (s, 3H, CH_3), 2 48 (s, 3H, ArCH_3), 3.10 (s, 6H, N(CH_3)$_2$), 3.14 (s, 6H, N(CH_3)$_2$), 3.02 - 3.14 (m, 6H, CH_2), 4.69 (brs, 1H, NH), 5 01 (brs,1H, NH), 6 83 (m, 2H, ArH), 6.92 (m, 2H, ArH), 7 44-7 71 (m, 7H, ArH , 2xbenzoH, meso-H), 8 56 (d, 1H benzoH) UV / Vis (λ_{max}, $CHCl_3$) 329 (ε 26690), 414 (57960), 616 (13250), 672 (25100)

3,8,12,18-Tetraethyl-3,7,11,17-tetramethyl-5,15-bis(4'-toluenesulfonyloxyphenyl)-3H-benzo[at]porphyrin (8a).
Sythesised by general procedure K using benzochlorin (**8**) (114mg). Yield of (**8a**) = 98mg, (90%)

^1H NMR ($CDCl_3$). δ -0.07 (t, 3H, CH_3 of 3-ethyl), 1 29 (t, 3H, CH_3), 1 32 (s, 3H, CH_3), 1 38 (t, 3H, CH_3), 1 48 (t, 3H, CH_3), 1.68 (s, 3H, CH_3), 1 69 (s, 3H, CH_3), 1 72 (s, 3H, CH_3), 1 86 (m, 2H, CH of 3-ethyl), 2 48 (s, 3H, ArCH_3), 2.50 (s, 3H, ArCH_3), 3.02 - 3 24 (m, 6H, CH_2), 4 35 (brs, 1H, NH), 4 55 (brs,1H, NH), 7.10 (m, 2H, benzoH, ArH), 7.24 (m, 2H, ArH), 7.37 (d, 4H, ArH), 7 59 (d, 1H, benzoH), 7.64-7 71 (m, 5H, ArH), 7 82-7.88 (m, 5H, ArH, meso-H), 8 62 (d, 1H benzoH) Anal Calc. for $C_{61}H_{60}N_4O_6S_2$ $2H_2O$ C, 70.08, H, 6.17 , N, 5.35 Found C, 69.72, H, 5 72, N, 5.03 FAB mass spectrum, m/z 1009 (M+1), requires 1008 (M+) UV / Vis (λ_{max}, CH_2Cl_2)· 337 (ε 27015), 418 (635890), 616 (12800), 669 (24440) ^{13}C NMR decoupled ($CDCl_3$). δ 8 53, 12.52, 13 54, 13 85, 15.64, 15 87, 16.24, 18 62, 18 85, 19 68, 21.75, 26 82, 33.23, 45.67, 58 06, 94 37, 106 99, 114 75, 117 36, 120 81, 120 85, 120 92, 122.16, 122 20, 128 32, 128.65, 128 76, 128.81, 128 85, 129.65, 129 78, 129.88, 131.92, 131 95, 132 59, 133 42, 133 54, 134 70, 135 32, 136 02, 137 51, 138 07, 138 29, 140 29, 142 95, 143 60, 144 23, 145 26, 145 57, 149 71, 149 78, 149 98, 156 84, 177 56

2,8,12,18-Tetraethyl-3,7,13,17-tetramethyl-5,15-bis(4'-methylphenyl)-2,3-dihydrocyclopenta[at]porphyrin-2^1-carboxaldehyde (13).
Synthesised by the method of Gunter and Robinson [6b] using. porphyrin (**9**) (97mg) Yield of purpurin (**13**) = 52mg, (53%) ^1H NMR ($CDCl_3$) δ -0.36 (t, 3H, CH_3 of 2-ethyl), 0 35 (brs, 1H, NH), 1 28 (brs, 1H, NH), 1 48 - 1 66 (m, 13H, 3xCH_3, CH_3 of 3-methyl, hidden CH of 2-ethyl), 2 10 (s, 3H, CH_3), 2 23 (s, 6H, 2xCH_3), 2 34 (m, 1H, CH of 2-ethyl), 2 59 (s, 3H, ArCH_3), 2 66 (s, 3H, ArCH_3), 3.53 - 3 78 (m, 6H, 3 x CH_2), 4.40 (q, 1H, 3-H), 7 07 (d, 1H, ArH), 7.24 (d, 1H, ArH), 7 43 (d, 1H, ArH), 7 51-7 59 (m, 4H, ArH), 7 93 (d of d, 1H, ArH), 8 07 (d , 1H, ArH), 9 36 (s, 1H, isocyclic ring-H), 9 42 (s, 1H, meso-H), 10 13 (s, 1H, CHO) FAB mass spectrum, m/z 713 (M+1), requires 712 (M+) UV / Vis (λ_{max}, CH_2Cl_2) 441 (ε 142600), 515 (8184), 586 (19535), 662 (10740), 708 (29436)

