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Organometallic C–C Coupling Reactions for Porphyrins

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Abbreviations used:

AcOH	Acetic acid
Ar	Aryl
ArLi	Aryllithium
AsPh ₃	Triphenylarsine
BPin	Pinacolborane
Bu ₄ NOAc	Tetrabutylammonium acetate
CaCO ₃	Calcium carbonate
CH ₂ Cl ₂	Dichloromethane
CuOAc	Copper(II) acetate
DDQ	2,3-Dichloro-5,6-Dicyanobenzoquinone
DIEA	N,N-Diisopropylethylamine
DME	Dimethoxyethane
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
Hal	Halogen
<i>i</i> Pr	<i>iso</i> -propyl
<i>i</i> -Pr ₂ NH	Isopropylamine
Mes	Mesityl
<i>n</i> Bu	<i>n</i> -butyl
<i>n</i> BuOH	<i>n</i> -Butanol
OEP	2,3,7,8,12,13,17,18-octaethylporphyrinato
P(<i>o</i> -Tol) ₃	Tri- <i>o</i> -tolylphosphine

Pd(dppf)Cl_2	1,1'-Bis(diphenylphosphino)ferrocene dichloropalladium(II)
Pd(OAc)_2	Palladium(II) acetate
$\text{Pd(PPh}_3)_4$	Tetrakis(triphenylphosphine)palladium(0)
$\text{Pd}_2(\text{dba})_3$	Tris(dibenzylideneacetone)dipalladium(0)
$\text{PdCl}_2(\text{dppe})$	1,2-bis(diphenylphosphino)ethane- <i>P,P'</i> -dichloropalladium
$\text{PdCl}_2(\text{PPh}_3)_2$	dichlorobis(triphenylphosphine)palladium (II)
PhLi	Phenyllithium
RLi	Organolithium reagent
sBu	<i>sec</i> -butyl
<i>t</i> Bu	<i>tert</i> -butyl
<i>t</i> BuLi	<i>t</i> -Butyllithium
THF	Tetrahydrofurane
TPP	5,10,15,20-Tetraphenylporphyrinato

I. Introduction

Organometallic reactions play an important role in modern synthetic chemistry. The ability to form a C–C bond in just one step makes this synthetic approach one of the most attractive tools to create or to modify organic molecules.^{1,2} Despite many methods available there is still a high demand for new and more effective synthetic strategies. The emerging new transition metal catalysts with widespread activities expand the variety of functionalities to be introduced into the substrates and allow the preparation of more elaborate and multifunctional synthons.³⁻⁵ Thus, applications of metal-catalyzed coupling reactions continue to grow rapidly providing an easy access to novel heteroatomic building blocks.^{6,7}

The increasing need for artificial multifunctional porphyrin-based systems required the development of new and more efficient reactions to introduce functional groups into the macrocycle and metal-catalyzed reactions fulfilled this need. In most cases these metal-catalyzed methods were initially developed for small aromatic molecules. Subsequently, they needed to be adapted by porphyrin chemists for specific applications in tetrapyrrole chemistry and proved to be immensely successful. In fact, many of significant breakthroughs in porphyrins chemistry of the past two decades and the increasing plethora of novel tetrapyrrolic compounds are solely based on advances in organometallic coupling reactions and their applications to porphyrin chemistry.

This chapter focuses on the utilization of organometallic approaches for the synthesis and transformation of the porphyrins. It includes organometallic porphyrins and “classic” non-porphyrin synthons, metal-mediated reactions, cyclization and rearrangement reactions. The

review covers the relevant literature from 1999 to 2009. Several earlier reviews have covered this field.⁸⁻¹³

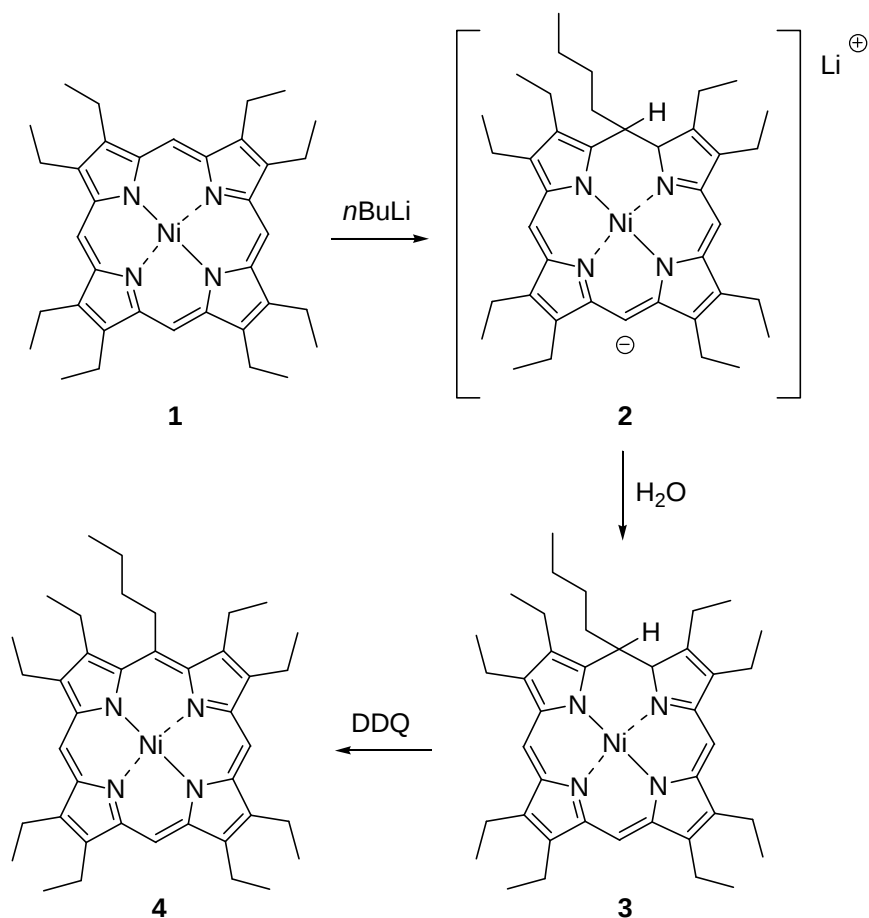
II. Organometallic transformations with RLi

A. Preparation of porphyrins

Next to the metal-catalyzed reactions described below the use of organolithium reagents for the direct functionalization of porphyrins has seen significant developments in the past decades.⁸ RLi reagents can be used for a wide variety of reactions and target systems and present one of the few nucleophilic substitution reactions for the modification of porphyrins. Typically, such reactions require activated porphyrins or are applicable only in special cases.¹⁴⁻¹⁷

In the nineties our group was involved in developing syntheses for highly substituted nonplanar porphyrins, which led us to study the reactivity of porphyrins with strong nucleophiles.¹⁸ During attempts to utilize Grignard reagents we found that 2,3,7,8,12,13,17,18-octaethylporphyrin (H₂OEP) derivatives reacted readily with *n*-butyl lithium to yield the meso alkylated species in quantitative yield.¹⁹ The reaction proceeds in a similar manner to the Ziegler alkylation, i.e. involves intermediary formation of a Meisenheimer-type complex **2**, which is hydrolyzed to a porphodimethene **3** and that in turn is oxidized to the product porphyrin **4**. Thus, the reaction follows an addition-oxidation mechanism. (Scheme 1) More detailed mechanistic, spectroscopic and deuterium labeling studies showed that two different intermediates have to be assumed for free base versus nickel porphyrins. The data were indicative of a porphodimethene for metalloporphyrins and a phlorin for free bases. Notably, the carbanion of the nickel(II)

complex **2** is stable towards hydrolysis and thus lends itself for use as a reactive nucleophile in further reactions.²⁰

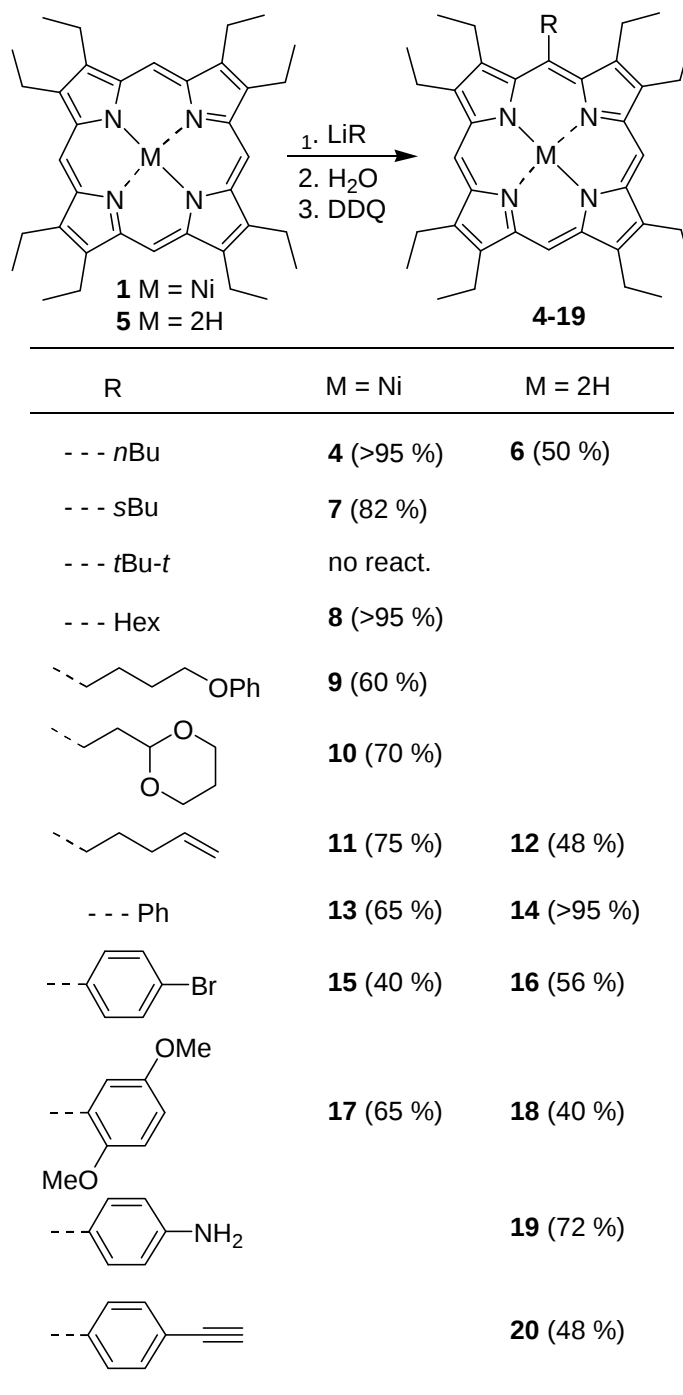


Scheme 1. Reaction of NiOEP **1** with *n*BuLi.

Overall, the reaction could be used with free base porphyrins, Ni, Zn, Cu, and Co porphyrins in yields ranging from 40 to 100%.²¹ Likewise, this method can be used with a large number of different organolithium reagents. With the exception of the sterically hindered *t*BuLi all LiR reagents gave good to excellent yields. Generally, alkyl lithium compounds typically gave

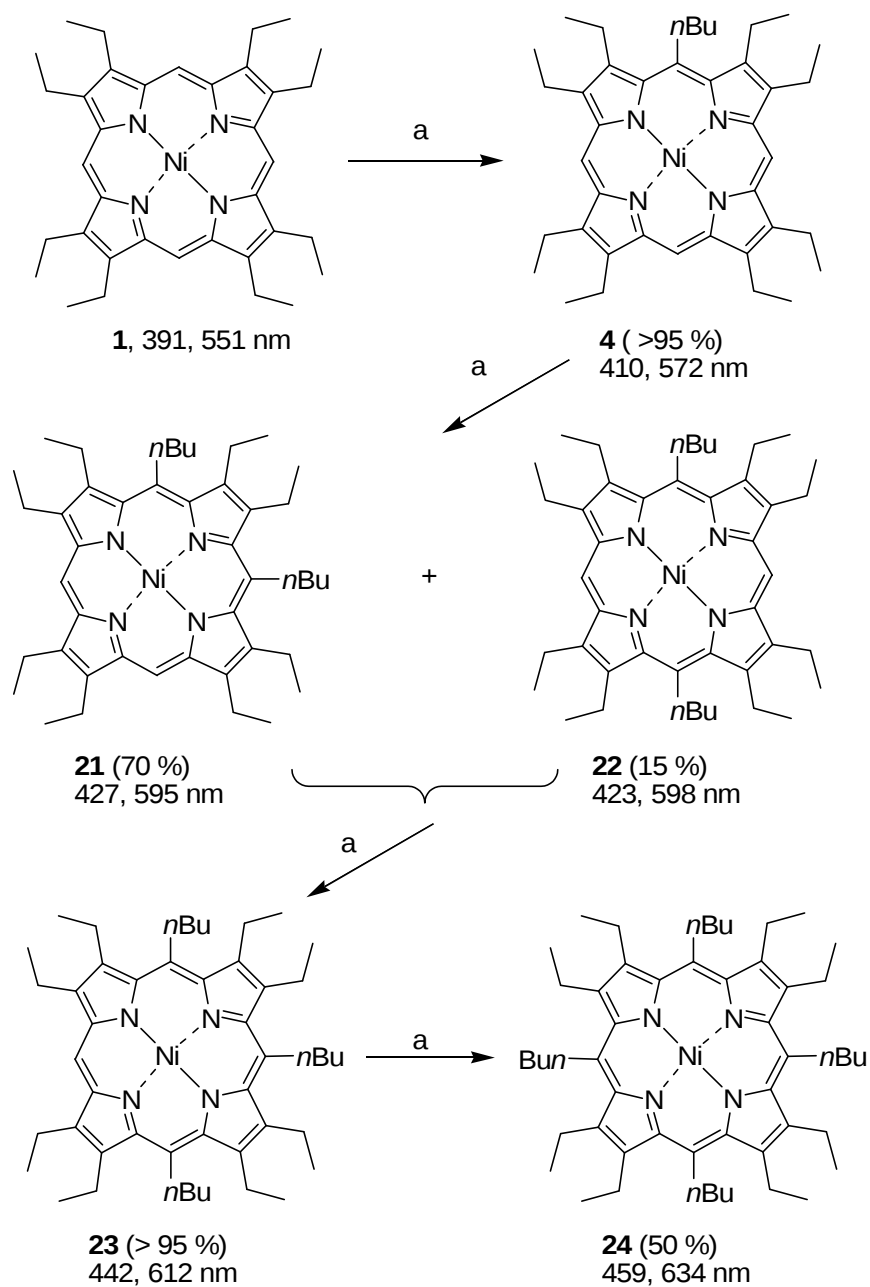
higher yields with metalloporphyrins while aryllithium reagents mostly gave better yields with free base porphyrins. Typical examples for reactions with OEP derivatives are given in Scheme

2.



Scheme 2. Reaction of OEP with various RLi.

The reaction proved equally applicable to further transformations of the substituted porphyrins. Thus, the reaction could be performed with OEP in a stepwise fashion until all four meso positions were substituted.^{19,21} These reactions provided an entry into various nonplanar and highly substituted porphyrins and successive substitutions were accompanied by significant alterations in the (photo)physical properties of the macrocycles, e.g. by increasing bathochromic shifts of the electronic absorption bands (see Scheme 3).^{19,22} A typical example for these novel systems are the highly ruffled 2,3,5,7,8,10,12,13,15,18,18,20-dodecaalkylporphyrins (e.g. **24**).²³ Using different RLi reagents in the stepwise reactions this method gives an alternative entry into various meso substituted ABCD-type porphyrin systems.

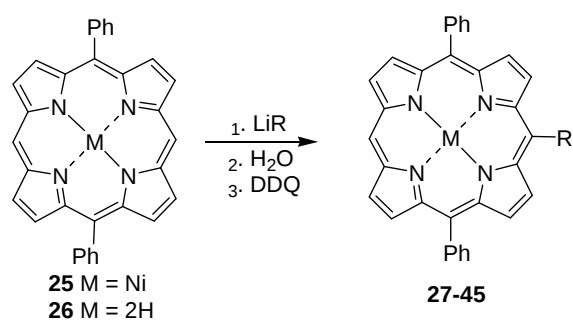


Scheme 3. Successive butylation of Ni(II)OEP. Numbers give main absorption bands and yields.

