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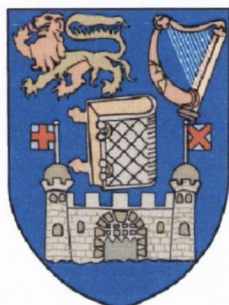
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Development and Investigation of Novel Transition Metal Mediated Reactions in Porphyrin Chemistry



Submitted by

Sabine Horn

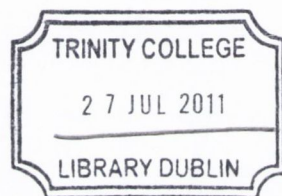
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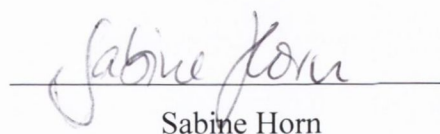


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Sabine Horn

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 medically 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 β -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(I) catalysed alkylation reaction was investigated as a new pathway towards alkylporphyrins. This included the *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(I) 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 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 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

Sabine Horn, Bob Cundell and Mathias O. Senge, "Exploration of the reaction of potassium organotrifluoroborates with porphyrins" *Tetrahedron Lett.* **2009**, 50, 2562–2565.

Sabine Horn, Katja Dahms and Mathias O. Senge, "Synthetic transformations of porphyrins – Advances 2004–2007" *J. Porphyrins Phthalocyanines* **2008**, 12, 1053–1077.

Cover Picture: Sabine Horn and Mathias O. Senge, "The Intermolecular Pauson-Khand Reaction of meso-Substituted Porphyrins" *Eur. J. Org Chem.* **2008**, 29, 4835.

Sabine Horn and Mathias O. Senge, "The Intermolecular Pauson-Khand Reaction of meso-Substituted Porphyrins" *Eur. J. Org Chem.* **2008**, 29, 4881–4890.

Sabine Horn, Natalia N. Sergeeva and Mathias O. Senge, "Conversion of Ni(II)-Allylporphyrins to α,β -unsaturated Formylporphyrins via a Nickel Promoted Reaction" *J. Org. Chem.* **2007**, 72, 5414–5417.

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 "The Pauson-Khand Reaction of Porphyrins" Tetrapyrrole Discussion Group Meeting, Dublin, Ireland, 12th – 14th Sep **2008**.

Sabine Horn and Mathias O. Senge "The Pauson-Khand Reaction of Porphyrins" 23rd International Conference on Organometallic Chemistry, Rennes, France, 13th – 18th Jul **2008**.

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

Katja Dahms, Eimear M. Finnigan, Sabine Horn, Natalia N. Sergeeva and Mathias O. Senge "Organometallic Reactions in Tetrapyrrole Chemistry" CSCB Symposium, Dublin, Ireland, 15th Dec **2006**.

Sabine Horn, Natalia N. Sergeeva and Mathias O. Senge "Suzuki cross-coupling reactions in tetrapyrrole chemistry", Fourth International Conference on Porphyrins and Phthalocyanines, Rome, Italy, 2th – 7th Jul **2006**.

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 <i>via</i> 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 ^1H 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
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Abbreviations

acac	acetylacetonate
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	<i>N,N</i> -dimethylformamide
dppf	1,1'-bis(diphenylphosphino)ferrocene
dtbbpy	4,4'-di- <i>tert</i> -butyl-2,2'-bispyridyl
equiv	equivalents
ES	electrospray
FT	Fourier transformations
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

MW	microwave
NBA	<i>N</i> -bromoacetamide
NBS	<i>N</i> -bromosuccinimide
NLO	non-linear optics
NMR	nuclear magnetic resonance
NOESY	nuclear Oberhauser effect spectroscopy
OAc	acetate
OEP	2,3,7,8,12,13,17,18-octaethylporphyrin
OTf	triflate
PDT	photodynamic therapy
Ph	phenyl
ppm	parts per million
q	quartet
R _f	retention factor
rt	room temperature
s	singlet
sep	septet
t	triplet
td	triplet of doublets
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TLC	thin-layer chromatography
TMS	trimethylsilane
TOF	time of flight
TPP	5,10,15,20-tetraphenylporphyrin
TPPTS	sodium triphenylphosphine trisulphonate
UV	ultraviolet
v/v	volume to volume
vis	visible

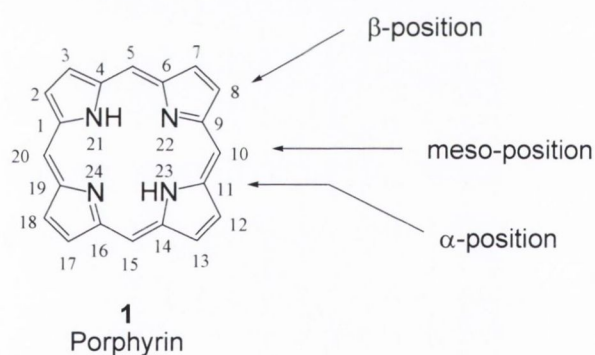
Chapter 1:

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).¹

The first porphyrin synthesis was published by Fischer in 1926,² confirming the aromatic macrocyclic structure initially proposed by Küster in 1913.³ 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 ($4n+2$).^{4,5} In free-base porphyrins two opposite β - β' carbon bonds possess more double bond character.⁶ 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).^{7,8} 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.⁹ The four inner nitrogen atoms (21–24) can form complexes with a wide variety of metal ions.¹⁰

Figure 1.1. IUPAC-nomenclature and designation of atoms.

Porphyrin **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.

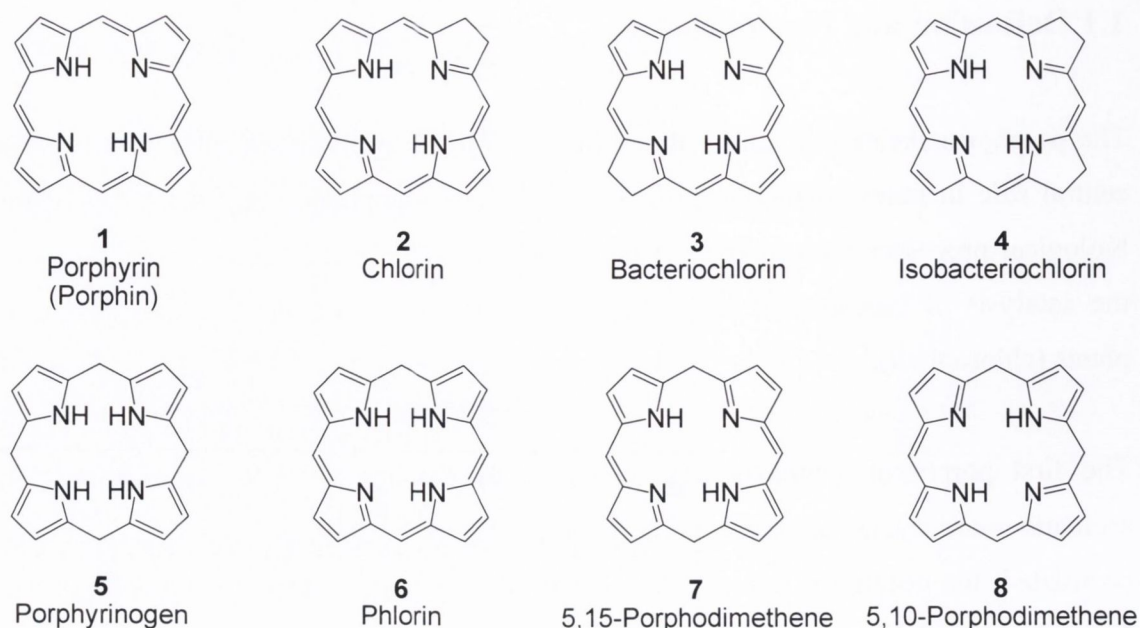


Figure 1.2. Tetrapyrrole classes.

1.2 Synthetic Considerations

Porphyrins substituted at the β -position occur in nature whereas meso-substitution is completely synthetic.¹¹ 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).¹²

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.^{13,14} 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.¹⁵ 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.¹³ In contrast, the synthesis of symmetrical meso-tetrasubstituted porphyrins, the so-called A₄-type (Figure 1.3), is easily accomplished in good yields.¹¹ The availability of diverse aldehydes leads to a wide range of various A₄-porphyrins.

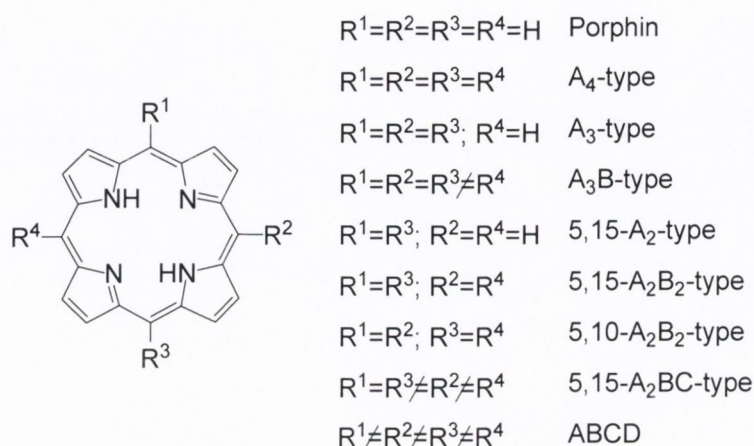
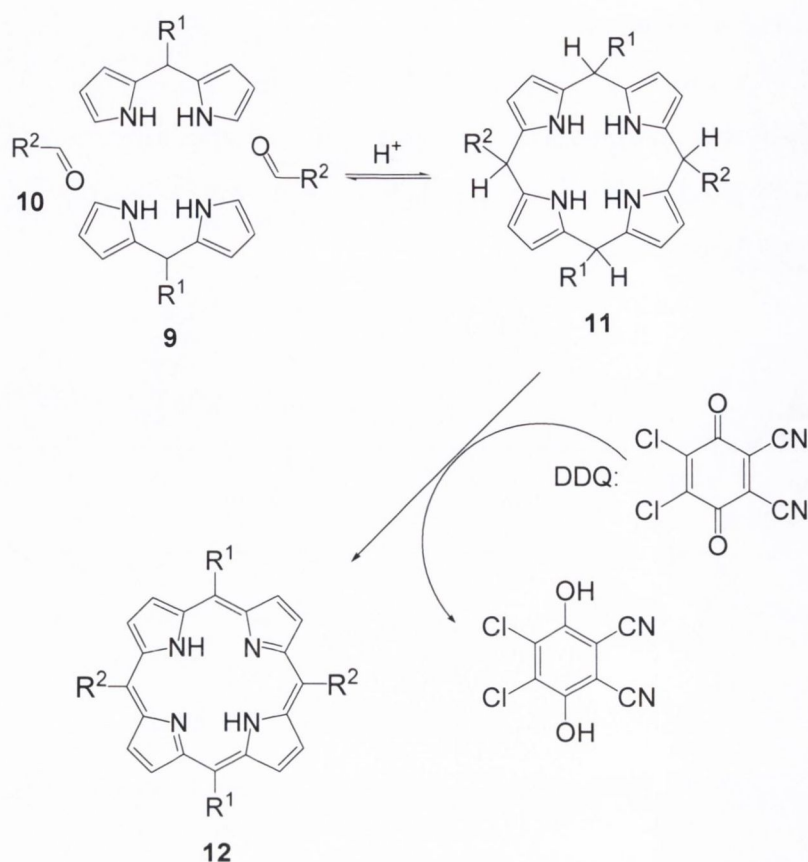


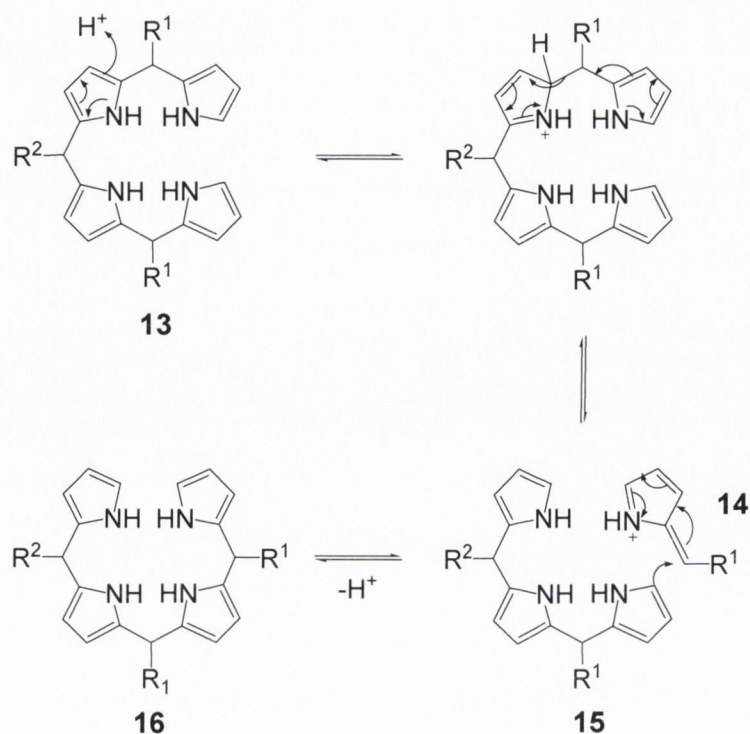
Figure 1.3. Examples for meso-substitution patterns using “ABCD”-nomenclature introduced by Lindsey.¹¹

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).¹⁶ 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**.



Scheme 1.1. MacDonald-type [2+2]-condensation reaction.

Unfortunately, this method can also produce by-products caused by scrambling.¹⁷ Under the given acidic conditions the bilane **13**, formed during the reaction, fragments into the pyrrole derivative **14** and a tripyrrane component **15** (Scheme 1.2). The recombination of **14** and **15** can lead to the formation of a different bilane **16**, resulting in a restructured substitution pattern of the porphyrin. Nevertheless, this [2+2]-condensation represents a reliable method for 5,15- A_2B_2 - and 5,15- A_2 -porphyrins in good yields and purity with the use of reaction conditions that minimises those exchange processes.¹⁸



Scheme 1.2. Mechanism of the scrambling process.

5,15- A_2 -porphyrins can be utilised in the synthesis of A_3B - and A_2BC -porphyrins. Various and different functional groups can be introduced stepwise into the free meso-positions using organolithium reagents,¹⁹ while halogenation allows the introduction of further functional groups, for instance *via* transition metal catalysed C-C cross-coupling reactions.²⁰

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.²¹ 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.²¹ Bulky groups for instance shield the reaction sites at the adjacent positions. Substituents with an electron-donating effect (alkyl, CO_2^- , O^-) tend to increase the electron density of the macrocycle and therefore make it more susceptible to electrophilic attacks. In contrast

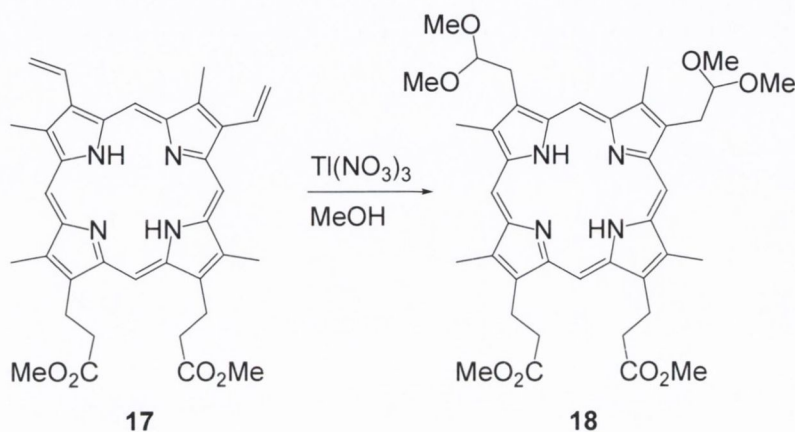
electron-withdrawing groups (aryl, CHO, NO₂) tend to decrease the electron density of the macrocycle. However, some substituents, such as aryl and vinyl, can occasionally be electron-donating by resonance when the porphyrin conformation allows overlap of the p-orbitals and an interaction of the two π -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.^{22,23} 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.

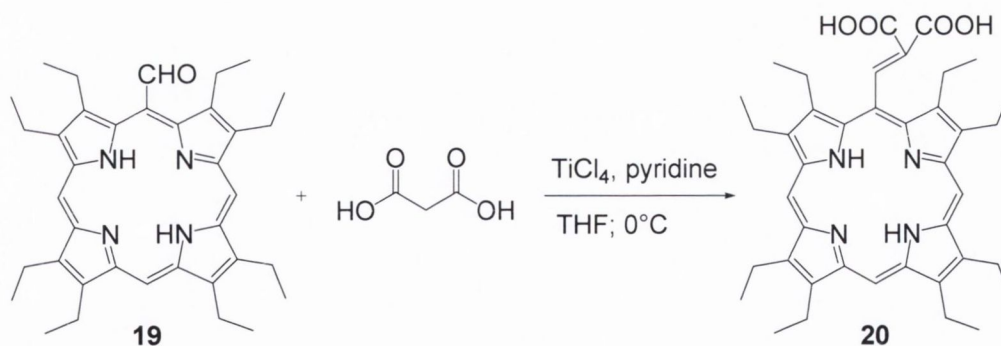
1.3.1 Transformation Reactions

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



Scheme 1.3. Transformation of vinyl-substituents into bis-acetals using thallium(III) nitrate.

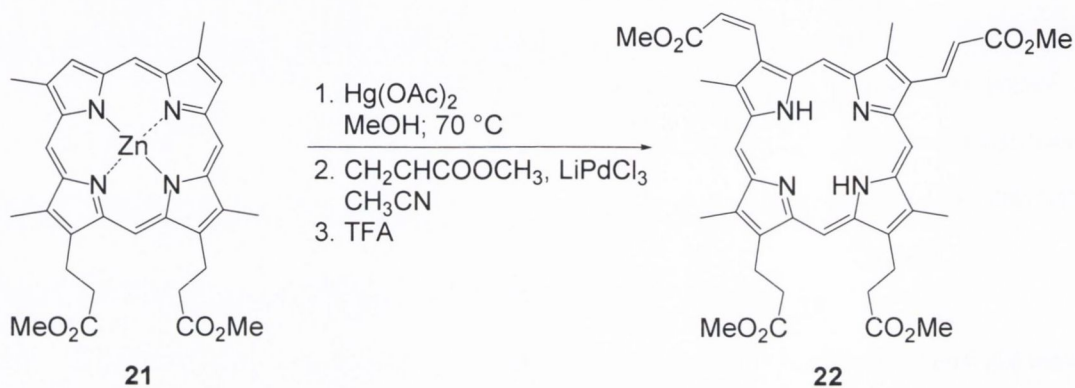
Titanium tetrachloride was used as a catalyst for the Knoevenagel condensation by Witte and Fuhrhop.²⁵ The formyl group of 5-formyl-OEP **19** was reacted with malonic acid to give the 2,2-dicarboxyvinyl analogue **20** in 68 % yield (Scheme 1.4).



Scheme 1.4. Variant of Knoevenagel condensation with titanium tetrachloride as catalyst.

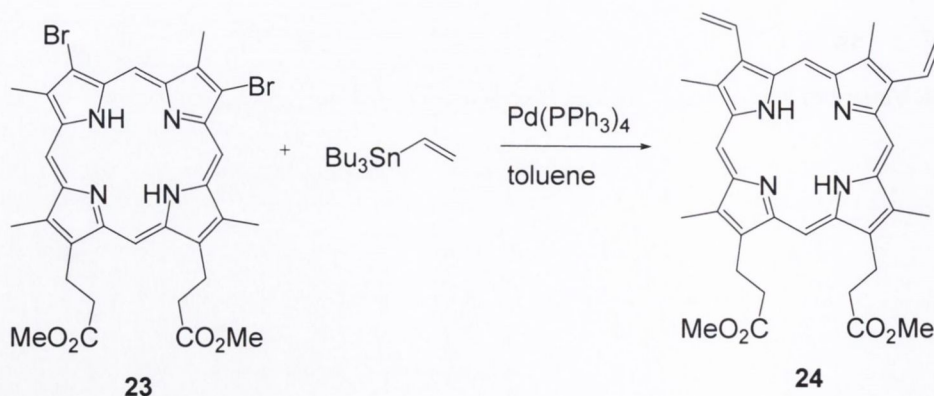
1.3.2 Palladium Catalysed Reactions

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.²⁶ The free β -positions of zinc(II) deuteroporphyrin IX dimethyl ester **21** were mercured and subsequently reacted with methyl acrylate using lithium trichloropalladate(II) as catalyst to give the analogue bis-acrylated compound **22**, 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.²⁷



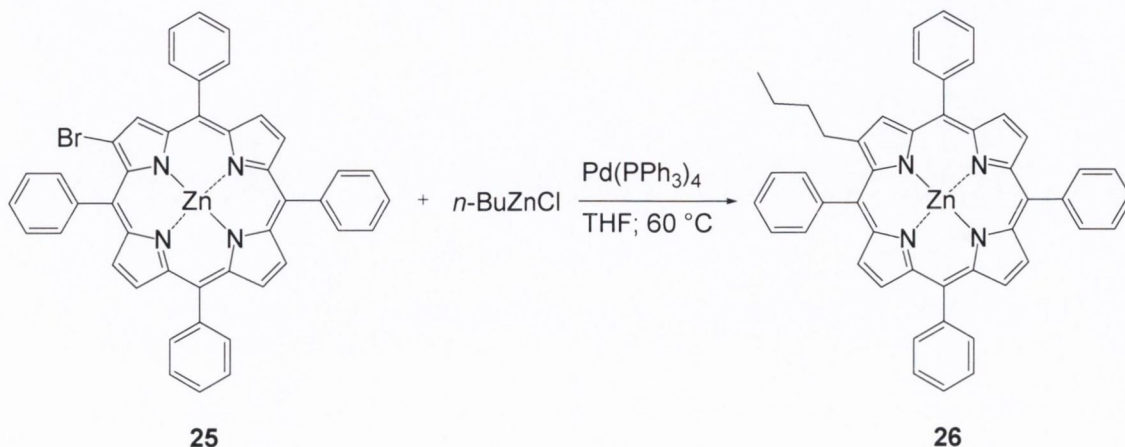
Scheme 1.5. Mercuration and palladium-olefin methodology.

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,²⁸ Negishi,²⁹ Sonogashira,³⁰ Heck³¹ and Suzuki reaction.³² The initial investigations were made by Smith and co-workers who first applied the Stille reaction to porphyrins.³³ 2,4-Dibromodeuteroporphyrin IX dimethyl ester **23** was reacted with tributylvinylstannane in the presence of a palladium catalyst to obtain protoporphyrin IX dimethyl ester **24** in 85 % yield (Scheme 1.6).



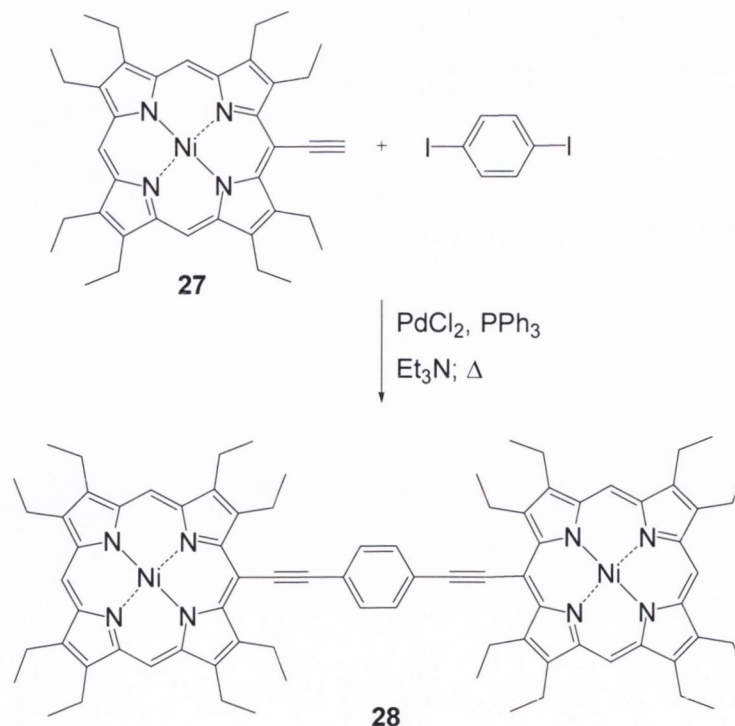
Scheme 1.6. First Stille reaction reported on porphyrin.

Therien and co-workers reported the synthesis of β -substituted porphyrins *via* the Negishi coupling reaction.³⁴ For instance, [2-butyl-5,10,15,20-tetraphenyl-porphyrinato]zinc (II) (2-*n*-butyl-TPP) **26** could be prepared in 92 % yield from zinc(II) 2-bromo-TPP **25** with *n*-butylzinc chloride under catalytic conditions (Scheme 1.7).



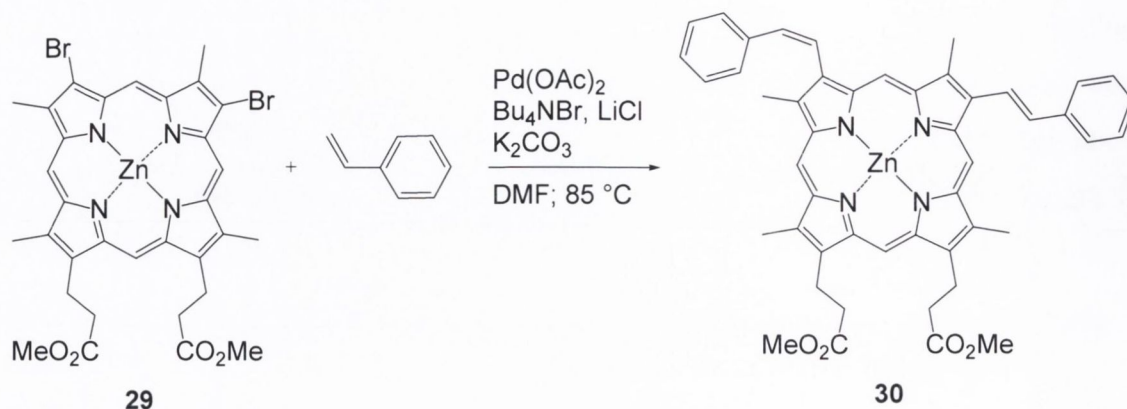
Scheme 1.7. Negishi reaction of 2-bromo-TPP zinc(II).

The Sonogashira reaction was used for the synthesis of a porphyrin dimer bridged by a 1,4-diethynylphenylene unit by Arnold and Nitschinsk.³⁵ Therefore, nickel(II) 5-ethynyl-OEP **27** was reacted with 1,4-diiodobenzene to obtain the dimer **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.^{36,37}



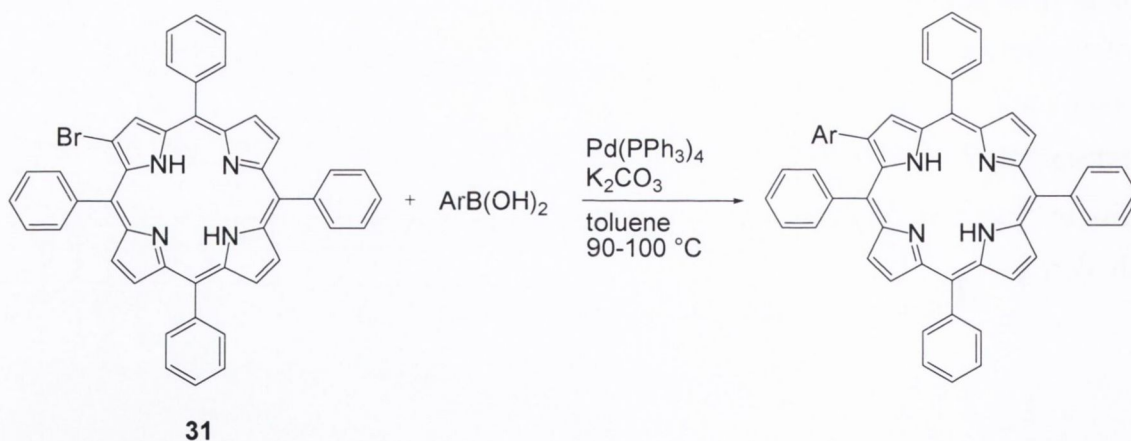
Scheme 1.8. Synthesis of porphyrin dimer *via* Sonogashira coupling reaction.

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



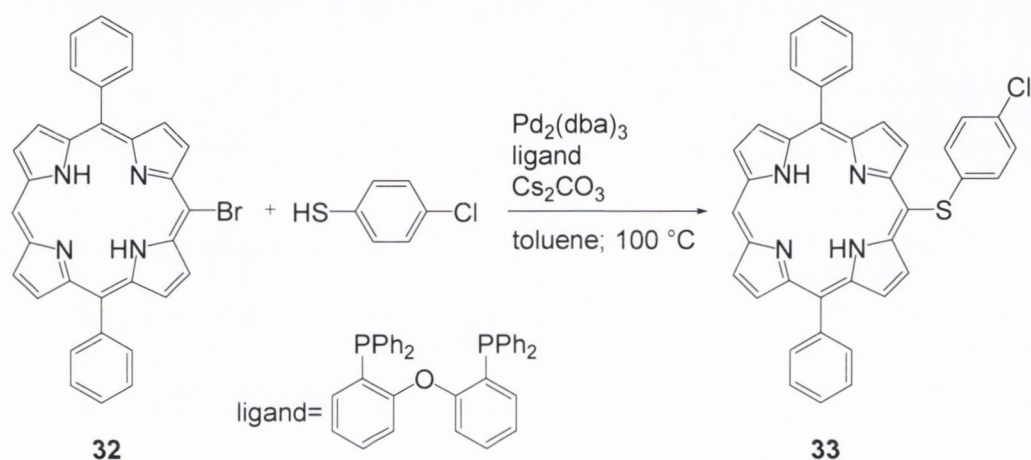
Scheme 1.9. Heck reaction on β -bromo porphyrin.

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



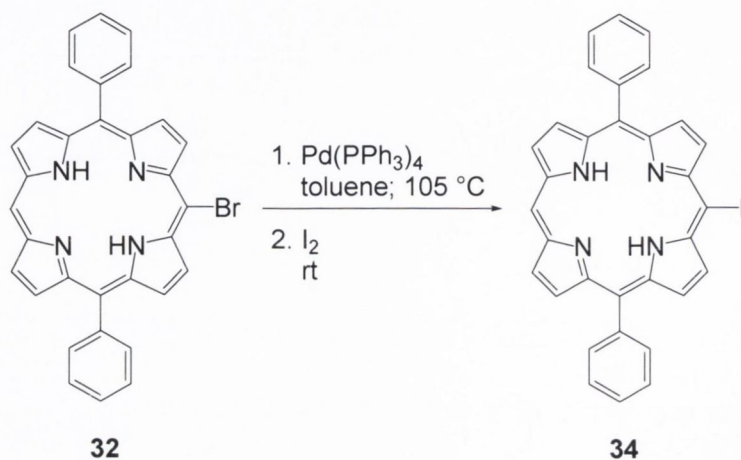
Scheme 1.10. General scheme for Suzuki reaction on β -bromo TPP.

Besides the well-known C-C coupling reactions, there are numerous examples for recently developed palladium catalysed reactions in porphyrin chemistry.^{11,41} Zhang and co-workers developed methods for palladium catalysed carbon-heteroatom bond formation reactions. Meso-oxy-,⁴² -amino- and -amidoporphyrins were synthesised in good to excellent yields.⁴³ The latest addition to these heteroatom-substituted porphyrins is the extension to C-S coupling reactions.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).



Scheme 1.11. Example for palladium catalysed C-S coupling on meso-bromoporphyrin.

A rather unusual example for the application of palladium in porphyrin synthesis was given by Arnold and co-workers.⁴⁵ 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 η^1 -palladio(II)porphyrin intermediate which is the reason for excess amounts of palladium catalyst.

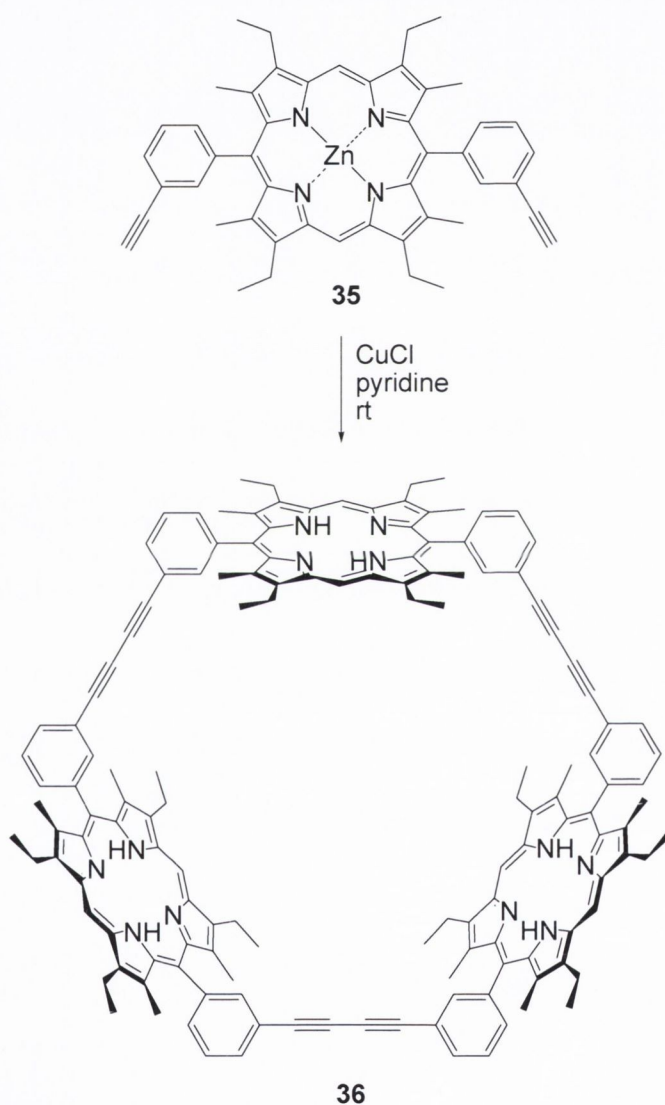


Scheme 1.12. Palladium catalysed halogen exchange reaction.

1.3.3 Other Transition Metal Catalysed Reactions

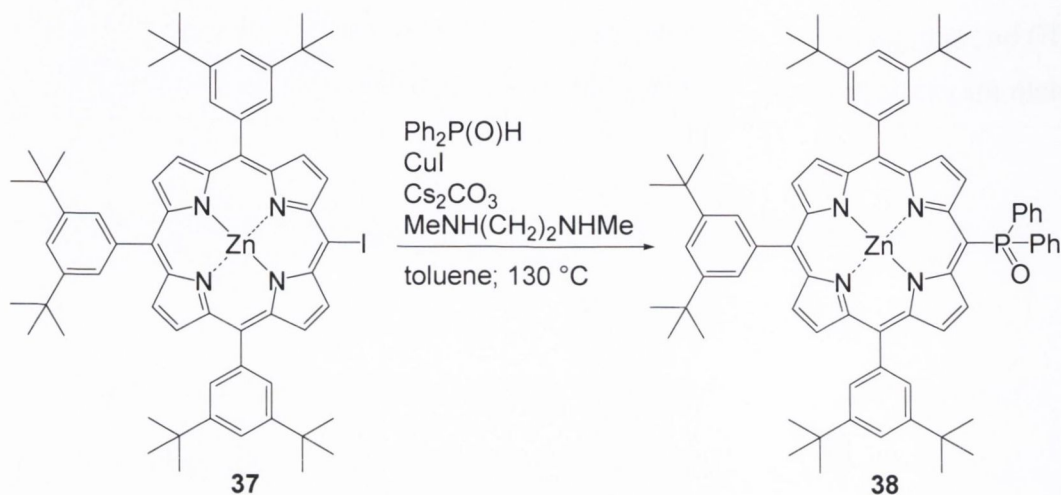
Although palladium is the most commonly used metal for catalytic reactions in organic chemistry, there are a number of other transition metals for C-C bond formation and transformation reactions that are just as well-known.

The Glaser coupling⁴⁶ was first applied to porphyrins by Anderson and Sanders.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).



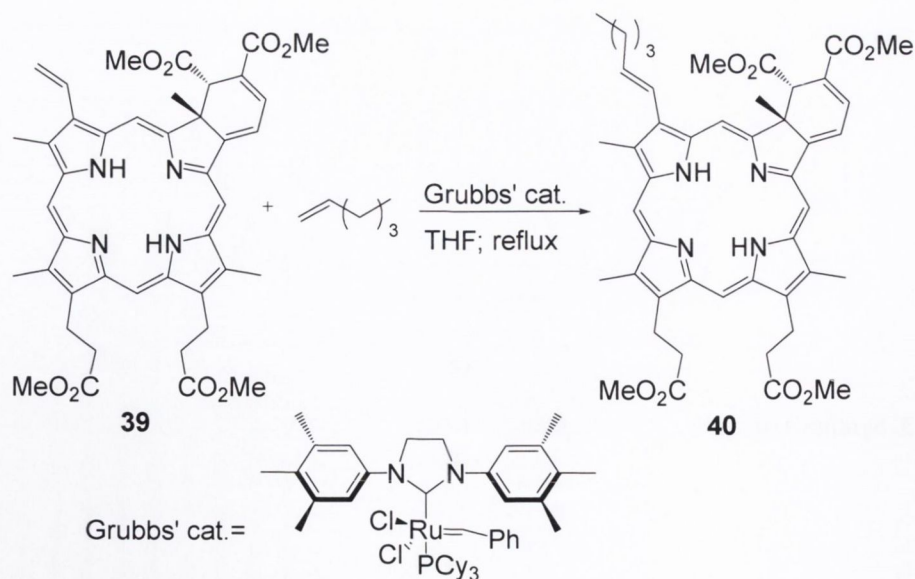
Scheme 1.13. Synthesis of cyclic trimer *via* Glaser coupling reaction.

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).



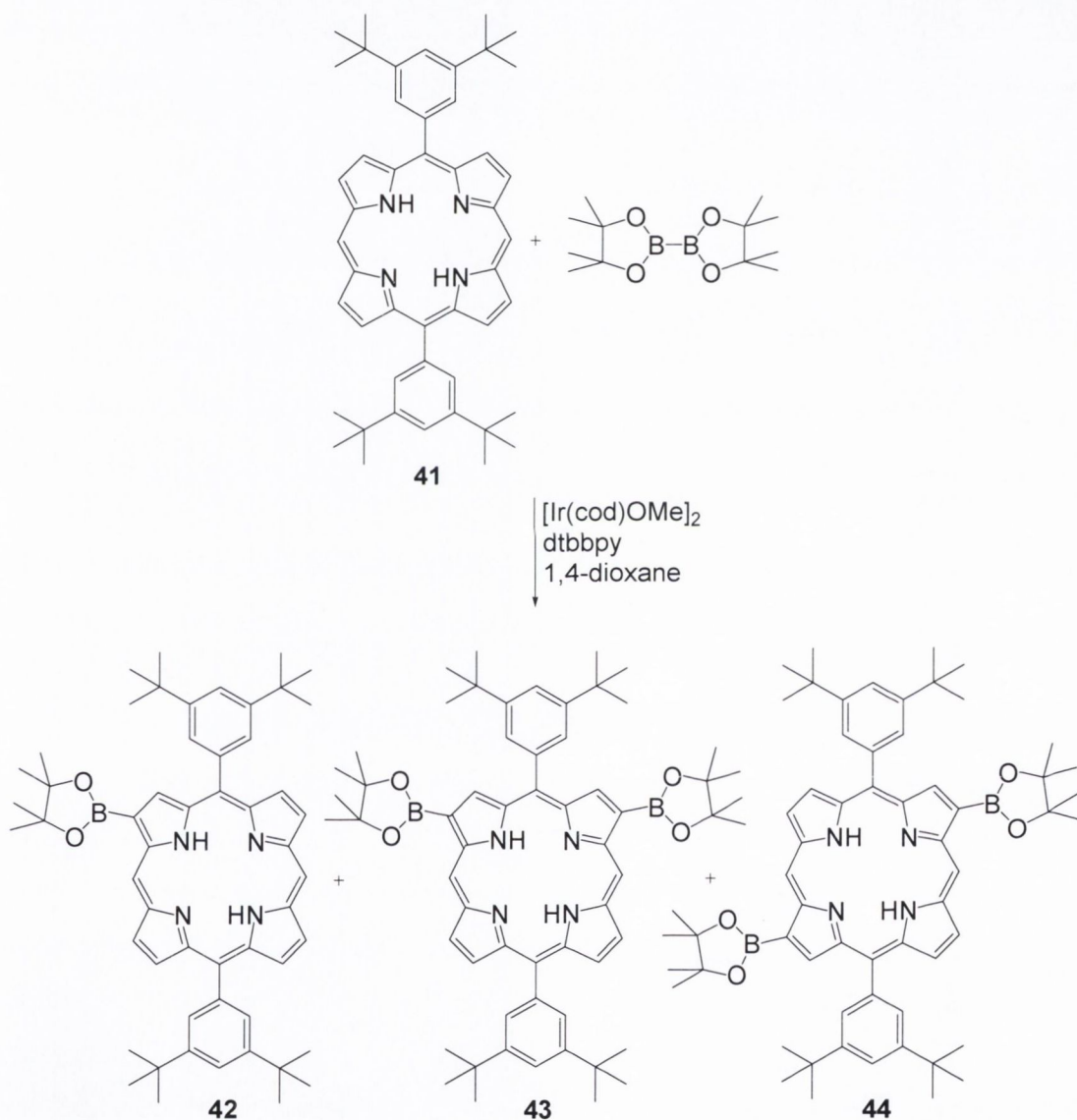
Scheme 1.14. Cu(I) catalysed C-P coupling reaction.

