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Development and Investigation of Novel Transition Metal Mediated Reactions in Porphyrin Chemistry

Submitted by

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Diploma of Chemistry, Technische Universität Berlin, Germany

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

Doctor of Philosophy

University of Dublin, Trinity College

March 2009
Declaration

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Sabine Horn
Summary

The aim of this work was to extend the number of existing pathways for the synthesis of porphyrins. The focus was directed towards the development and investigation of new transition metal catalysed reactions in porphyrin chemistry. These methods could then be used for the synthesis of distinct porphyrin systems for various applications.

A new pathway was discovered and investigated for the synthesis of acroleinylporphyrins. These compounds serve as precursors for the synthesis of benzochlorins which are highly promising candidates for photodynamic therapy. The new synthetic method included the conversion of allylporphyrins into nickel(II) acroleinylporphyrins in good yields via a nickel(II) mediated reaction. It demonstrates the first example of a nickel catalysed reaction in porphyrin chemistry. This methodology could be applied to aryl- and alkyl-substituted porphyrins with different substitution patterns. However, it was found to be limited to the meso-position of either free-base or nickel(II) metallated porphyrins. Nevertheless, the developed method offered a good alternative to the existing pathways for the synthesis of acroleinylporphyrins.

The Pauson-Khand reaction was studied for the first time as an alternative pathway for cyclisation reactions of porphyrin substituents at the meso-position. The porphyrin could serve as alkene as well as alkyne partner for the intermolecular Pauson-Khand reaction. However, steric considerations required the reaction centre to be at a certain distance from the macrocycle.

It was found that allylporphyrins were suitable compounds to serve as the alkene reaction partner. Reactions of allylporphyrins with phenylacetylene resulted in a good combined yield of the two regioisomers expected. However, this reaction was limited by the choice of the non-porphyrin alkyne partner and could only be carried out successfully with phenylacetylene.

Porphyrins could also serve as the alkyne reaction partner by using 4-ethynylphenyl as substituent. The reaction of 4-ethynylphenylporphyrin with norbornene and norbornadiene gave the corresponding Pauson-Khand products in good yields. Again, the reaction was limited by the choice of the non-porphyrin alkene partner which is a common problem of the intermolecular Pauson-Khand reaction.
Additionally, porphyrins could serve as the alkene and alkyne reaction partner in a sequential double Pauson-Khand reaction to form regioisomeric porphyrin dimers in a nearly quantitative combined yield. This demonstrated the potential of this method for the preparation of technically and medicinally relevant complex heterocycles.

To broaden the methods for the use of porphin as starting material for the synthesis of porphyrins, a study of various transition metal catalysed C-H bond activation reactions of porphin was undertaken. It turned out to be quite difficult to find appropriate reaction conditions for porphin as it decomposed under acidic conditions but did not react under basic conditions. The iridium(II) catalysed \( \beta \)-borylation of porphin led to trace amounts of the desired product as an inseparable mixture with starting material. This project turned out to be quite tedious considering the varying yield in porphin synthesis as well as the difficulties with the reactivity of porphin.

A rhodium(1) catalysed alkylation reaction was investigated as a new pathway towards alkylporphyrins. This included the \textit{in situ} formation of a zinc(I) ring-metallated porphyrin intermediate. Different methods were used for the synthesis of this intermediate. However, none of these attempts were successful and either starting material was recovered or dehalogenation of the starting material occurred. It was not possible to determine whether the conditions for the formation of the intermediate or the subsequent rhodium(1) catalysed alkylation reaction needed further alteration to give the desired alkyl-substituted porphyrins.

Finally, a different method was investigated to synthesise alkylporphyrins, namely the Suzuki cross-coupling reaction of various potassium organotrifluoroborates with directly brominated porphyrins. The method showed general applicability for the meso- and \( \beta \)-position of the macrocycle as well as for aryl- and alkyl-substituted porphyrins with different substitution patterns. The Suzuki coupling products were obtained in moderate to good yields, depending on the nature of the potassium organotrifluoroborate reagents. It was demonstrated that the use of potassium organotrifluoroborates offered a good alternative to their respective boronic acids or esters and a series of novel porphyrins could be synthesised in a straight-forward manner that would otherwise include numerous steps.
Publications


Conference Abstracts

Sabine Horn and Mathias O. Senge, “Exploration of the reaction of potassium organotrifluoroborates with porphyrins” CSCB Symposium, Dublin, Ireland, 12th Dec 2008.


Sabine Horn and Mathias O. Senge “First Pauson-Khand Reaction on Porphyrins” CSCB Symposium, Dublin, Ireland, 14th Dec 2007.


Für mich
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Table of Contents

Declaration II
Summary III
Publications V
Acknowledgements VIII
Abbreviations X

Chapter 1: Introduction
1.1 Definition and Nomenclature 2
1.2 Synthetic Considerations 3
1.3 Transition Metal Mediated Reactions 7
  1.3.1 Transformation Reactions 8
  1.3.2 Palladium Catalysed Reactions 9
  1.3.3 Other Transition Metal Catalysed Reactions 14
1.4 Objectives 17

Chapter 2: Acroleinylporphyrins via Nickel(II) Mediated Reaction
2.1 Background 20
2.2 Synthesis of Allylporphyrins 23
2.3 Acroleinylporphyrins via Nickel(II) Mediated Reaction 27
2.4 Spectroscopic Studies 36
  2.4.1 $^1$H Nuclear Magnetic Resonance (NMR) Spectroscopy 36
  2.4.3 Ultraviolet-visible (UV-vis) Spectroscopy 39
2.5 Conclusions 42

Chapter 3: The Pauson-Khand Reaction of Porphyrins
3.1 Background 44
3.2 The Pauson-Khand Reaction of Alkenylporphyrins 48
3.3 The Pauson-Khand Reaction of Alkynylporphyrins 51
3.4 Spectroscopic Studies 56
  3.4.1 $^1$H NMR Spectroscopy 56
  3.4.2 UV-vis Spectroscopy 61
3.5 Conclusions 62
Chapter 4: C-H Bond Activation Reactions of Porphin

4.1 Background 64
4.2 C-H Bond Activation Reactions of Porphin 66
4.3 Conclusions 70

Chapter 5: Rhodium(1) Catalysed Alkylation of Porphyrin

5.1 Background 72
5.2 Rhodium(1) Catalysed Alkylation of Porphyrin 73
5.3 Conclusions 77

Chapter 6: Suzuki Reaction of Potassium Organotrifluoroborates with Porphyrins

6.1 Background 79
6.2 Suzuki Reaction of Potassium Organotrifluoroborates with Porphyrins 80
6.3 Spectroscopic Studies 85
   6.3.1 $^1$H NMR Spectroscopy 85
   6.3.2 UV-vis Spectroscopy 87
6.4 Conclusions 89

Chapter 7: Experimental

7.1 Instrumentation and General Considerations 91
7.2 Allylporphyrins 92
   7.2.1 Synthesis of Starting Materials 92
   7.2.2 Synthesis of Allylporphyrins 93
7.3 Acroleinylporphyrins 103
7.4 Pauson-Khand Products of Alkenylporphyrins 110
   7.4.1 Synthesis of Starting Materials 110
   7.4.2 Pauson-Khand Products I 116
7.5 Pauson-Khand Products of Alkynylporphyrins 122
   7.5.1 Synthesis of Starting Materials 122
   7.5.2 Pauson-Khand Products II 131
7.6 Suzuki Reaction Using Potassium Organotrifluoroborates 136
   7.6.1 Synthesis of Starting Materials 136
   7.6.2 Suzuki Products 137

References 149
Abbreviations

acac  acetylacectonate
Ar  aryl
br  broad
Bu  butyl
calcd  calculated
cod  cyclooctadiene
COSY  correlation spectroscopy
d  doublet
dba  dibenzylideneacetone
DCM  dichloromethane
dd  doubledoublet
DDQ  2,3-dichloro-5,6-dicyanobenzoquinone
DMF  N,N-dimethylformamide
dppf  1,1'-bis(diphenylphosphino)ferrocene
dtbbpy  4,4'-di-tert-butyl-2,2'-bipyridyl
equiv  equivalents
ES  electrospray
FT  Fourier trasformations
GLC  gas-liquid chromatography
hex  hexyl
HRMS  high resolution mass spectrometry
IUPAC  International union of pure and applied chemistry
IR  infrared
LD  laser desorption
LUMO  lowest unoccupied molecular orbital
m  multiplet
m/z  mass-to-charge ratio
MALDI  matrix-assisted laser desorption/ionisation
Me  methyl
MeOH  methanol
mp  melting point
MS  mass spectrometry
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW</td>
<td>microwave</td>
</tr>
<tr>
<td>NBA</td>
<td>N-bromoacetamide</td>
</tr>
<tr>
<td>NBS</td>
<td>N-bromosuccinimide</td>
</tr>
<tr>
<td>NLO</td>
<td>non-linear optics</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>NOESY</td>
<td>nuclear Oberhauser effect spectroscopy</td>
</tr>
<tr>
<td>OAc</td>
<td>acetate</td>
</tr>
<tr>
<td>OEP</td>
<td>2,3,7,8,12,13,17,18-octaethylporphyrin</td>
</tr>
<tr>
<td>OTf</td>
<td>triflate</td>
</tr>
<tr>
<td>PDT</td>
<td>photodynamic therapy</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>q</td>
<td>quartet</td>
</tr>
<tr>
<td>R&lt;sub&gt;f&lt;/sub&gt;</td>
<td>retention factor</td>
</tr>
<tr>
<td>rt</td>
<td>room temperature</td>
</tr>
<tr>
<td>s</td>
<td>singlet</td>
</tr>
<tr>
<td>sep</td>
<td>septet</td>
</tr>
<tr>
<td>t</td>
<td>triplet</td>
</tr>
<tr>
<td>td</td>
<td>triplet of doublets</td>
</tr>
<tr>
<td>TFA</td>
<td>trifluoroacetic acid</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TLC</td>
<td>thin-layer chromatography</td>
</tr>
<tr>
<td>TMS</td>
<td>trimethylsilane</td>
</tr>
<tr>
<td>TOF</td>
<td>time of flight</td>
</tr>
<tr>
<td>TPP</td>
<td>5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin</td>
</tr>
<tr>
<td>TPPTS</td>
<td>sodium triphenylphosphine trisulfonate</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>v/v</td>
<td>volume to volume</td>
</tr>
<tr>
<td>vis</td>
<td>visible</td>
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Chapter 1:
Introduction
1.1 Definition and Nomenclature

The porphyrin skeleton 1 can be found in nature in every living creature as it plays a central role in many metabolic processes. Its metal complexes take part in essential biological processes such as the oxygen transport in the blood stream (haemoglobin), the catalysis of biochemical reactions (cytochrome P₄₅₀) and the energy transfer in plants (chlorophyll).

The first porphyrin synthesis was published by Fischer in 1926, confirming the aromatic macrocyclic structure initially proposed by Küster in 1913. As correctly postulated, the porphyrin framework consists of four pyrrole units linked together by four methine units to form a conjugated macrocycle. Only 18 of the 22 π-electrons take part in the aromatic system and therefore obey the Hückel-law for aromaticity (4n+2).

In free-base porphyrins two opposite β-β’ carbon bonds possess more double bond character. There are three different types of carbon atoms in a porphyrin unit and its positions are numbered according to the International Union of Pure and Applied Chemistry (IUPAC) recommendation (Figure 1.1). The positions 2, 3, 7, 8, 12, 13, 17 and 18 are known as the β-position, 5, 10, 15 and 20 as the meso-position and 1, 4, 6, 9, 11, 14, 16 and 19 as the α-position. The four inner nitrogen atoms (21–24) can form complexes with a wide variety of metal ions.

Porphyrrin 1 belongs to the class of tetrapyrroles and can be transformed into the according hydroporphyrins 2 to 8 by reduction (Figure 1.2). Chlorin 2, bacteriochlorin 3 and isobacteriochlorin 4 still possess a conjugated system, whereas porphyrinogen 5, phlorin 6 and porphodimethenes 7 and 8 have lost their aromatic character.
1.2 Synthetic Considerations

Porphyrrins substituted at the β-position occur in nature whereas meso-substitution is completely synthetic. However, meso-substituted porphyrins have found widespread use as models for biological processes. Depending on the type of substituents in the meso-positions, applications can be found in various areas ranging from physical chemistry, such as non-linear optics (NLO), to medicinal chemistry, such as photodynamic therapy (PDT). Symmetric porphyrins are synthetically more easily accessible than unsymmetric ones. Therefore, the most widely investigated porphyrins are $2,3,7,8,12,13,17,18$-octaethylporphyrin (H$_2$-OEP) and $5,10,15,20$-tetraphenylporphyrin (H$_2$-TPP).

Apart from total synthesis, which normally involves multiple steps, symmetric porphyrins are accessible by a condensation reaction of a pyrrole unit and an aldehyde. The use of 3,4-disubstituted pyrrole rings as starting materials leads to the formation of β-substituted porphyrins. Therefore, the design of the β-substitution pattern is limited by the synthesis of the pyrrole derivatives. This methodology can become quite tedious, for example, as the synthesis for 3,4-diethylpyrrole already involves four steps. Consequently, unsymmetrically β-substituted porphyrins are very complicated.
to synthesise and a mixed condensation of different pyrrole units with formaldehyde always leads to a variety of by-products. In contrast, the synthesis of symmetrical meso-tetrasubstituted porphyrins, the so-called A4-type (Figure 1.3), is easily accomplished in good yields. The availability of diverse aldehydes leads to a wide range of various A4-porphyrins.

\[ R^1=R^2=R^3=R^4=H \quad \text{Porphin} \]
\[ R^1=R^2=R^3=R^4 \quad \text{A4-type} \]
\[ R^1=R^2=R^3; \ R^4=H \quad \text{A3-type} \]
\[ R^1=R^2=R^3\neq R^4 \quad \text{A3B-type} \]
\[ R^1=R^3; \ R^2=R^4=H \quad 5,15-A2-type \]
\[ R^1=R^3; \ R^2=R^4 \quad 5,15-A2B2-type \]
\[ R^1=R^2; \ R^3=R^4 \quad 5,10-A2B2-type \]
\[ R^1=R^3\neq R^2\neq R^4 \quad 5,15-A2BC-type \]
\[ R^1\neq R^2\neq R^3\neq R^4 \quad \text{ABCD} \]

Figure 1.3. Examples for meso-substitution patterns using “ABCD”-nomenclature introduced by Lindsey.

Asymmetrically meso-substituted analogues can be obtained according to the same principle used for asymmetrically β-substituted porphyrins. The mixed condensation of pyrrole with different aldehydes gives a series of products distinguished by their substitution pattern (Figure 1.3). The yield for any particular porphyrin via this method is very low and chromatographic purification can be very difficult. Therefore, depending on the substitution pattern required, different synthetic routes have been employed in order to improve the yields of the desired porphyrins. The most common method for the synthesis of 5,15-A2B2- and 5,15-A2-porphyrins is given by a [2+2]-condensation reaction based on MacDonald et al. (Scheme 1.1). This reaction involves the acid catalysed condensation of dipyrromethane 9 with an aldehyde 10 to form the porphyrinogen 11. Subsequent oxidation with an oxidant such as 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) yields the corresponding porphyrin 12.
Unfortunately, this method can also produce by-products caused by scrambling. Under the given acidic conditions the bilane $\text{13}$, formed during the reaction, fragments into the pyrrole derivative $\text{14}$ and a tripyrrane component $\text{15}$ (Scheme 1.2). The recombination of $\text{14}$ and $\text{15}$ can lead to the formation of a different bilane $\text{16}$, resulting in a restructured substitution pattern of the porphyrin. Nevertheless, this $[2+2]$-condensation represents a reliable method for $5,15$-$\text{A}_2\text{B}_2$- and $5,15$-$\text{A}_2$-porphyrins in good yields and purity with the use of reaction conditions that minimises those exchange processes.
5,15-A₂-porphyrins can be utilised in the synthesis of A₃B- and A₂BC-porphyrins. Various and different functional groups can be introduced stepwise into the free meso-positions using organolithium reagents, while halogenation allows the introduction of further functional groups, for instance via transition metal catalysed C-C cross-coupling reactions.

However, the need for the development of new or improved synthetic pathways in porphyrin chemistry is still necessary and requires some consideration. The meso-position of porphyrins is more electrophilic than the β-position and therefore usually the preferred reaction site in electrophilic aromatic substitutions, electrophilic and nucleophilic additions, radical reactions, oxidations and reductions. However, the meso-position is sterically less accessible, especially when one or two of the adjacent β-positions are substituted. On the other hand, the β-positions are sterically favoured and undergo substitution and addition reactions.

Size and nature of substituents influence the reactivity of the macrocycle. Bulky groups for instance shield the reaction sites at the adjacent positions. Substituents with an electron-donating effect (alkyl, CO₂⁻, O⁻) tend to increase the electron density of the macrocycle and therefore make it more susceptible to electrophilic attacks. In contrast
electron-withdrawing groups (aryl, CHO, NO₂) tend to decrease the electron density of the macrocycle. However, some substituents, such as aryl and vinyl, can occasionally be electron-donating by resonance when the porphyrin conformation allows overlap of the p-orbitals and an interaction of the two π-electronic systems. The insertion of a metal ion into the porphyrin core can be a useful reaction step. Apart from protection of the inner nitrogen atoms from electrophilic reagents and strong bases, the coordinated metal also has an important inductive effect on the π-electron system of the porphyrin and therefore influences its reactivity. Zinc(II) for example, induces the highest negative charge into the porphyrin periphery and can be easily demetallated under acidic conditions. On the other hand, nickel(II) forms a more stable complex and can decrease the electron density of the porphyrin by π-back-bonding into semi-filled metal d-orbitals. In conclusion, the reactivity of porphyrins is influenced by the substituents already attached to the macrocycle as well as the metal ion coordinated to the inner core.

1.3 Transition Metal Mediated Reactions

Traditionally, the synthesis of porphyrins that possess one or more differing meso- or β-substituents involves a mixed condensation of appropriate aldehyde(s) with (substituted) pyrroles. However, this methodology bears several problems: the occurrence of side products makes purification quite tedious and not all reactants are compatible to protic or Lewis acidic reaction conditions. Therefore, the alteration of already substituted porphyrins are of great interest and the use of transition metals for catalytic coupling reactions or transformations of porphyrin substituents has grown rapidly over the last three decades.
1.3.1 Transformation Reactions

The first reactions in porphyrin chemistry using transition metals were reported in the 1970s. These reactions involve the transformation of porphyrin substituents into different functional groups. Smith and co-workers reported the transformation of the vinyl-substituents of the natural product protoporphyrin-IX dimethyl ester 17 into bis-acetals to afford the corresponding compound 18 in 92 % yield using thallium(III) nitrate (Scheme 1.3).²⁴

Titanium tetrachloride was used as a catalyst for the Knoevenagel condensation by Witte and Fuhrhop.²⁵ The formyl group of 5-formyl-OEP 19 was reacted with malonic acid to give the 2,2-dicarboxyvinyl analogue 20 in 68 % yield (Scheme 1.4).
1.3.2 Palladium Catalysed Reactions

The use of palladium as a catalyst for functionalisation of the porphyrin was initiated in 1980 by Smith and Langry who used a mercuration and palladium-olefin methodology. The free β-positions of zinc(II) deuteroporphyrin IX dimethyl ester were mercurated and subsequently reacted with methyl acrylate using lithium trichloropalladate(II) as catalyst to give the analogue bis-acrylated compound, after removal of zinc(II), in an overall yield of 31% (Scheme 1.5). This methodology could be used as a general synthetic pathway to attach various substituted olefins on the β-position of the porphyrin.

In the next two decades the most commonly used palladium catalysed reactions in organic chemistry for new C-C bond formations were applied to porphyrins, namely the Stille, Negishi, Sonogashira, Heck and Suzuki reaction. The initial investigations were made by Smith and co-workers who first applied the Stille reaction to porphyrins. 2,4-Dibromodeuteroporphyrin IX dimethyl ester was reacted with tributylvinylstannane in the presence of a palladium catalyst to obtain protoporphyrin IX dimethyl ester in 85% yield (Scheme 1.6).
Therien and co-workers reported the synthesis of β-substituted porphyrins via the Negishi coupling reaction.\textsuperscript{34} For instance, [2-butyl-5,10,15,20-tetraphenylporphyrinato]zinc (II) (2-n-butyl-TPP) \textsuperscript{26} could be prepared in 92 % yield from zinc(II) 2-bromo-TPP \textsuperscript{25} with n-butylzinc chloride under catalytic conditions (Scheme 1.7).

\begin{figure}
\centering
\includegraphics[width=\textwidth]{negishi反應.png}
\caption{Scheme 1.7. Negishi reaction of 2-bromo-TPP zinc(II).}
\end{figure}

The Sonogashira reaction was used for the synthesis of a porphyrin dimer bridged by a 1,4-diethynylphenylene unit by Arnold and Nitschinsk.\textsuperscript{35} Therefore, nickel(II) 5-ethynyl-OEP \textsuperscript{27} was reacted with 1,4-diiodobenzene to obtain the dimer \textsuperscript{28} in 60 % yield (Scheme 1.8). This coupling reaction was later applied to β- and meso-halogenated porphyrins to synthesise various alkenyl-substituted porphyrins.\textsuperscript{36,37}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{sonogashira反應.png}
\caption{Scheme 1.8. Synthesis of porphyrin dimer via Sonogashira coupling reaction.}
\end{figure}
Chapter 1: Introduction

Gauler and Risch reported the Heck reaction of the zinc(II) metallated analogue of compound \( \text{23} \) to synthesise styrene substituted porphyrins as well as 1,4-divinylbenzene linked dimers.\(^{38} \) The reaction of \( \text{29} \) with styrene gave \([3,8\text{-distyryldeuteroporphyrinato dimethyl ester}]\text{zinc(II)} \) \( \text{30} \) in 87 % yield (Scheme 1.9).

![Scheme 1.9. Heck reaction on \( \beta \)-bromo porphyrin.]

The first Suzuki cross-coupling reactions were also reported on the \( \beta \)-position of the porphyrin by Chan \textit{et al.}\(^{39} \) A series of \( \beta \)-aryl substituted TPPs was obtained in 50 % - 88 % yield from the reaction of \( \beta \)-bromo TPP \( \text{31} \) with various \( \beta \)-substituted aryl boronic acids (Scheme 1.10). Eight years later this methodology was developed for meso-bromo-substituted porphyrins.\(^{40} \)

![Scheme 1.10. General scheme for Suzuki reaction on \( \beta \)-bromo TPP.]
Chapter 1: Introduction

Besides the well-known C-C coupling reactions, there are numerous examples for recently developed palladium catalysed reactions in porphyrin chemistry.\textsuperscript{11,41} Zhang and co-workers developed methods for palladium catalysed carbon-heteroatom bond formation reactions. Meso-oxy-,\textsuperscript{42} amino- and amidoporphyrins were synthesised in good to excellent yields.\textsuperscript{43} The latest addition to these heteroatom-substituted porphyrins is the extension to C-S coupling reactions.\textsuperscript{44} Various different thiols were attached to meso-brominated porphyrins. For instance, the reaction of 5-bromo-10,20-diphenylporphyrin 32 with 4-chlorobenzenethiol in the presence of cesium carbonate, a palladium catalyst and appropriate ligand gave the sulfanyl-substituted analogue 5-(4-chlorophenylsulfanyl)-10,20-diphenylporphyrin 33 in 71% yield (Scheme 1.11).

\[
\begin{align*}
\begin{array}{c}
\text{Br} + \text{HS-Cl} & \xrightarrow{\text{Pd}_2(\text{dba})_3 \ \text{ligand} \ \text{Cs}_2\text{CO}_3 \ \text{toluene, 100 °C}} \text{NH N} = = \text{NH}
\end{array}
\end{align*}
\]

Scheme 1.11. Example for palladium catalysed C-S coupling on meso-bromoporpyrin.
A rather unusual example for the application of palladium in porphyrin synthesis was given by Arnold and co-workers. They reported a new method for selective iodination via a palladium mediated halogen exchange reaction. Compound 32 was first reacted with an excess of palladium reagent until full consumption of the starting material was observed before iodine was added to obtain 5-iodo-10,20-diphenylporphyrin 34 in 78% yield (Scheme 1.12). The reaction proceeds via a η¹-palladio(II)porphyrin intermediate which is the reason for excess amounts of palladium catalyst.

Scheme 1.12. Palladium catalysed halogen exchange reaction.
1.3.3 Other Transition Metal Catalysed Reactions

Although palladium is the most commonly used metal for catalytic reactions in organic chemistry, there are a number of other transition metals for C-C bond formation and transformation reactions that are just as well-known.

The Glaser coupling\textsuperscript{46} was first applied to porphyrins by Anderson and Sanders.\textsuperscript{47} The zinc(II) bisphenylacetylene substituted porphyrin 35 was reacted with copper(I) chloride to obtain the cyclic trimer 36 in 47\% yield after demetallation (Scheme 1.13).

Mantano et al. recently reported a Cu(I) catalysed C-P coupling reaction for the synthesis of meso-phosphorylporphyrins.\(^{48}\) The zinc(II) complex of 5-iodo-10,15,20-tris(3,5-di-tert-butylphenyl)porphyrin 37 was reacted with diphenylphosphane oxide in the presence of cesium carbonate and an amine using copper(I) iodide as the catalyst, to form the corresponding diphenylphosphoryl-substituted compound 38 in 72 % yield (Scheme 1.14).

\[\text{Ph}_2\text{P(O)H} \quad \text{CuI} \quad \text{Cs}_2\text{CO}_3 \quad \text{MeNH}(-\text{CH}_2\text{)}_2\text{NHMe}
\] 

\text{toluene; 130 °C}

\[\text{37} \quad \text{38}\]

**Scheme 1.14.** Cu(I) catalysed C-P coupling reaction.

The first cross-metathesis reaction\(^{49}\) was reported by Dolphin and co-workers on vinylchlorins and -porphyrins.\(^{50}\) Chlorin 39 was reacted with octene at the β-vinyl substituent in the presence of a 2\(^{nd}\) generation Grubbs’ catalyst (Scheme 1.15). The product 40 was obtained in 70 % yield with complete E-stereoselectivity.

\[\text{MeO}_2\text{C} \quad \text{CO}_2\text{Me} \quad \text{Grubbs’ cat.} \quad \text{THF; reflux} \quad \text{MeO}_2\text{C} \quad \text{CO}_2\text{Me}
\]

\[\text{39} \quad \text{40}\]

**Scheme 1.15.** Cross-metathesis reaction on vinylchlorin.
Osuka and co-workers developed a method for β-borylation of porphyrins via C-H bond activation using iridium as the catalyst.\textsuperscript{51} The reaction of 5,15-bis(2,5-di-tert-butylphenyl)porphyrin 41 with bis(pinacolato)diborane in the presence of an iridium catalyst and 4,4'-di-tert-butyl-2,2'-bipyridyl (dtbbpy) as ligand resulted in the formation of the mono-β-borylated compound 42 as the main product in 43\% yield, as well as a mixture of two isomeric di-β-borylated compounds 43 and 44 in a combined yield of 14\% (Scheme 1.16). Interestingly, the reaction took place at the β-position adjacent to the free meso-position which is most likely due to steric effects.

\textbf{Scheme 1.16.} Iridium catalysed β-borylation of via C-H bond activation.
1.4 Objectives

The development of new synthetic routes remains a crucial step to further advance the ever expanding range of applications for porphyrins. Thus, the use of transition metals for transformation reactions of porphyrin substituents or new bond formations in the meso- or β-position of the porphyrin represents a straight-forward approach as outlined in Chapter 1.3.

The aim of this work was to broaden these methods by developing and investigating novel transition metal mediated reactions in porphyrin chemistry. Ideally, these synthetic pathways involve simple starting materials and present a general method for various porphyrin systems.

The allyl-substituent on porphyrin was not studied as a functional group previously, although the synthesis of allylporphyrins only involves two steps. Generally, compounds with terminal double bonds can serve as precursors for catalytic reactions, such as cross-metathesis and the Pauson-Khand reaction. Surprisingly, when allylporphyrin was subjected to standard metalation conditions using nickel(II) acetate, the corresponding nickel(II) acroleinylporphyrin was formed. This transformation of the allyl-substituent into the acroleinyl-substituent was further investigated to determine the reaction conditions, optimise the yield and study the general application of this reaction to various porphyrin systems as well as aromatic non-porphyrin systems.

Additionally, allylporphyrins served as starting material for the intermolecular Pauson-Khand reaction. Although the Pauson-Khand reaction is well-known in organic chemistry and the most common method for the formation of cyclopentenones, it has not been used on porphyrins previously. It involves the reaction of an alkene with an alkyne and a carbon monoxide molecule in the presence of transition metal catalyst to form a cyclopentenone ring. Hence, the intermolecular Pauson-Khand reaction was investigated on porphyrins containing terminal alkene and alkyne substituents.

There are only a limited number of reactions on porphin, the parent porphyrin. Therefore, transition metal mediated C-H bond activation reactions were explored to introduce substituents on porphin directly for the synthesis of new porphyrins.
Also, the introduction of alkyl-substituents to the porphyrin core is limited to only a few synthetic methods. Attempts were made to broaden these pathways *via* a rhodium(1) catalysed reaction of zinc(I) ring-metallated porphyrins with iodoalkanes.

Finally, the Suzuki cross-coupling reaction on porphyrins was expanded to the use of potassium organotrifluoroborates instead of boronic acids or esters. The reaction conditions were optimised for porphyrin systems and the general application of this reaction was investigated.
Chapter 2:
Acroleinylporphyrins \textit{via} Nickel(II) Mediated Reaction
2.1 Background

Acroleinylporphyrins are of great interest as they serve as precursors for the synthesis of benzochlorins, which are highly promising candidates for photodynamic therapy.\(^{52,53}\) Cyclisation of the acroleinyl group of compound 45 onto the adjacent pyrrole subunit gave benzochlorin 46 in 50 % yield (Scheme 2.1).\(^{52}\)

![Scheme 2.1. Synthesis of benzochlorin (46).](image)

The first acroleinyl-substituted porphyrin was synthesised accidentally in 1970 by Nichol during an attempt to formylate the meso-position of protoporphyrin-IX dimethyl ester 17 via a Vilsmeier reaction.\(^{54}\) They obtained an isomeric mixture of mono-acroleinylporphyrin 47 and the diacroleinylporphyrin 48 in 7 % and 18 % yield, respectively (Scheme 2.2).\(^{55}\)

![Scheme 2.2. Synthesis of acroleinylporphyrins via Vilsmeier reaction.](image)

Smith and co-workers improved the yield of compound 48 to 38 % by reacting porphyrin 21 with acrolein, using the mercuration and palladium-olefin methodology (Scheme 2.3).\(^{27}\)
Chapter 2: Acroleinylporphyrins via Nickel(II) Mediated Reaction

Introduction of the acroleinyl group into the meso-position was first accomplished by Arnold et al. in 1978. Nickel(II) 5-acroleinyl-OEP was synthesised in three steps by a sequence of Vilsmeier formylation and Wittig reaction of nickel(II) OEP to obtain nickel(II) 5-vinyl-OEP, which was then purposely formylated using the Vilsmeier reaction again to give compound in an overall yield of 54 % (Scheme 2.4).