Reaction conditions: a) 1. *n*BuLi, THF, $-70\text{ }^{\circ}\text{C}$, 2. H_2O , 3. DDQ.

Note that the introduction of a second meso substituent occurs with a clear regioselective preference for the neighboring meso positions. This directing effect is more pronounced for

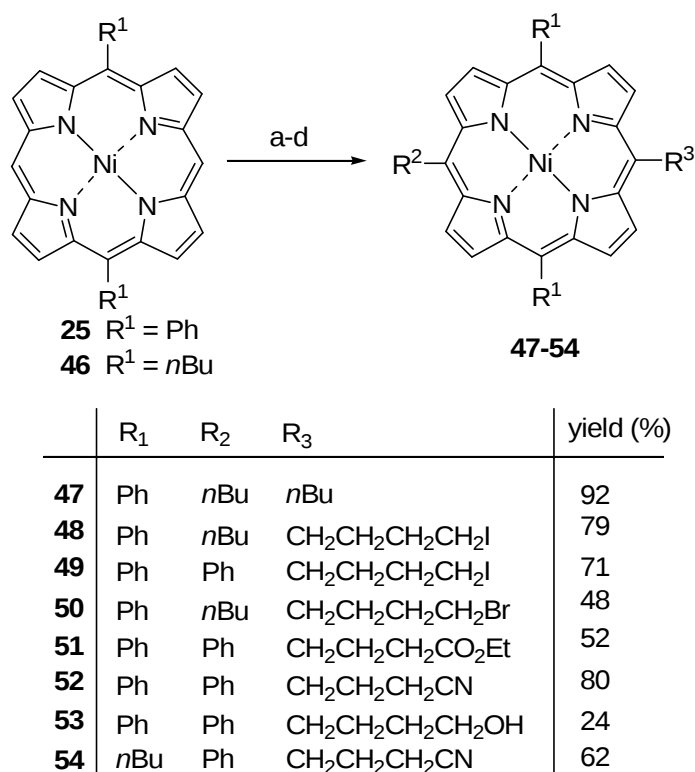
meso-aryl substituents than -alkyl residues and is the result of steric hindrance in the intermediate of the reaction.²⁰ There is also a clear regioselective preference for either the meso or β positions depending on the starting porphyrin. Krattinger and Callot showed that TPP can undergo both meso and β -alkylations with *n*BuLi and *t*BuLi.¹⁶ Reactions with 5,15-disubstituted porphyrins such as **24** and **25** using linear alkyl- and aryllithium reagents showed complete regioselectivity for the meso-position and resulted in the formation of the respective A₂B-type porphyrins **26-44** in good to excellent yields (Scheme 4).²⁴ Use of sterically more hindered RLi reagents resulted in the formation of phlorins, chlorins and ring-opened products as the result of β - and meso-addition reactions.²⁵



R	M = Ni	M = 2H
--- <i>n</i> Bu	27 (>95 %)	28 (94 %)
--- <i>i</i> Pi	29 (52 %) + byproducts	30 (30 %) + byproducts
--- <i>s</i> Bu	31 (65 %) + byproducts	32 (30 %) + byproducts
--- <i>t</i> Bu	33 (53 %) + byproducts	> 20 diff. products
	34 (73 %)	n.d.
--- N(CH ₃) ₂	n.d.	35 (75 %)
--- Ph	36 (92 %)	37 (89 %)
	n.d.	38 (86 %)
	n.d.	39 (80 %)
	n.d.	40 (83 %)
	n.d.	41 (30 %)
	n.d.	42 (78 %)
	n.d.	43 (82 %)
	n.d.	44 (78 %)
	n.d.	45 (85 %)

Scheme 4. Reaction of 5,15-diphenylporphyrins with various RLi.

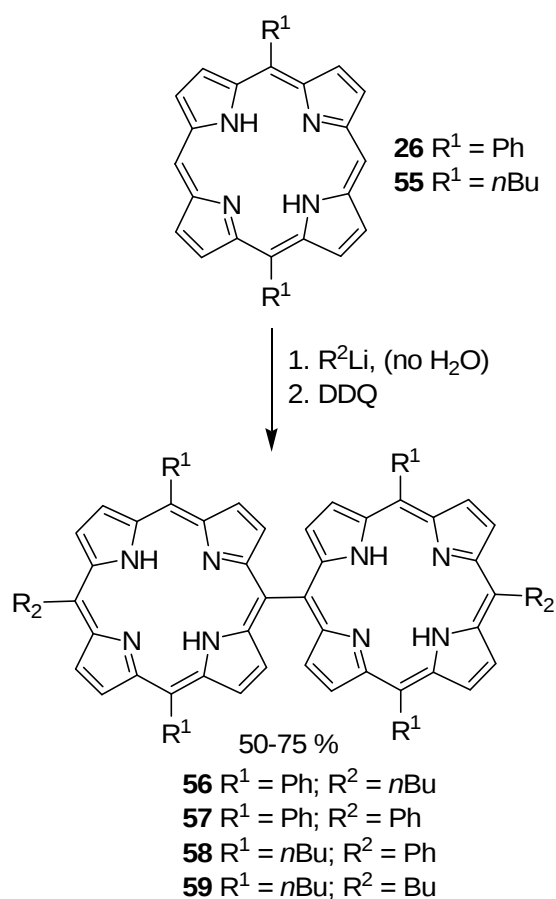
The presence of the phlorin/anionic intermediate offered the possibility for further modifications of the reaction. Thus, the *in situ* formed anion could be used as a nucleophile for the trapping of organic electrophiles. This allowed the development of a simple two-step one-pot reaction suitable for the introduction of base-stable functional groups. Typical reactions involved the reaction of a porphyrin with *n*BuLi or PhLi followed by hydrolysis of excess RLi and addition of alkyl iodides to yield the A₂BC-type porphyrins **47-54**(Scheme 5).²⁶ The reaction is also applicable to free base porphyrins.²⁷



Scheme 5. One-pot two-step reaction of 5,15-disubstituted nickel(II) porphyrins with $\text{R}^2\text{Li}/\text{R}^3\text{I}$.

Reaction conditions: a) LiR^2 , THF, $-70\text{ }^\circ\text{C}$; b) H_2O ; c) R^3I , 60 min, RT; d) air.

Another example is the preparation of directly meso-meso-linked bisporphyrins (Scheme 6). Reaction of free base porphyrins **26** and **55** with RLi but omitting the hydrolysis step resulted in the formation of the directly meso-meso linked bisporphyrins **56-59** through oxidation of the initial intermediate to a π -stabilized radical followed by radical dimerization.^{24,28} The respective nickel(II) complexes only yielded substitution products; no dimer formation was observed.²⁵ This method complements the various methods developed by Osuka's group for bis- and oligoporphyrins.²⁹



Scheme 6. Synthesis of directly meso-meso linked bisporphyrins.

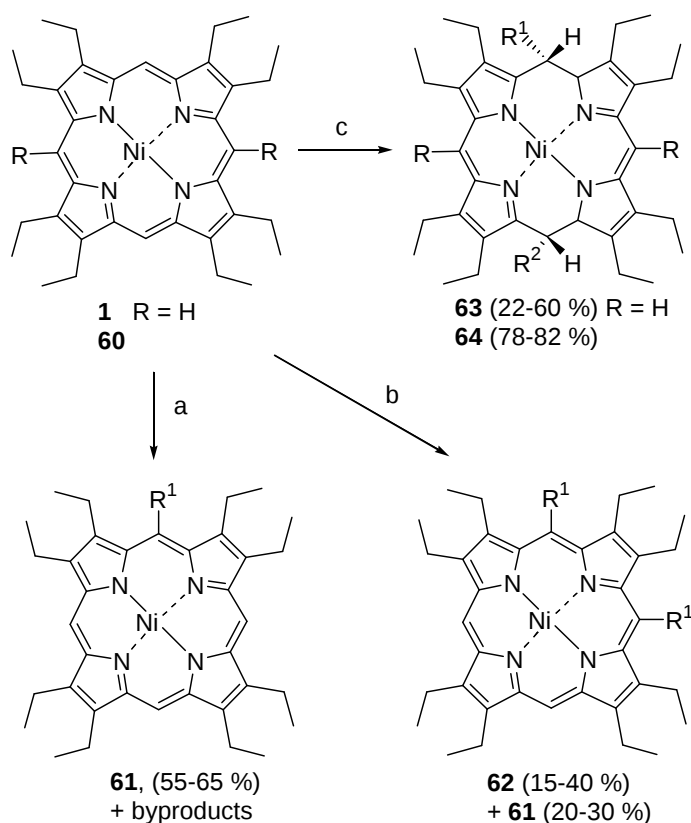
B. Preparation of hydroporphyrins

The reaction of porphyrins with RLi proceeds through an intermediary hydroporphyrin stage which opened the possibility to modify the reaction for the preparation of hydroporphyrins as well. One such modification was found to be possible via thermodynamic versus kinetic control of the reaction. The porphyrin substitution reactions were typically performed at low temperature under kinetic control. However, a switch to thermodynamic control allowed a convenient entry into meso hydroporphyrins, i.e. porphodimethenes. Porphodimethenes are a class of calixphyrins for which various syntheses have been reported.³⁰

During the synthesis of highly substituted porphyrins it was noted that use of sterically hindered precursor porphyrins resulted in the partial formation of a porphodimethene in addition to the target porphyrin.²¹ This porphodimethene was isolated although the standard workup included oxidation with DDQ and was also resistant towards oxidation with other oxidants. Upon raising the reaction temperature above $-80\text{ }^{\circ}\text{C}$, formation of these porphodimethene increased and became quantitative at temperatures above $-30\text{ }^{\circ}\text{C}$. These porphodimethenes were shown to have a *syn axial* configuration of the meso hydrogen. Thus, under thermodynamic conditions the intermediate is fixed in a configuration that is more difficult to oxidize than the normal intermediate of standard porphyrin formation reactions. The tendency of the intermediate to lock into the nonoxidizable form increases with the degree of conformational distortion already present in the parent porphyrin.

On the basis of these results a synthesis for porphodimethenes derived from OEP was derived (Scheme 7). For example, reaction of **1** under standard conditions with RLi/RI yielded the monosubstituted porphyrin **61** as the sole product. Direct oxidation of the intermediate after

addition of LiR and/or using an excess of LiR resulted in the formation of mixtures of mono- **61** and disubstituted **62** porphyrins. In contrast, trapping of the alkyl iodides at higher temperatures and with longer reaction times resulted in formation of the the decasubstituted porphodimethenes **63** in low to moderate yields. Use of the sterically more hindered porphyrins **60** gave the dodecasubstituted porphodimethenes **64** in good to excellent yields.³¹ Porphodimethenes could also be derived from 5,15-disubstituted porphyrins. Here, reaction with RLi and small alkyl iodides multiple meso substituted porphodimethenes were obtained. Similarly, use of co-catalysts in the reaction of meso-tetrasubstituted porphyrins allowed an entry into 5,10-porphodimethenes.^{32,33}

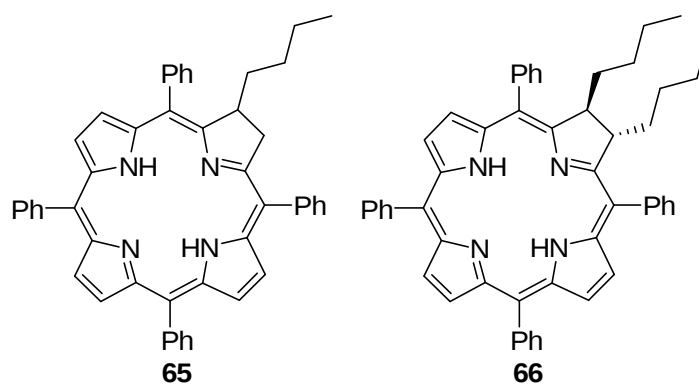


Scheme 7. Kinetic versus thermodynamic control in the reaction of Ni(II)OEP with R^1Li/R^2I .

Reaction conditions: a) 1. R^1Li , $T \ll RT$, 2. R^2I , $T < RT$, 3. DDQ; b) 1. large excess R^1Li , $T \ll$

RT , 2. DDQ; c) 1. R^1Li , $T \ll RT$, 2. R^2I , $T > RT$, 5–12 h.

The use of fully meso-substituted porphyrins in reactions with organolithium reagents also allows the preparation of porphodimethenes,²¹ phlorins,³⁴ and hydroporphyrins of the chlorin type.³³ Here the synthetic utility depends on the type of meso-substituted porphyrin. Meso Alkylporphyrins reacted with sterically unhindered organolithium reagents exclusively at the meso positions. In contrast meso arylporphyrins react in β -addition reactions to yield chlorins of the type **65** and **66** (Scheme 8).³⁵



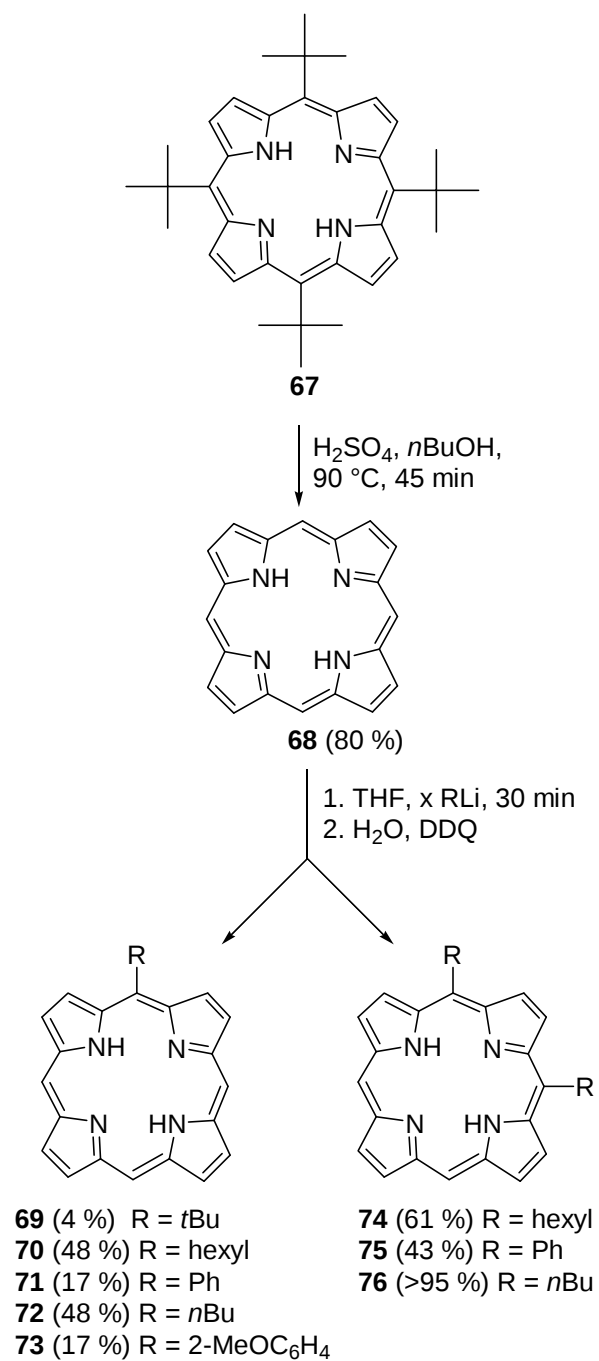
Scheme 8. Mono and disubstituted chlorins.

C. Synthetic applications

In recent years the methods described in this section have been applied to various applications. In addition to the preparation of highly substituted porphyrins mentioned above, synthetic projects included the synthesis of substituted benzoporphyrins,^{36,37} amphiphilic porphyrins for use in photodynamic therapy,³⁸⁻⁴¹ dimeric and trimeric porphyrins,⁴² and the use of other nucleophiles,^{43,44} e.g., the utility of the dithianyl anion for the preparation of formylporphyrins under basic conditions.^{45,46} Other applications were the synthesis of hydroxymethyl porphyrins

with (2-pyridyldimethylsilyl)methylolithium,⁴⁷ the preparation of meso amidinylporphyrins,⁴⁸ novel chlorins,⁴⁹ and as starting materials for peripherally metallated porphyrins.⁵⁰

A conceptionally important approach derives from the use of RLi reactions with unsubstituted porphyrin.⁵¹ This is based on the development of a convenient preparation of **68** via dealkylation of **67**. If this is used as an *in situ* method for the preparation of porphyrin immediately followed by addition of RLi a facile synthesis of mono- (**69-73**) and 5,10-meso-disubstituted (**74-76**)⁵² porphyrins without β -substituents is possible. Applied sequentially, this allowed an entry into ABCD-type porphyrins⁵¹ and into novel classes of 5,10-A₂B₂-type porphyrins, which proved useful for optical applications (Scheme 9).⁵³



Scheme 9. Preparation of A- and 5,10-A₂-type porphyrins.

