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Synthesis of Novel Polyaromatic and Heteropolyaromatic Molecules

Submitted by

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

Doctor of Philosophy

University of Dublin, Trinity College

July 2014
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Mia Davis
Summary

The aim of this work was to explore a number of different pathways for the synthesis of novel polyaromatic and heteroaromatic molecules. In particular, focus was directed towards the development of new preparative methods and the improvement of existing synthetic pathways for the synthesis of anthracenylporphyrins, triptycene scaffolds and subsequent triptycene-linked hexaporphyrin arrays.

A library of both symmetrically and unsymmetrically meso-tetrasubstituted anthracenylporphyrins were synthesised via condensation reaction and by Suzuki cross-coupling reactions. This comparative study showed that anthracenylporphyrins which were not accessible via Suzuki cross-coupling could be isolated via condensation reaction. However, the synthesis of anthracenylporphyrins which could be prepared via condensation reaction was limited by the cumbersome synthesis of the 5-substituted dipyrromethane precursors. Nevertheless, the developed method offered a good alternative to the Suzuki cross-coupling approach for the synthesis of dianthracenylporphyrins. This study also showed that the ruffled conformation adopted by Ni(II) porphyrins favours Suzuki cross-coupling reaction resulting in higher yields of Ni(II)anthracenylporphyrins than that of the corresponding free base or Zn(II)anthracenylporphyrins. A Suzuki cross-coupling reaction was also employed for the synthesis of an anthracene-linked porphyrin dimer.

Transition metal catalysed reactions were also investigated for the synthesis of novel hexa-substituted triptycene scaffolds for applications in light harvesting devices and molecular machines. A number of triptycene scaffolds were designed and isolated such that they that they could be used as precursors for further coupling reactions, thus, allowing access to elaborate highly complex molecular structures. A number of covalently-linked triptycene scaffolds with varying functionality were isolated relatively high yields via Sonogashira cross-coupling and Suzuki cross-coupling reactions. The $\pi$-conjugation of the triptycene scaffolds was also extended using Sonogashira cross-coupling and Glaser cross-coupling reactions.

Finally, in order to prove that the triptycene scaffolds were suitable for the synthesis of more complex elaborate structures, a triptycene-linked hexaporphyrin array was also synthesised. The reaction of the novel scaffold 2,3,6,7,14,15-hexaethynyltriptycene with 5-bromo-10,20-
diphenylporphyrin afforded the porphyrin hexamer in moderate yield using unoptimised reaction conditions.

Publications


Conference Abstracts


For my parents
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Abbreviations

acac acetylacetonate

Ar aromatic
Br  broad  butyl
Calcd  calculated  COSY  correlation spectroscopy  CDCI$_3$  deuterated chloroform
d  doublet  dba  dibenzylideneacetone  DCM  dichloromethane
dd  double doublet  DDQ  2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DIPA  Diisopropylamine  DMAP  4-Dimethylaminopyridine  DMF  N,N-dimethylformamide
DMSO  dimethyl sulphoxide  dtbbpy  4,4'-di-tert-butyl-2,2'-bipyridyl
Eq  equivalents  ES  electrospray  ESI  electrospray ionisation
Hex  hexyl  HRMS  high resolution mass spectrometry
IR  infrared  J  coupling constant measured in Hertz
Me  methyl  MeOH  methanol
m  multiplet  m/z  mass-to-charge ratio
mp  melting point  MS  mass spectrometry
MW  microwave  n-BuLi  n-butyllithium
n.d.  not detected  NLO  non-linear optics
NPM  N-Methylpyrrolidone  NMR  nuclear magnetic resonance
NOSEY  nuclear Oberhauser effect spectroscopy
OAc  acetate
OEP  2,3,7,8,12,13,17,18-octaethylporphyrin
OTf  triflate
PdCl₂(PPh₃)₂  dichlorobis(triphenylphosphine)palladium(II)
Pd(PPh₃)₄  tetrakis(triphenylphosphine)palladium(0)
Pd₂(dba)₃  tris(dibenzylideneacetone)dipalladium(0)
PDT  photodynamic therapy
Ph  phenyl
Rf  retention factor
RLi  organolithium reagent
rt  room temperature
s  singlet
SₓAr  electrophilic aromatic substitution
SₜAr  nucleophilic aromatic substitution
t  triplet
TBAF  tetra-\(n\)-butylammonium fluoride
TEA  triethylamine
TFA  trifluoroacetic acid
THF  tetrahydrofuran
TLC  thin layer chromatography
TOF  time of flight
UV  ultraviolet
v/v  volume to volume
vis  visible
\(\delta\)  chemical shift measured in parts per million (ppm)
\(\varepsilon\)  absorption coefficient
\(\lambda\)  wavelength measured in nanometre (nm)
Chapter 1
Introduction
1.1 Aromaticity and its history

Polyaromatic and polyheteroaromatic chemistry is a large branch of organic chemistry which is of major importance in research today. August Wilhelm von Hofmann first attempted to define aromaticity in 1855. He postulated that aromaticity was in fact a chemical property in which the stability of the molecule is stronger than would be expected by the stabilization through conjugation alone. In 1931 Hückel proposed that ‘amongst fully conjugated, planar, monocyclic polyolefins only those possessing $(4n + 2)$ π-electrons, where $n$ is an integer, will have special stability’. This is now known as Hückel’s rule. An aromatic compound was once defined as a hydrocarbon with alternating single and double bonds between each carbon atom. However, this definition does not suffice today, as antiaromatic compounds also have alternating single and double bonds. They are also planar, cyclic conjugated molecules but they are not classed as aromatic because they have an even number of pairs of π-electrons. Thus, the antiaromatic ring has $4n$ π-electrons and does not satisfy Hückel’s rule. A consequence of this is that they exhibit no aromatic characteristics and they are less stable than their aromatic counterparts. Non-aromatic compounds can in fact satisfy Hückel’s rule and can have $4n$ or $4n+2$ π electrons. However, they are not classed as aromatic due to distortion or disruption of the delocalisation of the π-electrons.

1.2 Polyaromatic and polyheteroaromatic compounds: Classes and synthesis

1.2.1 Polyaromatics

Polyaromatics or polyarenes are a class of aromatic compounds which consist of fused aromatic rings and do not contain heteroatoms (Figure 1.1). Larger polyarenes generally consist of six or more aromatic rings and smaller ones consist of six to three, anything smaller than three fused aromatic rings is not considered to be a polyaromatic compound.
Although there is no question that polyaromatic molecules are indeed aromatic, the degree of aromaticity can differ between each ring segment. Hückel’s rule is also not necessarily applicable for polyarenes whose stability is governed by Clar’s empirical finding.\(^4\) Clar deduced that the most stable structure of annulated benzenes is the one which possesses the maximum number of aromatic sextets separated by an entirely ‘empty’ six-membered ring. The electrons are said to be ‘semilocalised’ in disjoint \(\pi\)-sextets, \(i.e.\) the \(\pi\)-electrons of one ring are considered to be spin-coupled in the neighbouring ring. This means they in fact belong to the neighbouring moiety, thus forming their sextet substructure, forming isolated aromatic islands surrounded by the \(\pi\)-electron ‘empty’ rings or gaps. If triphenylene 1 and phenanthrene 2 are compared it can be seen that triphenylene has a completely vacant central ring whereas 2 has a ‘localised’ central ring in accordance with Clar’s rule.

### 1.2.1.1 Anthracene

Anthracene (3) is the simplest example of a polycyclic aromatic molecule. It consists of three fused benzene rings. It was first isolated from coal in 1833 but it was not until 1884 that 3 was synthesised by Karl Elbs as illustrated in Scheme 1.1.\(^5\)
The synthesis of 3 can be achieved through the dehydration type Elbs reaction by using an ortho methyl substituted benzophenone precursor 4 (Scheme 1.1). This reaction also facilitates the synthesis of larger, condensed linear polyaromatic molecules.5,6

Since then, 3 has been used as a precursor for a variety of applications ranging from dyes to electroluminescent devices and anti-cancer treatments. As a result, there has been much interest in the functionalisation of 3 in order to tailor its properties for specific applications.

Compound 3 exhibits a high quantum efficiency of photoluminescence7 and its derivatives exhibit interesting properties ranging from thermotropic liquid-crystal properties to light-light emitting properties.8-11 The emission characteristics of compound 3 also makes its suitable for sensors12 and solar cells.13 However, one of the major drawbacks of 3 is its ability to undergo dimerisation at the free meso-position due to the lack of photostability as illustrated in Scheme 1.2. The anthracene dimer 5 can revert back to the anthracene monomers 3 with the application of heat or by exposing it to UV irradiation lower than 300 nm.

![Scheme 1.2: Anthracene dimer isolation through exposure to UV light.](image)

Functionalisation of the fused benzene rings can give rise to enhanced fluorescence quantum efficiency and eliminates photostability issues.14 For example, 9,10-diphenylethynylatedanthracene exhibits a significant bathochromic shift of fluorescence and a higher quantum yield than other anthracene derivatives.15-17 More recently, there has also been interest in the synthesis of anthracene containing polymers for applications in material science.18-24
1.2.2 Iptycenes

Iptycenes are a class of structurally unique compounds consisting of arenes that are fused together through a bicycle[2.2.2]octane framework. The ‘iptycene’ concept was first proposed by Hart in 1981, based on triptycene 6, denoting the number of arene planes separated by the bridgehead system. There has been much interest in the development of iptycene derivatives, in particular 6 and pentiptycene 7 (Figure 1.2) due to the wide range of applications for which they can be tailored to, which include molecular machines, host-guest chemistry, ligand design, and intramolecular charge transfer.

![Figure 1.2: Structure of triptycene 6 and iptycene 7.](image)

The three-dimensional shape of iptycenes gives rise to an internal space otherwise known as free volume (Figure 1.3). This free volume promotes alignment in oriented polymers and liquid crystals in such a way that internal cavities are occupied by the host material, thus minimizing the free volume. It has been reported by Swager et al., that an iptycene polymer aligns orthogonally to host polymers when stretched, resulting in a molecular woven cloth. One general feature of the iptycene structure is that it prevents efficient crystal packing into pure crystalline lattices. The crystals tend to include solvent molecules into where one would expect...
to find free volume. The removal of the solvent molecules introduces free volume into
the crystal lattice.

Iptycenc containing polymers display solution-like emissive spectra and quantum
yields in the solid state. They are also exceptionally stable, even at high temperatures,
making them suitable for new vapour detection methods for ultratrace detection of
high explosives which is currently in use by The United States army.\textsuperscript{27}

1.2.2.1 Triptycene

The simplest member of the iptycene family is triptycene (6) and it is a C\textsubscript{20}
hydrocarbon with D\textsubscript{3h} symmetry. It was first isolated by Barlett \textit{et al.} in 1942 (Scheme
1.3).\textsuperscript{49}

\textbf{Scheme 1.3:} Bartlett synthesis of triptycene 6.\textsuperscript{49}
The reaction proceeds via Diels-Alder style reaction between compounds 3 and 8 to form adduct 9. The hydrogenation of 9 using copper chromite yielded 10. Subsequent oxidation using potassium bromate afforded triptycenedione 11 in good yield 93 %. Dioxime 12 was prepared by heating 11 together with hydroxylamine hydrochloride for 2 hours under reflux. Compound 12 was then reduced to the diamine derivative 13. Deamination of 13 was achieved using hypophosphorous acid which yielded the monochlorotriptycene 14. The formation of 14 can be attributed to the p-diazo substituent, which activates the N2-group toward replacement. As the first N2 group is replaced the remaining N2 group is eliminated thus yielding 14 as the major product. This was then reduced to yield 6 in an overall yield of 20 % (Scheme 1.3).\(^{49}\)

Craig and Wilcox\(^ {50}\) reported a more direct route for the synthesis of 6 in 1959, where it was reported that the triptycenedione 11 was reduced using LiAlH\(_4\) or NaBH\(_4\). The crude product was then heated under reflux in ethanolic hydrochloric acid and then subjected to chromatography on alumina to yield 6 in 15 % yield.\(^ {50}\) This paved the way for Wittig and Ludwig who reported a simple one step synthesis of 6 from 3 and benzyne 15 (Scheme 1.4). Anthranilic acid 16 was reacted with isopentyl nitrite 17 to generate 15 in situ, as illustrated in Scheme 1.4.\(^ {51}\) Various other precursors were also used to generate 15 in situ; the yields for the isolation of 6 ranged from 10 % to 59 %, the results of which are shown in Table 1.1.

\[ \text{Scheme 1.4: Generation of 15 in the synthesis of 6.} \]
Table 1.1: Precursors for the optimisation for the synthesis of 6.\textsuperscript{51}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Precursor</th>
<th>Activation</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{BrMg} )</td>
<td>Heat</td>
<td>28\textsuperscript{51}</td>
</tr>
<tr>
<td>2</td>
<td>( \text{Li} )</td>
<td>Room Temperature</td>
<td>10\textsuperscript{52}</td>
</tr>
<tr>
<td>3</td>
<td>( \text{N}_2 )</td>
<td>Heat</td>
<td>30\textsuperscript{53}</td>
</tr>
<tr>
<td>4</td>
<td>( \text{HOOC} )</td>
<td>Isopentyl nitrite Heat</td>
<td>59\textsuperscript{54}</td>
</tr>
<tr>
<td>5</td>
<td>( \text{t-BuOK} )</td>
<td>t-BuOK</td>
<td>21\textsuperscript{55}</td>
</tr>
<tr>
<td>6</td>
<td>( \text{Bu}_4\text{NF} )</td>
<td>Bu4NF</td>
<td>86\textsuperscript{56}</td>
</tr>
<tr>
<td>7</td>
<td>( \text{Li} )</td>
<td>Heat</td>
<td>11\textsuperscript{57}</td>
</tr>
</tbody>
</table>

An investigation into the reactivity of 15 towards substituted anthracenes W was undertaken by Klanderman et al.\textsuperscript{58} It was discovered that these compounds react to form Diels-Alder adducts with different substitution patterns. The central ring can attach at either the central ring A to form X or at either terminal positions B or C forming Y or Z, respectively (Scheme 1.5).

This study showed that the substituents in one ring do not influence the reactivity of another ring toward 15, the only exception is 9,10-diphenylanthracene. In fact, the reactivities generally mirror those of 3 toward maleic anhydride.\textsuperscript{58}
Scheme 1.5: Varying substitution patterns of the Diels-Alder adduct.

The unique structure of triptycene and triptycene derivatives makes them suitable for applications such as molecular inclusion compounds, coordination compounds with unusual geometries, molecular tweezers, nanosized molecular cages and for encapsulating small neutral molecules. Triptycene’s three-dimensional framework also gives rise to an electron rich cavity making it suitable for host-guest studies. Furthermore, triptycene 6 also exhibits unique electrochemical and photochemical properties which can make it a useful precursor for the synthesis of more elaborate iptycene complexes suitable for applications such as liquid crystals and polymers. Triptycene containing polymers are porous and are capable of absorbing gases due to the spatial orientation of the phenyl rings. The arrangement of the phenyl rings gives triptycene 6 its three blade ‘paddle like’ structure, which is capable of rotating around the axis running through the bridgehead, making it suitable for molecular machines. Further applications have also been reported recently for triptycene 6 as an anti-cancer agent and anti-malaria agent in the pharmaceutical industry.
1.2.3 Polyheteroaromatics

Aromatic and non-aromatic heterocycles have a wide variety of applications such as pharmaceuticals, organic conductors, insecticides and many more. One major difference between heteroaromatic compounds and polyaromatic compounds is that heteroaromatic compounds can act as ligands by binding to a metal, thus forming a coordination complex. This is true for the simplest of heteroaromatics such as phenanthroline 16 and its derivatives right up to the more elaborate porphyrins. This was clearly illustrated in a report by Baytekin et al. where they described a route to rigid divalent receptors 17, 18 and trivalent receptors 19 and interlocked molecules using phenanthroline-type tetralactam macrocycle precursors 20 (Scheme 1.6).

\[
\text{Scheme 1.6: Baytekin's synthesis of rigid di- and trivalent receptors and interlocked molecules using phenanthroline-type tetralactam macrocycle precursors.}^{95}
\]
Pyrrole (21) (Scheme 1.7), although a five membered ring system with delocalisation that differs from that of benzene, is still considered a heterocycle as it derives its aromaticity from the delocalisation of the lone pair from the nitrogen atom. As a result of this, the nitrogen atom cannot be protonated, thus making it non-basic. A number of pyrroles occur in nature but the importance of these is overshadowed by the tetrapyrrole derivatives, such as chlorophyll a (22), heme (23) and vitamin B_{12}.

Porphyrin chemistry is an ever expanding area of interest in the world of organic chemistry. Porphyrins are heterocyclic macrocycles consisting of four pyrrole type residues with the $\alpha$ carbons linked via methine bridges (Figure 1.4). Porphyrins are aromatic species which obey Hückel’s rule for aromaticity in that porphyrins contain $[4n+2]$ $\pi$-electrons, where $n = 4$. Although a porphyrin has 22 $\pi$-electrons, only 18 of these are involved in the aromatic system of the macrocycle. The remaining electrons are not involved in the aromaticity, thus Hückel’s rule is still valid for porphyrins. The electrons are delocalised, making the macrocycle highly conjugated, resulting in the porphyrins’ deep colour and is also responsible for the distinct absorption spectra porphyrins exhibit, the Soret band, which has a very high extinction coefficient. They are naturally occurring macrocycles and are sometimes referred to as the ‘pigment of life’. This is because they are well known as being components as hemes in hemoproteins in blood and chlorophylls in photoautotrophs, both of which are involved in many biological processes including energy transfer and food production for the latter. Porphyrins can be found in nature and are involved in and play a major role in a variety of functions such as oxygen transfer, electron transfer, oxidation catalysts and photosynthesis.

1.2.3.1 Porphyrins

The main function of porphyrins in nature is to chelate to metals, and these complexes subsequently play an integral role in biochemical processes (Figure 1.5). One of the...
most important porphyrins complexes in nature is hemoglobin which contains the Fe II protoporphyrin IX derivative 23.\textsuperscript{100,101}

In heme (23), the iron acts as a reversible binding site for oxygen, allowing it to be transported throughout an organism. Chlorophyll a (22) is responsible for the green pigment in Higher Plants, algae and cyanobacteria which is responsible for a majority of light absorption in the red and blue portions of the electromagnetic spectrum. It is based on a magnesium-chlorin complex, which contains a saturated bond between the 7 and 8 positions on the macrocyclic ring.\textsuperscript{101,102}

![Heme 23 and Chlorophyll a 22](image)

**Figure 1.5:** Heme 23 and chlorophyll a 22.

### 1.2.3.2 Synthesis of porphyrins

Historically, Thudichum\textsuperscript{103} isolated the first porphyrin in 1867 by treating hemoglobin with sulfuric acid. The correct porphyrin structure however, was first proposed by Küster in 1912. This was later confirmed by Fischer when he reported the first synthesis of porphine in 1926,\textsuperscript{104} the simplest of the porphyrin family. In 1929 Fischer went on to successfully synthesise heme.\textsuperscript{105} Rothemund then later synthesised porphine and meso tetrasubstituted porphyrins by condensation of pyrrole 21 with aldehydes.\textsuperscript{106,107}

Further developments of porphyrin synthesis was undertaken by Alder and Longo in 1967,\textsuperscript{108} who reported the concept of refluxing propionic acid to dissolve the aldehyde
and 21 to obtain crystalline porphyrins. However, the yields still remained relatively low at 20%. For the synthesis of 5,10,15,20-tetraphenylporphyrin yields of 30-40% were obtained by using acetic acid or acidified benzene (Scheme 1.7), which is now known as the Alder-Longo method.\(^{108}\)

\[
\begin{align*}
\text{NH} & \\
21 \text{ (1.0 eq.)} & \text{CH}_3\text{COOH} \\triangle, 30 \text{ min} & 25 \quad + \text{H}_2\text{O} \\
\text{R} & \text{CHO} \\
24 \text{ (1.0 eq.)} & \\
\text{R} & \text{Phenyl}
\end{align*}
\]

Scheme 1.7: Alder-Longo method for the synthesis of meso-substituted porphyrins.\(^{108}\)

At this time the desire to isolate novel and elaborate meso substituted porphyrins using milder conditions was still at the forefront of porphyrin chemists’ minds. Another successful method for the synthesis of porphyrins was developed by Lindsey \textit{et al.} in 1987.\(^{109}\) Here a one-pot reversible reaction of 21 and an aldehyde at room temperature was used. However, the oxidising agent employed in this case was 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ).\(^{109}\) The reaction was found to be quite sensitive to the concentration of the reactants and the acid catalyst. For 10 mM reactants, BF\(_3\)-etherate was found to be effective at 1 mM while TFA required a higher concentration of 20—50 mM.\(^{109}\) The Lindsey-type synthesis can accommodate a variety of both alkyl and aryl aldehydes, ranging from \textit{para, ortho,} and meta-
substituted benzaldehydes\textsuperscript{110-117} to heterocyclic aldehydes\textsuperscript{118} and organometallic units \textsuperscript{119} with an average yield of 30\% for fully symmetrical porphyrins.

Porphyrins with a 5,15-substitution pattern are useful for a variety of applications as well as useful building blocks for further functionalisation. This substitution pattern can be achieved via mixed aldehyde condensation reactions. However, due to the poor selectivity of this reaction by-products can be isolated,\textsuperscript{120} such as the 5,10-disubstituted porphyrin in about 25\% yield, thus lowering the yield of the desired 5,15-disubstituted porphyrin. Separation of the 5,15- and 5,10-substituted porphyrins involves cumbersome column chromatography. This is because the porphyrins have the same substituents on the periphery of the macrocycle, giving them very similar polarities.

Today, the most common method for the synthesis of 5,15-disubstituted porphyrins is a \([2+2]\) condensation reaction (Scheme 1.8) which was developed by MacDonald \textit{et al.}\textsuperscript{121}

\begin{center}
\textbf{Scheme 1.8} MacDonald-type \([2+2]\)-condensation reaction.\textsuperscript{121}
\end{center}

\[\text{R}^1 = \text{Phenyl, } \text{R}^2 = \text{H}, \text{5,15-}{\text{A}}_2\text{porphyrin} \]
\[\text{R}^1 = \text{alkyl/aryl, } \text{R}^2 = \text{H, 5,15-}{\text{A}}_2\text{porphyrin} \]
\[\text{R}^1 = \text{alkyl/aryl, } \text{R}^2 = \text{alkyl/aryl, 5,15-}{\text{A}}_2\text{porphyrin} \]
The reaction involves the acid-catalysed condensation of dipyrromethane 28 or its derivatives with an aldehyde to form the porphyrinogen intermediate 14. Subsequent oxidation with an oxidant such as 27 yields the corresponding porphyrin (Scheme 1.8).

1.3 Polyheteroaromatics and polyaromatic compounds: functionalisation reactions

Although the previously discussed reactions do offer a path to prepare a variety of simple aromatic hydrocarbons further functionalisation is required to tailor these molecules for specific applications.

1.3.1 Electrophilic aromatic substitution

Electrophilic aromatic substitution (S^EAr) reactions include halogenations, nitrations, Vilsmeier formylations, sulfonations and acylations. For the purpose of this thesis the focus will be on halogenation reactions only.

\[
\text{Scheme 1.9: General scheme for the synthesis of arylhalides.}
\]

One of the most important S^EAr reactions are halogenation reactions because aryl halides can act as useful building blocks or precursors for technically more elaborate molecules. In particular, arylhalides (Scheme 1.9) can act as precursors for the synthesis of boron derivatives which can then be used for C-C coupling reactions.

A catalyst is usually required for the halogenation of polyaromatic compounds. The catalysts most frequently used are metal halides that are capable of accepting electrons (i.e. Lewis acids such as FeBr₃, AlCl₃, and ZnCl₂). The catalyst activates the
bromine molecules by polarising them allowing attack from the nucleophilic aromatic ring. Interestingly, when anthracene (3) is reacted with molecular bromine addition takes place at the 9 and 10 positions to form 9,10-dibromo-9,10-dihydroanthracene 29. However, the addition products of halogenation readily undergo elimination to form the 9-substitution products such a 9-bromoanthracene 30 (Scheme 1.10).\footnote{127,128}

\begin{center}
\begin{align*}
\text{3} & \xrightarrow{\text{Br}_2 (1.0 \text{ eq.}) \atop \text{FeCl}_3 (0.001 \text{ eq.}) \atop \text{EtOAc} \atop \text{rt, 20 min.}} \text{29} \\
\text{29} & \xrightarrow{-\text{HBr} \atop 60^\circ \text{C}} \text{30}
\end{align*}
\end{center}

\textbf{Scheme 1.10:} Bromination of 3 to yield 30.\footnote{129}

The same strategy can be employed for chlorination, but not for iodination. The order of reactivity of the halogen atoms in $S_{E1}Ar$ reactions is $F_2 > Cl_2 > Br_2 > I_2$.\footnote{130} Molecular iodine is not reactive enough for electrophilic aromatic substitutions and fluorine is too reactive for the practical preparation of polyaromatic fluorine compound. As a consequence, iodination and fluorination must be carried out by other indirect means.\footnote{131}

Although complex, porphyrins are expected to undergo all the characteristic reactions of aromatic molecules; nucleophilic reactions such as those with organometallic reagents; and oxidation and reduction reactions. However, most electrophilic substitutions are employed on metallated porphyrins since these metallocycles are more stable to electrophilic attack whereas the free base porphyrins are easily protonated under acidic conditions.\footnote{132} There are two different sites at which these reactions can occur on the porphyrin periphery. Namely, the meso and the $\beta$-position. The two pyrrole units in porphyrins achieve an individual aromatic sextet of electrons resulting in the electron density being withdrawn from the neighbouring meso carbon atom, thus giving it a greater electrophilic character relative to the $\beta$-pyrrolic carbon. The meso carbon is sterically less accessible than the $\beta$-pyrrolic...
carbon, and even more so if the β-position has already been functionalised with a bulky group, thus the β-pyrrolic carbon is sterically favoured and readily undergo either substitution and/or addition reactions. This is illustrated in Scheme 1.11 as porphyrins 31 and 32 are generated when porphyrin 33 is reacted with NBS.

![Scheme 1.11: Bromination occurring at the β-position.](image)

_N-bromosuccinimide (NBS) and _N_-chlorosuccinimide (NCS) have proven to be successful halogenating agents for porphyrins._ For monohalogenation 1-1.5 equivalents of (NBS) or (NCS) is required. The competing reaction is this case is typically dihalogenation; however this by-product can be kept to a minimum yield if the reaction is carried out at 0 °C. A bromination reaction on free base substituted porphyrin (porphine) with NBS in CHCl₃ was performed by Longo _et al._ This reaction gave predominantly meso-brominated product as a mixture of 5-mono-, 5,15-di- and 5,10,15-tribromo porphyrins. Similarly, for 5,15-diphenylporphyrin 34 bromination occurs at the two available meso positions if two equivalents of NBS are used. This results in an A₂B₂-substituted porphyrin.

### 1.3.2 Nucleophilic aromatic substitution reactions with organolithium reagents

Another useful method for the functionalisation of both polyheteroaromatics and polyaromatic are nucleophilic aromatic substitution (_S_N_Ar_) reactions using organolithium reagents (Scheme 1.12).
Scheme 1.12: General scheme to illustrate the reaction of organolithium reagents and arylhalides.

Unsymmetric meso-tetrasubstituted porphyrins have applications in catalysis, as photosensitisers and in molecular recognition and nonlinear optics (NLO). Organolithium reagents react selectively at the meso position of porphyrin periphery. This makes them suitable for the synthesis of unsymmetric meso-tetrasubstituted porphyrin complexes.

It was thought for many years that for $S_nAr$ to take place on the porphyrin periphery activation of the porphyrin core was required which occurs for porphyrins with a high valence metal centre or if the porphyrin is already substituted with highly electron withdrawing groups. Senge and co-workers developed a method where nucleophilic substitution at the meso position via organolithium reactions will proceed with an unactivated porphyrin precursor. As a result, a library of unsymmetric porphyrins were synthesised by reacting $n$-butyllithium with a series of aryl bromides with yields as high as 93% (Scheme 1.13), when 10-15 equivalents of the organolithium reagent was used. An excess of organolithium reagent was required (10-15 equiv.) to ensure high yields of the desired products and to prevent the formation of ring-opened side products. Some of the porphyrin complexes isolated have since been used as precursors in the synthesis of more elaborate porphyrin arrays. This method is now considered a general pathway for the synthesis of unsymmetric porphyrins.
Scheme 1.13: Synthesis of unsymmetrical meso-porphyrins via reaction with organolithium reagents.\textsuperscript{147,150-153,155,156}

Sergeeva \textit{et al.}\textsuperscript{157} carried out an investigation into the synthesis of porphyrin dimers via Stille coupling. Initially, anthracene was thought to be a suitable linker between the two porphyrin macrocycles. The 9-tri(\textit{n}-butyl)stannylanthracene 49 could be conveniently synthesised on a large scale via organolithium reactions with \textit{i}-butyllithium 50, commercially available 30 and tri(\textit{n}-butyl)tin chloride at very low temperatures (Scheme 1.14).
However, when the reaction was carried out using 9,10-dibromoanthracene as the precursor the disubstituted derivative was not isolated and the major product which was recovered was anthracene in 71 % yield.

One of the earlier reported uses of organolithium reactions on triptycene 6 was reported by Iwamura et al.\textsuperscript{158,159} It was found that by reacting 1-bromotriptycene 51 with 42 in diethyl ether yielded the 9-triptyllithium 52. Subsequent reaction with oxygen in ether and 9-triptycene carbonyl chloride 53 at -70 °C resulted in the formation of 9-triptycyl-9-triptyceneperoxy 54 in 49 % yield as shown in Scheme 1.15.\textsuperscript{158}
1.3.3 *Transition metal catalysed carbon-carbon reactions*

Some of the most important reactions in chemistry are C-C bond-formation reactions as they provide key steps in the building of complex, bioactive molecules. Functionalisation is essential in order to tailor polyaromatics and heteropolyaromatics for specific applications. Carbon-carbon reactions are used in the construction of elaborate porphyrin complexes with differing physical, chemical, or optical properties by means of extending the π-conjugation.

Over the last 50 years, many C-C bond-forming methodologies have used transition metals to mediate the reactions. This is due to the high regioselectivity which is observed when using a transition metal catalyst for C-C coupling reactions. Of the transition metal catalysed coupling reactions, palladium-catalysed reactions have proven to be one of the most versatile and powerful metal-mediated transformations for porphyrin chemists over the past decades.

Palladium-catalysed cross-coupling reactions with organoboron compounds and organic electrophiles, namely halides or triflates, in the presence of a base have proved to be a powerful method for the formation of carbon-carbon bonds. Cross-coupling typically involves the oxidation of an aryl halide to a transition metal catalyst and ligand exchange resulting in a complex being formed. Reductive elimination of the product follows and catalyst is regenerated.

The most common of the metal-mediated reactions includes the Suzuki cross-coupling reaction, the Sonogashira cross-coupling reaction, the Heck reaction, the Stille reaction, the Negishi cross-coupling reaction and the Kumada cross-coupling reaction. All of these examples of metal-mediated cross-coupling reactions have proven to be invaluable tools for the synthesis of elaborate and complex molecules for an array of applications. Palladium catalysed cross-coupling reactions accommodate a wide variety of palladium(0) and palladium(II) catalysts and precursors.
1.3.3.1 *Suzuki cross-coupling*

The Suzuki cross-coupling reaction is a selective and general pathway for the synthesis of biaryl products (Scheme 1.16).\(^{169}\) Previously, biaryl compounds could be synthesised by coupling aryl halides using copper at very high temperature, known as the Ullmann reaction.\(^{170}\) However, for the synthesis of an asymmetric biaryl product the use of two different aryl halides can result in the formation of three biaryl products. By employing the Suzuki cross-coupling method the synthesis of asymmetric biaryl molecules is achievable without the formation of the by-products which would normally be formed under the Ullmann reaction conditions. In 1981 the first synthesis of biaryls by Suzuki cross-coupling was reported by using arylborane and haloarene precursors. The reaction proceeded under heterogeneous conditions and formed the coupled products selectively, thus giving high yields for the desired products.\(^{169}\)

\[
R\text{-}B(OH)\text{2} + R^1\text{-}X \xrightarrow{\text{Pd-catalyst, Base, solvent}} R\text{-}R^1
\]

Scheme 1.16: General scheme to illustrate the Suzuki cross-coupling reaction.

Due to their thermal stability during heating, phosphine-based palladium catalysts are generally employed for this reaction. Extremely high coupling reaction rates can sometimes be achieved by using palladium catalysts without a phosphine ligand, such as Pd(OAc)\text{2}. The steric hindrance of aryl halides is not a major factor in the formation of substituted biaryls, however, low yields result when *ortho*-disubstituted phenylboronic acids are used. There is no large difference between *meta-* and *para*-substituted phenylboronic acids, however, substituents at the *ortho*-position may greatly increase the rate of deboronation.\(^{160}\)
The reaction proceeds via oxidative addition of the organohalide 55 to Pd(0) 56 thus forming a Pd(II) complex 57. This is the rate determining step of the catalytic cycle. Initially, the complex is in cis conformation but quickly isomerises to the trans conformation. Inversion of stereochemistry occurs with benzylic or allylic halides, however when using vinyl halides the stereochemistry is retained. The next step is the transmetallation between the organopalladium(II) complex (R'-Pd-X) 58 and the organoboron compound 59. The role of base is to activate the boron-containing reagent 60. Organoboron compounds are highly covalent in character, and do not undergo transmetallation readily in the absence of base. The exact mechanism is unknown, however, it has been proposed that the base binds to the organoborane species depending on the base affinity for the organoborane. This makes the R group more nucleophilic and allows the R group to replace the halide anion on the palladium complex. Reductive elimination of 61 then results in the generation of the
coupled product 62 and the palladium catalyst 56 is regenerated, thus continuing the catalytic cycle (Scheme 1.17).

Liu et al.\(^{174}\) utilised the Suzuki cross-coupling approach for the synthesis of 9-naphthalene-2-yl-anthracene 63. The coupling partner, naphthalen-2-ylboronic acid 64, was first synthesised from 2-bromonaphthalene 65 as illustrated in Scheme 1.18. It was reported from this study that the contents of the catalyst and the reaction solvents can influence the progress of the reaction. It was concluded that the optimal conditions for the coupling of 64 and 30 required a 1:4 (mol) ratio of Pd(OAc)\(_2\) to PPh\(_3\), which can successfully form the reactive catalyst in 9:1 DME:H\(_2\)O.\(^{174}\)

![Scheme 1.18: Synthesis of 63 via Suzuki cross-coupling.\(^{174}\)](image)

Similarly, Swager et al. utilised the Suzuki cross-coupling reaction to produce conjugated polymer liquid crystal solutions. Fluorescent triptycene containing polymers were isolated by reacting 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl-ethenyl)triptycene derivatives 66 and 67 with two different 2,5-diodobenzene
precursors 68 and 69. The resulting polymers 70-73 were isolated in good yields of ~85 % in each case (Scheme 1.19).\textsuperscript{175}

\[
\text{Scheme 1.19: Swager's synthesis of conjugated polymers 70-73 via Suzuki cross-coupling.}\textsuperscript{175}
\]

A Suzuki cross-coupling reaction for the functionalisation of porphyrins in the β-position was reported by Chan \textit{et al.}\textsuperscript{176} A library of both aryl\textsuperscript{177} and alkyl\textsuperscript{178} β-substituted porphyrins were then isolated in reasonable yields (55 % - 88 %) from the corresponding β-bromoporphyrin. Further investigation was carried out by Shi \textit{et al.} who reported a method for which coupling at the meso position of bromoporphyrins could be achieved. The unsymmetric porphyrins were isolated in yields of 24 % - 78 %.\textsuperscript{179}

This methodology was then applied to porphyrins for the synthesis of boronylporphyrins by Hyslop \textit{et al.} who reported that boron ester groups could be attached to the meso position of the porphyrin periphery.\textsuperscript{180} The development of β-boronylporphyrins was undertaken later by Osuka \textit{et al.}\textsuperscript{181} who found that the presence of an iridium catalyst resulted in C-H bond activation. By using the conditions illustrated in Scheme 1.20, 5,15-bis(3,5-di-tert-butylphenyl)porphyrin 74 was converted to the mono-β-boronylated derivative 75 in 43 % yield when coupled with bis(pinacolato)diboron 76.\textsuperscript{181} Two stereomeric di-β-boronylporphyrins 77 and 78 were also obtained from the reaction with a combined yield of 14 % (Scheme 1.20).\textsuperscript{181}
The reaction taking place at the β-position instead of the free meso position was attributed to the fact that the β-position is more accessible because the meso-position is more sterically hindered. Osuka et al. and Senge et al. have since utilised this approach for the synthesis of covalently linked porphyrin dimers and arrays using borylporphyrin and bromoporphyrin precursors.

Scheme 1.20: Osuka’s synthesis of β-boronylporphyrins 75, 77 and 78.
1.3.3.2 Sonogashira cross-coupling

As in the Suzuki cross-coupling reaction, Sonogashira cross-coupling reactions also involve the coupling of an aryl or vinyl halide (Scheme 1.21). However, in the latter case, coupling occurs with a terminal alkyne. The reaction between aryl or alkenyl halides or triflates and terminal alkynes proceeds under basic conditions and usually requires the use of a copper iodide co-catalyst. This method has become paramount for the synthesis of arylalkynes and conjugated enynes.

\[
R - X + H - R^1 \xrightarrow{\text{Pd-catalyst, Cul, Et}_{3}N, \text{ solvent}} R - R^1
\]

Scheme 1.21: General scheme to illustrate the Sonogashira cross-coupling reaction.

The Sonogashira process usually proceeds smoothly when unstable aryl or vinyl iodides are used. The general reactivity order of the sp\(^2\) species is as follows; vinyl iodide > vinyl triflate > vinyl bromide > vinyl chloride > aryl iodide > aryl triflate > aryl bromide >> aryl chloride. If the organic halide system is “activated”, i.e. electron-poor, the forward reaction is even more favoured. Thus, deactivated aryl bromides are difficult starting materials for Sonogashira cross-coupling reactions. Similarly, aryl chlorides present a real challenge for any cross-coupling methodology if they are not strongly activated. Heck and Cassar first investigated this topic in 1975. Heck reported a method that employed a phosphane-palladium complex as a catalyst and triethylamine or piperidine as a base and solvent. Cassar’s procedure involved the use of a phosphane-palladium catalyst in combination with sodium methoxide as a base in DMF. However, Sonogashira and Hagihara reported in the same year that the addition of a catalytic amount of copper(I) iodide greatly accelerates the rate of the reaction, thus enabling alkynylation at room temperature. This was favourable over Heck and Cassar’s methods which both require high reaction temperatures. This reaction became known as the Sonogashira cross-coupling reaction and is now the most popular method for the alkynylation of aryl or alkenylhalides.
The copper-cocatalyzed Sonogashira reaction takes place through two independent catalytic cycles (Scheme 1.22). The terminal alkyne reagent is represented by ethynyltrimethylsilane 79 and base is represented by a tertiary amine 80; however other amines or inorganic bases perform similarly. The initial step involves the oxidative addition of the arylhalide or aryltriflate 55 to form the Pd(II) complex 57. The next step connects the palladium-cycle with the copper-cycle. The rate-determining step, transmetalation, generates 81 from the copper acetylide 82 formed in the Cu-cycle. *Cis/trans* isomerisation of 81 generates 83. Reductive elimination of 83 then results in the formation of the coupled alkyne product 84 with regeneration of the catalyst 56.

Toyota *et al.* used a series of Sonogashira coupling reactions to construct a novel π-conjugated anthracene-acetylene oligomer 85. Initially a suitable coupling partner was
prepared from the precursor 86 (Scheme 1.23). A Grignard reaction was used for the synthesis of 87 which was then subjected to a Sonogashira reaction with ethynyltrimethylsilane 79 to yield 88 in 49% yield. Each anthracene unit was then connected in a stepwise manor via Sonogashira cross-coupling reactions using compounds 88 or 89 (90, 92) followed by desilylation reactions (91, 93). The tetrameric intermediate 94 was prepared via a Sonogashira reaction using 1,8-diodoanthracene 95 as the coupling partner. This could then be cyclised using a final Sonogashira reaction affording 85 in reasonable yield of 31% as illustrated in Scheme 1.23.192

Scheme 1.23: Toyota’s synthesis of π-conjugated anthracene-acetylene oligomer 85 via Sonogashira cross-coupling reactions.192
In 2005, Lippard et al.\textsuperscript{193} utilised a series of dual Sonogashira coupling reactions incorporating a desilylation reaction for the synthesis of diethynyltriptycene-linked dipyridyl ligands.\textsuperscript{193} Initially, 2,3-dibromotriptycene \(96\) was reacted with \(79\) under Sonogashira reaction conditions and subsequent desilylation using potassium carbonate afforded \(95\) in 81 % yield. This was then used as a precursor for further Sonogashira reactions with a variety of functionally diverse 5-bromopyridines \(97-100\) to afford the diethynyltriptycene-linked dipyridyl ligands \(101-104\) with overall yields ranging from 40-50 % (Scheme 1.24).\textsuperscript{193}

![Scheme 1.24: Lippard's synthesis of diethynyltriptycene-linked dipyridyl ligands via Sonogashira cross-coupling reactions.\textsuperscript{193}](image)

The use of copper salts as co-catalysts in Sonogashira cross-coupling reactions is not without its drawbacks. Not only is it detrimental for the environment, but copper insertion can also occur when using free base porphyrin precursors. Homocoupling products of the terminal alkyne (Glaser coupling)\textsuperscript{194,195} often occur as a result of the in
*sit* *u* generation of acetylides and subsequent oxidation from air or/and oxidative agent. Significant efforts have been made to develop copper-free Sonogashira reaction conditions by increasing the reactivity of the catalytic system, thus making the use of copper avoidable. Some copper-free Sonogashira methodologies have been developed for coupling aryl iodides and activated aryl bromides with the traditional palladium complex Pd(PPh$_3$)$_2$Cl$_2$ (4 mol %) at 70 °C in neat piperidine. These copper free reaction conditions were first used in porphyrin chemistry by Arnold and Nitchinks, who reported the synthesis of a covalently-linked dimer. It has since proved to be a versatile and robust method for the synthesis of both β- and meso alkynyl porphyrins. This was demonstrated by Senge et al. who reported high yielding copper free Sonogashira reaction for the synthesis of unsymmetric porphyrin dimers. Two porphyrin monomers 105 and 106 were linked under copper-free conditions to yield the porphyrin dimer 107 in 64 % yield (Scheme 1.25).