This synthetic pathway was shortened by Vicente and Smith in 1991 by vinylogous Vilsmeier formylation of nickel(II) OEP directly, to obtain compound 45 in 85 % yield as well as nickel(II) 5,10-diacroleinyl-OEP in 55 % yield by using an excess of the Vilsmeier reagents (Scheme 2.5). However, it has been shown that the Vilsmeier formylation of porphyrins is not regioselective and can only be applied to copper(II) or nickel(II) metallated porphyrins. Therefore, the methodology of synthesising the vinyl-substituted porphyrin first before formylating it to the acroleinylporphyrin is more advisable for the design of a distinctive substitution pattern.
Nevertheless, vinylogous Vilsmeier reaction has also been used for the first synthesis of β-unsubstituted meso-acroleinylporphyrins by Boyle and Dolphin\cite{60} and still seems to be the method of choice for this type of compounds.\cite{61,62} Yields vary between 29 % and 63 %, depending on the aryl-substituent of the starting material 52, and, besides the desired mono-acroleinylporphyrin 53, the diacroleinylporphyrin 54 by-product was formed in trace amounts (Scheme 2.6).
2.2 Synthesis of Allylporphyrins

A previous synthesis of meso-allylporphyrins involved the condensation of 5-allyldipyrromethane with a dipyrromethane-dicarbinol with a yield of 44 %.63 The most straight-forward method for the introduction of the allyl-substituent onto the porphyrin structure is the Suzuki cross-coupling reaction.32 This reaction is well-known in porphyrin chemistry and usually involves brominated porphyrins and organoboron reagents.64 It has been used to obtain 2,3-diallylporphyrins in 14 % to 48 % yield by Smith and co-workers, previously.65

Therefore, the 5,15-A2-porphyrins: 5,15-diphenylporphyrin66 55, 5,15-bis(4-methylphenyl)porphyrin67 56, 5,15-dihexylporphyrin62 57 and 5,15-di(iso-propyl)porphyrin68 58 were synthesised by condensation reaction of dipyrromethane17 with the appropriate aldehyde according to literature procedure in 27 % to 52 % yield (Figure 2.1).59 These compounds were brominated under standard conditions30 to afford the starting materials 59,70 60,71 6222 and 63 in 62 % to 99 % yield. Compound 61, 5,15-dibromo-10,20-bis(4-butoxyphenyl)porphyrin, was kindly supplied by Dahms.73 Also, the two nickel(II) metallated analogues 64 and 65 were prepared from 60 and 62 as a second set of starting materials for the Suzuki cross-coupling reaction by using standard metallation conditions21 in 70 % and 64 % yield, respectively.

For a different substitution pattern, the A3-porphyrin 5,10,15-tris(4-methylphenyl)porphyrin74 66 was synthesised from compound 56 using organolithium reagents in 91 % yield75 and subsequently brominated to obtain the bromo-analogue porphyrin 6776 in 96 % yield (Figure 2.2).
Finally, the β-brominated compound 69 was prepared by bromination of TPP\textsuperscript{77} 68, which was kindly supplied by Dahms, in 46 % yield.\textsuperscript{78}

![Figure 2.2. A\textsubscript{3}- and β-substituted porphyrins as starting materials for Suzuki cross-coupling.](image)

With these different starting materials in hand, the Suzuki cross-coupling reactions were carried out according to literature procedure.\textsuperscript{40} The meso-bromoporphyrins 59 – 63 and 67 were dissolved in anhydrous THF in an oven-dried Schlenk-tube under argon atmosphere. K\textsubscript{3}PO\textsubscript{4} was added and the reaction mixture was degassed via three freeze-pump-thaw cycles and put under argon again. Allylboronic acid pinacol ester and Pd(PPh\textsubscript{3})\textsubscript{4} were added and the reaction mixture was heated to 80 °C in a sealed Schlenk-tube for 18 h. The progress of the reaction was monitored by thin layer chromatography (TLC) on silica gel (CH\textsubscript{2}Cl\textsubscript{2}/C\textsubscript{6}H\textsubscript{14} 1:1, v/v). The conversion was observed by the occurrence of a more polar spot on the TLC, a smaller retention factor than the starting material. After 18 h of heating no starting material was observed by TLC and the reaction was left to cool to room temperature. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane. The work-up of the reaction mixture was carried out by sequentially washing the crude product with a saturated solution of sodium bicarbonate, water and brine. The combined organic phase was dried over sodium sulphate. The crude product was purified by flash column chromatography on silica (CH\textsubscript{2}Cl\textsubscript{2}/C\textsubscript{6}H\textsubscript{14} 1:2, v/v) to obtain the corresponding meso-allylporphyrins 70 – 77 in 2 % to 95 % yield (Scheme 2.7).\textsuperscript{72}
Chapter 2: Acroleinylporphyrins *via* Nickel(II) Mediated Reaction

![Scheme 2.7. Synthesis of meso-allylporphyrins.](image)

The Suzuki cross-coupling reaction of 2-bromo-TPP 69 was carried out under slightly different conditions. K$_2$CO$_3$ was used as base and toluene as solvent and the reaction proceeded at a higher temperature, namely 110 °C. Work-up and purification was carried out in analogy to the meso-substituted compounds to obtain 2-allyl-TPP 78 in 66 % yield (Scheme 2.8).

![Scheme 2.8. Synthesis of 2-allyl-TPP.](image)
The yields of the allylporphyrins 70 to 78 were low to excellent. A by-product of this reaction was debrominated starting material. Compound 74 was achieved in the lowest yield by far at 2 %, due to the electron-donating effect of the alkyl-substituents on the reaction centre. No side-product could be obtained in this case and the remaining compound underwent decomposition. Insertion of nickel(II) decreases the electron density of the macrocycle by π-back-bonding into the semi-filled metal d-orbitals. Accordingly, by using the nickel(II) metallated starting material 65, the yield of compound 76 was 95 %, a large improvement on the analogous reaction with the free-base compound 62 to get porphyrin 73 in 50 % yield. This effect was not noticeable in comparing the reactions of the aryl-substituted compounds 60 and 64 to obtain porphyrins 71 and 73, respectively, as the aryl-substituents already have an electron-withdrawing effect on the reaction centre.

The crystal structure of porphyrin 71 shows the diallyl substitution pattern (Figure 2.3). The C52–C53 bond length is 1.313(2) Å, clearly indicating unsaturated bond character. The molecular conformation is flat, with a Δ24 of 0.03 Å. The allyl group is nearly perpendicular to the molecular plane with a C5–C51–C52–C53 torsion angle of 2.6°.

Figure 2.3. Molecular structure of 71 in the crystal. Hydrogen atoms have been omitted for clarity.
2.3 Acroleinylporphyrins via Nickel(II) Mediated Reaction

Initially, the free-base allylporphyrins were synthesised in order to study metathesis reactions on these compounds. However, treatment of porphyrin 71 with Grubbs’ I catalyst in anhydrous THF under argon atmosphere and 60 °C gave no reaction after six days.\(^5\)\(^8\) The progress of the reaction was monitored by TLC on silica gel (CH\(_2\)Cl\(_2\)/C\(_6\)H\(_{14}\) 1:1, v/v) and only decomposition of the starting material occurred. In an attempt to activate the allyl-substituents, compound 71 was metallated under standard conditions,\(^2\) namely nickel(II) acetate (3 equiv.) in N,N-dimethylformamide (DMF) at 130 °C. The reaction was monitored by TLC on silica gel (CH\(_2\)Cl\(_2\)/C\(_6\)H\(_{14}\) 1:1, v/v). The appearance of the nickel(II) metallated analogue can be observed clearly by the occurrence of a less polar bright red spot on the TLC in comparison to the purple spot of the starting material with a lower retention factor. As the insertion of nickel(II) proceeded very slowly, the reaction mixture was left heated overnight for completion. Next day the starting material was not observed by TLC but two additional green spots with a very low retention factor. The reaction mixture was left to cool to room temperature and the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane and purification was carried out by column chromatography on silica (ethyl acetate/C\(_6\)H\(_{14}\) 1:2, v/v). Surprisingly, not only the expected red nickel(II) derivative 79 was obtained as the first fraction of the column but two additional green compounds, which could be identified as the [5,15-diacroleinyl-10,20-bis(4-methylphenyl)porphyrinato]nickel(II) 80 as the second fraction of the column and the [5-acroleinyl-15-formyl-10,20-bis(4-methylphenyl)porphyrinato]-nickel(II) 81 as the last fraction (Scheme 2.9).\(^7\)\(^2\) Interestingly, diacroleinylporphyrin 80 was the main product of this reaction.
This conversion was further investigated using different amounts of nickel(II) acetate. Reaction of starting material 71 with 4, 6 and 8 equiv. of nickel(II) acetate had no influence on the yield of the main product 80, but the yield of compounds 79 and 81 decreased to traces only with increasing quantities of nickel(II) acetate. When less than 3 equiv. of nickel(II) acetate were added to the reaction, the formation of acroleinylporphyrins was not observed. This led to the conclusion that 1 equiv. of nickel(II) is needed for the insertion into the macrocycle and the remaining 2 equiv. for each allyl-substituent.
To analyse the function of the metal and ligand of nickel(II) acetate, the reaction was carried out using different transition metal(II) salts, namely palladium(II) and zinc(II) acetate as well as nickel(II) and zinc(II) chloride. However, none of these attempts resulted in the formation of any acroleinyl-substituted porphyrin. Thus, nickel(II) and the acetate played a significant role in the reaction mechanism.

Yamamoto et al. showed previously that the reaction of a nickel(0) complex with an allylic group can be promoted by acetic acid. Hence, the nickel(II) mediated reaction, illustrated in Scheme 2.9, was carried out with the addition of 0.1 mL of glacial acetic acid (DMF/glacial acetic acid 200:1, v/v) in an attempt to increase the yield. Indeed, diacroleinylporphyrin 80 was obtained in an improved yield of 60 %. A further increase of glacial acetic acid to 0.2 mL (DMF/glacial acetic acid 100:1, v/v) resulted in the optimised reaction conditions with a yield of 70 % for compound 80 and only traces of the by-products 79 and 81. However, when glacial acetic was replaced by hydrogen chloride the formation of compound 80 was not observed and only starting material was recovered.

To investigate the general application of this reaction to other porphyrin systems, the mono-allylporphyrin 77, the alkyl-substituted diallylporphyrin 73 and its nickel(II) analogue 76, as well as the β-allylporphyrin 78, were subjected to the optimised reaction conditions.

In the case of the mono-allylporphyrins 77 and 78, the quantity of nickel(II) acetate was altered accordingly to 2 equiv. as this compound only contains one allyl-group. The reaction of porphyrin 77 led to the successful formation of the three expected compounds 82 to 84 (Scheme 2.10). However, the yield of the nickel(II) acroleinylporphyrin 83 was lower at 26 % in comparison to its nickel(II) diacroleinyl-analogue 80, and the main product was [5-allyl-10,15,20-tris(4-methylphenyl)porphyrinato]nickel(II) 82 in 28 % yield.
The reaction of the alkyl-substituted allylporphyrins 73 and 76 with nickel(II) acetate resulted in the formation of the respective nickel(II) acroleinylporphyrin 85 (Scheme 2.11). Interestingly, the yield of compound 85 was identical for both reactions, with free-base porphyrin 73 and nickel(II) metallated analogue 76, at 20 %. No formation of any by-product was observed and the remaining starting material underwent decomposition. The same result was obtained when the reaction was carried out under milder conditions, namely 60 °C for 36 h.
Chapter 2: Acroleinylporphyrins via Nickel(II) Mediated Reaction

Scheme 2.11. Nickel(II) mediated reaction of alkyl-substituted diallylporphyrins.

The reaction of β-allyl-TPP 78 with nickel(II) acetate did not lead to the formation of the respective nickel(II) β-acroleinyl-TPP but only the standard metallated nickel(II) complex 86, on the basis of spectroscopic evidence (Scheme 2.12).

Scheme 2.12. Reaction of β-allyl-TPP with nickel(II) acetate.
As the reaction of the nickel(II) metallated compound 76 to give the acroleinyl-substituted analogue 85 gave the same yield as the reaction of the free-base 75, the influence of the inserted metal was investigated in more detail. Therefore, meso-diallylporphyrin 70 was metallated with zinc(II) by standard procedure\(^\text{10}\) to obtain the zinc(II) analogue 87 in 77% yield. When compound 87 was subjected to the optimised reaction conditions, only decomposition took place and small amounts of starting material were recovered (Scheme 2.13). Hence, the inserted nickel(II) must be crucial for the activation of the meso-allyl-substituent to convert to the acroleinyl group.

\[
\text{Ni(OAc)}_2 \xrightarrow{\text{AcOH}} \text{DMF, 130 °C} \xrightarrow{\text{Zn(II)}} 87
\]

Scheme 2.13. Reaction of zinc(II) metallated diallylporphyrin with nickel(II) acetate.

A closer look at the Suzuki cross-coupling reaction of [5,15-dibromo-10,20-bis(4-methylphenyl)porphyrinato]nickel(II) 64 with allylboronic acid pinacol ester in the presence of K\(_3\)PO\(_4\) with Pd(PPh\(_3\))\(_4\) as catalyst revealed the formation of [5-acroleinyl-15-allyl-10,20-ditolylporphyrinato]nickel(II) 88 in very small amounts (Scheme 2.14).

\[
\text{Br} \xrightarrow{\text{Pd(PPh\(_3\))\(_4\), K\(_3\)PO\(_4\)}} \text{THF, 80 °C} \xrightarrow{\text{CHO}} \text{Ni(II)}
\]

Due to this observation and the fact that palladium(II) and nickel(II) reagents often react similarly, compound 75 was reacted with Pd(PPh₃)₄ and Pd(OAc)₂ in the presence of glacial acetic acid in DMF at 130 °C for 12 h. Despite of the fact that the allyl-substituents were expected to be activated, only decomposition took place under these conditions.

In an approach to investigate the mechanism of the reaction, compound 71 was reacted with nickel(II) acetate in d₇-DMF at 115 °C in a sealed Schlenk-tube (in the absence of glacial acetic acid to simplify matters). The progress of the reaction was monitored by ¹H nuclear magnetic resonance (NMR) spectroscopy over a period of 24 h. The purpose of this experiment was to monitor the occurrence of any intermediate or by-product formed during the reaction. The use of a deuterated solvent allowed the direct removal of samples from the reaction mixture while the reaction took place, followed by immediate analysis at room temperature. This study revealed that conversion of compound 71 occurs as soon as the nickel(II) complex 75 of the starting material is formed. As the reaction only proceeds under thermal conditions and the measurements were carried out at room temperature, this could explain why no intermediates were detected. Hence, the mechanism of this transformation reaction can only be speculated upon.

Related studies showed that nickel catalysts are sometimes more effective than their palladium analogues for the reaction of allylic systems. The first reaction step could be identical to previous observations and involve the formation of a nickel-η³-allyl complex (Figure 2.4).

**Figure 2.4.** Possible intermediate during formation of diacroleinylporphyrins.
In one case the experimental data indicated a radical chain reaction mechanism initiated by heat, light or a reducing agent. All other reactions reported required a polar, coordinating solvent, such as DMF, as well as stoichiometric amounts of the nickel reagent. This is in agreement with the observations that the nickel(II) mediated reaction of diallylporphyrins required at least 3 equiv. of nickel(II) acetate to form the respective nickel(II) diacroleinylporphyrins. As mentioned earlier, 1 equiv. inserts into the porphyrin core, leaving 2 equiv. of nickel(II) acetate, one for each allyl-substituent. The formation of a \( \eta^3 \)-allyl-complex produces a partial positive charge at the carbon atoms C1 and C3 of the allylic group. These two positions are therefore susceptible to nucleophilic attacks; however, C1 is shielded by the macrocycle.

An alternative reaction mechanism is given by oxidation of the allyl-substituent with oxygen. Scheme 2.15 shows the suggested mechanism on compound 82 as an example. The first reaction step involves the formation of the \( \eta^3 \)-nickel(II)-allyl-complex I with the loss of a molecule of acetic acid. The \( \eta^3 \)-nickel(II)-allyl-complex I performs a nucleophilic attack to one oxygen atom of molecular oxygen. The second oxygen atom of molecular oxygen forms a hydrogen bond to the acidic proton of acetic acid and the former \( \eta^3 \)-nickel(II)-allyl-complex becomes a \( \eta^1 \)-nickel(II)-allyl-complex II. This complex undergoes \( \beta \)-hydrogen elimination with the loss of one water molecule as indicated in structure III. The final step involved the deprotonation of the \( \beta \)-carbonyl-hydrogen to form the acroleinyl-substituted product, compound 83.

Although the pathway of this mechanism is very plausible, it is not in consistency of the observations made during the investigations of the reaction. If a simple oxidation as illustrated in Scheme 2.15 took place the increase of equivalents of glacial acetic acid should only result in a shorter reaction time but not a higher yield of compound 83. Also, the formation of compound 83 should not be dependent on the specific use of glacial acetic acid but any acid in general. This was not observed as hydrogen chloride did not lead to the conversion of the allyl-substituent to the acroleinyl group. Hence, this reaction mechanism is mere speculation with no cogent observation as support.
Scheme 2.15. Speculated oxidation mechanism.
This new methodology for the conversion of an allyl group into an acroleinyl group was also applied to aromatic non-porphyrin systems to investigate its general application. However, when allylbenzene, 2-allylnaphthalene, 9-allylanthracene and 9-allylphenanthracene were subjected to the reaction conditions, the conversion of the allyl group was unsuccessful. It is possible that the allyl-substituent of these compounds were too electron-rich as the conversion was only successful with electron-poor nickel(II) porphyrins. Alternatively, the nickel(II) metal coordinated to the porphyrin core plays a significant role in the reaction mechanism and is missing in the case of the non-porphyrin compounds.

2.4 Spectroscopic Studies

2.4.1 $^1$H Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR spectra of porphyrins clearly show the aromatic character of the macrocycle. The $\beta$- and meso-protons are deshielded by the diamagnetic ring current and so their signals are shifted to lower field. As the meso-carbon atoms are more electron deficient than the $\beta$-carbon atoms, the meso-protons are shifted even further towards lower field than the $\beta$-protons. The effect of the diamagnetic ring current on the inner nitrogen protons is opposite to the effect on the protons outside of the macrocycle. The inner protons are shielded from the external magnetic field and are therefore shifted to higher field, further than the signal for trimethylsilane.$^{90,91}$
The $^1$H NMR spectroscopic time course study of the reaction of 5,15-diallyl-10,20-bis(4-methylphenyl)porphyrin 71 with nickel(II) acetate in d$_7$-DMF over a period of 24 h to give [5,15-diacroleinyl-10,20-bis(4-methylphenyl)porphyrinato]nickel(II) 80 shows the main features of the allyl- and acroleinyl-spectra (Figure 2.5).

![Figure 2.5. Nickel(II) mediated reaction of diallylporphyrin 71 in d$_7$-DMF, monitored by $^1$H NMR, 600 MHz, at rt.](image)

The top spectrum shows the starting material 71 before the reaction was started. After 1 h, the ratio between the starting material and its nickel(II) analogue 79 is already 4:3. The $^1$H signals of compound 79 are shifted to higher field in comparison to the free-base porphyrin 71. This is due to the fact that nickel(II) decreases the electron density of the macrocycle and therefore, the outer protons are less deshielded than in the case of the free-base analogue. After 2 h, the first characteristic signal of compound 80, namely that of the formyl-proton of the acroleinyl group, can be observed at 10.3 ppm.
Consumption of the starting material was complete after 5 h. The ratio of compounds 79 to 80 was 4:1 at that point in time. After 24 h the diacroleinylporphyrin 80 can be clearly identified as main product. Besides the occurrence of the formyl-proton, the differences between diacroleinylporphyrin 80 and diallylporphyrin 79 can be observed in the signals for protons H_a and H_b. Both signals appear at lower field in the spectrum of 80 as H_a of the acroleinyl group is attached to a double bond and H_b is adjacent to the formyl group.

Figure 2.6. ^1^H NMR, 400 MHz, at rt in CDCl_3 of products 82, 83 and 84 of nickel(II) mediated reaction of A_3B-substituted porphyrin.

^1^H NMR spectra of samples of pure compounds 82 to 84, resulting from the nickel(II) mediated reaction from the A_3B-type porphyrin 5-allyl-10,15,20-tris(4-methylphenyl)porphyrin 78, are shown in Figure 2.6. Generally, the lower symmetry of A_3B-type porphyrins in comparison to A_2B_2-type porphyrins can be seen in the splitting of the signals for the β-protons. In case of the A_2B_2-type porphyrins, there are two sets of doublets for the β-protons (Figure 2.5), whereas in the case of compound 82 there are three sets of signals. The influence of the substituents and hence symmetry on the electronic environment of the β-protons is clearly evident in the spectra of compounds 83 and 84 as these signals split further into four sets of doublets. The differences
between the three spectra are quite obvious and can be attributed to the different substituents. A different splitting pattern can be observed for $H_b$ of compound 83 in contrast to compound 82. The formation of a multiplet for compound 82 is a result of a four spin system, whereas the signal for $H_b$ of compound 83 splits into a double doublet as it is part of a three spin system. The signal for the formyl group in compound 84 is even further shifted to lower field at around 12 ppm, in comparison to the signal for the formyl group of compound 83 at around 10 ppm, as it is closer to the porphyrin macrocycle. Also, the formyl-substituent of compound 84 causes a shift of the neighbouring $\beta$-protons to lower field.

2.4.2 Ultraviolet-visible (UV-vis) Spectroscopy

One of the major characteristics of porphyrins is the colour, due to the intense absorption bands in the near-ultraviolet and visible region.

Metallated porphyrins show two electronic transitions in the visible region. The most intensive band is called B band or Soret band, after its discoverer, and represents a permitted $\pi,\pi^*$-transition. Q-bands can be detected in the region of longer wavelengths. They occur due to quasi-permitted $\pi,\pi^*$-transitions and show a vibrational fine structure. Free-base porphyrins generally possess lower symmetry in comparison to the metallated analogues which results in the elimination of degenerated excited states. This causes the occurrence of four Q-bands.
The UV-vis spectra of compounds 82 to 84 are illustrated in Figure 2.7. The Soret band of compound 84 is shifted bathochromically in comparison to compound 82 by 9 nm, due to the additional auxochrome. The Soret band of compound 83 is even further shifted as the acroleinyl-substituent allows for the extension of the π-conjugation of the porphyrin. This effect causes a bathochromic shift of the Soret band of 20 nm in comparison to the allyl-substituted porphyrin 82. Additionally, a bathochromical shift of the Q-bands can be observed by 21 nm as well as a different intensity pattern. The first Q-band of compound 82 has a higher absorbance and the second a very low one that it could not be assigned. The intensities of the Q-bands of compounds 83 and 84 are nearly the same with the second Q-band showing a slight higher absorbance.

Figure 2.7. UV-vis spectra of compounds 82 to 84 in DCM at rt. Baselines were adjusted arbitrarily.
The bathochromic shift is even larger in the case of the disubstituted porphyrins \(79\) to \(81\) (Figure 2.8). There is no difference of the Soret band of the diallylporphyrin \(79\) and the mono-allylporphyrin \(82\). Both can be found at 417 nm. The Soret bands of compounds \(80\) and \(81\) are shifted even further towards longer wavelengths in comparison to compounds \(83\) and \(84\) as these are disubstituted with auxochromic groups.
2.5 Conclusions

A series of allyl-substituted porphyrins was synthesised via the Suzuki cross-coupling reaction. The general application of this method to give various substitution patterns on porphyrins was demonstrated. It could be used to functionalise the meso-position of \(\text{A}_2\text{B}_2\) as well as \(\text{A}_3\text{B}\)-type porphyrins, for both aryl- and alkyl-substituted, as well as in the \(\beta\)-position. Electron withdrawing substituents (phenyl, tolyl) on the porphyrin support the reaction to obtain the Suzuki product in 62 % to 78 % yield. On the other hand, electron donating substituents (hexyl, \textit{iso}-propyl, butoxyphenyl) on the porphyrin seem to lower the reactivity to give the cross-coupling product in 41 % to 50 % yield and, in the case of 5,15-di(\textit{iso}-propyl)porphyrin, only in 2 % yield. However, the yield of the alkyl-substituted porphyrins could be increased by metal insertion of nickel(II) into the starting material.

Moreover, a new synthetic pathway was discovered and investigated with which to convert allylporphyrins into nickel(II) acroleinylporphyrins in up to 70 % yield via a nickel(II) mediated reaction. This is the first example of a nickel catalysed reaction in porphyrin chemistry. This methodology could be applied to \(\text{A}_2\text{B}_2\) as well as \(\text{A}_3\text{B}\)-type porphyrins, aryl- and alkyl-substituted. However, it was found to be limited to the meso-position of either free-base or nickel(II) metallated porphyrins. The reaction conditions were optimised and investigations were carried out to describe the reaction mechanism.
Chapter 3:
The Pauson-Khand Reaction of Porphyrrins
3.1 Background

The Pauson-Khand reaction is a formal [2+2+1] cycloaddition of an alkene, an alkyne and a carbon monoxide molecule in the presence of a transition metal to form a cyclopentenone system (Scheme 3.1). Since its discovery by Pauson and Khand in 1971 this reaction has remained the most flexible and atom-economical method for the synthesis of five-membered rings. It has been shown that cyclopentenones are versatile building blocks for the synthesis of natural products and that they exhibit biological activity.

![Scheme 3.1. The Pauson-Khand reaction.](image)

Originally, cobalt carbonyl was used as the transition metal complex for the Pauson-Khand reaction and it also served as a carbon monoxide source. The mechanism for this stoichiometric reaction, proposed by Magnus and co-workers, has been widely accepted (Scheme 3.2).

![Scheme 3.2. Postulated mechanism of the Pauson-Khand reaction.](image)
Initially, cobalt carbonyl coordinates to the alkyne to form the initial alkyne-hexacarbonylcobalt complex I. The next step is strongly endothermic and involves the loss of a carbon monoxide ligand. This creates a vacant coordination site on complex II for the alkene to coordinate on the cobalt to form the intermediate III. The alkene π-bond then inserts irreversibly into a cobalt-carbon bond to form the cobaltacycle IV. This step is believed to be rate-determining and establishes the regiochemistry and stereochemistry of the product. The last two steps involve insertion of a carbon monoxide molecule into a cobalt-carbon sp³ bond followed by reductive elimination and subsequent loss of a hexacarbonylcobalt molecule to form the cyclopentenone V. It has proven difficult to isolate any of the intermediates beyond complex I, and complex II could only be detected by mass spectrometry.

Although the first intramolecular version of the Pauson-Khand reaction was reported by Schore only ten years after the initial discovery, it has received most attention. This variation is thermodynamically more favoured and the formation of regioisomers can be excluded. In the case of the intermolecular Pauson-Khand reaction, the stereochemistry of the cobalto-intermediate IIIa and IIIb determines the regiochemistry of the products IV and V (Scheme 3.3).

For asymmetrically substituted alkynes (terminal and internal) insertion occurs exclusively at the alkyne carbon bearing the smaller substituent Rₛ. Consequently, the larger substituent Rₗ is always at the 2-position of the cyclopentenone. In contrast, the regiochemistry with respect to the alkene is generally less predictable. As shown in Scheme 3.3 the mono substituted alkene can coordinate in two possible ways to the
cobalt of complex IIIa and IIIb. In the reaction of a terminal alkyne with a monosubstituted alkene both regioisomers V and VI are formed, generally in a mixture of 1:1. In the case of a disubstituted alkyne isomer VI is obtained as the main product due to sterical factors. However, it is also known that the regiochemistry can be quite random and the reverse regioselectivity has been described for different promoters,\textsuperscript{107} different solvents and thermolyses.\textsuperscript{108} The reason for this unexpected selectivity remains unclear.\textsuperscript{109}

Additional to regiochemical challenges the intermolecular Pauson-Khand reaction appears to be synthetically more demanding. It has been limited by the poor reactivity and selectivity of simple alkenes. Sterically hindered alkenes are disfavoured and in many cases yields are only moderate. As a result, the intermolecular Pauson-Khand reaction has been restricted to strained alkenes, such as norbornene and norbornadiene, and there is a continuing need to widen the scope of this reaction.

The most common cyclisation reactions in porphyrin chemistry are Diels-Alder\textsuperscript{110} and the 1,3-dipolar cycloaddition reactions\textsuperscript{111} amongst other electrocyclic reactions.\textsuperscript{112} These methods have mostly been applied to the β-position of the porphyrin to form chlorins, isobacteriochlorins and bacteriochlorins.\textsuperscript{41} Recent advances include the use of microwave (MW) irradiation for the Diels-Alder reaction and the first 1,3-dipolar reactions at the meso-position of the porphyrin.
Silva et al. reported improvements of the Diels-Alder reaction of tetraarylporphyrin $89$ with pentacene under microwave assisted conditions (Scheme 3.4). The chlorin $90$ was obtained in 83 % yield, whereas the classic reaction conditions, namely heating in an oil bath at 200 °C for 8 h, only gave a yield at 22 %.

\[ \text{Scheme 3.4. Microwave assisted Diels-Alder reaction.} \]

The first cyclisation reactions of substituents in the meso-position of the porphyrin were only reported recently. Osuka and co-workers showed the reaction of an acetylene-substituted porphyrin $91$ with benzyl azide in the presence of copper(I) chloride to obtain the 1,3-dipolar cycloaddition product $92$ in 84 % yield (Scheme 3.5).

\[ \text{Scheme 3.5. 1,3-Dipolar cycloaddition at the meso-position of porphyrin.} \]
3.2 The Pauson-Khand Reaction of Alkenylporphyrins

Pauson and Khand investigated the reaction of styrene with phenylacetylene in an intermolecular fashion. In order to explore this reaction for porphyrins, the vinyl-substituted porphyrin, [5,10,15-tris(4-methylphenyl)-20-vinylporphyrinato]nickel(II) 94, was prepared via Suzuki cross-coupling reaction of 5-bromo-10,15,20-tris(4-methylphenyl)porphyrin 67 with vinylboronic acid pinacol ester to form compound 93 and subsequent metallation with nickel(II) acetate gave compound 94 in an overall yield of 37% (Figure 3.1). As a first attempt at the intermolecular Pauson-Khand reaction of porphyrins, the vinyl-substituted compound 94 was reacted with phenylacetylene and cobalt carbonyl. The reaction was carried out in a three-necked round bottom flask equipped with a reflux condenser under argon atmosphere. Phenylacetylene was dissolved in anhydrous THF. Cobalt carbonyl was added and the reaction mixture was stirred at room temperature for one hour until formation of the cobalt-acetylene complex. This could be monitored by TLC on silica gel (CH$_2$Cl$_2$/C$_6$H$_{14}$ 1:1, v/v) by the appearance of a polar peak, visible under UV light. Compound 94 was added and the reaction mixture was heated to reflux for four days. The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. Unfortunately, the only product that could be isolated from this reaction by column chromatography on silica (CH$_2$Cl$_2$/C$_6$H$_{14}$ 1:2, v/v) was the formyl-substituted analogue 84 in 11% yield. Possibly, the double bond of compound 94 is too close to the macrocycle and therefore too sterically hindered to take part in the reaction.

