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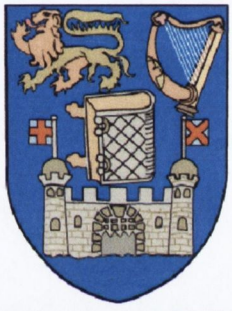
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# Synthesis, Reactivity and Modification of Novel meso-Substituted Porphyrins



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*Submitted by*

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Diploma of Chemistry, Universität Potsdam, Germany

*A thesis submitted to the University of Dublin, Trinity College for the degree of*

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University of Dublin, Trinity College March 2008

THESIS

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# Summary

The aim of this work was the synthesis, modification and characterisation of novel meso-substituted porphyrins. In particular, focus was directed towards the development of new synthetic pathways and the improvement of existing preparative methods.

Two different synthetic methods for the introduction of the formyl residue into the meso-position of the porphyrin macrocycle were investigated, together with studies of its transformation into a variety of functional groups. 1,3-Dithianylsubstituted porphyrins were used as synthons. Dithianylporphyrins can be synthesised by condensation reactions, with the mixed condensation versions giving rise to more stable derivatives. Alternatively, new C-C bonds were formed *via* organolithium compounds. Free base and the nickel(II) porphyrins were synthesised using 2-lithio-1,3-dithiane as the organolithium reagent. The products were stable but butylation occurred as a competitive reaction. Formylporphyrins were received from the dithianylporphyrins *via* acid-catalysed deprotection.

A variety of copper(II) and nickel(II) formylporphyrins were also synthesised in moderate to high yields by the Vilsmeier reaction. Grignard and Wittig reactions on a series of formylporphyrins were performed to demonstrate the wide application range of the formyl group as a precursor for obtaining more elaborately functionalised porphyrin molecules.

The preparation of basket-handle porphyrins in which the handle was directly linked to the meso-position, i.e. in the absence of an aromatic spacer, was also explored. (5,15-Diformyl-10,20-dihexylporphyrinato)nickel(II) and its reduced form, dihydroxymethyl-porphyrin served as precursors. The diformylporphyrin and 1,12-diaminododecane were used for the formation of an imine bridge. The formylsubstituted porphyrin was also treated with 1,10-decanediol to create an acetal linkage. In its reduced form, the porphyrin was reacted with 1,12-dibromododecane to form an ether bond. Nevertheless, all attempts did not lead the desired basket-handle porphyrins.

Exploratory reactions were performed to synthesise novel allenylporphyrins. First, Sonogashira cross-coupling was employed to introduce a propargyl electrophile that contained a terminal leaving group into the porphyrin moiety. Bromoporphyrins were used as precursors, but, due to numerous side reactions, no desired product was isolated.

The second method attempted was based upon the concept of the carbene rearrangement of the Doering-Moore-Skattebøl reaction. The first step required the synthesis of cyclopropylporphyrins *via* carbenes. Two porphyrins with unsaturated groups at the meso-position were used as starting materials and carbenes were generated *in situ*

from chloroform or bromoform and a strong base. However, no addition to the double bond was observed.

The Heck reaction was later used to introduce the 2,3-dichloro-1-propenyl residue into the meso-position of the porphyrin, with subsequent elimination of the geminal halides expected to yield the allene functionality. Unfortunately, this method was also unsuccessful in affording the desired allenylporphyrin.

A more recently reported method utilised two subsequent Horner-Wadsworth-Emmons (HWE) reactions and an attempt was made to apply this to the porphyrin systems described herein. The first HWE reaction yielded the alkenylphosphono compounds, but further reactions did not occur and the desired allenylporphyrins could not be formed using this synthetic pathway.

A last attempt was made using Pd-catalysed reactions. Although, the indium-mediated Pd-catalysed reaction did not give the target compound, Suzuki cross-coupling could be applied successfully, and the reaction of the commercially available allenyl boronic acid pinacol ester and a bromoporphyrin resulted in the corresponding allenylporphyrin.

Finally, the synthesis of porphyrin trimers linked by one triptycene unit as a rigid linker is described using 2,6,14-triiodotriptycene, which was generated in a three-step synthesis from triptycene. Reaction of triiodotriptycene with borolanylporphyrins under Suzuki cross-coupling conditions afforded three porphyrin trimers that were isolated in moderate yields.

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"Research is what I'm doing when I don't know what I'm doing."

Wernher von Braun

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***For 134340 aka Pluto - For me it will always be a planet!***

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# Abbreviations

| | |
|---|---|
| Ar | aromatic |
| BHP | basket-handle porphyrin |
| br | broad |
| BTIB | bis(trifluoroacetoxy)iodobenzene |
| calcd | calculated |
| $CDCl_3$ | deuterated chloroform |
| CIP | Cahn-Ingold-Prelog |
| $D_2O$ | deuteroxide |
| d | doublet |
| dd | double-doublet |
| DDQ | 2,3-dichloro-5,6-dicyano-1,4-benzoquinone |
| DFT | density functional theory |
| DMF | dimethylformamide |
| DMSO | dimethyl sulphoxide |
| dppe | 1,2-bis(diphenylphosphino)ethane |
| dppf | 1,1'-bis(diphenylphosphino)ferrocene |
| EI | electron impact |
| eq | equivalent |
| ES | electrospray |
| ESI | electrospray ionisation |
| FAB | fast atom bombardment |
| FT | Fourier transform |
| GC | gas chromatography |
| GIAO | gauge-including atomic orbital |
| HRMS | high resolution mass spectrometry |
| HWE | Horner-Wadsworth-Emmons |
| IR | infrared |
| IUPAC | international union of pure and applied chemistry |
| *J* | coupling constant measured in Hertz |
| LC | liquid chromatography |
| LD | laser desorption |
| LDA | lithium di(*iso*-propyl)amide |
| m | multiplet |
| m/z | mass-to-charge ratio |
| mp | melting point |
| MS | mass spectrometry |

| | |
|---|---|
| *n*-BuLi | *n*-butyllithium |
| NMR | nuclear magnetic resonance |
| NSD | normal structure decomposition |
| $PdCl_2(PPh_3)_2$ | dichlorobis(triphenylphosphine)palladium(II) |
| $Pd(PPh_3)_4$ | tetrakis(triphenylphosphine)palladium(0) |
| $Pd_2(dba)_3$ | tris(dibenzylideneacetone)dipalladium(0) |
| PDT | photodynamic therapy |
| Ph | phenyl |
| $R_f$ | retention factor |
| RLi | organolithium reagent |
| RMgX | Grignard reagent |
| rt | room temperature |
| s | singlet |
| $S_EAr$ | electrophilic aromatic substitution |
| SEM | (2-trimethylsilyl)ethoxymethyl |
| $S_NAr$ | nucleophilic aromatic substitution |
| t | triplet |
| TBAF | tetra-*n*-butylammonium fluoride |
| TBDMS | *tert*-butyldimethylsilyl |
| TFA | trifluoroacetic acid |
| THF | tetrahydrofuran |
| TLC | thin layer chromatography |
| TMEDA | *N,N,N',N'*-tetramethylethylendiamine |
| TOF | time of flight |
| UV | ultraviolet |
| v/v | volume to volume |
| vis | visible |
| VT | variable temperature |
| $\delta$ | chemical shift measured in parts per million (ppm) |
| $\varepsilon$ | absorption coefficient |
| $\lambda$ | wavelength measured in nanometre (nm) |

# CHAPTER 1:
# Introduction

## 1.1 Definition and nomenclature

The term porphyrin originates from the Greek word *porphura* meaning 'purple'. Porphyrins belong to an important class of tetrapyrroles (Figure 1.1) that consists of four pyrrole-subunits which are connected by four methine bridges. Küster postulated the macrocyclic structure of porphyrin **1** in 1913,[1] which was confirmed in 1926 when Fischer synthesised etioporphyrin I thereby demonstrating that the aromatic structure, initially proposed by Küster was correct.[2] The basic porphyrin structure contains 22 π-electrons but only 18 π-electrons are involved in the delocalisation of the aromatic system. Hence, it is in agreement with the [4n+2]-Hückel rule of aromaticity.[3,4] In free base porphyrins two opposite β,β' carbon bonds possess more double bond character.[5] The four nitrogen atoms are able to bind a variety of metal ions.[6]

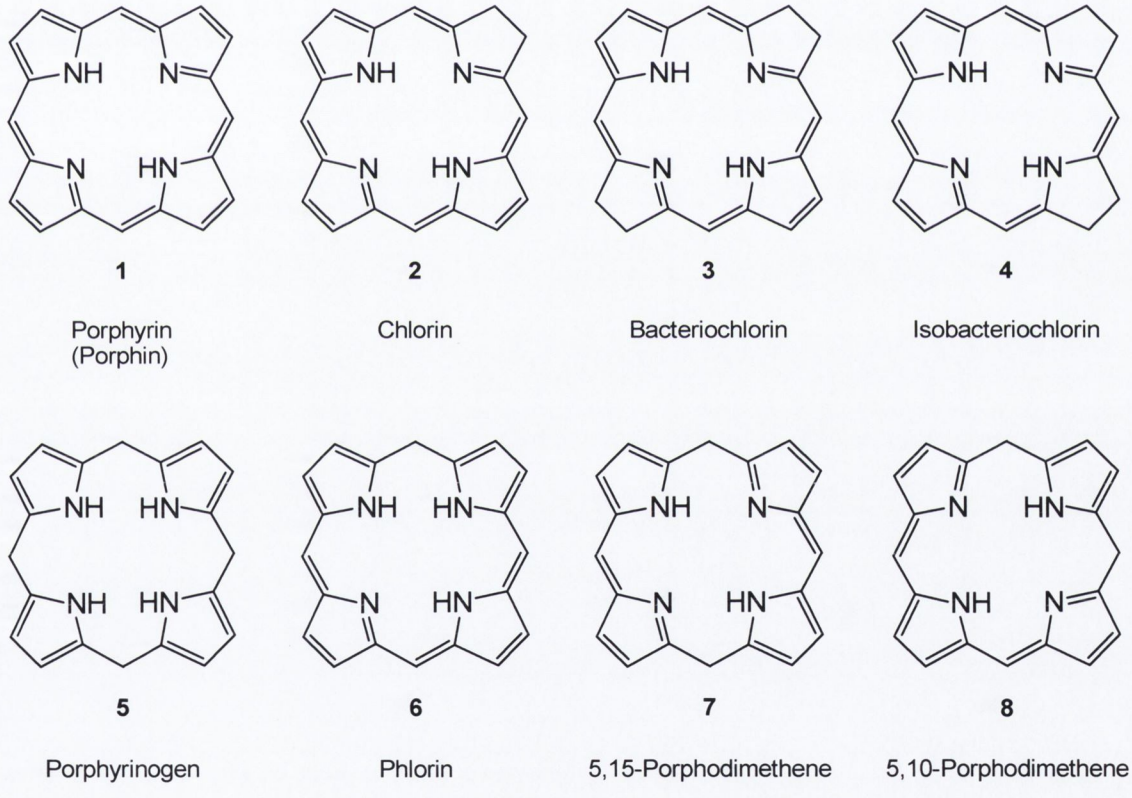



**Figure 1.1.** Important tetrapyrrole classes.

The reduction of porphyrin **1** can lead to the corresponding hydroporphyrins **2**-**8**, which also belong to the tetrapyrrole class. Chlorins (**2**), bacteriochlorins (**3**) and isobacteriochlorins (**4**) still have a conjugated π-electron system, whereas porphyrinogens (**5**), phlorins (**6**) and porphodimethenes (**7** and **8**) lose their aromatic character.

There are three different types of carbons in a porphyrin macrocycle and the numbering and positions of these atoms follow the rules of the International Union of Applied Chemistry (IUPAC).[7,8]

The carbon ring atoms are numbered 1-20 and the inner nitrogen atoms 21-24 (Figure 1.2). The positions 5, 10, 15 and 20 are called meso-positions ($C_{meso}$-H), whereas the positions 1, 4, 6, 9, 11, 14, 16 and 19 are labelled as α-positions ($C_{\alpha}$-H). Finally, the positions 2, 3, 7, 8, 12, 13, 17 and 18 are known as β-positions ($C_{\beta}$-H).

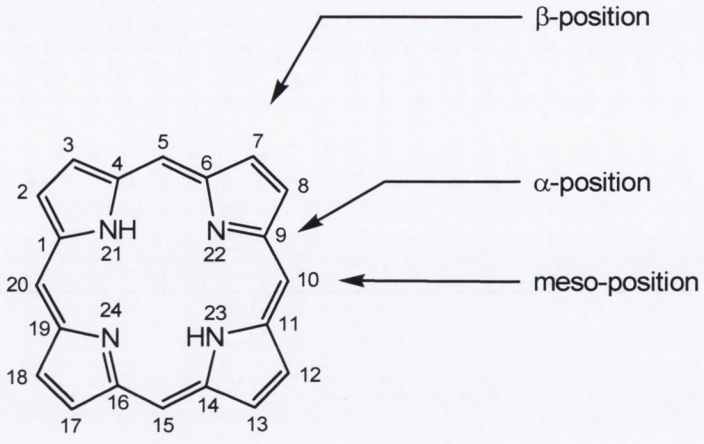



**Figure 1.2.** IUPAC-nomenclature and indication of atoms.

## 1.2 Classes of meso-substituted porphyrins

The possible patterns of meso-substitution[9] are shown in Figure 1.3 and are:

(1) monosubstitution: A-type.

(2) disubstitution: four types (two types of $A_2$ and two types of AB, respectively).

(3) trisubstitution: four types (one form of $A_3$, two types of $A_2B$ and one type of ABC).

(4) tetrasubstitution: seven types (one $A_4$, one $A_3B$, two types of $A_2B_2$, two types of $A_2BC$ and one ABCD).




**Figure 1.3.** Different classes of meso-substituted porphyrins.

## 1.3 Distortions of the porphyrin macrocycle

In spite of their delocalised aromatic nature, porphyrins frequently adopt a nonplanar conformation. The reason for the out-of-plane and in-plane displacement of the 24 atoms of the macrocycle is that this soft distortion requires less energy. Nonplanarity can be induced by a number of different factors, including metal and axial ligand effects, core substitution, steric crowding at the periphery, exchanging macrocycle atoms for larger heteroatoms, interruption of the aromatic system, reduction, and strapping of the macrocycle.[10,11]

### 1.3.1 Out-of-plane distortion

Scheidt and Lee suggested four major out-of-plane distortion modes[12] as shown in Figure 1.4:

(a) *ruf*fled: a 45° rotation around the major two-fold axis (perpendicular to the mean plane)

(b) *sad*dle: pyrrole rings are displaced, alternately, above and below the mean plane of the central 4N core; meso carbon atoms lie in plane or nearly in plane of the core

(c) *dom*ed: a slight 'stepping' of the core, appropriate to inversion symmetry a 'roof' folding along a line joining opposite meso carbon atoms

(d) *wav*e: two atoms of the meso- or β-position at the periphery are displaced, alternately, above and below the mean plane of the central 4N core

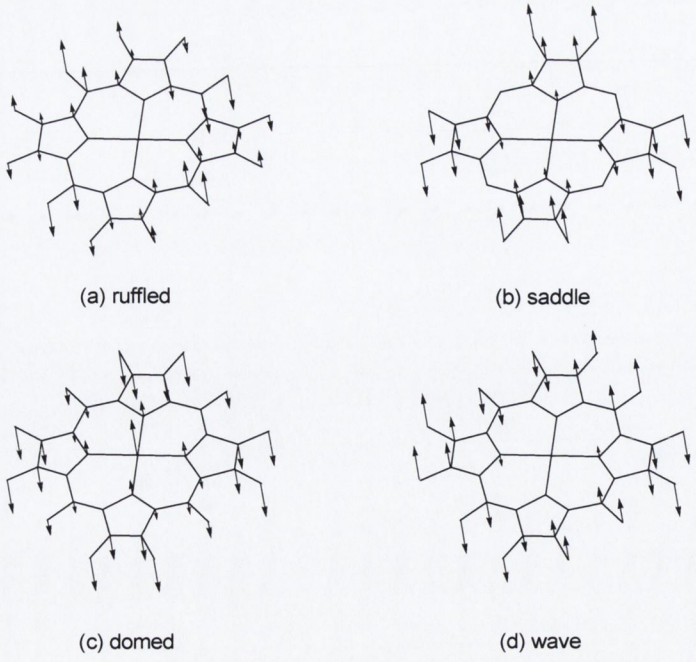



**Figure 1.4.** Out-of-plane distortion modes.[13]

The most often found distortion modes are *sad* and *ruf*.

### 1.3.2 In-plane distortion

There are five different in-plane distortion modes, which are depicted in Figure 1.5. The eigenvectors in the coordinate space indicate the direction and degree of the distortion.[11]

(a) and (b) *m-str* and *N-str* deformation: stretch along opposite methine bridges and pyrrole rings

(c) and (d) *trn* deformation: doubly-degenerate, deformations in x and y directions

(e) *bre* deformation: a macrocycle breathing deformation

(f) *rot* deformation: each pyrrole ring rotates in-phase (counterclockwise in Figure 1.4)

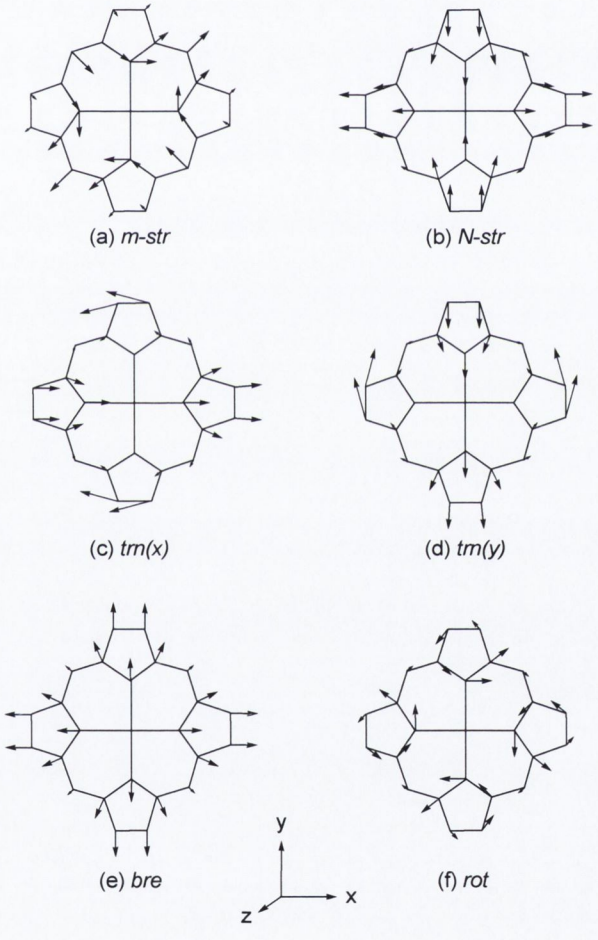



**Figure 1.5.** In-plane distortion modes of the porphyrin macrocycle. [11]

In most cases, the observed distortions can be described as a combination of the out-of-plane and in-plane modes.

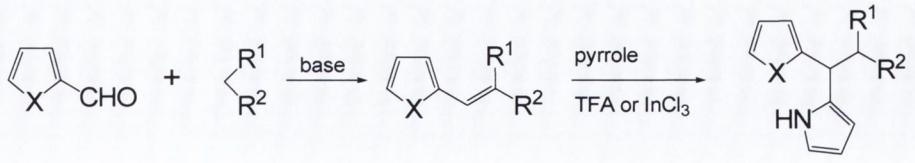
## 1.4 Advances in the synthesis of meso-substituted porphyrins

Meso-substituted porphyrins have always been of great interest even though, or maybe precisely because, they do not occur in nature but are accessible by laboratory synthesis only. Many applications have been found for meso-substituted porphyrins. Of special interest are the nonlinear optical properties of these materials,[14] arising due to their disc-like geometry, which allow energy transfer with molecular control. They have potential applications in optical communications,[15] data storage,[16] and electro-optical signal processing.[17] Of further importance is their use as photosensitisers for photodynamic therapy (PDT).[18,19] Meso-substituted porphyrins are stable and relatively easy to prepare, offering the possibility to design molecules with different properties through introduction of various substituents. Nevertheless, their synthesis remains a challenging task due to difficulties arising from purification and limited availability of suitable building blocks. A variety of different synthetic methods have been developed and investigated to create asymmetrically substituted porphyrins.[9,20,21] Most reported routes generally use acid-catalysed condensation reactions of meso-aryldipyrromethanes with aldehydes in order to obtain the desired product.[22]

### 1.4.1 Condensation reactions

The condensation of an aldehyde with a pyrrole or pyrrole derivative is amongst the longest known and best investigated pathway for the synthesis of porphyrins.[23-31] It represents a facile and straightforward method. However, investigations into its refinement and improvement are ongoing.

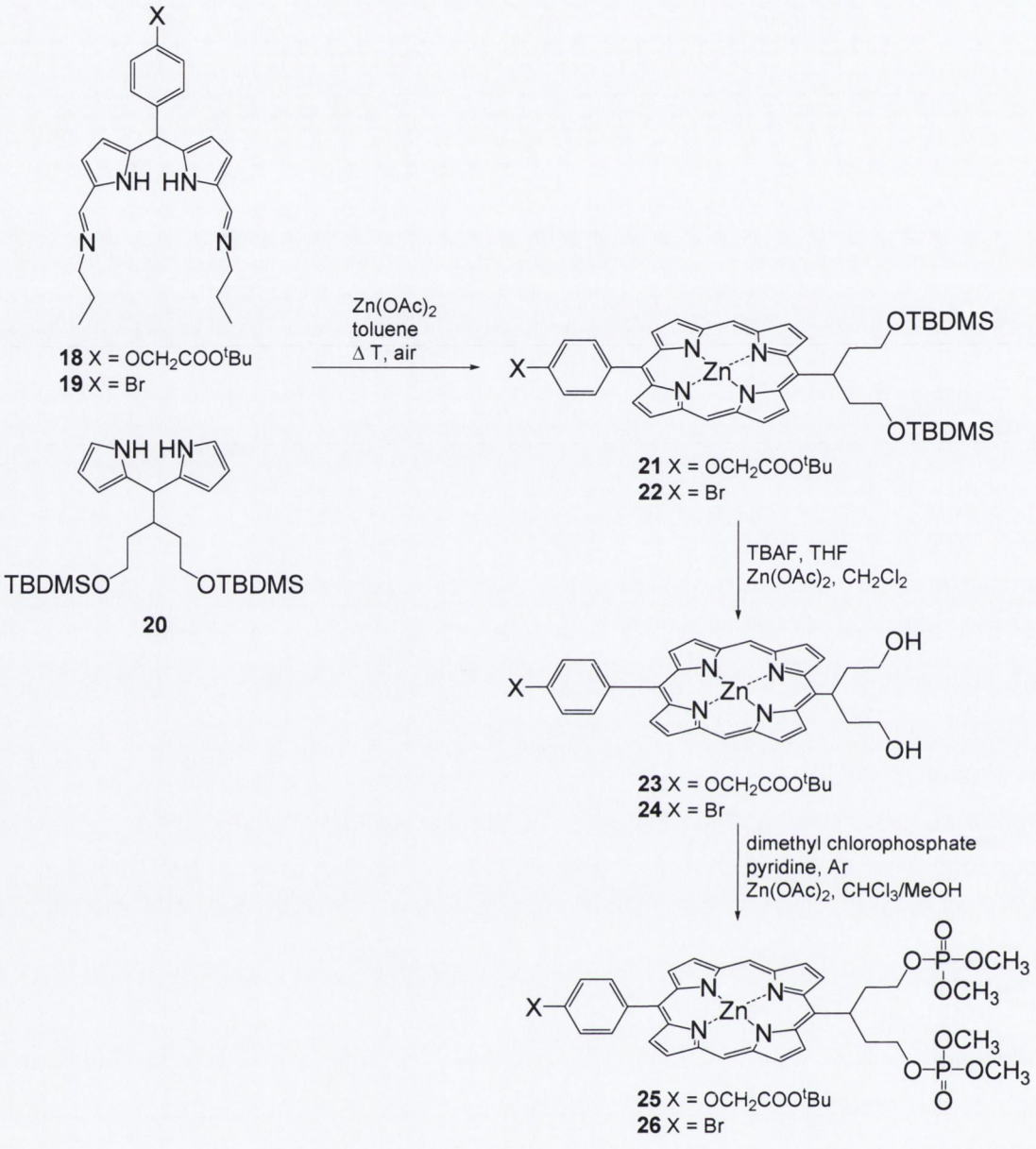
A different method developed by Hong *et al.*[32] first involves the synthesis of dipyrromethanes starting from 2-vinylsubstituted aromatic heterocycles such as pyrrole, thiophene and furan. By Aldol-type reaction of 2-formylpyrrole, 2-formylfuran or 2-formylthiophene with active methylene compounds, the corresponding 2-alkenyl derivates **9-13** were obtained in high yields (Scheme 1.1). A typical reaction involved treatment of 2-formylpyrrole and malononitrile with sodium acetate/methylammonium chloride in methanol. The alkenylpyrrole derivatives received were used for the synthesis of dipyrromethanes **14-17** by nucleophilic addition of pyrrole. Those dipyrromethanes were then used for the formation of porphyrins by [2+2]-condensation reactions.




**9** X = NH, $R^1 = R^2 = CN$
**10** X = NH, $R^1 = R^2 = CO_2Et$
**11** X = NH, $R^1$ = H, $R^2 = NO_2$
**12** X = O, $R^1$ = H, $R^2 = NO_2$
**13** X = S, $R^1$ = H, $R^2 = NO_2$
**14** X = NH, $R^1 = R^2 = CO_2Et$
**15** X = NH, $R^1$ = H, $R^2 = NO_2$
**16** X = O, $R^1$ = H, $R^2 = NO_2$
**17** X = S, $R^1$ = H, $R^2 = NO_2$

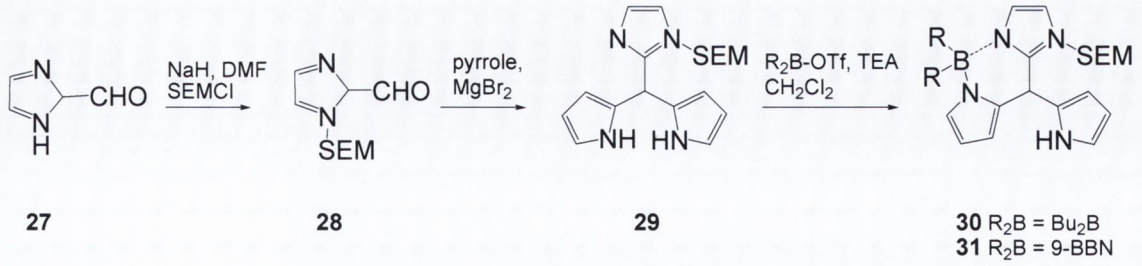
**Scheme 1.1.** Synthesis of dipyrromethanes starting from vinylsubstituted aromatic heterocycles.

A broad range of applications for porphyrins requires access to water-soluble, bioconjugatable derivatives.[33] Some examples include photosensitisers[34,35] and electron transporters in oxidation-reduction processes of cells[36] and in oxygen transport.[37] Dendritic alkyl groups attached to the porphyrin in the meso-position are known to confer high solubility in organic solvents. So-called 'swallowtail' motifs carrying a polar group (hydroxyl, dihydroxyphosphoryl, dihydroxyphosphoryloxy) at the end of each branch have been installed at the meso position in 5,15-AB-porphyrins.[38,39] The introduction of the swallowtail group was carried out using 1,9-bis(*N*-propylimino)dipyrromethane **18** or **19** in a condensation reaction with a dipyrromethane **20** (bearing a protected 1,5-dihydroxypent-3-yl unit at the 5-position), as illustrated in Scheme 1.2. The resulting zinc(II) porphyrins **21** and **22** were further treated with tetra-*n*-butylammonium fluoride (TBAF) in tetrahydrofuran (THF) resulting in the cleavage of the *tert*-butyldimethylsilyl (TBDMS) protecting group. The two hydroxyl groups in the corresponding swallowtail substituent of each of the resulting zinc(II) porphyrins, **23** and **24**, were transformed to the resulting diphosphate product **25** and **26**.




**Scheme 1.2.** Synthesis of water-soluble porphyrins containing symmetrically branched ('swallowtail') substituents.

Lindsey and co-workers developed a method for the design of imidazole-substituted metalloporphyrins that are valuable for studies of self-assembly and for applications where water solubility is required.[40] The syntheses involved dipyrromethanes, 1-acyldipyrromethanes, and 1,9-diacyldipyrromethanes bearing an imidazole group at the 5-position. First, the polar, reactive imidazole unit of the imidazole-2-carboxaldehyde precursor **27** was masked by introducing the 2-(trimethylsilyl)ethoxymethyl (SEM) group at the imidazole pyrrolic nitrogen (Scheme 1.3). The SEM-protected aldehyde **28** then was treated with an excess of pyrrole, yielding the protected 5-imidazolyldipyrromethane **29**. Second, a dialkylboron substituent was bound to the pyrrole of the dipyrromethane and coordinated to the imidazole imino nitrogen resulting in **30** and **31**, respectively. Several methods were examined, that utilised these dipyrromethanes to obtain $A_2B_2$-, $A_2BC$-, and 5,15-AB-porphyrins. The SEM group was later removed by acidic work-up.

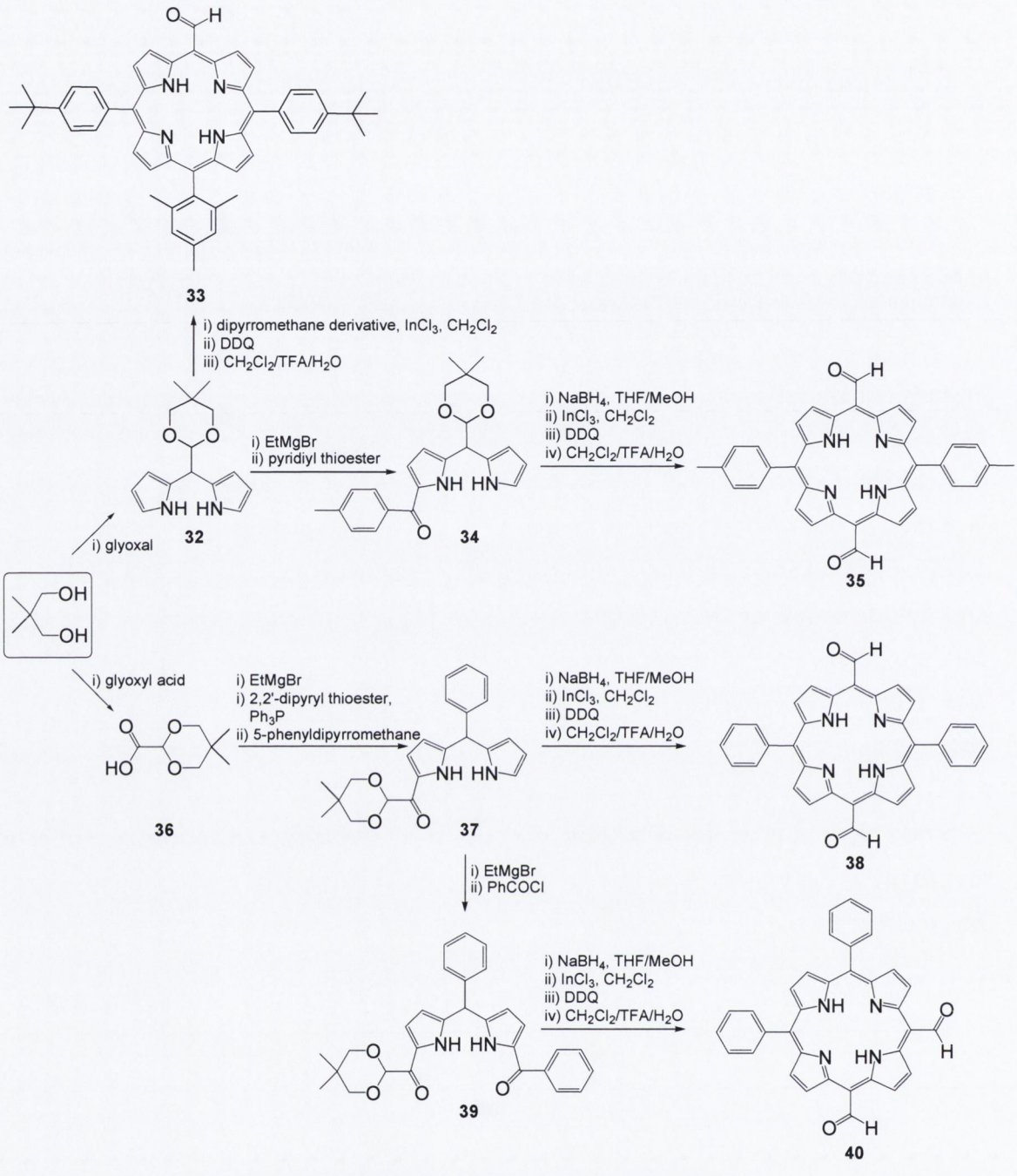



**27** **28** **29** **30** $R_2B = Bu_2B$ **31** $R_2B$ = 9-BBN

**Scheme 1.3.** Introduction of an imidazole unit masked by use of the SEM group at the imidazole pyrrolic nitrogen, and a dialkylboron motif bound to the pyrrole.

In addition, Lindsey and co-workers developed a new synthetic route towards free base formylporphyrins bearing one or two meso-formyl substituents (Scheme 1.4).[41] Glyoxal monoacetal was reacted with pyrrole to afford acetal-dipyrromethane **32**, which was used in further condensation reactions to provide the monoformylporphyrin **33**. Additionally, 1-acyldipyrromethane **34** was synthesised under standard acylation conditions from **32**, and further condensation reactions resulted in the diformylporphyrin **35**. Acetal-acid **36** was prepared from the reaction of glyoxyl acid monohydrate with neopentyl glycol and was used in the synthesis of 1-acyldipyrromethane **37**, which was employed in further condensation reactions to afford diformylporphyrin **38** and dipyrromethane **39**. 1,9-Diacyldipyrromethane **39** was condensed to the 5,10-diformylporphyrin **40**.

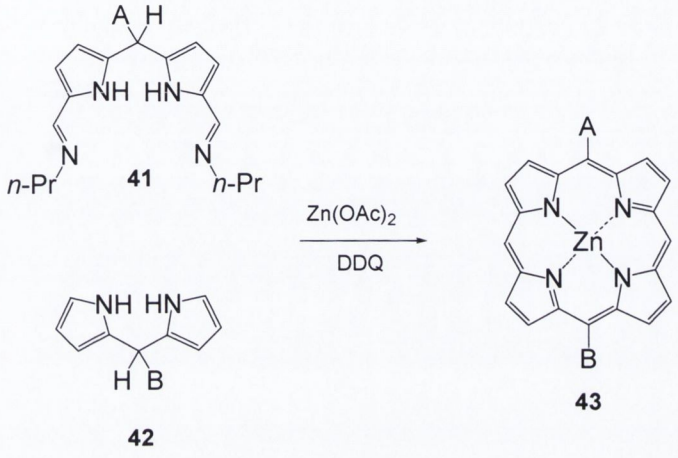
Similarly, Ono *et al.* described the preparation of meso-unsubstituted porphyrins with four formyl groups at the β-position.[42] Though, the formyl group in the pyrrole precursor was masked by a dithiolane group.




**Scheme 1.4.** Synthesis of free base formylporphyrins.

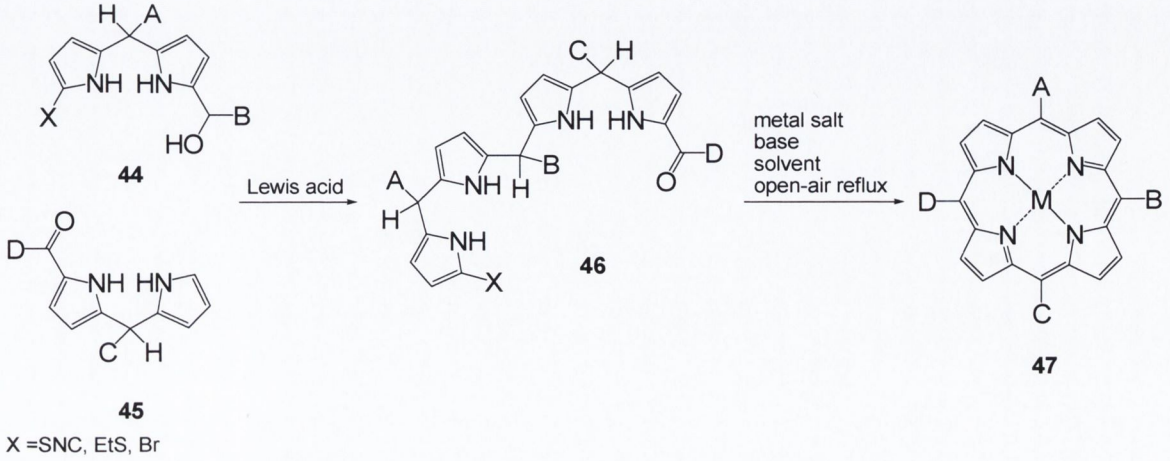
A different method developed by Lindsey and co-workers for the synthesis of 5,15-disubstituted porphyrins involved the condensation of an appropriately (i.e. A or B) functionalised bis(imino)substituted dipyrromethane **41** and an A- or B-substituted dipyrromethane **42**. The reaction was performed in refluxing ethanol containing zinc(II) acetate followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to provide the 5,15-disubstituted zinc(II) porphyrins **43** in moderate yields (Scheme 1.5).[43] The synthesis is compatible with a variety of substituents (e.g. alkyl, aryl, ester, acetal) and allows the synthesis of 5,15-AB-, $A_2$- and A-porphyrins. A second synthesis, yielding zinc(II) porphyrins bearing 5,15-AB-substituents has also been reported by Lindsey and co-workers.[44] This approach consisted of the 1,9-diformylation of a dipyrromethane,

conversion of the diformyldipyrromethane to the bis(imino) derivative, and subsequent reaction of the bis(imino)dipyrromethane and a dipyrromethane. In this way, a wide range of meso-substituents were introduced under reasonably mild conditions with final yields of approximately 30 %. The available substituent patterns for 5,15-AB-porphyrins included aryl/alkyl, aryl/aryl, but not alkyl/alkyl groups; for A-porphyrins the substituent had to be an aryl group.



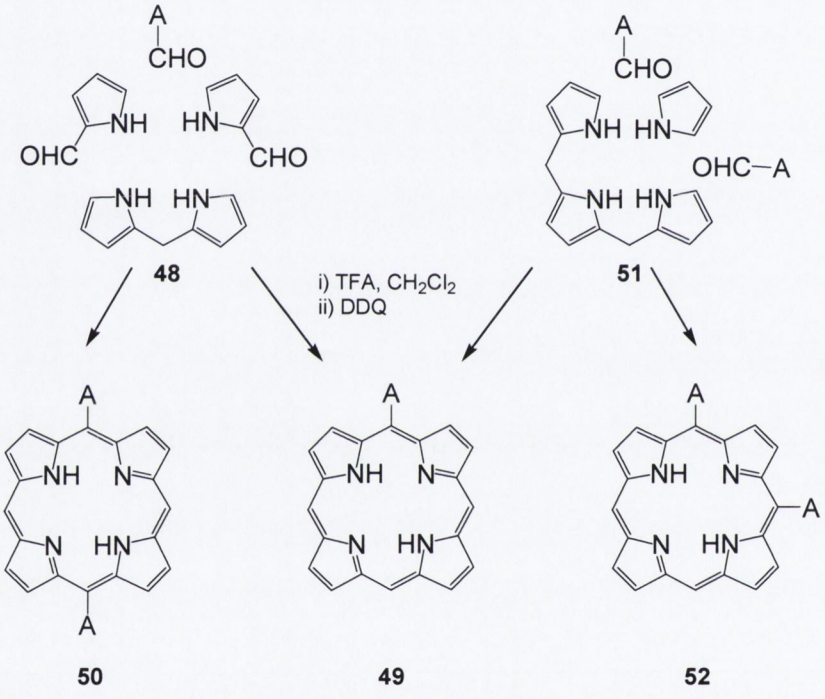

**Scheme 1.5.** Synthesis of 5,15-AB porphyrins with the A- or B-substituent on the dipyrromethane or the bis(imino)dipyrromethane.

An approach for ABCD-porphyrins **47** includes the direct synthesis of a 1-protected 1,9-acylbilane **46** by acid-catalysed condensation at high concentration of a 1-acyldipyrromethane **45** and a 9-protected dipyrromethane-1-carbinol **44** (derived from a 9-protected 1-acyldipyrromethane) (Scheme 1.6).[45] The three protecting groups thiocyanato, ethylthio, and bromo, were tested, but the bromo residue showed the highest efficiency as it is the better leaving group. A one-flask transformation of the 1-protected 1,9-acylbilane under basic, metal-templating conditions was also developed and gave the corresponding metalloporphyrin.



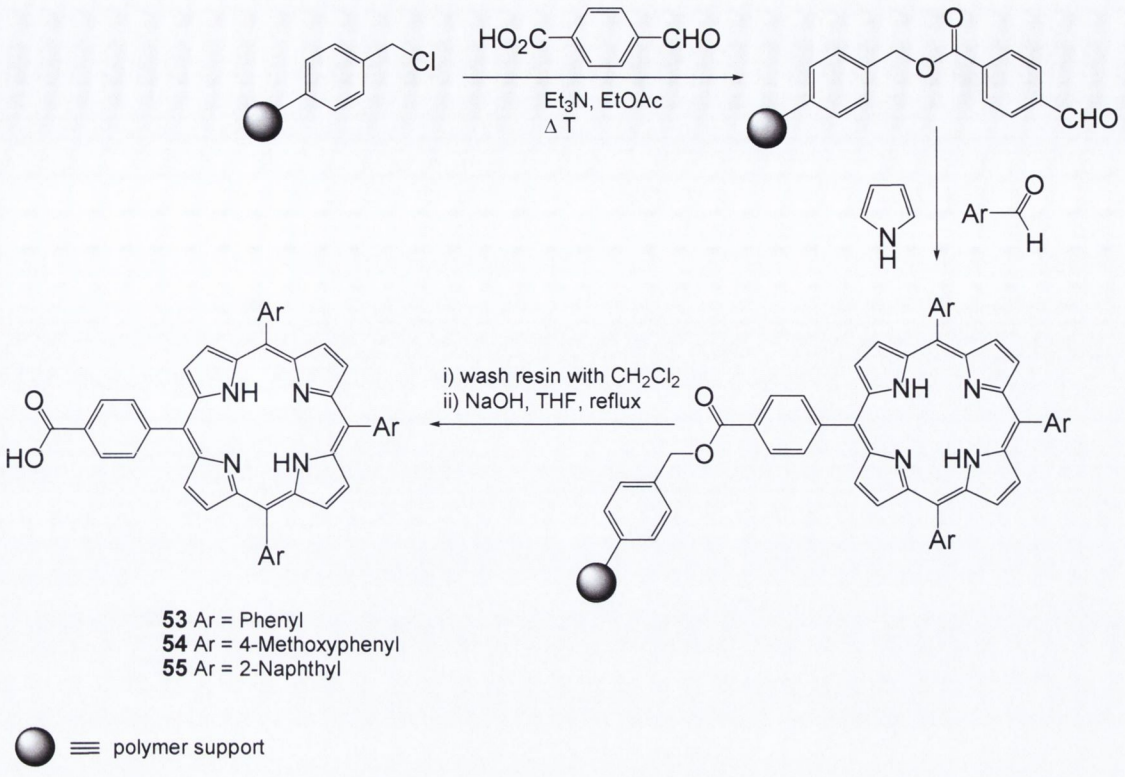

**Scheme 1.6.** Synthesis of ABCD-porphyrins *via* bilanes.

Senge and co-workers described an acid-catalysed [2+1+1] condensation method using dipyrromethane **48**, pyrrole-2-carbaldehyde, and an appropriate aldehyde to prepare 5-substituted porphyrins **49** (Scheme 1.7).[46] The only observed by-product were 5,15-disubstituted porphyrins **50**, which arose due to scrambling. A [3+1] approach of the simple condensation involved an unsubstituted tripyrrane **51**, pyrrole and various aldehydes. Thus, 5,10-disubstituted porphyrins **52** and monosubstituted porphyrins **49** were synthesised, with the latter product being formed as by-product due to scrambling (Scheme 1.7). The reactions were performed without difficulties and the desired compounds were easily separated from the observed side products.




**Scheme 1.7.** Synthesis of 5-, 5,10- and 5,15-meso-substituted porphyrins.

In 2005, Yang *et al.* developed a polymer-based approach for the synthesis of $A_3B$-porphyrins.[47] Here, the substituted aromatic aldehyde was first attached to a polymeric backbone (Scheme 1.8). The second step was a normal condensation reaction on the aldehyde group using pyrrole and an aromatic aldehyde. Only the $A_3B$-porphyrin was obtained from the polymer bound synthesis and compounds **53**-**55** were isolated in high purity. The polymer-supported species were readily separated from the small molecules present in the reaction medium by a simple filtration step. This method may also be extended to the preparation of monosubstituted porphyrins when using formaldehyde instead of an aromatic aldehyde, but this has not yet been attempted.




**53** Ar = Phenyl
**54** Ar = 4-Methoxyphenyl
**55** Ar = 2-Naphthyl

≡ polymer support

**Scheme 1.8.** Synthesis of tetrasubstituted porphyrins on polymers.

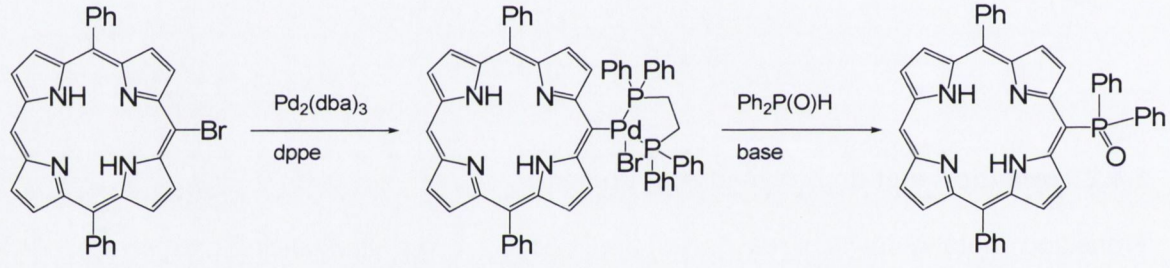
### 1.4.2 Transition metal-catalysed reactions

Transition metal-catalysed reactions offer a useful option for carbon-carbon as well as carbon-hetero atom bond formations. Complexes involving palladium tend to be the most common and widely employed catalysts.[48,49]

The cyano group is one of the most practical precursors for carbon bond formations and can be employed for subsequent transformations.[50,51] Several practical procedures are available for its introduction into the porphyrin moiety, though few facile methods exist for the preparation of porphyrins bearing more than one nitrile group.[52-55] The route developed by Takanami *et al.* involves a palladium-catalysed cyanation of bromoporphyrins using cyanoethylzinc bromide as a specific cyanating agent.[56] It provides an easy access to various cyanated zinc(II) porphyrins, including meso-mono- and meso-dicyanosubstituted zinc(II) complexes. This route is applicable to a wide range of mono- and dibromoporphyrins and affords the corresponding cyanoporphyrins in moderate to high yields.

Locos and Arnold investigated the palladium-catalysed coupling of vinyl derivatives with bromoporphyrins to produce a series of mono- and disubstituted alkenylporphyrins.[57] There are few articles describing Pd-catalysed couplings of alkenes to the porphyrin core,[58-65] however, Heck-type couplings are a useful method for the introduction of alkenes. Arnold and co-workers also developed methods for carbon-heteroatom bond formations, such as the preparation of peripherally palladated nickel(II) porphyrins using

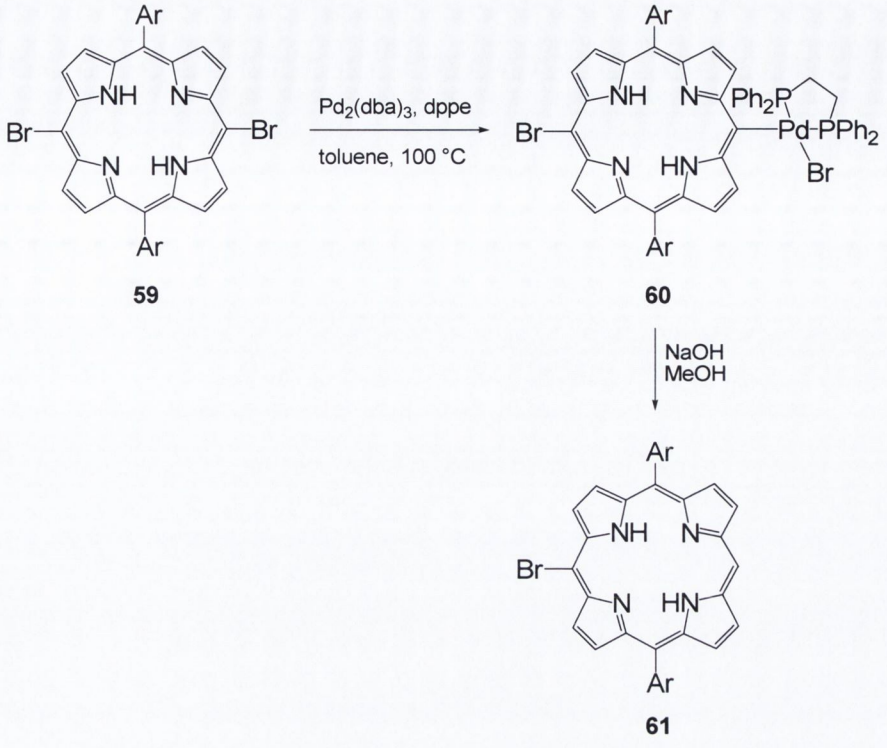
enantiopure chiral chelating diphosphines as supporting ligands on the attached palladium(II) fragment.[66] Both enantiomers of the complexes were obtained in good yields *via* oxidative addition of the starting bromoporphyrin to the $Pd^0L$ complex, which was generated *in situ* from tris(dibenzylideneacetone)dipalladium(0) [$Pd_2(dba)_3$] and the chiral ligand. Another carbon-heteroatom bond formation described by Arnold and co-workers provided porphyrins where one or two meso-positions were substituted by diphenylphosphine oxide groups. The carbon-phosphorus bond was introduced by the palladium-catalysed reaction of diphenylphosphine or its oxide with the appropriate bromoporphyrin.[67] Scheme 1.9 shows the palladium-catalysed reaction of 5-bromo-10,20-diphenylporphyrin **56** with 1,2-bis(diphenylphosphino)ethane (dppe), which resulted in the palladioporphyrin **57**. In a second step, the palladium moiety was cleaved by the introduction of the phosphine source and various phosphines and phosphine oxides were formed, such as compound **58**. The reaction mechanism is proposed to proceed *via* oxidative addition, phosphination, and reductive elimination steps.




**56** **57** **58**

**Scheme 1.9.** Introduction of diphenylphosphine oxide groups by Pd-catalysed reaction of diphenylphosphine oxide with a bromoporphyrin.

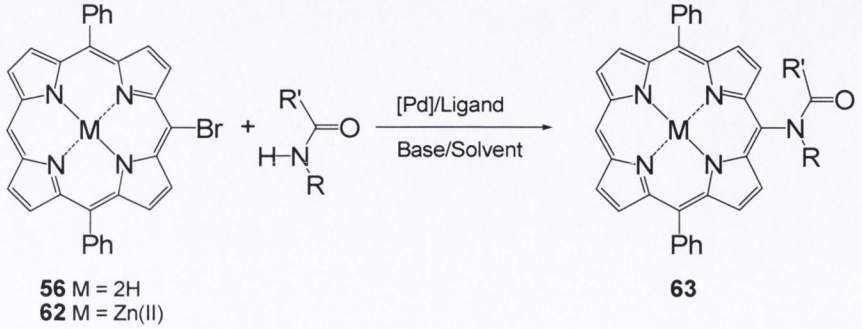
Likewise, Arnold and co-workers have developed a procedure for obtaining monobrominated diarylporphyrins from their dibrominated derivatives **59** (Scheme 1.10).[68] The synthesis is dependent upon interruption of the oxidative palladium addition following the insertion of only one palladium centre, resulting in porphyrin **60**. The incorporation of the second Pd-residue is much slower than the first due to the strong electron-donating properties of the $M(II)L_2Br$ moiety, which allows isolation of the monometallic species. In anticipation that elimination of the bromo-palladium(II) fragment might be faster with a *cis* ligand configuration, bidentate diphosphines, namely dppe and 1,1'-bis(diphenylphosphino)ferrocene (dppf) were used. The desired monobrominated porphyrin **61** could also be obtained when the reaction was performed as a one-pot procedure.




**Scheme 1.10** Preparation of monobrominated diarylporphyrins from dibrominated derivatives.

The oxidative addition of molecular $I_2$ to organopalladium(II) complexes has rarely been investigated.[69-72] Nevertheless, Arnold and co-workers developed an iodination based on this procedure for the preparation of meso-iodoporphyrins from bromoporphyrin precursors.[73] The halogen exchange was carried out *in situ*, starting from the bromoporphyrins and omitting the isolation of the $\eta^1$-palladioporphyrin intermediates. In this way, a variety of meso-iodoporphyrins were prepared in excellent yields.