^{13}C NMR decoupled ($CDCl_3$) δ 7.56, 13 42, 14 16, 14 65, 16 07, 17 11, 17 38, 19 24, 19 63, 20 25, 21 56, 21 66, 26 92, 54 50, 68 34, 102 03, 106 03, 115 35, 124 22, 128 19, 128 49, 128 74, 129 26, 129 82, 131 57, 132 27, 132 49, 133 18, 133 82, 134 87, 136 24, 136 97, 137 73, 138 08, 138 64, 140 19, 141 85, 142 96, 145 89, 148 23, 152 18, 155 84, 172 25, 182 01, 187 24.

2,8,12,18-Tetraethyl-3,7,13,17-tetramethyl-5,15-bis(4'-toluenesulfonyloxyphenyl)-2,3-dihydrocyclopenta[at]porphyrin-2^1-carboxaldehyde (14).
Synthesised as above using porphyrin (**10**) (109mg) Yield of purpurin (**14**) = 58mg (53%) ^1H NMR ($CDCl_3$) δ -0 38 (t, 3H, CH_3 of 2-ethyl), 0 22 (brs, 1H, NH), 1 12 (brs, 1H, NH), 1 42 (d, 3H, CH_3 of 3-methyl), 1 45 (m, 1H, hidden CH of 2-ethyl), 1 52 (t, 3H, CH_3), 1 59 (t, 3H, CH_3), 1.65 (t, 3H, CH_3), 2 14 (s, 3H, CH_3), 2 15 (s, 6H, 2xCH_3), 2 34 (m, 1H, CH of 2-ethyl), 2 51 (s, 6H, Tosyl CH_3), 3 53 - 3 78 (m, 6H, 3 x CH_2), 4 35 (q, 1H, 3-H), 7 09 (s, 2H, ArH), 7 24 (d, 1H, ArH), 7 28-7 44 (m, 5H, ArH), 7 60 (d of

d, 1H, ArH), 7.84 (d , 2H, TosylH), 7.89 (d,4H, Tosyl H), 7.97 (d of d, 1H, ArH), 8.13 (d, 1H, ArH), 9.35 (s, 1H, isocyclic ring-H), 9.46 (s, 1H, meso-H), 10 16 (s, 1H, CHO) Anal Calc for $C_{61}H_{60}N_4O_7S_2 \cdot$ C, 71 46; H, 5 90 ; N, 5.46. Found C, 71 78; H, 5.89; N, 5.30. UV / Vis (λ_{max}, Benzene): 336 (ε 18410), 442 (187140), 511 (6170), 546 (8880), 585 (24645), 653 (9015), 710 (54001).

^{13}C NMR decoupled ($CDCl_3$). δ 7 49, 13.51, 13.59, 14 35, 14 72, 16 05, 17.12, 17.36, 19.22, 19.61, 20 24, 21 78, 26.88, 30.89, 54 29, 68 34, 102 40, 106.22, 113.81, 121 51, 121 75, 121 98, 122 03, 122.11, 128.69, 128.83, 128.84, 129.86, 131.83, 132.02, 133.66, 132.82, 132.84, 133 45, 133 68, 134.95, 135.51, 136 40, 136.47, 138 44, 139 48, 140 64, 142 08, 143.38, 145 65, 145 68, 146.52, 148.37, 149.85, 150.09, 151 80, 155 37, 171 55, 182 20, 187 33

Hydrolysis of the Carbomethoxy Group in the Ni meso-Acrylate Diarylporphyrins. General Procedure D.