![Figure 3.1. Starting materials for the Pauson-Khand reaction of alkenylporphyrins.](image)

Hence, the allyl-substituted porphyrin 82, with an extra carbon atom between the porphyrin macrocycle and the terminal double bond, was subjected to the same reaction conditions (Scheme 3.6).
Indeed, the intermolecular Pauson-Khand reaction proceeded smoothly, and after 18 h the two products 100 and 101 were obtained in 19 % and 34 % yield, respectively. Compound 100 was obtained as the first fraction of column chromatography on silica gel (CH₂Cl₂/C₆H₁₄ 1:1, v/v) and regioisomer 101 was obtained as the second fraction. The reaction was also applied to the zinc(II) metallated analogue 95 and gave the respective products 102 and 103 in lower yields. To investigate the scope of this reaction further, the alkyl-substituted porphyrin 99 was prepared. The synthesis involved nucleophilic substitution of 5,15-dihexylporphyrin 57 with n-hexyllithium to obtain 5,10,15-trihexylporphyrin 96 in 26 % yield. Subsequent bromination gave compound 97 in 88 % yield and this was reacted with allylboronic acid pinacol acid under Suzuki conditions to give compound 98 in 60 % yield. Finally, porphyrin 98 was metallated using nickel(II) acetate to obtain the starting material 99 in 71 % yield. The Pauson-Khand reaction of the alkyl-substituted porphyrin 99 with phenylacetylene resulted in the formation of the two compounds 104 and 105, albeit in lower yields of...
14 % and 19 %, respectively, than in comparison with the nickel(II) aryl-substituted compounds 100 and 101.

To improve the yield of the intermolecular Pauson-Khand reaction, various possibilities have been reported in literature.\textsuperscript{94} The most promising ones seem to be either the replacement of cobalt by a different transition metal or the use of additives. Thus, cobalt carbonyl was replaced with molybdenum hexacarbonyl in the reaction of compound 82 with phenylacetylene.\textsuperscript{117,118} However, no reaction was observed and only starting material was recovered. As a second attempt to improve the yield of this reaction, N-methylmorpholine N-oxide was used as an additive.\textsuperscript{119} Again, only starting material was recovered. The addition of molecular sieves (4 Å) led to the formation of the desired compounds 100 and 101 but without improvement of the yield.\textsuperscript{120}

From the Pauson-Khand reaction of compound 82 with phenylacetylene using the initial reaction conditions, no starting material was recovered or detected by TLC. Looking at the reaction mechanism, the remaining equivalents of allylporphyrin 82 were possibly still inserted in complex IV (Scheme 3.6). However, attempts to isolate this complex were unsuccessful. Though, the existence of this intermediate could not be proven by Magnus and co-workers who postulated the mechanism nor has it been reported since.\textsuperscript{99} An attempt was conducted to force this intermediate to proceed in the reaction. This was completed by carrying out the reaction of allylporphyrin 82 with phenylacetylene and cobalt carbonyl in THF once again, this time in a sealed Schlenk tube. The solvent was degassed \textit{via} three freeze-pump-thaw cycles and the reaction mixture was stirred at 80 °C until no change was observed by TLC. Indeed, the combined yield of compounds 100 and 101 could be improved from 53 % to 72 %, respectively, after three days.

The Pauson-Khand products 100, 102, 104 and 101, 103, 105 comprise the two expected regioisomers in analogy to compounds V and VI according to the reaction mechanism (Scheme 3.3). The larger substituent of the alkyne reagent, namely the phenyl group, was always at the 2-position of the cyclopentenone. As the other residue of the alkyne reagent is a proton, complex III of the reaction mechanism is non-selective. Therefore, the residue of the terminal alkene, namely the porphyrin, occurred at the 4-position or, alternatively, at the 5-position of the resulting cyclopentenone. When the Pauson-Khand reaction was stopped after one day, the main products were the regioisomers 101, 103 and 105 with the porphyrin residue in the 4-position of the
cyclopentenone. This result seems plausible, as the porphyrin residue is rather bulky and the 2,4-disubstituted regioisomer is sterically more favoured. However, when the reaction of allylporphyrin 82 was left reacting for three days, the regioisomer 100 with the porphyrin residue on 5-position of the cyclopentenone was obtained in a slightly higher yield. As mentioned previously (Chapter 3.1), the occurrence of reverse regioselectivity in the intermolecular Pauson-Khand reaction is known but cannot be explained, yet.

The intermolecular Pauson-Khand reaction of allylporphyrin 82 was also carried out using different alkyne reagents. Phenylacetylene was replaced by ethynyltrimethylsilane, hexyne, dimethyl ethylacetylenedicarboxylate and propargyl toluene-4-sulfonate as alkyne reaction partner. Unfortunately, all of these attempts remained unsuccessful.

### 3.3 The Pauson-Khand Reaction of Alkynylporphyrins

The next step in the studies of the intermolecular Pauson-Khand reaction of porphyrins was to investigate the scope of a porphyrin as the alkyne reaction partner. Therefore, the acetylene group was introduced to the meso-position of other porphyrins (Figure 3.2). This was accomplished by reacting 5-bromo-10,15,20-tris(4-methylphenyl)porphyrin 67 with ethynyltrimethylsilane via Sonogashira reaction conditions according to the literature to obtain compound 106 in 72 % yield.\(^\text{121}\) Metallation with nickel(II) acetylacetonate gave the nickel(II) analogue 107 in 99 % yield and subsequent deprotection of the acetylene group resulted in the formation of the ethynyl-substituted porphyrin 108 in a quantitative yield.\(^\text{75}\)

![Figure 3.2. A,B-Type alkynylporphyrins as starting materials for the Pauson-Khand reaction.](image-url)
In analogy to the Pauson-Khand reaction of allylporphyrins with phenylacetylene, ethynylporphyrin 108 was reacted with allylbenzene and cobalt carbonyl in THF. Therefore, an oven-dried Schlenk-tube was put under argon atmosphere and charged with ethynylporphyrin 108 in anhydrous THF. The solvent was degassed via three freeze-pump-thaw cycles and put under argon again. Cobalt carbonyl was added and the reaction mixture was stirred at room temperature for one hour until formation of the cobalt-ethynylporphyrin-complex. This was monitored by TLC on silica gel (CH$_2$Cl$_2$/C$_6$H$_{14}$ 1:1, v/v) by the appearance of a green spot with a higher retention factor than the starting material. Then allylbenzene was added and the reaction mixture was heated to 80 °C in a sealed Schlenk-tube for 18 h. Next day the reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. Dry loaded column chromatography on silica gel (CH$_2$Cl$_2$/C$_6$H$_{14}$ 1:1, v/v) was carried out. However, no product was obtained and only decomposition took place. This can be related to the poor reactivity of the alkene partner as mentioned in Chapter 3.1. It was found that terminal alkenes usually result in low yields. De Bruin et al. showed that the lower the lowest unoccupied molecular orbital (LUMO) of the alkene, the higher the reactivity for the intermolecular Pauson-Khand reaction. Based on these studies they suggested the following order of reactivity for the thermal Pauson-Khand reaction: cyclohexene < cyclopentene < norborne. Hence, ethynylporphyrin 108 was reacted with cyclohexene, norborne and allylporphyrin 82; again unsuccessfully.

To create a more electron-rich ethynylporphyrin, the zinc(II) metallated analogue 109 and the alkyl-substituted compound 112 were prepared. Porphyrin 112 was synthesised using the same methods as for compound 108, namely Sonogashira reaction of 97 with ethynyltrimethylsilane to obtain compound 110 in 67 % yield, followed by metallation with nickel(II) acetylacetonate to compound 111 in 98 % yield and finally, deprotection to give porphyrin 112 in 99 % yield. The Pauson-Khand reactions of compounds 109 and 112 with norborne were again unsuccessful. Attempts to isolate the presumed initial alkyne-hexacarbonylcobalt complex of type I (Scheme 3.2) failed. Possibly, the alkyne group is too sterically hindered by the porphyrin macrocycle for the reaction to proceed, similar to the situation observed for vinylporphyrin 94 (Chapter 3.2). The mechanism of the Pauson-Khand reaction seems to be quite sterically demanding, which is conceivable when imagining complexes II and IV 3-dimensionally.
As the introduction of a spacer between the porphyrin macrocycle and the reaction centre was successful for alkenylporphyrins to take part in the Pauson-Khand reaction, the same method was applied to alkynylporphyrins. The most accessible porphyrin substituent bearing a terminal alkynyl group that is not directly linked to the meso-position was 4-ethynylphenyl.\textsuperscript{122,123} This substituent could easily be introduced to the macrocycle by nucleophilic substitution reaction of 5,15-bis(4-methylphenyl)porphyrin 56 with 4-ethynylphenyl lithium to obtain the 4-ethynylphenyl-substituted porphyrin 113 in 39 % yield (Figure 3.3). Metallation of compound 113 with nickel(II) acetylacetonate and zinc(II) acetate afforded the starting materials 114 and 115 in 78 % and 38 % yield, respectively.

![Figure 3.3. A_{2}B-Type alkynylporphyrins as starting materials for the Pauson-Khand reaction.](image.jpg)

The intermolecular Pauson-Khand reaction of alkynylporphyrins 114 and 115 with norbornene and norbornadiene succeeded and compounds 116 to 118 were obtained in good yields of 85 % and 78 %, respectively (Scheme 3.7). The regioselectivity of the products with regard to the cyclopentenone is in agreement with the theoretical expectations. The larger substituent of the alkyne reaction partner, namely the porphyrin, is located at the 2-position of the cyclopentenone. Several studies have shown that the Pauson-Khand reaction of norbornene and norbornadiene is completely \textit{exo-face} selective.\textsuperscript{124-128}
The yield of compound 118 was notably lower in comparison to compounds 116 and 117. Possibly, compound 118 reacted further with starting material 114 via a double Pauson-Khand reaction. However, the product mixture could not be analysed, as the amount of other fractions isolated was too small.
The double Pauson-Khand reaction on norbornadiene as a one-step procedure has been reported previously.\textsuperscript{124} It was achieved by using an excess of the alkyne. Accordingly, norbornadiene was reacted with a two-fold excess of the alkynylporphyrin \textit{114}. The main product of this reaction was the single Pauson-Khand product \textit{118} in 29\% yield. Other fractions isolated from this reaction were again insufficient for further analysis.

Hence, the double Pauson-Khand reaction was carried out in two steps. Compound \textit{118} was reacted with alkynylporphyrin \textit{114} and cobalt carbonyl (Scheme 3.8). Indeed, the two expected regioisomers \textit{119} and \textit{120} were obtained in a nearly quantitative combined yield of 50\% and 47\%, respectively. The stereochemistry of the second Pauson-Khand reaction on norbornadiene is also known to be \textit{exo-face} selective.\textsuperscript{127}

\begin{scheme}
\begin{center}
\includegraphics[width=\textwidth]{Scheme3.8.png}
\end{center}
\end{scheme}

\textbf{Scheme 3.8.} Synthesis of porphyrin dimers via two step double Pauson-Khand reaction.
3.4 Spectroscopic Studies

3.4.1 $^1$H NMR Spectroscopy

The two regioisomeric products 100 and 101, resulting from the Pauson-Khand reaction of allylporphyrin 82 with phenylacetylene, can easily be distinguished in their $^1$H NMR spectra (Figure 3.4).

![Figure 3.4](attachment:fig34.png)

There are two protons $H_b$ at the 5-position of the cyclopentenone of compound 101, whereas the signal for the proton $H_b$ at the same position of compound 100 integrates as one. This signal is also shifted towards lower field, as it is closer to the porphyrin macrocycle than the according signal $H_b$ of compound 101. The signals $H_c$ at the 4-position of the cyclopentenone, show the exact opposite. There are two proton signals for compound 100 and only one for compound 101, which is shifted towards lower field as it is closer to the porphyrin macrocycle in comparison to the $H_c$ signals of compound.
These two sets of $^1$H NMR signals, namely the ones for $H_b$ and $H_c$, are the ones that make it possible to differentiate between the two regioisomers. The signals for the protons $H_a$ and $H_d$ on the other hand, can be found in the same regions for both regioisomers 100 and 101 as the chemical environment for these two sets of signals are very similar.

For the initial assignment of the $^1$H NMR signals of the cyclopentenyl substituent HH-correlation spectroscopy (COSY) was carried out. Figure 3.5 shows the section of the 2-dimensional spectrum for the assignment of the signals of $H_a$, $H_b$ and $H_c$. A strong correlation can be observed for the two pairs of protons of $H_a$ and $H_b$ as they share one carbon atom, respectively. Additionally, correlations of $H_b$ with both pairs of $H_a$ and $H_c$ are clearly shown. This proves the assignment of this proton as the one in 5-position of the cyclopentenone ring, situated between two CH$_2$ signals.

The HH-COSY assignment was further proven by nuclear Oppenhaus$^r$ effect spectroscopy (NOESY). This measurement is based on correlations through space as opposed to interactions through bonds. Nevertheless, the same results can be observed. The protons $H_a$ correlate stronger with $H_b$ but also with $H_c$ as shown in the top spectrum.
of Figure 3.6. The second spectrum shows the correlation of \( H_b \) with \( H_a \) and \( H_c \). In the bottom spectrum a NOESY of \( H_c \) demonstrates the correlations to \( H_a \), \( H_b \) and \( H_d \).

Figure 3.6. NOESY measurements of compound 100 in CDCl\(_3\).
The $^1$H NMR spectra of the two regioisomeric porphyrin dimers 119 and 120 differ only slightly (Figure 3.7). Nevertheless, they can be distinguished by the four protons $H_b$ at the 4- and 5-position of each cyclopentenone, respectively. Although both compounds 119 and 120 are symmetrical, the fact that dimer 119 is mirror symmetric and dimer 120 is point symmetric is the reason for the differences in the $^1$H NMR spectra. Due to the mirror symmetry of compound 119, the four protons $H_b$ experience a different chemical environment, depending on whether they are at the 4- or 5-position of the two cyclopentenone rings. The two protons $H_b$ at the 5-position of each cyclopentenone ring are located between two carbonyl groups and therefore shifted towards lower field at
3.16 ppm. As the two protons H\textsubscript{b} at the 4-position of each cyclopentenone ring experience a completely different chemical environment, they appear in the \textsuperscript{1}H NMR as an individual peak at 2.84 ppm. The assignments of the \textsuperscript{1}H signals of the tetracyclic linker were achieved by comparison of the \textsuperscript{1}H NMR studies of Khand \textit{et al.} carried out on the same tetracyclic unit.\textsuperscript{124}

On the other hand, compound \textbf{120} is point symmetrical and therefore its \textsuperscript{1}H NMR spectrum is "more symmetrical" in comparison to the spectrum of compound \textbf{119}. Previous studies of the two isomeric tetracyclic linkers have shown that the proton H\textsubscript{b}, adjacent to the carbonyl group is rigidly held at a large angle.\textsuperscript{124} Therefore, the influence of one carbonyl group on the protons H\textsubscript{b} of compound \textbf{120} is not as big as the influence of two carbonyl groups as in compound \textbf{119}. Consequently, there is only one signal for all four H\textsubscript{b} protons in the \textsuperscript{1}H NMR spectrum of compound \textbf{120} at 3.06 ppm, located between the two signals for H\textsubscript{b} and H\textsubscript{b'} of compound \textbf{119}. The other proton signals, H\textsubscript{a}, H\textsubscript{c} and H\textsubscript{d}, of the two isomeric tetracyclic linkers are not influenced by the different symmetries of compounds \textbf{119} and \textbf{120} and can therefore be found in the same regions in the \textsuperscript{1}H NMR spectrum, respectively.
3.4.2 UV-vis Spectroscopy
The UV-vis spectra of the Pauson-Khand products hardly differ from their starting materials. This is demonstrated in Figure 3.8. The monomeric Pauson-Khand product 116 shows the same absorption maximum as its starting material 114 at 409 nm. Even the UV-vis spectrum of the porphyrin dimer 119 is only slightly different to starting material 114 with an absorption maximum of 410 nm. This is due to the fact that the linker of dimer 119 is not fully conjugated. Therefore, the two porphyrin units are not in conjugation with each other and the UV-vis spectrum of dimer 119 is not different to the one of a monomer, such as compound 116.

Figure 3.8. UV-vis spectra of compounds 114, 116 and 119 in DCM at rt. Baselines were adjusted arbitrarily.
3.5 Conclusions

It has been shown that the Pauson-Khand reaction offers an alternative pathway for cyclisation reactions of porphyrin substituents at the meso-position. The porphyrin could serve as alkene as well as alkyne partner for the intermolecular Pauson-Khand reaction. However, steric considerations required the reaction centre to be at a certain distance from the macrocycle.

When the porphyrin served as the alkene reaction partner, a distance of one carbon atom between the terminal double bond and the porphyrin macrocycle was necessary for the reaction to proceed. Reactions of allylporphyrins with phenylacetylene resulted in a combined yield of the expected two regioisomers of up to 72 %. However, this reaction was limited by the choice of the non-porphyrin alkyne partner and could only be carried out successfully with phenylacetylene.

A similar case was found for the intermolecular Pauson-Khand reaction using porphyrin as alkyne partner. When the terminal triple bond was directly linked to the porphyrin macrocycle the reaction did not proceed. This problem could be solved by the introduction of a spacer group. 4-Ethynylphenyl-substituted porphyrins reacted with norbornene and norbornadiene to give the corresponding Pauson-Khand products in up to 85 % yield. Again, the reaction was limited by the choice of the non-porphyrin alkene partner which is a common problem of the intermolecular Pauson-Khand reaction.

Additionally, porphyrins could serve as the alkene and alkyne reaction partner in a sequential double Pauson-Khand reaction to form regioisomeric porphyrin dimers in a nearly quantitative combined yield of 97 %. The two isomers could easily be separated by column chromatography and identified by $^1$H NMR spectroscopy. This demonstrated the potential of this method for the preparation of technically and medicinally relevant complex heterocycles.
Chapter 4:
C-H Bond Activation Reactions of Porphin
4.1 Background

Porphyrin (porphin) is the parent nucleus of every natural and synthetic porphyrin. It seems quite obvious to use porphin as starting material for the synthesis of porphyrins.

Initial investigations on the reactivity of porphin were reported in the 1970’s. Samuels et al. studied the halogenation of porphin. Amongst these reactions, bromination was the most successful. Treatment of porphin 1 with N-bromosuccinimide (NBS) gave \( \beta \)-monobromoporphyrin 121 in 41 % yield (Scheme 4.1).

\[
\begin{align*}
\text{NBS} & \quad \text{CCl}_4; 75 ^\circ C \\
1 & \quad \Rightarrow \quad 121
\end{align*}
\]

Scheme 4.1. \( \beta \)-Bromination of porphin.

Schlözer and Fuhrhop found that the regioselectivity of this reaction could be changed to the meso-position by using (porphyrinato)magnesium(II) 122 and \( N \)-bromoacetamide (NBA) to obtain tetrabromoporphyrin 123 after demetallation in 40 % yield (Scheme 4.2).

\[
\begin{align*}
\text{1. NBA} & \quad \text{tert-BuOH} \quad \text{2. HCl} \\
122 & \quad \Rightarrow \quad 123
\end{align*}
\]

Scheme 4.2. Meso-bromination of (porphyrinato)magnesium(II).
They also reported the Vilsmeier formylation of (porphyrinato)copper(II) 124 to form (formylporphyrinato)copper(II) 125 (Scheme 4.3).

\[ \text{CHO} \]

\[ \text{POCl}_3 \text{DMF} \]

Scheme 4.3. The Vilsmeier formylation of (porphyrinato)copper(II).

Nitration was carried out by Drach and Longo on porphin 1 using nitric and sulfuric acid to obtain the nitroporphyrin 126 in 70% yield (Scheme 4.4).

\[ \text{HNO}_3 \text{H}_2\text{SO}_4; 0 \hspace{1mm} ^\circ\text{C} \]

Scheme 4.4. Nitration of porphin.

Investigations of the reactivity of porphin were resumed nearly 30 years later after Neya and Funasaki published a straightforward procedure for the preparation of porphin in a higher yield. Senge and co-workers reported the nucleophilic substitution reaction of porphin 1 with organolithium reagents. For instance, the reaction of porphin 1 with \( n \)-hexyllithium (5 equiv.) gave 5,10-dihexylporphyrin 127 in 61% yield (Scheme 4.5).

\[ \text{1. } n\text{-HexLi} \text{THF, } -78 \hspace{1mm} ^\circ\text{C} \]

\[ \text{2. DDQ} \]

Scheme 4.5. Nucleophilic substitution reaction of porphin.
Shi and Wheelhouse reported the synthesis of tetraarylporphyrins directly from porphin 1 using the Suzuki cross-coupling reaction. The first step involved bromination of (porphyrinato)magnesium(II) 122 using NBA to obtain (tetrabromoporphyrinato)magnesium(II) 128 in 81% yield. The Suzuki reaction of compound 128 with arylboronic acid resulted in the formation of the tetraarylporphyrins 129 after demetallation in 42% to 70% yield (Scheme 4.6).

**Scheme 4.6.** Synthesis of tetraarylporphyrins using (porphyrinato)magnesium(II) as starting material.

### 4.2 C-H Bond Activation Reactions of Porphin

To broaden the range of applications using porphin as starting material for the synthesis of porphyrins, a study of transition metal catalysed C-H bond activation of porphin was undertaken. The preparation of porphin 1 was initiated from the synthesis of tetra-tert-butylporphyrin 130 in 9% yield, obtained by condensation of pyrrole and trimethylacetaldehyde (Scheme 4.7). The tert-butyl groups of compound 130 were then removed by treatment with sulphuric acid to obtain porphin 1 in yields that fluctuated between 1% to 44%.

**Scheme 4.7.** Synthesis of porphin.
The most common strategy for C-H bond activation of benzene and its derivatives is the use of a palladium catalyst.\(^{137}\) The first approach was based on an intermolecular palladium(II) catalysed C-H addition reaction of arenes to nitriles for the formation of aryl ketones.\(^ {138}\) In analogy to the procedure for benzene derivatives, porphin 1 was reacted with benzonitrile (0.5 equiv.), palladium(II) acetate (5 mol %) and catalytic amounts of trifluoroacetic acid in anhydrous toluene (Scheme 4.8). The reaction was carried out in a Schlenk-tube under argon atmosphere and was monitored by TLC on silica gel (CH\(_2\)Cl\(_2\)/C\(_6\)H\(_{14}\) 2:1, v/v). After 18 h no starting material was observed and the reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane and washed with water. The combined organic phase was dried over sodium sulphate and a \(^1\)H NMR of the crude reaction mixture was recorded. Unfortunately, porphin was destroyed under these harsh acidic conditions.

\[
\begin{array}{c}
\text{NH} \\
\text{N} \\
\text{N} \\
\text{H} \\
\text{N} \\
\text{N} \\
\text{H} \\
\end{array} \quad \text{NC} \quad \text{Pd(OAc)}_2 \\
\text{CH}_3 \quad \text{toluene; TFA} \\
\quad \text{100 °C}
\]

**Scheme 4.8.** Attempted reaction of porphin with benzonitrile.

Therefore, a different type of C-H bond activation reaction was investigated using basic conditions. Based on the palladium(II) catalysed C-C bond formation of heterocycles with aryl chlorides,\(^ {139}\) porphin 1 was reacted with phenyldichloride (Scheme 4.9). Therefore, porphin 1 was dissolved in anhydrous DMF in a Schlenk-tube under argon atmosphere. Phenyldichloride (1.5 equiv.), potassium phosphate (2 equiv.), palladium(II) acetate (0.1 equiv.) and 2-(biphenyl)di-tert-butylphosphine (0.2 equiv.) were added and the reaction mixture was heated to 125 °C. The progress of the reaction was monitored by TLC on silica gel (CH\(_2\)Cl\(_2\)/C\(_6\)H\(_{14}\) 2:1, v/v). However, after 5 days no difference was observed and only porphin was recovered.

\[
\begin{array}{c}
\text{NH} \\
\text{N} \\
\text{N} \\
\text{H} \\
\text{N} \\
\text{H} \\
\quad \text{Cl} \\
\end{array} \quad \text{Cl} \quad \text{Pd(OAc)}_2 \\
\text{DMF; 125 °C}
\]

**Scheme 4.9.** Attempted reaction of porphin with phenyldichloride.
Possibly, the free-base porphin 1 was not reactive enough, as this reaction was originally developed for electron-rich heterocycles. To induce a higher electronegativity to the macrocycle, metallation of porphin with magnesium(II) was attempted according to a literature procedure. However, it was not possible to isolate magnesium(II) porphin 122. This complex is known to be very labile and difficult to handle, so the focus of this project remained on free-base porphin.

Another approach to C-H bond activation of porphin 1 using the Suzuki cross-coupling reaction was carried out. Porphin 1 was reacted with 4-dimethylamino boronic acid and palladium(II) acetate (Scheme 4.10). Therefore, porphin 1 was dissolved in anhydrous DMF in a Schlenk-tube under argon atmosphere. The solution was degassed via three freeze-pump-thaw cycles and put under argon again. 4-Dimethylamino boronic acid (10 equiv.), palladium(II) acetate (0.1 equiv.), copper(II) trifluoromethanesulphonate (1 equiv.) and silver(I) oxide (1 equiv.) were added and the reaction mixture was heated in a sealed Schlenk-tube to 125 °C for 18 h. The reaction was monitored by TLC on silica (CH₂Cl₂/C₆H₁₄ 1:1, v/v). Again, no reaction was observed and only porphin was recovered.

The only known C-H bond activation reaction on porphyrins is the iridium(II) catalysed β-borylation developed by Osuka and co-workers. As this reaction has not been carried out on porphin 1 previously, it was subjected to the general reaction conditions, namely bis(pinacolato)diboron and iridium(II) catalyst (Scheme 4.11). Therefore, porphin 1 was dissolved in 1,4-dioxane in a Schlenk-tube under argon atmosphere. The solution was degassed via three freeze-pump-thaw cycles and put under argon again. Bis(pinacolato)diboron (0.5 to 8 equiv.), 4,4'-di-tert-butyl-2,2'-dipyridyl (0.01 equiv.) and (1,5-cyclooctadiene)(methoxy)iridium(I) dimer (5 mol %) were added and the reaction mixture was heated to 100 °C in a sealed Schlenk-tube. The progress of the reaction was monitored by TLC on silica (CH₂Cl₂/C₆H₁₄ 1:1, v/v). After 5 days the reaction was stopped as hardly any change could be observed by TLC. The solvent was
removed under reduced pressure and the crude reaction mixture was purified by column chromatography on silica gel (ethyl acetate/C₆H₁₄ 1:10, v/v).

Scheme 4.11. Iridium(II) catalysed β-borylation of porphin.

The reaction conditions were varied in regard to the amount of diboron reagent used. When 0.5 to 1.1 equiv. of diboron were used, monoborylated porphyrin 131 could be detected in the $^1$H NMR of the second fraction obtained by column chromatography. However, compound 131 was only obtained in trace amounts and only as a mixture with starting material porphin 1, which could not be separated by additional column chromatography on silica gel (CH₂Cl₂/C₆H₁₄ 1:1, v/v). When 8 equiv. of the diboron reagent was used, the formation of five different products was observed by TLC. Again, these products were only obtained in trace amounts and could not be separated by column chromatography on silica gel, despite numerous attempts.
4.3 Conclusions

Various transition metal catalysed C-H bond activation reactions were carried out on porphin. It turned out to be quite difficult to find appropriate reaction conditions for porphin. It decomposed under acidic conditions but did not react under basic conditions. Attempts to enhance the reactivity of porphin by metal insertion of magnesium(II) failed.

The iridium(II) catalysed β-borylation of porphin led to trace amounts of the desired product as a mixture with starting material. However, it was not possible to separate the β-borylated porphyrin from porphin by column chromatography and attempts to increase the yield of the product failed.

While the extension of new reactions of porphin for the synthesis of porphyrins seemed to be promising, this project turned out to be quite tedious considering the varying yield in porphin synthesis as well as the difficulties with the reactivity of porphin.
Chapter 5:
Rhodium(1) Catalysed Alkylation of Porphyrin
Chapter 5: Rhodium(1) Catalysed Alkylation of Porphyrin

5.1 Background

The introduction of alkyl-substituents onto the porphyrin macrocycle is of considerable interest for the synthesis of amphiphilic compounds suitable for PDT and the design of push-pull porphyrins for applications in NLO. However, apart from total synthesis, there is only a limited number of methods available for the introduction of an alkyl substituent onto the porphyrin macrocycle.

One of the most common pathways for the alkylation of porphyrins is the nucleophilic substitution reaction using alkyllithium reagents. Senge and Feng reported the synthesis of various alkyl-substituted porphyrins with or without functional groups on the alkyl chain. For instance, the reaction of 5,15-diphenylporphyrin \( \text{55} \) with \( n \)-butyllithium gave 5-butyl-10,15-diphenylporphyrin \( \text{132} \) in 94 % yield (Scheme 5.1). However, the use of secondary or tertiary alkyl reagents resulted in lower yields of the respective porphyrin with the formation of by-products. Additionally, functional groups on the alkyl chain needed to be protected and not all functionalised alkyllithium reagents led to the formation of the desired product.

\[
\begin{align*}
\text{55} & \quad \text{+ Li} - \quad \text{THF} -78^\circ C \\
\text{132} & \quad \text{2. } \text{H}_2\text{O} \\
& \quad \text{3. DDQ}
\end{align*}
\]

Scheme 5.1. Alkylation of porphyrin via nucleophilic substitution reaction.
Another method for the introduction of alkyl-substituents onto the porphyrin macrocycle is the Suzuki cross-coupling reaction of bromoporphyrin with alkylboronic acid. The only alkylboron reagent used in porphyrin chemistry is methylboronic acid. Zhou et al. reported the Suzuki reaction of 2,3,7,8,12,13,17,18-octabromoporphyrin 133 with methylboronic acid to obtain 2,3,7,8,12,13,17,18-octamethylporphyrin 134 in 74% yield (Scheme 5.2).\(^\text{144}\)

\[\text{Scheme 5.2. Alkylation of porphyrin via Suzuki cross-coupling reaction.}\]

\[\text{Zinc(I) ring-metallated porphyrins were reported previously, and used for a palladium(II) catalysed cross-coupling reaction with iodoarenes.}\]^\text{146}\ To broaden this procedure to iodoalkanes, the palladium(II) catalyst was unsuitable as it promotes β-hydrogen elimination of the iodoalkanes.\(^\text{147}\) However, it was found that this side-reaction could be inhibited by exchanging palladium(II) with rhodium(I).\(^\text{145}\)
Compounds 135 to 141 were prepared as starting materials (Figure 5.1). This involved the nucleophilic substitution reaction of 5,15-diphenylporphyrin 55 with phenyllithium to obtain 5,10,15-triphenylporphyrin 135 in 89% yield. Halogenation of compound 135 with iodine and NBS gave porphyrins 136 and 137 in 68% and 81% yield, respectively. Metallation of the halogenated compounds 136 and 137 with zinc(II) acetate resulted in the formation of the respective zinc(II) porphyrins 138 and 139 in 95% and 82% yield, respectively. The nickel(II) metallated porphyrins 140 and 141 were obtained by reaction of the free-base compounds 135 and 136 with nickel(II) acetylacetonate in 99% and 97% yield, respectively.