In 2004, Gao *et al.* showed that meso-amidoporphyrins can easily be synthesised by the direct reaction of meso-brominated porphyrins with amides *via* a palladium-catalysed amidation reaction.[74] A combination of palladium precursors $Pd(OAc)_2$ or $Pd_2(dba)_3$, the phosphine ligand Xantphos [9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene], and monobrominated porphyrins **56** and **62** were used for coupling with a wide range of amides to give the corresponding monosubstituted meso-amidoporphyrins **63** in high yields under mild conditions (Scheme 1.11). The reaction is also applicable to dibrominated porphyrins and results in disubstituted meso-amidoporphyrins.



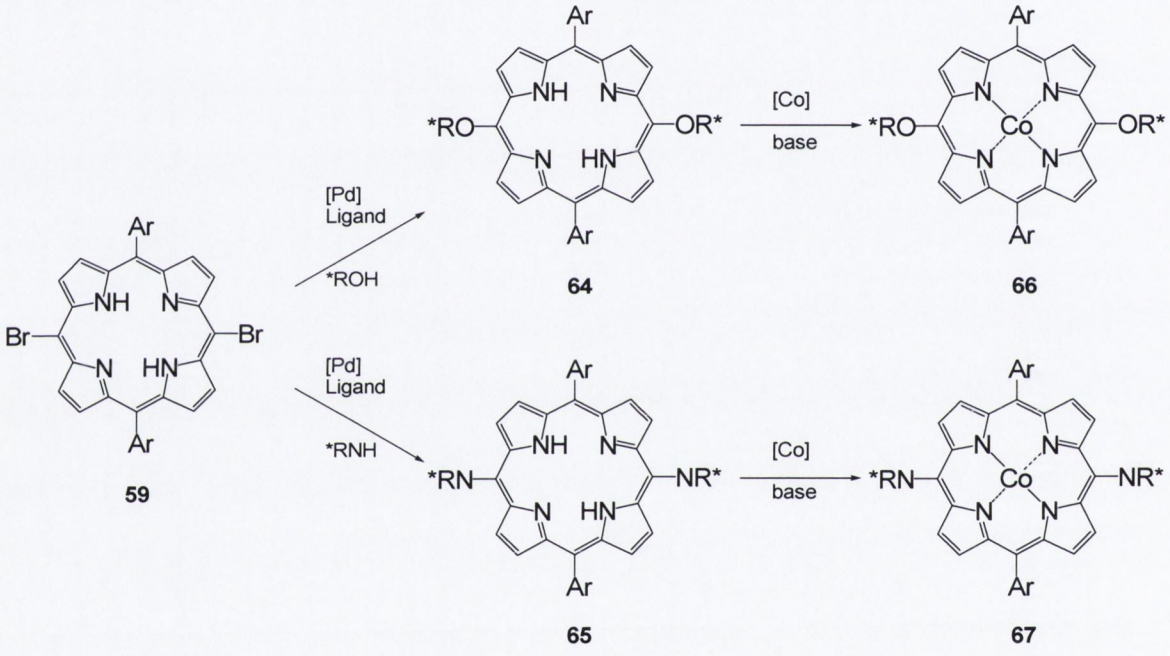

**56** M = 2H
**62** M = Zn(II)

**63**

**Scheme 1.11.** Synthesis of meso-amidoporphyrins by Pd-catalysed reactions of meso-brominated porphyrins with amides.

In addition, Gao *et al.* described a high yielding palladium-mediated C-S bond formation for the synthesis of new meso-arylsulphanyl- and alkylsulphanylsubstituted porphyrins, which was achieved by the direct reactions of meso-brominated porphyrins with thiols.[75] Selenols could also be used and led to the corresponding meso-selenosubstituted porphyrins.

Chen and co-workers reported the reaction of 5,15-dibromo-10,20-diarylporphyrins such as **59** with readily available chiral alcohols and amides. The reactions proceeded *via* palladium-mediated C-O and C-N bond formations to afford novel meso-chiral porphyrins **64** and **65** (Scheme 1.12).[76] Cobalt complexes of these chiral porphyrins (**66**, **67**) were prepared and shown to be effective catalysts for cyclopropanation of styrene with ethyl diazoacetate.



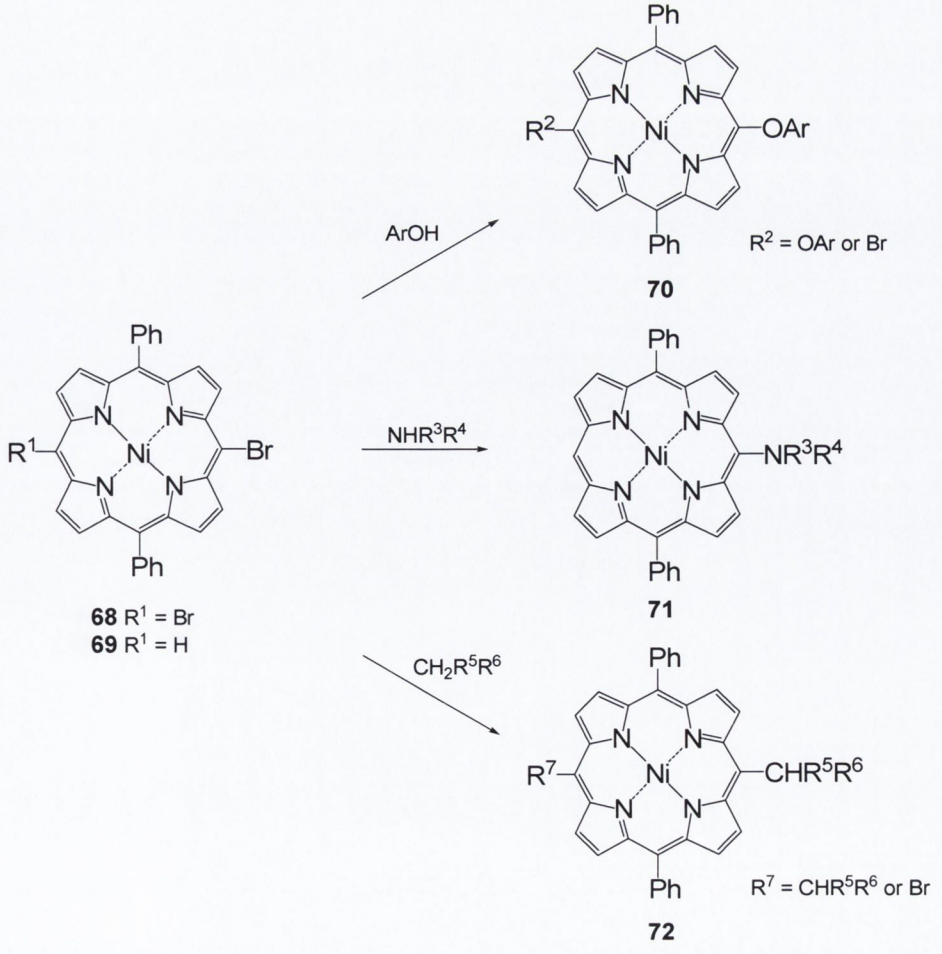

**Scheme 1.12.** Synthesis of novel meso-chiral porphyrins.

The introduction of fluorine or a fluoroalkyl group at the periphery of a porphyrin has significant influences on the properties of the porphyrin and is therefore of great interest.[77-84] A general and efficient method for preparing various perfluoroalkylated porphyrins by the Pd-catalysed cross-coupling of brominated porphyrins with perfluoroalkyl iodides in the presence of copper was developed by Lui and Chen.[85] The combination of $Pd_2(dba)_3$•$CHCl_3$ and $AsPh_3$ was the most effective catalyst system among the reaction conditions explored.

Matano *et al.* developed a copper-catalysed carbon-phosphorus cross-coupling reaction of a meso-iodoporphyrin with di-*n*-butyl phosphite and diphenylphosphane oxide. This method offers an efficient and general route for the synthesis of meso-phosphorylporphyrins.[86] It is also possible to use a copper-catalysed cross-coupling reaction of a meso-iodoporphyrin with benzenethiol or *n*-octanethiol for the

formation of meso-sulphanylporphyrins under Venkataraman conditions using copper(I) iodide, neocuproine and sodium tert-butoxide in toluene under reflux.[87] Oxidation with *m*-chloroperbenzoic acid led to the corresponding meso-sulphinylporphyrins.[88]

Senge and co-workers reported an example of a transition metal-catalysed reaction that is promoted by nickel, entailing the conversion of nickel(II) allylporphyrins to α,β-unsaturated formylporphyrins.[89] The starting allylporphyrins were obtained *via* Suzuki cross-coupling reactions and were isolated in moderate to high yields. Subsequent treatment of the allylporphyrins with nickel(II) acetate and catalytic amounts of glacial acidic acid in dimethylformamide (DMF) resulted in a mixture of nickel(II) allylporphyrin and nickel(II) acroleinylporphyrin, with the latter being the major product. Nickel is also used as a catalyst in the ligand-free reaction described by Chen and co-workers in which the nickel(II) bromoporphyrins **68** and **69** are used as precursors for C-O, C-N, and C-C cross-coupling reactions (Scheme 1.13).[90] $Ni(OAc)_2$ proved to be the most appropriate catalyst in DMF. $K_2CO_3$ was used as base. Several alcohols were employed for the formation of C-O bonds and gave the corresponding dietheration products **70** in high yields. An extension to various aliphatic and cyclic amines led to the formation of the desired meso-aminoporphyrins **71** and a series of carbon-based nucleophiles was also put to the test, yielding the corresponding C-C coupled porphyrins **72**.




**Scheme 1.13.** Nickel-catalysed C-O, C-N and C-C cross-coupling reactions.

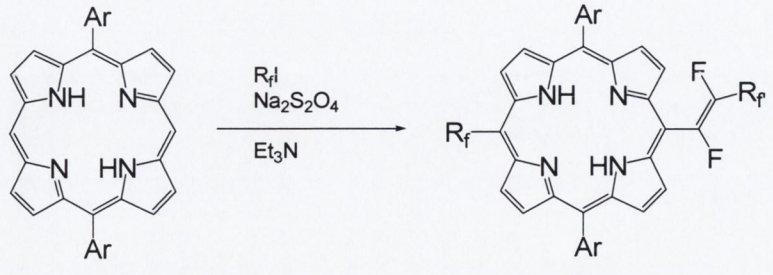
### 1.4.3 $S_EAr$ reactions

The most important electrophilic aromatic substitution ($S_EAr$) reactions in the synthesis of meso-substituted porphyrins are still nitration, halogenation, sulphonation, and Friedel-Crafts acylation or alkylation.

The electrophilic nitration, formylation or bromination of metallated 5-fluoroalkyl-10,20-diphenylporphyrin (fluoroalkyl = $CF_3$, $ClCF_2CF_2$, $n$-$C_6F_{13}$) were each investigated and found to proceed with high regioselectivity, exclusively affording the corresponding meso-substituted porphyrins. In contrast, the iodination mainly took place at the adjacent β site.[91]

In 2006, a series of nitrosubstituted 5,15-diarylporphyrins, featuring nitro groups either on the phenyl rings or on one of the two free meso-positions, was synthesised by Banfi *et al.*[92] Earlier studies on 5,15-diphenylporphyrin were reported by Arnold *et al.*[93] The meso-nitrosubstituted porphyrins were obtained by nitration of 5,15-diarylporphyrins with trifluoroacetic acid/sodium nitrite under particularly mild conditions. The nitration was carried out at a very low temperature (-78 °C) by adding a tenfold excess of $NaNO_2$ to a frozen mixture of the porphyrin in TFA. Gentle warming of the solution, followed by immediate quenching of the reaction mixture with aqueous sodium bicarbonate, allowed the recovery of the desired nitrated compounds in good yields.

Chen *et al.* have described the reaction of 5,10,15-triarylporphyrins with perfluoroalkyl iodides in the presence of $Na_2S_2O_4/NaHCO_3$ in dimethyl sulphoxide (DMSO)-$CH_2Cl_2$, which is another example of an electrophilic aromatic substitution reaction.[94] This reaction resulted in 2-polyfluoroalkyl-5,10,15-triarylporphyrin as well as 5,10,15-triaryl-20-polyfluoroalkylporphyrin. A similar approach was developed by Jin *et al.* involving the reaction of free base 5,15-diarylporphyrins such as **73** with fluoroalkyl iodides in the presence of $Na_2S_2O_4$ to give the desired product, 10,20-diaryl-5-[(*E*)-fluoroalkenyl]-15-(fluoroalkyl)porphyrins **74** (Scheme 1.14).[95]




**73** **74**

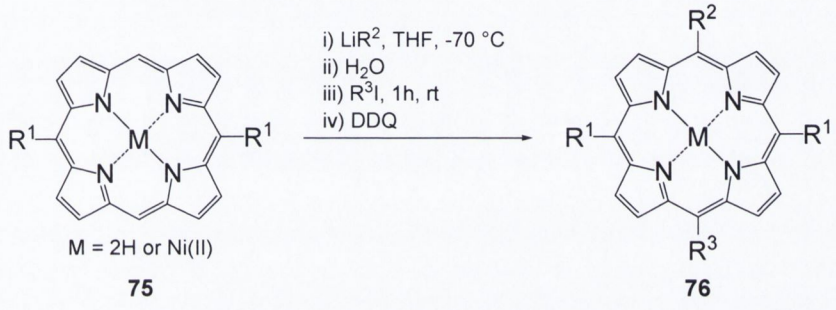
$R_f$ = fluoroalkyl

**Scheme 1.14.** Synthesis of fluoroalkylporphyrins *via* the reaction of free base 5,15-diarylporphyrins with fluoroalkyl iodides.

### 1.4.4 $S_NAr$ reactions

Nucleophilic aromatic substitution ($S_NAr$) reactions on unactivated porphyrins provide another approach that is applicable to the preparation of meso-substituted porphyrin systems.

The use of organolithium reagents for $S_NAr$ reactions is a complementary and more selective synthesis for obtaining meso-substituted porphyrins.[96-98] Treatment of 5,15-diarylporphyrins such as **75** with an organolithium reagent and an alkyl iodide results in the formation of $A_2BC$-type meso-tetrasubstituted porphyrins **76** in a one-pot synthesis, as reported by Shaker and Senge (Scheme 1.15).[99]




**Scheme 1.15.** One-pot synthesis of $A_2BC$-type meso-tetrasubstituted free base porphyrins.

The first reactions of porphyrin Grignard reagents, formed from the treatment of bromoporphyrins with Rieke magnesium were investigated by Chen and co-workers.[100] The Grignard reagents were tested using a variety of aldehydes and ketones. Aliphatic ketones resulted in the isolation of unexpected products as the reaction did not take place on the carbonyl position but on the $\alpha$-carbon. No products were detected when aromatic ketones were employed, however, aromatic aldehydes afforded the anticipated products in moderate yields. Debromination of the porphyrin was observed with aliphatic aldehydes.

## 1.5 Objectives

A lot of work and effort has been invested in the research and development of new synthetic routes towards novel porphyrin systems. A few examples are already shown in chapter 1.4.

The aim of this work was to broaden the existing synthetic methods for the design of novel meso-substituted porphyrins by introducing and transforming different functional groups. The reactions used were either new to or partially investigated in the field of porphyrin chemistry.

The incorporation of the 1,3-dithianyl group as a masking group for the formyl group *via* condensation reaction has been investigated previously in our group. The intention was to carry on this work, for instance by stabilising the porphyrin macrocycle with different substituents, which could be introduced *via* mixed condensation reactions. Furthermore, organolithium reactions were explored as an alternative route for the introduction of the dithianyl group into the porphyrin moiety. After successful deprotection the reactivity of the novel, sterically unhindered formylporphyrins was investigated. Well characterised reactions such as Wittig and Grignard offer a possibilty of direct comparison of the unhindered porphyrins to more steric hindered porphyrin arrangements. This study showed how adjacent substituents to the formyl group would influence its reactivity.

Additionally, formylporphyrins can be used as precursors for novel basket-handle porphyrins. In contrast to established basket-handle porphyrin systems, an attempt was made to link the bridge directly to the meso-position of the formylporphyrin without the need for an aromatic linker. Several approaches were trialled for the transformation of the formyl group into imine, ether or acetal linkages. Also, the bridge can be varied further creating different cavities for prospective molecule trapping or ion binding.

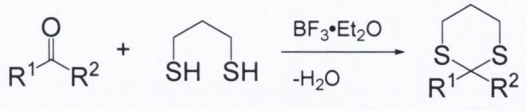
The allene substituent can be introduced as a second functional group using common methods. The Sonogashira cross-coupling reaction can be used to introduce a propargyl residue with a leaving group. The carbene rearrangement *via* the Doering-Moore-Skattebøl reaction offers another route towards allenylporphyrins. Additionally, more contemporary attempts can be employed, for example the application of the Horner-Wadsworth-Emmons reaction on porphyrin systems or the Suzuki cross-coupling reaction using the allenyl boronic acid pinacol ester as linker to bromoporphyrins.

As a third project, the synthesis of novel porphyrin arrays using triptycene as a rigid, 120° orienting, three-pronged scaffold was attempted. The triiodotriptycene molecule was prepared starting from triptycene and employed in several Suzuki cross-coupling reactions with previously synthesised borylated porphyrins.

# CHAPTER 2:
# Dithianylporphyrins

## 2.1 Basic principles

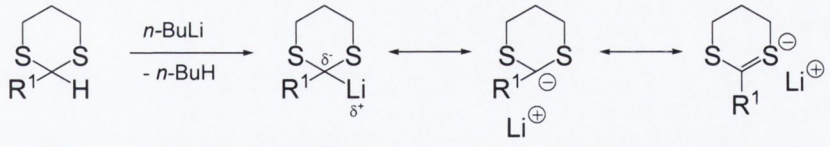
Thiols, most commonly 1,3-propanedithiol, **78**, react with carbonyl compounds (**77**) in the presence of an acid catalyst to give thioacetals (**79**), as shown in Scheme 2.1. The thermodynamic drive for this process is stronger than for formation of more commonly encountered oxygen-based acetals. Cyclic dithioacetal derivatives of 1,3-propanedithiol - termed dithianes - are easy to prepare, exhibit high stability towards hydrolysis, and are incredibly reactive towards alkylation. For these reasons, dithianes are very important in organic synthesis.[101]




**77** **78** **79**

**Scheme 2.1.** Synthesis of 1,3-dithianes.

1,3-Dithianes have a relatively acidic C-H bond ($pK_a$ = 31.3) at the carbon between the two sulphur atoms.[102] The reason for this acidity is polarisation due to the adjacent sulphur atoms, which stabilises the negative charge in the resulting carbanion. Treatment of 1,3-dithianes with organolithium reagents such as *n*-butyllithium allows the exchange of the proton with a lithium atom (Scheme 2.2) and the result is a 2-lithio-1,3-dithiane **81**.[103] The carbon-lithium bond of this species is covalent in nature but it is highly polarised because of the very electropositive metal centre. The chemical behaviour of **81** is thus similar to that of compounds containing formal negatively charged carbon atoms, i. e. carbanions.




**80** **81**

**Scheme 2.2.** Reaction of 1,3-dithiane with *n*-BuLi.

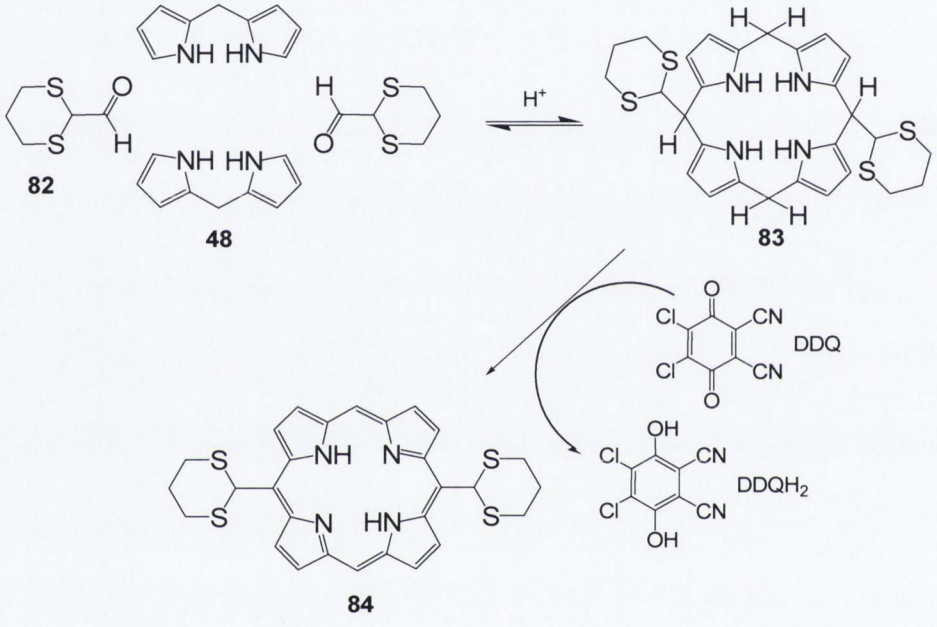
Another outcome of this resonance stabilisation is that the normally electrophilic carbonyl carbon atom has been converted to a good nucleophile. Typically, the oxygen atom of a carbonyl unit is more electronegative than the carbon atom, thus the carbonyl carbon reacts as an electrophile. However, the dithiane group 'masks' the carbonyl group and reverses the polarity. This type of reactivity has been exploited in the umpolung reactions introduced by Seebach and Corey.[103-106]

There are several methods for the hydrolysis of the dithianyl group. Examples include photolytic cleavage,[107] metal coordination,[108,109] alkylation,[110-112] and the use of chemical oxidants[113-115] or ammonium salts.[116]

## 2.2 Synthesis of dithianylporphyrins

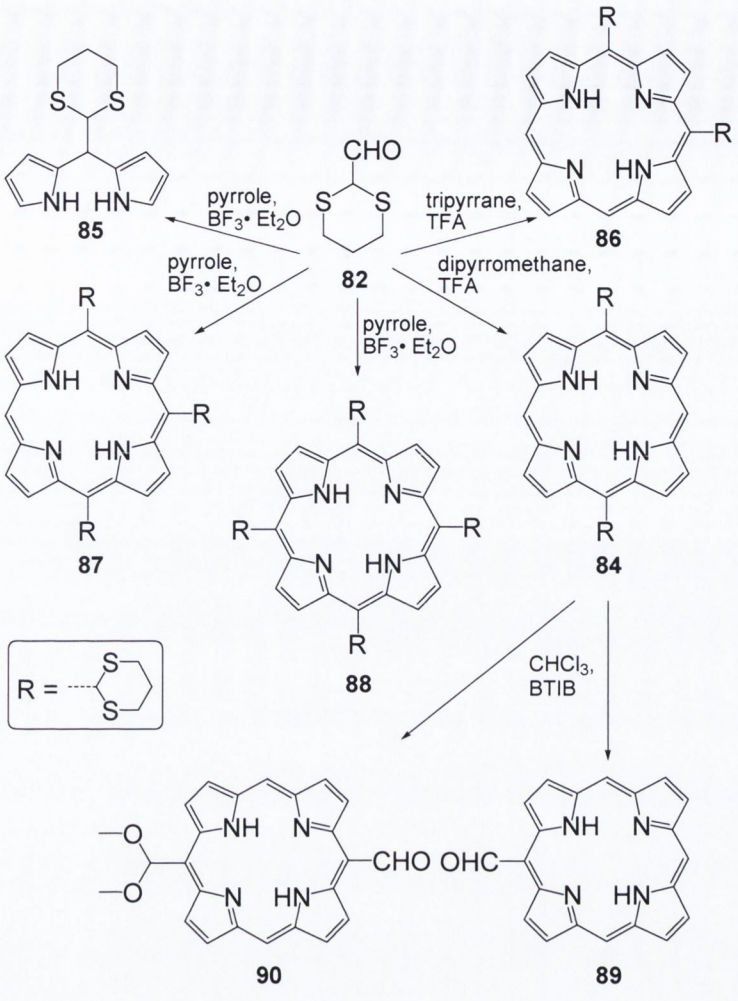
### 2.2.1 Condensation reactions

As mentioned in section 1.4.1, one of the simplest and oldest methods for the preparation of meso-substituted porphyrins is the classical condensation reaction using a dipyrromethane and an aldehyde. The key synthon for the preparation of dithianylporphyrins *via* condensation reactions is 2-formyl-1,3-dithiane **82** (Scheme 2.3).[117,118]




**Scheme 2.3.** [2+2] Condensation reaction of dipyrromethane **48** with 2-formyl-1,3-dithiane **82**.

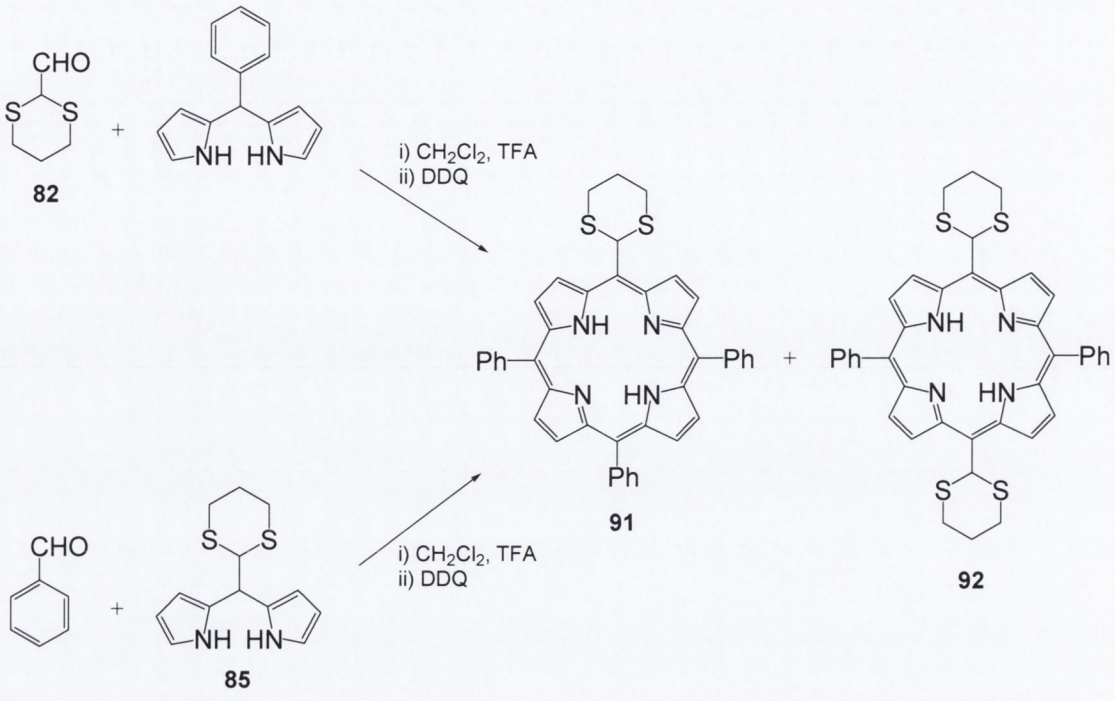
The [2+2] condensation reaction of 2-formyl-1,3-dithiane **82** with dipyrromethane **48** resulted in the porphyrinogen **83** which was oxidised by DDQ to the corresponding porphyrin **84**. The reaction of **82** with pyrrole produced the 1,3-dithianyldipyrromethane **85** in almost quantitative yield (96 %). Depending on the reaction conditions, and stoichiometry employed, the porphyrins **84** and **86** to **88**, having two to four meso dithianyl residues, were prepared in low to moderate yields (Scheme 2.4).[119] The oxidative dethioacetalisation is rather difficult due to the low stability and solubility of dithianylporphyrins with more than two dithianyl residues or with dithianyl residues in a 5,10 regiochemical arrangement. The instability is a result of the increased steric tension in such systems together with the high reactivity of the dithianyl residues.[120]




**Scheme 2.4.** Condensation reactions involving 2-formy-1,3-dithiane **82**.

Although many different reagents for the dethioacetalisation were tested, only porphyrins having one or two dithianyl residues could be converted into the corresponding formylporphyrins. Using bis(trifluoroacetoxy)iodobenzene (BTIB), porphyrin **84** was converted into either the monoformylporphyrin **89** or the acetal **90**, while porphyrins such as **87** or **88** always resulted in the formation of complex mixtures with partially deprotected groups and loss of individual meso-substituents.[119,121,122]

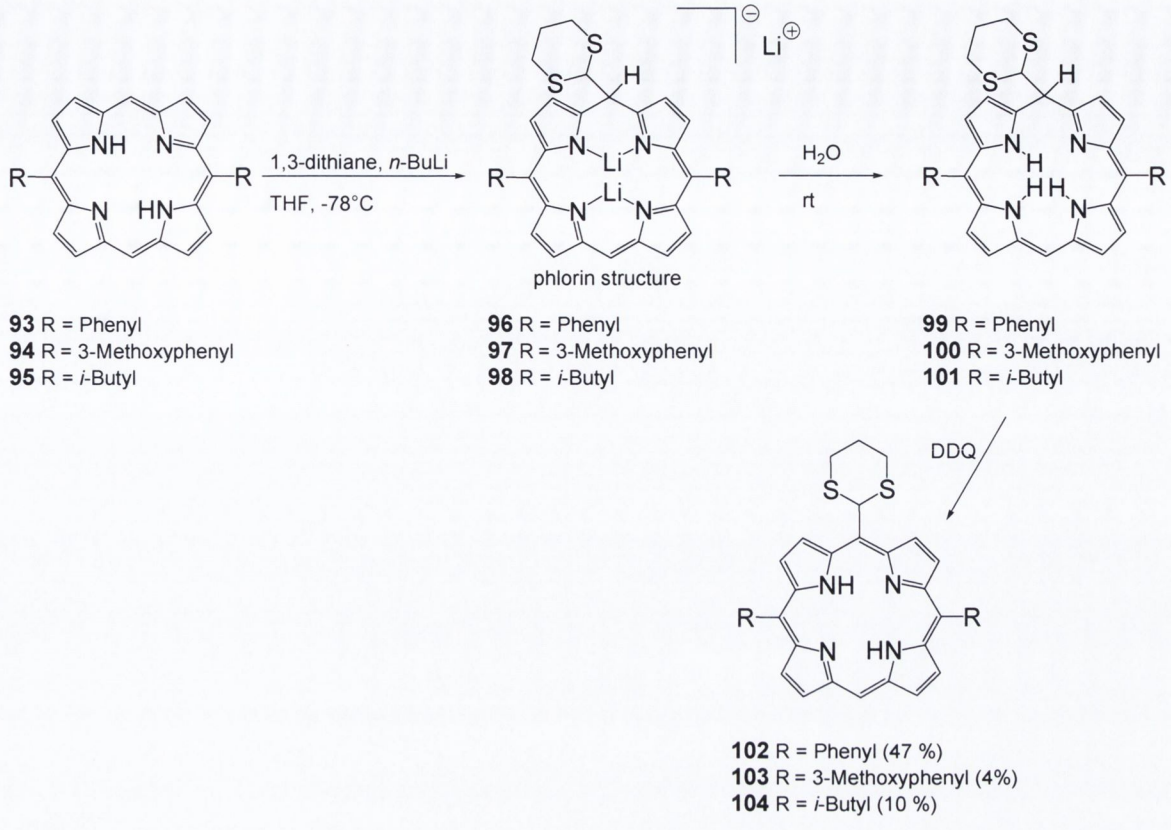
In order to increase the solubility of the dithianylporphyrins, mixed condensation reactions were attempted in which either 2-formyl-1,3-dithiane **82** and 5-phenyldipyrromethane or 1,3-dithianyldipyrromethane **85** and benzaldehyde were used as starting materials (Scheme 2.5).[123,124] Depending on the reaction conditions employed, the porphyrins **91** and **92** were isolated in yields of 2-4 % or 2-3 %, respectively. The appearance of compound **91** is due to scrambling during the condensation process.[125-127]




**Scheme 2.5.** Mixed condensation for the preparation of meso-substituted dithianylporphyrins.

### 2.2.2 Organolithium reactions

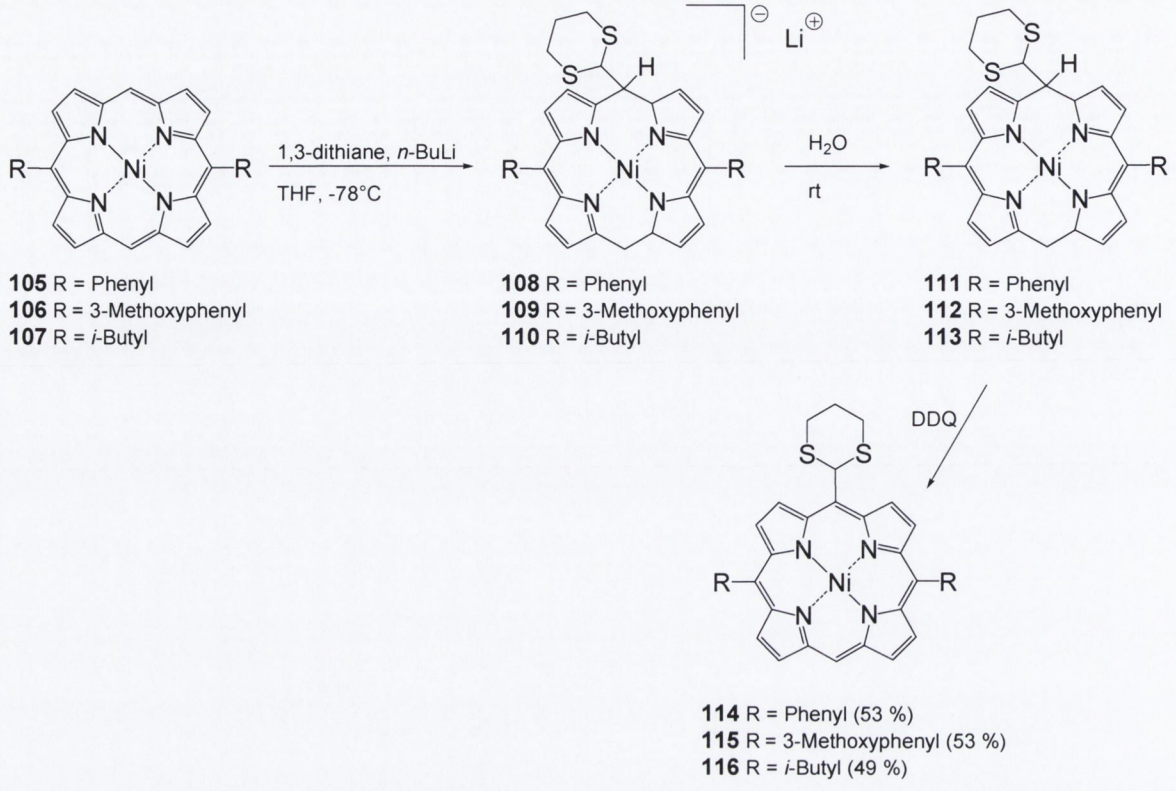
An alternative method for the introduction of the dithianyl residue to the porphyrin architecture is *via* the formation of a C-C bond by using organolithium reagents.[96,97,128-130] This technique can be applied to a number of different porphyrins carrying various substituents due to the relatively mild reaction conditions required. It can be utilised for both free base and metalloporphyrins and typically gives good to excellent yields. A special example involves the treatment of 1,3-dithiane with *n*-butyllithium in THF at -30 °C to generate 2-lithio-1,3-dithiane **81** *in situ*, which can subsequently be reacted with the appropriate porphyrins.[103] Effectively, this approach provides an entry to formylporphyrins under nucleophilic conditions.[42,121,122]




**Scheme 2.6.** Reaction of free base porphyrins with 2-lithio-1,3-dithiane.

Investigation of this reaction was carried out with the 5,15-disubstituted porphyrins **93-95** and **105-107** at -78 °C in THF under argon atmosphere. The mechanism for the reaction with free base porphyrins is slightly different from that involved in the metalloporphyrin derivatives.[97,98,129] For the former case, the first step comprised the addition of the 1,3-dithianyl residue to the basic porphyrin macrocycle and the coordination of two lithium atoms to the inner nitrogen atoms. The result is a phlorin-type structure, **96-98**, which after quenching with water, affords the intermediates **99-101** (Scheme 2.6). Subsequent oxidation with DDQ results in the desired porphyrins **102-104** in 4-47 % yield.

Similarly, the first step of the reaction of 2-lithio-1,3-dithiane **81** with the metalloporphyrins **105-107** is a dithianyl addition reaction to form the Meisenheimer-type complexes **108-110** (Scheme 2.7). Hydrolysis with water yields the porphodimethenes **111-113**, which are easily oxidised with DDQ to give the desired porphyrins **114-116** in 49-53 % yield. Nickel(II) porphyrins generally gave higher yields than the free base porphyrins, and due to the steric hindrance of the bulky dithianyl residue, the yields are comparable to those of *iso*-propyllithium or *sec*-butyllithium reactions.[131]




**105** R = Phenyl
**106** R = 3-Methoxyphenyl
**107** R = *i*-Butyl

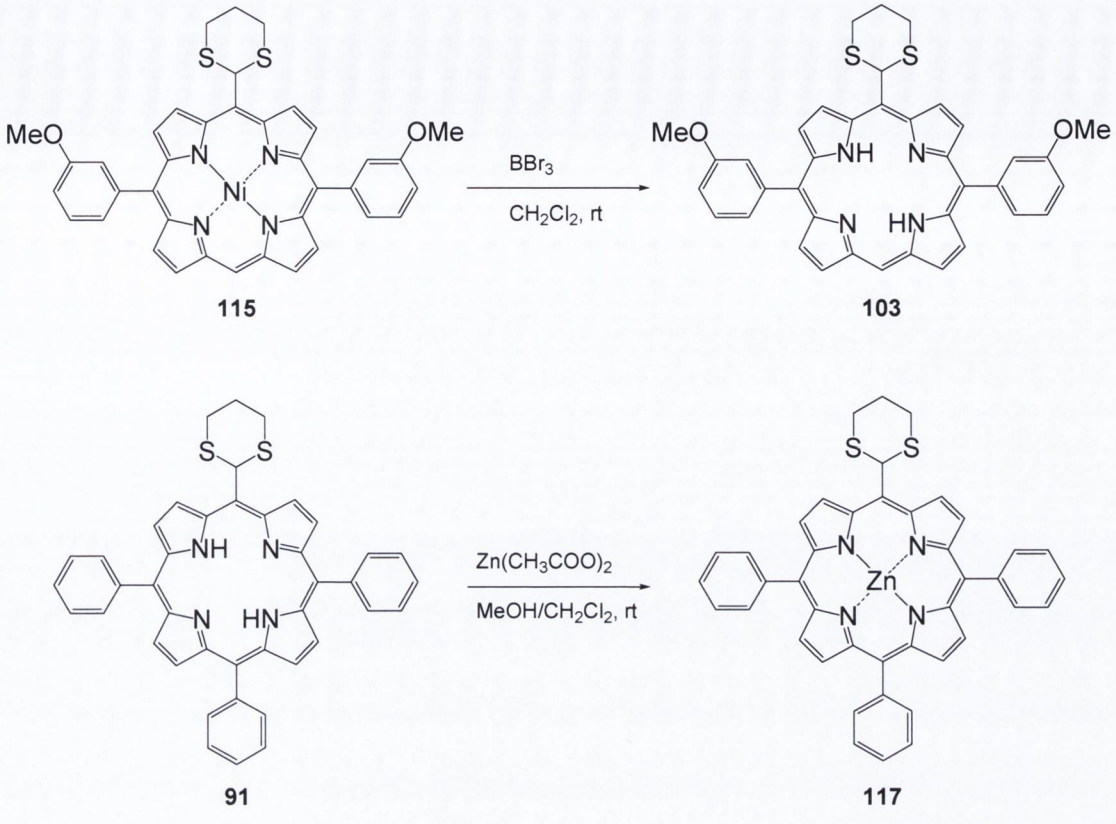
**108** R = Phenyl
**109** R = 3-Methoxyphenyl
**110** R = *i*-Butyl

**111** R = Phenyl
**112** R = 3-Methoxyphenyl
**113** R = *i*-Butyl

**114** R = Phenyl (53 %)
**115** R = 3-Methoxyphenyl (53 %)
**116** R = *i*-Butyl (49 %)

**Scheme 2.7.** Reaction of metalloporphyrins with 2-lithio-1,3-dithiane.

Dithianylporphyrins such as **91** and **115** are stable enough to withstand metallation and demetallation sequences, respectively (Scheme 2.8). The nickel(II) porphyrin **115** was successfully demetallated with $BBr_3$, albeit in only 24 % yield.[132] The free base porphyrin **91** was converted to the zinc(II) porphyrin **117** in 53 % yield under standard metallation conditions with zinc acetate and methanol in dichloromethane.[6]



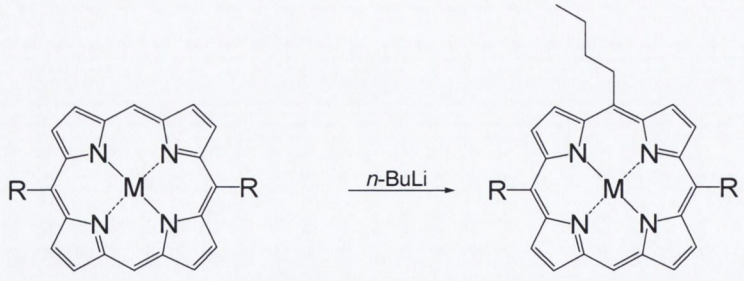

**115** **103**

**91** **117**

**Scheme 2.8.** Metallation and demetallation of dithianylporphyrins.

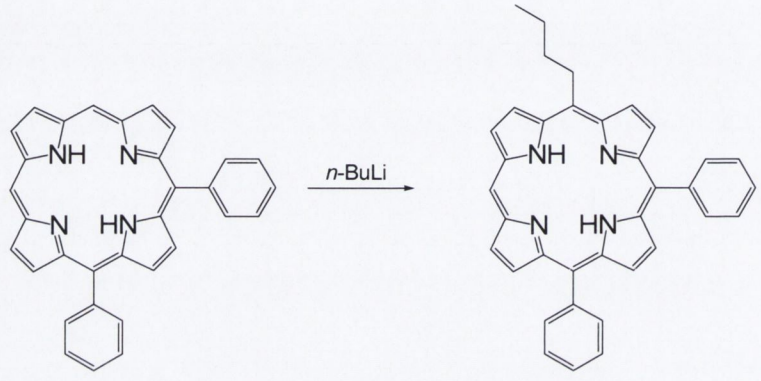
### 2.2.3 Side products

Typically, the reaction of 1,3-dithiane with *n*-butyllithium at -30 °C in THF under inert atmosphere forms 2-lithio-1,3-dithiane, which can be used for subsequent, low temperature reactions with a variety of porphyrins. Occasionally, however, the 2-lithio-1,3-dithiane is not formed and the *n*-butyllithium instead reacts directly with the porphyrin moiety, resulting in the formation of the novel, but undesired, *n*-butylporphyrins **118**-**120** and **122** (Scheme 2.9).




**94** M = 2H, R = 3-Methoxyphenyl
**95** M = 2H, R = *i*-Butyl
**107** M = Ni(II), R = *i*-Butyl

**118** M = 2H, R = 3-Methoxyphenyl (24 %)
**119** M = 2H, R = *i*-Butyl (15 %)
**120** M = Ni(II), R = *i*-Butyl (28 %)




**121** **122** (26 %)

**Scheme 2.9.** Side products formed during treatment with organolithium reagents.

An X-ray structural analysis of compound **120** was performed and the results are illustrated in Figures 2.1 and 2.2.

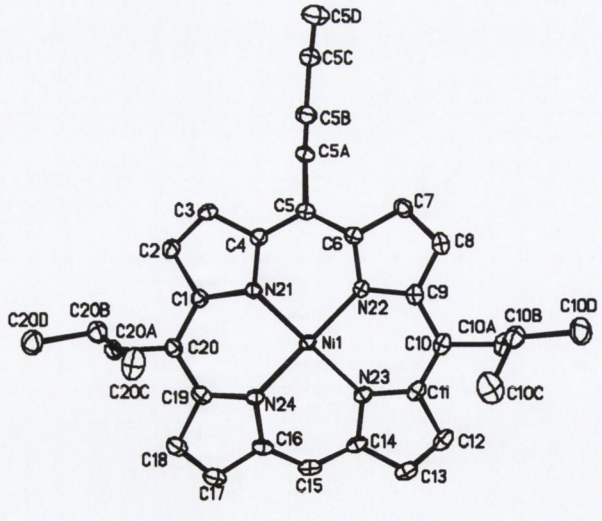



**Figure 2.1.** View of the molecular structure of one of the two independent molecules of **120** in the crystal. Hydrogen atoms have been omitted for clarity, ellipsoids are drawn for 50 % occupancy.

The compound crystallised with two crystallographically independent molecules in the unit cell. A top view of the molecular structure is shown in Figure 2.1. All three alkyl side chains point towards the same face of the porphyrin molecule. The molecules form a close-spaced lattice structure in which neighbouring porphyrins are oriented in a

perpendicular fashion with respect to each other, as depicted in Figure 2.2. The edge of one molecule points with a β-hydrogen atom towards the nickel(II) centre of the next molecule and the hydrogen nickel separations are small with H22A···Ni(1) 2.593 Å, H12A···Ni(2) 2.667 Å, H32A···Ni(1) 2.757 Å, and H2A···Ni(2) 2.635 Å, respectively. Thus, the two faces of each macrocycle core are blocked by a neighbouring macrocycle in edge-on fashion.

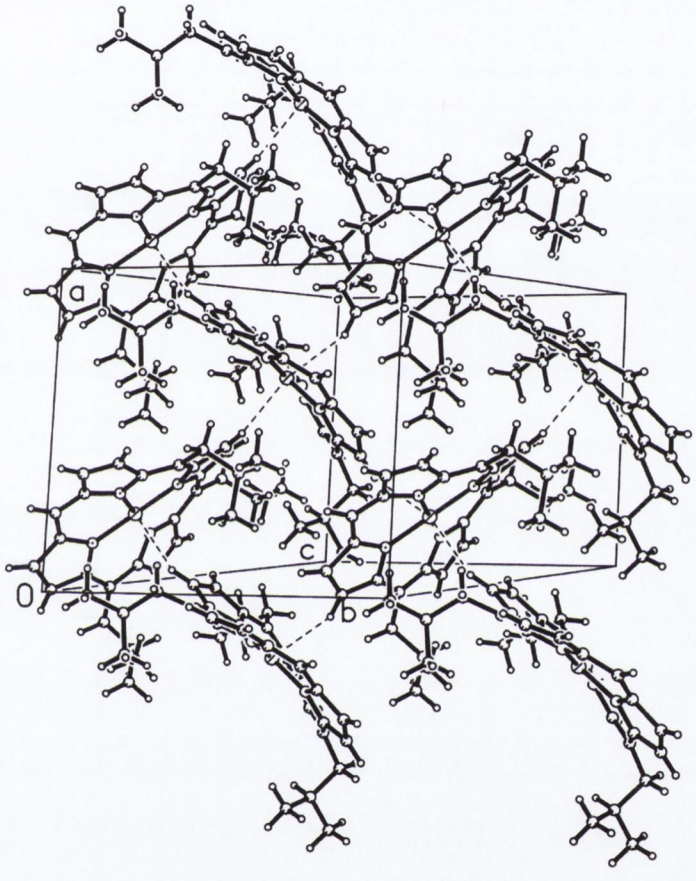



**Figure 2.2.** View of the molecular arrangement of **120** in the crystal. Dashed lines indicate short Ni···H separations.

The compound is characterised by an overall ruffled conformation as indicated by mean displacements of the $C_m$ atoms ($C_m$ = meso carbon) by about 0.6 Å (Figure 2.3), which is in line with expectations for a sterically unhindered nickel(II) meso-alkylporphyrin. The degree of displacement of the $C_m$ atoms is similar to that found for symmetric (5,10,15,20-tetraalkylporphyrinato)-nickel(II) systems.[120]. Both molecules exhibit the same conformation with only minor differences evident in the structural parameters and bond lengths and angles of each. Only negligible differences are found in displacements for substituted versus unsubstituted meso-carbon atoms. One of the molecules exhibits a small degree of *sad* distortion and both show a contribution from *bre* in-plane distortion.

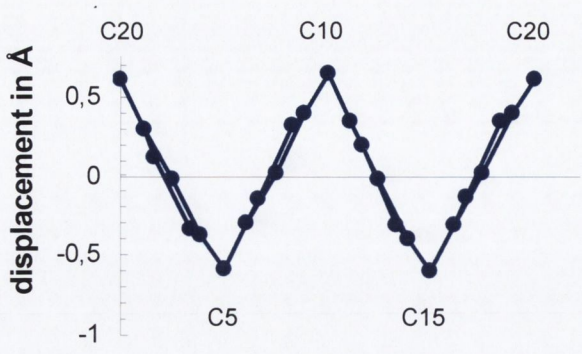



**Figure 2.3.** View of the skeletal deviations in molecule 1 of **120**. The sequence of meso-carbon atoms is C20, C5, C10, C15, C20 from left to right.

## 2.3 Spectroscopic studies

### 2.3.1 $^1$H Nuclear Magnetic Resonance (NMR) spectroscopy

NMR studies clearly confirm the aromatic character of porphyrins. The diamagnetic ring current deshields the β-protons as well as the meso-protons. The meso-protons are shifted further towards lower field than the β-protons because they are attached to more electron-deficient carbons. On the other hand, the inner protons attached to the nitrogen atoms are shifted to higher field, beyond the tetramethylsilane signal. This is again due to the ring current, which deshields protons outside the macrocycle from the external magnetic field, but shields them if they are inside the macrocycle.[133,134]

The $^1$H NMR spectra of all the dithianylporphyrins exhibit very broad signals for the β-protons flanking the dithianyl residues.[135] Variable temperature (VT) $^1$H NMR studies for porphyrin **102** showed that above the coalescence temperature of 334 K, the $^1$H NMR resonances of the β-protons adjacent to the dithianyl residue are fused (Figure 2.4). Below this temperature they resolve into two broad resonances. Further cooling of the sample causes decoalescence of each of these resonances into two sets.

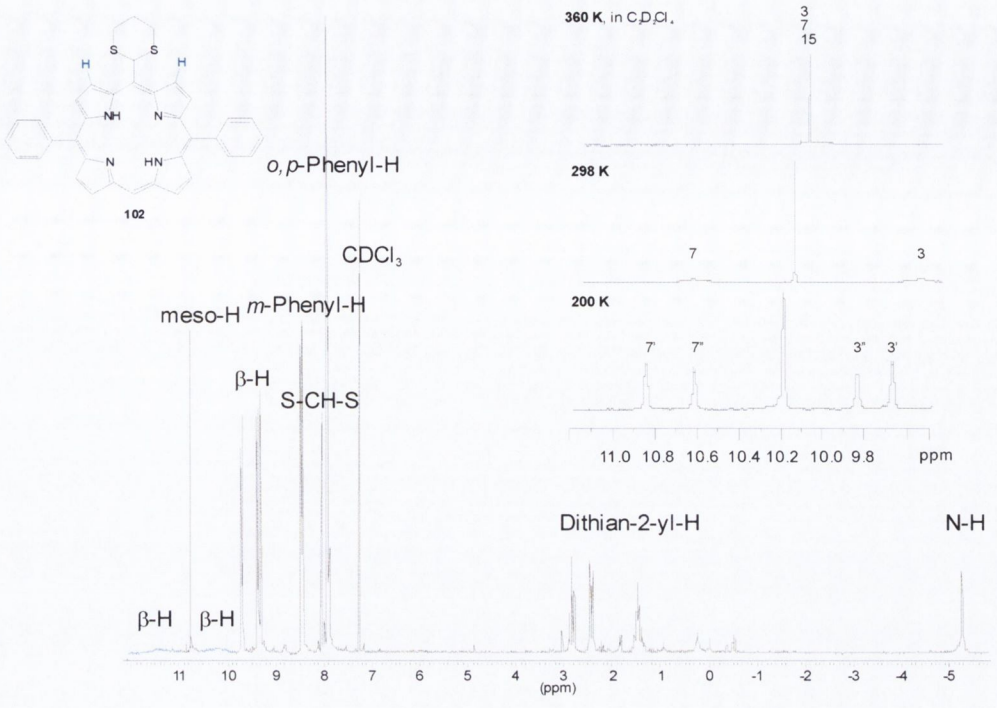



**Figure 2.4.** $^1$H NMR spectrum of **102** with 128 scans, 300 MHz in $CDCl_3$, at rt and VT study of the β-protons (200, 298 and 360 K).

In contrast, the signals for the β-protons of the nickel(II) complex **114** split only once in the temperature range studied (Figure 2.5). For all the dithianylporphyrins, the resonances for the β-protons become sharper with decreasing temperature, indicating that intramolecular hydrogen bonds between the β-protons and the sulphur atoms prevent the free rotation of the dithianyl residues.