![Scheme 1.25: Copper-free Sonogashira reaction for covalently-linked porphyrin dimer 107.](image)
Furthermore, Sonogashira cross-coupling reactions have also been utilised for the synthesis of elaborate multiporphyrin arrays. The extended conjugation in these arrays gives them a rigid, covalently linked framework, thus making them suitable for applications in light harvesting.\textsuperscript{200-202}

### 1.3.3.3 Glaser cross-coupling

Although palladium-catalysed reactions have proved both versatile and an effective method for the formation of C-C bonds in organic chemistry, other transition metals can be applied for similar synthetic applications. One of the most common of these which is used in organic chemistry and porphyrin chemistry alike is the Glaser coupling reaction (Scheme 1.26).\textsuperscript{203} This approach provides access to arylene ethynylene type molecules.

![Scheme 1.26: General scheme to illustrate the Glaser cross-coupling reaction.](image)

Although copper was one of the first transition metals used for the functionalisation of C-H bonds, methods that utilise copper catalysis for conversion of C-H bonds to C-C bonds are less common than the likes of palladium and other transition metals.\textsuperscript{205} The Glaser-Hay cross-coupling involves the use of a copper catalyst for alkyne dimerisation which was first reported in 1869.\textsuperscript{203} Zhang \textit{et al.}\textsuperscript{206} utilised the Glaser cross-coupling reaction for the synthesis a nanosized cages. Zhang and co-workers became interested in the development of new supramolecular systems which incorporated triptycene 6 for its unique 3D rigid structure. 2,7,14-Triiodotriptycene 108 was used as the starting precursor. This was subjected to palladium catalysed Sonogashira coupling with ((3-ethynylphenyl)ethynyl)trimethylsilane 109 to give 2,7,14-tris((3-((trimethylsilyl)-ethynyl)phenyl)ethynyl)triptycene 110 in 60 % yield. Subsequent deprotection resulted in the isolation of 111 in good yield. The Glaser cross-coupling reaction was then used to synthesise a nanosized cage compound 112 with high symmetry in 58 % yield (Scheme 1.27).\textsuperscript{206}
Swager et al.\textsuperscript{207} recently developed a successful method for the synthesis of fluorescent macrocycles based on 1,3-butadiyne-bridged dibenzo[a\^]anthracene subunits via Glaser coupling. This multistep synthesis involved the initial construction of a functionalised dibenzo[a\^]anthracene building block. Subsequent installation of free alkyne groups on one side of the polycyclic aromatic framework \textbf{113} and a final cyclization based on a modified Glaser coupling afforded \textbf{114} and \textbf{115} in reasonable yields of 41\% and 47\%, respectively (Scheme 1.28).
Likewise, the Glaser reaction has proven very useful in porphyrin chemistry. It has been previously used to construct a number of diphenylbutadiyne-linked multiporphyrin complexes.\textsuperscript{200,208-221} A good example of this was reported by Lindsey and co-workers\textsuperscript{222} in 2002 which is illustrated in Scheme 1.29. The Glaser cross-coupling reaction was used to form a dimer from porphyrin precursors 116 and 117 which were isolated via mixed condensation reaction and subsequent metallation. This synthetic pathway resulted in the isolation of the porphyrin dyad 118 in 46 % yield.


Scheme 1.29: Synthesis of porphyrin dimers via Glaser coupling.

1.4 Applications

1.4.1 Models for photo-initiated charge transfer

The development of compounds suitable for photo-initiated charge transfer is of interest for chemists in the scientific community. The understanding of the mechanisms of photoinitiated charge separation and development of models of biological photosynthesis is paramount for the improvement of the capture and storage of solar energy. Understanding how nature performs the intrinsic complex function of photosynthesis, allows researchers to use this knowledge for the construction of efficient artificial light harvesting devices.
The process of photosynthesis in nature is a complex one which involves the organisation of the various component molecules within a protein matrix, thus the task of making model systems to mimic the photoinitiated charge is a challenging one. The molecules are organised via covalent linkages which are based on electron donors and acceptors which mimic the charge separation function. Models known as dyads represent the simplest model for charge separation and consist of a chromophore covalently linked to an electron donor or acceptor.

Many dyad models consist of a porphyrin covalently linked to a quinone, which can undergo photoinitiated charge transfer under the correct conditions. Upon irradiation these compounds form the excited singlet state of the porphyrin which either decays or donates an electron to the covalently linked quinone moiety to form a charge separated state. A successful charge separate state eventually recombines to reform the ground photosynthetic reaction centre which then produces a long-lived charge separation. Photoinitiated electron transfer occurs in a number of steps in the natural photosynthetic process. To improve these synthetic models and mimic the natural photosynthetic mechanism, triads consisting of two donors and one acceptor or two acceptors and one donor have been developed. The lifetimes of the charge separated states are increased due to the covalent linking of these groups initiating multistep electron transfer.

The understanding of the mechanism of photosynthesis and the assembly of pigments for natural light harvesting has been studied intensely. Overlapping molecules, of a special pair of bacteriochlorophyll (Figure 1.6), make up the reaction centre for the photosynthetic process. It is in fact the overlap of these two molecules and indeed their near perfect two-fold symmetry that allow them to act as the primary electron donors initially during photosynthesis. The light absorption characteristics of the molecule are optimised by the substituents on the periphery of the macrocycle. These substituents together with the long phytol hydrocarbon chain, also aid in anchoring the chromophore within the light-harvesting proteins. The metal centre found in chlorophyll fine-tunes the light absorbing and energy-transfer characteristics or the molecule. It also acts as the centre for binding water which is the source for electron replacement.
Figure 1.6: Schematic representation of the photosynthetic reaction centre isolated from \textit{Rhodopseudomonas viridis}.\textsuperscript{227}
The photosynthetic reaction centre as isolated from the purple bacterium *Rhodopseudomonas viridis* is illustrated in Figure 1.6. Upon excitation, an electron is transferred from the special pair to bacteriophytin (BPh). An intermediate bacteriochlorophyll molecule (BCl) that is in close proximity to the primary electron donors facilitates this process. The excitation is further relayed to the menaquinone and then to the final electron acceptor, ubiquinone, which is facilitated by a histidine-glutamine iron complex.

Two almost symmetrical arms are formed by BCl, BPh and quinones, L and M, from the *special pair* which span the cytoplasmic membrane. The L side is highly favoured in the chain of electron transfer. This is due to slight conformational differences between the two sides. The relatively large distance between the redox sites promotes a much longer charge-separated state after electron transfer occurs from the *special pair* to the quinone residue.

The special pair is capable of absorbing light in order to generate electronic excitation; however, it is not sufficient to saturate its maximum turnover rate by itself. Energy is supplied by the light harvesting proteins and the chlorophyll molecules. Chlorophyll can serve as light-harvesting antennae by capturing the sunlight and funnelling the electronic excitation towards the reaction centre. X-ray crystallography, electron microscopy and molecular modelling have all played a vital role in determining the organisation of the proteins that is responsible for bacterial photosynthesis.

The antennae for *Rhodopseudomonas viridis* usually consist of a number of small light harvesting proteins (LH-II), which contain two orthogonal rings of bacteriochlorophyll *b* molecules. One ring contains an octameric aggregate of sixteen chlorophyll molecules and the second slightly larger ring contains eight, as illustrated in Figure 1.7a.

The LH-II protein lies in close proximity to a larger light harvesting protein, LH-II shown in Figure 1.7b. Both proteins are co-planar, thus allowing the maximum amount of electronic interaction between them. LH-I consists of thirty two
chlorophyll molecules which form a ring encompassing the reaction centre and its chromophores. This resulting planar organisation is optimal for energy transfer from the outer light-harvesting complexes. Excitation transfer occurs in the order LH-II8 → LH-II16 → LH-I → RC. This results in an energy cascade from the outer light harvesting proteins, which in turn fuels the reaction centre to generate an electron for photosynthesis at a rate of about 1000 times per second.

Figure 1.7: The relative positions of bacteriochlorophyll b in a) LH-I protein and b) LH-II in bacteria.228

1.4.2 Photodynamic therapy (PDT)

Photodynamic therapy is an anti cancer treatment that combines a photosensitiser, O2 and light to produce a therapeutic effect.231-234 PDT is a selective treatment modality
that affects mainly the target tissue. A photosensitiser is administrated intravenously to the patient and accumulates around the tumour site. A beam of light with the same frequency as the porphyrins absorption maximum is then directed at the tumour site. This activates the photosensitiser via photoexcitation which in the presence of ground-state (triplet) oxygen ($^{3}\text{O}_2$) results in the formation of highly reactive singlet oxygen. These oxygen free radicals are toxic and can damage cells via photo-oxidative reactions, resulting in cell necrosis or cell apoptosis.\textsuperscript{235,236} A simple Jablonski diagram (Figure 1.8) illustrates the photochemical process involved in PDT.

![Jablonski diagram](image)

**Figure 1.8:** A simple Jablonski diagram.

Porphyrsins are good photosensitisers for PDT due to their cyclic conjugated electronic structure. They are capable of absorbing light and transferring it to molecular oxygen, thus forming radicals that are capable of damaging proteins, lipids, cell components and nucleic acids. The efficacy of PDT relies heavily on the molecular features of the photosensitising agent.\textsuperscript{237} A suitable photosensitiser should be non toxic in the absence of light, yet absorb light of longer wavelengths (600-800 nm) for deeper tissues penetration allowing treatment of tumours that would be difficult to remove by means of surgery. It should be selective and amphiphilic in character in order to pass through the lipid membrane.

McCaughan is perhaps most apt in his description of the potential associated with the study of photosensitisers:
‘Photodynamic therapy is an entirely new treatment modality and its development can be likened to that of the discovery of antibiotics. This is just the beginning and its possible uses are only limited by imagination’.238
1.5 Objectives

The development of new synthetic routes remains a crucial step to further advance the ever expanding range of applications in polyaromatic and polyheteroaromatic chemistry. The aim of this work was to broaden these methods by developing and investigating transition metal mediated reactions, organolithium reactions and condensation reactions for the synthesis of highly conjugated porphyrin monomers, dimers and arrays. Ideally, these synthetic pathways should involve simple starting materials and present a general method for various porphyrin systems. This project, therefore, had three main aims.

The first was to synthesise and characterise a series of novel symmetrically and unsymmetrically meso-tetrasubstituted anthracenylporphyrins. A series of both metallo- and free-base anthracenylporphyrins was planned for this project. The strategy behind the synthesis of these anthracenylporphyrins was to investigate the influence the metallo- and free-base porphyrins precursors had on the overall success of the reactions.

The oxidative fusing of the anthracene moiety to the β-positions of the porphyrin periphery was also to be investigated. It was expected that fusing the anthracenylporphyrins would cause a significant bathochromic shift to the near-IR region of the electromagnetic spectrum as a result of extending the π-conjugation of the systems. This bathochromic shift would make fused-anthracenylporphyrins potential candidates for PDT. Furthermore, a synthetic pathway for the synthesis of novel anthracene-linked porphyrin dimers was also desired for this section of the project.

The second aim was to synthesise and characterise a series of covalently linked triptycene scaffolds. In particular, triptycene scaffolds with highly conjugated ‘arms’ in the six most outer positions of triptycene were desired. The triptycene scaffolds were designed to be suitable precursors for further coupling reactions to allow access to elaborate highly complex molecular structures. Furthermore, scaffolds bearing ethynyl functional groups at the six outer most positions were particularly sought
after. This is because these types of triptycene scaffolds would allow for further post-polymerisation reactions to afford rigid, rod-like, anisotropic, high modulus structures.

These scaffolds needed to be isolated in relatively high yields from simple precursors and exhibit high solubility. Several approaches were to be investigated to determine the optimum conditions for the synthesis of novel covalently-linked triptycene scaffolds.

As discussed in section 1.4.1 multiporphyrin arrays have a wide range of applications such as molecular electronics, nonlinear optics and models for photoinitiated charge transfer. For these reasons the third aim of this project was to synthesise multichromophoric species, particularly for light harvesting applications. The development of a new molecular architecture with a high density of chromophores, while retaining the spatial integrity of the system was to be investigated. While triptycene-linked porphyrin trimers have been reported within our group the isolation of a triptycene-linked hexaporphyrin array has remained elusive. Multiporphyrin arrays have been reported for inclusion in light harvesting systems, however, the solubility of the multiporphyrin system decreases as the number of porphyrins in the system increases. For these reasons triptycene-linked arrays were proposed to be good candidates for light harvesting systems. This is due to the increased solubility of the system as a consequence of the triptycene scaffold and its 3-D structure. The synthesis of both directly linked and ethyne-linked hexaporphyrin arrays was to be investigated via Suzuki cross-coupling and Sonogashira cross-coupling reactions.
Chapter 2:
Anthracenylporphyrins
2.1 Introduction and applications of anthracenylporphyrins

Porphyrins with meso-anthracenyl residues are currently being studied for a variety of applications ranging from photodynamic therapy,\textsuperscript{91} two-photon absorption,\textsuperscript{92} nonlinear optics,\textsuperscript{93,241-243} organic semiconductors\textsuperscript{244} and photovoltaics.\textsuperscript{94,245,246} This is related to the ability of anthracene moieties to allow and control reversible multiple electron-transfer processes\textsuperscript{247} and their potential to yield systems with extended \( \pi \)-conjugation. Such expanded porphyrin systems also show interesting structural and functional features and possess unique metal coordination properties.\textsuperscript{248}

The anthracenylporphyrins which were targeted possess both aryl and alkyl meso substituents on the porphyrin periphery as illustrated in Figure 2.1. The aryl meso-substituted anthracenylporphyrins were desired due to the bathochromic shift which is observed as a result of extending the \( \pi \)-conjugation of the macrocycle making them suitable candidates for PDT. Alkyl meso-substituted anthracenylporphyrins were also desired to prevent aggregation. Aggregation is often seen in dye molecules as a result of \( \pi \)-stacking, which would result in a decrease in efficiency of the system.

![Figure 2.1: Mono- and dianthracenylporphyrin.](image)

Even more intriguing are the methods of extending the \( \pi \)-conjugation of a porphyrin macrocycle by triply-fusing anthracenylporphyrins via oxidative intramolecular ring closure.\textsuperscript{249,250} The geometry of anthracene matches the geometry of a porphyrin. This indicates that anthracene is a suitable moiety to fuse to the porphyrin periphery, while retaining planarity of the macrocycle. These fused chromophores offer potential in photodynamic cancer therapy due to the expected red shift which is associated with
the extension of the π-conjugation of the macrocycle. This red shift overcomes potential problems associated with absorption and light scattering by the tissue, thus increasing penetration and enabling treatment to a wider variety of tumours.\textsuperscript{91,251} These advances clearly indicate the potential of anthracenylporphyrins and require the development of appropriate methods for their synthesis.

2.2 Substituted anthracenes

2.2.1 Synthesis of 9-substituted anthracenes via Suzuki cross-coupling reactions

Initially, some exploratory syntheses on the functionalisation of anthracene using Suzuki cross-coupling reactions was undertaken. It was anticipated the anthracenylporphyrins would exhibit poor solubility, particularly if the anthracene moiety was successfully triply fused to the porphyrin periphery. Therefore, compounds 123-125 where chosen as precursors for later cross coupling reactions which would increase the solubility of the macrocycle (Scheme 2.1). It was proposed that phenyl substituents at the 9 position of the anthracene moiety would increase the solubility of the anthracenylporphyrin systems. The anthracene derivative 126 was also synthesised as a precursor for later coupling reactions to prevent aggregation from occurring (Scheme 2.1).

The reaction of boronic acid derivatives 119-122 with 9-bromoanthracene (30) required optimisation because the use of standard conditions only resulted in the isolation of debrominated starting material. Anthracenes 123-126 were isolated in reasonable yields of 41-67 % by using the conditions which are illustrated in Scheme 2.1. Anthracene 123 was brominated using 1.5 equivalents of NBS and 0.5 equivalents of pyridine and stirred at room temperature in chloroform to yield 127 in good yield (Scheme 2.1). This confirmed that bromination takes place at the 10 position of the anthracene derivatives, making them suitable coupling reagents for boronylporphyrins.
Scheme 2.1: Synthesis of anthracene derivatives via Suzuki coupling reactions.

Figure 2.2: X-ray crystal structure of compound 124. Displacement ellipsoids are drawn at the 50% probability level.

Figure 2.2 shows the X-ray crystal structure of 124, which illustrates that the phenyl ring is orthogonal to the anthracenyl plane with a dihedral angle of 71.65°. As shown in Scheme 2.1, a number of anthracene derivatives with different electronic properties 123-126 could be synthesised successfully. While compounds such as 123 or 124 could be obtained in good yields, the preparation of difunctionalised derivatives is still unsatisfactory. When the boronic acid derivatives 119-122 (Scheme
2.1) were coupled to 10-bromoanthracene-9-boronic acid under the same reaction conditions, compounds 123 and 124 were isolated in lower yields. The desired 9-aryl-10-boronic acid anthracene derivatives were not formed. An example for an entry into compounds suitable for porphyrin modification is the conversion of 123 into 127 using NBS (Scheme 2.1).

2.3 Synthesis of porphyrin precursors

2.3.1 Synthesis of meso-disubstituted porphyrins

This section describes the various strategies used to isolate the porphyrin precursors which were used to synthesise anthracenylporphyrins. Three types of substitution were considered for these anthracenylporphyrins, namely $A_2B_2$, $A_2B_C$ and $A_3B$ substituted porphyrins.

The synthesis of both aryl and alkyl meso-disubstituted porphyrins requires the synthesis of dipyrromethane precursors for the condensation reaction. Initially, a classic method which was reported over a decade ago was used, from which 128 could be isolated in up to 43 % yield.\(^{253}\) However, the synthesis of 128 was achieved in yields of up to 60 % using a modified method developed by Lindsey \textit{et al.}\(^{254}\) This method uses indium chloride (InCl$_3$) and a Lewis catalyst with neat pyrrole 21 and formaldehyde 129, as shown in Scheme 2.2.\(^{254}\) The alleviation of an anhydrous basic workup and the omission of any extraction techniques led to a much better efficiency in the removal of pyrrole. As a result, this method is more favourable over the previous method which was used for the synthesis of dipyrromethane 128.
Scheme 2.2: Synthesis of $\Lambda_2$-type porphyrins via 2+2 condensation reaction.

A series of alkyl and aryl 5,15-porphyrins were synthesised by reacting aldehydes 130-132 with 128 under the modified condensation reaction conditions originally reported by Lindsey et al.\cite{109,255} The resulting porphyrinogen intermediates 25, 133, 134 were oxidised using DDQ to yield porphyrins 5,15-diphenylporphyrin 34\textsuperscript{256} (54 %) and 5,15-dihexylporphyrin 135\textsuperscript{257} (27 %) respectively. The coupling of anthracene derivatives to aryl and alkyl meso-substituted porphyrins could then be compared. Furthermore, 5,15-bis(3,5-di-$t$-butylphenyl)porphyrin 75\textsuperscript{258} (31 %) was also chosen as suitable precursor because of its increased solubility by comparison to the other precursors synthesised for this project (Scheme 2.2).
2.3.2 Synthesis of $A_2B$ porphyrins via organolithium reactions

For the synthesis of monoanthracenylporphyrins, trisubstituted porphyrin precursors were first synthesised. This allows easy access to monobrominated porphyrins which can be used in the final coupling reaction. This in turn reduces side reactions and favours the coupling reaction of the monosubstituted anthracenylporphyrin. 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 (Scheme 2.3). The Suzuki cross coupling approach was considered for the synthesis of 5,10,15-triarylporphyrins, however, reduced yields and selectivity made the organolithium reaction a more attractive approach.

Scheme 2.3: Functionalisation of $A_2$-type porphyrins using organolithium reagents and metallation to yield $A_3$-type and $A_2B$-type metalloporphyrins.
The trisubstituted porphyrins 5,10,15-triphenylporphyrin 136 and 5-phenyl-10,20-bis(3,5-di-t-butyl)porphyrin 137 were subsequently synthesised by subjecting 34 and 74 to nucleophilic substitution using 138 at 0 °C. Similarly, 5,10,15-trihexylporphyrin 139 was also isolated by subjecting 135 to nucleophilic substitution using 140 at -70 °C, as shown in Scheme 2.3. This procedure has been thoroughly explored for the synthesis of A3-type and A2B-type porphyrins by Senge et al.\(^ {150,151,153,262-265}\) Initially, the reaction of the organic nucleophile with free base porphyrins generates phlorin-type intermediates 141-143. This is converted to the anionic species 144-146 \textit{in situ}. Hydrolysis of the anionic species with water gives 10,20-dihydroporphyrins 147-149 which is subsequently oxidised by DDQ to yield porphyrins 136, 137 and 139 in excellent yield (Scheme 2.3). The free base porphyrins 136 and 137 were reacted with nickel(II)acetylacetonate and the resulting nickel(II) complexes (150, 151) were isolated in good yields of 91 % and 94 %, respectively. Similarly, the free base derivatives 136 and 137 were also converted to the respective zinc(II) complexes 152 and 153 in good yields of 87 % and 85 %. The free base 139 was also converted to the respective zinc(II) 154 and nickel(II) 155 complexes. The lower yields of 76 % and 75 % for 154 and 155 are considered to be a result of the reduced solubility of 139 (Scheme 2.3).\(^ {261}\)

\section*{2.3.3. Bromination of porphyrins}

Halogenated porphyrins are of inherent value as they are suitable starting materials for palladium cross-coupling reactions, thus making them suitable building blocks for elaborate complexes. Bromination and, more recently, iodination have been established as routine syntheses for starting materials in the porphyrin field.\(^ {144,269}\)

The 5,15-disubstituted porphyrins precursors were dissolved in chloroform and reacted with NBS (Scheme 2.4).\(^ {270}\) The electrophilic substitution of bromine on porphyrins 136, 137, 139 and 150-155 produced 156-164 in almost quantitative yields (87-94 %) when using 1.5 equiv. of NBS, (Scheme 2.4). The synthesis of 156-158 has previously been reported using a different synthetic methodology.\(^ {259,272}\) However, the use of organolithium reactions and subsequent bromination reactions has proven to be high yielding and as a result other synthetic methods were not explored. For the synthesis of 159 the reaction time can be
reduced by increasing the reaction temperature to reflux. The reduced yield for 159 can be attributed to the poor solubility of the porphyrin precursor 139.

Scheme 2.4: Synthesis of bromoporphyrins 156-164 using NBS.

2.4 Synthesis of anthracenylporphyrins

For the synthesis of anthracenylporphyrins the efficiency of three different preparative methods was explored. One method we envisaged to be successful was a standard 2+2 condensation reaction. This has been proven to be an effective method for A$_2$B$_2$-type porphyrins in previous studies, and thus it was applied to the synthesis of A$_2$B$_2$-type anthracenylporphyrins. The yield of the reaction is limited by the synthesis of the precursor pyrrole derivatives and by the possibility of scrambling, as illustrated in Scheme 2.5.
Although this method significantly favours the synthesis of 5,15-A₂B₂- and 5,15-A₂-porphyrins, by-products can also be isolated from this reaction as a result of scrambling.¹⁴⁶

During the reaction, the acidic conditions causes the formation of the bilane A which then fragments into a pyrrole derivative B and a tripyrrane C. The recombination of B and C can lead to the formation of a different bilane D as illustrated in Scheme 2.5. This results in a different substitution pattern on the porphyrin periphery which can result in the formation of A₃B-trisubstituted pattern. However, the scrambling products can be removed by column chromatography. Therefore, the MacDonald [2+2] condensation is still considered the most reliable method for the synthesis of 5,15-A₂B₂- and 5,15-A₂- meso-substituted porphyrins.¹⁴⁶

**Scheme 2.5: Mechanism of the scrambling process.**²⁷⁴
Another method which was used for the synthesis of anthracenylporphyrins was the palladium-catalysed Suzuki cross-coupling reaction.\textsuperscript{275} This appeared to be the most straightforward method, and it was thought that it would result in higher yields than the condensation reaction. This reaction is widely used in porphyrin chemistry and has shown its potential for the synthesis of a wide variety of A\textsubscript{3}B-type porphyrins.\textsuperscript{265,276-278}

2.4.1 Condensation reactions

The simplest method for the preparation of A\textsubscript{2}B\textsubscript{2}-type porphyrins is by condensation reaction. Thus, the synthesis of anthracenylporphyrins using the condensation method was investigated. The symmetric 5,10,15,20-tetra(9-anthracenyl)porphyrin \textbf{165} was first reported by Volz and Schäffer\textsuperscript{279} followed by an improved synthesis by Tohara and Sato.\textsuperscript{280} It was reported that anthracene carboxaldehyde \textbf{166} when reacted with pyrrole \textbf{21} could be used to synthesise \textbf{165} via condensation in 1-3 % yield (Scheme 2.6).\textsuperscript{280}

![Scheme 2.6: Literature synthesis of \textbf{165} via condensation reaction.\textsuperscript{280}]

A one-pot condensation reaction for the synthesis of 5,15-dianthracenyl-10,20-dihexylporphyrin \textbf{167} first required the synthesis of 5-hexylpyrromethane \textbf{168},\textsuperscript{281} which was isolated in a reasonable yield of 54 % from hexanal \textbf{169} and \textbf{21} (Scheme 2.7). This was then used in a condensation reaction with \textbf{166} using TEA, TFA and
DDQ (Scheme 2.7). The major product which was isolated from this reaction was 167 (10 %) as illustrated in Scheme 2.7. The scrambling by-product, 5-anthracenyl-10,15,20-trihexylporphyrin 170, was also formed during the reaction. However, cumbersome column chromatography prevented the isolation of 170 from this mixture in its pure form. The relevant fraction was metallated with Zn(II)(OAc)₂ and could be purified using preparative TLC and subsequent recrystallisation, to yield 171 and 172 in their pure states. Compound 167 was also converted into the nickel(II) derivative 173 for comparative analyses by heating compound 167 and Ni(II)(acac)₂ under reflux in toluene (Scheme 2.7).

\[
\begin{align*}
\text{(i)} & \quad \text{InCl}_3 (0.3 \text{ eq.}), \text{dry CH}_2\text{Cl}_2, 55 \degree\text{C, Ar}, 2.5 \text{ h}; \quad \text{(ii)} \quad \text{NaOH (10% aq., w/v)}; \\
\text{(iii)} & \quad \text{TFA (0.25 eq.), rt, Ar, 14 h}; \quad \text{(iv)} \quad \text{DDQ (13.0 eq.) 30 min, TEA (43.0 eq.)}; \\
\text{(v)} & \quad \text{a) Zn(OAc)₂ (1.5 eq.) in MeOH, CHCl₃, 60 °C, b) Ni(acac)₂ (1.5 eq.), toluene, 120 °C, 0.5 h.}
\end{align*}
\]

**Scheme 2.7:** Synthesis of dianthracenylporphyrins using anthraldehyde via 2+2 condensation reaction.

Another meso-substituted dipyrromethane derivative 174 was synthesised in reasonable yield from 1-ethylpropanal 175 and 21. A condensation reaction was also
carried out using 174 and 166 as precursors. Here, chromatography was much easier due to decreased scrambling and less side-product formation. The scrambling product 176 was formed in less than 1% yield and as a result was not fully characterised. Overall, this reaction gave a good yield of 14% for compound 177. Again, the free base was converted into the respective zinc(II) 178 and nickel(II) 179 complexes (Scheme 2.7).

2.4.2 Organolithium reactions

Another alternative for the synthesis of the anthracenylporphyrins is the substitution of porphyrins with a free meso-position using an anthracenyl lithium derivative. This method has worked well with many other RLi reagents\textsuperscript{264,282-284} and could be applied for the preparation of anthracenyl-2,3,7,8,12,13,17,18-octaethylporphyrins (Scheme 2.8).\textsuperscript{285}

\begin{center}
\centering
\includegraphics[width=\textwidth]{scheme2_8}
\end{center}

\textbf{Scheme 2.8: Attempted synthesis of compound 181 through organolithium substitution.}

Thus, a $S_{N}Ar$ reaction on porphyrin 136 using anthracenyl lithium 180 was also attempted (Scheme 2.8). Using the standard methodology established by the Senge group,\textsuperscript{264,282-284} the anthracenyl lithium was prepared \textit{in situ} by reacting compound 30 with $n$-butyllithium 42 at -78 $^\circ$C. However, addition of porphyrin 136 to the dark-red
solution did not, upon hydrolysis, result in the expected colour change to green. Repeated attempts to synthesise the desired monoanthracenylporphyrin 181 failed, most likely due to the poor formation of 180. As no butylporphyrin was isolated as a generic side product, the organolithium reagent may have formed and subsequently decomposed.

2.4.3 Suzuki cross-coupling reactions

Palladium-mediated cross-coupling reactions have evolved into versatile methods for carbon-carbon bond formation. Initially, it was believed that Suzuki coupling would be the most efficacious way of coupling an aromatic compound to the porphyrin periphery. The Suzuki cross-coupling reaction has proven particularly useful for the coupling of aryl halides and porphyrin boron esters. Thus, it seemed the most straightforward synthetic route for the synthesis of anthracenylporphyrins. Compound 30 was reacted with compound 182 under the modified conditions originally established by Hyslop and Therien to synthesise anthracenylporphyrin 181 (Scheme 2.9).

![Scheme 2.9: Attempts at synthesising 181.](image)

However, coupling did not occur and the major product which was isolated was the deborylated porphyrin precursor 136 (Scheme 2.8). A polar green compound was also isolated from the reaction mixture. Unfortunately, $^1$H NMR studies indicated that it was not worth pursuing any further as it did not appear to be a porphyrin. Looking at this unexpected result, different bromides were used under similar conditions to see if
coupling could be achieved. Two different bromides, 1-bromonaphthalene 183 and 4-bromobenzonitrile 184, were used in test reactions (Scheme 2.10).

![Scheme 2.10: Attempts to couple arylbromides to 182.](image)

Unfortunately, the result for 183 and 184 were the same as what was observed for 30 (Scheme 2.9), and porphyrins 185 and 186 were not isolated (Scheme 2.10). The major product isolated from the reaction mixture was the porphyrin precursor 182 (Scheme 2.10).

The synthesis of the desired anthracenylporphyrin 181 using the Suzuki cross-coupling reaction proved unsuccessful under the initial reaction conditions (Scheme 2.9). The decision was made to reverse the functional groups of the porphyrin and the anthracene in the hope that this would favour the coupling reaction. Attention was turned towards the synthesis of borylanthracenes 187 and 188 as illustrated in Scheme 2.11.
Borylanthracenes 187 and 188 were synthesised in good yields by coupling pinacolborane 189 to 9-bromoanthracene 30 or 9,10-dibromoanthracene 185, respectively. The freshly synthesised 187 and 5-bromo-10,15,20-triphenylporphyrin 156 were subjected to the same coupling conditions as shown in Scheme 2.10. However, the coupled product again was not isolated after column chromatography with the major products isolated from the reaction mixture being the debrominated porphyrin precursor 136 (Scheme 2.8), 187 (Scheme 2.11) and anthracene (3). It was clear that the reaction conditions used in this case were not suitable for the synthesis of anthracenylporphyrin, thus an optimisation of the reaction conditions was carried out.

2.4.3.1 Synthesis of palladium catalysts

It was decided to synthesise the palladium catalysts which were to be used in the Suzuki cross-coupling reaction to ensure the optimum efficacy was being achieved. As shown in Scheme 2.12, the Pd(0) catalyst Pd(PPh₃)₄, 190, was synthesised by the method of adding the triphenylphosphine 191 to PdCl₂ 192 in DMSO, and heating to 140 °C under argon, until no PdCl₂ was visible. The heat source was subsequently
removed, and after 15 minutes of vigorous stirring, hydrazine hydrate was added, resulting in yellow precipitate which was the desired Pd(0) catalyst. The precipitate 190 was subsequently collected under inert atmosphere in good yield of 81 % (Scheme 2.12).

\[
\text{PdCl}_2 + \begin{array}{c}
\text{Ph} \\
\text{P} \\
\text{Ph} \\
\text{P} \\
\text{P} \\
\text{Ph}
\end{array}
\xrightarrow{\begin{array}{c}
\text{H}_2\text{NNH}_2\text{H}_{2}\text{O (4.0 eq.)} \\
\text{DMSO} \\
140^\circ\text{C, 3 h}
\end{array}}
\begin{array}{c}
\text{Ph} \\
\text{P} \\
\text{P} \\
\text{D} \\
\text{P} \\
\text{Ph}
\end{array}
\]

\[
192 \ (1.0 \text{ eq.}) \quad 191 \ (4.13 \text{ eq.}) \quad 190 \ 81\%
\]

**Scheme 2.12:** Synthesis of Pd(0) catalyst 190.\(^{289}\)

A Pd(II) catalyst 193 (Scheme 2.13) was also synthesised as it has increased stability and longer shelf life than that of 190 (Scheme 2.12). The chloride salt 193 was synthesised by the addition of PdCl\(_2\) 192 and the relevant phosphine ligand 191 to benzonitrile 194 and heated to 180 °C for 30 minutes under argon (Scheme 2.13). After this time, the heat was removed and the mixture was allowed to cool slowly overnight. The yellow crystals of 193 were collected the following day by filtration (Scheme 2.13).\(^{290}\)

\[
\text{PdCl}_2 + \begin{array}{c}
\text{Ph} \\
\text{P} \\
\text{Ph} \\
\text{P} \\
\text{P} \\
\text{Ph}
\end{array}
\xrightarrow{\begin{array}{c}
\text{PhCN} \\
180^\circ\text{C, 30 min}
\end{array}}
\begin{array}{c}
\text{Ph} \\
\text{P} \\
\text{P} \\
\text{D} \\
\text{P} \\
\text{Ph}
\end{array}
\]

\[
192 \ (1.0 \text{ eq.}) \quad 191 \ (2.22 \text{ eq.}) \quad 193 \ 93\%
\]

**Scheme 2.13:** Synthesis of Pd(II) catalyst 193.\(^{290}\)

### 2.4.3.2 Synthesis of monoanthracenylporphyrins

The failure of the previous attempts to synthesise anthracenylporphyrin 181 indicated that barium hydroxide and water was not suitable reagents in the Suzuki coupling
involving porphyrins and anthracene derivatives. The base was changed to \( \text{K}_3\text{PO}_4 \), the solvent was also changed to THF and the freshly prepared catalyst 190 was also used (Scheme 2.14). The reaction mixture was subjected to column chromatography from which the desired anthracenyl porphyrin 181 was isolated in 21 % yield (Scheme 2.14). Again the products of the competing debromination and deborylation reactions were also isolated. Efforts were then focused on reducing the competing reactions, in an effort to increase the yield of the desired anthracenylporphyrins.

**Scheme 2.14**: Synthesis of 181 via Suzuki cross-coupling reaction.

The freshly prepared catalysts 190 and 193 were used to test a variety of reaction conditions using a series of porphyrins to yield both alkyl and aryl mono-anthracenylporphyrins. The yields of the optimisation of the reaction conditions are illustrated in Table 2.1. Overall the success of this reaction was found to be dependent on a number of factors: the position of the functional group, the palladium catalyst and the metal in the center of the porphyrin. The optimisation of the reaction conditions for the coupling of compounds 136 and 187 (Scheme 2.14) showed that use of the catalyst 190 (Scheme 2.12) gave only moderate conversion (15 – 21 %) in dry THF with \( \text{K}_3\text{PO}_4 \) (Table 2.1, entry 2) or \( \text{Cs}_2\text{CO}_3 \) (Table 2.1, entry 6). Freshly prepared 193 (Scheme 2.13) proved to be a better catalyst in conjunction with AsPh\(_3\) and gave moderate conversion in DMF (30 %) and acceptable results in THF (48 %) (Table 2.1, entries 3 and 4). DME/water and DMF/toluene were also found to be unsuitable solvents. Use of the zinc(II) derivative 152 gave a significantly lower yield (15 %) while the nickel(II) derivative 150 proved to be superior (81 % yield) (Table 2.1, entries 7 and 8).
Scheme 2.15: Generic example of the cross-coupling reaction between porphyrins and anthracenes.

Table 2.1: Reaction conditions for the synthesis of mono-anthracenylporphyrins.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R¹</th>
<th>R²</th>
<th>M</th>
<th>X</th>
<th>Y</th>
<th>Catalyst</th>
<th>Base</th>
<th>Temp/Solvent</th>
<th>Yield/Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Phenyl</td>
<td>Phenyl</td>
<td>2H</td>
<td>Br</td>
<td>Br</td>
<td>Pd(PPh₃)₄</td>
<td>Ba(OH)₂ 8 (H₂O)</td>
<td>80 °C/DME/H₂O</td>
<td>n.d.</td>
</tr>
<tr>
<td>2</td>
<td>Phenyl</td>
<td>Phenyl</td>
<td>2H</td>
<td>Br</td>
<td>Br</td>
<td>Pd(PPh₃)₄</td>
<td>K₂PO₄</td>
<td>67 °C/THF</td>
<td>21 % /181</td>
</tr>
<tr>
<td>3</td>
<td>Phenyl</td>
<td>Phenyl</td>
<td>2H</td>
<td>Br</td>
<td>Br</td>
<td>PdCl₂(PPh₃)₂/AsPh₃</td>
<td>C₆H₅CO₂</td>
<td>80 °C/DMF</td>
<td>30 % /181</td>
</tr>
<tr>
<td>4</td>
<td>Phenyl</td>
<td>Phenyl</td>
<td>2H</td>
<td>Br</td>
<td>Br</td>
<td>PdCl₂(PPh₃)₂/AsPh₃</td>
<td>C₆H₅CO₂</td>
<td>67 °C/THF</td>
<td>48 % /181</td>
</tr>
<tr>
<td>5</td>
<td>Phenyl</td>
<td>Phenyl</td>
<td>2H</td>
<td>Br</td>
<td>Br</td>
<td>PdCl₂(PPh₃)₂/AsPh₃</td>
<td>C₆H₅CO₂</td>
<td>67 °C/THF</td>
<td>60 % /181</td>
</tr>
<tr>
<td>6</td>
<td>Phenyl</td>
<td>Phenyl</td>
<td>2H</td>
<td>Br</td>
<td>Br</td>
<td>Pd(PPh₃)₄</td>
<td>C₆H₅CO₂</td>
<td>67 °C/THF</td>
<td>15 % /181</td>
</tr>
<tr>
<td>7</td>
<td>Phenyl</td>
<td>Phenyl</td>
<td>Nii(II)</td>
<td>Br</td>
<td>Br</td>
<td>PdCl₂(PPh₃)₂/AsPh₃</td>
<td>C₆H₅CO₂</td>
<td>67 °C/THF</td>
<td>81 % /195</td>
</tr>
<tr>
<td>8</td>
<td>Phenyl</td>
<td>Phenyl</td>
<td>Zn(II)</td>
<td>Br</td>
<td>Br</td>
<td>PdCl₂(PPh₃)₂/AsPh₃</td>
<td>C₆H₅CO₂</td>
<td>67 °C/THF</td>
<td>15 % /196</td>
</tr>
<tr>
<td>9</td>
<td>3,5-Di-tert-butylphenyl</td>
<td>Phenyl</td>
<td>2H</td>
<td>Br</td>
<td>Br</td>
<td>PdCl₂(PPh₃)₂/AsPh₃</td>
<td>C₆H₅CO₂</td>
<td>67 °C/THF</td>
<td>49 % /197</td>
</tr>
<tr>
<td>10</td>
<td>3,5-Di-tert-butylphenyl</td>
<td>Phenyl</td>
<td>Nii(II)</td>
<td>Br</td>
<td>Br</td>
<td>PdCl₂(PPh₃)₂/AsPh₃</td>
<td>C₆H₅CO₂</td>
<td>67 °C/THF</td>
<td>85 % /198</td>
</tr>
<tr>
<td>11</td>
<td>3,5-Di-tert-butylphenyl</td>
<td>Phenyl</td>
<td>Zn(II)</td>
<td>Br</td>
<td>Br</td>
<td>PdCl₂(PPh₃)₂/AsPh₃</td>
<td>C₆H₅CO₂</td>
<td>67 °C/THF</td>
<td>12 % /199</td>
</tr>
<tr>
<td>12</td>
<td>Hexyl</td>
<td>Hexyl</td>
<td>2H</td>
<td>Br</td>
<td>Br</td>
<td>PdCl₂(PPh₃)₂/AsPh₃</td>
<td>C₆H₅CO₂</td>
<td>67 °C/THF</td>
<td>40 % /200</td>
</tr>
<tr>
<td>13</td>
<td>Hexyl</td>
<td>Hexyl</td>
<td>Nii(II)</td>
<td>Br</td>
<td>Br</td>
<td>PdCl₂(PPh₃)₂/AsPh₃</td>
<td>C₆H₅CO₂</td>
<td>67 °C/THF</td>
<td>57 % /201</td>
</tr>
<tr>
<td>14</td>
<td>Hexyl</td>
<td>Hexyl</td>
<td>Zn(II)</td>
<td>Br</td>
<td>Br</td>
<td>PdCl₂(PPh₃)₂/AsPh₃</td>
<td>C₆H₅CO₂</td>
<td>67 °C/THF</td>
<td>6 % /167</td>
</tr>
</tbody>
</table>
Likewise, Pd$_2$(dba)$_3$/AsPh$_3$ and Cs$_2$CO$_3$ in dry THF proved to be a good combination and converted compound 136 into the desired anthracene derivative 181 in about 60% yield (Table 2.1, entry 5). These results are in agreement with the observed high activity of some of these catalysts$^{291}$ and the applicability of the palladium complex Pd$_2$(dba)$_3$ in the presence of a tertiary phosphine ligand and a base.$^{291-293}$ Using the optimised conditions, a number of anthracenylporphyrins were prepared and characterised (Scheme 2.15, Table 2.1).