III. Palladium mediated C–C coupling reactions

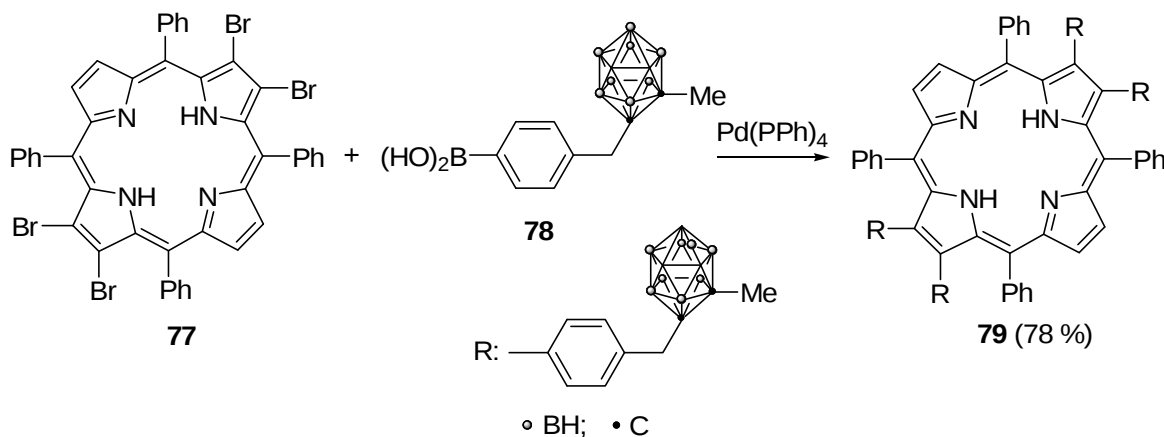
Palladium-catalyzed reactions are one of the most favourite methods available for the synthesis of natural porphyrin analogues and artificial porphyrin systems.^{9,10,13} They are characterized by mild reaction conditions, are high suitable for many functional groups, give high chemical yields, have facile reaction procedures and use readily accessible starting materials. These properties and the short synthetic sequences involved offer significant benefits. Bromoporphyrins are the key starting materials and can easily be obtained via bromination.⁹ Bromination of the meso positions is more easily achieved than that of the β -positions, where selective bromination is difficult and inseparable mixtures often obscure further transformations.¹³ In the context of this chapter we will focus on palladium catalyzed reactions involving the synthesis and transformation of the porphyrin monomers. Fused and oligomeric porphyrin systems will be described elsewhere [EDITOR PUT IN REFERENCE TO RELEVANT BOOK CHAPTER].

A. Suzuki-type C–C coupling reactions

Organoboronates are some of the best known and powerful examples of organometallic synthons and they serve as excellent precursors in Suzuki-type C–C couplings.⁵⁴ As an alternative to bromoporphyrins, borylated porphyrins obtained via a palladium-catalyzed reaction of bromoporphyrins with pinacolborane or bispinacolborane, can be used as starting materials in these transformations. Here, the first synthesis of boronyl porphyrins was reported by Therien et al.⁵⁵ and this breakthrough opened a new era in the organometallic chemistry of porphyrin analogues. This strategy was also adapted for the synthesis of β -boronyl porphyrins and used to

prepare the first β,β -directly linked dimers.⁵⁶ Later it was shown that, alternatively, an iridium catalyzed direct C-H borylation can be employed for the regioselective β -borylation of porphyrins⁵⁷ and corroles.⁵⁸ However, it is difficult to control the number of boronyl groups introduced. Depending on the diboron reagent used mono-, di-, and tetraboronyl porphyrins can be prepared. This approach is dependent on steric constraints and requires a careful choice of the porphyrin substrates. It can also be used to introduce boronyl groups at peripheral aryl position of the porphyrin.⁵⁹

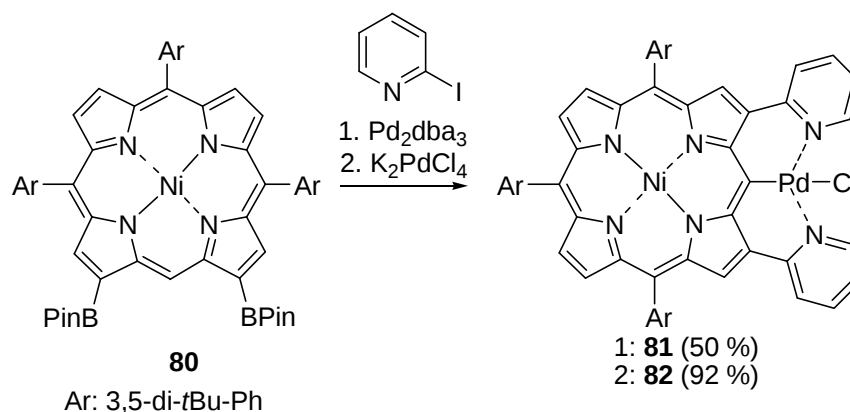
Recent years have seen many specific applications of Suzuki reactions for porphyrins. For example, the relevance of carborane-containing porphyrins for boron neutron capture elicited the synthesis of multifunctionalized carboranyl porphyrins via reaction of 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrin **77** with carboranyl-modified benzylboronic acid **78** to give the tetrasubstituted compound **79** in 78% (Scheme 10).⁶⁰



Scheme 10. Synthesis of carborane functionalized porphyrin.

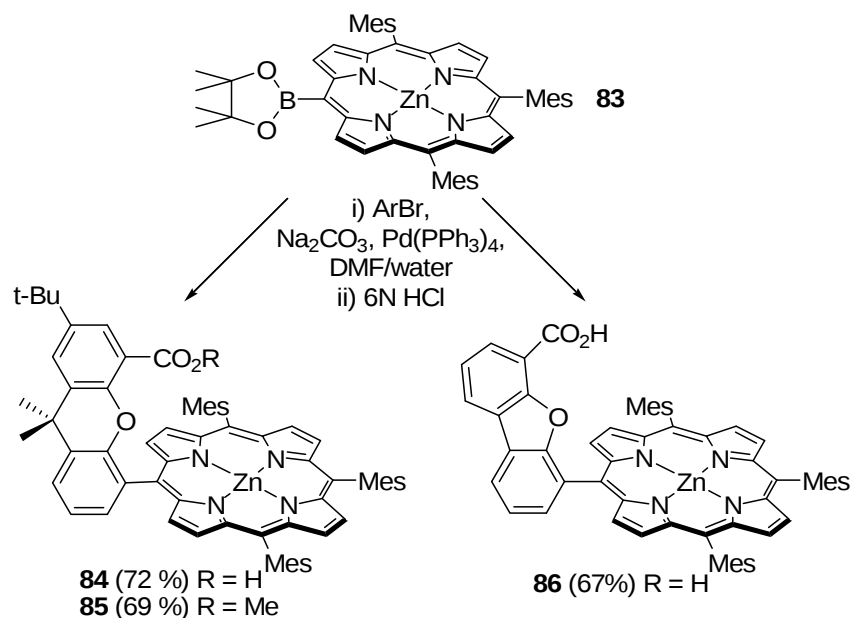
Heterometallic porphyrins could be prepared starting from a meso boronyl porphyrin and (4-bromophenyl)subporphyrin boron-complex to yield the phenylene-bridged subporphyrin-

porphyrin hybrids in 7-19% yields.⁶¹ Pincer complexes of type **82** can be prepared via Suzuki reaction to yield dipyrindinyl porphyrin **81** in 50% followed by complexation with palladium providing the organometallic molecule **82** in 92% yield (Scheme 11).⁶²



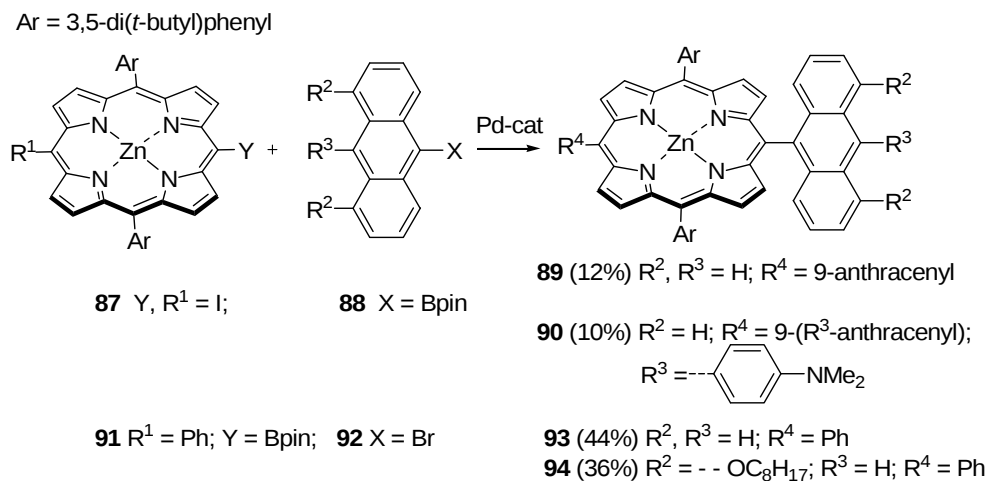
Scheme 11. Synthesis of porphyrin pincer complexes.

Other examples utilizing C-C couplings for the synthesis of heterometallic porphyrins were given through the reaction of porphyrin monotriflate with ferrocene diboronic acid to yield a ferrocene-porphyrin dyad in 18%. Although, the porphyrin naphthyl triflate is sterically hindered, this approach was shown to be also successful for the preparation of various co-facially linked conjugates in yields of 55-78%.⁶³ Likewise, precursors for a proton-coupled electron transfer network were synthesised via the coupling of boronyporphyrin **83** and the corresponding bromides, affording the face-to-face xanthene **84** and **85** and dibenzofurane porphyrins **86** in 67- 72% yield (Scheme 12).⁶⁴



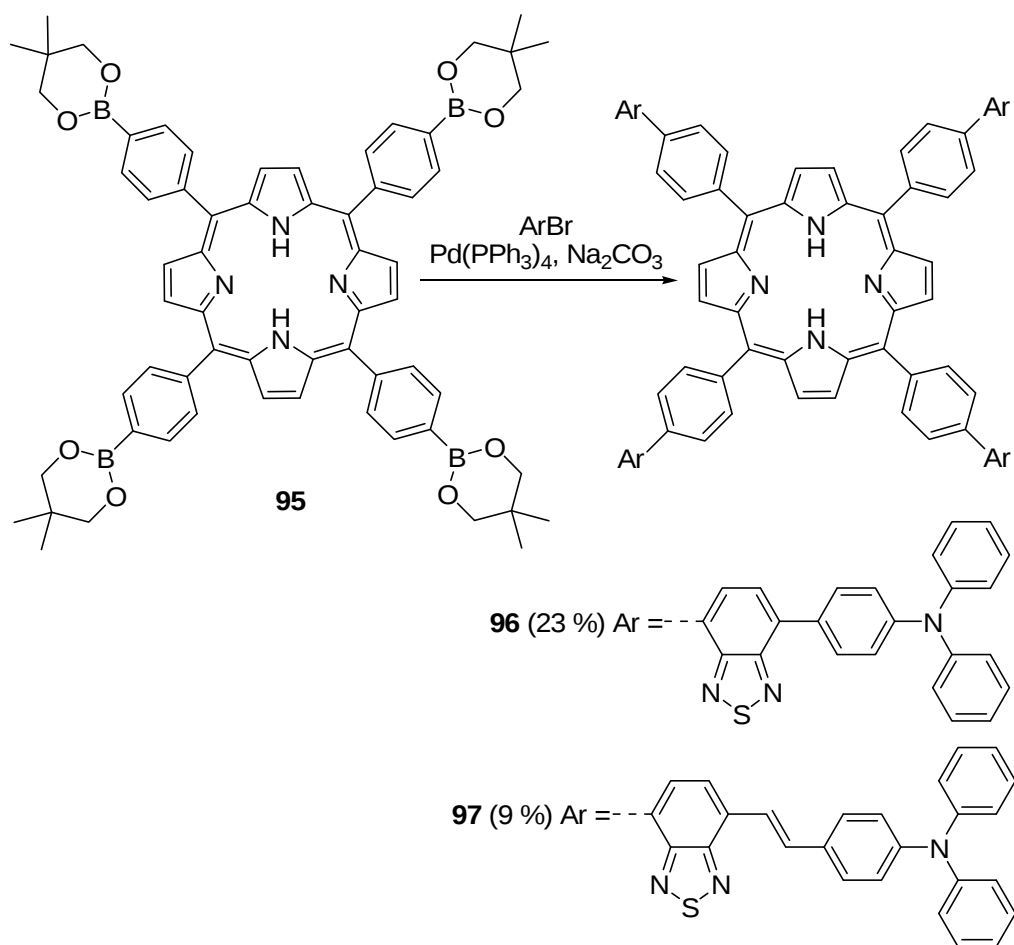
Scheme 12. Synthesis of face-to-face xanthene and dibenzofurane porphyrins.

In the context of fused porphyrin systems anthraporphyrins with large π -conjugated chromophores have a favorable geometry to form a flat material when fused and may possess enhanced electronic properties. Their synthetic access is still limited; however it has been shown that a Suzuki-type reaction of either a boronyl anthracene **88** (10-12% for **89** and **90**)⁶⁵ or a boronyl porphyrin **91** (36-44% for **93** and **94**)⁶⁶ can be used for the synthesis of the precursor anthraporphyrins (Scheme 13).



Scheme 13. Synthesis of anthraporphyrins.

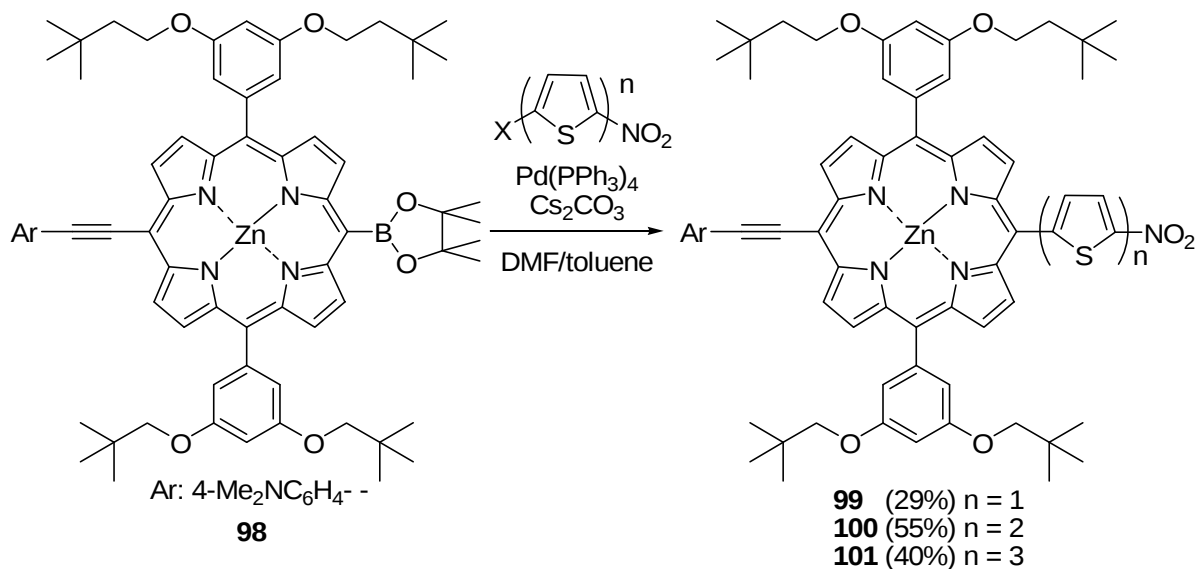
More straightforward systems include porphyrin benzothiadiazole chromophores **96** and **97** which were prepared in 9-23% yield via Suzuki C-C coupling reactions of the 5,10,15,20-tetrakis(4-boronate)phenyl porphyrin **95** in the presence of $\text{Pd}(\text{PPh}_3)_4$ and CaCO_3 in aq. DME (Scheme 14).⁶⁷ Nevertheless, the syntheses of polyaromatic, conjugated chromophores continues to be quite challenging and leaves room for further developments in this area.