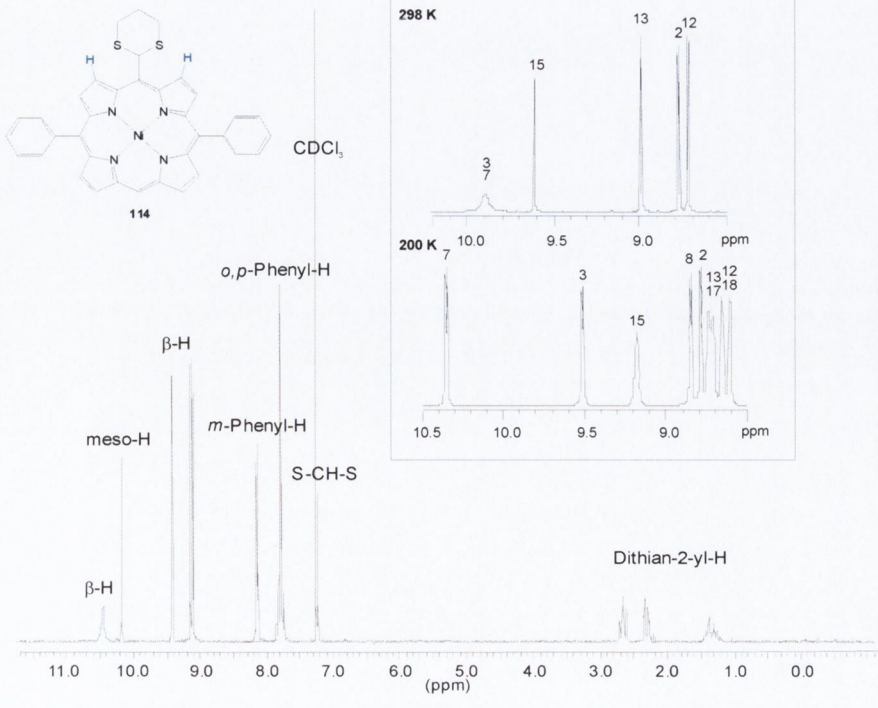



**Figure 2.5.** $^1$H NMR spectrum of **114** with 128 scans, 300 MHz in $CDCl_3$, at rt and VT study of the β-protons (200 and 298 K).

### 2.3.2 Ultraviolet-visible (UV-vis) spectroscopy

Porphyrins are compounds of remarkable colours. Hence, they are characterised by intense absorption bands in the near-ultraviolet and visible region.

Metalloporphyrins show two electronic transitions in the visible region. The more intense band is called the B band or Soret band after its discoverer and represents the permitted $\pi,\pi^*$-transitions.[136] It has a very large extinction coefficient and is characteristic for the macrocyclic conjugation. At longer wavelengths, Q bands, with significantly lower intensitiy than the Soret band, can be detected. The Q bands represent the quasi-permitted $\pi,\pi^*$ transitions and show additional vibrational fine structure. Free base porphyrins possess a lower symmetry in comparison to metallated porphyrins, resulting in the appearance of four rather than two Q bands.[137]

The UV-vis spectra of compounds **92**, **93** and **102** are shown in Figure 2.6. It can be seen that with the introduction of one dithianyl group, the Soret band is red-shifted by approximately 10 nm (406 nm for compound **93** *vs.* 419 nm for compound **102**). The incorporation of a second dithianyl substituent shifts the Soret band even further.

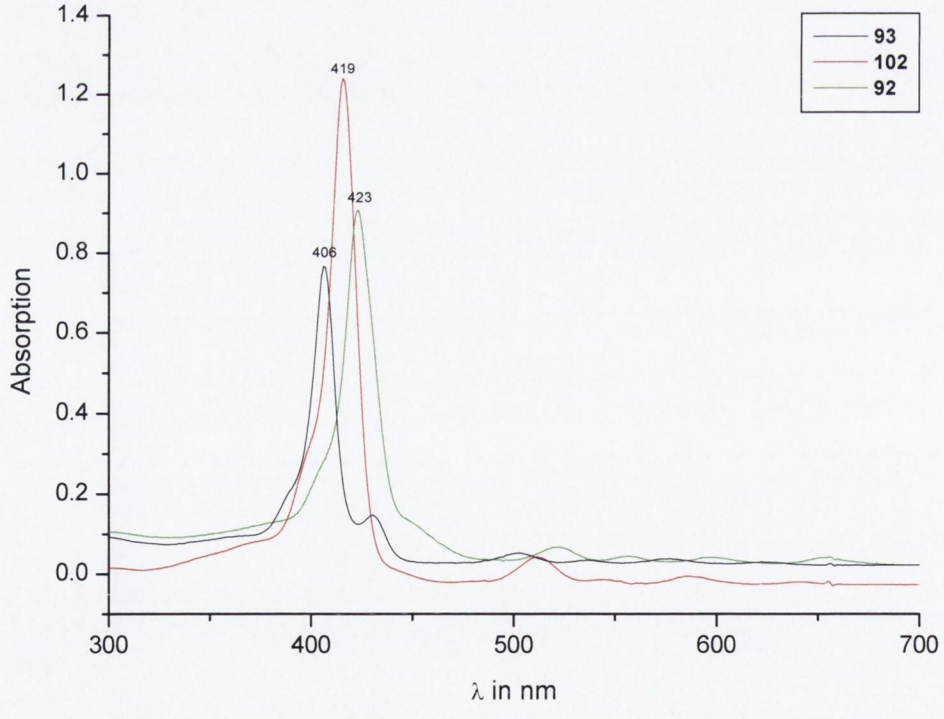
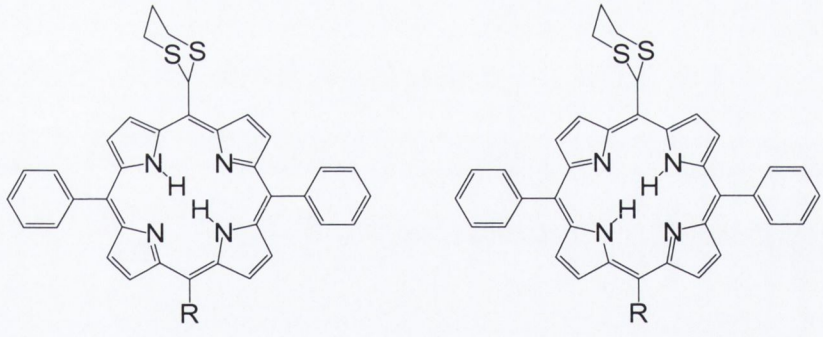



**Figure 2.6.** UV-vis spectra of free base diphenylporphyrin **93** and dithianylporphyrins **92** and **102** in $CH_2Cl_2$ at rt. Baselines have been adjusted arbitrarily.

## 2.4. Theoretical studies

Through our collaboration with Philipp Wacker and Prof. Kleinpeter, Universität Potsdam, Germany, the conformational landscape of 1,3-dithianylporphyrins was investigated. The rotational behaviour of the dithianyl substituents in the meso-position and experimental results for the energy barriers were gained by $^1$H NMR investigations at various temperatures. Quantum chemical calculations were performed on Origin2000 and 1.7 MHz Linux based personal computer using the GAUSSIAN 03 software package. For geometry optimisation of the ground state structures and for NMR chemical shift calculations the theory level B3LYP and basis set 6-31G** were used. Chemical shift calculations were performed using the gauge-including atomic orbital (GIAO) approach. For energetic evaluations the transition state geometries and ground state structures were calculated at the same theory level using the 6-31G basis set. The geometry optimisations of ground and transition states were performed without any symmetry restrictions and were followed by frequency calculations to verify the character of the stationary point obtained. The study revealed the existence of different NH-*trans*-tautomers with regard to the orientation of the dithianyl substituents for the free base porphyrins **91**, **92** and **102** (Figure 2.7). This is a result of the restricted rotation of the dithianyl group.




**91** R = 1,3-Dithianyl
**92** R = Phenyl
**102** R = H

A B

**Figure 2.7.** Two trans tautomers for **91**, **92** and **102**.

The calculation of the global minima structures for the free base porphyrins **91**, **92** and **102** revealed that the B tautomer is higher in energy.

Relatively ruffled porphyrin core conformations were established for the transition states of the dithianyl rotation, resulting in a lower rotational energy barrier for the nickel(II) complex **114** compared to the free base systems (Figure 2.8).

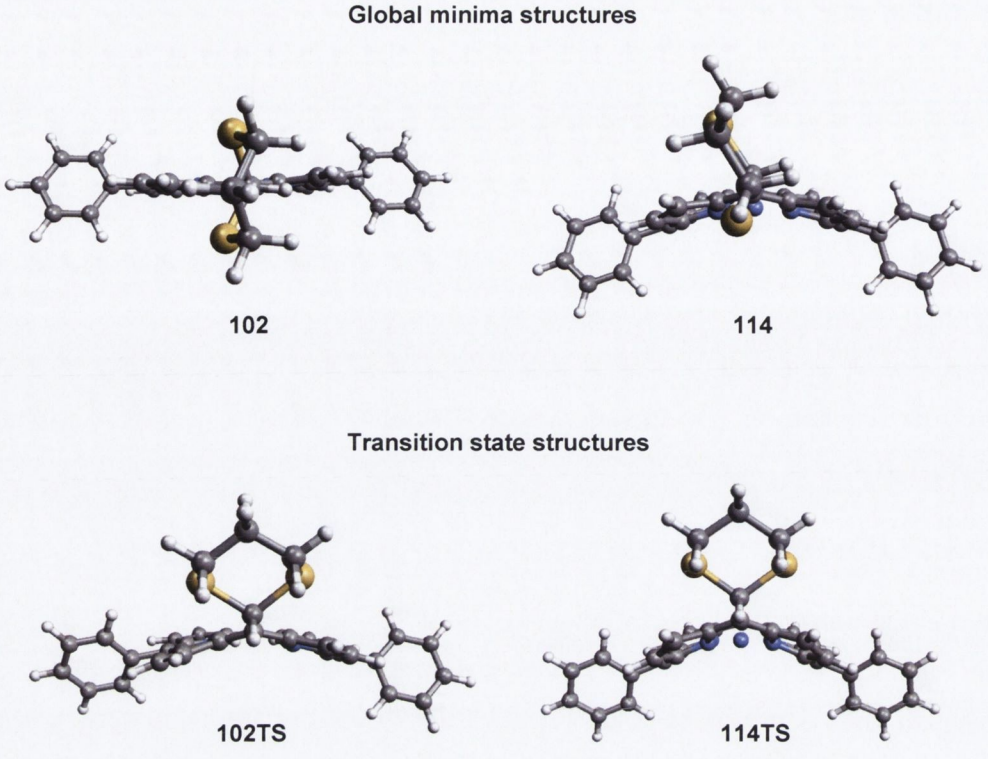



**Figure 2.8.** Ground and transition states for **102** and **114**.

Computational data revealed the similarity of the conformation of the porphyrin macrocycle in both the transition state and global minimum structure of the nickel(II) complex **114**, and also gave a structural basis for the lower rotational barrier in metalloporphyrins compared to the free base systems. This supports the crucial interplay between core conformation, metal effects, and substituent type, orientation and conformation on the landscape of tetrapyrrole.[135]

Further investigations involved theoretical studies of the mechanism of the NH-tautomerism in a series of meso-dithianylporphyrins having different substitution pattern (Figure 2.6). Quantum chemical calculations were again performed on Origin2000 and 1.7 GHz Linux based personal computer using the GAUSSIAN 03 software package. For geometry optimisation of all structures, B3LYP and basis set 6-31G were used. The geometry optimisations of ground and transition states were performed without any symmetry restrictions and were followed by frequency calculations to verify the character of the stationary point obtained. Generally, two mechanisms are possible for the inner proton-exchange. In the synchronous mechanism, both inner protons jump simultaneously *via* a second-order saddle-point (SS), whereas in the asynchronous pathway the *trans-trans* conversion takes place step by step as shown for porphin in Figure 2.9.

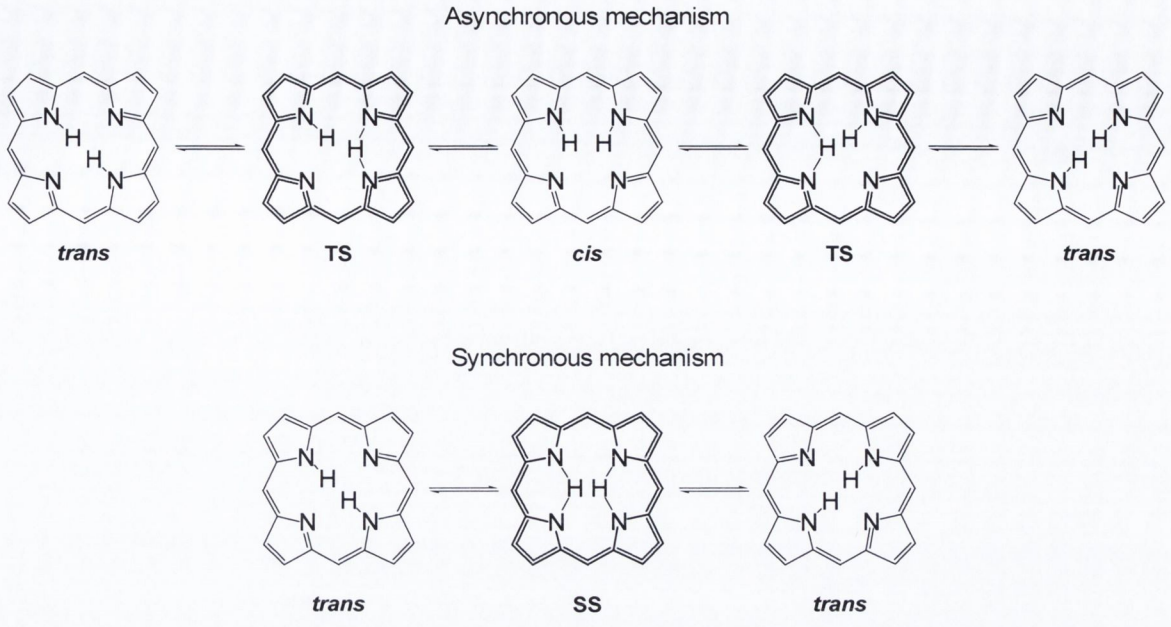



**Figure 2.9.** Asynchronous and synchronous mechanism of the inner proton-hopping tautomerism process of porphin.

Dependent on the substitution for the synchronous pathway, two saddle points of significantly different energy were calculated. Furthermore, four distinctive asynchronous NH-tautomerism pathways were explored.

The macrocyclic conformations of the geometries obtained were analysed with normal structure decomposition (NSD) analyses and the calculated energy barriers of the preferred pathways agreed well with experimental activation enthalpies, as determined by VT-NMR spectroscopy.[11,138] In conclusion, the investigation of the NH-tautomerism showed that there is a strong interplay between the in-plane *m-str* and the out-of-plane *ruf* distortion.[139]

## 2.5 Conclusions

Two new routes were developed for the incorporation of the dithianyl group into the porphyrin moiety. In the first approach dithianylporphyrins could be synthesised by condensation reactions, with the mixed condensation versions giving rise to more stable derivatives affording porphyrins **91** and **92** in modest yields.

The formation of new C-C bonds *via* alkylation with organolithium compounds was chosen as a second route for the preparation of dithianylporphyrins. The free base porphyrins **102-104** and the nickel(II) porphyrins **114-116** were synthesised in low to moderate yields using 2-lithio-1,3-dithiane as organolithium reagent. The products thus obtained were stable, but a competitive butylation reaction also occurred and the compounds **118-120** and **122** were isolated as side products.

The robustness of compounds **91** and **115** towards metallation and demetallation reactions were exemplary. The demetallated product **103** was obtained from **115** in the

relatively low yield of 24 %, whilst the metallated porphyrin **117** was obtained from compound **91** in a moderate yield of 53 %.

The conformational landscape of the dithianylporphyrins was explored and the rotational behaviour of the dithianyl group was investigated by VT-NMR spectroscopy and molecular modelling. Furthermore, the NH-tautomerism was examined theoretically.

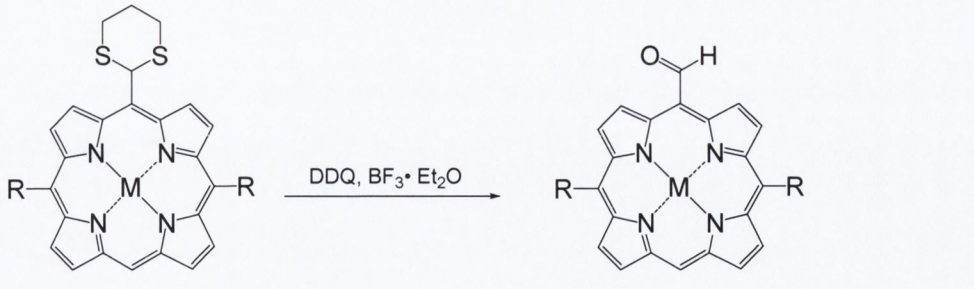
# CHAPTER 3: Formylporphyrins and their reactivity

## 3.1 Synthesis of formylporphyrins

The formyl group is a functional group that allows asymmetric modification of meso-substituted porphyrins and has been widely used in the field of porphyrin chemistry.[140-146] Nevertheless, surprisingly few reactions have been reported using meso-substituted formylporphyrins as precursors for the further functionalisation of porphyrin frameworks. The examples studied to date possess either meso- or β-substituents that are adjacent to the formyl group, which can cause *peri* interactions that result in a deformation of the macrocycle[147-153] or facilitate complex rearrangement reactions.[154,155] Herein is described an investigation into the synthesis of β-unsubstituted meso-formylporphyrins and their reactions with Grignard and Wittig reagents in an attempt to further develop the use of these crucial intermediates in porphyrin chemistry.

### 3.1.1 Deprotection of dithianylporphyrins

A novel method for the synthesis of formylporphyrins is the deprotection of dithianylporphyrins. It was found that the treatment of dithianylporphyrins with DDQ and $BF_3$•$Et_2O$ in dichloromethane led to facile dethioacetalisation affording the corresponding formylporphyrins **123-125** in yields ranging from 39-94 % (Scheme 3.1).[156]




**102** R = Phenyl, M = 2H
**114** R = Phenyl, M = Ni(II)
**115** R = 3-Methoxyphenyl, M = Ni(II)

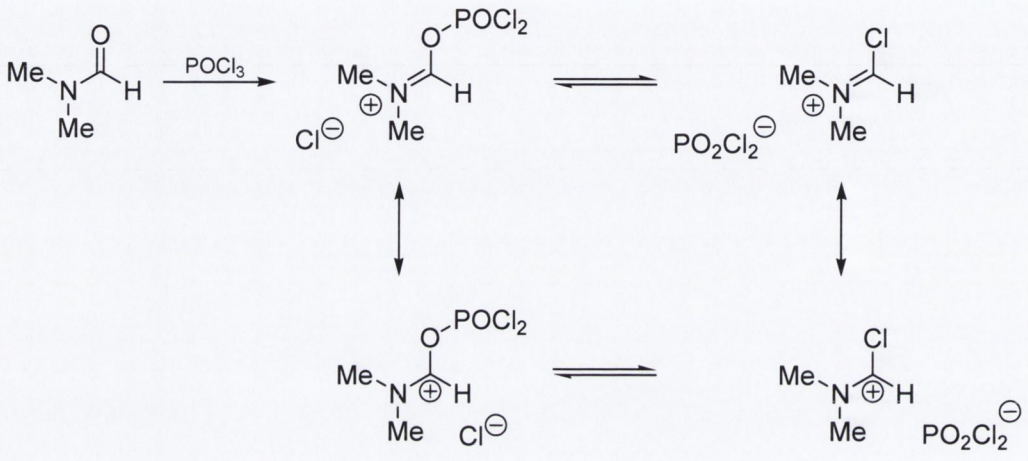
**123** R = Phenyl, M = 2H (44 %)
**124** R = Phenyl, M = Ni(II) (39 %)
**125** R = 3-Methoxyphenyl, M = Ni(II) (94 %)

**Scheme 3.1.** Deprotection of dithianylporphyrins.

The dithianyl group allows the preparation of free base formylporphyrins without prior activation through conversion to the copper(II) or nickel(II) complex, which is required for classic porphyrin formylation reactions.

### 3.1.2 Vilsmeier reactions

The most common method of porphyrin formylation is almost certainly the Vilsmeier reaction,[6,141,157-161] the basis of which is the formation of the zwitterionic Vilsmeier complex **126**, as shown in Scheme 3.2.

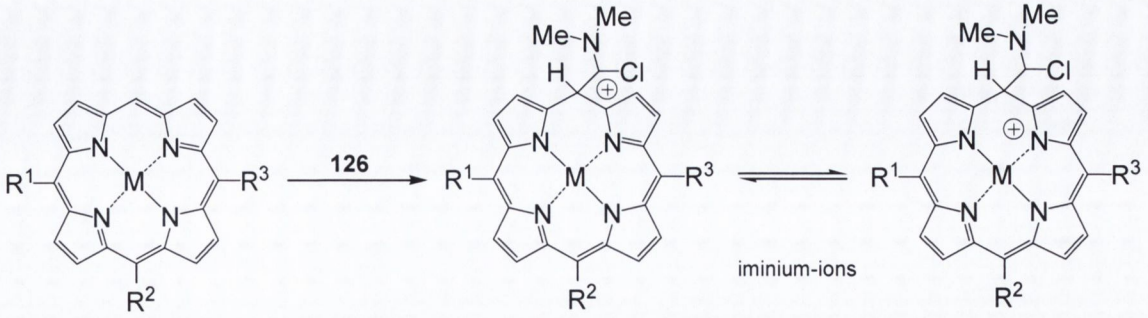



Vilsmeier complex **126**

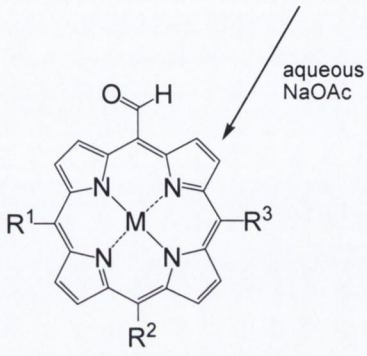
**Scheme 3.2.** Formation of the Vilsmeier complex.

The complex is obtained by reaction of phosphorus oxychloride ($POCl_3$) with DMF at 0 °C and represents the reactive electrophile. This iminium ion is weaker in its reactivity than for example, an oxonium ion, which is used in Friedel-Crafts acylations. Hence, Vilsmeier formylation only takes place with activitated, electron rich aromatic compounds. Indeed, this is why formylation only occurs with copper(II) or nickel(II) porphyrins. Furthermore, porphyrins possess two reactive sites for electrophilic substitution, the meso- and the β-position and the electronegativity of the porphyrin determines which site will react. Therefore, another reason for the use of metallated porphyrins for formylation is that metals coordinated to the inner nitrogens increase the electronegativity of the porphyrin moiety, which results exclusively in reaction at the meso-position.[162]

Only two formyl groups can be attached to the porphyrin framework as the formyl group is electron-withdrawing. Thus, every formyl substituent introduced further deactivates the porphyrin.




**105** M = Ni(II), $R^1$ = $R^3$ = Phenyl, $R^2$ = H
**106** M = Ni(II), $R^1$ = $R^3$ = 3-Methoxyphenyl, $R^2$ = H
**127** M = Cu(II), $R^1$ = $R^3$ = 3-Methoxyphenyl, $R^2$ = H
**128** M = Ni(II), $R^1$ = $R^3$ = Hexyl, $R^2$ = H
**129** M = Cu(II), $R^1$ = $R^3$ = Hexyl, $R^2$ = H
**130** M = Cu(II), $R^1$ = $R^3$ = *i*-Butyl, $R^2$ = H
**131** M = Ni(II), $R^1$ = $R^3$ = 1-Ethylpropyl, $R^2$ = H
**132** M = Cu(II), $R^1$ = $R^3$ = 1-Ethylpropyl, $R^2$ = H
**133** M = Cu(II), $R^1$ = $R^2$ = Phenyl, $R^3$ = H




**124, 134, 137, 138, 141** M = Ni(II)
**135, 136, 139, 140, 142, 143** M = Cu(II)

**Scheme 3.3.** Vilsmeier reactions.

The reaction mechanism for the formylation of the copper(II) and nickel(II) porphyrins **105**, **106**, and **127-133** is shown in Scheme 3.3. Metallation was achieved by standard conditions with nickel(II) acetate in DMF, nickel(II) acetylacetonate in toluene under reflux, or copper(II) acetate in dichloromethane at room temperature.[6]

**Table 3.1.** Yields of formylporphyrins obtained by Vilsmeier reaction.

| Product | M | $R^1$ | $R^2$ | $R^3$ | Yield [%] | Starting material |
|---|---|---|---|---|---|---|
| **124** | Ni(II) | Phenyl | H | $R^1$ | 59 | **105** |
| **134** | Ni(II) | 3-Methoxyphenyl | CHO | $R^1$ | 48 | **106** |
| **135** | Cu(II) | 3-Methoxyphenyl | H | $R^1$ | 13 | **127** |
| **136** | Cu(II) | 3-Methoxyphenyl | CHO | $R^1$ | 20 | **127** |
| **137** | Ni(II) | Hexyl | H | $R^1$ | 60 | **128** |
| **138** | Ni(II) | Hexyl | CHO | $R^1$ | 42 | **128** |
| **139** | Cu(II) | Hexyl | CHO | $R^1$ | 18 | **129** |
| **140** | Cu(II) | *i*-Butyl | H | $R^1$ | 47 | **130** |
| **141** | Ni(II) | 1-Ethylpropyl | CHO | $R^1$ | 7 | **131** |
| **142** | Cu(II) | 1-Ethylpropyl | CHO | $R^1$ | 97 | **132** |
| **143** | Cu(II) | Phenyl | $R^1$ | CHO | 77 | **133** |

The method used for the Vilsmeier formylation was adapted from the procedure reported for similar porphyrins by Johnson *et al.*[53] The Vilsmeier complex was formed *in situ* and subsequent reaction with the porphyrin in 1,2-dichloroethane at 80 °C resulted in the stable iminium ions, from which the desired formylporphyrins **124** and **134-143** were obtained after aqueous work-up. Yields are summarised in Table 3.1. In general, the relatively low yields obtained were a result of difficulties encountered during separation of the mono- and diformylated porphyrin derivatives. Compounds **124**, **137** and **138** were used as starting material for further reactions.

### 3.1.3 Spectroscopic studies

#### *3.1.3.1 $^1$H NMR spectroscopy*

The most diagnostic resonance in an $^1$H NMR spectrum of a formylporphyrin is the low-field singlet, typically appearing between 11 and 13 ppm, which is due to the aldehyde proton. Figure 3.1 shows part of the $^1$H NMR spectrum of **137** and from this it can be seen that, in comparison to the dithianylporphyrin spectra, the β-protons give rise to sharp doublets. The β-protons adjacent to the formyl group are shifted downfield to a further extend than the proton of the free meso-position.

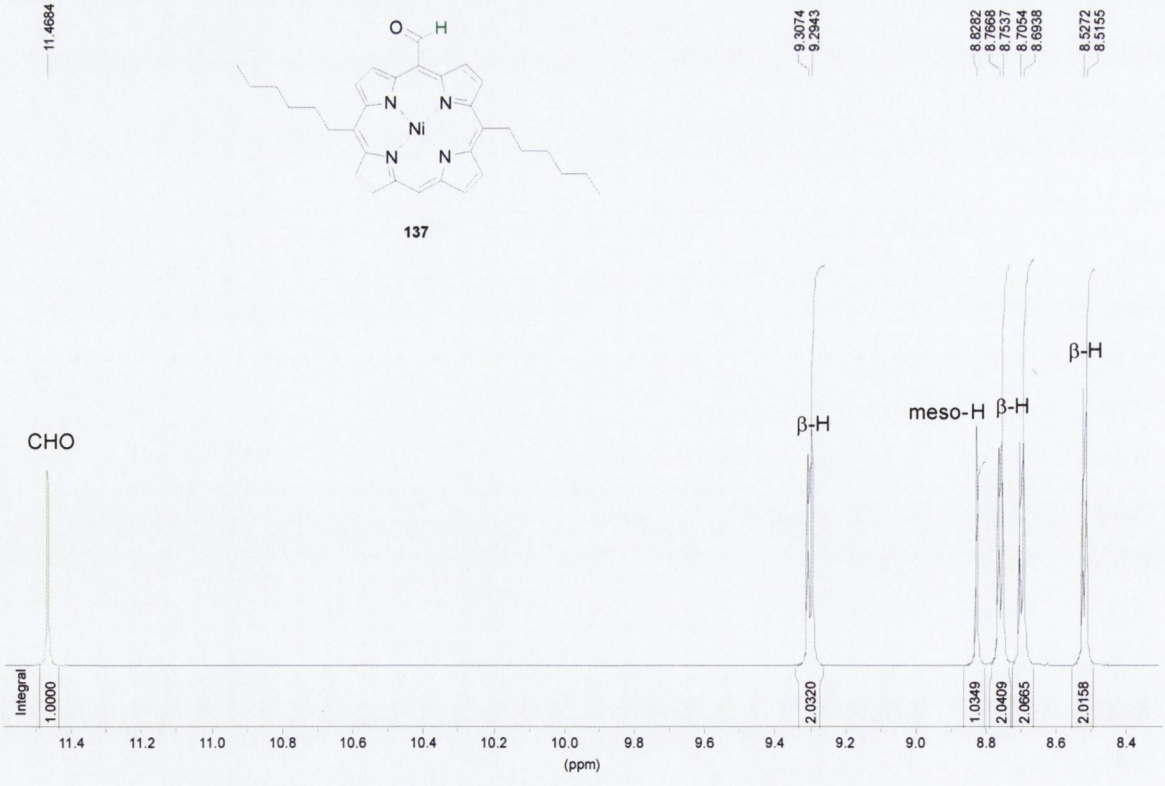



**Figure 3.1.** $^1$H NMR spectrum of **137** with 32 scans, 400 MHz in $CDCl_3$, at rt.

### *3.1.3.2 UV-vis spectroscopy*

Figure 3.2 shows the UV-vis spectra of compounds **128**, **137** and **138**. A clear bathochromic shift of the Soret band from 402 nm for **128** to 425 nm for **138** can be observed, due to the introduction of the formyl group as an additional auxochrome. Hence, formylporphyrins are recognisable by their emerald green colour, which is in contrast to the red colour more typical of metalloporphyrins.

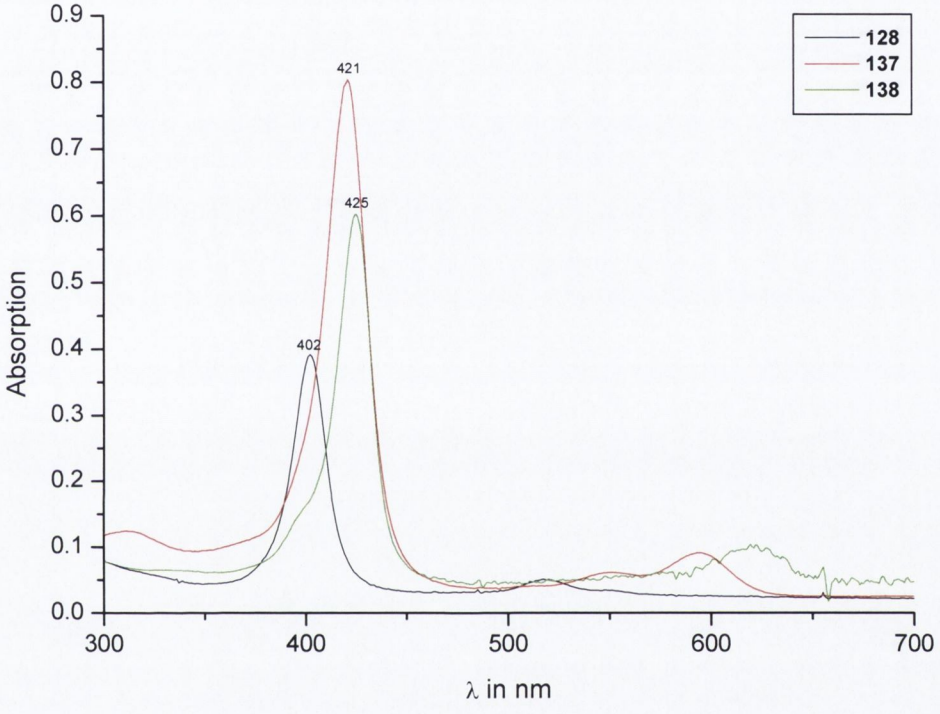



**Figure 3.2.** UV-vis spectra of nickel(II) dihexylporphyrin **128** and compounds **137** and **138** in $CH_2Cl_2$ at rt. Baselines have been adjusted arbitrarily.

## 3.2 Grignard reactions

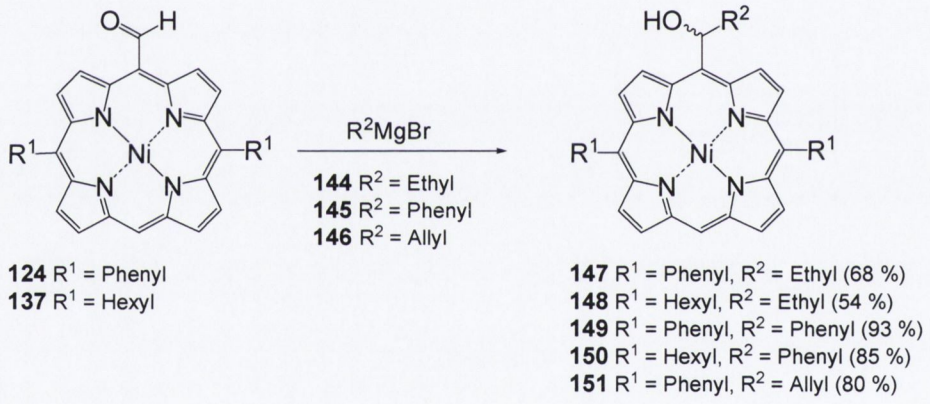
### 3.2.1 Synthetic investigations

Chemical modification of the formyl group on the porphyrin moiety may be achieved through the use of Grignard reactions.[163] Arnold *et al.* reported the reaction of 2,3,7,8,12,13,17,18-octaethyl-5-formylporphyrin with methylmagnesium iodide to yield the corresponding meso-(1-hydroxyethyl) derivative, but only as a crude product since decomposition to the meso-vinyl compound rapidly occurred.[164] Smith and co-workers continued these studies using several Grignard reagents such as methylmagnesium bromide, ethylmagnesium bromide, and benzylmagnesium chloride and an acid.[165] Surprisingly, they did not obtain the expected carbinol compounds but instead observed direct meso-alkylation on the 15-position opposite to the formyl group. Studies of

β-substituted formylporphyrins with organometallic reagents (RLi) show comparable yields and products to those obtained with RMgX.[166]

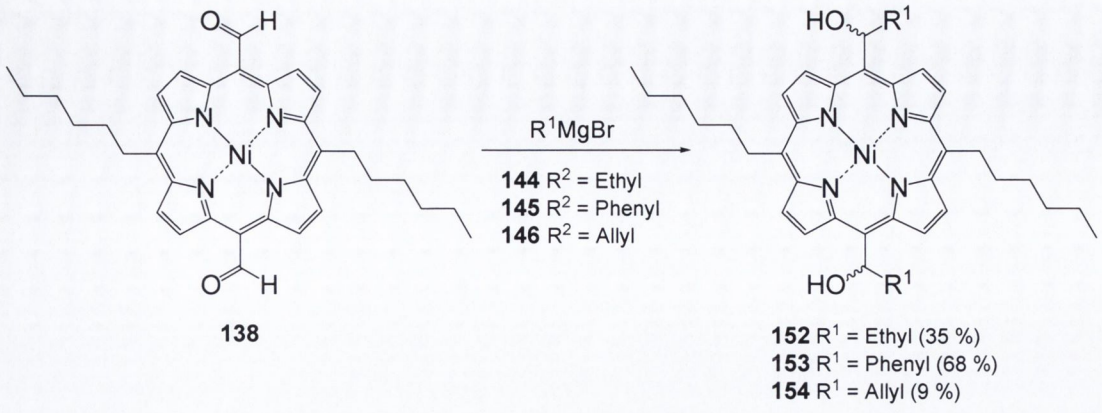
The formylporphyrins **124**, **137**, and **138** were treated with the commercially available Grignard reagents ethylmagnesium bromide **144**, phenylmagnesium bromide **145**, and allylmagnesium bromide **146** to obtain compounds **147-154**, as shown in Schemes 3.4 and 3.5. The reaction between the formylporphyrins and phenyl- and allylmagnesium bromide were performed in dry THF under argon at ambient temperature, whereas the reaction with ethylmagnesium bromide was carried out at an elevated temperature (75 °C), as suggested by Arnold *et al.*[164]

An excess of 10 equivalents of the Grignard reagents was used for the monoformylated porphyrin **124** and **137** and compounds **147-151** were isolated in yields ranging from 54 % to 93 % (Scheme 3.4). In contrast to the behaviour of organolithium reagents, the Grignard reagents reacted only with the formyl group and not with the free meso-position.




**Scheme 3.4.** Grignard reactions on monoformylporphyrins.

The diformylated porphyrin **138** was functionalised by treatment with 20 equivalents of the appropriate Grignard compounds, according to Scheme 3.5. Interestingly, the disubstituted (1-hydroxypropyl)- (**152**) and (1-hydroxybut-3-enyl)porphyrin (**154**) compounds thus isolated in yields of 35 and 9 %, respectively, following chromatographic purification were found to be unstable. Both porphyrins **152** and **154** were characterised by $^1$H-NMR spectroscopy but no further characterisation could be accomplished due to product decomposition. Similar problems were encountered by Arnold *et al.* in their reactions of 5-formyloctaethylporphyrin with methylmagnesium bromide and phenylmagnesium bromide **145**.[164] In contrast, this difficulty did not occur in the reactions of ethylmagnesium bromide (**144**) or allylmagnesium bromide (**146**) with the monoformylated porphyrins **124** and **137**, respectively. In the reaction with phenylmagnesium bromide (**145**), both the mono- and disubstituted products proved to be stable and compound **153** was isolated in 68 % yield.




**Scheme 3.5.** Grignard reactions on diformylporphyrin **138**.

Compound **151**, obtained from the reaction of formylporphyrin **124** with allylmagnesium bromide is particularly interesting, in light of the potential to investigate the activating or deactivating influence of the adjacent hydroxyl group in further reactions such as metathesis.

An X-ray structural analysis of compound **149** was attempted. Single crystals were obtained using a dichloromethane/methanol solvent mixture, however, the resulting molecular structure contained a methoxy group in place of the expected hydroxyl group. Most likely, the methoxy group resulted from the methanol attacking the hydroxyl substituent. A top view of the resulting molecular structure is shown in Figure 3.3. The methoxy-**149** compound crystallised as a racemic mixture.

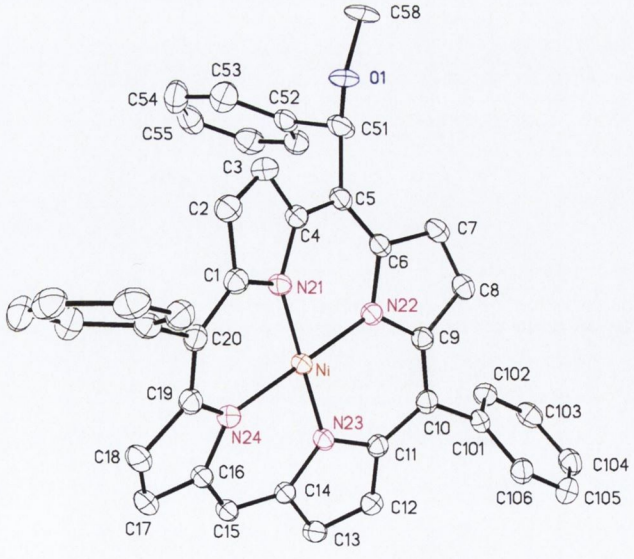



**Figure 3.3.** View of the molecular structure of methoxy-**149** in the crystal. Hydrogen atoms and on one of the enantiomeric forms have been omitted for clarity, ellipsoids are drawn for 50 % occupancy.

Overall the structure is that of a typical ruffled nickel(II) porphyrin with the largest $C_m$ displacements observed for the alkyl substituted position 5. It represents a typical ruffled

Overall the structure is that of a typical ruffled nickel(II) porphyrin with the largest $C_m$ displacements observed for the alkyl substituted position 5. It represents a typical ruffled structure with only minor contributions from *sad* distortion. Furthermore, the molecules form a close spaced lattice structure characterised by π-stacking of the porphyrin macrocycles. The closest intramolecular contacts are Ni···H15 3.032 Å and Ni···H203 2.767 Å. The latter are NOT bonding interactions.

### 3.2.2 Spectroscopic studies

#### *3.2.2.1 $^1$H NMR spectroscopy*

Figure 3.4a shows the $^1$H NMR spectrum of compound **149** in deutero-chloroform ($CDCl_3$). The spectrum in blue (Figure 3.4b) represents the same sample upon the addition of deuterium oxide ($D_2O$). In Figure 3.4a, the doublet resonance at 3.3 ppm is readily attributed to the hydroxyl group, as confirmed by the disappearance of this signal in the latter spectrum due to exchange with the deuterium atoms of $D_2O$. The signal at 8.03-8.04 ppm (shown enlarged in red) is assigned to the adjacent alkyl CH-proton and appears as a doublet due to coupling with the OH proton in a) and as a singlet upon the addition of deuterium oxide in b).

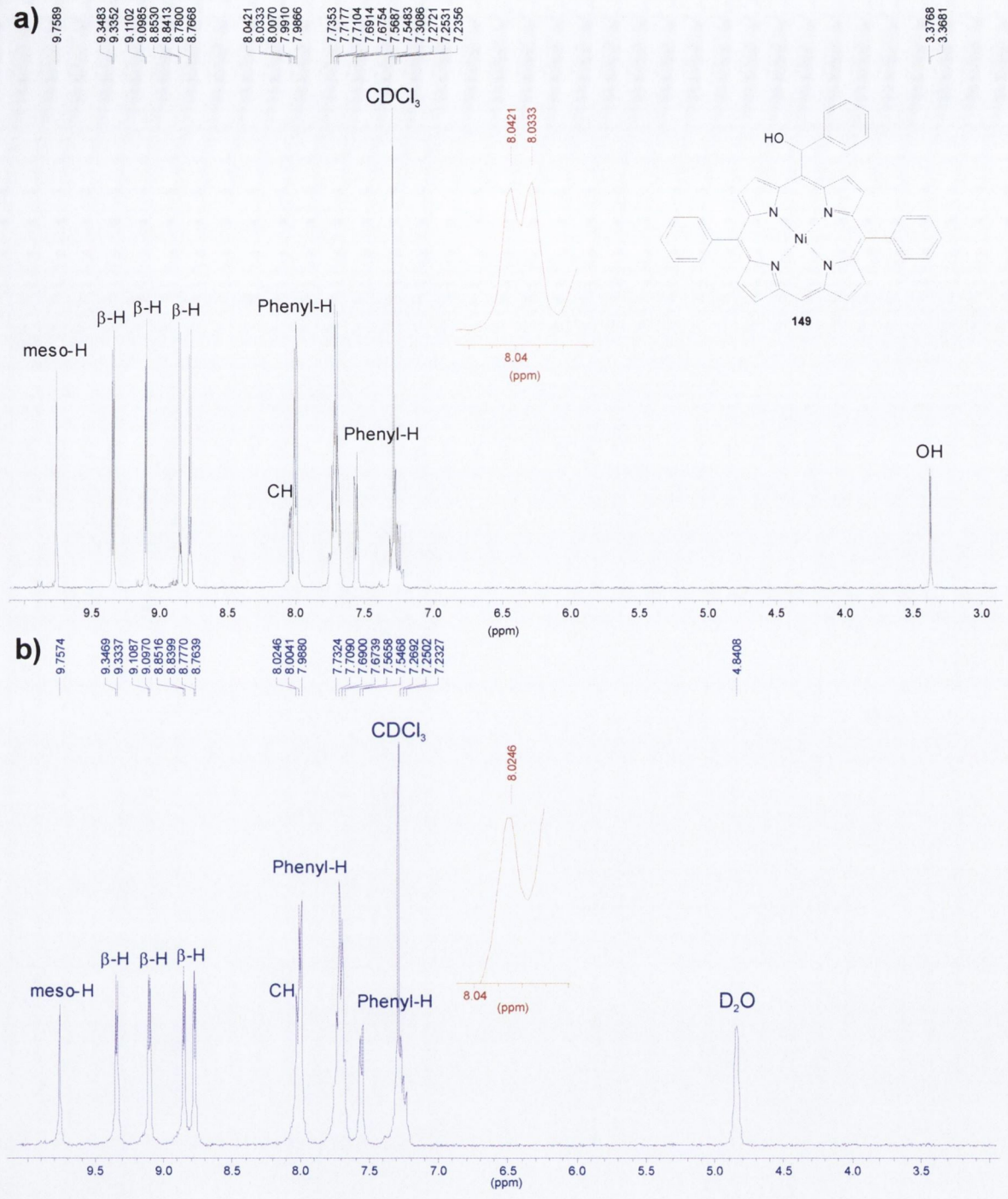



**Figure 3.4.** a) $^{1}H$ NMR spectrum of **149** with 32 scans, 400 MHz in $CDCl_3$, at rt (black); b) upon addition of $D_2O$ (blue). Inset: expansion of the region showing the alkyl CH resonance (red).

### *3.2.2.2 UV-vis spectroscopy*

The UV-visible spectra of the nickel(II) porphyrins **124**, **147**, **149** and **151** are displayed in Figure 3.5. The Soret bands of the Grignard products are blue (hypsochromically) shifted by 7-8 nm relative to that of compound **124**, but they are slightly red shifted (2-10 nm) compared to nickel(II) 5,15-diphenylporphyrin **91**, (shown in Figure 2.6). Evidently, the

introduction of these new groups to the meso-position of the porphyrin moiety does not significantly influence the habit of the absorption spectrum.

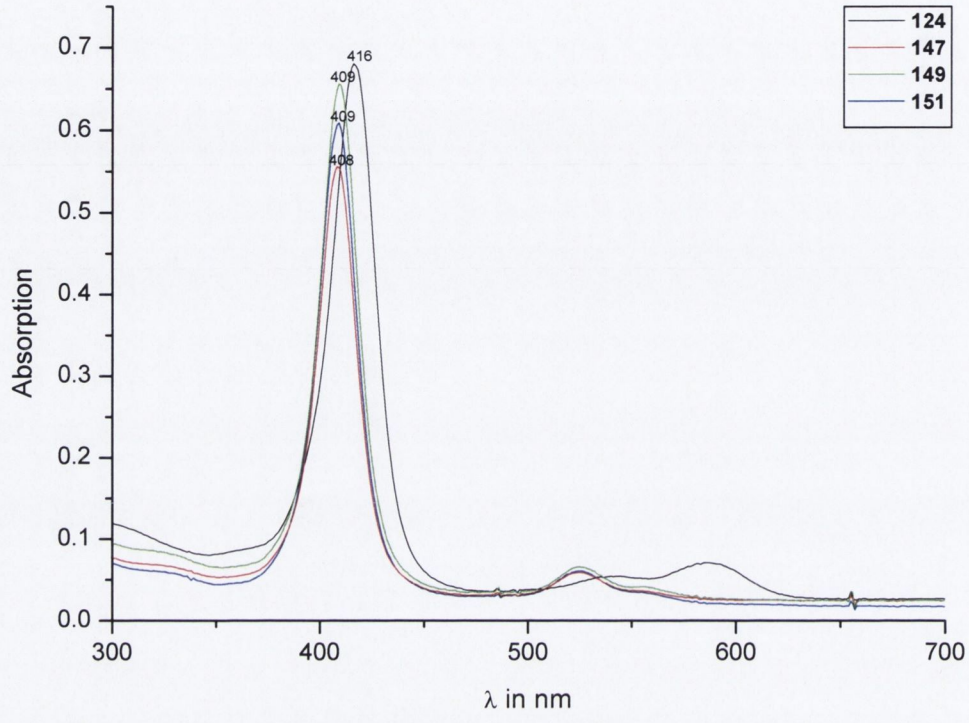



**Figure 3.5.** UV-vis spectra of compounds **124**, **147**, **149** and **151** in $CH_2Cl_2$ at rt. Baselines have been adjusted arbitrarily.

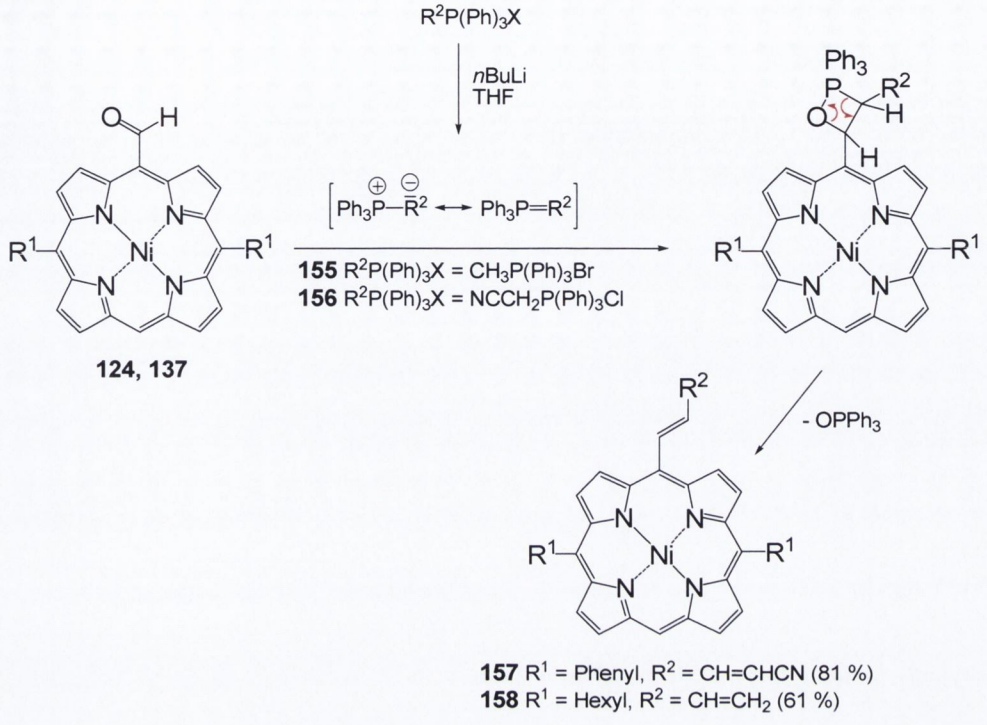
## 3.3 Wittig reactions

### 3.3.1 Synthetic investigations

A further reaction for the transformation of formyl groups is the Wittig reaction.[167] For β-substituted porphyrins, the Wittig reaction has been investigated in some detail. Callot reported the reactions of (2,3,7,8,12,13,17,18-octaethyl-5-formylporphyrinato)nickel(II) and 2-formyl-5,10,15,20-tetraphenylporphyrin with several Wittig reagents, with product yields ranging from 29 to 93 %.[168] Further Wittig condensations were reported by Arnold *et al.* who prepared various meso-vinyl derivates of nickel(II) porphyrins in yields ranging from 44 to 70 %.[169]

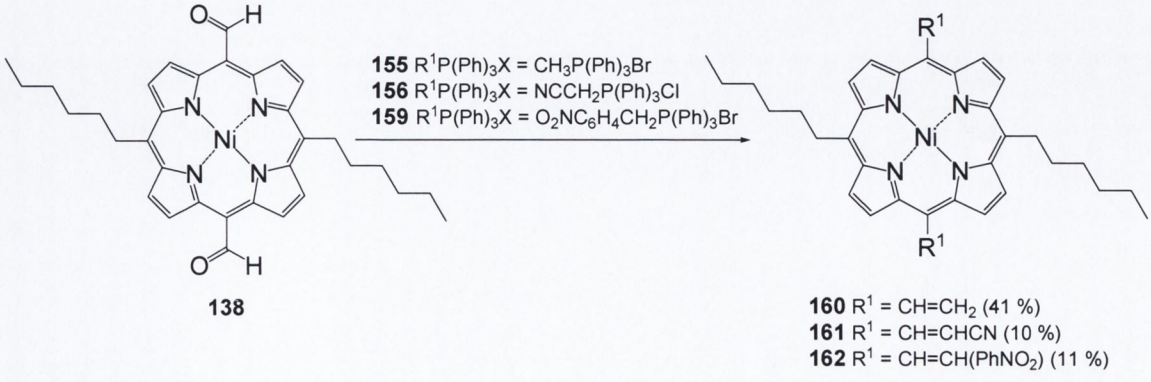
The reactions of commercially available methyltriphenylphosphonium bromide **155** and (cyanomethyl)triphenylphosphonium chloride **156** with 5-formylporphyrins **124** and **137**, respectively, were investigated. An excess of the phosphonium halide was suspended in dry THF and *n*-butyllithium was added dropwise at room temperature to form the ylide *in situ* before adding the respective formylporphyrin. Oxaphosphonate intermediates were

formed as a result of a [2+2] cycloaddition before the elimination of phosphine oxide and afforded the vinylporphyrins **157** and **158**, isolated in the *E*-conformation in 81 and 61 % yield, respectively (Scheme 3.6).




**Scheme 3.6.** Wittig reactions of monoformylporphyrins.

Scheme 3.7 illustrates the reaction of diformylporphyrin **138** with methyltriphenylphosphonium bromide **155**, (cyanomethyl)triphenylphosphonium chloride **156** and (4-nitrophenyl)triphenylphosphonium bromide **159** to the corresponding products **160-162**. Compounds **161** and **162** were only isolated in high purity in 10 % and 11 % yield, due to separation problems from their side products. In contrast, compound **160** was received in a moderate yield of 41 %.




**Scheme 3.7.** Wittig reactions of porphyrin **138**.

The yields of Wittig reactions of meso-substituted porphyrins are comparable to the results obtained for β-substituted porphyrins. Callot reported the synthesis of 5-vinyl-2,3,7,8,12,13,17,18-octaethylporphyrin from the formyl precursor in 27 % yield. For reactions with different residues adjacent to the double bond he obtained yields ranging from 69 to 93 %. [168] Similarly, Arnold *et al.* investigated different Wittig reactions of 5-formyloctaethylporphyrin and 5-formyletioporphyrin I, preparing various meso-vinyl derivates of nickel(II) porphyrins in yields ranging from 44 % to 70 %.[169]

Another synthetic approach for the preparation of porphyrins with unsaturated residues was described by Locos and Arnold in 2006, involving the Heck coupling of bromoporphyrins with acrylonitrile.[57] In this way, the mono- and disubstituted alkenylporphyrins were isolated as an inseparable mixture of *E*- and *Z*-isomers. In our case, by employing the Wittig reaction, the cyanoethenylporphyrin **157** was isolated only as the *E*-isomer in a very good yield of 81 %.