The first cross-metathesis reaction⁴⁹ 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 2nd generation Grubbs' catalyst (Scheme 1.15). The product **40** was obtained in 70 % yield with complete *E*-stereoselectivity.



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.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.



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.

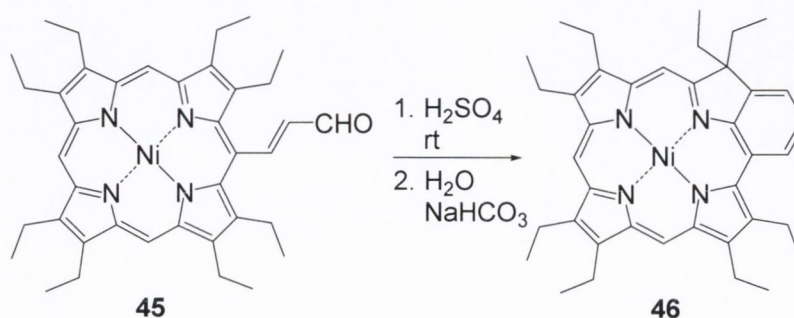
Also, the introduction of alkyl-substituents to the porphyrin core is limited to only a few synthetic methods. Attempts were made to broaden these pathways *via* a rhodium(1) catalysed reaction of zinc(I) ring-metallated porphyrins with iodoalkanes.

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 *via* Nickel(II)
Mediated Reaction

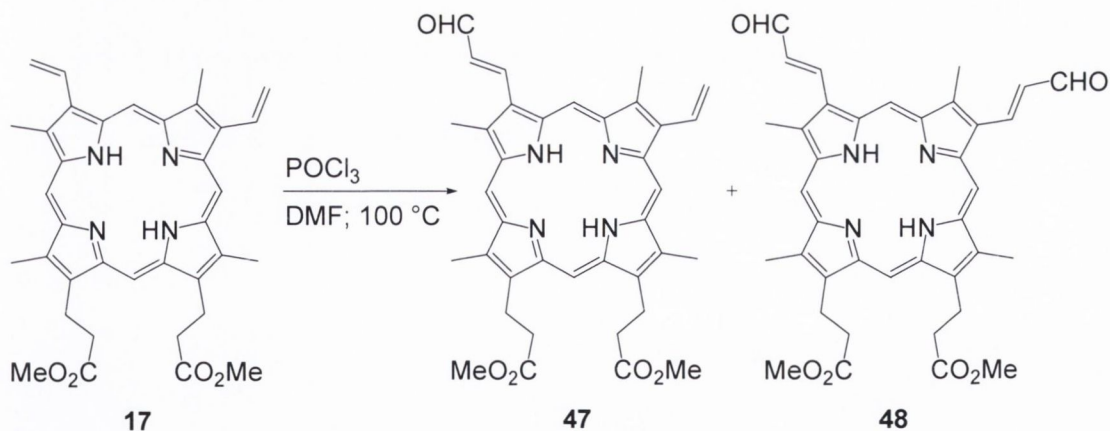
2.1 Background

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



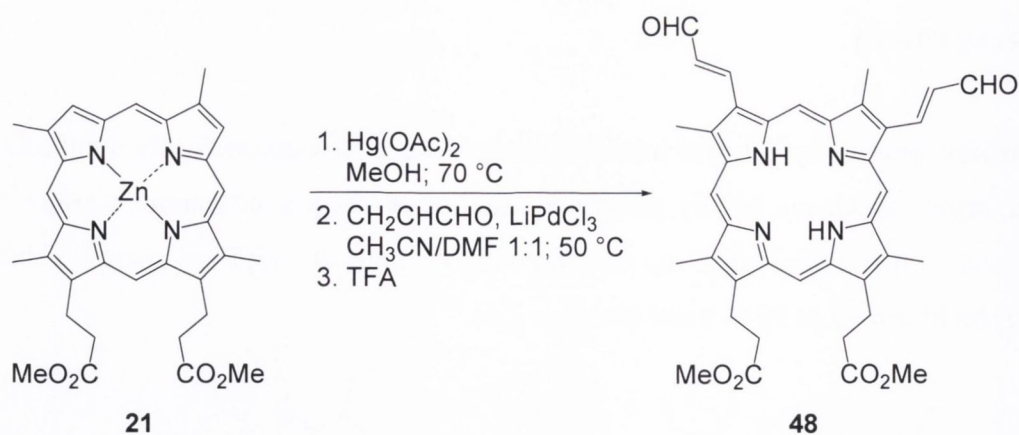
Scheme 2.1. Synthesis of benzochlorin (**46**).

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



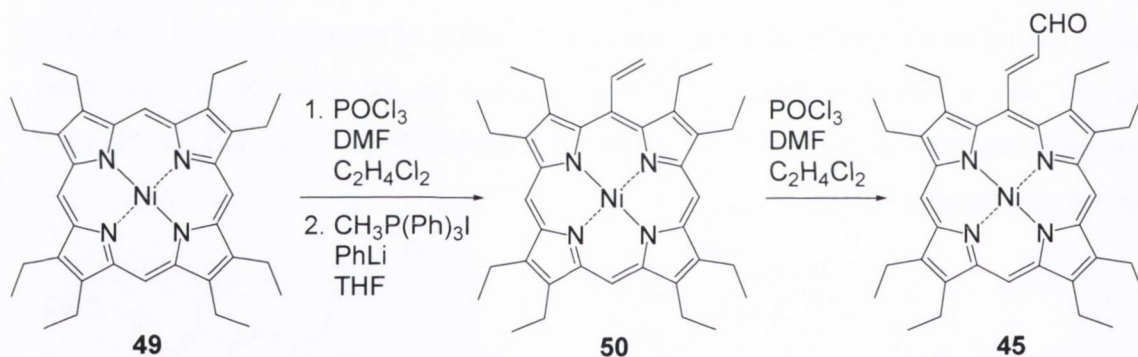
Scheme 2.2. Synthesis of acroleinylporphyrins via Vilsmeier reaction.

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



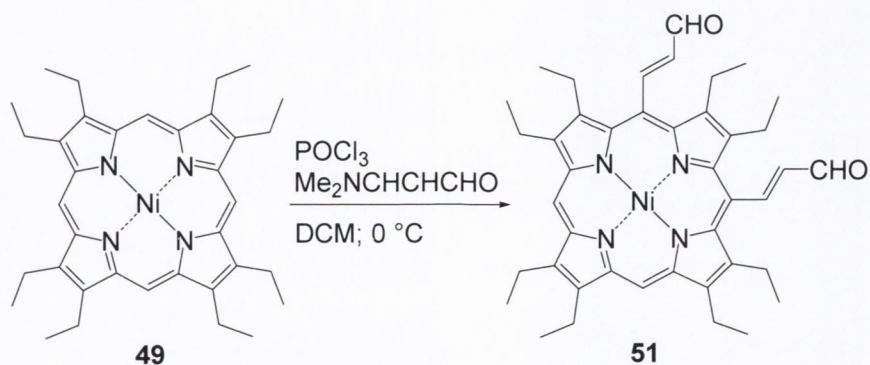
Scheme 2.3. Synthesis of acroleinylporphyrin *via* mercuration and palladium-olefin methodology.

Introduction of the acroleinyl group into the meso-position was first accomplished by Arnold *et al.* in 1978.⁵⁶ Nickel(II) 5-acroleinyl-OEP **45** was synthesised in three steps by a sequence of Vilsmeier formylation and Wittig reaction⁵⁷ of nickel(II) OEP **49** to obtain nickel(II) 5-vinyl-OEP **50**, which was then purposely formylated using the Vilsmeier reaction again to give compound **45** in an overall yield of 54 % (Scheme 2.4).



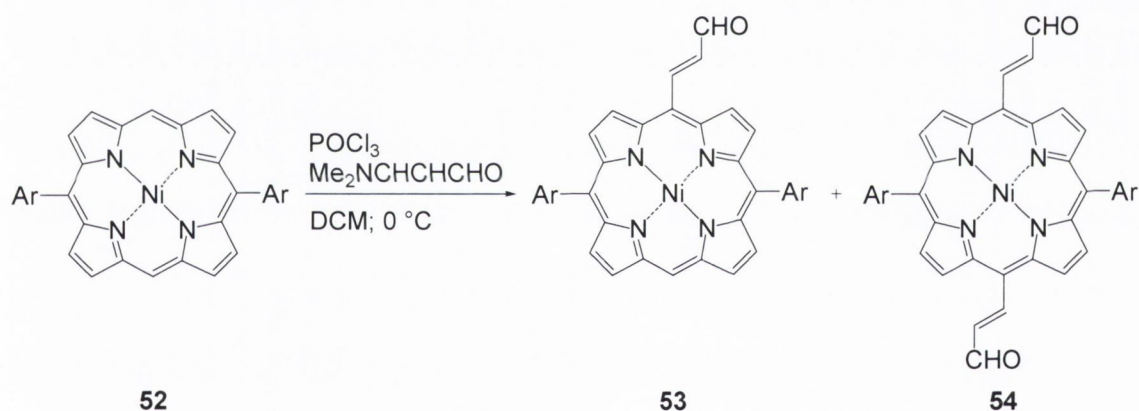
Scheme 2.4. Meso-acroleinylporphyrin *via* sequential Vilsmeier and Wittig reaction.

This synthetic pathway was shortened by Vicente and Smith in 1991 by vinylogous Vilsmeier formylation of nickel(II) OEP **49** directly, to obtain compound **45** in 85 % yield as well as nickel(II) 5,10-diacroleinyl-OEP **51** in 55 % yield by using an excess of the Vilsmeier reagents (Scheme 2.5).⁵² 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.⁵⁸ 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.⁵⁹



Scheme 2.5. Diacroleinylporphyrin *via* vinylogous Vilsmeier reaction.

Nevertheless, vinylogous Vilsmeier reaction has also been used for the first synthesis of β -unsubstituted meso-acroleinylporphyrins by Boyle and Dolphin⁶⁰ and still seems to be the method of choice for this type of compounds.^{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).

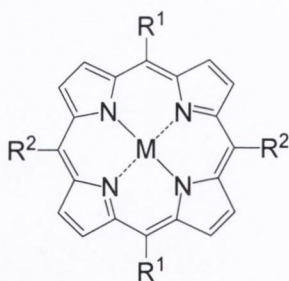


Scheme 2.6. Synthesis of β -unsubstituted meso-acroleinylporphyrins.

2.2 Synthesis of Allylporphyrins

A previous synthesis of meso-allylporphyrins involved the condensation of 5-allyldipyrromethane with a dipyrromethane-dicarbonyl 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- A_2 -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).⁶⁹ These compounds were brominated under standard conditions²⁰ to afford the starting materials **59**,⁷⁰ **60**,⁷¹ **62**⁷² 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.



- 55** $R^1=Ph$; $R^2=H$; $M=2H$
- 56** $R^1=4-MePh$; $R^2=H$; $M=2H$
- 57** $R^1=n-C_6H_{13}$; $R^2=H$; $M=2H$
- 58** $R^1=iso-C_3H_7$; $R^2=H$; $M=2H$
- 59** $R^1=Ph$; $R^2=Br$; $M=2H$
- 60** $R^1=4-MePh$; $R^2=Br$; $M=2H$
- 61** $R^1=4-BuOPh$; $R^2=Br$; $M=2H$
- 62** $R^1=n-C_6H_{13}$; $R^2=Br$; $M=2H$
- 63** $R^1=iso-C_3H_7$; $R^2=Br$; $M=2H$
- 64** $R^1=4-MePh$; $R^2=Br$; $M=Ni(II)$
- 65** $R^1=n-C_6H_{13}$; $R^2=Br$; $M=Ni(II)$

Figure 2.1. 5,15-Porphyrins as starting materials for Suzuki cross-coupling.

For a different substitution pattern, the A_3 -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 **67**⁷⁶ in 96 % yield (Figure 2.2).

Finally, the β -brominated compound **69** was prepared by bromination of TPP⁷⁷ **68**, which was kindly supplied by Dahms, in 46 % yield.⁷⁸

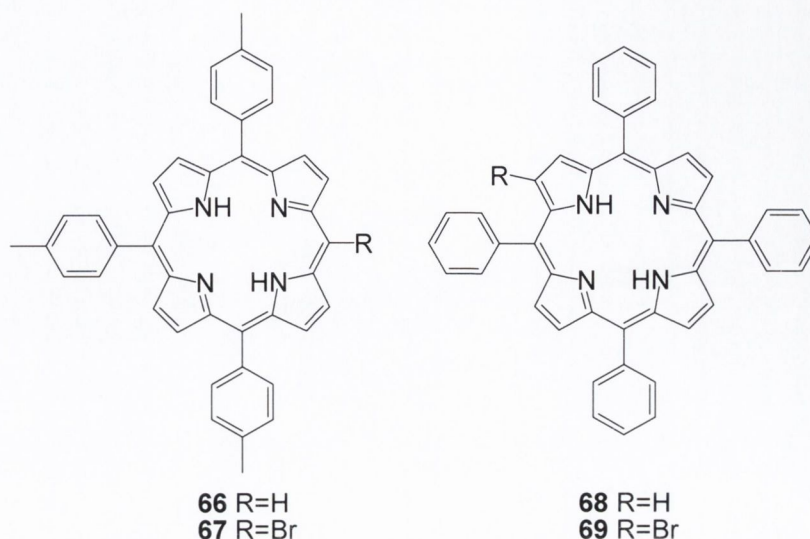
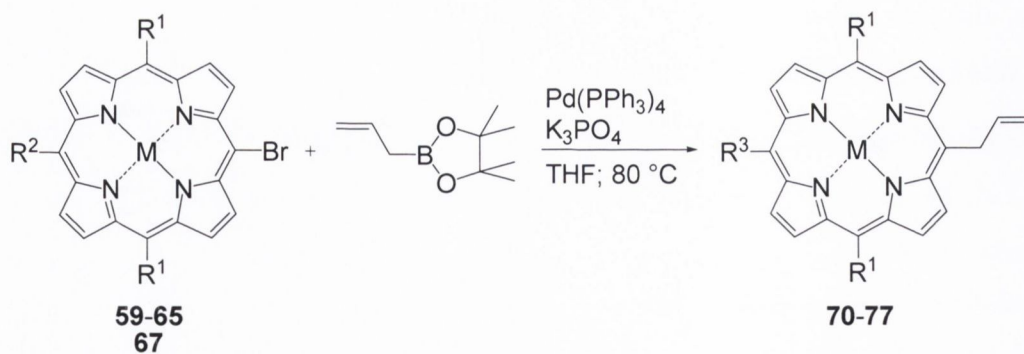


Figure 2.2. A₃- and β -substituted porphyrins as starting materials for Suzuki cross-coupling.

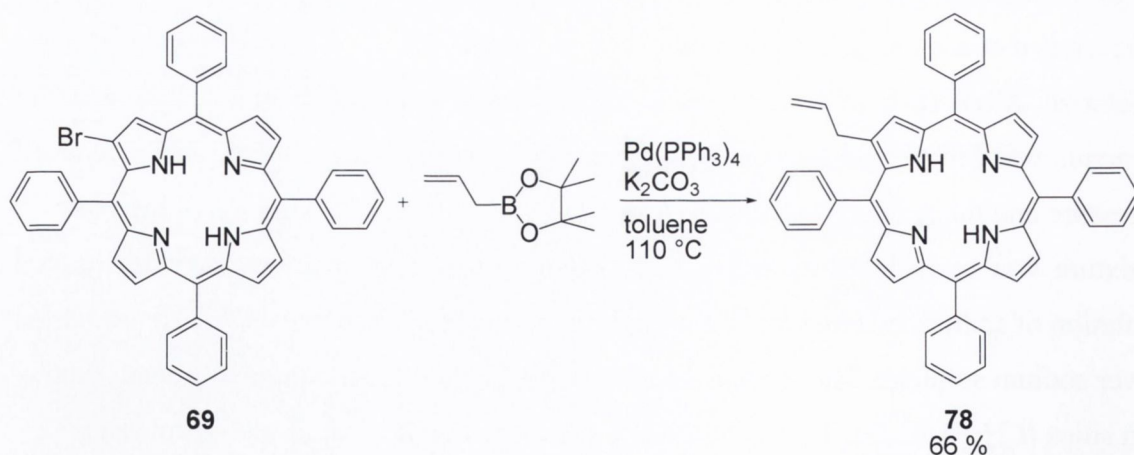
With these different starting materials in hand, the Suzuki cross-coupling reactions were carried out according to literature procedure.⁴⁰ The meso-bromoporphyrins **59** – **63** and **67** were dissolved in anhydrous THF in an oven-dried Schlenk-tube under argon atmosphere. K₃PO₄ was added and the reaction mixture was degassed *via* three freeze-pump-thaw cycles and put under argon again. Allylboronic acid pinacol ester and Pd(PPh₃)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 (CH₂Cl₂/C₆H₁₄ 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 (CH₂Cl₂/C₆H₁₄ 1:2, v/v) to obtain the corresponding meso-allylporphyrins **70** – **77** in 2 % to 95 % yield (Scheme 2.7).⁷²



Entry	R ¹	R ²	R ³	M	Product	Yield
59	Ph	Br	allyl	2H	70	78 %
60	4-MePh	Br	allyl	2H	71	86 %
61	4-BuOPh	Br	allyl	2H	72	50 %
62	<i>n</i> -C ₆ H ₁₃	Br	allyl	2H	73	50 %
63	<i>iso</i> -C ₃ H ₇	Br	allyl	2H	74	2 %
64	4-MePh	Br	allyl	Ni(II)	75	88 %
65	<i>n</i> -C ₆ H ₁₃	Br	allyl	Ni(II)	76	95 %
67	4-MePh	4-MePh	4-MePh	2H	77	74 %

Scheme 2.7. Synthesis of meso-allylporphyrins.

The Suzuki cross-coupling reaction of 2-bromo-TPP **69** was carried out under slightly different conditions.⁷⁹ K₂CO₃ 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.

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.²¹ 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 Δ_{24} of 0.03 Å.⁸⁰ The allyl group is nearly perpendicular to the molecular plane with a C5–C51–C52–C53 torsion angle of 2.6°.

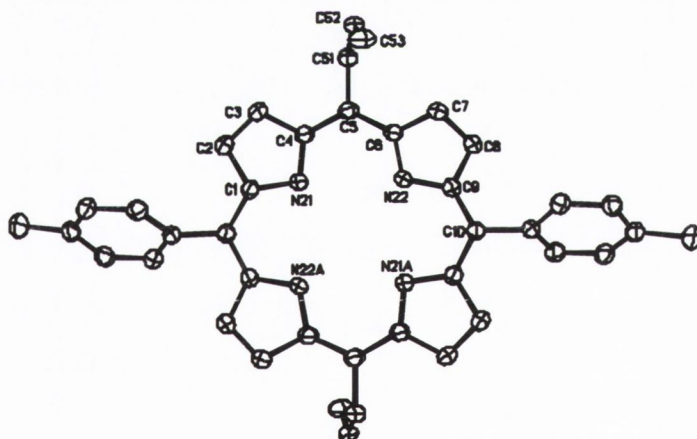
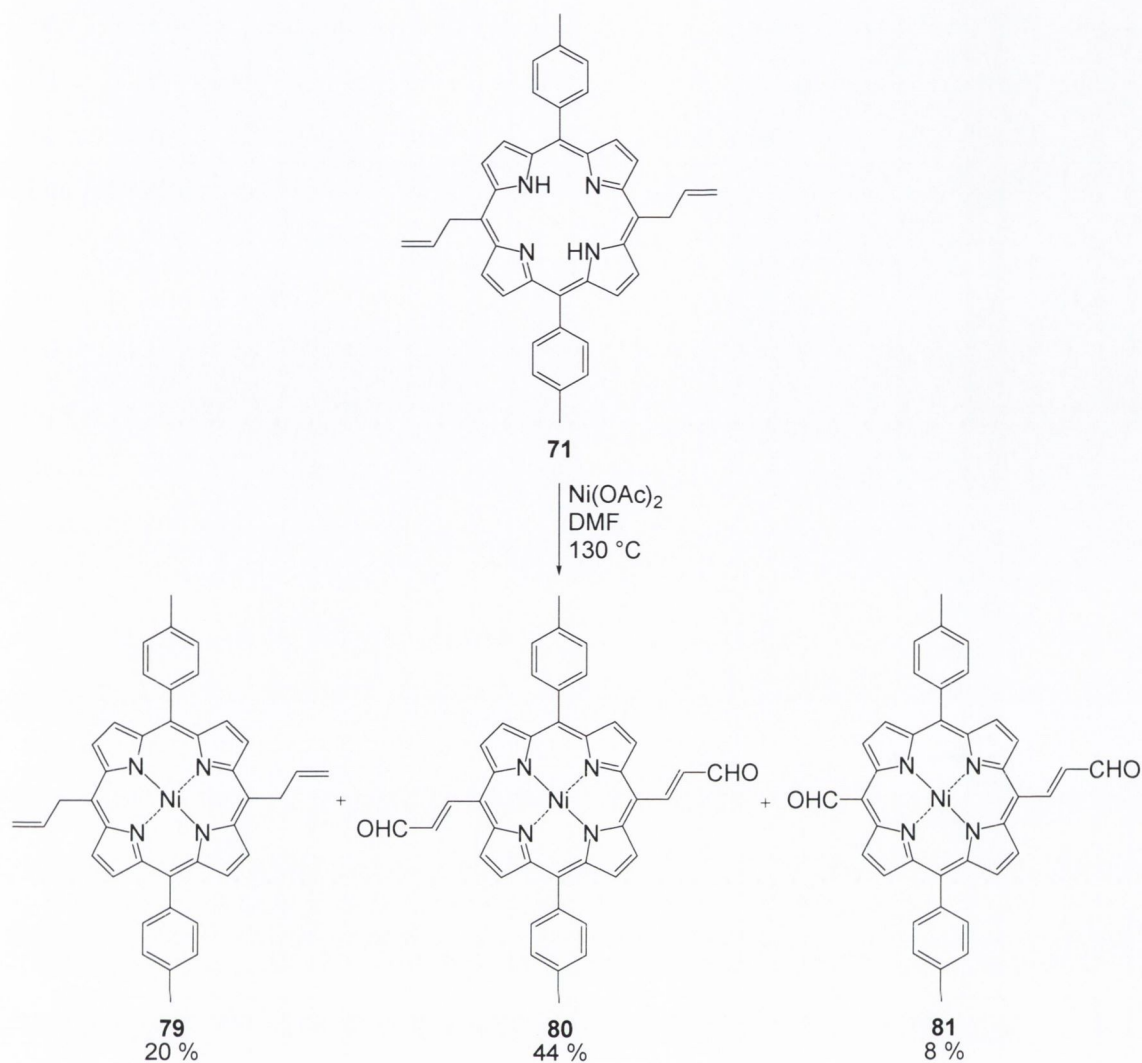


Figure 2.3. Molecular structure of **71** in the crystal. Hydrogen atoms have been omitted for clarity.

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.^{65,81} The progress of the reaction was monitored by TLC on silica gel (CH₂Cl₂/C₆H₁₄ 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,²¹ namely nickel(II) acetate (3 equiv.) in *N,N*-dimethylformamide (DMF) at 130 °C. The reaction was monitored by TLC on silica gel (CH₂Cl₂/C₆H₁₄ 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/C₆H₁₄ 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).⁷² Interestingly, diacroleinylporphyrin **80** was the main product of this reaction.



Scheme 2.9. Reaction of allylporphyrin with nickel(II) acetate.

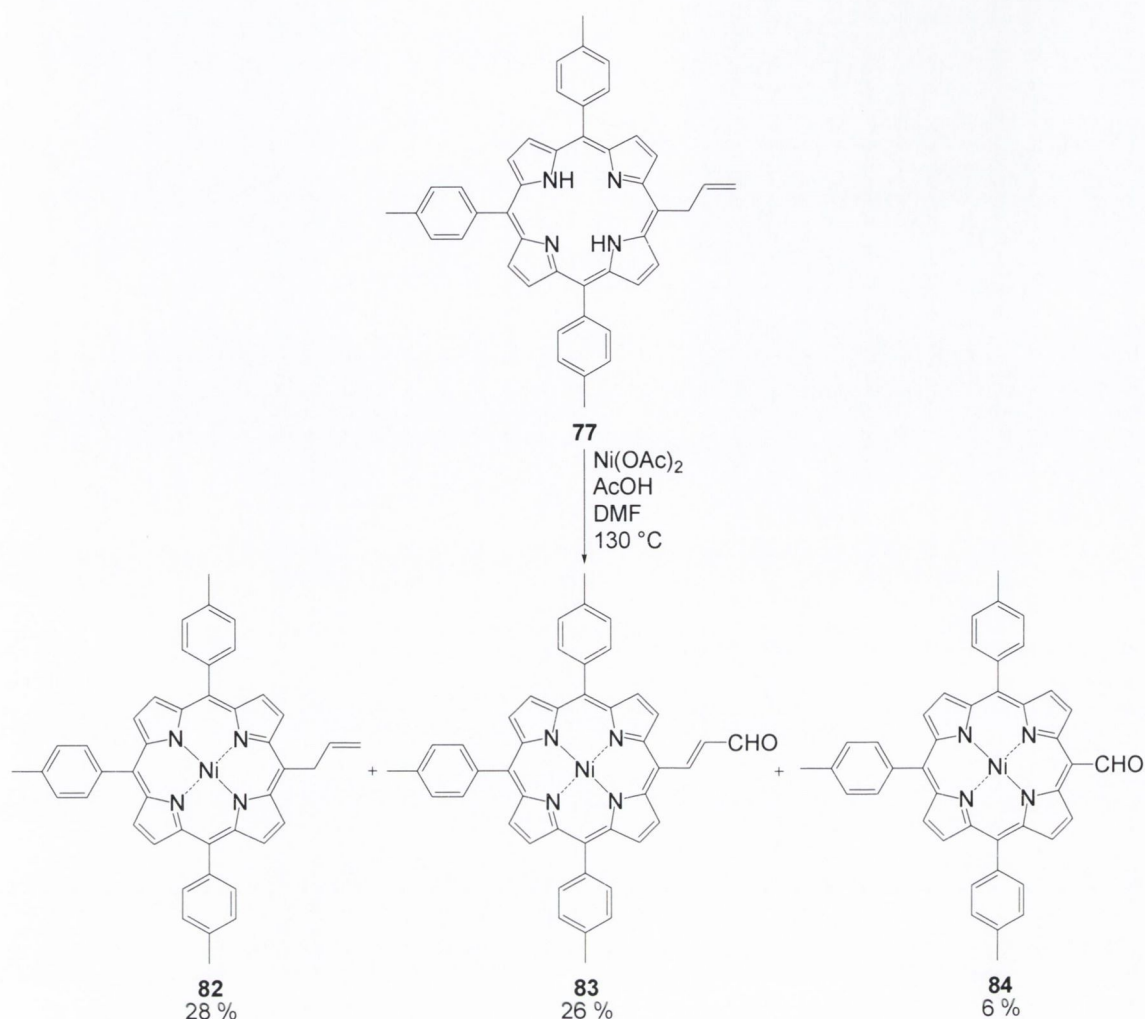
This conversion was further investigated using different amounts of nickel(II) acetate. Reaction of starting material **71** with 4, 6 and 8 equiv. of nickel(II) acetate had no influence on the yield of the main product **80**, but the yield of compounds **79** and **81** decreased to traces only with 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.⁸² 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.

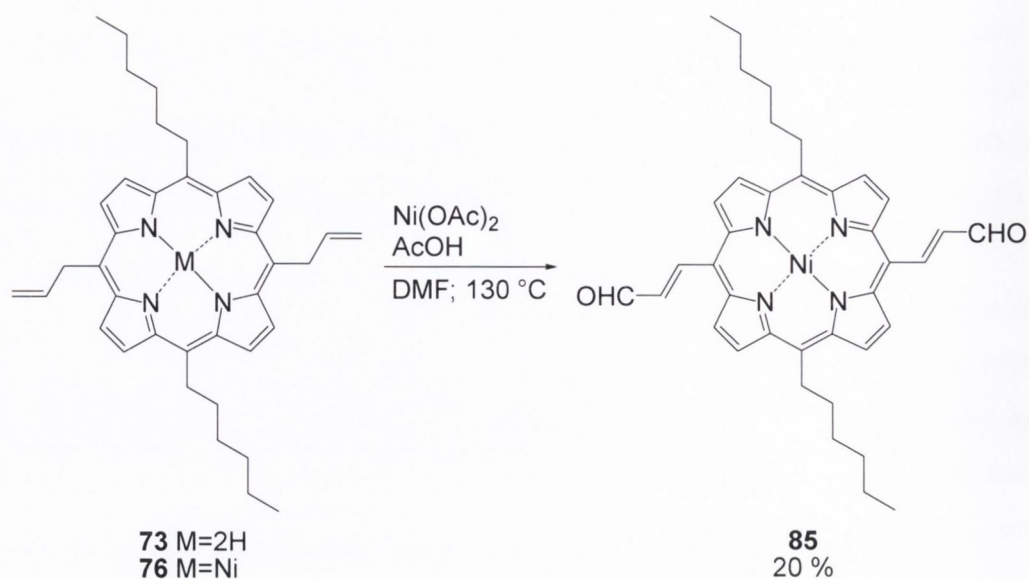
To investigate the general application of this reaction to other porphyrin systems, the mono-allylporphyrin **77**, the alkyl-substituted diallylporphyrin **73** and its nickel(II) analogue **76**, as well as the β -allylporphyrin **78**, were subjected to the optimised reaction conditions.

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.



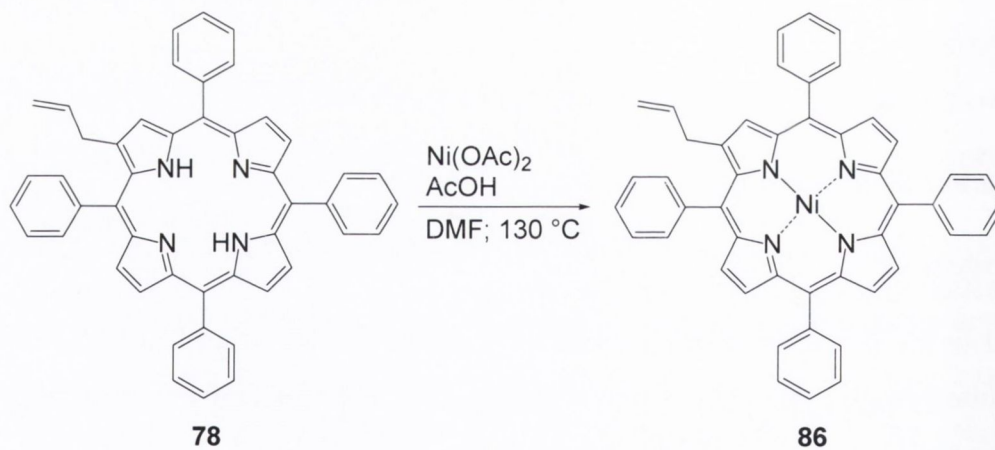
Scheme 2.10. Nickel(II) mediated reaction of mono-allylporphyrin.

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.



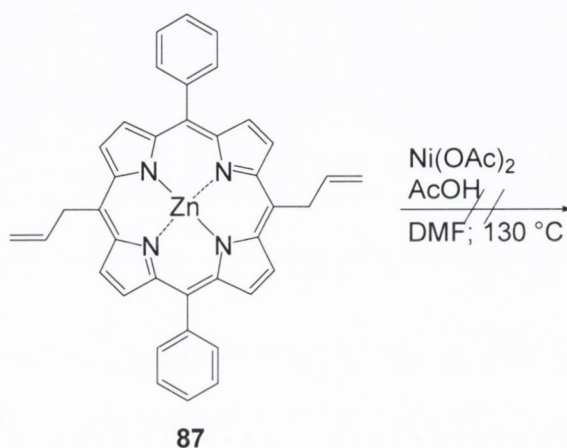
Scheme 2.11. Nickel(II) mediated reaction of alkyl-substituted diallylporphyrins.

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).



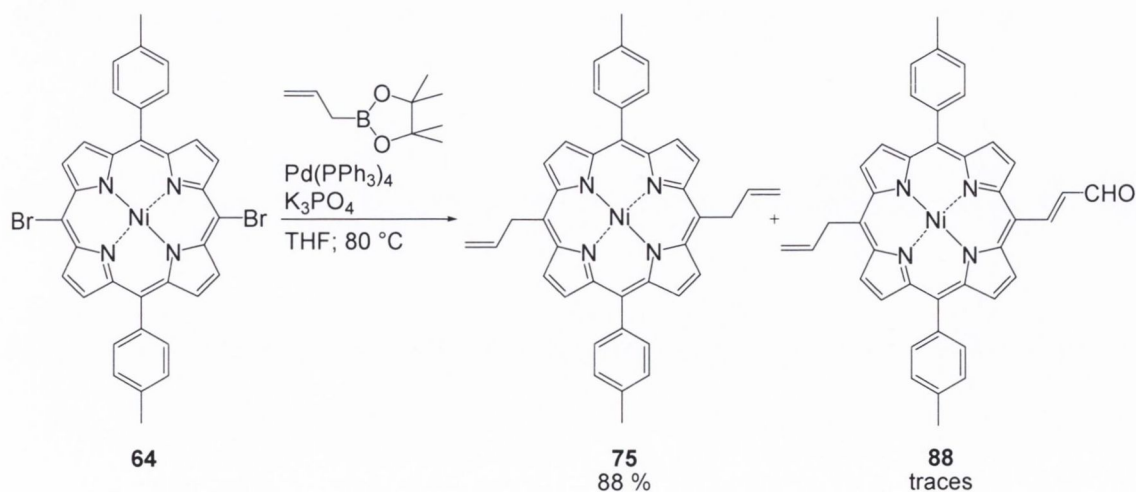
Scheme 2.12. Reaction of β -allyl-TPP with nickel(II) acetate.

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 procedure¹⁰ 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.



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_3PO_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).



Scheme 2.14. Suzuki coupling of nickel(II) metallated diallylporphyrin.

Due to this observation and the fact that palladium(II) and nickel(II) reagents often react similarly,⁸³ compound **75** was reacted with $\text{Pd}(\text{PPh}_3)_4$ and $\text{Pd}(\text{OAc})_2$ 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 d_7 -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.⁸⁴⁻⁸⁶ The first reaction step could be identical to previous observations and involve the formation of a nickel- η^3 -allyl complex (Figure 2.4).⁸⁷⁻⁸⁹

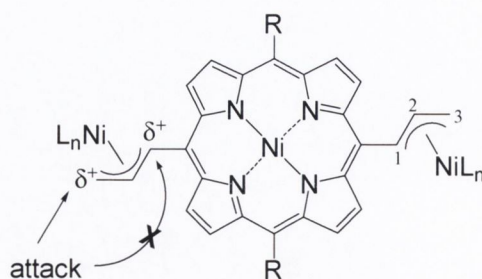
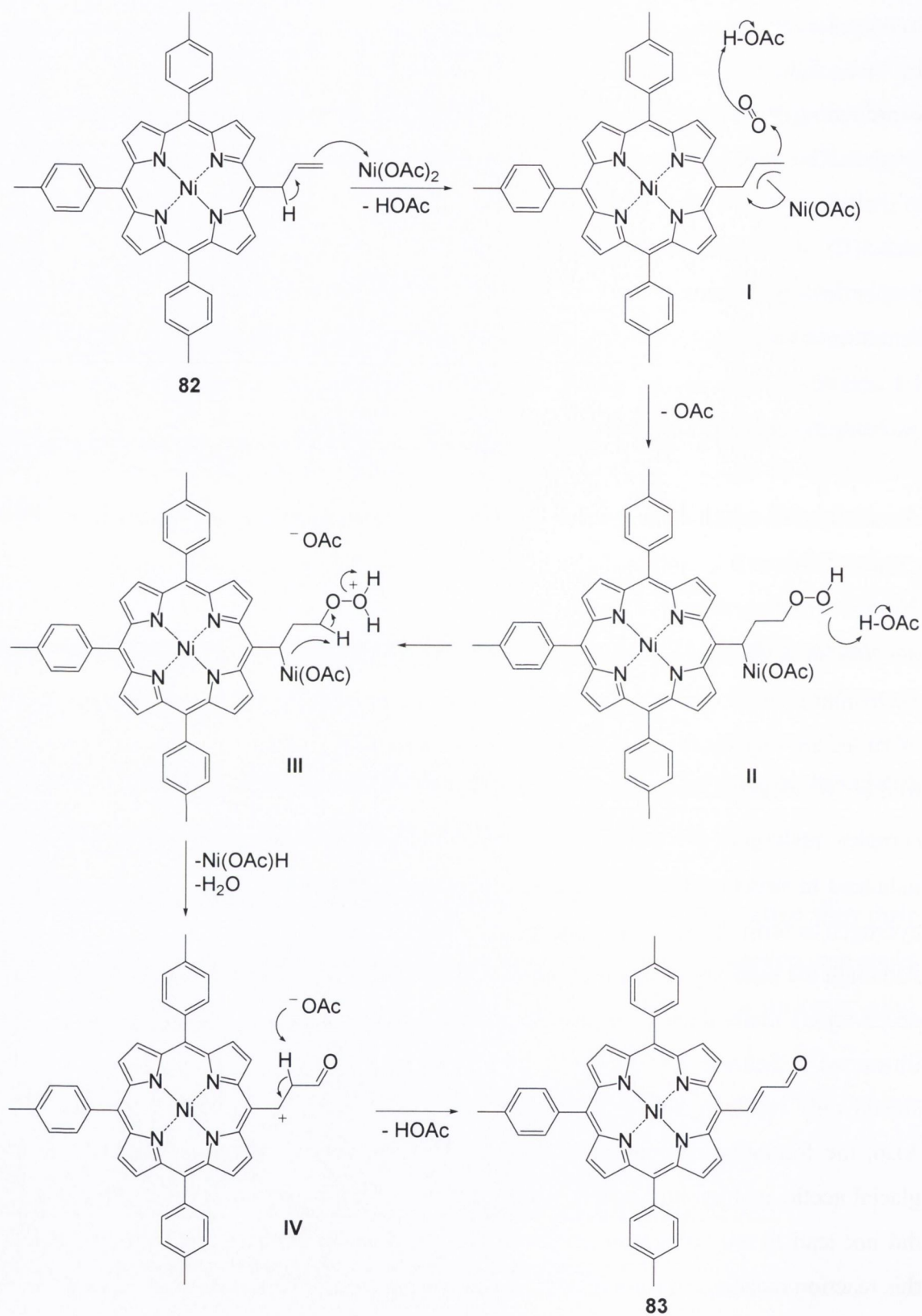


Figure 2.4. Possible intermediate during formation of diacroleinylporphyrins.

In one case the experimental data indicated a radical chain reaction mechanism initiated by heat, light or a reducing agent.⁸⁷ 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 η^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 η^3 -nickel(II)-allyl-complex **I** with the loss of a molecule of acetic acid. The η^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 η^3 -nickel(II)-allyl-complex becomes a η^1 -nickel(II)-allyl-complex **II**. This complex undergoes β -hydrogen elimination with the loss of one water molecule as indicated in structure **III**. The final step involved the deprotonation of the β -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 ^1H Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR spectra of porphyrins clearly show the aromatic character of the macrocycle. The β - 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 β -carbon atoms, the meso-protons are shifted even further towards lower field than the β -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 ^1H 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** show the main features of the allyl- and acroleinyl-spectra (Figure 2.5).