Scheme 14. Benzothiadiazole porphyrins synthesized via Suzuki reaction.

Prompted by their interesting optical and nonlinear optical properties conjugated porphyrin chromophores **99-101** bearing nitrothiophenyl and nitropolythiophenyl substituents

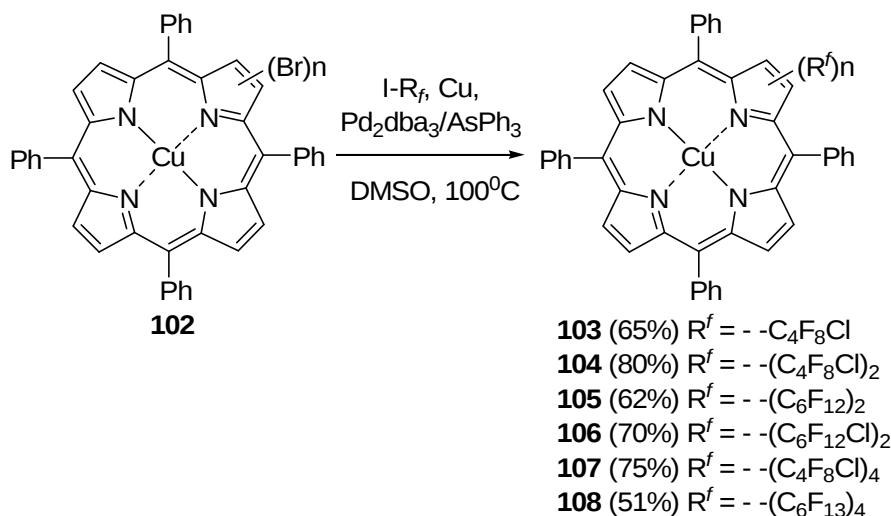
were synthesised via palladium mediated C-C coupling using meso boronyporphyrin **98** as the starting materials (Scheme 15).⁶⁸



Scheme 15. Synthesis of nitropolythiophenyl porphyrins.

β -Octabrominated meso-tetraarylporphyrins are interesting compounds due to their ease of preparation. Derivatization of the fully octabrominated TPP β -positions proceeded quite well giving rise to the various octaaryl derivatives in 30-58% yields.⁶⁹ Porphyrins with electron-withdrawing groups, such as trifluoromethyl, are difficult to brominate, however, if this step is overcome, they could be functionalized further at the β -positions to give the β -monoarylporphyrins in 51-98%. For example, the β -diphenyl-5,10,15,20-tetratrimethylporphyrin could be prepared in 44% yield.⁷⁰ An alternative route to β and meso perfluoroalkylated porphyrins was given through Pd-Cu catalyzed coupling reactions involving just the halogenated counterparts.⁷¹ Here, the brominated porphyrins reacted with the perfluoroalkyl iodides in the presence of Pd₂(dba)₃/AsPh₃ and copper to give a range of meso

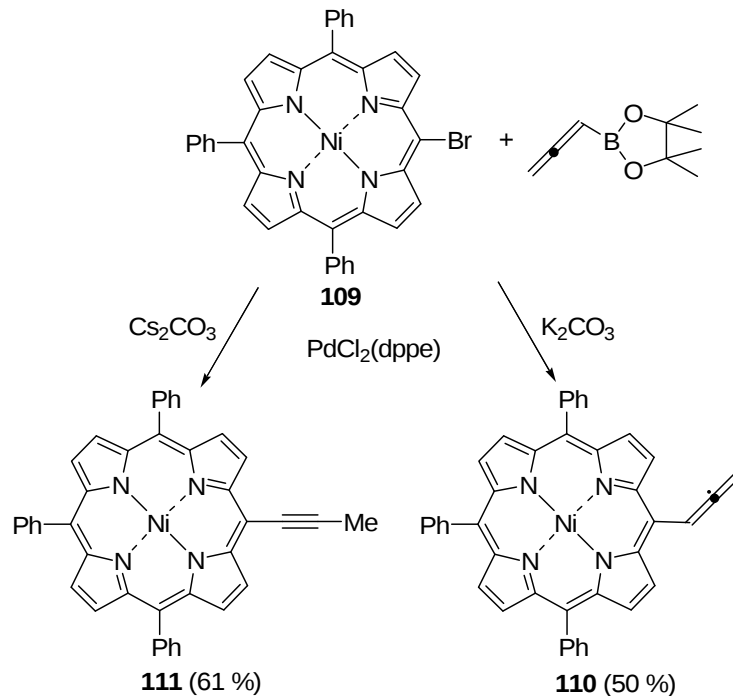
and β -perfluoroalkylated porphyrins in 40-85% and 51-85% (**103-108**) yields, respectively (Scheme 16).



Scheme 16. Synthesis of β -perfluoroalkylated porphyrins.

In addition to the organolithium approach described earlier, unsymmetrically meso substituted porphyrins can also be prepared via palladium catalyzed methods. In general terms due to the reactive nature of the meso positions for the necessary bromination step, modification of the meso positions is easier in comparison to the β sites. Thus, various meso mono-, di- and tetra-functionalized porphyrins could be prepared using Suzuki reactions in excellent yields.⁷² Mild reaction conditions over several hours enabled the introduction of heteroaromatic and various aryl residues into the macrocycles to yield A_3B -,⁷³ A_2B_2 -⁷⁴ and A_2BC -type⁷⁵ porphyrins.

In terms of novel functional groups Pd-catalyzed Suzuki couplings proved to be effective for the synthesis of allenyl porphyrins.⁷⁶ Depending on the reaction conditions, the reaction proceeded via the formation of an allene **110** or its rearrangement product, the respective - 1-propynyl porphyrin **111** (Scheme 17).



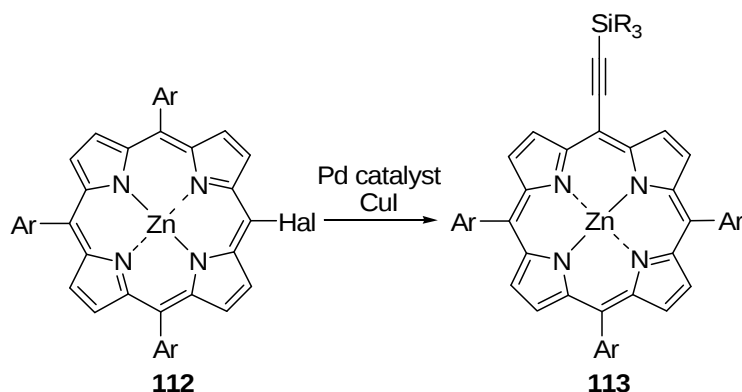
Scheme 17. Formation of allenyl and alkynyl porphyrins.

Thus far boronates have been used almost exclusively in reactions with porphyrins. However, as an alternative, the RBF_3K salts can be used for Suzuki-type transformation with a bromoporphyrin, in the presence of $\text{Pd}(\text{dppf})\text{Cl}_2$. The reaction was effective for introduction of non-aromatic residues resulting in a series of substituted porphyrins in 21-75% yield.⁷⁷

B. Sonogashira C-C coupling reactions

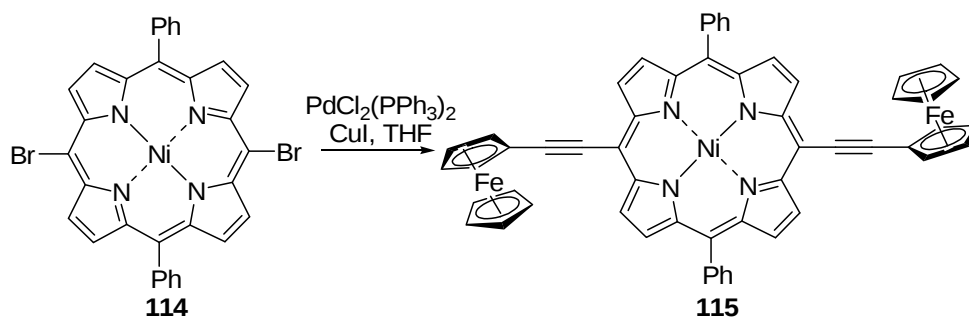
Ethynyl substituted porphyrin chromophores are used as efficient candidates for applications in push-pull systems to enhance absorption in the visible region.[EDITOR REFER TO CHAPTER BY OSUKA] Ethynyl bridges have a strong π -conjugation and allow effective electronic

interactions within the system. Often alkynyl substituted porphyrins have been used to construct large assemblies of porphyrin units. Here, Sonogashira coupling is widely used for the introduction of these residues. Reactions typically utilize a bromo/iodo precursor and terminal acetylene in the presence of a Pd-catalyst. Direct introduction of the alkynyl residue can be achieved via the reaction of an iodo- or bromoporphyrin **112** with alkynyl compounds in the presence of CuI and a Pd-catalyst (Scheme 18).^{42,78-84}



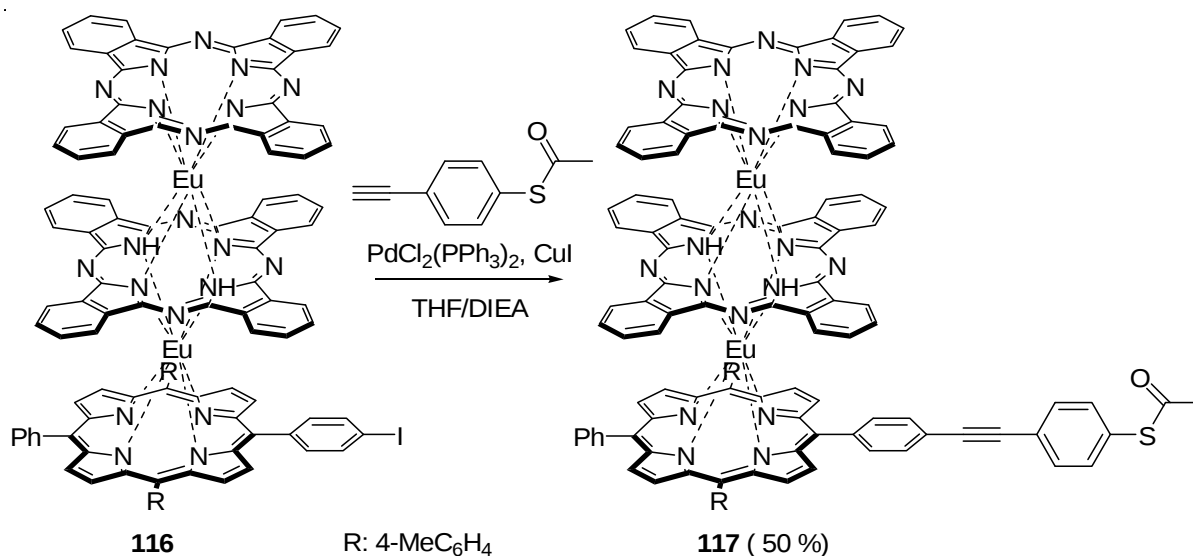
Scheme 18. Synthesis of acetylenic porphyrins via Sonogashira coupling.

Several examples of new applications have been reported. One example is the incorporation of ferrocenyl units through an ethynyl linker. The reaction utilized 5,15-dibromoporphyrin **114** and ferrocenyl acetylene in the presence of $\text{PdCl}_2(\text{PPh}_3)_2$ -CuI in THF to give **115** in a yield of 66% (Scheme 19).⁸⁵



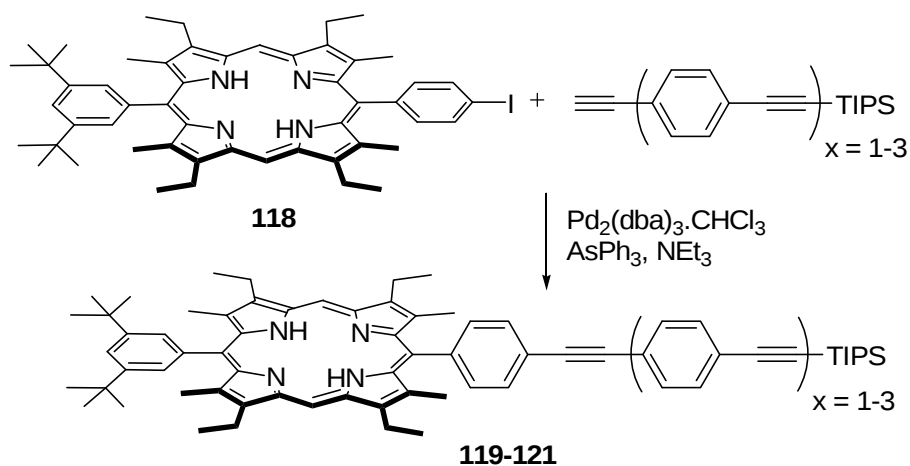
Scheme 19. Synthesis of ferrocenyl porphyrin.

Another example of Sonogashira couplings is the preparation of β -tetrasubstituted porphyrins via the reaction of the metallated 2,4-diiododeuteroporphyrin-IX with dodecyne in the presence of a palladium catalyst.⁸⁶ It can also be used for introduction of fluorine containing acetylenes into the macrocycle in up to 95% yield, thus providing a wide scope of applications for fluoroporphyrins.⁸⁷ Sonogashira reactions have been widely used to modify the porphyrin periphery for the synthesis of more complex porphyrin architectures. For example, silyl protected alkynyl porphyrins can be cleaved and a free ethylene-group can be used for further alterations, generally involving organometallic reactions. Some examples employing the terminal alkynyl porphyrins in Sonogashira C–C coupling reactions have been presented.^{88,89} Alternatively, haloaryl porphyrins can be coupled to non-porphyrin acetylenes to provide an easy access to the various porphyrinyl compounds.^{90,91} As an example, a direct modification of the triple-decker sandwich complex **116** via Sonogashira reaction is shown in Scheme 20.⁹¹

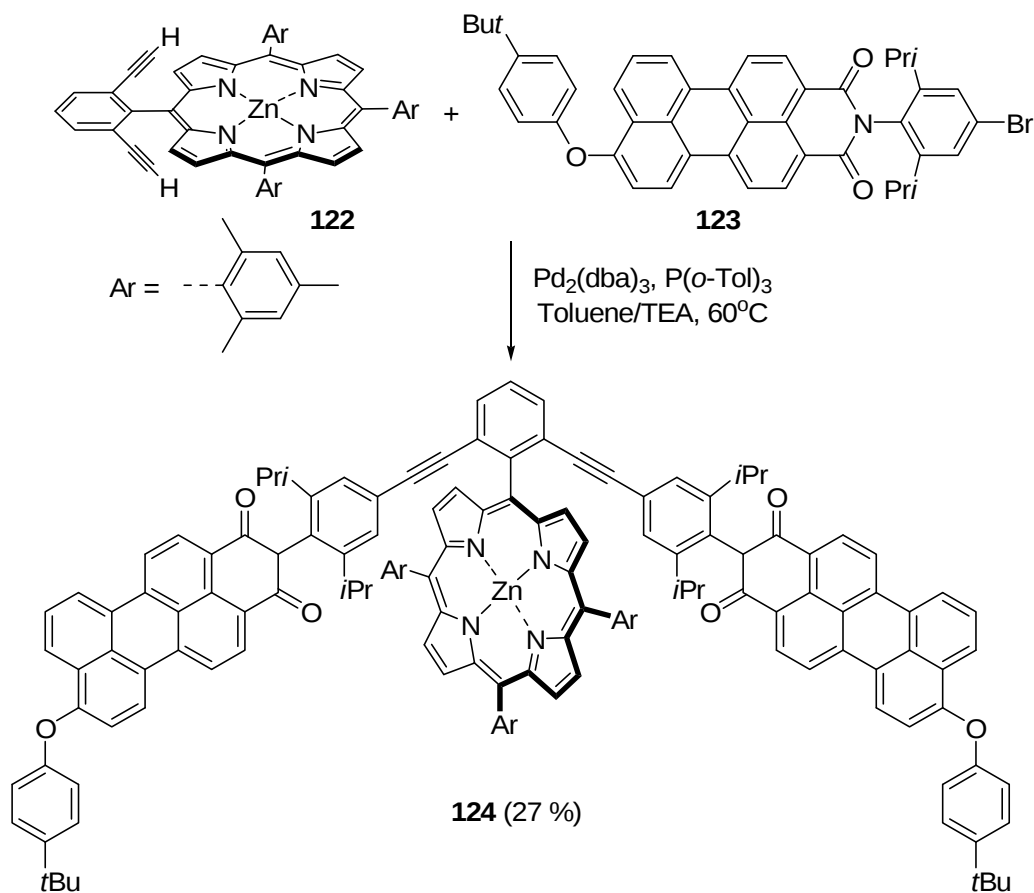


Scheme 20. Synthesis of thiol-derivatised europium porphyrinic triple-decker sandwich complexes.