![Figure 5.1. Starting materials for rhodium(1) catalysed alkylation reaction.](image)

In analogy to the literature procedure for the preparation of zinc(I) ring-metallated porphyrin, a solution of Rieke-zinc(0) was prepared (Scheme 5.3).

![Scheme 5.3. Preparation of Rieke-zinc(0).](image)

This solution containing activated zinc(0) was added to porphyrin 138 in THF and left reacting overnight to form the zinc(I) ring-metallated porphyrin 142 in situ (Scheme 5.4). Subsequently, the rhodium(II) catalyst and 1,1'-bis(diphenylphosphino)ferrocene (dpff) were added to the reaction mixture to generate the rhodium(1) catalyst, Rh-dpff, before iodopentane was added. The reaction was stopped after five days as no change was observed by TLC and only starting material was recovered.
The reaction was repeated using different conditions. The Rh-dppf reagent was generated separately before it was added to the reaction mixture and the amount was increased from 0.1 equiv. to 2.5 equiv. Also, the amount of iodopentane was increased from 1 equiv. to 2, 5 and 10 equiv., respectively, and the amount of Rieke-zinc(0) was increased from 1 equiv. to 1.5 and 3 equiv., respectively. Again, only starting material was recovered.

The bromo-substituted compound 139 was also subjected to the reaction conditions using a higher temperature of 80 °C after addition of iodopentane. This alteration was unsuccessful and only starting material was recovered.

When the nickel(II) metallated compounds 140 and 141 were used as starting materials dehalogenation took place and porphyrin 143 was formed (Scheme 5.5).

**Scheme 5.4.** Proposed rhodium(I) catalysed alkylation reaction of zinc(II) porphyrin using Rieke-zinc(0).

**Scheme 5.5.** Rhodium(1) catalysed alkylation reaction of nickel(II) porphyrin using Rieke-zinc(0).
As all attempts with Rieke-zinc(0) failed, a different method was used for the preparation of zinc(I) ring-metallated porphyrins. Compounds 138 and 140 were reacted with activated zinc(0) and trimethylsilyl chloride at 70 °C before the addition of rhodium(1) catalyst and iodopentane (Scheme 5.6). However, only dehalogenation took place and compounds 143 and 144 were generated from the reaction mixture. Alterations of the reaction conditions, regarding amounts of catalyst and iodopentane as well as temperature increase, did not lead to a different result.

Scheme 5.6. Rhodium(0) catalysed alkylation reaction using activated zinc(0) powder.

The zinc(I) ring-metallated porphyrin reported previously, was assumed to be formed due to the observation that the amount of zinc(0) in the solution decreased, however it could not be isolated. Zinc(I) metallated arenes are also known to be unstable and decompose on air. Hence, the presence of any zinc(I) metallated compound can only be confirmed indirectly by gas-liquid chromatography (GLC). Therefore, intermediate 142 could not be isolated nor detected by TLC.
5.3 Conclusions

A rhodium(I) catalysed alkylation reaction was investigated for porphyrins. This included the \textit{in situ} formation of a zinc(I) ring-metallated porphyrin intermediate. Different methods were used for the synthesis of this intermediate. Additionally, the conditions for the subsequent rhodium(I) alkylation reaction were varied. However, none of these attempts were successful and either starting material was recovered or dehalogenation of the starting material occurred to form the according dehalogenated porphyrin.

This investigated reaction seemed to be a highly promising pathway for the introduction of alkyl-substituents onto the porphyrin macrocycle, especially as a similar reaction using zinc(I) ring-metallated porphyrins was reported, previously. However, this method contains a large number of uncertainties since reagents as well as intermediates were formed \textit{in situ}. Therefore, it was not possible to determine whether the conditions for the formation of the intermediate or the subsequent rhodium(I) catalysed alkylation reaction needed further alteration to give the desired alkyl-substituted porphyrins.
Chapter 6: 
Suzuki Reaction of Potassium Organotrifluoroborates with Porphyrrins
6.1 Background

The Suzuki cross-coupling reaction owes its popularity to the fact that it is a very straight-forward method with a high regio- and stereoselectivity as well as tolerance towards a wide range of functional groups.\(^{155}\)

It employs the palladium(0) catalysed reaction of an organohalide with an organoboron compound to form a new carbon-carbon bond in the presence of an appropriate base (Scheme 6.1).

\[
\text{Pd(0) catalyst} \quad R^1-X + (\text{HO})_2B-R^2 \xrightarrow{\text{base}} R^1-R^2 + (\text{HO})_2B-X
\]

Scheme 6.1. General outline of the Suzuki cross-coupling reaction.

The mechanism of the Suzuki coupling reaction is best described by a catalytic cycle (Scheme 6.2).\(^{156}\) The first step (a) is an oxidative addition of the organohalide to the palladium(0) catalyst \(I\) to form a palladium(II) species \(II\). Next, transmetallation (b) transfers substituent \(R^2\) from boron, activated by a base, to palladium, generating the palladium complex \(III\). Step c describes the cis-trans rearrangement of the ligands on palladium(II) to form complex \(IV\). Finally, reductive elimination (d) takes place to obtain the coupling product and regenerate the palladium(0) catalyst \(I\).

Scheme 6.2. Catalytic cycle of Suzuki cross-coupling reaction.
The Suzuki cross-coupling reaction is a very important tool for the synthesis of new porphyrin species and represents the most popular method among palladium catalysed reactions.\(^{64}\) It has been extensively studied on every position of the porphyrin as well as in every possible way: the β-position,\(^{39}\) the meso-position,\(^{40}\) on aryl-substituents\(^{157}\) and with porphyrins serving as the boron reaction partner.\(^{158}\) As mentioned earlier (Chapter 5.1), hardly any alkylboronic derivatives were used in the reaction with halogenated porphyrins.

It has been shown previously, that alkylboronic acids and esters give lower yields in comparison to aryl and alkenyl analogues, unless highly toxic thallium bases are used.\(^{159-161}\) Presumably, this is due to difficulties in the transmetallation step (b) between the boronic acid and the palladium(II) species II (Scheme 6.2).\(^{161}\)

To overcome these problems, Molder and co-workers have enlarged the application of the Suzuki cross-coupling reaction to include the use of potassium alkyltrifluoroborates.\(^{162}\) The major advantages of potassium organotrifluoroborates in comparison to the respective organoboronic acids and esters is their greater nucleophilicity and higher air stability.\(^{163}\) Hence, there are a number of commercially available potassium organotrifluoroborates that cannot be obtained as the boronic acid or ester analogues due to instability.

**6.2 Suzuki Reaction of Potassium Organotrifluoroborates with Porphyrins**

The only reaction of potassium organotrifluoroborates with porphyrins was reported by van Lier and co-workers.\(^{164}\) The Suzuki coupling reaction of compound 145 with potassium vinyltrifluoroborate gave the 4-vinylphenyl-substituted analogue 146 in 56 % yield (Scheme 6.3). The reaction took place at the halogenated aryl-substituent of the zinc(II) metallated porphyrin 145 and was targeted at cationic porphyrins. Besides potassium vinyltrifluoroborate only two other potassium aryltrifluoroborates were used in the coupling reaction and no other porphyrin was investigated.
To investigate the general application of this reaction on uncharged porphyrins, various potassium organotrifluoroborates were reacted with directly meso- and β-brominated porphyrins containing aryl- and alkyl-substituents in different substitution patterns (Figure 6.1). Compound 148 was synthesised by iodination of porphyrin 66 to form compound 147,\(^{76}\) followed by metallation using nickel(II) acetylacetonate in an overall yield of 43\%. As methodologies for the introduction of alkyl-substituents onto the porphyrin macrocycle are limited and problematic (see Chapter 5.1), the Suzuki coupling reaction was focussed on the use of potassium alkyltrifluoroborates.

Figure 6.1. Starting materials for reaction with potassium organotrifluoroborates.
For ease of comparison with literature data the reaction of compound 67 with potassium vinyltrifluoroborate was chosen as a model reaction (Scheme 6.4). The conditions of Molander et al. were changed and optimised according to standard conditions for the Suzuki coupling reaction of meso-brominated porphyrins, and vinylporphyrin 93 was obtained in 61% yield.

\[
\text{NH} \quad \text{N} \quad \text{Br} + \text{KF}_3\text{B}^- \quad \text{Pd(dppf)Cl}_2 \quad \text{Cs}_2\text{CO}_3
\]

\[
\text{THF/H}_2\text{O 10:1} \quad 80^\circ\text{C}
\]

\[
\text{NH} \quad \text{N} \quad \text{HN}
\]

Scheme 6.4. Suzuki coupling reaction of potassium vinyltrifluoroborate with meso-bromoporphyrin.

In comparison, the reaction of potassium vinyltrifluoroborate with bromoaryl-substituted porphyrin 145 gave the coupling product 146 in 56% yield (Scheme 6.3). Using vinylboronic acid pinacol ester in the Suzuki reaction of compound 67, compound 93 was formed in 52% yield (Chapter 3.2). This result is in agreement with observations made by Molander and co-workers that potassium organotrifluoroborates give slightly higher yields than their boronic acid or ester analogues.

To further investigate the scope of this method, various potassium organotrifluoroborates were reacted with porphyrin 67 under the optimised conditions to obtain compounds 149 to 155 in low to good yields of 16% to 75% (Scheme 6.5). As a side product debrominated starting material, compound 66, was obtained in varying amounts. For the synthesis of compound 153, double the amount of potassium organotrifluoroborate reagent was needed, as well as a longer reaction time of 36 h to fully consume the starting material. All other reactions were complete after 18 h. The reaction conditions were tolerant towards various functional groups, such as carbonyl, cyano, amido, amino and ester groups. The boronic acid or ester analogues of the potassium organotrifluoroborates used for the synthesis of porphyrins 151 to 155 are not commercially available and an approach to synthesise compounds 149 to 155 via a
different pathway would include several steps. Alternatively, compound 150 could be obtained by reaction of 5,10,15-tris(4-methylphenyl)porphyrin 66 with methyllithium in a nucleophilic substitution reaction. However, it has been reported that this reagent presents problems due to multiple reactions at the meso-position.\footnote{\textsuperscript{167-169}}

\begin{center}
\begin{tabular}{ccc}
R & Product & Yield [\%] \\
\hline
 & 149 & 21 \\
 & 150 & 29 \\
 & 151 & 73 \\
 & 152 & 26 \\
OMe & 153 & 16 \\
\end{tabular}
\end{center}

\begin{center}
\begin{tabular}{ccc}
R & Product & Yield [\%] \\
\hline
 & 154 & 21 \\
 & 155 & 75 \\
\end{tabular}
\end{center}

\textbf{Scheme 6.5.} Suzuki coupling reaction of compound 67 with various potassium organotrifluoroborates.

The next aspect of exploring the Suzuki coupling reaction of potassium organotrifluoroborates with porphyrins involved investigating the method with different types of porphyrin. Therefore, alkyl-substituted porphyrin 97, \( \beta \)-brominated compound 69 and the dibromo-\( \text{A}_3\text{B}_2 \) porphyrin 60 were reacted with potassium cyanoethyltrifluoroborate under the optimised conditions to obtain compounds 156 to 158 in 25% to 70% yield (Figure 6.2). The yield of alkyl-substituted porphyrin 156 is lower at 25% in comparison to the aryl-substituted analogue 151 with a yield of 73%. This is due to the electron-donating effect of the alkyl-substituents and has been observed previously in the Suzuki cross-coupling reaction with boronic esters (Chapter 2.2).\footnote{\textsuperscript{72}}
In the reaction of dibromoporphyrin 60 the amounts of potassium cyanoethyltrifluoroborate and caesium carbonate were doubled according to the number of bromide-substituents. The yield of 35 % for \( \text{A}_3\text{B}_2\) -porphyrin 158 is significantly lower than that of \( \text{A}_2\text{B}_1\) -porphyrin 151. The isolation of compound 158 by column chromatography was rather problematic as the retention factor of compound 158 was very close to the retention factor of the debrominated by-product 56, which led to the lower isolated yield of 35 %. The mono-coupled product was not observed. The difference in the reaction of potassium cyanoethyltrifluoroborate with meso-monobrominated porphyrin 67 or \( \beta\)-monobrominated porphyrin 69 was very small. The \( \beta\)-substituted product 157 was obtained in 70 % yield, nearly the same result as for the meso-substituted product 151 with a yield of 73 %.

In an attempt to synthesise a methyl-bridged porphyrin dimer, compound 67 was reacted with potassium bromomethyltrifluoroborate using the optimised conditions. However, no reaction was observed and only starting material was recovered. Therefore, the more reactive porphyrin 148 was subjected to the same reaction conditions (Scheme 6.6). Surprisingly, the only product obtained was the directly meso-meso linked bisporphyrin 159 in 10 % yield. The formation of this dimer is possibly due to self-addition of another compound 148.
6.3 Spectroscopic Studies

6.3.1 $^1$H NMR Spectroscopy

As mentioned earlier the $^1$H NMR spectra of porphyrins are influenced by the ring current of the macrocycle (Chapter 2.4.1). Protons located on the outside of the porphyrin macrocycle are therefore shifted towards lower field. Although meso- and β-protons are both located directly on the aromatic ring, they experience a different influence of the ring current. Protons at the β-position of porphyrins are less influenced by the ring current than protons at the meso-position due to the higher electron deficiency of meso-carbon atoms in comparison to β-carbon atoms. Therefore, meso-protons are even further shifted towards lower field than β-protons.

This effect also influences the proton signals of the meso- and β-substituents and is demonstrated by comparison of the $^1$H NMR spectra of meso-cyanoethyl-substituted compound 151 with β-cyanoethyl-substituted porphyrin 157 (Figure 6.3). The $^1$H NMR signal for the two protons $H_a$ of compound 151 is shifted further towards lower field at 5.46 ppm in comparison to the signal for the two protons $H_a$ of compound 157 at 3.23 ppm. The same effect can be observed for the $^1$H NMR signal for proton $H_b$. As this proton is further away from the macrocycle, the effect is smaller and the difference of this signal for compound 151 in comparison to compound 157 is only 0.78 ppm.
The substituent at the \( \beta \)-position of compound 157 also affects the location of the \( \beta \)-protons in the spectrum. Alkyl-substituents at the \( \beta \)-position of porphyrins have a shielding effect on the macrocycle.\(^{170}\) Therefore, the signals for the \( \beta \)-protons of compound 157 are shifted towards higher field at 8.67 ppm to 8.87 ppm. In comparison, the signals for the \( \beta \)-protons of \( \beta \)-unsubstituted compound 151 are located further downfield at 8.85 ppm to 9.45 ppm.
6.3.2 UV-vis Spectroscopy

The UV-vis spectra of compounds 149 to 158 differ only slightly with the Soret band at 418 nm to 421 nm, respectively. This is due to the fact that the substituents of these compounds are mainly alkyl-groups with no interaction of the porphyrin π-system. However, the introduction of a fourth meso-substituent into the macrocycle in comparison to only three meso-substituents results in a bathochromic shift of the Soret band. This can be observed in the spectra of compound 66 and compound 152 (Figure 6.4). The presence of a fourth substituent in the meso-position causes a bathochromic shift of the Soret band from 414 nm for compound 66 to 421 nm for compound 152.

![Image](image.png)

Figure 6.4. UV-vis spectra of compounds 66 and 152 in DCM at rt. Baselines were adjusted arbitrarily.
The UV-vis spectrum of the directly meso-meso linked porphyrin dimer 159 shows an interesting feature, characteristic for this type of bisporphyrin (Figure 6.5). The Soret band shows a split which is due to the oblique geometry of the porphyrin dimer. Therefore, two wavelengths can be observed for the Soret band at 418 nm and 447 nm.

Figure 6.5. UV-vis spectra of compound 159 in DCM at rt. Baselines were adjusted arbitrarily.
6.4 Conclusions

The Suzuki cross-coupling reaction of various potassium organotrifluoroborates with directly brominated porphyrins was investigated. The reaction conditions were optimised for the use with porphyrins and were tolerant towards a wide range of functional groups. The method showed general application for the meso- and β-position of the macrocycle as well as for aryl- and alkyl-substituted porphyrins with different substitution patterns. The Suzuki coupling products were obtained in low to good yields of 16 % to 75 %, depending on the nature of the potassium organotrifluoroborate reagents. The investigation was focused on the use of potassium alkyltrifluoroborates to broaden the few pathways existing for the synthesis of alkylporphyrins. It was demonstrated that the use of potassium organotrifluoroborates offered a good alternative to their respective boronic acids or esters. Due to their higher air stability in comparison to their boronic acid or ester analogues, there is a large number of commercially available potassium organotrifluoroborates that made it possible to synthesise a series of novel porphyrins in a straight-forward manner that would otherwise include numerous steps.
Chapter 7:
Experimental
7.1 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: doubledoublet, td: triplet of doublets, t: triplet, q: quartet, sep: septet, 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. CHN-analysis were unsuccessful. 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. Melting points were acquired on a Stuart SMP10 melting point apparatus and are uncorrected. Thin layer chromatography (TLC) was performed on silica gel 60F$_{254}$ (Merck) precoated aluminum 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. Toluene was dried by filtration through a layer of Fluka Al$_2$O$_3$ (basic) and degassed with argon for 10 min before it was used. Pd(dppf)$_2$Cl$_2$ and potassium organotrifluoroborates were provided by Frontier Scientific, Inc. All commercial chemicals were supplied by Aldrich and used without further purification.
7.2 Allylporphyrins

7.2.1 Synthesis of Starting Materials

5,10,15-Tris(4-methylphenyl)porphyrin 66. A 1 L 3-necked round-bottom flask was charged with \( p \)-bromotoluene (5 g, 29.31 mmol, 14 equiv.) in dry diethyl ether (100 mL) under Ar. \( n \)-Butyllithium (14 mL, 35.1 mmol, 17.2 equiv., 2.5 M in hexane) was added drop-wise at \(-70^\circ C\) over 30 min. After the addition was complete the reaction mixture was allowed to warm to rt and was stirred for 1 h (colour change to white). Next, 5,15-bis(4-methylphenyl)porphyrin 56 (1 g, 2.04 mmol, 1 equiv.) dissolved in THF (500 mL) under Ar and cooled to \(-20^\circ C\) was added. The combined reaction mixture was stirred at rt for 1 h (colour change to brown), then water (5 mL, colour change to emerald green) and DDQ (2.1 g, 9.25 mmol, 4 equiv.) were added (colour change to red). After 1 h the crude product was filtered through a layer of silica gel and recrystallised from \( \text{CH}_2\text{Cl}_2/\text{MeOH} \) (1:3, v/v). The product was obtained as purple crystals in 1.08 g (1.86 mmol, 91 %) yield. Analytical data were as reported by Lindsey and co-workers.\(^{76}\)
7.2.2 Synthesis of Allylporphyrins

**General Procedure:** Bromoporphyrin (59-67) (1 equiv.) was placed into a round-bottom flask under argon atmosphere and dissolved in anhydrous THF (60 mL). Allylboronic acid pinacol ester (10–20 equiv.), Pd(PPh$_3$)$_4$ (0.1 equiv.) and K$_3$PO$_4$ (20–40 equiv.) were added and the reaction mixture was heated under reflux at 80 °C (bath) for 18 h. 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 dichloromethane. The crude product mixture was washed sequentially with a saturated solution of sodium bicarbonate, water and brine. The organic phase was dried with sodium sulfate and the solvent was removed under reduced pressure. Purification of the product was carried out by column chromatography on silica gel (CH$_2$Cl$_2$/C$_6$H$_{14}$, 1:1, v/v).

**5,15-Diallyl-10,20-diphenylporphyrin 70.** By using 5,15-dibromo-10,20-diphenylporphyrin 59 (100 mg, 0.16 mmol) as starting material, allylboronic acid pinacol ester (0.6 mL, 3.2 mmol, 20 equiv.), K$_3$PO$_4$ (1.4 g, 6.4 mmol, 40 equiv.) and Pd(PPh$_3$)$_4$ (18 mg, 0.016 mmol) the product was obtained in 68.2 mg (0.126 mmol, 78 %) yield of purple crystals: mp >300 °C; R$_f$=0.42 (CH$_2$Cl$_2$/C$_6$H$_{14}$, 2:1, v/v); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$=2.63 (s, br, 2H, NH), 5.16 (d, $^3$J=17.0 Hz, 2H, CH$_2$CH=CHH), 5.24 (d, $^3$J=9.9 Hz, 2H, CH$_2$CH=CHH), 5.76 (d, $^3$J=5.2 Hz, 4H, CH$_2$CH=CH$_2$), 6.86 (m, 2H, CH$_2$CH=CH$_2$), 7.78 (m, 6H, H$_A$), 8.22 (m, 4H, H$_A$), 8.89 (d, $^3$J=4.7 Hz, 4H, H$_B$), 9.44 (d, $^3$J=4.7 Hz, 4H, H$_B$) ppm; $^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$=38.4, 115.4, 115.7, 118.8, 126.1, 127.2, 127.6 (br), 131.4 (br), 134.0, 141.0, 142.0, 146.2 (br) ppm; IR:
3331 (NH), 3071 (C=CH₂), 3006 (Ar-H), 2921 (CH₃) cm⁻¹; UV/vis (CH₂Cl₂): \( \lambda_{\text{max}} \) (lg ε)=417 (5.6), 514 (4.5), 549 (4.4), 600 (4.4), 656 (4.4) nm; HRMS (ES⁺): calcd for C₃₈H₃₀N₄ [M+H]^⁺ 543.2543, found 543.2549.

5,15-Diallyl-10,20-bis(4-methylphenyl)porphyrin 71. By using 5,15-dibromo-10,20-bis(4-methylphenyl)porphyrin 60 (100 mg, 0.154 mmol) as starting material, allylboronic acid pinacol ester (0.6 mL, 3.08 mmol, 20 equiv.), K₃PO₄ (1.3 g, 6.16 mmol, 40 equiv.) and Pd(PPh₃)₄ (18 mg, 0.0154 mmol) product was obtained in 55 mg (0.096 mmol, 62 %) yield of dark purple crystals: mp >300 °C; Rₚ=0.60 (CH₂Cl₂/C₆H₁₄, 1:1, v/v); \(^1^H\) NMR (600 MHz, CDCl₃): \( \delta=2.63 \) (s, br, 2H, NH), 2.75 (s, 6H, C₆H₄CH₃), 5.16 (d, \(^3^J=17.0 \) Hz, 2H, CH₂CH=CH₂), 5.24 (d, \(^3^J=10.5 \) Hz, 2H, CH₂CH=CH₂), 5.76 (d, \(^3^J=5.5 \) Hz, 4H, CH₂CH=CH₂), 6.86 (m, 2H, CH₂CH=CH₂), 7.59 (d, \(^3^J=7.2 \) Hz, 4H, H₆), 8.10 (d, \(^3^J=7.2 \) Hz, 4H, H₆), 8.92 (d, \(^3^J=4.4 \) Hz, 4H, H₆), 9.43 (d, \(^3^J=4.4 \) Hz, 4H, H₆) ppm; \(^1^3^C\) NMR (100.6 MHz, CDCl₃): \( \delta=21.4, 38.7, 115.5, 116.0, 119.2, 127.2, 134.2, 137.2, 139.4, 141.4 \) ppm; IR: 3312 (NH), 3008 (Ar-H), 2932 (CH₃), 2857 (CH₂) cm⁻¹; UV/vis (CH₂Cl₂): \( \lambda_{\text{max}} \) (lg ε)=419 (5.3), 517 (3.0), 553 (3.9), 595 (2.8), 653 (3.9) nm; HRMS (ES⁺): calcd for C₄₀H₃₄N₄ [M+H]^⁺ 571.2862, found 571.2872.
5,15-Diallyl-10,20-bis(4-butoxyphenyl)porphyrin 72. By using 5,15-dibromo-10,20-bis(4-butoxyphenyl)porphyrin 61 (100 mg, 0.131 mmol) as starting material, allylboronic acid pinacol ester (0.5 mL, 2.62 mmol, 20 equiv.), K$_3$PO$_4$ (1.1 g, 5.24 mmol, 40 equiv.) and Pd(PPh$_3$)$_4$ (15 mg, 0.0131 mmol) the product was obtained in 45 mg (0.08 mmol, 50 %) yield of purple crystals: mp >300 ºC; R$_f$=0.71 (CH$_2$Cl$_2$/C$_6$H$_{14}$, 2:1, v/v); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$=2.62 (s, br, 2H, NH), 1.15 (t, 6H, $^3$J=7.5 Hz, OCH$_3$CH$_2$CH$_3$), 1.71 (m, 4H, OC$_2$H$_4$CH$_2$CH$_3$), 2.01 (m, 4H, OCH$_2$CH$_2$CH$_2$H), 4.29 (t, $^3$J=6.4 Hz, 4H, OCH$_2$CH$_2$CH$_2$H), 5.16 (d, $^3$J=17.0 Hz, 2H, CH$_2$CH=CH=CH$_2$), 5.23 (d, $^3$J=9.9 Hz, 2H, CH$_2$CH=CH=CH$_2$), 5.75 (d, $^3$J=5.5 Hz, 4H, CH$_2$CH=CH=CH$_2$), 6.85 (m, 2H, CH$_2$CH=CH=CH$_2$), 7.29 (d, $^3$J=7.9 Hz, 4H, $H_{A1}$), 8.10 (d, $^3$J=8.5 Hz, 4H, $H_{A1}$), 8.92 (d, $^3$J=5.0 Hz, 4H, $H_{B1}$), 9.42 (d, $^3$J=5.0 Hz, 4H, $H_{B1}$) ppm; $^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$=13.6, 19.0, 31.1, 38.3, 67.5, 112.1, 115.1, 115.6, 118.6, 127.4, 131.5, 134.1, 135.0, 141.0, 158.4, 206.6 ppm; UV/vis (CH$_2$Cl$_2$): $\lambda_{max}$ (lg e)=421 (5.8), 447 (5.1), 519 (4.8), 555 (4.7), 598 (4.7) nm; HRMS (ES+): calcd for C$_{46}$H$_{46}$N$_4$O$_2$ [M+H]$^+$ 687.3699, found 687.3673.
5,15-Diallyl-10,20-dihexylporphyrin 73. By using 5,15-dibromo-10,20-dihexylporphyrin 62 (100 mg, 0.16 mmol) as starting material, allylboronic acid pinacol ester (0.6 mL, 3.2 mmol, 20 equiv.), K$_3$PO$_4$ (1.4 g, 6.4 mmol, 40 equiv.) and Pd(PPh$_3$)$_4$ (18 mg, 0.016 mmol) the product was obtained in 45 mg (0.08 mmol, 50 %) yield as purple needles: mp 167 °C; R$_f$=0.64 (CH$_2$Cl$_2$/C$_6$H$_{14}$, 1:1, v/v); $^1$H NMR (600 MHz, CDCl$_3$): $\delta$=2.62 (s, br, 2H, NH), 0.95 (t, $^3$J=7.0 Hz, 6H, C$_3$H$_{10}$CH$_3$), 1.41 (m, 4H, C$_4$H$_8$CH$_2$CH$_3$), 1.52 (m, 4H, C$_3$H$_6$CH$_2$CH$_2$CH$_3$), 1.82 (m, 4H, C$_2$H$_4$CH$_2$C$_2$H$_4$CH$_3$), 2.51 (m, 4H, CH$_2$CH$_2$C$_3$H$_6$CH$_3$), 4.92 (t, $^3$J=8.2 Hz, 4H, CH$_2$C$_4$H$_8$CH$_3$), 5.16 (d, $^3$J=15.7 Hz, 2H, CH$_2$CH=CHCH$_3$), 5.23 (d, $^3$J=10.5 Hz, 2H, CH$_2$CH=CHCH$_3$), 5.72 (d, $^3$J=5.9 Hz, 4H, CH$_2$CH=CHCH$_3$), 6.86 (m, 2H, CH$_2$CH=CHCH$_3$) 9.46 (s, 8H, $H_\beta$) ppm; $^{13}$C NMR (150.9 MHz, CDCl$_3$): $\delta$=14.2, 22.8, 30.3, 31.9, 35.5, 38.7, 39.0, 114.3, 115.9, 118.8, 141.6 ppm; IR: 3315 (NH), 2953 (CH$_2$), 2916 (CH$_2$), 2846 (CH$_3$) cm$^{-1}$; UV/vis (CH$_2$Cl$_2$): $\lambda_{max}$ (lg $\varepsilon$)=418 (6.0), 520 (5.0); 556 (4.9), 559 (4.8) nm; HRMS (ES+): calcd for C$_{38}$H$_{46}$N$_4$ [M+H]$^+$ 559.3801, found 559.3776.
5,15-Diallyl-10,20-diisopropylporphyrin 74. By using 5,15-dibromo-10,20-di(iso-propyl)porphyrin 63 (100 mg, 0.18 mmol) as starting material, allylboronic acid pinacol ester (0.7 mL, 3.6 mmol, 20 equiv.), K₃PO₄ (1.5 g, 7.2 mmol, 40 equiv.) and Pd(PPh₃)₄ (21 mg, 0.018 mmol) the product was obtained in 1.5 mg (0.003 mmol, 2 %) yield of purple crystals: mp >300 °C; Rf=0.45 (CH₂Cl₂/C₆H₁₄, 1:1, v/v); ¹H NMR (400 MHz, CDCl₃): δ=−2.30 (s, br, 2H, NH), 2.40 (d, ³J=7.5 Hz, 12H, CH(CH₃)₂), 5.22 (d, ³J=17.0 Hz, 2H, CH₂CH=CHH), 5.27 (d, ³J=9.9 Hz, 2H, CH₂CH=CHH), 5.56 (sep, ³J=7.5 Hz, 2H, CH(CH₃)₂), 5.69 (d, ³J=5.6 Hz, 4H, CH₂CH=CH₂), 6.88 (m, 2H, CH₂CH=CH₂), 9.45 (d, ³J=5.3 Hz, 4H, H₁₃), 9.59 (d, ³J=5.3 Hz, 4H, H₁₃) ppm; ¹³C NMR (100.6 MHz, CDCl₃): δ=28.3, 34.5, 38.9, 113.6, 115.5, 124.2, 128.1, 128.4, 130.4, 141.3 ppm; UV/vis (CH₂Cl₂): λₘₐₓ (lg ε)=436 (4.2), 590 (3.1), 644 (3.2), 722 (2.9) nm; HRMS (ES+): calcd for C₃₂H₃₄N₄ [M+H]⁺ 475.2862, found 475.2878.
[5,15-Diallyl-10,20-bis(4-methylphenyl)porphyrinato]nickel(II) 75. By using [5,15-dibromo-10,20-bis(4-methylphenyl)porphyrinato]nickel(II) 64 (100 mg, 0.154 mmol) as starting material, allylboronic acid pinacol ester (0.6 mL, 3.08 mmol, 20 equiv.), K$_3$PO$_4$ (1.3 g, 6.16 mmol, 40 equiv.) and Pd(PPh$_3$)$_4$ (18 mg, 0.0154 mmol) the product was obtained in 55 mg (0.096 mmol, 62 %) yield of red crystals: mp 216 °C; R$_f$=0.56 (CH$_2$Cl$_2$/C$_6$H$_{14}$, 1:2, v/v); $^1$H NMR (600 MHz, CDCl$_3$): $\delta$=2.67 (s, 6H, C$_6$H$_4$CH$_3$), 5.25 (m, 8H, CH$_2$CH=CH$_2$, CH$_2$CH=CH$_2$), 6.72 (m, 2H, CH$_2$CH=CH$_2$), 7.50 (d, $^3$J=7.6 Hz, 4H, $H_A$), 7.87 (d, $^3$J=7.6 Hz, 4H, $H_A$), 8.78 (d, $^3$J=4.8 Hz, 4H, $H_B$), 9.25 (d, $^3$J=4.8 Hz, 4H, $H_B$) ppm; $^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$=21.5, 29.7, 38.0, 77.2, 115.9, 127.5, 129.5, 132.6, 133.5, 140.9 ppm; UV/vis (CH$_2$Cl$_2$): $\lambda_{max}$ (log $\varepsilon$)=417 (5.0), 533 (4.1) nm; HRMS (ES+): calcd for C$_{40}$H$_{33}$N$_4$Ni [M+H]$^+$ 627.2059, found 627.2054.
[5,15-Diallyl-10,20-dihexylporphyrinato]nickel(II) 76. By using [5,15-dibromo-10,20-dihexylporphyrinato]nickel(II) 65 (100 mg, 0.144 mmol) as starting material, allylboronic acid pinacol ester (0.5 mL, 2.88 mmol, 20 equiv.), K$_3$PO$_4$ (1.2 g, 5.76 mmol, 40 equiv.) and Pd(PPh$_3$)$_4$ (17 mg, 0.0144 mmol) the product was obtained in 84 mg (0.137 mmol, 95 %) yield as red needles: mp 163 °C; R$_f$=0.80 (CH$_2$Cl$_2$/$C_6$H$_{14}$, 1:1, v/v); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$=0.92 (t, $^3$J=6.9 Hz, 6H, $C_5$H$_{10}$CH$_2$), 1.37 (m, 8H, $C_3$H$_6$CH$_2$CH$_2$CH$_3$), 1.58 (m, 4H, $C_2$H$_4$CH$_2$C$_2$H$_4$CH$_3$), 2.24 (m, 4H, CH$_2$CH$_2$C$_3$H$_6$CH$_3$), 4.42 (t, $^3$J=8.3 Hz, 4H, CH$_2$C$_4$H$_8$CH$_3$), 5.12 (d, $^3$J=5.9 Hz, 4H, CH$_2$CH=CH$_2$), 5.22 (d, $^3$J=8.8 Hz, 2H, CH$_3$CH=CHH), 5.28 (d, $^3$J=15.7 Hz, 2H, CH$_3$CH=CHH), 6.70 (m, 2H, CH$_2$CH=CH$_2$), 9.20 (s, 8H, H$_8$) ppm; $^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$=14.1, 22.7, 30.0, 31.7, 33.9, 37.3, 37.8, 113.0, 115.6, 117.2, 129.7, 129.8, 141.1, 141.2 ppm; IR: 3072 (C=CH$_2$), 2953 (CH$_2$), 2917 (CH$_2$), 2846 (CH$_3$) cm$^{-1}$; UV/vis (CH$_2$Cl$_2$): $\lambda_{max}$ (lg e)=419 (6.1); 537 (3.0) nm; HRMS (ES+): calcd for $C_{38}H_{44}N_4Ni$ [M+H]$^+$ 614.2919, found 614.2929.
Chapter 7: Experimental