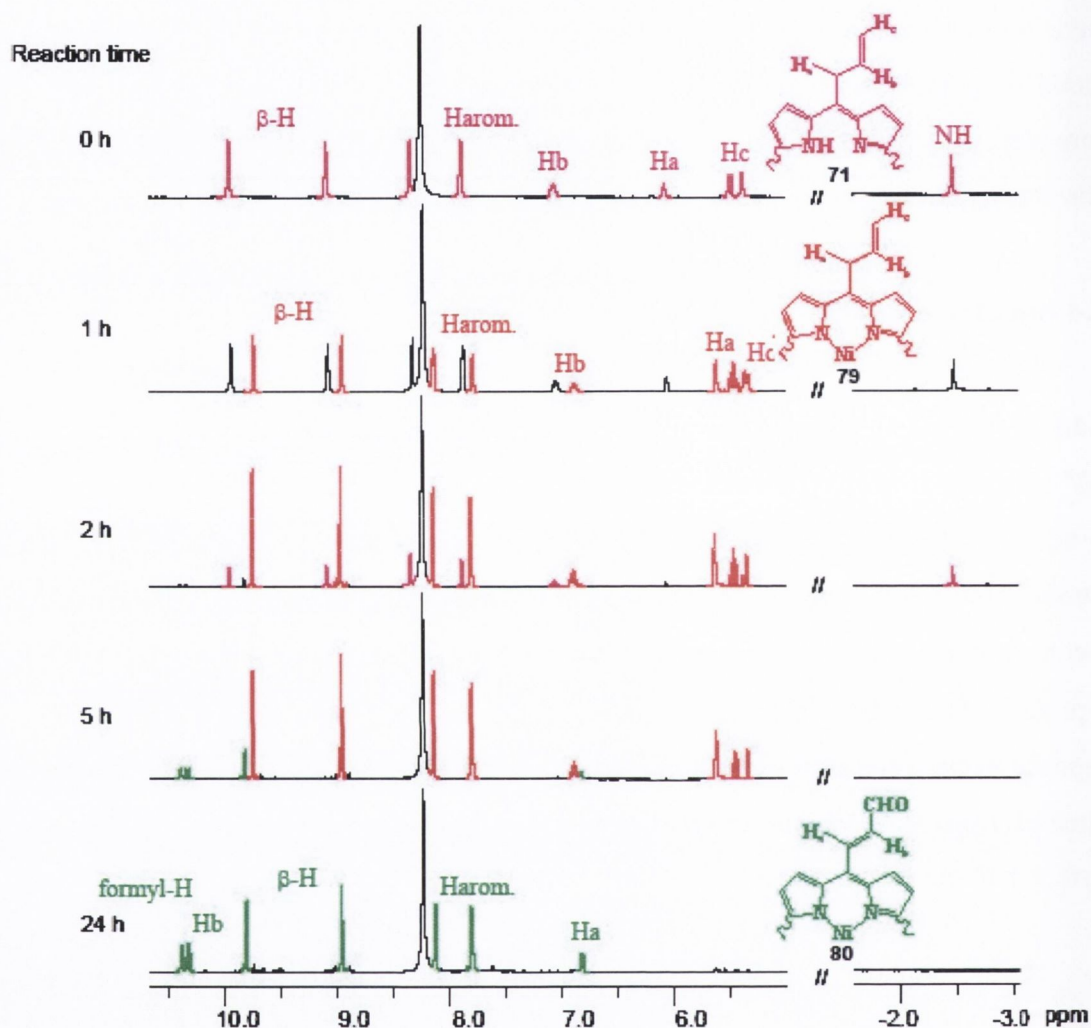


Figure 2.5. Nickel(II) mediated reaction of diallylporphyrin **71** in d_7 -DMF, monitored by ^1H NMR, 600 MHz, at rt.

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 ^1H 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.

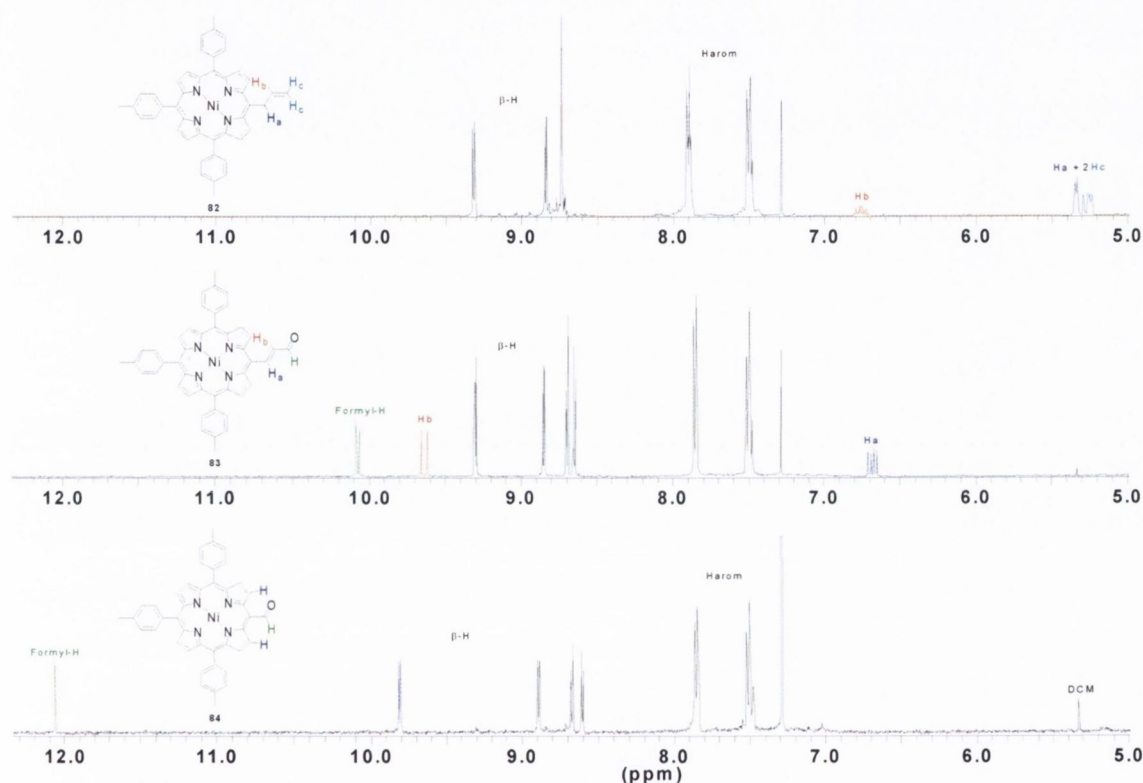


Figure 2.6. ^1H NMR, 400 MHz, at rt in CDCl_3 of products **82**, **83** and **84** of nickel(II) mediated reaction of A_3B -substituted porphyrin.

^1H 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 β -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 π, π^* -transition.⁹² Q-bands can be detected in the region of longer wavelengths. They occur due to quasi-permitted π, π^* -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.⁹³

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.

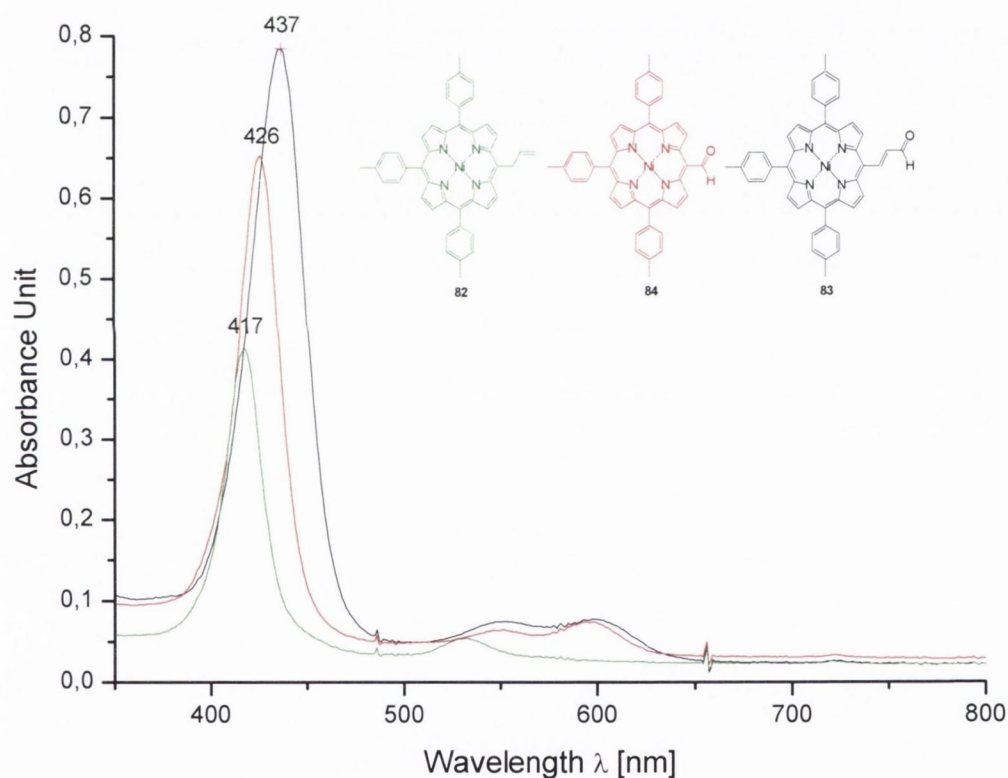


Figure 2.7. UV-vis spectra of compounds **82** to **84** in DCM at rt. Baselines were adjusted arbitrarily.

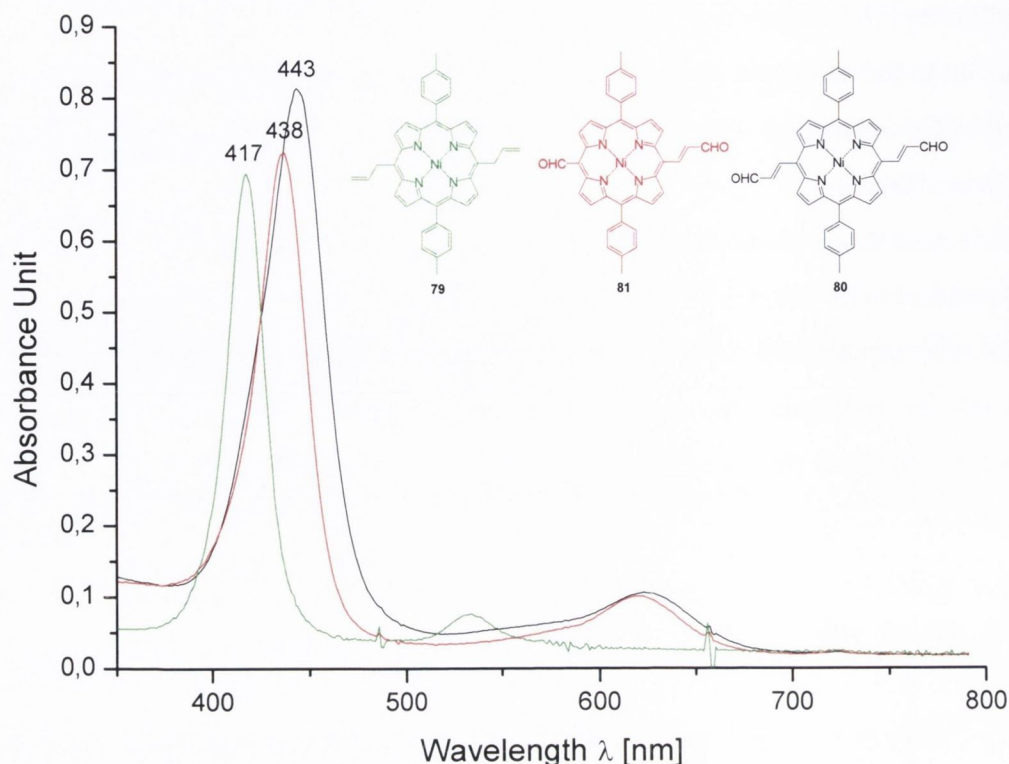


Figure 2.8. UV-vis spectra of compounds **79** to **81** in DCM at rt. Baselines were adjusted arbitrarily.

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

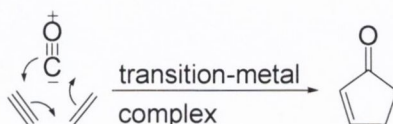
A series of allyl-substituted porphyrins was synthesised *via* the Suzuki cross-coupling reaction. The general application of this method to give various substitution patterns on porphyrins was demonstrated. It could be used to functionalise the meso-position of A₂B₂- as well as A₃B-type porphyrins, for both aryl- and alkyl-substituted, as well as in the β -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, *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(*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 A₂B₂- as well as A₃B-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 descry the reaction mechanism.

Chapter 3:
The Pauson-Khand Reaction of
Porphyrins

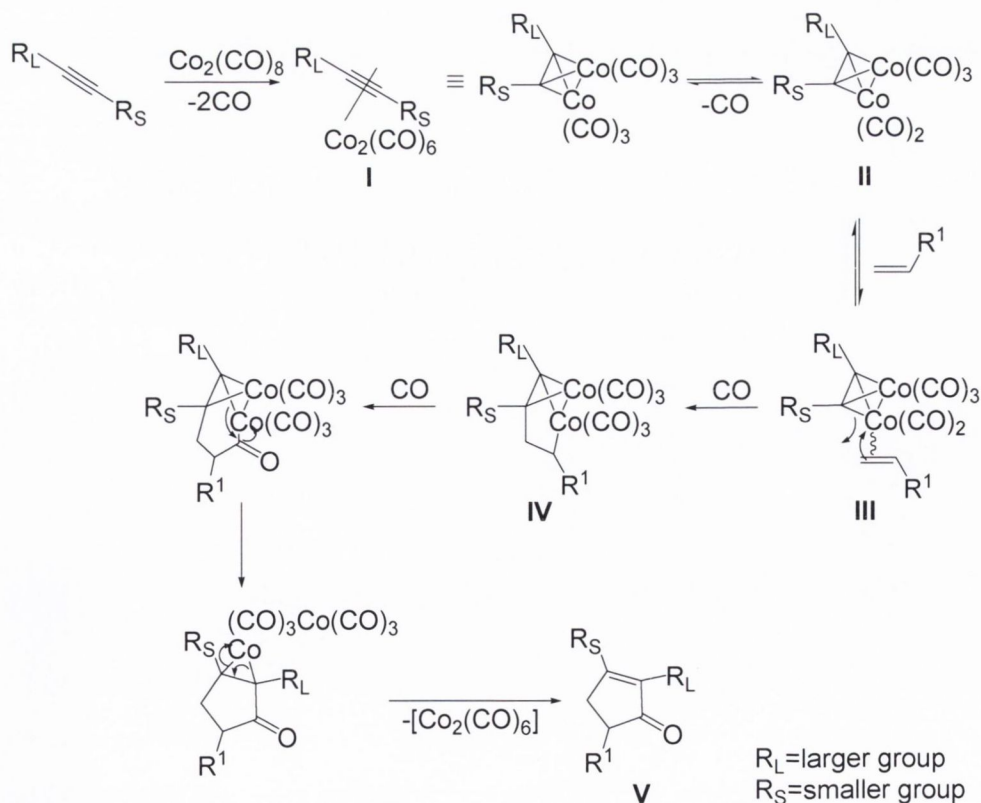
3.1 Background

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).⁹⁴ Since its discovery by Pauson and Khand in 1971⁹⁵ this reaction has remained the most flexible and atom-economical method for the synthesis of five-membered rings.⁹⁶ It has been shown that cyclopentenones are versatile building blocks for the synthesis of natural products and that they exhibit biological activity.^{97,98}



Scheme 3.1. The Pauson-Khand reaction.

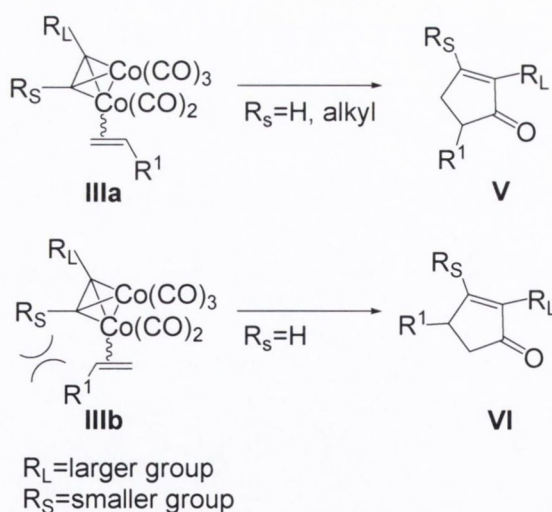
Originally, cobalt carbonyl was used as the transition metal complex for the Pauson-Khand reaction and it also served as a carbon monoxide source. The mechanism for this stoichiometric reaction, proposed by Magnus and co-workers, has been widely accepted (Scheme 3.2).^{99,100}



Scheme 3.2. Postulated mechanism of the Pauson-Khand reaction.

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.^{101,102} The last two steps involve insertion of a carbon monoxide molecule into a cobalt-carbon sp^3 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.¹⁰³

Although the first intramolecular version of the Pauson-Khand reaction was reported by Schore¹⁰⁴ only ten years after the initial discovery, it has received most attention.¹⁰⁵ 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).



Scheme 3.3. Possible regioisomers from Pauson-Khand reaction.

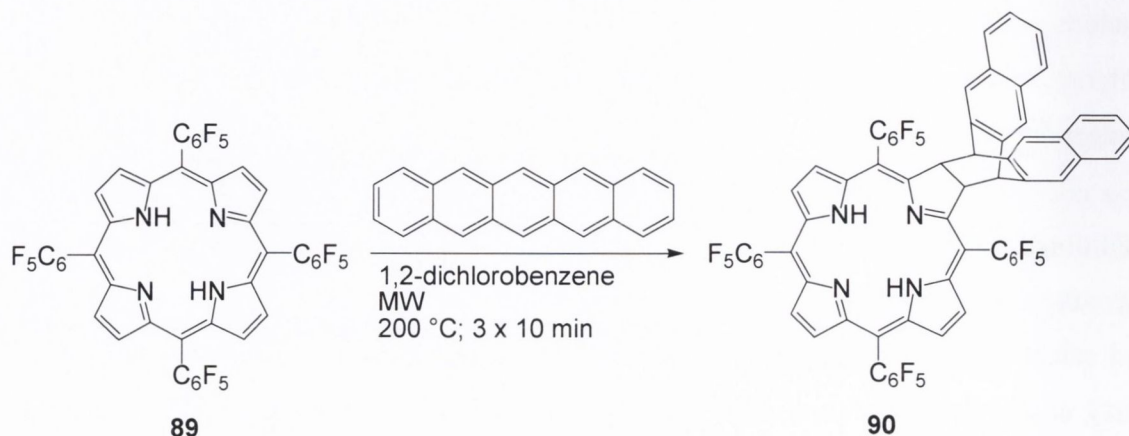
For asymmetrically substituted alkynes (terminal and internal) insertion occurs exclusively at the alkyne carbon bearing the smaller substituent R_S .¹⁰⁶ Consequently, the larger substituent R_L is always at the 2-position of the cyclopentenone. In contrast, the regiochemistry with respect to the alkene 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,¹⁰⁷ different solvents and thermolyses.¹⁰⁸ The reason for this unexpected selectivity remains unclear.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.

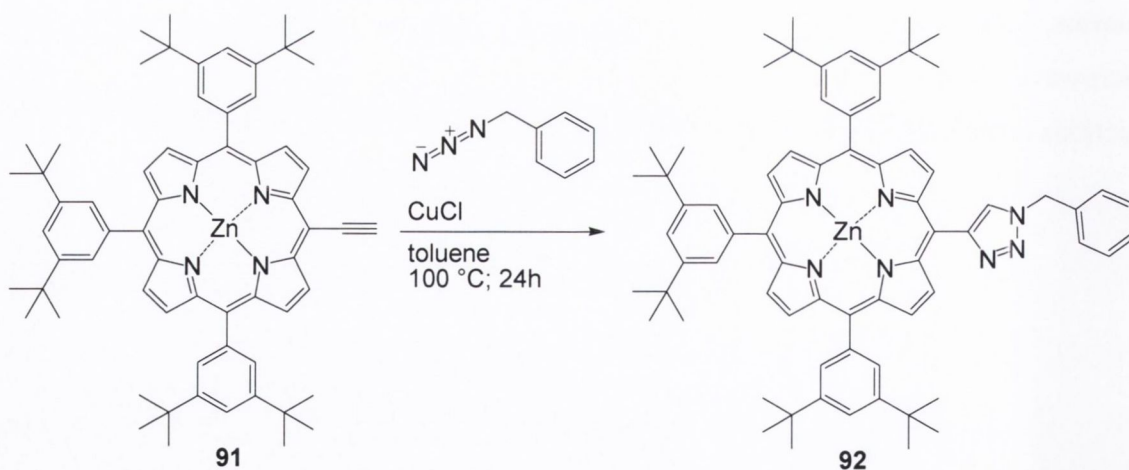
The most common cyclisation reactions in porphyrin chemistry are Diels-Alder¹¹⁰ and the 1,3-dipolar cycloaddition reactions¹¹¹ amongst other electrocyclic reactions.¹¹² These methods have mostly been applied to the β -position of the porphyrin to form chlorins, isobacteriochlorins and bacteriochlorins.⁴¹ 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).¹¹³ 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 %.



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.¹¹⁴ 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).¹¹⁵



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.¹¹⁶ In order to explore this reaction for porphyrins, the vinyl-substituted porphyrin, [5,10,15-tris(4-methylphenyl)-20-vinylporphyrinato]nickel(II) **94**,⁷⁵ 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 condensor 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 ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$ 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 ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$ 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.

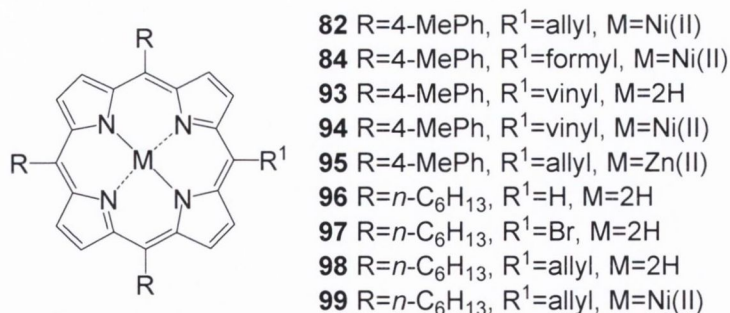
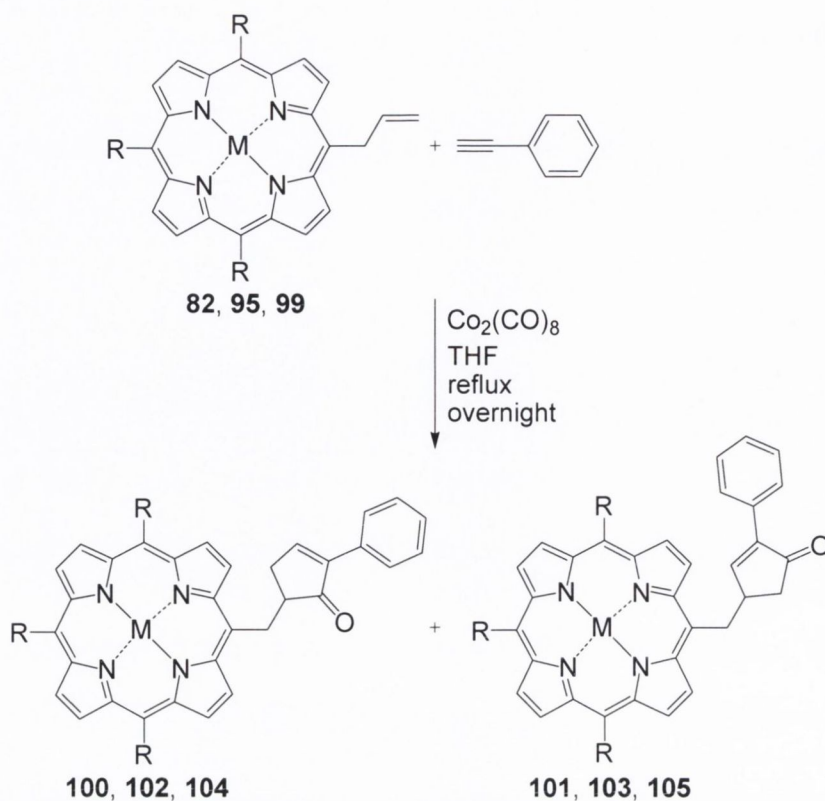


Figure 3.1. Starting materials for the Pauson-Khand reaction of alkenylporphyrins.

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).



Entry	R	M	Product	Yield [%]
82	4-MePh	Ni(II)	100, 101	19, 34
95	4-MePh	Zn(II)	102, 103	8, 15
99	<i>n</i> -C ₆ H ₁₃	Ni(II)	104, 105	14, 19

Scheme 3.6. The Pauson-Khand reaction of allylporphyrins.

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.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.^{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.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.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.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 *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.

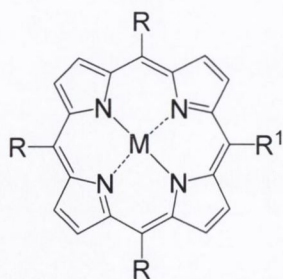
The Pauson-Khand products **100**, **102**, **104** and **101**, **103**, **105** comprise the two expected regioisomers in analogy to compounds **V** and **VI** according to the reaction mechanism (Scheme 3.3). The larger substituent of the alkyne reagent, namely the phenyl group, was always at the 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.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.⁷⁵



- 106** R=4-MePh, R¹=TMS-ethynyl, M=2H
107 R=4-MePh, R¹=TMS-ethynyl, M=Ni(II)
108 R=4-MePh, R¹=ethynyl, M=Ni(II)
109 R=4-MePh, R¹=ethynyl, M=Zn(II)
110 R=*n*-C₆H₁₃, R¹=TMS-ethynyl, M=2H
111 R=*n*-C₆H₁₃, R¹=TMS-ethynyl, M=Ni(II)
112 R=*n*-C₆H₁₃, R¹=ethynyl, M=Ni(II)

Figure 3.2. A₃B-Type alkynylporphyrins as starting materials for the Pauson-Khand reaction.

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 ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$ 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 ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$ 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.¹⁰² Based on these studies they suggested the following order of reactivity for the thermal Pauson-Khand reaction: cyclohexene < cyclopentene < norbornene. Hence, ethynylporphyrin **108** was reacted with cyclohexene, norbornene 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 norbornene 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.^{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.

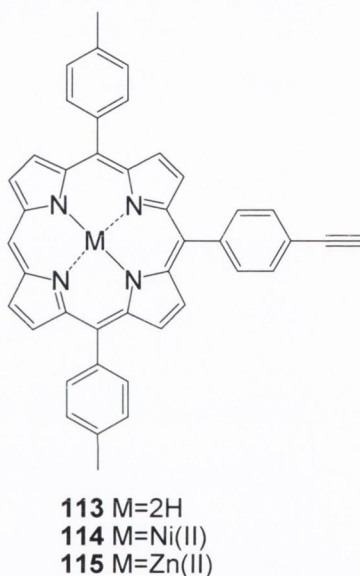
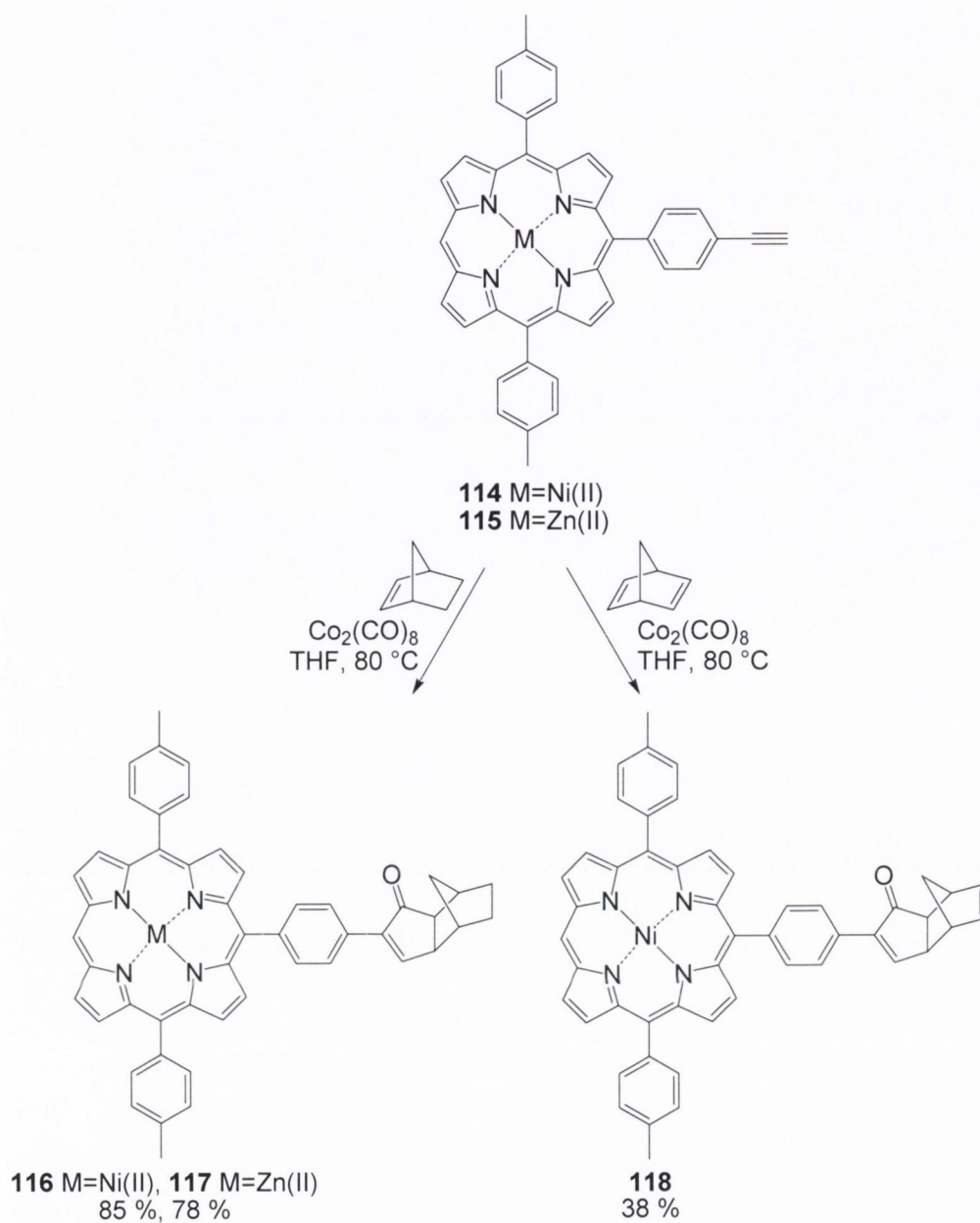


Figure 3.3. A₂B-Type alkynylporphyrins as starting materials for the Pauson-Khand reaction.

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 *exo*-face selective.¹²⁴⁻¹²⁸

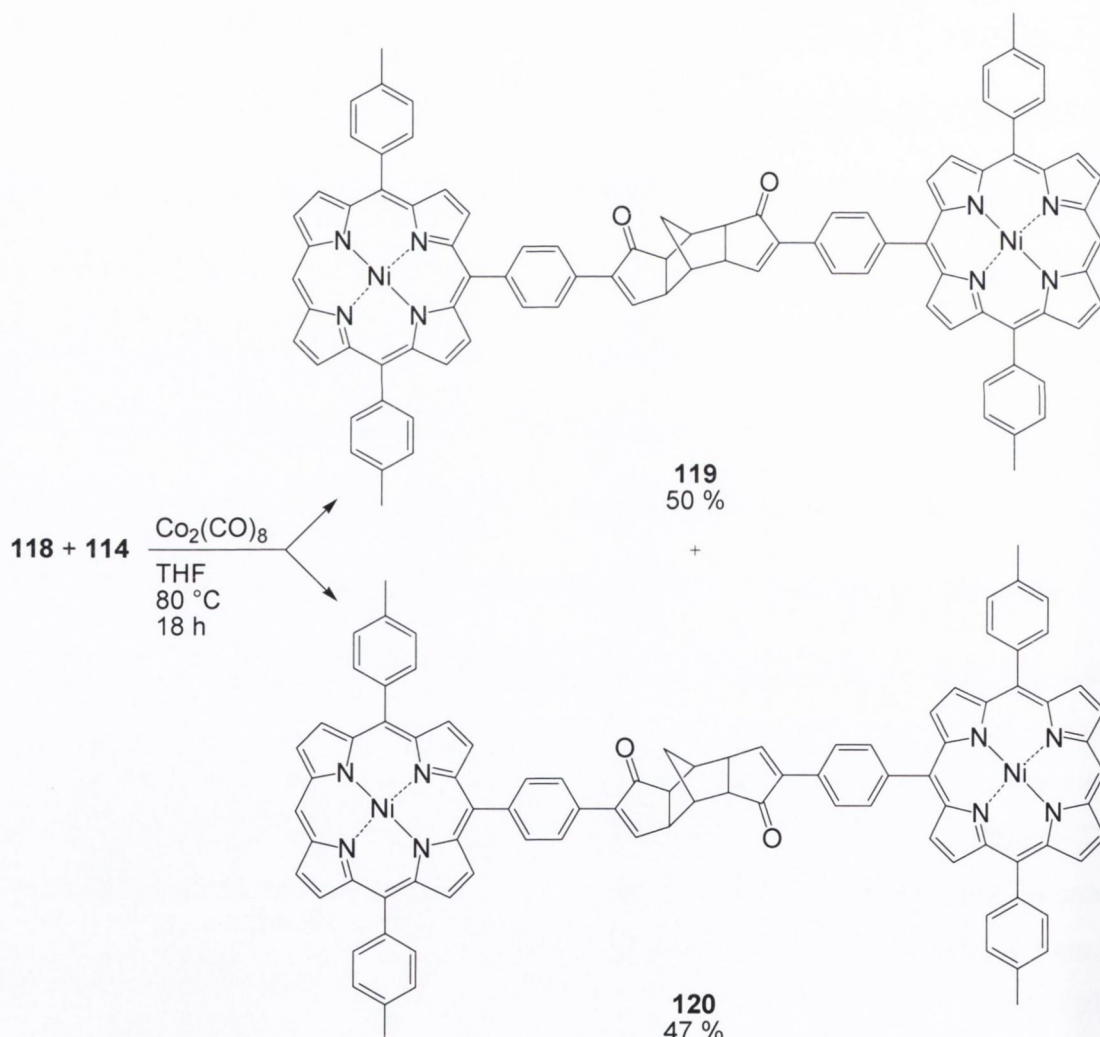


Scheme 3.7. The Pauson-Khand reaction of alkynylporphyrins.

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.¹²⁴ 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.¹²⁴ It was achieved by using an excess of the alkyne. Accordingly, norbornadiene was reacted with a two-fold excess of the alkynylporphyrin **114**. The main product of this reaction was the single Pauson-Khand product **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 **118** was reacted with alkynylporphyrin **114** and cobalt carbonyl (Scheme 3.8). Indeed, the two expected regioisomers **119** and **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 *exo*-face selective.¹²⁷



Scheme 3.8. Synthesis of porphyrin dimers *via* two step double Pauson-Khand reaction.

3.4 Spectroscopic Studies

3.4.1 ^1H 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 ^1H NMR spectra (Figure 3.4).

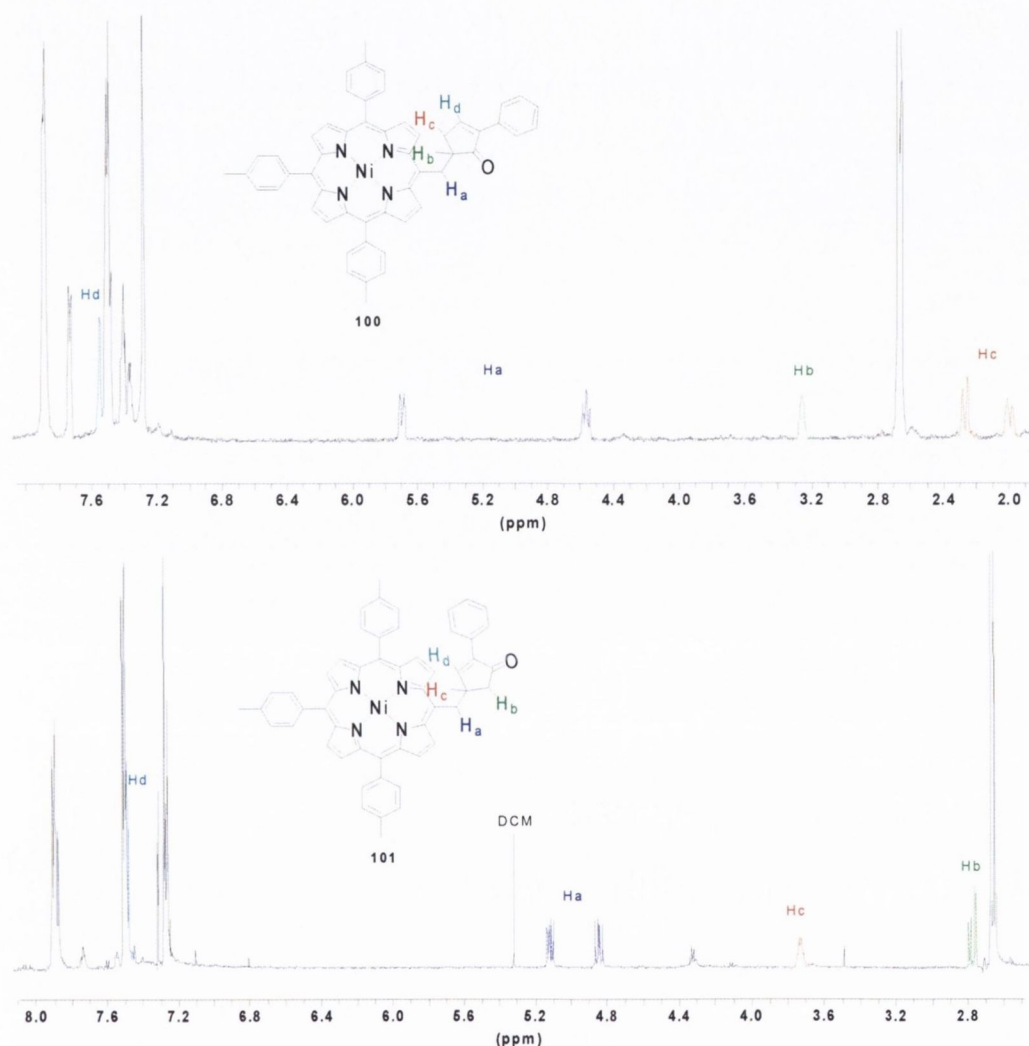


Figure 3.4. ^1H NMR spectra of compounds **100** and **101** in CDCl_3 .

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

100. These two sets of ^1H 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 ^1H 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.

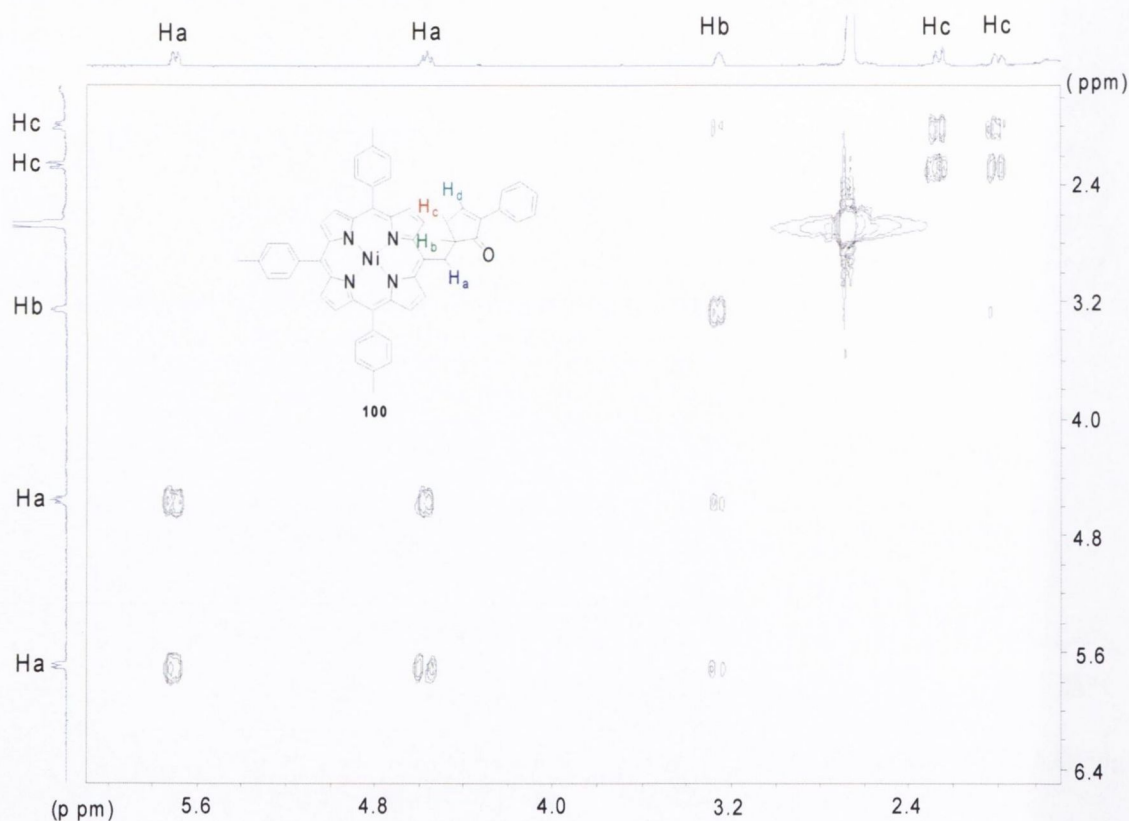


Figure 3.5. Section of HH-COSY of compound **100** in CDCl_3 .