Ni(II)anthracenylporphyrins 195, 198, 201 were isolated in higher yields than either the free base counterparts 181, 197, 200 or the zinc(II) 196, 199, 167 porphyrins (Table 2.1). For the aryl substituted porphyrins, this phenomenon can be attributed to the more ruffled conformation of Ni(II) meso-arylporphyrin precursors 157, 163 (Scheme 2.4).$^{294}$ The ruffled conformation gives the bulky anthracenyl residue easier access to the meso position.$^{149}$ When coupling was attempted using Zn(II) porphyrins 158, 161, 164 (Scheme 2.4), the starting material was the major product isolated from the reaction mixture. Anthracenylporphyrins 196, 199 and 167 were isolated in low yields (Table 2.1, entries 8, 11 and 14).

### 2.4.3.3 Synthesis of dianthracenylporphyrins

The synthesis of meso-dianthracenylporphyrins was also investigated using the same cross-coupling reaction conditions which had proven successful for the synthesis of monoanthracenylporphyrins. The dibromoporphyrin precursors 202-207 were prepared by reacting 5,15-substituted porphyrins 34, 74 and 135 (scheme 2.3) with Ni(II)(acac)$_2$ under reflux in toluene. The free base and metalloporphyrins precursors were then brominated using three equivalents of NBS in chloroform. The reaction of (5,15-dibromo-10,20-dihexylporphyrinato)nickel(II) 205 yielded the desired dianthracenylporphyrin 208 in good yield (Scheme 2.16). However, the reaction time had to be increased from 16 hours to 48 hours for the high yield of 77% to be obtained. Initial analytical evidence ($^1$H NMR, HRMS) indicated that the side product of this reaction 209 was formed in 5% yield after column chromatography of the crude reaction mixture (Scheme 2.16).
Scheme 2.16: Synthesis of dianthracenylporphyrins.

When the free base 5,15-dibromo-10,20-dihexylporphyrin 204 was coupled with 187 for up to 72 hours, only 12 % of 210 was recovered, however, 211 was not formed. The remaining porphyrin fraction which was isolated was the starting material 204. Increasing the reaction time showed no improvement in yield and still 211 was not formed (Scheme 2.16). It was thought that poor solubility of the precursor 204 by comparison to the nickel derivative 205 could be hindering the reaction from taking place, as repeated attempts to prepare 211 using this method failed.

Similar results were obtained for the synthesis of aryl-anthracenylporphyrins 212-219 (Scheme 2.16). The highest yields obtained for dianthracenylporphyrins 214 (84 %) and 218 (81 %) were achieved when the nickelated porphyrin precursors 203 and 207 were used in the reaction. Initial $^1$H NMR and mass spectroscopic analysis indicated the side product 219 had been formed during the synthesis of 218 in 2 % yield (Scheme 2.16).

It was also noted that the reaction proceeded more quickly for the nickel derivatives than the corresponding free base porphyrin precursors 202 and 206. The reactions were monitored by TLC from which it could be determined that the starting material had been completely consumed after 12 hours for the synthesis of 214 and 218.
However, when monitoring the reaction for the synthesis of 212 and 216 the starting material was still evident by TLC after 72 hours. The competing reaction in these cases was debromination, which was less evident when using nickelated porphyrin precursors. These results provide further evidence that Ni(II) porphyrins are more suitable for Suzuki cross-coupling reactions than the corresponding free base or Zn(II) porphyrin derivatives (Scheme 2.16).

Using these conditions, dibrominated porphyrin precursors could also be converted into the monobromo-monoanthracenylporphyrin derivatives 220-225 by using 1.5 equivalents of 187. When porphyrin 204 was coupled with 187 for 12 hours, 50 % of 222 was isolated, with no debrominated or dianthracenylporphyrin isolated (Scheme 2.17). The remainder of porphyrin isolated was starting material 204. When the corresponding nickel(II) porphyrin precursor 205 was subjected to the same reaction conditions debrominated starting material was the main product recovered. The desired 223 was not recovered from the reaction mixture (Scheme 2.17). The side products of the reaction, monoanthracenyl- 209 and dianthracenylporphyrin 208 (Scheme 2.16), were both isolated in ≤ 10 % yield.

\[
\begin{align*}
\text{PdCl}_2(\text{PPPh}_3)_2/ \text{AsP} & \text{h}_3 (0.2 \text{ eq.)} \\
\text{Cs}_2\text{CO}_3 (5.0 \text{ eq.)} & \\
\text{THF} & 67 ^\circ \text{C, 12 h} \\
\end{align*}
\]

\[187\ (1.5 \text{ eq.}) \]

\[R^1 = \text{Phenyl, } M = 2H \quad 202 \]
\[R^1 = \text{Phenyl, } M = \text{Ni}(\text{II}) \quad 203 \]
\[R^1 = \text{Hexyl, } M = 2H \quad 204 \]
\[R^1 = \text{Hexyl, } M = \text{Ni}(\text{II}) \quad 205 \]
\[R^1 = 3,5\text{-Di-tert-butyl-phenyl}, M = 2H \quad 206 \]
\[R^1 = 3,5\text{-Di-tert-butyl-phenyl, } M = \text{Ni}(\text{II}) \quad 207 \]

\[R^1 = \text{Phenyl, } M = 2H \quad 18\% \quad 220 \]
\[R^1 = \text{Phenyl, } M = \text{Ni}(\text{II}) \quad \text{n.d.} \quad 221 \]
\[R^1 = \text{Hexyl, } M = 2H \quad 50\% \quad 222 \]
\[R^1 = \text{Hexyl, } M = \text{Ni}(\text{II}) \quad \text{n.d.} \quad 223 \]
\[R^1 = 3,5\text{-Di-tert-butyl-phenyl, } M = 2H \quad 21\% \quad 224 \]
\[R^1 = 3,5\text{-Di-tert-butyl-phenyl, } M = \text{Ni}(\text{II}) \quad 10\% \quad 225 \]

**Scheme 2.17:** Synthesis of 5-anthracenyl-15-bromo-porphyrin derivatives 220-225 via Suzuki cross-coupling.

It was also found that when using aryl substituted porphyrin precursor 203 and the hexyl substituted porphyrin precursor 205, the respective products 221 and 223 were not isolated (Scheme 2.17). Preliminary \(^1\)H NMR analysis showed that the mono-
anthracenylporphyrins 215 and 209 (Scheme 2.16) were formed as by-products of the reaction. However, this was not the case when free base porphyrins 202 and 204 were subjected to the same cross-coupling reaction conditions. The desired bromoanthracenylporphyrins 220 and 222 could be isolated in 18 % and 50 % yield when using 1.5 equivalents of 187 as shown in Scheme 2.17. A similar result was obtained for the synthesis of compounds 224 and 225 as a higher yield was isolated for the free base monobromoanthracenylporphyrin 224 then the corresponding Ni(II) derivative 225. These results indicate that debromination occurs more readily for Ni(II) porphyrins than that of the corresponding free base porphyrins. This synthetic pathway can thus open the way for the preparation of functionalised anthracenylporphyrins via subsequent modification of the remaining bromo group.

2.5 Oxidative fusing reactions

Oxidative fusing reactions have been previously reported for the synthesis of triply-fused porphyrin dimers by Osuka et al. The oxidative fusing of an anthracene-linked porphyrin would be expected to cause a bathochromic shift that would surpass that of triply-fused directly linked porphyrin dimers. This expected result would be a consequence of the overlapping of the π orbitals of both the anthracene linker and the porphyrin moieties of the dimer system. Numerous attempts were made to triply fuse anthracenylporphyrin 181 following the procedure which had proven to be successful for the synthesis of triply-fused dimers (Scheme 2.18).

\[
\begin{align*}
\text{Ph} \quad (\text{OTf})_3 (4.0 \text{ eq.}) & \quad \text{DDQ (4.0 eq)} \quad \text{Ph} \\
\text{toluene} & \quad 120 \degree \text{C}, 24 \text{ h} \\
M = 2\text{H} & \quad 181 \\
M = \text{Ni(II)} & \quad 195 \\
M = 2\text{H} & \quad 226 \text{ n.d.} \\
M = \text{Ni(II)} & \quad 227 \text{ n.d.}
\end{align*}
\]

Scheme 2.18: Attempted synthesis of triply-linked anthracenylporphyrins 226 and 227.
After allowing the reaction to stir overnight, investigation by TLC analysis showed the complete consumption of the starting material 181 to form a distinct blue component with a very low rf value. After isolating this compound, an unambiguous $^1$H NMR spectrum could not be obtained, however, mass spectroscopic analysis indicated that 226 had not been formed. The reaction was attempted again using the equivalent Ni(II) porphyrin 195 to investigate the influence of the nickel centre on the success of the reaction. The reaction was monitored by TLC which showed again complete consumption of starting material. After chromatographic purification of the reaction mixture, the $^1$H NMR spectrum showed that the oxidative conditions employed produced a complicated array of products. It was concluded that these products could not be separated by chromatography following further analysis by TLC. The mixture was sent for mass spectroscopic analysis from which it was concluded that the desired triply-linked anthracenylporphyrin 227 had not been formed (Scheme 2.18).

It was at this time that Anderson et al. reported the synthesis of fused bis-anthracene porphyrin monomers and dimers. In this study it was found that the oxidative ring closure reaction would only go to completion if FeCl$_3$ was used with Sc(OTf)$_3$. As expected, the fused compounds displayed a significant red-shift with maxima in the near-IR at 973 and 1495 nm. As a method had now been reported for the oxidative fusing of anthracenylporphyrins, my attention turned to establishing a synthetic method for the synthesis of anthracene-linked porphyrin dimers which could also be fused via an oxidative ring closure reaction.

### 2.6 Synthesis of anthracene-linked dimers

Having established suitable cross-coupling reaction conditions for the synthesis of both mono and disubstituted anthracenylporphyrins; it seemed rational to investigate if the same reaction conditions could afford anthracene-linked dimers. To make further use of the mono-anthracenylporphyrins, it was attempted to brominate anthracenylporphyrin 181 to make compound 228 (Scheme 2.19). It was thought that if 228 could be isolated in reasonable yield, it could then be used as a precursor for a further cross-coupling reaction with a boronylporphyrin to afford an anthracene-
linked dimer. Two conditions were investigated for the synthesis of 228. Initially, 181 was subjected to the most commonly used method used for the bromination of porphyrins using NBS in chloroform. The reaction was monitored by TLC from which it could be determined that no reaction was taking place. Increasing the reaction temperature to reflux and increasing the reaction time showed no improvement of this result, the desired 228 still was not formed. The recovery of the 181 was easily achieved by passing the solution through a short silica plug with CH₂Cl₂ and removing the solvent. This was then used to investigate and alternative method for the bromination of anthracenylporphyrins. Anthracenylporphyrin 181 was dissolved in carbon tetrachloride and reacted with molecular bromine for 1 hour. However, it was determined from ¹H NMR spectroscopic analysis that multiple porphyrin-based products had been formed during the reaction, none of which were the desired compound 228. Preliminary results indicated that bromination was not occurring specifically at the 10-position of the anthracene moiety, thus this synthetic pathway was quickly deemed unsuitable for the synthesis of 228 (Scheme 2.19).

![Scheme 2.19: Attemps to synthesise 228.](image-url)
The next most rational approach for the synthesis of anthracene-linked dimers was the coupling of porphyrin and anthracene derivatives using an excess of the porphyrin precursor. When trying to couple porphyrin \( 182 \) with 9,10-dibromoanthracene \( 185 \) to achieve an anthracene-linked porphyrin dimer \( 229 \), 5.0 equivalents of the boronporphyrin precursor \( 182 \) was used (Scheme 2.20). Under these conditions the major product which was isolated was deborylated porphyrin precursor \( 136 \) (Scheme 2.3). The other porphyrin containing compound was the starting material \( 182 \). The reaction was repeated using nickel(II) porphyrin \( 230 \) and compound \( 185 \) under the same reaction conditions. Coupling was achieved and gave the respective dinuclear porphyrin \( 231 \) in 31 % yield when 10 equivalents of \( 230 \) was reacted with \( 185 \) for 48 hours (Scheme 2.20). Interestingly, no product formation was observed when the zinc(II) porphyrin \( 232 \) was used as the porphyrin precursor. The failed formation of the anthracene-linked dimers \( 229 \) and \( 233 \) when using free base porphyrins and zinc(II) porphyrins, respectively, again confirming that the ruffled conformation of nickel(II) porphyrins favours these types of meso-coupling reactions (Scheme 2.20).

\[
\text{Scheme 2.20: Synthesis of anthracene-linked dimers via Suzuki cross-coupling.}
\]
2.7 Spectroscopic studies

2.7.1 NMR Spectroscopy

The \(^1\)H NMR spectra of porphyrins are very different to most other compounds. Their chemical shifts are, in general, strongly dependent upon the distance and orientation in relation to the delocalisation pathway of the \(\pi\)-electrons of the porphyrin. Protons above or inside the porphyrin macrocycle are in the shielding region of the ring current effect, whereas those in the plane of the macrocycle, but on the porphyrin periphery are in the deshielding region.\(^{298}\) The \(^1\)H NMR spectrum of 181 is shown in Figure 2.3.

![Spectroscopic studies](image-url)

**Figure 2.3**: \(^1\)H NMR, HH COSY and NOESY NMR experiments performed on 181 in CDCl\(_3\) at rt.
To determine the exact chemical shift of every proton in the spectrum, HH COSY and NOESY experiments were also carried out, thus the assignment of each peak is also shown in Figure 2.3.

Contrary to the mono-substituted anthracenylporphyrins the dianthracenylporphyrins showed two doublets associated with the eight β-Hs (Figure 2.4). The decreased number of resonances for the dianthracenylporphyrin derivatives can be attributed to the increased symmetry of the macrocycle.

**Figure 2.4:** $^1$H NMR and CH COSY spectrum of 172 in CDCl$_3$ at rt.
The chemical shifts of the anthracenyl and porphyrin hydrogen atoms follow the trend of increasing downfield shift in the order of Ni(II) < Zn(II) < 2H, as illustrated in Figure 2.5.

![Chemical shifts](image)

**Figure 2.5:** Comparison of \(^1\)H NMR spectra for compounds 167, 172 and 173 in CDCl\(_3\) at rt.

### 2.7.2 UV-vis spectroscopy

Porphyrrins absorb light in near-ultraviolet and visible region. This is what gives porphyrins their characteristic colour. Metalloporphyrins exhibit two electronic transitions in the visible region. The Soret band is the most intense of these transitions which represents a permitted \(\pi-\pi^*\) transitions.\(^{299}\) At longer wavelengths Q-bands can be seen which occur due to quasi-permitted \(\pi-\pi^*\) transitions. Free base porphyrins possess decreased symmetry when compared to that of the metalloporphyrins. As a result of this decreased symmetry four Q-bands occur due to elimination of degenerated excited states.\(^{300}\)

Extending the \(\pi\)-conjugation of the porphyrin system causes a bathochromic or red-shift of the Soret band. Furthermore, the Soret band experiences decreased intensity and band broadening as a result of the extended conjugation of the porphyrin macrocycle. Similarly, a bathochromic shift and band broadening is also observed for
porphyrins bearing electron withdrawing groups. These electron withdrawing groups also cause an increase of the intensity of the Q bands.

The effect of extending the conjugation of the porphyrin is illustrated in Figure 2.6. As the π-system is expanded the Soret band is increasingly red-shifted. This is particularly evident when comparing compound 167 (Scheme 2.2) to 214 (Scheme 2.16) as the Soret band has shifted by 12 nm. The Q bands have also been red-shifted and intensified as a result of the extension of the π-system of the macrocycle. The extent of which the porphyrin is red shifted follows the trend of how electron withdrawing or electron donating the various substituents are (Figure 2.6).

![Figure 2.6: UV-vis spectra of porphyrins 167 and 214 in CH2Cl2 at rt. Baselines were adjusted arbitrarily.](image)

Porphyrrins can also undergo a bathochromic shift as a result of different metal centres. The degree of the red shift the porphyrins exhibits is dependent on the metal centre. The electronegativity of the metal centre has a large bearing on the extent of which the porphyrin experiences a bathochromic shift and the anthracenylporphyrin follow the order of Ni(II) > Zn(II) > 2H.
2.8 X-ray crystallographic studies

Compound 214 crystallised in a monoclinic space group on an inversion center and exhibits a more or less planar conformation (Figure 2.7). The $\Delta 24$ value (deviation of the 24 macrocycle atoms from their least-squares plane) is 0.03 Å, and only minor $w_{av}$ and $r_{uf}$ contributions (e.g., $Cm$ displacements of $0.04 - 0.1$ Å) were found. The average Ni–N bond length is 1.964(3) Å, indicative of an almost planar porphyrin. The anthracenyl units are orthogonal to the 4N-plane (87.6°) while the phenyl rings are slightly tilted to the 4N-plane (108.7°).

![Figure 2.7: View of the molecular structure of 214 in the crystal form. Hydrogen atoms have been removed for clarity; displacement ellipsoids are drawn at the 50% probability level.](image)

The porphyrin molecules form a very closely packed lattice in the crystal. Two hydrogen atoms from the phenyl residue are in a bifurcated close contact to a neighbouring nickel atom (Ni · · ·H20F = 2.838 Å, Ni · · ·H20G = 3.152 Å) (Figure 2.8). As a result, the meso-substituents are tilted slightly upwards and downwards from the macrocycle. For example, the *ipso* carbons of the phenyl and anthracenyl residues are displaced from the 4N-plane by 0.13 and 0.19 Å, respectively.
Figure 2.8: View of the molecular packing of the porphyrin molecules of 214 in the crystal. Dashed lines indicate close H···Ni contacts.

The molecular structure of 198 is shown in Figure 2.9. The porphyrin exhibits the classic $\eta_6$ distortion with alternating up and down $Cm$ displacements of 0.54 to 0.61 Å. The overall $\Delta 24$ displacement is 0.29 Å. These displacements are similar to those of other meso-tetraaryl-Ni(II)porphyrins, and the nonplanar character is also evident by the average Ni–N bond length of 1.919(3) Å. Likewise, the meso-aryl residues are almost orthogonal to the 4N-plane of the macrocycle. The relevant dihedral angles for the residues at C5, C10, C15, and C20 are 97.3, 105.3, 81.6, and 94.2°, respectively. The crystal structure is rather similar to that of 201 (Table 2.1, entry 13). Again, the meso-phenyl ring of one molecule is rather close to the Ni center of a neighbouring porphyrin. However, here the “coordination” is “monodentate” with the closest contact being Ni···H15E (2.731 Å).
The molecular structure of 201 (Table 2.1, entry 13) also exhibits a planar macrocycle. This is indicated by a $\Delta 24$ of 0.01 Å and an average Ni–N bond length of 1.960(2) Å. The anthracenyl residues are almost orthogonal to the plane of the four nitrogen atoms (96.2°). In the crystal packing there are no close contacts. The anthracene residues prevent π-stacking of the porphyrins, and the hexyl side chains are oriented between neighbouring anthracenyl substituents and hinder π-stacking as well. The observation of both planar and nonplanar Ni(II) porphyrins in this series indicates the conformational flexibility of these systems.}

2.9 Conclusion

This chapter reports upon the synthesis of mono- and disubstituted anthracenylporphyrins. Two synthetic pathways proved to be effective for the synthesis of anthracenylporphyrin derivatives, namely the Suzuki cross-coupling and condensation reactions. Furthermore, a series of anthrace derivatives was also synthesised via Suzuki cross-coupling reaction. It was found that Ni(II) porphyrins are favoured for the synthesis of meso-aryl-substituted anthracenylporphyrins and
anthracene-linked porphyrin dimers via Suzuki cross-coupling reaction. When comparing the two synthetic methods for the synthesis of disubstituted anthracenylporphyrins, the condensation reaction has many advantages over the Suzuki cross-coupling reaction. The condensation is a more cost-efficient method, requiring less analysis, time and waste resulting thus in greener chemistry. Furthermore, it is a synthetic pathway to access previously unreported dialkyldianthracenylporphyrins which were poorly formed or not at all via Suzuki cross-coupling reactions. These alkyl residues prevent aggregation by hindering \( \pi \) stacking, thus increasing the efficacy of the system.

Attempts to oxidatively fuse anthracenylporphyrin 181 failed using an adapted method reported by Osuka et al.\(^{295}\) A method to do so was since reported by Anderson et al.\(^{250}\) who found oxidative fusing of anthracenylporphyrins could be achieved under the same conditions that were used by Osuka et al.,\(^{295}\) with the addition of FeCl\(_3\) to the reaction mixture. Furthermore, the attachment of long alkoxy groups to the anthracene moiety gives increased solubility to anthracenylporphyrin, thus, allowing for the oxidative fusing to occur.

A method for the first anthracene-linked dimer via Suzuki cross-coupling reaction is also reported. Future work in this area would be to use a similar method for oxidative fusing of the anthracene-linked dimer as was reported by Anderson et al.\(^{250}\) for the fusion of anthracenyl monomers and dimers.
Chapter 3

Synthesis of Novel Triptycene Scaffolds
3.1 Introduction

Supramolecular chemistry is an area of chemistry which focuses on the assembly of small molecules to form large complex systems. As part of my research, the focus was turned to the synthesis of triptycene scaffolds that allowed easy access to highly functionalised structures. As highlighted in Chapter 1, the shape and structure of triptycene gives it unique physical properties, i.e. the nature of its ring fusion maintains the overall shape of the molecule. The free internal volume characteristic of triptycene occurs as a result of the rigid shape coupled with the space swept out by the aromatic faces (Chapter 1, Section 1.2.2). The internal free volume is defined by the overall cylindrical space swept out by the rotating triptycene. Taking advantage of these voids can provide a unique opportunity to produce elaborate novel supramolecular structures through appropriate host selection such as liquid crystals and polymers. In order expand the diversity of triptycene scaffolds for such applications; we envisioned suitably functionalised triptycene scaffolds bearing boron ester or ethynyl moieties would be amenable to additional functionalisation through transition metal cross-coupling reactions.

In recent years, triptycenes and its 9,10-substituted derivatives have found applications in the construction of new molecular machines. Therefore, it seemed rational to investigate the versatility of the bromination of an array of 9,10-substituted triptycene derivatives with varying degrees of functionality. These could then be used as precursors for transition metal cross-coupling reactions in order to synthesise highly conjugated polymers. The addition of flexible side chains and/or more elaborate functional groups is expected to inhibit strong π-π associations and allow for further functionalisation reactions. The inhibition of the π-π associations is required to ensure the high solubility of the resulting arrays and polymers. Attempts to synthesise both triptycene scaffolds that retain IFV and triptycene scaffolds which have varying functionality at the bridgehead positions are discussed herein.
3.2 Synthesis of anthracene precursors

Anthracene derivatives act as precursors for the Diels-Alder reaction for the synthesis of triptycene derivatives as discussed in Chapter 1, Section 1.2.2.1. A series of 9,10-substituted anthracene derivatives first had to be synthesised to act as precursors for the synthesis of 9,10-disubstituted triptycenes. These could then be subjected to the Diels-Alder type reaction. Two synthetic pathways were investigated for the synthesis of 9,10-disubstituted anthracene derivatives which included organolithium reactions and electrophilic aromatic substitution reactions.

3.2.1 Organolithium reactions

Initially, the synthesis of 9,10-disubstituted anthracenes was carried out via organolithium reaction. Anthraquinone 234 was dissolved in anisole (235) and dry hexane and degassed using the freeze-thaw technique. The solution was cooled to 0 °C and organolithium reagents 138, 140 and 236 in n-hexane were slowly added via syringe (Scheme 3.1). A colour change from yellow to dark green was observed as expected and the solution was brought to room temperature and the reaction was left over night under an inert atmosphere and quenched with 5 mL aqueous aluminium chloride. The residue was dissolved in THF and added dropwise to a solution of tin(II) chloride in acetic acid 237 and stirred for 1 day as illustrated in Scheme 3.1.

![Scheme 3.1: Synthesis of 9,10-disubstituted anthracenes 238-241 via organolithium reactions.](image-url)
The reaction proceeded smoothly when using the least sterically demanding 140 reagent giving the double addition product 9,10-dihexylanthracene\textsuperscript{315} 238 in good yield of 61 %. The reaction with 138 was slow to proceed resulting in a mixture of both 9-phenylanthracene\textsuperscript{316} 239 and 9,10-diphenylanthracene\textsuperscript{317} 240 derivatives being formed. The single addition product 239 was also isolated in 23 % yield which may be as a result of steric hindrance. This resulted in a low yield of 36 % for 240.\textsuperscript{317} Gentle heating of the reaction mixture to 40 °C and increasing the reaction time to 48 hours showed an increased yield of 45 % for 240 whereas the yield of 239 was reduced to 11 % under the same reaction conditions. When the reaction was carried out using sec-butyllithium 236 the desired 9,10-disubstituted anthracene 241 was not isolated. An ambiguous \textsuperscript{1}H NMR spectrum made it impossible to identify the products of the reaction. This may be as a result of 236 being more basic than the primary organolithium reagents such as \textsuperscript{n}-hexyllithium. Steric hindrance may also prevent the formation of 241 as the linear alkylolithium reagents seem to proceed well (Scheme 3.1).

More elaborate 9,10-disubstituted anthracene derivatives were prepared by allowing commercially available arylhalides 242-249 to react with \textsuperscript{n}-butyllithium 42 at -78 °C. These reactions were carried out under an inert atmosphere with the intent of generating the corresponding lithium salts 250-257, which could then act as nucleophiles towards the carbonyl groups of 234 (Scheme 3.2).

The 9,10-disubstituted anthracenes 258,\textsuperscript{318} 259,\textsuperscript{319} 260 and 261\textsuperscript{320} were obtained in poor yields ranging from 6-19 %, illustrated in Scheme 3.2. However, as a consequence of the poor/failed generation of the lithium salts, nucleophilic attack did not occur for 9,10-disubstituted anthracenes 262-265. As a result only starting materials and degradation products were recovered from the reaction mixtures.
**Scheme 3.2:** Generation of lithium salts for the synthesis of 9,10-disubstituted anthracenes.

### 3.2.2 Suzuki cross-coupling reactions

Another method for the introduction of aryl and alkyl substituents onto the central positions of the anthracene system is the Suzuki cross-coupling reaction. It was speculated that by using Suzuki cross-coupling reaction conditions mono- and disubstituted anthracene derivatives could be isolated with improved yields than that for the organolithium reactions. Furthermore, using the Suzuki cross-coupling reaction allows for larger scale reactions than is possible for the organolithium reaction. This is due to the inherent dangers associated with organolithium reagents, in particular the pyrophoricity of the organolithium reagents themselves.\(^{22}\) Thus, larger quantities of anthracene precursors could be isolated in one Suzuki cross-coupling reaction. A series of reactions were then carried out for the synthesis of 9,10-disubstituted anthracene derivatives (Scheme 3.3). Commercially available 185 was reacted with various commercially available aryl boron esters 76, 266-268 using a
palladium(II) dichloride catalyst 193 and the mild base potassium phosphate. These reaction conditions yielded 9,10-disubstituted anthracene derivatives 261 and 259 in improved yields of 69 % and 38 %, respectively (Scheme 3.3). However, no coupling was observed when using 266 as the boron reagent. This reaction seemed to be favoured if stronger electron withdrawing boron ester derivatives were used as starting precursors.

Compound 118 was also synthesised by using bis(pinacolato)diboron 76 as the precursor for this coupling reaction. The reaction was carried out in dry THF and the base was changed to cesium carbonate to afford 118 in 61 % yield (Scheme 3.3). These reaction conditions seemed to favour the formation of 118 then the reaction conditions which were described in Chapter 2, Section 2.4.3.

![Reaction scheme](image)

**Scheme 3.3:** Synthesis of 9,10-substituted anthracene derivatives via Suzuki cross-coupling.

Attempts to synthesise 9-substituted anthracene derivatives via the palladium catalysed Suzuki cross-coupling reactions were also investigated. It was thought that mono-substitution would not only be more specific but that the coupling of an electron withdrawing group could allow a pathway for the synthesis of a push-pull
type system. Compound 30 was used as the starting aryl halide precursor. Together with potassium phosphate and a palladium dichloride catalyst, thiophene boronic acid 270 and allyl boronic acid 271 were reacted with 30 in dry THF (Scheme 3.4). Progress of the reactions was monitored by TLC however, no coupled products were isolated. The major product isolated from the reaction in both cases was anthracene (3). The reactions were repeated using cesium carbonate instead of potassium carbonate. The reactions were monitored for a period of 24 hours by TLC but 3-(anthracen-9-yl)thiophene 272 was not formed during the reaction. However, the reaction did work well for the synthesis of 9-allylanthracene 273 which was isolated in 62 % yield (Scheme 3.4). A reaction time longer than 24 hours showed no improvement in yield. The competing reaction in this case was debromination of the anthracene precursor.

\[
\begin{align*}
\text{PdCl}_2(P\text{Ph}_3)_2 &/ \text{Pd}(P\text{Ph}_3)_4 (0.2 \text{ eq.}) \\
&+ \text{Cs}_2\text{CO}_3 (5.0 \text{ eq.}) \\
\text{Dry THF} &+ 67 \degree \text{C, 16 h} \\
R^1 = \text{allyl} &\rightarrow 273 62\% \\
\text{thiophene} &\rightarrow 272 \text{ n.d.}
\end{align*}
\]

Scheme 3.4: Synthesis of 273 via Suzuki cross-coupling.

3.2.3 Electrophilic aromatic substitution

Organic azides are known to engage in useful organic reactions such as the coupling of an azide group and a terminal alkyne. This is known as click chemistry and is now a commonly used reaction for ethynyl linked systems. These copper catalysed reactions are normally carried out at room temperature under mild conditions and have a wide scope with high yields. For this reason, the synthesis of azido anthracene derivatives which could be used as precursors for azido triptycenes was investigated.
The synthesis of azido anthracenes 274 and 275 (Scheme 3.5) first requires the synthesis of the precursors 9,10-diaminoanthracene 276325 and 9-aminoanthracene 277.326

**Scheme 3.5:** Synthesis of 276-280 and attempted azidation reactions.

Anthracene (3) was reacted with nitric acid at 75 °C for 24 hours to form 9,10-dinitroanthracene 278 (Scheme 3.5).327 The crude mixture of this reaction was reduced using palladium on carbon and sodium borohydride to yield 276 in 47% overall yield as shown in (Scheme 3.5). For the synthesis of 277, anthracene 3 was allowed to react with nitric acid and HCl to form 9-chloro-10-nitro-9,10-dihydroanthracene 279.328 Dehydrochlorination was achieved using sodium hydroxide.
and glacial acetic acid to afford 9-nitroanthracene 280 in a reasonable yield of 51% (Scheme 3.5). Oxidised anthracene was also present in the reaction mixture which may have been as a result of exposure to light or to oxygen being present in the reaction vessel. This was removed by passing the reaction mixture through a short silica plug using EtOAc/n-hexane (5:95). In its pure form, compound 280 was then dissolved in THF and reduced by tin(II) chloride and hydrochloric acid. Upon recrystallisation compound 277 was isolated in 43% yield (Scheme 3.5).

Initially, an adapted procedure reported by Séverac et al.\textsuperscript{267} was investigated for the conversion of aminoanthracenes to azidoanthracenes. To a stirred solution of 277 in TFA at 0 °C a solution of 2 equiv. of NaN\textsubscript{3} in H\textsubscript{2}O was added dropwise and stirred for 10 minutes. This was followed by the addition of a solution of NaN\textsubscript{3} in H\textsubscript{2}O which was added dropwise (Scheme 3.5). The reaction mixture was stirred at 0 °C for 45 minutes and monitored by TLC. Preliminary analytical evidence (\textsuperscript{1}H NMR, HRMS) suggested that oxidised anthracene was present and the desired 9-azidoanthracene 274 was not formed.

Another approach which was investigated to convert compounds 277 and 276 to compounds 274 and 275 were carried out according to a procedure reported by Tor et al.\textsuperscript{329} This two-step synthesis first required the synthesis of trifluoromethanesulfonyl azide 281 as it is not commercially available (Scheme 3.6). Trifluoromethanesulfonic anhydride 282 was reacted with sodium azide 283 in CHCl\textsubscript{3} and H\textsubscript{2}O at 0 °C for 2 hours. This afforded 281 which was then reacted separately with 277 and 276, using copper sulphate and triethylamine in CH\textsubscript{2}Cl\textsubscript{2} (Scheme 3.6). However, subsequent work up and column chromatography showed that the desired products, 274 and 275, were not isolated using this synthetic pathway. \textsuperscript{1}H NMR showed no peaks in the aromatic region which may have been as a result of the degradation of the aminoanthracene derivatives 277 and 276. Repeated attempts to synthesise the desired products (276, 277) proved unsuccessful using this methodology. This synthetic pathway was deemed impractical for the synthesis of triptycine scaffolds and thus, was not pursued any further.
3.3 Synthesis of 9,10-disubstituted triptycene derivatives

Having successfully synthesised a series of both alkyl and aryl substituted anthracene precursors, exploratory reactions were carried out in an attempt to synthesis 9,10-disubstituted triptycenes. As previously discussed in chapter 1 (Section 1.2.2.1), anthracenes can be used as the precursor for the synthesis of triptycenes. A benzyne intermediate is created *in situ* using anthranilic acid 16 and isopropyl nitrite 17 (Scheme 1.4). Benzyne acts as the dienophile in the Diels-Alder type reaction with which the anthracene precursors acts as the diene resulting in the formation of triptycene.

3.3.1 Diels-Alder reaction

Anthranilic acid 16 was dissolved in THF and added dropwise over 4 hours to a solution of 17 and the 9,10-substituted anthracene derivatives 118, 238, 240, 259, 261, 273, 276 and 277 in refluxing chloroform (Scheme 3.7). This procedure was adapted from one reported by Friedman *et al.* Slow addition of 16 is paramount in order to keep the benzyne concentration very low and so prevent a potential hazard of explosion, as well as to avoid side reactions from occurring. After 30 minutes the solvent was removed and the remaining solids were dissolved in *p*-xylene and maleic
anhydride 283, as illustrated in Scheme 3.7. The solution was heated under reflux for 15 minutes, followed by an aqueous work up and plug filtration before the solvent was removed.

A yellow residue was isolated which was confirmed to be 9,10-dihexyltriptycene 284 by NMR and mass spectrometry analysis. When anthracenes 276 and 277 were used as precursors for this reaction a brown/yellow residue was isolated. These residues were later confirmed to be 9-aminotriptycene 285 and 9,10-diaminotriptycene 286 by NMR analysis and mass spectrometry (Scheme 3.7). However, triptycenes 287-291 could not be isolated from the reaction mixture. It was speculated that having electron donating groups at the central positions of the anthracene precursor prevented or interfered with the formation of the triptycene precursors. It was noted that the yield of the triptycene derivative was directly related to the electron donating ability of the central functional group. The highest yield obtained in the sequence was for 286 which was isolated in good yield of 58% (Scheme 3.7).

Scheme 3.7: Synthesis of 9,10-substituted triptycene derivatives 284, 285 and 286.

Amines are electron donating and would strongly activate the central ring of the anthracene system. The yield of the 9,10-substituted triptycene derivatives increases
as the electron donating effect of the 9,10-sutstituted moieties increases. The lowest yield obtained for the 9,10-substituted triptycenes was for 284 which was isolated in 17 % yield. Interestingly, when compound 118 was subjected to the Diels-Alder type reaction with the intent of isolating compound 291 the major product which was isolated was unsubstituted triptycene (Scheme 3.7). When the reaction was being monitored by TLC triptycene was not apparent in the reaction mixture. It was thought that the boron ester groups were being cleaved during the tedious column chromatography, thus compound 291 was deemed to be unsuitable precursor for the purposes of this project. As a result, the reaction was not perused any further.

3.3.2 Bromination of triptycene 9,10-disubstituted triptycene derivatives

For the synthesis of triptycene based scaffolds, it was thought that a good starting point was to extended the scope of King’s work,\textsuperscript{314} who reported the bromination of the six outermost positions of triptycenes.\textsuperscript{314} It seemed most rational to test the hypothesis that this reaction was versatile enough to brominate an array of triptycene derivatives, and so carry out further transition metal catalysed cross-coupling reactions. Triptycenes 284-286\textsuperscript{58,130,333,334} and unsubstituted triptycene 6 were dissolved in chloroform and reacted with molecular bromine using an iron catalyst and heated under reflux for 1 hour. Subsequent recrystallisation from n-hexane afforded 292 in its pure form in 61 % yield (Scheme 3.8). Increasing the reaction time to twelve hours resulted in the isolation of 2,3,6,7,14,15-hexabromo-9,10-dihexyltriptycene 293\textsuperscript{298,333} was isolated in reasonable yield of 56 %. Varying the equivalents of bromine resulted in a decreased yield or no improvement in yield.
Scheme 3.8: Bromination of triptycene derivatives.

The $^1$H NMR spectrum of 293 showed a singlet in the aromatic region, similar to is observed for 292, which was shifted slightly upfield due to the influence the two hexyl moieties exert on the diamagnetic current of the system. When triptycenes 285-286 were subjected to the same reaction conditions the desired triptycene derivatives could not be recovered. As the desired triptycenes 294-295 were not detected in mass spectrometry it concluded this method was only suitable for 9,10-aliphatic triptycene derivatives. The failed formation of compounds 294-295 could be attributed to the coordination of the lewis acid (FeBr$_3$) to the lone pair of the nitrogen. Preliminary NMR analysis showed that neither the starting material nor the desired triptycene derivatives were present. Furthermore, preliminary analysis showed that degradation of the precursor had in fact occurred; indicating that using a super stoichiometric quantity of the catalyst would not facilitate the formation of the desired products 294-295.

It was at this point that a new synthetic strategy was employed for the synthesis of triptycene scaffolds. In particular, triptycene scaffolds which would retain the free internal volume after further functionalisation were desired.
3.4 Synthesis of triptycene derivatives which retain IFV of iptycenes

3.4.1 Suzuki cross-coupling reactions

The synthesis of boron esters is a long established method for the synthesis of precursors which can undergo Suzuki cross-coupling reactions.\textsuperscript{169} They are a fundamental part of organic chemistry due to their ability to construct carbon-carbon bonds. Furthermore, they can exhibit a high degree of stereocontrol in the carbon-carbon bond formation.\textsuperscript{335} For these reasons one triptycene scaffold which was envisaged to make an interesting precursor for further functionalisation of the triptycene periphery is $296$, as illustrated in Scheme 3.9.

Initially, compound $292$ was subjected to the boronylation reaction established by Therien \textit{et al.}\textsuperscript{288} using 4,4,5,5-tetramethyl-1,3,2-dioxaborolane $76$, however the boron ester moiety was not coupled to the periphery of the triptycene molecule. All that could be isolated from this reaction was the starting triptycene precursor $292$ and the debrominated triptycene $6$. An optimisation of this reaction was carried using a variety of reaction conditions. Compound $297$ was formed when $292$ was reacted with 36.0 equivalents of pinacolborane $189$, cesium carbonate in heated under reflux conditions in dry THF (Scheme 3.9). However, due to the low yield obtained for this reaction the formation of $297$ could only be confirmed by mass spectrometry. Nonetheless, this was an important result as it confirmed that substitution can readily take place at two neighbouring positions on the triptycene periphery without the problems associated with steric hindrance. Increasing the equivalents of the boron reagent showed no improvement in the yield of compound $297$, nor was compound $296$ formed.

Further investigations were carried out and it was deduced that compound $296$ could be isolated when compound $292$ was reacted with bis(pinacolato)diboron $189$, cesium carbonate in refluxing THF under Suzuki cross-coupling conditions (Scheme 3.9). One main new product that was observed by TLC which was determined to be compound $296$ by mass spectrometry analysis of the crude mixture, however, this
compound was unstable. After the crude mixture was subjected to column chromatography, there were numerous new fractions that were apparent by TLC. Furthermore, the major product which had previously been observed by TLC was no longer present. Purification via column chromatography proved to be an ineffective method for the isolation of compound 296. The boron ester moieties were cleaved from the triptycene periphery whilst passing through the silica column, as a result triptycene 6 was all that could be recovered after chromatography.

Scheme 3.9: Synthesis of compounds 296 and 297 via Suzuki cross-coupling reaction.

An optimisation of the reaction was carried out in order to try and alleviate the necessity of cumbersome purification techniques. The optimisation of this reaction is illustrated in Table 3.1. Column chromatography can be avoided if 48.0 equivalents of 189 is used followed by extraction with ethylacetate resulting in the isolation of the desired compound 296 in reasonable yield of 36% (Table 3.1, entry 5).
Table 3.1: Tested reaction conditions during the optimisation for the synthesis of 296.

<table>
<thead>
<tr>
<th>Ent.</th>
<th>Boronyl reagent</th>
<th>Equiv.</th>
<th>Base</th>
<th>Solvent</th>
<th>Product</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pinacol borane</td>
<td>30</td>
<td>K_3PO_4</td>
<td>THF</td>
<td>296</td>
<td>n.d.</td>
</tr>
<tr>
<td>2</td>
<td>Pinacol borane</td>
<td>36</td>
<td>Cs_2CO_3</td>
<td>THF</td>
<td>297</td>
<td>Trace</td>
</tr>
<tr>
<td>3</td>
<td>Pinacol borane</td>
<td>60</td>
<td>Cs_2CO</td>
<td>DMF</td>
<td>296</td>
<td>Trace</td>
</tr>
<tr>
<td>4</td>
<td>Bis(pinacolato)diboron</td>
<td>36</td>
<td>TEA</td>
<td>THF</td>
<td>296</td>
<td>7%</td>
</tr>
<tr>
<td>5</td>
<td>Bis(pinacolato)diboron</td>
<td>48</td>
<td>Cs_2CO_3</td>
<td>THF</td>
<td>296</td>
<td>36%</td>
</tr>
</tbody>
</table>

3.4.2 Synthesis of hexaethynyliptycene derivatives

Ethynyl functionality is an attractive building block for triptycene derivatives due to its potential for extended conjugation, its simple linear geometry and its wide accessibility through a range of syntheses.