The Wittig products bear unsaturated substituents and can therefore be useful substrates for metathesis [170-172] or Diels-Alder reactions,[173-175] which can then have applications in photodynamic therapy [176,177] or nanoscience.[178,179]

### 3.3.2 Spectroscopic studies

#### *3.3.2.1 $^1$H NMR spectroscopy*

Figure 3.6 shows the $^1$H NMR spectrum of compound **157** as a representative example for all the Wittig products. The most significant resonances are highlighted in orange and represent the protons of the alkenyl substituent, which appear as doublets. The magnitude of the coupling constant (15.5 Hz) is indicative of the *E*-conformation.

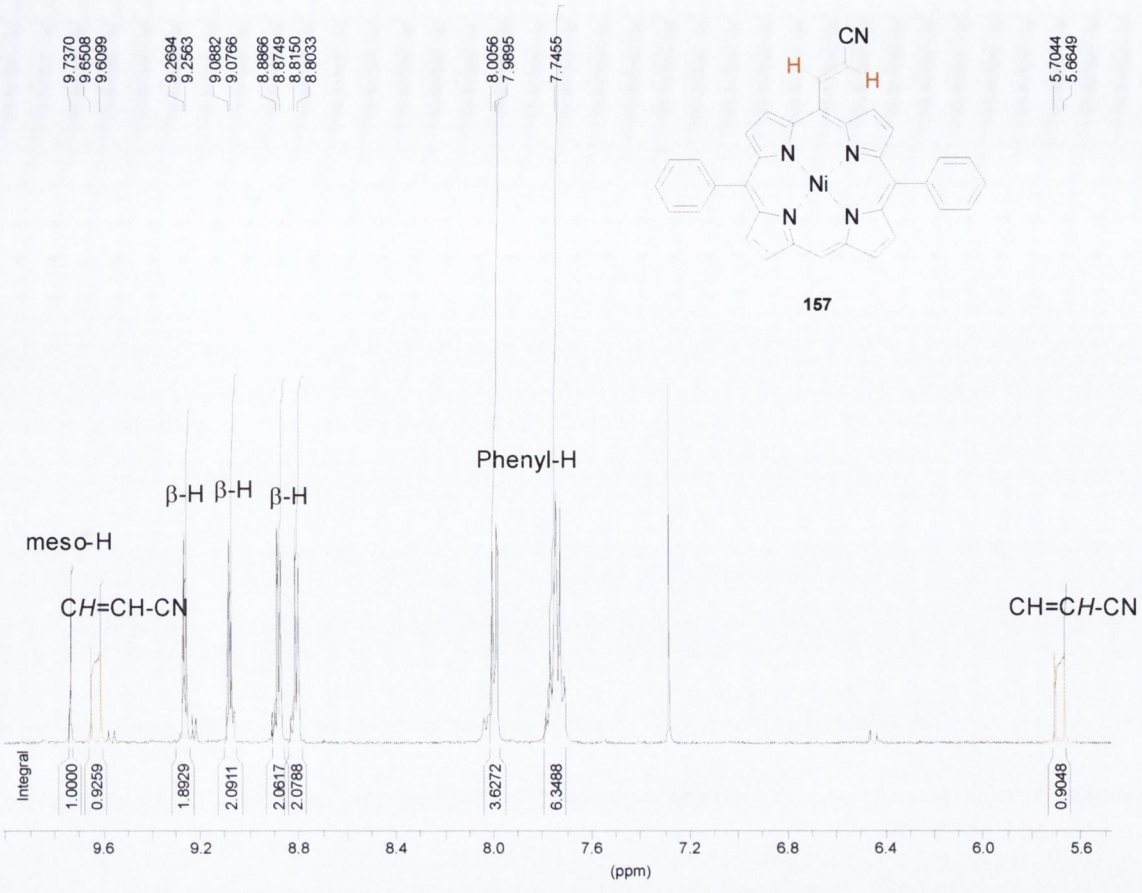



**Figure 3.6.** $^{1}$H NMR spectrum of **157** with 32 scans, 400 MHz in $CDCl_3$, at rt.

### *3.3.2.2 UV-vis spectroscopy*

Figure 3.7 illustrates the UV-vis spectra of compounds **138**, **160**, **161** and **162**. The introduction of the vinyl residue in compound **160** has no significant influence on the absorption spectrum in comparison to the starting material. In contrast, the ethenylcyano group in **161** shifts the Soret band bathochromically by 15 nm and, in case of **162**, the ethenyl(4-nitrophenyl) substituent results in a shift of the absorption by 38 nm. Compared to 5,15-(dihexylporphyrinato)nickel(II) **128** ($\lambda_{max}$ = 402 nm, Figure 3.2), all of the unsaturated substituents induce a bathochromic shift. The ethenyl(4-nitrophenyl) substituent combines several auxochromic groups, which together serve to markedly shift the Soret band.

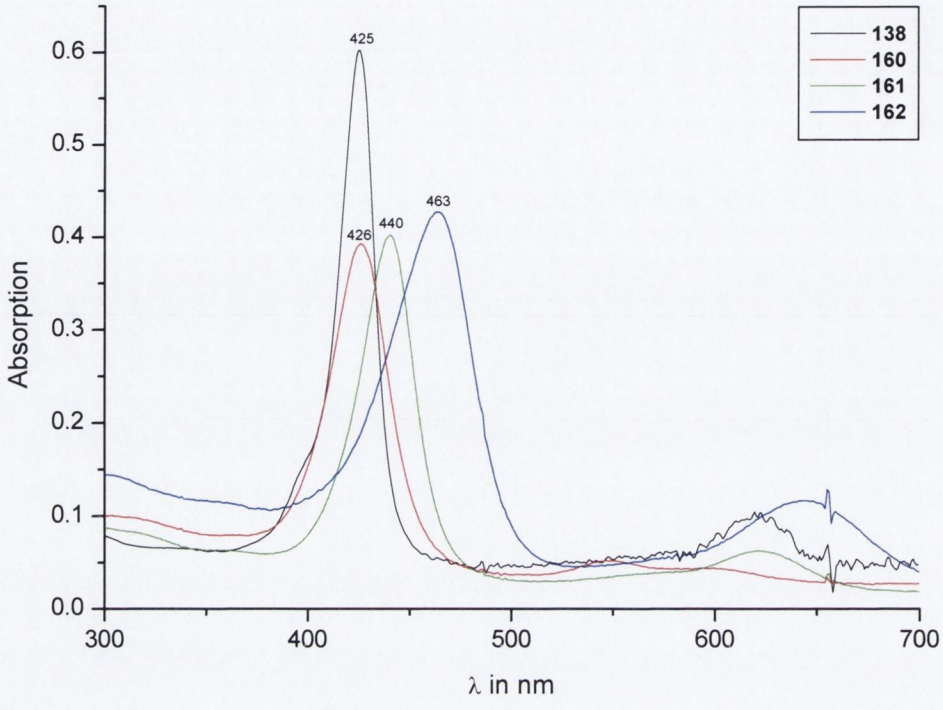



**Figure 3.7.** UV-vis spectra of compounds **138**, **160**, **161** and **162** in $CH_2Cl_2$ at rt. Baselines have been adjusted arbitrarily.

## 3.4 Conclusions

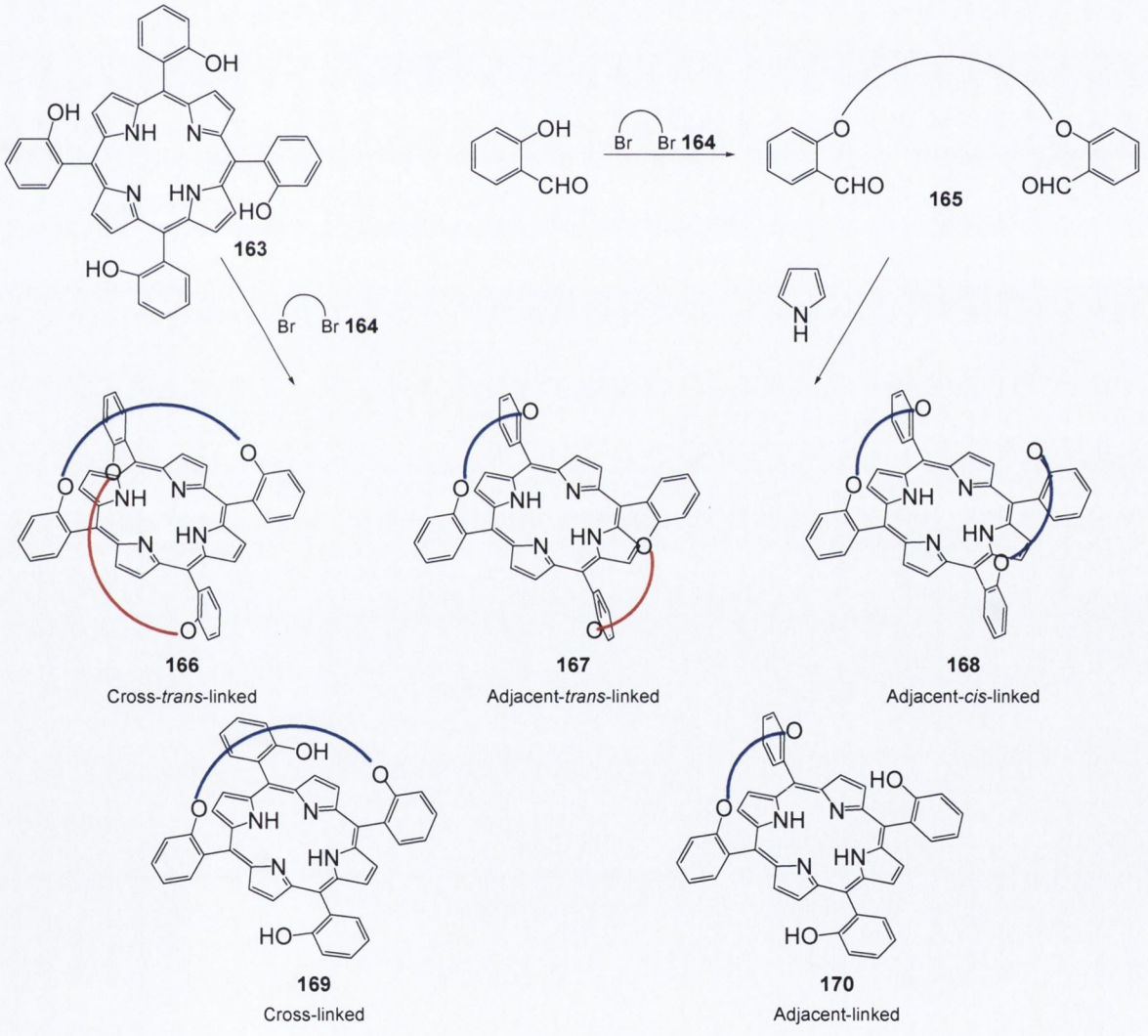
It has been demonstrated that the deprotection of dithianylporphyrins offers a new pathway for the preparation of formylporphyrins such as **123-125** in the free base form as well as for metalloporphyrins under mild reaction conditions with yields, comparable to the Vilsmeier reaction. Nonetheless, the Vilsmeier reaction remains the most common way for introducing a formyl group into the porphyrin moiety and was used for the successful synthesis of compounds **124** and **134-143**.

To demonstrate the use of the formyl group for the further functional elaboration of porphyrins, studies of Grignard and Wittig reactions of 5,15-disubstituted porphyrins were performed. The yields of the porphyrins prepared by Grignard reactions, **147-154**, and those prepared using Wittig reagents, **157** and **158**, and **160-162** ranged from 9 to 93 % and 10 to 81 %, respectively. These yields are generally much better than those obtained from similar reactions with 5-formyl-2,3,7,8,12,13,17,18-octaethylporphyrins. Hence, the lower steric hindrance present in the 5,15-substituted porphyrins facilitates their reactivity and, as a result, the yields and stability of the resulting porphyrins.

# CHAPTER 4:
# Basket-handle porphyrins

## 4.1 Basic principles

The reactivity of the formyl unit in formylsubstituted porphyrins offers extraordinary potential for obtaining more exotic porphyrin derivatives and one possible application for formylporphyrins is the transformation into basket-handle porphyrins (BHPs). These species are important in photocatalytic reactions and show promising nonlinear optical properties. BHPs were mentioned for the first time in 1979 by Momenteau, and typically involve two opposite meso-phenyl substituents that are bridged by a suitable chain, i.e. the basket-handle.[180,181] At present, there are two main types of basket-handle porphyrins, namely ether- and amide-linked derivatives.

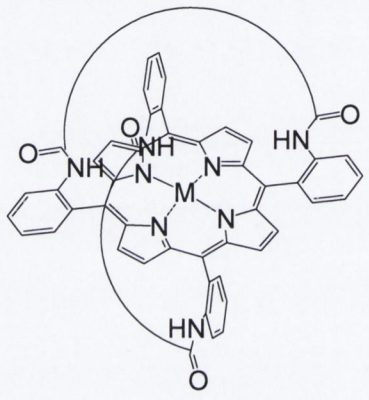



**Scheme 4.1.** Synthesis of ether-linked basket-handle porphyrins and its different isomers. blue: bridge above porphyrin level, red: bridge underneath porphyrin level.

Scheme 4.1 shows the two synthetic methods that currently exist for the formation of ether-linked BHPs, and the five possible isomers. The first pathway requires the initial synthesis of 5,10,15,20-tetrakis(2-hydroxyphenyl)porphyrin (**163**) and the subsequent reaction of this tetrasubstituted porphyrin with a dibromoalkylchain (**164**).[182,183] The

second approach employs salicylaldehyde, which reacts with the alkyl chain **164** to afford a dialdehyde derivative **165** that undergoes a following condensation reaction with pyrrole to provide the ether-linked BHP molecules.[181] The first synthesis leads to three of doubly-bridged porphyrin isomers **166-168** and two of mono-bridged BHP derivatives, **169** and **170**. In contrast, the second route yields only the doubly-bridged porphyrin derivatives **166-168**.

Basket-handle porphyrins with an amide bridge (**171**)[184] have also been reported (Figure 4.1), being prepared from the treatment of a tetraaminophenylporphyrin with a diacyl chloride.




**171**

**Figure 4.1.** Amide-bridged (**171**) basket-handle porphyrin.

Commonly, all BHP derivatives described have a phenyl group attached to the meso-position of the porphyrin unit and the linking chain is connected *via* the *ortho*-substituent of this phenyl group.

To date, there are no reports for the synthesis of basket-handle porphyrins wherein the linking bridge is directly attached to the meso-carbon of the porphyrin moiety, i.e. without a phenyl spacer. Meso-formyl substituents may provide an entry into such systems and, accordingly, formylporphyrin **138** was tested for the formation of mono-bridged basket-handle porphyrins.

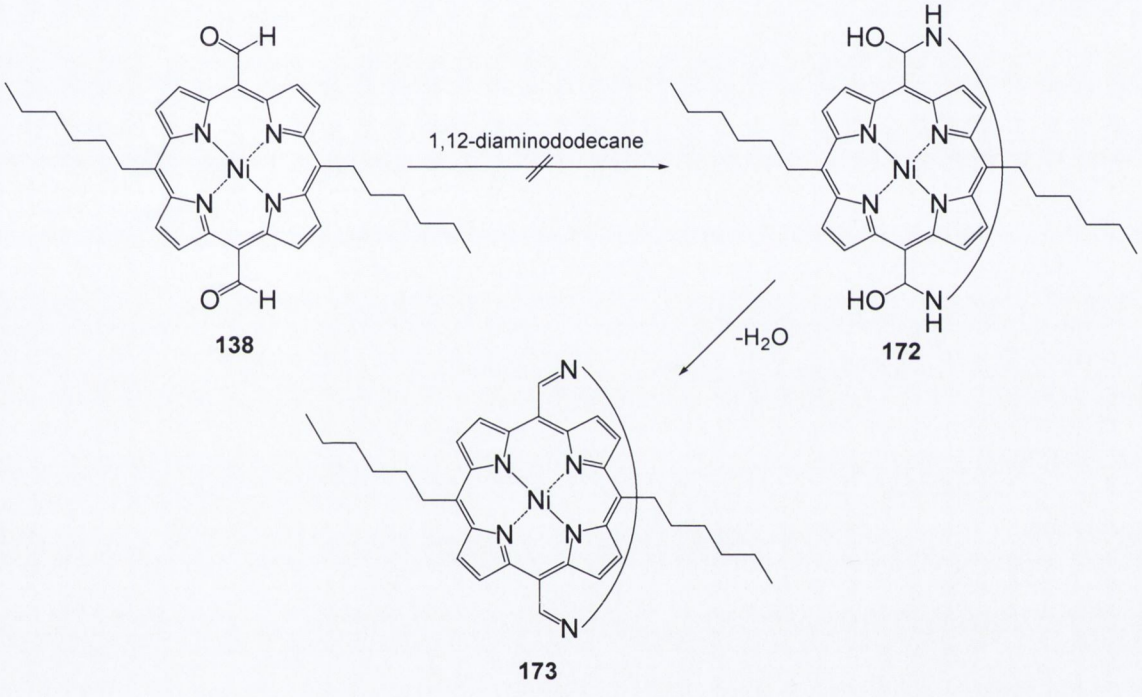
## 4.2 Synthetic studies

### 4.2.1 Imine-linked basket-handle porphyrins

The preparation of an imine-linked basket-handle porphyrin by the reaction of an amine with the formylporphyrin **138** was attempted first. So far, meso- and β-iminoporphyrins have been prepared, and two pathways exist for their formation. In one approach, the formylporphyrin reacts with an amine in benzene, either at ambient temperature or upon

heating.[185] Alternatively, the porphyrin may be functionalised with the amino group and subsequently undergoes reaction with the appropriate aldehyde.[186]

Compound **138**, 1,12-diaminododecane and sodium sulphate were dissolved in dichloromethane and stirred at rt (Scheme 4.2), according to the general method for the preparation of imines described by Blaney *et al.*[187] As this only led to the recovery of starting material, the mixture was heated to reflux for three days. However, the only porphyrin recovered was again compound **138**. A change of the solvent to acetonitrile and an increase of the reaction temperature from 40 to 60 °C did not lead to the hemiaminal intermediate **172** nor the desired bis(imine)-linked compound **173**.

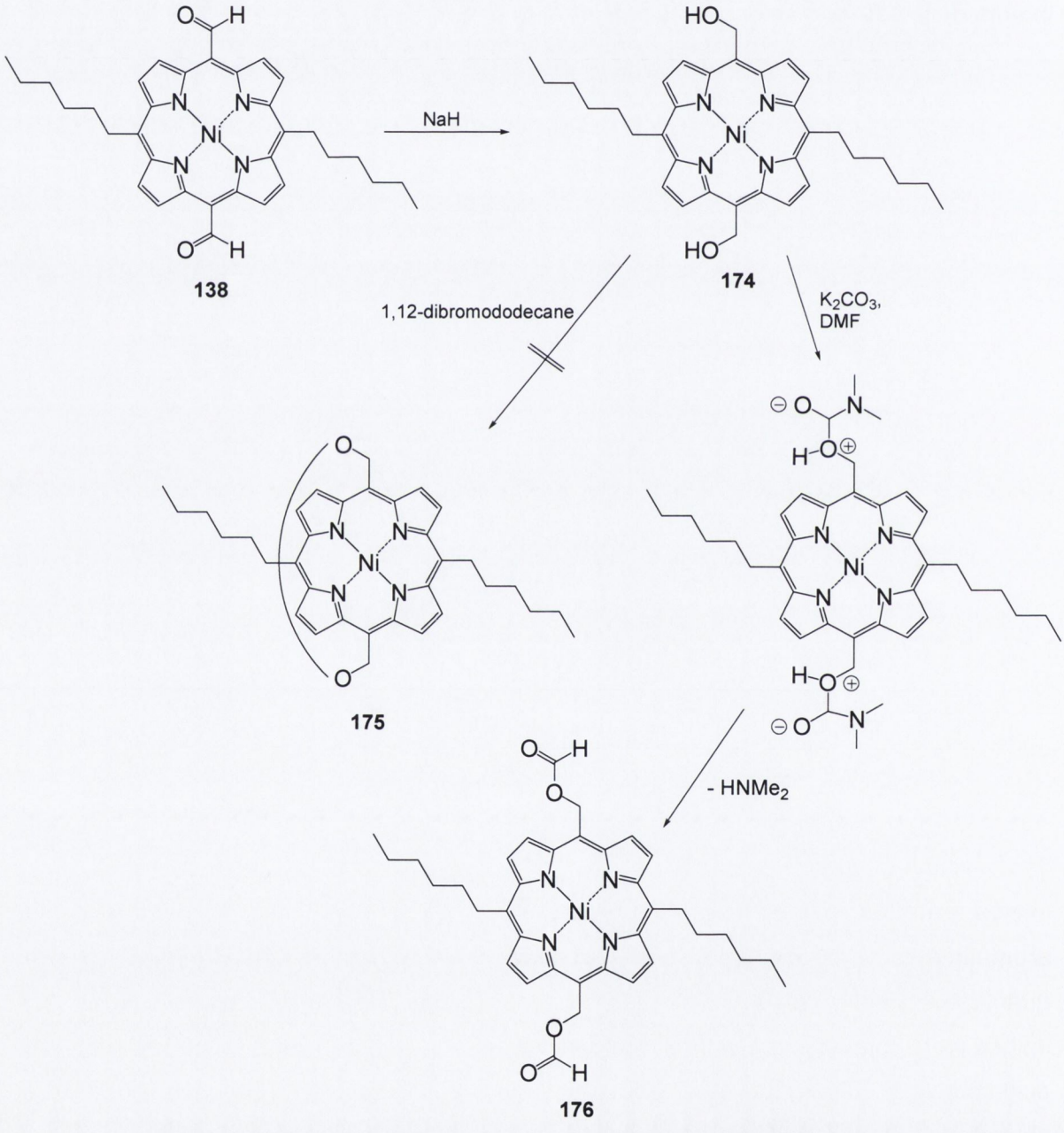



**Scheme 4.2.** Attempted synthesis of imine-linked basket-handle porphyrins.

The reaction of an aldehyde with an amine was first discovered by Schiff and, as a result, imines are often referred to as Schiff bases.[188,189] Schiff also found that, in the case of aromatic aldehydes, the reaction was particularly facile and afforded the imines in near quantitative yield. Indeed, it was reported that aromatic aldehydes were so reactive that imines were formed even without the removal of water, but in general the reaction was acid-catalysed. Therefore, the above reaction of compound **138** was repeated in chloroform with the addition of a catalytic amount of hydrochloric acid and an excess of sodium sulphate at 60 °C. Again, this variation only resulted in the recovery of starting material **138**.

### 4.2.2 Ether-linked basket-handle porphyrins

The formation of an ether-linkage has been described for the preparation of BHPs from tetraarylporphyrin precursors[180,181,190,191] and may provide an alternative approach to basket-handle porphyrins in which the bridge is directly linked at the meso-position. The most common ether synthesis was discovered by Alexander Williamson in 1850,[192] and involves the nucleophilic substitution of an alkyl halide by an alkoxide.




**Scheme 4.3.** Attempted synthesis of ether-linked basket-handle porphyrins.

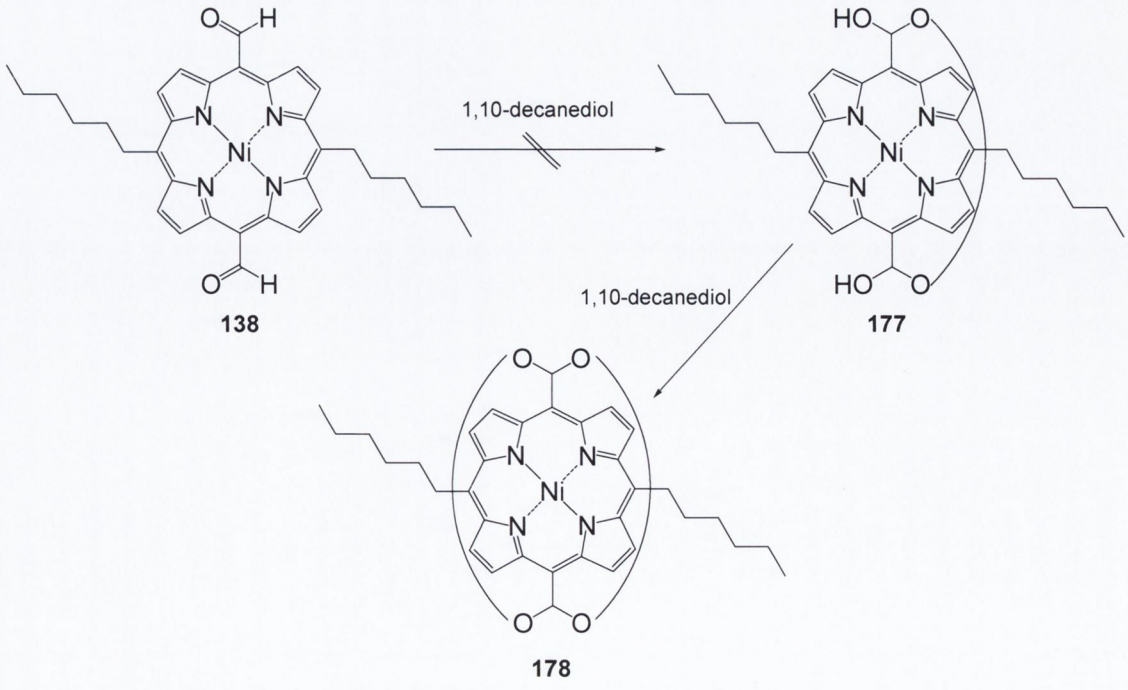
Formylporphyrin **138** was reduced nearly quantitatively to the dihydroxymethylporphyrin **174** using sodium hydride, following the procedure of Johnson and Oldfield.[53] The hydroxymethylporphyrin **174** was then reacted with 1,12-dibromododecane under basic

conditions in dry DMF, analogous to the procedure described by Momenteau for the preparation of the tetraaryl-BHPs.[181] The isolated product was, however, not the expected BHP **175** but compound **176** (Scheme 4.3), presumably due to a reaction with the solvent. When the reaction was repeated using dry toluene as solvent only starting material was recovered.

A procedural modification was made in an attempt to increase the reactivity of potassium carbonate by adding 18-crown-6. For crown ethers, the interior of the central cavity is water like, whereas the exterior is hydrocarbon like. Hence, the potassium ions are caught in the centre of the 18-crown-6 molecule and can be carried into the organic solvent, i.e. the carbonate ions are essentially unsolvated or 'naked' and therefore quite reactive.[193] Nevertheless, none of the desired products were isolated by applying this modification. In a further attempt, potassium hydroxide was used as a base in refluxing ethanol, but in this case the porphyrin was entirely destroyed.

### 4.2.3 Acetal-linked basket-handle porphyrins

Acetals are often used as protecting groups for aldehydes or ketones, thus acetal formation may provide a different route towards the synthesis of basket-handle porphyrins. The acid-catalysed addition of an alcohol to an aldehyde initially forms a hemiacetal intermediate, which cannot generally be isolated. Exceptions are sugars, which form stable, cyclic hemiacetals comprising five- or six-membered rings. In the presence of excess alcohol, the hydroxyl group present in the hemiacteal is substituted by a second alkoxy group to afford the more stable acetal species.[194]




**138** **177** **178**

**Scheme 4.4.** Attempted preparation of basket-handle porphyrins *via* acetal formation.

Porphyrin **138** was reacted with an excess of 1,10-decanediol and a catalytic amount of *p*-toluenesulphonic acid in toluene under reflux in an argon atmosphere (Scheme 4.4), according to the procedure described by Éll *et al.* for the preparation of acetal-protected substituted benzaldehyde.[195] Formation of the hemiacetal **177** and the acetal **178** could not be detected, and only starting material was recovered. A 100-fold increase in the amount of acid employed resulted in complete porphyrin decomposition.

## 4.3 Conclusions

To date, basket-handle porphyrins have been synthesised either with an ether or an amide bridge. In all reported cases, an aromatic spacer was used to attach the bridge to the porphyrin skeleton.

Our aim was to create basket-handle porphyrins in which the basket-handle was directly linked to the meso-position. Formylporphyrin **138** and its reduced form, hydroxymethylporphyrin **174**, served as precursors for initial investigations. Compound **138** was treated with 1,12-diaminododecane and 1,10-decanediol for the attempted formation of an imine-bridged and an acetal-linked BHP, respectively. Compound **138** was additionally reduced to the hydroxymethylporphyrin **174** and subsequently reacted with 1,12-dibromo-dodecane to form an ether bond. However, all attempts were unsuccessful and did not lead to the desired basket-handle porphyrins. A plausible reason for the reluctance towards BHP formation is that the alkyl chain is not flexible enough to bend over the porphyrin moiety, especially given the established reactivity of meso-formyl substituent towards further functionalisation, as discussed in the previous chapter.

# CHAPTER 5:
# Allenylporphyrins

## 5.1 Basic principles

Cumulated dienes are often known as allenes. The central carbon in allenes is sp-hybridised and, as a result, the double bond array is linear with respect to the two terminal carbon atoms ($sp^2$-hybridised). Since the π-bonds of allenes are orthogonally disposed, the planes defined by the end carbon substituents are perpendicular to one another. The two π-bonds are not in conjugation with each other because they are not co-planar. An interesting consequence of this configuration is that allenes having two different substituents on each of the terminal carbon atoms are chiral.

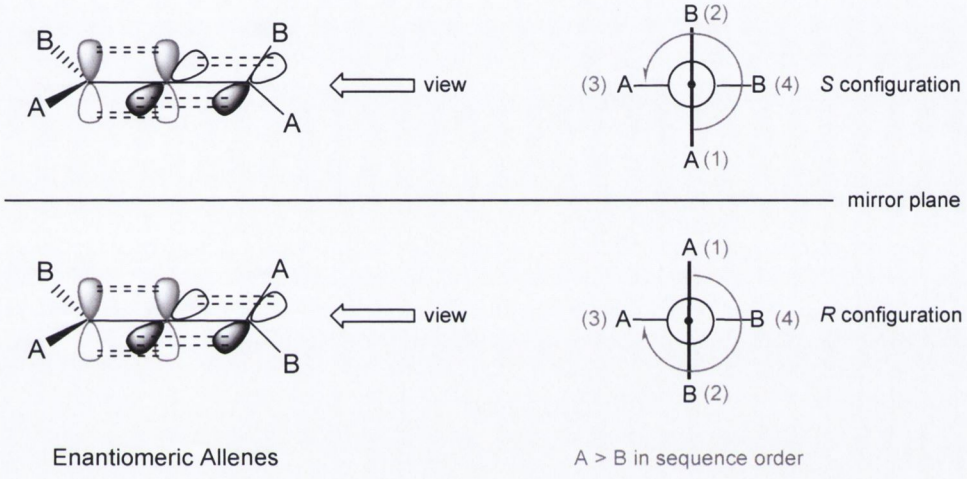



**Figure 5.1.** Stereochemistry of allenes.

This phenomenon is demonstrated in Figure 5.1, which shows an allene with different residues A and B, on each of the terminal carbon atoms, where A has the higher Cahn-Ingold-Prelog (CIP) priority. Only the substituents at one end of the allene project above and below the plane containing the rest of the molecule, and the two possible relative orientations for these groups give rise to *R* and *S* enantiomers. The unusual stereochemistry of such systems was successfully predicted by van't Hoff in 1875.[196]

The high degree of unsaturation and the readily accessible π-bond system of allenes renders them extremely reactive towards the common electrophilic addition reactions. For instance, most allenes react rapidly with chlorine and bromine to form 2,3-dihalopropenes.[197] Furthermore, allenes can participate in Diels-Alder reactions in two ways. Firstly, if one of the allenic π-bonds is conjugated with a double bond, it reacts as a typical conjugated diene.[198,199] Secondly, allenes also behave as dienophiles, especially when bearing electron-withdrawing substituents.[200] Rearrangements to isomeric acetylenes and conjugated dienes are also common and represent possible obstacles during addition and substitution reactions.[201]

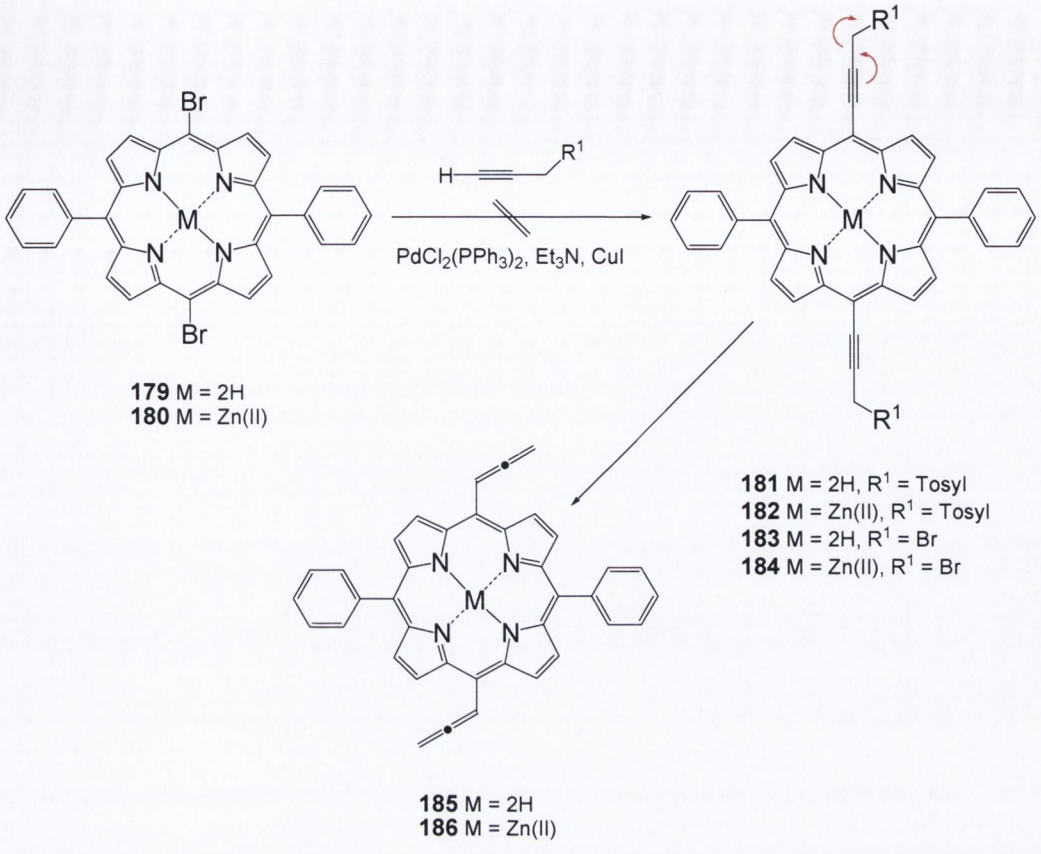
Allenes possess potential applications as dyes, drugs, antioxidants and in polymers or co-polymers suitable for paints, fibers, elastomers, printable films and heat- or corrosion-resistant materials.[197,202,203] Allenes comprise an unsaturated system of cumulated double bonds that offer the possibility of transformation into different functional groups *via* Diels-Alder or metathesis reactions. Thus, when incorporated into the porphyrin moiety, the reactivity of the allene unit represents a new entry for the synthesis of a number of asymmetric porphyrins. Furthermore, cumulated dienes are rigid and chiral, which may confer interesting properties to the resulting allenylporphyrins. Finally, allenes also occur in natural products,[204,205] thus allenylporphyrins could be useful for biological or medicinal applications.

## 5.2 Synthetic studies

### 5.2.1 Allenes from propargyl electrophiles

The most commonly employed synthesis for terminal allenes begins with propargyl electrophiles that bear a terminal leaving group.[206-208] Rearrangement and loss of the leaving group at the propargyl substituent affords the terminal allene. Sonogashira cross-coupling is employed to introduce the desired propargyl residues to the precursor molecule. The reaction of terminal alkynes with aryl or vinyl halides is performed with a palladium catalyst, a copper(I) co-catalyst, and an amine base and typically requires anhydrous, anaerobic conditions.[209]

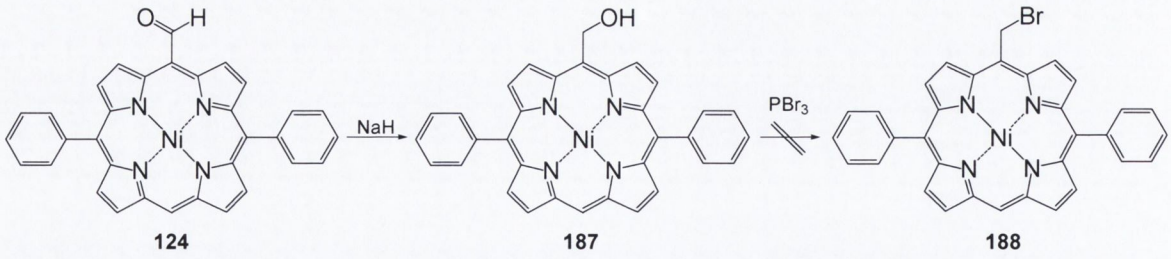
The dibromoporphyrin **179** or **180** were dissolved in THF and treated with triethylamine, $PdCl_2(PPh_3)_2$, copper(I) iodide and the respective propargyl compound under reflux and an argon atmosphere (Scheme 5.1), analogous to the procedure reported for the preparation of arylethynylporphyrins and trimethylsilylethynylporphyrins.[210,211]




**Scheme 5.1.** Attempted Sonogashira cross-coupling reaction.

Neither the dipropargylporphyrins **181-184** nor the corresponding allenylporphyrins **185** and **186** were isolated, however, and only starting material and an insoluble polymer were obtained. Increasing the equivalents of CuI and triethylamine or decreasing the amount of porphyrin used did not lead to the desired products. A plausible explanation for this behaviour is that the propargyl compounds necessarily carry good leaving groups and may react with themselves under the conditions employed. It is also possible that the desired porphyrins are formed, but react again with either the propargyl compound or starting dibromoporphyrin.

Consequently, to minimise steric hindrance, it was attempted to introduce the bromo group at a position more remote from the porphyrin ring. Formylporphyrin **124** was quantitatively reduced with sodium hydride to the corresponding alcohol **187** (Scheme 5.2). Unfortunately, the hydroxymethylporphyrin **187** proved to be thermally unstable, rapidly decomposing at temperatures above 50 °C. An electrophilic substitution reaction to exchange the hydroxyl group with a bromo group was nonetheless attempted using phosphorus tribromide at 0 °C.[212] However, the desired bromoporphyrin **188** was not formed, perhaps due to the instability of the precursor.

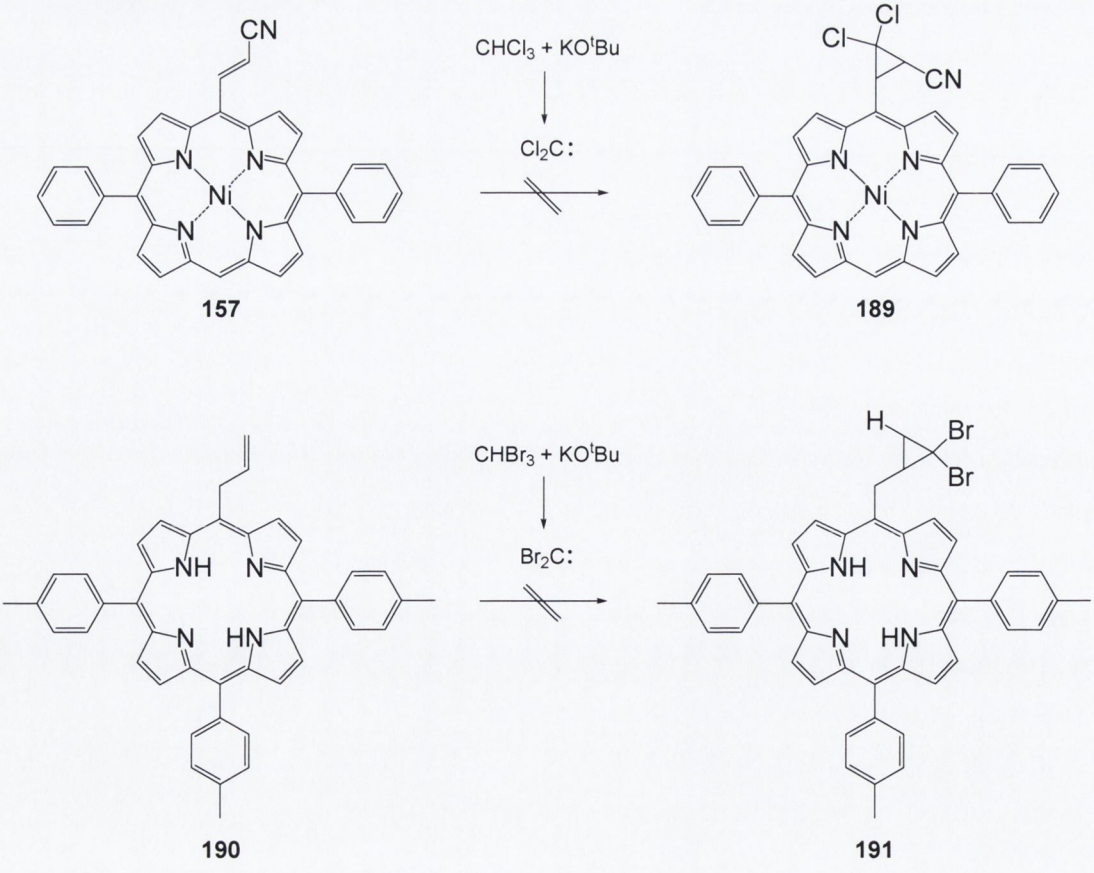



**Scheme 5.2.** Attempted synthesis of bromomethylporphyrin.

### 5.2.2 Carbene rearrangement: the Doering-Moore-Skattebøl reaction

A second attempt for the preparation of allenylporphyrins involved the synthesis of cyclopropylporphyrins *via* carbenes. Geminal dihalo cyclopropane derivates can be converted to allenes by reaction with an organolithium base,[213] and this method has obvious advantages in that olefins can be easily prepared and few side reactions occur.

The formation of cyclopropane derivatives *via* addition to olefins is among the unique and characteristic reactions of carbenes. Carbenes can exist in two states, the singlet state and the triplet state, depending on the substituents at the carbon atom. Singlet carbenes possess a pair of electrons and an $sp^2$-hybridised carbon atom and can be generated from chloroform or bromoform and potassium *tert*-butoxide. Typically, these molecules are short lived and therefore very reactive.[214]

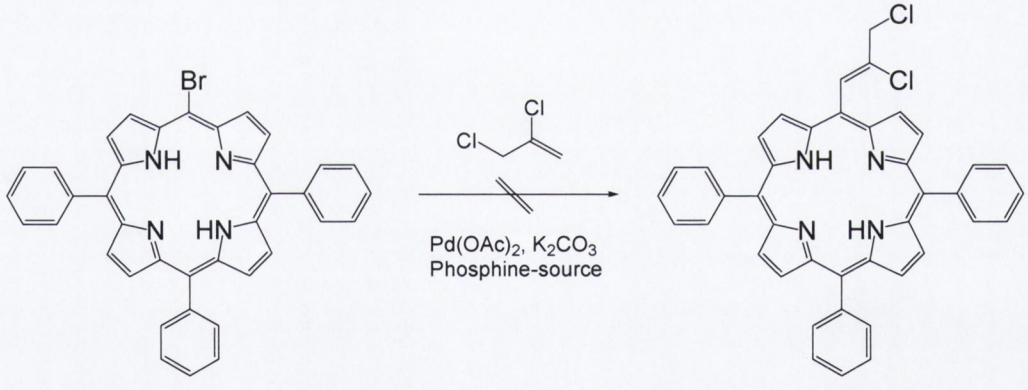



**Scheme 5.3.** Attempted cyclopropanation of porphyrins **157** and **190**.

Cyclopropanation of the vinyl substituent of porphyrin **157**, synthesised by a Wittig reaction as discussed in Chapter 3.3. was attempted by treatment with dichlorocarbene, which was formed *in situ* from chloroform and potassium *tert*-butoxide (Scheme 5.3).[215] A strong reaction of the base with chloroform was observed but no formation of the desired product **189** was detected. Similarly, the reaction of porphyrin **190**,[83] in which the double bond is more remote from the porphyrin skeleton, with dibromocarbene did not lead to porphyrin **191**. The reaction was generally performed at rt under argon, but the porphyrins **189** and **191** were also not formed upon increasing the reaction temperature.

### 5.2.3 Heck cross-coupling reactions

The introduction of 2,3-dichloro-1-propene into the porphyrin moiety *via* a Heck cross-coupling reaction offers a different route towards allenylporphyrins. Since allenes may result from the elimination reaction of two such vicinal halogen atoms,[216] it has been previously demonstrated that the palladium catalysed Heck cross-coupling reaction is a useful technique for attaching alkenyl substituents to both the β- and meso-positions of porphyrins in high yields.[57,60,62,64,65,217]




**192** **193**

**Scheme 5.4.** Attempted Heck coupling reaction of porphyrin **192** with 2,3-dichloro-1-propene.

According to the procedure explored by Locos[218], bromoporphyrin **192** was reacted with palladium acetate, triphenylphosphine and 2,3-dichloro-1-propene under basic conditions in a DMF-toluene solvent mixture (Scheme 5.4). However, only starting material was recovered. Similarly, utilising the more steric hindered di-*tert*-butylbiphenylphosphine did not lead to the desired porphyrin **193**.

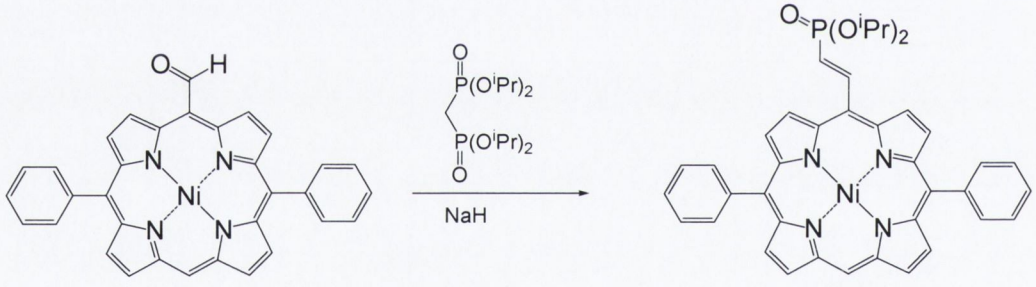
Alkenes used for the Heck reaction are often electron-deficient, but chlorine atoms belong to the chameleon-like class of substituents that show no significant electron-withdrawing or -donating effect. It is therefore possible that 2,3-dichloro-1-propene is not sufficiently electron-deficient to react under the Heck coupling conditions.

### 5.2.4 Horner-Wadsworth-Emmons (HWE) reactions

In 1958, Horner reported a modified Wittig reaction in which stabilised phosphonate carbanions were reacted with aldehydes (or ketones).[219,220] Wadsworth and Emmons later defined the reaction further.[221-223] In comparison to the phosphonium ylides used in the Wittig reaction, phosphonate stabilised carbanions used in the so-called Horner-Wadsworth-Emmons (HWE) reactions are more nucleophilic and more basic.

The HWE reaction has been successfully applied to the synthesis of allenes.[224,225] For example, Tomioka and co-workers described a one-pot procedure for the synthesis of functionalised allenes using two sequential HWE olefination reactions.[226] The first reaction occurred between an aldehyde and methylenebisphosphonate to give an alkenylphosphonate. This was followed by a direct deprotonation with LDA and then treatment with aldehydes to afford an hydroxyalkenylphosphonate, which could be converted into the corresponding allene by a subsequent HWE olefination reaction.

Scheme 5.5 shows the reaction of the monoformylporphyrin **124** and tetra(*iso*-propyl) methylenebisphosphonate promoted by sodium hydride in THF at rt. The reaction yielded the corresponding alkenylphosphonoporphyrin **194** in 73 %.

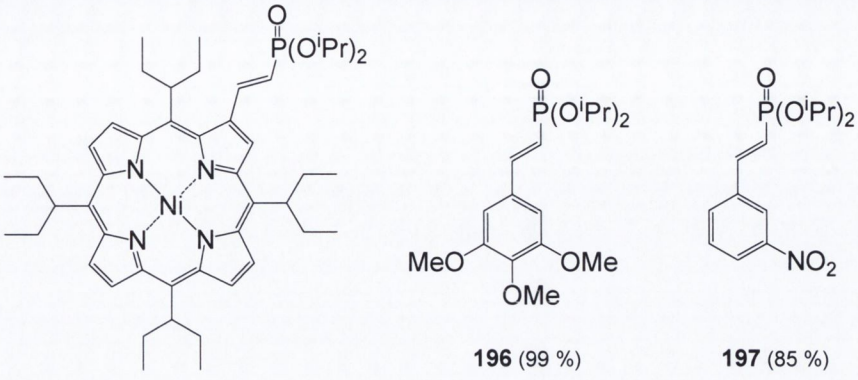



**124** **194** (73 %)

**Scheme 5.5.** Synthesis of alkenylphosphonate **194**.

The alkenylphosphono compounds **195-197**, illustrated in Figure 5.2, were synthesised following this same procedure and were isolated in high yields ranging from 80-99 %. To investigate the scope of the reaction compound **195** was synthesised starting from [2-formyl-5,10,15,20-tetrakis(1-ethylpropyl)porphyrinato]nickel(II), mainly because the reactivity of meso- and β-positions differ.[227] Unfortunately, subsequent formation of the vinylanion which could then react with another aldehyde in a Baylis-Hillman type reaction[228,229] to give the required hydroxyalkenylphosphonates, failed. Lithium di(*iso*-propyl)amide (LDA) and *tert*-butyllithium were used as bases to form the vinylanion. The reaction of alkenylphosphonoporphyrin **194**, LDA, and different aldehydes only resulted in the recovery of starting material. When *tert*-butyllithium was used for the initial step, the porphyrin was destroyed. In the reversed case, **196** and **197** were reacted with the lithium base and formylporphyrin **124** was added. However, no reaction occurred and only

starting material was recovered. A plausible reason for the reactive reticence may be steric hindrance caused by the bulky *iso*-propoxy residues attached to the phosphorus atom.




**195** (80 %) **196** (99 %) **197** (85 %)

**Figure 5.2.** Synthesised alkenylphosphonates.

### *5.2.4.1 $^1$H NMR spectroscopy*

Figure 5.3 shows the $^1$H NMR spectrum of compound **194** in which diagnostic resonances for the *iso*-propyl and the vinyl protons are clearly identifiable. The alkenyl proton adjacent to the phosphonate group appears as a double-doublet at 9.79 ppm with coupling constants of $^2J_{HP}$ = 22 Hz and $^3J_{HH}$ = 17 Hz and the vicinal proton appears as a triplet with a coupling constant of $^3J_{HH}$ = 17 Hz. The proton-proton coupling constant of 17 Hz indicates an *E*-conformation for the olefinic double bond.

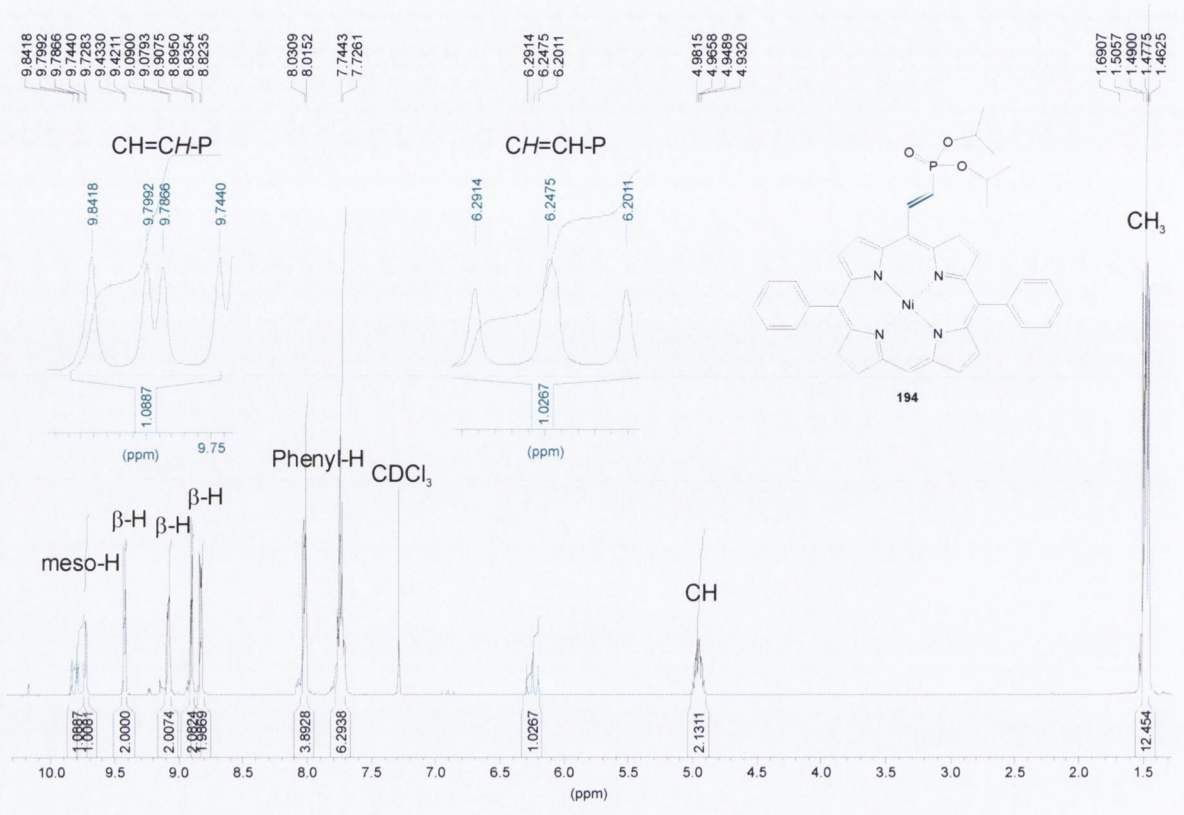



**Figure 5.3.** $^{1}$H NMR spectrum of **194** with 32 scans, 400 MHz in $CDCl_3$, at rt.

### *5.2.4.2 UV-vis spectroscopy*

Figure 5.4 shows the UV-vis spectra of compounds **105** and **194**. The introduction of the new chromophoric group, the alkenylphosphonate substituent, results in a marked bathochromic shift of the Soret band from 400 to 415 nm.