The HH-COSY assignment was further proven by nuclear Overhauser 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 topspectrum

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 .

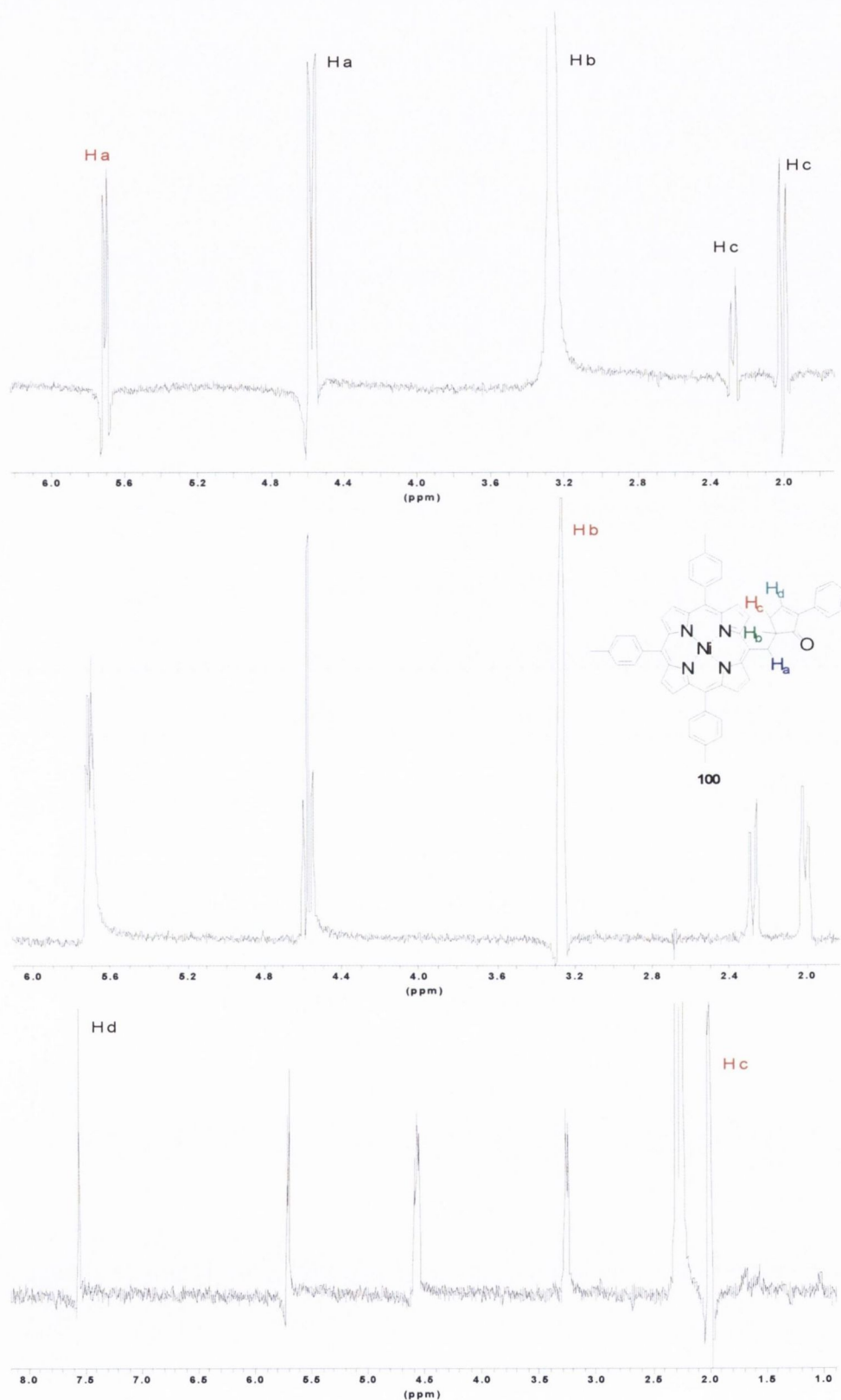


Figure 3.6. NOESY measurements of compound **100** in $CDCl_3$.

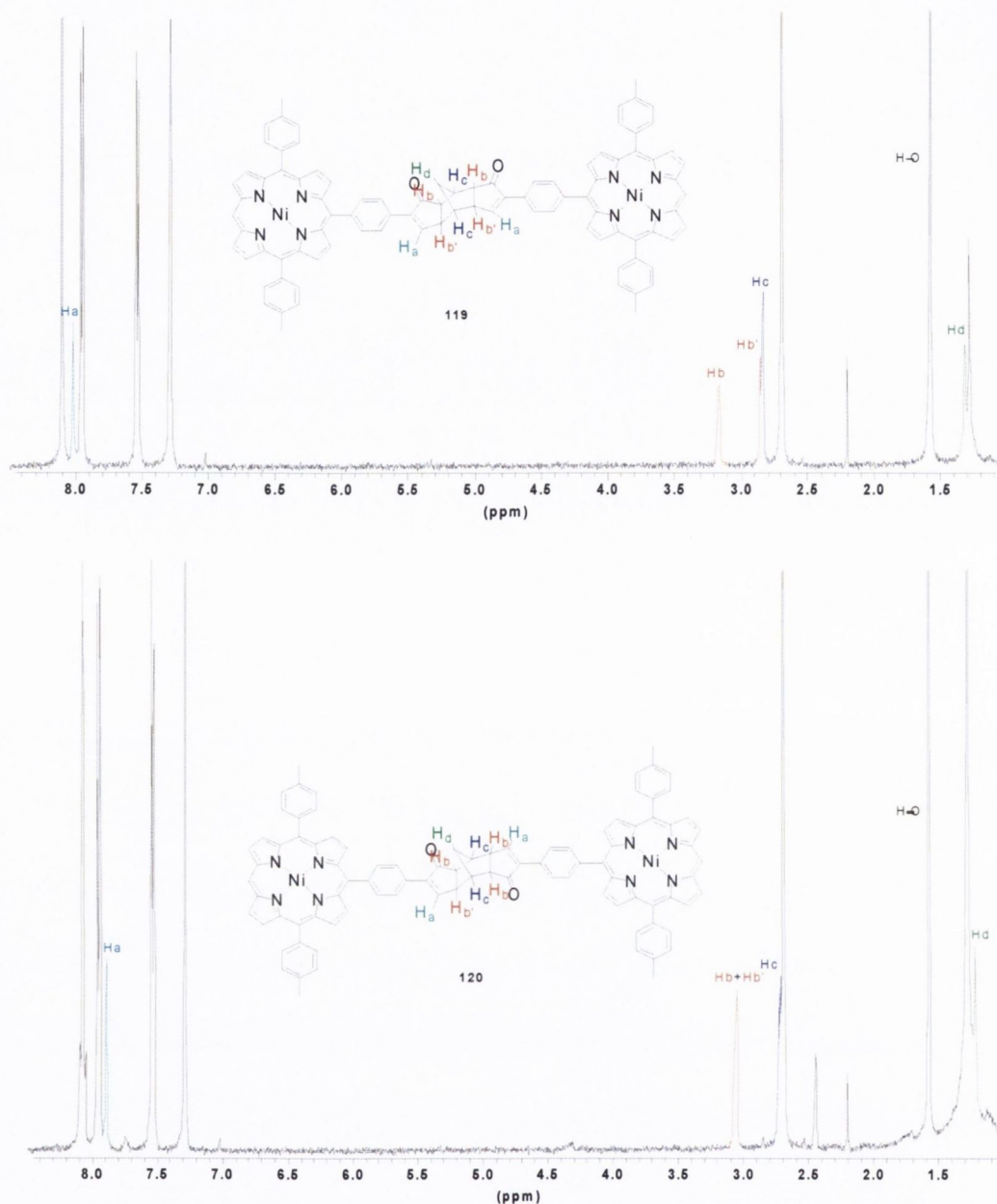


Figure 3.7. ^1H NMR spectra of compounds **119** and **120** in CDCl_3 .

The ^1H 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 ^1H 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 $H_{b'}$ at the 4-position of each cyclopentenone ring experience a completely different chemical environment, they appear in the 1H NMR as an individual peak at 2.84 ppm. The assignments of the 1H signals of the tetracyclic linker were achieved by comparison of the 1H NMR studies of Khand *et al.* carried out on the same tetracyclic unit.¹²⁴

On the other hand, compound **120** is point symmetrical and therefore its 1H NMR spectrum is “more symmetrical” in comparison to the spectrum of compound **119**. Previous studies of the two isomeric tetracyclic linkers have shown that the proton H_b , adjacent to the carbonyl group is rigidly held at a large angle.¹²⁴ Therefore, the influence of one carbonyl group on the protons H_b of compound **120** is not as big as the influence of two carbonyl groups as in compound **119**. Consequently, there is only one signal for all four H_b protons in the 1H NMR spectrum of compound **120** at 3.06 ppm, located between the two signals for H_b and $H_{b'}$ of compound **119**. The other proton signals, H_a , H_c and H_d , of the two isomeric tetracyclic linkers are not influenced by the different symmetries of compounds **119** and **120** and can therefore be found in the same regions in the 1H 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**.

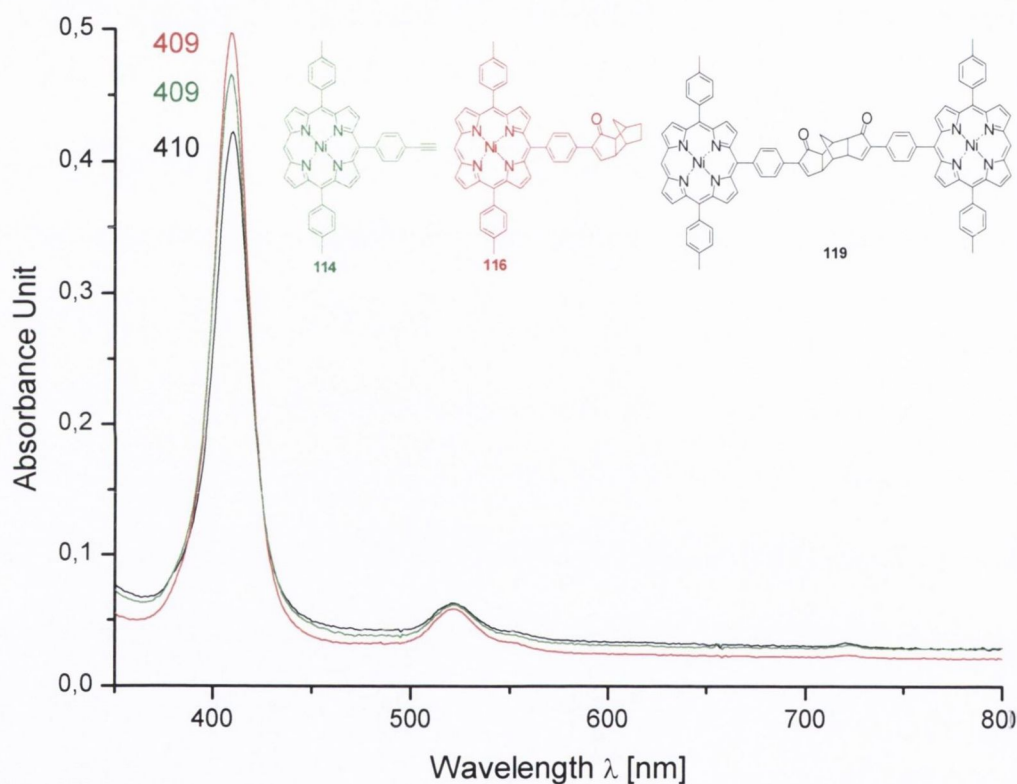


Figure 3.8. UV-vis spectra of compounds **114**, **116** and **119** in DCM at rt. Baselines were adjusted arbitrarily.

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.

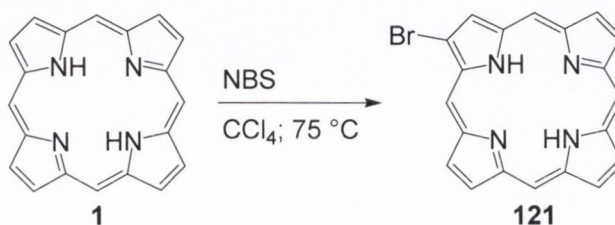
Additionally, porphyrins could serve as the alkene and alkyne reaction partner in a sequential double Pauson-Khand reaction to form regioisomeric porphyrin dimers in a nearly quantitative combined yield of 97 %. The two isomers could easily be separated by column chromatography and identified by ^1H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

Chapter 4:
C-H Bond Activation Reactions of
Porphin

4.1 Background

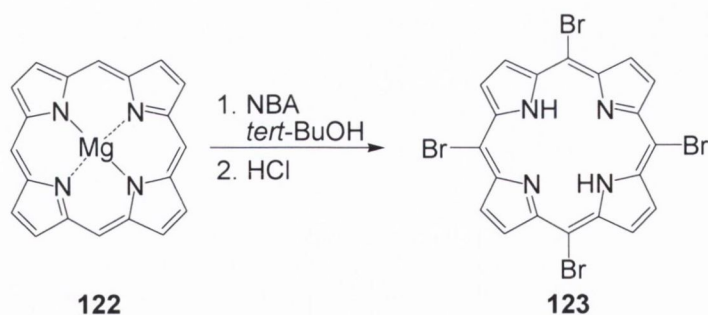
Porphyrin (porphin) is the parent nucleus of every natural and synthetic porphyrin. It seems quite obvious to use porphin as starting material for the synthesis of porphyrins.

Initial investigations on the reactivity of porphin were reported in the 1970's. Samuels *et al.* studied the halogenation of porphin.¹²⁹ Amongst these reactions, bromination was the most successful. Treatment of porphin **1** with *N*-bromosuccinimide (NBS) gave β -monobromoporphyrin **121** in 41 % yield (Scheme 4.1).



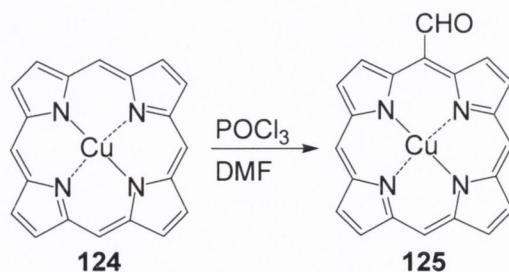
Scheme 4.1. β -Bromination of porphin.

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).¹³⁰



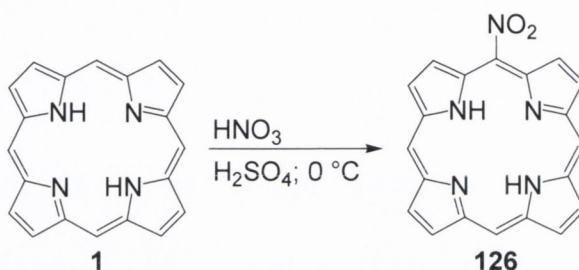
Scheme 4.2. Meso-bromination of (porphyrinato)magnesium(II).

They also reported the Vilsmeier formylation of (porphyrinato)copper(II) **124** to form (formylporphyrinato)copper(II) **125** (Scheme 4.3).¹³⁰



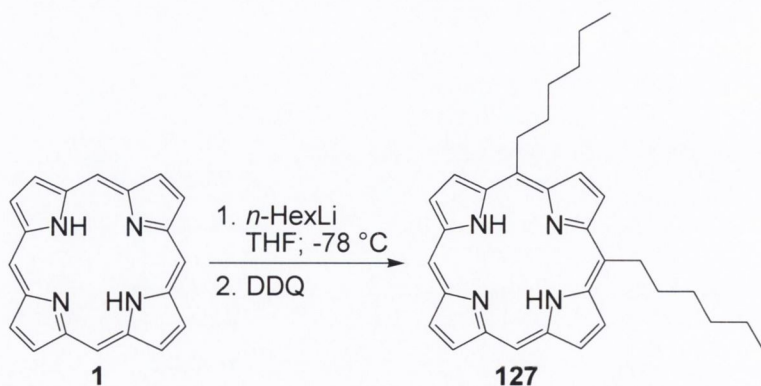
Scheme 4.3. The Vilsmeier formylation of (porphyrinato)copper(II).

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).¹³¹



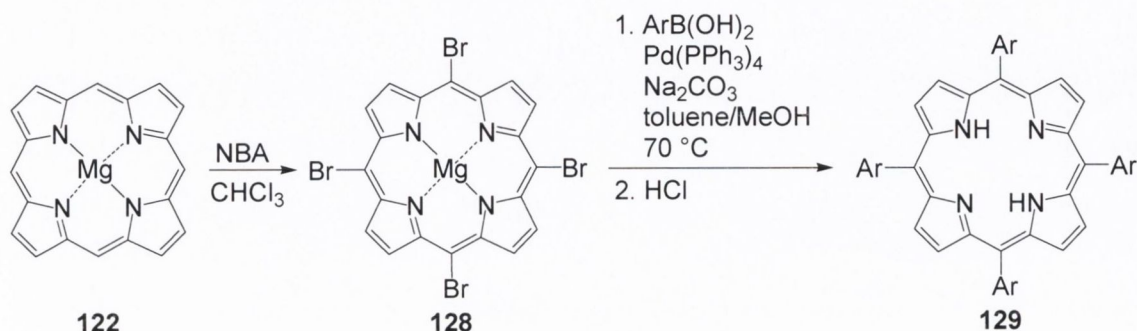
Scheme 4.4. Nitration of porphin.

Investigations of the reactivity of porphin were resumed nearly 30 years later after Neya and Funasaki published a straight-forward procedure for the preparation of porphin in a higher yield.¹³² Senge and co-workers reported the nucleophilic substitution reaction of porphin **1** with organolithium reagents.^{133,134} For instance, the reaction of porphin **1** with *n*-hexyllithium (5 equiv.) gave 5,10-dihexylporphyrin **127** in 61 % yield (Scheme 4.5).



Scheme 4.5. Nucleophilic substitution reaction of porphin.

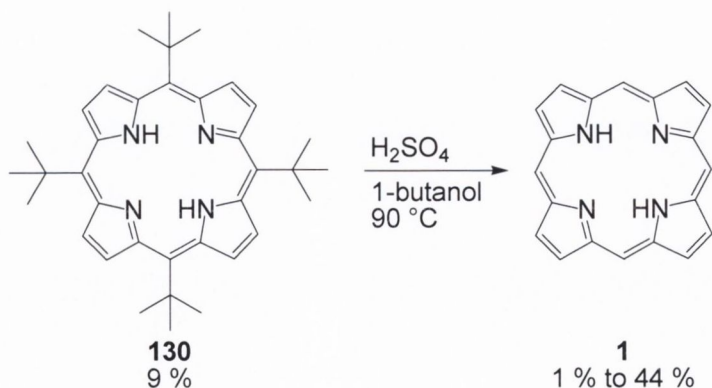
Shi and Wheelhouse reported the synthesis of tetraarylporphyrins directly from porphin **1** using the Suzuki cross-coupling reaction.¹³⁵ The first step involved bromination of (porphyrinato)magnesium(II) **122** using NBA to obtain (tetrabromoporphyrinato)magnesium(II) **128** in 81 % yield. The Suzuki 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.

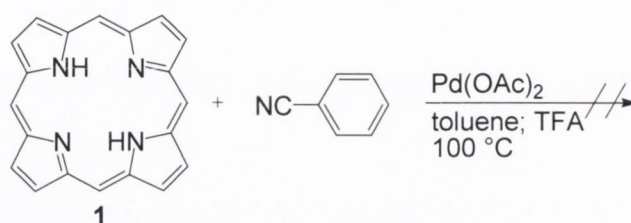
4.2 C-H Bond Activation Reactions of Porphin

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).¹³⁶ 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 %.¹³²



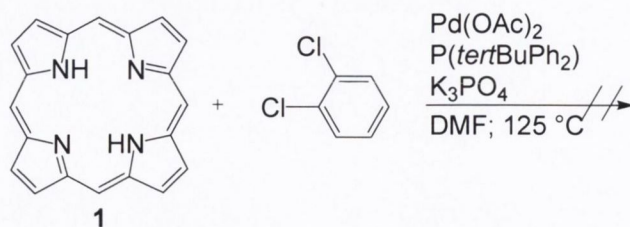
Scheme 4.7. Synthesis of porphin.

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 ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$ 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 ^1H NMR of the crude reaction mixture was recorded. Unfortunately, porphin was destroyed under these harsh acidic conditions.



Scheme 4.8. Attempted reaction of porphin with benzonitrile.

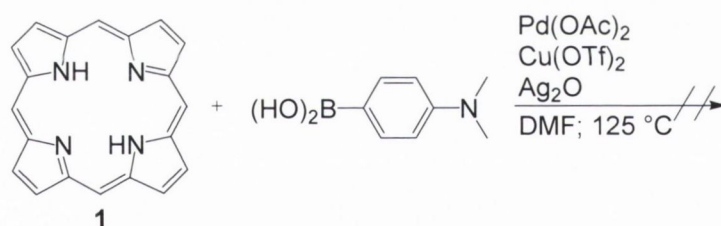
Therefore, a different type of C-H bond activation reaction was investigated using basic conditions. Based on the palladium(II) catalysed C-C bond formation of heterocycles with aryl chlorides,¹³⁹ porphin **1** was reacted with phenyldichloride (Scheme 4.9). Therefore, porphin **1** was dissolved in 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 ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$ 2:1, v/v). However, after 5 days no difference was observed and only porphin was recovered.



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.¹³⁵ 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.

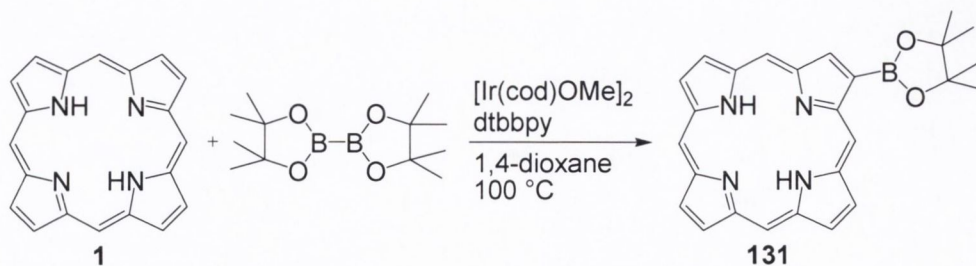
Another approach to C-H bond activation of porphin **1** using the Suzuki cross-coupling reaction was carried out.¹⁴⁰ Porphin **1** was reacted with 4-dimethylamino boronic acid and palladium(II) acetate (Scheme 4.10). Therefore, porphin **1** was dissolved in anhydrous DMF in a Schlenk-tube under argon 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.



Scheme 4.10. Attempted Suzuki coupling of porphin by C-H activation reaction.

The only known C-H bond activation reaction on porphyrins is the iridium(II) catalysed β -borylation developed by Osuka and co-workers.⁵¹ 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 ¹H 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.

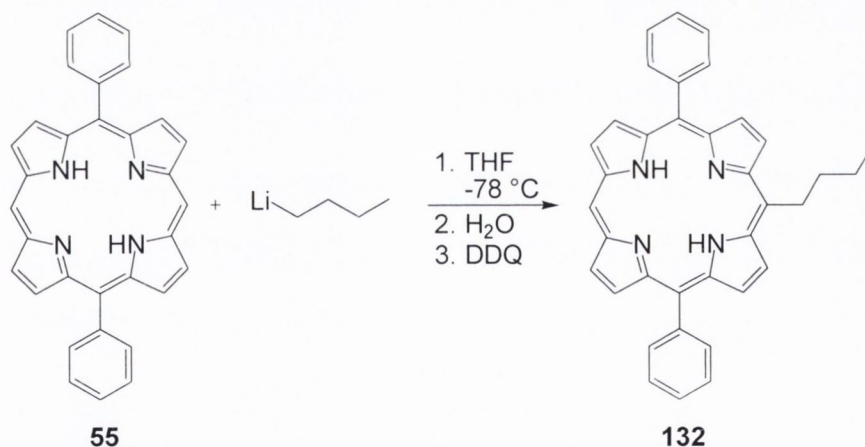
While the extension of new reactions of porphin for the synthesis of porphyrins seemed to be promising, this project turned out to be quite tedious considering the varying yield in porphin synthesis as well as the difficulties with the reactivity of porphin.

Chapter 5:
Rhodium(1) Catalysed Alkylation of
Porphyrin

5.1 Background

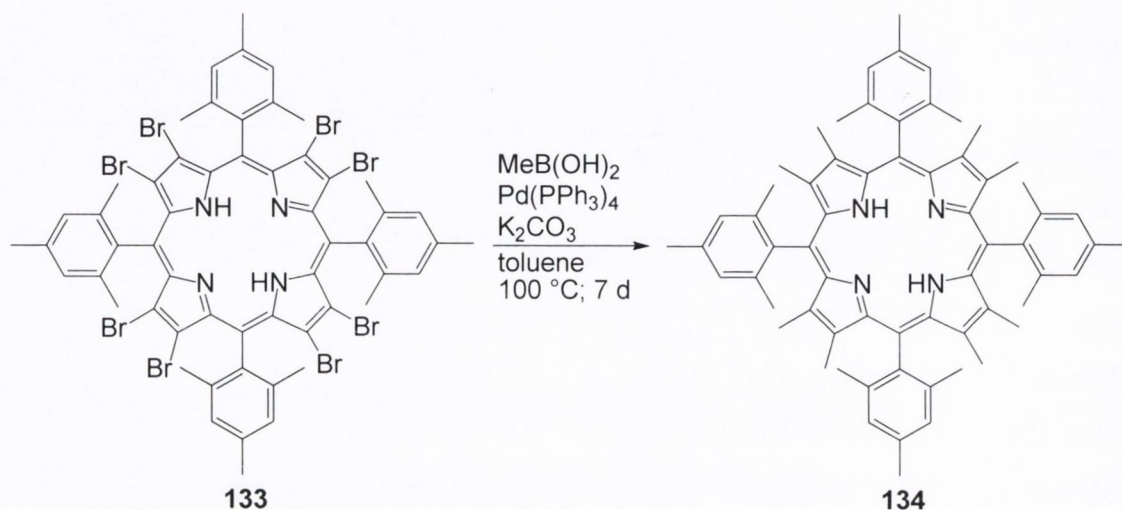
The introduction of alkyl-substituents onto the porphyrin macrocycle is of considerable interest for the synthesis of amphiphilic compounds suitable for PDT and the design of push-pull porphyrins for applications in NLO.^{141,142} However, apart from total synthesis, there is only a limited number of 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.¹⁹ Senge and Feng reported the synthesis of various alkyl-substituted porphyrins with or without functional groups on the alkyl chain.¹⁴³ For instance, the reaction of 5,15-diphenylporphyrin **55** with *n*-butyllithium gave 5-butyl-10,15-diphenylporphyrin **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.



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).¹⁴⁴



Scheme 5.2. Alkylation of porphyrin via Suzuki cross-coupling reaction.

5.2 Rhodium(1) Catalysed Alkylation of Porphyrin

Due to the limited number of procedures available for alkylation of porphyrins, a new method was investigated. The candidate: a rhodium(1) cross-coupling reaction between alkyl halides and a zinc(I) ring-metallated porphyrin, according to a literature procedure for arenes.¹⁴⁵

Zinc(I) ring-metallated porphyrins were reported previously, and used for a palladium(II) catalysed cross-coupling reaction with iodoarenes.¹⁴⁶ To broaden this procedure to iodoalkanes, the palladium(II) catalyst was unsuitable as it promotes β -hydrogen elimination of the iodoalkanes.¹⁴⁷ However, it was found that this side-reaction could be inhibited by exchanging palladium(II) with rhodium(1).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.¹⁴⁸ Halogenation of compound **135** with iodine and NBS gave porphyrins **136** and **137** in 68 % and 81 % yield, respectively.^{71,149} 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.⁷⁶ 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.¹⁴⁸

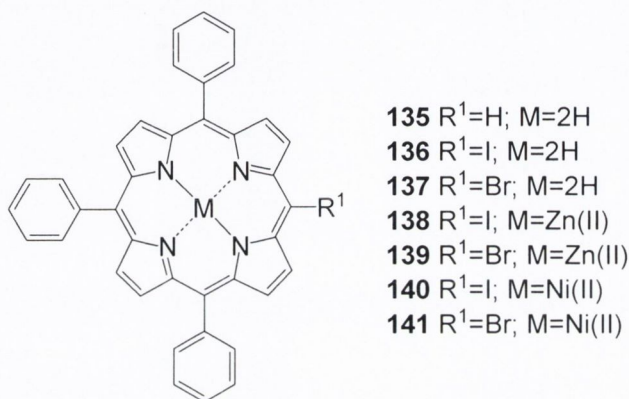
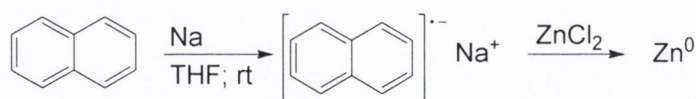


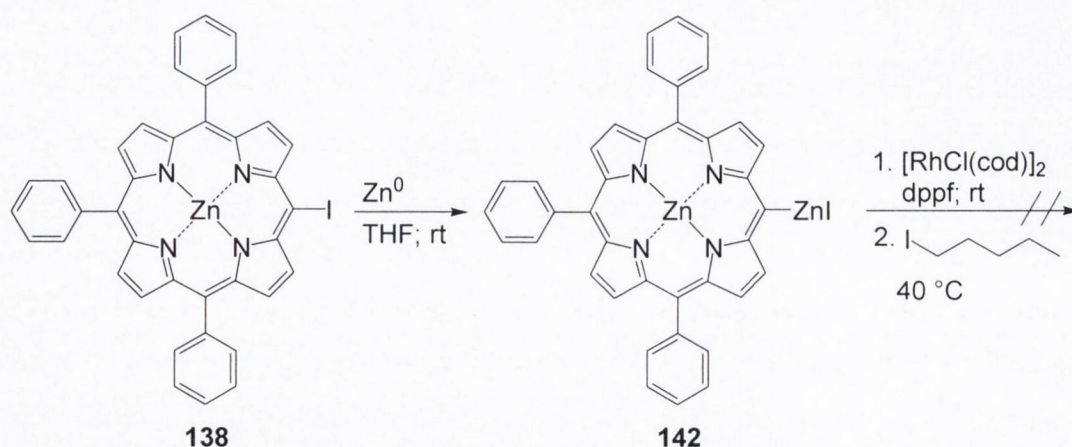
Figure 5.1. Starting materials for rhodium(I) catalysed alkylation reaction.

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).¹⁵⁰⁻¹⁵³



Scheme 5.3. Preparation of Rieke-zinc(0).

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).¹⁴⁶ Subsequently, the rhodium(II) catalyst and 1,1'-bis(diphenylphosphino)ferrocene (dppf) were added to the reaction mixture to generate the rhodium(I) catalyst, Rh-dppf, before iodopentane was added. The reaction was stopped after five days as no change was observed by TLC and only starting material was recovered.

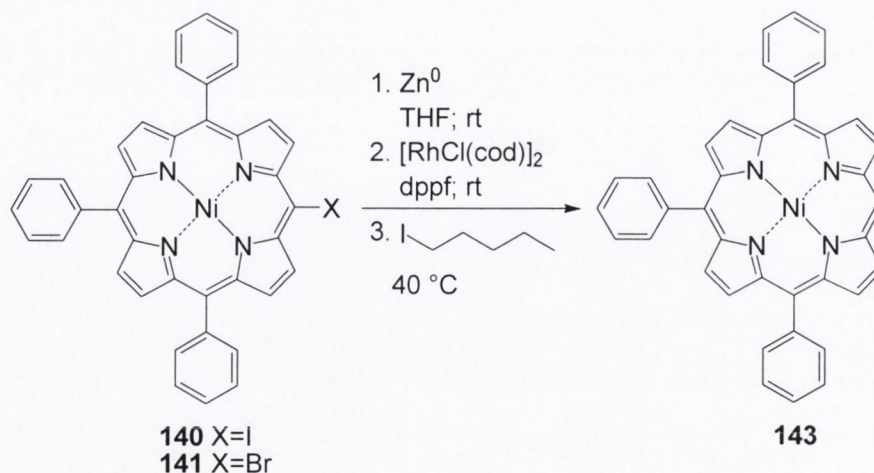


Scheme 5.4. Proposed rhodium(1) catalysed alkylation reaction of zinc(II) porphyrin using Rieke-zinc(0).

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.

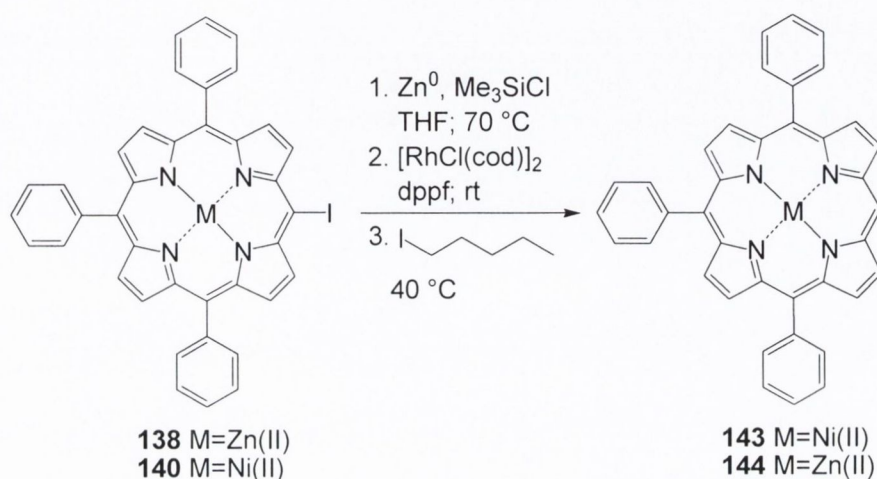
The bromo-substituted compound **139** was also subjected to the reaction conditions using a higher temperature of 80°C after addition of iodopentane. This alteration was unsuccessful and only starting material was recovered.

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



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.¹⁵⁴ Compounds **138** and **140** were reacted with activated zinc(0) and trimethylsilyl chloride at 70 °C before the addition of rhodium(I) catalyst and iodopentane (Scheme 5.6). However, only dehalogenation took place and compounds **143** and **144** were generated from the reaction mixture.⁷⁶ 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).^{153,154} Therefore, intermediate **142** could not be isolated nor detected by TLC.

5.3 Conclusions

A rhodium(1) catalysed alkylation reaction was investigated for porphyrins. This included the *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(1) 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.

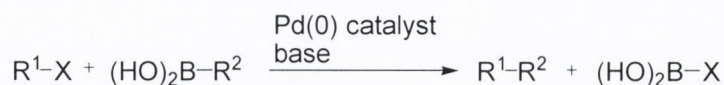
This investigated reaction seemed to be a highly promising pathway for the introduction of alkyl-substituents onto the porphyrin macrocycle, especially as a similar reaction using zinc(I) ring-metallated porphyrins was reported, previously. However, this method contains a large number of uncertainties since reagents as well as intermediates were formed *in situ*. Therefore, 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.

Chapter 6:
Suzuki Reaction of Potassium
Organotrifluoroborates with
Porphyrins

6.1 Background

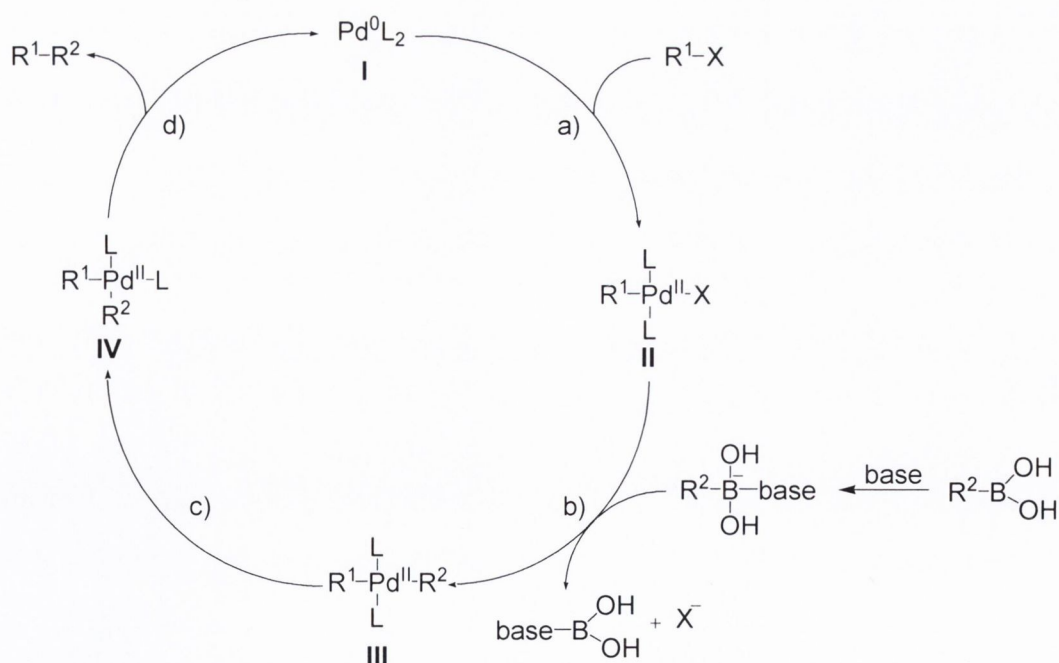
The Suzuki cross-coupling reaction owes its popularity to the fact that it is a very straight-forward method with a high regio- and stereoselectivity as well as tolerance towards a wide range of functional groups.¹⁵⁵

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).



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.

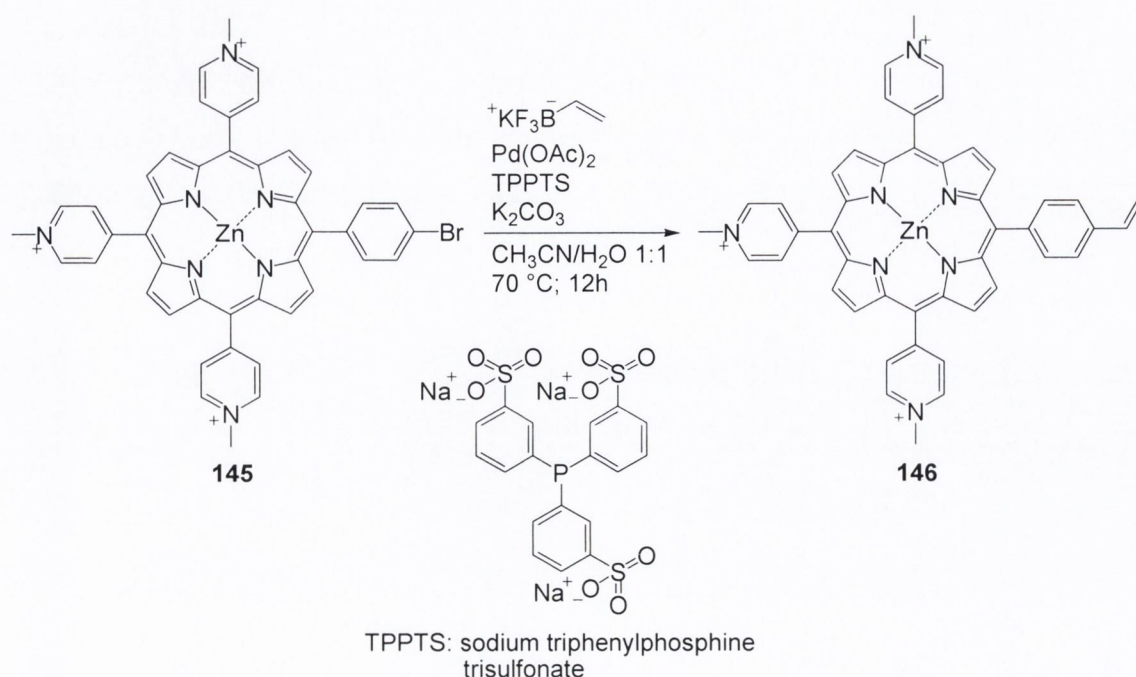
The Suzuki cross-coupling reaction is a very important tool for the synthesis of new porphyrin species and represents the most popular method among palladium catalysed reactions.⁶⁴ It has been extensively studied on every position of the porphyrin as well as in every possible way: the β -position,³⁹ the meso-position,⁴⁰ on aryl-substituents¹⁵⁷ 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, Molander 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.



Scheme 6.3. Suzuki coupling reaction of potassium vinyltrifluoroborate with cationic porphyrin.

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.