5-Allyl-10,15,20-tris(4-methylphenyl)porphyrin 77. By using 5-bromo-10,15,20-tris(4-methylphenyl)porphyrin 67 (100 mg, 0.152 mmol) as starting material, allylboronic acid pinacol ester (0.6 mL, 3.04 mmol, 20 equiv.) K$_3$PO$_4$ (1.3 g, 6.08 mmol, 40 equiv.) and Pd(PPh$_3$)$_4$ (18 mg, 0.0152 mmol) the product was obtained in 70 mg (0.113 mmol, 74 %) yield as purple crystals; mp >300 °C; R$_f$=0.60 (CH$_2$Cl$_2$/C$_6$H$_{14}$, 1:1, v/v); $^1$H NMR (400 MHz, CDCl$_3$): δ=-2.70 (s, br, 2H, NH), 2.70 (s, 3H, C$_6$H$_4$H$_2$), 2.73 (s, 6H, C$_6$H$_4$CH$_3$), 5.16 (d, $^3$J=18.6 Hz, 1H, CH$_2$CH=CHH), 5.23 (d, $^3$J=8.8 Hz, 1H, CH$_2$CH=CHH), 5.79 (d, $^3$J=4.9 Hz, 2H, CH$_2$CH=CH$_2$), 6.87 (m, 1H, CH$_2$CH=CH$_2$), 7.56 (m, 6H, H$_A$), 8.09 (m, 6H, H$_A$), 8.83 (s, 4H, H$_B$), 8.95 (d, $^3$J=4.9 Hz, 2H, H$_B$), 9.47 (d, $^3$J=4.9 Hz, 2H, H$_B$) ppm; $^{13}$C NMR (100.6 MHz, CDCl$_3$): δ=21.5, 39.0, 115.9, 116.1, 119.7, 119.8, 127.3, 127.4, 130.9 (br), 134.4, 137.3, 139.1, 139.4, 141.5 ppm; UV/vis (CH$_2$Cl$_2$): $\lambda_{max}$ (lg ε)=420 (5.6), 519 (4.6), 552 (4.5), 593 (4.5), 650 (4.5) nm; HRMS (ES+): calcd for C$_{44}$H$_{36}$N$_4$ [M+H]$^+$ 621.3018, found 621.3030.
2-Allyl-5,10,15,20-tetraphenylporphyrin 78. 2-Bromo-5,10,15,20-tetraphenylporphyrin 69 (50 mg, 0.07 mmol; 1 equiv.) was placed into a round-bottom flask under argon atmosphere and dissolved in anhydrous toluene (15 mL). Allylboronic acid pinacol ester (0.06 mL, 0.35 mmol; 5 equiv.), Pd(PPh₃)₄ (8.0 mg, 0.007 mmol; 0.1 equiv.) and K₂CO₃ (97.0 mg, 0.7 mmol; 10 equiv.) were added and the reaction mixture was heated under reflux at 100 °C for 18 h. The progress of the reaction was followed by TLC. After consumption of the starting material the solvent was evaporated to dryness under reduced pressure and the residue was dissolved in dichloromethane. The crude product was washed with a saturated solution of sodium bicarbonate, water and brine. The organic phase was dried with sodium sulfate and the solvent was evaporated to dryness under reduced pressure. Purification of the product was carried out by column chromatography on silica (CH₂Cl₂/C₆H₁₄, 1:2, v/v). The product was obtained in 30 mg (0.046 mmol, 66 %) yield as purple crystals: mp >300 °C; Rf=0.60 (CH₂Cl₂/C₆H₁₄, 1:1, v/v); ¹H NMR (400 MHz, CDCl₃): δ=−2.77 (s, br. 2H, NH), 3.62 (d, 3J=6.2 Hz, 2H, CH₂CH=CH₂), 4.95 (dd, 3J=14.5 Hz, 2J=1.8 Hz, 1H, CH₂CH=CH₂), 4.97 (d, 3J=17.0 Hz, 1H, CH₂CH=CH₂), 7.77 (m, 12H, 8.21 (m, 6H, 8.63 (dd, 3J=4.8 Hz, 3J=7.7 Hz, 2H, H₆), 8.76 (d, 3J=5.9 Hz, 2H, H₂), 8.81 (d, 3J=4.8 Hz, 1H, H₆), 8.87 (m, 2H, H₂) ppm; ¹³C NMR (100.6 MHz, CDCl₃): δ=34.6, 116.2, 118.9, 119.7, 120.0, 120.5, 126.5, 126.6, 126.7, 126.9, 127.6, 127.7, 128.2, 129.6 (br), 132.3, (br), 133.4, 134.4, 134.5, 134.6, 137.1, 137.5, 141.9, 142.0, 142.3 ppm; IR: 3301 (NH), 2920 (CH₂) cm⁻¹; UV/vis (CH₂Cl₂): λₘₐₓ (lg ε)=418 (5.7), 515 (4.6), 549 (4.4), 590 (4.4), 642 (4.4) nm; HRMS (ES+): calcd for C₄₇H₃₄N₄ [M+H]⁺ 655.2862, found 655.2845.
5,15-Diallyl-10,20-diphenylporphyrin 70 (56 mg, 0.103 mmol; 1 equiv.) was placed into a round-bottom flask and dissolved in 65 mL of dichloromethane. ZnO (40 mg, 0.412 mmol; 4 equiv.) and TFA (2 drops) were added and the reaction mixture was stirred at rt for 3 h. The progress of the reaction was followed by TLC. After consumption of the starting material the crude mixture was filtered through a layer of silica gel and the red fraction was washed off with dichloromethane. The solvent was evaporated to dryness under reduced pressure and the product was obtained in 48.3 mg (0.08 mmol, 77%) yield as red crystals: mp >300 °C; Rf=0.45 (CH$_2$Cl$_2$/C$_6$H$_{14}$, 1:1, v/v); $^1$H NMR (600 MHz, d$_6$-acetone): δ=5.14 (d, $^3$J=10.3 Hz, 2H, CH$_2$CH=C/CH), 5.23 (d, $^3$J=15.4 Hz, 2H, CH$_2$CH=C/CH), 5.87 (d, $^3$J=5.9 Hz, 4H, CH$_2$CH=CH$_2$), 6.87 (m, 2H, CH$_2$CH=CH$_2$), 7.82 (m, 6H, H$_A$), 8.20 (m, 4H, H$_A$), 8.86 (d, $^3$J=4.4 Hz, 4H, H$_B$), 9.64 (d, $^3$J=5.1 Hz, 4H, H$_B$) ppm; $^{13}$C NMR (150.9 MHz, CDCl$_3$): δ=39.2, 115.0, 117.0, 120.0, 126.8, 127.7, 129.5, 132.2, 134.7, 142.8, 143.9, 149.8, 150.8 ppm; UV/vis (CH$_2$Cl$_2$): $\lambda_{max}$ (lg ε)=421 (5.9), 552 (4.9) nm; HRMS (ES+): calcd for C$_{36}$H$_{28}$N$_4$Zn [M+H]$^+$ 604.1605, found 604.1618.
7.3 Acroleinylporphyrins

**General Procedure:** Allylporphyrin (71, 73, 76-78, 87) (1 equiv.) was placed into a round-bottom flask and dissolved in DMF (20 mL). Ni(OAc)$_2$·4H$_2$O (3 equiv. for diallylporphyrin, 2 equiv. for mono-allylporphyrin) and glacial acetic acid (0.2 mL) were added and the reaction mixture was heated at 115 °C for 18 h. The progress of the reaction was followed by TLC. After consumption of the starting material the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (ethyl acetate/C$_6$H$_4$, 1:2, v/v).

The product was obtained in 34 mg (0.074 mmol, 70 %) yield of green crystals: mp >300 °C; $R_f$=0.54 (ethyl acetate/C$_6$H$_4$, 1:2, v/v); $^1$H NMR (400 MHz, CDC$_3$): $\delta$=2.67 (s, 6H, C$_6$H$_4$CH$_3$), 6.55 (dd, $^3$J=7.7 Hz, $^3$J=15.4 Hz, 2H, CH=CHCHO), 7.49 (d, $^3$J=7.7 Hz, 4H, $H_A$), 7.76 (d, $^3$J=7.7 Hz, 4H, $H_A$), 8.68 (d, $^3$J=5.0 Hz, 4H, $H_B$), 9.14 (d, $^3$J=5.0 Hz, 4H, $H_B$), 9.44 (d, $^3$J=15.4 Hz, 2H, CH=CHCHO), 10.02 (d, $^3$J=7.7 Hz, 2H, CH=CHCHO) ppm; $^{13}$C NMR (100.6 MHz, CDC$_3$): $\delta$=21.5, 110.1, 120.8, 128.0, 131.5, 133.3, 134.1, 136.3, 138.0, 140.6, 141.8, 142.0, 150.5, 192.0 ppm; IR: 2918 (CHO), 1670 (C=O) cm$^{-1}$; UV/vis (CH$_2$Cl$_2$): $\lambda_{max}$ (lg $\varepsilon$)=443 (5.2), 622 (4.4) nm; LRMS (ES$^+$): calcd for C$_{40}$H$_{28}$N$_4$NiO$_2$ [M+H]$^+$ 655.4, found 655.3.
[5-Acroleinyl-15-formyl-10,20-bis(4-methylphenyl)porphyrinato]nickel(II) 81. The title compound was obtained as a side-product of the synthesis of [5,15-diacroleinyl-10,20-bis(4-methylphenyl)porphyrinato]nickel(II) 80 in 3.7 mg (0.006 mmol, 8%) yield of light green crystals: mp >300 °C; Rf=0.65 (CH2Cl2); 1H NMR (600 MHz, CDCl3):

\[
\begin{align*}
\delta & = & 2.67 \text{ (s, 6H, C}_6\text{H}_4\text{C} = \text{CH}) , \\
& & 6.66 \text{ (dd, }^3J=7.4 \text{ Hz, }^3J=15.5 \text{ Hz, 1H, CH=CHCHO) ,} \\
& & 7.52 \text{ (d, }^3J=7.8 \text{ Hz, 4H, } H_{\text{Ar}} \text{),} \\
& & 7.82 \text{ (d, }^3J=7.8 \text{ Hz, 4H, } H_{\text{Ar}} \text{),} \\
& & 8.76 \text{ (d, }^3J=4.9 \text{ Hz, 2H, } H_{\beta} \text{),} \\
& & 8.82 \text{ (d, }^3J=5.0 \text{ Hz, 2H, } H_{\beta} \text{),} \\
& & 9.25 \text{ (d, }^3J=5.0 \text{ Hz, 2H, } H_{\beta} \text{),} \\
& & 9.58 \text{ (d, }^3J=15.6 \text{ Hz, 1H,} \\
& & \text{CH=CHCHO),} \\
& & 9.75 \text{ (d, }^3J=5.0 \text{ Hz, 2H, } H_{\beta} \text{),} \\
& & 10.10 \text{ (d, }^3J=7.4 \text{ Hz, 1H, CH=CHCHO),} \\
& & 11.99 \text{ (s, 1H,CHO) ppm; } \text{^13C NMR (100.6 MHz, CDCl3):} \\
\delta & = & 21.3, 29.5, 112.4, 121.4, \\
& & 127.8, 131.4, 131.7, 133.1, 133.6, 135.4, 136.1, 138.0, 139.9, 141.4, 142.4, 143.2, \\
& & 143.6, 150.2 \text{ ppm; IR: 2929 (CHO), 2856 (CH}_3\text{), 1733 (C=O cm}^{-1}\text{; UV/vis (CH}_2\text{Cl}_2):} \\
\lambda_{\text{max (lg }\varepsilon)} & = & 438 (3.4), 622 (2.6) \text{ nm.}
\end{align*}
\]
[5-ALLYL-10,15,20-TRIS(4-METHYLPHENYL)PORPHYRINATO]NICKEL(II) 82. The title compound was obtained as a side-product of the synthesis of [5-acroleinyl-10,15,20-tris(4-methylphenyl)porphyrinato]nickel(II) 83 in 12.3 mg (0.018 mmol, 28%) yield as red crystals: mp 100 °C; Rf=0.63 (CH2Cl2/C6H14, 1:2, v/v); 1H NMR (600 MHz, CDCl3): δ=2.63 (s, 3H, C6H4CH3), 2.64 (s, 6H, C6H4CH3), 5.22 (m, 2H, CH2CH=CH2), 5.32 (d, 3J=5.9 Hz, 2H, CH2CH=CH2), 6.73 (m, 1H, CH2CH=CH2), 7.46 (m, 6H, HAr), 7.86 (m, 6H, HAr), 8.70 (s, 4H, HAr), 8.80 (d, 3J=4.6 Hz, 2H, HAr), 9.29 (d, 3J=4.7 Hz, 2H, HAr) ppm; 13C NMR (100.6 MHz, CDCl3): δ=21.0, 38.1, 115.9, 118.5, 127.6, 129.5, 133.1, 132.7, 133.6, 137.3, 137.9, 141.0, 142.2, 142.4, 142.5, 142.7 ppm; IR: 3021 (C=CH2), 2917 (CH2) cm⁻¹; UV/vis (CH2Cl2): λmax (log ε)=417 (5.7), 531 (4.8) nm; HRMS (ES+): calcd for C44H34N4Ni [M+H]+ 677.2215, found 677.2233.
[5-Acroleinyl-10,15,20-tris(4-methylphenyl)porphyrinato]nickel(II) 83. By using 5-allyl-10,15,20-tris(4-methylphenyl)porphyrin 77 (40 mg, 0.065 mmol) as starting material and Ni(OAc)$_2$ (49 mg, 0.195 mmol, 3 equiv.) the product was obtained in 11.6 mg (0.017 mmol, 26%) yield of dark green crystals: mp 105 °C; R$_f$=0.48 (CH$_2$Cl$_2$/C$_6$H$_{14}$, 2:1, v/v); $^1$H NMR (400 MHz, CDCl$_3$): $\delta=2.64$ (s, 3H, C$_6$H$_4$CH$_3$), 2.66 (s, 6H, C$_6$H$_4$CH$_3$), 6.67 (dd, $^3$J=7.4 Hz, $^3$J=15.4 Hz, 1H, CH=CHCHO), 7.49 (t, $^3$J=7.7 Hz, 6H, $H_A$), 7.85 (d, $^3$J=7.7 Hz, 6H, $H_A$), 8.64 (d, $^3$J=5.3 Hz, 2H, $H_B$), 8.70 (d, $^3$J=4.7 Hz, 2H, $H_B$), 8.85 (d, $^3$J=4.7 Hz, 2H, $H_B$), 9.30 (d, $^3$J=4.7 Hz, 2H, $H_B$), 9.63 (d, $^3$J=15.2 Hz, 1H, CH=CHCHO), 10.07 (d, $^3$J=7.7 Hz, 1H, CH=CHCHO) ppm; $^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta=21.0, 107.4, 119.6, 120.8, 127.3, 13.4, 131.8, 132.5, 132.9, 133.0, 133.6, 137.2, 140.7, 141.0, 141.8, 142.7, 151.2, 191.7 ppm; IR: 3022 (CH=CH), 2918 (CHO), 2852 (CH$_3$), 1670 (C=O) cm$^{-1}$; UV/vis (CH$_2$Cl$_2$): $\lambda_{max}$ (lg $\varepsilon$)=437 (5.1), 552 (4.1), 598 (4.1) nm.
5-Formyl-10,15,20-tris(4-methylphenyl)porphyrinato[nickel(II)] 84. The title compound was obtained as a side-product of the synthesis of [5-acroleinyl-10,15,20-tris(4-methylphenyl)porphyrinato]nickel(II) 83 in 2.4 mg (0.004 mmol, 6%) yield of bright green crystals: mp 81°C; Rf=0.66 (CH₂Cl₂/C₆H₁₄, 1:2, v/v); ¹H NMR (400 MHz, CDCl₃): δ=2.65 (s, 3H, C₆H₄CH₃), 2.67 (s, 6H, C₆H₄CH₃), 7.50 (t, 3J=8.0 Hz, 6H, H₆), 7.85 (d, 3J=8.0 Hz, 6H, H₆), 8.60 (d, 3J=4.7 Hz, 2H, H₂β), 8.68 (d, 3J=4.7 Hz, 2H, H₂β), 8.88 (d, 3J=5.2 Hz, 2H, H₂α), 9.80 (d, 3J=5.2 Hz, 2H, H₂α), 12.0 (s, 1H, CHO) ppm; ¹³C NMR (100.6 MHz, CDCl₃): δ=21.0, 120.6, 127.3, 130.1, 131.4, 132.9, 135.0, 136.5, 137.3, 140.5, 141.5, 143.9, 192.3 ppm; UV/vis (CH₂Cl₂): λ_{max} (lg ε)=426 (4.8), 552 (3.8), 593 (3.9) nm.
[5,15-Diacryl-10,20-dihexylporphyrinato]nickel(II) 85. By using 5,15-diallyl-10,20-dihexylporphyrin 73 (32 mg, 0.057 mmol) as starting material and Ni(OAc)$_2$ (43 mg, 0.171 mmol, 3 equiv.) the product was obtained in 7.3 mg (0.011 mmol, 20 %) or 10.3 mg (0.016 mmol; 20 %) yield, respectively, as green crystals: mp 181 °C; R$_f$=0.58 (ethyl acetate/C$_6$H$_{14}$, 1:2, v/v); $^1$H NMR (600 MHz, CDCl$_3$): $\delta$=0.88 (t, 6H, $^3$J=7.0 Hz, C$_5$H$_{10}$CH$_3$), 1.31 (m, 8H, C$_3$H$_6$CH$_2$CH$_2$CH$_3$), 1.57 (m, 4H, C$_2$H$_4$CH$_2$C$_2$H$_4$CH$_3$), 2.18 (m, 4H, CH$_2$CH$_2$C$_3$H$_6$CH$_3$), 4.29 (t, $^3$J=7.9 Hz, 4H, CH$_2$C$_4$H$_8$CH$_3$), 6.47 (dd, $^3$J=7.2 Hz, $^3$J=15.2 Hz, 2H, CH=CHCHO), 9.11 (m, 8H, H$_{10}$), 9.33 (d, $^3$J=15.2 Hz, 2H, CH=CHCHO), 9.97 (d, $^3$J=7.6 Hz, 2H, CH=CHCHO) ppm; $^{13}$C NMR (150.9 MHz, CDCl$_3$): $\delta$=14.1, 22.6, 29.7, 29.9, 31.6, 33.8, 37.2, 109.2, 120.6, 131.3, 131.8, 139.7, 141.4, 141.6, 150.5, 191.9 ppm; IR: 2920 (CH$_2$), 2850 (CHO), 1666 (C=O) cm$^{-1}$; UV/vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (lg $\varepsilon$)=448 (5.3), 637 (4.6) nm; HRMS (ES$^+$): calcd for C$_{38}$H$_{40}$N$_4$NiO$_2$ [M+H]$^+$ 643.2581, found 643.2583.
[5-Acroleinyl-15-allyl-10, 20-ditolylporphyrinato]nickel(II) 88. The title compound was obtained as a side-product of the synthesis of [5, 15- diallyl-10,20-bis(4-methylphenyl)porphyrinato]nickel(II) 75 in traces amounts of green crystals: $^1$H NMR (600 MHz, CDCl$_3$): $\delta=2.67$ (s, 3H, C$_6$H$_4$CH$_3$), 5.23 (m, 4H, CH$_2$CH=CH$_2$, CH$_2$CH=CH$_2$), 6.67 (m, 2H, CH$_2$CH=CH$_2$, CH=CHCHO), 7.51 (d, $^3$J=7.3 Hz, 4H, HA)$_2$), 7.85 (d, $^3$J=7.3 Hz, 4H, HA)$_2$), 8.70 (d, $^3$J=4.5 Hz, 2H, HA), 8.81 (d, $^3$J=4.5 Hz, 2H, HA), 9.22 (d, $^3$J=4.5 Hz, 2H, HA), 9.27 (d, $^3$J=4.5 Hz, 2H, HA), 9.61 (d, $^3$J=15.2 Hz, 1H, CH=CHCHO), 10.07 (d, $^3$J=7.3 Hz, 1H, CH=CHCHO) ppm; $^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta=21.2$, 37.7, 116.0, 119.6, 127.6, 130.2, 130.5, 132.6, 133.2, 133.9, 136.9, 137.5, 140.3, 140.7, 141.2, 141.9, 142.6, 151.3, 191.9 ppm.
7.4 Pauson-Khand Products of Alkenylporphyrins

7.4.1 Synthesis of Starting Materials

5,10,15-Tris(4-methylphenyl)-20-vinylporphyrin 93. A 50 mL Schlenk-tube was filled with argon and charged with 5-bromo-10,15,20-tris(4-methylphenyl)phenylporphyrin 67 (300 mg, 0.455 mmol, 1 equiv.) in dry THF (50 mL). K3PO4 (2.0 g, 9.1 mmol, 20 equiv.) was added and the solution was degassed via three freeze-pump-thaw cycles and put under argon atmosphere again. Vinylboronic acid pinacol ester (0.8 mL, 4.55 mmol, 10 equiv.) and Pd(PPh3)4 (53 mg, 0.0455 mmol, 0.1 equiv.) were added and the reaction mixture was heated to 80 °C for 18 h. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane. The crude product was washed sequentially with a saturated solution of sodium bicarbonate, water and brine and dried over sodium sulfate. Purification was carried out by dry loaded column chromatography on silica gel (CH2Cl2/C6H14, 1:2, v/v). The product was obtained after recrystallisation from CH2Cl2/MeOH (1:3, v/v) as purple crystals in 144 mg (0.24 mmol, 52 %) yield: mp >300 °C; Rf =0.43 (CH2Cl2/C6H14, 1:1, v/v); 1H NMR (400 MHz, CDCl3): δ=−2.67 (s, br, 2H, NH), 2.73 (s, 3H, C6H4NH), 2.73 (s, 6H, C6H4CH3), 6.15 (dd, 3J=17.5 Hz, 2J=1.8 Hz, 1H, CH=CH1), 6.59 (dd, 3J=11.7 Hz, 2J=1.8 Hz, 1H, CH=CH1), 7.57 (d, 3J=8.2 Hz, 4H, H4), 7.59 (d, J=7.6 Hz, 2H, H5), 8.09 (d, 3J=7.6 Hz, 4H, H4), 8.12 (d, 3J=7.6 Hz, 2H, H5), 8.84 (s, 4H, H6), 9.26 (dd, 3J=17.0 Hz, 3J=11.1 Hz, 1H, CH=CH2), 9.50 (d, 3J=5.3 Hz, 2H, H6) ppm; 13C NMR (100.6 MHz, CDCl3):
5,10,15-Tris(4-methylphenyl)-20-vinylporphyrinato|nickel(II) 94. A 50 mL 2-necked round bottom flask was charged with 5,10,15-tris(4-methylphenyl)-20-vinylporphyrin 93 (70 mg, 0.116 mmol, 1 equiv.) and Ni(acac)₂ (45 mg, 0.174 mmol, 1.5 equiv.) in toluene (30 mL). The reaction mixture was heated to reflux until completion (~30 min, monitored by TLC). The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane. The crude product was filtered through a layer of silica gel and washed off with dichloromethane. After recrystallisation from CH₂Cl₂/MeOH (1:3, v/v) the product was obtained as dark red needles in 54.6 mg (0.08 mmol, 71 %) yield: mp 212 °C; Rᵣ=0.85 (CH₂Cl₂/C₆H₁₄, 1:1, v/v); H NMR (400 MHz, CDCl₃): δ=2.65 (s, 3H, C₆H₄CH₃), 2.66 (s, 6H, C₆H₄CH₃), 5.64 (dd, 3J= 7.5 Hz, 2J=1.8 Hz, 1H, CH=CHH), 5.68 (dd, 3J=17.5 Hz, 2J=1.8 Hz, 1H, CH=CHH), 7.48 (d, 3J=7.6 Hz, 4H, Hₐ), 7.50 (d, 3J=7.6 Hz, 2H, Hₐ), 7.88 (d, 3J=5.9 Hz, 4H, Hₐ), 7.89 (d, 3J=5.9 Hz, 2H, Hₐ), 8.71 (d, 3J=4.7 Hz, 2H, Hₐ), 8.72 (d, 3J=5.3 Hz, 2H, Hₐ), 8.84 (d, 3J=5.3 Hz, 2H, Hₐ), 8.96 (dd, 3J=17.0 Hz, 3J=11.0 Hz, 1H, CH=CH₂), 9.35 (d, 3J=4.7, 2H, Hₐ) ppm; C NMR (100.6 MHz, CDCl₃): δ=21.0, 114.5, 118.2, 127.2, 127.6, 130.9, 131.6, 131.7, 132.1, 133.0, 133.1, 135.4, 136.9,
5,10,15-Trihexylporphyrin 96. A 1 L 3-necked round-bottom flask was filled with argon and charged with 5,15-dihexylporphyrin 57 (940 mg, 1.967 mmol, 1 equiv.) in dry THF (500 mL). The solution was cooled to -78 °C and n-hexyllithium (5.13 mL, 11.8 mmol, 6 equiv., 2.3 M in hexane) was added dropwise over 20 min. After complete addition, the reaction mixture was kept stirring at -78 °C for 15 min before it was allowed to warm to rt (colour change to brown). After 1 h, water (4 mL, colour change to emerald green) and DDQ (2.7 g, 11.8 mmol, 6 equiv.) were added (colour change to red). Triethylamine (3 mL) was added after an additional hour of stirring and the crude product was filtered through a layer of silica. After recrystallisation from CH<sub>2</sub>Cl<sub>2</sub>/MeOH (1:3, v/v) the product was obtained in 290 mg (0.516 mmol, 26 %) yield as purple needles: mp 142 °C; R<sub>f</sub> =0.22 (CH<sub>2</sub>Cl<sub>2</sub>/C<sub>6</sub>H<sub>14</sub>, 1:2, v/v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ=-2.84 (s, br, 2H, NH), 0.97 (t, <sup>3</sup>J=7.3 Hz, 6H, C<sub>3</sub>H<sub>10</sub>CH<sub>3</sub>), 0.99 (t, <sup>3</sup>J=7.6 Hz, 3H, C<sub>5</sub>H<sub>11</sub>CH<sub>3</sub>), 1.44 (m, 6H, C<sub>6</sub>H<sub>8</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.56 (m, 6H, C<sub>3</sub>H<sub>6</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.84 (m, 6H, C<sub>2</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>2</sub>H<sub>4</sub>CH<sub>3</sub>), 2.56 (m, 6H, CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>), 4.99 (t, <sup>3</sup>J=8.2 Hz, 4H, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>), 5.08 (t, <sup>3</sup>J=8.2 Hz, 2H, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>), 9.31 (d, <sup>3</sup>J=4.7 Hz, 2H, H<sub>β</sub>), 9.52 (d, <sup>3</sup>J=4.7 Hz, 2H, H<sub>β</sub>), 9.55 (d, <sup>3</sup>J=4.7 Hz, 2H, H<sub>β</sub>), 9.62 (d, <sup>3</sup>J=4.7 Hz, 2H, H<sub>β</sub>), 9.96 (s, 1H, H<sub>meso</sub>) ppm; <sup>13</sup>C NMR (150.9 MHz, CDCl<sub>3</sub>): δ=13.9, 22.6, 30.1, 30.2, 31.7, 31.8, 34.9, 35.3, 36.1, 38.5, 38.7, 38.9, 102.8, 118.5, 119.9, 120.2, 127.7, 128.1, 128.5, 131.1, 145.1 (br), 146.6 (br) ppm: UV/vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (lg ε)=412 (5.5), 512 (4.6), 545 (4.5), 591 (4.4), 647 (4.4) nm; HRMS (ES+): calcd for C<sub>38</sub>H<sub>50</sub>N<sub>4</sub> [M+H]<sup>+</sup> 563.4114, found 563.4124.
5-Bromo-10,15,20-trihexylporphyrin 97. A 250 mL round-bottom flask was charged with 5,10,15-trihexylporphyrin 96 (222 mg, 0.39 mmol, 1 equiv.) in chloroform (100 mL). N-Bromosuccinimide (NBS, 83 mg, 0.468 mmol, 1.2 equiv.) and pyridine (0.2 mL) were added and the reaction mixture was stirred at rt until completion (~30 min, monitored by TLC). The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane. The crude product was filtered through a layer of silica gel and washed off with dichloromethane. After recrystallisation from CH₂Cl₂/MeOH (1:3, v/v) the product was obtained in 220 mg (0.34 mmol, 88%) yield as brown needles: mp 133 °C; Rₚ=0.41 (CH₂Cl₂/C₆H₁₄, 1:2, v/v); ¹H NMR (400 MHz, CDCl₃): δ=2.66 (s, br, 2H, N //), 0.97 (t, J=7.3 Hz, 6H, C₅H₁₀CH₃), 0.99 (t, J=7.6 Hz, 3H, C₅H₁₀CH₃), 1.43 (m, 6H, C₄H₈CH₂CH₃), 1.54 (m, 6H, C₃H₆CH₂CH₂CH₃), 1.82 (m, 6H, C₂H₄CH₂C₂H₄CH₃), 2.51 (m, 6H, CH₂CH₂CH₂C₂H₄CH₃), 4.91 (m, 6H, CH₂C₄H₈CH₃), 9.45 (d, J=5.2 Hz, 2H, Hₗ), 9.46 (d, J=5.8 Hz, 2H, Hₗ), 9.50 (d, J=5.2 Hz, 2H, Hₗ), 9.67 (d, J=4.7 Hz, 2H, Hₗ) ppm; ¹³C NMR (100.6 MHz, CDCl₃): δ=14.2, 22.8, 30.2, 30.3, 31.9, 35.4, 35.8, 38.7, 38.8, 101.1, 119.9, 120.4, 128.7 (br), 131.9 (br) ppm; UV/vis (CH₂Cl₂): λ_max (lg ε)=420 (6.3), 521 (5.2), 557 (5.2), 602 (5.1), 661 (5.1) nm; HRMS (ES+): calcd for C₅₈H₄₉N₄Br [M+H]+ 641.3219, found 641.3227.
5-Allyl-10,15,20-trihexylporphyrin 98. A 50 mL Schlenk-tube was filled with argon and charged with 5-bromo-10,15,20-trihexylporphyrin 97 (300 mg, 0.468 mmol, 1 equiv.) in dry THF (50 mL). K$_3$PO$_4$ (2.0 g, 9.36 mmol, 20 equiv.) was added and the solution was degassed via three freeze-pump-thaw cycles and put under argon again. Allylboronic acid pinacol ester (0.9 mL, 4.68 mmol, 10 equiv.) and Pd(PPh$_3$)$_4$ (54 mg, 0.0468 mmol, 0.1 equiv.) were added and the reaction mixture was heated to 80 °C for 18 h. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane. The crude product mixture was washed sequentially with a saturated solution of sodium bicarbonate, water and brine and dried over sodium sulfate. Purification was carried out by dry loaded column chromatography on silica gel (CH$_2$Cl$_2$/C$_6$H$_{14}$, 1:2, v/v). After recrystallisation from CH$_2$Cl$_2$/MeOH (1:3, v/v) the product was obtained in 170 mg (0.28 mmol, 60 %) yield as purple crystals: mp 114 °C; R$_f$=0.49 (CH$_2$Cl$_2$/C$_6$H$_{14}$, 1:1, v/v); $^1$H NMR (400 MHz, CDC$_3$): δ=-2.59 (s, br, 2H, NH), 0.97 (t, $^3$J=7.3 Hz, 6H, C$_5$H$_{10}$CH$_3$), 0.99 (t, $^3$J=7.6 Hz, 3H, C$_5$H$_{10}$CH$_3$), 1.43 (m, 6H, C$_4$H$_8$CH$_2$CH$_3$), 1.54 (m, 6H, C$_3$H$_6$CH$_2$CH$_2$CH$_3$), 1.85 (m, 6H, C$_2$H$_4$CH$_2$C$_2$H$_4$CH$_3$), 2.54 (m, 6H, CH$_2$CH$_2$C$_3$H$_6$CH$_3$), 4.95 (m, 6H, CH$_2$C$_4$H$_8$CH$_3$), 5.18 (d, $^3$J=17.0 Hz, 1H, CH$_2$CH=CHH), 5.25 (d, $^3$J=9.9 Hz, 1H, CH$_2$CH=CHH), 5.74 (d, $^3$J=5.3 Hz, 2H, CH$_2$CH=CH$_2$), 6.88 (m, 1H, CH$_2$CH=CH$_2$), 9.48 (d, $^3$J=4.8 Hz, 4H, H$_{9}$), 9.50 (d, $^3$J=5.2 Hz, 4H, H$_{9}$) ppm; $^{13}$C NMR (100.6 MHz, CDC$_3$): δ=14.2, 22.8, 30.4, 31.9, 35.5, 35.6, 38.8, 39.0, 113.9, 115.9, 118.6, 118.9, 126.6 (br), 128.2 (br), 141.7 ppm; IR: 3319 (NH), 3121 (C=CH$_2$), 2953 (CH$_2$), 2918 (CH$_2$), 2850 (CH$_3$) cm$^{-1}$; UV/vis (CH$_2$Cl$_2$): $\lambda_{max}$ (lg ε)=419 (5.6), 520 (4.6), 555 (4.5), 600 (4.5), 659 (4.5) nm; HRMS (ES+): calcd for C$_{41}$H$_{54}$N$_4$ [M+H]$^+$ 603.4427, found 603.4423.
Chapter 7: Experimental