Sonogashira coupling requires the presence of CuI as a co-catalyst and metallated porphyrins have to be used in order to avoid undesired metallation by copper. Unfortunately there only few copper-free methods available for this transformation. For example, a palladium catalyzed coupling between free base iodoporphyrins and terminal alkynes provides an access to the various polyalkynyl (**119-121**)^{92,93} and perylene (**124**)⁹⁴ porphyrins in good yields (Scheme 21 and 22). These copper-free methods feature relatively high loading conditions, namely NEt₃ (100 equiv), Pd₂(dba)₃·CHCl₃ (15 mol %) and 10 equivs of AsPh₃ per Pd in CH₂Cl₂/MeOH, 1:1 solvent mixture.⁹⁵

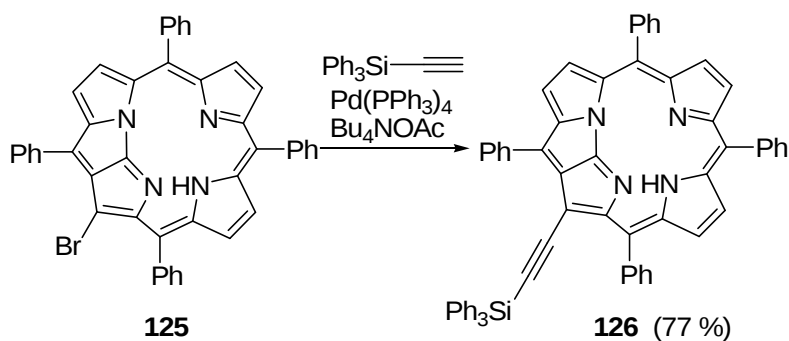


Scheme 21. Synthesis of polyalkynyl porphyrins.



Scheme 22. Synthesis of perylenebased porphyrins.

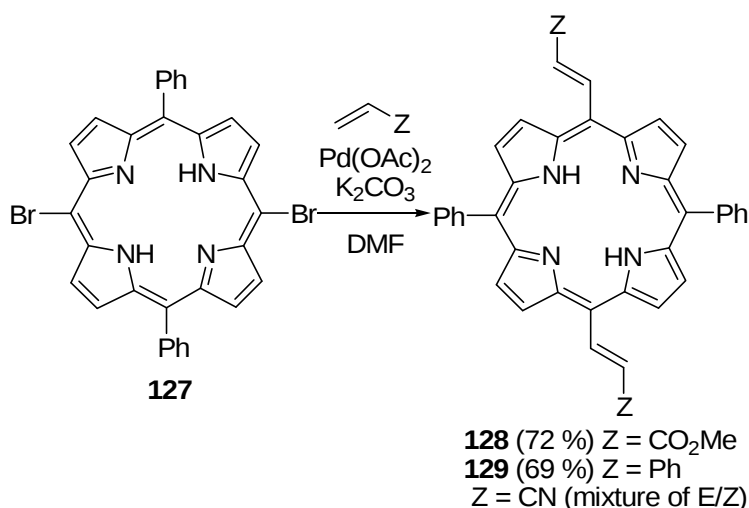
Internally substituted N-confused and N-fused porphyrins can also undergo these types of coupling.⁹⁶ In case of N-fused porphyrins **125**, the typical copper-mediated conditions do not work well. The reaction was carried out without amine and copper salt but with the addition of Bu_4NOAc providing the desired derivatives **126** in excellent yield (Scheme 23).



Scheme 23. Sonogashira coupling of an N-fused porphyrin with an acetylene derivative.

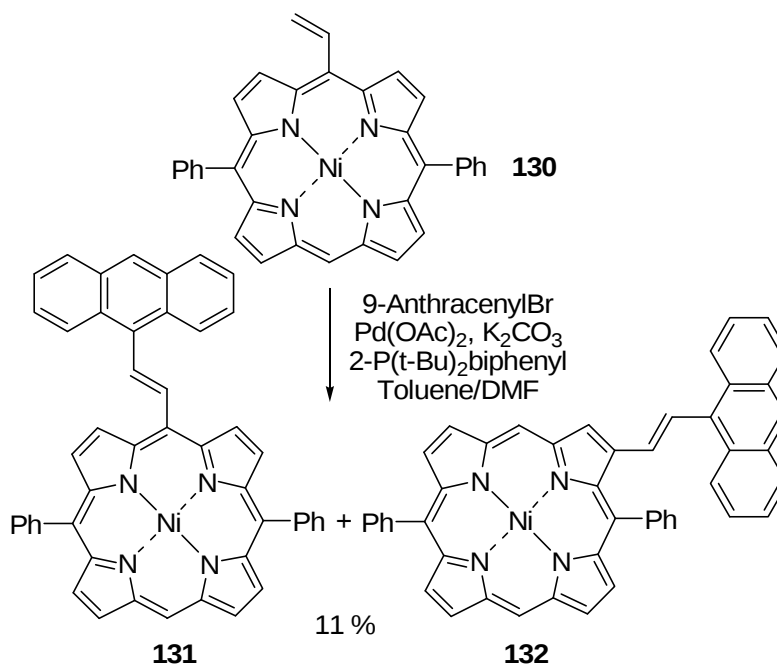
C. Heck and Stille coupling reactions

Another alternative approach involving palladium-mediated couplings for C–C-bond construction are the Heck and Stille reactions. The Heck approach has been used to introduce the alkenyl substituents into either the meso or β positions. Detailed investigations of the direct coupling of some typical Heck-type alkenes such as acrylates, styrenes and acrylonitrile with meso bromoporphyrins **127** have been carried out (Scheme 24).⁹⁷



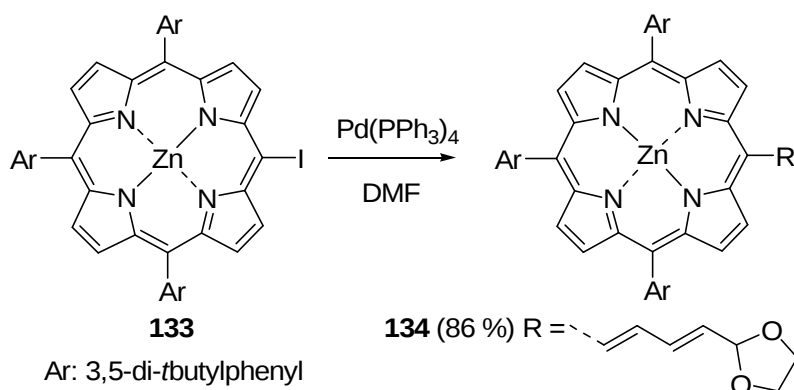
Scheme 24. Synthesis of alkenyl porphyrins via Heck coupling.

The Heck reaction can also be used to modify a porphyrin at its peripheral position.⁹⁸ For example, alkenyl porphyrin **130** reacts with 9-bromoanthracene forming meso and β adducts **131** and **132** in an overall yield of 11% (Scheme 25). Likewise, β -derivatization of protoporphyrin-IX via Heck-type transformation has been successfully accomplished in the presence of a palladium catalyst. Here a porphyrin with two alkenyl units reacted with several haloaryl derivatives to yield substituted arylvinylidene porphyrins.⁹⁹



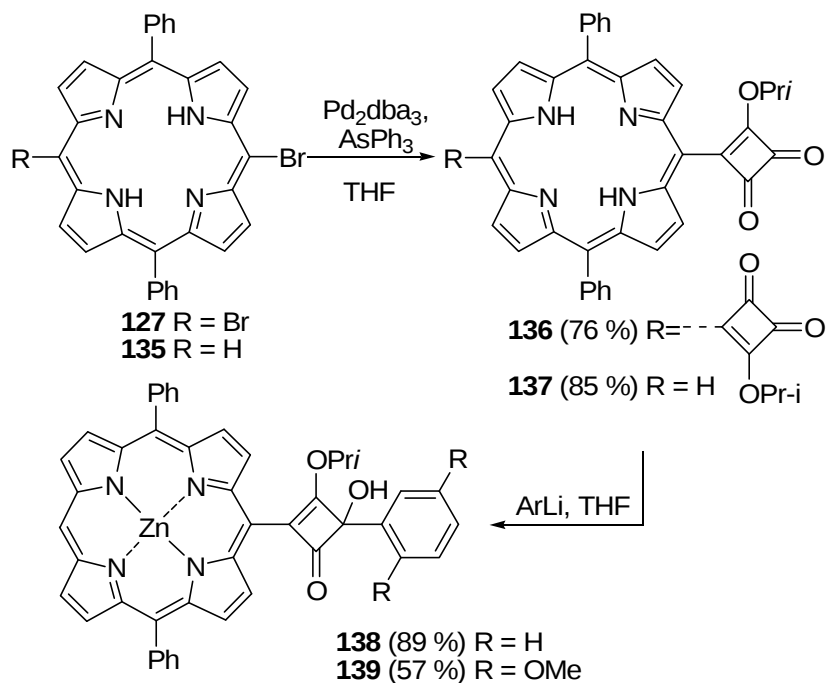
Scheme 25. Synthesis of alkenyl porphyrins via Heck coupling.

The Stille coupling represents a simple approach for the synthesis of novel materials, including tin reagents and coupling products. Tin compounds can be easily prepared starting from the corresponding bromides and can then be used for C–C bond formation in the presence of a catalyst. Moreover, the precursors are commercially available and the tin reagents are cheap to prepare compared to the related boronates widely utilized for Suzuki coupling. However, in contrast to the other methods described here, the latter has not been widely used. Only few examples have been reported so far for the synthesis of novel porphyrin molecules and porphyrin dimers.^{100,101} Here, the conversion of the iodoporphyrin **133** into porphyrin butadiene derivative **134** has been achieved in the presence of Pd(PPh₃)₄ at 80 °C in DMF in 86% (Scheme 26).¹⁰²



Scheme 26. Synthesis of porphyrin butadiene derivative via Stille coupling.

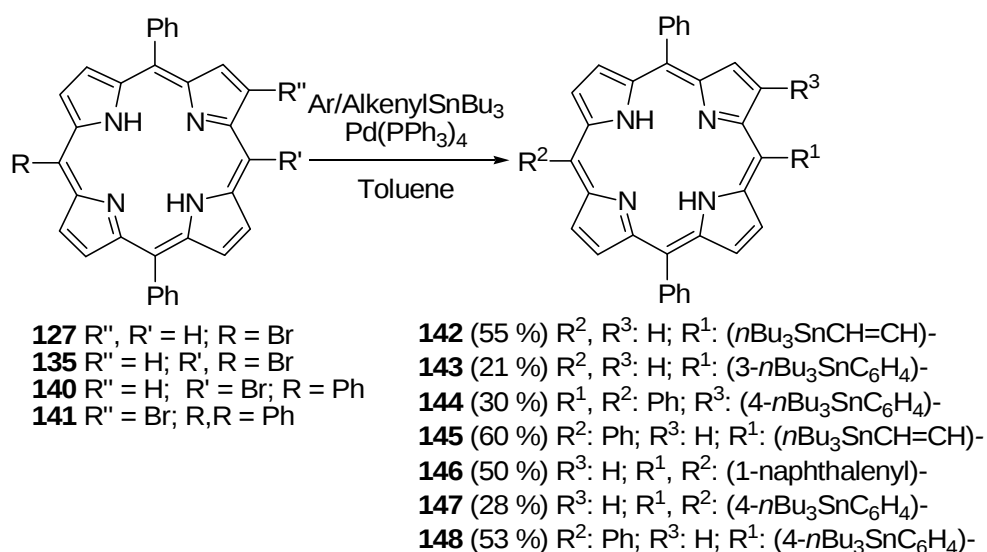
Another example illustrates a complex organometallic approach for the synthesis of porphyrin-quinone systems.¹⁰³ The first step is a Stille reaction of the bromoporphyrins **127** and **135** and *n*-butylstannylcyclobutendione in the presence of a Pd-catalyst followed by an organolithium reaction of ArLi to give the 1,2-adducts **136** and **137** (Scheme 27). The squarylporphyrins **138-139** are finally converted via thermal rearrangement and air oxidation into a porphyrin-quinone.



Scheme 27. Synthesis of squarylporphyrins via an organometallic approach.

The Stille reaction also proved to be quite successful for the synthesis of members of the N-confused porphyrin series. E.g., brominated N-confused porphyrin silver complexes reacted with aryl stannanes (e.g., 2-furyl, 2-thienyl and phenylethynyl) to form the Stille-adducts in 63-76% yield.¹⁰⁴

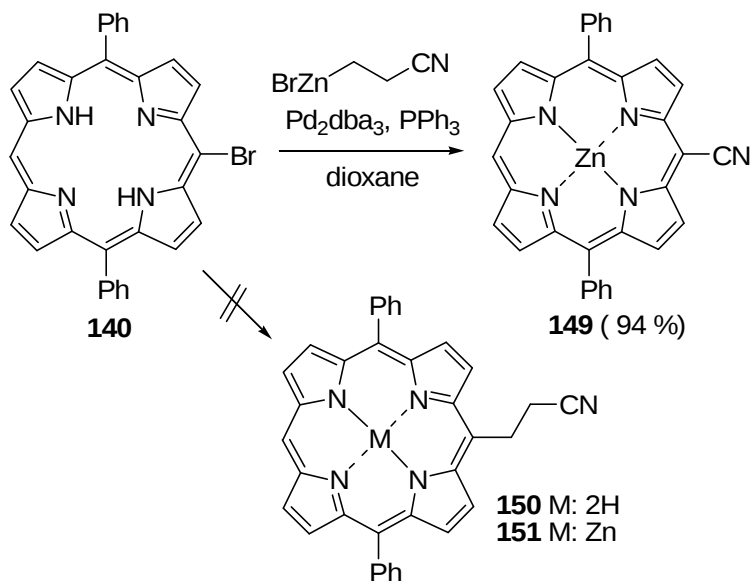
Generally, C-C bond formation is performed using haloporphyrins and non-porphyrin tin-counterparts. Recently, it has been shown that stannyl porphyrins can also be prepared via Stille reactions using organostannanes. This method can be used for meso and β porphyrins to provide the respective porphyrinyl stannanes **142-148** as convenient building blocks (Scheme 28).¹⁰⁵



Scheme 28. Synthesis of a series of tin porphyrins via Stille C-C coupling.

Non-Stille organometallic approaches using organozinc reagents have been developed for porphyrin modifications. For example, palladium catalyzed cyanation using cyanomethyl zinc bromides, provided a convenient route to meso **149** and β -cyanoporphyrins in 50-94% yields.

Moreover, no ethylcyanoporphyrins **150-151** were formed under these conditions giving solely the cyano compounds (Scheme 29).¹⁰⁶



Scheme 29. Synthesis of cyanoporphyrins.