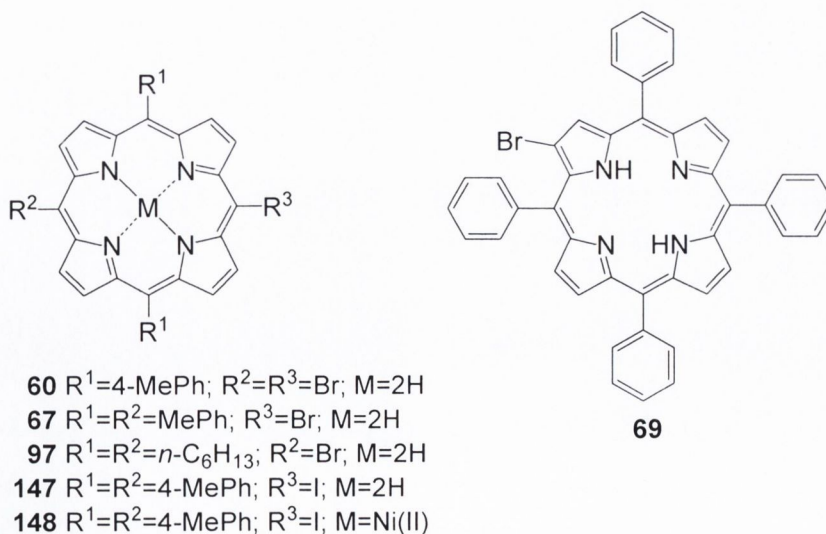
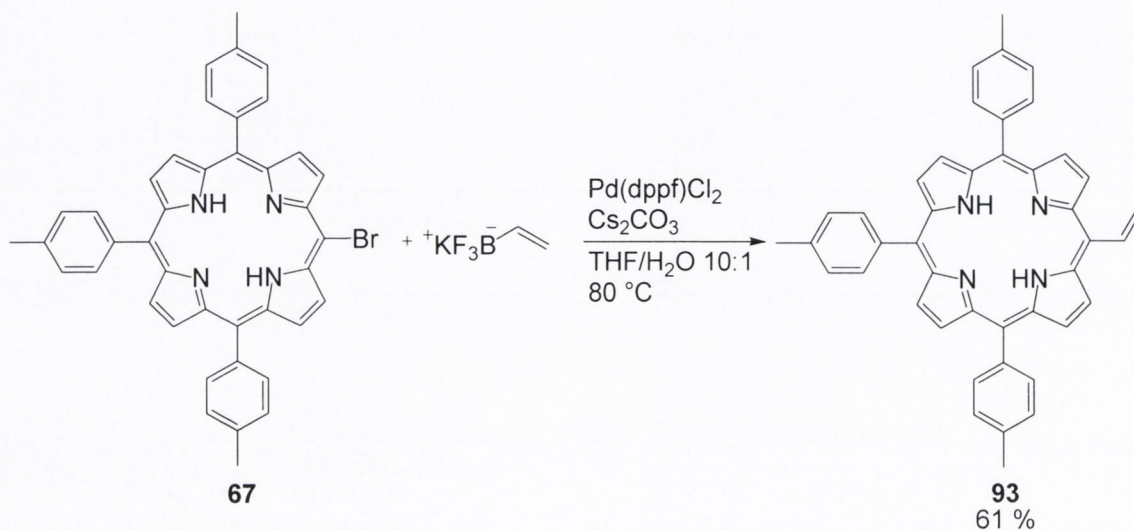


Figure 6.1. Starting materials for reaction with potassium organotrifluoroborates.

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.*^{162,165} were changed and optimised according to standard conditions for the Suzuki coupling reaction of meso-brominated porphyrins,⁴⁰ and vinylporphyrin **93** was obtained in 61 % yield.¹⁶⁶

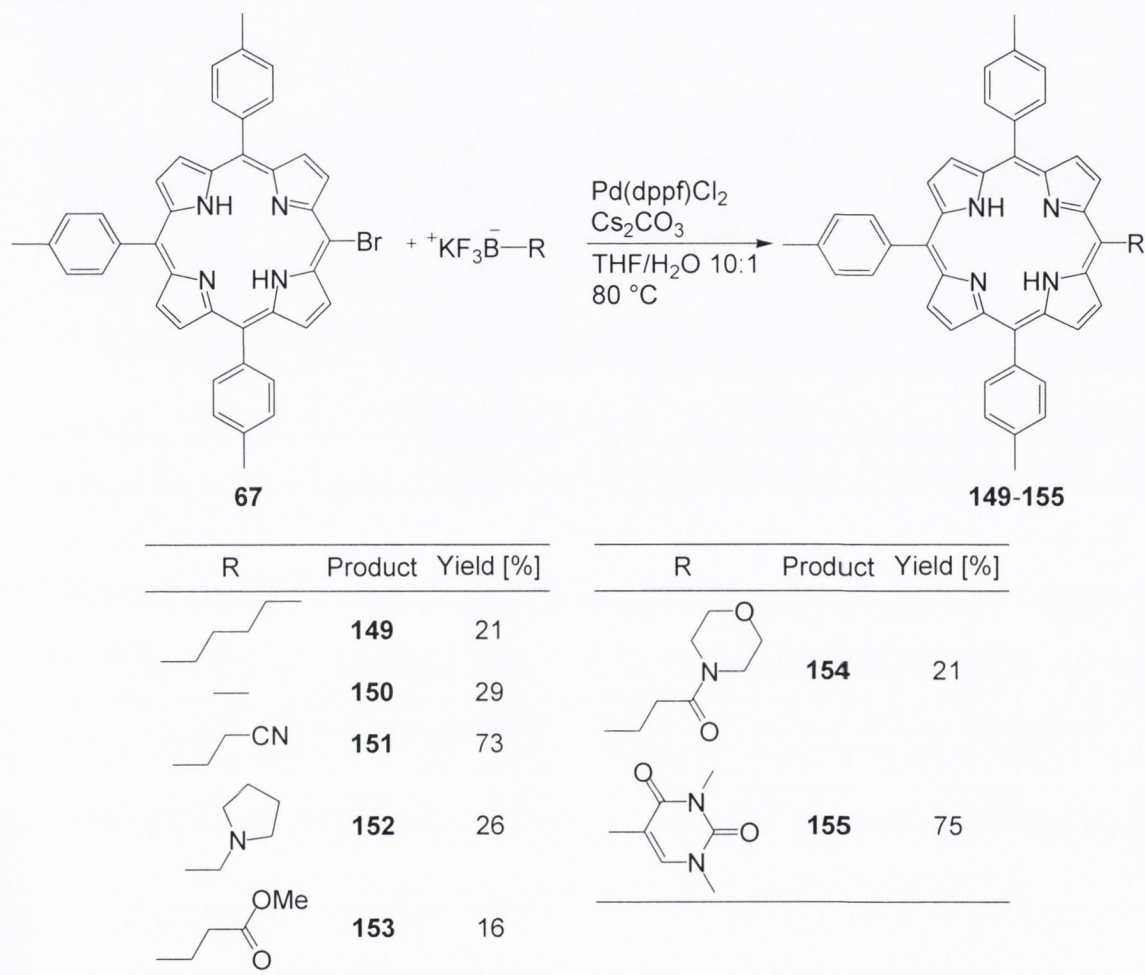


Scheme 6.4. Suzuki coupling reaction of potassium vinyltrifluoroborate with meso-bromoporphyrin.

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).⁷⁵ 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.¹⁶²

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.¹⁶⁷⁻¹⁶⁹



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**, β -brominated compound **69** and the dibromo-A₂B₂ 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).⁷²

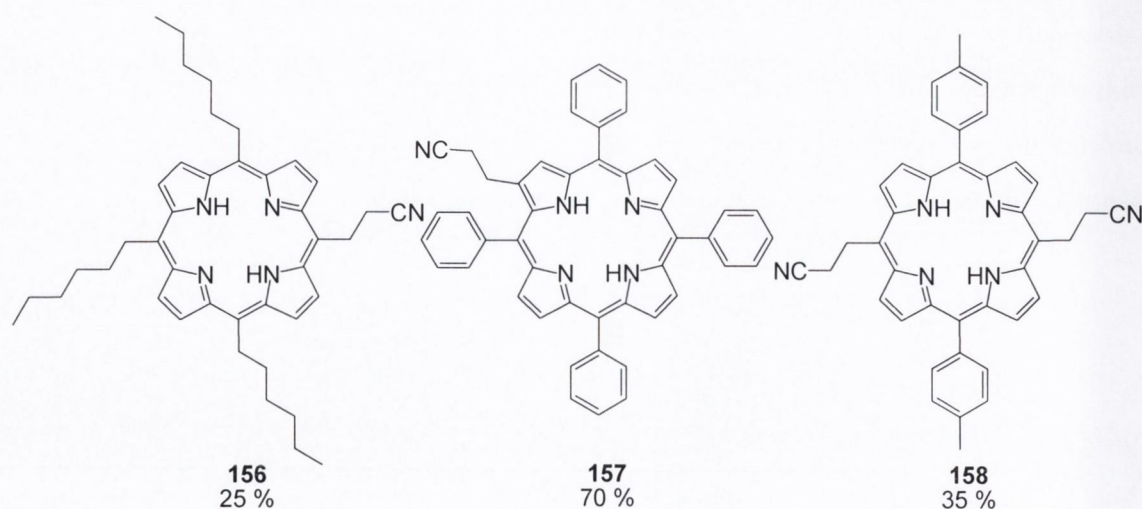
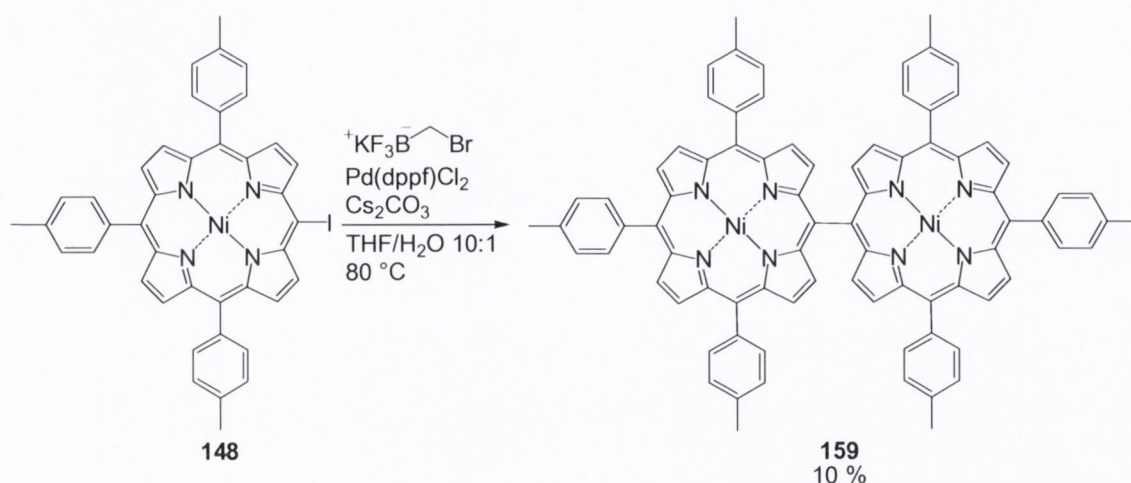


Figure 6.2. Products of Suzuki coupling reaction with potassium cyanoethyltrifluoroborates.

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 A_2B_2 -porphyrin **158** is significantly lower than that of A_3B -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 β -monobrominated porphyrin **69** was very small. The β -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**.



Scheme 6.6. Suzuki coupling reaction of potassium bromomethyltrifluoroborate with porphyrin **148**.

6.3 Spectroscopic Studies

6.3.1 ${}^1\text{H}$ NMR Spectroscopy

As mentioned earlier the ${}^1\text{H}$ 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.⁹⁰ 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 ${}^1\text{H}$ NMR spectra of meso-cyanoethyl-substituted compound **151** with β -cyanoethyl-substituted porphyrin **157** (Figure 6.3). The ${}^1\text{H}$ 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 ${}^1\text{H}$ 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.

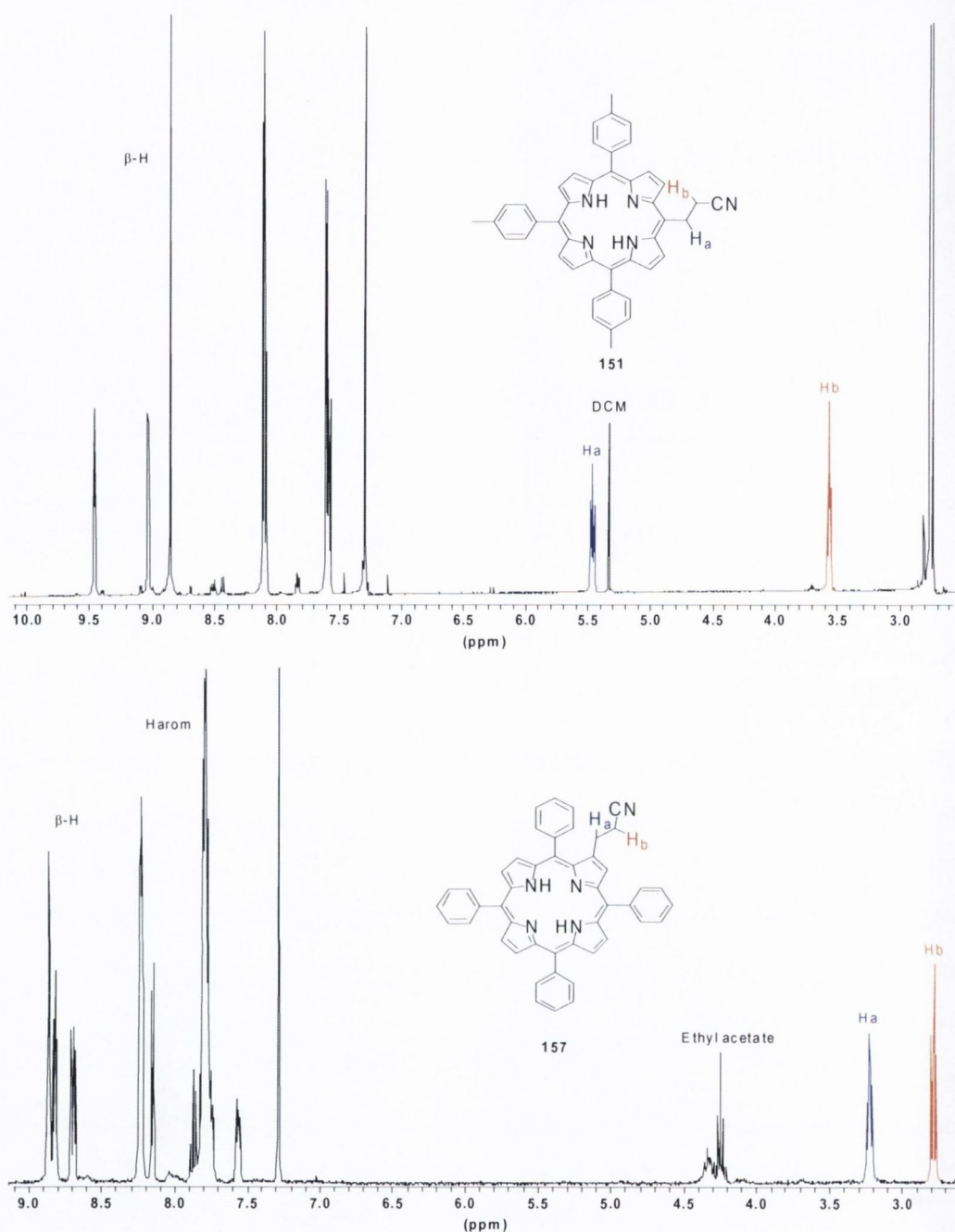


Figure 6.3. ^1H NMR spectra of compounds **151** and **157** in CDCl_3 .

The substituent at the β -position of compound **157** also effects the location of the β -protons in the spectrum. Alkyl-substituents at the β -position of porphyrins have a shielding effect on the macrocycle.¹⁷⁰ Therefore, the signals for the β -protons of compound **157** are shifted towards higher field at 8.67 ppm to 8.87 ppm. In comparison, the signals for the β -protons of β -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**.

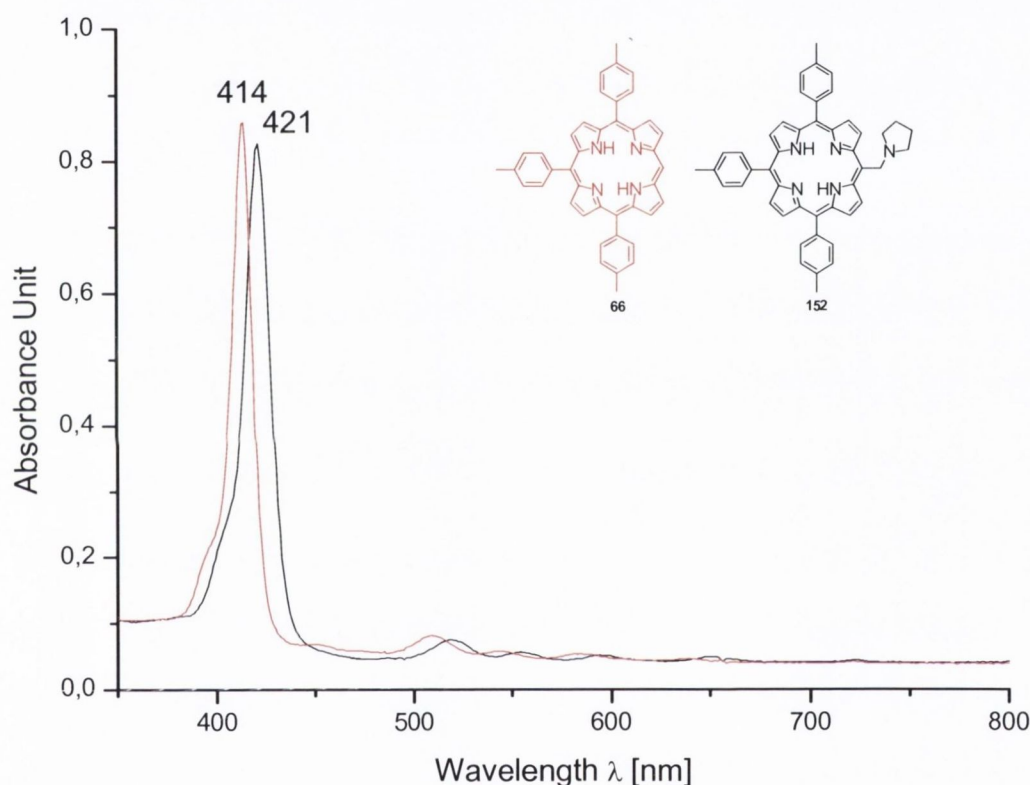


Figure 6.4. UV-vis spectra of compounds **66** and **152** in DCM at rt. Baselines were adjusted arbitrarily.

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.^{171,172} Therefore, two wavelengths can be observed for the Soret band at 418 nm and 447 nm.

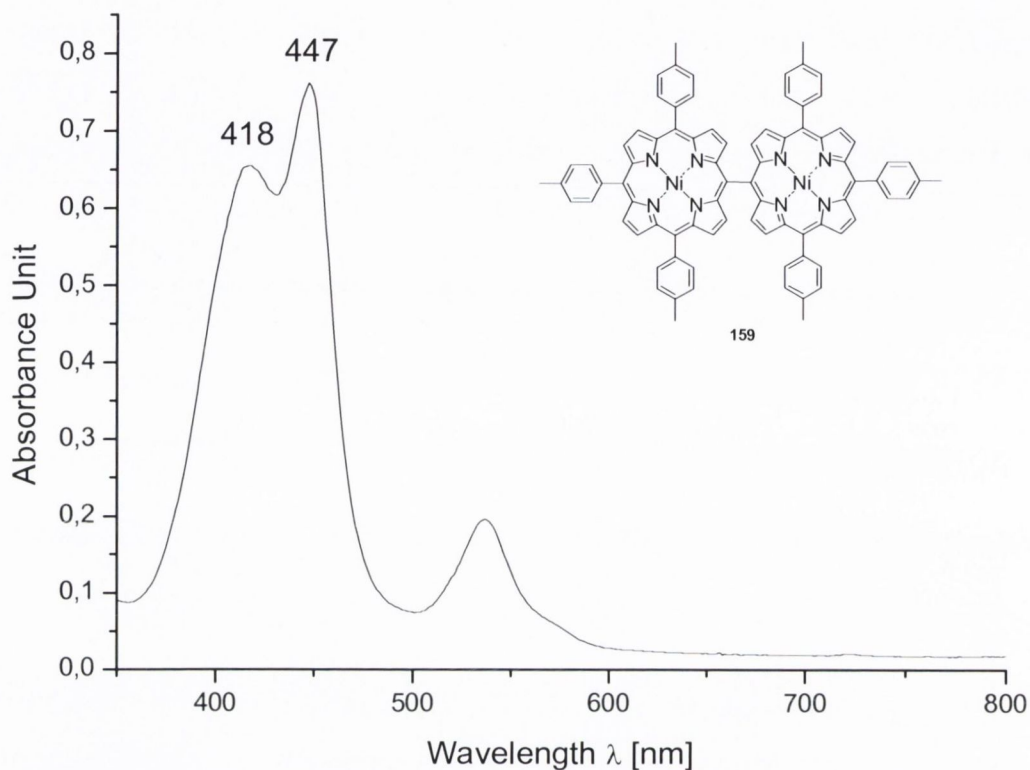


Figure 6.5. UV-vis spectra of compound **159** in DCM at rt. Baselines were adjusted arbitrarily.

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:

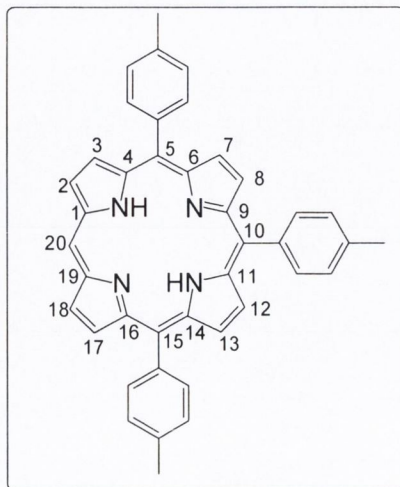
Experimental

7.1 Instrumentation and General Considerations

^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 (400.13 MHz for ^1H NMR; 100.61 MHz for ^{13}C NMR) and/or Bruker AV 600 (600.13 MHz for ^1H 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*TM 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 60F₂₅₄ (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 Al₂O₃ (basic) and degassed with argon for 10 min before it was used. Pd(dppf)₂Cl₂ and potassium organotrifluoroborates were provided by Frontier Scientific, Inc. All commercial chemicals were supplied by Aldrich and used without further purification.

7.2 Allylporphyrins

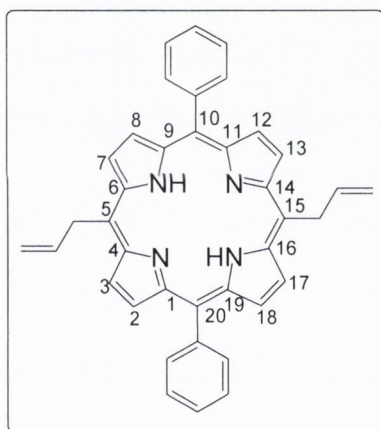
7.2.1 Synthesis of Starting Materials



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 °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 °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 CH₂Cl₂/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

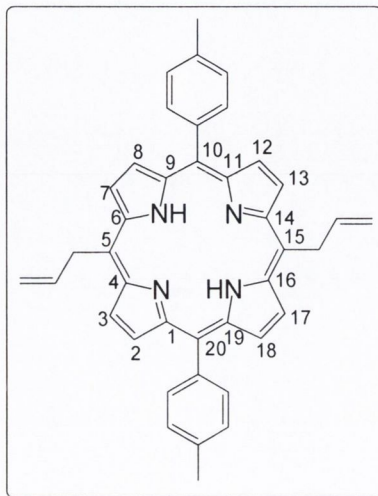
7.2.2 Synthesis of Allylporphyrins

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.), $\text{Pd}(\text{PPh}_3)_4$ (0.1 equiv.) and K_3PO_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 ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$, 1:1, v/v).

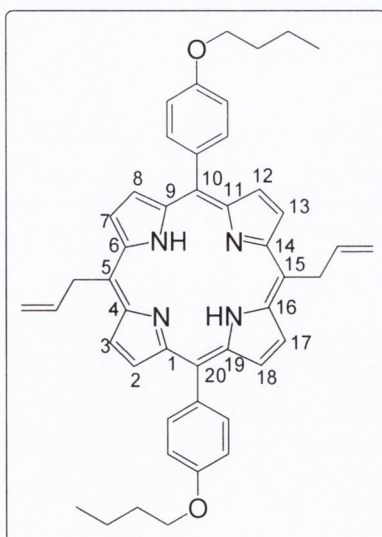


5,15-Diallyl-10,20-diphenylporphyrin 70. By using 5,15-dibromo-10,20-diphenylporphyrin **59** (100 mg, 0.16 mmol) as starting material, allylboronic acid pinacol ester (0.6 mL, 3.2 mmol, 20 equiv.), K_3PO_4 (1.4 g, 6.4 mmol, 40 equiv.) and $\text{Pd}(\text{PPh}_3)_4$ (18 mg, 0.016 mmol) the product was obtained in 68.2 mg (0.126 mmol, 78 %) yield of purple crystals: mp >300 °C; R_f =0.42 ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$, 2:1, v/v); ^1H NMR (400 MHz, CDCl_3): δ =−2.63 (s, br, 2H, NH), 5.16 (d, 3J =17.0 Hz, 2H, $\text{CH}_2\text{CH}=\text{CHH}$), 5.24 (d, 3J =9.9 Hz, 2H, $\text{CH}_2\text{CH}=\text{CHH}$), 5.76 (d, 3J =5.2 Hz, 4H, $\text{CH}_2\text{CH}=\text{CH}_2$), 6.86 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 7.78 (m, 6H, H_{Ar}), 8.22 (m, 4H, H_{Ar}), 8.89 (d, 3J =4.7 Hz, 4H, H_β), 9.44 (d, 3J =4.7 Hz, 4H, H_β) ppm; ^{13}C NMR (100.6 MHz, CDCl_3): δ =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:

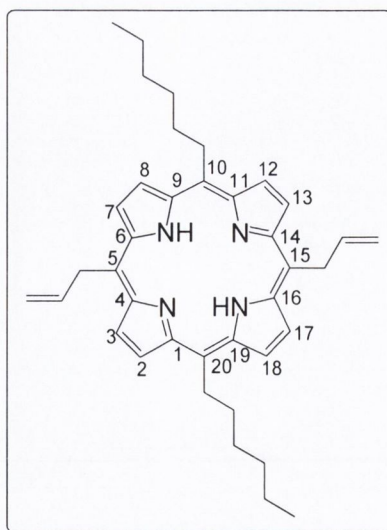
3331 (NH), 3071 (C=CH₂), 3006 (Ar-H), 2921 (CH₂) cm⁻¹; UV/vis (CH₂Cl₂): $\lambda_{\max}$ (lg ϵ)=417 (5.6), 514 (4.5), 549 (4.4), 600 (4.4), 656 (4.4) nm; HRMS (ES⁺): calcd for C₃₈H₃₀N₄ [M+H]⁺ 543.2543, found 543.2549.



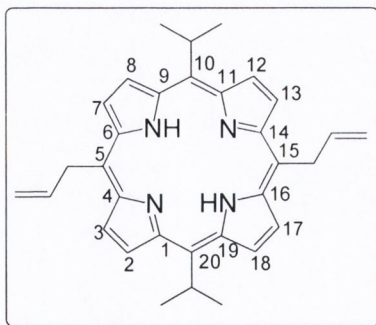
5,15-Diallyl-10,20-bis(4-methylphenyl)porphyrin 71. By using 5,15-dibromo-10,20-bis(4-methylphenyl)porphyrin **60** (100 mg, 0.154 mmol) as starting material, allylboronic acid pinacol ester (0.6 mL, 3.08 mmol, 20 equiv.), K₃PO₄ (1.3 g, 6.16 mmol, 40 equiv.) and Pd(PPh₃)₄ (18 mg, 0.0154 mmol) product was obtained in 55 mg (0.096 mmol, 62 %) yield of dark purple crystals: mp >300 °C; R_f=0.60 (CH₂Cl₂/C₆H₁₄, 1:1, v/v); ¹H NMR (600 MHz, CDCl₃): δ =-2.63 (s, br, 2H, NH), 2.75 (s, 6H, C₆H₄CH₃), 5.16 (d, ³J=17.0 Hz, 2H, CH₂CH=CHH), 5.24 (d, ³J=10.5 Hz, 2H, CH₂CH=CHH), 5.76 (d, ³J=5.5 Hz, 4H, CH₂CH=CH₂), 6.86 (m, 2H, CH₂CH=CH₂), 7.59 (d, ³J=7.2 Hz, 4H, H_{Ar}), 8.10 (d, ³J=7.2 Hz, 4H, H_{Ar}), 8.92 (d, ³J=4.4 Hz, 4H, H_β), 9.43 (d, ³J=4.4 Hz, 4H, H_β) ppm; ¹³C NMR (100.6 MHz, CDCl₃): δ =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): $\lambda_{\max}$ (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.



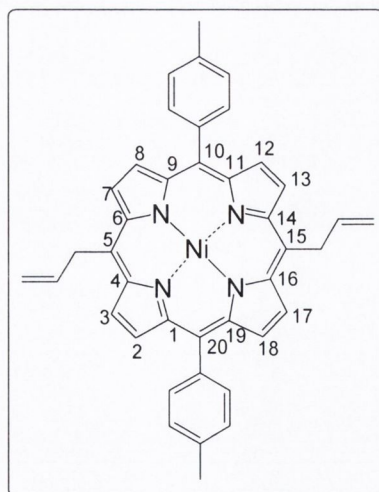
5,15-Diallyl-10,20-bis(4-butoxyphenyl)porphyrin 72. By using 5,15-dibromo-10,20-bis(4-butoxyphenyl)porphyrin **61** (100 mg, 0.131 mmol) as starting material, allylboronic acid pinacol ester (0.5 mL, 2.62 mmol, 20 equiv.), K_3PO_4 (1.1 g, 5.24 mmol, 40 equiv.) and $Pd(PPh_3)_4$ (15 mg, 0.0131 mmol) the product was obtained in 45 mg (0.08 mmol, 50 %) yield of purple crystals: mp $>300\text{ }^\circ\text{C}$; $R_f=0.71$ (CH_2Cl_2/C_6H_{14} , 2:1, v/v); 1H NMR (400 MHz, $CDCl_3$): $\delta=-2.62$ (s, br, 2H, NH), 1.15 (t, 6H, $^3J=7.5$ Hz, $OC_3H_6CH_3$), 1.71 (m, 4H, $OC_2H_4CH_2CH_3$), 2.01 (m, 4H, $OCH_2CH_2C_2H_5$), 4.29 (t, $^3J=6.4$ Hz, 4H, $OCH_2C_2H_5CH_3$), 5.16 (d, $^3J=17.0$ Hz, 2H, $CH_2CH=CHH$), 5.23 (d, $^3J=9.9$ Hz, 2H, $CH_2CH=CHH$), 5.75 (d, $^3J=5.5$ Hz, 4H, $CH_2CH=CH_2$), 6.85 (m, 2H, $CH_2CH=CH_2$), 7.29 (d, $^3J=7.9$ Hz, 4H, H_{Ar}), 8.10 (d, $^3J=8.5$ Hz, 4H, H_{Ar}), 8.92 (d, $^3J=5.0$ Hz, 4H, H_β), 9.42 (d, $^3J=5.0$ Hz, 4H, H_β) 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_2Cl_2): λ_{max} (lg ϵ)=421 (5.8), 447 (5.1), 519 (4.8), 555 (4.7), 598 (4.7) nm; HRMS (ES $^+$): calcd for $C_{46}H_{46}N_4O_2$ $[M+H]^+$ 687.3699, found 687.3673.



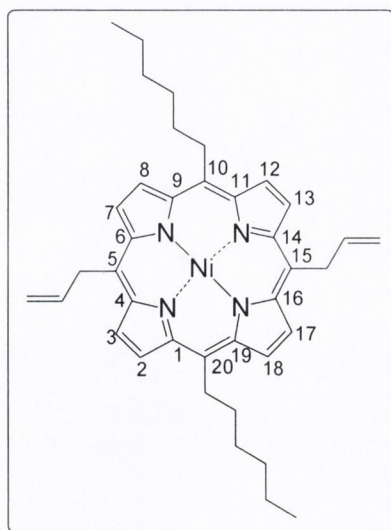
5,15-Diallyl-10,20-dihexylporphyrin 73. By using 5,15-dibromo-10,20-dihexylporphyrin **62** (100 mg, 0.16 mmol) as starting material, allylboronic acid pinacol ester (0.6 mL, 3.2 mmol, 20 equiv.), K_3PO_4 (1.4 g, 6.4 mmol, 40 equiv.) and $Pd(PPh_3)_4$ (18 mg, 0.016 mmol) the product was obtained in 45 mg (0.08 mmol, 50 %) yield as purple needles: mp 167 °C; $R_f=0.64$ (CH_2Cl_2/C_6H_{14} , 1:1, v/v); 1H NMR (600 MHz, $CDCl_3$): $\delta=-2.62$ (s, br, 2H, NH), 0.95 (t, $^3J=7.0$ Hz, 6H, $C_5H_{10}CH_3$), 1.41 (m, 4H, $C_4H_8CH_2CH_3$), 1.52 (m, 4H, $C_3H_6CH_2CH_2CH_3$), 1.82 (m, 4H, $C_2H_4CH_2C_2H_4CH_3$), 2.51 (m, 4H, $CH_2CH_2C_3H_6CH_3$), 4.92 (t, $^3J=8.2$ Hz, 4H, $CH_2C_4H_8CH_3$), 5.16 (d, $^3J=15.7$ Hz, 2H, $CH_2CH=CHH$), 5.23 (d, $^3J=10.5$ Hz, 2H, $CH_2CH=CHH$), 5.72 (d, $^3J=5.9$ Hz, 4H, $CH_2CH=CH_2$), 6.86 (m, 2H, $CH_2CH=CH_2$) 9.46 (s, 8H, H_β) 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_2Cl_2): λ_{max} (lg ϵ)=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.



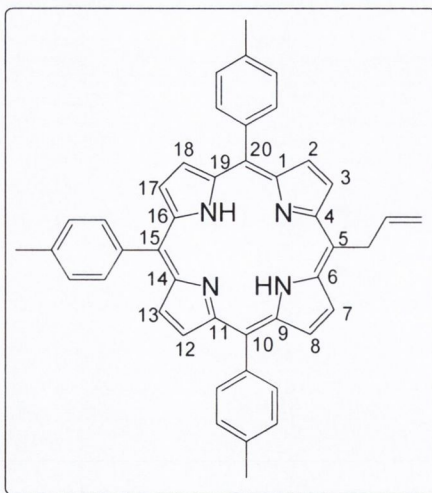
5,15-Diallyl-10,20-diisopropylporphyrin 74. By using 5,15-dibromo-10,20-di(*iso*-propyl)porphyrin **63** (100 mg, 0.18 mmol) as starting material, allylboronic acid pinacol ester (0.7 mL, 3.6 mmol, 20 equiv.), K_3PO_4 (1.5 g, 7.2 mmol, 40 equiv.) and $Pd(PPh_3)_4$ (21 mg, 0.018 mmol) the product was obtained in 1.5 mg (0.003 mmol, 2 %) yield of purple crystals: mp $>300\text{ }^\circ\text{C}$; $R_f=0.45$ (CH_2Cl_2/C_6H_{14} , 1:1, v/v); 1H NMR (400 MHz, $CDCl_3$): $\delta=-2.30$ (s, br, 2H, NH), 2.40 (d, $^3J=7.5$ Hz, 12H, $CH(CH_3)_2$), 5.22 (d, $^3J=17.0$ Hz, 2H, $CH_2CH=CHH$), 5.27 (d, $^3J=9.9$ Hz, 2H, $CH_2CH=CHH$), 5.56 (sep, $^3J=7.5$ Hz, 2H, $CH(CH_3)_2$), 5.69 (d, $^3J=5.6$ Hz, 4H, $CH_2CH=CH_2$), 6.88 (m, 2H, $CH_2CH=CH_2$), 9.45 (d, $^3J=5.3$ Hz, 4H, H_β), 9.59 (d, $^3J=5.3$ Hz, 4H, H_β) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta=28.3$, 34.5, 38.9, 113.6, 115.5, 124.2, 128.1, 128.4, 130.4, 141.3 ppm; UV/vis (CH_2Cl_2): λ_{max} (lg ϵ)=436 (4.2), 590 (3.1), 644 (3.2), 722 (2.9) nm; HRMS (ES $^+$): calcd for $C_{32}H_{34}N_4$ $[M+H]^+$ 475.2862, found 475.2878.



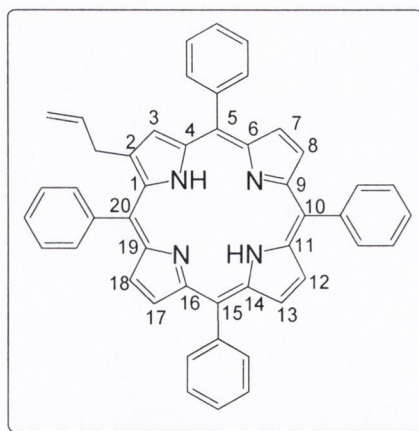
[5,15-Diallyl-10,20-bis(4-methylphenyl)porphyrinato]nickel(II) 75. By using [5,15-dibromo-10,20-bis(4-methylphenyl)porphyrinato]nickel(II) **64** (100 mg, 0.154 mmol) as starting material, allylboronic acid pinacol ester (0.6 mL, 3.08 mmol, 20 equiv.), K_3PO_4 (1.3 g, 6.16 mmol, 40 equiv.) and $Pd(PPh_3)_4$ (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_2Cl_2/C_6H_{14} , 1:2, v/v); 1H NMR (600 MHz, $CDCl_3$): $\delta=2.67$ (s, 6H, $C_6H_4CH_3$), 5.25 (m, 8H, $CH_2CH=CH_2$, $CH_2CH=CH_2$), 6.72 (m, 2H, $CH_2CH=CH_2$), 7.50 (d, $^3J=7.6$ Hz, 4H, H_{Ar}), 7.87 (d, $^3J=7.6$ Hz, 4H, H_{Ar}), 8.78 (d, $^3J=4.8$ Hz, 4H, H_β), 9.25 (d, $^3J=4.8$ Hz, 4H, H_β) 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_2Cl_2): λ_{max} (lg ϵ)=417 (5.0), 533 (4.1) nm; HRMS (ES⁺): calcd for $C_{40}H_{33}N_4Ni$ $[M+H]^+$ 627.2059, found 627.2054.



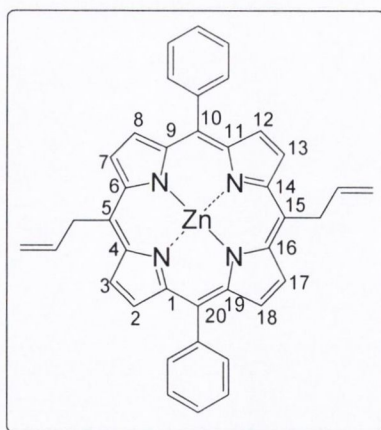
[5,15-Diallyl-10,20-dihexylporphyrinato]nickel(II) 76. By using [5,15-dibromo-10,20-dihexylporphyrinato]nickel(II) **65** (100 mg, 0.144 mmol) as starting material, allylboronic acid pinacol ester (0.5 mL, 2.88 mmol, 20 equiv.), K_3PO_4 (1.2 g, 5.76 mmol, 40 equiv.) and $Pd(PPh_3)_4$ (17 mg, 0.0144 mmol) the product was obtained in 84 mg (0.137 mmol, 95 %) yield as red needles: mp 163 °C; $R_f=0.80$ (CH_2Cl_2/C_6H_{14} , 1:1, v/v); 1H NMR (400 MHz, $CDCl_3$): $\delta=0.92$ (t, $^3J=6.9$ Hz, 6H, $C_5H_{10}CH_3$), 1.37 (m, 8H, $C_3H_6CH_2CH_2CH_3$), 1.58 (m, 4H, $C_2H_4CH_2C_2H_4CH_3$), 2.24 (m, 4H, $CH_2CH_2C_3H_6CH_3$), 4.42 (t, $^3J=8.3$ Hz, 4H, $CH_2C_4H_8CH_3$), 5.12 (d, $^3J=5.9$ Hz, 4H, $CH_2CH=CH_2$), 5.22 (d, $^3J=8.8$ Hz, 2H, $CH_2CH=CHH$), 5.28 (d, $^3J=15.7$ Hz, 2H, $CH_2CH=CHH$), 6.70 (m, 2H, $CH_2CH=CH_2$), 9.20 (s, 8H, H_β) 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_2Cl_2): λ_{max} (lg ϵ)=419 (6.1); 537 (3.0) nm; HRMS (ES⁺): calcd for $C_{38}H_{44}N_4Ni$ $[M+H]^+$ 614.2919, found 614.2929.



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_3PO_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_2Cl_2/C_6H_{14} , 1:1, v/v); 1H NMR (400 MHz, $CDCl_3$): $\delta=-2.70$ (s, br, 2H, NH), 2.70 (s, 3H, $C_6H_4CH_3$), 2.73 (s, 6H, $C_6H_4CH_3$), 5.16 (d, $^3J=18.6$ Hz, 1H, $CH_2CH=CHH$), 5.23 (d, $^3J=8.8$ Hz, 1H, $CH_2CH=CHH$), 5.79 (d, $^3J=4.9$ Hz, 2H, $CH_2CH=CH_2$), 6.87 (m, 1H, $CH_2CH=CH_2$), 7.56 (m, 6H, H_{Ar}), 8.09 (m, 6H, H_{Ar}), 8.83 (s, 4H, H_β), 8.95 (d, $^3J=4.9$ Hz, 2H, H_β), 9.47 (d, $^3J=4.9$ Hz, 2H, H_β) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta=21.5$, 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_2Cl_2): λ_{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.