[5-Allyl-10,15,20-triheptylporphyrinato]nickel(II) 99. A 50 mL 2-necked round-bottom flask was charged with 5-allyl-10,15,20-triheptylporphyrin 98 (170 mg, 0.28 mmol, 1 equiv.) and Ni(acac)₂ (108 mg, 0.42 mmol, 1.5 equiv.) in toluene (50 mL). The reaction mixture was heated to reflux until completion (~30 min, monitored by TLC). The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane. The crude product was filtered through a layer of silica gel and washed off with dichloromethane. The product was obtained in 132 mg (0.20 mmol, 71 %) yield as a red low melting solid: Rf=0.67 (CH₂Cl₂/C₆H₁₄, 1:2, v/v); ¹H NMR (400 MHz, CDCl₃): δ=0.93 (t, ³J=7.3 Hz, 6H, C₅H₁₀CH₃), 0.95 (t, ³J=7.5 Hz, 3H, C₅H₁₀CH₃), 1.34 (m, 6H, C₄H₈CH₂CH₃), 1.43 (m, 6H, C₅H₁₀CH₂CH₂CH₃), 1.59 (m, 6H, C₂H₄CH₂C₂H₄CH₃), 2.26 (m, 6H, CH₂CH₂C₃H₆CH₃), 4.48 (m, 6H, CH₂C₄H₈CH₃), 5.18 (d, ³J=5.9 Hz, 2H, CH₂CH=CH₂), 5.23 (d, ³J=10.0 Hz, 1H, CH₂CH=CH₂), 5.31 (d, ³J=17.5 Hz, 1H, CH₂CH=CH₂), 6.71 (m, 1H, CH₂CH=CH₂), 9.25 (d, ³J=4.8 Hz, 4H, Hβ), 9.26 (d, ³J=5.2 Hz, 4H, Hα) ppm; ¹³C NMR (100.6 MHz, CDCl₃): δ=14.2, 22.7, 30.1, 31.8, 33.9, 37.3, 37.9, 112.6, 115.6, 117.1, 117.3, 129.7, 129.8, 129.9, 141.0, 141.1, 141.2 ppm; UV/vis (CH₂Cl₂): λmax (lg ε)=420 (5.4), 539 (4.5), 570 (4.3), nm; HRMS (ES+): calcd for C₄₁H₅₂N₄Ni [M+H]^⁺ 659.3624, found 659.3593.
7.4.2 Pauson-Khand Products I

**General Procedure:** Phenylacetylene (10 equiv.) was placed into a round-bottom flask under argon in dry THF (20 mL). Co$_2$(CO)$_8$ (10 equiv.) was added, and the reaction mixture was stirred at rt until formation of the complex (~1 h, monitored by TLC). Then allylporphyrin (82, 95, 99) (1 equiv.) was added and the reaction mixture was heated at 80 °C for 18 h. The crude products were purified by dry loaded column chromatography on silica gel (CH$_2$Cl$_2$/$C_6$H$_{14}$, 1:1, v/v). The first fraction of the column was assumed to be the remaining Co-phenylacetylene-porphyrin complex. Recrystallisation was carried out from CH$_2$Cl$_2$/MeOH (1:3, v/v).

![Chemical Structure](image)

[5,10,15-Tris(4-methylphenyl)-20-(5-methyl-2-phenylcyclopent-2-enonyl)-porphyrinato]nickel(II) 100. By using [5-allyl-10,15,20-tris(4-methylphenyl)porphyrinato]nickel(II) 82 (40 mg, 0.059 mmol) as starting material, phenylacetylene (60 µL, 0.59 mmol) and Co$_2$(CO)$_8$ (202 mg, 0.59 mmol) the reaction was carried out in a Schlenk-tube and the solution was degassed via three freeze-pump-thaw cycles and refilled with argon. The product was obtained as the second fraction by column chromatography followed by recrystallisation as red crystals in 18.8 mg (0.023 mmol, 39 %) yield: mp 146 °C; $R_f$=0.21 (CH$_2$Cl$_2$/$C_6$H$_{14}$, 1:1, v/v); $^1$H NMR (400 MHz, CDCl$_3$): $\delta=1.97$ (m, 1H, C=CHCH$_2$CHCH$_2$), 2.25 (m, 1H, C=CHCH$_2$CHCH$_2$), 2.66 (s, 3H, C$_6$H$_4$CH$_3$), 2.67 (s, 6H, C$_6$H$_4$CH$_3$), 3.24 (m, 1H, C=CHCH$_2$CHCH$_2$), 4.55 (dd, $^3J=14.0$ Hz, $^2J=11.1$ Hz, 1H, C=CHCH$_2$CHCH$_2$), 5.69 (dd, $^3J=14.6$ Hz, $^2J=4.1$ Hz, 1H, C=CHCH$_2$CHCH$_2$), 7.39 (d, $^3J=5.9$ Hz, 1H, $H_{A1}$), 7.43
(m, 2H, $H_{Ar}$), 7.49 (d, $^3J$=7.0 Hz, 4H, $H_{Ar}$), 7.49 (d, $^3J$=7.6 Hz, 2H, $H_{Ar}$), 7.55 (dd, $^3J$=2.9 Hz, $^1J$=1.8 Hz, 1H, C=CHCH$_2$CHCH$_2$), 7.73 (d, $^3J$=6.4 Hz, 2H, $H_{Ar}$), 7.88 (d, $^3J$=3.5 Hz, 4H, $H_{Ar}$), 7.89 (d, $^3J$=3.5 Hz, 2H, $H_{Ar}$), 8.74 (d, $^3J$=4.1 Hz, 2H, $H_\beta$), 8.74 (d, $^3J$=4.6 Hz, 2H, $H_\beta$), 8.88 (d, $^3J$=4.7 Hz, 2H, $H_\beta$), 9.44 (d, $^3J$=5.3 Hz, 2H, $H_\beta$) ppm; $^1$C NMR (150.9 MHz, CDCl$_3$): $\delta$=14.1, 21.5, 22.7, 29.4, 29.7, 31.9, 32.8, 35.0, 52.3, 114.5, 118.6, 127.0, 127.6, 128.4, 129.7, 131.6, 132.3, 133.1, 133.6, 137.4, 142.2, 142.4, 142.8, 157.3, 207.8 ppm; IR: 3022 (CH=C), 2918 (CH$_2$), 2850 (CH$_3$), 1698 (C=0) cm$^{-1}$; UV/vis (CH$_2$Cl$_2$): $\lambda_{max}$ (lg $\varepsilon$)=419 (5.4), 523 (4.7) nm; HRMS (ES$^+$): calcd for C$_{53}$H$_{40}$N$_4$NiO [M+H]$^+$ 807.2634, found 807.2648.

$[5,10,15$-Tris(4-methylphenyl)-20-(4-methyl-2-phenylcyclopent-2-enonyl)-porphyrinato]$\text{nickel(II)}$ 101. The product was obtained as the third fraction by column chromatography of the reaction above. Recrystallisation gave 15.7 mg (0.019 mmol, 33%) yield of red crystals: mp 182 °C; $R_f$=0.16 (CH$_2$Cl$_2$/C$_6$H$_{14}$, 1:1, v/v); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$=2.63 (m, 1H, COCH$_2$CH), 2.66 (s, 3H, C$_6$H$_4$CH$_3$), 2.68 (s, 6H, C$_6$H$_4$CH$_3$), 2.77 (dd, $^3J$=18.7 Hz, $^2J$=6.4 Hz, 1H, COCH$_2$CH), 3.70 (m, 1H, COCH$_2$CH), 4.80 (dd, $^3J$=14.0 Hz, $^2J$=9.4 Hz, 1H, COCH$_2$CHCH$_2$), 5.10 (dd, $^3J$=14.0 Hz, $^2J$=7.0 Hz, 1H, COCH$_2$CHCH$_2$), 7.28 (m, 5H, $H_{Ar}$), 7.49 (s, 1H, CH=CCO), 7.50 (d, $^3J$=4.7 Hz, 4H, $H_{Ar}$), 7.51 (d, $^3J$=7.6 Hz, 2H, $H_{Ar}$), 7.89 (d, $^3J$=5.3 Hz, 4H, $H_{Ar}$), 7.91 (d, $^3J$=7.0 Hz, 2H, $H_{Ar}$), 8.76 (d, $^3J$=4.7 Hz, 2H, $H_\beta$), 8.76 (d, $^3J$=5.3 Hz, 2H, $H_\beta$), 8.88 (d, $^3J$=5.3 Hz, 2H, $H_\beta$), 9.28 (d, $^3J$=5.3 Hz, 2H, $H_\beta$) ppm; $^1$C NMR (150.9 MHz, CDCl$_3$): $\delta$=13.9, 21.3, 22.5, 29.5, 30.8, 31.8, 43.1, 43.5, 113.3, 118.6, 118.7, 127.0,
127.5, 128.2, 128.3, 129.0, 131.0, 132.2, 132.9, 133.4, 133.5, 137.3, 137.6, 137.63, 142.0, 142.2, 142.4, 142.5, 142.8, 160.9, 206.1 ppm; IR: 3022 (CH=C), 2918 (CH$_2$), 2851 (CH$_3$), 1702 (C = O) cm$^{-1}$; UV/vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (lg ε)=419 (5.6), 531 (4.6) nm; HRMS (ES+): calcd for C$_{53}$H$_{40}$N$_4$NiO [M+H]$^+$ 807.2634, found 807.2663.

[5,10,15-Tris(4-methylphenyl)-20-(5-methyl-2-phenylcyclopent-2-enonyl)-porphyrinato]zinc(II) 102 By using [5-allyl-10,15,20-bis(4-methylphenyl)porphyrinato]zinc(II) 95 (40 mg, 0.059 mmol) as starting material, phenylacetylene (65 µL, 0.59 mmol) and Co$_2$(CO)$_8$ (202 mg, 0.59 mmol) the product was obtained as the second fraction by column chromatography followed by recrystallisation as purple crystals in 3.8 mg (4 µmol, 8 %) yield; mp >300 °C; R$_f$=0.19 (CH$_2$Cl$_2$/C$_6$H$_{14}$, 1:1, v/v); $^1$H NMR (600 MHz, CDCl$_3$): δ=2.31 (m, 1H, C=CHCH$_2$CHCH$_2$), 2.73 (s, 3H, C$_6$H$_4$CH$_3$), 2.76 (s, 6H, C$_6$H$_4$CH$_3$), 2.95 (m, 1H, C=CHCH$_2$CHCH$_2$), 3.83 (m, 1H, C=CHCH$_2$CHCH$_2$), 4.94 (dd, $^3$J=14.7 Hz, $^2$J=11.0 Hz, 1H, C=CHCH$_2$CHCH$_2$), 7.41 (t, $^3$J=7.3 Hz, 1H, H$_{Ar}$), 7.48 (dd, $^3$J=7.3 Hz, $^3$J=7.3 Hz, 2H, H$_{Ar}$), 7.58 (d, $^3$J=7.3 Hz, 2H, H$_{Ar}$), 7.58 (d, $^3$J=5.9 Hz, 2H, H$_{Ar}$), 7.60 (d, $^3$J=5.1 Hz, 2H, H$_{Ar}$), 7.75 (dd, $^3$J=2.8 Hz, $^3$J=2.4 Hz, 1H, C=CHCH$_2$CHCH$_2$), 7.86 (d, $^3$J=7.4 Hz, 2H, H$_{Ar}$), 8.10 (d, $^3$J=7.3 Hz, 2H, H$_{Ar}$), 8.11 (d, $^3$J=5.9 Hz, 2H, H$_{Ar}$), 8.13 (d, $^3$J=7.3 Hz, 2H, H$_{Ar}$), 8.95 (d, $^3$J=5.2 Hz, 2H, H$_{β}$), 8.95 (d, $^3$J=5.2 Hz, 2H, H$_{β}$), 8.88 (d, $^3$J=4.7 Hz, 2H, H$_{β}$), 9.69 (d, $^3$J=4.4 Hz, 2H, H$_{β}$) ppm; $^{13}$C NMR (150.9 MHz, CDCl$_3$): δ=13.9, 21.4, 22.5, 29.2, 29.5, 30.7, 33.0, 36.3, 54.6, 117.3, 120.7, 127.0, 127.1, 128.4, 128.8, 131.6,
[5,10,15-Tris(4-methylphenyl)-20-(4-methyl-2-phenylcyclopent-2-enonyl)-porphyrinato]zinc(II) 103 The product was obtained as the third fraction of the reaction above by column chromatography followed by recrystallisation as purple crystals in 7.3 mg (9 µmol, 15 %) yield: mp >300 °C; Rf=0.12 (CH<sub>2</sub>Cl/CH<sub>3</sub>OH, 9:1, v/v);

$^1$H NMR (400 MHz, CDCl<sub>3</sub>): $\delta$=2.74 (s, 3H, C<sub>6</sub>H<sub>4</sub>C/3), 2.75 (s, 6H, C<sub>6</sub>H<sub>4</sub>C/3), 2.88 (m, 2H, COCH<sub>2</sub>CH), 4.14 (m, 1H, COCH<sub>2</sub>CH), 5.07 (dd, $^3$J=14.7 Hz, $^2$J=9.8 Hz, 1H, COCH<sub>2</sub>CH), 5.35 (dd, $^3$J=14.7 Hz, $^2$J=6.9 Hz, 1H, COCH<sub>2</sub>CH), 7.29 (s, 2H, H<sub>Ar</sub>), 7.50 (m, 3H, H<sub>Ar</sub>), 7.56 (s, 1H, CH=CCO), 7.59 (d, $^3$J=3.9 Hz, 4H, H<sub>Ar</sub>), 7.60 (d, $^3$J=1.9 Hz, 4H, H<sub>Ar</sub>), 8.10 (d, $^3$J=7.9 Hz, 4H, H<sub>Ar</sub>), 8.13 (d, $^3$J=2.9 Hz, 2H, H<sub>Ar</sub>), 8.96 (d, $^3$J=3.9 Hz, 2H, H<sub>Ar</sub>), 9.04 (d, $^3$J=3.9 Hz, 2H, H<sub>Ar</sub>), 9.44 (d, $^3$J=4.9 Hz, 2H, H<sub>Ar</sub>), ppm; $^{13}$C NMR (150.9 MHz, CDCl<sub>3</sub>): $\delta$=13.9, 21.4, 22.5, 29.2, 29.5, 31.8, 40.5, 43.3, 45.4, 53.2, 115.9, 120.9, 121.1, 127.1, 127.2, 128.2, 128.3, 128.4, 131.2, 131.9, 132.0, 132.6, 134.2, 134.3, 136.9, 137.0, 139.6, 139.7, 142.2, 149.8, 150.2, 150.5, 161.6, 206.5 ppm; IR: 3021 (CH=C), 2919 (CH<sub>2</sub>), 2851 (CH<sub>3</sub>), 1702 (C=O) cm$^{-1}$; UV/vis (CH<sub>2</sub>Cl<sub>2</sub>): $\lambda_{max}$ (lg $\varepsilon$)=422 (5.6), 552 (4.5), 588 (4.4) nm; HRMS (ES+): calcd for C<sub>53</sub>H<sub>40</sub>N<sub>4</sub>OZn [M+H]$^+$ 813.2572, found 813.2585.
[5,10,15-Trihexyl-20-(5-methyl-2-phenylcyclopent-2-enonyl)porphyrinato]nickel(II) 104. By using [5-allyl-10,15,20-trihexylporphyrinato]nickel(II) 99 (45.5 mg, 0.069 mmol) as starting material, phenylacetylene (76 μL, 0.69 mmol) and Co₂(CO)₈ (236 mg, 0.69 mmol) the product was obtained as the second fraction by column chromatography followed by recrystallisation as red crystals in 7.4 mg (9 μmol, 14 %) yield: mp 102 °C; Rf=0.15 (CH₂Cl₂/C₆H₁₄, 1:1, v/v); ¹H NMR (600 MHz, CDCl₃): δ=0.92 (t, ³J=7.2 Hz, 6H, C₅H₁₀(CH₃), 0.92 (t, ³J=7.2 Hz, 3H, C₅H₁₀(CH₃), 1.35 (m, 6H, C₆H₈CH₂CH₃), 1.43 (m, 6H, C₃H₆CH₂CH₂CH₂CH₃), 1.58 (m, 6H, C₂H₄CH₂C₂H₄CH₃), 1.89 (m, 1H, C=CHCH₂CHCH₂), 2.12 (m, 1H, C=CHCH₂CHCH₂), 2.26 (m, 6H, CH₂CH₂C₃H₄CH₃), 3.12 (m, 1H, C=CHCH₂CHCH₂), 4.42 (dd, ³J=14.3 Hz, ²J=11.3 Hz, 1H, C=CHCH₂CHCH₂), 5.61 (dd, ³J=14.7 Hz, ²J=14.1 Hz, 1H, C=CHCH₂CHCH₂), 7.37 (t, ³J=7.2 Hz, 1H, H₉), 7.42 (dd, ³J=7.5 Hz, ²J=7.2 Hz, 2H, H₈), 7.52 (m, 1H, C=CHCH₂CHCH₂), 7.73 (d, ³J=7.5 Hz, 2H, H₉), 9.28 (d, ³J=5.3 Hz, 2H, H₈), 9.28 (d, ³J=6.4 Hz, 2H, H₉), 9.30 (d, ³J=5.3 Hz, 2H, H₈), 9.37 (d, ³J=4.9 Hz, 2H, H₉), ppm; ¹³C NMR (150.9 MHz, CDCl₃): δ=13.9, 22.5, 29.9, 31.6, 32.6, 33.8, 34.6, 37.0, 37.1, 51.8, 112.6, 117.0, 117.2, 126.9, 128.3, 129.7, 129.8, 130.1, 131.5, 140.9, 141.0, 141.1, 142.1, 157.2, 207.7 ppm; IR: 2952 (CH₂), 2920 (CH₃), 2851 (CH₃), 1697 (C=O) cm⁻¹; UV/vis (CH₂Cl₂): λmax (lg ε)=421 (5.3), 540 (4.5), 574 (4.3) nm; HRMS (ES⁺): calcd for C₅₀H₅₈N₄NiO [M+H]^+ 789.4042, found 789.4028.
\[5,10,15\text{-Trihexyl-20-(4-methyl-2-phenylcyclopent-2-enonyl)porphyrinato}\text{-nickel(II)}\text{ 105.}\] The product was obtained as the third fraction of the reaction above by column chromatography followed by recrystallisation as red crystals in 10.3 mg (0.013 mmol, 19 %) yield: mp 136 °C; \(R_f=0.23\) (CH\(_2\)Cl\(_2\)/C\(_6\)H\(_{14}\), 1:1, v/v); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta=0.92\) (t, \(J=7.3\) Hz, 6H, C\(_5\)H\(_{10}\)CH\(_3\)), 0.92 (t, \(J=7.3\) Hz, 3H, C\(_5\)H\(_{10}\)CH\(_3\)), 1.35 (m, 6H, C\(_4\)H\(_8\)CH\(_2\)CH\(_3\)), 1.44 (m, 6H, C\(_3\)H\(_6\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.59 (m, 6H, C\(_2\)H\(_4\)CH\(_2\)C\(_2\)H\(_4\)CH\(_3\)), 2.28 (m, 6H, CH\(_2\)CH\(_2\)C\(_3\)H\(_6\)CH\(_3\)), 2.60 (m, 1H, COCH\(_2\)CH), 2.74 (m, 1H, COCH\(_2\)CH), 3.59 (m, 1H, COCH\(_2\)CH), 4.51 (m, 6H, CH\(_2\)C\(_4\)H\(_8\)CH\(_3\)), 4.71 (dd, \(J=13.9\) Hz, \(J=9.4\) Hz, 1H, COCH\(_2\)CHCH\(_2\)CH), 4.99 (dd, \(J=14.3\) Hz, \(J=7.2\) Hz, 1H, COCH\(_2\)CHCH\(_2\)CH), 7.26 (s, 1H, CH=CCO), 7.26 (d, \(J=1.9\) Hz, 2H, H\(_{\alpha}\)), 7.27 (d, \(J=1.5\) Hz, 1H, H\(_{\alpha}\)), 7.51 (m, 2H, H\(_{\alpha}\)), 9.23 (d, \(J=5.3\) Hz, 2H, H\(_{\beta}\)), 9.29 (d, \(J=4.9\) Hz, 2H, H\(_{\beta}\)), 9.30 (d, \(J=5.7\) Hz, 4H, H\(_{\beta}\)) ppm; \(^13\)C NMR (150.9 MHz, CDCl\(_3\)): \(\delta=13.9, 22.5, 29.5, 29.9, 31.6, 33.9, 37.2, 38.9, 43.1, 43.2, 111.6, 117.2, 117.4, 127.0, 128.1, 128.2, 129.3, 129.8, 129.9, 131.1, 131.1, 140.9, 141.2, 141.3, 142.3, 161.1, 206.2 ppm; IR: 2951 (CH\(_2\)), 2919 (CH\(_2\)), 2851 (CH\(_3\)), 1701 (C=O) cm\(^{-1}\); UV/vis (CH\(_2\)Cl\(_2\)): \(\lambda_{\text{max}}\) (lg \(\varepsilon\))=421 (5.5), 538 (4.8), 570 (4.6) nm; HRMS (ES+): calcd for C\(_{50}\)H\(_{58}\)N\(_4\)NiO\([\text{M+H}]^+\) 789.4042, found 789.4020.
7.5 Pauson-Khand Products of Alkynylporphyrins

7.5.1 Synthesis of Starting Materials

5,10,15-Tris(4-methylphenyl)-20-trimethylsilylethynylporphyrin 106

A 100 mL Schlenk-tube was filled with argon and charged with 5-bromo-10,15,20-tris(4-methylphenyl)porphyrin 67 (200 mg, 0.30 mmol; 1 equiv.) in dry THF/triethylamine (60 mL, 1:3, v/v). The solution was degassed via five freeze-pump-thaw cycles and put under argon again. Ethynyltrimethylsilane (0.4 mL, 3.0 mmol, 10 equiv.), copper(I)iodide (14 mg, 0.075 mmol, 0.25 equiv.) and Pd(PPh₃)₂Cl₂ (25 mg, 0.036 mmol, 0.12 equiv.) were added and the reaction mixture was stirred at rt for 18 h. Dichloromethane (60 mL) was added and the solution was washed with water and dried over sodium sulfate. After purification by dry loaded column chromatography on silica gel (CH₂Cl₂/C₆H₁₄, 1:2, v/v), the product was obtained in 146 mg (0.216 mmol, 72 %) yield as purple crystals: mp >300 °C; Rf=0.41 (CH₂Cl₂/C₆H₁₄, 1:2, v/v); ¹H NMR (400 MHz, CDCl₃): δ=2.40 (s, br, 2H, NH), 0.63 (s, 9H, SiCH₃), 2.72 (s, 3H, C₆H₄CH₃), 2.74 (s, 6H, C₆H₄CH₃), 7.56 (d, J=8.2 Hz, 2H, HA), 7.59 (d, J=8.2 Hz, 4H, H₂), 8.07 (d, J=8.2 Hz, 2H, HA), 8.10 (d, J=8.2 Hz, 4H, H₂), 8.80 (s, 4H, H'), 8.93 (d, J=4.7 Hz, 2H, H') ppm; ¹³C NMR (100.6 MHz, CDCl₃): δ=0.4, 21.6, 29.7, 98.7, 101.7, 107.2, 121.1, 121.2, 127.4, 127.5, 130.6 (br), 131.9 (br), 134.4, 134.5, 137.5 ppm; UV/vis (CH₂Cl₂): λ_max (lg ε)=429 (5.7), 529 (4.6), 568 (4.6), 604 (4.4), 657 (4.5) nm; HRMS (ES+): calcd for C₄₆H₄₀N₄Si [M+H]⁺ 677.3101, found 677.3095.
[5,10,15-Tris(4-methylphenyl)-20-trimethylsilylethynylporphyrinato]-nickel(II)