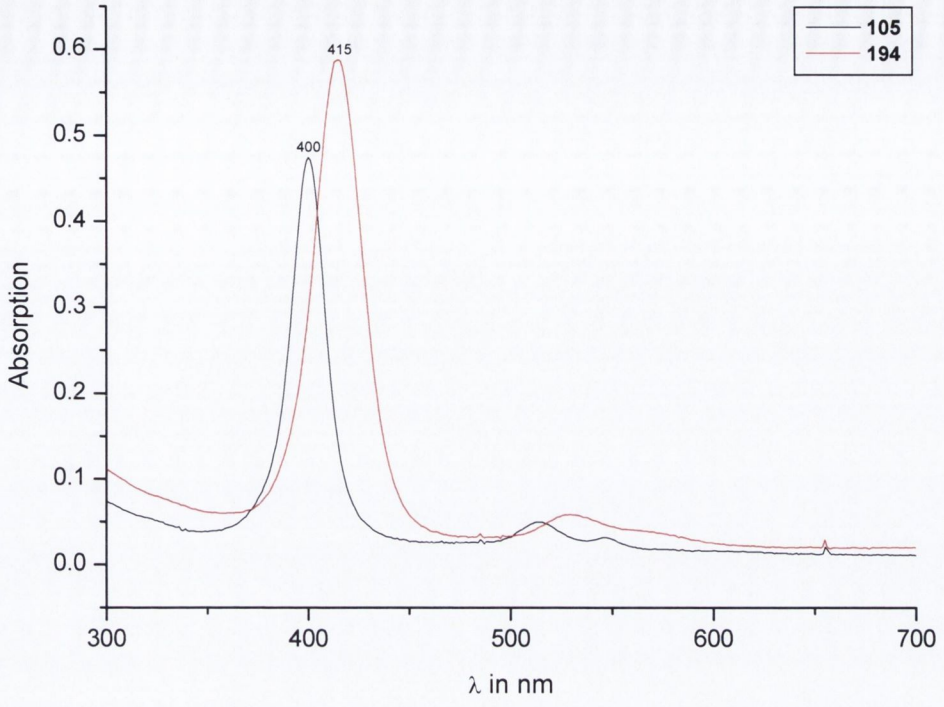
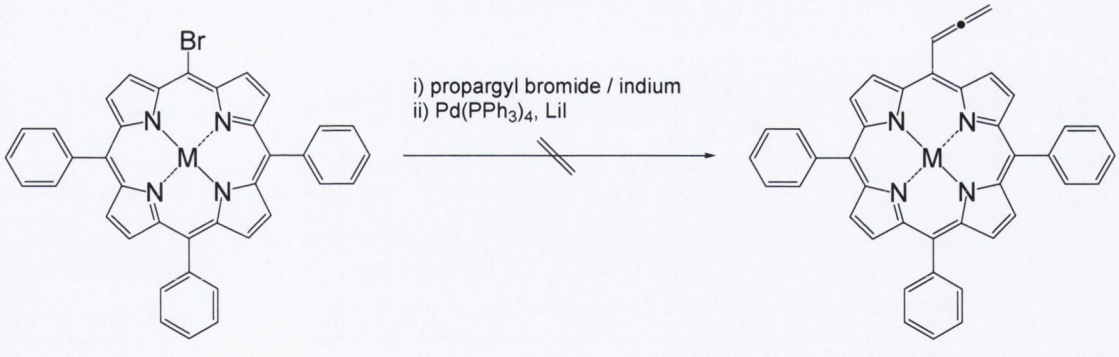



**Figure 5.4.** UV-vis spectra of compounds **105** and **194** in $CH_2Cl_2$ at rt. Baselines have been adjusted arbitrarily.

### 5.2.5 Palladium-catalysed cross-coupling reactions

A relatively new approach towards the formation of allenylporphyrins using allenylindium reagents, which can be generated *in situ* from propargyl bromide, has been reported.[230]




**192** M = 2H
**198** M = Ni(II)
**199** M = Zn(II)

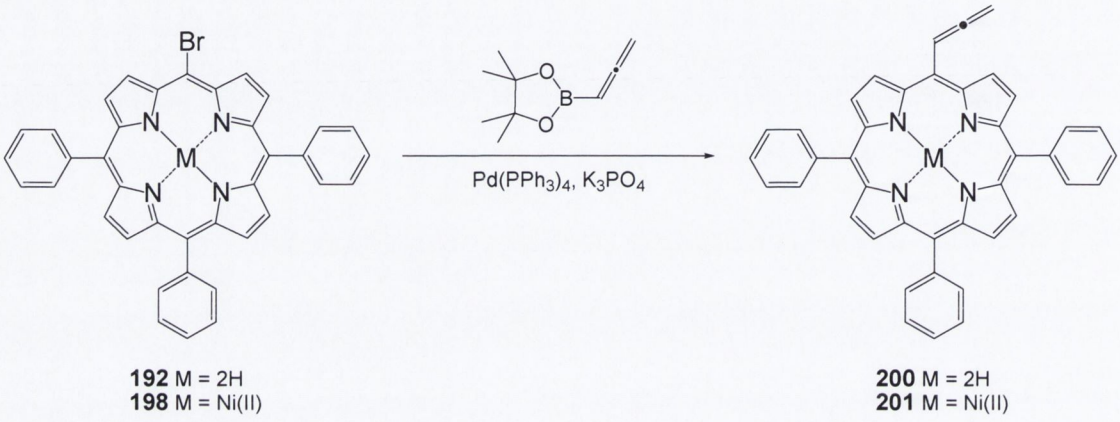
**200** M = 2H
**201** M = Ni(II)
**202** M = Zn(II)

**Scheme 5.6.** Attempted Pd-catalysed coupling reaction of allenylindium and bromoporphyrins **192**, **198** and **199**.

In an analogous fashion, the Pd-catalysed coupling of the allenylindium reagent with the bromoporphyrins **192**, **198** and **199** in DMF at rt and under reflux in an argon atmosphere was attempted, but the desired products **200**-**202** were not detected (Scheme 5.6).

Suzuki cross-coupling reactions have been successfully applied in the field of porphyrin chemistry, particularly in the synthesis of β-arylsubstituted porphyrins,[231-233] but also for

the preparation of meso-substituted porphyrins,[83,234,235] and the recent commercial availability of the allenyl boronic acid pinacol ester offered another promising route for the synthesis of allenylporphyrins. Consequently, the bromoporphyrins **192** and **198** were reacted with the allenyl compound under the same Suzuki cross-coupling reaction conditions [$Pd(PPh_3)_4$ catalyst, potassium phosphate base] (Scheme 5.7), that were successfully employed by Shi and Boyle for the preparation of asymmetrically substituted meso-phenylporphyrins.[235]




**192** M = 2H
**198** M = Ni(II)

**200** M = 2H
**201** M = Ni(II)

**Scheme 5.7.** Suzuki cross-couplings with allenyl boronic acid pinacol ester.

Using this protocol, the free base porphyrin **200** could not been obtained, however, the nickel(II) porphyrin **201** was isolated in 9 % yield. To increase the yield, the base was changed to the milder potassium carbonate, but by applying this modification no allenylporphyrin **201** was formed. So far, it has not been possible to optimise the procedure to increase the yield further.

### *5.2.5.1 $^1$H NMR spectroscopy*

Figure 5.5 shows the $^1$H NMR spectrum of **201**. The allene shows the characteristically large coupling constant between the protons at the opposite ends of the cumulated π-system, with an exceptionally large four bond coupling constant of $^4J_{HH}$ = 6 Hz. Allenes show one of the largest reported long-range couplings and this is attributed to the σ-π interaction between the electrons of the C-H bond and the double bond furthest from it. The vinylic proton resonances at 8.31 ppm. The position of the vinyl proton resonance in allenes is shifted to higher field than in simple olefins and indicates that the central sp-hybridised carbon atom exerts a long-range shielding of the terminal protons.

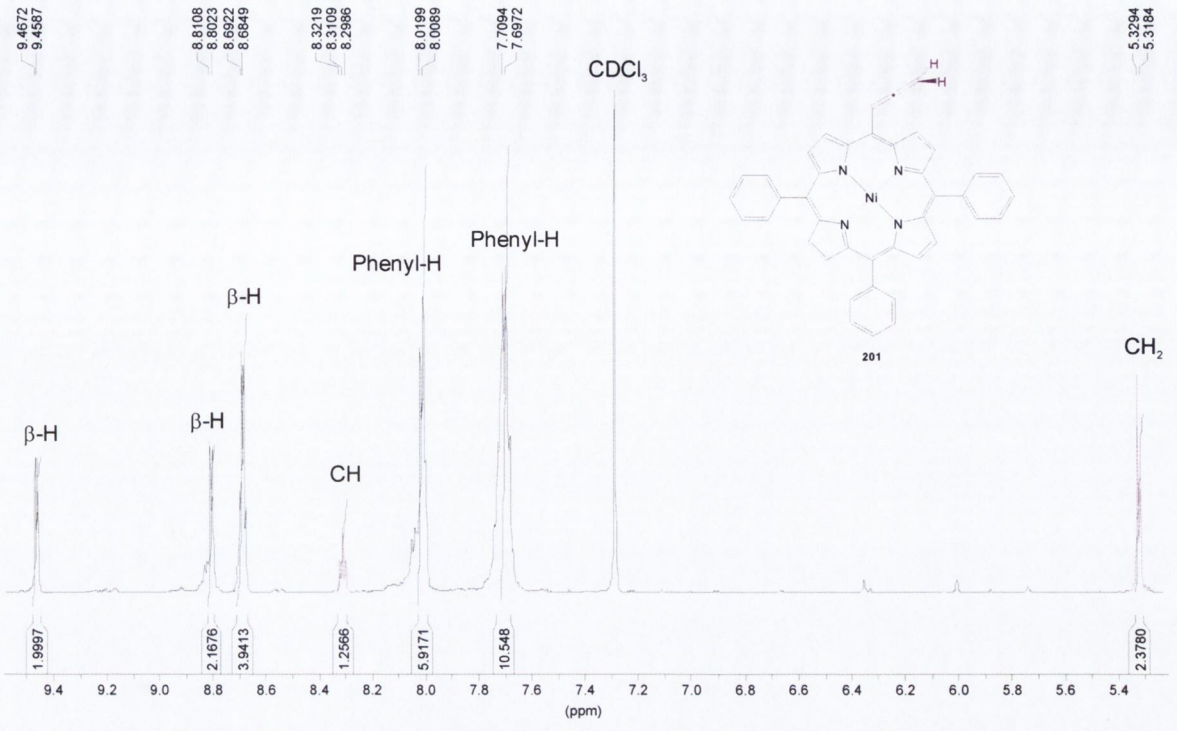



**Figure 5.5.** $^{1}$H NMR spectrum of **201** with 32 scans, 600 MHz in $CDCl_3$, at rt.

### *5.2.5.2 UV-vis spectroscopy*

Figure 5.6 shows the electronic absorption spectra of (5,10,15-triphenylporphyrinato)nickel(II) and the allenylporphyrin **201**. The Soret band is shifted bathochromically by approximately 10 nm as a result of the introduction of the allene residue.

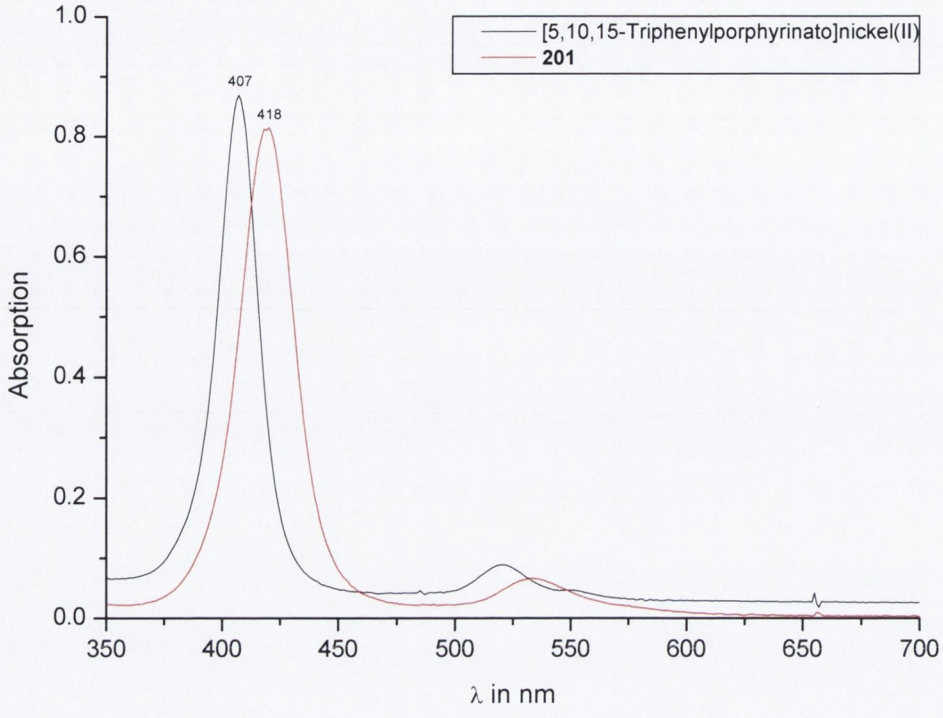



**Figure 5.6.** UV-vis spectra of (5,10,15-triphenylporphyrinato)nickel(II) and **201** in $CH_2Cl_2$ at rt. Baselines have been adjusted arbitrarily.

### *5.2.5.3 IR spectroscopy*

The infrared (IR) spectrum of allenylporphyrin **201** is illustrated in Figure 5.7.

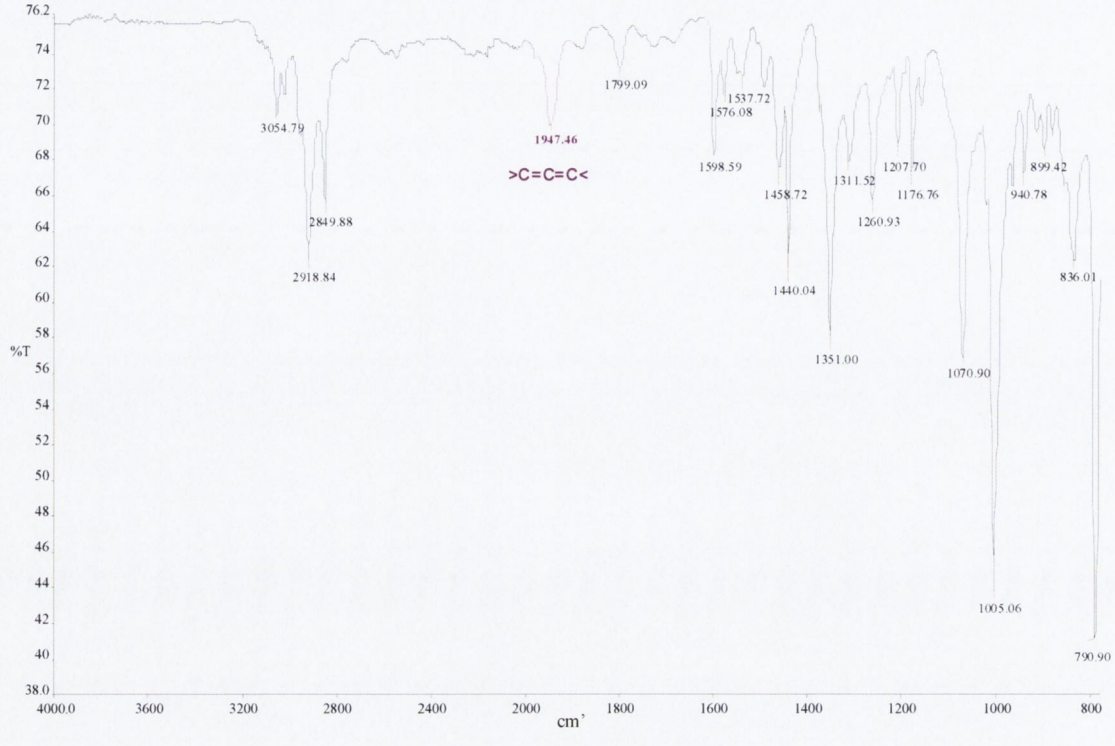



**Figure 5.7.** FT-IR spectrum of **201** at rt.

The most typical infrared absorption for allenes appears in the region of 1930-1980 $cm^{-1}$ and symbolises an asymmetric stretching mode along the >C=C=C< axis. It is commonly called the allene band and appears at 1947 $cm^{-1}$ for compound **201**.[236]

## 5.3 Conclusions

A number of synthetic methods were employed with the aim of preparing novel allenylporphyrins. The most common way to synthesise allenes uses propargyl electrophiles that have a terminal leaving group. Sonogashira cross-coupling was employed to introduce the propargyl substituent into the porphyrin moiety using bromoporphyrins **179** and **180** as precursors. However, due to numerous side reactions, the desired products were not isolated.

The second method attempted exploit the carbene rearrangement of the Doering-Moore-Skattebøl reaction. The first step required the synthesis of cyclopropylporphyrins *via* carbenes and porphyrins **157** and **190**, containing unsaturated groups at the meso-position, were used as starting materials. The necessary carbenes were generated *in situ* from chloroform or bromoform and a strong base, however, no addition to the double bond occurred.

The elimination of geminal dihalo groups may also lead to allenes and a Heck reaction was used to introduce the 2,3-dichloro-1-propenyl residue into the meso-position of porphyrin **192**. Unfortunately, this method also failed to generate the desired allenylporphyrin.

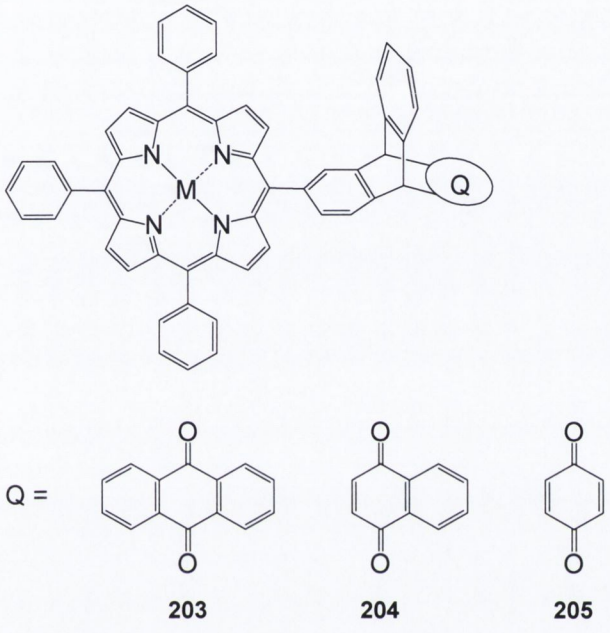
A more recently reported synthetic strategy uses two Horner-Wadsworth-Emmons reactions. The first HWE reaction resulted in the alkenylphosphono compounds **195-197** in high yields, but further reactions did not occur and the desired allenylporphyrins could not be formed in this way.

Pd-catalysed reactions were also attempted. Although, the indium-mediated Pd-catalysed reaction did not give the target compound, Suzuki cross-coupling could be applied successfully. The reaction between commercially available allenyl boronic acid pinacol ester and bromoporphyrin **198** resulted in the allenylporphyrin **201** in 9 % yield.

# CHAPTER 6:
# Porphyrin trimers

## 6.1 Basic principles

Wasielewski and Niemczyk first introduced a triptycene residue into the porphyrin moiety in 1984.[237] A quinone substituent was incorporated into the triptycene group, so that the functionalised molecules **203-205** possessed a porphyrin electron donor and a quinone electron acceptor (Figure 6.1).

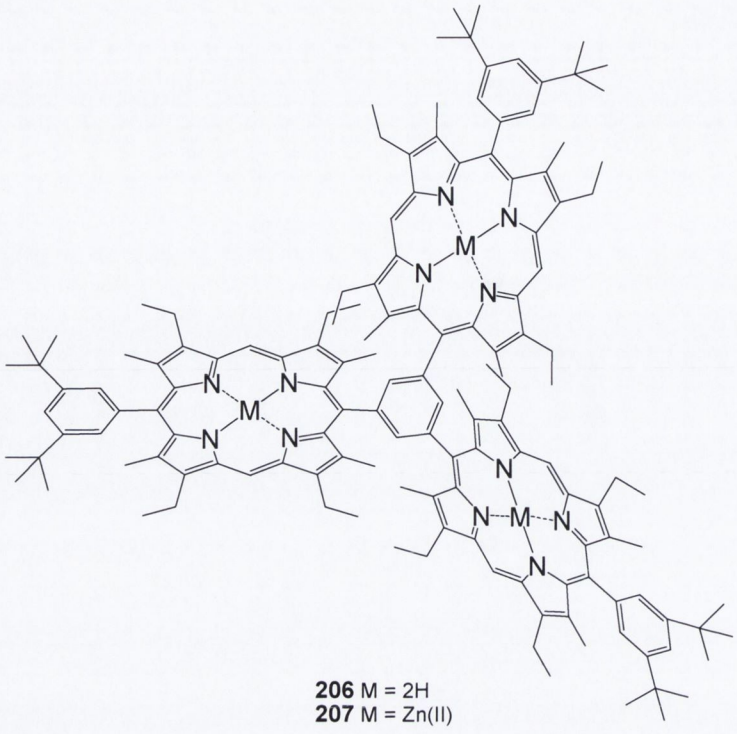



**203** **204** **205**

**Figure 6.1.** Structures of porphyrins covalently linked to quinone systems.

The meso-triphenyltriptycenylporphyrin-quinones **203-205** were prepared by mixed condensation reactions of pyrrole, benzaldehyde and the corresponding triptycene-quinone aldehyde. The resulting porphyrins were used for the study of photoinduced electron transfer reactions, as they represented model systems with well-defined donor-acceptor distances and orientations.[238-240]

Osuka *et al.* later described the first porphyrin oligomer in which three porphyrin units were attached to one benzene ring (Figure 6.2).[241] The porphyrin trimers **206** and **207** were obtained after an 11-step synthesis in overall yields of 13 %.




**206** M = 2H
**207** M = Zn(II)

**Figure 6.2.** Structure of porphyrin trimers **206** and **207**.

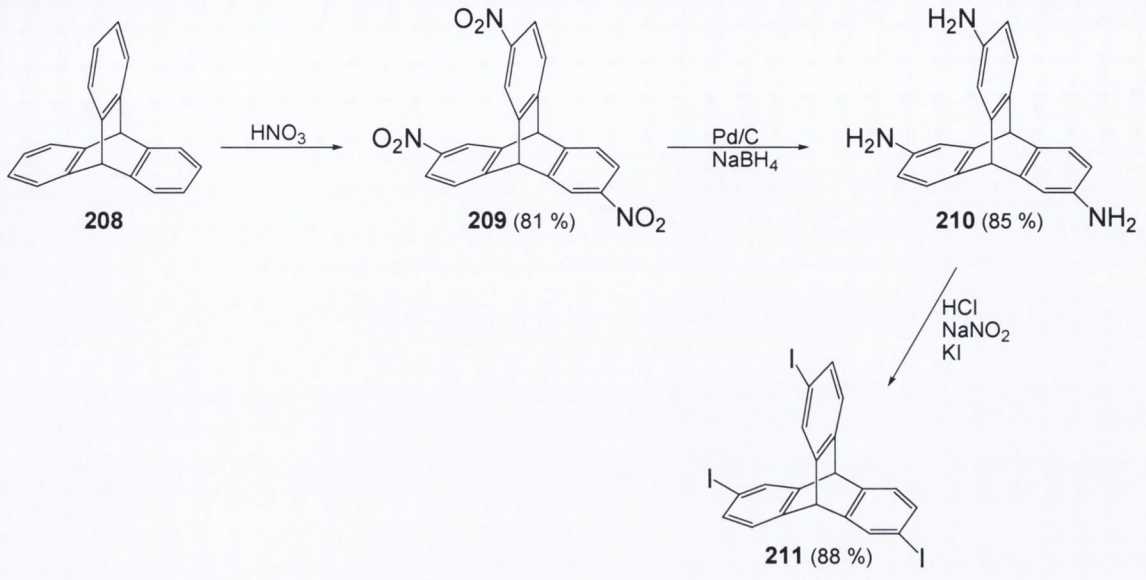
Herein is described an attempt to prepare porphyrin trimers in which each porphyrin unit is covalently linked to a central triptycene residue *via* Suzuki cross-coupling reaction. Suzuki cross-coupling with borylated porphyrins as synthons have been reported previously.[242-245] For instance, such reactions were used for the coupling of two porphyrins linked by an additional molecule, e.g. phenyl or diphenyl or derivatives of carbazole, dibenzofuran, or xanthene.[242,246,247]

Compounds with highly conjugated $\pi$ systems have attracted considerable attention as promising organic materials for electronic devices[248,249] and there has been increasing interest in the design and construction of porphyrin arrays with well-defined geometries for this purpose.[250] Multi-porphyrin architectures are desirable systems as they provide rigid frameworks *via* relatively easy synthetic pathways. Furthermore, the antenna chlorophylls in photosynthetic bacteria are arranged as macrorings to absorb and transfer solar energy efficiently.[251] This biological importance of multi-porphyrin arrays makes them an attractive research target.

## 6.2 Synthetic studies

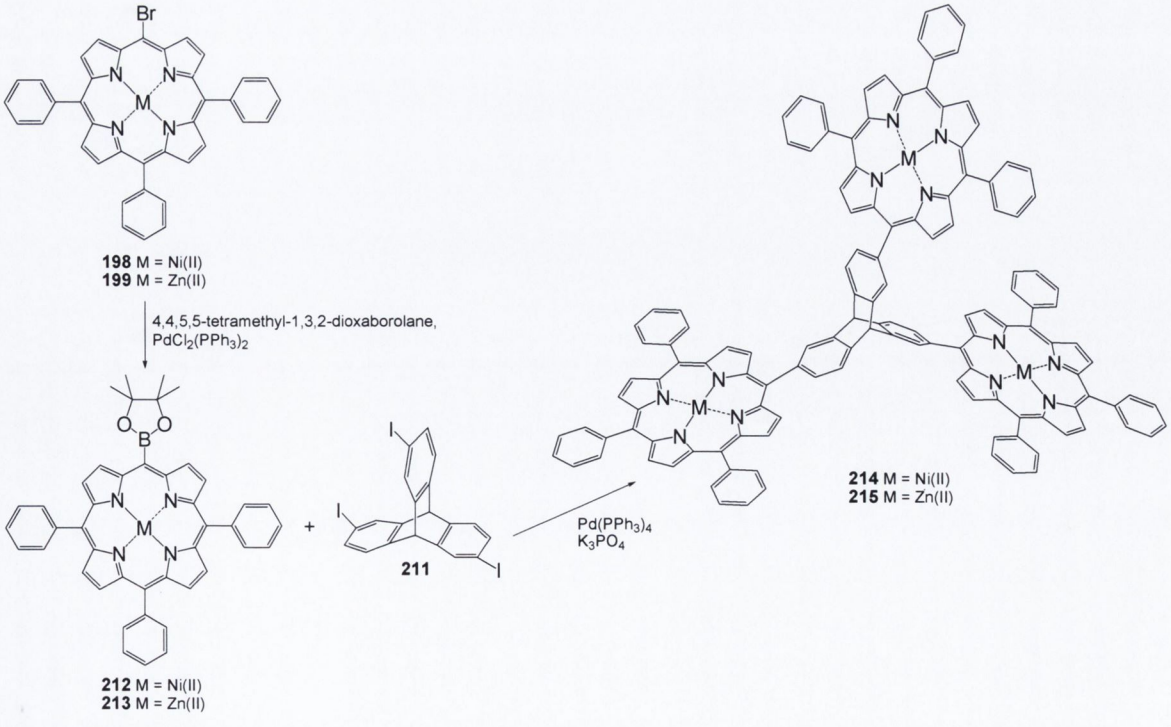
Firstly, commercially available triptycene **208** was reacted with nitric acid under reflux conditions to obtain the 2,6,14-trinitrotriptycene **209** in 81 % yield according to a procedure detailed by Zhang *et al.*[252] The nitro groups were subsequently reduced to amino groups to afford 2,6,14-triaminotriptycene **210**. This was followed by the

Sandmeyer reaction,[253,254] resulting in the formation of 2,6,14-triiodotriptycene **211** in an overall yield of 61 %.



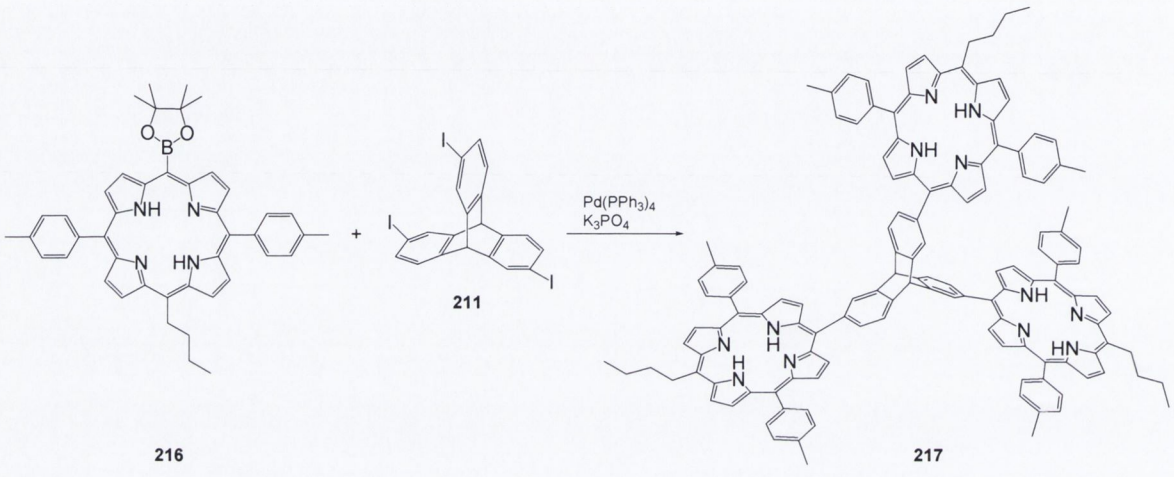

**Scheme 6.1.** Three-step synthesis of 2,6,14-triiodotriptycene **211**.

Furthermore, bromoporphyrins **198** and **199** were reacted with 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (pinacolborane) under Pd-catalysed conditions in a manner similar to that described by Therien and co-workers.[242] Debromination of the starting material was a competitive reaction, thus a ten-fold excess of pinacolborane was used.




**Scheme 6.2.** Formation of triptycene-linked porphyrin trimers **214** and **215** *via* Suzuki cross-coupling.

The borylated porphyrins **212** and **213** were obtained in 51 and 29 % yield, respectively. In the following step, **212** and **213** were reacted with 2,6,14-triiodotriptycene **211** in a Suzuki cross-coupling reaction using conditions analogous to these described by Chng *et al.* for the preparation of 4,6-bis[5-(10,15,20-trimesitylporphyrinyl)]dibenzofuran.[246] Following work-up, the desired porphyrin trimers **214** and **215** were isolated in 22 and 18 % yield, respectively.




**Scheme 6.3.** Synthesis of triptycene-linked porphyrin **217** *via* Suzuki cross-coupling from **216** with 2,6,14-triiodotriptycene **211**.

Scheme 6.3 shows the synthesis of the free base porphyrin trimer **217**. The reaction was performed the same way as described for the metallated porphyrins **214** and **215**. The Suzuki cross-coupling reaction of **216**[255] and 2,6,14-triiodotriptycene **211** resulted in **217** in 16 % yield. The yield of the free base trimer is comparable to both metallated trimers, which leads to the conclusion that the inserted metal has no major influence on the reaction process.

## 6.3 Spectroscopic studies

### 6.3.1 $^1$H NMR spectroscopy

Figure 6.3 shows the $^1$H NMR spectrum of compound **217** in which the resonances for the CH-protons of the triptycene molecule are clearly visible at 6.13 and 6.26 ppm. The six NH-protons appear at -2.60 to -2.67 ppm as three 2H singlets, with each resonance being attributed to one porphyrin macrocycle. This shows distinctly that three porphyrin molecules are attached to one triptycene residue. Other resonances in the spectrum are not highly resolved due to the size and rigidity of the porphyrin oligomer, but the number and integration of the existing signals are consistent with compound **217**. Moreover, the molecular composition is confirmed by high resolution mass spectrometry (HRMS) measurements.

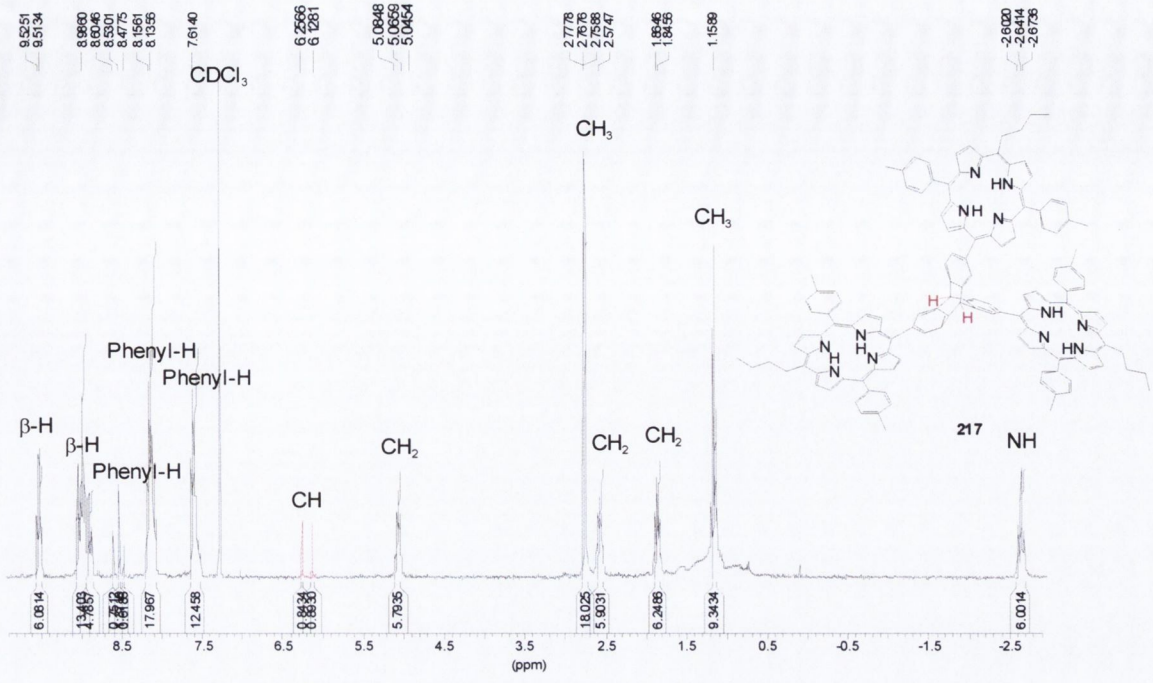



**Figure 6.3.** $^{1}$H NMR spectrum of **217** with 32 scans, 400 MHz in $CDCl_3$, at rt.

### 6.3.2 UV-vis spectroscopy

The electronic absorption spectra were measured for all three porphyrin trimers and are illustrated in Figure 6.4. All three compounds show Soret bands that are shifted by approximately 5 nm to higher wavelengths than those of the corresponding monomeric precursor porphyrins.

Osuka *et al.* described a splitting of the Soret band for the metallated compound **207** due to exciton coupling.[241] However, this phenomenon was not observed for the free base porphyrin **206**. It is noteworthy that, in comparison, the metallated trimers linked to triptycene **214** and **215** showed only one distinct Soret band, whilst the free base trimer **217** showed a split Soret band with absorptions at 422 and 446 nm.

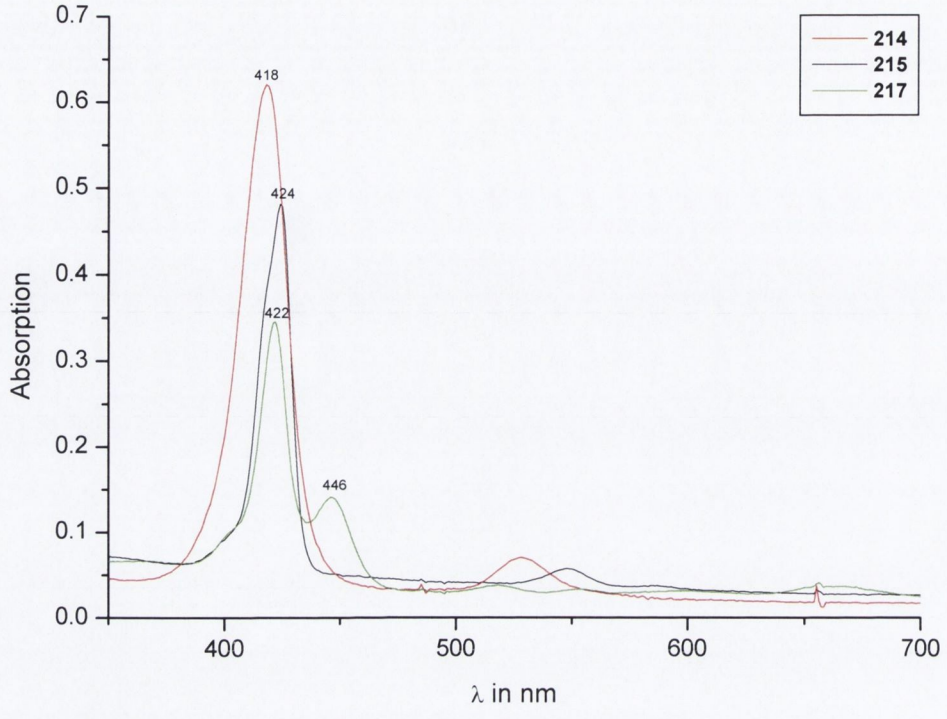



**Figure 6.4.** UV-vis spectra of porphyrin trimers **214**, **215** and **217** in $CH_2Cl_2$ at rt. Baselines have been adjusted arbitrarily.

## 6.4 Conclusions

This chapter describes the synthesis of porphyrin trimers linked by a central triptycene molecule. Firstly, 2,6,14-triiodotriptycene **211** was generated in a three-step synthesis from commercially available triptycene. The borylated porphyrins **212**, **213** and **216** were then prepared and treated with **211** under Suzuki cross-coupling conditions. The desired porphyrin trimers **214**, **215** and **217** were isolated in unoptimised yields of 16-22 %. No significant difference between the reaction of free base, zinc(II) or nickel(II) porphyrin was hereby determined, which implicates that this reaction is applicable to different porphyrin systems. This protocol therefore provides a straightforward approach for obtaining porphyrin trimers.

It is also conceivable to introduce bromo or iodo residues in different positions on the triptycene molecule and to consequently extend the synthesis to the preparation of several different oligomeric porphyrin-triptycene arrays.

# CHAPTER 7:
# Experimental

## 7.1 Instrumentation and general considerations

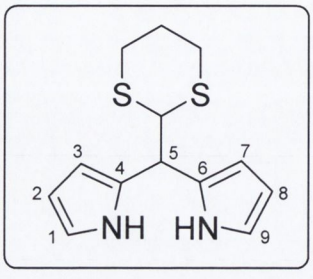
$^{1}H$ and $^{13}C$ NMR spectra were recorded on Bruker Avance 300 (300 MHz for $^{1}H$ NMR; 63 MHz for $^{13}C$ NMR) (Potsdam University) or Bruker DPX 400 (400.13 MHz for $^{1}H$ NMR; 100.61 MHz for $^{13}C$ NMR) and/or Bruker AV 600 (600.13 MHz for $^{1}H$ NMR; 150.90 MHz for $^{13}C$ NMR) instruments (Trinity College Dublin). Chemical shifts are reported in ppm referred to tetramethysilane set at 0.00 ppm. Data are reported as follows: chemical shift, multiplicity (s: singlet, d: doublet, dd: double-doublet, t: triplet, br: broad, m: multiplet), integration, coupling constants (*J* in Hz) and assignment. High resolution mass spectrometry and low resolution mass spectrometry were recorded on Finnigan SSQ 710 GC/MS or GC–TOF and ESI / APCI-Q-$TOF_{micro}$ (Potsdam University) or LCT Orthogonal Acceleration TOF Electrospray mass spectrometer (TCD) or Micromass/Waters Corp. USA Quattro *micro*™ LC-MS/MS systems (UCD), respectively. UV-vis measurements were performed on Carl-Zeiss-Jena® Diodearray Spectrometer Specord S100 (Potsdam University) or Shimadzu Multispec-1501 (TCD). IR spectroscopy was performed using Perkin Elmer Spektrum 100, FT-IR spectrometer. X-ray crystallography was carried out on CCD X-ray Diffractometer Rigaku Saturn-724. Microanalysis was measured on Exeter Analytical CE-440 elemental analyser (UCD). Melting points were acquired on Stuart SMP10 melting point apparatus and are uncorrected. Thin layer chromatography (TLC) was performed on silica gel $60F_{254}$ (Merck) precoated aluminium sheets. Chromatography on silica gel was carried out using a forced flow of the indicated solvent system on either Fluka Silica Gel 60 (230-400 mesh) or Fluka $AlB_{2B}OB_{3B}$ (basic). Tetrahydrofuran (THF) was distilled from sodium/benzophenone under argon. All commercial chemicals were supplied by Aldrich and used without further purification. Other conditions were as described before.[256]

## 7.2 Starting materials

Dipyrromethane **48**,[31] 5-phenyldipyrromethane,[31] 5,15-diphenylporphyrin **93**,[257,258] 5,15-bis(3-methoxyphenyl)porphyrin **94**,[259-261] 5,15-di(*iso*-butyl)porphyrin **95**,[259,261] 5,15-dihexylporphyrin,[259,261] 5,15-bis(1-ethylpropyl)porphyrin[46,260], 5,10-diphenylporphyrin **121**,[262,263] 5,10,15-triphenylporphyrin[131,264] were prepared, metallated[265] or brominated[266] according to literature procedures.

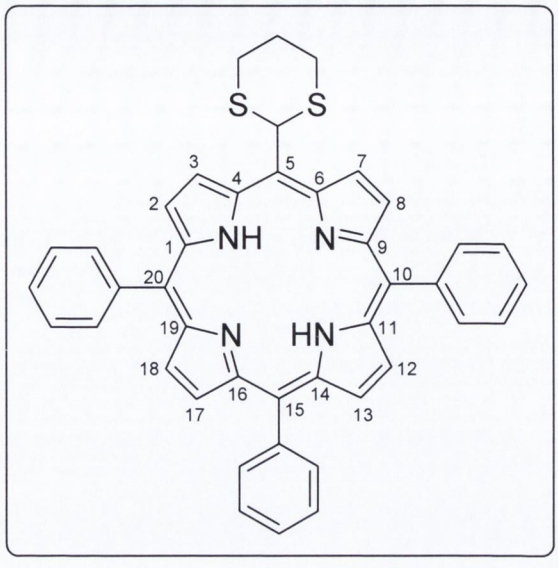
## 7.3 Dithianylporphyrins

### 5-(1,3-Dithian-2-yl)-dipyrromethane 85



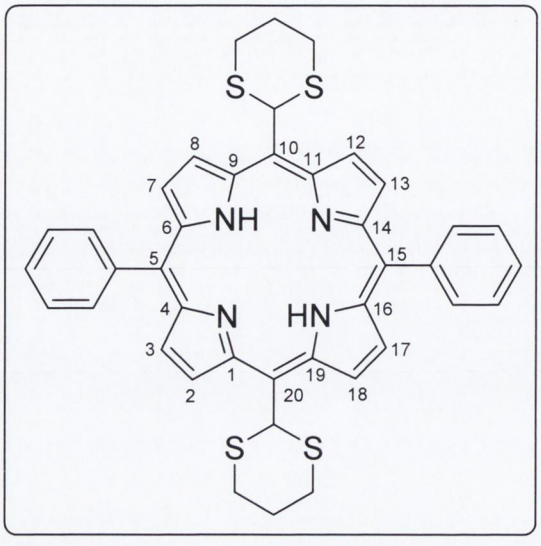

A mixture of 1.48 g (10 mmol) 2-formyl-1,3-dithiane **82** and 400 ml pyrrole was purged with argon for 10 min, followed by addition of 500 µl $BF_3$•$Et_2O$. After 20 min the same amount of acid was added again. After 40 min the reaction was terminated by addition of 16.7 ml 0.1 M NaOH. The solution was washed several times with water and the solvent removed under reduced pressure yielding a yellow oil as crude product. Column chromatography (silica gel, *n*-hexane:$CH_2Cl_2$, 1:2, 1% $NEt_3$, v/v) followed by recrystallisation from *n*-hexane gave a white solid in 2.54 g, (9.62 mmol, 96 %): *Mp* 51 °C; $^1$H NMR (270 MHz, $CDCl_3$, 47 °C): $\delta$= 1.86 ppm (m, 1H, $CH_2$-C$H_{2eq}$-$CH_2$), 2.10 (m, 1H, $CH_2$-C$H_{2ax}$$CH_2$), 2.90 (m, 4H, S-C$H_2$), 4.52 (d, 1H, $^3J$=4.4 Hz, C-C*H*-C), 4.66 (d, 1H, $^3J$=4.4 Hz, S-C*H*-S), 6.11 (m, 2H, 2,8-CH-CH=C*H*), 6.19 (m, 2H, 1,9-C*H*), 6.71 (m, 2H, 3,7-CH=C*H*), 8.49 (br s, 2H, N*H*); $^{13}$C NMR (126 MHz, $CDCl_3$, 47 °C): $\delta$= 25.49 ppm, 31.15, 43.24, 53.37, 107.92, 108.18, 117.40, 129.52; MS (200 °C, 80 eV): *m/z* = 264 (77) $[M]^{\bullet+}$, 145 (100) $[M\text{-}C_4H_7S_2]^{\bullet+}$, 119 (80) $[M\text{-}C_9H_9N_2]^{\bullet+}$; HRMS $[C_{13}H_{16}N_2S_2]$: calcd 264.0755 found 264.0775; [$C_{13}H_{16}N_2S_2$, 264.40 g mol$^{-1}$]: anal. calcd C 59.05, H 6.10, N 10.59, found C 59.35, H 6.27, N 10.32.

**5-(1,3-Dithian-2-yl)-10,15,20-triphenylporphyrin 91**



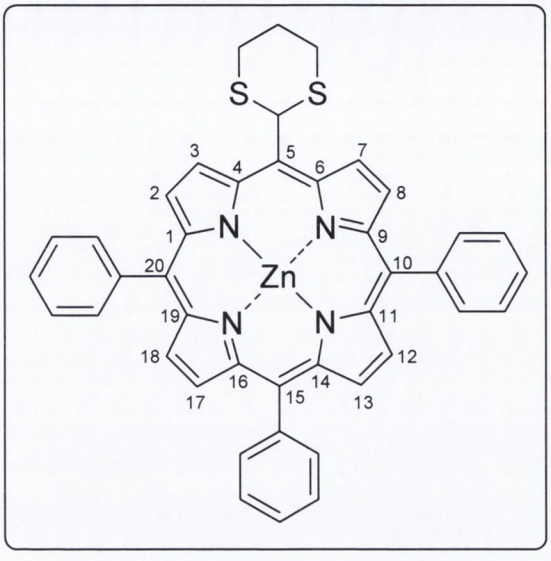

A solution of 2-formyl-1,3-dithiane **82** (1g, 6.7 mmol) and 5-phenyldipyrromethane (1.49 g, 6.7 mmol) was dissolved in dry dichloromethane (1.7 l) under argon and exclusion of light. After 1 h TFA (110 µl) was added and the reaction mixture was stirred for 12 h. The reaction was quenched with DDQ (3.9 g, 17.2 mmol), followed by filtration through a silica plug. The product was purified by column chromatography on silica gel with dichloromethane : *n*-hexane (2:1, v/v). The product was received as the first fraction after recrystallisation from dichloromethane/methanol as purple crystals: yield: 70 mg (0.11 mmol, 3 %): *Mp* > 310 °C; $^1$H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta$= -2.65 ppm (br s, 2H, N*H*), 2.50 (m, 2H, $CH_2$-C*H*$_2$-$CH_2$), 3.28 (m, 2H, S-C$H_{2eq}$), 3.61 (m, 2H, S-C$H_{2ax}$), 7.72 (s, 1H, S-C*H*-S), 7.77 (m, 9H, Ar$_H$), 8.20 (m, 6H, Ar$_H$), 8.79 (m, 4H, 12,13,17,18-$H_\beta$), 8.92 (d, 2H, $^3J$=4.4 Hz, 2,8-$H_\beta$), 10.02 (m, 2H, 3,7-$H_\beta$); $^{13}$C NMR (63 MHz, $CDCl_3$, 20 °C): $\delta$= 26.17 ppm, 35.76, 54.06, 114.05, 120.32, 121.19, 126.61, 126.74, 127.75, 131.17, 134.49, 141.73, 142.29; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 424 nm (5.41), 518 (4.24), 552 (3.83), 593 (3.74), 650 (3.57); MS (pos. FAB, 3 kV), *m/z* (%)= 657 (100) $[M+H]^+$, 656 (73) $[M]^{\bullet+}$, 580 (37) $[M\text{-}C_6H_5, +H]^{\bullet+}$, 503 (28) $[M\text{-}2xC_6H_5+H]^+$; HRMS [$C_{42}H_{32}N_4S_2$]: calcd 656.2068, found 656.2043; [$C_{42}H_{32}N_4S_2$, 656.86 g mol$^{-1}$]: anal. calcd C 76.80, H 4.91, N 8.53, found C 76.95, H 5.21, N 8.88.

**5,15-Diphenyl-10,20-bis(1,3-dithian-2-yl)porphyrin 92**




A solution of 2-formyl-1,3-dithiane **82** (1g, 6.7 mmol) and 5-phenyldipyrromethane (1.49 g, (6.7 mmol) was dissolved in dry dichloromethane (1.7 l) under argon and exclusion of light. After 1 h TFA (110 µl) was added and the reaction mixture was stirred for 12 h. The reaction was quenched with DDQ (3.9 g, 17.2 mmol), followed by filtration through a silica plug. The product was purified by column chromatography on silica gel with dichloromethane : *n*-hexane (2:1, v/v). The product was received as second fraction after recrystallisation from dichloromethane/methanol as purple crystals in (40 mg, 0.057 mmol) 2 % yield: *Mp* > 310 °C; $^{1}$H NMR (300 MHz, $CDCl_3$, 47 °C): $\delta$= -2.59 ppm (br s, 2H, N-H), 2.47 (m, 4H, $CH_2$-$CH_2$-$CH_2$), 3.27 (m, 2H, S-C$H_{2eq}$), 3.60 (m, 2H, S-C$H_{2ax}$), 7.69 (s, 2H, S-C*H*-S), 7.75 (m, 6H, $Ar_H$), 8.14 (m, 4H, $Ar_H$), 8.78 (d, 4H, $^{3}J$=5.1 Hz, 3,7,13,17-$H_\beta$), 9.90 (br s, 4H, 2,8,12,18-$H_\beta$); $^{13}$C NMR (63 MHz, $CDCl_3$, 47°C): $\delta$= 26.17 ppm, 35.72, 53.75, 115.06, 120.42, 126.57, 127.81, 130.06, 134.43, 142.37, 146.32; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 423 nm (5.31), 521 (4.24), 556 (3.92), 598 (3.78), 654 (3.71), MS (pos. FAB, 3 kV): *m/z* (%)= 699 (100) $[M+H]^+$, 698 (73) $[M]^{\bullet+}$; HRMS [$C_{40}H_{34}N_4S_4$]: calcd 698.1666, found 698.1644; [$C_{40}H_{34}N_4S_4$, 698.98 g $mol^{-1}$]: anal. calcd C 68.73, H 8.02, N 4.90, found C 68.52, H 8.25, N 4.77.