To the Ni *meso*-acrylate porphyrin dissolved in tetrahydrofuran was added a KOH / methanol (10%) solution and the resulting solution refluxed until hydrolysis was complete as judged by tlc (15min). The solvent was removed by rotary evaporation and the brown residue acidified with glacial acetic acid. Chloroform was added and the organic layer washed well with water. The organic layer wash dried over sodium sulfate, filtered and evaporated to dryness to give the crude carboxylic acid porphyrin

2, 8, 12, 18-Tetraethyl-3, 7, 13, 17-tetramethyl-5,15-bis(4'-methylphenyl)porphyrin-10-propenoic acid (15a).
Synthesised using method G using porphyrin (**15**) (0 2 g), tetrahydrofuran (70mL), 10% KOH / methanol (10mL), acetic acid (15 mL) Yield of (**15a**) = 0 19 g, (92%) ^1H NMR ($CDCl_3$) δ 1.52 (t, 6H, 2 x CH_3), 1.54 (t, 6H, 2 x CH_3), 2 12 (s, 6H, 2 xCH_3), 2 17 (s, 6H, 2 x CH_3), 2.59 (s, 6H, $ArCH_3$), 3 53 (m, 8H, 4 x CH_2), 5.18 (d, 1H, vinyl Hβ), 7.38 (d, 4H, ArH), 7 58 (brs, 4H, ArH), 9.07 (s, 1H, meso-H), 9 56 (d, 1H, vinyl H)

5,15-Bis(4'-dimethylaminophenyl)-2, 8, 12, 18-tetraethyl-3, 7, 13, 17-tetramethylporphyrin-10-propenoic acid (16a).
Synthesised using method G using porphyrin (**16**) (0.5 g), tetrahydrofuran (75mL), 10% KOH / methanol (5mL), acetic acid (15 mL) Yield of (**16a**) = 0.48 g, (97%). ^1H NMR ($CDCl_3$). δ 1 50 (t, 6H, 2 x CH_3), 1.56 (t, 6H, 2 x CH_3), 2 15 (s, 6H, 2 xCH_3), 2 20 (s, 6H, 2 x CH_3), 3 14 (s, 12H, $N(CH_3)_2$), 3.56 (m, 8H, 4 x CH_2), 5.28 (d, 1H, vinyl Hβ), 6 95 (d, 4H, ArH), 7 56 (brs, 4H, ArH), 9 07 (s, 1H, meso-H), 9.60 (d, 1H, vinyl H)

Synthesis of the Ni Diaryl Dimers and Ni meso-Vinyl Diaryporphyrins. General Procedure E.

The crude Ni carboxylic acid porphyrin was dissolved in glacial acetic acid and the solution bought to rapid reflux until the colour changed from green to brown (~1min) The reaction was cooled quickly and methylene chloride added The organic layer was washed well with water, dried over sodium sulfate and the solvent removed by rotary evaporation The residue was dissolved in a minimum amount of 1·1 methylene chloride / petroleum spirit (bp 60-70°C) or 1:1 CCl_4 / petroleum spirit (bp. 60-70°C) and chromatographed on silica using the same solvent system The first and second major brown fractions were collected and evaporated to dryness to give the Ni *meso*-vinyl diarylporphyrin and diaryl dimer respectively The diaryl dimer fraction was recrystallized from methylene chloride / acetonitrile, as brown round beads.

[2, 8, 12, 18-Tetraethyl-3, 7, 13, 17-tetramethyl-5,15-bis(4'-methylphenyl)-10-vinyl-porphyrinato(2-)]nickel(II) (17).
Synthesised by method E using, porphyrin (**15a**) (0 74 g), acetic acid (25mL). Flash column chromatography was carried out using 1 1 CCl_4 / petroleum spirit (bp. 60-70°C) as eluent The first fraction contained the *meso*-vinyl diarylporphyrin Yield of (**17**) = 165 2mg, (22%)