D. Macromolecules: Dendrimers and conjugated polymers

While most work dealt with simple porphyrin molecules, organometallic approaches have been developed as well for the synthesis of macromolecules such as dendritic porphyrins and polymeric constructs. This strategy has been used to modify other systems such as the Wang resin¹⁰⁷ and nanotubes.¹⁰⁸ Dendrimers are three-dimensional, nanoscopic materials assembled from an inner core and a regular array of the branching units. Organometallic synthesis is a key step to attach the modified dendrons to a porphyrin core unit yielding the macromolecules. Dendritic porphyrins with fluorene unit were prepared via palladium mediated Suzuki-type reaction.¹⁰⁹ Likewise, syntheses for the porphyrin cored benzoquinone-polyphenylene

$\text{RB(OH)}_2, \text{Pd(PPh}_3)_4$

152

153 (57 %)

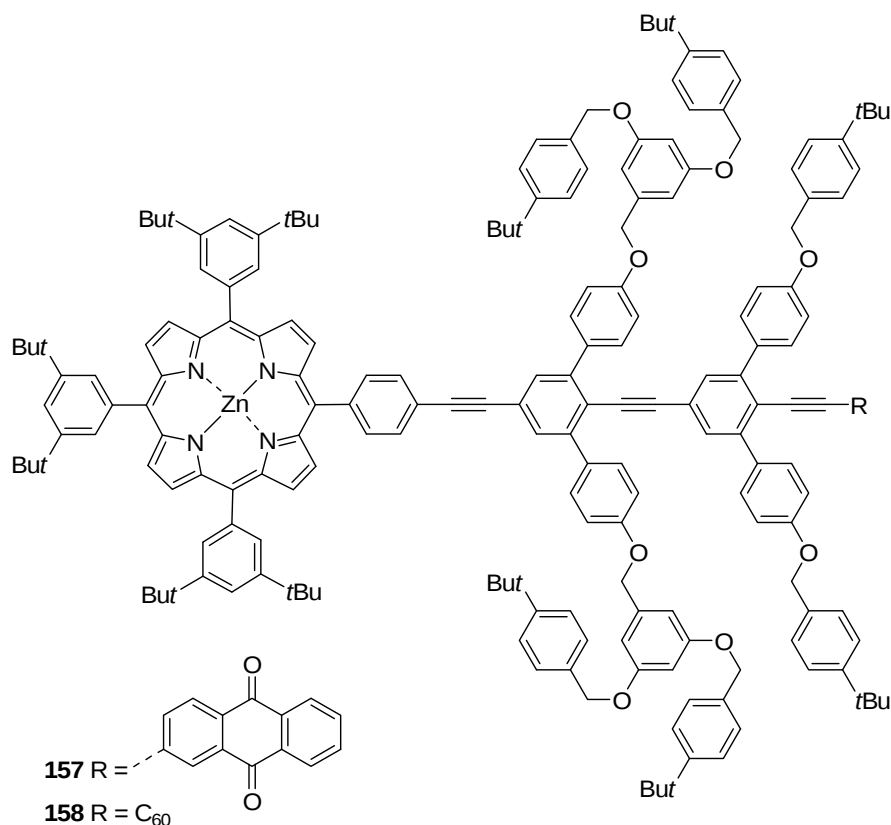
154 (24 %)

155 (11 %)

R =

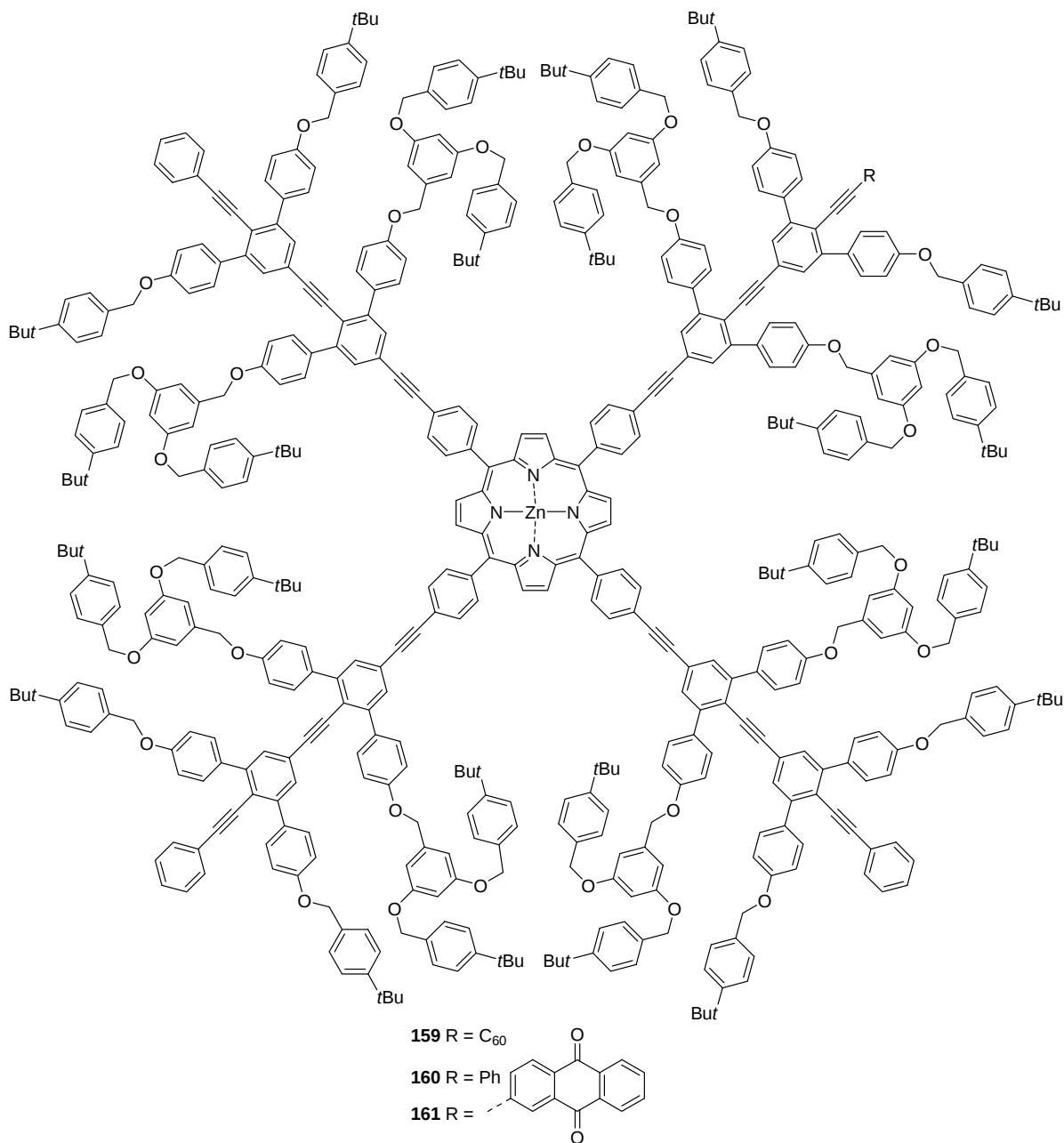
Sonogashira coupling reactions have proven to be successful for the synthesis and modification of dendrimers.¹¹²⁻¹¹⁶ Work involved the synthesis of a series of snowflake-shaped

dendrimers and dendrones for energy transfer studies. The dendrons with the terminal anthraquinonyl and C₆₀ residues were prepared using an organometallic methodology. Subsequent Sonogashira couplings resulted in the formation of the final anthraquinonyl containing dendron that was iodated and coupled again via Sonogashira reaction with the a 5-(4-acetylenylphenyl)-10,15,20-tris(3,5-tert.butylphenyl)porphyrinato-zinc **156** in the presence of PdCl₂(PPh₃)₂, CuI and *i*Pr₂NH in THF, giving the desired dendrimer **157** in 36% yields (Scheme 31).¹¹² In the case of fullereryl compounds, the TBS-protected alkynyl dendron can be prepared in the same manner using the palladium-catalyzed Sonogashira reaction followed by deprotection of the TBS group. The resulting terminal alkynyl dendron reacted with lithium bis(trimethylsilyl)amide in the presence of C₆₀ in THF, followed by protonation with TFA and due to a partial demetallation was treated with ZnOAc₂ to give **158**.¹¹³



Scheme 31. Structure of dendrons synthesised via Sonogashira coupling

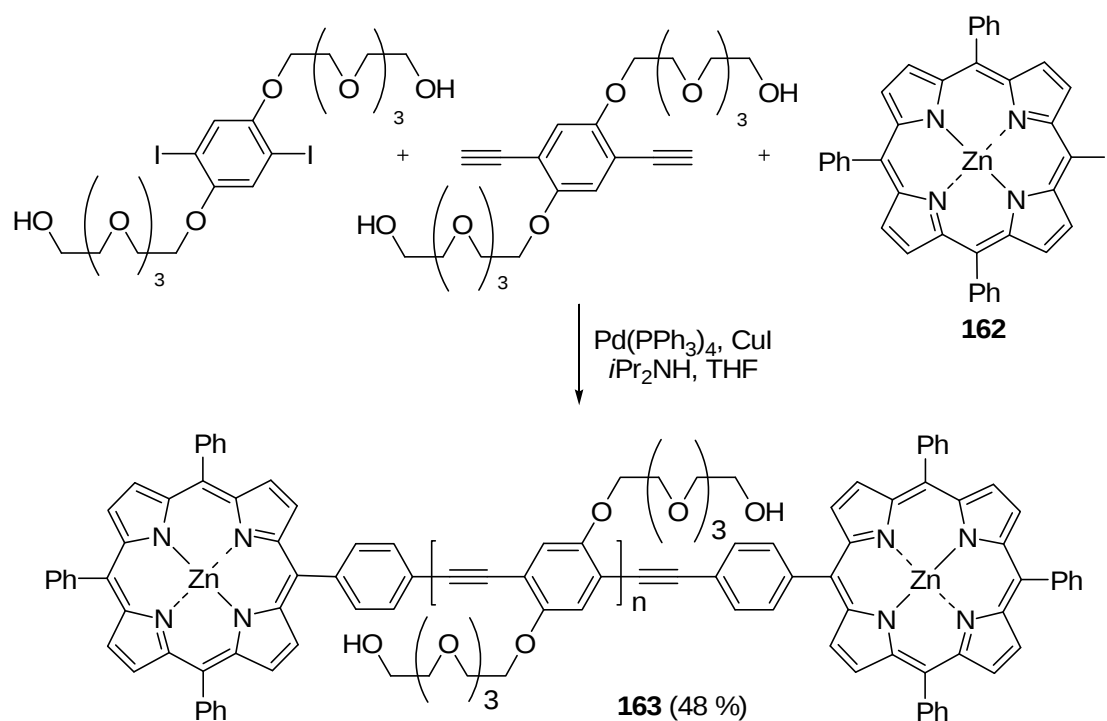
Construction of the snowflake-shaped dendrimers **159-161** with fullerene C_{60} and the anthraquinonyl substituents was performed in the same manner; these compounds have been synthesised in 38% (**159** for C_{60}) and 36% (**161** for anthraquinonyl residue) yields, respectively (Scheme 32).^{112,113}



Scheme 32. Structure of snowflake-shaped dendrimer synthesised via Sonogoshira coupling

Conjugated polymers are interesting targets for industrial applications and several approaches have been developed to assemble porphyrin-containing polymers. For example, the Suzuki approach has been used for the synthesis of polyfluorene copolymers containing porphyrin and/or thiophene units.^{117,118} These transformations proceed smoothly and require just a dibromoporphyrin, a brominated spacer and boron trifluoride in the presence of Pd(PPh₃)₄. Alternatively, Heck coupling reactions can also be used for the design of conjugated porphyrin materials.¹¹⁹

Rigid rod-like polymers are prone to aggregation. However, the combination of dendrimers and linear polymer backbone can be employed to overcome this problem. Porphyrin-containing dendronized polymers have been prepared using a macromonomer strategy. Suzuki polycondensation of Frechet-type dendrones with a diboronic porphyrin gave access to polymeric materials in 87-94%.¹²⁰ Hyperbranched fluorenyl porphyrin cored polymers could be synthesized in a similar manner.^{121,122} Alternatively, Sonogashira coupling of a diethynyl porphyrin and diiodo-functionalized Frechet-type dendrones proved successful for the production of conjugated polymers in 71-84% yields.¹²³ Similarly, perylene-porphyrin rod-like oligomers,¹²⁴ and the porphyrin-polyphenylene-ethynylene systems^{125,126} for light-harvesting applications were prepared via Sonogashira coupling reactions (Scheme 33).



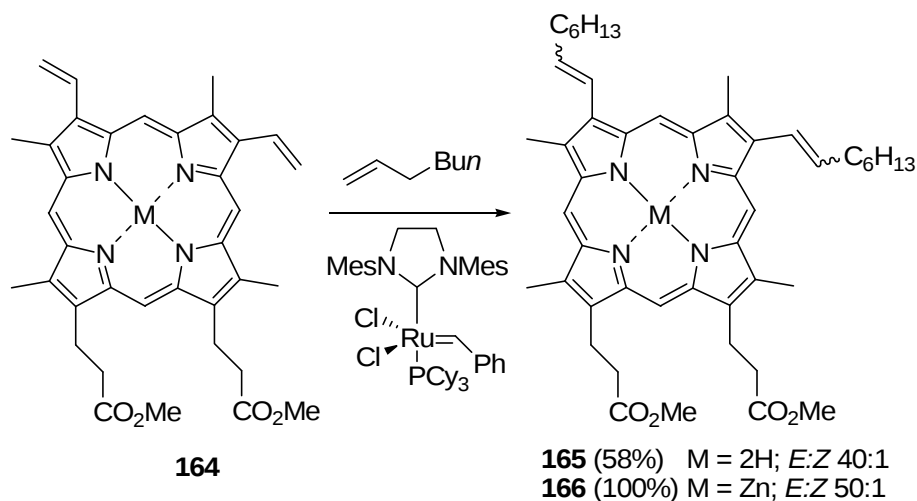
Scheme 33. Synthesis of porphyrin end-capped water-soluble poly(phenyleneethynylene).

IV. Metal mediated C-C coupling reactions

A. Ruthenium catalyzed C-C coupling reactions

Ruthenium catalyzed reactions, particularly olefin metathesis, are widely used in synthetic chemistry for the preparation of various materials. Depending on structure and reactivity of the organic building blocks, a selection of suitable Ru-catalysts can be employed.^{127,128} Porphyrins and their derivatives can also be modified using this approach. Several examples applying cross-metathesis in porphyrin related fields focused on the transformations of long unsaturated side chains attached via aryl or ether spacers to a porphyrin core. These studies were aimed at the synthesis of porphyrin arrays and boxes,¹²⁹⁻¹³⁶ or porphyrins with peptide backbones¹³⁷ and

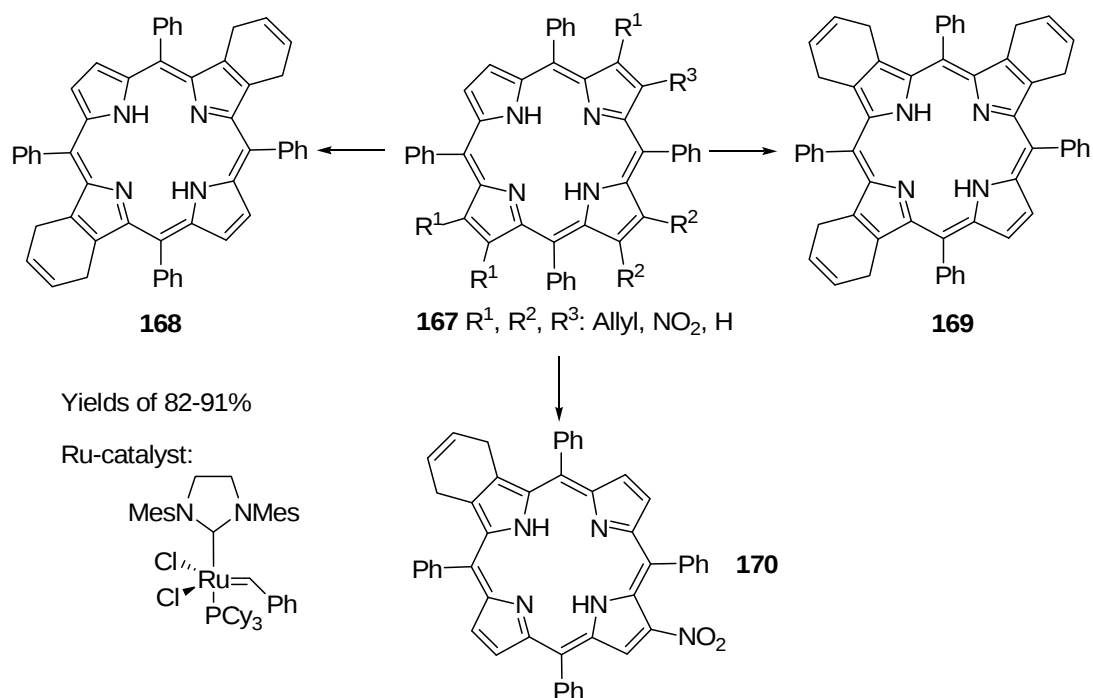
polymeric chains¹³⁸. Olefin cross-metathesis can also be used for the direct functionalization of porphyrin macrocycles. Examples include modifications of β vinyl chlorins and β vinyl porphyrins **164** catalyzed by a 2nd generation Grubbs catalyst (Scheme 34).^{139,140}



Yields and E:Z ratios were calculated based on the crude ¹H NMR spectra

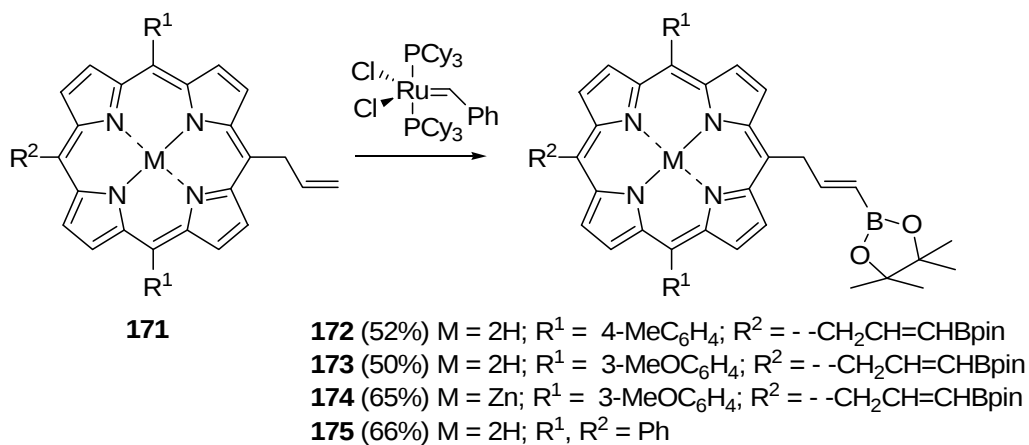
Scheme 34. Modification of β vinyl porphyrins via metathesis.