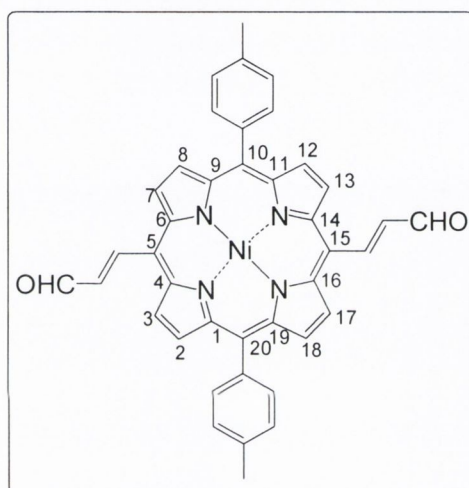
2-Allyl-5,10,15,20-tetraphenylporphyrin 78. 2-Bromo-5,10,15,20-tetraphenylporphyrin **69** (50 mg, 0.07 mmol; 1 equiv.) was placed into a round-bottom flask under argon atmosphere and dissolved in anhydrous toluene (15 mL). Allylboronic acid pinacol ester (0.06 mL, 0.35 mmol; 5 equiv.), Pd(PPh₃)₄ (8.0 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; R_f=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=CHH), 5.11 (d, ³J=9.9 Hz, 1H, CH₂CH=CHH), 6.16 (m, 1H, CH₂CH=CH₂), 7.77 (m, 12H, H_{Ar}), 8.10 (d, ³J=7.0 Hz, 2H, H_{Ar}), 8.21 (m, 6H, H_{Ar}), 8.63 (dd, ³J=4.8 Hz, ³J=7.7 Hz, 2H, H_β), 8.76 (d, ³J=5.9 Hz, 2H, H_β), 8.81 (d, ³J=4.8 Hz, 1H, H_β), 8.87 (m, 2H, H_β) 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): λ_{max} (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.



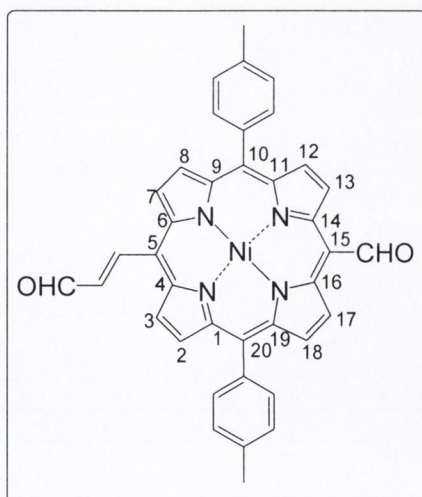
[5,15-Diallyl-10,20-diphenylporphyrinato]zinc(II) 87. 5,15-Diallyl-10,20-diphenylporphyrin **70** (56 mg, 0.103 mmol; 1 equiv.) was placed into a round-bottom flask and dissolved in 65 mL of dichloromethane. ZnO (40 mg, 0.412 mmol; 4 equiv.) and TFA (2 drops) were added and the reaction mixture was stirred 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; R_f =0.45 ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$, 1:1, v/v); ^1H NMR (600 MHz, d_6 -acetone): δ =5.14 (d, 3J =10.3 Hz, 2H, $\text{CH}_2\text{CH}=\text{CHH}$), 5.23 (d, 3J =15.4 Hz, 2H, $\text{CH}_2\text{CH}=\text{CHH}$), 5.87 (d, 3J =5.9 Hz, 4H, $\text{CH}_2\text{CH}=\text{CH}_2$), 6.87 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 7.82 (m, 6H, H_{Ar}), 8.20 (m, 4H, H_{Ar}), 8.86 (d, 3J =4.4 Hz, 4H, H_β), 9.64 (d, 3J =5.1 Hz, 4H, H_β) 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_2Cl_2): λ_{max} (lg ϵ)=421 (5.9), 552 (4.9) nm; HRMS (ES $^+$): calcd for $\text{C}_{38}\text{H}_{28}\text{N}_4\text{Zn}$ $[\text{M}+\text{H}]^+$ 604.1605, found 604.1618.

7.3 Acroleinylporphyrins

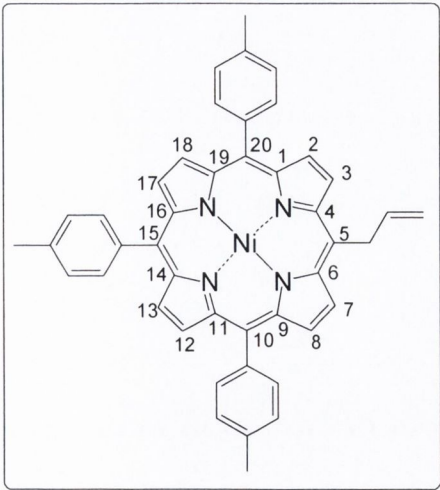
General Procedure: Allylporphyrin (**71**, **73**, **76-78**, **87**) (1 equiv.) was placed into a round-bottom flask and dissolved in DMF (20 mL). $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (3 equiv. for diallylporphyrin, 2 equiv. for mono-allylporphyrin) and glacial acetic acid (0.2 mL) were 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_6H_{14} , 1:2, v/v).



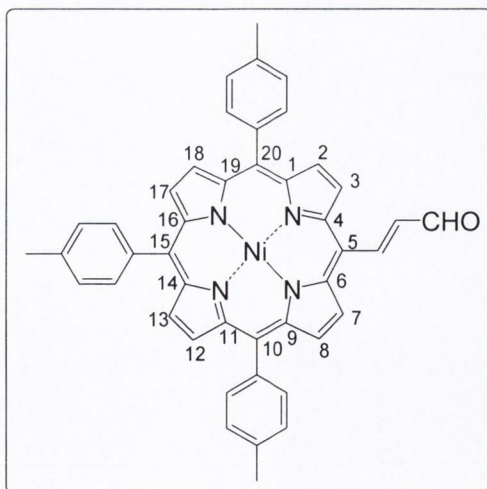
[5,15-Diallyl-10,20-bis(4-methylphenyl)porphyrinato]nickel(II) 80. By using 5,15-diallyl-10,20-bis(4-methylphenyl)porphyrin **71** (42 mg, 0.074 mmol) as starting material and $\text{Ni}(\text{OAc})_2$ (55 mg, 0.222 mmol, 3 equiv.) the product was obtained in 34 mg (0.052 mmol, 70 %) yield of green crystals: mp >300 °C; R_f =0.54 (ethyl acetate/ C_6H_{14} , 1:2, v/v); ^1H NMR (400 MHz, CDCl_3): δ =2.67 (s, 6H, $\text{C}_6\text{H}_4\text{CH}_3$), 6.55 (dd, 3J =7.7 Hz, 3J =15.4 Hz, 2H, $\text{CH}=\text{CHCHO}$), 7.49 (d, 3J =7.7 Hz, 4H, H_{Ar}), 7.76 (d, 3J =7.7 Hz, 4H, H_{Ar}), 8.68 (d, 3J =5.0 Hz, 4H, H_β), 9.14 (d, 3J =5.0 Hz, 4H, H_β), 9.44 (d, 3J =15.4 Hz, 2H, $\text{CH}=\text{CHCHO}$), 10.02 (d, 3J =7.7 Hz, 2H, $\text{CH}=\text{CHCHO}$) ppm; ^{13}C NMR (100.6 MHz, CDCl_3): δ =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 ($\text{C}=\text{O}$) cm^{-1} ; UV/vis (CH_2Cl_2): λ_{max} (lg ϵ)=443 (5.2), 622 (4.4) nm; LRMS (ES⁺): calcd for $\text{C}_{40}\text{H}_{28}\text{N}_4\text{NiO}_2$ $[\text{M}+\text{H}]^+$ 655.4, found 655.3.



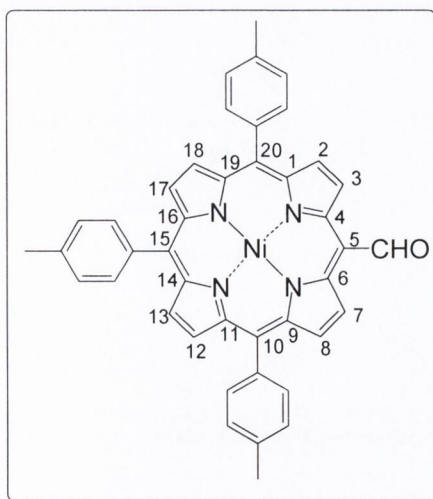
[5-Acroleinyl-15-formyl-10,20-bis(4-methylphenyl)porphyrinato]nickel(II) 81. The title compound was obtained as a side-product of the synthesis of [5,15-diacroleinyl-10,20-bis(4-methylphenyl)porphyrinato]nickel(II) **80** in 3.7 mg (0.006 mmol, 8 %) yield of light green crystals: mp >300 °C; $R_f=0.65$ (CH_2Cl_2); ^1H NMR (600 MHz, CDCl_3): $\delta=2.67$ (s, 6H, $\text{C}_6\text{H}_4\text{CH}_3$), 6.66 (dd, $^3J=7.4$ Hz, $^3J=15.5$ Hz, 1H, $\text{CH}=\text{CHCHO}$), 7.52 (d, $^3J=7.8$ Hz, 4H, H_{Ar}), 7.82 (d, $^3J=7.8$ Hz, 4H, H_{Ar}), 8.76 (d, $^3J=4.9$ Hz, 2H, H_β), 8.82 (d, $^3J=5.0$ Hz, 2H, H_β), 9.25 (d, $^3J=5.0$ Hz, 2H, H_β), 9.58 (d, $^3J=15.6$ Hz, 1H, $\text{CH}=\text{CHCHO}$), 9.75 (d, $^3J=5.0$ Hz, 2H, H_β), 10.10 (d, $^3J=7.4$ Hz, 1H, $\text{CH}=\text{CHCHO}$), 11.99 (s, 1H, CHO) ppm; ^{13}C NMR (100.6 MHz, CDCl_3): $\delta=21.3$, 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 ppm; IR: 2929 (CHO), 2856 (CH_3), 1733 ($\text{C}=\text{O}$) cm^{-1} ; UV/vis (CH_2Cl_2): λ_{max} (lg ϵ)=438 (3.4), 622 (2.6) nm.



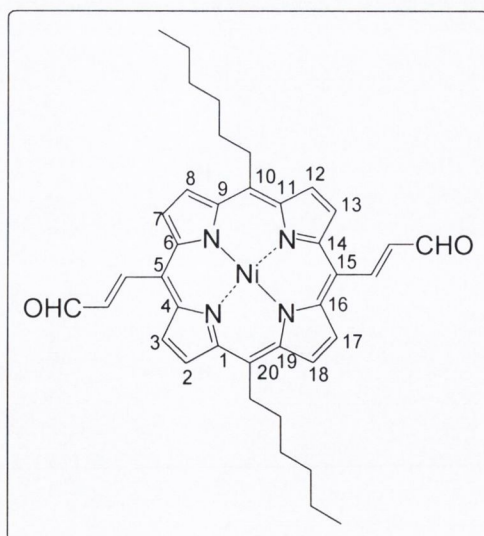
[5-Allyl-10,15,20-tris(4-methylphenyl)porphyrinato]nickel(II) 82. The title compound was obtained as a side-product of the synthesis of [5-acroleinyl-10,15,20-tris(4-methylphenyl)porphyrinato]nickel(II) **83** in 12.3 mg (0.018 mmol, 28 %) yield as red crystals: mp 100 °C; $R_f=0.63$ ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$, 1:2, v/v); ^1H NMR (600 MHz, CDCl_3): $\delta=2.63$ (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.64 (s, 6H, $\text{C}_6\text{H}_4\text{CH}_3$), 5.22 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.32 (d, $^3J=5.9$ Hz, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 6.73 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 7.46 (m, 6H, H_{Ar}), 7.86 (m, 6H, H_{Ar}), 8.70 (s, 4H, H_β), 8.80 (d, $^3J=4.6$ Hz, 2H, H_β), 9.29 (d, $^3J=4.7$ Hz, 2H, H_β) ppm; ^{13}C NMR (100.6 MHz, CDCl_3): $\delta=21.0$, 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 ($\text{C}=\text{CH}_2$), 2917 (CH_2) cm^{-1} ; UV/vis (CH_2Cl_2): λ_{max} ($\lg \epsilon$)=417 (5.7), 531 (4.8) nm; HRMS (ES+): calcd for $\text{C}_{44}\text{H}_{34}\text{N}_4\text{Ni}$ $[\text{M}+\text{H}]^+$ 677.2215, found 677.2233.



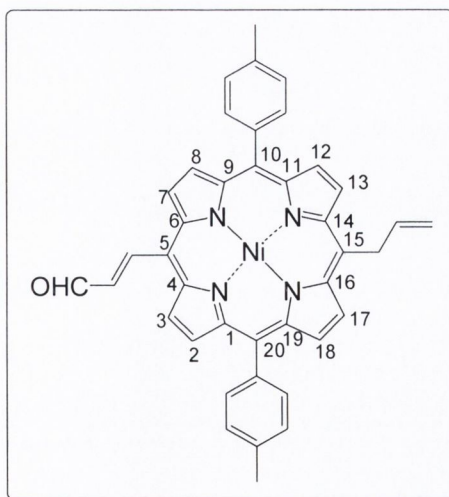
[5-Acroleinyl-10,15,20-tris(4-methylphenyl)porphyrinato]nickel(II) 83. By using 5-allyl-10,15,20-tris(4-methylphenyl)porphyrin **77** (40 mg, 0.065 mmol) as starting material and $\text{Ni}(\text{OAc})_2$ (49 mg, 0.195 mmol, 3 equiv.) the product was obtained in 11.6 mg (0.017 mmol, 26 %) yield of dark green crystals: mp 105 °C; $R_f=0.48$ ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$, 2:1, v/v); ^1H NMR (400 MHz, CDCl_3): $\delta=2.64$ (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.66 (s, 6H, $\text{C}_6\text{H}_4\text{CH}_3$), 6.67 (dd, $^3J=7.4$ Hz, $^3J=15.4$ Hz, 1H, $\text{CH}=\text{CHCHO}$), 7.49 (t, $^3J=7.7$ Hz, 6H, H_{Ar}), 7.85 (d, $^3J=7.7$ Hz, 6H, H_{Ar}), 8.64 (d, $^3J=5.3$ Hz, 2H, H_β), 8.70 (d, $^3J=4.7$ Hz, 2H, H_β), 8.85 (d, $^3J=4.7$ Hz, 2H, H_β), 9.30 (d, $^3J=4.7$ Hz, 2H, H_β), 9.63 (d, $^3J=15.2$ Hz, 1H, $\text{CH}=\text{CHCHO}$), 10.07 (d, $^3J=7.7$ Hz, 1H, $\text{CH}=\text{CHCHO}$) 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 ($\text{CH}=\text{CH}$), 2918 (CHO), 2852 (CH_3), 1670 ($\text{C}=\text{O}$) cm^{-1} ; UV/vis (CH_2Cl_2): λ_{max} ($\lg \epsilon$)=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 ; $R_f=0.66$ ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$, 1:2, v/v); ^1H NMR (400 MHz, CDCl_3): $\delta=2.65$ (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.67 (s, 6H, $\text{C}_6\text{H}_4\text{CH}_3$), 7.50 (t, $^3J=8.0$ Hz, 6H, H_{Ar}), 7.85 (d, $^3J=8.0$ Hz, 6H, H_{Ar}), 8.60 (d, $^3J=4.7$ Hz, 2H, H_β), 8.68 (d, $^3J=4.7$ Hz, 2H, H_β), 8.88 (d, $^3J=5.2$ Hz, 2H, H_β), 9.80 (d, $^3J=5.2$ Hz, 2H, H_β), 12.0 (s, 1H, CHO) ppm; ^{13}C NMR (100.6 MHz, CDCl_3): $\delta=21.0$, 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 (CH_2Cl_2): λ_{max} (lg ϵ)=426 (4.8), 552 (3.8), 593 (3.9) nm.



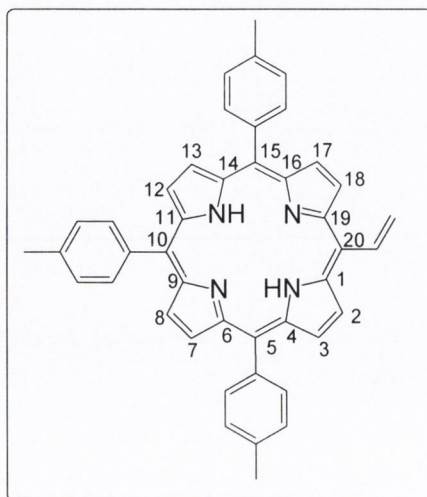
[5,15-Diacroleinyl-10,20-dihexylporphyrinato]nickel(II) 85. By using 5,15-diallyl-10,20-dihexylporphyrin **73** (32 mg, 0.057 mmol) as starting material and Ni(OAc)₂ (43 mg, 0.171 mmol, 3 equiv.) the product was obtained in 7.3 mg (0.011 mmol, 20 %) or 10.3 mg (0.016 mmol; 20 %) yield, respectively, as green crystals: mp 181 °C; R_f =0.58 (ethyl acetate/C₆H₁₄, 1:2, v/v); ¹H NMR (600 MHz, CDCl₃): δ =0.88 (t, 6H, ³*J*=7.0 Hz, C₅H₁₀CH₃), 1.31 (m, 8H, C₃H₆CH₂CH₂CH₃), 1.57 (m, 4H, C₂H₄CH₂C₂H₄CH₃), 2.18 (m, 4H, CH₂CH₂C₃H₆CH₃), 4.29 (t, ³*J*=7.9 Hz, 4H, CH₂C₄H₈CH₃), 6.47 (dd, ³*J*=7.2 Hz, ³*J*=15.2 Hz, 2H, CH=CHCHO), 9.11 (m, 8H, *H*_β), 9.33 (d, ³*J*=15.2 Hz, 2H, CH=CHCHO), 9.97 (d, ³*J*=7.6 Hz, 2H, CH=CHCHO) ppm; ¹³C NMR (150.9 MHz, CDCl₃): δ =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 (CH₂), 2850 (CHO), 1666 (C=O) cm⁻¹; UV/vis (CH₂Cl₂): $\lambda_{\max}$ (lg ϵ)=448 (5.3), 637 (4.6) nm; HRMS (ES⁺): calcd for C₃₈H₄₀N₄NiO₂ [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: ^1H NMR (600 MHz, CDCl_3): δ =2.67 (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$), 5.23 (m, 4H, $\text{CH}_2\text{CH}=\text{CH}_2$, $\text{CH}_2\text{CH}=\text{CH}_2$), 6.67 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$, $\text{CH}=\text{CHCHO}$), 7.51 (d, $^3J=7.3$ Hz, 4H, H_{Ar}), 7.85 (d, $^3J=7.3$ Hz, 4H, H_{Ar}), 8.70 (d, $^3J=4.5$ Hz, 2H, H_{β}), 8.81 (d, $^3J=4.5$ Hz, 2H, H_{β}), 9.22 (d, $^3J=4.5$ Hz, 2H, H_{β}), 9.27 (d, $^3J=4.5$ Hz, 2H, H_{β}), 9.61 (d, $^3J=15.2$ Hz, 1H, $\text{CH}=\text{CHCHO}$), 10.07 (d, $^3J=7.3$ Hz, 1H, $\text{CH}=\text{CHCHO}$) ppm; ^{13}C NMR (100.6 MHz, CDCl_3): δ =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.

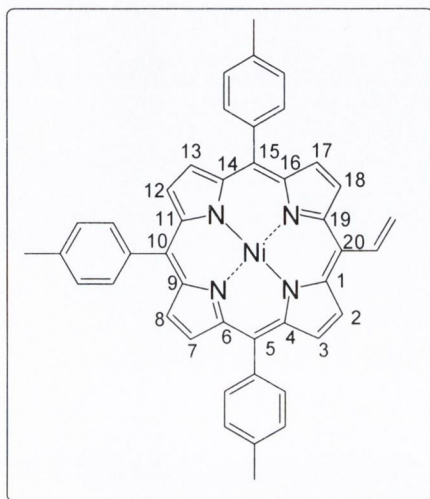
7.4 Pauson-Khand Products of Alkenylporphyrins

7.4.1 Synthesis of Starting Materials



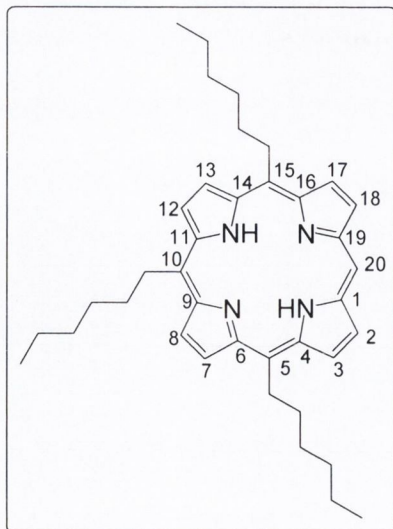
5,10,15-Tris(4-methylphenyl)-20-vinylporphyrin 93. A 50 mL Schlenk-tube was filled with argon and charged with 5-bromo-10,15,20-tris(4-methylphenyl)phenylporphyrin **67** (300 mg, 0.455 mmol, 1 equiv.) in dry THF (50 mL). K_3PO_4 (2.0 g, 9.1 mmol, 20 equiv.) was added and the solution was degassed *via* three freeze-pump-thaw cycles and put under argon atmosphere again. Vinylboronic acid pinacol ester (0.8 mL, 4.55 mmol, 10 equiv.) and $Pd(PPh_3)_4$ (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 (CH_2Cl_2/C_6H_{14} , 1:2, v/v). The product was obtained after recrystallisation from $CH_2Cl_2/MeOH$ (1:3, v/v) as purple crystals in 144 mg (0.24 mmol, 52 %) yield: mp >300 °C; R_f =0.43 (CH_2Cl_2/C_6H_{14} , 1:1, v/v); 1H NMR (400 MHz, $CDCl_3$): δ = -2.67 (s, br, 2H, NH), 2.73 (s, 3H, $C_6H_4CH_3$), 2.73 (s, 6H, $C_6H_4CH_3$), 6.15 (dd, 3J =17.5 Hz, 2J =1.8 Hz, 1H, CH=CHH), 6.59 (dd, 3J =11.7 Hz, 2J =1.8 Hz, 1H, CH=CHH), 7.57 (d, 3J =8.2 Hz, 4H, H_{Ar}), 7.59 (d, J =7.6 Hz, 2H, H_{Ar}), 8.09 (d, 3J =7.6 Hz, 4H, H_{Ar}), 8.12 (d, 3J =7.6 Hz, 2H, H_{Ar}), 8.84 (s, 4H, H_β), 8.95 (d, 3J =4.7 Hz, 2H, H_β), 9.26 (dd, 3J =17.0 Hz, 3J =11.1 Hz, 1H, CH=CH₂), 9.50 (d, 3J =5.3 Hz, 2H, H_β) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$):

δ =21.6, 117.0, 120.1, 120.2, 127.3, 127.4, 127.6, 131.1 (br), 134.5, 137.4, 137.5, 139.2 ppm; IR: 3318 (NH), 3022 (C=CH₂), 2917 (CH₃) cm⁻¹; UV/vis (CH₂Cl₂): $\lambda_{\max}$ (lg ϵ)=421 (6.0), 521 (5.0), 556 (4.9), 596 (4.87), 653 (4.86) nm; HRMS (ES⁺): calcd for C₄₃H₃₄N₄ [M+H]⁺ 607.2862, found 607.2861.

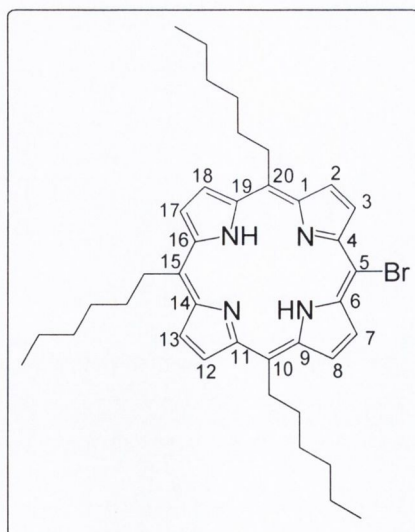


[5,10,15-Tris(4-methylphenyl)-20-vinylporphyrinato]nickel(II) 94. A 50 mL 2-necked round bottom flask was charged with 5,10,15-tris(4-methylphenyl)-20-vinylporphyrin **93** (70 mg, 0.116 mmol, 1 equiv.) and Ni(acac)₂ (45 mg, 0.174 mmol, 1.5 equiv.) in toluene (30 mL). The reaction mixture was heated 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; R_f=0.85 (CH₂Cl₂/C₆H₁₄, 1:1, v/v); ¹H 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, H_{Ar}), 7.50 (d, ³J=7.6 Hz, 2H, H_{Ar}), 7.88 (d, ³J=5.9 Hz, 4H, H_{Ar}), 7.89 (d, ³J=5.9 Hz, 2H, H_{Ar}), 8.71 (d, ³J=4.7 Hz, 2H, H_β), 8.72 (d, ³J=5.3 Hz, 2H, H_β), 8.84 (d, ³J=5.3 Hz, 2H, H_β), 8.96 (dd, ³J=17.0 Hz, ³J=11.0 Hz, 1H, CH=CH₂), 9.35 (d, ³J=4.7, 2H, H_β) ppm; ¹³C 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,

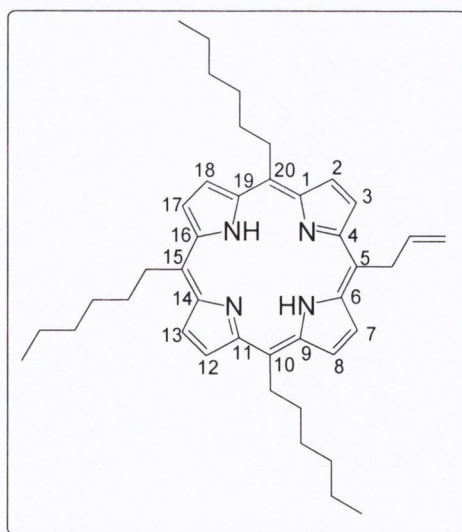
137.3, 140.8, 141.5, 141.9 ppm; UV/vis (CH_2Cl_2): λ_{max} ($\lg \epsilon$)=420 (5.5), 535 (4.7) nm; HRMS (ES⁺): calcd for $\text{C}_{43}\text{H}_{32}\text{N}_4\text{Ni}$ $[\text{M}+\text{H}]^+$ 663.2059, found 663.2031.



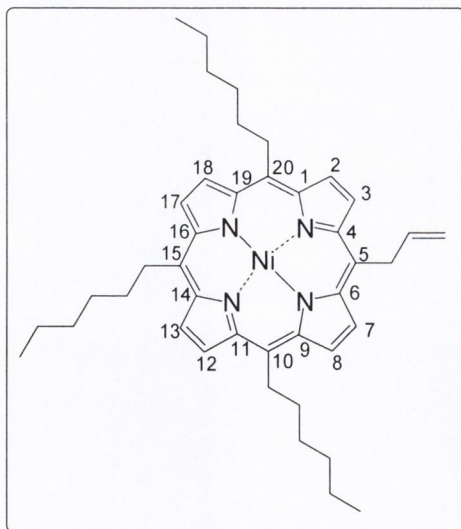
5,10,15-Trihexylporphyrin 96. A 1 L 3-necked round-bottom flask was filled with argon and charged with 5,15-dihexylporphyrin **57** (940 mg, 1.967 mmol, 1 equiv.) in dry THF (500 mL). The solution was cooled to $-78\text{ }^\circ\text{C}$ and *n*-hexyllithium (5.13 mL, 11.8 mmol, 6 equiv., 2.3 M in hexane) was added dropwise over 20 min. After complete addition, the reaction mixture was kept stirring at $-78\text{ }^\circ\text{C}$ 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 $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (1:3, v/v) the product was obtained in 290 mg (0.516 mmol, 26 %) yield as purple needles: mp $142\text{ }^\circ\text{C}$; R_f =0.22 ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$, 1:2, v/v); ^1H NMR (400 MHz, CDCl_3): δ =−2.84 (s, br, 2H, NH), 0.97 (t, 3J =7.3 Hz, 6H, $\text{C}_5\text{H}_{10}\text{CH}_3$), 0.99 (t, 3J =7.6 Hz, 3H, $\text{C}_5\text{H}_{10}\text{CH}_3$), 1.44 (m, 6H, $\text{C}_4\text{H}_8\text{CH}_2\text{CH}_3$), 1.56 (m, 6H, $\text{C}_3\text{H}_6\text{CH}_2\text{CH}_2\text{CH}_3$), 1.84 (m, 6H, $\text{C}_2\text{H}_4\text{CH}_2\text{C}_2\text{H}_4\text{CH}_3$), 2.56 (m, 6H, $\text{CH}_2\text{CH}_2\text{C}_3\text{H}_6\text{CH}_3$), 4.99 (t, 3J =8.2 Hz, 4H, $\text{CH}_2\text{C}_4\text{H}_8\text{CH}_3$), 5.08 (t, 3J =8.2 Hz, 2H, $\text{CH}_2\text{C}_4\text{H}_8\text{CH}_3$), 9.31 (d, 3J =4.7 Hz, 2H, H_β), 9.52 (d, 3J =4.7 Hz, 2H, H_β), 9.55 (d, 3J =4.7 Hz, 2H, H_β), 9.62 (d, 3J =4.7 Hz, 2H, H_β), 9.96 (s, 1H, H_{meso}) ppm; ^{13}C NMR (150.9 MHz, CDCl_3): 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, 119.8, 119.9, 120.2, 127.7, 128.1, 128.5, 131.1, 145.1 (br), 146.6 (br) ppm; UV/vis (CH_2Cl_2): λ_{max} ($\lg \epsilon$)=412 (5.5), 512 (4.6), 545 (4.5), 591 (4.4), 647 (4.4) nm; HRMS (ES⁺): calcd for $\text{C}_{38}\text{H}_{50}\text{N}_4$ $[\text{M}+\text{H}]^+$ 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; *R*_f=0.41 (CH₂Cl₂/C₆H₁₄, 1:2, v/v); ¹H NMR (400 MHz, CDCl₃): δ=−2.66 (s, br, 2H, NH), 0.97 (t, ³*J*=7.3 Hz, 6H, C₅H₁₀CH₃), 0.99 (t, ³*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, CH₂CH₂C₃H₆CH₃), 4.91 (m, 6H, CH₂C₄H₈CH₃), 9.45 (d, ³*J*=5.2 Hz, 2H, *H*_β), 9.46 (d, ³*J*=5.8 Hz, 2H, *H*_β), 9.50 (d, ³*J*=5.2 Hz, 2H, *H*_β), 9.67 (d, ³*J*=4.7 Hz, 2H, *H*_β) 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 C₃₈H₄₉N₄Br [M+H]⁺ 641.3219, found 641.3227.



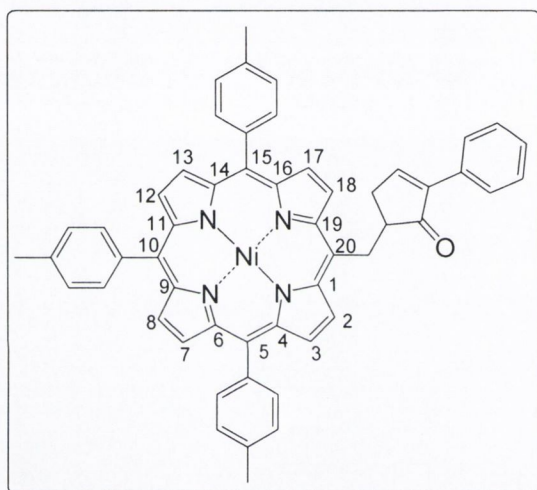
5-Allyl-10,15,20-trihexylporphyrin 98. A 50 mL Schlenk-tube was filled with argon and charged with 5-bromo-10,15,20-trihexylporphyrin **97** (300 mg, 0.468 mmol, 1 equiv.) in dry THF (50 mL). K_3PO_4 (2.0 g, 9.36 mmol, 20 equiv.) was added and the solution was degassed via three freeze-pump-thaw cycles 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_2Cl_2/C_6H_{14} , 1:2, v/v). After recrystallisation from $CH_2Cl_2/MeOH$ (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_2Cl_2/C_6H_{14} , 1:1, v/v); 1H NMR (400 MHz, $CDCl_3$): $\delta=-2.59$ (s, br, 2H, NH), 0.97 (t, $^3J=7.3$ Hz, 6H, $C_5H_{10}CH_3$), 0.99 (t, $^3J=7.6$ Hz, 3H, $C_5H_{10}CH_3$), 1.43 (m, 6H, $C_4H_8CH_2CH_3$), 1.54 (m, 6H, $C_3H_6CH_2CH_2CH_3$), 1.85 (m, 6H, $C_2H_4CH_2C_2H_4CH_3$), 2.54 (m, 6H, $CH_2CH_2C_3H_6CH_3$), 4.95 (m, 6H, $CH_2C_4H_8CH_3$), 5.18 (d, $^3J=17.0$ Hz, 1H, $CH_2CH=CHH$), 5.25 (d, $^3J=9.9$ Hz, 1H, $CH_2CH=CHH$), 5.74 (d, $^3J=5.3$ Hz, 2H, $CH_2CH=CH_2$), 6.88 (m, 1H, $CH_2CH=CH_2$), 9.48 (d, $^3J=4.8$ Hz, 4H, H_β), 9.50 (d, $^3J=5.2$ Hz, 4H, H_β) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta=14.2, 22.8, 30.4, 31.9, 35.5, 35.6, 38.8, 39.0, 113.9, 115.9, 118.6, 118.9, 126.6$ (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_2Cl_2): λ_{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.



[5-Allyl-10,15,20-trihexylporphyrinato]nickel(II) 99. A 50 mL 2-necked round-bottom flask was charged with 5-allyl-10,15,20-trihexylporphyrin **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: $R_f=0.67$ (CH₂Cl₂/C₆H₁₄, 1:2, v/v); ¹H NMR (400 MHz, CDCl₃): $\delta=0.93$ (t, ³ $J=7.3$ Hz, 6H, C₅H₁₀CH₃), 0.95 (t, ³ $J=7.5$ Hz, 3H, C₅H₁₀CH₃), 1.34 (m, 6H, C₄H₈CH₂CH₃), 1.43 (m, 6H, C₃H₆CH₂CH₂CH₃), 1.59 (m, 6H, C₂H₄CH₂C₂H₄CH₃), 2.26 (m, 6H, CH₂CH₂C₃H₆CH₃), 4.48 (m, 6H, CH₂C₄H₈CH₃), 5.18 (d, ³ $J=5.9$ Hz, 2H, CH₂CH=CH₂), 5.23 (d, ³ $J=10.0$ Hz, 1H, CH₂CH=CHH), 5.31 (d, ³ $J=17.5$ Hz, 1H, CH₂CH=CHH), 6.71 (m, 1H, CH₂CH=CH₂), 9.25 (d, ³ $J=4.8$ Hz, 4H, H_β), 9.26 (d, ³ $J=5.2$ Hz, 4H, H_β) ppm; ¹³C NMR (100.6 MHz, CDCl₃): $\delta=14.2$, 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): $\lambda_{\max}$ (lg ϵ)=420 (5.4), 539 (4.5), 570 (4.3), nm; HRMS (ES⁺): calcd for C₄₁H₅₂N₄Ni [M+H]⁺ 659.3624, found 659.3593.

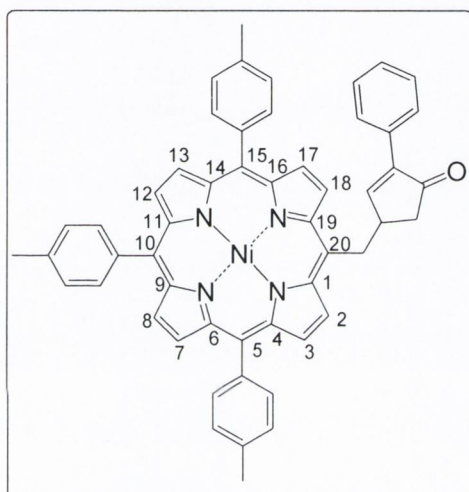
7.4.2 Pauson-Khand Products I

General Procedure: Phenylacetylene (10 equiv.) was placed into a round-bottom flask under argon in dry THF (20 mL). $\text{Co}_2(\text{CO})_8$ (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 ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$, 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 $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (1:3, v/v).



[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 $\text{Co}_2(\text{CO})_8$ (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 ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$, 1:1, v/v); ^1H NMR (400 MHz, CDCl_3): δ =1.97 (m, 1H, $\text{C}=\text{CHCH}_2\text{CHCH}_2$), 2.25 (m, 1H, $\text{C}=\text{CHCH}_2\text{CHCH}_2$), 2.66 (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.67 (s, 6H, $\text{C}_6\text{H}_4\text{CH}_3$), 3.24 (m, 1H, $\text{C}=\text{CHCH}_2\text{CHCH}_2$), 4.55 (dd, 3J =14.0 Hz, 2J =11.1 Hz, 1H, $\text{C}=\text{CHCH}_2\text{CHCH}_2$), 5.69 (dd, 3J =14.6 Hz, 2J =4.1 Hz, 1H, $\text{C}=\text{CHCH}_2\text{CHCH}_2$), 7.39 (d, 3J =5.9 Hz, 1H, H_{Ar}), 7.43

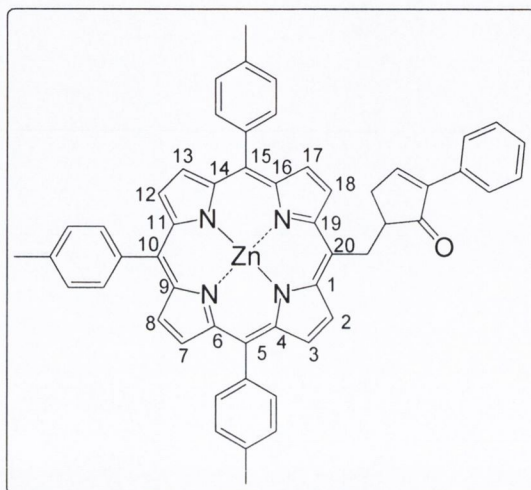
(m, 2H, H_{Ar}), 7.49 (d, $^3J=7.0$ Hz, 4H, H_{Ar}), 7.49 (d, $^3J=7.6$ Hz, 2H, H_{Ar}), 7.55 (dd, $^3J=2.9$ Hz, $^3J=1.8$ Hz, 1H, $C=CHCH_2CHCH_2$), 7.73 (d, $^3J=6.4$ Hz, 2H, H_{Ar}), 7.88 (d, $^3J=3.5$ Hz, 4H, H_{Ar}), 7.89 (d, $^3J=3.5$ Hz, 2H, H_{Ar}), 8.74 (d, $^3J=4.1$ Hz, 2H, H_β), 8.74 (d, $^3J=4.6$ Hz, 2H, H_β), 8.88 (d, $^3J=4.7$ Hz, 2H, H_β), 9.44 (d, $^3J=5.3$ Hz, 2H, H_β) ppm; ^{13}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=O) cm^{-1} ; UV/vis (CH_2Cl_2): λ_{max} (lg ϵ)=419 (5.4), 523 (4.7) nm; HRMS (ES $^+$): calcd for $C_{53}H_{40}N_4NiO$ $[M+H]^+$ 807.2634, found 807.2648.



[5,10,15-Tris(4-methylphenyl)-20-(4-methyl-2-phenylcyclopent-2-enonyl)-

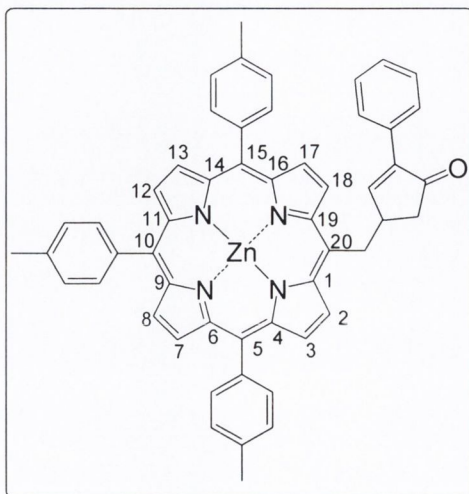
porphyrinato]nickel(II) 101. The product was obtained as the third fraction by column chromatography of the reaction above. Recrystallisation gave 15.7 mg (0.019 mmol, 33 %) yield of red crystals: mp 182 °C; $R_f=0.16$ (CH_2Cl_2/C_6H_{14} , 1:1, v/v); 1H NMR (400 MHz, $CDCl_3$): $\delta=2.63$ (m, 1H, $COCH_2CH$), 2.66 (s, 3H, $C_6H_4CH_3$), 2.68 (s, 6H, $C_6H_4CH_3$), 2.77 (dd, $^3J=18.7$ Hz, $^2J=6.4$ Hz, 1H, $COCH_2CH$), 3.70 (m, 1H, $COCH_2CH$), 4.80 (dd, $^3J=14.0$ Hz, $^2J=9.4$ Hz, 1H, $COCH_2CHCH_2$), 5.10 (dd, $^3J=14.0$ Hz, $^2J=7.0$ Hz, 1H, $COCH_2CHCH_2$), 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_β), 8.76 (d, $^3J=5.3$ Hz, 2H, H_β), 8.88 (d, $^3J=5.3$ Hz, 2H, H_β), 9.28 (d, $^3J=5.3$ Hz, 2H, H_β) ppm; ^{13}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, 132.22, 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 (CH₂), 2851 (CH₃), 1702 (C=O) cm⁻¹; UV/vis (CH₂Cl₂): λ_{max} (lg ε)=419 (5.6), 531 (4.6) nm; HRMS (ES⁺): calcd for C₅₃H₄₀N₄NiO [M+H]⁺ 807.2634, found 807.2663.