107. A 50 mL 2-necked round bottom flask was charged with 5,10,15-tris(4-methylphenyl)-20-trimethylsilylethynylporphyrin 106 (100 mg, 0.148 mmol; 1 equiv.) and Ni(acac)₂ (57 mg, 0.222 mmol, 1.5 equiv.) in toluene (30 mL). The reaction mixture was heated to reflux until completion (~30 min, monitored by TLC). The solvent was removed under reduced pressure and the residue was dissolve in dichloromethane. The crude product was filtered through a layer of silica gel and washed off with dichloromethane. The solvent was removed under reduced pressure and the product was obtained in a quantitative yield (107 mg, 0.146 mmol, 99 %) as purple crystals: mp >300 °C; Rf=0.86 (CH₂Cl₂/C₆H₁₄, 1:1, v/v); ¹H NMR (400 MHz, CDCl₃): δ=0.56 (s, 9H, SiC/Zs), 2.65 (s, 3H, C₆H₄CH₃), 2.68 (s, 6H, C₆H₄CH₃), 7.49 (d, ³J=8.0 Hz, 4H, Hₐₐ), 7.51 (d, ³J=8.0 Hz, 2H, Hₐₐ), 7.88 (d, ³J=4.8 Hz, 4H, Hₐₐ), 7.90 (d, ³J=5.2 Hz, 2H, Hₐₐ), 8.69 (d, ³J=5.3 Hz, 2H, Hₐₐ), 8.71 (d, ³J=4.7 Hz, 2H, Hₐₐ), 8.83 (d, ³J=4.7 Hz, 2H, Hₐₐ), 9.51 (d, ³J=4.7 Hz, 2H, Hₐₐ) ppm; ¹³C NMR (100.6 MHz, CDCl₃): δ=1.1, 29.7, 102.2, 119.5, 119.6, 126.9, 127.1, 127.8, 127.9, 132.5, 132.6, 133.2, 133.4, 133.5, 133.6, 133.7, 140.4, 140.5, 142.4, 142.8, 143.0, 143.1 ppm; IR: 3054 (Ar-H), 2957 (CH₃), 2921 (CH₃), 2851 (CH₃), 2163 (C=C) cm⁻¹; UV/vis (CH₂Cl₂): λₘₜₙ (lg e)=417 (5.2), 533 (4.5) nm.
[5-Ethynyl-10,15,20-tris(4-methylphenyl)porphyrinato]nickel(II) 108. A 100 mL round-bottom flask was charged with [5-trimethylsilylethynyl-10,15,20-tris(4-methylphenyl)porphyrinato]nickel(II) 107 (108 mg, 0.146 mmol, 1 equiv.) and tetrabutylammonium fluoride (61 mg, 0.234 mmol, 1.6 equiv.) in dichloromethane (50 mL). The reaction mixture was stirred at rt until completion (~30 min, monitored by TLC). The crude product was filtered through a short layer of silica and washed off with dichloromethane. After the solvent was removed under reduced pressure, the product was obtained in a quantitative yield (97 mg, 0.146 mmol, 100 %) as dark red crystals: mp >300 °C; Rf=0.63 (CH$_2$Cl$_2$/C$_6$H$_4$, 1:2, v/v); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$=2.66 (s, 3H, C$_6$H$_4$C), 2.68 (s, 6H, C$_6$H$_4$CH$_3$), 4.08 (s, 1H, C=CH), 7.49 (d, $^3$J=8.8 Hz, 2H, H$_{Ar}$), 7.52 (d, $^3$J=8.2 Hz, 4H, H$_{Ar}$), 7.88 (d, $^3$J=6.5 Hz, 2H, H$_{Ar}$), 7.90 (d, $^3$J=7.6 Hz, 4H, H$_{Ar}$), 8.71 (d, $^3$J=4.7 Hz, 2H, H$_{b}$), 8.73 (d, $^3$J=5.3 Hz, 2H, H$_{b}$), 8.85 (d, $^3$J=4.7 Hz, 2H, H$_{b}$), 9.54 (d, $^3$J=4.7 Hz, 2H, H$_{b}$) ppm; $^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$=21.5, 29.8, 84.1, 84.2, 96.9, 119.8, 120.8, 127.6, 127.7, 131.4, 132.1, 132.5, 133.3, 133.5, 133.6, 137.5, 137.6, 137.7, 142.5, 142.6, 143.4, 145.1 ppm; IR: 3286 (C=CH), 3022 (Ar-H), 2850 (CH$_3$) cm$^{-1}$; UV/vis (CH$_2$Cl$_2$): $\lambda_{max}$ (lg e)=423 (5.5), 537 (4.7), 571 (4.6) nm; HRMS (ES+): calcd for C$_{43}$H$_{30}$N$_4$Ni [M+H]$^+$ 661.1902, found 661.1870.
10,15,20-Trihexyl-5-trimethylsilylethynylporphyrin 110. A 50 mL Schlenk-tube was filled with argon and charged with 5-bromo-10,15,20-trihexylporphyrin 97 (100 mg, 0.156 mmol, 1 equiv.) in dry THF/triethylamine (40 mL, 3:1, v/v). The solution was degassed via five freeze-pump-thaw cycles and put under argon again. Ethynyltrimethylsilane (0.2 mL, 1.56 mmol, 10 equiv.), copper(I)iodide (8 mg, 0.039 mmol, 0.25 equiv.) and Pd(PPh\(_3\))\(_2\)Cl\(_2\) (13 mg, 0.019 mmol, 0.12 equiv.) were added and the reaction mixture was stirred at rt for 18 h. Dichloromethane (30 mL) was added and the solution was washed with water and dried over sodium sulfate. The product was obtained as purple crystals in 69 mg (0.10 mmol, 67 %) yield: mp 119 °C; R\(_f\)=0.71 (CH\(_2\)Cl\(_2\)/C\(_6\)H\(_{14}\), 1:1, v/v); \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ= -2.40 (s, br, 2H, NH), 0.68 (s, 9H, SiC\(_3\)), 0.97 (t, \(^3\)J=7.3 Hz, 6H, C\(_5\)H\(_{10}\)C\(_3\)), 0.99 (t, \(^3\)J=7.6 Hz, 3H, C\(_5\)H\(_{10}\)CH\(_3\)), 1.43 (m, 6H, C\(_6\)H\(_{5}\)CH\(_2\)CH\(_3\)), 1.53 (m, 6H, C\(_5\)H\(_{6}\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.79 (m, 6H, C\(_5\)H\(_{4}\)CH\(_2\)C\(_2\)H\(_4\)CH\(_3\)), 2.47 (m, 6H, CH\(_2\)CH\(_2\)C\(_3\)H\(_6\)CH\(_3\)), 4.81 (t, \(^3\)J=8.1 Hz, 4H, CH\(_2\)C\(_4\)H\(_8\)CH\(_3\)), 4.86 (t, \(^3\)J=8.1 Hz, 2H, CH\(_2\)C\(_4\)H\(_8\)CH\(_3\)), 9.33 (d, \(^3\)J=5.1 Hz, 2H, H\(_{\beta}\)), 9.38 (d, \(^3\)J=4.2 Hz, 2H, H\(_{\beta}\)), 9.40 (d, \(^3\)J=4.2 Hz, 2H, H\(_{\beta}\)), 9.65 (d, \(^3\)J=4.8 Hz, 2H, H\(_{\beta}\)) ppm; \(^1\)C NMR (100.6 MHz, CDCl\(_3\)): δ=0.5, 14.2, 22.8, 30.3, 30.4, 31.9, 36.3, 37.0, 38.6, 38.9, 96.8, 100.7, 107.6, 120.3, 121.8, 128.6 (br), 130.7 (br) ppm; IR: 3314 (NH), 2951 (CH\(_2\)), 2919 (CH\(_2\)), 2848 (CH\(_3\)), 2132 (C=C) cm\(^{-1}\); UV/vis (CH\(_2\)Cl\(_2\)): λ\(_{\max}\) (lg ε)=428 (5.8), 532 (4.7), 571 (4.8), 611 (4.6), 669 (4.7) nm; HRMS (ES+): calcd for C\(_{43}\)H\(_{58}\)N\(_4\)Si [M+H]\(^+\) 659.4509, found 659.4494.
[10,15,20-Trihexyl-5-trimethylsilylethynylporphyrinato]nickel(II) 111. A 50 mL 2-necked round-bottom flask was charged with 10,15,20-trihexyl-5-trimethylsilylethynylporphyrin 110 (44 mg, 0.066 mmol, 1 equiv.) and Ni(acac)₂ (25 mg, 0.1 mmol, 1.5 equiv.) in toluene (20 mL). The reaction mixture was heated to reflux until completion (~2 h, monitored by TLC). The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane. The crude product was filtered through a layer of silica gel and washed off with dichloromethane. After the solvent was removed under reduced pressure the product was obtained in 46 mg (0.064 mmol, 98 %) yield of a red low melting solid; Rf=0.95 (CH₂Cl₂/C₆H₄, 1:1, v/v); 

\^H NMR (400 MHz, CDCl₃): δ=0.59 (s, 9H, SiCH₃), 0.92 (t, \(J =7.2\) Hz, 6H, C₅H₁₀CH₃), 0.94 (t, \(J =7.2\) Hz, 3H, C₃H₁₀CH₃), 1.34 (m, 6H, C₆H₈CH₂CH₃), 1.43 (m, 6H, C₃H₆CH₂CH₂CH₃), 1.60 (m, 6H, C₂H₄CH₂C₂H₄CH₃), 2.26 (m, 6H, CH₂CH₂C₃H₆CH₃), 4.42 (m, 6H, CH₂C₄H₈CH₃), 9.18 (d, \(J =5.0\) Hz, 2H, \(H_β\)), 9.20 (d, \(J =2.1\) Hz, 2H, \(H_β\)), 9.22 (d, \(J =2.0\) Hz, 2H, \(H_β\)), 9.42 (d, \(J =5.0\) Hz, 2H, \(H_β\)) ppm; \(^{13}\)C NMR (100.6 MHz, CDCl₃): δ=0.4, 14.2, 22.7, 29.8, 30.1, 30.2, 31.8, 34.0, 34.2, 37.4, 37.5, 96.4, 101.2, 105.5, 118.4, 119.6, 129.3, 129.8, 130.2, 131.7, 140.9, 141.4, 142.2, 143.9 ppm; UV/vis (CH₂Cl₂): \(λ_{max}\) (lg ε)=428 (5.3), 548 (4.4), 585 (4.3) nm; HRMS (ES+): calcd for C₄₃H₅₆N₄NiSi [M+H]^+ 715.3706, found 715.3718.
[5-Ethynyl-10,15,20-trihexylporphyrinato]nickel(II) \textbf{112}. A 50 mL round bottom flask was charged with \textit{[10,15,20-trihexyl-5-trimethylsilylthynylporphyrinato]nickel(II)} \textbf{111} (46 mg, 0.064 mmol, 1 equiv.) and tetrabutylammonium-fluoride (25 mg, 0.1 mmol, 1.6 equiv.) in dichloromethane (20 mL). The reaction mixture was stirred at rt until completion (~30 min, monitored by TLC). The crude product was filtered through a short layer of silica gel and washed off with dichloromethane. After the solvent was removed under reduced pressure the product was obtained in 41 mg (0.06 mmol, 99 \%) yield of a red low melting solid: 

R\textsubscript{f}=0.89 (CH\textsubscript{2}Cl\textsubscript{2}/C\textsubscript{6}H\textsubscript{14}, 1:1, v/v); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \delta=0.94 (t, \textit{J}=7.2 Hz, 6H, C\textsubscript{5}H\textsubscript{10}CH\textsubscript{3}), 0.96 (t, \textit{J}=7.2 Hz, 3H, C\textsubscript{6}H\textsubscript{11}CH\textsubscript{3}), 1.37 (m, 6H, C\textsubscript{4}H\textsubscript{8}CH\textsubscript{2}CH\textsubscript{3}), 1.43 (m, 6H, C\textsubscript{3}H\textsubscript{6}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 1.59 (m, 6H, C\textsubscript{4}H\textsubscript{8}CH\textsubscript{2}CH\textsubscript{3}), 2.25 (m, 6H, CH\textsubscript{2}CH\textsubscript{2}C\textsubscript{5}H\textsubscript{11}CH\textsubscript{3}), 4.04 (s, 1H, C=CH\textsubscript{2}), 4.32 (t, \textit{J}=8.1 Hz, 2H, CH\textsubscript{2}C\textsubscript{4}H\textsubscript{8}CH\textsubscript{3}), 4.37 (t, \textit{J}=8.0 Hz, 4H, CH\textsubscript{2}C\textsubscript{4}H\textsubscript{8}CH\textsubscript{3}), 9.12 (d, \textit{J}=5.0 Hz, 2H, H\textsubscript{β}), 9.14 (d, \textit{J}=5.0 Hz, 2H, H\textsubscript{β}), 9.19 (d, \textit{J}=4.8 Hz, 2H, H\textsubscript{β}), 9.42 (d, \textit{J}=4.8 Hz, 2H, H\textsubscript{β}) ppm; \textsuperscript{13}C NMR (100.6 MHz, CDCl\textsubscript{3}): \delta=14.2, 22.7, 29.8, 30.0, 30.1, 31.8, 33.9, 34.2, 37.4, 37.6, 83.6, 84.2, 94.9, 118.4, 119.7, 129.3, 129.8, 130.3, 131.4, 140.8, 141.4, 142.2, 143.9 ppm; UV/vis (CH\textsubscript{2}Cl\textsubscript{2}): \lambda_{\text{max}} (lg \varepsilon)=425 (5.6), 545 (4.6), 581 (4.5) nm; HRMS (ES\textsuperscript{+}): calcd for C\textsubscript{40}H\textsubscript{48}N\textsubscript{4}Ni [M+H]\textsuperscript{+} 643.3311, found 643.3282.
5-(4-Ethynylphenyl)-10,20-bis(4-methylphenyl)porphyrin 113. A 250 mL 3-necked round-bottom flask was filled with argon and charged with p-bromobenzene (1.113 g, 6.15 mmol, 15 equiv.) in 3 mL dry diethyl ether. n-Butyllithium (4.9 mL, 12.3 mmol, 30 equiv., 2.5 M in hexane) was added dropwise at -78 °C over 1 h. After the addition was complete the reaction mixture was warmed to 45 °C and dry THF (2 mL) was added until a white solid was formed. 5,15-Bis(4-methylphenyl)porphyrin 56 (200 mg, 0.41 mmol, 1 equiv.) dissolved in dry THF (150 mL) was added quickly and the reaction mixture was stirred at rt for 18 h (colour change to brown). Water (2 mL, colour change to emerald green) and DDQ (1.4 g, 6.15 mmol, 15 equiv.) were added (colour change to red). After 1 h the crude product was filtered through a layer of silica gel and washed off with dichloromethane. After recrystallisation from CH$_2$Cl$_2$/MeOH (1:3, v/v) the product was obtained in 95 mg (0.16 mmol, 39 %) yield as purple crystals: mp >300 °C; R$_f$=0.24 (CH$_2$Cl$_2$/C$_6$H$_{14}$, 1:4, v/v); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$= 2.99 (s, br, 2H, N/H), 2.75 (s, 6H, C$_6$H$_4$CH$_3$), 3.35 (s, 1H, C=CH), 7.01 (d, $^3$J=7.6 Hz, 4H, H$_{Ar}$), 7.91 (d, $^3$J=8.2 Hz, 2H, H$_{Ar}$), 8.15 (d, $^3$J= 7.6 Hz, 4H, H$_{Ar}$), 8.21 (d, $^3$J=7.6 Hz, 2H, H$_{Ar}$), 8.86 (d, $^3$J=4.7 Hz, 2H, H$_{p}$), 8.97 (d, $^3$J=4.7 Hz, 2H, H$_{p}$), 9.08 (d, $^3$J=4.1 Hz, 2H, H$_{p}$), 9.37 (d, $^3$J=4.7 Hz, 2H, H$_{p}$), 10.25 (s, 1H, H$_{meso}$) ppm; $^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$=21.1, 77.8, 83.3, 104.5, 118.8, 119.4, 121.1, 127.2, 129.9, 130.5, 133.9, 134.2, 137.0, 138.3, 142.9, 145.3 (br), 146.7 (br) ppm; IR: 3294 (C=CH), 3024 (Ar-H) cm$^{-1}$; UV/vis (CH$_2$Cl$_2$): $\lambda_{max}$ (lg e)=414 (5.7), 509 (4.6), 543 (4.4), 582 (4.4), 639 (4.4) nm; HRMS (ES+): calcd for C$_{42}$H$_{30}$N$_4$ [M+H]$^+$ 591.2549, found 591.2524.
A 100 mL 2-necked round-bottom flask was charged with 5-(4-ethynylphenyl)-10,20-bis(4-methylphenyl)porphyrin (176 mg, 0.3 mmol, 1 equiv.) and Ni(acac)$_2$ (116 mg, 0.45 mmol, 1.5 equiv.) in toluene (50 mL). The reaction mixture was heated to reflux until completion (~4 h, monitored by TLC). The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane and filtered through a layer of silica gel. After recrystallisation from CH$_2$Cl$_2$/MeOH (1:3, v/v) the product was obtained as red needles in 166 mg (0.257 mmol, 86 %) yield: mp >300 ºC; Rf=0.77 (CH$_2$Cl$_2$/C$_6$H$_{14}$, 1:1, v/v); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$=2.69 (s, 6H, C$_6$H$_4$C/H); 7.53 (d, $^3$J=7.6 Hz, 4H, $H_{ar}$); 7.84 (d, $^3$J=8.2 Hz, 2H, $H_{ar}$); 7.94 (d, $^3$J=7.6 Hz, 4H, $H_{ar}$); 8.01 (d, $^3$J=7.6 Hz, 2H, $H_{ar}$); 8.76 (d, $^3$J=4.7 Hz, 2H, $H_{b}$); 8.84 (d, $^3$J=5.3 Hz, 2H, $H_{b}$); 8.95 (d, $^3$J=4.7 Hz, 2H, $H_{b}$); 9.16 (d, $^3$J=4.7 Hz, 2H, $H_{b}$); 9.86 (s, 1H, $H_{meso}$) ppm; $^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$=21.5, 78.2, 83.6, 104.7, 118.2, 118.9, 121.6, 127.6, 130.6, 131.6, 132.2, 132.3, 132.7, 133.6, 133.7, 137.9, 141.8, 141.9, 142.8, 142.9, 143.0 ppm; UV/vis (CH$_2$Cl$_2$): $\lambda_{max}$ ($lg c$)=409 (5.4), 523 (4.6), 550 (4.4) nm; HRMS (ES+): calcd for C$_{42}$H$_{28}$N$_4$Ni [M+H]$^+$ 647.1746, found 647.1755.
130 Chapter 7: Experimental

[5-(4-Ethynylphenyl)-10,20-bis(4-methylphenyl)porphinato]zinc(II) 115: A 100 mL round bottom flask was charged with 5-(4-ethynylphenyl)-10,20-bis(4-methylphenyl)porphyrin 113 (76 mg, 0.03 mmol, 1 equiv.) in dichloromethane (50 mL). Zn(OAc)$_2$ (10 mg, 0.045 mmol, 1.5 equiv.) dissolved in methanol (5 mL) was added and the reaction mixture was stirred at rt until completion (~1 h, monitored by TLC). The crude product was filtered through a layer of silica gel. After the solvent was removed under reduced pressure the product was obtained quantitatively (84 mg, 0.03 mmol, 99 %) as pink crystals: mp >300 °C; R$_f$=0.46 (CH$_2$Cl$_2$/C$_6$H$_{14}$, 1:1, v/v); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$=2.76 (s, 6H, C$_6$H$_4$CH$_3$), 3.34 (s, 1H, C=CH), 7.61 (d, 3J=7.6 Hz, 4H, $H_{Ar}$), 7.92 (d, 3J=7.6 Hz, 2H, $H_{Ar}$), 8.14 (d, 3J=8.2 Hz, 4H, $H_{Ar}$), 8.21 (d, 3J=8.2 Hz, 2H, $H_{Ar}$), 8.97 (d, 3J=4.7 Hz, 2H, $H_{p}$), 9.06 (d, 3J=4.7 Hz, 2H, $H_{p}$), 9.13 (d, 3J=4.7 Hz, 2H, $H_{p}$), 9.38 (d, 3J=4.1 Hz, 2H, $H_{p}$), 10.23 (s, 1H, H$_{meso}$) ppm; $^{13}$C NMR (100.6 MHz, CDCl$_3$): $\delta$=21.6, 83.8, 105.9, 120.2, 120.8, 121.3, 127.4, 130.3, 131.5, 131.7, 132.1, 132.7, 134.4, 134.5, 137.2, 139.6, 143.7, 149.3, 149.7, 150.3 ppm; IR: 3298 (C≡CH), 3022 (Ar-H) cm$^{-1}$; UV/vis (CH$_2$Cl$_2$): $\lambda_{max}$ (lg $\varepsilon$)=415 (5.7), 542 (4.8) nm; HRMS (ES$^+$): calcd for C$_{42}$H$_{30}$N$_4$ [M]$^+$ 652.1605, found 652.1588.
7.5.2 Pauson-Khand Products II

**General Procedure:** 4-Ethynylphenylporphyrin (114, 115) (1 equiv.) was placed into a Schlenk tube under argon in dry THF (20 mL). The solution was degassed via three freeze-pump-thaw cycles and refilled with argon. Next Co$_2$(CO)$_8$ (10 equiv.) was added, and the reaction mixture was stirred at rt until formation of the complex (~1 h, monitored by TLC). Norbornene or norbornadiene (2 equiv.) was added, and the reaction mixture was heated at 80 °C for 18 h. The crude products were purified by dry loaded column chromatography on silica gel (CH$_2$Cl$_2$/C$_6$H$_{14}$, 1:1, v/v). The first fraction of the column was assumed to be the remaining Co-porphyrin-norbornene/norbornadiene complex and the product was obtained as the second fraction. Recrystallisation was carried out from CH$_2$Cl$_2$/MeOH (1:3, v/v).

[5,15-Bis(4-methylphenyl)-10-(4-phenyltricyclopentadiene)12-decayan-3-onyl]-porphyrinato]nickel(II) 116. By using [5-(4-ethynylphenyl)-10,20-bis(4-methylphenyl)porphyrinato]nickel(II) 114 (40 mg, 0.062 mmol) and norbornene (12 mg, 0.124 mmol) as starting material, the product was obtained after recrystallisation as purple crystals in 40.4 mg (0.053 mmol, 85 %) yield: mp >300 °C; R$_f$=0.24 (CH$_2$Cl$_2$/C$_6$H$_{14}$, 1:1, v/v); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$=1.14 (d, $^3$J=10.5 Hz, 1H, CH$_2$CH), 1.31 (dd, $^3$J=11.7 Hz, $^3$J= 10.5 Hz, 1 H, CHCH$_2$CH), 1.46 (m, 2H, C=CH(CH)$_2$CH$_2$), 1.77 (m, 2H, CO(CH)$_2$CH$_2$), 2.42 (s, 1H, COCHCH$_2$), 2.54 (d, $^3$J=5.3 Hz, 1H, COCHCH$_2$), 2.64 (s, 1H, C=CHCHCH$_2$), 2.69 (s, 6H, C$_6$H$_{14}$CH$_3$), 2.87 (d, $^3$J=2.9 Hz, 1H, C=CHCHCH$_2$), 7.53 (d, $^3$J=7.0 Hz, 4H, $H_A$), 7.94 (d,
Chapter 7: Experimental

\[ \text{\( V = 5.9 \text{ Hz, } 4H, H_{\alpha} \), 8.06 (s, 4H, } H_{\alpha} \), 8.81 (d, \( J = 5.9 \text{ Hz, } 2H, H_{\beta} \), 8.83 (d, \( J = 4.7 \text{ Hz, } 2H, H_{\beta} \), 8.95 (d, \( J = 4.7 \text{ Hz, } 2H, H_{\beta} \), 9.16 (d, \( J = 4.7 \text{ Hz, } 2H, H_{\beta} \), 9.86 (s, 1H, \( H_{\text{meso}} \)) ppm; \( ^{13} \text{C NMR (100.6 MHz, CDCl}_3 \)): \( \delta = 21.1, 28.0, 28.8, 31.0, 28.1, 39.2, 45.5, 54.7, 104.1, 118.3, 118.4, 125.0, 127.2, 130.5, 131.5, 131.6, 131.7, 137.2, 133.2, 136.9, 137.5, 140.9, 141.8, 142.3, 142.5, 145.5, 160.4, 208.9 \text{ ppm; IR: } 3024 (\text{Ar-H, } 2943 (\text{CH}_2), 2869 (\text{CH}_3) 1692 (\text{C=O}) \text{ cm}^{-1}; \text{UV/vis (CH}_2\text{Cl}_2): \lambda_{\text{max}} (\lg \varepsilon) = 409 (5.8), 522 (4.9), 550 (4.7) \text{ nm; HRMS (ES+): calcld for C}_{50}\text{H}_{38}\text{N}_4\text{NiO } [M+H]^+ 769.2477, \text{ found 769.2479.}} \]

[5,15-Bis(4-methylphenyl)-10-(4-phenyltricyclo[5.2.1.0^26]deca-4-en-3-onyl)-porphyrinato]zinc(II) 117. By using [5-(4-ethynylphenyl)-10,20-bis(4-methylphenyl)porphyrinato]zinc(II) 115 (40 mg, 0.061 mmol) and norbornene (11 mg, 0.122 mmol) as starting materials, after recrystallisation the product was obtained as pink crystals in 36.7 mg (0.047 mmol, 78 %) yield: mp >300 \text{ °C; } R_t=0.31 (\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}, 1:1, v/v); \text{H NMR (400 MHz, CDCl}_3): \delta = 0.99 (d, \( J = 6.4 \text{ Hz, } 1H, \text{CHCH}_2\text{CH})), 1.14 (d, \( J = 11.1 \text{ Hz, } 1H, \text{CHCH}_2\text{CH})), 1.46 (m, 2H, C=CH(CH)_2CH_2)), 1.78 (m, 2H, CO(CH)_2CH_2)), 2.44 (d, \( J = 2.3 \text{ Hz, } 1H, \text{COCHCHCH}_2)), 2.48 (d, \( J = 5.3 \text{ Hz, } 1H, \text{COCHCHCH}_2)), 2.58 (s, 1H, C=CHCHCHCH_2)), 2.76 (s, 6H, C_6H_5CH_3)), 2.88 (s, 1H, C=CHCHCHCH_2)), 7.61 (d, \( J = 7.6 \text{ Hz, } 4H, H_{\alpha})), 7.98 (d, \( J = 2.9 \text{ Hz, } 1H, C=CH)), 8.07 (d, \( J = 8.2 \text{ Hz, } 2H, H_{\alpha})), 8.15 (d, \( J = 7.6 \text{ Hz, } 4H, H_{\alpha})), 8.25 (d, \( J = 7.6 \text{ Hz, } 2H, H_{\alpha})), 9.01 (d, \( J = 4.7 \text{ Hz, } 2H, H_{\beta})), 9.04 (d, \( J = 4.7 \text{ Hz, } 2H, H_{\beta})), 9.15 (d, \( J = 4.7 \text{ Hz, } 2H, H_{\beta})), 9.43 (d, \( J = 4.7 \text{ Hz, } 2H, H_{\beta})), 10.29 (s, 1H, \( H_{\text{meso}} \)) ppm; \( ^{13} \text{C NMR (150.9 MHz, CDCl}_3): \delta = 21.0, 21.4, 22.5, 23.7, 26.9, 28.4, 34.7, 38.4, 39.5, 47.9, 54.9, 105.7, 120.6, 120.7, 124.9,
Chapter 7: Experimental

125.4, 127.2, 128.1, 130.5, 131.5, 131.7, 131.8, 132.4, 132.5, 134.3, 134.4, 135.6, 136.9, 139.6, 139.7, 142.9, 145.1, 145.9, 148.7, 149.5, 149.8, 150.2, 150.3, 150.4, 160.6, 186.0, 209.2 ppm; IR: 2920 (CH₃), 2852 (CH₃), 1672 (C=O) cm⁻¹; UV/vis (CH₂Cl₂): λmax (log ε)=415 (6.2), 543 (5.1), 582 (4.9) nm; HRMS (ES+): calcd for C₅₀H₃₈N₄OZn [M]+ 774.2337, found 774.2338.

[5,15-Bis(4-methylphenyl)-10-(4-phenyltricyclo[5.2.1.0²⁶]deca-4,8-dien-3-onyl)porphyrinato]nickel(II) 118. By using [5-(4-ethynylphenyl)-10,20-bis(4-methylphenyl)porphyrinato]nickel(II) 114 (50 mg, 0.077 mmol) and norbornadiene (14 mg, 0.154 mmol) as starting materials, after recrystallisation the product was obtained as red crystals in 22.2 mg (0.028 mmol, 38 %) yield: mp >300 °C; Rf=0.21 (CH₂Cl₂/C₆H₁₄, 1:1, v/v); ¹H NMR (400 MHz, CDCl₃): δ=1.56 (d, 3J=1.2 Hz, 2H, CHCH₂CH), 2.64 (d, 3J=5.3 Hz, 2H, COCHCH), 2.69 (s, 6H, C₆H₄CH₃), 2.94 (s, 1H, C=CHCHCH), 3.01 (m, 1H, C=CHCHCH), 3.17 (d, 3J=1.2 Hz, 1H, COCHCH), 6.35 (dd, 3J=5.3 Hz, 3J=2.9 Hz, 1H, CH=CH), 6.43 (dd, 3J=5.3 Hz, 3J=2.9 Hz, 1H, CH=CH), 7.53 (d, 3J=7.6 Hz, 4H, H₅Ar), 7.94 (d, 3J=8.2 Hz, 4H, H₅Ar), 7.99 (d, 3J=2.9 Hz, 1H, C=CH), 8.06 (d, 3J=8.8 Hz, 2H, H₅Ar), 8.06 (d, 3J=8.8 Hz, 2H, H₅Ar), 8.80 (d, 3J=4.7 Hz, 2H, H₆b), 8.83 (d, 3J=4.7 Hz, 2H, H₆b), 9.16 (d, 3J=4.7 Hz, 2H, H₆b), 9.86 (s, 1H, H₆meso) ppm; ¹³C NMR (150.9 MHz, CDCl₃): δ=21.3, 41.4, 43.4, 44.2, 49.3, 53.6, 104.4, 118.6, 125.3, 127.5, 130.9, 131.7, 131.8, 131.9, 132.5, 133.5, 133.7, 137.1, 137.3, 137.9, 138.5, 141.3, 142.1, 142.6, 142.7, 142.8, 146.9, 160.2, 207.8 ppm; IR: 3024 (Ar-H), 2966 (CH₂), 2874 (CH₃), 1693 (C=O) cm⁻¹; UV/vis (CH₂Cl₂): λmax (log ε)=409 (5.7), 523
(4.7), 548 (4.5) nm; HRMS (MALDI LD+): calcd for C_{50}H_{36}N_{4}O_{2}Ni [M]^+ 766.2243, found 766.2251.