An efficient method for the synthesis of diaryl ethynes was reported by Cheng et al.\textsuperscript{338} which used a palladium-catalysed reaction with aryl bromides and acetylene. It was also reported that the reaction could be carried out under copper and amine free conditions. This was derived from calcium carbide \textit{in situ}, affording the diaryl ethynes in one-pot reaction in reasonable to excellent yields.\textsuperscript{338} This method employed aminophosphines as ligands, which can be synthesised relatively easily, are air-stable and, most importantly, show high activity in copper and amine free alkynylation reactions.\textsuperscript{339,340} However, reacting compound 292 with compound 298, Pd(OAc)_2 (299), (4-ethynylphenyl)trimethylsilane 300 and K_2CO_3 in THF did not yield the desired triptycene system 301 (Scheme 3.10). The reaction was not specific as a multitude of products which had formed during the progress of the reaction were apparent by TLC. Further analysis by NMR and mass spectrometry indicated that the major products formed were triptycene dimer derivatives. Furthermore, it was
concluded from the preliminary results that coupling had not occurred and that no coupling had occurred between (4-ethynylphenyl)trimethylsilane (300) and compound 292. It was at this point that this reaction was deemed unsuitable for the synthesis of highly conjugated triptycene scaffolds and thus was deemed impractical.

Scheme 3.10: Synthesis of triptycene scaffold 302 via Sonogashira cross-coupling reaction.

The next most rational approach was the Sonogashira reaction which has proven to be a useful tool for extending conjugation through ethynyl groups over a recent number of years. However, the synthesis of the starting precursors suitable for Sonogashira cross-coupling can involve tedious multi-step procedures which can result in overall low yields. An investigation was carried out to determine if
Sonogashira cross-coupling could be forced to occur at the six outer positions of compound 292.

Compound 292 was reacted with a copper catalyst, palladium catalyst and trimethysilylacetylene 87 under inert atmosphere in a dried Schlenk tube. These classic Sonogashira conditions did not yield the desired 2,3,6,7,14,15-hexakis((trimethylsilyl)ethynyl)triptycene 302. Triptycene 6 was isolated from the reaction and a brown solid which could not be identified. An investigation was carried out using a variety of solvents and reaction conditions from which it was deduced that increasing the reaction temperature to reflux resulted in a trace amount of the desired product 302 being detected by mass spectrometry. The yield of this reaction however was \(< 1\%\) which was unacceptable. Increasing the number of equivalents of 87 showed no improvement in yield. However, by using DMF instead of THF and heating the reaction under reflux at the higher temperature of 155 °C for two days (Scheme 3.10) improved the yield of 302 slightly to \(> 5\%\). This result was certainly not good enough for the purpose in which it was intended.

3.4.2.1 Microwave assisted Sonogashira cross-coupling reaction

Having concluded that the traditional Sonogashira methodology was an unsuitable synthetic pathway for the synthesis of compound 302 due to the low yields obtained for the desired product, the use of a microwave assisted Sonogashira reaction was explored. Wang et al.\(^{343}\) described an efficient method for the synthesis of ethynylarylboronic acids through microwave-facilitated Sonogashira coupling reaction starting from bromoaryl boronic acids. The introduction of microwave reactions has solved many safety and reproducibility issues, allowing the formation of several hundred milligrams of the product per run. This method also avoids long reaction times and the use of an excess of the expensive precursor trimethysilylacetylene 87.\(^{344,345}\) Furthermore, it was also reported that the use of a microwave assisted Sonogashira reaction results in higher yields whilst using a reduced amount of palladium catalyst.\(^{346}\) Trimethysilylacetylene 87 together with compound 292, (triphenylphosphine)palladium(II)dichloride 193, triphenylphosphine 191, copper iodide, diethylamine (DEA) and dimethylformamide (DMF) was irradiated with a microwave for 40 % minutes at a temperature of 130 °C. The use of
column chromatography resulted in the isolation of the desired compound 302 in 32 % yield.

Microwave reactions\(^{347,348}\) maintain the reaction temperature whilst using a sealed tube and so a series of reactions were carried out to determine the optimum temperature and reaction time. It was found that conducting the reaction at 120 °C for 35 minutes gave 53 % isolated yield of the desired product 302 (Scheme 3.11). The deprotection of the trimethylsilyl group was achieved by reacting compound 302 with tetra-n-butylammonium fluoride 303 (TBAF) in CH\(_2\)Cl\(_2\) at room temperature overnight (Scheme 3.11). Passing the mixture through a short silica plug in 1:5 EtOAc:n-hexane and removal of the solvent yielded the desired 2,3,6,7,14,15-hexaethynyltriphylene 304 as a pale yellow solid. The cleavage of the trimethylsilyl group was accomplished in 76 % yield (Scheme 3.11).

Scheme 3.11: Synthesis of triptycene scaffold 302 via microwave assisted Sonogashira cross-coupling and its deprotected derivative 304.
3.5 Synthesis of highly conjugated triptycene scaffolds with increased IFV

Triptycene can be extended by increasing the size of its arene blades\textsuperscript{349} with a few reported exceptions.\textsuperscript{350,351} The most common uses of extended triptycenes has primarily been as starting materials for the synthesis of more elaborate ipyocene complexes.\textsuperscript{352} This has been demonstrated by Pascal's synthesis of dodecaphenyltriptycene.\textsuperscript{353}

Having established a suitable synthetic pathway for the synthesis of compounds \textbf{302} and \textbf{304} it seemed rational to investigate whether the conjugation of these triptycene systems could be extended further as a different approach to increasing the blade perpendicularly. Two transition metal catalysed approaches were investigated: the microwave assisted Sonogashira cross-coupling reaction and Glaser cross-coupling reaction.

3.5.1 Microwave assisted Sonogashira cross-coupling

Given that the microwave assisted Sonogashira reaction was found to be a suitable method for extending the conjugation of the triptycene it seemed rational to first investigate if the same methodology would work if the functional groups were reversed.

For this Sonogashira reaction ((4-bromophenyl)ethynyl)trimethylsilane \textbf{305} was used as the aryl halide was coupled to each of the six ethynyl groups of \textbf{304}. Using the same microwave conditions as previously described for the synthesis of \textbf{302} resulted in the formation of 2,3,6,7,14,15-hexakis((4-((trimethylsilyl)ethynyl)phenyl)-ethynyl)triptycene (\textbf{306}) (\textsuperscript{1}H NMR, C-H Cosy, HRMS). This was then be deprotected using TBAF (\textbf{303}) resulting in the isolation of 2,3,6,7,14,15-hexakis[(4-ethynyl|phenyl)ethynyl]-triptycene \textbf{307} as a yellow solid in a yield of 63 % (Scheme 3.12).

3.5.2 Glaser coupling reaction

Glaser coupling has proven successful for triptycene based molecular cages and monodisperse oligo(1,4-phenyleneethynylene-alt-1,4-triptyceneethynylene).\textsuperscript{354,355} Chen et al. followed a similar synthetic pathway for the synthesis of nanoscale triptycene based molecular cage like structures.\textsuperscript{66} A large excess of 87, piperdine, copper(I) chloride and copper(II) acetate were reacted with 304. After 2 hours the reaction mixture was purified on a silica column using EtOAc/n-hexane, 1:5, v/v. Recrystallisation from CH\textsubscript{2}Cl\textsubscript{2}/MeOH yielded 2,3,6,7,14,15-hexakis((trimethylsilyl)-buta-1,3-diyn-1-yl)-triptycene 308 as a pale yellow solid in 16 % yield, as illustrated in Scheme 3.13.

3.6 Spectroscopy

3.6.1 NMR Spectroscopy

The $^1$H NMR spectroscopic pattern of the aromatic triptycene protons depends heavily on the overall symmetry of the molecule. As a consequence, the pattern of the aromatic protons of triptycene can be used to distinguish the symmetry of the overall system and thus can be used to deduce whether substitution occurred at all six positions. It is convenient to begin this comparison by looking at triptycene 6 as a standard molecule to observe the different substituent effects. Figure 3.1 shows the $^1$H NMR spectrum of compound 306. The bridgehead C-H protons can clearly be identified as one singlet at 5.43 ppm and the aromatic protons of the triptycene also appear as a singlet at 7.63 ppm. By comparison with 6 the presence of the trimethylsilane groups gives rise to a sharp singlet which is observed at 0.28 ppm that integrates to 54 protons. The six phenyl groups are represented as a multiplet in the aromatic region which integrates to 24 protons.
Figure 3.1: $^1$H NMR and CH COSY experiments performed on 306 in CDCl$_3$ at rt.

Figure 3.2 shows the $^1$H NMR spectra of 302 and 308. The resonance of the bridgehead C-H proton for both triptycene complexes is visible at 5.37 ppm. The six aromatic protons for both systems are represented by a sharp singlet at 7.53 ppm which can be attributed to the high symmetry and deshielding by the diamagnetic ring current. Cleavage of the trimethylsilyl groups from 302 was confirmed when comparing the spectra of compounds 302 and 304. For 302, a large singlet at 0.23 ppm represented the seventy two protons of the six trimethylsilyl moieties. After deprotection this singlet had completely disappeared and had given rise to a singlet at 3.30 ppm. This corresponds to the six protons and is indicative of the six ethynyl groups of 304. A chemical shift was not observed for the aromatic or bridgehead protons, this is due to the trimethylsilane groups having minimal influence on the electromagnetic ring current.

Similarly, the spectrum for the product of the Glaser coupling reaction 308 shows high degrees of symmetry (Figure 3.2). The aromatic protons and the bridge head
protons are each represented by sharp singlets that integrate accordingly. The most diagnostic resonance is the 72 proton singlet which represents the TMS groups. This appears at 0.25 ppm which when compared with the spectra of 302 was slightly shifted up field. This can be attributed to the protons being more shielded then those of compound 302 as a result of the extra ethynyl linker extending the TMS groups further away from the triptycene core.

**Figure 3.2:** $^1$H NMR comparison of triptycene scaffolds 302 and 308 in CDCl$_3$ at rt.

The $^1$H NMR spectra of the two ethynyl-triptycene systems 302 and 308 differ only by slight upfield shifts as a result of the extended conjugation resulting from the additional ethynyl linkers. However, by using $^{13}$C NMR they can be distinguished by the presence of the extra peaks at 83.7 and 84.1 ppm which are a result of the additional ethynyl group of 308. This also results in a significant downfield shift of the ethynyl carbons which were already attached to the triptycene periphery as illustrated in Figure 3.3.
3.6.2 UV-vis Spectroscopy

When the UV-vis absorption spectrum of compounds 304 and 307 were compared, a significant bathochromic shift and an increased intensity of the absorption peaks was observed. This can be attributed to the extended conjugation the additional phenyl-ethynyl groups exhibits on the triptycene system. The additional phenyl-ethynyl groups caused a bathochromic shift of 28 nm as a direct result of extending the $\pi$ conjugation.

![Figure 3.4: Comparison of the UV-vis spectra of 304 and 307 in THF at rt. Baselines were adjusted arbitrarily.](image)
3.7 Conclusion

Transition metal-catalysed carbon-carbon bond formation is an undoubtedly fast-growing research field with enormous academic and industrial interest. This chapter describes the transition metal-catalysed synthesis of hexasubstituted triptycene scaffolds. Highly symmetric rigid and functionalised triptycene derivatives have been successfully synthesized which are suitable for further transformation reactions. The triptycene derivatives possess $D_{3h}$-symmetry and can serve as versatile molecular building blocks for the synthesis of more elaborate and complex structures.

A triptycene scaffold bearing six boron ester moieties (296) was generated from the previously reported 2,3,6,7,14,15-hexabromotriptycene scaffold $292^{314}$ via the palladium-catalysed Suzuki cross-coupling reaction. This scaffold can serve as a precursor for further Suzuki cross-coupling reactions in the synthesis of elaborate supramolecular systems.

Furthermore, the conjugation of triptycene was extended at the six outer positions via microwave assisted Sonogashira cross-coupling reactions. Microwave heating seems to be particularly competitive with the traditional Schlenk tube/flask method, as it brought long reaction times down to minutes and increased the yield. In addition, the use of the microwave for Sonogashira cross-coupling reactions improved the reproducibility of the reaction and minimised waste by using stoichiometric quantities of expensive reagents. The product of this reaction 2,3,6,7,14,15-hexakis((trimethylsilyl)ethynyl)triptycene $302$, following deprotection afforded a novel triptycene scaffold 2,3,6,7,14,15-hexaethynyltriptycene $304$. This scaffold then proved to be a suitable precursor for both further Sonogashira cross-coupling reactions and for Glaser cross-coupling reactions to yield highly conjugated symmetric rigid triptycene scaffolds. These novel triptycene derivatives have potential applications in material chemistry, supramolecular chemistry and molecular machines.$^{28,29,356}$

This new synthetic pathway has opened up a whole range of triptycene scaffolds which can be easily synthesised through similar means. All of the novel triptycene
scaffolds discussed in this chapter showed exceptional solubility despite some of them being highly conjugated. This is an important property as it enables further functionalisation reactions to be carried out with relative ease. It is in fact conceivable to repeat the Sonogashira cross-coupling and deprotection reactions, thus extending the conjugated arms of the triptycene scaffold further. This in turn would also increase the free volume, thus making suitable conjugated triptycene systems for a variety of applications. The π extended triptycene scaffold bearing neighbouring ethynyl groups (304) also affords the opportunity for cyclization reactions to create higher-order planarised triptycene π systems. It is also plausible that these ethynyl-triptycene scaffolds (304, 307) could also be subjected to ‘click’ reactions with organic azides. Overall, the novel triptycene scaffolds which have been synthesised have opened the door to an endless library of supramolecular systems with the potential of a wide range of applications.
Chapter 4

Synthesis of Rigid Covalently-Linked Hexaporphyrin Arrays
4.1 Introduction

Macromolecules have been of interest since the beginning of the twenty first century for their unique properties of broad applicability which includes; molecular electronics,357 nonlinear optics,358 models for photoinitiated charge transfer,359 biological and materials chemistry.360-365 They also provide basic knowledge in photophysics, photobiology and photochemistry. Macromolecules are extremely large molecules that exhibit functions and properties that are not evident or existent in small molecules. The design and development of synthetic methods for the synthesis of multiporphyrin arrays is currently being undertaken by many researchers in the scientific community.366

Multiporphyrin species have been under investigation for the purposes of light harvesting devices because of their versatility. Specifically, their excited-state properties can be fine-tuned by substituting the meso or β positions as well as incorporating different central metals to the macrocycle. Multichromophore systems can mimic the role of the light harvesting antenna components for artificial photosynthesis367-369 and in-dye sensitized solar cells.370 It was thought that for this reason that triptycene-linked porphyrin arrays would be efficient light-harvesting complexes in order to capture and transfer light energy in a cascade of energy transfer steps. Furthermore, porphyrin architectures with defined three-dimensional structures have been employed in diverse studies371 and are members of a broader class of shape-persistent nanoscale molecular architectures that have elicited wide interest.372-374 In order to expand the diversity of the triptycene scaffolds which were synthesised in Chapter 3,43 it was thought that the boron triptycene scaffold 296 (Chapter 3, Section 3.4.1) and the π-extended triptycene scaffold 304 (Chapter 3, Section 3.4.2.1) would be amenable to further six fold cross-coupling reactions using bromoporphyrin precursors. The pathways explored for the synthesis of triptycene-linked hexaporphyrin arrays is discussed herein.
4.2 Synthesis of porphyrin precursors

4.2.1 Synthesis of $A_2$, $A_2B$, $A_2BC$ porphyrins

Meso-substituted porphyrins were isolated via condensation reaction of various substituted aldehydes and dipyrromethane. 5,15 $A_2$-type porphyrins 34, 142, 309-311 were isolated in reasonable yields ranging from 27-41% (Scheme 4.1). 255

\[ \text{R}^1 = 1\text{-Methylpropyl; } R^2 = H \quad 311 \text{ 33}\% \]
\[ \text{R}^1 = 1\text{-Ethylpropyl; } R^2 = H \quad 310 \text{ 30}\% \]
\[ \text{R}^1 = 4\text{-Methyl-C}_6\text{H}_4; R^2 = H \quad 309 \text{ 31}\% \]
\[ \text{R}^1 = \text{Hexyl; } R^2 = H \quad 142 \text{ 27}\% \]
\[ \text{R}^1 = \text{Ph; } R^2 = H \quad 34 \text{ 41}\% \]

\[ \text{R}^1 = 1\text{-Methylpropyl; } R^2 = H; M = \text{Ni}(II) \quad 315 \text{ 88}\% \]
\[ \text{R}^1 = 1\text{-Ethylpropyl; } R^2 = H; M = \text{Ni}(II) \quad 314 \text{ 94}\% \]
\[ \text{R}^1 = 4\text{-Methyl-C}_6\text{H}_4; R^2 = H; M = \text{Ni}(II) \quad 313 \text{ 83}\% \]
\[ \text{R}^1 = \text{Ph; } R^2 = H; M = \text{Ni}(II) \quad 312 \text{ 92}\% \]

\[ \text{R}^1 = \text{Ph; } R^2 = \text{Ph; } M = 2\text{H} \quad 156 \text{ 87}\% \]
\[ \text{R}^1 = \text{Hexyl, } R^2 = \text{Hexyl, } M = 2\text{H} \quad 159 \text{ 74}\% \]
\[ \text{R}^1 = 1\text{-Ethylpropyl, } R^2 = \text{H,M = Ni(II)} \quad 316 \text{ 77}\% \]
\[ \text{R}^1 = 4\text{-Methyl-C}_6\text{H}_4; R^2 = \text{H; } M = 2\text{H} \quad 317 \text{ 57}\% \]
\[ \text{R}^1 = 4\text{-Methyl-C}_6\text{H}_4; R^2 = \text{H; } M = \text{Ni(II)} \quad 318 \text{ 70}\% \]
\[ \text{R}^1 = \text{Ph; } R^2 = \text{H; } M = 2\text{H} \quad 319 \text{ 63}\% \]
\[ \text{R}^1 = \text{Ph; } R^2 = \text{H}; M = \text{Ni(II)} \quad 320 \text{ 71}\% \]
\[ \text{R}^1 = 1\text{-Methylpropyl, } R^2 = \text{H,M = Ni(II)} \quad 321 \text{ 74}\% \]
\[ \text{R}^1 = 1\text{-Methylpropyl, } R^2 = \text{Br,M = Ni(II)} \quad 322 \text{ 89}\% \]

i) $R^2\text{Li (6.0 to 8.0 eq.), dry THF, } -78\text{ °C to r.t., NH}_4\text{Cl, DDQ (10.0 eq.) ii) Ni(acac)}_2 \text{(1.5 eq.), toluene, 120 °C, 1 h. iii) NBS (0.8–3.0 equiv.), CHCl}_3, \text{ pyridine, 1–3 h.}

Scheme 4.1: Synthesis of meso-substituted bromoporphyrin precursors 156, 157, 159, 316-322.
Porphyrids with nickel(II) centres were synthesised because it was thought that they would promote further coupling and functionalisation reactions due to the classic ruffled conformation which is exhibited by these complexes. Metallation was carried out using nickel(II)acetylacetonate in toluene and heated under reflux to yield porphyrins 312-315 in good yields of up to 80%. Nucleophilic addition followed by hydrolysis and oxidation using DDQ yielded trisubstituted A2B-type porphyrins 139, 136, 150 in yields ranging from 33-80%.152,264 Bromination was carried out using NBS to yield bromoporphyrins 156, 157, 159, 316-322 in yields ranging from 57-91% (Scheme 4.1).270

It was anticipated that steric effects could hinder the coupling at all six outer positions of the triptycene scaffolds, particularly for the Suzuki cross-coupling reaction to yield the directly linked hexaporphyrin arrays. By introducing porphyrins with linkers bearing the boron ester moiety it was thought that any problems associated with steric hindrance could be eliminated (Scheme 4.2).

Scheme 4.2: Synthesis of meso substituted bromoporphyrin precursors 323 and 324.
A one-pot condensation reaction for the synthesis of 5,15-bis(3-bromophenyl)-10,20-diphenylporphyrin 323 first required the synthesis of 5-phenyldipyrromethane 325, as described in chapter two (Section 2.4.1) for the synthesis of substituted dipyrromethane derivatives 16, 168 and 174. 5-Phenyldipyrromethane 325 was isolated in reasonable yield of 58%281 and was then used in a condensation reaction with 4-bromobenzaldehyde 326 using TEA, TFA and DDQ, resulting in the formation of compound 323 in 28% yield. Metallation of porphyrin 323 was carried out using nickel(II)acetylacetonate to yield [5,15-bis(3-bromophenyl)-10,20-diphenylporphyrinato]nickel(II) 324 in excellent yield of 91% (Scheme 4.2).

4.2.2 Synthesis of boronylporphyrins

Boronylporphyrins have proven to be excellent precursors for C-C coupling reaction and this has been well documented over recent decades.160 It seemed rational to investigate if such boronylporphyrin precursors could be used for the synthesis of triptycene linked hexaporphyrin arrays via Suzuki cross-coupling reaction. Thus, meso-substituted boronylporphyrins with varying functionality were first synthesised.

Boronylation of bromoporphyrins 156 and 157 was carried out using a modified method developed by Therien et al.288 (Scheme 4.3). The reaction was monitored by TLC and after 16 hours it was apparent that the starting material had been completely consumed.

![Scheme 4.3: Synthesis of meso-substituted boronylporphyrins 182 and 327](image-url)

- 105 -
The competing reaction in these cases was debromination of the starting porphyrin precursors. However, these competing reactions could be minimised by using 10-15 equivalents of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane 189 resulting in the desired boronylporphyrins 182 and 327 being isolated in yields of 36 % and 51 %, respectively, after column chromatography (Scheme 4.3).

Dibromoporphyrin 324 was also subjected to the same Suzuki cross-coupling conditions as described above.288 It was anticipated that varying the number of equivalents used of the boron ester precursor would promote the formation of the monoboronester porphyrin complex 328. Unfortunately the desired 328 could only be obtained in poor yield of 12 %. The competing reaction in this case was debromination resulting in 5,10,15,20-tetraphenylporphyrinato(ll)nickel 329 being the major product formed with a yield of 64 % (Scheme 4.4). The optimisation of this reaction was carried out and initially the base was changed from the stronger Cs2CO3 to the weaker K3PO4. This certainly favoured the reaction with the yield of the desired 328 increasing to 19 %. The yield of 329 was only detected in trace amounts. However these reaction conditions also yielded the porphyrin dimer 330 which was isolated in 14 % yield. Although an interesting dimer which certainly has other applications in porphyrin chemistry it was not suitable for the coupling reactions which were intended for triptycene. Thus, the goal was to eliminate the formation of the dimer and again increase the yield of 328 further. Under the same conditions bis(pinacolato)diboron (76) was used instead of pinacolborane (189) which resulted in the formation of the mono- and diporphyrin borate derivatives 328 and 331 in 32 % and 41 % yield, respectively (Scheme 4.4).

Reducing the quantity of bis(pinacolato)diboron (76) from 5 to 2 equivalents resulted in the desired mono-porphyrin borate being isolated in 48 % yield (Scheme 4.4). It was noted, that when the reaction was carried out using the free base derivative of the porphyrin precursor 323, the only reaction which took place was debromination of the porphyrin precursor. Varying the equivalents of bis(pinacolato)diboron (76) and reaction conditions showed that debromination could be reduced. However, the desired free base boronylporphyrin could not be isolated unless compound 324 was used as the precursor.
Scheme 4.4: Synthesis of boronylporphyrins 328, 330 and 331 via Suzuki cross-coupling.

4.2.3 Synthesis of porphyrins bearing a phenylethynyl moiety via organolithium reaction

Precursors for a Sonogashira reaction require one aryl halide and one ethyne moiety. Interporphyrin interaction occurs when there is a strong overlap of π-orbitals. This overlap can occur by either cofacial arrangements or by the addition of a conjugating bridge. Thus, porphyrins with ethynyl groups are seemed like attractive precursors for the synthesis of triptycene linked hexaporphyrin arrays.
The obvious synthetic route for the synthesis of porphyrins bearing an acetylene moiety on the porphyrin periphery was by nucleophilic substitution. This method has long been established within the Senge group and has proven to be a successful reaction using a variety of porphyrin precursors. Commercially available 1-bromo-4-ethynylbenzene 332 was reacted with n-butyllithium (42). The reaction is temperature sensitive and thus was carried out at -78 °C under inert conditions to generate the reactive aryllithium intermediate. Porphyrins 318, 320-323 in THF were added slowly to the reaction mixture. The reaction was brought to room temperature and allowed to react for a further hour. Subsequent work up and purification yielded porphyrins 333-337 in varying yields of 53-94 %, as shown in Scheme 4.5.

Scheme 4.5: Synthesis of porphyrins bearing a phenylethynyl moiety 333-337 at the meso-position via organolithium reaction.

Highly substituted porphyrins possessing aryl meso-substituents are also desirable compounds for optical applications due to the potential to fine-tune their physiochemical properties via conformational control. It was previously reported
by Senge et al. that octaethylporphyrin (OEP) readily undergoes nucleophilic substitution. Direct aryl meso-substituted OEP derivatives were isolated and more specifically bearing a 4-ethynylphenyl residue. For this reason, octaethylporphyrin was synthesised according to a procedure developed by Sessler et al. and then metallated using nickel(II)acetylacetonate to yield [2,3,7,8,12,13,17,18-octaethylporphyrinato]nickel(II) in good yield of 91%. It was subjected to the same organolithium reaction as described above to yield [2,3,7,8,12,13,17,18-octaethyl-5-(4-ethynylphenyl)porphyrinato]nickel(II) in 88% (Scheme 4.6). This procedure had been optimised for the synthesis of free base OEP derivatives which reported the isolation of 2,3,7,8,12,13,17,18-octaethyl-5-(4-ethynylphenyl)porphyrin in 72% yield. The significant improvement in yield can be attributed to the ruffled conformation of nickel porphyrins, thus making the meso-position more accessible to the bulky aryl residue.

**Scheme 4.6**: Synthesis of porphyrin 40 via organolithium reaction.

### 4.3 Synthesis of iodotriptycene precursors

The coupling of boronylporphyrins to the 2,6,14-triiodotriptycene 341 has been reported within the Senge group recently. As iodine is a better leaving group than bromine it was anticipated that using 292 may hinder the formation of larger multiporphyrin arrays. With this in mind, attention was turned to the synthesis of both 341 and 2,3,6,7,14,15-hexaiodotriptycene 342 (Scheme 4.7). It was hoped that the increased reactivity of the iodotriptycene derivatives would enable the hexaporphyrin array to be formed.
Commercially available triptycene was heated under reflux in nitric acid to yield 2,6,14-trinitrotriptycene 343 in good yield of 63% following a procedure published by Zhang et al.\textsuperscript{60} This was then reduced to the triamino derivative 344 in good yield of 74%. Subjecting 344 to the Sandmeyer reaction afforded 341 in 20% yield (Scheme 4.7).\textsuperscript{382,383}

\begin{center}
\includegraphics[width=0.9\textwidth]{scheme47.png}
\end{center}

\textbf{Scheme 4.7:} Synthesis of 341 via Sandmeyer reaction.

A similar synthetic pathway as described above was investigated for the synthesis of 342 and is shown in Scheme 4.8. Mastalerz et al.\textsuperscript{384} reported a convenient one-step pathway for the synthesis of 2,3,6,7,14,15-hexanitrotriptycene 345. This method not only obviates cumbersome column chromatography but also reduces the number of steps previously required for the synthesis of 2,3,6,7,14,15-hexaaminotriptycene 346 as reported by MacLachlan et al.\textsuperscript{385} The intention was to reduce compound 345 to 346 and finally carry out the Sandmeyer reaction to afford compound 342. Initially, triptycene 6 was suspended in fuming nitric acid and heated to 85 °C for 4 hours. Subsequent work up and recrystallisation from DMF yielded a yellow residue which
was later confirmed by NMR analysis and mass spectrometry to be the desired 345 in 20 % yield. Reduction of the nitro residues to amino residues yielded compound 346 in low yield of 12 % (Scheme 4.8). It has been reported that compound 346 readily undergoes oxidation upon exposure to oxygen resulting in the rapid decomposition of the triptycene system. Triptycene 346 was subjected to the Sandmeyer reaction (Scheme 4.8), however, compound 342 failed to form. A brown solid was recovered which could not be identified by NMR spectroscopic analysis which appeared to be degradation products as there were no resonance peaks in the aromatic region of the \(^1\)H NMR spectrum. It is plausible that the instability of the precursor 346 hindered the formation of the desired product.

\[
\begin{align*}
\text{fuming HNO}_3 (18.0 \text{ eq.}) & \quad 85 ^\circ \text{C, 4 h} \\
\text{Pd/C, 10 wt. \% (2.6 eq.)} & \quad \text{NaBH}_4 (0.5 \text{ eq.}) \\
\text{NH}_2 \text{HCl (95.0 eq.)} & \quad \text{NH}_2 \text{H}_2\text{O} \\
\text{80 ^\circ \text{C, 2 h}} & \quad \text{80 ^\circ \text{C, 2 h}} \\
\end{align*}
\]

**Scheme 4.8: Attempted synthesis of 342.**

It was then thought that using a similar synthetic pathway as was reported by King *et al.* could afford compound 342 if molecular iodine was substituted for molecular bromine. aluminium chloride was thought to be a more suitable catalyst and thus was reacted with molecular iodine and triptycene 6 in chloroform and heated under reflux for twenty four hours. However, NMR spectroscopic analysis confirmed that the compound 6 was all that was recovered from the reaction mixture. The repeated failure to form the iodo-substituted 342 product using this reaction indicated that molecular iodine was not reactive enough to halogenate triptycene.
4.4 Optimisation of Suzuki cross-coupling reaction conditions for hexa-substituted triptycenes

As compound 292\textsuperscript{314} proved useful as a precursor for palladium-catalysed cross-coupling reactions in the chapter three, it seemed rational to investigate if it was a suitable precursor for the synthesis of triptycene-linked hexaporphyrin arrays. A series of test reactions were carried out to ensure that coupling would indeed take place at all six positions using commercially available boronesters 119, 347-349 (Scheme 4.9).

![Scheme 4.9: Synthesis of hexasubstituted triptycene derivatives 350-353 via Suzuki cross-coupling.](image)

During the optimisation of this reaction it was found that electron withdrawing substituents on the boron esters favoured this reaction. The highest yield of 32\% was obtained when compound 292 was coupled with 3-aminophenyl boronic ester to give compound 350. No reaction took place when the electron donating 4-(methoxycarbonyl)phenyl boronester 119 was used under the same reaction conditions as shown in Scheme 4.9.
4.5 Synthesis of triptycene-linked porphyrin arrays

4.5.1 Suzuki cross-coupling approach

Having established suitable reaction conditions for the coupling of aryl boron esters to triptycene 292, both alkyl and aryl substituted boronylporphyrins 182, 327 and 328 were then subjected to the same Suzuki cross-coupling conditions as described above. Unfortunately, no coupled product could be isolated from this reaction. The starting material and dehalogenated/deborylated starting materials were recovered. Increasing the reaction time and increasing the equivalents of the boronylporphyrins showed no improvement in the progress of the reaction. Initially, it was suspected that steric hindrance could have been a contributing factor for the failed efforts to synthesise the desired hexaporphyrin arrays. However, it was concluded that it was not the major contributory factor. The phenyl spacer group in the boron porphyrin precursor 328 should have overcome any problems associated with steric hindrance and resulted in the formation of the corresponding porphyrin hexamer if this indeed was the case. Again, it was thought that the major contributing factor preventing the formation of the directly linked porphyrin arrays was the reduced reactivity of bromo groups by comparison to iodo groups.

It was decided to test the reaction conditions and reagents by synthesising one of the triptycene-linked porphyrin trimers previously reported by the Senge group.\textsuperscript{42} Triptycene 341 was reacted with boronylporphyrin 327 which resulted in the formation of the porphyrin trimer 354 in an impure state which was detected using mass spectroscopy (Scheme 4.10). This was not purified or characterised any further as this result confirmed that the method and the reagents used are suitable for the Suzuki coupling of boronylporphyrins to halogenated triptycene. It was thought that the decreased reactivity of compound 292 by comparison to porphyrin 341 could be hindering any coupling from occurring. It was at this point that compound 292 was deemed to be an unsuitable precursor for the synthesis of directly hexaporphyrin arrays.
The boronyltriptycene scaffold 296 was isolated in low yield via a Suzuki cross-coupling reaction as described in Chapter 3. Triptycene 296 is an unstable complex that does not survive column chromatography and its stability at room temperature is also questionable, nevertheless, if stored in the fridge under argon it seems to remain stable. Triptycene 296 was subjected to further cross-coupling reactions with a number of bromoporphyrin derivatives 156, 157, 159, 321-323. The procedure was modified from one which was previously reported for the synthesis of triptycene-linked porphyrin trimers. However, coupling was not achieved at any position and complete deboronylation of 296 had occurred. Debromination of the porphyrin precursors was also observed although some of the brominated porphyrin could be re-isolated using column chromatography and reused for further reactions. Despite repeated attempts to isolate hexaporphyrin arrays using the triptycene scaffold 296, no coupled product could be isolated, with compound 6 being the major product isolated from all of the reaction mixtures (Scheme 4.11). It was at this point that the focus was turned to synthesis triptycene linked hexaporphyrin arrays via Sonogashira cross-coupling reaction.

Scheme 4.10: Synthesis of triptycene linked trimer 354 via Suzuki cross-coupling.
Scheme 4.11: Attempted synthesis of directly linked hexaporphyrin arrays via Suzuki cross-coupling.

4.5.2 Sonogashira cross-coupling approach

A Sonogashira cross-coupling approach was also investigated for triptycene-linked hexaporphyrin arrays. The intention was to isolate a high order planarized triptycene-porphyrin complex with an extended π-system. Porphyrins bearing a phenylethynyl moiety (228-232) were subjected to the same conditions which had already proven
successful for the synthesis of triptycene-linked porphyrin trimers via Sonogashira cross-coupling reactions by the Senge group.\textsuperscript{42}

\begin{align*}
R^1 &= \text{Ph, } R^2 = \text{H, } M = \text{2H} \quad 333 \\
R^1 &= \text{Ph, } R^2 = \text{H, } M = \text{Ni(II)} \quad 335 \\
R^1 &= \text{p-Tolyl, } R^2 = \text{H, } M = \text{2H} \quad 334 \\
R^1 &= \text{1-Ethylpropyl, } R^2 = \text{H, } M = \text{Ni(II)} \quad 336 \\
R^1 &= \text{1-Methylpropy, } R^2 = \text{H, } M = \text{Ni(II)} \quad 337
\end{align*}

\begin{align*}
&\text{TEA} \\
&\text{PdCl}_2(\text{PPh}_3)_2 \\
&\text{THF} \\
&67 \degree \text{C, 16 h}
\end{align*}

\begin{align*}
R^1 &= \text{Ph, } R^2 = \text{H, } M = \text{Cu(II)} \quad 355 \quad 51\% \\
R^1 &= \text{p-Tolyl, } R^2 = \text{H, } M = \text{Cu(II)} \quad 356 \quad 55\%
\end{align*}

\textbf{Scheme 4.12:} Attempted synthesis of triptycene linked hexaporphyrin arrays via copper-catalysed Sonogashira reaction.

The reaction was monitored by TLC from which it was deduced that the starting material had been completely consumed after twelve hours. It was also evident that many side products had formed during the course of the reaction. NMR analysis indicated the desired triptycene-linked porphyrin arrays were not formed. The failure of this reaction was attributed to competing reactions. In this case debromination of the triptycene precursor 292 was evident by \textsuperscript{1}H NMR spectroscopic analysis. The major competing reaction when free base porphyrin precursors 333 and 334 were used in the reaction was copper insertion to the core of the porphyrin macrocycle 355 and 356 (Scheme 4.12). Insertion of the copper ion into free base porphyrins has been well documented particularly as a side reaction of Sonogashira cross-coupling reactions.
The most utilised method for the prevention of copper insertion is the use of a copper-free Sonogashira cross-coupling reaction.\textsuperscript{208}

It was then decided to use copper-free reaction conditions so as to omit the competing reaction of copper insertion which was observed when using a copper catalyst as shown in Scheme 4.12. It was also decided to reverse the functionality of the triptycene and porphyrin precursors. This approach would make further use of the novel triptycene scaffold 304 that was synthesised in chapter 3. Furthermore, it would also alleviate the use of compound 292 as a precursor, which was desirable, as compound 292 had proven unsuccessful for the triptycene-porphyrin Suzuki cross-coupling reaction described in section 4.3.1.

\begin{align*}
\begin{array}{c}
\text{304} \\
\text{Pd$_2$dba} \\
\text{AsPh$_3$} \\
\text{TEA} \\
\text{THF}
\end{array}
\end{align*}

\begin{align*}
R^1 &= \text{Ph}, R^2 = \text{Ph}, M = 2\text{H} \quad 333 \\
R^1 &= \text{p-Tolyl}, R^2 = \text{H}, M = 2\text{H} \quad 334 \\
R^1 &= \text{1-Ethylpropyl}, R^2 = \text{H}, M = \text{Ni(II)} \quad 336 \\
R^1 &= \text{1-Methylpropyl}, R^2 = \text{H}, M = \text{Ni(II)} \quad 337
\end{align*}

\textbf{Scheme 4.13:} Attempted synthesis of triptycene-linked hexaporphyrin arrays \textit{via} copper-free Sonogashira reaction.

Porphyrins 159 and 317 were deemed to be suitable precursors for copper-free Sonogashira coupling due to their poor solubility. Porphyrins 333, 336, 334 and 337 were chosen as starting materials. The bromoporphyrin precursors were reacted with 304 under the same reaction conditions which had previously been reported by the Senge group for the synthesis of porphyrin trimers (Scheme 4.13).\textsuperscript{42} The reaction was unsuccessful as no coupling was observed and debromination of the porphyrin
precursors was the dominant reaction. It was concluded at this time that the reaction conditions certainly favoured coupling of iodo derivatives over bromo derivatives to the ethyne moiety whether it be on the triptycene or the porphyrin periphery. The reactivity of the sp$^2$ species of aryl iodides is significantly greater than that of aryl bromides. The Sonogashira process usually runs smoothly when the more expensive and unstable aryl iodides are used. The reaction proceeds if the organic halide system is "activated" or electron-poor. Thus, deactivated aryl bromides are difficult starting materials for coupling reactions, if not strongly activated and can prove to be difficult precursors.\textsuperscript{184}

4.5.3 Microwave assisted Sonogashira cross-coupling approach

It was at this point that it was speculated that the previously established method for the synthesis compound 302 could be applied for the synthesis of hexaporphyrin arrays. The triptycene scaffold 304 was used as the ethynyl precursor for the reaction in order to eliminate the tedious preparation of ethynyl bearing porphyrins which can only be synthesised on a small scale. A test reaction was carried out using compounds 333 and 304 using the same reaction conditions as described for the synthesis of 302. However, the desired hexaporphyrin array was not formed with most of the starting precursors being isolated without being modified in anyway. It was noted that poor solubility of the porphyrin 333 could be hindering the progress of this reaction, thus, the amount of DMF used in the reaction was increased from 0.5 mL to 5 mL. The products of this reaction again showed that coupling of compounds 304 and 333 was not achieved. The competing reaction in this case was partial debromination of porphyrin 333. The microwave tube size was a limiting factor taking the porphyrin solubility into account. As a result the reaction was then scaled down to allow for the addition of a further 5 mL of DMF and the quantity of diethylamine (DEA) was also increased to 12.6 mL. The more soluble precursor 5-bromo-10,20-diphenylporphyrin 321 was chosen for the next test reaction. The reaction mixture was subjected to 40 minutes of microwave irradiation. The mixture was passed through a short silica plug with CH$_2$Cl$_2$ and the solvent was reduced. Column chromatography and subsequent recrystallisation from CH$_2$Cl$_2$ afforded the hexaporphyrin array 2,3,6,7,14,15-hexakis(4-(5,15-diphenylporphyrin)ethynyl)triptycene 357 in 12 % yield as illustrated in Scheme 4.14.
Scheme 4.14: Synthesis of compound 357 via microwave assisted Sonogashira cross-coupling.

The major product isolated from the reaction was debrominated starting material with a copper metal centre. It was noted that the solubility of compound 357 far surpassed what was expected as it was soluble in CH₂Cl₂, THF, chloroform and partially soluble in hexane. This extraordinary solubility can be attributed to the spherical or three-dimensional shape that 357 adopts. This shape is solely due to the unique structure of
the triptycene scaffold. The addition of a three-dimensional core to macrocycles will affect both the solubility of macrocycle as a whole.

4.6   Spectroscopy

4.6.1  $^1$H NMR spectroscopy

The $^1$H NMR assignment of (phenylethynyl)porphyrin monomers is relatively simple. The chemical shifts of each proton can easily be assigned from the 1D spectrum as illustrated in Figure 4.1. Generally, the lower symmetry of $A_3B$ or $A_2BC$-type porphyrins in comparison to $A_2B_2$-type porphyrins can be seen in the splitting of the signals for the $\beta$-protons. The influence of the substituents and hence symmetry on the electronic environment of the $\beta$-protons is clearly evident in the spectrum of porphyrin 337 as these signals split further into four sets of doublets (Figure 4.1).

![Figure 4.1: $^1$H NMR spectra of 337 in CDCl$_3$ at rt.](image)

The presence of the phenylethynyl moiety at the meso-position of the porphyrin periphery gives rise to a sharp singlet at 3.68 ppm. This is indicative of the terminal proton of ethynyl group and integrates to one proton. Furthermore, the presence of the phenyl group gave rise to two doublets at 7.83 and 7.93 ppm.
Figure 4.2 shows the $^1$H NMR spectrum of compound 357 in which the resonances for the bridgehead protons of the triptycene molecule are clearly visible at 5.37 ppm. The twelve NH-protons give only one signal at -2.48 ppm due to the complete symmetry of this triptycene-porphyrin system. This shows distinctly that six porphyrin molecules are attached to one triptycene scaffold. The β- and meso-protons are deshielded by the diamagnetic ring current and so their signals are shifted to lower field than would be observed for the corresponding porphyrin monomer.