^1H NMR ($CDCl_3$) δ 1.46 (t, 6H, 2 x CH_3), 1 52 (t, 6H, 2 x CH_3), 2 07 (s, 6H, 2 xCH_3), 2 14 (s, 6H, 2 x CH_3), 2 58 (s, 6H, $ArCH_3$), 3 53 (m, 8H, 4 x CH_2), 4 60 (d of d, 1H, vinyl*trans*-Hβ), 5 82 (d of d, 1H, vinyl *cis*-Hβ), 7 36 (d, 4H, ArH), 7 63 (d, 4H, ArH), 8 80 (d of d, 1H, vinyl Hα), 9 12 (s, 1H, meso-H) UV / visible (λ_{max}, $CHCl_3$) 424 (ε 110540), 549 (8390), 582 (8445)

5,15-Bis(4'-dimethylaminophenyl)-2, 8, 12, 18-tetraethyl-3, 7, 13, 17-tetramethyl-10-vinyl-porphyrinato-(2-)]nickel(II) (18).
Synthesised by method E using porphyrin (**16a**) (0 5 g), acetic acid (25mL) Flash column chromatography was carried out using 1 1 methylene chloride / petroleum spirit (bp· 60-70°C) as eluent The first major brown fraction contained porphyrin (**18**) Yield of (**18**) = 0 16 g, (34%)

^{1}H NMR ($CDCl_3$): δ 1.49 (t, 6H, 2 x CH_3), 1.57 (t, 6H, 2 x CH_3), 2 19 (s, 6H, 2 xCH_3), 2.27 (s, 6H, 2 x CH_3), 3 17 (s, 12H, $N(CH_3)_2$), 3 53 (m, 8H, 4 x CH_2), 4.76 (d of d, 1H, vinyl*trans*-Hβ), 5.89 (d of d, 1H, vinyl *cis*-Hβ), 6.98 (d, 4H, ArH), 7.64 (d, 4H, ArH), 8.87 (d of d, 1H, vinyl Hα), 9.16 (s, 1H, meso-H).

1-{[2',8',12',18'-Tetraethyl-3',7',13',17'-tetramethyl-5',15'-bis(4"-methylphenyl)-10'-ethylidene-10',20'-dihydroporphyrinato(2-)]nickel(II)-20'-yl}-2-{[2"",8"",12"",18""-tetraethyl-3"",7"",13"",17""-tetramethyl-5"",15""-bis(4""-methylphenyl)porphyrinato(2-)]nickel(II)-20""-yl}ethene (19).

Synthesised by method E using: porphyrin (**15a**) (0.74 g), acetic acid (25mL) Flash column chromatography was carried out using 1.1 CCl_4 / petroleum spirit (bp. 60-70^{0}C) as eluent. The second fraction contained the diarylporphyrin dimer. Yield of dimer (**19**) = 105 1mg, (15%)

^{1}H NMR ($CDCl_3$) (see text for symbols) δ 0.71 (t, 3H, A or A'CH_3), 0 74 (t, 3H, A or A'CH_3), 0 81 (t, 3H, A or A'CH_3), 0.91 (t, 3H, A or A'CH_3), 1 09 (s, 3H, B or B'CH_3), 1 14 (s, 3H, B or B'CH_3), 1.18 (s, 3H, B or B'CH_3), 1 23 (t, 6H, ECH_3), 1 26 (s, 3H, B or B'CH_3), 1 55 (t, 9H, FCH_3, G CH_3), 2.05 (s, 6H, D CH_3), 2 00-2 26 (m, 8H, A or A'CH_2), 2 16 (s, 6H, C CH_3), 2 41 (s, 6H, porphodimethene ArCH_3), 2 43 (s, 6H, porphodimethene ArCH_3), 2 58 (s, 6H, porphyrin ArCH_3), 3.57 (q, 4H, FCH_2), 3 81 (m, 4H, ECH_2), 4 67 (d, 1H, methine H proton), 5 39 (d of d, 1H, H vinylHβ), 5 88 (q, 1H, G H), 6 92 (t, 2H, ArH), 7 17 (t, 2H, ArH), 7 27 (m, 2H, ArH), 7 34 (d, 6H, Ar H), 7 61 (brs, 4H, ArH), 9 05 (s, 1H, meso-H), 9 08 (d, 1H, H vinyl Hα) FAB mass spectrum, m/z 1482 (M+2), requires m/z 1480 (M+) UV / visible (λ_{max}, $CHCl_3$) 434 , 561 nm