A new route to benzoporphyrins has been developed via a combined organometallic approach.¹⁴¹ Here, β -allyl-tetraphenylporphyrins **167** synthesized via Suzuki coupling were converted in the presence of a 2nd generation Grubbs catalyst into the products of intramolecular ring-closure metathesis **168-170** in 82-91% yields. These adducts were then treated with DDQ oxidizing them to the benzoporphyrins in almost quantitative yields (Scheme 35).



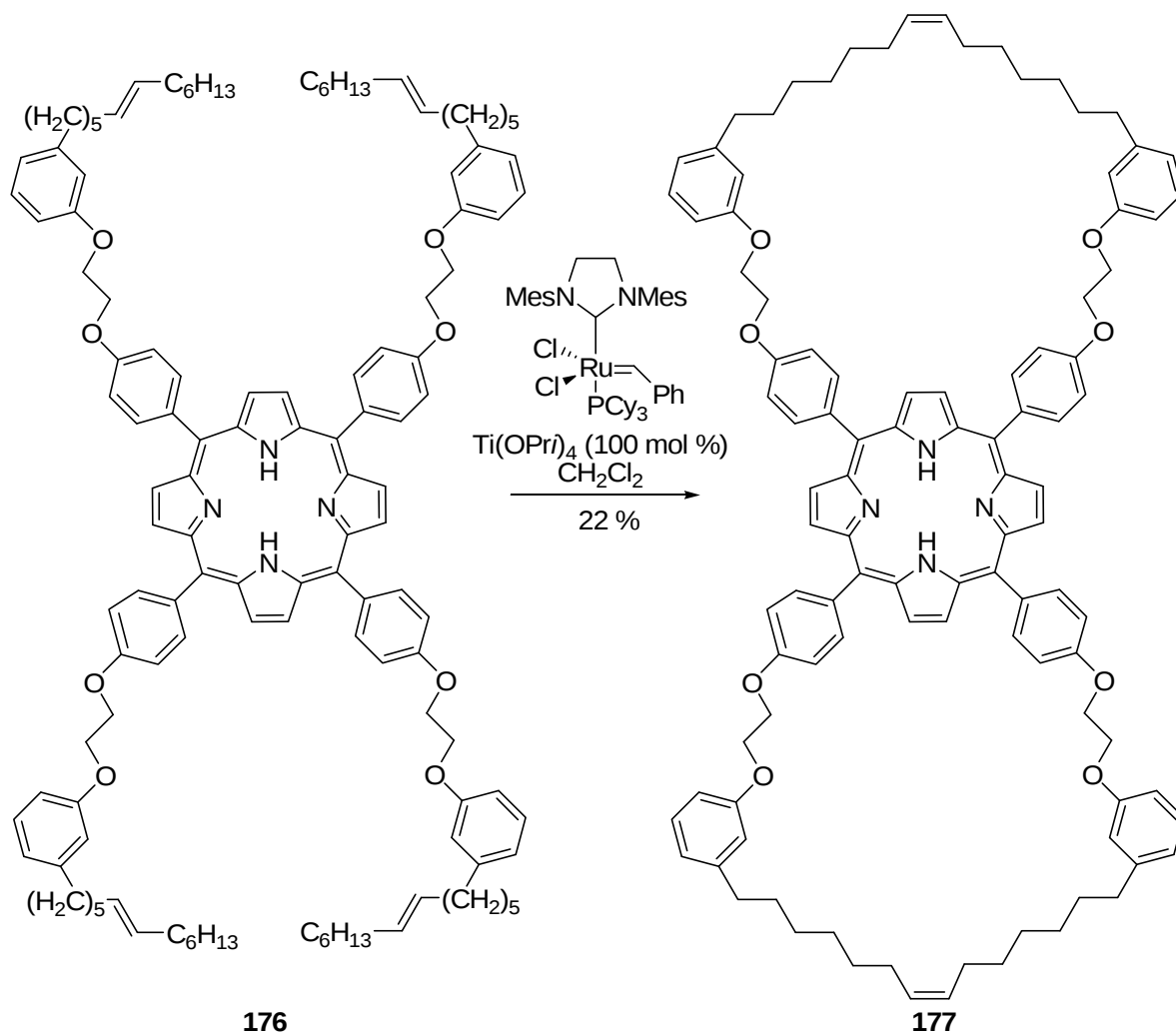
Scheme 35. An approach to benzoporphyrins.

Other examples of meso allyl porphyrin utilizations in metathesis transformations involved the synthesis of porphyrins with unsaturated side chains. For example, porphyrins **172-175** with mono and bis-substituted unsaturated boronyl residues could be prepared in good yields (52-66%) using a Grubbs 1st generation catalyst. In all cases complete *E*-stereoselectivity (100%) was observed (Scheme 36).¹⁴²



Scheme 36. Synthesis of boronyl porphyrins via metathesis.

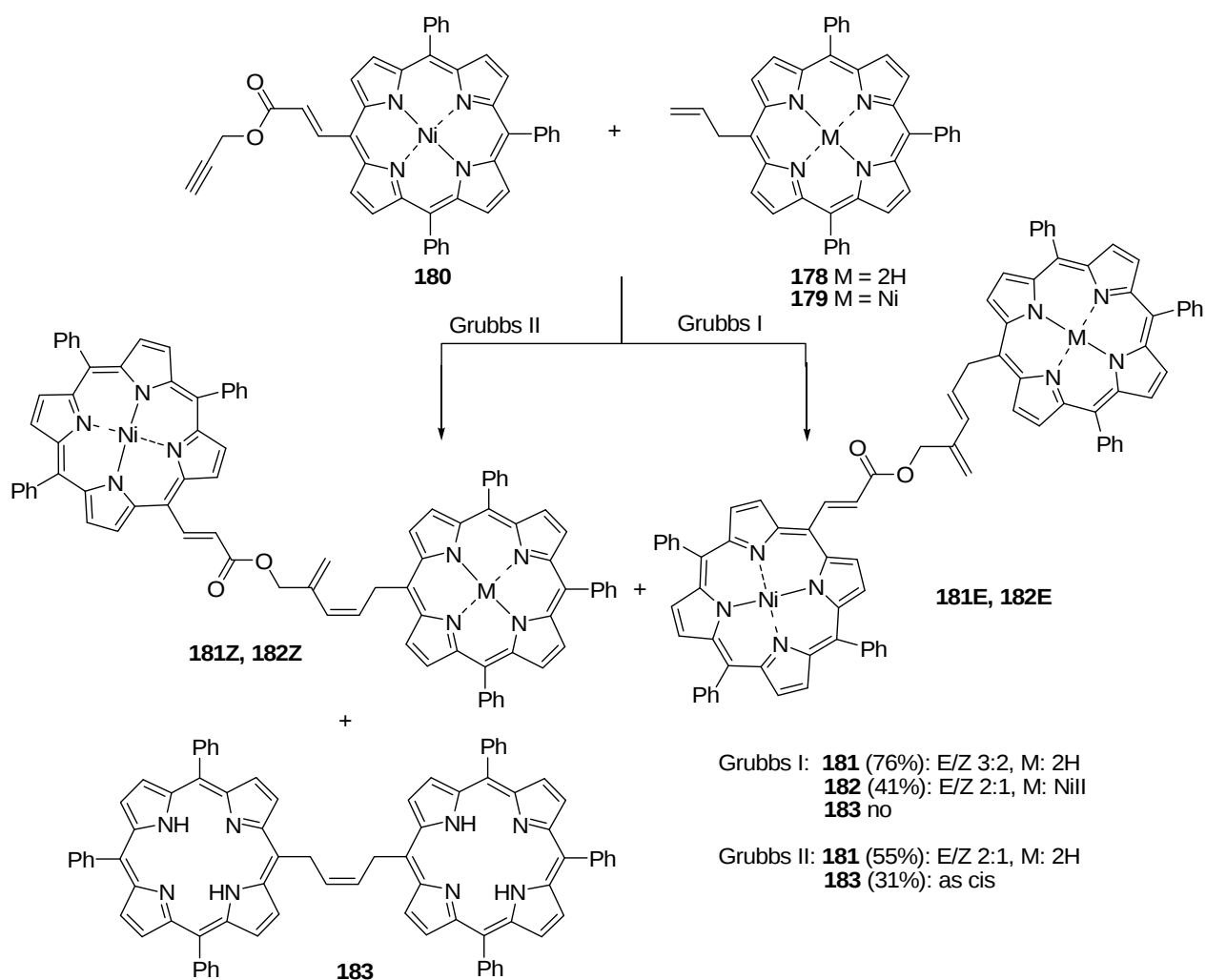
Another example included the synthesis of hybrid cardanol-based porphyrins via cross-metathesis or intramolecular ring-closure metathesis.^{143,144} Examination of the different Grubbs catalysts showed that the Hoveyda-Grubbs catalyst was most efficient for the preparation of these compounds **177** (Scheme 37).



Scheme 37. Synthesis of cardanol-based porphyrins.

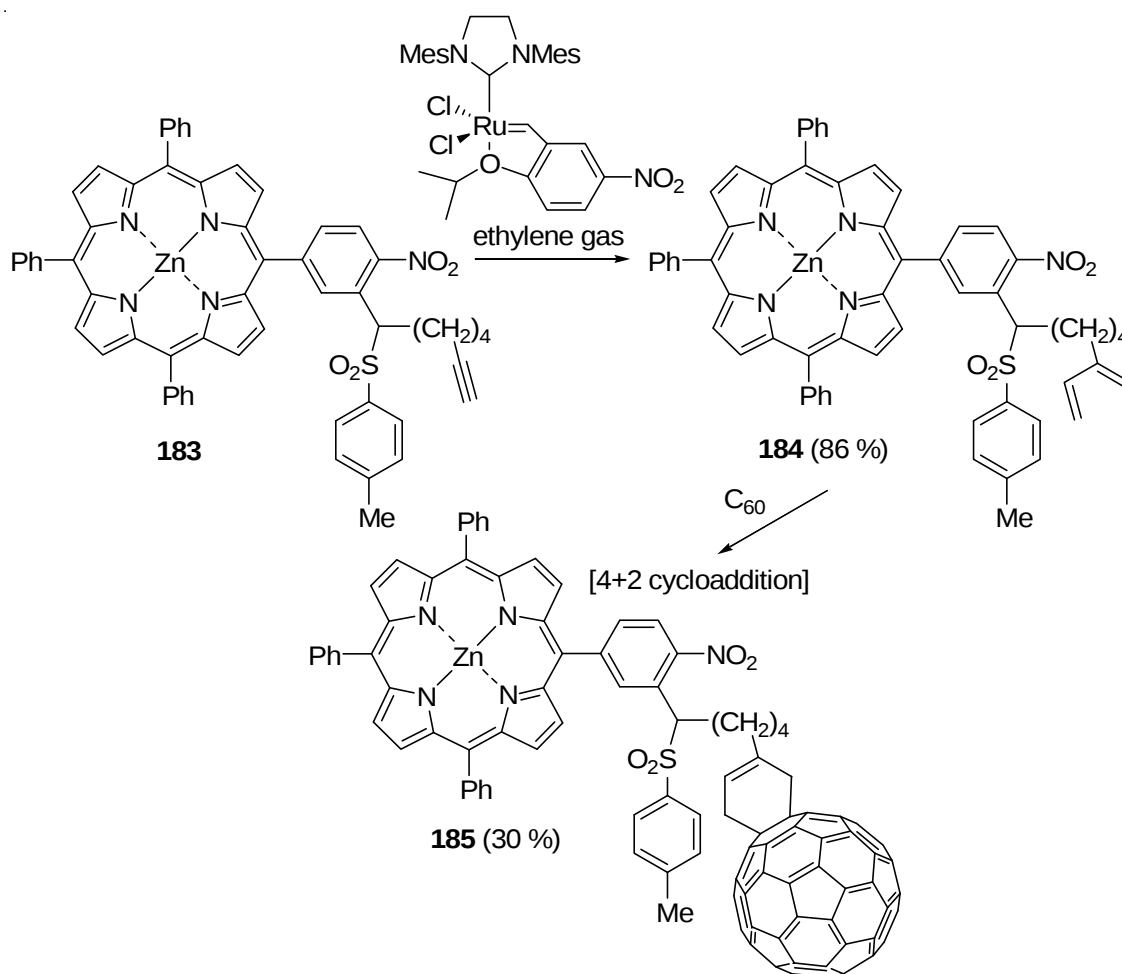
Another potential method is the enyne metathesis, a unique and interesting transformation involving the reaction between an alkene and an alkyne partner. Enyne metathesis can be used

for the synthesis of the porphyrin butadiene derivatives. For example, porphyrin propargyl ester and allyl porphyrins **178** and **179** could be converted into synthetically useful 1,3-disubstituted butadiene derivatives **181** and **182**.¹⁴⁵ Depending on the catalysts used, enyne metathesis of porphyrin **180** and allyl porphyrin **178** can result in the different product formations. In the case of Grubbs II catalyst, a competing CM homodimerisation of allyl porphyrin **178** took place, resulting in a mixture of alkene **183** (31%, *cis* isomer) and the 1,3-disubstituted butadiene derivatives **181** (55%) (Scheme 38).



Scheme 38. Enyne metathesis of **180** and allyl porphyrins **178**, **179**. Synthesis of 1,3-disubstituted butadienes **181** and **182**.

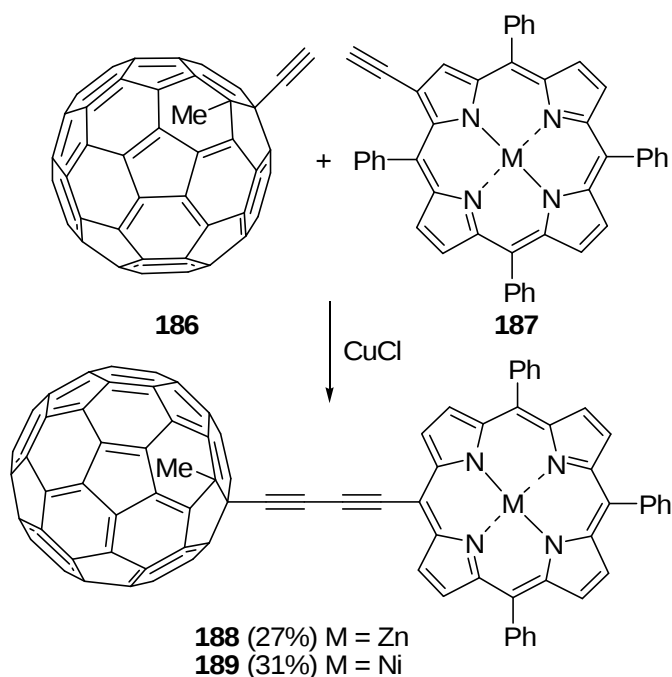
Butadienyl compounds offer themselves toward structural elaboration via Diels–Alder and other cycloaddition reactions. Hence, a synthetic approach for porphyrin-fullerene dyads, adapted from a chlorin synthesis,¹⁴⁶ has been developed via enyne metathesis followed by [4+2] cycloaddition to fullerene.¹⁴⁷ The 2-substituted butadienyl porphyrin **184** could be prepared in 86% yield from a porphyrin alkynyl derivative **183** and ethene in the presence of Hoveyda-Grubbs catalyst and was converted into the porphyrin-fullerene dyad **185** via Diels-Alder reaction in 31% yield (Scheme 39).