**[5-(1,3-Dithian-2-yl)-10,15,20-triphenyl)porphyrinato]zinc(II) 117**

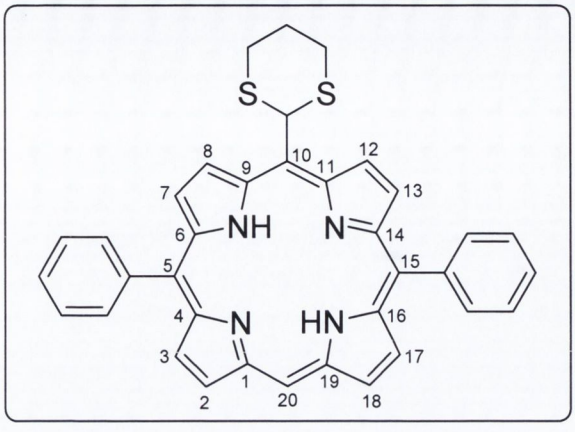



To a solution of 5-(1,3-dithian-2-yl)-10,15,20-triphenylporphyrin **91** (50 mg, 0.08 mmol) in 10 ml dichloromethane under argon at rt methanol (0.5 ml) and zinc acetate (200 mg, 1.09 mmol) were added and the mixture was stirred for 30 min. The organic phase was then washed with water and dried over sodium sulphate. After recrystallisation from dichloromethane/methanol purple crystals were obtained. Yield: 29 mg (1.43 mmol, 53 %) *Mp* > 300 °C, $R_f$=0.57 ($CH_2Cl_2$:*n*-hexane, 2:1, v/v), $^1$H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta$= 2.25 ppm (m, 2H, $CH_2$-C$H_2$-$CH_2$), 3.10 (m, 2H, S-C$H_2$), 3.58 (m, 2H, S-C$H_2$), 7.75 (m, 10H, S-C*H*-S, Ar$_H$), 8.15 (m, 6H, Ar$_H$), 8.76 (d, 2H, $^3J$=4.6 Hz, $H_\beta$), 8.82 (d, 2H, $^3J$=4.7 Hz, $H_\beta$), 8.95 (d, 2H, $^3J$=4.7 Hz, $H_\beta$), 9.76 (d, 2H, $^3J$=5.0 Hz, $H_\beta$); UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 425 nm (5.86), 555 (4.30), 600 (3.82); MS (ESI): *m/z* (%)= 718 (100) $[M]^{\bullet+}$; HRMS (EI) [$C_{42}H_{30}N_4S_2Zn$]: calcd 718.1203, found 718.1170.

**General procedure A – Synthesis of dithianylporphyrins *via* organolithium reagents**

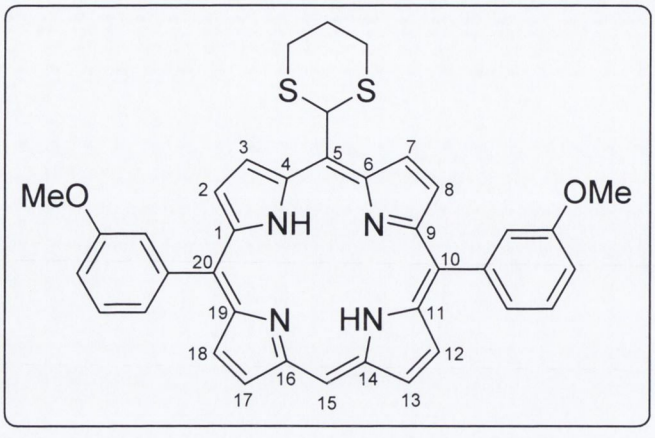
A dried out, septum-equipped Schlenk-flask under argon was charged with 1,3-dithiane (1.16 g, 9.64 mmol). The flask was evacuated for 30 min with an oil pump and 25 ml of freshly distilled THF was added. The solution was cooled to -40 °C and *n*-butyllithium (3.84 ml of a 2.5 M solution, 9.6 mmol) was added dropwise *via* a syringe through the septum. The reaction mixture was stirred for 2 h at -30 to -40 °C. The solution of the organometallic compound was cooled to -78 °C and mixed with a suspension (-78 °C) of 0.45 mmol porphyrin in 20 ml of absolute THF. After transfer of the porphyrin suspension, *N,N,N',N'*-tetramethylethylenediamine (0.25 ml, 1.6 mmol) was added and the reaction mixture turned dark-brown. After stirring for 1 min the cold bath was removed and the reaction mixture was stirred for 15 min. Water (6 ml) was added *via* a syringe resulting in an immediate colour change to dark-green. The mixture was stirred for 15 min at room temperature, followed by addition of 10 ml of a solution of DDQ (0.6 g in 10 ml THF, ca. 0.75 mmol) resulting in a colour change to purple. Stirring was continued for 15 min followed by filtration of the reaction mixture through 200 ml silica gel and washing with dichloromethane. The eluted porphyrin fractions were evaporated to dryness and washed with *n*-hexane (2 × 10 ml). The residue was purified by column chromatography on silica gel in dichloromethane : *n*-hexane 3:1, v/v and the target compounds obtained as the second fraction after recrystallisation from dichloromethane/methanol.

**5,15-Diphenyl-10-(1,3-dithian-2-yl)porphyrin 102**




5,15-Diphenylporphyrin **93** was reacted following procedure A, yield: 120 mg (0.207 mmol, 47 %) of purple crystals. *Mp* 290 °C; $R_f$=0.2 ($CH_2Cl_2$:*n*-hexane, 3:1, v/v); $^1$H NMR (250 MHz, $CDCl_3$, 20 °C): $\delta$= -3.03 ppm (br s, 2H, N*H*), 2.53 (m, 2H, $CH_2$-C$H_2$-$CH_2$), 3.31 (m, 2H, S-C$H_2$), 3.63 (m, 2H, S-C$H_2$), 7.78 (m, 6H, Ar$_H$), 7.87 (s, 1H, S-C*H*-S), 8.21 (m, 4H, Ar$_H$), 8.92 (dd, 4H, $^3J$=8.1 Hz, $^3J$=4.7 Hz, 2,3,17,18-$H_\beta$), 9.25 (d, 2H, $^3J$=4.6 Hz, 7,13-$H_\beta$), 9.71 (br s, 1H, 8- or 12-$H_\beta$), 10.12 (s, 1H, $H_{meso}$), 10.71 (br s, 1H, 8- or 12-$H_\beta$); $^{13}$C NMR (63 MHz, $CDCl_3$, 20 °C): $\delta$= 26.21 ppm, 35.87, 54.51, 105.74, 114.53, 126.74, 127.77, ~132, 134.60, 141.90; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 416 nm (5.49), 512 (4.02), 544 (3.23), 586 (3.45), 640 (2.72); MS (EI, 80 eV, 200 °C): *m/z* (%)= 580 (100) [$M^+$], 519 (33) [$M^+$–$C_2H_5S$], 506 (62) [$M^+$–$C_3H_6S$], 476 (86) [$M^+$–$C_3H_4S_2$], 462 (17) [$M^+$–$C_4H_6S_2$], 290 (8) [$M^{2+}$]; HRMS (EI) [$C_{36}H_{28}N_4S_2$]: calcd 580.1755, found 580.1772.

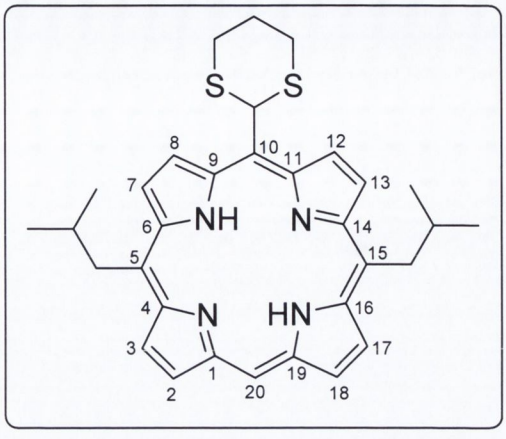
**5-(1,3-Dithian-2-yl)-10,20-bis(3-methoxyphenyl)porphyrin 103**




5,15-Bis(3-methoxyphenyl)porphyrin **94** was reacted following procedure A, yield: 15 mg (0.02 mmol, 4 %) of purple crystals; *Mp* 268 °C; $R_f$=0.09 ($CH_2Cl_2$:*n*-hexane, 1:1, v/v); $^1$H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta$= -3.03 ppm (br s, 2H, N*H*); 2.55 (m, 2H, $CH_2$-C$H_2$-$CH_2$), 3.33 (m, 2H, S-C$H_2$), 3.64 (m, 2H, S-C$H_2$), 4.00 (s, 6H, OC$H_3$), 7.37 (m, 2H, $Ar_H$), 7.69 (m, 2H, $Ar_H$), 7.82 (m, 5H, $Ar_H$ + S-C*H*-S), 8.98 (m, 4H, 12,13,17,18-$H_\beta$), 9.27 (d, 2H, $^3J$=4.5 Hz, 2,8-$H_\beta$), 9.65 (br s, 1H, 3- or 7-$H_\beta$), 10.14 (s, 1H, $H_{meso}$),10.63 (br s, 1H, 3- or 7-$H_\beta$); $^{13}$C NMR (63 MHz, $CDCl_3$, 20 °C): $\delta$= 35.88 ppm, 55.54, 113.71, 120.47, 127.55, 127.71, 127.80, 143.21, 158.02; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 417 nm (5.29), 513 (3.81), 557 (3.38), 588 (3.41), 648 (3.25); MS (EI, 80 eV, 200 °C): *m/z* (%)= 640 (2) $[M]^{\bullet+}$, 580 (5) [$M^+$-$C_2H_4S$], 522 (7) [$M^+$-$C_4H_6S_2$]; HRMS (EI) [$C_{38}H_{32}N_4O_2S_2$]: calcd 640.1967, found 640.1979.

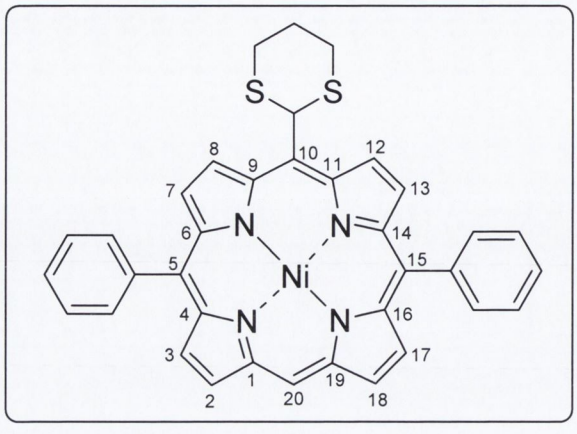
Alternatively this compound was prepared *via* demetallation of **115**. The nickel(II) complex **115** (70 mg, 0.1 mmol) was dissolved under argon in 15 ml dry dichloromethane and cooled to 0 °C. $BBr_3$ (4 ml) was added dropwise and the red solution turned green. After removal of the cold bath the mixture was stirred for 12 h at rt. Water was then added slowly for hydrolysis and the mixture was extracted with water (2 × 20 ml) and saturated $NaHCO_3$ solution (20 ml) and dried with $Na_2SO_4$. The solvent was removed under reduced pressure and recrystallisation from $CH_2Cl_2$/$CH_3OH$ gave 15 mg (0.02 mmol, 24%) of the title compound.

**5,15-Di(*iso*-butyl)-10-(1,3-dithian-2-yl)porphyrin 104**



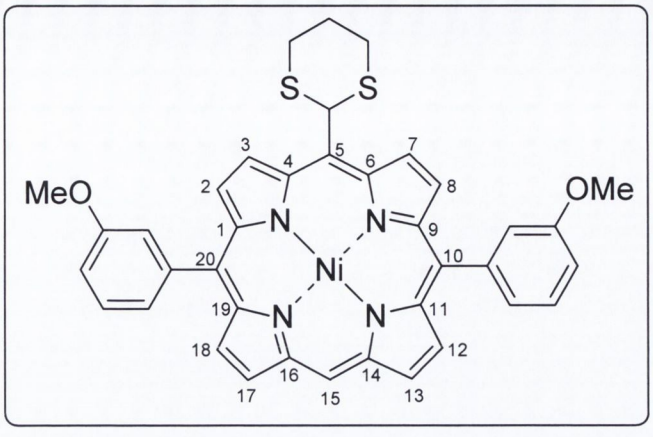

5,15-Di(*iso*-butyl)porphyrin **95** was reacted following procedure A, yield: 24 mg (0.044 mmol, 10 %) of purple crystals: *Mp* 268 °C; $R_f$=0.30 ($CH_2Cl_2$:*n*-hexane, 1:1, v/v); $^1$H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta$= -2.91 ppm (s, 2H, N*H*), 1.19 (d, 12H, $^3J$ = 6.6 Hz, $CH(CH_3)_2$), 2.57 (m, 2H, $CH(CH_3)_2$), 2.76 (m, 2H, $CH_2CH$), 3.35 (m, 2H, S-$CH_2$), 3.66 (m, 2H, S-$CH_2$), 4.81 (d, $^3J$=7.2 Hz, 4H, $CH_2$-CH), 7.89 (s, 1H, S-C*H*-S), 9.27 (d, 2H, $^3J$=5.0 Hz, $H_\beta$), 9.45 (d, 2H, $^3J$=4.6 Hz, $H_\beta$), 9.52 (d, 2H, $^3J$=5.0 Hz, $H_\beta$), 9.77 (br s, 1H, $H_\beta$), 9.98 (s, 1H, 20-$H_{meso}$), 10.78 (br s, 1H, $H_\beta$); $^{13}$C NMR (63 MHz, $CDCl_3$, 20 °C): $\delta$= 23.32 ppm, 26.32, 35.95, 36.65, 36.71, 43.41, 54.98, 104.93, 113.18, 120.99; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 416 nm (5.57), 514 (4.17), 547 (3.58), 590 (3.63), 646 (3.45); MS (EI, 70 eV): *m/z* (%)= 540 (1) $[M]^{\bullet+}$, 423 (2) $[M^+-C_2H_4S]$, 407 (40) $[M^+-C_5H_9S_2]$; HRMS (EI) $[C_{32}H_{36}N_4S_2]$: calcd 540.2381, found 540.2394.

**[5,15-Diphenyl-10-(1,3-dithian-2-yl)porphyrinato]nickel(II) 114**



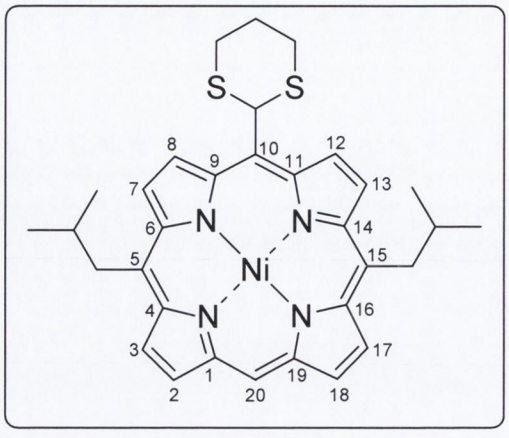

(5,15-Diphenylporphyrinato)nickel(II) **105** was reacted following procedure A, yield: 140 mg (0.22 mmol, 53 %) of purple crystals: *Mp* > 300 °C; $R_f$=0.60 ($CH_2Cl_2$:*n*-hexane, 1:1, v/v); $^1$H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta$= 2.45 ppm (m, 2H, $CH_2$-C$H_2$-$CH_2$) 3.22 (m, 2H, S-C$H_2$), 3.45 (m, 2H, S-C$H_2$), 7.24 (s, 1H, S-C*H*-S), 7.69 (m, 6H, $Ar_H$), 7.99 (m, 4H, $Ar_H$), 8.78 (m, 4H, 2,3,17,18-$H_\beta$), 9.02 (d, 2H, $^3J$=4.8 Hz, 7,13-$H_\beta$), 9.65 (s, 1H, $H_{meso}$), 9.88 (br s, 2H, 8,12-$H_\beta$); $^{13}$C NMR (63 MHz, $CDCl_3$, 20 °C): $\delta$= 26.00 ppm, 35.20, 52.77, 104.99, 112.55, 118.37, 126.87, 127.73, 132.32, 132.37, 133.66, 140.54, 141.88, 142.14, 142.55; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 413 nm (5.09), 529 (4.07), 560 (3.71); MS (70 eV): *m/z* (%)= 636 (4) $[M]^{\bullet+}$, 575 (7) $[M^+-C_2H_5S]$, 562 (10) $[M^+-C_3H_6S]$, 532 (2.5) $[M^+-C_3H_4S_2]$, 518 (4) $[M^+-C_4H_6S_2]$, 318 (2) $[M]^{2+}$; HRMS (EI) $[C_{36}H_{26}N_4NiS_2]$: calcd 636.0952, found 636.0956.

**[5-(1,3-Dithian-2-yl)-10,20-bis(3-methoxyphenyl)porphyrinato]nickel(II) 115**




[5,15-Bis(3-methoxyphenyl)porphyrinato]nickel(II) **106** was reacted following procedure A, yield: 167 mg (0.239 mmol, 53 %) of purple crystals: *Mp* > 300 °C; $R_f$=0.10 ($CH_2Cl_2$:*n*-hexane, 1:1, v/v); $^1$H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta$= 2.44 ppm (m, 2H, $CH_2$-C$H_2$-$CH_2$), 3.22 (m, 2H, S-C$H_2$), 3.49 (m, 2H, S-C$H_2$), 3.94 (s, 6H, OC$H_3$), 7.25 (m, 4H, Ar$_H$), 7.60 (m, 5H, Ar$_H$ + S-C*H*-S), 8.82 (m, 4H, 12,13,17,18-$H_\beta$), 9.02 (d, $^3J$=4.8 Hz, 2H, 2,8-$H_\beta$), 9.65 (s, 1H, $H_{meso}$), 9.87 (br s, 2H, 3,7-$H_\beta$); $^{13}$C NMR (63 MHz, $CDCl_3$, 20 °C): $\delta$= 25.99 ppm, 35.20, 52.75, 55.42, 105.02, 112.58, 113.58, 118.14, 119.57, 126.68, 127.75, 132.44, 132.64, 141.17, 141.76, 141.83, 142.19, 142.44, 158.13; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 413 nm (5.13), 529 (4.16), 560 (3.80); MS (EI, 70 eV): *m/z* (%)= 698 (2) $[M]^{\cdot+}$), 537 (2.5) $[M^+-C_2H_5S]$, 624 (2) $[M^+-C_3H_6S]$, 349 (1) $[M]^{2+}$; HRMS (EI) $[C_{38}H_{30}N_4NiO_2S_2]$: calcd 696.1164, found 696.1138.

**[5,15-Di(*iso*-butyl)-10-(1,3-dithian-2-yl)porphyrinato]nickel(II) 116**



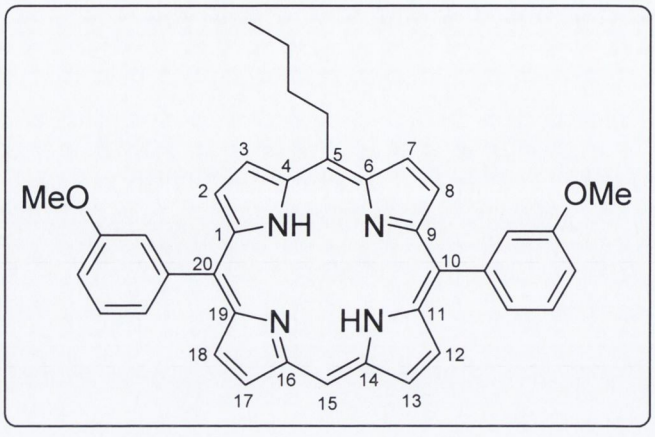

[5,15-Di(*iso*-butyl)porphyrinato]nickel(II) **107** was reacted following procedure A, yield: 128 mg (0.214 mmol, 49 %) of purple crystals: *Mp* 250 °C; $R_f$=0.30 ($CH_2Cl_2$:*n*-hexane, 1:1, v/v); $^1$H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta$= 0.84 ppm (d, 12H, $^3J$ = 6.6 Hz, CH(C$H_3$)$_2$), 2.22 (m, 2H, C$H$(CH$_3$)$_2$), 2.46 (m, 2H, C$H_2$CH), 3.24 (m, 2H, S-C$H_2$), 3.49 (m, 2H, S-C$H_2$), 4.52 (d, 4H, $^3J$ = 7.2 Hz, C$H$-CH$_2$), 7.14 (s, 1H, S-C$H$-S), 9.03 (d, 2H, $^3J$=5.2 Hz, 7,13-$H_\beta$), 9.30 (dd, 4H, $^3J$=6.0 Hz, $^3J$=5.0 Hz, 2,3,17,18-$H_\beta$), 9.47 (s, 1H, $H_{meso}$), 9.86 (br s, 2H, 8,12-$H_\beta$); $^{13}$C NMR (63 MHz, $CDCl_3$, 20 °C): $\delta$= 22.99 ppm, 26.09, 34.38, 35.19, 42.14, 52.65, 104.05, 111.22, 116.46, 130.41, 132.46, 139.87, 141.02, 142.00, 142.87; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 416 nm (5.45), 534 (4.11), 568 (3.59); MS (EI, 70 eV): *m/z* (%)= 596 (5) [M]$^{\bullet+}$, 553 (6) [M$^+$-$C_2H_5S$], 535 (7) [M$^+$-$C_3H_7$], 522 (11) [M$^+$-$C_3H_6S$], 492 (4) [M$^+$-$C_3H_4S_2$], 481 (17.5) [M$^+$-$C_8H_{18}$], 298 (2) [M]$^{2+}$; HRMS (EI) [$C_{32}H_{34}N_4S_2Ni$]: calcd 596.1578, found 596.1576.

## 7.4 Butylporphyrins

### General procedure B – Synthesis of butyl-2-ylporphyrins

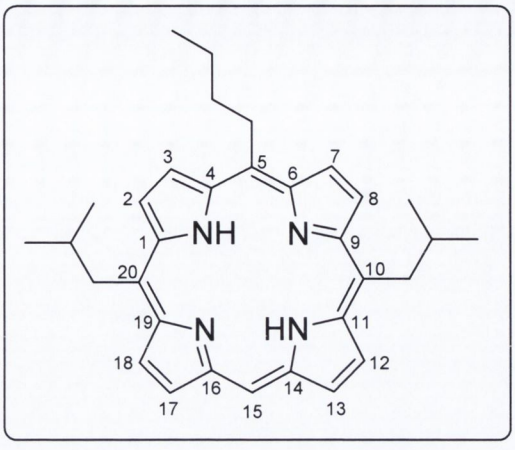
Porphyrin (1 eq.) was placed in a Schlenk flask and dissolved in dry THF under argon. The solution was cooled down to -78 °C. Then *n*-butyllithium (20 eq., 2.5 M solution in *n*-hexane) and *N,N,N',N'*-tetramethylethylendiamine (3.3 eq.) were added dropwise. The mixture was allowed to warm up to room temperature and was stirred for additional 30 minutes. The reaction was quenched with 3 ml water and stirred for another 15 min. DDQ (5.5 eq.) was added. Stirring was continued for 15 min followed by filtration of the reaction mixture through 200 ml silica gel and washing with dichloromethane. The eluted porphyrin fractions were evaporated to dryness.

**5-Butyl-10,20-bis(3-methoxyphenyl)porphyrin 118**



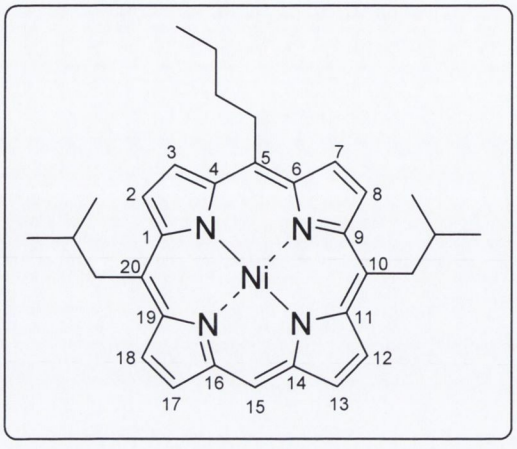

5,15-Bis(3-methoxyphenyl)porphyrin **94** was reacted according to procedure B. The residue was dissolved in dichloromethane and purified *via* column chromatography on silica gel with dichloromethane (h = 45 cm, ø = 3 cm). The product was obtained as purple crystals after recrystallisation from dichloromethane/methanol 52.1 mg (0.09 mmol, 24 %): *Mp* > 310 °C; $R_f$=0.8 ($CH_2Cl_2$:*n*-hexane, 3:1, v/v); $^1$H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta$= -2.96 ppm (s, 2H, N*H*), 1.15 (t, 3H, $^3J$=7.3 Hz, $CH_2$-C$H_3$), 1.84 (m, 2H, C$H_2$-$CH_3$), 2.57 (m, 2H, $CH_2$-C$H_2$-$CH_2$), 4.02 (s, 6H, OC$H_3$), 5.08 (t, 2H, $^3J$=7.9 Hz, C$H_2$-$CH_2$-$CH_2$), 7.39 (m, 2H, Ar$_H$), 7.69 (m, 2H, Ar$_H$), 7.85 (m, 4H, Ar$_H$), 9.04 (m, 4H, $H_\beta$), 9.26 (d, 2H, $^3J$=4.7 Hz, $H_\beta$), 9.55 (d, 2H, $^3J$=4.9 Hz, $H_\beta$), 10.09 (s, 1H, $H_{meso}$); $^{13}$C NMR (63 MHz, $CDCl_3$, 20 °C): $\delta$= 14.19 ppm, 23.65, 35.61, 41.09, 55.05, 103.99, 113.48, 118.75, 120.56, 121.15, 127.52, 127.72, 131.15, 143.38, 158.03; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 413 nm (5.27), 509 (4.06), 543 (3.50), 584 (3.63), 640 (3.32); MS (EI, 70 eV): *m/z* (%)= 578 (86) [$M^+$], 535 (100) [$M^+$-$C_3H_7$], 289 (2) [$M^{2+}$]; HRMS (ES+) [$C_{38}H_{34}N_4O_2$]: calcd 578.2682, found 578.2684.

**5-Butyl-10,20-di(*iso*-butyl)porphyrin 119**




5,15-Di(*iso*-butyl)porphyrin **95** was reacted according to procedure B. The residue was dissolved in dichloromethane and purified *via* column chromatography on silica gel with dichloromethane : *n*-hexane (1:1, v/v, h = 45 cm, ø = 3 cm). The product was obtained as purple crystals after recrystallisation from dichloromethane/methanol 14.2 mg (0.03 mmol, 15 %): *Mp* 195 °C, $R_f$=0.5 ($CH_2Cl_2$:*n*-hexane, 1:1, v/v); $^1$H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta$= -2.83 ppm (s, 2H, N*H*), 0.97 (t, 3H, $^3J$=7.3 Hz, $CH_2$-C$H_3$), 1.21 (d, 12H, $^3J$=6.6 Hz, CH(C$H_3$)$_2$), 1.87 (m, 2H, C$H_2$-$CH_3$), 2.58 (m, 2H, $CH_2$-C$H_2$-$CH_2$), 2.79 (m, 2H, C*H*(C$H_3$)$_2$), 4.84 (d, 4H, $^3J$=7.3 Hz, C$H_2$-CH), 5.08 (t, 2H, $^3J$=8.0 Hz, C$H_2$-$CH_2$-$CH_2$), 9.29 (d, 2H, $^3J$=4.7 Hz, 13,17-$H_\beta$), 9.51 (dd, 4H, $^3J$=4.9 Hz, $^3J$=4.7 Hz, 2,8,12,18-$H_\beta$), 9.61 (d, 2H, $^3J$=4.9 Hz, 3,7-$H_\beta$), 9.96 (s, 1H, $H_{meso}$); $^{13}$C NMR (75 MHz, $CDCl_3$, 20 °C): $\delta$= 14.22 ppm, 23.36, 23.77, 36.02, 36.72, 41.16, 43.36, 53.41, 103.06, 117.45, 119.95, 128.30, 128.52, 128.74, 131.13; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 413 nm (4.22), 512 (3.95), 542 (3.63), 588 (3.32), 645 (3.16); MS (EI, 70 eV): *m/z* (%)= 478 (52) [$M^+$], 435 (100) [$M^+$–$C_3H_7$], 392 (12) [$M^+$–$C_6H_{14}$], 239 (3) [$M^{2+}$]; HRMS (ES+) [$C_{32}H_{38}N_4$+H]: calcd 479.3175, found 479.3142.

**[5-Butyl-10,20-di(*iso*-butyl)porphyrinato]nickel(II) 120**



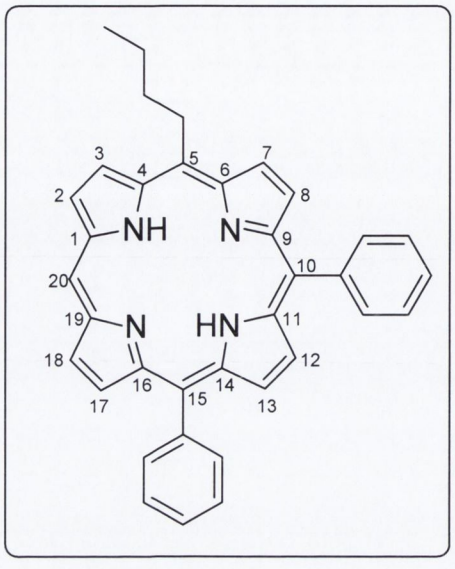

[5,15-Di(*iso*-butyl)porphyrinato]nickel(II) **107** was reacted according to procedure B. The residue was dissolved in dichloromethane and purified *via* column chromatography on silica gel with dichloromethane : *n*-hexane (1:3, v/v, h = 48 cm, ø = 3 cm). The product was obtained as purple crystals after recrystallisation from dichloromethane/methanol 27.2 mg (0.05 mmol, 28 %): *Mp* > 310 °C, $R_f$=0.7 ($CH_2Cl_2$:*n*-hexane, 1:3, v/v); $^1$H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta$= 0.88 ppm (d, 12H, $^3J$=6.6 Hz, $CH(CH_3)_2$), 1.05 (t, 3H, $^3J$=7.3 Hz, $CH_2$-$CH_3$), 1.60 (m, 2H, $CH_2$-$CH_3$), 2.30 (m, 4H, $CH(CH_3)_2$ + $CH_2$-$CH_2$-$CH_2$), 4.56 (m, 6H, $CH_2$-$CH_2$-$CH_2$ + $CH_2$-CH), 9.05 (d, 2H, $^3J$=4.9 Hz, $H_\beta$), 9.34 (d, 2H, $^3J$=4.9 Hz, $H_\beta$), 9.36 (s, 4H, $H_\beta$), 9.49 (s, 1H, $H_{meso}$); $^{13}$C NMR (63 MHz, $CDCl_3$, 20 °C): $\delta$= 14.03 ppm, 23.04, 23.45, 34.04, 34.51, 39.62, 42.27, 102.61, 115.82, 117.98, 129.61, 130.21, 130.55, 132.03, 140.74, 141.59, 142.23, 142.28; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 411 nm (5.55), 528 (4.29); MS (EI, 70 eV): *m/z* (%)= 534 (89) [$M^+$], 491 (100) [$M^+$-$C_3H_7$], 448 (18) [$M^+$-$C_6H_{14}$], 267 (2) [$M^{2+}$]; HRMS (ES+)[$C_{32}H_{36}N_4Ni$]: calcd 534.2293, found 534.2300.

*Experimental for X-ray:* The crystals were immersed in hydrocarbon oil (Paraton N®), suitable single crystals selected under the microscope, mounted on a glass fiber and placed in the low-temperature $N_2$ stream on the diffractometer.[267] Intensity data for all compounds were collected with a Bruker Smart CCD system using graphite monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) with $\varphi$ and $\omega$ scans. The intensities were corrected for Lorentz and polarisation effects. Absorption corrections were applied using the program Sadabs,[268] extinction effects were disregarded. The structure was solved using the program SIR92.[269] Refinements were carried out by full-matrix least squares on $|F^2|$ with the program SHELXL-97 using all data.[270] Nonhydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were placed into geometrically calculated positions and refined using a ridging model.

*Refinement details:* The outer carbon atoms of the butyl chains show high thermal librational movement.

*Normal-coordinate structural decomposition:* The theoretical background and development of this method has been described by Shelnutt and co-workers.[11,138] For calculations we used the NSD engine program-version 3.0, as provided on the internet under the URL http://jasheln.unm.edu/jasheln/content/nsd/NSDengine/nsd_index.htm.

**5-Butyl-10,15-diphenylporphyrin 122**

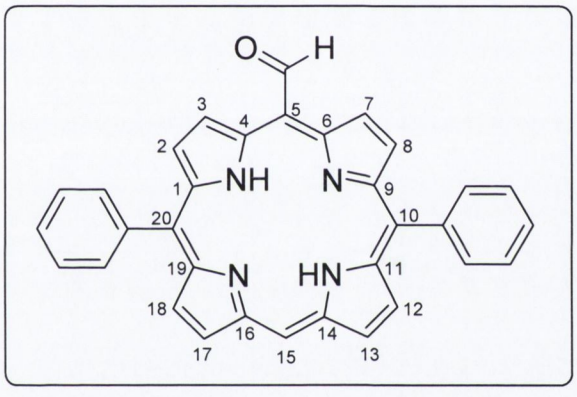



5,10-Diphenylporphyrin **121** was reacted according to procedure B. The residue was dissolved in dichloromethane and purified *via* column chromatography on silica gel with dichloromethane : *n*-hexane (1:1, v/v, h = 44 cm, ø = 3 cm).The product was obtained as purple crystals after recrystallisation from dichloromethane/methanol 31.7 mg (0.06 mmol, 26 %): *Mp* 155 °C; $R_f$=0.6 ($CH_2Cl_2$:*n*-hexane, 1:1, v/v); $^1$H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta$= -2.90 ppm (s, 2H, N*H*), 1.15 (t, 3H, $^3J$=7.3 Hz, $CH_2$-C$H_3$), 1.84 (m, 2H, C$H_2$-$CH_3$), 2.56 (m, 2H, $CH_2$-C$H_2$-$CH_2$), 5.04 (t, 2H, $^3J$=7.9 Hz, C$H_2$-$CH_2$-$CH_2$), 7.78 (m, 6H, Ar$_H$), 8.23 (m, 4H, Ar$_H$), 8.84 (dd, 2H, $^3J$=4.8 Hz, $H_\beta$), 8.94 (d, 1H, $^3J$=4.8 Hz, $H_\beta$), 8.98 (d, 1H, $^3J$=4.6 Hz, $H_\beta$), 9.30 (d, 1H, $^3J$=4.7 Hz, $H_\beta$), 9.40 (d, 1H, $^3J$=4.7 Hz, $H_\beta$), 9.50 (d, 1H, $^3J$=4.9 Hz, $H_\beta$), 9.60 (d, 1H, $^3J$=4.7 Hz, $H_\beta$), 10.14 (s, 1H, $H_{meso}$); $^{13}$C NMR (75 MHz, $CDCl_3$, 20 °C): $\delta$= 14.21 ppm, 23.66, 34.89, 40.89, 104.30, 118.81, 119.96, 120.18, 126.46, 126.82, 127.64, 128.43, 130.39, 131.00, 131.27, 131.61, 131.78, 134.42, 134.65, 141.71, 142.82; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 412 nm (5.33), 509 (4.23), 543 (3.68), 585 (3.26), 641 (3.06); MS (EI, 70 eV): *m/z* (%)= 518 (98) [$M^+$], 475 (100) [$M^+$-$C_3H_7$], 259 (4) [$M^{2+}$]; HRMS (ES+) [$C_{36}H_{30}N_4$]: calcd 519.2549, found 519.2579.

## 7.5 Formylporphyrins

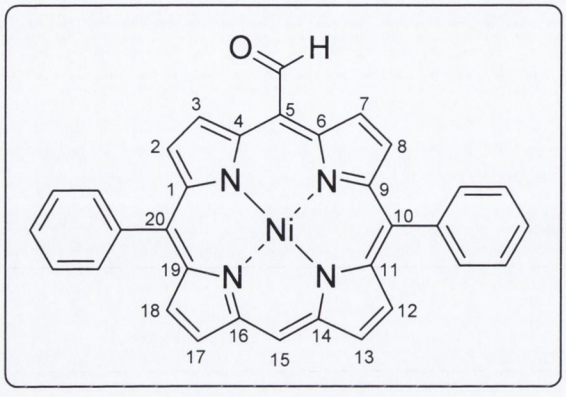
**General procedure C – Deprotection of the dithianylporphyrins:** To a solution of dithianylporphyrin (0.06 mmol) in dichloromethane (60 ml) DDQ (500 mg, 2.20 mmol) and $BF_3$•$Et_2O$ (0.5 ml, 9.95 mmol) were added and the colour of the red solution changed over yellow to green. After stirring for 45 min the reaction was quenched by the addition of aqueous sodium hydrogen carbonate. The organic phase was washed with a saturated solution of sodium hydrogen carbonate several times, followed by drying over anhydrous sodium sulphate and evaporation of the solvent in vacuum. After filtration through silica gel and recrystallisation from dichloromethane/methanol the pure product was obtained.

**5-Formyl-10,20-diphenylporphyrin 123**



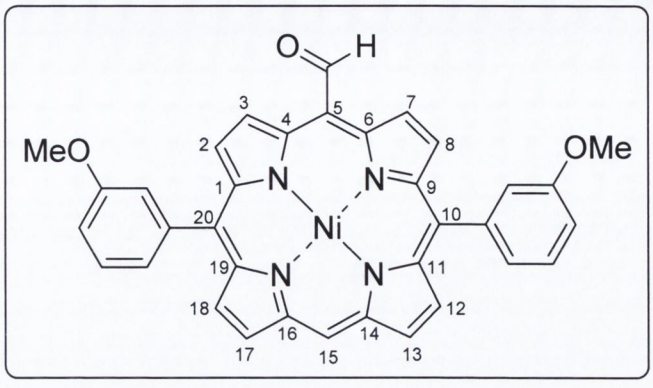

5,15-Diphenyl-10-(1,3-dithian-2-yl)porphyrin **102** was deprotected following procedure C, yield: 13 mg (0.03 mmol, 44 %) of purple crystals: *Mp* > 310 °C; $R_f$=0.53 ($CH_2Cl_2$:*n*-hexane, 2:1, v/v); $^1$H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta$= -2.54 ppm (br s, 2H, N*H*), 7.81 (m, 6H, Ar$_H$), 8.18 (dd, 4H, $^3J$=6.0 Hz, $^4J$=1.5 Hz, Ar$_H$), 8.85 (d, 2H, $^3J$=4.5 Hz, $H_\beta$), 9.02 (d, 2H, $^3J$=4.9 Hz, 2,8-$H_\beta$), 9.22 (d, 2H, $^3J$=4.5 Hz, $H_\beta$), 10.11 (d, 2H, $^3J$=4.7 Hz, 3,7-$H_\beta$), 10.18 (s, 1H, $H_{meso}$), 12.52 (s, 1H, C*H*O); $^{13}$C NMR (63 MHz, $CDCl_3$, 20 °C): $\delta$= 108.08 ppm, 109.87, 122.13, 124.92, 126.94, 127.80, 128.10, 128.64, 130.19, 131.18, 133.86, 134.42, 141.18, 195.15; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 411 nm (5.49), 508 (3.95), 561 (3.47), 581 (3.56), 647 nm (3.30); MS (70 eV): *m/z* (%)= 490 (23) $[M]^{\bullet+}$, 462 (6) $[M^+$-CO], 245 (16) $[M]^{2+}$; HRMS (EI) [$C_{33}H_{22}N_4O$]: calcd 490.1794, found 490.1777.

**(5-Formyl-10,20-diphenylporphyrinato)nickel(II) 124**




[5,15-Diphenyl-10-(1,3-dithian-2-yl)porphyrinato]nickel(II) **105** was deprotected following procedure C, yield: 13 mg (0.02 mmol, 39 %) of purple crystals: *Mp* 215 °C; $R_f$=0.59 ($CH_2Cl_2$:*n*-hexane, 2:1, v/v); $^1$H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta$= 7.72 ppm (m, 6H, $Ar_H$), 7.98 (dd, 4H, $^3J$=5.8 Hz, $^4J$=1.5 Hz, $Ar_H$), 8.74 (d, 2H, $^3J$=4.8 Hz, $H_\beta$), 8.89 (d, 2H, $^3J$=5.2 Hz, 2,8-$H_\beta$), 9.05 (d, 2H, $^3J$=4.8 Hz, $H_\beta$), 9.75 (s, 1H, $H_{meso}$), 9.86 (d, 2H, $^3J$=5.2 Hz, 3,7-$H_\beta$), 12.13 (s, 1H, C*H*O); $^{13}$C NMR (63 MHz, $CDCl_3$, 20 °C): $\delta$= 106.49 ppm, 108.59, 111.61, 127.04, 128.08, 130.53, 132.38, 133.19, 133.53, 135.29, 141.80, 144.26, 173.52; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 417 nm (5.31), 545 (3.75), 589 (3.94), MS (EI, 70 eV): *m/z* (%)= 546 (18) $[M]^{\bullet+}$, 517 (16) $[M^+$-CHO], 440 (52) $[M^+$-$C_7H_6O]$; HRMS (EI) $[C_{33}H_{20}N_4NiO]$: calcd 546.0991, found: 546.0989.

**[5-Formyl-10,20-bis(3-methoxyphenyl)porphyrinato]nickel(II) 125**



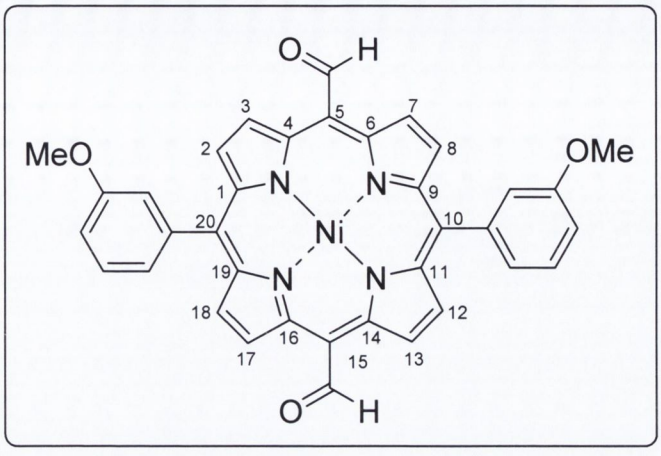

[5-Dithian-2-yl-10,20-bis(3-methoxyphenyl)porphyrinato]nickel(II) **106** was deprotected following procedure C, yield: 34 mg (0.05 mmol, 94 %) of dark purple crystals: *Mp* > 300 °C; $R_f$=0.26 ($CH_2Cl_2$:*n*-hexane, 2:1, v/v); $^1$H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta$= 3.95 ppm (s, 6H, OC$H_3$), 7.58 (m, 8H, Ar$_H$), 8.77 (d, 2H, $^3J$=4.8 Hz, $H_\beta$), 8.93 (d, 2H, $^3J$=5.2 Hz, 2,8-$H_\beta$), 9.03 (d, 2H, $^3J$=4.8 Hz, $H_\beta$), 9.72 (s, 1H, $H_{meso}$), 9.84 (d, 2H, $^3J$=5.2 Hz, 3,7-$H_\beta$), 12.11 (s, 1H, C*H*O); $^{13}$C NMR (100.6 MHz, $CDCl_3$, 20 °C): $\delta$= 29.07 ppm, 55.02, 105.91, 108.15, 113.26, 119.15, 119.77, 126.09, 127.53, 130.09, 132.01, 132.79, 134.93, 140.64, 140.82, 141.40, 143.64, 143.85, 157.77, 192.70; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 419 nm (4.69), 545 (3.47), 592 (3.56); MS (ESI): *m/z* (%)= 606 (100) $[M]^{\bullet+}$; HRMS (EI) [$C_{35}H_{24}N_4NiO_3$] calcd 606.1202, found 606.1190.

**General procedure D – Synthesis of formylporphyrins *via* Vilsmeier reaction:** A 100 ml three-necked flask equipped with a reflux condenser containing anhydrous DMF (75 eq.) was charged dropwise and slowly with $POCl_3$ (74 eq.) at 0-2 °C under an argon atmosphere. After 20 min the $POCl_3$-DMF complex solidified. After removal of the ice-bath, 1,2-dichloroethane (5 ml) was added and the solution was heated gently to 50 °C. The metalloporphyrin (0.1-1.5 g) was added slowly at 50 °C as a solution in 1,2-dichloroethane (25 ml). After complete addition the mixture was heated to 90 °C for 12 h. After cooling with an ice-bath a saturated aqueous sodium acetate solution was added very carefully and then the mixture was heated to 80 °C for 3 h for completion of the hydrolysis. After cooling to rt the porphyrin was extracted into dichloromethane (3 x), followed by washing once with water, twice with aqueous sodium hydrogen carbonate, and then finally twice with brine. Finally, the organic phase was dried with anhydrous sodium sulphate and the solvent was evaporated under reduced pressure.

**(5-Formyl-10,20-diphenylporphyrinato)nickel(II) 124**

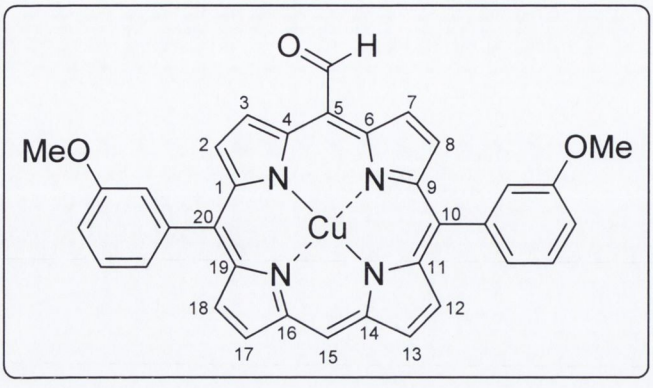
For the Vilsmeier-complex 2.7 ml (34.7 mmol) dry DMF and 3.06 ml (33.4 mmol) $POCl_3$ were used for the monoformylation of 500 mg (0.96 mmol) (5,15-diphenylporphyrinato)nickel(II) **105** following procedure D. Yield: 308 mg (0.56 mmol, 59 %). Full characterisation was described earlier for the deprotection of dithianylporphyrin **105**.

**[5,15-Diformyl-10,20-bis-(3-methoxyphenyl)porphyrinato]nickel(II) 134**



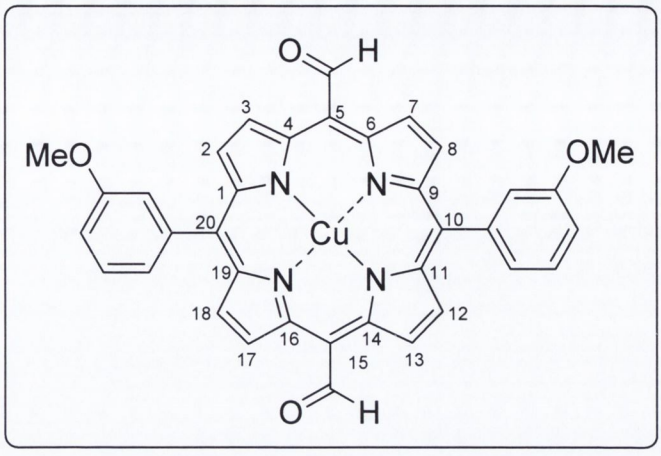

Prepared by reaction of **106** following procedure D. After column chromatography on silica gel (h = 34 cm, ø = 3 cm), the second fraction contained **134** and dark green crystals were obtained after recrystallisation from dichloromethane/methanol (52.4 mg, 0.08 mmol, 48 %): *Mp* 254 °C; $R_f$=0.3 ($CH_2Cl_2$:*n*-hexane, 2:1, v/v); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 3.98 ppm (s, 6H, OC$H_3$), 7.31 (m, 2H, Ar$_H$), 7.47 (m, 2H, Ar$_H$), 7.52 (m, 2H, Ar$_H$), 7.62 (m, 2H, Ar$_H$), 8.81 (d, 4H, $^3J$=5.1 Hz, $H_\beta$), 9.73 (d, 4H, $^3J$=4.7 Hz, $H_\beta$), 11.97 (s, 2H, C*H*O); $^{13}$C NMR (150 MHz, $CDCl_3$, 20 °C): $\delta$= 55.36 ppm, 108.27, 113.69, 119.42, 121.16, 126.23, 127.98, 131.76, 134.90, 140.22, 142.22, 142.62, 158.14, 192.47, 192.49; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 429 nm (7.11), 632 (3.85); MS (ES+): *m/z* (%)= 635 (8) [$M^{+\bullet}$], 544 (14) [$M^+$-$OCH_3$-$OCH_3$-CHO], 317 (11) [$M^{2+}$]; HRMS (ES+) [$C_{36}H_{24}N_4O_4Ni$+H]: calcd 635.1229, found 635.1245.

**[5-Formyl-10,20-bis-(3-methoxyphenyl)porphyrinato]copper(II) 135**



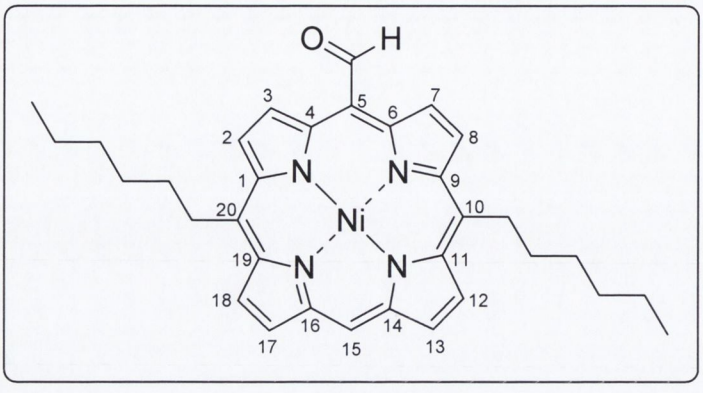

Prepared by reaction of **127** following procedure D. After column chromatography on alumina with dichloromethane (h = 43 cm, ø = 3 cm), the first fraction containing the product and dark purple crystals were obtained after recrystallisation from dichloromethane/methanol (20.6 mg, 0.03 mmol, 13 %): *Mp* 285 °C; $R_f$=0.63 ($CH_2Cl_2$:*n*-hexane, 2:1, v/v); UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 418 nm (5.42), 548 (4.33), 592 (4.51); MS (ES): *m/z* (%)= 612 (35) [$M^{\bullet+}$], 551 (87) [($^{63}$Cu-M)$^+$-$OCH_3$-CHO], 267 (5) [$M^{2+}$].

**[5,15-Diformyl-10,20-bis-(3-methoxyphenyl)porphyrinato]copper(II) 136**



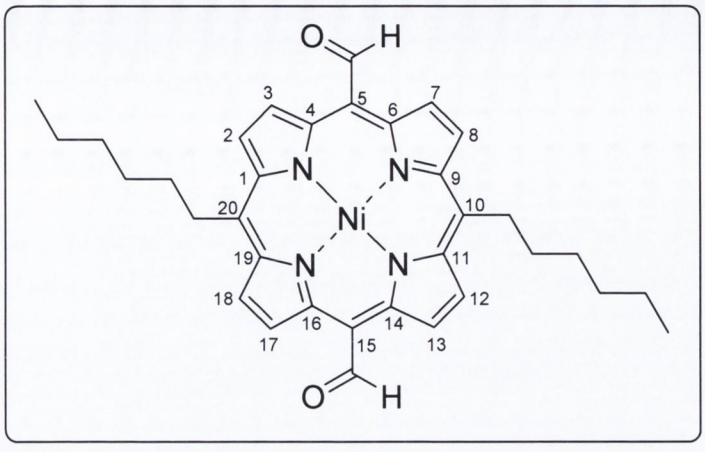

This compound was obtained as a second product from the reaction to prepare **135** After column chromatography on alumina with dichloromethane (h = 43 cm, ø = 3 cm), the second fraction contained product **136** and dark green crystals were received after recrystallisation from dichloromethane/methanol (32.5 mg, 0.05 mmol, 20 %): *Mp* > 310 °C; $R_f$=0.28 ($CH_2Cl_2$:*n*-hexane, 2:1, v/v); UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 432 nm (4.89), 628 (4.03); MS (ES): *m/z* (%)= 611 (5) [$M^+$-CHO].

**(5-Formyl-10,20-dihexylporphyrinato)nickel(II) 137**



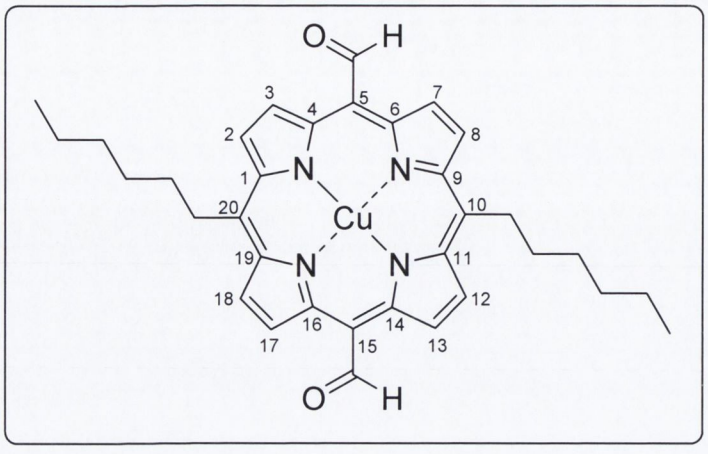

(5,15-Dihexylporphyrinato)nickel(II) **128** was reacted following procedure D. After column chromatography on silica gel (h = 34 cm, ø = 3 cm), the first fraction contained product **137** and purple crystals were collected after recrystallisation from dichloromethane/methanol (275 mg, 0.49 mmol, 60 %): *Mp* 149 °C; $R_f$=0.68 ($CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 0.97 ppm (t, 6H, $^3J$= 7.0 Hz, C$H_3$), 1.38 (m, 8H, C$H_2$-$CH_3$ + C$H_2$-$CH_2$-$CH_3$); 1.53 (m, 4H, C$H_2$-$CH_2$-$CH_2$-$CH_3$), 2.09 (m, 4H, C$H_2$-$CH_2$-$CH_2$-$CH_2$-$CH_3$), 3.85 (t, 4H, $^3J$=8.1 Hz, C$H_2$-$CH_2$-$CH_2$-$CH_2$-$CH_2$-$CH_3$), 8.52 (d, 2H, $^3J$=4.5 Hz, $H_\beta$), 8.70 (d, 2H, $^3J$=4.6 Hz, $H_\beta$), 8.76 (d, 2H, $^3J$=5.2 Hz, $H_\beta$), 8.83 (s, 1H, $H_{meso}$), 9.30 (d, 2H, $^3J$=5.2 Hz, $H_\beta$), 11.47 (s, 1H, C*H*O); $^{13}$C NMR (100.6 MHz, $CDCl_3$, 20 °C): $\delta$= 13.76 ppm, 22.28, 29.62, 31.24, 33.34, 37.14, 103.76, 106.82, 118.83, 127.86, 129.34, 130.91, 132.17, 139.32, 139.34, 142.04, 142.80, 191.88; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 421 nm (5.30), 550 (4.19), 594 (4.44); HRMS (ES+) [$C_{33}H_{36}N_4ONi$]: calcd 562.2243, found 562.2256; [$C_{33}H_{36}N_4ONi$, 563.37 g mol$^{-1}$] anal. calcd C 70.36, H 6.44, N 9.95, found C 70.21, H 6.39, N 9.93.