![Figure 4.2: $^1$H NMR spectra of 357 in CDCl$_3$ at rt.](image)

As seen for 337, the influence of the substituents on the electronic environment of the β-protons is clearly evident. Again four doublets are clear in the spectrum of compound 357. Also, the ethynyl substituent linking the porphyrin to the triptycene scaffold in 357 causes a shift of the neighbouring β-protons to lower field. The meso-carbon atoms are less electron deficient than the β-carbon atoms with the exception of the β-carbon atoms adjacent to the free meso-carbon. As a result the β-protons, numbered 11, 12 and 13 are shifted even further towards lower field than the meso-proton. Some 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 357. Moreover, the molecular composition is confirmed by high resolution mass spectrometry measurements. The high resolution mass spectrum for the synthesised porphyrin array 357 was completely in agreement with the calculated molecular weight. The triptycene-linked hexaporphyrin array 357 gave a peak at $m/z = 3159.1584 \,[M^+]$ as shown in Figure 4.3.

![Isotope model](image)

**Figure 4.3:** Mass spectrum and corresponding isotope model for 357.

### 4.6.2 UV-vis Spectroscopy

In order to investigate the influence of conjugated substituents on the porphyrin periphery, the absorption of porphyrins 34, 333, 339 and 340 were compared. Despite the substitution pattern, the addition of phenylethynyl functional groups to the porphyrins periphery resulted in a red-shift. The decrease of the HOMO-LUMO gap found for alkynyl porphyrins can be attributed to the change in the distribution of the electron density as a result of the extended conjugation of the system. The effect on the UV-visible spectrum of porphyrins from increasing the conjugation on the
porphyrin periphery is shown in Figure 4.4. In this case, Ni(II)porphyrins 339, 340 and free base porphyrins 34, 333 were used as an example, however, similar results were observed for all porphyrins bearing the phenylethynyl moiety at the meso position.

![Figure 4.4](attachment:Figure_4.4.png)

**Figure 4.4:** UV-vis comparison of 34, 333, 339 and 340 in CH₂Cl₂ at rt. Baselines were adjusted arbitrarily.

The electronic absorption spectra was measured for compound 357 and compared to that of 304 and 34 as illustrated in Figure 4.5.

![Figure 4.5](attachment:Figure_4.5.png)

**Figure 4.5:** UV-vis comparison of 34, 307 and 357 in CH₂Cl₂ at rt. Baselines were adjusted arbitrarily.
A broadening of the Soret band along with a decrease in intensity is also observed as the as the π-system is expanded. The spectrum clearly illustrates that the Soret band is bathochromically shifted by 10 nm when compared to that of the monomeric porphyrin precursor. Additionally, a bathochromic shift of the Q-bands is also observed along with a greater intensity pattern. The most apparent of these shifts was observed for the second Q-band which was bathochromically shifted by 21 nm (Figure 4.5).

The red shift which is observed for the porphyrin hexamer 357 can be attributed to the extending of the conjugation of each porphyrin in the array. For carbon-carbon bridges, alkyne linkers create the best circumstances for the π-orbital overlapping of porphyrins and it substituents. As each porphyrin unit of the hexaporphyrin array is linked via meso-substitution, the red shift can be attributed to a raising of the $a_{2u}$ orbital and lowering of one $e_g$ orbital. This results in a loss of degeneracy in the frontier orbitals and a decrease in the HOMO-LUMO gap. Extending the conjugation of the macrocycle changes the distribution of the electron density of the system, resulting in the decreased HOMO-LUMO gap for alkynyl substituted porphyrins.

4.7 Conclusions

This chapter explored various synthetic pathways with the aim of isolating triptycene-linked hexaporphyrin arrays to mimic the role of the light harvesting antenna components for artificial photosynthesis.

Previously reported methods for the synthesis of triptycene-linked porphyrin trimers were explored but were found to be unsuitable pathways for the synthesis of triptycene-linked hexaporphyrin arrays. The Suzuki cross-coupling reaction and the Sonogashira cross-coupling approach were investigated, however, repeated attempts of both previously reported methods failed to isolate triptycene-linked hexaporphyrin arrays. This was due to the reduced reactivity of the 2,3,6,7,14,15-bromotriptycene precursor by comparison to the 2,6,14-triiodotriptycene precursor which had proven to be successful for the synthesis of triptycene-linked trimers.
Efforts to synthesise 2,3,6,7,14,15-hexaiodotriptycene, for use in later coupling reactions, failed due to the instability of the 2,3,6,7,14,15-hexaaminotriptycene precursor. However, further investigation revealed that the coupling of the porphyrin moieties to a triptycene scaffold was indeed feasible via microwave assisted Sonogashira cross-coupling reaction. By making use of the 2,3,6,7,14,15-hexaethynyltriptycene scaffold described in chapter 3, a novel synthetic pathway to access triptycene-linked hexa porphyrin arrays was established. This method alleviates the synthesis of the porphyrins bearing a phenylethynyl moiety which can be a tedious reaction which should be done on small scales.

The triptycene anchor plays the role of a rigid scaffold, keeping the porphyrin units at predetermined distances. This allows for a three-dimensional structural arrangement of the chromophores, guaranteeing the supramolecular nature of the array. Furthermore, hexaporphyrin array exhibited exceptional solubility which can be also attributed to the 3-dimensional structure of the system.

This microwave mediated synthetic method is a platform which now allows access to more complex triptycene-linked hexaporphyrin arrays. The optimisation of this reaction needs be to be investigated further, incorporating both metallo- and free base porphyrins which should have varying functionality on the porphyrin periphery. It is also conceivable to introduce a halogen on the free meso-position of each porphyrin unit. In doing so, that site could be used to carry out further coupling reactions and thus, further extending the π-conjugation of the system as a whole.
Chapter 5

Experimental
5.1 Instrumentation and General Considerations

$^1$H and $^{13}$C NMR spectra were recorded on a 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). Chemical shifts are reported in ppm referred to tetramethylsilane set at 0.00 ppm. Data are reported as follows: chemical shifts, multiplicity (s: singlet, d: doublet, dd: double doublet, td: triplet of doublets, t: triplet, q: quartet, br: broad, m: multiplet), coupling constants ($J$ in Hz), integration and assignment. High resolution mass spectrometry (HRMS) was carried out on a Micromass/Waters Corp. USA liquid chromatography time-of-flight (TOF) spectrometer equipped with an electrospray source or a matrix-assisted laser desorption/ionisation (MALDI) Q TOF Premier MS system. Low resolution mass spectrometry was recorded on a Micromass/Waters Corp. USA Quattro micro™ LC-MS/MS. UV-vis absorption spectroscopy was performed on a Shimadzu MultiSpec-1501. Infrared (IR) spectroscopy was carried out on a Perkin Elmer Spectrum 100 Fourier Transformations (FT) IR spectrometer. Microwave reactions were carried out using a Biotage Initiator microwave synthesiser. Melting points were acquired on a Stuart SM.P.10 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 Fluka Silica Gel 60 (230-400 mesh). Tetrahydrofuran (THF) and diethyl ether were distilled over sodium/benzophenone under nitrogen. All commercial chemicals were supplied by Aldrich and used without further purification.
5.2 Starting materials

5.2.1 Synthesis of meso-substituted dipyrromethanes

Dipyrromethane 128, 5-hexyldipyrromethane 168, 5-(1-ethylpropyl)dipyrromethane 174 and 5-phenyldipyrromethane 325 were prepared according using a modified procedure reported by Lindsey et al.254

5.2.2 5,15-Disubstituted porphyrin precursors

5,15-Diphenylporphyrin 34,387,388 5,15-dihexylporphyrin 135,389 5,15-bis(4-methoxyphenyl)porphyrin 207,147,265,390 5,15-bis(3,5-di-tert-butylphenyl)porphyrin 74,109 5,15-bis(2-ethylpropyl)porphyrin 310,151,262 5,15-ditolyporphyrin 309,387 5,15-bis(4-bromophenyl)-10,20porphyrin 323387 were prepared via MacDonald [2+2] condensation reaction.146

5.2.3 5,10,20-Trisubstituted porphyrin precursors

5,10,15-Triphenylporphyrin 136,391 5,10,15-trihexylporphyrin 139261 and 5,15-bis(3,5-di-tert-butylphenyl)-10-phenylporphyrin 137,392 were prepared using Senge methodology.393 All porphyrin precursors were metallated394 and brominated146 according to literature procedures.
5,10,15-trihexylporphyrin 139 (526 mg, 1.00 mmol, 1.0 equiv.) was placed in a 100 mL flask with Ni(acac)$_2$ (388 mg, 1.50 mmol, 1.5 equiv.). Toluene (50 mL) was added, and the mixture was heated under reflux for 3 hours. The progress of the reaction was monitored by TLC using CH$_2$Cl$_2$/n-hexane (1:2, v/v). Upon completion of the reaction, the solvent was removed *in vacuo*, and the product was isolated after passage through a plug of silica gel using CH$_2$Cl$_2$ as the eluent. Recrystallisation of the product using CH$_2$Cl$_2$/MeOH yielded 155 as orange crystals (465 mg, 0.75 mmol, 75 %); M.p. = 291-293 °C; R$_f$ = 0.68 (CH$_2$Cl$_2$/n-hexane, 1:2, v/v).

δ$_H$ (400 MHz, CDCl$_3$): 0.90 (t, $J$ = 7.3 Hz, 6H, CH$_3$, H-17), 0.95 (t, $J$ = 7.6 Hz, 3H, CH$_3$, H-11), 1.40-1.44 (m, 6H, CH$_2$, H-10, H-16), 1.53-1.58 (m, 6H, CH$_2$, H-9, H-15), 1.80-1.87 (m, 6H, CH$_2$, H-8, H-14), 2.53-2.58 (m, 6H, CH$_2$, H-7, H-13), 4.97 (t, $J$ = 8.0 Hz, 4H, CH$_2$, H-12), 5.08 (t, $J$ = 8.0 Hz, 2H, CH$_2$, H-6), 9.29 (d, $J$ = 4.7 Hz, 2H, $H_p$, H-5), 9.48 (d, $J$ = 4.7 Hz, 2H, $H_p$, H-3), 9.57 (d, $J$ = 4.7 Hz, 2H, $H_p$, H-2), 9.90 ppm (s, 1H, $H_{meso}$, H-1).
δc (100 MHz, CDCl₃): 13.9, 22.1, 30.3, 30.5, 31.4, 31.8, 34.9, 35.5, 36.3, 38.4, 38.7, 38.9, 103.1, 118.8, 120.0, 120.2, 120.6, 127.8, 128.3, 128.9, 131.2, 142.8, 144.0 ppm


UV/vis (CH₂Cl₂): λmax (lg ε): 419 (5.42), 533 (4.17), 559 nm (3.81).

5.2.4 5-Bromo-10,15,20-trisubstituted porphyrin precursors

(5-Bromo-10,15,20-trihexylporphyrinato)zinc(II) (161)

Porphyrrin 154 (313 mg, 0.50 mmol, 1.0 equiv.) was placed in a 100 mL flask with NBS (267 mg, 1.50 mmol, 3.0 equiv.). The mixture was dissolved in chloroform (100 mL) and pyridine (0.4 μL, 0.05 mmol, 0.1 equiv.) was added, and the mixture was stirred at room temperature for 3 hours. The progress of the reaction was monitored by TLC using CH₂Cl₂/n-hexane (1:2, v/v). Upon completion of the reaction, the solvent was removed in vacuo, and the product was isolated after passage through a plug of silica gel using CH₂Cl₂ as the eluent. Recrystallisation of the product using CH₂Cl₂/MeOH yielded 161 as orange crystals (282 mg, 0.40 mmol, 80 %); M.p. > 300 °C; Rf = 0.69 (CH₂Cl₂/n- hexane, 1:2, v/v).
δ_H (400 MHz, CDCl₃): 0.94 (t, J = 7.1 Hz, 6H, CH₃, H-16), 0.98 (t, J = 7.5 Hz, 3H, CH₃, H-10), 1.41-1.45 (m, 6H, CH₂, H-9, H-15), 1.55-1.59 (m, 6H, CH₂, H-8, H-14), 1.80-1.86 (m, 6H, CH₂, H-7, H-13), 2.51-2.55 (m, 6H, CH₂, H-6, H-12), 4.94-5.06 (m, 6H, CH₂, H-5, H-11), 9.45 (d, J = 4.8 Hz, 2H, H_β, H-4), 9.48 (d, J = 4.8 Hz, 2H, H_β, H-3), 9.50 (d, J = 4.8 Hz, 2H, H_β, H-2), 9.67 ppm (d, J = 4.8 Hz, 2H, H_β, H-1).

δ_C (100 MHz, CDCl₃): 14.1, 22.4, 30.5, 31.4, 31.9, 32.2, 35.0, 35.7, 36.5, 38.7, 38.9, 39.1, 103.3, 119.0, 120.4, 120.6, 121.2, 127.7, 128.5, 129.0, 131.8, 142.6, 144.1 ppm.

HRMS (m/z -ES): [M+H]^+ calcd. for C₃₈H₄₈BrN₄Zn 703.2356, found 703.2315.

UV/vis (CH₂Cl₂): λ_max (lg ε): 418 (4.60), 534 (3.61), 556 nm (2.18).

(5-Bromo-10,15,20-trihexylporphyrinato)nickel(II) (160)

Porphyрин 155 (309 mg, 0.50 mmol, 1.0 equiv.) was placed in a 100 mL flask with NBS (267 mg, 1.50 mmol, 3.0 equiv). The mixture was dissolved in chloroform (100 mL) and pyridine (0.4 μL, 0.05 mmol, 0.1 equiv.) was added, and the mixture was stirred at room temperature for 3 hours. The progress of the reaction was monitored
by TLC using CH₂Cl₂/n-hexane (1:2, v/v). Upon completion of the reaction, the solvent was removed in vacuo, and the product was isolated after passage through a plug of silica gel using CH₂Cl₂ as the eluent. Recrystallisation of the product using CH₂Cl₂/MeOH yielded 160 as orange crystals (306 mg, 0.44 mmol, 87 %) yield; M.p. ≥ 300 °C; Rᵣ = 0.69 (CH₂Cl₂/n-hexane, 1:2, v/v).

δH (400 MHz, CDCl₃): 0.97 (t, J = 7.6 Hz, 6H, CH₃, H-16), 0.99 (t, J = 7.5 Hz, 3H, CH₃, H-10), 1.42-1.48 (m, 6H, CH₂, H-9, H-15), 1.58-1.63 (m, 6H, CH₂, H-8, H-14), 1.85-1.92 (m, 6H, CH₂, H-7, H-13), 2.54-2.59 (m, 6H, CH₂, H-6, H-12), 4.99 (t, J = 7.8 Hz, 4H, CH₂, H-11), 5.08 (t, J = 7.8 Hz, 2H, Hβ, H-4), 9.51 (d, J = 4.8 Hz, 2H, Hβ, H-3), 9.63 (d, J = 4.8 Hz, 2H, Hβ, H-2), 9.69 ppm (d, J = 4.8 Hz, 2H, Hβ, H-1).

δC (100 MHz, CDCl₃): 14.3, 22.5, 30.6, 31.6, 32.2, 32.7, 35.5, 35.9, 38.1, 38.4, 39.5, 39.7, 103.5, 119.3, 121.0, 121.6, 122.4, 127.9, 129.0, 129.6, 132.3, 142.8, 144.5 ppm.

HRMS (m/z -ES): [M⁺] calcd. for C₃₈H₄₁BrN₄Ni 696.2338, found 696.2361.

UV/vis (CH₂Cl₂): λmax (lg ε): 424 (4.80), 540 (3.11), 572 nm (2.98).

5.3 Anthracenylporphyrins

5.3.1 Procedure A: general procedure for the preparation of 9-monosubstituted anthracenes via Suzuki cross-coupling.

To a stirred slurry of K₃PO₄ (1.00 g, 4.70 mmol, 5.0 equiv.) in anhydrous THF (150 mL), 9-bromoanthracene 30 (128 mg, 0.50 mmol, 1.0 equiv.), Pd(PPh₃)₄ (1.08g, 0.94 mmol, 0.2 equiv.) and a boronic acid derivative (2.50 mmol, 5.0 equiv.) were added. The reaction mixture was heated to 67 °C, shielded from light and stirred for 12 hours.
The reaction was monitored by TLC using EtOAc/n-hexane (5:95, v/v) as the mobile phase. The solvent was removed and the mixture was taken up in EtOAc and washed with saturated aqueous NaHCO₃ (3 x 50 mL), water (3 x 50 mL) and dried over NaSO₄. The organic solvent was evaporated, and the crude mixture was dry loaded onto a silica column, and the anthracene derivative was isolated using EtOAc/n-hexane (5:95, v/v) as the mobile phase. The crude product was recrystallised from CH₂Cl₂/n-hexane.

**Methyl 4-(anthracen-9-yl)benzoate (123)**

![Methyl 4-(anthracen-9-yl)benzoate](image)

Prepared *via* Suzuki cross-coupling reaction according to procedure A above using 4-methoxycarbonylphenylboronic acid (450 mg, 2.50 mmol, 5.0 equiv.) to yield 123 as yellow crystals (19 mg, 0.03 mmol, 60 %); M.p. = 172 – 174 °C; Rf = 0.47 (EtOAc/n-hexane, 5:95).

δ₁H (400 MHz, CDCl₃): 3.99 (s, 3H, CH₃, H-8), 7.38 (app. t, J = 7.5 Hz, 2H, Ar-H, H-5), 7.50 (app. t, J = 7.5 Hz, 2H, Ar-H, H-4), 7.58 (d, J = 8.0 Hz, 2H, Ar-H, H-2), 7.62-7.66 (m, 2H, Ar-H, H-1), 8.12 (d, J = 7.5 Hz, 2H, Ar-H, H-3), 8.62 ppm (s, 1H, Ar-H, H-7).

δ₁C (100 MHz, CDCl₃): 51.9, 125.1, 125.5, 126.1, 126.9, 128.2, 129.4, 129.5, 129.7, 131.2, 132.3, 135.6, 143.7, 166.8 ppm.

HRMS (m/z -ES): [M+H]⁺ calcd. for C₂₂H₁₇O₂ 313.1219, found 313.1229.
UV/vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (lg ε): 343 (5.54), 360 (5.80), 380 (5.58), 401 (5.60), 427 nm (5.63).

9-(4-(N,N-Dimethylamino)phenyl)anthracene (124)

Prepared via Suzuki cross-coupling reaction according to procedure A above using (4-(dimethylamino)phenyl)boronic acid (495 mg, 2.50 mmol, 5.0 equiv.) to yield 124 as yellow crystals (505 mg, 1.70 mmol, 67 %); M.p. = 256-258 °C, lit. M.p. = 256 °C.$^{351}$ $R_f = 0.52$ (EtOAc/n-hexane, 5:95). Analytical data were as reported in literature.$^{395,396}$

$\delta_H$ (400 MHz, CDCl$_3$): 3.12 (s, 6H, CH$_3$, H-8), 6.99 (d, $J = 8.0$ Hz, 2H, Ar-H, H-1), 7.32 (app. t, $J = 9.1$ Hz, 2H, Ar-H, H-5), 7.39 (app. t, $J = 8.4$ Hz, 2H, Ar-H, H-4), 7.50 (d, $J = 8.0$ Hz, 2H, Ar-H, H-2), 8.09 (d, $J = 9.1$ Hz, 2H, Ar-H, H-6), 8.29 (d, $J = 9.1$ Hz, 2H, Ar-H, H-3), 8.51 ppm (s, 1H, Ar-H, H-7).

4-(Anthracen-9-yl)phenol (125)
Prepared via Suzuki cross-coupling reaction according to procedure A above using 4-hydroxyphenylboronic acid (345 mg, 2.50 mmol, 5.0 equiv.) to yield 125 as yellow crystals (143 mg, 0.53 mmol, 53 %); M.p. = 176-178 °C; lit. M.p. = No melting point given in literature;\textsuperscript{397} R\textsubscript{f} = 0.58 (EtOAc/n-hexane, 5:95). Analytical data were as reported in literature.\textsuperscript{397}

\[\delta_{\text{H}} (400 \text{ MHz, CDCl}_3): \ 6.87 \ (d, J = 7.6 \text{ Hz}, 2\text{H}, \text{Ar-H, H-1}), \ 7.36 \ (\text{app. t}, J = 8.9 \text{ Hz}, 2\text{H}, \text{Ar-H, H-5}), \ 7.46 \ (\text{app. t}, J = 7.5 \text{ Hz}, 2\text{H}, \text{Ar-H, H-4}), \ 7.60 \ (d, J = 7.6 \text{ Hz}, 2\text{H}, \text{Ar-H, H-2}), \ 8.07 \ (d, J = 9.1 \text{ Hz}, 2\text{H}, \text{Ar-H, H-6}), \ 8.13 \ (d, J = 8.1 \text{ Hz}, 2\text{H}, \text{Ar-H, H-3}), \ 8.51 \text{ ppm (s, 1H, H-7)}.\]

HRMS (m/z -ES): [M+H] \textsuperscript{+} calcd. for C_{20}H_{15}O 271.1123; found 271.1131.

9-n-Butylanthracene (126)

Prepared via Suzuki cross-coupling reaction according to procedure A above using butylboronic acid (255 mg, 2.50 mmol, 5.0 equiv.) to yield 126 as yellow crystals (240 mg, 1.025 mmol, 41 %); M.p. = 64-66 °C, lit. M.p. = 64-66 °C;\textsuperscript{398} R\textsubscript{f} = 0.81 (EtOAc/n-hexane, 5:95). Analytical data were as reported in literature.\textsuperscript{398}

\[\delta_{\text{H}} (400 \text{ MHz, CDCl}_3): \ 0.82 \ (t, J = 8.5 \text{ Hz}, 3\text{H}, \text{CH}_3, \text{H-9}), \ 1.51\text{-}1.57 \ (m, 2\text{H}, \text{CH}_2, \text{H-8}), \ 1.64\text{-}1.71 \ (m, 2\text{H}, \text{CH}_2, \text{H-7}), \ 3.12 \ (t, J = 8.5 \text{ Hz}, 2\text{H}, \text{CH}_2, \text{H-6}), \ 6.99 \ (\text{app. t}, J = 8.4 \text{ Hz}, 2\text{H}, \text{Ar-H, H-2}), \ 7.26 \ (\text{app. t}, J = 8.4 \text{ Hz}, 2\text{H}, \text{Ar-H, H-3}), \ 7.89 \ (d, J = 8.2 \text{ Hz}, 2\text{H}, \text{Ar-H, H-}]

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1), 8.15 (d, \(J = 8.0\) Hz, 2H, Ar-\(H, H-4\)), 8.31 ppm (s, 1H, Ar-\(H, H-5\)).

2-(Anthracen-9-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (111)

A 100 mL Schlenk flask was charged with 9-bromoanthracene 30 (85 mg, 0.33 mmol, 1.0 equiv.) and dried under vacuum. Dry toluene (20 mL) and dry triethylamine (0.59 mL, 4.21 mmol, 12.8 equiv.) was 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 (0.47 mL, 3.24 mmol, 9.8 equiv.) and dichlorobis(tri-phenylphosphine)palladium(II) (13.6 mg, 0.02 mmol, 0.6 equiv.) were added. The Schlenk tube was sealed and heated to 120 °C overnight. The reaction was cooled and quenched with a saturated aqueous KCl (10 mL) solution, washed with water and dried over anhydrous Na\(_2\)SO\(_4\). The organic solvents were removed in vacuo and subjected to purification via column chromatography to yield 111 as a yellow powder (52 mg, 0.17 mmol, 50 %); M.p. = 138-140 °C, lit. M.p. = 138-140 °C; \(^{399}\) R\(_f\) = 0.81 (CH\(_2\)Cl\(_2\)/n-hexane 1:2, v/v). Analytical data were as reported in literature.\(^{399}\)

\[\delta_H (400\text{ MHz, CDCl}_3):\] 1.24 (s, 12H, CH\(_3\), H-6), 7.41-7.63 (m, 4H, Ar-\(H, H-2, H-3\)), 7.91-7.96 (m, 2H, H-4), 8.39 (s, 1H, H-5), 8.43 ppm (d, \(J = 8.2\) Hz, 2H, H-1).
Methyl 4-(10-bromoanthracen-9-yl)benzoate (127)

To a solution of 123 (19 mg, 0.03 mmol, 1.0 equiv.) in chloroform (250 mL) and pyridine (75 μL), NBS (8 mg, 0.045 mmol, 1.5 equiv.) was added, and the mixture was stirred at room temperature for 2 hours. The progress of the reaction was monitored by TLC at five minute intervals using EtOAc/n-hexane (5:95, v/v) as the eluent. The reaction was quenched with acetone (25 mL) and the solvent reduced and passed through a plug of silica using CH₂Cl₂. Recrystallisation of the product using CH₂Cl₂/MeOH yielded 127 as yellow crystals (12 mg, 0.03 mmol, 93%); M.p. = 105-107 °C; Rf = 0.31(EtOAc/n-hexane, 5:95).

δ_H (400 MHz, CD3OD): 4.05 (s, 3H, C = H3, H-7), 7.42 (app. t, J = 7.3 Hz, 2H, Ar-H, H-5), 7.53 (app. t, J = 7.5 Hz, 2H, Ar-H, H-4), 7.62-7.70 (m, 4H, Ar-H, H-1, H-2), 8.30 (d, J = 7.6 Hz, 2H, Ar-H, H-3), 8.65 ppm (d, J = 7.5 Hz, Ar-H, 2H, H-6).

δ_C (100 MHz, CDCl3): 52.4, 125.4, 126.0, 126.9, 127.1, 128.1, 129.8, 130.2, 130.3, 131.4, 136.4, 139.1, 143.6, 166.8 ppm.

HRMS (m/z -ES): [M+H]^+ calcd. for C22H16BrO2 391.0034; found 391.0047.

UV/vis (CH₂Cl₂): λ_max (lg ε): 333 (5.52), 350 (5.54), 367 (5.56), 387 (5.59), 419 nm (5.62).
5.3.2 Palladium Catalysts

Tetrakis(triphenylphosphine)palladium(0) (190)

Produced using an adapted procedure from a method that was reported by Coulson et al.\textsuperscript{289} Palladium(II) chloride (28.4 mg, 0.16 mmol, 1.0 equiv.), triphenylphosphine (165.3 mg, 0.66 mmol, 4.1 equiv.) and DMSO (18 mL) were added to a Schlenk flask and charged with argon. The reaction was heated to 140 °C and stirred until PdCl\textsubscript{2} was no longer visible in the reaction mixture. A colour change from pale yellow to bright yellow was observed during the progress of the reaction. The heat source was removed and the mixture was stirred for a further 15 minutes. Hydrazine hydrate (38\mu L, 80 % w/w, 0.64 mmol, 0.4 equiv.) was then added dropwise forming a pale yellow precipitate. The precipitate was filtered under nitrogen using a sintered glass funnel. The palladium catalyst was then washed with EtOH (2 X 5 mL) and then ether (2 X 5 mL). The pale yellow product was transferred to a round bottom flask and dried under vacuum, before being stored under argon.

Dichlorobis(triphenylphosphine)palladium(II) (193)

Produced using an adapted procedure which was reported by Suzuki et al.\textsuperscript{290} A 25 mL pear-shaped flask was equipped with a magnetic stirring bar and a reflux condenser connected to an argon inlet and purged with argon. Palladium(II) chloride (300 mg, 1.69 mmol, 1.0 equiv.), triphenylphosphine (975 mg, 3.72 mmol, 2.2 equiv.) and benzonitrile (10 mL) were added. The mixture was heated to 180 °C, and allowed to
stir for 20 minutes, resulting in a clear red solution. The solution was cooled to room temperature over a period of 1 hour and allowed to stand overnight. The bright orange crystals that precipitated were filtered, washed with ether (3 X 5 mL) and dried under vacuum to give 193 as an orange solid (1.10 g, 92.9 %).

5.3.3 Procedure B: general procedure for the condensation approach for the preparation of anthracenylporphyrins.

9-Anthracenylaldehyde (206 mg, 1.00 mmol, 1.0 equiv.) was dissolved in 1.00 L of dry CH₂Cl₂ and a substituted dipyrromethane derivative was then added. The mixture was degassed by bubbling a stream of argon through the mixture for 30 minutes. Trifluoroacetic acid was added dropwise to the mixture via a syringe. The reaction was shielded from light and allowed to stir for 14 hours under argon at room temperature. DDQ was added to the mixture and was allowed to stir for a further 30 minutes. Triethylamine (TEA) was added, and the mixture was allowed to stir for a further hour. The solvent was reduced to 500 mL, and the mixture was passed through a large silica plug, using CH₂Cl₂ as the eluent. The porphyrin containing fractions were collected and purified further by column chromatography using CH₂Cl₂/n-hexane (1:2, v/v) as the mobile phase. The desired product fraction was recrystallised from CH₂Cl₂ and MeOH.

5,15-Dianthracenyl-10,20-dihexylporphyrin (167)
Prepared via procedure B from 9-anthracenylaldehyde (206 mg, 1.00 mmol, 1.0 equiv.), 5-hexyldipyrromethane (230 mg, 1.00 mmol, 1.0 equiv.), trifluoroacetic acid (24 μL, 0.25 mmol, 0.25 equiv.), DDQ (2.93 g, 13.00 mmol, 13 equiv.) and TEA (15 mL) to yield 167 as purple crystals (83 mg, 0.10 mmol, 10 %); M.p. ≥ 300 °C; Rf = 0.7 (CH₂Cl₂/n-hexane, 1:2).

δ_H (400 MHz, CDCl₃):
-2.05 (s, 2H, NH, H-1), 0.82-0.93 (m, 6H, CH₃, H-14), 1.29-1.34 (m, 4H, CH₂, H-13), 1.40-1.48 (m, 4H, CH₂, H-12), 1.62-1.65 (m, 4H, CH₂, H-11), 2.48-2.53 (m, 4H, CH₂, H-10), 4.89 (t, J = 8.4 Hz, 4H, Ar-H, H-9), 7.06 (app. t, J = 7.4 Hz, 4H, Ar-H, H-5), 7.10 (d, J = 8.7 Hz, 4H, Ar-H, H-4), 7.46 (app. t, J = 7.4 Hz, 4H, Ar-H, H-6), 7.79-7.86 (m, 8H, Ar-H, H-7, H₁₃, H-2), 8.99 (s, 2H, Ar-H, H-8), 9.13 ppm (d, J = 4.3 Hz, 4H, H₁₃, H-3).

δ_C (100 MHz, CDCl₃):
13.9, 22.5, 30.0, 31.6, 34.2, 37.5, 114.4, 118.3, 125.0, 125.6, 127.7, 128.0, 128.6, 129.7, 130.8, 132.5, 133.9, 134.7, 142.1, 142.6 ppm.

HRMS (m/z -ES):
[M+H]^+ calcd. for C₆₀H₃₅N₄ 830.4348, found 830.4315.

UV/vis (CH₂Cl₂):
λ_max (lg ε): 423 (4.60), 534 (3.61), 580 (2.78), 653 nm (2.92).
(5,15-Dianthracenyl-10,20-dihexylporphyrinato)zinc(II) (172)

Porphyrin 167 (41 mg, 0.05 mmol, 1.0 equiv.) was isolated via procedure B and placed in a 100 mL flask with Zn(acac)\(_2\) (21 mg, 0.008 mmol, 1.5 equiv.). MeOH (50 mL) was added, and the mixture was heated under reflux for 3 hours. The progress of the reaction was monitored by TLC using CH\(_2\)Cl\(_2\)/n-hexane (1:2, v/v). Upon completion of the reaction, the solvent was removed \textit{in vacuo}, and the product was isolated after passage through a plug of silica gel using CH\(_2\)Cl\(_2\) as the eluent. Recrystallisation of the product using CH\(_2\)Cl\(_2\)/MeOH yielded 172 as purple crystals (39 mg, 0.044 mmol, 88%); M.p. ≥ 300 °C; \(R_f = 0.6\) (CH\(_2\)Cl\(_2\)/n-hexane, 1:2).

\(\delta_H\) (400 MHz, CDCl\(_3\)): 0.75 (t, \(J = 9.0\) Hz, 6H, CH\(_3\), H-13), 1.30-1.36 (m, 4H, CH\(_2\), H-12), 1.38-1.43 (m, 4H, CH\(_2\), H-11), 1.61-1.67 (m, 4H, CH\(_2\), H-10), 2.51-2.56 (m, 4H, CH\(_2\), H-9), 4.88 (t, \(J = 7.2\) Hz, 4H, CH\(_2\), H-8), 7.02 (app. t, \(J = 7.6\) Hz, 4H, Ar-H, H-4), 7.08 (d, \(J = 8.6\) Hz, 4H, Ar-H, H-3), 7.49 (app. t, \(J = 7.3\) Hz, 4H, Ar-H, H-5), 7.90-7.95 (m, 8H, Ar-H, H-6, \(H_{\beta}\), H-1), 8.96 (s, 2H, Ar-H, H-7), 9.17 ppm (d, \(J = 4.8\) Hz, 4H, \(H_{\beta}\), H-2).

\(\delta_C\) (100 MHz, CDCl\(_3\)): 14.0, 22.7, 29.3, 31.9, 35.9, 38.8, 113.7, 119.1, 125.0, 125.7, 127.3, 127.8, 128.8, 129.7, 130.8, 132.4, 134.1, 134.9, 142.0, 142.3 ppm.
HRMS (m/z -ES): [M+H]^+ calcd. for C_{60}H_{53}N_{4}Zn 892.3483, found 892.3529.

UV/vis (CH_2Cl_2): \( \lambda_{\text{max}} \) (lg \( \varepsilon \)) = 424 (4.94), 522 (3.82), 560 nm (2.68).

(5,15-Dianthracenyl-10,20-dihexylporphyrinato)nickel(II) (173)

Porphyrin 167 (41 mg, 0.05 mmol, 1.0 equiv.) was isolated via procedure B and placed in a 100 mL flask with Ni(acac)_2 (21 mg, 0.08 mmol, 1.5 equiv.). Toluene (50 mL) was added, and the mixture was heated under reflux for 3 hours. The progress of the reaction was monitored by TLC using CH_2Cl_2/n-hexane (1:2, v/v). Upon completion of the reaction, the solvent was removed in vacuo and the product was isolated after passage through a plug of silica gel using CH_2Cl_2 as the eluent. Recrystallisation of the product using CH_2Cl_2/MeOH yielded 173 as orange crystals (34 mg, 0.038 mol, 76 %); M.p. \( \geq \) 300 °C; R_f = 0.94 (CH_2Cl_2/n-hexane, 1:2).

\[ \delta_{\text{H}} \ (400 \text{ MHz, CDCl}_3): \]
0.88 (t, \( J = 7.5 \text{ Hz}, 6\text{H}, \text{CH}_3\), H-13), 1.31-1.37 (m, 4H, CH_2, H-12), 1.39-1.46 (m, 4H, CH_2, H-11), 1.61-1.67 (m, 4H, CH_2, H-10), 2.56-2.61 (m, 4H, CH_2, H-9), 4.82 (t, \( J = 8.2 \text{ Hz}, 4\text{H}, \text{CH}_2\), H-8), 7.12 (app. t, \( J = 7.5 \text{ Hz}, 4\text{H}, \text{Ar-H}, \text{H-4}\)), 7.15 (d, \( J = 8.6 \text{ Hz}, 4\text{H}, \text{Ar-H}, \text{H-3}\)), 7.50 (app. t, \( J = 7.2 \text{ Hz}, 4\text{H}, \text{Ar-H}, \text{H-5}\)), 8.42-8.47 (m, 8H, Ar-H, H-6, H_6, H-1), 8.90 (s, 2H, Ar-H, H-7), 9.32 (d, \( J = 5.1 \text{ Hz}, 4\text{H}, H_6, \text{H-2}\)).
\( \delta_c \) (100 MHz, CDCl\(_3\)): 13.9, 22.5, 30.0, 31.5, 34.1, 37.5, 113.5, 118.3, 124.9, 125.6, 127.7, 128.0, 128.4, 129.7, 130.8, 132.5, 134.4, 134.7, 142.4, 142.7 ppm.

HRMS (m/z -ES): \([\text{M}+\text{H}]^+\) calcd. for C\(_{60}\)H\(_{55}\)Ni \(886.3545\), found 886.3546.

UV/vis (CH\(_2\)Cl\(_2\)): \(\lambda_{\text{max}} \text{ (lg } \varepsilon) = 420 \text{ (4.27), 534 (3.97), 566 nm (2.69).}\)

**5,15-Dianthracenyl-10,20-bis(1-ethylpropyl)porphyrin (177)**

Prepared via procedure B from 9-anthracenylaldehyde (206 mg, 1.00 mmol, 1.0 equiv.), 5-ethylpropyldipyrrromethane (216 mg, 1.0 mmol, 1.0 equiv.), trifluoroacetic acid (24 \(\mu\)L, 0.25 mmol, 0.25 equiv.), DDQ (2.93 g, 13.00 mmol, 13 equiv.) and TEA (15 mL) to yield 177 as purple crystals (112 mg, 0.14 mmol, 14 %); M.p. \(\geq 300\) °C; \(R_f = 0.73\) (CH\(_2\)Cl\(_2\)/n-hexane, 1:2).

\(\delta_h\) (400 MHz, CDCl\(_3\)): -2.22 (s, 2H, NH, H-1), 0.97 (t, \(J = 7.1\) Hz, 12H, CH\(_3\), H-11), 2.72-2.79 (m, 8H, CH\(_2\), H-10), 4.87-4.93 (m, 2H, CH, H-9), 7.04 (app. t, \(J = 7.3\) Hz, 4H, H-5), 7.12 (d, \(J = 8.1\) Hz, 4H, H-4), 7.48 (app. t, \(J = 7.3\) Hz, 4H, H-6), 7.74 (d, \(J = 5.1\) Hz, 4H, \(H_\beta\), H-3), 8.32 (d, \(J = 8.7\) Hz, 4H, H-7), 8.80 (s, 2H, H-8), 9.02 ppm (d, \(J = 5.1\) Hz, 4H, \(H_\beta\), H-2).
δ_C (100 MHz, CDCl₃): 14.1, 34.5, 41.2, 124.8, 125.0, 125.5, 125.8, 127.0, 127.2, 127.6, 128.0, 128.5, 128.8, 130.7, 131.5, 132.7, 135.0 ppm

HRMS (m/z -ES): [M]^+ calcd. for C₅₈H₄₀N₄ 802.4035, found 802.4035.

UV/vis (CH₂Cl₂): \( \lambda_{\text{max}} (\log \epsilon) = 422 \ (4.38), \ 522 \ (3.21), \ 558 \ (2.92), \ 600 \ (2.79), \ 654 \text{ nm} \ (2.81). \)


Porphyrin 177 (56 mg, 0.07 mmol, 1.0 equiv.) was isolated via procedure B and placed in a 100 mL flask with Zn(acac)₂ (31 mg, 0.12 mmol, 1.5 equiv.). MeOH (50 mL) was added and the mixture was heated under reflux for 3 hours. The progress of the reaction was monitored by TLC using CH₂Cl₂/\( \beta \)-hexane (1:2, v/v). Upon completion of the reaction, the solvent was removed in vacuo, and the product was isolated after passage through a plug of silica gel using CH₂Cl₂ as the eluent. Recrystallisation of the product using CH₂Cl₂/MeOH yielded 178 as purple/green crystals (54 mg, 0.06 mmol, 82 %); M.p. ≥ 300 °C; R_f = 0.56 (CH₂Cl₂/\( \beta \)-hexane, 1:2).

δ_H (400 MHz, CDCl₃): 0.93 (s, 12H, CH₃, H-10), 2.73-2.77 (m, 8H, CH₂, H-9), 4.89-4.94 (m, 2H, CH, H-8), 7.01 (app. t, J = 8.1 Hz, 4H, H-4), 7.12 (d, J = 9.0 Hz, 4H, H-3), 7.44 (app. t, J = 7.7 Hz, 4H, H-5), 8.27 (d, J = 4.7 Hz, 4H, H₉, H-2),
8.35 (d, $J = 8.0$ Hz, 4H, H-6), 8.89 (s, 2H, H-7), 9.03 ppm (d, $J = 5.2$ Hz, 4H, H-1).

δ_C (100 MHz, CDCl₃):
14.2, 34.6, 40.2, 124.1, 124.8, 125.3, 126.0, 127.4, 128.0, 128.4, 128.7, 129.4, 130.7, 132.3, 133.6, 135.1, 135.8 ppm.

HRMS (m/z -ES):
[M]⁺ calcd. for C₅₈H₄₈N₄Zn 864.3170, found 864.3173.

UV/vis (CH₂Cl₂):
$\lambda_{\text{max}}$ (lg $\varepsilon$) = 424 (4.61), 540 (3.91), 589 nm (3.08).


Porphyrin 177 (56 mg, 0.07 mmol, 1.0 equiv.) was isolated via procedure B and placed in a 100 mL flask with Ni(acac)₂ (31 mg, 0.12 mmol, 1.5 equiv.). Toluene (50 mL) was added, and the mixture was heated under reflux for 3 hours. The progress of the reaction was monitored by TLC using CH₂Cl₂/n-hexane (1:2, v/v). Upon completion of the reaction, the solvent was removed in vacuo and the product was isolated after passage through a plug of silica gel using CH₂Cl₂ as the eluent. Recrystallisation of the product using CH₂Cl₂/MeOH yielded 179 as orange crystals (44 mg, 0.05 mmol, 71 %); M.p. ≥ 300 °C; $R_f$ = 0.94 (CH₂Cl₂/n-hexane, 1:2).

δ_H (400 MHz, CDCl₃):
0.93 (t, 12H, CH₃, H-10), 2.76-2.81 (m, 8H, CH₂, H-9), 4.96-5.01 (m, 2H, CH, H-8), 7.08 (app. t, $J = 7.4$ Hz, 4H, H-4), 7.19 (d, $J = 7.5$ Hz, 4H, H-3), 7.46 (app. t, $J =
7.5 Hz, 4H, H-5), 8.06 (d, $J = 4.4$ Hz, 4H, $H_β$, H-2), 8.22 (d, $J = 8.0$ Hz, 4H, H-6), 8.82 (s, 2H, H-7), 9.07 ppm (d, $J = 4.4$ Hz, 4H, $H_β$, H-1).