^{13}C decoupled NMR ($CDCl_3$) δ 12 82, 12 97, 13 18, 13 34, 14 51, 14 58, 15.29, 15 35, 15 46, 15 60, 15 62, 17 07, 17 24, 17.46, 17 55, 17 64, 18 19, 19 35, 21.41, 21 57, 21 89, 40 48, 95 75, 109.60, 117 12, 126 15, 128 08, 128 17, 128 23, 129.09, 129 35, 129 44, 129.61, 130 07, 130 88, 131 33, 131.38, 131 71, 132 52, 133 08, 133 17, 133 61, 135 50, 135 65, 137 49, 138 12, 138 20, 138 24, 138 34, 138 90, 139 33, 139 57, 139 72, 140 98, 142 31, 142 43, 144 98, 147 36, 148 30, 151 34, 153.24, 153 98, 154 35

1-{[5',15'-bis(4"-dimethylaminophenyl)-2',8',12',18'-tetraethyl-3',7',13',17'-tetramethyl-10'-ethylidene-10',20'-dihydroporphyrinato(2-)]nickel(II)-20'-yl}-2-{[5"",15""-bis(4""-dimethylaminophenyl)-2"",8"",12"",18""-tetraethyl-3"",7"",13"",17""-tetramethylporphyrinato(2-)]nickel(II)-20""-yl}ethene (20).

Synthesised by method E using porphyrin (**16a**) (0.5 g), acetic acid (25mL) Flash column chromatography was carried out using 1 ·1 methylene chloride / petroleum spirit (bp· 60-70^{0}C) as eluent The second major brown fraction contained the porphyrin dimer (**20**) Yield of dimer (**20**) = 0 24 g, (50%) ^{1}H NMR ($CDCl_3$) (see text for symbols) δ 0 72 (t, 3H, A or A'CH_3), 0 75 (t, 3H, A or A'CH_3), 0 83 (t, 3H, A or A'CH_3), 0 91 (t, 3H, A or A'CH_3), 1 18 (s, 6H, B or B'CH_3), 1 23 (t, 6H, ECH_3), 1 27 (s, 3H, B or B'CH_3), 1 28 (s, 3H, B or B'CH_3), 1 54 (t, 6H, FCH_3), 1 58 (d, 3H, G CH_3), 2 12 (s, 6H, D CH_3), 2 00-2 30 (m, 8H, A or A'CH_2), 2 23 (s, 6H, C CH_3), 2 98 (s, 6H, porphodimethene ArCH_3), 2 99 (s, 6H, porphodimethene ArCH_3), 3 12 (s, 6H, porphyrin ArCH_3), 3 57 (q, 4H, FCH_2), 3 81 (m, 4H, ECH_2), 4 71 (d, 1H, methine H proton), 5 48 (d of d, 1H, H vinylHβ), 5.89 (q, 1H, G H), 6 70-7 00 (brm, 10H, ArH), 7 28 (brm, 2H, ArH), 7.55 (brs, 4H, ArH), 9 04 (s, 1H, meso-H), 9 09 (d, 1H, H vinyl Hα) FAB mass spectrum, m/z 1598 (M+2), requires m/z 1596 (M+) Anal Calcd for $C_{100}H_{112}N_{12}Ni_2 H_2O$ C, 74 25, H, 6 99, N, 10 38 Found C, 74.00, H, 7 28, N, 10 10 UV / visible (λ_{max}, $CHCl_3$). 434 (ε 156295), 561 (28350)

^{13}C decoupled NMR ($CDCl_3$) δ 12 98, 13 14, 13 33, 13 56, 14 55, 14 69, 15 27, 15 37, 15 51, 15 65, 17 09, 17 28, 17 59, 17 67, 18 24, 19 35, 21 89, 40 48, 40 57, 40 80, 95 45, 109 85, 111 46, 112 40, 117 39, 125 86, 126 64, 126 82, 129 00, 129.47, 130 10, 130 25, 130 57, 130 97, 131 09, 131 15, 131 43, 132 87, 133 27, 133 66, 133 80, 134 25, 138.35, 138 40, 138 47, 139 02, 139 15, 139 40, 139 78, 140 33, 141 00, 142 89, 143 03, 144 55, 147 07, 147 98, 150 16, 150 26, 151 19, 153 10, 153 76, 154 07

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