**(5,15-Diformyl-10,20-dihexylporphyrinato)nickel(II) 138**



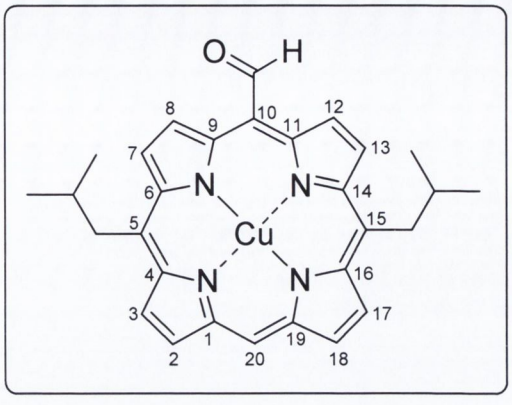

Prepared by reaction of **128** following procedure D. After column chromatography on silica gel eluting with dichloromethane (h = 56 cm, ø = 3 cm), the second fraction gave product **138** and dark purple crystals were obtained after recrystallisation from dichloromethane/methanol (46.4 mg, 0.078 mmol, 42 %): *Mp* 199 °C; $R_f$=0.46 ($CH_2Cl_2$:*n*-hexane, 2:1, v/v); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 0.84 ppm (t, 6H, $^3J$=7.0 Hz, C$H_3$), 1.25 (m, 8H, C$H_2$-C$H_2$-$CH_3$), 1.36 (m, 4H, C$H_2$-$CH_2$-$CH_2$-$CH_3$), 1.86 (m, 4H, C$H_2$-$CH_2$-$CH_2$-$CH_2$-$CH_3$), 4.16 (t, 4H, $^3J$=7.7 Hz, C$H_2$-$CH_2$-$CH_2$-$CH_2$-$CH_2$-$CH_3$), 8.93 (d, 4H, $^3J$=4.7 Hz, $H_\beta$), 9.38 (d, 4H, $^3J$=4.7 Hz, $H_\beta$), 11.52 (s, 2H, C*H*O); $^{13}$C NMR (100 MHz, $CDCl_3$, 20 °C): $\delta$= 13.58 ppm, 22.07, 29.29, 31.09, 33.13, 36.21, 105.97, 120.27, 131.01, 131.45, 140.15, 140.94, 191.36; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 425 nm (5.11), 622 (3.14); MS (ES+): *m/z* (%)= 591 (13) [$M^{+\bullet}$], 304 (2) [$M^{2+}$].

**(5,15-Diformyl-10,20-dihexylporphyrinato)copper(II) 139**



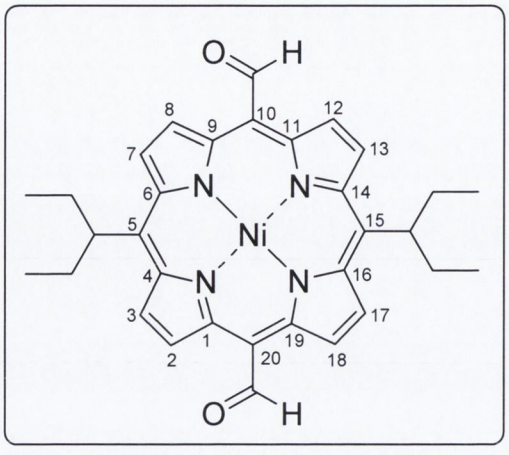

This compound was obtained by the reaction of (5,15-dihexylporphyrinato)copper(II) **129** according to procedure D. The second fraction from column chromatography on silica gel eluting with dichloromethane:*n*-hexane (2:1, v/v) and recrystallisation from dichloromethane and methanol gave the product as green crystals (10 mg, 0.02 mmol, 18 %): *Mp* 292 °C; $R_f$=0.35 ($CH_2Cl_2$:*n*-hexane, 2:1, v/v); UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 427 nm (5.16), 572 (3.56), 626 (4.12); MS (EI, 70 eV): *m/z* (%)= 595 (1) $[M]^{\bullet+}$, 298 (1) $[M]^{2+}$; HRMS (ES+) [$C_{34}H_{36}CuN_4O_2$]: calcd 595.2291, found 595.5298.

**[5,15-Di(*iso*-butyl)-10-formylporphyrinato]copper(II) 140**



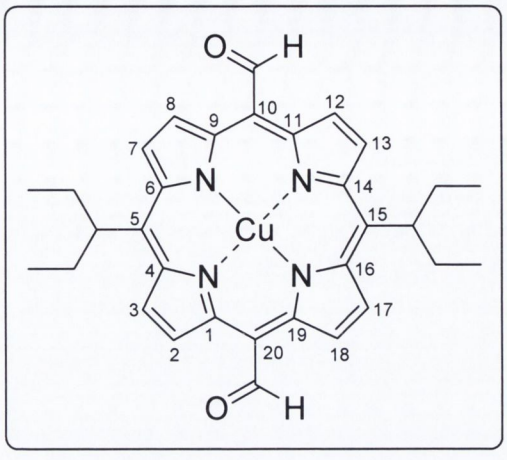

Prepared by reaction of [5,15-di(*iso*-butyl)porphyrinato]copper(II) **130** following procedure D. The first fraction from column chromatography on silica gel eluting with dichloromethane:*n*-hexane (2:1, v/v) followed by recrystallisation from dichloromethane and methanol gave the pure product as purple crystals (12.1 mg, 0.02 mmol) in 47 % yield: *Mp* > 310 °C, $R_f$=0.55 ($CH_2Cl_2$:*n*-hexane, 2:1, v/v); UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 419 nm (5.98), 550 (3.89), 593 (4.09); MS (EI, 70 eV): *m/z* (%)= 511 (13) $[M]^{\bullet+}$, 468 (2) $[M-C_3H_7]^+$; HRMS (ESI) [$C_{29}H_{28}CuN_4O$ + H]: calcd 512.1637, found 512.1631.

**[5,15-Bis(1-ethylpropyl)-10,20-diformylporphyrinato]nickel(II) 141**



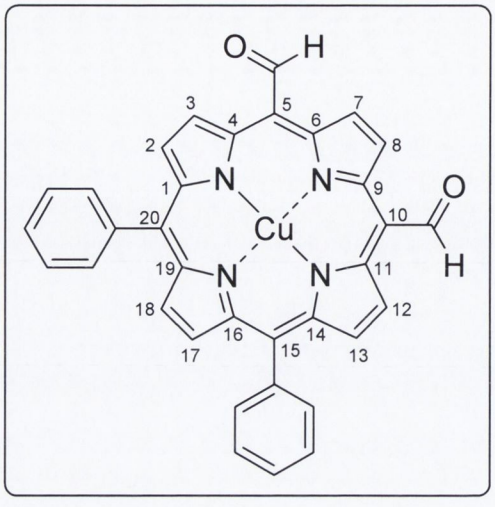

Prepared by reaction of [5,15-bis(1-ethylpropyl)porphyrinato]nickel(II) **131** following procedure D. After column chromatography on silica gel with dichloromethane (h = 56 cm, ø = 3 cm), the fraction containing pure product (36.3 mg, 0.065 mmol) 6.5 % yield, was obtained: *Mp* 251 °C; $R_f$=0.59 ($CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 0.92 ppm (t, 6H, $^3J$=7.3 Hz, C$H_3$), 2.62 (m, 4H, C$H_2$-$CH_3$), 4.25 (m, 2H, C$H$-($CH_2$-$CH_3$)$_2$, 9.38 (d, 4H, $^3J$=5.0 Hz, $H_\beta$), 9.73 (d, 4H, $^3J$=5.0 Hz, $H_\beta$), 11.89 (s, 2H, C$H$O); $^{13}$C NMR (100.6 MHz, $CDCl_3$, 20 °C): $\delta$= 13.73 ppm, 29.59, 33.38, 49.24, 107.52, 125.16, 132.36, 133.44, 140.78, 142.32, 192.30; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 435 nm (4.93), 633 (4.41); MS (ES+): *m/z* (%)= 563 (21) [$M^{+\bullet}$], 281 (2) [$M^{2+}$]; HRMS (ES+) [$C_{32}H_{32}N_4O_2Ni$+H]: calcd 563.1957, found 563.1960.

**[5,15-Bis(1-ethylpropyl)-10,20-diformylporphyrinato]copper(II) 142**




Prepared by reaction of [5,15-bis(1-ethylpropyl)porphyrinato]copper(II) **132** following procedure D. The second fraction of column chromatography on silica gel eluting with dichloromethane : *n*-hexane (2:1, v/v) followed by recrystallisation from dichloromethane and methanol gave the pure product as purple crystals (31 mg, 0.06 mmol) in 97 % yield: *Mp* 299 °C; $R_f$=0.52 ($CH_2Cl_2$:*n*-hexane, 2:1, v/v); UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 429 nm (5.15), 580 (3.49), 630 (4.14); MS (70 eV): *m/z* (%)= 541 (2) $[M\text{-}CHO]^{\bullet+}$, 539(3) $[M\text{-}CHO]^{\bullet+}$, 396 (7) $[M\text{-}C_{11}H_{23}O]^+$, 71 (26) $[C_5H_{11}]^+$.

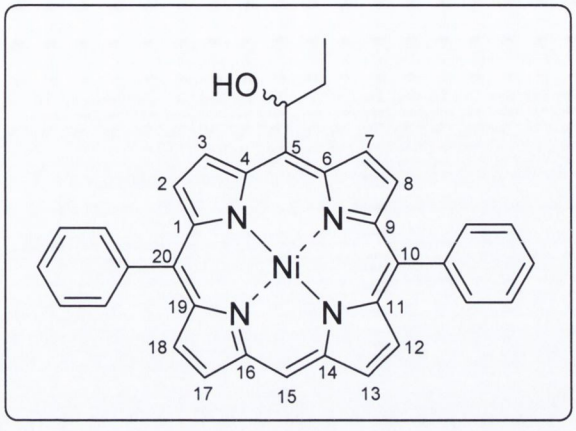
**(5,10-Diformyl-15,20-diphenylporphyrinato)copper(II) 143**




Prepared by reaction of (5,10-diphenylporphyrinato)copper(II) **133** following procedure D. After column chromatography on silica gel (h = 46 cm, ø = 3 cm) with dichloromethane the first fraction containing pure product was obtained as dark green crystals after recrystallisation from dichloromethane/methonal 45.1 mg, (0.077 mmol, 77 %) yield: *Mp* 220 °C; $R_f$=0.4 ($CH_2Cl_2$:*n*-hexane, 3:1, v/v); UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 432 nm (4.45), 562 (3.50), 602 (3.43); MS (EI, 70 eV): *m/z* (%)= 581 (4) [$M^{+\bullet}$], 552 (1) [$M^+$-CHO], 523 (2) [$M^+$-$C_2H_2O_2$], 445 (2) [$M^+$-$C_2H_2O_2$-$C_6H_6$]; HRMS (ESI) [$C_{34}H_{22}N_4O_2Cu$]: calcd 581.1039, found 581.1042.

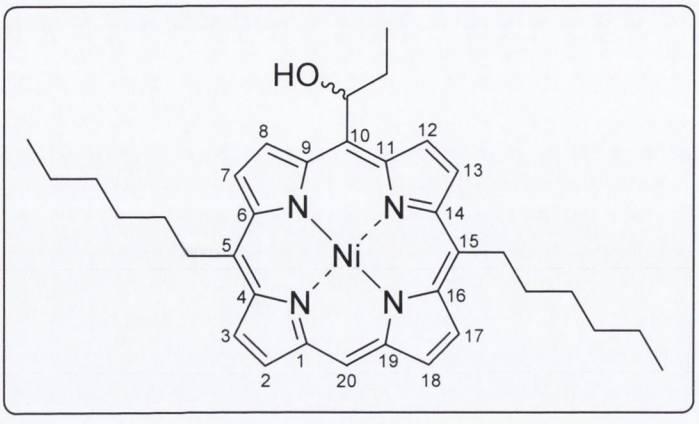
## 7.6 Grignard products

### [5-*rac*-(1-Hydroxypropyl)-10,20-diphenylporphyrinato]nickel(II) 147



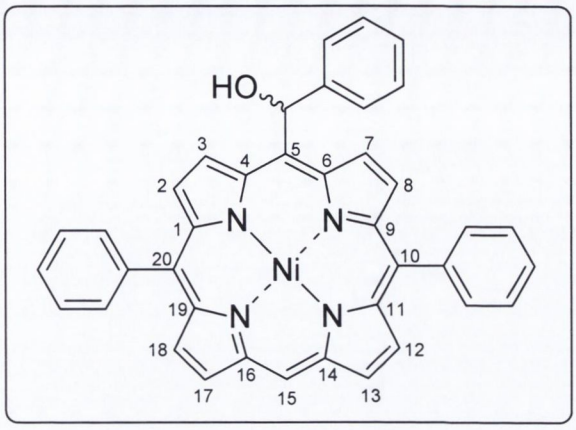

(5-Formyl-10,20-diphenylporphyrinato)nickel(II) **124** (30 mg, 0.05 mmol) was dissolved in dry THF. Ethylmagnesium bromide solution **144** (170 µl, 0.5 mmol, 3M in diethyl ether) was added. The reaction mixture was stirred at room temperature for 12 h and the reaction was quenched with 10 ml aqueous saturated ammonium chloride solution. The layers were separated and the aqueous layer extracted with dichloromethane. The organic layer was washed several times with water. The solvent was evaporated and the product was purified by column chromatography on silica gel with dichloromethane (h = 36 cm, ø = 3 cm). The first fraction gave pure product after recrystallisation from dichloromethane/methonal as dark red crystals (21.6 mg, 0.037 mmol, 68 %): *Mp* 99 °C; $R_f$=0.5 ($CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 0.98 ppm (t, 3H, $^3J$=7.3 Hz, C$H_3$), 2.57 (m, 1H, C$H_2$), 2.84 (m, 1H, C$H_2$), 3.21 (s, 1H, O$H$), 6.68 (t, 1H, $^3J$=7.3 Hz, C$H$), 7.71 (m, 6H, Ar$_H$), 7.99 (m, 4H, Ar$_H$), 8.83 (dd, 4H, $^3J$=10.4 Hz, $^4J$=4.8 Hz, $H_\beta$), 9.09 (d, 2H, $^3J$=5.1 Hz, $H_\beta$), 9.63 (d, 2H, $^3J$=5.1 Hz, $H_\beta$), 9.73 (s, 1H, $H_{meso}$); $^{13}$C NMR (100.6 MHz, $CDCl_3$, 20 °C): $\delta$= 11.45 ppm, 29.29, 35.63, 104.09, 117.64, 117.99, 126.47, 127.32, 130.00, 131.90, 132.10, 132.23, 133.23, 140.22, 140.50, 141.18, 141.84; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 409 nm (4.84), 525 (3.84), 556 (3.43); HRMS (ES+) [$C_{35}H_{26}N_4NiO$]: calcd 576.1460, found 576.1481.

**[5,15-Dihexyl-10-*rac*-(1-hydroxypropyl)porphyrinato]nickel(II) 148**




(5-Formyl-10,20-dihexylporphyrinato)nickel(II) **137** (30 mg, 0.05 mmol) was dissolved in dry THF and ethylmagnesium bromide solution **144** (85 µl, 0.25 mmol, 3M in diethyl ether) was added. The reaction mixture was heated to reflux at 75 °C for 12 h. The reaction was quenched with 10 ml aqueous saturated ammonium chloride solution. The layers were separated; the aqueous layer was extracted with dichloromethane. The organic layer was washed several times with water. The solvent was evaporated and the product was purified by column chromatography on silica gel with dichloromethane (h = 29 cm, ø = 3 cm), the first fraction gave the product as dark red crystals after recrystallisation from dichloromethane/methonal (15.9 mg, 0.03 mmol, 54 %): *Mp* 49 °C; $R_f$=0.32 ($CH_2Cl_2$:*n*-hexane, 1:4 , v/v); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 0.91 ppm (t, 9H, $^3J$=7.3 Hz, C$H_3$), 1.33 (m, 4H, C$H_2$-$CH_3$), 1.41 (m, 4H, C$H_2$-$CH_2$-$CH_3$); 1.57 (m, 4H, C$H_2$-$CH_2$-$CH_2$-$CH_3$), 2.24 (m, 4H, C$H_2$-$CH_2$-$CH_2$-$CH_2$-$CH_3$), 4.56 (t, 4H, $^3J$=8.0 Hz, C$H_2$-$CH_2$-$CH_2$-$CH_2$-$CH_2$-$CH_3$), 9.06 (d, 2H, $^3J$=4.2 Hz, $H_\beta$), 9.32 (dd, 4H, $^3J$=5.4 Hz, $^4J$=2.2 Hz, $H_\beta$), 9.36 (d, 2H, $^3J$=5.0 Hz, $H_\beta$), 9.48 (s, 1H, $H_{meso}$); $^{13}$C NMR (100.6 MHz, $CDCl_3$, 20 °C): $\delta$= 8.02 ppm, 13.72, 19.52, 22.26, 29.29, 29.65, 29.88, 31.20, 31.36, 33.48, 33.59, 36.94, 37.06, 45.37, 53.01, 102.50, 114.49, 116.83, 125.11, 128.79, 129.13, 129.27, 131.025, 131.68, 135.32, 139.73, 140.25; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 415 nm (4.88), 532 (3.94).

**[5-*rac*-(1-Hydroxybenzyl)-10,20-diphenylporphyrinato]nickel(II) 149**




Compound **124** (100 mg, 0.17 mmol) was dissolved in dry THF and phenylmagnesium bromide solution **145** (1.7 ml, 1.7 mmol, 1M in THF) was added. The reaction mixture was stirred at room temperature for 12 h. The reaction was quenched with 10 ml aqueous saturated ammonium chloride solution. The layers were separated, the aqueous layer extracted with dichloromethane. The organic layer was washed several times with water. The solvent was evaporated and the product was purified by column chromatography on silica gel with dichloromethane (h = 21 cm, ø = 3 cm). The first fraction gave the product as dark purple crystals after recrystallisation from dichloromethane/methonal (99.6 mg, 0.16 mmol, 93 %): *Mp* 236 °C; $R_f$=0.51 ($CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 3.37 ppm (d, 1H, $^3J$=3.5 Hz, CHO*H*), 7.28 (m, 5H, $Ar_H$ + $CDCl_3$), 7.55 (m, 2H, $Ar_H$), 7.71 (m, 6H, $Ar_H$), 8.00 (m, 4H, $Ar_H$), 8.08 (br d, 1H, $^3J$=3.5 Hz, C*H*OH), 8.79 (d, 2H, $^3J$=5.2 Hz, $H_\beta$), 8.85 (d, 2H, $^3J$=4.8 Hz, $H_\beta$), 9.12 (d, 2H, $^3J$=4.8 Hz, $H_\beta$), 9.37 (d, 2H, $^3J$=5.2 Hz, $H_\beta$), 9.78 (s, 1H, $H_{meso}$); $^{13}$C NMR (100.6 MHz, $CDCl_3$, 20 °C): $\delta$= 74.62 ppm, 104.60, 125.88, 126.27, 126.40, 126.47, 127.36, 127.69, 130.26, 132.02, 132.16, 132.72, 133.01, 133.11, 133.22, 140.12, 141.35, 141.93, 142.19; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 409 nm (5.08), 525 (4.08), 554 (3.73); HRMS (ES+) [$C_{39}H_{26}N_4ONi$]: calcd 624.1460, found 624.1474.

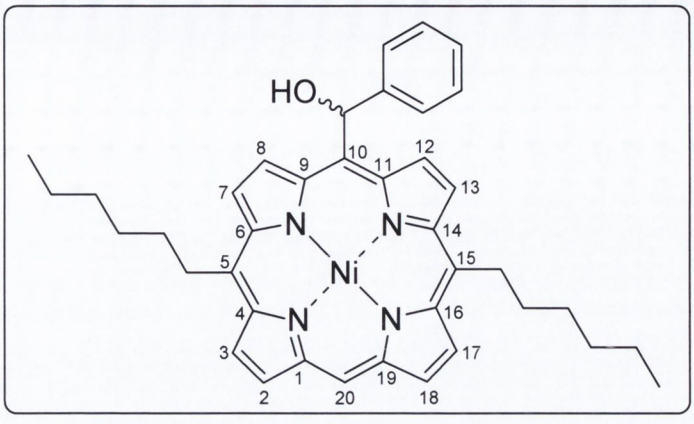
*Experimental for X-ray* [5-*rac*-(1-Methoxybenzyl)-10,20-diphenylporphyrinato]nickel(II): The crystals were obtained from recrystallisation of compound **149** with dichloromethane/methanol. The methoxy group most likely resulted from the methonal attaching the hydroxyl group. The crystals were immersed in hydrocarbon oil (Paraton N®), suitable single crystals selected under the microscope, mounted on a glass fiber and placed in the low-temperature $N_2$ stream on the diffractometer.[267] Intensity data for all compounds were collected with a Bruker Smart CCD system using graphite monochromated Mo-$K_a$ radiation ($\lambda$ = 0.71073 Å) with $\varphi$ and $\omega$ scans. The intensities were corrected for Lorentz and polarisation effects. Absorption corrections were applied using

an empirical absorption correction, extinction effects were disregarded. The structure was solved using using direct methods.[271] Refinements were carried out by full-matrix least squares on $|F^2|$ with the program SHELXL-97 using all data.[270] Nonhydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were placed into geometrically calculated positions and refined using a ridging model.

*Refinement details:* The compound crystallised as the racemic mixture of the two enantiomers. The two "crystallographically disordered" positions were refined with 50 % occupany each. No hydrogen atoms were included in the refinement for the disordered positions.

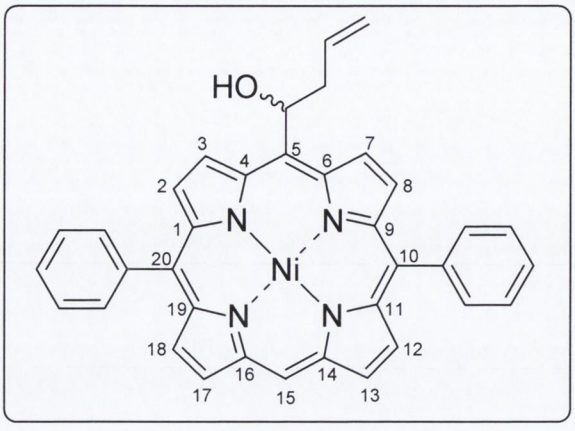
*Normal-coordinate structural decomposition:* The theoretical background and development of this method has been described by Shelnutt and coworkers.[11,138] For calculations we used the NSD engine program-version 3.0, as provided on the internet under the URL http://jasheln.unm.edu/jasheln/content/nsd/NSDengine/nsd_index.htm.

**[5,15-Dihexyl-10-*rac*-(1-hydroxybenzyl)porphyrinato]nickel(II) 150**



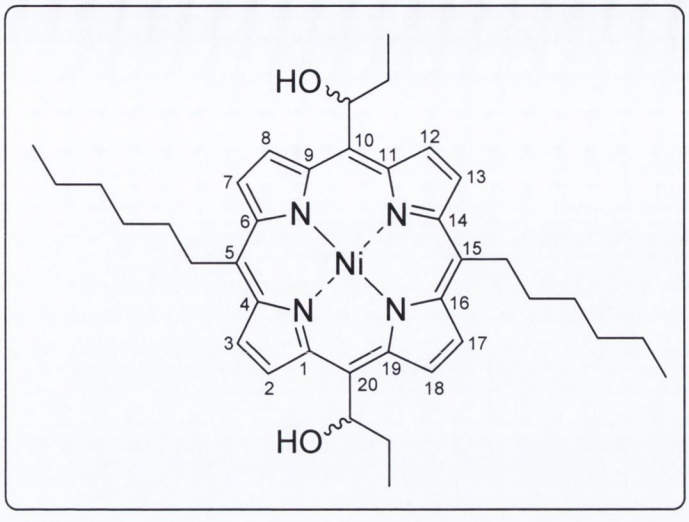

Porphyrin **137** (30 mg, 0.05 mmol) was dissolved in dry THF and phenylmagnesium bromide solution **145** (0.5 ml, 0.5 mmol, 1M in THF) was added. The reaction mixture was stirred at room temperature for 1 h. The reaction was quenched with 10 ml aqueous saturated ammonium chloride solution. The layers were separated and the aqueous layer was extracted with dichloromethane. The organic layer was washed several times with water. The solvent was evaporated and the product was purified by column chromatography on silica gel with dichloromethane (h = 28 cm, ø = 3 cm), the first fraction gave the product as purple crystals after recrystallisation from dichloromethane/methonal (29.1 mg, 0.045 mmol) in 85 % yield: *Mp* 136 °C; $R_f$=0.71 ($CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 0.93 ppm (t, 6H, $^3J$=7.0 Hz, C$H_3$), 1.37 (m, 8H, C$H_2$-$CH_2$-$CH_3$ + C$H_2$-$CH_3$); 1.59 (m, 4H, C$H_2$-$CH_2$-$CH_2$-$CH_3$), 2.26 (m, 4H, C$H_2$-$CH_2$-$CH_2$-$CH_2$-$CH_3$), 3.27 (br s, 1H, CHO*H*), 4.44 (t, 4H, $^3J$=7.6 Hz, C$H_2$-$CH_2$-$CH_2$-$CH_2$-$CH_2$-$CH_3$), 7.29 (m, 5H, Ar$_H$ + $CDCl_3$), 7.52 (m, 2H, Ar$_H$), 7.79 (br s, 1H, C*H*OH), 9.07 (d, 2H, $^3J$=4.6 Hz, $H_\beta$), 9.16 (d, 2H, $^3J$=5.2 Hz, $H_\beta$), 9.20 (d, 2H, $^3J$=5.5 Hz, $H_\beta$), 9.28 (d, 2H, $^3J$=4.6 Hz, $H_\beta$), 9.51 (s, 1H, $H_{meso}$); $^{13}$C NMR (100.6 MHz, $CDCl_3$, 20 °C): $\delta$= 13.71 ppm, 22.25, 29.64, 31.32, 33.55, 37.07, 74.36, 103.46, 115.47, 117.09, 125.89, 127.64, 129.26, 129.78, 130.39, 132.07, 140.05, 140.72, 140.88, 141.87, 146.42; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 412 nm (5.21), 530 (4.18), 564 (3.71); HRMS (ES+) [$C_{39}H_{42}N_4ONi$]: calcd 640.2712, found 640.2741.

**[5-*rac*-(1-Hydroxybut-3-enyl)-10,20-diphenylporphyrinato]nickel(II) 151**




Compound **124** (30 mg, 0.05 mmol) was dissolved in dry THF and allylmagnesium bromide solution **146** (0.5 ml, 0.5 mmol, 1M in diethyl ether) was added. The reaction mixture was stirred at room temperature for 12 h. Subsequent work-up was as described for **147**. Yield: 26 mg (0.044 mmol, 80 %) of purple crystals after recrystallisation from dichloromethane/methonal; *Mp* 96 °C; $R_f$=0.42 ($CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 3.15-3.18 ppm (m, 2H, CH(O*H*)(C$H_2$)), 3.53 (m, 1H, CH(OH)(C$H_2$)), 5.04 (dd, 1H, $^3J$=10.0 Hz, $^4J$= 1.0 Hz, CH=C$H_2$), 5.19 (dd, 1H, $^3J$=16.1 Hz, $^4J$= 1.0 Hz, CH=C$H_2$), 5.88 (dd, 1H, $^3J$=5.0 Hz, $^4J$= 4.0 Hz, C*H*=CH$_2$), 6.71 (C*H*(OH)(CH$_2$)), 7.63 (m, 6H, Ar$_H$), 7.89 (m, 4H, Ar$_H$), 8.71 (d, 2H, $^3J$=5.0 Hz, $H_\beta$), 8.74 (d, 2H, $^3J$=5.0 Hz, $H_\beta$), 8.98 (d, 2H, $^3J$=5.0 Hz, $H_\beta$), 9.51 (d, 2H, $^3J$=5.0 Hz, $H_\beta$), 9.60 (s, 1H, $H_{meso}$); $^{13}$C NMR (100.6 MHz, $CDCl_3$, 20 °C): $\delta$= 47.25 ppm, 74.00, 104.16, 117.14, 117.52, 117.69, 126.46, 127.32, 129.87, 131.92, 132.10, 132.32, 133.23, 134.98, 140.18, 140.29, 141.16, 141.84, 141.87; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 408 nm (5.01), 524 (4.04), 556 (3.61); HRMS (ES+) [$C_{36}H_{26}N_4NiO$]: calcd 588.1460, found 588.1479.

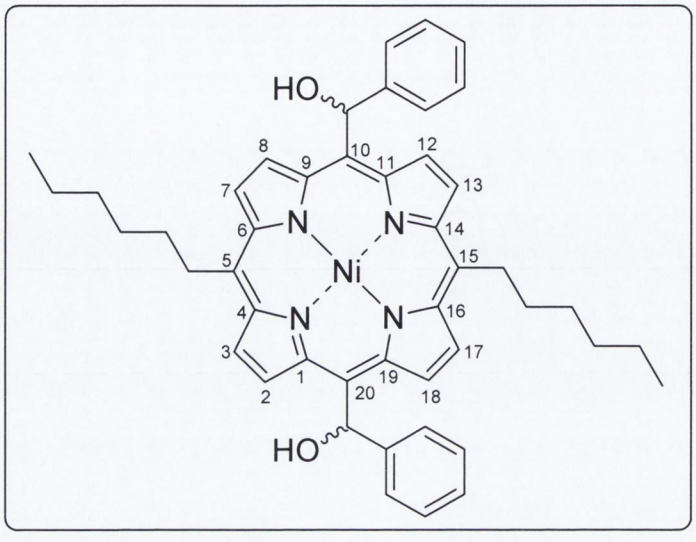
**[5,15-Dihexyl-10,20-*rac*-bis(1-hydroxypropyl)porphyrinato]nickel(II) 152**




The diformylporphyrin **138** (50 mg, 0.08 mmol) was dissolved in dry THF and ethylmagnesium bromide solution **144** (285 µl, 0.85 mmol, 3M in diethyl ether) was added. The reaction mixture was stirred at room 75 °C for 12 h. Subsequent work-up was as described for **147**. Yield: 18.2 mg (0.03 mmol, 35 %) of purple crystals; *Mp* 97 °C; $R_f$=0.71 ($CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 0.91 ppm (m, 12H, C*H*$_3$), 1.33 (m, 8H, C*H*$_2$-CH$_3$ + C*H*$_2$-CH$_2$-CH$_3$); 1.55 (m, 4H, C*H*$_2$-CH$_2$-CH$_2$-CH$_3$), 2.21 (m, 4H, C*H*$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$), 2.43 (m, 2H, CH-C*H*$_2$-CH$_3$), 2.76 (m, 2H, CH-C*H*$_2$-CH$_3$), 3.19 (br s, 2H, CHO*H*), 4.40 (t, 4H, $^3J$=7.9 Hz, C*H*$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$), 6.47 (t, 2H, $^3J$=7.3 Hz, C*H*OH), 9.20 (d, 4H, $^3J$=4.7 Hz, $H_\beta$), 9.51 (d, 4H, $^3J$=4.7 Hz, $H_\beta$).

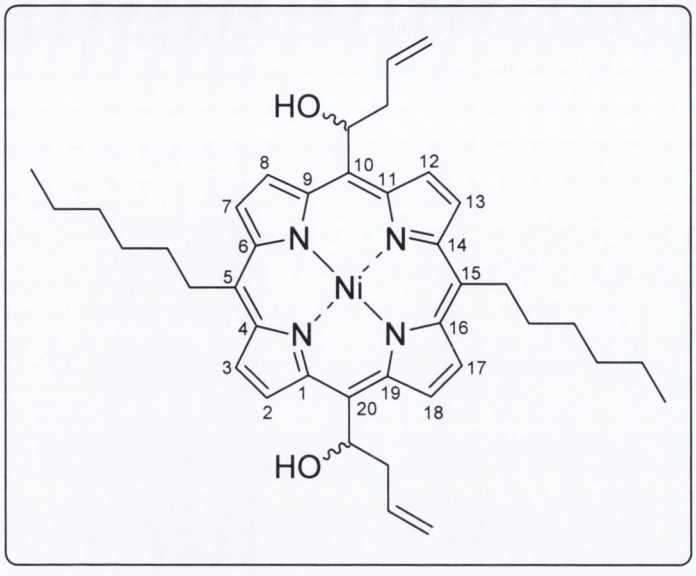
Compound **152** was too unstable to carry out further characterisation.

**[5,15-Dihexyl-10,20-*rac*-bis(1-hydroxybenzyl)porphyrinato]nickel(II) 153**




The diformylporphyrin **138** (50 mg, 0.08 mmol) was dissolved in dry THF and phenylmagnesium bromide solution (1.6 ml, 1.6 mmol, 1M in THF) was added. The reaction mixture was stirred at room temperature for 12 h. Subsequent work-up was as described for **147**. Yield: 40.6 mg (0.05 mmol, 68 %) of purple crystals; *Mp* 147 °C; $R_f$=0.22 ($CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 0.89 ppm (t, 6H, $^3J$=7.5 Hz, C$H_3$), 1.33 (m, 8H, C$H_2$-$CH_3$ + C$H_2$-$CH_2$-$CH_3$); 1.54 (m, 4H, C$H_2$-$CH_2$-$CH_2$-$CH_3$), 2.19 (m, 4H, C$H_2$-$CH_2$-$CH_2$-$CH_2$-$CH_3$), 4.38 (t, 4H, $^3J$=7.9 Hz, C$H_2$-$CH_2$-$CH_2$-$CH_2$-$CH_2$-$CH_3$), 7.28 (m, 9H, Ar$_H$ + $CDCl_3$), 7.55 (m, 4H, Ar$_H$), 7.80 (br s, 2H, C*H*OH), 9.14 (d, 4H, $^3J$=5.3 Hz, $H_\beta$), 9.21 (d, 4H, $^3J$=5.3 Hz, $H_\beta$); $^{13}$C NMR (100.6 MHz, $CDCl_3$, 20 °C): $\delta$= 13.69 ppm, 22.25, 29.59, 31.28, 33.45, 36.97, 125.89, 126.29, 127.69, 130.07, 130.94; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 420 nm (4.99), 541 (4.11), 574 (3.71); HRMS (ES+) [$C_{46}H_{48}N_4O_2Ni$]: calcd 746.3131, found 746.3107.

**[5,10-Dihexyl-10,20-*rac*-bis(1-hydroxybut-3-enyl)porphyrinato]nickel(II) 154**

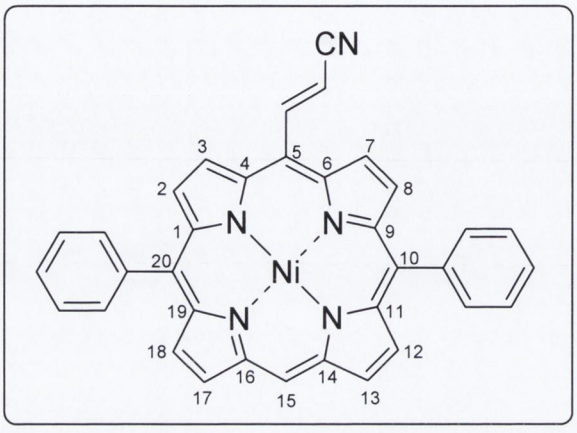



The diformylporphyrin **138** (30 mg, 0.05 mmol) was dissolved in dry THF and allylmagnesium bromide solution (1 ml, 1 mmol, 1M in THF) was added. The reaction mixture was stirred at room temperature for 12 h. Subsequent work-up was as described for **147**. Yield: 3.03 mg (0.005 mmol, 9 %) of purple crystals; *Mp* 100 °C; $R_f$=0.14 ($CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 0.90 ppm (t, 6H, $^3J$=7.3 Hz, C$H_3$), 1.40 (m, 8H, C$H_2$-$CH_3$ + C$H_2$-$CH_2$-$CH_3$); 1.63 (m, 4H, C$H_2$-$CH_2$-$CH_2$-$CH_3$), 2.21 (m, 4H, C$H_2$-$CH_2$-$CH_2$-$CH_2$-$CH_3$), 3.16 (br s, 2H, CHO*H*), 4.09 (dd, 4H, $^3J$=6.4 Hz, $^3J$=7.0 Hz, C$H_2$CHOH), 4.44 (t, 4H, $^3J$=7.9 Hz, C$H_2$-$CH_2$-$CH_2$-$CH_2$-$CH_2$-$CH_3$), 5.15 (d, 2H, $^3J$=9.9 Hz, CH=C$H_2$), 5.29 (d, 2H, $^3J$=17.5 Hz, CH=C$H_2$), 5.97 (m, 2H, C*H*=$CH_2$), 6.65 (m, 2H, C*H*OH), 9.23 (d, 4H, $^3J$=5.3 Hz, $H_\beta$), 9.53 (d, 4H, $^3J$=4.7 Hz, $H_\beta$).

Compound **154** was too unstable to carry out further characterisation.

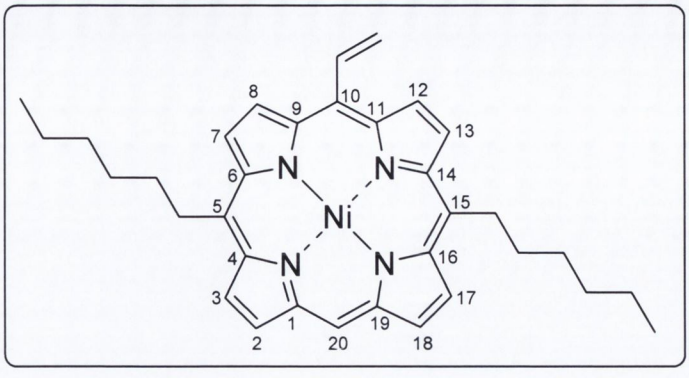
## 7.7 Wittig products

### [5-(*E*)-Cyanoethenyl-10,20-diphenylporphyrinato]nickel(II) 157



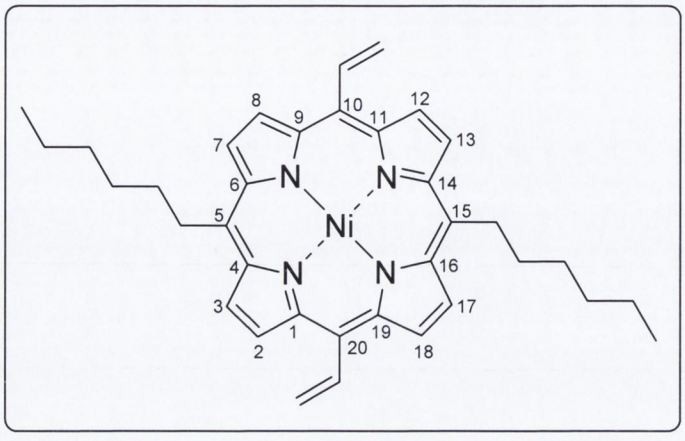

To a suspension of (cyanomethyl)triphenylphosphonium bromide **156** (52 mg, 0.15 mmol) in dry THF *n*-butyllithium (0.04 ml, 2.5M in hexane) was added and the suspension was stirred for 5 min followed by addition of (5-formyl-10,15-diphenylporphyrinato)nickel(II) **124** (30 mg, 0.05 mmol). The reaction mixture was stirred at room temperature for 2 h and then heated to 75 °C for 12 h. A suspension of (cyanomethyl)triphenylphosphonium bromide (52 mg, 0.15 mmol) and *n*-butyllithium (0.04 ml, 2.5M in hexane) in dry THF was added. The mixture was stirred for 12 h and quenched with water. Dichloromethane was added and the phases were separated. The organic layer was washed with water several times. The solvent was evaporated and the product was purified by column chromatography on silica gel with dichloromethane (h = 30 cm, ø = 3 cm), the first fraction giving the title compound as purple crystals after recrystallisation from dichloromethane/methanol (25.5 mg, 0.044 mmol, 81 %): *Mp* 295 °C; $R_f$=0.84 ($CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 5.68 ppm (d, 1H, $^3J$=15.5 Hz, C$H_3$), 7.74 (m, 6H, Ar$_H$), 7.99 (m, 4H, Ar$_H$), 8.81 (d, 2H, $^3J$=4.6 Hz, $H_\beta$), 8.88 (d, 2H, $^3J$=4.7 Hz, $H_\beta$), 9.08 (d, 2H, $^3J$=4.6 Hz, $H_\beta$), 9.26 (d, 2H, $^3J$=4.6 Hz, $H_\beta$), 9.63 (d, 1H, $^3J$=15.5 Hz, C$H$), 9.74 (s, 1H, $H_{meso}$); $^{13}$C NMR (100.6 MHz, $CDCl_3$, 20 °C): $\delta$= 105.85 ppm, 107.85, 108.05, 113.64, 117.78, 119.01, 126.65, 127.61, 129.88, 132.49, 133.18, 133.49, 139.66, 139.92, 141.43, 141.96, 142.66, 149.69; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 420 nm (5.31), 536 (4.31), 576 (4.12); HRMS (ES+) [$C_{35}H_{22}N_5Ni$]: calcd 570.1229, found 570.1230.

**(5,15-Dihexyl-10-vinylporphyrinato)nickel(II) 158**



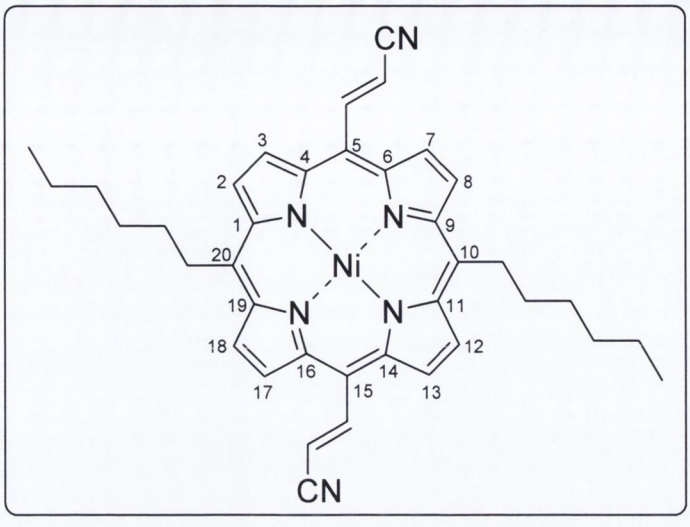

To a suspension of methyltriphenylphosphonium bromide **155** (50 mg, 0.14 mmol) in dry THF *n*-butyllithium (0.03 ml, 2.5M in hexane) was added and the suspension was stirred for 5 min. Addition of (5-formyl-10,15-dihexylporphyrinato)nickel(II) **137** (30 mg, 0.05 mmol) was followed by stirring for 1 h at room temperature. The mixture was quenched with water, dichloromethane was added and the phases were separated. The organic layer was washed with water several times. The solvent was evaporated and the product was purified by column chromatography on silica gel with dichloromethane : *n*-hexane (1:1, v/v, h = 30 cm, ø = 3 cm), the first fraction gave the title compound as dark red crystals after recrystallisation from dichloromethane/methanol (17.2 mg, 0.03 mmol, 61 %): *Mp* 92 °C; $R_f$=0.65 ($CH_2Cl_2$:*n*-hexane=1:2, v/v); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 0.93 ppm (t, 6H, $^3J$= 7.1 Hz, C$H_3$), 1.38 (m, 8H, C$H_2$-$CH_3$ + C$H_2$-$CH_2$-$CH_3$); 1.62 (m, 4H, C$H_2$-$CH_2$-$CH_2$-$CH_3$), 2.31 (m, 4H, C$H_2$-$CH_2$-$CH_2$-$CH_2$-$CH_3$), 4.57 (t, 4H, $^3J$=8.2 Hz, C$H_2$-$CH_2$-$CH_2$-$CH_2$-$CH_2$-$CH_3$), 5.60 (dd, 1H, $^3J$=17.4 Hz, $^4J$=1.6 Hz, CH=C$H_2$), 6.32 (dd, 1H, $^3J$=11.0 Hz, $^4J$=1.2 Hz, CH=C$H_2$), 8.95 (dd, 1H, $^3J$=17.7 Hz, $^4J$= 11.0 Hz, C$H$=$CH_2$), 9.08 (d, 2H, $^3J$=4.7 Hz, $H_\beta$), 9.34 (dd, 4H, $^3J$=8.7 Hz, $^4J$=4.7 Hz, $H_\beta$), 9.41 (d, 2H, $^3J$=5.4 Hz, $H_\beta$), 9.51 (s, 1H, $H_{meso}$); $^{13}$C NMR (100.6 MHz, $CDCl_3$, 20 °C): $\delta$= 13.69 ppm, 22.24, 29.28, 29.64, 29.88, 31.35, 33.63, 36.97, 102.89, 114.01, 117.00, 125.09, 127.46, 129.14, 129.32, 131.18, 131.86, 135.55, 139.44, 140.94, 141.31; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 414 nm (4.81), 534 (3.84), 622 (2.04).

**(5,15-Dihexyl-10,20-divinylporphyrinato)nickel(II) 160**



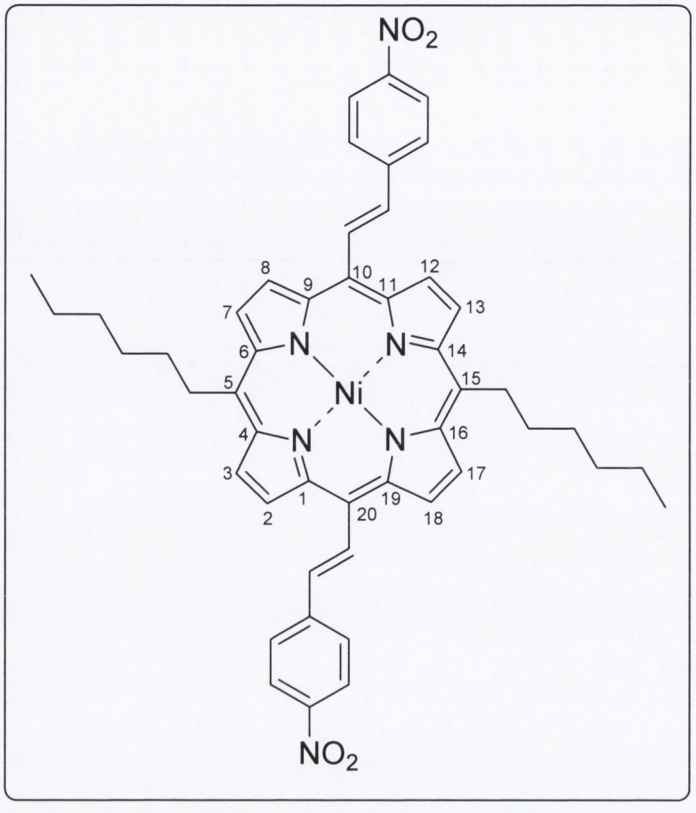

To a suspension of methyltriphenylphosphonium bromide **155** (150 mg, 0.42 mmol) in dry THF *n*-butyllithium (0.1 ml, 2.5M in hexane) was added and the suspension was stirred for 5 min. (5,15-Diformyl-10,15-dihexylporphyrinato)nickel(II) **138** (30 mg, 0.05 mmol) was added and the reaction mixture was stirred for 90 min at room temperature. Subsequent work-up was as described for **157** and gave purple crystals (12.2 mg, 0.02 mmol, 41 %): *Mp* 123 °C; $R_f$=0.17 ($CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 0.92 ppm (t, 6H, $^3J$=7.3 Hz, C$H_3$), 1.33 (m, 8H, C$H_2$-$CH_3$ + C$H_2$-$CH_2$-$CH_3$); 1.58 (m, 4H, C$H_2$-$CH_2$-$CH_2$-$CH_3$), 2.25 (m, 4H, C$H_2$-$CH_2$-$CH_2$-$CH_2$-$CH_3$), 4.45 (t, 4H, $^3J$= 8.2 Hz, C$H_2$-$CH_2$-$CH_2$-$CH_2$-$CH_2$-$CH_3$), 5.53 (dd, 2H, $^3J$=17.6 Hz, $^4J$=1.7 Hz, CH=C$H_2$), 6.25 (dd, 2H, $^3J$=11.1 Hz, $^4J$=1.5 Hz, CH=C$H_2$), 8.83 (dd, 2H, $^3J$=16.8 Hz, $^3J$=10.7 Hz, C$H$=$CH_2$), 9.22 (d, 4H, $^3J$=5.1 Hz, $H_\beta$), 9.29 (d, 4H, $^3J$=5.2 Hz, $H_\beta$); $^{13}$C NMR (100.6 MHz, $CDCl_3$, 20 °C): $\delta$= 13.72 ppm, 22.24, 29.30, 29.61, 31.34, 33.45, 36.78, 113.57, 117.27, 127.57, 128.03, 128.10, 128.29, 129.30, 129.36, 131.40, 133.22, 133.41, 135.13; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 426 nm (4.94), 548 (4.19), 596 (3.88).

**[5,15-(*E*)-Dicyanoethenyl-10,20-dihexylporphyrinato]nickel(II) 161**




To a suspension of (cyanomethyl)triphenylphosphonium chloride **156** (340 mg, 1 mmol) in dry THF *n*-butyllithium (0.4 ml, 2.5M in hexane) was added and the suspension was stirred for 5 min. Following the addition of (5,15-diformyl-10,15-dihexylporphyrinato)nickel(II) **138** (30 mg, 0.05 mmol) the reaction mixture was stirred at room temperature. After 1 h (cyanomethyl)triphenylphosphonium chloride (340 mg, 1 mmol) and *n*-butyllithium (0.4 ml, 2.5M in hexane) were added and the mixture was stirred for 12 h. Subsequent work-up was as described for **157**. Yield: 3.3 mg (5 µmol, 10 %) dark green crystals; *Mp* 142 °C; $R_f$=0.62 ($CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 0.92 ppm (t, 6H, $^3J$=7.2 Hz, C$H_3$), 1.35 (m, 4H, C$H_2$-$CH_3$), 1.42 (m, 4H, C$H_2$-$CH_2$-$CH_3$); 1.59 (m, 4H, C$H_2$-$CH_2$-$CH_2$-$CH_3$), 2.22 (m, 4H, C$H_2$-$CH_2$-$CH_2$-$CH_2$-$CH_3$), 4.38 (t, 4H, $^3J$=8.5 Hz, C$H_2$-$CH_2$-$CH_2$-$CH_2$-$CH_2$-$CH_3$), 5.67 (d, 1H, $^3J$=16.2 Hz, C$H_3$), 9.17 (d, 4H, $^3J$=4.9 Hz, $H_\beta$), 9.23 (d, 4H, $^3J$=4.9 Hz, $H_\beta$), 9.42 (d, 1H, $^3J$=16.2 Hz, C$H$); $^{13}$C NMR (150 MHz, $CDCl_3$, 20 °C): $\delta$= 13.91 ppm, 22.45, 29.55, 29.83, 31.52, 33.71, 37.19, 67.83, 108.30, 108.75, 117.95, 120.36, 131.26, 131.39, 131.52, 139.19, 141.66, 148.83; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 440 nm (4.86), 571 (3.71), 625 (4.05).