$\delta_C$ (100 MHz, CDCl$_3$): 14.6, 37.3, 41.6, 124.3, 124.8, 125.4, 126.2, 127.4, 128.0, 128.6, 128.9, 129.1, 130.7, 132.5, 133.8, 135.0, 136.1 ppm.

HRMS ($m/z$ -ES): [M]$^+$ calcd. for C$_{58}$H$_{48}$N$_4$Ni 858.3232, found 858.3196.

UV/vis (CH$_2$Cl$_2$): $\lambda_{max}$ (lg $\varepsilon$) = 424 (4.56), 544 (3.73), 595 nm (3.22).

5.3.4 Procedure C: Suzuki cross-coupling approach for the preparation of anthracenylporphyrins.

To a stirred slurry of Cs$_2$CO$_3$ in anhydrous THF (250 mL), a brominated porphyrin precursor,$^{392}$ 9-borylanthracene$^{288}$ and PdCl$_2$(PPh$_3$)$_2$/AsPh$_3$ or Pd$_2$(dba)$_2$ were added. The reaction mixture was heated to 67 °C, shielded from light and stirred 12 hours. The reaction was monitored by TLC using CH$_2$Cl$_2$/n-hexane (1:2, v/v) as the mobile phase. The solvent was removed and the mixture was taken up in EtOAc and was washed with saturated aqueous NaHCO$_3$ (3 X 100 mL), water (3 X 100 mL) and dried over Na$_2$SO$_4$. The organic solvent was evaporated, and the crude mixture was dry-loaded onto a silica column. The anthracenylporphyrin was isolated using CH$_2$Cl$_2$/n-hexane (1:2, v/v) as the mobile phase. The solvent was removed, and the anthracenylporphyrins were further purified by recrystallisation from CH$_2$Cl$_2$/MeOH.
5-Anthracenyl-10,15,20-triphenylporphyrin (181)

Prepared via procedure C using Cs₂CO₃ (163 mg, 0.50 mmol, 5.0 equiv.), 5-bromo-10,15,20-triphenylporphyrin (62 mg, 0.10 mmol, 1.0 equiv.), 9-borylanthracene²⁸⁸ (152 mg, 0.50 mmol, 5.0 equiv.) and PdCl₂(PPh₃)₂/AsPh₃ (20 mg, 0.02 mmol, 0.2 equiv.) to yield 181 as purple crystals (28 mg, 0.035 mmol, 35 %); M.p. ≥ 300 °C; R₉
= 0.6 (CH₂Cl₂/n-hexane, 1:2).

δ_H (400 MHz, CDCl₃): -2.37 (s, 2H, NH, H-1), 7.01 (app. t, J = 7.6 Hz, 2H, Ar-H, H-7), 7.13 (d, J = 8.1 Hz, 2H, Ar-H, H-6), 7.48 (app. t, J = 7.6 Hz, 2H, Ar-H, H-8), 7.70-7.86 (m, 11H, Ar-H, H-5, H-12, H-13, H-15, H-16), 8.21-8.35 (m, 8H, Ar-H, H-9, H-11, H-14), 8.71 (d, J = 5.0 Hz, 2H, Hβ, H-4), 8.91 (d, J = 5.0 Hz, 4H, Hβ, H-2, H-3), 8.96 ppm (s, 1H, Ar-H, H-10).

δ_C (100 MHz, CDCl₃): 115.6, 120.0, 124.9, 125.6, 126.5, 127.6, 127.9, 128.1, 128.5, 128.9, 130.2, 130.8, 131.7, 132.1, 132.8, 134.3, 135.2, 135.8, 136.2, 136.6, 139.3, 141.6, 142.2, 143.0, 143.7, 146.6, 147.1 ppm.

HRMS (m/z -ES): [M+H]^+ calcd. for C₆₀H₃₅N₄ 714.2783, found 714.2796.
UV/vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 423 (5.05), 521 (4.85), 555 (4.65), 598 (4.45), 654 nm (4.40).

(5-Anthracenyl-10,15,20-triphenylporphyrinato)nickel(II) (195)

Prepared via procedure C using Cs$_2$CO$_3$ (163 mg, 0.50 mmol, 5.0 equiv.), (5-bromo-10,15,20-triphenylporphyrinato)nickel(II) (67 mg, 0.10 mmol, 1.0 equiv.), 9-borylanthracene$^{288}$ (152 mg, 0.50 mmol, 5.0 equiv.) and PdCl$_2$(PPh$_3$)$_2$/AsP$_3$ (20 mg, 0.02 mmol, 0.2 equiv.) to yield 195 as orange crystals (63 mg, 0.081 mmol, 81 %); M.p. $\geq 300$ °C; $R_f$ = 0.7 (CH$_2$Cl$_2$/n-hexane, 1:2).

$\delta_H$ (400 MHz, CDCl$_3$):


$\delta_C$ (100 MHz, CDCl$_3$):

116.2, 120.7, 125.3, 125.9, 127.0, 127.8, 128.4, 128.7, 129.5, 130.9, 131.3, 132.0, 133.1, 134.9, 136.0, 136.5, 137.2, 137.7, 138.4, 140.3, 142.1, 142.9, 144.0, 144.6, 145.1, 147.0, 147.8 ppm.
HRMS ($m/z$ -ES): \([\text{M+H}]^+\) calcd. for \(C_{52}H_{33}N_4Ni\) 770.1980, found 770.1924.

UV/vis (CH$_2$Cl$_2$): \(\lambda_{\text{max}} (\lg \varepsilon) = 426 (5.86), 528 (4.03), 552 \text{ nm (3.71)}.\)

(5-Anthracenyl-10,15,20-triphenylporphyrinato)zinc(II) (196)

Prepared via procedure C using Cs$_2$CO$_3$ (163 mg, 0.50 mmol, 5.0 equiv.), (5-bromo-10,15,20-triphenylporphyrinato)nickel(II) (68 mg, 0.10 mmol, 1.0 equiv.), 9-borylanthracene$^{288}$ (152 mg, 0.50 mmol, 5.0 equiv.) and PdCl$_2$ (PPh$_3$)$_2$/AsPh$_3$ (20 mg, 0.02 mmol, 0.2 equiv.) to yield 196 as purple crystals (12 mg, 0.015 mmol, 15 %); M.p. \(\geq 300 \degree\text{C}; R_f = 0.6\) (CH$_2$Cl$_2$/n-hexane, 1:2).

\(\delta_H\) (400 MHz, CDCl$_3$):

7.02 (app. t, \(J = 7.6 \text{ Hz, 2H, Ar-H, H-6}\)), 7.19 (d, \(J = 8.0 \text{ Hz, 2H, Ar-H, H-5}\)), 7.47 (app. t, \(J = 7.8 \text{ Hz, 2H, Ar-H, H-7}\)), 7.74-7.81 (m, 11H, Ar-H, H-4, H-11, H-12, H-14, H-15), 8.20-8.29 (m, 8H, Ar-H, H-8, H-10, H-13), 8.66 (d, \(J = 4.8 \text{ Hz, 2H, } H_{\beta}\)), 8.73 (d, \(J = 4.8 \text{ Hz, 4H, } H_{\beta}\)), 8.96 ppm (s, 1H, Ar-H, H-9).

\(\delta_C\) (100 MHz, CDCl$_3$):

115.9, 120.4, 125.2, 125.7, 126.8, 127.5, 128.2, 128.6, 129.2, 130.4, 131.0, 131.8, 132.8, 133.6, 135.8, 136.3, 136.9, 137.6, 138.2, 139.4, 140.0, 141.9, 142.6, 144.1, 144.5, 146.7, 147.4 ppm.
HRMS (m/z -ES): [M+H]^+ calcd. For C_{52}H_{33}N_{4}Zn 776.1918, found 776.1954.

UV/vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 425 (5.83), 551 (4.82), 592 nm (3.74).

5-Anthracenyl-10,20-bis(3,5-di-tert-butylphenyl)-15-phenylporphyrin (197)

Prepared via procedure C using Cs$_2$CO$_3$ (163 mg, 0.50 mmol, 5.0 equiv.), 5-bromo-10,20-bis(3,5-di-tert-butylphenyl)-15-phenylporphyrin (84 mg, 0.10 mmol, 1.0 equiv.), 9-borylanthracene$^{288}$ (152 mg, 0.50 mmol, 5.0 equiv.), and PdCl$_2$(PPh$_3$)$_2$/AsPh$_3$ (20 mg, 0.02 mmol, 0.2 equiv.) to yield 197 as purple crystals (46 mg, 0.05 mmol, 49 %); M.p. $\geq$ 300 °C; $R_f$ = 0.92 (CH$_2$Cl$_2$/n-hexane, 1:2).

$\delta_H$ (400 MHz, CDCl$_3$): -2.47 (s, 2H, NH, H-1), 1.50 (s, 36H, CH$_3$, H-16), 6.89 (app. t, $J = 7.5$ Hz, 2H, Ar-H, H-7), 7.03 (d, $J = 8.1$ Hz, 2H, Ar-H, H-6), 7.39 (app. t, $J = 7.5$ Hz, 2H, Ar-H, H-8), 7.70-7.78 (m, 5H, Ar-H, H-12, H-14, H-15), 8.03 (d, $J = 1.9$ Hz, 4H, Ar-H, H-11), 8.21-8.27 (m, 4H, Ar-H, H-9, H-13), 8.31 (d, $J = 4.4$ Hz, 2H, $H_{\beta}$, H-5), 8.79 (d, $J = 4.8$ Hz, 2H, $H_{\beta}$, H-4), 8.94 (s, 1H, Ar-H, H-10), 9.01 ppm (d, $J = 5.1$ Hz, 4H, $H_{\beta}$, H-2, H-3).
δ_C (100 MHz, CDCl₃):
31.6, 34.9, 114.1, 121.0, 122.2, 122.6, 124.0, 124.7, 125.7, 126.3, 126.8, 128.1, 128.4, 128.7, 129.0, 129.3, 130.1, 130.3, 130.6, 131.5, 131.7, 132.0, 132.3, 132.6, 133.0, 134.2, 134.5, 135.6, 137.0 ppm.

HRMS (m/z -ES):
[M]^+ calcd. for C₆₈H₅₆N₄ 938.5287, found 938.5217.

UV/vis (CH₂Cl₂):
λ_max (lg ε) = 422 (6.67), 519 (5.47), 533 (5.32), 597 nm (5.10).


Prepared via procedure C using Cs₂CO₃ (163 mg, 0.50 mmol, 5.0 equiv.), [5-bromo-10,20-bis(3,5-di-tert-butylphenyl)-15-phenylporphyrinato]nickel-(II) (90 mg, 0.10 mmol, 1.0 equiv.), 9-borylanthracene²⁸⁸ (152 mg, 0.50 mmol, 5.0 equiv.), and PdCl₂(PPh₃)₂/AsPh₃ (20 mg, 0.02 mmol, 0.2 equiv.) to yield 198 as orange crystals (85 mg, 0.085 mmol, 85 %); M.p. ≥ 300 °C; R_f = 0.95 (CH₂Cl₂/n-hexane, 1:2).

δ_H (400 MHz, CDCl₃):
1.51 (s, 36H, CH₃, H-15), 7.02 (app. t, J = 7.5 Hz, 2H, Ar-H, H-6), 7.13 (d, J = 8.6 Hz, 2H, Ar-H, H-5), 7.48 (app. t, J = 7.5 Hz, 2H, Ar-H, H-7), 7.76-7.84 (m, 5H, Ar-H, H-11, H-13, H-14), 8.17 (d, J = 1.8 Hz, 4H, Ar-
8.28-8.33 (m, 4H, Ar-H, H-8, H-12), 8.38 (d, J = 4.6 Hz, 2H, H-4), 8.77 (d, J = 4.7 Hz, 2H, H-3), 8.94 (s, 1H, Ar-H, H-9), 9.02 ppm (d, J = 4.9 Hz, 4H, H-1, H-2).

δC (100 MHz, CDCl₃):

31.0, 33.8, 114.6, 121.9, 122.3, 122.7, 124.4, 125.3, 126.1, 127.2, 127.9, 128.3, 128.6, 128.9, 129.1, 129.4, 129.9, 130.2, 130.8, 132.0, 132.2, 132.6, 132.8, 133.0, 133.4, 134.5, 134.7, 135.9, 137.6 ppm.

HRMS (m/z -ES):

[M⁺] calcd. for C₅₈H₆₄N₄Ni 994.4484, found 994.4429.

UV/vis (CH₂Cl₂):

λ_max (log ε) = 420 (4.66), 528 (4.56), 654 nm (4.28).

[5-Anthracenyl-10,20-bis(3,5-di-tert-butylphenyl)-15-phenylporphyrinatolo zinc(II) (199)

Prepared via procedure C using Cs₂CO₃ (163 mg, 0.50 mmol, 5.0 equiv.), [5-bromo-10,20-bis(3,5-di-tert-butylphenyl)-15-phenylporphyrinatolo zinc(II) (90 mg, 0.10 mmol, 1.0 equiv.), 9-borylanthracene²⁸⁸ (152 mg, 0.50 mmol, 5.0 equiv.), and PdCl₂(PPh₃)₂/AsPh₃ (20 mg, 0.02 mmol, 0.2 equiv.) to yield 199 as orange crystals (92 mg, 0.09 mmol, 85 %); M.p. ≥ 300 °C, lit. M.p. not reported;²⁴⁹ Rₕ = 0.91 (CH₂Cl₂/n-hexane, 1:2). Analytical data were as reported in literature.²⁴⁹

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δ\textsubscript{H} (400 MHz, CDCl\textsubscript{3}): 1.52 (s, 36H, CH\textsubscript{3}, H-15), 7.01 (app. t, \(J = 7.6\) Hz, 2H, Ar-\(H\), H-6), 7.11 (d, \(J = 8.6\) Hz, 2H, Ar-\(H\), H-5), 7.45 (app. t, \(J = 7.8\) Hz, 2H, Ar-\(H\), H-7), 7.73-7.81 (m, 5H, Ar-\(H\), H-11, H-13, H-14), 8.08 (d, 4H, \(J = 1.6\) Hz, Ar-\(H\), H-10), 8.26-8.31 (m, 4H, Ar-\(H\), H-8, H-12), 8.35 (d, \(J = 4.6\) Hz, 2H, H\(_{\beta}\), H-4), 8.76 (d, \(J = 4.7\) Hz, 2H, H\(_{\beta}\), H-3), 8.90 (s, 1H, Ar-\(H\), H-9), 9.02 ppm (d, \(J = 4.9\) Hz, 4H, H\(_{\beta}\), H-1, H-2).

HRMS (\textit{m}/\textit{z} -ES): [M]\textsuperscript{+} calcd. for C\textsubscript{68}H\textsubscript{64}N\textsubscript{4}Zn 1000.4422, found 1000.4437.

5-Anthracenyl-10,15,20-trihexylporphyrin (200)

![5-Anthracenyl-10,15,20-trihexylporphyrin](image)

Prepared via procedure C using Cs\textsubscript{2}CO\textsubscript{3} (163 mg, 0.50 mmol, 5.0 equiv.), 5-bromo-10,15,20-trihexylporphyrin (64 mg, 0.10 mmol, 1.0 equiv.), 9-borylanthracene\textsuperscript{288} (152 mg, 0.50 mmol, 5.0 equiv.), and PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}/AsPh\textsubscript{3} (20 mg, 0.02 mmol, 0.2 equiv.) to yield 200 as purple crystals (29 mg, 0.04 mmol, 40 %); M.p. \(\geq 300\) °C; \(R_f = 0.69\) (CH\textsubscript{2}Cl\textsubscript{2}/n-hexane, 1:2).

δ\textsubscript{H} (400 MHz, CDCl\textsubscript{3}): −2.31 (s, 2H, NH, H-1), 0.91-0.96 (m, 6H, CH\textsubscript{3}, H-16), 1.00 (t, \(J = 7.4\) Hz, 3H, CH\textsubscript{3}, H-22), 1.35-1.54 (m, 12H, CH\textsubscript{2}, H-14, H-15, H-20, H-21), 1.80-1.96 (m, 6H, CH\textsubscript{2}, H-13, H-19), 2.52-2.63 (m, 6H, CH\textsubscript{2}, H-12, H-18), 4.94
(5-Anthracenyl-10,15,20-trihexylporphyrinato)nickel(II) (201)

(5-Anthracenyl-10,15,20-trihexylporphyrinato)nickel(II) (201)
Prepared via procedure C using Cs₂CO₃ (163 mg, 0.50 mmol, 5.0 equiv.), (5-bromo-10,15,20-triheptylporphyrinato)nickel(II) (70 mg, 0.10 mmol, 1.0 equiv.), 9-borylanthracene\(^{288}\) (152 mg, 0.50 mmol, 5.0 equiv.), and PdCl₂(PPH₃)₂/AsPh₃ (20 mg, 0.02 mmol, 0.2 equiv.) to yield **201** as orange crystals (45 mg, 0.06 mmol, 57%); M.p. ≥ 300 °C; R\(f\) = 0.75 (CH₂Cl₂/n-hexane, 1:2).

\[\delta_H (400 \text{ MHz, CDCl}_3):\]

- 0.94-1.03 (m, 9H, CH₃, H-15, H-21),
- 1.44-1.51 (m, 6H, CH₂, H-14, H-20),
- 1.56-1.61 (m, 6H, CH₂, H-13, H-19),
- 1.84-1.90 (m, 6H, CH₂, H-12, H-18),
- 2.54-2.59 (m, 6H, CH₂, H-11, H-17),
- 4.95 (t, J = 8.5 Hz, 4H, CH₂, H-10),
- 4.57 (t, J = 8.5 Hz, 2H, CH₂, H-16),
- 6.99 (app. t, J = 8.2 Hz, 2H, Ar-H, H-6),
- 7.20 (d, J = 7.7 Hz, 2H, Ar-H, H-5),
- 7.55 (app. t, J = 8.2 Hz, 2H, Ar-H, H-7),
- 8.28 (d, J = 5.4 Hz, 2H, H\(_{β}\), H-1),
- 8.40 (d, J = 9.6 Hz, 2H, Ar-H, H-8),
- 8.90 (s, 1H, Ar-H, H-9),
- 9.31 (d, J = 5.4 Hz, 2H, H\(_{β}\), H-2),
- 9.60 (d, J = 5.4 Hz, 2H, H\(_{β}\), H-3),
- 9.78 ppm (d, J = 5.4 Hz, 2H, H\(_{β}\), H-4).

\[\delta_C (100 \text{ MHz, CDCl}_3):\]

- 13.6, 22.2, 23.2, 28.4, 28.8, 30.5, 31.3, 35.6, 35.9, 38.2, 38.5, 43.8, 113.9, 119.3, 121.7, 122.1, 124.9, 125.6, 126.2, 126.5, 128.2, 128.6, 129.3, 129.8, 130.4, 131.9, 132.5, 133.6, 135.0, 136.1, 143.6 ppm.

HRMS (\(m/z\) -ES):

- [M]\(^+\) calcd. for C\(_52\)H\(_{56}\)N\(_4\)Ni 794.3858, found 794.3893.

UV/vis (CH₂Cl₂):

- \(\lambda_{\text{max}} (\text{lg} \epsilon) = 421 (5.66), 522 (4.67), 554 \text{ nm (3.59).}\)
(5-Anthracenyl-10,15,20-trihexylporphyrinato)zinc(II) (167)

Prepared via general procedure C using Cs₂CO₃ (163 mg, 0.50 mmol, 5.0 equiv.), (5-bromo-10,15,20-trihexylporphyrinato)zinc(II) (71 mg, 0.10 mmol, 1.0 equiv.), 9-borylanthracene²⁸⁸ (152 mg, 0.50 mmol, 5.0 equiv.) and PdCl₂(PPh₃)₂/AsPh₃ (20 mg, 0.02 mmol, 0.2 equiv.) to yield 167 as purple crystals (5 mg, 0.006 mmol, 6 %); M.p. ≥ 300 °C; Rₖ = 0.6 (CH₂Cl₂/n-hexane, 1:2).

δ_H (400 MHz, CDCl₃): 0.91-0.96 (m, 6H, CH₃, H-15), 1.00 (t, J = 8.0 Hz, 3H, CH₃, H-21), 1.38-1.55 (m, 12H, CH₂, H-13, H-14, H-19, H-20), 1.79-1.92 (m, 6H, CH₂, H-12, H-18), 2.50-2.62 (m, 6H, CH₂, H-11, H-17), 4.95 (t, J = 9.0 Hz, 4H, CH₂, H-10), 5.15 (t, J = 8.3 Hz, 2H, CH₂, H-16), 7.01 (app. t, J = 6.6 Hz, 2H, Ar-H, H-6), 7.18 (d, J = 8.1 Hz, 2H, Ar-H, H-5), 7.55 (app. t, J = 6.9 Hz, 2H, Ar-H, H-7), 8.23 (d, J = 5.1 Hz, 2H, H₆, H-1), 8.32 (d, J = 8.1 Hz, 2H, Ar-H, H-8), 8.91 (s, 1H, Ar-H, H-9), 9.24 (d, J = 4.6 Hz, 2H, H₇, H-2), 9.53 (d, J = 5.1 Hz, 2H, H₆, H-3), 9.67 ppm (d, J = 5.1 Hz, 2H, H₇, H-4).

δ_C (100 MHz, CDCl₃): 13.7, 22.2, 23.0, 27.4, 28.9, 29.7, 31.4, 35.1, 35.9, 38.0, 38.7, 43.4, 113.5, 119.8, 121.5, 122.0, 124.7, 125.1, 125.9, 127.0, 128.3, 128.8, 129.5, 130.1, 130.6, 132.2, 132.8, 133.1, 134.5, 135.8, 142.8 ppm.

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HRMS (m/z -ES): [M$^+$] calcd. for C$_{52}$H$_{56}$N$_4$Zn 800.3796, found 800.3818.

UV/vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 450 (5.11), 519 nm (4.51), 551 nm (3.12)

**5,15-Dianthracenyl-10,20-diphenylporphyrin (212)**

Prepared *via* procedure C using Cs$_2$CO$_3$ (163 mg, 0.50 mmol, 5.0 equiv.), (5,15-dibromo-10,20-diphenylporphyrin (62 mg, 0.10 mmol, 1.0 equiv.), 9-borylanthracene$^{288}$ (304 mg, 1.00 mmol, 10.0 equiv.), and PdCl$_2$(PPh$_3$)$_2$/AsPh$_3$ (20 mg, 0.02 mmol, 0.2 equiv.) to yield 212 as purple crystals (28 mg, 0.04 mmol, 35 %); M.p. $\geq$ 300 °C; R$_f$ = 0.6 (CH$_2$Cl$_2$/n-hexane, 1:2).

$\delta$$_{H}$ (400 MHz, CDCl$_3$): -2.36 (s, 2H, NH, H-1), 7.06 (app. t, $J$ = 7.3 Hz, 4H, Ar-H, H-5), 7.17 (d, $J$ = 7.6 Hz, 4H, Ar-H, H-4), 7.50 (app. t, $J$ = 7.1 Hz, 4H, Ar-H, H-6), 7.66-7.78 (m, 6H, Ar-H, H-10, H-11), 8.20 (d, $J$ = 7.0 Hz, 4H, Ar-H, H-9), 8.28-8.37 (m, 8H, Ar-H, H-3, H-7), 8.70 (d, $J$ = 5.1 Hz, 4H, $H_9$, H-2), 8.98 ppm (s, 2H, Ar-H, H-8).

$\delta$$_{C}$ (100 MHz, CDCl$_3$): 118.2, 121.0, 124.7, 125.4, 126.3, 127.1, 127.4, 127.8, 128.0, 130.5, 131.8, 132.2, 133.0, 133.9, 134.8, 139.3, 141.6, 142.4 ppm.

HRMS (m/z -ES): [M+H]$^+$ calcd. for C$_{60}$H$_{59}$N$_4$ 814.3096, found 814.3082.
UV/vis (CH₂Cl₂): \( \lambda_{\text{max}} (\log \varepsilon) = 430 \ (5.26), \ 523 \ (4.71), \ 559 \ (4.57), \ 601 \ (4.43), \ 650 \ \text{nm} \ (4.11) \). 

**(5,15-Dianthracenyl-10,20-diphenylporphyrinato)nickel(II) (214)**

Prepared via procedure C using Cs₂CO₃ (163 mg, 0.50 mmol, 5.0 equiv.), (5,15-dibromo-10,20-diphenylporphyrinato)nickel(II) (67 mg, 0.10 mmol, 1.0 equiv.), 9-borylanthracene²⁸⁸ (304 mg, 1.00 mmol, 10.0 equiv.), and PdCl₂(PPh₃)₂/AsPh₃ (20 mg, 0.02 mmol, 0.2 equiv.) to yield 214 as orange crystals (73 mg, 0.08 mmol, 81 %); M.p. ≥ 300 °C; Rₕ = 0.9 (CH₂Cl₂/n-hexane, 1:2).

\( \delta \)H (400 MHz, CDCl₃): 7.06-7.15 (m, 8H, Ar-H, H-4, H-3), 7.48 (app. t, \( J = 7.0 \) Hz, 4H, Ar-H, H-5), 7.60-7.67 (m, 6H, Ar-H, H-9, H-10), 8.23 (d, \( J = 7.0 \) Hz, 4H, H₈, H-8), 8.22-8.30 (m, 8H, Ar-H, H-6, H-2), 8.63 (d, \( J = 5.1 \) Hz, 4H, H₈, H-1), 8.95 ppm (s, 2H, Ar-H, H-7).

\( \delta \)C (100 MHz, CDCl₃): 118.8, 121.4, 125.0, 125.7, 126.6, 127.6, 127.8, 127.9, 128.2, 130.8, 132.2, 132.6, 133.5, 134.4, 135.8, 140.6, 142.7, 143.8 ppm.

HRMS (m/z -ES): [M]⁺ calcd. for C₄₆H₃₆N₄Ni 870.2293, found 870.2302.

UV/vis (CH₂Cl₂): \( \lambda_{\text{max}} (\log \varepsilon) = 435 \ (4.57), \ 529 \ (4.25), \ 656 \ \text{nm} \ (4.16) \).
5,15-Dianthracenyl-10,20-bis(3,5-di-tert-butylphenyl)porphyrin (216)

Prepared via procedure C using Cs$_2$CO$_3$ (163 mg, 0.50 mmol, 5.0 equiv.), [5,15-bromo-10,20-bis(3,5-di-tert-butylphenyl)porphyrinato]nickel(II) (85 mg, 0.10 mmol, 1.0 equiv.), 9-borylanthracene$^{288}$ (304 mg, 1.00 mmol, 10.0 equiv.), and PdCl$_2$(PPh$_3$)$_2$/AsP$_3$ (20 mg, 0.02 mmol, 0.2 equiv.) to yield 216 as purple crystals (26 mg, 0.025 mmol, 25%); M.p. $>$ 300 °C; $R_f$ = 0.7 (CH$_2$Cl$_2$/n-hexane, 1:2).

$\delta$$_H$ (400 MHz, CDCl$_3$): -2.40 (s, 2H, NH, H-1), 1.42 (s, 36H, CH$_3$, H-11), 7.03 (app. t, $J$ = 7.1 Hz, 4H, Ar-H, H-5), 7.19 (d, $J$ = 7.0 Hz, 4H, Ar-H, H-4), 7.47 (app. t, $J$ = 7.1 Hz, 4H, Ar-H, H-6), 7.71 (d, $J$ = 1.9 Hz, 2H, Ar-H, H-10), 7.96 (d, $J$ = 2.1 Hz, 4H, Ar-H, H-9), 8.33 (d, $J$ = 4.8 Hz, 4H, $H_\beta$, H-3), 8.41 (d, $J$ = 7.1 Hz, 4H, Ar-H, H-7), 8.81 (d, $J$ = 4.9 Hz, 4H, $H_\beta$, H-2), 9.18 ppm (s, 2H, Ar-H, H-8).

$\delta$$_C$ (100 MHz, CDCl$_3$): 32.0, 34.4, 117.0, 120.4, 120.8, 121.3, 122.6, 123.8, 124.4, 124.9, 127.0, 127.8, 128.4, 132.4, 132.6, 134.6, 135.9, 137.6, 140.6, 142.7 ppm.

HRMS ($m/z$ -ES): [M+H]$^+$ calcd. for C$_{76}$H$_{70}$N$_4$ 1039.5600, found
UV/vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 427 (4.51), 529 (4.22), 604 (4.17), 656 nm (4.13).


Prepared via general procedure C using Cs$_2$CO$_3$ (163 mg, 0.50 mmol, 5.0 equiv.), [5,15-dibromo-10,20-bis(3,5-di-tert-butylphenyl)porphyrinato]nickel(II) (90 mg, 0.10 mmol, 1.0 equiv.), 9-borylanthracene$^{288}$ (304 mg, 1.00 mmol, 10.0 equiv.), and PdCl$_2$(PPh$_3$)$_2$/AsPh$_3$ (20 mg, 0.02 mmol, 0.2 equiv.) to yield 218 as orange crystals (89 mg, 0.08 mmol, 81%); M.p. $\geq$ 300 °C; R$_f$ = 0.8 (CH$_2$Cl$_2$/n-hexane, 1:2).

$\delta_H$ (400 MHz, CDCl$_3$):

1.45 (s, 36H, CH$_3$, H-10), 7.06 (app. t, $J$ = 7.3 Hz, 4H, Ar-H, H-4), 7.20 (d, $J$ = 7.5 Hz, 4H, Ar-H, H-3), 7.51 (app. t, $J$ = 7.3 Hz, 4H, Ar-H, H-5), 7.74 (d, $J$ = 2.0 Hz 2H, Ar-H, H-9), 8.01 (d, $J$ = 1.8 Hz, 4H, Ar-H, H-8), 8.40 (d, $J$ = 4.8 Hz, 4H, $H_\beta$, H-2), 8.48 (d, $J$ = 7.3 Hz, 4H, Ar-H, H-6), 8.89 (d, $J$ = 4.8 Hz, 4H, Ar-H, H-1), 9.27 ppm (s, 2H, Ar-H, H-7).
δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>):
32.3, 37.7, 117.8, 120.7, 121.0, 122.3, 122.9, 123.6,
124.8, 125.2, 127.4, 128.2, 128.5, 132.8, 133.1, 135.1,
136.3, 138.1, 142.2, 144.3 ppm.

HRMS (m/z -ES):
[M]<sup>+</sup> calcd. for C<sub>76</sub>H<sub>68</sub>N<sub>4</sub>Ni 1094.4797, found 1094.4742.

UV/vis (CH<sub>2</sub>Cl<sub>2</sub>):
λ<sub>max</sub> (lg ε) = 434 (4.81), 534 (4.62), 671 nm (4.19).

5-Anthracenyl-10,15-diphenylporphyrin (213)

Prepared via procedure C using Cs<sub>2</sub>CO<sub>3</sub> (163 mg, 0.50 mmol, 5.0 equiv.), (5, 15-
dibromo-10,20-diphenylporphyrin (62 mg, 0.10 mmol, 1.0 equiv.), 9-
borylanthracene<sup>388</sup> (304 mg, 1.00 mmol, 10.0 equiv.), and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>/AsPh<sub>3</sub> (20
mg, 0.02 mmol, 0.2 equiv.) to yield 213 as purple crystals (11 mg, 0.02 mmol, 17 %);
M.p. ≥ 300 °C; R<sub>f</sub> = 0.6 (CH<sub>2</sub>Cl<sub>2</sub>/n-hexane, 1:2).

δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>):
-2.32 (s, 2H, NH, H-1), 7.06 (app. t, J = 7.6 Hz, 2H, Ar-
H, H-7), 7.10 (d, J = 7.8 Hz, 2H, Ar-H, H-6), 7.46 (app.
t, J = 7.6 Hz, 2H, Ar-H, H-8), 7.69-7.78 (m, 6H, Ar-H,
H-12, H-13), 8.10 (d, J = 7.1 Hz, 4H, Ar-H, H-11), 8.22
(d, J = 5.1 Hz, 2H, H<sub>β</sub>, H-5), 8.27 (d, J = 4.8 Hz, 2H,
Ar-H, H-9), 8.48 (s, 1H, H-10), 8.69 (d, J = 4.8 Hz, 2H,
δC (100 MHz, CDCl3):
120.3, 121.0, 124.9, 125.2, 125.7, 126.8, 127.7, 128.0, 128.2, 128.6, 131.8, 132.0, 132.2, 132.5, 132.9, 133.8, 134.2, 139.9, 142.2, 142.7, 143.1, 143.8, 148.8 ppm.

HRMS (m/z -ES): [M+H]⁺ calcd. for C₄₆H₃₁N₄ 638.2470, found 638.2454.

UV/vis (CH₂Cl₂):
λmax (lg ε) = 420 (4.55), 516 (3.72), 549 (3.39), 591 (3.32), 648 nm (3.17).

5-Anthracenyl-10,20-bis(3,5-di-tert-butylphenyl)porphyrin (217)

Prepared via procedure C using Cs₂CO₃ (163 mg, 0.50 mmol, 5.0 equiv.), 5,15-dibromo-10,20-bis(3,5-di-tert-butylphenyl)porphyrin (85 mg, 0.10 mmol, 1.0 equiv.), 9-borylanthracene²⁸⁸ (46 mg, 0.15 mmol, 1.5 equiv.) and PdCl₂(PPh₃)₂/AsPh₃ (20 mg, 0.02 mmol, 0.2 equiv.) to yield 217 as purple crystals (16 mg, 0.02 mmol, 18 %); M.p. ≥ 300 °C; Rf = 0.7 (CH₂Cl₂/n-hexane, 1:2).

δH (400 MHz, CDCl₃):
-2.41 (s, 2H, NH, H-1), 1.51 (s, 36H, CH₃, H-14), 7.02 (app. t, J = 7.2 Hz, 2H, Ar-H, H-8), 7.13 (d, J = 7.5 Hz, 2H, Ar-H, H-7), 7.45 (app. t, J = 7.2 Hz, 2H, Ar-H, H-
9), 7.79 (d, J = 2.1 Hz, 2H, Ar-H, H-13), 8.11 (d, J = 1.7 Hz, 4H, Ar-H, H-12), 8.34 (d, J = 4.8 Hz, 2H, Hβ, H-6), 8.71 (d, J = 9.0 Hz, 2H, Ar-H, H-10), 8.80 (d, J = 4.8 Hz, 2H, Hβ, H-5), 8.97 (d, J = 4.6 Hz, 2H, Hβ, H-4), 9.05 (d, J = 4.6 Hz, 2H, Ar-H, H-3), 9.14 (s, 1H, Ar-H, H-11), 9.27 ppm (s, 1H, Hmeso, H-2).

δC (100 MHz, CDCl3): 31.8, 37.2, 119.3, 121.5, 124.1, 124.7, 125.2, 126.3, 126.8, 127.1, 127.7, 130.3, 130.5, 130.8, 131.0, 131.3, 132.6, 133.4, 134.5, 137.8, 139.6, 141.4, 141.8, 142.3, 144.9 ppm.

HRMS (m/z -ES): [M+H]^+ calcd. for C_{62}H_{63}N_{9} 862.4974, found 862.4939.

UV/vis (CH2Cl2): λmax (lg ε) = 424 (4.47), 523 (4.16), 551 (3.99), 599 (3.09), 648 nm (3.01).

5-Anthracenyl-15-bromo-10,20-diphenylporphyrin (220)

Prepared via procedure C using Cs2CO3 (163 mg, 0.50 mmol, 5.0 equiv.), 5,15-dibromo-10,20-diphenylporphyrin (62 mg, 0.10 mmol, 1.0 equiv.), 9-borylanthracene288 (46 mg, 0.15 mmol, 1.5 equiv.) and PdCl2(PPh3)2/AsPPh3 (20 mg, 0.02 mmol, 0.2 equiv.) to yield 220 as purple crystals (13 mg, 0.02 mmol, 18%); M.p. ≥ 300 °C; Rf = 0.5 (CH2Cl2/n-hexane, 1:2).
$\delta_H$ (400 MHz, CDCl$_3$): -2.46 (s, 2H, NH, H-1), 7.03 (app. t, $J = 7.5$ Hz, 2H, Ar-H, H-7), 7.12 (d, $J = 7.3$ Hz, 2H, Ar-H, H-6), 7.49 (app. t, 2H, Ar-H, H-8), 7.70-7.78 (m, 6H, Ar-H, H-12, H-13), 8.23 (d, $J = 7.5$ Hz, 4H, Ar-H, H-11), 8.29 (d, $J = 4.8$ Hz, 2H, $\beta_H$, H-5), 8.31 (d, $J = 7.3$ Hz, 2H, Ar-H, H-9), 8.70 (d, $J = 4.8$ Hz, 2H, $\beta_H$, H-4), 8.88-8.93 (m, 4H, $\beta_H$, H-2, H-3), 8.97 ppm (s, 1H, Ar-H, H-10).

$\delta_C$ (100 MHz, CDCl$_3$): 115.0, 120.0, 120.6, 120.9, 125.0, 125.2, 126.1, 126.3, 127.1, 127.3, 127.6, 127.8, 128.2, 128.4, 128.8, 131.6, 134.7, 134.9, 135.2, 135.3, 135.8, 143.4, 143.6 ppm.

HRMS (m/z -ES): $[M]^+$ calcd. for C$_{46}$H$_{29}$BrN$_4$ 716.1576, found 716.1563.

UV/vis (CH$_2$Cl$_2$): $\lambda_{max}$ (lg $\varepsilon$) = 425 (4.48), 520 (3.65), 556 (3.33), 599 (3.27), 643 nm (3.18).

5-Anthracenyl-15-bromo-10,20-dihexylporphyrin (222)

![5-Anthracenyl-15-bromo-10,20-dihexylporphyrin (222) structure](image)

Prepared via procedure C using Cs$_2$CO$_3$ (163 mg, 0.50 mmol, 5.0 equiv.), 5,15-dibromo-10,20-dihexylporphyrin (63 mg, 0.10 mmol, 1.0 equiv.), 9-borylanthracene$^{288}$ (46 mg, 0.15 mmol, 1.5 equiv.) and PdCl$_2$(PPh$_3$)$_2$/AsPh$_3$ (20 mg,
0.02 mmol, 0.2 equiv.) to yield 222 as purple crystals (40 mg, 0.05 mmol, 50 %); M.p. ≥ 300 °C; Rf = 0.5 (CH₂Cl₂/n-hexane, 1:2).

δ_H (400 MHz, CDCl₃):
-2.37 (s, 2H, NH, H-1), 0.93 (t, J = 7.2 Hz, 6H, CH₃, H-16), 1.38-1.42 (m, 4H, CH₂, H-15), 1.47-1.53 (m, 4H, CH₂, H-14), 1.77-1.83 (m, 4H, CH₂, H-13), 2.47-2.54 (m, 4H, CH₂, H-12), 4.90 (t, J = 8.1 Hz, 4H, CH₂, H-11), 7.05 (app. t, J = 7.0 Hz, 2H, Ar-H, H-7), 7.11 (d, J = 8.3 Hz, 2H, Ar-H, H-6), 7.49 (app. t, J = 7.0 Hz, 2H, Ar-H, H-8), 8.26 (d, J = 4.6 Hz, 2H, Hβ, H-4), 8.33 (d, J = 8.7 Hz, 2H, Ar-H, H-9), 8.97 (s, 1H, Ar-H, H-10), 9.11 (d, J = 4.6 Hz, 2H, Hβ, H-5), 9.21 (d, J = 5.1 Hz, 2H, Hβ, H-3), 9.24 ppm (d, J = 5.1 Hz, 2H, Hβ, H-2).

δ_C (100 MHz, CDCl₃):
14.0, 22.5, 30.1, 31.4, 34.1, 37.6, 114.8, 118.4, 120.5, 121.8, 122.6, 124.9, 125.7, 125.9, 127.3, 127.9, 128.1, 128.5, 130.7, 133.2, 133.9, 134.3, 135.0, 141.8, 142.0 ppm.

HRMS (m/z -ES):
[M]+ calcd. for C₄₆H₄₅BrN₄ 732.2828, found 732.2861.

UV/vis (CH₂Cl₂):
λ_max (lg ε) = 420 (4.32), 517 (3.89), 571 (3.46), 592 (3.30), 651 nm (3.05).
5-Anthracenyl-15-bromo-10,20-bis(3,5-di-tert-butylphenyl)porphyrin (224)

Prepared via procedure C using Cs₂CO₃ (163 mg, 0.50 mmol, 5.0 equiv.), 5,15-dibromo-10,20-bis(3,5-di-tert-butylphenyl)porphyrin (84 mg, 0.10 mmol, 1.0 equiv.), 9-borylanthracene²⁸⁸ (46 mg, 0.15 mmol, 1.5 equiv.) and PdCl₂(PPh₃)₂/AsPh₃ (20 mg, 0.02 mmol, 0.2 equiv.) to yield 224 as purple crystals (24 mg, 0.02 mmol, 21 %); M.p. ≥ 300 °C; Rᵣ = 0.6 (CH₂Cl₂/n-hexane, 1:2).

δ_H (400 MHz, CDCl₃): -2.40 (s, 2H, NH, H-1), 1.54 (s, 36H, CH₃, H-13), 7.05 (app. t, J = 7.2 Hz, 2H, Ar-H, H-7), 7.13 (d, J = 8.4 Hz, 2H, Ar-H, H-6), 7.79-7.88 (m, 4H, Ar-H, H-12, H-8), 8.08-8.13 (m, 4H, Ar-H, H-11), 8.24 (d, J = 4.8 Hz, 2H, H₇, H-5), 8.31 (d, J = 4.8 Hz, 2H, Ar-H, H-9), 8.70 (d, J = 4.8 Hz, 2H, H₈, H-3), 9.25 ppm (d, J = 4.8 Hz, 2H, H₉, H-2).

δ_C (100 MHz, CDCl₃): 31.6, 35.9, 117.6, 121.1, 125.0, 125.2, 125.7, 126.1, 127.1, 127.7, 127.9, 128.0, 128.1, 128.5, 129.7, 130.7, 131.5, 133.4, 134.0, 135.0, 135.6, 138.6, 140.5, 141.4, 142.1 ppm.