4,10-Bis{[5,15-bis(4-methylphenyl)-10-phenylporphyrinato]nickel(II)}tetracyclo[5.2.1.0^{2,6}.0^{8,12}]trideca-4,9-dien-3,11-dione 119. By using [5-(4-ethynylphenyl)-10,20-bis(4-methylphenyl)porphyrinato]nickel(II) 114 (26 mg, 0.039 mmol) and [5,15-bis(4-methylphenyl)-10-(4-phenyltricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-onyl)porphyrinato]nickel(II) 118 (30 mg, 0.039 mmol) as starting materials, the product was obtained as the second fraction of the column chromatography after recrystallisation in 28 mg (0.019 mmol, 50 %) yield as red crystals: mp >300 °C; R_f=0.69 (CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3): δ=1.31 (s, 2H, CHCH_2CH), 2.69 (s, 12H, C_6H_4CH_3), 2.84 (m, 4H, C=CHCHCH=CH=C, CH_2CH), 3.16 (m, 2H, COCHCH=CHCO), 7.54 (d, ^3J=7.6 Hz, 8H, H_\text{Ar}), 7.95 (d, ^3J=8.2 Hz, 8H, H_\text{Ar}), 8.02 (d, ^3J=2.34 Hz, 2H, C=CH), 8.09 (s, 8H, H_\text{Ar}), 8.81 (d, ^3J=5.3 Hz, 4H, H_\beta), 8.84 (d, ^3J=4.7 Hz, 4H, H_\beta), 8.95 (d, ^3J=4.7 Hz, 4H, H_\beta), 9.17 (d, ^3J=4.7 Hz, 4H, H_\beta), 9.86 (s, 2H, H_{\text{meso}}) ppm; ^13C NMR (100.6 MHz, CDCl_3): δ=21.5, 29.7, 41.3, 47.2, 55.1, 104.6, 118.6, 118.8, 125.6, 127.6, 130.4, 131.9, 132.1, 132.2, 132.7, 133.7, 133.9, 137.5, 141.8, 142.2, 142.8, 142.9, 143.0, 146.6, 159.2, 207.8 ppm; IR: 2918 (CH_2), 1699 (C=O) cm^{-1}; UV/vis (CH_2Cl_2): λ_{max} (lg ε)=410 (5.6), 521 (4.9), 551 (4.7) nm; HRMS (MALDI LD+): calcd for C_{93}H_{64}N_{8}O_{2}Ni_{2} [M]^+ 1440.3859, found 1440.3795.
4,10-Bis[[5,15-bis(4-methylphenyl)-10-phenylporphyrinato]nickel(II)]tetracyclo-
[5.2.1.0^2,6.0^8,12]trideca-4,10-dien-3,9-dione 120. The product was obtained as the third
fraction of the reaction above after recrystallisation in 26.5 mg (0.018 mmol, 47 %)
yield as red crystals: mp >300 °C; Rf=0.19 (CH₂Cl₂); ^1H NMR (400 MHz, CDCl₃):
δ=1.22 (s, 2H, CHCH₂CH₂), 2.69 (s, 12H, C₆H₄CH₂), 2.72 (d, ^3J=5.3 Hz, 2H,
CHCH₂CH₂), 3.06 (m, 4H, COCHCH₂), 7.53 (d, ^3J=7.6 Hz, 8H, H₄Ar), 7.89 (d, ^3J=1.8 Hz,
2H, C=CH), 7.95 (d, ^3J=8.2 Hz, 8H, H₄Ar), 8.06 (d, ^3J=8.8 Hz, 4H, H₂Ar), 8.09 (d, ^3J=8.2
Hz, 4H, H₂Ar), 8.81 (d, ^3J=5.3 Hz, 4H, H₂β), 8.85 (d, ^3J=5.3 Hz, 4H, H₂β), 8.95 (d, ^3J=4.7
Hz, 4H, H₂β), 9.17 (d, ^3J=4.7 Hz, 4H, H₂β), 9.86 (s, 2H, Hmeso) ppm; ^13C NMR (100.6
MHz, CDCl₃): δ=21.1, 29.3, 40.5, 41.2, 47.7, 53.5, 104.2, 118.2, 118.3, 125.1, 127.2,
129.9, 131.4, 131.6, 131.8, 132.2, 133.3, 133.5, 137.0, 137.5, 141.3, 141.7, 142.3,
142.4, 142.5, 145.9, 158.4, 206.7 ppm; IR: 3024 (Ar-H), 2919 (CH₂), 2851 (CH₃), 1704
(C=O) cm⁻¹; UV/vis (CH₂Cl₂): λ_max (lg ε)=410 (5.7), 521 (4.9), 548 (4.7) nm; HRMS
7.6 Suzuki Reaction Using Potassium Organotrifluoroborates

7.6.1 Synthesis of Starting Materials

[5-Iodo-10,15,20-tris(4-methylphenyl)porphyrinato]nickel(II) 148. A 100 mL 2-necked round-bottom flask was charged with 5-iodo-10,15,20-tris(4-methylphenyl)porphyrin 147 (50 mg, 0.07 mmol, 1 equiv.) and Ni(acac)₂ (27 mg, 0.11 mmol, 1.5 equiv.) in toluene (50 mL). The reaction mixture was heated to reflux until completion (~3 h, monitored by TLC). The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane and filtered through a layer of silica gel. After recrystallisation from CH₂Cl₂/MeOH (1:3, v/v) the product was obtained as red needles in 43 mg (0.057 mmol, 80 %) yield: mp 236 °C; R_f=0.78 (CH₂Cl₂/C₆H₁₄, 1:1, v/v); ¹H NMR (600 MHz, CDCl₃): δ=2.66 (s, 3H, C₆H₄CH₃), 2.68 (s, 6H, C₆H₄CH₃), 7.50 (t, ³J=7.5 Hz, 6H, H₁₄), 7.88 (d, ³J=7.3 Hz, 6H, H₁₄), 8.71 (d, ³J=4.4 Hz, 2H, H₉), 8.73 (d, ³J=5.1 Hz, 2H, H₉), 8.79 (d, ³J=4.4 Hz, 2H, H₉), 9.51 (d, ³J=5.1 Hz, 2H, H₈), ppm; ¹³C NMR (150.9 MHz, CDCl₃): δ=21.4, 119.5, 127.6, 132.5, 132.6, 133.4, 133.5, 133.6, 137.5, 137.6, 137.7, 141.9, 142.9, 143.0, 143.5, 144.4 ppm; UV/vis (CH₂Cl₂): λ_max (lg ε)=421 (5.8), 535 (4.9) nm; HRMS (ES+): calcd for C₄₁H₅₉N₄Ni [M+H]^+ 763.0849, found 763.0895.
7.6.2 Suzuki Products

**General procedure:** A 20 mL Schlenk-tube was put under argon and charged with porphyrin (60, 67, 69, 97, 148) (1 equiv.) and Cs₂CO₃ (20 equiv.) in THF/H₂O (10:1, v/v). The solution was degassed via three freeze-pump-thaw cycles and put under argon again. Potassium organotrifluoroborate (10 equiv.) and Pd(dppf)Cl₂ (0.25 equiv.) were added and the reaction mixture was heated to 80 °C for 18 h. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane. The crude product was washed with a saturated solution of sodium bicarbonate, water and brine. The organic phase was dried over magnesium sulfate and the crude product was purified by column chromatography on silica (CH₂Cl₂/n-hexane, 1:1, v/v).

![Porphyrin structure](image)

5,10,15-Tris(4-methylphenyl)-20-pentylporphyrin 149. By using 5-bromo-10,15,20-tris(4-methylphenyl)porphyrin 67 (30 mg, 0.045 mmol), Cs₂CO₃ (318 mg, 0.9 mmol), Pd(dppf)Cl₂ (8 mg, 0.01125 mmol) and potassium n-pentyltrifluoroborate (80 mg, 0.45 mmol) the product was obtained as purple crystals in 6.2 mg (0.01 mmol, 21%) yield: mp >300 °C; Rₚ=0.52 (CH₂Cl₂/C₆H₁₄, 1:1, v/v); ¹H NMR (600 MHz, CDCl₃): δ=-2.68 (s, br, 2H, NH), 1.00 (t, ³J=7.3 Hz, 3H, (CH₂)₄CH₃), 1.59 (t, ³J=7.7 Hz, 2H, (CH₂)₃CH₂CH₃), 1.83 (t, ³J=7.7 Hz, 2H, (CH₂)₂CH₂CH₂CH₃), 2.59 (t, ³J=7.3 Hz, 2H, CH₂CH₂(CH₂)₂CH₃), 2.73 (s, 3H, C₆H₄CH₃), 2.75 (s, 6H, C₆H₄CH₃), 5.05 (t, ³J=8.1 Hz, 2H, CH₂CH₃(CH₂)₂CH₃), 7.57 (d, ³J=7.3 Hz, 2H, HA), 7.59 (d, ³J=7.3 Hz, 4H, HA), 8.10 (d, ³J=8.1 Hz, 2H, HA), 8.12 (d, ³J=7.3 Hz, 4H, HA), 8.83 (s, 4H, Hβ), 8.96 (d, ³J=4.4 Hz, 2H, Hβ), 9.50 (d, ³J=5.1 Hz, 2H, Hβ) ppm; ¹³C NMR (150.9 MHz, CDCl₃):
δ=14.0, 21.4, 22.6, 32.6, 35.4, 38.4, 119.2, 119.4, 120.2, 127.2, 127.3, 131.1, 134.3, 134.3, 137.1, 139.1, 139.4 ppm; IR: 3311 (NH), 3027 (Ar-H), 2951 (CH₂), 2919 (CH₂), 2855 (CH₃) cm⁻¹; UV-vis (CH₂Cl₂): λ_{max} (lg ε)=419 (5.7), 517 (4.6), 553 (4.5), 593 (4.4), 649 (4.4) nm; HRMS (ES+): calcd for C₄₆H₄₃N₄ [M+H]^+ 651.3488, found 651.3495.

5-Methyl-10,15,20-tris(4-methylphenyl)porphyrin 150. By using 5-bromo-10,15,20-tris(4-methylphenyl)porphyrin 67 (30 mg, 0.045 mmol), Cs₂CO₃ (318 mg, 0.9 mmol), Pd(dppf)Cl₂ (8 mg, 0.01125 mmol) and potassium methyltrifluoroborate (55 mg, 0.45 mmol) the product was obtained as purple crystals in 7.8 mg (0.013 mmol, 29 %) yield: mp >300 °C; R_f=0.43 (CH₂Cl₂/C₆H₁₄, 1:1, v/v); 'H NMR (400 MHz, CDCl₃): δ=−2.63 (s, br, 2H, NH), 2.72 (s, 3H, C₆H₄CH₃), 2.75 (s, 6H, C₆H₄CH₃), 4.71 (s, 3H, CH₃), 7.57 (d, 3J=8.0 Hz, 2H, HA), 7.59 (d, 3J=7.8 Hz, 4H, HA), 8.10 (d, 3J=7.5 Hz, 2H, HA), 8.12 (d, 3J=7.8 Hz, 4H, HA), 8.84 (s, 4H, Hβ), 8.96 (d, 3J=4.8 Hz, 2H, Hβ), 9.53 (d, 3J=4.8 Hz, 2H, Hβ) ppm; C NMR (100.6 MHz, CDCl₃): δ=21.1, 21.6, 114.6, 119.3, 119.7, 127.4, 127.5, 130.8 (br.), 131.4 (br.), 134.5, 137.2, 137.3, 139.2, 139.5 ppm; IR: 3316 (NH), 3023 (Ar-H), 2917 (CH₃), 2855 (CH₃) cm⁻¹; UV-vis (CH₂Cl₂): λ_{max} (lg ε)=419 (5.6), 517 (4.5), 552 (4.4), 593 (4.4), 651 (4.4) nm; HRMS (ES+): calcd for C₄₂H₃₅N₄ [M+H]^+ 595.2862, found 595.2843.
5-Cyanoethyl-10,15,20-tris(4-methylphenyl)porphyrin 151. By using 5-bromo-10,15,20-tris(4-methylphenyl)porphyrin 67 (30 mg, 0.045 mmol), Cs₂CO₃ (318 mg, 0.9 mmol), Pd(dppf)Cl₂ (8 mg, 0.01125 mmol) and potassium 2-cyanoethyltrifluoroborate (73 mg, 0.45 mmol) the product was obtained as purple crystals in 21.1 mg (0.033 mmol, 73%) yield: mp >300 °C; Rᵣ=0.58 (CH₂Cl₂/C₆H₁₄, 1:1, v/v); ¹H NMR (600 MHz, CDCl₃): δ=−2.75 (s, br, 2H, NH), 2.72 (s, 3H, C₆H₄CH₃), 2.76 (s, 6H, C₆H₃CH₂), 3.56 (t, ²J=8.1 Hz, 2H, CH₂CH₂CN), 5.46 (t, ³J=8.1 Hz, 2H, CH₂CH₂CN), 7.58 (d, ²J=8.1 Hz, 2H, H₉₈), 7.60 (d, ²J=7.3 Hz, 4H, H₁₀₂₄), 8.09 (d, ³J=7.3 Hz, 2H, H₉₈), 8.11 (d, ³J=8.1 Hz, 4H, H₁₀₂₄), 8.85 (s, 4H, H₁₀₂₄), 9.03 (d, ³J=5.1 Hz, 2H, H₀₈), 9.46 (d, ²J=4.4 Hz, 2H, H₀₈) ppm; ¹³C NMR (150.9 MHz, CDCl₃): δ=21.4, 23.9, 31.0, 113.2, 118.9, 120.1, 120.5, 127.2, 127.3, 134.3, 137.3, 137.4, 138.8, 139.0 ppm; IR: 3316 (NH), 3023 (Ar-H), 2915 (CH₂), 2244 (C≡N) cm⁻¹; UV-vis (CH₂Cl₂): λ_max (log ε)=419 (5.7), 516 (4.6), 551 (4.5), 592 (4.5), 648 (4.4) nm; HRMS (ES⁺): calcd for C₄₄H₃₆N₅ [M+H]⁺ 634.2971, found 634.3000.
5,10,15-Tris(4-methylphenyl)-20-methylpyrrolidylporphyrin 152. By using 5-bromo-10,15,20-tris(4-methylphenyl)porphyrin 67 (30 mg, 0.045 mmol), Cs₂CO₃ (318 mg, 0.9 mmol), Pd(dpdpf)Cl₂ (8 mg, 0.01125 mmol) and potassium 1-trifluoroboratomethylpyrrolidine (86 mg, 0.45 mmol) the product was obtained as purple crystals in 7.9 mg (0.012 mmol, 26%) yield: mp >300 °C; Rf=0.26 (ethyl acetate); ¹H NMR (400 MHz, CDCl₃): δ=2.77 (s, br, 2H, NH), 1.82 (s, br, 4H, NCH₂(CH₂)₂), 2.72 (s, 3H, C₆H₄CH₃), 2.75 (s, 6H, C₆H₄CH₃), 2.94 (s, br, 4H, NCH₂(CH₂)₂CH₂), 6.00 (s, br, 2H, CH₂N), 7.57 (d, ³J=5.9 Hz, 2H, Hₘ), 7.59 (d, ³J=6.9 Hz, 4H, Hₘ), 8.10 (d, ³J=4.9 Hz, 2H, Hₘ), 8.12 (d, ³J=7.8 Hz, 4H, Hₘ), 8.85 (d, ³J=2.9 Hz, 4H, Hₘ), 8.98 (d, ³J=4.9 Hz, 2H, Hₘ), 9.69 (d, ³J=3.9 Hz, 2H, Hₘ) ppm; ¹³C NMR (100.6 MHz, CDCl₃): δ=21.1, 23.1, 29.3, 53.8, 53.9, 126.9, 127.0, 130.4, 131.3, 133.9, 134.0, 136.9, 138.6, 139.0 ppm; IR: 3312 (NH), 3021 (Ar-H), 2919 (CH₃), 2853 (CH₃), 1669 (CH₂N) cm⁻¹; UV-vis (CH₂Cl₂): λₘₐₓ (lg ε)=421 (5.4), 519 (4.3), 554 (4.2), 594 (4.2), 651 (4.1) nm; HRMS (ES+): calcd for C₄₆H₄₂N₅ [M+H]⁺ 664.3461, found 664.3440.
5-Methylproprionatyl-10,15,20-tris(4-methylphenyl)porphyrin 153. By using 5-bromo-10,15,20-tris(4-methylphenyl)porphyrin 67 (30 mg, 0.045 mmol), Cs$_2$CO$_3$ (318 mg, 0.9 mmol), Pd(dpdpf)Cl$_2$ (8 mg, 0.01125 mmol) and potassium 3-trifluoroboratopropionate methyl ester (175 mg, 0.9 mmol, 20 equiv.) the product was obtained as purple crystals in 4.9 mg (0.007 mmol, 16%) yield: mp >300 °C; $R_f$=0.28 (CH$_2$Cl$_2$/C$_6$H$_{14}$, 1:1, v/v); $^1$H NMR (600 MHz, CDCl$_3$): δ=-2.72 (s, br, 2H, NH), 2.73 (s, 3H, C$_6$H$_4$CH$_3$), 2.75 (s, 6H, C$_6$H$_4$CH$_3$), 3.59 (t, $^3$J=8.4 Hz, 2H, CH$_2$CH$_2$OCH$_3$), 3.80 (s, 3H, CH$_2$CH$_2$OCH$_3$), 5.42 (t, $^3$J=8.4 Hz, 2H, CH$_2$CH$_2$OCH$_3$), 7.57 (d, $^3$J=8.1 Hz, 2H, $H_{Ar}$), 7.59 (d, $^3$J=7.3 Hz, 4H, $H_{Ar}$), 8.09 (d, $^3$J=8.8 Hz, 2H, $H_{Ar}$), 8.11 (d, $^3$J=7.3 Hz, 4H, $H_{Ar}$), 8.84 (s, 4H, $H_{p}$), 8.98 (d, $^3$J=4.4 Hz, 2H, $H_{p}$), 9.53 (d, $^3$J=4.4 Hz, 2H, $H_{p}$) ppm; $^{13}$C NMR (150.9 MHz, CDCl$_3$): δ=21.4, 30.5, 41.7, 51.7, 116.6, 119.7, 119.8, 127.2, 127.3, 13.08, 131.7, 134.3, 137.2, 139.0, 139.2, 173.1 ppm; IR: 3310 (NH), 3026 (Ar-H), 2918 (CH$_2$), 2850 (CH$_3$), 1731 (C=O) cm$^{-1}$; UV-vis (CH$_2$Cl$_2$): $\lambda_{max}$ (lg $e$)=419 (5.6), 516 (4.5), 552 (4.3), 593 (4.2), 651 (4.2) nm; HRMS (ES+): calcd for C$_{45}$H$_{39}$N$_4$O$_2$ [M+H]$^+$ 667.3073, found 667.3093.
5,10,15-Tris(4-methylphenyl)-20-morpholinopropanolylporphyrin 154. By using
5-bromo-10,15,20-tris(4-methylphenyl)porphyrin 67 (30 mg, 0.045 mmol), Cs₂CO₃
(318 mg, 0.9 mmol), Pd(dppe)Cl₂ (8 mg, 0.01125 mmol) and potassium
3-morpholino-3-oxopropyl trifluoroborate (112 mg, 0.45 mmol) the product was
obtained as purple crystals in 6.7 mg (0.009 mmol, 21%) yield: mp 273 °C;
Rₑ=0.69 (ethyl acetate); ¹H NMR (600 MHz, CDCl₃): δ=—2.70 (s, br, 2H, NH), 2.73 (m,
5H, C₆H₄CH₃, CH₂O), 2.76 (s, 6H, C₆H₄CH₃), 2.91 (t, ³J=4.4 Hz, 2H, NCH₂), 3.47 (t,
³J=4.8 Hz, 2H, OCH₂), 3.57 (t, ³J=8.1 Hz, 2H, CH₂CH₂CO), 3.66 (t, ³J=4.4 Hz, 2H,
CH₂N), 5.47 (t, ³J=9.2 Hz, 2H, CH₂CH₂CO), 7.58 (d, ³J=8.8 Hz, 2H, H₆), 7.60 (d,
³J=7.3 Hz, 4H, H₆, H₆), 8.10 (d, ³J=4.4 Hz, 2H, H₆, H₆), 8.11 (d, ³J=8.1 Hz, 4H, H₆, H₆), 8.85 (s,
4H, H₆), 8.99 (d, ³J=4.4 Hz, 2H, H₆), 9.53 (d, ³J=4.4 Hz, 2H, H₆) ppm; ¹³C NMR (150.9
MHz, CDCl₃): δ=21.5, 30.9, 40.7, 41.9, 45.7, 65.8, 66.5, 117.5, 119.8, 119.9, 127.4,
127.5, 131.0, 131.8, 134.0, 134.4, 134.5, 137.3, 137.4, 139.1, 139.3, 170.8 ppm; IR:
3313 (NH), 3023 (Ar-H), 2917 (CH₂), 1637 (C=O) cm⁻¹; UV-vis (CH₂Cl₂): λₘₐₓ
( lg ε)=419 (5.5), 518 (4.5), 552 (4.4), 592 (4.4), 647 (4.4) nm; HRMS (ES+): calcd for
C₄₈H₄₄N₅O₂ [M+H]⁺ 722.3495, found 722.3404.
5-(N,N-Dimethyluracil)-10,15,20-tris(4-methylphenyl)porphyrin 155. By using 5-bromo-10,15,20-tris(4-methylphenyl)porphyrin 67 (30 mg, 0.045 mmol), Cs₂CO₃ (318 mg, 0.9 mmol), Pd(dppf)Cl₂ (8 mg, 0.01125 mmol) and potassium 1,3-dimethyluracil-5-trifluoroborate (111 mg, 0.45 mmol) the product was obtained as purple crystals in 24.2 mg (0.034 mmol, 75%) yield: mp >300 °C; Rf=0.23 (ethyl acetate/C₆H₄, 1:2, v/v); ¹H NMR (600 MHz, CDCl₃): δ=−2.73 (s, br, 2H, NH), 2.73 (s, 3H, C₆H₄), 2.74 (s, 6H, C₆H₄CH₃), 3.72 (s, 3H, NCH₂CH₂), 3.75 (s, 3H, CONCH₂CO), 7.59 (m, 6H, H₆), 8.00 (s, 1H, CH), 8.12 (m, 6H, H₆), 8.87 (d, 3J=3.7 Hz, 4H, H₆), 8.94 (d, 3J=3.7 Hz, 2H, H₆), 9.06 (d, 3J=4.4 Hz, 2H, H₆) ppm; ¹³C NMR (150.9 MHz, CDCl₃): δ=21.4, 28.6, 37.3, 107.8, 115.2, 120.3, 121.1, 127.2, 127.3, 127.4, 128.2, 128.3, 129.7, 131.9, 134.3, 134.4, 137.3, 138.9, 139.0, 145.2, 152.2, 164.1, 206.7 ppm; IR: 3312 (NH), 3025 (Ar-H), 2919 (CH₃), 2851 (CH₃), 2705 (NCH₃), 1710 (C=O), 1648 (C=O) cm⁻¹; UV-vis (CH₂Cl₂): λₘₐₓ (lg ε)=420 (5.8), 516 (4.6), 551 (4.4), 591 (4.3), 648 (4.3) nm; HRMS (ES+): calcd for C₄₇H₃₉N₆O₂ [M+H]⁺ 719.3126, found 719.3134.
5-Cyanoethyl-10,15,20-trihexylporphyrin 156. By using 5-bromo-10,15,20-trihexylporphyrin 97 (30 mg, 0.047 mmol), Cs₂CO₃ (318 mg, 0.9 mmol), Pd(dppf)Cl₂ (9 mg, 0.01175 mmol) and potassium 2-cyanoethyltrifluoroborate (76 mg, 0.47 mmol) the product was obtained as purple crystals in 7.1 mg (0.0115 mmol, 25%) yield: mp 117 °C; Rf=0.18 (CH₂Cl₂/C₆H₁₄, 1:1, v/v); ¹H NMR (400 MHz, CDCl₃): δ=−2.73 (s, br, 2H, NH), 0.99 (t, ³J=7.3 Hz, 9H, CH₃), 1.45 (m, 6H, (CH₂)₄CH₂CH₃), 1.55 (m, 6H, (CH₂)₃CH₂CH₂CH₃), 1.84 (m, 6H, (CH₂)₂CH₂(CH₂)₂CH₃), 2.53 (m, 6H, CH₂CH₂(CH₂)₂CH₃), 3.47 (t, ³J=8.8 Hz, 2H, CH₂CH₂CN), 4.94 (m, 6H, CH₂(CH₂)₃CH₃), 5.32 (t, ³J=8.8 Hz, 2H, CH₂CH₂CN), 9.39 (d, ³J=4.8 Hz, 2H, H₆), 9.49 (d, ³J=4.8 Hz, 4H, H₆), 9.53 (d, ³J=5.0 Hz, 2H, H₆) ppm; ¹³C NMR (100.6 MHz, CDCl₃): δ=13.7, 22.3, 23.4, 29.3, 30.7, 31.5, 35.2, 38.4, 110.9, 117.4, 118.8, 119.5, 126.5 (br.), 128.4, 129.3 (br.), 130.5 ppm; IR: 3315 (NH), 2951 (CH₂), 2919 (CH₂), 2850 (CH₃), 2245 (C≡N) cm⁻¹; UV-vis (CH₂Cl₂): λₑₘₚ₅ (lg ε)=418 (5.6), 518 (4.5), 554 (4.4), 600 (4.3), 656 (4.3) nm; HRMS (ES+): calcd for C₄₁H₅₄N₅ [M+H]^⁺ 616.4379, found 616.4367.
2-Cyanoethyl-5,10,15,20-tetraphenylporphyrin 157. By using 2-bromo-5,10,15,20-tetraphenylporphyrin 69 (30 mg, 0.043 mmol), Cs$_2$CO$_3$ (318 mg, 0.9 mmol), Pd(dppf)Cl$_2$ (8 mg, 0.01125 mmol) and potassium 2-cyanoethyltrifluoroborate (70 mg, 0.43 mmol) the product was obtained as purple crystals in 20.2 mg (0.03 mmol, 70%) yield: mp 123 °C; R$_f$=0.22 (CH$_2$Cl$_2$/C$_6$H$_{14}$, 1:1, v/v); $^1$H NMR (400 MHz, CDCl$_3$): δ=−2.75 (s, br, 2H, NH), 2.78 (t, $^3$J=7.3 Hz, 2H, CH$_2$CH$_2$CN), 3.22 (t, $^3$J=7.6 Hz, 2H, CH$_2$CH$_2$CN), 7.79 (m, 12H, $H_{Ar}$), 8.15 (d, $^3$J=7.0 Hz, 2H, $H_{Ar}$), 8.24 (m, 6H, $H_{Ar}$), 8.68 (d, $^3$J=4.7 Hz, 1H, $H_{β}$), 8.71 (s, 1H, $H_{β}$), 8.81 (d, $^3$J=4.7 Hz, 1H, $H_{β}$), 8.83 (d, $^3$J=4.7 Hz, 1H, $H_{β}$), 8.87 (m, 3H, $H_{β}$) ppm; $^{13}$C NMR (100.6 MHz, CDCl$_3$): δ=18.6, 25.8, 118.8, 118.9, 119.8, 120.2, 126.2, 126.26, 126.3, 126.85, 127.3, 127.4, 128.3, 130.4, 130.8, 132.8, 134.0, 134.1, 134.2, 141.3, 141.7, 141.9, 167.3 ppm; IR: 3305 (NH), 3053 (Ar-H), 2954 (CH$_2$), 2919 (CH$_2$), 2245 (C≡N) cm$^{-1}$; UV-vis (CH$_2$Cl$_2$): λ$_{max}$ (lg ε)=419 (5.4), 516 (4.2), 551 (4.0), 591 (3.9), 648 (3.9) nm; HRMS (ES+): calcd for C$_{47}$H$_{34}$N$_5$ [M+H]$^+$ 668.2814, found 668.2836.
5,15-Dicyanoethyl-10,20-bis(4-methylphenyl)porphyrin 158. By using 5,15-dibromo-10,20-bis(4-methylphenyl)porphyrin 60 (30 mg, 0.046 mmol), Cs₂CO₃ (649 mg, 1.8 mmol, 40 equiv.), Pd(dppf)Cl₂ (8 mg, 0.0115 mmol) and potassium 2-cyanoethyltrifluoroborate (149 mg, 0.9 mmol, 20 equiv.) the product was obtained as purple crystals in 9.4 mg (0.016 mmol, 35%) yield: mp >300 °C; Rᵣ=0.22 (CH₂Cl₂/C₆H₁₄, 2:1, v/v); ¹H NMR (400 MHz, CDCl₃): δ = -2.80 (s, br, 2H, NH), 2.77 (s, 6H, C₆H₄CH₃), 3.56 (t, 3J=7.9 Hz, 4H, CH₂CH₂CN), 5.41 (t, 3J=7.9 Hz, 4H, CH₂CH₂CN), 7.61 (d, 3J=7.6 Hz, 4H, Hν), 8.09 (d, 3J=7.6 Hz, 4H, Hν), 9.00 (d, 3J=4.7 Hz, 4H, Hβ), 9.43 (d, 3J=5.3 Hz, 4H, Hβ) ppm; ¹³C NMR (100.6 MHz, CDCl₃): δ=21.1, 23.6, 30.5, 113.6, 118.6, 120.0, 127.0, 132.2, 133.0, 134.0, 137.3, 138.5 ppm; IR: 3324 (NH), 3971 (CH₂), 3916 (CH₂), 2244 (C≡N) cm⁻¹; UV-vis (CH₂Cl₂): λ_max (lg ε)=418 (5.6), 516 (4.4), 551 (4.4), 594 (4.4), 650 (4.4) nm; HRMS (ES+): calcd for C₄₀H₃₃N₆ [M+H]^+ 597.2759, found 597.2767.
5,5'-Bis{(10,15,20-tris(4-methylphenyl)porphyrinato)nickel(II)} 159. By using [5-iodo-10,15,20-tris(4-methylphenyl)porphyrinato]nickel(II) 148 (30 mg, 0.039 mmol), Cs₂CO₃ (275 mg, 0.8 mmol), Pd(dppf)Cl₂ (7 mg, 0.01 mmol) and potassium bromomethyltrifluoroborate (70 mg, 0.39 mmol) the product was obtained as red crystals in 4.9 mg (0.0039 mmol, 10%) yield: mp > 300 °C; Rₛ=0.45 (CH₂Cl₂/C₆H₁₄, 1:2, v/v); ¹H NMR (400 MHz, CDCl₃): δ=2.60 (s, 12H, C₆H₄CH₃), 2.70 (s, 6H, C₆H₄CH₃), 7.44 (d, 3=8.2 Hz, 8H, H₆), 7.55 (d, 3=7.6 Hz, 4H, H₆), 7.92 (d, 3=7.6 Hz, 8H, H₆), 7.99 (d, 3=7.6 Hz, 4H, H₆), 8.08 (d, 3=5.3 Hz, 4H, H₆), 8.57 (d, 3=5.3 Hz, 4H, H₆), 8.82 (d, 3=5.3 Hz, 4H, H₆), 8.85 (d, 3=4.7 Hz, 4H, H₆) ppm; ¹³C NMR (100.6 MHz, CDCl₃): δ=21.0, 21.1, 119.3, 127.1, 127.2, 131.5, 131.8, 131.9, 133.1, 133.2, 133.5, 136.9, 137.0, 137.4, 137.6, 141.9, 142.2, 142.8, 146.2 ppm; IR: 2917 (CH₃) cm⁻¹; UV-vis (CH₂Cl₂): λₘₐₓ (lg ε)=418 (5.7), 447 (5.8), 537 (5.2), 571 (3.7) nm; HRMS (MALDI LD+): calcd for C₈₂H₅₈N₈Ni₂ [M⁺] 1270.349, found 1270.351.
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