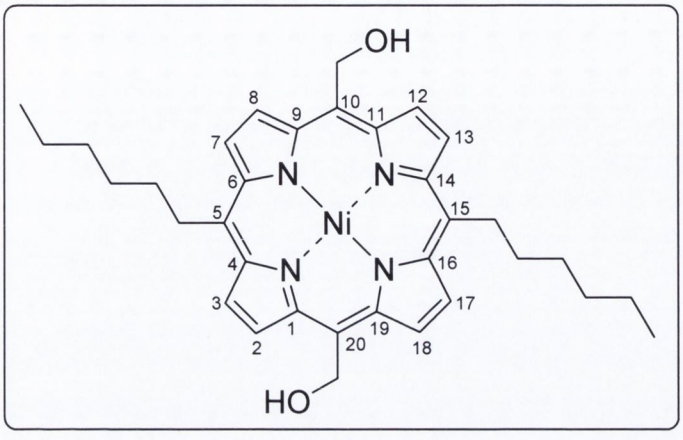
**[5,15-Dihexyl-10,20-bis(4-(*E*)-nitrophenylethenyl)porphyrinato]nickel(II) 162**




To a suspension of (4-nitrophenyl)triphenylphosphonium bromide **159** (134 mg, 0.28 mmol) in dry THF *n*-butyllithium (0.07 ml, 2.5M in hexane) was added and the suspension was stirred for 5 min. (5,15-Diformyl-10,15-dihexylporphyrinato)nickel(II) **138** (30 mg, 0.055 mmol) was added and the reaction mixture was stirred for 2 days at room temperature. It was quenched with water, dichloromethane was added and the phases were separated. The organic layer was washed with water several times. The solvent was evaporated and the product was purified by column chromatography on silica gel with dichloromethane (h = 28 cm, ø = 3 cm) to yield purple crystals after recrystallisation from dichloromethane/methanol (4.8 mg, 0.006 mmol, 11 %): *Mp* 296 °C; $R_f$=0.44 ($CH_2Cl_2$:*n*-hexane, 2:1, v/v); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 0.91 ppm (t, 6H, $^3J$=7.3 Hz, C*H*$_3$), 1.31 (m, 8H, C*H*$_2$-CH$_3$ + C*H*$_2$-CH$_2$-CH$_3$); 1.42 (m, 4H, C*H*$_2$-CH$_2$-CH$_2$-CH$_3$), 2.24 (m, 4H, C*H*$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$), 4.41 (t, 4H, $^3J$=7.9 Hz, C*H*$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$), 6.75 (d, 2H, $^3J$=15.8 Hz, C*H*), 7.84 (d, 4H, $^3J$=8.8 Hz, Ar$_H$), 8.35 (d, 4H, $^3J$=8.2 Hz, Ar$_H$), 9.20 (d, 4H, $^3J$=4.7 Hz, $H_\beta$), 9.25 (d, 4H, $^3J$=5.3 Hz, $H_\beta$) 9.28 (s, 2H, C*H*); $^{13}$C NMR (150 MHz, $CDCl_3$, 20 °C): $\delta$= 11.00 ppm, 13.68, 22.19, 24.83, 28.61, 29.26, 29.58, 31.29, 33.38, 34.22, 36.77, 111.92, 118.82, 123.94, 126.48, 129.99, 131.29, 139.58, 140.69, 140.93, 143.19, 146.51; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 465 nm (5.17), 646 (4.61).

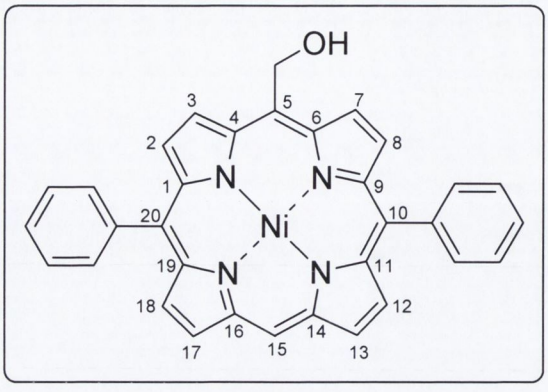
## 7.8 Formylreduction

### (5,15-Dihexyl-10,20-dihydroxymethylporphyrinato)nickel(II) 174




(5,15-Diformyl-10,20-dihexylporphyrinato)nickel(II) **138** (150 mg, 0.26 mmol) was dissolved in 50 ml chloroform. A solution of sodium borohydride (104 mg, 2.74 mmol) in aqueous ethanol (105 ml, water:ethanol = 1:6, v/v) was added. The reaction mixture was stirred for 30 min at room temperature. The phases were separated and the organic layer washed again with water. The product was purified by column chromatography on silica gel with chloroform (h = 34 cm, ø = 3 cm). The pure product was obtained as red crystals after recrystallisation from dichloromethane/methanol: 145.3 mg (0.24 mmol, 96 %): *Mp* 184 °C; $R_f$=0.17 ($CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 0.91 ppm (t, 6H, $^3J$=7.4 Hz, C$H_3$), 1.33 (m, 4H, C$H_2$-$CH_3$), 1.41 (m, 4H, C$H_2$-$CH_2$-$CH_3$); 1.57 (m, 4H, C$H_2$-$CH_2$-$CH_2$-$CH_3$), 2.24 (m, 4H, C$H_2$-$CH_2$-$CH_2$-$CH_2$-$CH_3$), 2.59 (br s, 2H, $CH_2OH$), 4.16 (t, 4H, $^3J$=8.1 Hz, C$H_2$-$CH_2$-$CH_2$-$CH_2$-$CH_2$-$CH_3$), 6.39 (s, 4H, C$H_2$OH), 9.29 (d, 4H, $^3J$=5.1 Hz, $H_\beta$), 9.38 (d, 4H, $^3J$=5.1 Hz, $H_\beta$); $^{13}$C NMR (100.6 MHz, $CDCl_3$, 20 °C): $\delta$= 13.98 ppm, 22.51, 29.86, 31.61, 33.80, 37.32, 63.03, 112.92, 118.00, 129.36, 130.41, 140.94, 141.94; MS (ES+) *m/z* (%): 595 (3) [$M^{+\bullet}$], 577 (7) [$M^{+\bullet}$-$H_2O$], 559 (38) [$M^{+\bullet}$-$(H_2O)_2$], 267 (4) [$M^{2+}$]; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 415 nm (5.72), 536 (3.91); HRMS (ES+)[$C_{34}H_{40}N_4O_2Ni$]: calcd 594.2505, found 594.2501.

**(5-Hydroxymethyl-10,20-diphenylporphyrinato)nickel(II) 187**



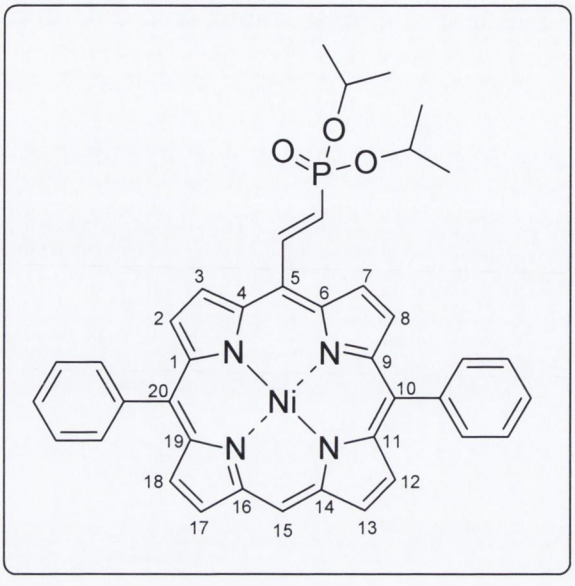

(5-Formyl-10,20-diphenylporphyrinato)nickel(II) **124** (100 mg, 0.18 mmol) was dissolved in 50 ml chloroform. A solution of sodium borohydride (34 mg, 0.9 mmol) in aqueous ethanol (105 ml, water:ethanol = 1:6, v/v) was added. The reaction mixture was stirred for 2 h at room temperature. The phases were separated and the organic layer washed again with water. The product was purified by column chromatography on silica gel with chloroform : *n*-hexane (1:1, v/v, h = 44 cm, ø = 3 cm) and dark red crystals were obtained after recrystallisation from dichloromethane/methanol in (96.6 mg, 0.17 mmol) 98 % yield: *Mp* 229 °C; $R_f$=0.23 ($CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 2.76 ppm (t, 1H, $^3J$=5.5 Hz, $CH_2OH$), 4.95 (m, 2H, $CH(CH_3)_2$), 6.64 (d, 2H, $^3J$=5.8 Hz, $CH_2OH$), 7.74 (m, 6H, $Ar_H$), 8.03 (m, 4H, $Ar_H$), 8.87 (d, 2H, $^3J$=4.7 Hz, $H_\beta$), 8.91 (d, 2H, $^3J$=5.3 Hz, $H_\beta$), 9.11 (d, 2H, $^3J$=4.7 Hz, $H_\beta$), 9.49 (d, 2H, $^3J$=5.3 Hz, $H_\beta$), 9.79 (s, 1H, $H_{meso}$), $^{13}$C NMR (100.6 MHz, $CDCl_3$, 20 °C): $\delta$= 63.15 ppm, 104.71, 113.55, 118.13, 126.48, 127.38, 128.46, 131.93, 132.17, 132.78, 133.31, 140.24, 141.91, 142.08, 142.11, 142.32; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 406 nm (5.76), 521 (4.82), 552 (4.46); HRMS (ES+) [$C_{33}H_{22}N_4NiO$]: calcd 548.1147, found 548.1131.

## 7.9 Phosphonates

### General procedure E – Synthesis of phosphonates

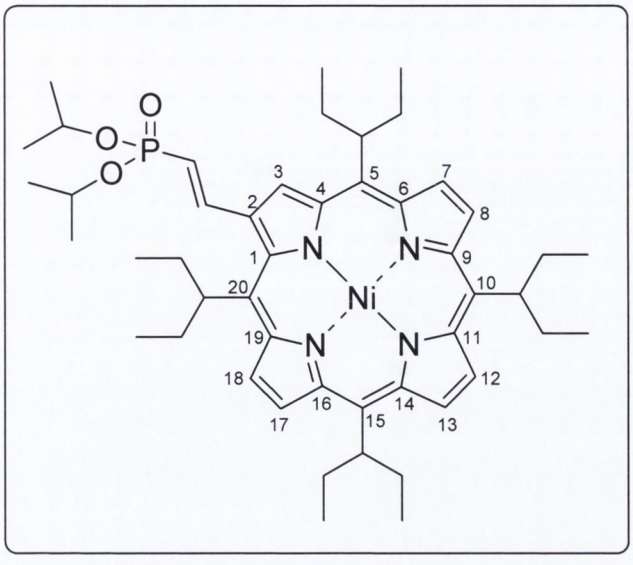
Tetra(*iso*-propyl) methylenebisphosphonate (1 eq.) was added to a suspension of sodium hydride (1.5 eq.) in dry THF at 0 °C. The mixture was stirred for 30 min before the respective aldehyde was added. The solution was stirred overnight at room temperature. Subsequently, the reaction mixture was quenched with saturated $NH_4Cl$-solution, extracted with ethyl acetate and washed with brine. The residue was purified by column chromatography on silica gel.

**[5-(*E*)-Di(*iso*-propyl)ethenylphosphono-10,20-diphenylporphyrinato]nickel(II) 194**



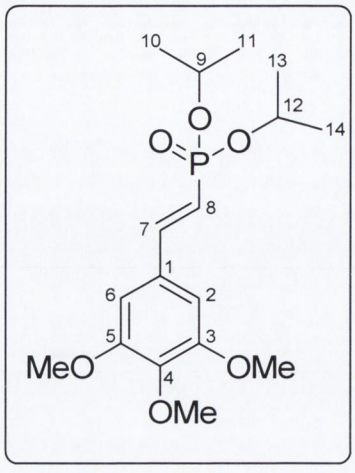

Prepared by reaction of compound **124** following procedure E. The first fraction of column chromatography on silica gel eluting with ethyl acetate : *n*-hexane (4:1, v/v, h = 39 cm, ø = 3 cm) gave the pure product as purple crystals after recrystallisation from dichloromethane/methanol (284.9 mg, 0.4 mmol) in 73 % yield: *Mp* 183 °C; $R_f$=0.6 (ethyl acetate:*n*-hexane, 4:1, v/v); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 1.47 ppm (d, 6H, $^3J$=6.0 Hz, C$H_3$), 1.50 ppm (d, 6H, $^3J$=6.3 Hz, C$H_3$), 4.95 (m, 2H, C$H$(C$H_3$)$_2$), 6.24 (t, 2H, $^3J_{HHP}$=17.9 Hz, C$H$=CH-P), 7.74 (m, 6H, Ar$_H$), 8.02 (m, 4H, Ar$_H$), 8.83 (d, 2H, $^3J$=4.8 Hz, $H_\beta$), 8.90 (d, 2H, $^3J$=5.0 Hz, $H_\beta$), 9.08 (d, 2H, $^3J$=4.5 Hz, $H_\beta$), 9.43 (d, 2H, $^3J$=4.8 Hz, $H_\beta$), 9.72 (s, 1H, $H_{meso}$), 9.79 (dd, 1H, $^3J_{HHP}$=17.1 Hz, $^2J_{HP}$=22.1 Hz, CH=C$H$-P); $^{13}$C NMR (100.6 MHz, $CDCl_3$, 20 °C): $\delta$= 24.26 ppm, 70.84, 70.90, 105.48, 111.58, 111.81, 118.90, 127.02, 127.92, 130.43, 130.97, 132.28, 132.59, 132.74, 133.36, 133.67, 140.43, 140.78, 141.99, 142.39, 142.77; $^{31}$P NMR (162 MHz, $CDCl_3$, 20 °C): $\delta$= 14.73 ppm; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 415 nm (5.17), 529 (4.17), 566 (3.87); HRMS (ES+) [$C_{40}H_{35}N_4NiO_3P$+H]: calcd 709.1879, found 709.1862.

**[2-(*E*)-Di(*iso*-propyl)ethenylphosphono-5,10,15,20-tetra(1-ethylpropyl)porphyrinato]nickel(II) 195**



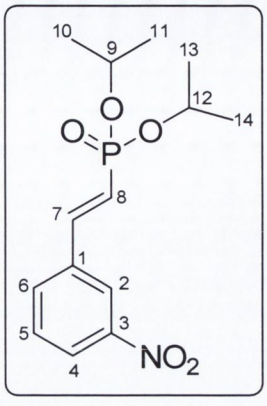

Prepared by reaction of [2-formyl-5,10,15,20-tetrakis(1-ethylpropyl)porphyrinato]nickel(II) following procedure E. The first fraction of column chromatography on silica gel eluting with ethyl acetate : *n*-hexane (4:1, v/v, h = 41 cm, ø = 3 cm) gave the pure product as purple crystals after recrystallisation from 1,4-dioxane/water (312.3 mg, 0.37 mmol) in 80 % yield: *Mp* 144 °C; $R_f$=0.77 (ethyl acetate:*n*-hexane, 4:1, v/v); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 0.88 ppm (t, 6H, $^3J$=7.3 Hz, $CH_2CH_3$), 1.01 (t, 18H, $^3J$=7.3 Hz, $CH_2CH_3$), 1.59 (d, 6H, $^3J$=6.4 Hz, $(CH_3)_2CH$), 1.61 (d, 6H, $^3J$=6.4 Hz, $(CH_3)_2CH$), 2.68 (m, 16H, $CH_2CH_3$), 4.14 (t, 1H, $^3J$=7.0 Hz, $CHCH_2$), 4.23 (m, 3H, $CHCH_2$), 4.94 (m, 2H, $CHCH_3$), 6.24 (dd, 1H, $^3J$=16.9 Hz, $^3J$=20.5 Hz, CH=CH-P), 8.80 (dd, 1H, $^3J_{HHP}$=16.9 Hz, $^2J_{HP}$=20.5 Hz, CH=CH-P), 9.16 (d, 1H, $^3J$=4.7 Hz, $H_\beta$), 9.19 (s, 4H, $H_\beta$), 9.23 (s, 1H, $H_\beta$), 9.26 (d, 1H, $^3J$=5.3 Hz, $H_\beta$); $^{13}$C NMR (100.6 MHz, $CDCl_3$, 20 °C): $\delta$= 13.61 ppm, 14.09, 14.12, 24.15, 24.19, 24.23, 24.27, 32.55, 33.36, 33.46, 48.84, 49.24, 49.31, 67.12, 70.59, 70.64, 117.49, 119.36, 120.56, 120.78, 120.96, 121.64, 130.45, 130.67, 130.72, 130.96, 131.17, 132.43, 132.59, 137.88, 139.73, 140.39, 142.46, 145.57; $^{31}$P NMR (162 MHz, $CDCl_3$, 20 °C): $\delta$= 17.82 ppm; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 431 nm (4.70), 556 (3.91), 593 (3.54); HRMS (ES+) [$C_{48}H_{67}N_4NiO_3P$+H]: calcd 837.4383, found 837.4377.

**(*E*)-Di(*iso*-propyl)-3,4,5-trimethoxystyrylphosphonate 196**




Prepared by reaction of 3,4,5-trimethoxbenzaldehyde following procedure E. The first fraction of column chromatography on silica gel eluting with ethyl acetate : *n*-hexane (4:1, v/v, h = 35 cm, ø = 3 cm) gave the pure product as white crystals after recrystallisation from dichloromethane/methanol (1.74 g, 5.0 mmol) in 99 % yield: *Mp* 77 °C; $R_f$=0.4 (ethyl acetate:*n*-hexane, 4:1, v/v); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 1.34 ppm (d, 6H, $^3J$=6.0 Hz, C$H_3$), 1.38 (d, 6H, $^3J$=6.3 Hz, C$H_3$), 3.88 (s, 3H, 4-OC$H_3$), 3.89 (s, 6H, 3,5-OC$H_3$), 4.72 (m, 2H, C$H$($CH_3$)$_2$); 6.17 (t, 1H, $^3J_{HHP}$=17.2 Hz, C*H*-7), 6.73 (s, 2H, $Ar_{H\text{-}2,6}$), 7.40 (dd, 1H, $^3J_{HHP}$=17.3 Hz, $^2J_{HP}$=22.3 Hz, C*H*-8), $^{13}$C NMR (100.6 MHz, $CDCl_3$, 20 °C): $\delta$= 24.05 ppm, 24.10, 29.70, 56.14, 60.96, 70.43, 70.48, 104.76, 113.83, 115.75, 130.49, 130.73, 139.79, 147.65, 147.72, 153.40; $^{31}$P NMR (162 MHz, $CDCl_3$, 20 °C): $\delta$= 17.46 ppm; IR: $\nu$= 1120 cm$^{-1}$ (P-O-alkyl), 1232 (P=O), 1377 (d, C($CH_3$)$_2$); HRMS (ES+) [2x$C_{17}H_{27}O_6P$]: calcd 739.2988, found 739.2980.

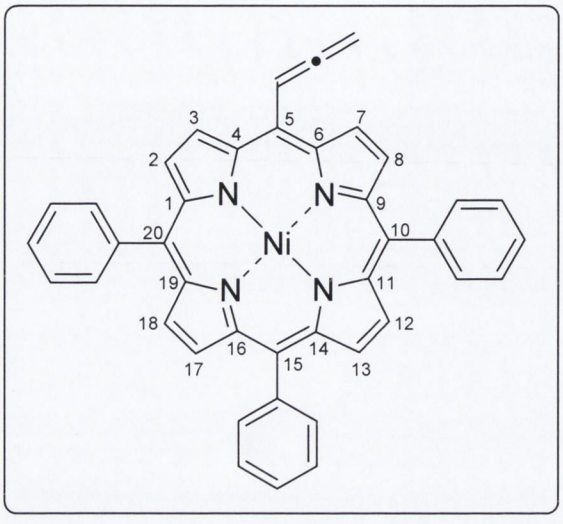
**(*E*)-Di(*iso*-propyl)-3-nitrostyrylphosphonate 197**




Prepared by reaction of 3-nitrobenzaldehyde following procedure E. The first fraction of column chromatography on silica gel eluting with ethyl acetate : *n*-hexane (4:1, v/v, h = 37 cm, ø = 2.5 cm) gave the pure product as yellow crystals after recrystallisation from dichloromethane/methanol (1.71 g, 5.6 mmol) in 85 % yield: *Mp* 64 °C; $R_f$=0.38 (ethyl acetate:*n*-hexane, 4:1, v/v); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 1.36 ppm (d, 6H, $^3J$=6.3 Hz, C$H_3$), 1.40 (d, 6H, $^3J$=6.3 Hz, C$H_3$), 4.72-4.81 (m, 2H, C$H$($CH_3$)$_2$); 6.45 (dd, 1H, $^3J$=16.0 Hz, $^3J$=17.6 Hz, C$H$-7), 7.53 (dd, 1H, $^3J_{HHP}$=4.8 Hz, $^2J_{HH}$=17.6 Hz, C$H$-8), 7.60 (dd, 1H, $^3J$=8.0 Hz, $^3J$=8.0 Hz, Ar$_{H\text{-}5}$), 7.80 (d, 2H, $^3J$=6.3 Hz, Ar$_{H\text{-}6}$), 8.24 (d, 2H, $^3J$=8.0 Hz, Ar$_{H\text{-}4}$), 8.38 (s, 1H, C$H$-2), $^{13}$C NMR (100.6 MHz, $CDCl_3$, 20 °C): $\delta$= 24.05 ppm, 24.09, 24.14, 70.90, 70.96, 118.77, 120.66, 121.91, 124.36, 129.96, 133.51, 136.70, 136.93, 144.62, 144.69, 148.67; $^{31}$P NMR (162 MHz, $CDCl_3$, 20 °C): $\delta$= 15.26 ppm; IR: $\nu$= 1120 cm$^{-1}$ (P-O-alkyl), 1231 (P=O), 1377 (d, C($CH_3$)$_2$), 1527 (Ph-$NO_2$); HRMS (ES+) [$C_{14}H_{20}NO_5PNa$]: calcd 336.0977, found 336.0991.

## 7.10 Allenylporphyrin

### (5-Allenyl-10,15,20-triphenylporphyrinato)nickel(II) 201



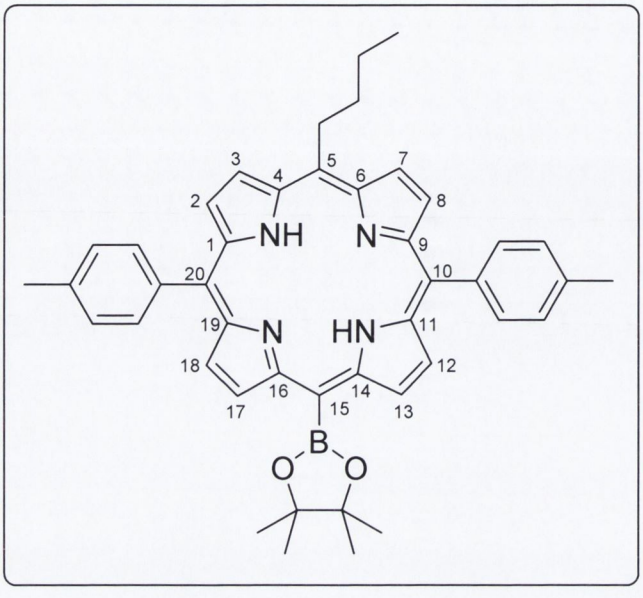

The bromoporphyrin **198** (30 mg, 0.045 mmol) and potassium carbonate (190.8 mg, 0.9 mmol) were placed in a Schlenk tube and dried under vacuum. Dry THF (20 ml) was added. The solution was degassed *via* three freeze-pump-thaw cycles, before the vessel was purged with argon. Allenyl boronic acid pinacol ester (81 µl, 0.45 mmol) and tetrakis(triphenylphosphine)palladium(0) (5.1 mg, 0.0045 mmol) were then added, and the Schlenk tube was sealed and stirred at 80 °C overnight. Dichloromethane was added and the organic phase was washed with aqueous saturated sodium hydrogencarbonate solution, water and brine. The residue was purified by column chromatography on silica gel with eluting with dichloromethane : *n*-hexane (1:3, v/v, h = 49 cm, ø = 3 cm). Red crystals were obtained after recrystallisation from dichloromethane/methanol in (2.6 mg, 0.004 mmol) 9 % yield: $R_f$=0.46 ($CH_2Cl_2$:*n*-hexane, 1:2, v/v); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 5.32 ppm (d, 2H, $^4J$=6.6 Hz, CH=C=C$H_2$), 7.70 (m, 9H, Ar$_H$), 8.01 (m, 6H, Ar$_H$), 8.31 (t, 1H, $^4J$=7.0 Hz, C$H$=C=C$H_2$), 8.68 (d, 2H, $^3J$=4.2 Hz, $H_\beta$), 8.70 (d, 2H, $^3J$=4.4 Hz, $H_\beta$), 8.81 (d, 2H, $^3J$=5.1 Hz, $H_\beta$), 9.46 (d, 2H, $^3J$=5.1 Hz, $H_\beta$); $^{13}$C NMR (100.6 MHz, $CDCl_3$, 20 °C): $\delta$= 29.27 ppm, 92.05, 109.22, 118.38, 118.53, 126.43, 126.46, 127.29, 130.27, 131.68, 131.75, 132.19, 133.20, 140.20, 140.22, 140.44, 141.06, 141.40, 141.89, 142.05, 142.13, 142.18, 215.61; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 420 nm (5.41), 534 (4.32); IR: $\nu$= 696 cm$^{-1}$ (aromatic H), 737 (aromatic H), 1537 (N-H), 1947 (C=C=C), 3054 (aromatic H).

## 7.11 Borylated porphyrins

### General procedure F – Synthesis of dioxaborolanylporphyrin

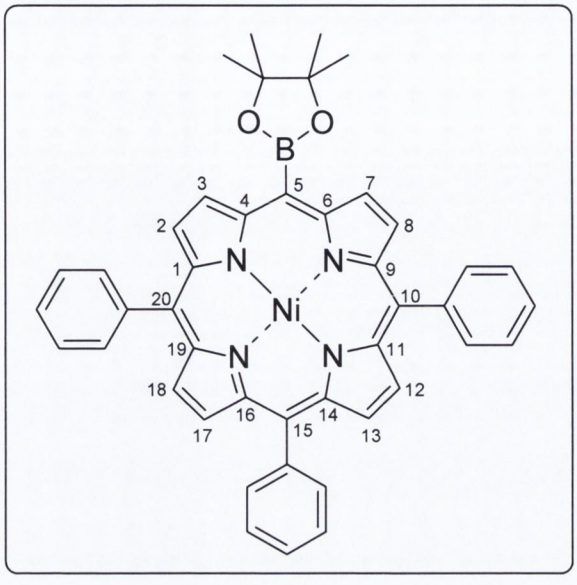
The bromoporphyrin (1 eq.) was placed in a Schlenk tube and dried under vacuum. Dry 1,2-dichloroethane (20 ml) and dry triethylamine (13 eq.) were added under argon. The solution was degassed *via* three freeze-pump-thaw cycles, before the vessel was purged with argon. 4,4,5,5-Tetramethyl-1,3,2-dioxaborolane (10 eq.) and dichlorobis(triphenylphosphine)palladium(II) (0.03 eq) were then added, and the Schlenk tube was sealed and stirred at 90 °C overnight. The reaction was quenched carefully with a saturated KCl solution, washed with water, and dried over $Na_2SO_4$. The solvent was removed under reduced pressure.

**5-Butyl-15-(4',4',5',5'-tetramethyl-[1',3',2']dioxaborolan-2'-yl)-10,20-bis(4-methylphenyl)porphyrin 216[255]**



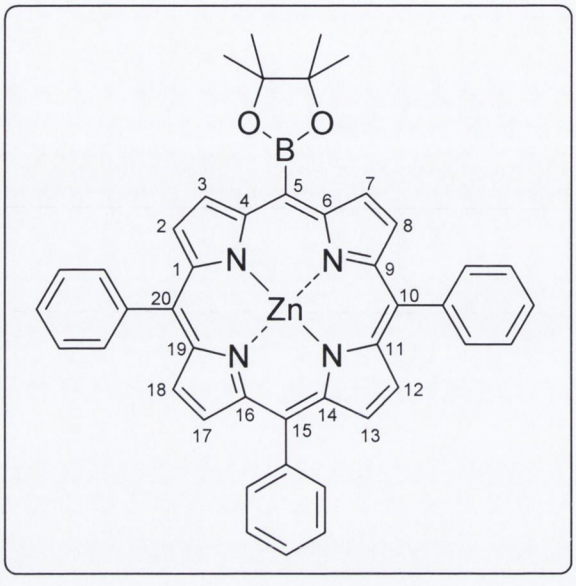

Prepared by reaction of 5-bromo-15-butyl-10,20-ditolylporphyrin following procedure F. The crude product was purified by column chromatography on silica gel dichloromethane : *n*-hexane (1:2, v/v) and gave the pure product as second fraction as purple crystals after recrystallisation from dichloromethane/methanol (207.3 mg, 0.308 mmol) in 48 % yield: *Mp* 260 °C; $R_f$=0.37 ($CH_2Cl_2$:*n*-hexane, 1:1, v/v); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 1.14 ppm (t, 3H, $^3J$=7.4 Hz, $CH_2$-C$H_3$), 1.84 (s, 14H, C$H_3$ + C$H_2$-$CH_3$), 2.55 (m, 2H, $CH_2$-C$H_2$-$CH_2$), 2.76 (s, 6H, Tolyl-C$H_3$), 5.04 (t, 2H, $^3J$=7.9 Hz, C$H_2$-$CH_2$-$CH_2$-$CH_3$), 7.59 (d, 4H, $^3J$=7.8 Hz, Ar$_H$), 8.10 (d, 4H, $^3J$=7.8 Hz, Ar$_H$), 8.92 (d, 2H, $^3J$=4.8 Hz, $H_\beta$), 8.95 (d, 2H, $^3J$=4.8 Hz, $H_\beta$), 9.49 (d, 2H, $^3J$=4.8 Hz, $H_\beta$), 9.82 (d, 2H, $^3J$=4.8 Hz, $H_\beta$), $^{13}$C NMR (100.6 MHz, $CDCl_3$, 20 °C): $\delta$= 14.24 ppm, 21.58, 23.71, 25.33, 35.28, 40.94, 85.06, 119.58, 122.50, 127.29, 134.45, 137.24, 139.67; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 417 nm (5.35), 517 (4.22), 549 (3.79), 589 (3.77), 644 (3.53); HRMS (ES+) [$C_{44}H_{45}BN_4O_2$+H]: calcd 673.3714, found 673.3685.

**[5-(4',4',5',5'-Tetramethyl-{1',3',2'}dioxaborolan-2'-yl)-10,15,20-triphenylporphyrinato]nickel(II) 212**




Produced from the bromoporphyrin **198** following procedure F. The crude product was purified by column chromatography on silica gel dichloromethane : *n*-hexane (1:2, v/v, h = 31 cm, ø = 6 cm) and gave the pure product as second fraction as purple crystals after recrystallisation from dichloromethane/methanol, yield: 201.5 mg (0.28 mmol, 51 %): *Mp* 230 °C; $R_f$=0.53 ($CH_2Cl_2$:*n*-hexane, 1:1, v/v); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): δ= 1.72 ppm (s. 12H, C$H_3$), 7.71 (m, 9H, Ar$_H$), 8.02 (m, 6H, Ar$_H$), 8.70 (d, 2H, $^3J$=4.9 Hz, $H_\beta$), 8.74 (d, 2H, $^3J$=4.9 Hz, $H_\beta$), 8.86 (d, 2H, $^3J$=5.1 Hz, $H_\beta$), 9.79 (d, 2H, $^3J$=5.1 Hz, $H_\beta$); $^{13}$C NMR (100.6 MHz, $CDCl_3$, 20 °C): $\delta$= 24.73 ppm, 84.39, 118.25, 126.38, 127.23, 127.29, 131.12, 131.86, 132.61, 133.18, 133.26, 133.54, 140.33, 140.44, 141.25, 141.45, 142.48, 146.44; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 413 nm (5.27), 528 (4.21), 569 (3.78); HRMS (ES+) [$C_{44}H_{35}BN_4NiO_2$+H]: calcd 721.2285, found 721.2272.

**[5-(4',4',5',5'-Tetramethyl-{1',3',2'}dioxaborolan-2'-yl)-10,15,20-triphenylporphyrinato]zinc(II) 213**



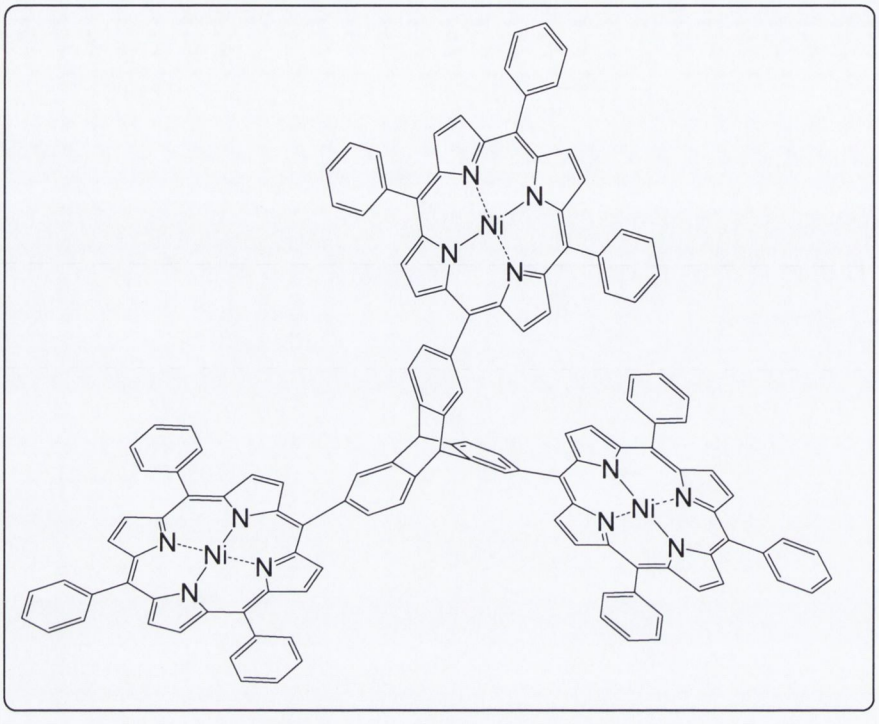

Produced from the bromoporphyrin **199** following procedure F. The crude product was purified by column chromatography on silica gel dichloromethane : *n*-hexane (1:2, v/v, h = 24 cm, ø = 3 cm) and gave the pure product as second fraction as purple crystals after recrystallisation from dichloromethane/methanol, yield: 108.7 mg (0.15 mmol, 29 %): *Mp* 148 °C; $R_f$=0.17 ($CH_2Cl_2$:*n*-hexane, 1:1, v/v); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 1.83 ppm (s, 12H, C$H_3$), 7.72 (m, 9H, Ar$_H$), 8.17 (m, 6H, Ar$_H$), 8.83 (d, 2H, $^3J$=4.7 Hz, $H_\beta$) 8.85 (d, 2H, $^3J$=4.9 Hz, $H_\beta$), 8.99 (d, 2H, $^3J$=4.7 Hz, $H_\beta$), 9.83 (d, 2H, $^3J$=4.7 Hz, $H_\beta$); $^{13}$C NMR (100.6 MHz, $CDCl_3$, 20 °C): $\delta$= 25.02 ppm, 84.91, 120.64, 122.30, 126.20, 127.13, 127.19, 131.24, 131.85, 132.56, 132.69, 134.02, 134.17, 142.44, 142.55, 149.02, 149.69, 150.09, 154.10; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 417 nm (5.13), 546 (4.27), 581 (3.57); HRMS (ES+) [$C_{44}H_{35}BN_4O_2Zn$+H]: calcd 727.2223, found 727.2206.

## 7.12 Porphyrin trimers

### General procedure G – Synthesis of porphyrin trimers

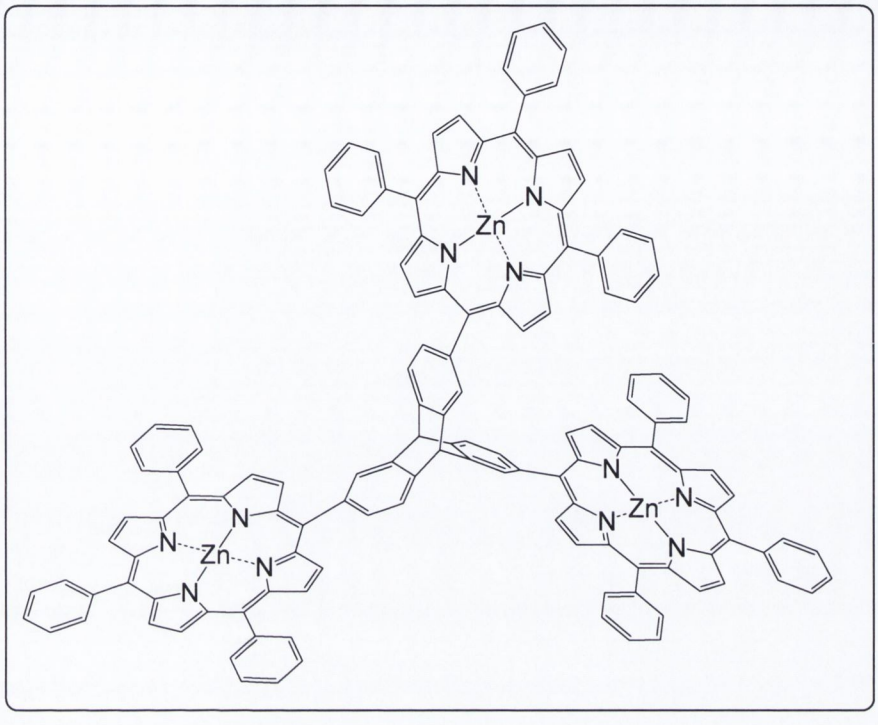
The borolanylporphyrin (1 eq.), 2,6,14-triiodotriptycene (0.3 eq.), potassium phosphate (4 eq.) and tetrakis(triphenylphosphine)palladium(0) (0.1 eq.) were place in a Schlenk tube and dissolved in anhydrous DMF under argon. The mixture was heated at 100 °C overnight. The solvent was removed and the residue was redissolved in dichloromethane and washed with aqueous sodium hydrogencarbonate solution.

**2,6,14-[Tris(5,10,15-triphenylporphyrinato)nickel(II)]triptycene 214**



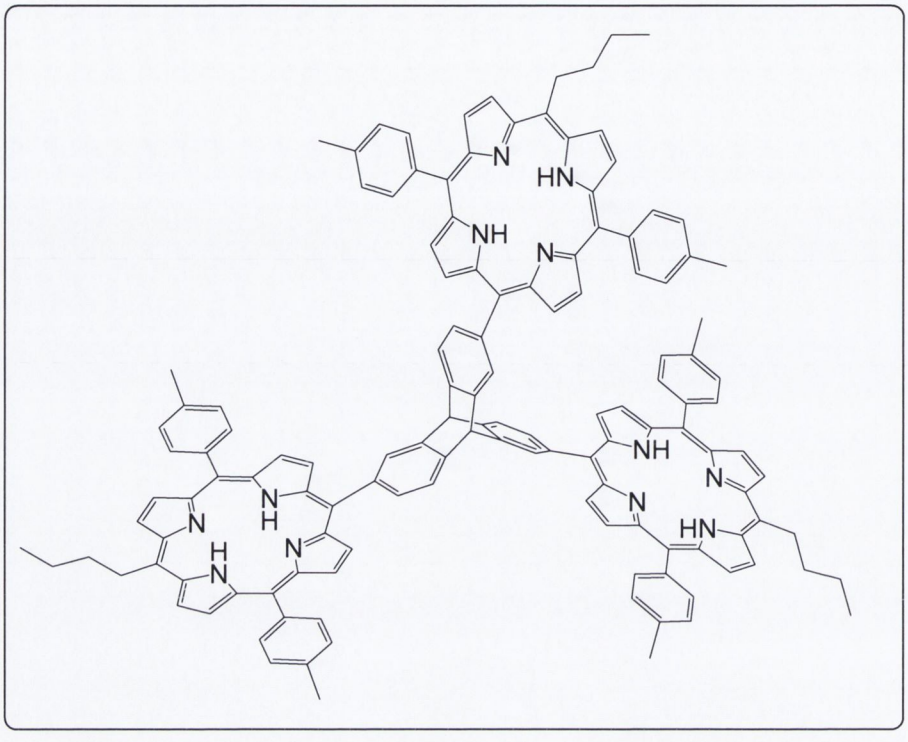
Produced from the borolanylporphyrin **212** following procedure G. The crude product was purified by dry-loaded column chromatography on silica gel, dichloromethane : *n*-hexane (1:2, v/v, h = 53 cm, ø = 3 cm) and gave the pure product as second fraction as orange crystals after recrystallisation from dichloromethane/methanol, yield: 20.6 mg (0.01 mmol, 22 %): *Mp* > 310°C; $R_f$=0.47 ($CH_2Cl_2$:*n*-hexane, 1:1, v/v); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 5.96 ppm (s, 1H, C*H*), 6.10 (s, 1H, C*H*), 7.71 (m, 30H, $Ar_H$), 8.05 (m, 21H, $Ar_H$), 8.18 (s, 1H, $Ar_H$), 8.25 (s, 1H, $Ar_H$), 8.33 (s, 1H, $Ar_H$), 8.78 (m, 16H, $H_\beta$), 8.92 (m, 8H, $H_\beta$); $^{13}$C NMR (150.9 MHz, $CDCl_3$, 20 °C): $\delta$= 13.99 ppm, 22.56, 29.24, 29.58, 31.80, 53.97, 54.01, 118.83, 118.84, 118.87, 118.91, 118.96, 122.43, 126.69, 126.71, 127.56, 129.43, 131.16, 132.02, 132.06, 132.29, 132.36. 132.42, 133.57, 138.02, 140.80; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 418 nm (5.54), 528 (5.06); HRMS (LD+) [$C_{134}H_{80}N_{12}Ni_3$]: calcd 2030.4689, found 2030.4669.

**2,6,14-[Tris(5,10,15-triphenylporphyrinato)zinc(II)]triptycene 215**




Produced from the borolanylporphyrin **213** following procedure G. The crude product was purified by column chromatography on silica gel dichloromethane : *n*-hexane (1:1, v/v, h = 30 cm, ø = 3 cm) and gave the pure product as second fraction as purple crystals after recrystallisation from dichloromethane/methanol, yield: 18.3 mg (0.009 mmol, 18 %): *Mp* > 310 °C; $R_f$=0.09 ($CH_2Cl_2$:*n*-hexane, 2:1, v/v); $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta$= 6.16 ppm (s, 1H, C*H*), 6.31 (s, 1H, C*H*), 7.81 (m, 30H, $Ar_H$), 8.30 (m, 21H, $Ar_H$), 8.51 (s, 1H, $Ar_H$), 8.59 (s, 1H, $Ar_H$), 8.69 (s, 1H, $Ar_H$), 9.03 (m, 18H, $H_\beta$), 9.22 (m, 6H, $H_\beta$); $^{13}$C NMR (150.9 MHz, $CDCl_3$, 20 °C): $\delta$= 14.01 ppm, 22.59, 29.26, 29.56, 29.60, 31.83, 36.26, 121.01, 121.07, 121.12, 122.27, 126.47, 127.40, 130.53, 131.89, 131.92, 132.00, 132.29, 134.35, 134.38, 140.04, 142.79, 144.09, 144.92; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 424 nm (5.49), 549 (4.92), 587 (4.32).

**2,6,14-Tris[5-butyl-10,15-bis(4-methylphenyl)porphyrin-20-yl]triptycene 217**



Produced from the borolanylporphyrin **216** following procedure G. The crude product was purified by column chromatography on silica gel dichloromethane : *n*-hexane (1:1, v/v, h = 31 cm, ø = 3 cm) and gave the pure product as the sixth fraction as purple crystals after recrystallisation from dichloromethane/methanol, yield: 8.9 mg (0.005 mmol, 16 %): *Mp* 237 °C; $R_f$=0.13 ($CH_2Cl_2$:*n*-hexane, 1:1, v/v); $^1$H NMR (600 MHz, $CDCl_3$, 20 °C): $\delta$= -2.64 ppm (s, 2H, N*H*), -2.61 (s, 2H, N*H*), -2.57 (s, 2H, N*H*), 1.16 (t, 12H, $^3J$=7.3 Hz, C$H_3$), 1.85 (m, 6H, C$H_2$-CH$_3$), 2.57 (m, 6H, CH$_2$-C$H_2$-CH$_2$), 2.77 (m, 18H, $C_6H_5$-C$H_3$), 5.06 (m, 6H, C$H_2$-CH$_2$-CH$_2$-CH$_3$), 6.13 (s, 1H, C*H*), 6.26 (s, 1H, C*H*), 7.61 (m, 12H, Ar$_H$), 8.14 (m, 18H, Ar$_H$), 8.48 (s, 1H, Ar$_H$), 8.53 (s, 1H, Ar$_H$), 8.60 (s, 1H, Ar$_H$), 8.91 (m, 5H, $H_\beta$), 8.99 (m, 13H, $H_\beta$), 9.51 (m, 6H, $H_\beta$); $^{13}$C NMR (150.9 MHz, $CDCl_3$, 20 °C): $\delta$= 13.97 ppm, 14.06, 21.41, 22.54, 23.51, 29.21, 29.56, 31.79, 35.11, 40.75, 54.17, 119.25, 119.46, 116.53, 120.29, 122.34, 127.19, 128.69, 130.47, 130.75, 132.04, 134.33, 137.05, 137.08, 137.15, 139.30, 139.43, 144.11, 144.87; UV/vis ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$)= 422 nm (5.40), 446 (5.01), 518 (4.44), 554 (4.25), 593 (4.04), 649 (4.05); HRMS (ES+) [$C_{134}H_{110}N_{12}$+2H]: calcd 1888.9133, found 1888.9158.

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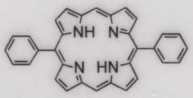
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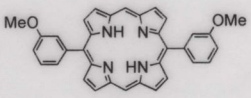
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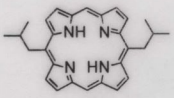
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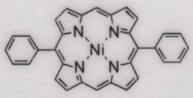
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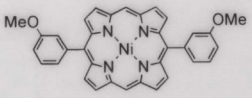
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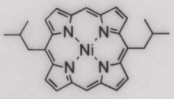
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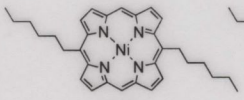
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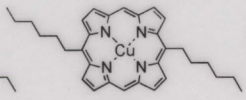
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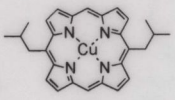
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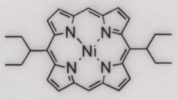
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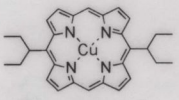
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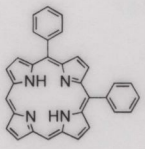
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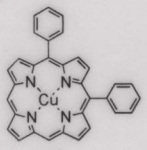
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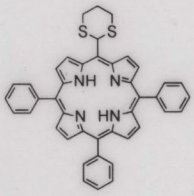
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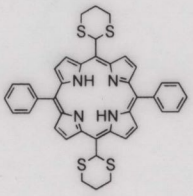
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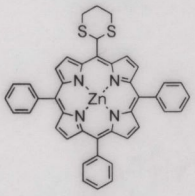
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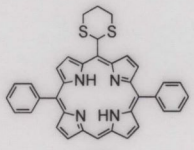
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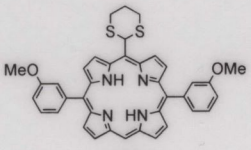
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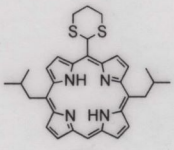
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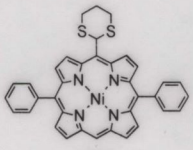
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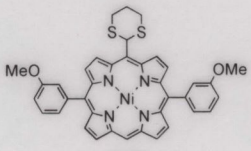
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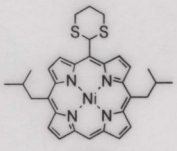
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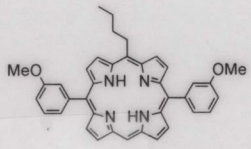
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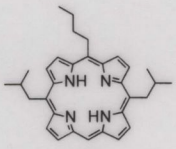
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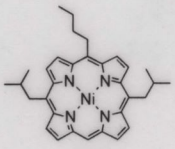
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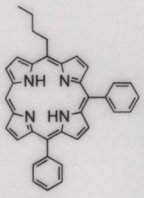
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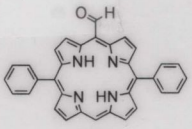
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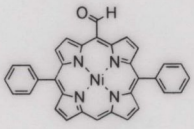
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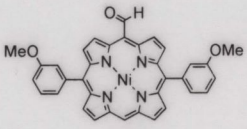
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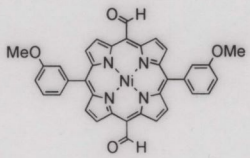
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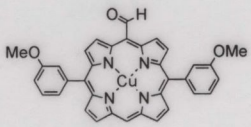
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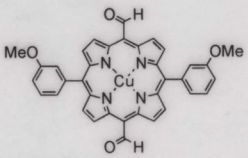
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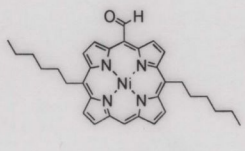
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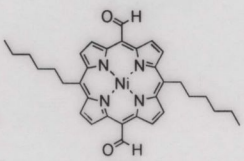
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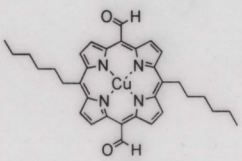
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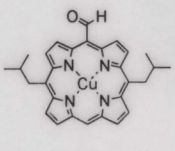
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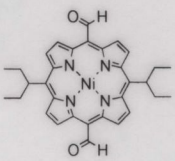
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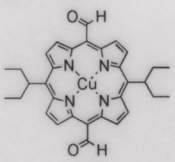
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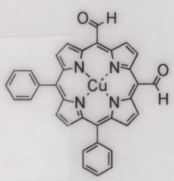
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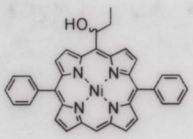
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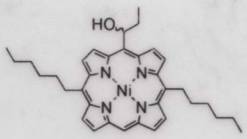
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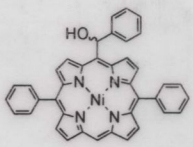
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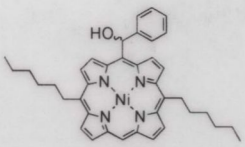
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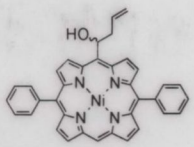
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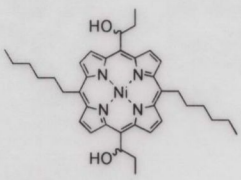
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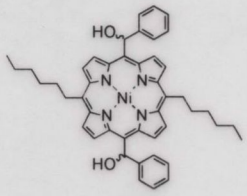
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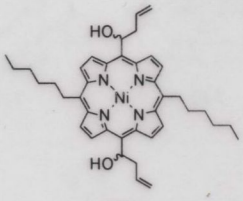
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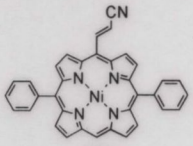
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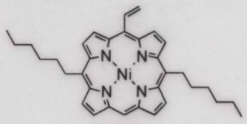
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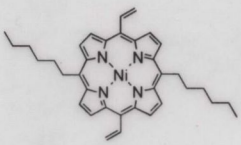
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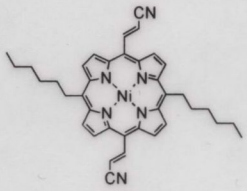
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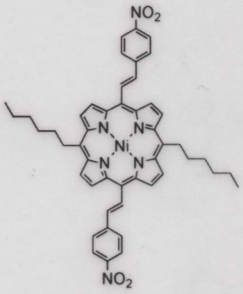
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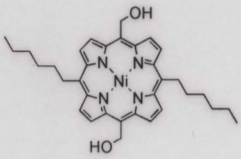
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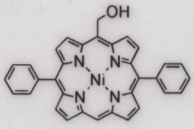
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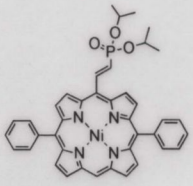
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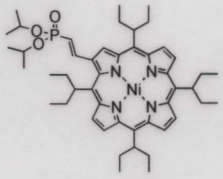
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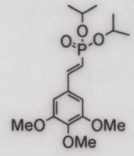
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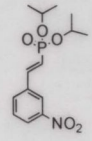
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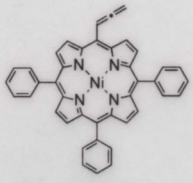
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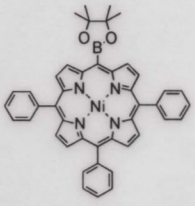
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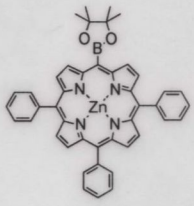
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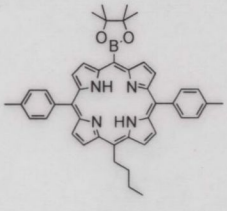
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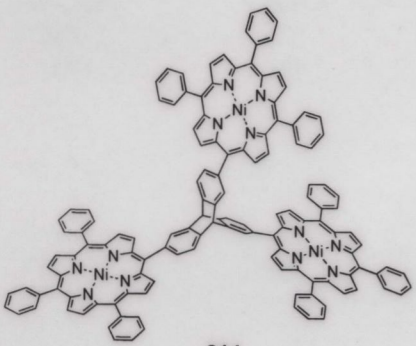
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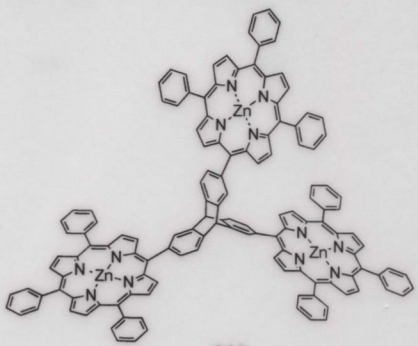
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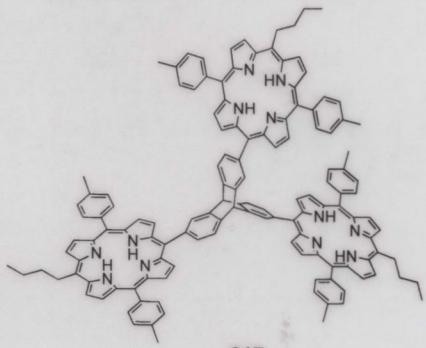
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