HRMS (m/z -ES): [M]⁺ calcd. for C₆₀H₆₁BrN₄ 940.4080, found 940.4106.
UV/vis \((\text{CH}_2\text{Cl}_2)\): \(\lambda_{\text{max}} (\lg \varepsilon) = 415 (4.38), 527 (4.15), 556 (3.93), 599 (3.37), 653 \text{ nm} (3.26)\).


Prepared via procedure C using Cs₂CO₃ (163 mg, 0.50 mmol, 5.0 equiv.), [5,15-dibromo-10,20-bis(3,5-di-tert-butylphenyl)triphenylporphyrinato] nickel(II) (90 mg, 0.10 mmol, 1.0 equiv.), 9-borylanthracene\(^\text{288}\) (46 mg, 0.15 mmol, 1.5 equiv.) and \(\text{PdCl}_2(\text{PPh}_3)_2/\text{AsPh}_3\) (20 mg, 0.02 mmol, 0.2 equiv.) to yield **225** as orange crystals (10 mg, 0.01 mmol, 10 %); M.p. \(\geq 300 \, ^\circ\text{C}\); \(R_f = 0.8\) \((\text{CH}_2\text{Cl}_2/\text{n-hexane}, 1:2)\).

\(\delta_H (400 \, \text{MHz, CDCl}_3):\) 1.54 (s, 36H, \(\text{CH}_3\), H-12), 7.12 (app. t, \(J = 7.6 \, \text{Hz}\), 2H, Ar-\(H\), H-6), 7.17 (d, \(J = 8.2 \, \text{Hz}\), 2H, Ar-\(H\), H-5), 7.86-7.93 (m, 4H, Ar-\(H\), H-7, H-11), 7.90-7.97 (m, 4H, Ar-\(H\), H-10), 8.28 (d, \(J = 4.8 \, \text{Hz}\), 2H, \(H_\beta\), H-4), 8.36 (d, \(J = 8.7 \, \text{Hz}\), 2H, Ar-\(H\), H-8), 8.72 (d, \(J = 4.8 \, \text{Hz}\), 2H, \(H_\beta\), H-3), 8.94-8.98 (m, 3H, \(H_\beta\), Ar-\(H\), H-2, H-9), 9.28 ppm (d, \(J = 5.6 \, \text{Hz}\), 2H, \(H_\beta\), H-1).

\(\delta_C (100 \, \text{MHz, CDCl}_3):\) 31.5, 35.8, 117.8, 121.3, 125.1, 125.5, 125.9, 126.5, 127.1, 127.8, 128.2, 128.4, 128.8, 130.2, 131.4, 132.0,
133.7, 134.3, 134.9, 135.6, 136.1, 139.3, 141.3, 142.1, 142.8 ppm.

HRMS (m/z -ES): [M]^+ calcd. for C_{46}H_{59}BrN_{4}Ni 996.3277, found 996.3287.

UV/vis (CH2Cl2): \( \lambda_{\text{max}} (\log \varepsilon) = 418 (4.10), 529 (3.23), 654 \) nm (3.42).

9,10-Bis[(10,15,20-triphenylporphyrin-5-ylato)nickel(II)]anthracene (231)

To a stirred slurry of Cs2CO3 (212 mg, 0.65 mmol, 5.0 equiv.) in anhydrous THF, [5-bromo-10,15,20-triphenylporphyrinato]nickel(II) 230 (937 mg, 1.30 mmol, 10.0 equiv.), 9,10-dibromoanthracene 185 (43 mg, 0.13 mmol, 1.0 equiv.) and PdCl2(PPh3)2 (20 mg, 0.02 mmol, 0.2 equiv.) were added. The reaction mixture was heated to 67 °C, shielded from light and stirred for 48 hours. The reaction was monitored by TLC using CH2Cl2/n-hexane (1:2, v/v) as the mobile phase. This mixture was washed with saturated aqueous NaHCO3 (3 X 100 mL), water (3 X 100 mL) and dried over Na2SO4. The organic solvent was evaporated and the crude mixture was dry loaded onto a silica column. The anthracenylporphyrin dimer 231 was isolated using CH2Cl2/n-hexane (1:2, v/v) as the mobile phase. The solvent was removed, and the anthracenylporphyrin was further purified by recrystallisation from CH2Cl2/MeOH yielding 231 as orange crystals (54 mg, 0.04 mmol, 31 %); M.p. \( \geq 300 \) °C; \( R_f = 0.88 \) (CH2Cl2/n-hexane, 1:2).
\[ \delta_H \text{ (400 MHz, CDCl}_3\text{):} \]

7.35-7.40 (m, 4H, Ar-\(H\), H-6), 7.45-7.49 (m, 4H, Ar-\(H\), H-5), 7.51-7.58 (m, 6H, Ar-\(H\), H-9, H-12), 7.63 (m 12H, Ar-\(H\), H-8, H-11), 7.74-7.78 (m, 12H, Ar-\(H\), H-7, H-10), 8.10 (d, \(J = 5.1 \text{ Hz}, 4\text{H}, H_\beta, H-4\)), 8.61 (d, \(J = 5.1 \text{ Hz}, 4\text{H}, H_\beta, H-3\)), 8.80 (d, \(J = 4.7 \text{ Hz}, 4\text{H}, H_\beta, H-2\)),

8.84 ppm (d, \(J = 4.7 \text{ Hz}, 4\text{H}, H_\beta, H-1\)).

\[ \delta_C \text{ (100 MHz, CDCl}_3\text{):} \]

120.6, 120.9, 124.9, 125.3, 125.6, 125.8, 126.0, 128.2, 128.7, 129.4, 129.7, 131.2, 132.0, 132.7, 133.1, 134.8, 137.0, 142.2, 142.5, 146.3, 146.7, 147.1, 150.3 ppm.

HRMS (m/z -ES): \([M]^+ \text{ calcd. for } C_{90}H_{54}N_8Ni}_2 1362.3178, \text{ found } 1362.3221.

UV/vis (CH\(_2\)Cl\(_2\)): \(\lambda_{\text{max}} (\lg \varepsilon) = 404 (4.32), 500 (4.00), 532 (4.07), 577 \text{ nm (3.58).} \)

5.4 Novel Triptycene Scaffolds

5.4.1 Anthracene Precursors

Procedure D: general procedure for the preparation of 9,10-disubstituted derivatives \textit{via} simple organolithium reaction.

Anthraquinone was added to a stirred solution of aryl/alkyllithium in hexane (100 mL) and anisole (100 mL) at room temperature. The reaction was stirred for 1 day and quenched by addition of a saturated solution of ammonium chloride (50 mL). The organic layer was separated, washed with water (2 \(\times\) 200 mL), and evaporated. The resulting residue was dissolved in THF (75 mL) and added dropwise to a solution of tin dichloride in acetic acid (300 mL). The resulting suspension was stirred for 1 day, and the organic material was extracted with hexane (1.00 L). The organic extract was washed with 5% ammonium hydroxide (500 mL) and evaporated to dryness. The residue was crystallized from 2-propanol to give pure desired anthracene derivatives.
9,10-Dihexylanthracene (238)

Prepared via organolithium reaction according to the procedure D using anthraquinone (10.40 g, 50.00 mmol, 1.0 equiv.), hexyllithium (10.9 mL of a 2.5 M solution in hexane, 0.273 mol, 6.0 equiv.) and tin dichloride (56.25 g, 0.25 mol, 5.0 equiv.). The residue was crystallized from 2-propanol to yield 238 as a yellow powder (10.40 g, 30.00 mmol, 61 %); M.p. = 87-89 °C, lit. M.p. = 87-88 °C;\(^{400}\) R\(_f\) = 0.88 (EtOAc/n-hexane 1:5, v/v). Analytical data were as reported in literature.\(^{400}\)

\(\delta_H\) (400 MHz, CDCl\(_3\)): 0.95 (t, \(J = 7.4\) Hz, 6H, CH\(_3\), H-8), 1.27-1.32 (m, 8H, CH\(_2\), H-6, H-7), 1.43-1.47 (m, 4H, CH\(_2\), H-5), 1.76-1.79 (m, 4H, CH\(_2\), H-4), 3.36 (t, \(J = 8.2\) Hz, 4H, Ar-H, H-3), 7.30 (dd, \(J = 7.4, 1.5\) Hz, 4H, Ar-H, H-1), 7.90 ppm (dd, \(J = 7.6, 1.5\) Hz, 4H, Ar-H, H-2).

9,10-Diphenylanthracene (240)
Prepared via organolithium reaction according to procedure D using anthraquinone (10.4 g, 50.00 mmol, 1.0 equiv.), phenyllithium (10.9 mL of a 2.5 M solution in hexane, 0.273 mol, 6.0 equiv.) and tin dichloride (56.25 g, 0.25 mol, 5.0 equiv.). The residue was crystallized from 2-propanol and the crude mixture was dry loaded onto a silica column using EtOAc/n-hexane (5:95, v/v) as the mobile phase. The desired disubstituted anthracene 240 (7.60 g, 23.00 mmol, 45 %) and 239 (2.9 g, 11.50 mmol, 23 %) were isolated as a yellow powder; M.p. = 245-247 °C, lit. M.p. = 245-246 °C; \( R_f = 0.57 \) (EtOAc/n-hexane 1:5, v/v). Analytical data were as reported in literature. \(^{401}\)

\[ \delta_H (400 \text{ MHz, CDCl}_3): \]

- 7.39-7.43 (m, 4H, Ar-H, H-5),
- 7.43-7.55 (m, 10H, Ar-H, H-1, H-2, H-3)
- 7.84-7.91 ppm (m, 4H, Ar-H, H-4).

9-Phenylanthracene (239)

The mono-substituted derivative 239 was also isolated from the above reaction mixture as a yellow powder (2.9 g, 11.50 mmol, 23 %); M.p. = 154-156 °C, lit. M.p. = 154-156 °C; \( R_f = 0.61 \) (EtOAc/n-hexane 1:5, v/v). Analytical data were as reported in literature. \(^{403-405}\)

\[ \delta_H (400 \text{ MHz, CDCl}_3): \]

- 6.91 (d, \( J = 8.0 \text{ Hz} \), 3H, Ar-H, H-1, H-2),
- 7.36-7.60 (m, 6H, Ar-H, H-3, H-5, H-6),
- 8.02 (d, \( J = 9.0 \text{ Hz} \), 2H, Ar-H, H-7),
- 8.13 (d, \( J = 8.5 \text{ Hz} \), 2H, Ar-H, H-4),
- 8.54 ppm (s, 1H, Ar-H, H-8).
Procedure E: general procedure for organolithium reactions with anthracene *via* generation of lithium salt.

A 100 mL 3-neck round-bottom flask was dried under high vacuum, purged with argon and charged with a suitable aryl bromide precursor (3.00 mmol). Dry diethyl ether (15 mL) was added and the solution was cooled to -78 °C. *n*-Butyllithium (1.2 mL of a 2.5 M solution in hexane, 3.6 mmol) was added dropwise over 1 h at -78 °C. The reaction mixture was warmed to -40 °C and dry THF was added until a white/pink suspension formed (~2 mL). Anthraquinone 234 (55 mg, 0.25 mmol) was dissolved in hexane (10 mL) and anisole (10 mL). The mixture was added dropwise to the solution and stirred at room temperature for one day. The reaction was quenched by addition of a 5 % solution of ammonium chloride (30 mL). The organic layer was separated, washed with water (2 × 25 mL), and evaporated. The resulting residue was dissolved in THF (75 mL) and added dropwise to a solution of tin dichloride (3.33 g, 17.5 mmol) in acetic acid (21 mL). The resulting suspension was stirred for 24 h, and the organic material was extracted with hexane (100 mL). The organic extract was washed with 5 % ammonium hydroxide (50 mL) and evaporated to dryness. The residue was crystallized from 2-propanol to give pure desired anthracene derivatives.

**9,10-Bis(4-aminophenyl)anthracene (258)**

![Structure of 9,10-Bis(4-aminophenyl)anthracene (258)](image)

Prepared *via* organolithium reaction according to procedure E above using 4-bromoaniline (620 mg, 3.00 mmol, 1.0 equiv.) to yield 258 as a yellow powder (6 mg,
0.015 mmol, 6 %); M.p. ≥ 300 °C, lit. M.p. > 300 °C; R_f = 0.36 (EtOAc/n-hexane 1:5, v/v). Analytical data were as reported in literature.

δ_H (400 MHz, CDCl_3): 3.58 (br. s, 4H, NH_2), 7.01-7.06 (m, 4H, Ar-H, H-4), 7.40-7.45 (m, 8H, Ar-H, H-1, H-2), 7.76-7.81 ppm (m, 4H, Ar-H, H-3).

9,10-Bis(4-ethynylphenyl)anthracene (260)

Prepared via organolithium reaction according to procedure E above using 4-ethynylbenzene (644 mg, 3.60 mmol, 14.4 equiv.) to yield 260 as a yellow powder (15 mg, 0.04 mmol, 6 %); M.p. = 217-219 °C; R_f = 0.53 (EtOAc/n-hexane 1:5, v/v).

δ_H (400 MHz, CDCl_3): 3.12 (s, 2H, CH, H-5), 7.23-7.27 (m, 4H, Ar-H, H-4), 7.60-7.64 (m, 8H, Ar-H, H-1, H-2), 7.93-7.98 ppm (m, 4H, Ar-H, H-3).

δ_C (100 MHz, CDCl_3): 80.7, 81.9, 124.7, 125.1, 126.3, 126.9, 127.8, 130.2, 137.0, 138.6 ppm.

HRMS (m/z -ES): [M]^+ calcd. for C_{30}H_{18} 378.1409, found 378.1443.

UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 361 (5.31), 378 (5.70), 401 nm (5.14).
Procedure F: general procedure for the preparation of 9,10-disubstituted anthracenes via Suzuki cross-coupling.

To a stirred slurry of $K_3PO_4$ in anhydrous THF of 9,10-dibromoanthracene (185), a boronic acid derivative and Pd(PPh$_3$)$_4$ were added. The reaction mixture was heated to 67 °C, shielded from light and stirred overnight. The reaction was monitored by TLC using EtOAc/n-hexane (5:95, v/v) as the mobile phase. The solvent was removed and the mixture was taken up with EtOAc and was washed with saturated aqueous NaHCO$_3$, water and dried over NaSO$_4$. The organic solvent was evaporated, and the crude mixture was dry loaded onto a silica column, and the anthracene derivative was isolated using EtOAc/n-hexane (5:95, v/v) as the mobile phase. The crude product was recrystallised using CH$_2$Cl$_2$/n-hexane.

9,10-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)anthracene (118)

Prepared via Suzuki cross-coupling reaction according to procedure F using $K_3PO_4$ (528 mg, 2.50 mmol, 5.0 equiv.), 9,10-dibromoanthracene 185 (165 mg, 0.50 mmol, 1.0 equiv.), bis(pinacolato)diboron (1.27 g, 5.00 mmol, 10.0 equiv.) and Pd(PPh$_3$)$_4$ (1.16 g, 0.10 mmol, 0.2 equiv.) to yield 118 as a yellow powder (133 mg, 0.31 mmol, 61 %); M.p. = 129-131 °C, lit. M.p. not reported; $R_f = 0.82$ (EtOAc/n-hexane 5:95, v/v). Analytical data were as reported in literature.$^{409}$

$\delta_H$ (400 MHz, CDCl$_3$): 1.24 (s, 24H, $CH_3$, H-3), 7.41 (dd, $J = 8.1$, 1.6 Hz, 4H, Ar-$H$, H-1), 8.29 ppm (dd, $J = 8.1$, 1.6 Hz, 4H, Ar-$H$, H-2).
9,10-Bis(4-hydroxyphenyl)anthracene (259)

Prepared via Suzuki cross-coupling reaction according to procedure F using K$_3$PO$_4$ (528 mg, 2.50 mmol, 5.0 equiv.), 9,10-dibromoanthracene 185 (165 mg, 0.50 mmol, 1.0 equiv.), 4-hydroxyphenylboronic acid (690 mg, 5.00 mmol, 10.0 equiv.) and Pd(PPh$_3$)$_4$ (1.16 g, 0.10 mmol, 0.2 equiv.) to yield 259 as a yellow powder (138 mg, 0.38 mmol, 38 %); M.p. = 219-221 °C, lit. M.p. not reported; R$_f$ = 0.47 (EtOAc/n-hexane 5:95, v/v). Analytical data were as reported in literature.$^8$

$\delta_H$ (400 MHz, CDCl$_3$): 6.98 (d, $J = 7.5$ Hz, 4H, Ar-H, H-1), 7.40-7.44 (m, 4H, Ar-H, H-4), 7.60 (d, $J = 7.5$ Hz, 4H, Ar-H, H-2), 7.99-8.03 ppm (m, 4H, Ar-H, H-3).

9,10-Bis(4-bromophenyl)anthracene (261)
Prepared via Suzuki cross-coupling reaction according to procedure F using K$_3$PO$_4$ (528 mg, 2.50 mmol, 5.0 equiv.), 9,10-dibromoanthracene $\textbf{185}$ (165 mg, 0.50 mmol, 1.0 equiv.), 4-bromophenylboronic acid (1.05 g, 5.00 mmol, 10 equiv.) and Pd(PPh$_3$)$_4$ (1.16 g, 0.10 mmol, 0.2 equiv.) to yield $\textbf{261}$ as a yellow powder (171 mg, 0.35 mmol, 69 %); M.p. = 222-224 °C, lit. M.p. = 222-224 °C; $^\dagger$ R$_f$ = 0.44 (EtOAc/n-hexane 5:95, v/v). Analytical data were as reported in literature.$^\ddagger$

$\delta_H (400$ MHz, CDCl$_3$): 7.38-7.43 (m, 4H, Ar-H, H-4), 7.56-7.64 (m, 8H, Ar-H, H-1, H-2), 7.93-7.96 ppm (m, 4H, Ar-H, H-3).

$\textbf{9-Allylanthracene (273)}$

To a stirred slurry of Cs$_2$CO$_3$ (815 mg, 2.50 mmol, 5.0 equiv.) in anhydrous THF, 9-bromoanthracene $\textbf{30}$ (128 mg, 0.50 mmol, 1 equiv.), allylboronic acid (430 mg, 5.00 mmol, 5.0 equiv.) and PdCl$_2$(PPh$_3$)/Pd(PPh$_3$)$_4$ (929 mg, 0.10 mmol, 0.2 equiv.) were added. The reaction mixture was heated to 67 °C, shielded from light and stirred overnight. The reaction was monitored by TLC using EtOAc/n-hexane (5:95, v/v) as the mobile phase. The solvent was removed and the mixture was taken up in EtOAc and washed with a saturated solution of NaHCO$_3$, water and dried over Na$_2$SO$_4$. The organic solvent was evaporated, and the crude mixture was dry loaded onto a silica column and the anthracene derivative was isolated using EtOAc/n-hexane (5:95, v/v) as the mobile phase. The product was recrystallised using CH$_2$Cl$_2$/MeOH to yield $\textbf{273}$ as a yellow powder (68 mg, 0.31 mmol, 62 %); M.p. = 64-66 °C, lit. M.p. = 64°C; $^0$ R$_f$ = 0.9 (EtOAc/n-hexane 5:95, v/v). Analytical data were as reported in literature.$^\ddagger$

$\delta_H (400$ MHz, CDCl$_3$): 4.26 (d, $J = 5.6$ Hz, 2H, CH$_2$, H-6), 4.85 (dd, $J = 9.2$, 1.6 Hz, 1H, CH, H-8), 5.06 (dd, $J = 14.6$, 1.6 Hz, 1H, H-5).
9,10-Diaminoanthracene (276)

Anthracene 3 (1.0 g, 5.60 mmol, 1.0 equiv.) was suspended in concentrated nitric acid (10 mL, 24.10 mmol, 4.3 equiv.). The mixture was heated to 75 °C and stirred for 24 hours. The reaction mixture was cooled to room temperature, poured into water (1.00 L) and stirred for 1 hour. The pale yellow precipitate was collected by suction filtration, washed with water, and dried in air to give approximately 1 g of the crude intermediate 9-nitroanthracene 278. The crude mixture was dissolved in dry CH₂Cl₂ (20 mL) and dry MeOH (20 mL) and palladium on carbon (1.4 g, 10 wt. %, 13.0 mmol, 2.32 equiv.) was added. The suspension was placed in an ice bath and sodium borohydride (2.44 g, 65 mmol, 11.6 equiv.) was added slowly. After 30 minutes, the reaction mixture was filtered and the solvent was evaporated. The residue was taken up in CH₂Cl₂ and was washed with water (20 mL X 2) and brine (20 mL X 2). The organic solvent was removed in vacuo to yield 276 as a white solid (550 mg, 2.63 mmol, 47 %); M.p. = 140-142 °C, lit. M.p. = 140-142 °C. Analytical data were in accordance to the literature.

δH (400 MHz, CDCl₃): 3.61 (br. s, 4H, NH₂, H-3), 7.28-7.32 (m, 4H, Ar-H, H-1), 7.79-7.83 ppm (m, 4H, Ar-H, H-2).

CH, H-9), 6.28-6.33 (m, 1H, CH, H-7), 7.31-7.36 (m, 4H, Ar-H, H-3, H-4), 7.56-7.63 ppm (m, 5H, Ar-H, H-1, H-2, H-5).
9-Nitroanthracene (280)

![Diagram of 9-Nitroanthracene (280)]

Anthracene 3 (10.0 g, 56.00 mmol, 1.0 equiv.) was suspended in glacial acetic acid (40 ml, 0.70 mol, 12.5 equiv.) and stirred at room temperature. Concentrated nitric acid (4 mL, 0.95 mol, 1.7 equiv.) was added dropwise and the mixture was stirred vigorously for 1 hour to form a clear solution. A mixture of concentrated HCl (50 mL) and glacial acetic acid (50 mL) was added slowly resulting in a pale yellow precipitate. This was filtered, washed with glacial acetic acid (3 X 25 mL) and again thoroughly with water until the washings were neutral. The resulting yellow solid was treated with a warm solution (60–70 °C) of 10 % aqueous NaOH (200 mL), filtered, washed with warm water until the washings were neutral, air-dried and recrystallised from glacial acetic acid to yield 280 as a fluffy yellow solid (6.37 g, 28.60 mmol, 51 % yield); M.p. = 145-147 °C, lit. M.p. = 145-146 °C. Analytical data were as reported in literature.\(^\text{415,416}\)

$$\delta_H \text{ (400 MHz, CDCl}_3\text{): } 7.30-7.36 \text{ (m, 4H, Ar-H, H-3, H-4), 7.94 (d, } J = 8.2 \text{ Hz, 2H, Ar-H, H-2), 8.18 (d, } J = 8.0 \text{ Hz, 2H, Ar-H, H-5), 8.33 ppm (s, 1H, Ar-H, H-1).}$$

9-Aminoanthracene (277)

![Diagram of 9-Aminoanthracene (277)]
9-Nitroanthracene 280 (7.24 g, 32.50 mmol) was suspended in glacial acetic acid (145 mL) and heated to 70–80 °C for 2 hours. SnCl₂ (31.00 g, 163.2 mmol) in concentrated HCl (110 mL) was added dropwise to the clear solution. The resulting yellow precipitate was stirred at 80 °C for a further 30 minutes, cooled to room temperature, filtered, washed with concentrated HCl (3 X 10 mL), treated with a solution of 5 % NaOH (50 mL) for approximately 15 minutes, filtered, washed thoroughly with water until the washings were neutral and vacuum-dried at 50 °C for 6 hours to yield 277 as a yellow powder (2.70 g, 13.90 mmol, 43 % yield); M.p. = 165-167 °C, lit. M.p. = 165-170 °C. Analytical data were in accordance with the literature.

δH (400 MHz, CDCl₃): 3.54 (br. s, 2H, NH₂, H-6), 7.29-7.37 (m, 4H, Ar-H, H-3, H-4), 7.79-7.86 (m, 4H, Ar-H, H-2, H-5), 7.90 ppm (s, Ar-H, 1H, H-1).

5.4.2 9- and 9,10-Substituted Triptycenes

9,10-Dihexyltriptycene (284)

Anthranilic acid 16 (1.97 g, 14.40 mmol, 2.25 equiv.) was dissolved in THF (90 mL) and added dropwise over 4 hours to a solution of isoamyl nitrite (2.1 mL, 15.40 mmol, 2.4 equiv.) and 9,10-dihexylanthracene 238 (2.21 g, 6.40 mmol, 1.0 equiv.) in chloroform (250 mL) and heated under reflux. After the addition was complete, the reaction was stirred under reflux for a further 15 minutes and the solvent was evaporated to dryness. The remaining solids were dissolved in xylenes (200 mL), and maleic anhydride (1.50 g, 15.40 mmol, 2.4 equiv.) was added. This mixture was heated under reflux for 15 minutes and allowed to cool. Aqueous workup and
filtration through a plug of silica gel yielded 284 as a yellow powder (459 mg, 1.09 mmol, 17 %); M.p. ≥ 300 °C lit. M.p. not reported; \( R_f = 0.61 \) (CH\(_2\)Cl\(_2\)/n-hexane, 1:1, v/v). Analytical data were as reported in literature. \(^{333}\)

\[ \delta_H \text{ (400 MHz, CDCl}_3\text{): } 1.18 \text{ (t, } J = 7.4 \text{ Hz, 6H, } CH_3, H-8) , 1.68-1.92 \text{ (m, 16H, } CH_2, H-4, H-5, H-6, H-7) , 2.20-2.26 \text{ (m, 4H, } CH_2, H-3) , 7.13 \text{ (dd, } J = 8.1, 1.7 \text{ Hz, 6H, Ar-H, H-1) , 7.56 \text{ ppm (dd, } J = 8.3, 1.7 \text{ Hz, 6H, Ar-H, H-2).} \]

HRMS \( (m/z \text{-ES)}: [M]^+ \text{ calcd. for C}_{32}H_{38} 422.2974, \text{ found 422.2911.} \]

9-Aminotriptycenc (285)

Anthranilic acid 16 (1.06 g, 7.80 mmol, 2.25 equiv.) was dissolved in THF (90 mL) and added dropwise over 4 hours to a solution of isoamyl nitrite (1.1 mL, 8.28 mmol, 2.4 equiv.) and 9-aminoanthracene 277 (928 mg, 3.45 mmol, 1.0 equiv.) in chloroform (65 mL) and heated under reflux. After the addition was complete, the reaction was stirred under reflux for a further 15 minutes and the solvent was evaporated to dryness. The remaining solids were dissolved in xylenes (50 mL), and maleic anhydride (813 mg, 8.30 mmol, 2.4 equiv.) was added. This mixture was heated under reflux for 15 minutes and allowed to cool. Aqueous workup and filtration through a plug of silica gel yielded 285 as a brown powder (323 mg, 1.20 mmol, 36 %); M.p. = 216-218 °C, lit. M.p. = 218 °C; \(^{419}\) \( R_f = 0.77 \) (CH\(_2\)Cl\(_2\)/n-hexane, 1:1, v/v). Analytical data were as reported in literature. \(^{419}\)
\( \delta_H (400 \text{ MHz, CDCl}_3): \)

- 3.06 (br. s, 2H, NH\(_2\), H-3), 5.19 (s, 1H, CH, H-4), 7.03 (dd, \( J = 7.3, 2.1 \text{ Hz}, 6\text{H}, \text{Ar-}H, \text{H-1} \)), 7.25 ppm (dd, \( J = 7.3, 2.1 \text{ Hz}, 6\text{H}, \text{Ar-}H, \text{H-2} \)).

**9,10-Diaminotriptycene (286)**

![9,10-Diaminotriptycene (286)](image)

Anthranilic acid 16 (1.06 g, 7.80 mmol, 2.25 equiv.) was dissolved in THF (90 mL) and added dropwise over 4 hours to a solution of isoamyl nitrite (1.1 mL, 8.28 mmol, 2.4 equiv.) and 9,10-diaminoanthracene 276 (717 mg, 3.45 mmol, 1.0 equiv.) in chloroform (65 mL) and heated under reflux. After the addition was complete, the reaction was stirred under reflux for a further 15 minutes and the solvent was evaporated to dryness. The remaining solids were dissolved in xylenes (50 mL), and maleic anhydride (813 mg, 8.30 mmol, 2.4 equiv.) was added. This mixture was heated under reflux for 15 minutes and allowed to cool. Aqueous workup and filtration through a plug of silica gel yielded 286 as a brown powder (568 mg, 2.00 mmol, 58 %); M.p. = 290-292 °C, lit. M.p. = 290-292 °C;\(^{334} \) R\(_f\) = 0.72 (CH\(_2\)Cl\(_2\)/n-hexane, 1:1, v/v). Analytical data were as reported in literature.\(^{334} \)

\( \delta_H (400 \text{ MHz, CDCl}_3): \)

- 5.85 (br. s, 4H, NH\(_2\), H-3), 7.01-7.06 (m, 6H, Ar-\( H\), H-1), 7.21-7.28 ppm (m, 6H, Ar-\( H\), H-2).
5.4.3 2,3,6,7,14,15-Hexasubstituted triptycene scaffolds

2,3,6,7,14,15-Hexabromotriptycene (292)

Triptycene 6 (1.07 g, 4.20 mmol, 1.0 equiv.) was dissolved in chloroform (80 mL) in a round-bottom flask. Iron filings (30 mg, 0.50 mmol, 0.1 equiv.) were added, and the solution was stirred at 25 °C for 15 minutes. Bromine (1.35 mL, 26.3 mmol, 6.3 equiv.) was added, and the solution was heated under reflux for 1 hour, during which time the initially reddish-brown solution turned reddish-orange. The flask was removed from heat, and chloroform and excess bromine were removed under vacuum. The resulting brown powder was dissolved in chloroform (100 mL) and flushed through a pad of silica using chloroform as eluent (100 mL). The filtrate was evaporated to dryness. The crude white powder crystallized from acetone to yield 292 as white powder. The mother liquor was evaporated to dryness and recrystallised again to afford a second crop to give a combined yield of 292 (1.84 g, 2.55 mmol, 61 %); M.p. > 300 °C, lit. M.p. > 350 °C.\(^{314}\) Analytical data were as reported in literature.\(^{314}\)

\[ \delta_H (400 \text{ MHz, CDCl}_3): \quad 5.23 \text{ (s, 2H, CH-H-2), 7.59 ppm (s, 6H, Ar-H, H-1).} \]
2,3,6,7,14,15-Hexabromo-9,10-dihexyltriptycene (293)

Triptycene 284 (363 mg, 1.05 mmol, 1.0 equiv.) was dissolved in chloroform (80 mL) in a round-bottom flask. Iron filings (6 mg, 0.10 mmol, 0.1 equiv.) were added, and the solution was stirred at 25 °C for 15 minutes. Bromine (0.2 mL, 6.60 mmol, 6.3 equiv.) was added, and the solution was heated under reflux for 12 hours, during which time the initially reddish-brown solution turned reddish-orange. The flask was removed from heat, and chloroform and excess bromine were removed under vacuum. The resulting brown powder was dissolved in chloroform (25 mL) and flushed through a pad of silica using additional chloroform as eluent (50 mL). The filtrate was evaporated to dryness. The crude white powder crystallized from acetone to yield 293 as a white powder. The mother liquor was evaporated to dryness and recrystallised again to afford a second crop to give a combined yield of compound 293 (250 mg, 0.273 mmol 26 %); M.p. > 300 °C lit. M.p. not reported; Analytical data were as reported in literature.\textsuperscript{333}

\(\delta_H\) (400 MHz, CDCl\textsubscript{3}): 1.16 (t, \(J = 7.4\) Hz, 6H, CH\textsubscript{3}, H-7), 1.75-2.05 (m, 16H, CH\textsubscript{2}, H-3, H-4, H-5, H-6), 2.41-2.76 (m, 4H, CH\textsubscript{2}, H-2), 7.51 ppm (s, 6H, Ar-H, H-1).

HRMS \(m/z\) -ES: \([M+H]^+\) calcd. for C\textsubscript{32}H\textsubscript{33}Br\textsubscript{6} 890.7683, found 890.7640.

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Triptycene 292\textsuperscript{314} (180 mg, 0.25 mmol, 1.0 equiv.) was placed into a round-bottom flask under argon atmosphere and dissolved in anhydrous THF (100 mL). Bis(pinacolato)diboron (3.01 g, 12.00 mmol, 48.0 equiv.), \( \text{PdCl}_2(\text{PPh}_3)_2 \) (9 mg, 0.013 mmol, 0.05 equiv.) and \( \text{CS}_2 \text{CO}_3 \) (815 mg, 2.50 mmol, 10.0 equiv.) were added and the reaction mixture was heated to 67 °C for 18 hours. The progress of the reaction was followed by TLC. After consumption of the starting material the solvent was removed under reduced pressure and the residue was dissolved in \( \text{CH}_2\text{Cl}_2 \). The crude product mixture was washed sequentially with a saturated aqueous NaHCO\(_3\) (3 X 50 mL), water (3 X 50 mL) and brine (3 X 50 mL). The organic phase was dried with NaSO\(_4\) and the solvent was removed under reduced pressure. Recrystallisation from EtOAc/\( \eta \)-hexane yielded 296 as a white solid (91 mg, 0.90 mmol, 36%); M.p. = 128-130 °C; \( R_f = 0.23 \); (EtOAc/\( \eta \)-hexane, 1:5, v/v).

\( \delta_H \) (400 MHz, CDCl\(_3\)): 1.31 (s, 72H, \( CH_3 \), H-3), 5.41 (s, 2H, CH, H-2), 7.60 ppm (s, 6H, Ar-H, H-1).

\( \delta_C \) (100 MHz, CDCl\(_3\)): 24.9, 54.0, 83.6, 128.9, 132.2, 145.8 ppm.

HRMS (\( m/z \) -ES): [M]\(^+\) calcd. for \( \text{C}_{56}\text{H}_{80}\text{B}_6\text{O}_{12} \) 1010.6208, found 1010.6243.

UV/vis (\( \text{CH}_2\text{Cl}_2 \)): \( \lambda_{\text{max}} \) (lg \( e \)) = 219 (4.07), 257 nm (3.15).
**2,3,6,7,14,15-Hexakis[(trimethylsilyl)ethynyl]-triptycene (302)**

A mixture of triptycene 292 (180 mg, 0.25 mmol, 1.0 equiv.), PdCl₂(PPh₃)₂ (107 mg, 0.16 mmol, 0.6 equiv.), Cul (30 mg, 0.16 mmol, 0.6 equiv.) triphenylphosphine (79 mg, 0.30 mmol, 1.2 equiv.), trimethylsilylacetylene (980 mg, 10.00 mmol, 40.0 equiv.), and diethylamine (12.6 mL, 0.12 mmol, 0.5 equiv.) in dimethylformamide (DMF, 0.5 mL) was irradiated using a microwave at 120 °C for 35 minutes in a heavy-walled glass vial sealed with a teflon septum. The reaction mixture was then filtered and washed with CH₂Cl₂. The filtrate was concentrated under reduced pressure and the yellow residue was purified by column chromatography on silica gel (EtOAc/n-hexane, 5:95, v/v) to yield 302 as a yellow/brown powder (111 mg, 0.12 mmol, 53 %); M.p. ≥ 300 °C; Rᵢ = 0.86 (CH₂Cl₂/n-hexane, 1:2, v/v).

δ₁H (400 MHz, CDCl₃): 0.22 (s, 54H, CH₃, H-3), 5.20 (s, 2H, CH, H-2), 7.39 ppm (s, 6H, Ar-H, H-1).

δC (100 MHz, CDCl₃): 0.1, 52.6, 98.2, 103.1, 123.5, 127.5, 143.4 ppm.

HRMS (m/z -ES): [M+H]⁺ calcd. for C₅₀H₆₅Si₆ 831.3467, found 831.3456.

UV/vis (CH₂Cl₂): λ_max (lg ε) = 229 (4.92), 247nm (3.14).
2,3,6,7,14,15-Hexaethynyl-triptycene (304)

Triptycene 302 (208 mg, 0.25 mmol, 1.0 equiv.) was dissolved in CH₂Cl₂ (50 mL) and TBAF (1M in THF) (1.5 mL, 1.50 mmol, 6.0 equiv.) was added and the mixture was stirred for 12 hours at room temperature. The reaction was monitored by TLC using CH₂Cl₂/n-hexane (1:1, v/v). Upon completion, the solution was filtered through a plug of silica using CH₂Cl₂ as eluent. Solvent was removed in vacuo and the residue recrystallised using CHCl₃/MeOH to yield 304 as a yellow solid (76 mg, 0.19 mmol, 76 %); M.p. = 297-299 °C; Rᵣ = 0.78 (EtOAc/n-hexane, 1:5, v/v).

δₓ (400 MHz, CDCl₃): 3.26 (s, 6H, CH, H-3), 5.33 (s, 2H, CH, H-2), 7.51 ppm (s, 6H, Ar-H, H-1).

δₓ (100 MHz, CDCl₃): 52.2, 80.9, 81.5, 122.8, 127.8, 143.5 ppm.


UV/vis (CH₂Cl₂): λₓmax (lg ε) = 230 (4.94), 253 nm (3.40).
2,3,6,7,14,15-Hexakis[(4-ethynylphenyl)ethynyl]-triptycene (307)

Triptycene 306 (286 mg, 0.20 mmol, 1.0 equiv.) was dissolved in CH₂Cl₂ and TBAF (1M in THF) (1.5 mL, 1.50 mmol, 6.0 equiv.) was added and the mixture was stirred at room temperature for 12 hours. The reaction was followed by TLC using CH₂Cl₂/n-hexane (1:1, v/v). Upon completion, the solution was filtered through a plug of silica using CH₂Cl₂ as eluent. The solvent was removed in vacuo and the residue recrystallised using CH₂Cl₂/MeOH to yield 307 as a yellow solid (120 mg, 0.12 mmol, 63 %); M.p. > 300 °C; Rf = 0.63 (EtOAc/n-hexane, 1:5, v/v).

δ_H (400 MHz, CDCl₃): 3.18 (s, 6H, CH, H-4), 5.43 (s, 2H, CH, H-5), 7.43-7.51 (m, 24H, Ar-H, H-2, H-3), 7.59 ppm (s, 6H, Ar-H, H-1).

δ_C (100 MHz, CDCl₃): 50.9, 79.2, 83.2, 90.2, 90.9, 131.5, 131.6, 131.7, 132.2, 133.1, 143.6 ppm.

HRMS (m/z -ES): [M]⁺ calcd. for C₈₀H₅₈ 998.2974, found 998.2966.

UV/vis (CH₂Cl₂): λ_max (lg ε) = 249 (5.03), 281 nm (3.80).
2,3,6,7,14,15-Hexakis[(trimethylsilyl)buta-1,3-diyn-1-yl]-triptycene (308)

To a slurry of CuCl (552 mg, 5.63 mmol, 45.0 equiv.), ethynyltrimethylsilane (306 mg, 3.125 mmol, 25.0 equiv.) and Cu(OAc)$_2$ (1.36 g, 7.50 mmol, 60.0 equiv.) in dry pyridine (20 mL) was added dropwise a solution of 304 (50 mg, 0.125 mmol, 1.0 equiv.) in dry pyridine (10 mL, 3.40 mmol, 27.2 equiv.) at 60 °C. The mixture was stirred for an additional 2 hours at the same temperature. The mixture was then cooled and the pyridine was removed *in vacuo*. The residue was taken up in CH$_2$Cl$_2$ (50 mL) and washed with 1.0 M aqueous HCl (3 x 30 mL). The aqueous solution was extracted with CH$_2$Cl$_2$ (2 x 30 mL). The organic extracts were combined, washed successively with saturated aqueous NaHCO$_3$ (2 x 50 mL) and brine (2 x 50 mL), dried over Na$_2$SO$_4$. The organic extracts were then concentrated and subjected to column chromatography on silica gel eluted with CH$_2$Cl$_2$ and petroleum ether (1:5) to yield 308 as a yellow solid (19 mg, 0.02 mmol, 16 %) yield; M.p. ≥ 300 °C; $R_f$ = 0.89 (EtOAc/n-hexane, 1:5, v/v).

$\delta_H$ (400 MHz, CDCl$_3$): 0.25 (s, 54H, $CH_3$, H-3), 5.37 (s, 2H, $CH$, H-2), 7.42 ppm (s, 6H, Ar-$H$, H-1).

$\delta_C$ (100 MHz, CDCl$_3$): 0.6, 52.0, 83.7, 84.1, 97.8, 102.6, 124.6, 127.0, 142.8 ppm.

HRMS ($m/z$ -ES): [M]$^+$ calcd. for C$_{62}$H$_{62}$Si$_6$ 975.3545, found 975.3527.
UV/vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (lg e) = 287 nm (3.67).

5.5 Rigid covalently linked hexaporphyrin arrays

5.5.1 Porphyrin starting materials

5,15-Bis(1-methylpropyl)porphyrin (311)

The method used was adapted from the procedure of Lindsey et al.$^{109}$ A reaction vessel was charged with CH$_2$Cl$_2$ (2000 mL), dipyrromethane 128 (3.61 g, 24.80 mmol, 1.0 equiv.) and 2-methylbutanal (2.13 g, 24.80 mmol, 1.0 equiv.). A rubber septum was used to seal the top of the bottle and the solvent was degassed with a stream of argon for 30 minutes. Trifluoroacetic acid (191 µL, 2.48 mmol, 0.1 equiv.) was injected into the vessel dropwise via a syringe, then the vessel was shielded from light and the reaction was allowed to stir for 16 hours under argon at room temperature. The septum was removed, DDQ (11.6 g, 51.10 mmol, 2.1 equiv.) was added to the mixture and the reaction mixture was allowed to stir for a further 30 minutes at room temperature. Triethylamine (12.5 mL) was added to quench the reaction and the crude mixture was reduced to 500 mL before being subjected to chromatography using CH$_2$Cl$_2$/n-hexane (1:2, v/v) as an eluent. The porphyrin containing fractions were collected and dried and the dark purple residue was recrystallised using CH$_2$Cl$_2$/MeOH to yield 311 as purple crystals (3.87 g, 9.18 mmol, 37%); M.p. = 297-299 °C; R$_f$ = 0.53 (CH$_2$Cl$_2$/n-hexane, 1:2, v/v).
δ_H (400 MHz, CDCl₃): -2.39 (s, 2H, NH, H-1), 0.95 (t, J = 7.5 Hz, 6H, CH₃, H-7), 2.35 (d, J = 7.5 Hz, 6H, CH₃, H-8), 2.67-2.73 (m, 4H, CH₂, H-6), 4.82-4.86 (m, 2H, CH, H-5), 9.16 (d, J = 4.7 Hz, 4H, H₇, H-4), 9.55 (d, J = 4.7 Hz, 4H, H₈, H-3), 9.61 ppm (s, 2H, H_meso, H-2).