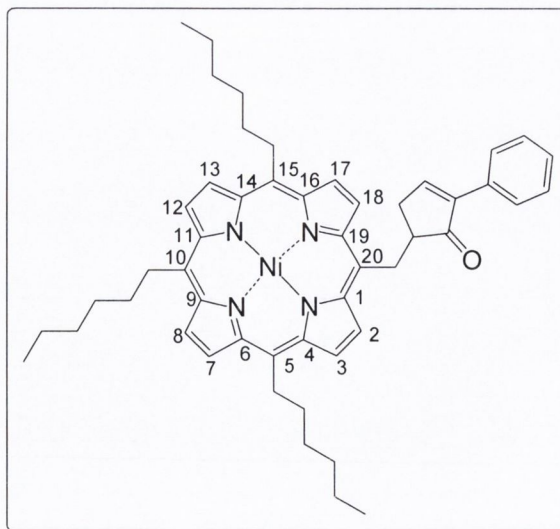
[5,10,15-Tris(4-methylphenyl)-20-(5-methyl-2-phenylcyclopent-2-enonyl)-porphyrinato]zinc(II) 102 By using [5-allyl-10,15,20-bis(4-methylphenyl)porphyrinato]zinc(II) **95** (40 mg, 0.059 mmol) as starting material, phenylacetylene (65 μL, 0.59 mmol) and Co₂(CO)₈ (202 mg, 0.59 mmol) the product was obtained 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 (CH₂Cl₂/C₆H₁₄, 1:1, v/v); ¹H NMR (600 MHz, CDCl₃): δ=2.31 (m, 1H, C=CHCH₂CHCH₂), 2.73 (s, 3H, C₆H₄CH₃), 2.76 (s, 6H, C₆H₄CH₃), 2.95 (m, 1H, C=CHCH₂CHCH₂), 3.83 (m, 1H, C=CHCH₂CHCH₂), 4.94 (dd, ³J=14.7 Hz, ²J=11.0 Hz, 1H, C=CHCH₂CHCHH), 5.98 (dd, ³J=14.7 Hz, ²J=4.4 Hz, 1H, C=CHCH₂CHCHH), 7.41 (t, ³J=7.3 Hz, 1H, H_{Ar}), 7.48 (dd, ³J=7.3 Hz, ³J=7.3 Hz, 2H, H_{Ar}), 7.58 (d, ³J=7.3 Hz, 2H, H_{Ar}), 7.58 (d, ³J=5.9 Hz, 2H, H_{Ar}), 7.60 (d, ³J=5.1 Hz, 2H, H_{Ar}), 7.75 (dd, ³J=2.8 Hz, ³J=2.4 Hz, 1H, C=CHCH₂CHCH₂), 7.86 (d, ³J=7.4 Hz, 2H, H_{Ar}), 8.10 (d, ³J=7.3 Hz, 2H, H_{Ar}), 8.11 (d, ³J=5.9 Hz, 2H, H_{Ar}), 8.13 (d, ³J=7.3 Hz, 2H, H_{Ar}), 8.95 (d, ³J=5.2 Hz, 2H, H_β), 8.95 (d, ³J=5.2 Hz, 2H, H_β), 8.88 (d, ³J=4.7 Hz, 2H, H_β), 9.69 (d, ³J=4.4 Hz, 2H, H_β) ppm; ¹³C NMR (150.9 MHz, CDCl₃): 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,

131.8, 131.9, 132.6, 134.2, 136.9, 139.7, 142.2, 149.8, 149.9, 150.1, 150.4, 157.1, 207.9 ppm; IR: 2920 (CH₂), 2852 (CH₃), 1698 (C=O) cm⁻¹; UV/vis (CH₂Cl₂): λ_{max} (lg ε)=422 (5.9), 551 (4.8), 589 (4.6) nm; HRMS (ES⁺): calcd for C₅₃H₄₀N₄OZn [M+H]⁺ 813.2572, found 813.2590.



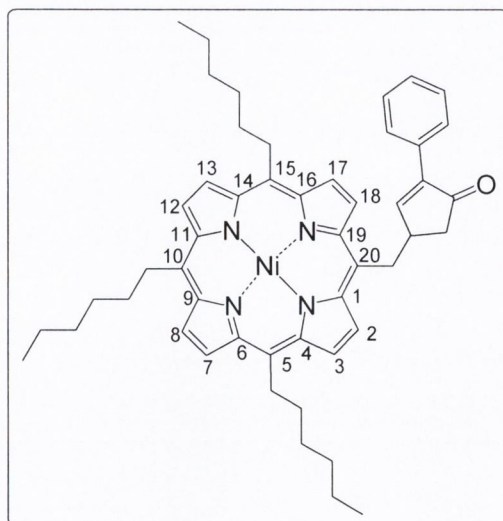
[5,10,15-Tris(4-methylphenyl)-20-(4-methyl-2-phenylcyclopent-2-enonyl)-

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; R_f=0.12 (CH₂Cl₂/C₆H₁₄, 1:1, v/v); ¹H NMR (400 MHz, CDCl₃): δ=2.74 (s, 3H, C₆H₄CH₃), 2.75 (s, 6H, C₆H₄CH₃), 2.88 (m, 2H, COCH₂CH), 4.14 (m, 1H, COCH₂CH), 5.07 (dd, ³J=14.7 Hz, ²J=9.8 Hz, 1H, COCH₂CHCHH), 5.35 (dd, ³J=14.7 Hz, ²J=6.9 Hz, 1H, COCH₂CHCHH), 7.29 (s, 2H, H_{Ar}), 7.50 (m, 3H, H_{Ar}), 7.56 (s, 1H, CH=CCO), 7.59 (d, ³J=3.9 Hz, 4H, H_{Ar}), 7.60 (d, ³J=1.9 Hz, 4H, H_{Ar}), 8.10 (d, ³J=7.9 Hz, 4H, H_{Ar}), 8.13 (d, ³J=2.9 Hz, 2H, H_{Ar}), 8.96 (d, ³J=3.9 Hz, 2H, H_β), 8.96 (d, ³J=3.9 Hz, 2H, H_β), 9.04 (d, ³J=3.9 Hz, 2H, H_β), 9.44 (d, ³J=4.9 Hz, 2H, H_β) ppm; ¹³C NMR (150.9 MHz, CDCl₃): δ=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 (CH₂), 2851 (CH₃), 1702 (C=O) cm⁻¹; UV/vis (CH₂Cl₂): λ_{max} (lg ε)=422 (5.6), 552 (4.5), 588 (4.4) nm; HRMS (ES⁺): calcd for C₅₃H₄₀N₄OZn [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 μ L, 0.69 mmol) and $\text{Co}_2(\text{CO})_8$ (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 μ mol, 14 %) yield: mp 102 $^{\circ}\text{C}$; $R_f=0.15$ ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$, 1:1, v/v); ^1H NMR (600 MHz, CDCl_3): $\delta=0.92$ (t, $^3J=7.2$ Hz, 6H, $\text{C}_5\text{H}_{10}\text{CH}_3$), 0.92 (t, $^3J=7.2$ Hz, 3H, $\text{C}_5\text{H}_{10}\text{CH}_3$), 1.35 (m, 6H, $\text{C}_4\text{H}_8\text{CH}_2\text{CH}_3$), 1.43 (m, 6H, $\text{C}_3\text{H}_6\text{CH}_2\text{CH}_2\text{CH}_3$), 1.58 (m, 6H, $\text{C}_2\text{H}_4\text{CH}_2\text{C}_2\text{H}_4\text{CH}_3$), 1.89 (m, 1H, $\text{C}=\text{CHCH}_2\text{CHCH}_2$), 2.12 (m, 1H, $\text{C}=\text{CHCH}_2\text{CHCH}_2$), 2.26 (m, 6H, $\text{CH}_2\text{CH}_2\text{C}_3\text{H}_6\text{CH}_3$), 3.12 (m, 1H, $\text{C}=\text{CHCH}_2\text{CHCH}_2$), 4.42 (dd, $^3J=14.3$ Hz, $^2J=11.3$ Hz, 1H, $\text{C}=\text{CHCH}_2\text{CHCHH}$), 4.51 (m, 6H, $\text{CH}_2\text{C}_4\text{H}_8\text{CH}_3$), 5.61 (dd, $^3J=14.7$ Hz, $^2J_{\text{H,H}}=4.1$ Hz, 1H, $\text{C}=\text{CHCH}_2\text{CHCHH}$), 7.37 (t, $^3J=7.2$ Hz, 1H, H_{Ar}), 7.42 (dd, $^3J=7.5$ Hz, $^3J=7.2$ Hz, 2H, H_{Ar}), 7.52 (m, 1H, $\text{C}=\text{CHCH}_2\text{CHCH}_2$), 7.73 (d, $^3J=7.5$ Hz, 2H, H_{Ar}), 9.28 (d, $^3J=5.3$ Hz, 2H, H_{β}), 9.28 (d, $^3J=6.4$ Hz, 2H, H_{β}), 9.30 (d, $^3J=5.3$ Hz, 2H, H_{β}), 9.37 (d, $^3J=4.9$ Hz, 2H, H_{β}) ppm; ^{13}C NMR (150.9 MHz, CDCl_3): $\delta=13.9$, 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 (CH_2), 2920 (CH_2), 2851 (CH_3), 1697 ($\text{C}=\text{O}$) cm^{-1} ; UV/vis (CH_2Cl_2): λ_{max} (lg ϵ)=421 (5.3), 540 (4.5), 574 (4.3) nm; HRMS (ES $^{+}$): calcd for $\text{C}_{50}\text{H}_{58}\text{N}_4\text{NiO}$ [$\text{M}+\text{H}$] $^{+}$ 789.4042, found 789.4028.

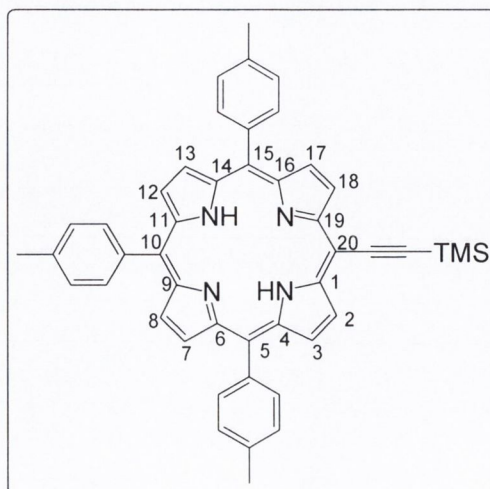


[5,10,15-Trihexyl-20-(4-methyl-2-phenylcyclopent-2-enonyl)porphyrinato]-

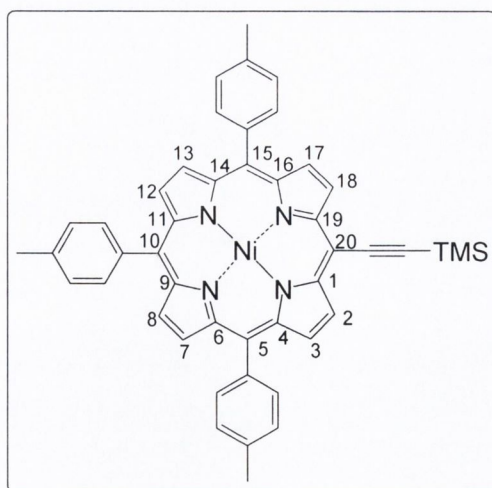
nickel(II) 105. The product was obtained as the third fraction of the reaction above by column chromatography followed by recrystallisation as red crystals in 10.3 mg (0.013 mmol, 19 %) yield: mp 136 °C; $R_f=0.23$ ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$, 1:1, v/v); ^1H NMR (600 MHz, CDCl_3): $\delta=0.92$ (t, $^3J=7.3$ Hz, 6H, $\text{C}_5\text{H}_{10}\text{CH}_3$), 0.92 (t, $^3J=7.3$ Hz, 3H, $\text{C}_5\text{H}_{10}\text{CH}_3$), 1.35 (m, 6H, $\text{C}_4\text{H}_8\text{CH}_2\text{CH}_3$), 1.44 (m, 6H, $\text{C}_3\text{H}_6\text{CH}_2\text{CH}_2\text{CH}_3$), 1.59 (m, 6H, $\text{C}_2\text{H}_4\text{CH}_2\text{C}_2\text{H}_4\text{CH}_3$), 2.28 (m, 6H, $\text{CH}_2\text{CH}_2\text{C}_3\text{H}_6\text{CH}_3$), 2.60 (m, 1H, COCH_2CH), 2.74 (m, 1H, COCH_2CH), 3.59 (m, 1H, COCH_2CH), 4.51 (m, 6H, $\text{CH}_2\text{C}_4\text{H}_8\text{CH}_3$), 4.71 (dd, $^3J=13.9$ Hz, $^2J=9.4$ Hz, 1H, $\text{COCH}_2\text{CHCHH}$), 4.99 (dd, $^3J=14.3$ Hz, $^2J=7.2$ Hz, 1H, $\text{COCH}_2\text{CHCHH}$), 7.26 (s, 1H, $\text{CH}=\text{CCO}$), 7.26 (d, $^3J=1.9$ Hz, 2H, H_{Ar}), 7.27 (d, $^3J=1.5$ Hz, 1H, H_{Ar}), 7.51 (m, 2H, H_{Ar}), 9.23 (d, $^3J=5.3$ Hz, 2H, H_{β}), 9.29 (d, $^3J=4.9$ Hz, 2H, H_{β}), 9.30 (d, $^3J=5.7$ Hz, 4H, H_{β}) ppm; ^{13}C NMR (150.9 MHz, CDCl_3): $\delta=13.9$, 22.5, 29.5, 29.9, 31.6, 33.9, 37.2, 38.8, 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 ($\text{C}=\text{O}$) cm^{-1} ; UV/vis (CH_2Cl_2): λ_{max} (lg ϵ)=421 (5.5), 538 (4.8), 570 (4.6) nm; HRMS (ES $^+$): calcd for $\text{C}_{50}\text{H}_{58}\text{N}_4\text{NiO}$ $[\text{M}+\text{H}]^+$ 789.4042, found 789.4020.

7.5 Pauson-Khand Products of Alkynylporphyrins

7.5.1 Synthesis of Starting Materials

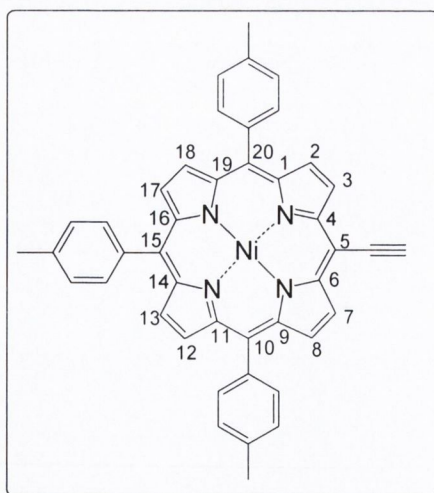


5,10,15-Tris(4-methylphenyl)-20-trimethylsilyl ethynylporphyrin 106 A 100 mL Schlenk-tube was filled with argon and charged with 5-bromo-10,15,20-tris(4-methylphenyl)porphyrin **67** (200 mg, 0.30 mmol; 1 equiv.) in dry THF/triethylamine (60 mL, 1:3, v/v). The solution was degassed via five freeze-pump-thaw 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 $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (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 ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$, 1:2, v/v), the product was obtained in 146 mg (0.216 mmol, 72 %) yield as purple crystals: mp $>300^\circ\text{C}$; $R_f=0.41$ ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$, 1:2, v/v); ^1H NMR (400 MHz, CDCl_3): $\delta=-2.40$ (s, br, 2H, NH), 0.63 (s, 9H, SiCH_3), 2.72 (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.74 (s, 6H, $\text{C}_6\text{H}_4\text{CH}_3$), 7.56 (d, $^3J=8.2$ Hz, 2H, H_{Ar}), 7.59 (d, $^3J=8.2$ Hz, 4H, H_{Ar}), 8.07 (d, $^3J=8.2$ Hz, 2H, H_{Ar}), 8.10 (d, $^3J=8.2$ Hz, 4H, H_{Ar}), 8.80 (s, 4H, H_β), 8.93 (d, $^3J=4.7$ Hz, 2H, H_β), 9.66 (d, $^3J=4.7$ Hz, 2H, H_β) ppm; ^{13}C NMR (100.6 MHz, CDCl_3): $\delta=0.4$, 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 (CH_2Cl_2): λ_{max} (lg ϵ)=429 (5.7), 529 (4.6), 568 (4.6), 604 (4.4), 657 (4.5) nm; HRMS (ES $^+$): calcd for $\text{C}_{46}\text{H}_{40}\text{N}_4\text{Si}$ $[\text{M}+\text{H}]^+$ 677.3101, found 677.3095.

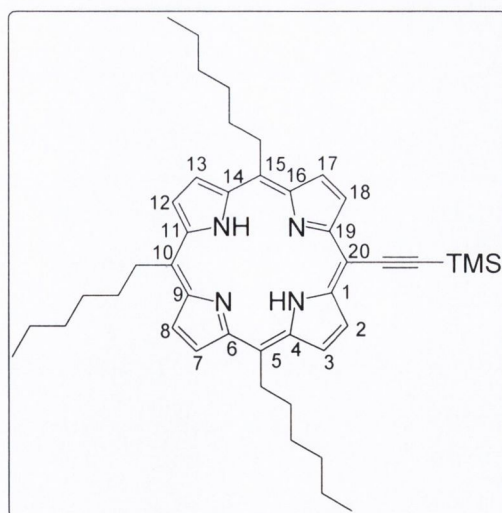


[5,10,15-Tris(4-methylphenyl)-20-trimethylsilylethynylporphyrinato]-nickel(II)

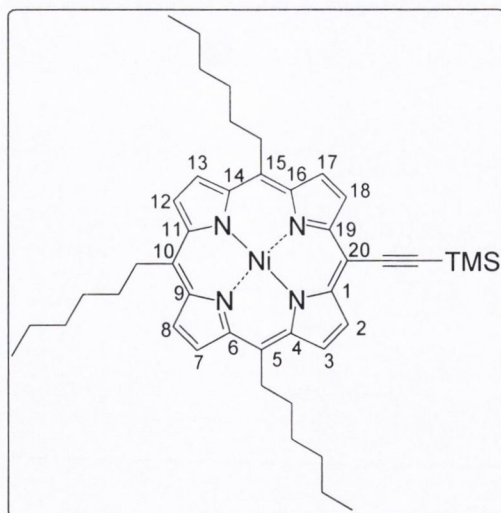
107. A 50 mL 2-necked round bottom flask was charged with 5,10,15-tris(4-methylphenyl)-20-trimethylsilylethynylporphyrin **106** (100 mg, 0.148 mmol; 1 equiv.) and Ni(acac)₂ (57 mg, 0.222 mmol, 1.5 equiv.) in toluene (30 mL). The reaction mixture was heated to reflux until completion (~30 min, monitored 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; $R_f=0.86$ (CH₂Cl₂/C₆H₁₄, 1:1, v/v); ¹H NMR (400 MHz, CDCl₃): $\delta=0.56$ (s, 9H, SiCH₃), 2.65 (s, 3H, C₆H₄CH₃), 2.68 (s, 6H, C₆H₄CH₃), 7.49 (d, ³ $J=8.0$ Hz, 4H, H_{Ar}), 7.51 (d, ³ $J=8.0$ Hz, 2H, H_{Ar}), 7.88 (d, ³ $J=4.8$ Hz, 4H, H_{Ar}), 7.90 (d, ³ $J=5.2$ Hz, 2H, H_{Ar}), 8.69 (d, ³ $J=5.3$ Hz, 2H, H_β), 8.71 (d, ³ $J=4.7$ Hz, 2H, H_β), 8.83 (d, ³ $J=4.7$ Hz, 2H, H_β), 9.51 (d, ³ $J=4.7$ Hz, 2H, H_β) ppm; ¹³C NMR (100.6 MHz, CDCl₃): $\delta=1.1$, 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): λ_{max} (lg ϵ)=417 (5.2), 533 (4.5) nm.



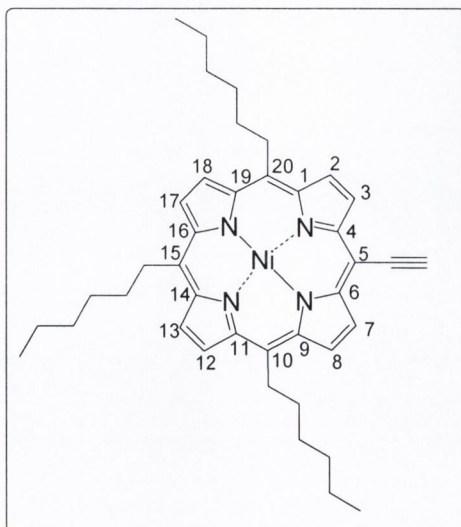
[5-Ethynyl-10,15,20-tris(4-methylphenyl)porphyrinato]nickel(II) 108. A 100 mL round-bottom flask was charged with [5-trimethylsilylethynyl-10,15,20-tris(4-methylphenyl)porphyrinato]nickel(II) **107** (108 mg, 0.146 mmol, 1 equiv.) and tetrabutylammoniumfluoride (61 mg, 0.234 mmol, 1.6 equiv.) in dichloromethane (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; R_f =0.63 ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$, 1:2, v/v); ^1H NMR (400 MHz, CDCl_3): δ =2.66 (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.68 (s, 6H, $\text{C}_6\text{H}_4\text{CH}_3$), 4.08 (s, 1H, $\text{C}\equiv\text{CH}$), 7.49 (d, 3J =8.8 Hz, 2H, H_{Ar}), 7.52 (d, 3J =8.2 Hz, 4H, H_{Ar}), 7.88 (d, 3J =6.5 Hz, 2H, H_{Ar}), 7.90 (d, 3J =7.6 Hz, 4H, H_{Ar}), 8.71 (d, 3J =4.7 Hz, 2H, H_β), 8.73 (d, 3J =5.3 Hz, 2H, H_β), 8.85 (d, 3J =4.7 Hz, 2H, H_β), 9.54 (d, 3J =4.7 Hz, 2H, H_β) ppm; ^{13}C NMR (100.6 MHz, CDCl_3): δ =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 ($\text{C}\equiv\text{CH}$), 3022 (Ar-H), 2850 (CH_3) cm^{-1} ; UV/vis (CH_2Cl_2): λ_{max} (lg ϵ)=423 (5.5), 537 (4.7), 571 (4.6) nm; HRMS (ES⁺): calcd for $\text{C}_{43}\text{H}_{30}\text{N}_4\text{Ni}$ [$\text{M}+\text{H}$]⁺ 661.1902, found 661.1870.



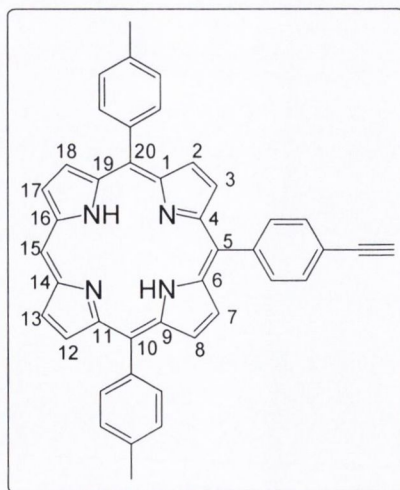
10,15,20-Trihexyl-5-trimethylsilyl ethynylporphyrin 110. A 50 mL Schlenk-tube was filled with argon and charged with 5-bromo-10,15,20-trihexylporphyrin **97** (100 mg, 0.156 mmol, 1 equiv.) in dry THF/triethylamine (40 mL, 3:1, v/v). The solution was degassed via five freeze-pump-thaw cycles and put 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(PPh₃)₂Cl₂ (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 (CH₂Cl₂/C₆H₁₄, 1:1, v/v); ¹H NMR (400 MHz, CDCl₃): δ=−2.40 (s, br, 2H, NH), 0.68 (s, 9H, SiCH₃), 0.97 (t, ³J=7.3 Hz, 6H, C₅H₁₀CH₃), 0.99 (t, ³J=7.6 Hz, 3H, C₅H₁₀CH₃), 1.43 (m, 6H, C₄H₈CH₂CH₃), 1.53 (m, 6H, C₃H₆CH₂CH₂CH₃), 1.79 (m, 6H, C₂H₄CH₂C₂H₄CH₃), 2.47 (m, 6H, CH₂CH₂C₃H₆CH₃), 4.81 (t, ³J=8.1 Hz, 4H, CH₂C₄H₈CH₃), 4.86 (t, ³J=8.1 Hz, 2H, CH₂C₄H₈CH₃), 9.33 (d, ³J=5.1 Hz, 2H, *H*_β), 9.38 (d, ³J=4.2 Hz, 2H, *H*_β), 9.40 (d, ³J=4.2 Hz, 2H, *H*_β), 9.65 (d, ³J=4.8 Hz, 2H, *H*_β) ppm; ¹³C NMR (100.6 MHz, CDCl₃): 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 (CH₂), 2919 (CH₂), 2848 (CH₃), 2132 (C≡C) cm^{−1}; UV/vis (CH₂Cl₂): λ_{max} (lg ε)=428 (5.8), 532 (4.7), 571 (4.8), 611 (4.6), 669 (4.7) nm; HRMS (ES⁺): calcd for C₄₃H₅₈N₄Si [M+H]⁺ 659.4509, found 659.4494.



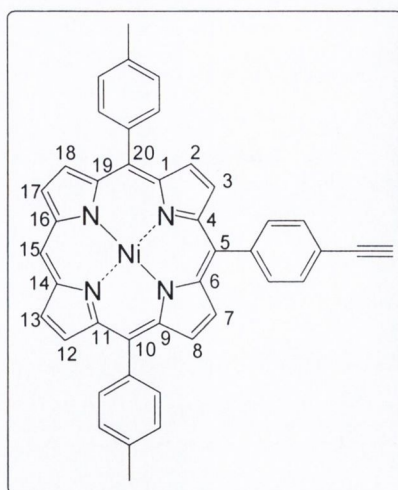
[10,15,20-Trihexyl-5-trimethylsilylethynylporphyrinato]nickel(II) 111. A 50 mL 2-necked round-bottom flask was charged with 10,15,20-trihexyl-5-trimethylsilylethynylporphyrin **110** (44 mg, 0.066 mmol, 1 equiv.) and Ni(acac)₂ (25 mg, 0.1 mmol, 1.5 equiv.) in toluene (20 mL). The reaction mixture was 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: $R_f=0.95$ (CH₂Cl₂/C₆H₁₄, 1:1, v/v); ¹H NMR (400 MHz, CDCl₃): $\delta=0.59$ (s, 9H, SiCH₃), 0.92 (t, ³ $J=7.2$ Hz, 6H, C₅H₁₀CH₃), 0.94 (t, ³ $J=7.2$ Hz, 3H, C₅H₁₀CH₃), 1.34 (m, 6H, C₄H₈CH₂CH₃), 1.43 (m, 6H, C₃H₆CH₂CH₂CH₃), 1.60 (m, 6H, C₂H₄CH₂C₂H₄CH₃), 2.26 (m, 6H, CH₂CH₂C₃H₆CH₃), 4.42 (m, 6H, CH₂C₄H₈CH₃), 9.18 (d, ³ $J=5.0$ Hz, 2H, H_β), 9.20 (d, ³ $J=2.1$ Hz, 2H, H_β), 9.22 (d, ³ $J=2.0$ Hz, 2H, H_β), 9.42 (d, ³ $J=5.0$ Hz, 2H, H_β) ppm; ¹³C NMR (100.6 MHz, CDCl₃): $\delta=0.4$, 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): $\lambda_{\max}$ (lg ϵ)=428 (5.3), 548 (4.4), 585 (4.3) nm; HRMS (ES⁺): calcd for C₄₃H₅₆N₄NiSi [M+H]⁺ 715.3706, found 715.3718.



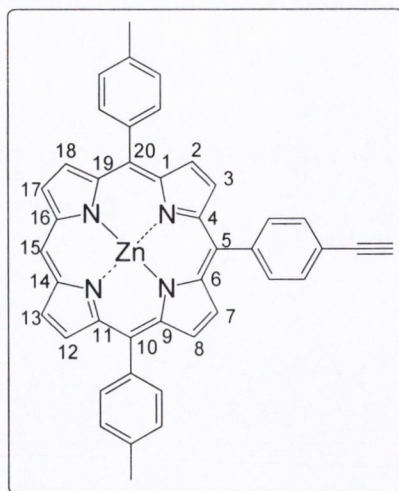
[5-Ethynyl-10,15,20-trihexylporphyrinato]nickel(II) 112. A 50 mL round bottom flask was charged with [10,15,20-trihexyl-5-trimethylsilylethynylporphyrinato]nickel(II) **111** (46 mg, 0.064 mmol, 1 equiv.) and tetrabutylammonium-fluoride (25 mg, 0.1 mmol, 1.6 equiv.) in dichloromethane (20 mL). The reaction 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: $R_f=0.89$ ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$, 1:1, v/v); ^1H NMR (400 MHz, CDCl_3): $\delta=0.94$ (t, $^3J=7.2$ Hz, 6H, $\text{C}_5\text{H}_{10}\text{CH}_3$), 0.96 (t, $^3J=7.2$ Hz, 3H, $\text{C}_5\text{H}_{10}\text{CH}_3$), 1.37 (m, 6H, $\text{C}_4\text{H}_8\text{CH}_2\text{CH}_3$), 1.43 (m, 6H, $\text{C}_3\text{H}_6\text{CH}_2\text{CH}_2\text{CH}_3$), 1.59 (m, 6H, $\text{C}_2\text{H}_4\text{CH}_2\text{C}_2\text{H}_4\text{CH}_3$), 2.25 (m, 6H, $\text{CH}_2\text{CH}_2\text{C}_3\text{H}_6\text{CH}_3$), 4.04 (s, 1H, $\text{C}\equiv\text{CH}$), 4.32 (t, $^3J=8.1$ Hz, 2H, $\text{CH}_2\text{C}_4\text{H}_8\text{CH}_3$), 4.37 (t, $^3J=8.0$ Hz, 4H, $\text{CH}_2\text{C}_4\text{H}_8\text{CH}_3$), 9.12 (d, $^3J=5.0$ Hz, 2H, H_β), 9.14 (d, $^3J=5.0$ Hz, 2H, H_β), 9.19 (d, $^3J=4.8$ Hz, 2H, H_β), 9.42 (d, $^3J=4.8$ Hz, 2H, H_β) ppm; ^{13}C NMR (100.6 MHz, CDCl_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_2Cl_2): λ_{max} ($\lg \epsilon$)=425 (5.6), 545 (4.6), 581 (4.5) nm; HRMS (ES⁺): calcd for $\text{C}_{40}\text{H}_{48}\text{N}_4\text{Ni}$ $[\text{M}+\text{H}]^+$ 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 $-78\text{ }^{\circ}\text{C}$ over 1 h. After the addition was complete the reaction mixture was warmed to $-45\text{ }^{\circ}\text{C}$ 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 $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (1:3, v/v) the product was obtained in 95 mg (0.16 mmol, 39 %) yield as purple crystals: mp $>300\text{ }^{\circ}\text{C}$; $R_f=0.24$ ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$, 1:4, v/v); ^1H NMR (400 MHz, CDCl_3): $\delta=-2.99$ (s, br, 2H, NH), 2.75 (s, 6H, $\text{C}_6\text{H}_4\text{CH}_3$), 3.35 (s, 1H, $\text{C}\equiv\text{CH}$), 7.01 (d, $^3J=7.6\text{ Hz}$, 4H, H_{Ar}), 7.91 (d, $^3J=8.2\text{ Hz}$, 2H, H_{Ar}), 8.15 (d, $^3J=7.6\text{ Hz}$, 4H, H_{Ar}), 8.21 (d, $^3J=7.6\text{ Hz}$, 2H, H_{Ar}), 8.86 (d, $^3J=4.7\text{ Hz}$, 2H, H_{β}), 8.97 (d, $^3J=4.7\text{ Hz}$, 2H, H_{β}), 9.08 (d, $^3J=4.1\text{ Hz}$, 2H, H_{β}), 9.37 (d, $^3J=4.7\text{ Hz}$, 2H, H_{β}), 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 ($\text{C}\equiv\text{CH}$), 3024 (Ar-H) cm^{-1} ; UV/vis (CH_2Cl_2): λ_{max} (lg ϵ)=414 (5.7), 509 (4.6), 543 (4.4), 582 (4.4), 639 (4.4) nm; HRMS (ES $^{+}$): calcd for $\text{C}_{42}\text{H}_{30}\text{N}_4$ [$\text{M}+\text{H}$] $^{+}$ 591.2549, found 591.2524.



[5-(4-Ethynylphenyl)-10,20-bis(4-methylphenyl)porphyrinato]nickel(II) 114. A 100 mL 2-necked round-bottom flask was charged with 5-(4-ethynylphenyl)-10,20-bis(4-methylphenyl)porphyrin **113** (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 CH₂Cl₂/MeOH (1:3, v/v) the product was obtained as red needles in 166 mg (0.257 mmol, 86 %) yield: mp >300 °C; R_f=0.77 (CH₂Cl₂/C₆H₁₄, 1:1, v/v); ¹H NMR (400 MHz, CDCl₃): δ=2.69 (s, 6H, C₆H₄CH₃), 3.30 (s, 1H, C≡CH), 7.53 (d, ³J=7.6 Hz, 4H, H_{Ar}), 7.84 (d, ³J=8.2 Hz, 2H, H_{Ar}), 7.94 (d, ³J=7.6 Hz, 4H, H_{Ar}), 8.01 (d, ³J=7.6 Hz, 2H, H_{Ar}), 8.76 (d, ³J=4.7 Hz, 2H, H_β), 8.84 (d, ³J=5.3 Hz, 2H, H_β), 8.95 (d, ³J=4.7 Hz, 2H, H_β), 9.16 (d, ³J=4.7 Hz, 2H, H_β), 9.86 (s, 1H, H_{meso}) ppm; ¹³C NMR (100.6 MHz, CDCl₃): δ=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 (CH₂Cl₂): λ_{max} (lg ε)=409 (5.4), 523 (4.6), 550 (4.4) nm; HRMS (ES⁺): calcd for C₄₂H₂₈N₄Ni [M+H]⁺ 647.1746, found 647.1755.

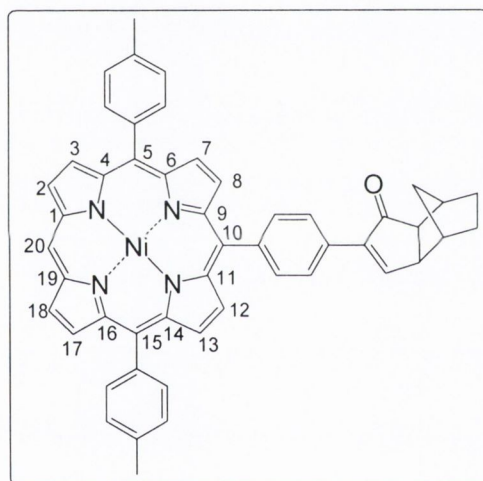


[5-(4-Ethynylphenyl)-10,20-bis(4-methylphenyl)porphyrinato]zinc(II) 115: A

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). $\text{Zn}(\text{OAc})_2$ (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; $R_f=0.46$ ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$, 1:1, v/v); ^1H NMR (400 MHz, CDCl_3): $\delta=2.76$ (s, 6H, $\text{C}_6\text{H}_4\text{CH}_3$), 3.34 (s, 1H, $\text{C}\equiv\text{CH}$), 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_β), 9.06 (d, $^3J=4.7$ Hz, 2H, H_β), 9.13 (d, $^3J=4.7$ Hz, 2H, H_β), 9.38 (d, $^3J=4.1$ Hz, 2H, H_β), 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 ($\text{C}\equiv\text{CH}$), 3022 (Ar-H) cm^{-1} ; UV/vis (CH_2Cl_2): λ_{max} (lg ϵ)=415 (5.7), 542 (4.8) nm; HRMS (ES⁺): calcd for $\text{C}_{42}\text{H}_{30}\text{N}_4$ $[\text{M}]^+$ 652.1605, found 652.1588.

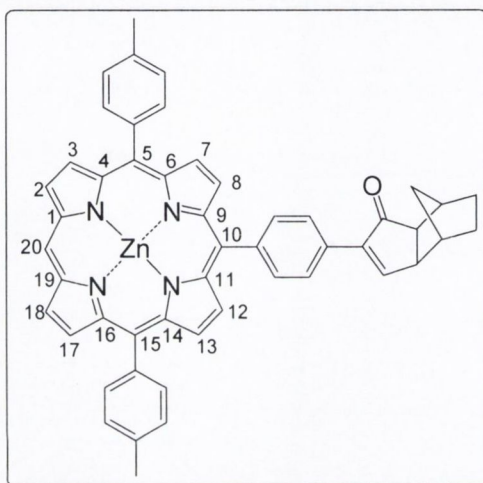
7.5.2 Pauson-Khand Products II

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 $\text{Co}_2(\text{CO})_8$ (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 ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$, 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 $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (1:3, v/v).



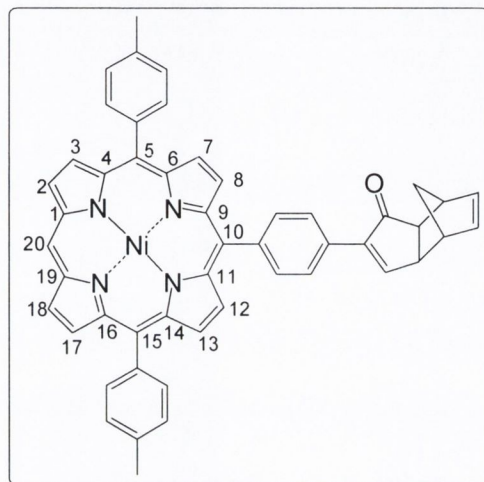
[5,15-Bis(4-methylphenyl)-10-(4-phenyltricyclo[5.2.1.0^{2,6}]]deca-4-en-3-onyl)-porphyrinato]nickel(II) 116. By using [5-(4-ethynylphenyl)-10,20-bis(4-methylphenyl)porphyrinato]nickel(II) **114** (40 mg, 0.062 mmol) and norbornene (12 mg, 0.124 mmol) as starting material, the product was obtained after recrystallisation as purple crystals in 40.4 mg (0.053 mmol, 85 %) yield: mp >300 °C; R_f =0.24 ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$, 1:1, v/v); ^1H NMR (400 MHz, CDCl_3): δ =1.14 (d, 3J =10.5 Hz, 1H, CHCH_2CH), 1.31 (dd, 3J =11.7 Hz, 3J = 10.5 Hz, 1 H, CHCH_2CH), 1.46 (m, 2H, $\text{C}=\text{CH}(\text{CH}_2)\text{CH}_2$), 1.77 (m, 2H, $\text{CO}(\text{CH})_2\text{CH}_2$), 2.42 (s, 1H, COCHCHCH_2), 2.54 (d, 3J =5.3 Hz, 1H, COCHCHCH_2), 2.64 (s, 1H, $\text{C}=\text{CHCHCHCH}_2$), 2.69 (s, 6H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.87 (d, 3J =2.9 Hz, 1H, $\text{C}=\text{CHCHCHCH}_2$), 7.53 (d, 3J =7.0 Hz, 4H, H_{Ar}), 7.94 (d,

$^3J=5.9$ Hz, 4H, H_{Ar}), 7.96 (s, 1H, C=CH), 8.06 (s, 4H, H_{Ar}), 8.81 (d, $^3J=5.9$ Hz, 2H, H_β), 8.83 (d, $^3J=4.7$ Hz, 2H, H_β), 8.95 (d, $^3J=4.7$ Hz, 2H, H_β), 9.16 (d, $^3J=4.7$ Hz, 2H, H_β), 9.86 (s, 1H, H_{meso}) ppm; ^{13}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 ppm; IR: 3024 (Ar-H), 2943 (CH_2), 2869 (CH_3) 1692 (C=O) cm^{-1} ; UV/vis (CH_2Cl_2): λ_{max} (lg ϵ)=409 (5.8), 522 (4.9), 550 (4.7) nm; HRMS (ES $^+$): calcd for $C_{50}H_{38}N_4NiO$ $[M+H]^+$ 769.2477, found 769.2479.