Scheme 39. Synthesis of porphyrin-fullerene dyad.

B. Copper, nickel, cobalt and rhodium C-C coupling reactions

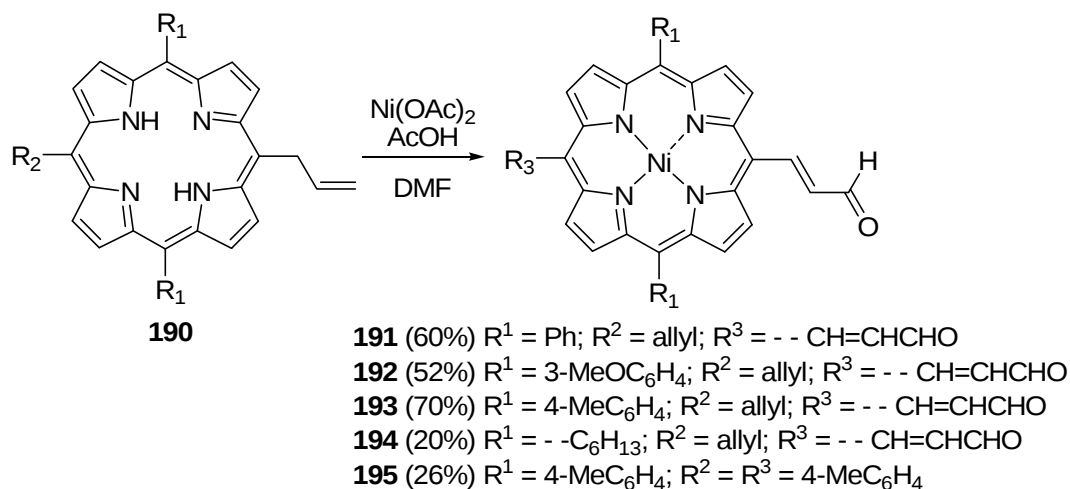
With the exception of the Pd-catalyzed reactions described above, copper is used more frequently than other metals in metal-mediated C-C and C-X coupling reactions. Typical reactions include Glaser couplings and the “click reaction”. Glaser coupling can be used to assemble doubly linked acetylene bridges and is mainly utilized for the synthesis of porphyrin arrays. Surprisingly, only a few examples have been reported so far for the preparation of porphyrin monomers.^{150,151} One example is the preparation of fullerene-porphyrin dyads **188** and **189** using a C–C coupling between the fullerene derivative **186** and an acetylenyl porphyrin **187** in the presence of CuCl (Scheme 40).¹⁴⁸ Another example illustrated the synthesis of the bishexylthiophene-pyridine-porphyrin systems. Such compounds could be prepared from ethynyl pyridine and terminal diethynyl porphyrins in the presence of CuOAc.¹⁴⁹



Scheme 40. Fullerene-porphyrin dyads via Glaser C-C coupling.

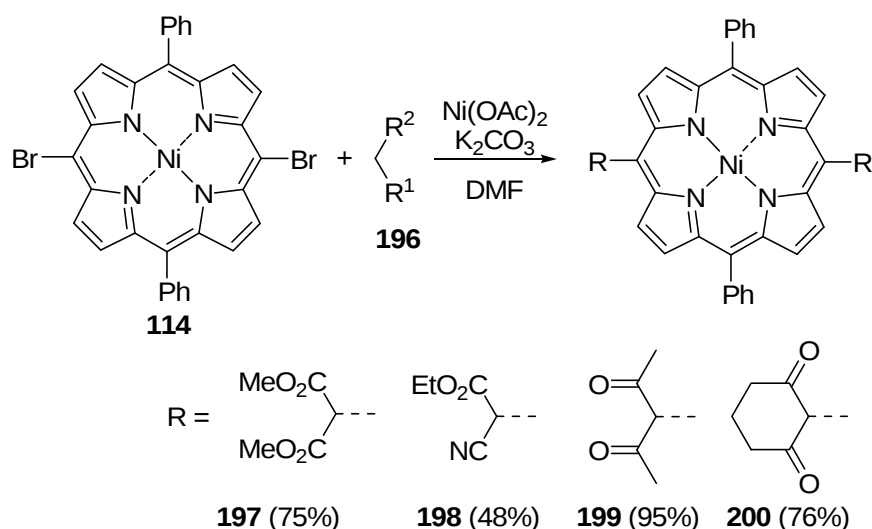
At a first glance nickel complexes show a similar behavior towards organic systems as palladium reagents and the two metal catalysts may act in a similar way in each step of the overall catalytic cycle. However, it has been noted that nickel complexes are more effective in certain catalytic reactions than the analogous palladium catalysts.

One of the predominant theories is based on the formation of η^1 and/or η^3 -complexes involving the allyl systems. Experimental data indicate that the reaction proceeds via a radical chain mechanism, which can be initiated by heat, light, or reducing agents. These coupling reactions require a polar, coordinating solvent such as DMF, as well as stoichiometric amounts of nickel. A new route to α,β -unsaturated formylporphyrins **191-195** involved synthesis of allyl porphyrins **190** via Suzuki coupling reaction in 50-95% yields followed by reaction with nickel acetate in DMF providing mono- and diacroleinylporphyrins **191-195** in up to 70% yield (Scheme 41).¹⁵⁰



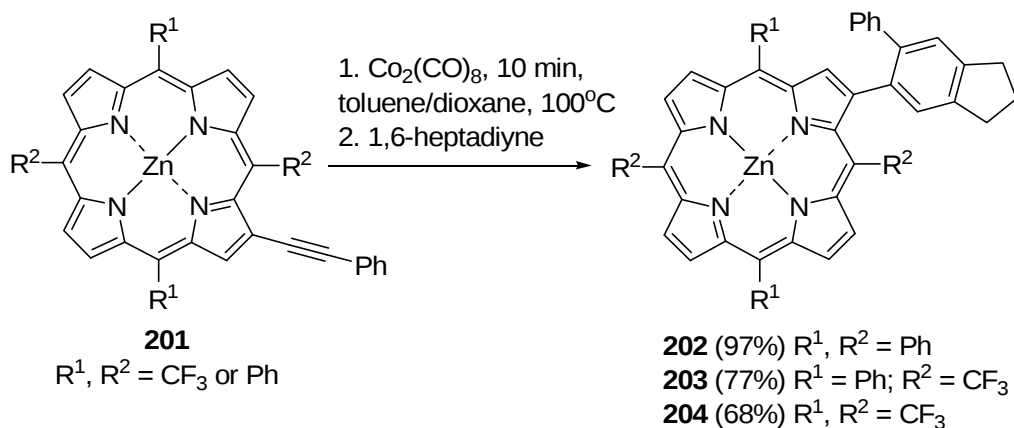
Scheme 41. Synthesis of α,β -unsaturated formylporphyrins via Ni-catalyzed reaction.

It has also been shown that a nickel catalyzed C–C coupling of meso dibromoporphyrin nickel complexes **114** with carbonyl compounds **196** resulted in the formation of a novel porphyrin series of carbonyl and carboxy porphyrins **197-200** in 48-95% yields (Scheme 42).¹⁵¹ The catalytic system operates simply and effectively under mild conditions and allows a convenient entry into a series of potentially useful meso functionalized porphyrins on a large scale. The authors speculated that the mechanism of this reaction should follow the catalytic cycle of nickel-catalyzed cross-coupling of simple aromatic halides.



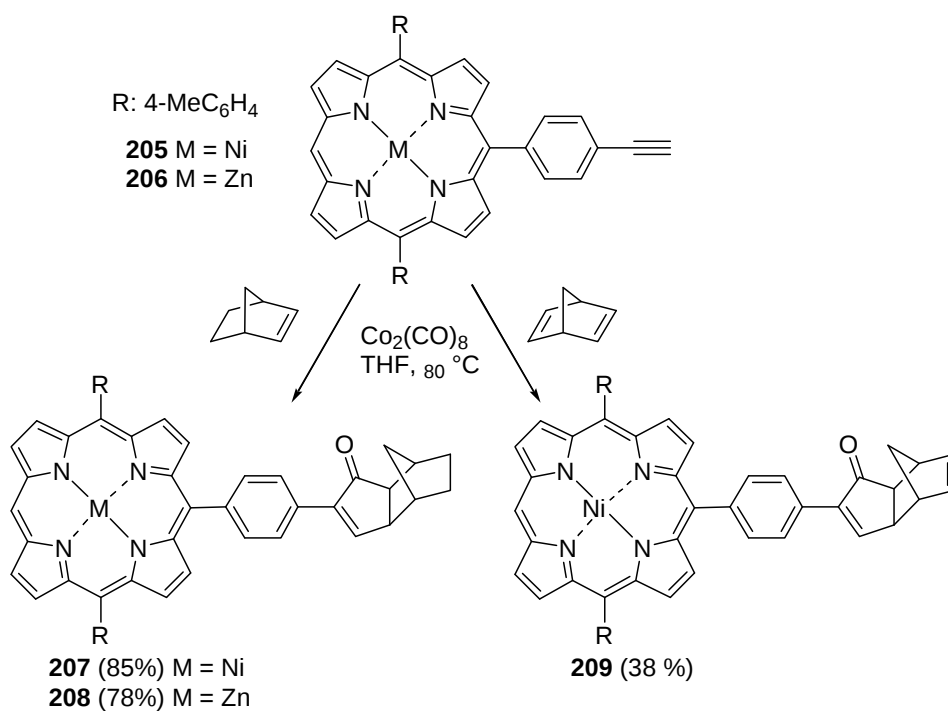
Scheme 42. Ni-catalyzed approach for the synthesis of carbonyl and carboxy porphyrins.

Most examples of cobalt mediated C–C transformations involving porphyrins are cyclization reactions. For example, cobalt-mediated [2+2+2] cycloadditions allow a facile control of the nature of macrocycle-to-macrocycle connectivity and have been used for the synthesis of the monomeric porphyrins **202-204** and face-to-face porphyrin dimers (Scheme 43).¹⁵²



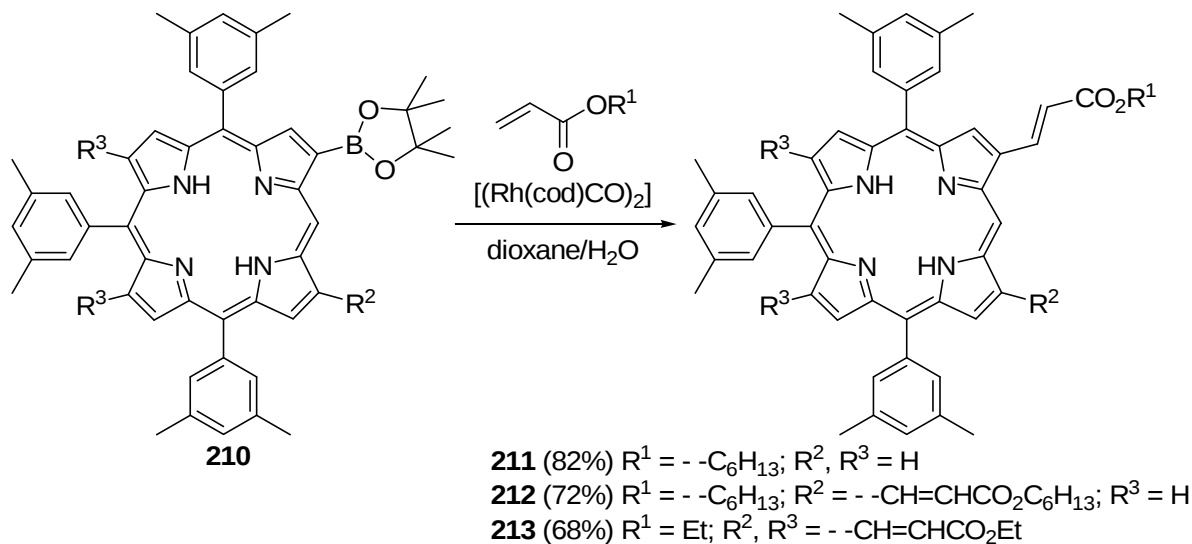
Scheme 43. Cobalt mediated [2+2+2] cycloaddition. Synthesis of β -aryl porphyrins.

Another example is the Pauson-Khand reaction, a flexible and atom economical method for the synthesis of five-membered rings. It involves the reaction of an alkene, an alkyne and a carbon monoxide molecule in a transition-metal mediated coupling to form a cyclopentenone system. The Pauson-Khand porphyrin adducts **207-209** could easily be prepared using cobalt mediated C–C couplings in 38-85% yields (Scheme 44).¹⁵³



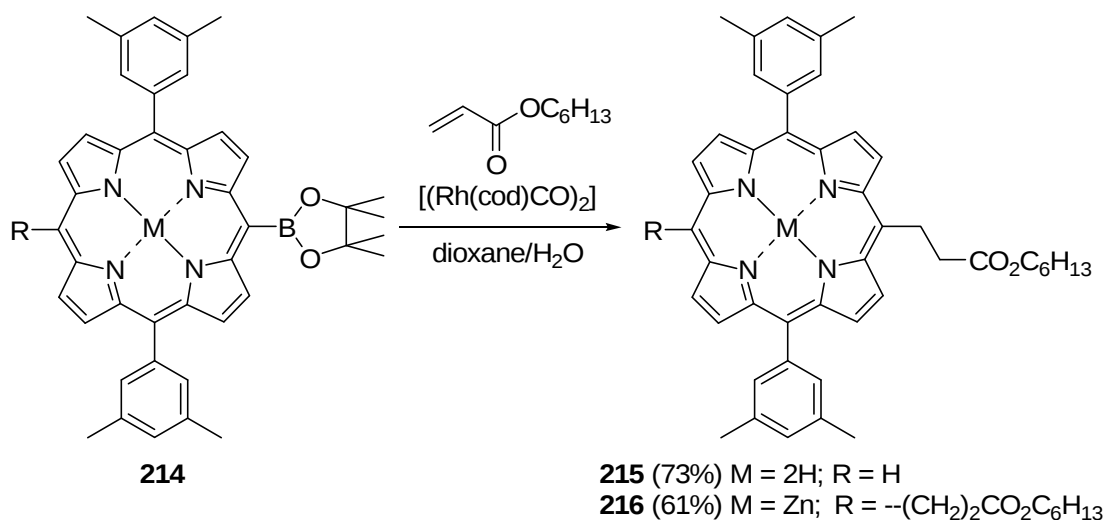
Scheme 44. Synthesis of porphyrin derivatives via Co-mediated Pauson-Khand reaction.

Rhodium catalysis is a well-established method in organic synthesis.^{154,155} However, it has not yet been widely employed in for porphyrin synthesis. Finally, a “Heck-like” introduction of α,β - and α,β,χ,δ -unsaturated substituents into porphyrins **211-213** under Rh-catalysis using β -borylporphyrins **210** has been reported recently (Scheme 45).¹⁵⁶



Scheme 45. Synthesis of α,β - and α,β,χ,δ -unsaturated porphyrin derivatives via Rh-catalysis.

Interestingly, the reaction of meso borylporphyrins **214** and acrylates under the same conditions provided exclusively the saturated esters **215** and **216** as the products of 1,4-conjugate addition. These transformations seem to be highly reaction site depended (β vs. meso) (Scheme 46).



Scheme 46. Synthesis of porphyrin ester derivatives via Rh-catalysis.

Acknowledgments

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