δ_C (100 MHz, CDCl₃): 12.6, 23.7, 32.8, 39.4, 103.7, 119.9, 128.0, 130.7, 137.6, 140.0 ppm.

HRMS (m/z -ES): [M+H]^+ calcd. for C_{28}H_{31}N_4 423.2549, found 423.2551.

UV/vis (CH₂Cl₂): λ_max (lg ε) = 401 (4.96), 514 (3.87), 548 (3.73), 590 (3.10), 630 nm (2.97).

[5,15-(1-Ethylpropyl)porphyrinato]nickel(II) (314)

Porphyрин 310 (450 mg, 1.00 mmol, 1.0 equiv) was isolated via condensation reaction and placed in a 100 mL flask with Ni(acac)₂ (388 mg, 1.50 mmol, 1.5 equiv.). Toluene (50 mL) was added, and the mixture was heated under reflux for 3 hours. The progress of the reaction was monitored by TLC using CH₂Cl₂/n-hexane (1:2, v/v) as eluent. Upon completion of the reaction, the solvent was removed in vacuo, and the product was isolated after passage through a plug of silica gel using CH₂Cl₂ as the eluent. Recrystallisation of the product using CH₂Cl₂/MeOH yielded 314 as orange crystals (460 mg, 0.94 mmol, 94%); M.p. = 280-282 °C; R_f= 0.45 (CH₂Cl₂/n-hexane, 1:2, v/v).
\[ \delta_H (400 \text{ MHz, CDCl}_3): \quad 0.93 \text{ (t, } J = 7.4 \text{ Hz, } 12\text{H, CH}_3, \text{ H-6)}, \ 2.72-2.77 \text{ (m, } 8\text{H, CH}_2, \text{ H-5),} \ 4.69-4.74 \text{ (m, } 2\text{H, CH, H-4),} \ 9.14 \text{ (d, } J = 5.1 \text{ Hz, } 4\text{H, } H\beta, \text{ H-3),} \ 9.54 \text{ (d, } J = 5.1 \text{ Hz, } 4\text{H, } H\beta, \text{ H-2),} \ 9.67 \text{ ppm (s, } 2\text{H, } H_{\text{meso}}, \text{ H-1).} \]

\[ \delta_C (100 \text{ MHz, CDCl}_3): \quad 14.0, \ 33.7, \ 49.4, \ 103.4, \ 120.1, \ 130.9, \ 132.0, \ 140.3, \ 142.4 \text{ ppm.} \]

HRMS (m/z -ES): \[ [\text{M+H}]^+ \text{ calcd. for } C_{30}H_{33}N_4Ni \ 507.2059, \ \text{found} \ 507.2126. \]

UV/vis (CH\text{Cl}_2): \[ \lambda_{\text{max}} (\lg \varepsilon) = 405 \ (4.11), \ 523 \text{ nm (3.92).} \]

\textbf{[5,15- Bis(1-Methylpropyl)porphyrinato]nickel(II) (315)}

Porphyrin 311 (422 mg, 1.00 mmol, 1.0 equiv.) was isolated via condensation reaction and placed in a 100 mL flask with Ni(acac)_2 (388 mg, 1.50 mmol, 1.5 equiv.). Toluene (50 mL) was added, and the mixture was heated under reflux for 3 hours. The progress of the reaction was monitored by TLC using CH\text{Cl}_2/n-hexane (1:2, v/v). Upon completion of the reaction, the solvent was removed \textit{in vacuo}, and the product was isolated after passage through a plug of silica gel using CH\text{Cl}_2 as the eluent. Recrystallisation of the product using CH\text{Cl}_2/MeOH yielded 315 as orange crystals (421 mg, 0.88 mmol, 88 %); M.p. = 291-293 °C; R_f = 0.68 (CH\text{Cl}_2/n-hexane, 1:2, v/v).
\[ \delta_H (400 \text{ MHz, CDCl}_3): \]

0.95 (t, \( J = 7.5 \text{ Hz}, 6\text{H}, \text{CH}_3, \text{H}-6), 2.32 (d, 6\text{H}, \( J = 7.5 \text{ Hz}, \text{CH}_3, \text{H}-7), 2.65-2.69 (m, 4\text{H}, \text{CH}_2, \text{H}-5), 4.72-4.78 \]

(m, 2\text{H}, \text{CH}, \text{H}-4), 9.11 (d, \( J = 4.7 \text{ Hz}, 4\text{H}, \text{H}_\beta, \text{H}-3),

9.51 (d, \( J = 4.7 \text{ Hz}, 4\text{H}, \text{H}_\beta, \text{H}-2), 9.56 \text{ ppm (s, 2H, } \text{H}_{\text{meso}, \text{H}-1}).

\[ \delta_C (100 \text{ MHz, CDCl}_3): 13.5, 26.1, 34.2, 41.3, 102.9, 120.9, 130.4, 131.7, 139.8, 141.2 \text{ ppm.} \]

HRMS (m/z -ES):

\[ [\text{M}]^+ \text{ calcd. for } \text{C}_{28}\text{H}_{28}\text{N}_4\text{Ni} 478.1667, \text{found 478.1677.} \]

UV/vis (CH\text{Cl}_2):

\[ \lambda_{\text{max}} (\text{lg } \varepsilon) = 403 \text{ (5.10), 522nm (3.94).} \]

**[5,15-Bis(4-bromophenyl)-10,20-porphyrinato]nickel(II) (324)**

Porphyрин 323 (385 mg, 0.50 mmol, 1.0 equiv.) was isolated via condensation reaction and placed in a 100 mL flask with Ni(acac)\textsubscript{2} (192 mg, 0.75 mmol, 1.5 equiv.). Toluene (50 mL) was added, and the mixture was heated under reflux for 3 hours. The progress of the reaction was monitored by TLC using CH\text{Cl}_2/n-hexane (1:2, v/v). Upon completion of the reaction, the solvent was removed in vacuo and the product was isolated after passage through a plug of silica gel using CH\text{Cl}_2 as the eluent. Recrystallisation of the product using CH\text{Cl}_2/MeOH yielded 324 as orange crystals (380 mg, 0.46 mmol, 91 %); M.p. > 300 °C; \( R_f = 0.88 \) (CH\text{Cl}_2/n-hexane, 1:2, v/v).
δ_H (400 MHz, CDCl₃): 7.68-7.74 (m, 6H, Ar-H, H-6, H-7), 7.82 (d, J = 8.2 Hz, 4H, Ar-H, H-5), 7.89 (d, J = 8.9 Hz, 4H, Ar-H, H-3), 8.04 (d, J = 7.6 Hz, 4H, Ar-H, H-4), 8.74 (d, J = 5.5 Hz, 4H, H_β, H-1), 8.79 ppm (d, J = 5.5 Hz, 4H, H_β, H-2).

δ_C (100 MHz, CDCl₃): 124.3, 128.4, 130.1, 130.9, 131.9, 132.2, 132.8, 132.6, 133.4, 135.8, 139.7, 140.2, 141.0, 146.3 ppm.

HRMS (m/z -ES): [M]^+ calcd. for C_{44}H_{26}Br_{2}N_{4}Ni 825.9878, found 825.9871.

UV/vis (CH₂Cl₂): λ_max (lg ε) = 415 (5.76), 528 nm (4.48).


Porphyрин 311 (239 mg, 0.50 mmol, 1.0 equiv.) was isolated via condensation reaction and placed in a 100 mL flask with NBS (267 mg, 1.50 mmol, 3.0 equiv). The mixture was dissolved in chloroform (100 mL) and pyridine (0.4 μL, 0.05 mmol, 0.1 equiv.) was added, and the mixture was stirred at room temperature for 3 hours. The progress of the reaction was monitored by TLC using CH₂Cl₂/n-hexane (1:2, v/v). Upon completion of the reaction, the solvent was removed in vacuo, and the product was isolated after passage through a plug of silica gel using CH₂Cl₂ as the eluent. Recrystallisation of the product using CH₂Cl₂/MeOH yielded 322 as orange crystals.
(280 mg, 0.44 mmol, 89 %) yield; M.p. ≥ 300 °C; R_f = 0.69 (CH_2Cl_2/n- hexane, 1:2, v/v).

δ_H (400 MHz, CDCl_3): 0.92 (t, J = 7.4 Hz, 6H, CH_3, H-5), 2.21 (d, J = 7.1 Hz, 6H, CH_3, H-6), 2.51-2.56 (m, 4H, CH_2, H-4), 4.45-4.50 (m, 2H, CH, H-3), 9.25 (d, J = 4.8 Hz, 4H, H_P, H-2), 9.33 ppm (d, J = 4.8 Hz, 4H, H_P, H-1).

δ_C (100 MHz, CDCl_3): 13.4, 26.0, 34.1, 41.3, 101.0, 123.1, 131.6, 133.2, 139.7, 141.5 ppm.

HRMS (m/z -ES): [M]^+ calcd. for C_{28}H_{26}Br_{2}N_{4}Ni 633.9878, found 633.9885.

UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 427 (5.14), 552 nm (3.05).

[5-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-10,15,20-triphenylporphyrinato]nickel(II) (327)

A 100 mL Schlenk flask was charged with porphyrin 157 (468 mg, 0.65 mmol, 1.0 equiv.) dried under vacuum. Dry 1,2-dichloroethane (20 mL) and dry triethylamine (0.8 mL, 4.20 mmol, 8.0 equiv.) were added under argon. The solution was degassed via 3 freeze-pump-thaw cycles before the vessel was purged with argon. 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.94 mL, 3.30 mmol, 5.0 equiv.) and
dichlorobis(triphenylphosphine)palladium(II) (8 mg, 0.01 mmol, 0.2 equiv.) were added. The Schlenk tube was sealed and heated to 90 °C overnight. The reaction was quenched with a saturated KCl (10 mL) solution, washed with water (3 X 20 mL) and dried over Na2SO4. The organic solvents were removed in vacuo and subjected to purification via column chromatography. Recrystallisation of the product using CH2Cl2/MeOH yielded 327 as red crystals (236 mg, 0.33 mmol, 51 %); Rf = 0.53 (CH2Cl2/n-hexane, 1:1, v/v); M.p. = 229-231 °C, lit. M.p. = 230 °C. Analytical data were as reported in literature.43

\[ \delta_H (400 \text{ MHz, CDCl}_3) : 1.88 (s, 12H, CH3, H-11), 7.64-7.73 (m, 9H, Ar-H, H-6, H-7, H-9, H-10), 8.16-8.22 (m, 6H, Ar-H, H-5, H-8), 8.72 (d, J = 4.6 \text{ Hz}, 2H, Hé, H-1), 8.85 (d, J = 4.6 \text{ Hz}, 2H, Hé, H-3), 8.97 (d, J = 4.6 \text{ Hz}, 2H, Hé, H-2), 9.89 \text{ ppm (d, J = 4.6 Hz, 2H, Hé, H-4).} \]

[5-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-10,15,20porphyrinato]nickel(II) (224)

A 100 mL Schlenk flask was charged with porphyrin 324 (260 mg, 0.25 mmol, 1.0 equiv.), Pd(PPh3)4 (58 mg, 0.50 mmol, 0.2 equiv.) and dried under high vacuum. Dry THF (10 ml) and K3PO4 (265 mg, 1.25 mmol, 5.0 equiv.) was added and the solution was degassed by three freeze-pump-thaw cycles, before the flask was purged with argon. Bis(pinacolato)doboron (127 mg, 0.50 mmol, 2.0 equiv.) was added and the flask was sealed and stirred at 67 °C for 16 hours. The reaction was followed by TLC.
using \( \text{CH}_2\text{Cl}_2/n\text{-hexane} \) (2:1, \( v/v \)). The reaction was quenched with saturated KCl solution (10 mL), washed with water (3 X 20 mL), and dried with MgSO\(_4\). The solvent was removed \( \text{in vacuo} \) and the residue was subjected to column chromatography using \( \text{CH}_2\text{Cl}_2/n\text{-hexane} \) (1:2, \( v/v \)) and recrystallised from \( \text{CH}_2\text{Cl}_2/n\text{-hexane} \) to yield \( \textbf{328} \) as red/orange crystals (95 mg, 0.12 mmol, 48\%); \( R_f = 0.23 \) (\( \text{CH}_2\text{Cl}_2/n\text{-hexane}, 1:2, v/v \)); M.p. \( > 300 \, ^\circ \text{C} \).

\[ \delta_{\text{H}} \] (400 MHz, CDCl\(_3\)):

\[ 1.31 \text{ (s, \text{12H, CH}_3, H-13)}, \quad 8.04-8.12 \text{ (m, \text{15H, Ar-H, H-6, H-7, H-8, H-10, H-11, H-12})}, \quad 8.16-8.21 \text{ (m, \text{4H, Ar-H, H-5, H-6})}, \quad 8.80 \text{ ppm (app. s, 8H, H}_\beta\text{, H-1, H-2, H-3, H-4)}. \]

\[ \delta_{\text{C}} \] (100 MHz, CDCl\(_3\)):

26.1, 83.2, 118.5, 118.6, 120.3, 120.8, 121.4, 124.6, 124.9, 125.7, 126.4, 126.9, 127.3, 128.7, 131.8, 132.6, 132.9, 133.3, 134.3, 140.1, 140.5, 142.0, 142.2, 143.4, 145.3 ppm.

HRMS (\( m/\text{z} \)-ES):

\[ [\text{M}]^+ \text{ calcd. for C}_{50}\text{H}_{39}\text{BN}_4\text{NiO}_2 \text{ 769.2520, found 796.2534}. \]

UV/vis (CH\(_2\text{Cl}_2\)):

\[ \lambda_{\text{max}} (\text{lg } \varepsilon) = 417 \, (5.01), \quad 529 \, (3.93), \quad 618 \, \text{nm (3.44)}. \]

\[ 5,5'-\text{(1,4-Dibenzene)-bis}[[10,15,20-\text{triphenylporphyrinato} \text{nickel(II)}] \text{ (330)} \]
A 100 mL Schlenk flask was charged with porphyrin 324 (260 mg, 0.25 mmol, 1.0 equiv.), Pd(PPh₃)₄ (58 mg, 0.50 mmol, 0.2 equiv.) and dried under high vacuum. Dry THF (10 ml) and K₃PO₄ (265 mg, 1.25 mmol, 5.0 equiv.) was added and the solution was degassed via three freeze-pump-thaw cycles, before the flask was purged with argon. Pinacol borolane (198 mg, 1.25 mmol, 5.0 equiv.) was added and the flask was sealed and stirred at 67 °C for 16 hours. The reaction was followed by TLC using CH₂Cl₂/n-hexane (2:1, v/v). The reaction was quenched with saturated KCl solution (10 mL), washed with water (3 X 20 mL), and dried with MgSO₄. The solvent was removed in vacuo and the residue was subjected to column chromatography using CH₂Cl₂/n-hexane (1:2, v/v) and recrystallised from CH₂Cl₂/n-hexane to yield 330 as red/orange crystals (56 mg, 0.04 mmol, 14 %); Rₜ = 0.19 (CH₂Cl₂/n-hexane, 1:2, v/v); M.p. ≥ 300 °C.

δₜ (400 MHz, CDCl₃): 1.28 (s, 24H, C/H₃, H-12), 7.74 (d, J = 7.5 Hz, 16H, Ar-H, H-6, H-8, H-9), 7.86-7.90 (m, 16H, Ar-H, H-5, H-7, H-10), 8.14 (d, J = 7.5 Hz, 4H, Ar-H, H-11) 8.92 ppm (app. s, 16H, H₆, H-1, H-2, H-3, H-4).

δₜ (100 MHz, CDCl₃): 24.9, 85.4, 116.2, 120.4, 122.6, 123.2, 123.9, 125.8, 126.3, 126.7, 129.2, 129.8, 130.7, 132.0, 133.4, 134.1, 135.6, 136.0, 136.3, 136.8, 137.2, 138.2, 140.3, 141.0, 143.6 ppm.

HRMS (m/z -ES): [M+H]+ calcd. for C₁₀₀H₁₇₁B₂N₈Ni₂O₄ 1591.4883 found, 1591.4826.

UV/vis (CH₂Cl₂): λₘₐₓ (lg ε) = 414 (5.71), 505 (5.09), 541 (4.16), 578 nm (3.63).
[5,15-Bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-10,20-porphyrinato]nickel(II) (331)

A 100 mL Schlenk flask was charged with porphyrin 324 (260 mg, 0.25 mmol, 1.0 equiv.), Pd(PPh<sub>3</sub>)<sub>4</sub> (58 mg, 0.50 mmol, 0.2 equiv.) and dried under high vacuum. Dry THF (10 ml) and K<sub>3</sub>P<sub>4</sub> (265 mg, 1.25 mmol, 5.0 equiv.) were added and the solution was degassed by three freeze-pump-thaw cycles before the flask was purged with argon. Bis(pinacolato)diboron (127 mg, 0.50 mmol, 2.0 equiv) was added and the flask was sealed and stirred at 67 °C for 16 hours. The reaction was followed by TLC using CH<sub>2</sub>Cl<sub>2</sub>/n-hexane (1:2, v/v). The reaction was quenched with saturated KCl solution (10 mL), washed with water (3 X 20 mL), and dried with MgSO<sub>4</sub>. The solvent was removed in vacuo and the residue was subjected to column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/n-hexane (1:2, v/v) and recrystallised from CH<sub>2</sub>Cl<sub>2</sub>/n-hexane to yield 331 as red crystals (91 mg, 0.01 mmol, 41 %); R<sub>f</sub> = 0.5 (CH<sub>2</sub>Cl<sub>2</sub>/n-hexane, 1:2, v/v); M.p. = 287-289 °C.

δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>): 1.37 (s, 24H, CH<sub>3</sub>, H-10), 7.52-7.55 (m, 6H, Ar-H, H-8, H-9), 7.57-7.62 (m, 8H, Ar-H, H-5, H-7), 7.70 (d, J = 7.5 Hz 4H, Ar-H, H-6), 8.00-8.06 (m, 4H, H-2, H-3), 8.76 ppm (d, J = 4.2 Hz, 4H, H<sub>1</sub>, H-1, H-4).

δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>): 24.9, 88.4, 126.7, 127.7, 128.3, 128.4, 131.8, 131.9, 132.0, 132.6, 133.1, 133.5, 135.1, 139.2, 140.7, 145.4 ppm.
HRMS (m/z -ES): \[ \text{[M]}^+ \text{ calcd. for } C_{56}H_{50}B_2N_4NiO_4 \ 922.3372, \text{ found} \ 922.3375. \]

UV/vis (CH$_2$Cl$_2$): \( \lambda_{\text{max}} \ (\varepsilon) = 415 \ (5.10), \ 528 \text{ nm} \ (3.97). \)

Procedure G: general procedure for phenylacetylene porphyrin organolithium reactions

A 100 mL three-neck round-bottom flask was dried under high vacuum, purged with argon and charged with 1-bromo-4-ethynylbenzene. Dry diethyl ether (15 mL) was added and the solution was cooled to -70 °C. n-Butyllithium was added dropwise over 1 hour at -70 °C. The reaction mixture was warmed to -40 °C and ~2 mL dry THF was added until a white/pink suspension formed. The porphyrin precursor was dissolved in THF (~80 mL) and added rapidly to the vigorously stirred solution and the reaction was stirred at room temperature for a further 4 hours (colour changed to brown). Saturated aqueous ammonium chloride (2 mL, colour changed to green) and DDQ were added. After 1 hour, the crude product was filtered through a layer of silica gel using CH$_2$Cl$_2$ as eluent. Recrystallisation from CH$_2$Cl$_2$/MeOH yielded the desired phenylethynylporphyrin.

5-(4-Ethynylphenyl)-10,20-diphenylporphyrin (333)

Prepared via organolithium reaction according to procedure G from 1-bromo-4-ethynylbenzene (270 mg, 1.50 mmol, 6.0 equiv.), n-butyllithium (0.8 mL of a 2.5 M
solution in hexane, 2.00 mmol, 8.0 equiv.), 5-bromo-10,20-diphenylporphyrin 321 (135 mg, 0.25 mmol, 1.0 equiv.) and DDQ (850 mg, 3.75 mmol, 15.0 equiv.) to yield 333 as purple crystals (84 mg, 0.15 mmol, 68 %); M.p. > 300 °C, lit. M.p. > 300 °C;\textsuperscript{420} R_f = 0.36 (CH_2Cl_2/n-hexane, 1:2, v/v). Analytical data were as reported in literature.\textsuperscript{420}

\[ \delta_H (400 MHz, CDCl_3): \]
-2.89 (s, 2H, NH, H-1), 3.40 (s, 1H, CH, H-9), 7.65–7.78 (m, 6H, Ar-H, H-11, H-12), 7.86 (d, J = 7.6 Hz, 2H, Ar-H, H-7), 8.20 (d, J = 7.6 Hz, 2H, Ar-H, H-8), 8.04–8.09 (m, 4H, Ar-H, H-10), 8.80 (d, J = 4.8 Hz, 2H, H_β, H-5), 8.88 (d, J = 4.8 Hz, 2H, H_β, H-6), 9.06 (d, J = 4.8 Hz, 2H, H_β, H-3), 10.13 ppm (s, 1H, H_meso, H-2).

[5-(4-Ethynylphenyl)-10,20-diphenylporphyrinato]nickel(II) (334)

![Diagram of 5-(4-Ethynylphenyl)-10,20-diphenylporphyrinato]nickel(II) (334)

Prepared via organolithium reaction according to procedure G from 1-bromo-4-ethynylbenzene (270 mg, 1.50 mmol, 6.0 equiv.), n-butyllithium (0.8 mL of a 2.5 M solution in hexane, 2.0 mmol, 8.0 equiv.), [5-bromo-10,20-diphenylporphyrinato]nickel(II) 322 (150 mg, 0.25 mmol, 1.0 equiv.) and DDQ (850 mg, 3.75 mmol, 15.0 equiv.) to yield 334 as red/purple crystals (130 mg, 0.21 mmol, 83 %) yield; M.p. ≥ 300 °C, lit. M.p. > 300 °C;\textsuperscript{154} R_f = 0.72 (CH_2Cl_2/n-hexane, 1:1, v/v). Analytical data were as reported in literature.\textsuperscript{154}
$\delta_\text{H} (400 \text{ MHz, CDCl}_3)$: 3.33 (s, 1H, CH, H-8), 7.73-7.78 (m, 6H, Ar-H, H-10, H-11), 7.85 (d, $J = 7.5$ Hz, 4H, Ar-H, H-9), 8.02 (d, $J = 7.3$ Hz, 2H, Ar-H, H-7), 8.85 (d, $J = 4.8$ Hz, 2H, Ar-H, H-5), 9.03 (d, $J = 4.8$ Hz, 2H, Ar-H, H-3), 9.21 (d, $J = 4.8$ Hz, 2H, Ar-H, H-2), 9.88 ppm (s, 1H, Ar-H, H-1).

5-(4-Ethynylphenyl)-10,20-ditolyIporphyrin (335)

Prepared via organolithium reaction according to procedure G above from 1-bromo-4-ethynylbenzene (270 mg, 1.50 mmol, 6.0 equiv.), n-butyllithium (0.8 mL of a 2.5 M solution in hexane, 2.00 mmol, 8.0 equiv.), [5-bromo-10,20-ditolyIporphyrinato]nickel(II) 320 (157 mg, 0.25 mmol, 1.0 equiv.) and DDQ (850 mg, 3.75 mmol, 15.0 equiv.) to yield 335 as purple crystals (97 mg, 0.15 mmol, 76 %); M.p. $>$ 300 °C, lit. M.p. $>$ 300 °C; $R_f = 0.77$ (CH$_2$Cl$_2$/n-hexane, 1:1, v/v). Analytical data were as reported in literature.$^{261}$

$\delta_\text{H} (400 \text{ MHz, CDCl}_3)$: 2.93 (s, 6H, CH$_3$, H-11), 3.07 (s, 1H, CH, H-8), 7.08 (d, $J = 7.6$ Hz, 4H, Ar-H, H-10), 7.93 (d, $J = 7.9$ Hz, 4H, Ar-H, H-9), 8.23 (d, $J = 7.6$ Hz, 4H, Ar-H, H-6), 8.32 (d, $J = 7.6$ Hz, 4H, Ar-H, H-7), 8.92 (d, $J = 4.8$ Hz, 2H, H$_\beta$, H-4), 9.06 (d, $J = 4.8$ Hz, 2H, H$_\beta$, H-5), 9.18 (d, $J = 4.8$ Hz, 2H, H$_\beta$, H-3), 9.18 (d, $J = 4.8$ Hz, 2H, H$_\beta$, H-2), 9.88 ppm (s, 1H, Ar-H, H-1).
Hz, 2H, Hβ, H-3), 9.38 (d, J = 4.8 Hz, 2H, Hβ, H-2), 10.17 ppm (s, 1H, Ar-H, H-1).

5-(4-Ethynylphenyl)-10,20-bis(1-ethylpropyl)porphyrinato]nickel(II) (336)

Prepared via organolithium reaction according to procedure G above from 1-bromo-4-ethynylbenzene (270 mg, 1.50 mmol, 6.0 equiv.), n-butyllithium (0.8 mL of a 2.5 M solution in hexane, 2.00 mmol, 8.0 equiv.), [5-bromo-10,20-bis(2-ethylpropyl)porphyrinato]nickel(II) 318 (127 mg, 0.25 mmol, 1.0 equiv.) and DDQ (850 mg, 3.75 mmol, 15.0 equiv.) to yield 336 as red crystals (147 mg, 0.21 mmol, 82%); M.p. ≥ 300 °C; Rf = 0.56 (CH2Cl2/n-hexane, 1:2, v/v).

δH (400 MHz, CDCl3): 0.98 (t, J = 7.4 Hz, 12H, CH3, H-11), 2.23 (d, J = 7.1 Hz, 8H, CH2, H-10), 3.38 (s, 1H, CH, H-8), 4.61-4.71 (m, 2H, CH, H-9), 7.82 (d, J = 7.9 Hz, 2H, Ar-H, H-6), 7.95 (d, J = 7.9 Hz, 2H, Ar-H, H-7), 8.70 (d, J = 5.2 Hz, 2H, Hβ, H-4), 9.09 (d, J = 5.2 Hz, 2H, Hβ, H-3), 9.37 (d, J = 5.2 Hz, 2H, Hβ, H-5), 9.41-9.51 ppm (m, 3H, Ar-H, Hmeso/ Hβ, H-2, H-1).

δC (100 MHz, CDCl3): 13.4, 34.1, 41.4, 77.6, 83.2, 102.6, 116.2, 121.0, 121.6, 130.1, 130.2, 130.7, 131.4, 131.9, 132.0, 133.0, 139.2, 140.5, 140.1, 141.2 ppm.
HRMS (m/z -ES): [M]^+ calcd. for C_{38}H_{36}N_{4}Ni 606.2293, found 606.2272.

UV/vis (CH_2Cl_2): \( \lambda_{\text{max}} (\lg \varepsilon) = 412 \ (5.31), 535 \text{ nm} \ (3.87), 550 \text{ nm} \ (3.03). \)

5-(4-Ethynylphenyl)-10,20-bis(1-methylpropyl)porphyrinato|nickel(II) (337)

Prepared \textit{via} organolithium reaction according to procedure G from 1-bromo-4-ethynylbenzene (270 mg, 1.50 mmol, 6.0 equiv.), n-butyllithium (0.8 mL of a 2.5 M solution in hexane, 2.00 mmol, 8.0 equiv.), [5,15-bis(2-methylpropyl)porphyrinato|nickel(II) 323 (120 mg, 0.25 mmol, 1.0 equiv.) and DDQ (850 mg, 3.75 mmol, 15.0 equiv.) to yield 337 as red crystals (139 mg, 0.24 mmol, 94 %); M.p. \( \geq 300 \text{ C}; R_f = 0.56 \) (CH_2Cl_2/n-hexane, 1:2, v/v).

\( \delta_H \) (400 MHz, CDCl_3):

- 0.95 (t, \( J = 7.2 \text{ Hz}, 6\text{H}, CH_3, H-11\)), 2.31 (d, \( J = 7.1 \text{ Hz}, 6\text{H}, CH_3, H-12\)), 2.59-2.66 (m, 4\text{H}, CH_2, H-10), 3.41 (s, 1\text{H}, CH, H-8), 4.65-4.70 (m, 2\text{H}, CH, H-9), 7.83 (d, \( J = 7.9 \text{ Hz}, 2\text{H}, Ar-H, H-6\)), 7.93 (d, \( J = 7.9 \text{ Hz}, 2\text{H}, Ar-H, H-7\)), 8.70 (d, \( J = 5.0 \text{ Hz}, 2\text{H}, H_\beta, H-3\)), 9.08 (d, \( J = 4.8 \text{ Hz}, 2\text{H}, H_\beta, H-4\)), 9.36 (d, \( J = 5.0 \text{ Hz}, 2\text{H}, H_\beta, H-2\)), 9.45 (d, \( J = 4.8 \text{ Hz}, 2\text{H}, H_\beta, H-5\)), 9.48 ppm (s, 1\text{H}, Ar-H, H-1).
δ_C (100 MHz, CDCl₃): 13.4, 26.1, 34.1, 41.4, 77.6, 83.2, 102.6, 116.2, 121.0, 121.6, 126.5, 130.1, 130.2, 130.7, 131.4, 131.9, 132.2, 133.0, 139.2, 140.0, 141.1 ppm.

HRMS (m/z -ES): [M]^+ calcd. for C_{36}H_{32}N_{4}Ni 578.1980, found 578.1923.

UV/vis (CH₂Cl₂): \( \lambda_{\text{max}} (\log \varepsilon) = 414 (5.75), 532 (4.02), 541 \text{ nm} (3.10). \)

[5-(4-Ethynylphenyl)-octaethylporphyrinato]nickel(II) (340)

Prepared via organolithium reaction according to procedure G from 1-bromo-4-ethynylbenzene (270 mg, 1.50 mmol, 6.0 equiv.), n-butyllithium (0.8 mL of a 2.5 M solution in hexane, 2.00 mmol, 8.0 equiv.), [2,3,7,8,12,13,17,18-octaethylporphyrinato]nickel(II) 339 (148 mg, 0.25 mmol, 1.0 equiv.) and DDQ (850 mg, 3.75 mmol, 15.0 equiv.) to yield 340 as red/purple crystals (152 mg, 0.22 mmol, 88%); M.p. > 300 °C; R_f = 0.49 (CH₂Cl₂/ n-hexane, 1:2, v/v).

δ_H (400 MHz, CDCl₃): 0.98 (t, \( J = 7.4 \text{ Hz}, 6\text{H}, CH_{3}, \text{H-13} \)), 1.97 (t, \( J = 7.4 \text{ Hz}, 6\text{H}, CH_{3}, \text{H-9} \)), 2.18-2.24 (m, 12H, CH₃, H-6, H-9), 2.73-2.79 (m, 4H, CH₂, H-12), 3.38 (s, 1H, CH, H-5), 4.05-4.18 (m, 12H, CH₂, H-7, H-8, H-10), 7.92 (d, \( J = 7.1 \text{ Hz}, 2\text{H, Ar-H, H-3} \)), 8.25 (d, \( J = 7.1 \text{ Hz}, 2\text{H, H-4} \)), 9.33 (s, 1H, \( H_{\text{meso}}, \text{H-1} \)), 9.45 ppm (s, 2H, \( H_{\text{meso}}, \text{H-2} \)).

(Note: The alkyl carbons 10, 12 and 11, 13 are homootopic)
\[ \delta_c (100 \text{ MHz}, \text{CDCl}_3): \ 13.4, 18.0, 26.1, 29.3, 34.1, 41.4, 77.6, 83.2, 102.6, 116.2, 121.0, 121.6, 126.5, 130.1, 130.2, 130.7, 131.4, 131.9, 132.2, 133.0, 139.2, 140.0, 141.1 \text{ ppm}. \]

HRMS (m/z -ES): \[ [M]^+ \text{ calcd. for C}_{44}H_{48}N_4Ni 690.3232, \text{ found 690.3242}. \]

UV/vis (CH\(_2\)Cl\(_2\)): \[ \lambda_{\text{max}}(\lg \varepsilon) = 418 (5.02), 536 (3.61), 579 \text{ nm (2.97)}. \]

5.5.2 Triptycene precursors

2,6,14-Trinitrotriptycene (343)

Triptycene 6 (2.5 g, 10.00 mmol, 1.0 equiv.) was dissolved in concentrated HNO\(_3\) (100 mL, 65 %, 1.60 mol, 155.0 equiv.), and heated to 75 °C for 24 hours. The brown solution was cooled to room temperature then poured into H\(_2\)O (1 L) and stirred. The precipitate was collected, washed with cold water (3 X 500 mL) and dried in air. The crude product was separated by column chromatography using CH\(_2\)Cl\(_2\)/\(n\)-hexane (1:4, v/v) as eluent to yield 343 as a yellow powder (2.45 g, 6.3 mmol, 63 %); M.p. = 174-176 °C, lit. M.p. = 173-176 °C;\(^{385}\) R\(_f\) = 0.47 (CH\(_2\)Cl\(_2\)/\(n\)-hexane, 1:4, v/v). Analytical data were in accordance to the literature.\(^{385,421}\)

\[ \delta_h (400 \text{ MHz}, \text{CDCl}_3): \ 5.73 \text{ (s, 1H, CH, H-5), 5.80 (s, 1H, CH, H-4), 7.86-7.91 (m, 3H, Ar-H, H-1), 8.08-8.13 (m, 3H, Ar-H, H-2), 8.27-8.32 ppm (m, 3H, Ar-H, H-3)}. \]
2,6,14-Triaminotriptycene (344)

Triptycene 343 (1.00 g, 2.60 mmol, 1.0 equiv) was dissolved in dry CH₂Cl₂ (20 mL) and dry MeOH (20 mL) and palladium on carbon (1.40 g, 10 wt. %, 3.38 mmol, 1.3 equiv.) was added. The suspension was placed in an ice bath and sodium borohydride (25 mg, 0.65 mmol, 0.25 equiv.) was added slowly. After 30 minutes, the reaction mixture was filtered and taken up in CH₂Cl₂. The mixture was washed with water (2 X 40 mL) and brine (2 X 40 mL) and dried over MgSO₄. The organic solvent was removed in vacuo to yield 344 as a white powder (568 mg, 1.90 mmol, 74 %); M.p. = 281-283 °C, lit. M.p. = 279-283 °C; Rᵢ = 0.43 (CH₂Cl₂/n-hexane, 1:4, v/v). Analytical data were in accordance to the literature.⁵⁸⁵,⁴²²

δₓ (400 MHz, CDCl₃): 3.46 (br. s, 6H, NH₂, H-1), 5.23 (s, 1H, CH, H-5), 5.27 (s, 1H, CH, H-6), 6.29-6.33 (m, 3H, Ar-H, H-2), 6.54-6.58 (m, 3H, Ar-H, H-3), 6.78-6.82 ppm (m, 3H, Ar-H, H-4).

2,6,14-Triiodotriptycene (341)
Triptycene 344 (660 mg, 2.20 mmol, 1.0 equiv.) was dissolved in concentrated hydrochloric acid (5 mL, 0.21 mol, 95.0 equiv.) and water (10 mL). The reaction mixture was cooled in an ice bath. Sodium nitrite (501 mg, 7.30 mmol, 3.3 equiv.) was dissolved in water (10 mL) and added to the reaction mixture over a period of 10 minutes. Potassium iodide (2.75 g, 16.50 mmol, 7.5 equiv.) was dissolved in H2O (5 mL) and added to the reaction mixture over 30 minutes. The mixture was heated to 80 °C for 2 hours, cooled, and then extracted with CH2Cl2 (3 X 30 mL). The combined extracts were washed with saturated aqueous NaHSO4 (2 X 20 mL), dried over anhydrous Na2SO4 and concentrated in vacuo to remove the organic solvents. The crude product was subjected to column chromatography on silica gel using CH2Cl2/n-hexane (1:4, v/v) as eluent to yield 341 as a white powder (278 mg, 0.44 mmol, 20 %): M.p. = 155-157 °C, lit. M.p. = 155-157 °C; Rf = 0.51 (CH2Cl2/n-hexane, 1:4, v/v). Analytical data were in accordance to the literature.

δH (400 MHz, CDCl3): 5.17-5.21 (m, 2H, CH, H-4), 7.08 (d, J = 7.6 Hz, 3H, Ar-H, H-1), 7.31 (dd, J = 7.5, 1.6 Hz, 3H, Ar-H, H-2), 7.74 ppm (d, J = 1.6 Hz, 3H, Ar-H, H-3).

2,3,6,7,14,15-Hexanitrotriptycene (345)

Triptycene (5.15 g, 20.20 mmol, 1.0 eq.) was suspended in fuming nitric acid (150 mL, 100 %) and heated to 85 °C for 4 hours. The reaction mixture was cooled to room temperature, poured into water (1.0 L), and stirred for 1 hour. The pale yellow (slightly pink) precipitate was collected by suction filtration, washed with water (500 mL), and dried in air. Recrystallization from boiling DMF after cooling to room temperature afforded 345 as yellow crystals (2.12 g, 4.04 mmol, 20 %): M.p. 113-115 °C; lit. M.p. = 113 °C; Analytical data were as reported in literature.
\[ \delta_H (400 \text{ MHz, CDCl}_3): \quad 5.19 \text{ (s, 2H, CH, H-1), 8.29 ppm (s, 6H, Ar-H, H-2)}. \]

**2,3,6,7,14,15-Hexaaminotriptycene (346)**

Triptycene 345 (1.36 g, 2.60 mmol, 1.0 equiv.) was dissolved in dry CH\(_2\)Cl\(_2\) (20 mL) and dry MeOH (20 mL) and palladium on carbon (2.80 g, 10 wt. %, 4.80 mmol, 2.6 equiv.) was added. The suspension was placed in an ice bath and sodium borohydride (48 mg, 1.25 mmol, 0.5 equiv.) was added slowly. After 30 minutes, the reaction mixture was filtered and extracted with CH\(_2\)Cl\(_2\) (2 × 30 mL). The organic phase was washed with water (2 × 40 mL) and brine (2 × 40 mL). The organic solvent was removed *in vacuo* to yield 346 as a brown powder (148 mg, 0.43 mmol, 12 %) with ~90 % purity (\(^1\)H NMR). This compound is air-sensitive and attempts to purify the compound further through methods such as chromatography were unsuccessful and resulted in further decomposition. Compound 346 was used without further purification. M.p. = 181-183 °C, lit. M.p. = 181-184 °C; \(R_f = 0.24\) (CH\(_2\)Cl\(_2\)/n-hexane, 1:4, v/v). Analytical data were in accordance to the literature.\(^{385}\)

\[ \delta_H (400 \text{ MHz, CDCl}_3): \quad 3.40 \text{ (br. s, 12H, NH}_2, \text{ H-1), 5.19 \text{ (s, 2H, CH, H-2), 7.03 ppm (s, 6H, Ar-H, H-3)}.} \]
5.5.3 Multi-porphyrin array

2,3,6,7,14,15-Hexakis[4-(5,15-diphenylporphyrin)ethynyl]triptycene (357)

A mixture of triptycene 304 (50 mg, 0.125 mmol, 1.0 equiv.), PdCl₂(PPh₃)₂ (52 mg, 0.07 mmol, 0.6 equiv.), Cul (15 mg, 0.08 mmol, 0.64 equiv.) triphenylphosphine (40 mg, 0.15 mmol, 1.2 equiv.), 5-bromo-10,15-diphenylporphyrin (2.84 g, 5.25 mmol, 42.0 equiv.) and diethylamine (12.6 mL, 0.12 mmol, 0.95 equiv.) in DMF (5 mL) was irradiated in a microwave at 120 °C for 40 minutes in a heavy-walled glass vial sealed with a teflon septum. The reaction mixture was then filtered through silica using CH₂Cl₂ (250 mL). The filtrate was concentrated under reduced pressure and the yellow residue was purified by first using a short silica plug (CH₂Cl₂/n-hexane, 1:1, v/v) followed by column chromatography on silica gel (CH₂Cl₂/n-hexane, 1:3, v/v) to yield 357 as a purple crystalline solid (47 mg, 0.015 mmol, 12 %); M.p. ≥ 300 °C; Rf = 0.42 (CH₂Cl₂/n-hexane, 1:1, v/v).

δH (400 MHz, CDCl₃): -2.48 (s, 12H, NH, H-1), 5.37 (s, 2H, CH, H-13), 6.82-6.85 (m, 12H, Ar-H, H-9), 7.18-7.34 (m, 12H, Ar-H, H-8), 7.56 (s, 6H, Ar-H, H-12), 7.71-7.78 (m, 12H, Ar-H, H-10), 7.81-7.86 (m, 12H, Ar-H, H-7), 8.24-8.29 (m,
12H, Ar-H, H-11), 8.77 (d, J = 4.5 Hz, 12H, H$_{\beta}$, H-3),
8.97 (app. m, 12H, H$_{\beta}$, H-6), 9.30 (d, J = 4.5 Hz, 12H,
H$_{\beta}$, H-4), 10.01-10.06 (app. m, 12H, H$_{\beta}$, H-5), 10.24
ppm (s, J = 4.5 Hz, 6H, H$_{\text{meso}}$, H-2).

HRMS (m/z -ES): [M]$^+$ calcd. for C$_{224}$H$_{34}$N$_{24}$ 3159.1223, found 3159.1584.

UV/vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 428 (5.14), 527 (3.97), 572 (4.10), 605
(3.81), 664 nm (3.95).
Chapter 6

References
References

152. M. O. Senge, *Accounts of Chemical Research* 2005, **38**, 733.