[5,15-Bis(4-methylphenyl)-10-(4-phenyltricyclo[5.2.1.0^{2,6}]]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 °C; $R_f=0.31$ (CH_2Cl_2/C_6H_{14} , 1:1, v/v); 1H NMR (400 MHz, $CDCl_3$): $\delta=0.99$ (d, $^3J=6.4$ Hz, 1H, CHCH₂CH), 1.14 (d, $^3J=11.1$ Hz, 1H, CHCH₂CH), 1.46 (m, 2H, C=CH(CH)₂CH₂), 1.78 (m, 2H, CO(CH)₂CH₂), 2.44 (d, $^3J=2.3$ Hz, 1H, COCHCHCH₂), 2.48 (d, $^3J=5.3$ Hz, 1H, COCHCHCH₂), 2.58 (s, 1H, C=CHCHCHCH₂), 2.76 (s, 6H, C₆H₄CH₃), 2.88 (s, 1H, C=CHCHCHCH₂), 7.61 (d, $^3J=7.6$ Hz, 4H, H_{Ar}), 7.98 (d, $^3J=2.9$ Hz, 1H, C=CH), 8.07 (d, $^3J=8.2$ Hz, 2H, H_{Ar}), 8.15 (d, $^3J=7.6$ Hz, 4H, H_{Ar}), 8.25 (d, $^3J=7.6$ Hz, 2H, H_{Ar}), 9.01 (d, $^3J=4.7$ Hz, 2H, H_β), 9.04 (d, $^3J=4.7$ Hz, 2H, H_β), 9.15 (d, $^3J=4.7$ Hz, 2H, H_β), 9.43 (d, $^3J=4.7$ Hz, 2H, H_β), 10.29 (s, 1H, H_{meso}) ppm; ^{13}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,

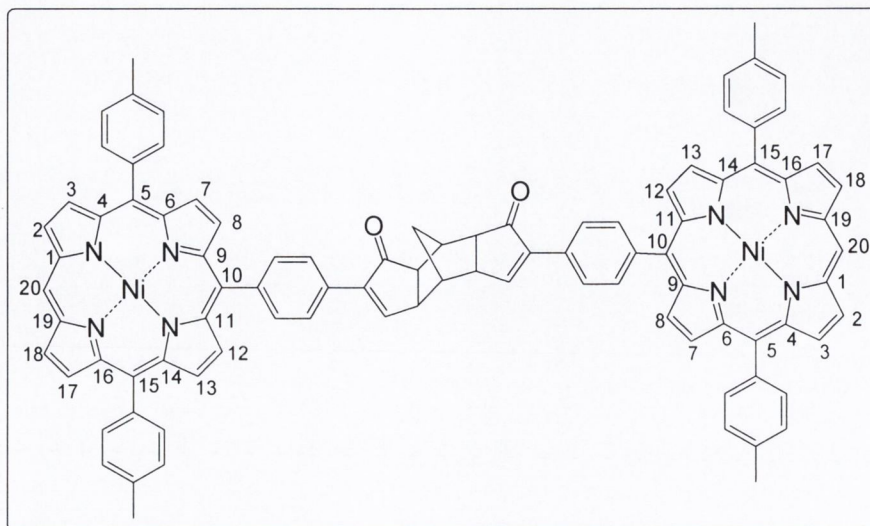
125.4, 127.2, 128.1, 130.5, 131.5, 131.7, 131.8, 132.4, 132.5, 134.3, 134.4, 135.6, 136.9, 139.6, 139.7, 142.9, 134.1, 145.3, 145.9, 148.7, 149.5, 149.8, 150.2, 150.3, 1501.4, 160.6, 186.0, 209.2 ppm; IR: 2920 (CH₂), 2852 (CH₃), 1672 (C=O) cm⁻¹; UV/vis (CH₂Cl₂): λ_{max} (lg ϵ)=415 (6.2), 543 (5.1), 582 (4.9) nm; HRMS (ES⁺): calcd for C₅₀H₃₈N₄OZn [M]⁺ 774.2337, found 774.2338.



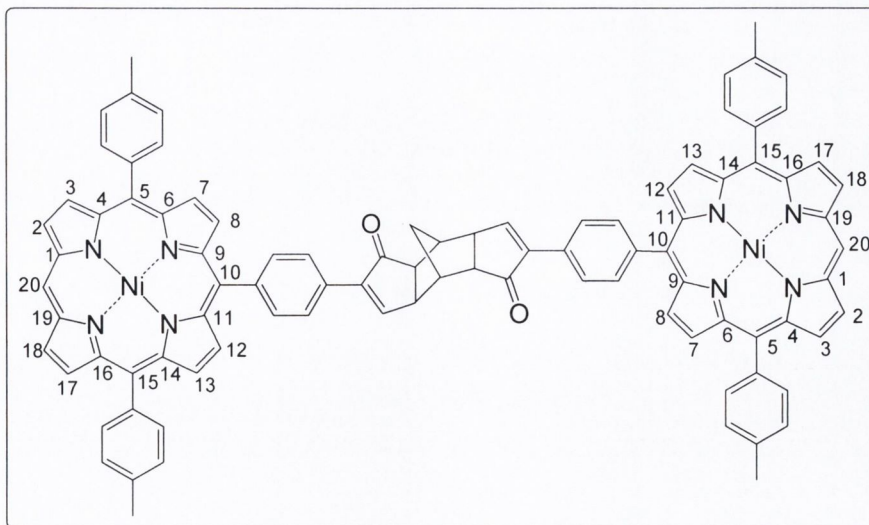
[5,15-Bis(4-methylphenyl)-10-(4-phenyltricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-onyl)-

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; R_f =0.21 (CH₂Cl₂/C₆H₁₄, 1:1, v/v); ¹H NMR (400 MHz, CDCl₃): δ =1.56 (d, ³ J =1.2 Hz, 2H, CHCH₂CH), 2.64 (d, ³ J =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, ³ J =1.2 Hz, 1H, COCHCH), 6.35 (dd, ³ J =5.3 Hz, ³ J =2.9 Hz, 1H, CH=CH), 6.43 (dd, ³ J =5.3 Hz, ³ J =2.9 Hz, 1H, CH=CH), 7.53 (d, ³ J =7.6 Hz, 4H, H_{Ar}), 7.94 (d, ³ J =8.2 Hz, 4H, H_{Ar}), 7.99 (d, ³ J =2.9 Hz, 1H, C=CH), 8.06 (d, ³ J =8.8 Hz, 2H, H_{Ar}), 8.06 (d, ³ J =8.8 Hz, 2H, H_{Ar}), 8.80 (d, ³ J =4.7 Hz, 2H, H_β), 8.83 (d, ³ J =4.7 Hz, 2H, H_β), 8.94 (d, ³ J =5.3 Hz, 2H, H_β), 9.16 (d, ³ J =4.7 Hz, 2H, H_β), 9.86 (s, 1H, H_{meso}) 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): λ_{max} (lg ϵ)=409 (5.7), 523

(4.7), 548 (4.5) nm; HRMS (MALDI LD+): calcd for $C_{50}H_{36}N_4ONi$ $[M]^+$ 766.2243, found 766.2251.



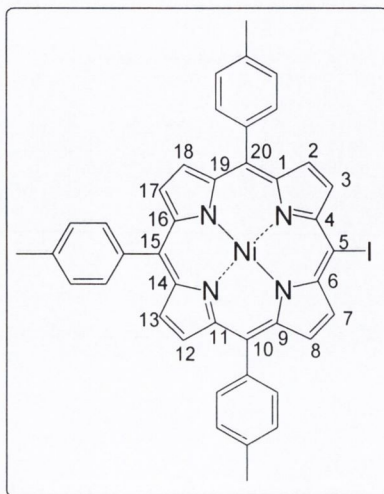
4,10-Bis{[5,15-bis(4-methylphenyl)-10-phenylporphyrinato]nickel(II)}tetracyclo-[5.2.1.0^{2,6}.0^{8,12}]trideca-4,9-dien-3,11-dione 119. By using [5-(4-ethynylphenyl)-10,20-bis(4-methylphenyl)porphyrinato]nickel(II) **114** (26 mg, 0.039 mmol) and [5,15-bis(4-methylphenyl)-10-(4-phenyltricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-onyl)porphyrinato]nickel(II) **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, $C=CHCHCHCHCH=C$, CH_2CH), 3.16 (m, 2H, $COCHCHCHCO$), 7.54 (d, 3J =7.6 Hz, 8H, H_{Ar}), 7.95 (d, 3J =8.2 Hz, 8H, H_{Ar}), 8.02 (d, 3J =2.34 Hz, 2H, $C=CH$), 8.09 (s, 8H, H_{Ar}), 8.81 (d, 3J =5.3 Hz, 4H, H_β), 8.84 (d, 3J =4.7 Hz, 4H, H_β), 8.95 (d, 3J =4.7 Hz, 4H, H_β), 9.17 (d, 3J =4.7 Hz, 4H, H_β), 9.86 (s, 2H, H_{meso}) ppm; ^{13}C 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 $C_{93}H_{64}N_8O_2Ni_2$ $[M]^+$ 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; $R_f=0.19$ (CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3): $\delta=1.22$ (s, 2H, CHCH_2CH), 2.69 (s, 12H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.72 (d, $^3J=5.3$ Hz, 2H, CHCH_2CH), 3.06 (m, 4H, COCHCH), 7.53 (d, $^3J=7.6$ Hz, 8H, H_{Ar}), 7.89 (d, $^3J=1.8$ Hz, 2H, $\text{C}=\text{CH}$), 7.95 (d, $^3J=8.2$ Hz, 8H, H_{Ar}), 8.06 (d, $^3J=8.8$ Hz, 4H, H_{Ar}), 8.09 (d, $^3J=8.2$ Hz, 4H, H_{Ar}), 8.81 (d, $^3J=5.3$ Hz, 4H, H_β), 8.85 (d, $^3J=5.3$ Hz, 4H, H_β), 8.95 (d, $^3J=4.7$ Hz, 4H, H_β), 9.17 (d, $^3J=4.7$ Hz, 4H, H_β), 9.86 (s, 2H, H_{meso}) ppm; ^{13}C NMR (100.6 MHz, CDCl_3): $\delta=21.1$, 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 (CH_2), 2851 (CH_3), 1704 ($\text{C}=\text{O}$) cm^{-1} ; UV/vis (CH_2Cl_2): λ_{max} (lg ϵ)=410 (5.7), 521 (4.9), 548 (4.7) nm; HRMS (MALDI LD⁺): calcd for $\text{C}_{93}\text{H}_{64}\text{N}_8\text{O}_2\text{Ni}_2$ $[\text{M}]^+$ 1440.3859, found 1440.3929.

7.6 Suzuki Reaction Using Potassium Organotrifluoroborates

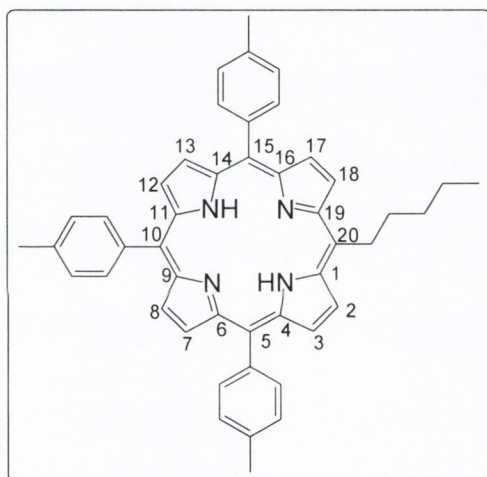
7.6.1 Synthesis of Starting Materials



[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, ³*J*=7.5 Hz, 6H, *H*_{Ar}), 7.88 (d, ³*J*=7.3 Hz, 6H, *H*_{Ar}), 8.71 (d, ³*J*=4.4 Hz, 2H, *H*_β), 8.73 (d, ³*J*=5.1 Hz, 2H, *H*_β), 8.79 (d, ³*J*=4.4 Hz, 2H, *H*_β), 9.51 (d, ³*J*=5.1 Hz, 2H, *H*_β), 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 C₄₁H₃₀N₄INi [M+H]⁺ 763.0849, found 763.0895.

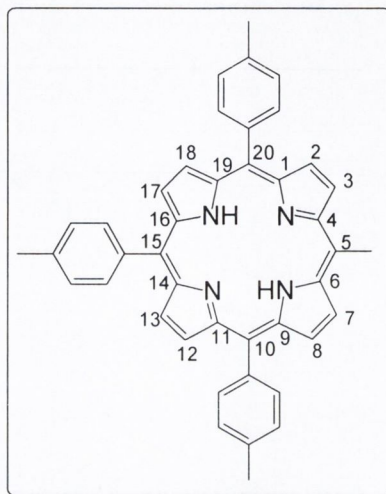
7.6.2 Suzuki Products

General procedure: A 20 mL Schlenk-tube was put under argon and charged with porphyrin (**60**, **67**, **69**, **97**, **148**) (1 equiv.) and Cs_2CO_3 (20 equiv.) in THF/ H_2O (10:1, v/v). The solution was degassed *via* three freeze-pump-thaw cycles and put under argon again. Potassium organotrifluoroborate (10 equiv.) and $\text{Pd}(\text{dppf})\text{Cl}_2$ (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 ($\text{CH}_2\text{Cl}_2/n$ -hexane, 1:1, v/v).

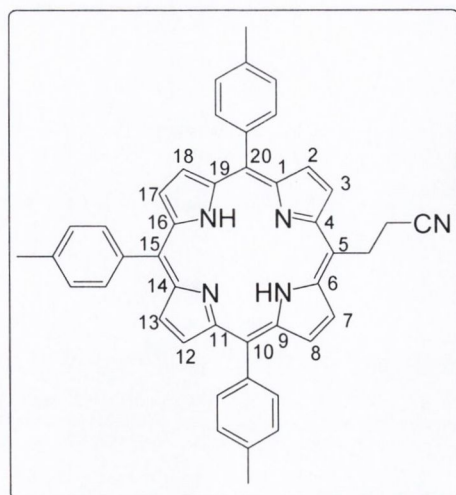


5,10,15-Tris(4-methylphenyl)-20-pentylporphyrin 149. By using 5-bromo-10,15,20-tris(4-methylphenyl)porphyrin **67** (30 mg, 0.045 mmol), Cs_2CO_3 (318 mg, 0.9 mmol), $\text{Pd}(\text{dppf})\text{Cl}_2$ (8 mg, 0.01125 mmol) and potassium *n*-pentyltrifluoroborate (80 mg, 0.45 mmol) the product was obtained as purple crystals in 6.2 mg (0.01 mmol, 21%) yield: mp >300 °C; $R_f=0.52$ ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$, 1:1, v/v); ^1H NMR (600 MHz, CDCl_3): $\delta=-2.68$ (s, br, 2H, NH), 1.00 (t, $^3J=7.3$ Hz, 3H, $(\text{CH}_2)_4\text{CH}_3$), 1.59 (t, $^3J=7.7$ Hz, 2H, $(\text{CH}_2)_3\text{CH}_2\text{CH}_3$), 1.83 (t, $^3J=7.7$ Hz, 2H, $(\text{CH}_2)_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.59 (t, $^3J=7.3$ Hz, 2H, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 2.73 (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.75 (s, 6H, $\text{C}_6\text{H}_4\text{CH}_3$), 5.05 (t, $^3J=8.1$ Hz, 2H, $\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 7.57 (d, $^3J=7.3$ Hz, 2H, H_{Ar}), 7.59 (d, $^3J=7.3$ Hz, 4H, H_{Ar}), 8.10 (d, $^3J=8.1$ Hz, 2H, H_{Ar}), 8.12 (d, $^3J=7.3$ Hz, 4H, H_{Ar}), 8.83 (s, 4H, H_β), 8.96 (d, $^3J=4.4$ Hz, 2H, H_β), 9.50 (d, $^3J=5.1$ Hz, 2H, H_β) ppm; ^{13}C NMR (150.9 MHz, CDCl_3):

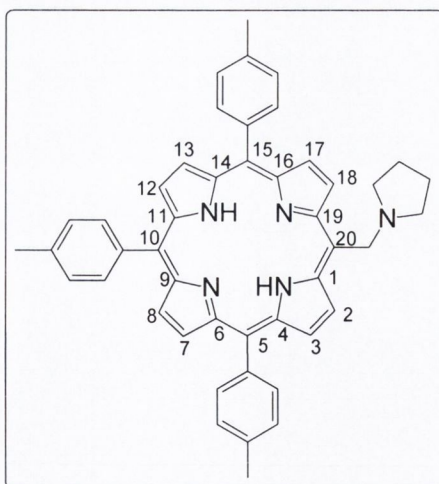
δ =14.0, 21.4, 22.6, 32.6, 35.4, 38.4, 119.2, 119.4, 120.2, 127.2, 127.3, 131.1, 134.3, 134.3, 137.1, 139.1, 139.4 ppm; IR: 3311 (NH), 3027 (Ar-H), 2951 (CH₂), 2919 (CH₂), 2855 (CH₃) cm⁻¹; UV-vis (CH₂Cl₂): $\lambda_{\max}$ (lg ϵ)=419 (5.7), 517 (4.6), 553 (4.5), 593 (4.4), 649 (4.4) nm; HRMS (ES⁺): calcd for C₄₆H₄₃N₄ [M+H]⁺ 651.3488, found 651.3495.



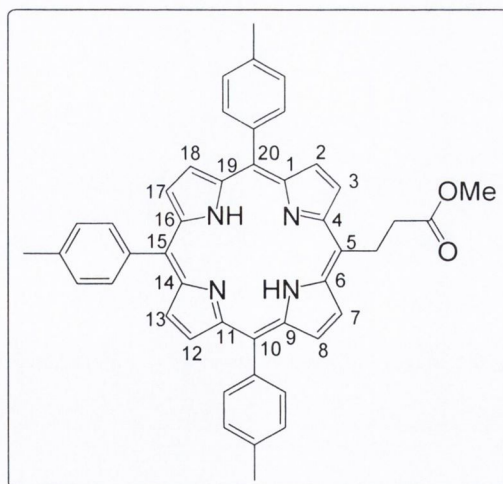
5-Methyl-10,15,20-tris(4-methylphenyl)porphyrin 150. By using 5-bromo-10,15,20-tris(4-methylphenyl)porphyrin **67** (30 mg, 0.045 mmol), Cs₂CO₃ (318 mg, 0.9 mmol), Pd(dppf)Cl₂ (8 mg, 0.01125 mmol) and potassium methyltrifluoroborate (55 mg, 0.45 mmol) the product was obtained as purple crystals in 7.8 mg (0.013 mmol, 29 %) yield: mp >300 °C; R_f=0.43 (CH₂Cl₂/C₆H₁₄, 1:1, v/v); ¹H 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, H_{Ar}), 7.59 (d, ³J=7.8 Hz, 4H, H_{Ar}), 8.10 (d, ³J=7.5 Hz, 2H, H_{Ar}), 8.12 (d, ³J=7.8 Hz, 4H, H_{Ar}), 8.84 (s, 4H, H_β), 8.96 (d, ³J=4.8 Hz, 2H, H_β), 9.53 (d, ³J=4.8 Hz, 2H, H_β) ppm; ¹³C 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): $\lambda_{\max}$ (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.



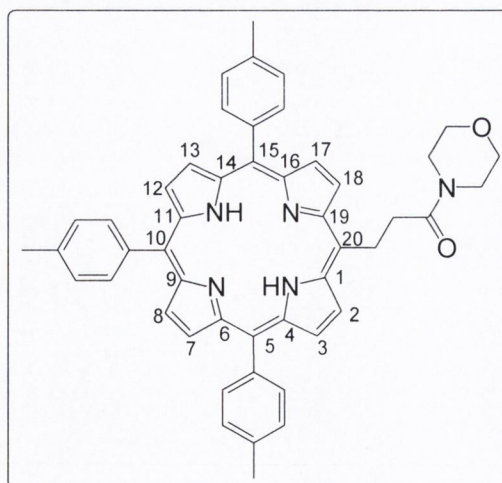
5-Cyanoethyl-10,15,20-tris(4-methylphenyl)porphyrin 151. By using 5-bromo-10,15,20-tris(4-methylphenyl)porphyrin **67** (30 mg, 0.045 mmol), Cs_2CO_3 (318 mg, 0.9 mmol), $\text{Pd}(\text{dppf})\text{Cl}_2$ (8 mg, 0.01125 mmol) and potassium 2-cyanoethyltrifluoroborate (73 mg, 0.45 mmol) the product was obtained as purple crystals in 21.1 mg (0.033 mmol, 73%) yield: mp $>300^\circ\text{C}$; $R_f=0.58$ ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$, 1:1, v/v); ^1H NMR (600 MHz, CDCl_3): $\delta=-2.75$ (s, br, 2H, NH), 2.72 (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.76 (s, 6H, $\text{C}_6\text{H}_4\text{CH}_3$), 3.56 (t, $^3J=8.1$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{CN}$), 5.46 (t, $^3J=8.1$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{CN}$), 7.58 (d, $^3J=8.1$ Hz, 2H, H_{Ar}), 7.60 (d, $^3J=7.3$ Hz, 4H, H_{Ar}), 8.09 (d, $^3J=7.3$ Hz, 2H, H_{Ar}), 8.11 (d, $^3J=8.1$ Hz, 4H, H_{Ar}), 8.85 (s, 4H, H_β), 9.03 (d, $^3J=5.1$ Hz, 2H, H_β), 9.46 (d, $^3J=4.4$ Hz, 2H, H_β) ppm; ^{13}C NMR (150.9 MHz, CDCl_3): $\delta=21.4$, 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 (CH_2), 2244 ($\text{C}\equiv\text{N}$) cm^{-1} ; UV-vis (CH_2Cl_2): λ_{max} (lg ϵ)=419 (5.7), 516 (4.6), 551 (4.5), 592 (4.5), 648 (4.4) nm; HRMS (ES $^+$): calcd for $\text{C}_{44}\text{H}_{36}\text{N}_5$ $[\text{M}+\text{H}]^+$ 634.2971, found 634.3000.



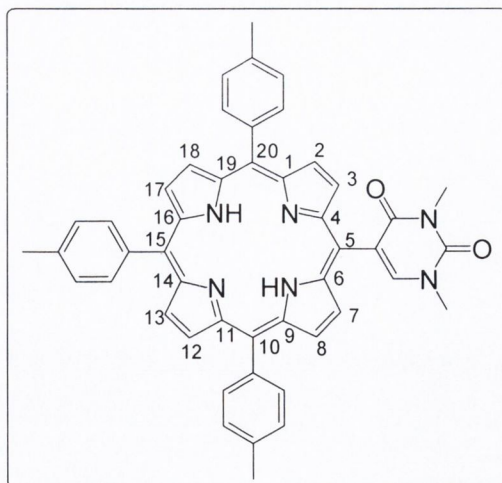
5,10,15-Tris(4-methylphenyl)-20-methylpyrrolidylporphyrin 152. By using 5-bromo-10,15,20-tris(4-methylphenyl)porphyrin **67** (30 mg, 0.045 mmol), Cs_2CO_3 (318 mg, 0.9 mmol), $\text{Pd}(\text{dppf})\text{Cl}_2$ (8 mg, 0.01125 mmol) and potassium 1-trifluoroboratomethylpyrrolidine (86 mg, 0.45 mmol) the product was obtained as purple crystals in 7.9 mg (0.012 mmol, 26%) yield: mp $>300\text{ }^\circ\text{C}$; $R_f=0.26$ (ethyl acetate); ^1H NMR (400 MHz, CDCl_3): $\delta=-2.77$ (s, br, 2H, NH), 1.82 (s, br, 4H, $\text{NCH}_2(\text{CH}_2)_2$), 2.72 (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.75 (s, 6H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.94 (s, br, 4H, $\text{NCH}_2(\text{CH}_2)_2\text{CH}_2$), 6.00 (s, br, 2H, CH_2N), 7.57 (d, $^3J=5.9$ Hz, 2H, H_{Ar}), 7.59 (d, $^3J=6.9$ Hz, 4H, H_{Ar}), 8.10 (d, $^3J=4.9$ Hz, 2H, H_{Ar}), 8.12 (d, $^3J=7.8$ Hz, 4H, H_{Ar}), 8.85 (d, $^3J=2.9$ Hz, 4H, H_β), 8.98 (d, $^3J=4.9$ Hz, 2H, H_β), 9.69 (d, $^3J=3.9$ Hz, 2H, H_β) ppm; ^{13}C NMR (100.6 MHz, CDCl_3): $\delta=21.1$, 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 (CH_2), 2853 (CH_3), 1669 (CH_2N) cm^{-1} ; UV-vis (CH_2Cl_2): λ_{max} (lg ϵ)=421 (5.4), 519 (4.3), 554 (4.2), 594 (4.2), 651 (4.1) nm; HRMS (ES $^+$): calcd for $\text{C}_{46}\text{H}_{42}\text{N}_5$ $[\text{M}+\text{H}]^+$ 664.3461, found 664.3440.



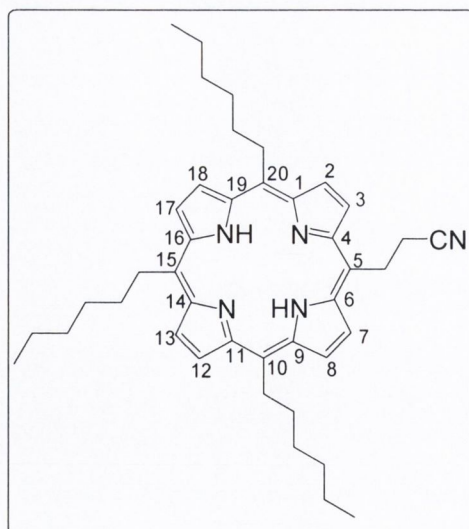
5-Methylpropionatyl-10,15,20-tris(4-methylphenyl)porphyrin 153. By using 5-bromo-10,15,20-tris(4-methylphenyl)porphyrin **67** (30 mg, 0.045 mmol), Cs_2CO_3 (318 mg, 0.9 mmol), $\text{Pd}(\text{dppf})\text{Cl}_2$ (8 mg, 0.01125 mmol) and potassium 3-trifluoroboratopropionate methyl ester (175 mg, 0.9 mmol, 20 equiv.) the product was obtained as purple crystals in 4.9 mg (0.007 mmol, 16%) yield: mp $>300^\circ\text{C}$; $R_f=0.28$ ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$, 1:1, v/v); ^1H NMR (600 MHz, CDCl_3): $\delta=-2.72$ (s, br, 2H, NH), 2.73 (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.75 (s, 6H, $\text{C}_6\text{H}_4\text{CH}_3$), 3.59 (t, $^3J=8.4$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{OCH}_3$), 3.80 (s, 3H, $\text{CH}_2\text{CH}_2\text{OCH}_3$), 5.42 (t, $^3J=8.4$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{OCH}_3$), 7.57 (d, $^3J=8.1$ Hz, 2H, H_{Ar}), 7.59 (d, $^3J=7.3$ Hz, 4H, H_{Ar}), 8.09 (d, $^3J=8.8$ Hz, 2H, H_{Ar}), 8.11 (d, $^3J=7.3$ Hz, 4H, H_{Ar}), 8.84 (s, 4H, H_β), 8.98 (d, $^3J=4.4$ Hz, 2H, H_β), 9.53 (d, $^3J=4.4$ Hz, 2H, H_β) ppm; ^{13}C NMR (150.9 MHz, CDCl_3): $\delta=21.4$, 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 ($\text{C}=\text{O}$) cm^{-1} ; UV-vis (CH_2Cl_2): λ_{max} (lg ϵ)=419 (5.6), 516 (4.5), 552 (4.3), 593 (4.2), 651 (4.2) nm; HRMS (ES $^+$): calcd for $\text{C}_{45}\text{H}_{39}\text{N}_4\text{O}_2$ $[\text{M}+\text{H}]^+$ 667.3073, found 667.3093.



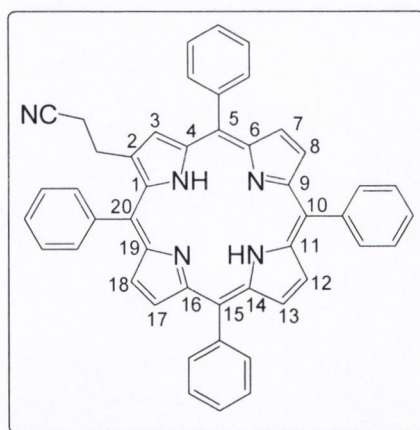
5,10,15-Tris(4-methylphenyl)-20-morpholinopropanolylporphyrin 154. By using 5-bromo-10,15,20-tris(4-methylphenyl)porphyrin **67** (30 mg, 0.045 mmol), Cs_2CO_3 (318 mg, 0.9 mmol), $\text{Pd}(\text{dppf})\text{Cl}_2$ (8 mg, 0.01125 mmol) and potassium 3-morpholino-3-oxopropyl trifluoroborate (112 mg, 0.45 mmol) the product was obtained as purple crystals in 6.7 mg (0.009 mmol, 21%) yield: mp 273 °C; $R_f=0.69$ (ethyl acetate); ^1H NMR (600 MHz, CDCl_3): $\delta=-2.70$ (s, br, 2H, NH), 2.73 (m, 5H, $\text{C}_6\text{H}_4\text{CH}_3$, CH_2O), 2.76 (s, 6H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.91 (t, $^3J=4.4$ Hz, 2H, NCH_2), 3.47 (t, $^3J=4.8$ Hz, 2H, OCH_2), 3.57 (t, $^3J=8.1$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{CO}$), 3.66 (t, $^3J=4.4$ Hz, 2H, CH_2N), 5.47 (t, $^3J=9.2$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{CO}$), 7.58 (d, $^3J=8.8$ Hz, 2H, H_{Ar}), 7.60 (d, $^3J=7.3$ Hz, 4H, H_{Ar}), 8.10 (d, $^3J=4.4$ Hz, 2H, H_{Ar}), 8.11 (d, $^3J=8.1$ Hz, 4H, H_{Ar}), 8.85 (s, 4H, H_β), 8.99 (d, $^3J=4.4$ Hz, 2H, H_β), 9.53 (d, $^3J=4.4$ Hz, 2H, H_β) ppm; ^{13}C NMR (150.9 MHz, CDCl_3): $\delta=21.5$, 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 (CH_2), 1637 ($\text{C}=\text{O}$) cm^{-1} ; UV-vis (CH_2Cl_2): λ_{max} (lg ϵ)=419 (5.5), 518 (4.5), 552 (4.4), 592 (4.4), 647 (4.4) nm; HRMS (ES $^+$): calcd for $\text{C}_{48}\text{H}_{44}\text{N}_5\text{O}_2$ $[\text{M}+\text{H}]^+$ 722.3495, found 722.3404.



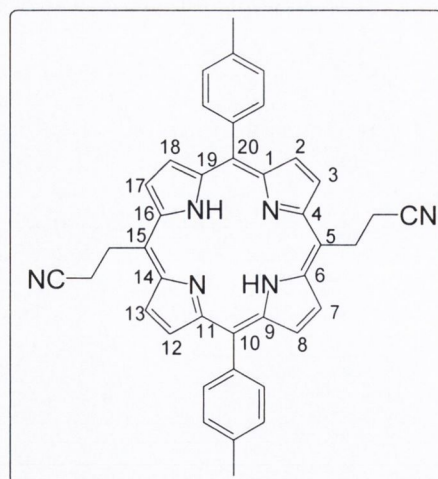
5-(*N,N*-Dimethyluracil)-10,15,20-tris(4-methylphenyl)porphyrin 155. By using 5-bromo-10,15,20-tris(4-methylphenyl)porphyrin **67** (30 mg, 0.045 mmol), Cs_2CO_3 (318 mg, 0.9 mmol), $\text{Pd}(\text{dppf})\text{Cl}_2$ (8 mg, 0.01125 mmol) and potassium 1,3-dimethyluracil-5-trifluoroborate (111 mg, 0.45 mmol) the product was obtained as purple crystals in 24.2 mg (0.034 mmol, 75%) yield: mp $>300^\circ\text{C}$; $R_f=0.23$ (ethyl acetate/ C_6H_{14} , 1:2, v/v); ^1H NMR (600 MHz, CDCl_3): $\delta=-2.73$ (s, br, 2H, NH), 2.73 (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.74 (s, 6H, $\text{C}_6\text{H}_4\text{CH}_3$), 3.72 (s, 3H, NCH_3CH), 3.75 (s, 3H, CONCH_3CO), 7.59 (m, 6H, H_{Ar}), 8.00 (s, 1H, CH), 8.12 (m, 6H, H_{Ar}), 8.87 (d, $^3J=3.7$ Hz, 4H, H_β), 8.94 (d, $^3J=3.7$ Hz, 2H, H_β), 9.06 (d, $^3J=4.4$ Hz, 2H, H_β) ppm; ^{13}C NMR (150.9 MHz, CDCl_3): $\delta=21.4$, 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 (CH_3), 2851 (CH_3), 2705 (NCH_3), 1710 ($\text{C}=\text{O}$), 1648 ($\text{C}=\text{O}$) cm^{-1} ; UV-vis (CH_2Cl_2): λ_{max} (lg ϵ)=420 (5.8), 516 (4.6), 551 (4.4), 591 (4.3), 648 (4.3) nm; HRMS (ES $^+$): calcd for $\text{C}_{47}\text{H}_{39}\text{N}_6\text{O}_2$ $[\text{M}+\text{H}]^+$ 719.3126, found 719.3134.



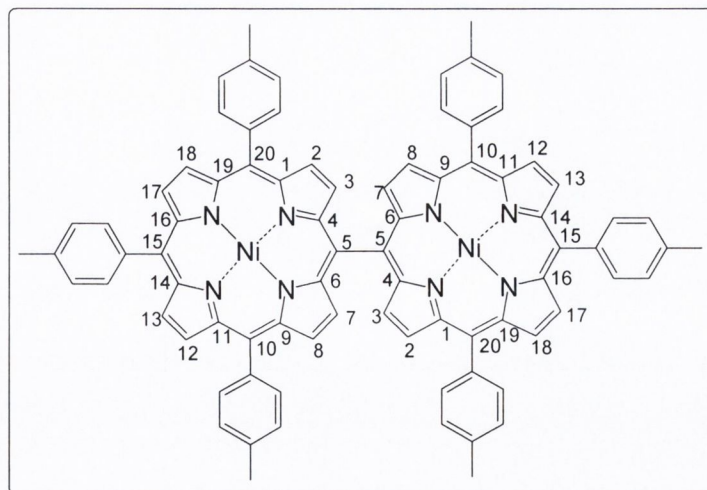
5-Cyanoethyl-10,15,20-trihexylporphyrin 156. By using 5-bromo-10,15,20-trihexylporphyrin **97** (30 mg, 0.047 mmol), Cs_2CO_3 (318 mg, 0.9 mmol), $\text{Pd}(\text{dppf})\text{Cl}_2$ (9 mg, 0.01175 mmol) and potassium 2-cyanoethyltrifluoroborate (76 mg, 0.47 mmol) the product was obtained as purple crystals in 7.1 mg (0.0115 mmol, 25%) yield: mp 117 °C; $R_f=0.18$ ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$, 1:1, v/v); ^1H NMR (400 MHz, CDCl_3): $\delta=-2.73$ (s, br, 2H, NH), 0.99 (t, $^3J=7.3$ Hz, 9H, CH_3), 1.45 (m, 6H, $(\text{CH}_2)_4\text{CH}_2\text{CH}_3$), 1.55 (m, 6H, $(\text{CH}_2)_3\text{CH}_2\text{CH}_2\text{CH}_3$), 1.84 (m, 6H, $(\text{CH}_2)_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 2.53 (m, 6H, $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 3.47 (t, $^3J=8.8$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{CN}$), 4.94 (m, 6H, $\text{CH}_2(\text{CH}_2)_4\text{CH}_3$), 5.32 (t, $^3J=8.8$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{CN}$), 9.39 (d, $^3J=4.8$ Hz, 2H, H_β), 9.49 (d, $^3J=4.8$ Hz, 4H, H_β), 9.53 (d, $^3J=5.0$ Hz, 2H, H_β) ppm; ^{13}C NMR (100.6 MHz, CDCl_3): $\delta=13.7$, 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 (CH_2), 2919 (CH_2), 2850 (CH_3), 2245 ($\text{C}\equiv\text{N}$) cm^{-1} ; UV-vis (CH_2Cl_2): λ_{max} (lg ϵ)=418 (5.6), 518 (4.5), 554 (4.4), 600 (4.3), 656 (4.3) nm; HRMS (ES⁺): calcd for $\text{C}_{41}\text{H}_{54}\text{N}_5$ $[\text{M}+\text{H}]^+$ 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_2CO_3 (318 mg, 0.9 mmol), $\text{Pd}(\text{dppf})\text{Cl}_2$ (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; $R_f=0.22$ ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$, 1:1, v/v); ^1H NMR (400 MHz, CDCl_3): $\delta=-2.75$ (s, br, 2H, NH), 2.78 (t, $^3J=7.3$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{CN}$), 3.22 (t, $^3J=7.6$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{CN}$), 7.79 (m, 12H, H_{Ar}), 8.15 (d, $^3J=7.0$ Hz, 2H, H_{Ar}), 8.24 (m, 6H, H_{Ar}), 8.68 (d, $^3J=4.7$ Hz, 1H, H_β), 8.71 (s, 1H, H_β), 8.81 (d, $^3J=4.7$ Hz, 1H, H_β), 8.83 (d, $^3J=4.7$ Hz, 1H, H_β), 8.87 (m, 3H, H_β) ppm; ^{13}C NMR (100.6 MHz, CDCl_3): $\delta=18.6$, 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 ($\text{C}\equiv\text{N}$) cm^{-1} ; UV-vis (CH_2Cl_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 $\text{C}_{47}\text{H}_{34}\text{N}_5$ $[\text{M}+\text{H}]^+$ 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 mmg, 0.046 mmol), Cs_2CO_3 (649 mg, 1.8 mmol, 40 equiv.), $\text{Pd}(\text{dppf})\text{Cl}_2$ (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 $>300^\circ\text{C}$; $R_f=0.22$ ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$, 2:1, v/v); ^1H NMR (400 MHz, CDCl_3): $\delta=-2.80$ (s, br, 2H, NH), 2.77 (s, 6H, $\text{C}_6\text{H}_4\text{CH}_3$), 3.56 (t, $^3J=7.9$ Hz, 4H, $\text{CH}_2\text{CH}_2\text{CN}$), 5.41 (t, $^3J=7.9$ Hz, 4H, $\text{CH}_2\text{CH}_2\text{CN}$), 7.61 (d, $^3J=7.6$ Hz, 4H, H_{Ar}), 8.09 (d, $^3J=7.6$ Hz, 4H, H_{Ar}), 9.00 (d, $^3J=4.7$ Hz, 4H, H_β), 9.43 (d, $^3J=5.3$ Hz, 4H, H_β) ppm; ^{13}C NMR (100.6 MHz, CDCl_3): $\delta=21.1$, 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 (CH_2), 3916 (CH_2), 2244 ($\text{C}\equiv\text{N}$) cm^{-1} ; UV-vis (CH_2Cl_2): λ_{max} (lg ϵ)=418 (5.6), 516 (4.4), 551 (4.4), 594 (4.4), 650 (4.4) nm; HRMS (ES $^+$): calcd for $\text{C}_{40}\text{H}_{33}\text{N}_6$ $[\text{M}+\text{H}]^+$ 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), Cs_2CO_3 (275 mg, 0.8 mmol), $\text{Pd}(\text{dppf})\text{Cl}_2$ (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 $>300\text{ }^\circ\text{C}$; $R_f=0.45$ ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$, 1:2, v/v); ^1H NMR (400 MHz, CDCl_3): $\delta=2.60$ (s, 12H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.70 (s, 6H, $\text{C}_6\text{H}_4\text{CH}_3$), 7.44 (d, $^3J=8.2$ Hz, 8H, H_{Ar}), 7.55 (d, $^3J=7.6$ Hz, 4H, H_{Ar}), 7.92 (d, $^3J=7.6$ Hz, 8H, H_{Ar}), 7.99 (d, $^3J=7.6$ Hz, 4H, H_{Ar}), 8.08 (d, $^3J=5.3$ Hz, 4H, H_β), 8.57 (d, $^3J=5.3$ Hz, 4H, H_β), 8.82 (d, $^3J=5.3$ Hz, 4H, H_β), 8.85 (d, $^3J=4.7$ Hz, 4H, H_β) ppm; ^{13}C NMR (100.6 MHz, CDCl_3): $\delta=21.0$, 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 (CH_3) cm^{-1} ; UV-vis (CH_2Cl_2): λ_{max} (lg ϵ)=418 (5.7), 447 (5.8), 537 (5.2), 571 (3.7) nm; HRMS (MALDI LD $^+$): calcd for $\text{C}_{82}\text{H}_{58}\text{N}_8\text{Ni}_2$ $[\text{M}]^+$ 1270.349, found 1270.351.

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