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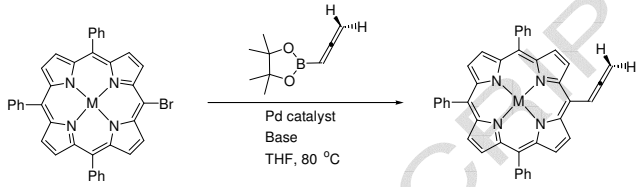

Palladium-catalysed Suzuki-Miyaura cross-coupling is the simplest and most efficient method for attaching an unsubstituted allene, a novel substituent and potential functional group, to the porphyrin periphery.

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Allenylporphyrins: A new motif on the porphyrin periphery

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Abstract— Palladium-catalysed Suzuki-Miyaura cross-coupling proved to be the simplest and most efficient method for attaching an unsubstituted allene, a novel substituent and potential functional group, to the porphyrin periphery. Comparative studies on various allenyl synthetic pathways show that this method, which makes use of a bromoporphyrin and allenylboronate, affords the corresponding allenylporphyrin in the presence of an appropriate base and THF.

The synthesis and functionalisation of porphyrins is of interest to organic chemists. Tetrapyrroles play pivotal, diverse roles in Nature[1] and there is a continuing desire to exploit their properties for applications in medicine,[2] catalysis[3] and nano materials.[4] As a result, functional group interconversion and synthetic transformations spanning the field of porphyrin chemistry are constantly being explored and improved.[5] One niche in the area of synthetic transformations that appears to have received little to no attention with porphyrins, however, is the use of 1,2-propadiene, or allene.

Allenes represent a versatile functional group that can be utilised as a building block in a variety of synthetic transformations.[6] With the emergence of efficient protocols for their preparation, allenes have allowed chemists to access a variety of structurally interesting products that possess biological, chiral and optical activity.[7]

While cumulenic porphyrin dimers linked by two carbons have been explored for their impressive optical properties,[8] these dimers are quinoidal in nature, which results in exceptionally perturbed electronic absorption spectra. To the best of our knowledge, no studies have been performed on the utilization of cumulative double bonds on porphyrins for their chiral and biological aspects, hence this has become the aim of our investigation.

Of the methods we envisaged being successful for allene synthesis on the macrocycle periphery, the Horner-Wadsworth-Emmons (HWE) reaction appealed the most due to its versatility in allene generation[9] and its need for a formylporphyrin precursor. Formylporphyrins are commonly used precursors the utility of which has recently been expanded succesfully from solely metalloporphyrins to include their metal-free analogues.[10]

Applying the one-pot double olefination procedure designed by Tomioka and co-workers[11] to formylporphyrin **1** (Scheme 1), the HWE reaction using tetraisopropyl methylenebisphosphonate and NaH worked well and the extremely polar intermediate **2** could be isolated by simple chromatography in very good yield. Interestingly though, both in the one-pot procedure, and using the isolated intermediate **2**, the second olefination reaction could not be realised under a variety of conditions. This olefination reaction occurs through nucleophilic substitution of an *in situ* generated carbanion intermediate by an aldehyde.[11] However, in our case, when using either benzaldehyde or hexanal in conjunction with LDA, the result was the unexpected substitution of diisopropylamine from the base onto the alkenephosphonate to generate porphyrin **4**. Reaction of diisopropylamine with **2** occurred seemingly regardless of the temperature used (–80 °C to 60 °C. Use of the non-nucleophilic base, ^{t}BuOK, only resulted in partial dehydrophosphonation to yield the alkynylporphyrin **3** in modest amounts when the reaction mixture was heated to 60 °C after addition of the base. Using the metal-free analogue **6**, which was synthesised by Heck coupling, only starting material was retrieved from the reaction mixture.

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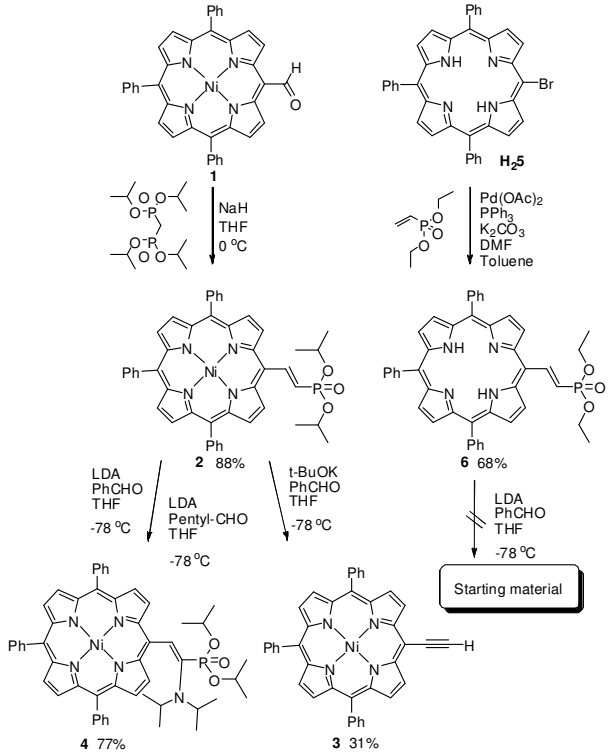
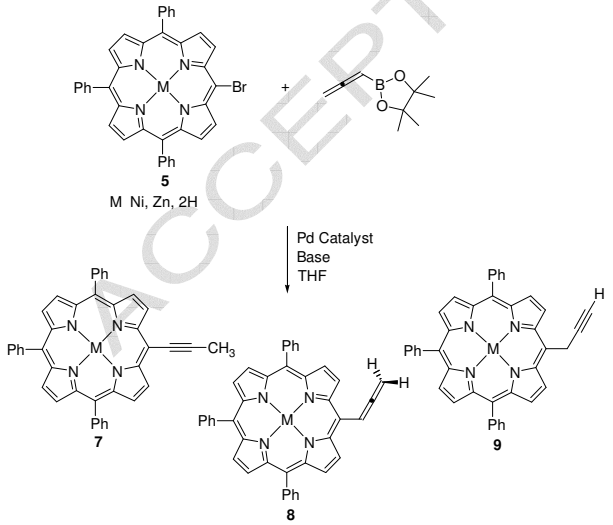


Scheme 1.

As the double HWE reaction did not afford the desired result, we tried a more unconventional synthetic route to allenes by using the allenylboronic acid pinacol ester reagent and Suzuki coupling (Scheme 2). Previously, this particular reagent has been used mainly to take advantage of the allene in three- and four-component reactions and in Ru^{II} catalysis to generate alkenylboronates.[12,13]



Scheme 2.

All Suzuki coupling reactions were attempted using a ten-fold excess of the allenylboronate, and the reaction mixture was degassed by three freeze-pump-thaw cycles before being heated to the desired temperature. Using a variety of conditions to couple the allenylboronate to the bromoporphyrin, it was discovered that very few conditions resulted in the consumption of the bromo starting material. However, when successful, depending on the base and metalloporphyrin used, either the 1-propynyl-, **7**, allenyl-, **8**, or 2-propynylporphyrin, **9** could be isolated after column chromatography. The results of the investigations to find the optimum conditions for attaching the allene to the porphyrin are shown in Table 1.

Except for when K_3PO_4 was used as base, the Suzuki coupling was relatively unsuccessful when carried out at reflux in THF. Even using K_3PO_4, coupling only occurred with the Ni^{II} bromoporphyrin, and the use of this with a strong base resulted in rearrangement of the allene to the more stable 1-propynylporphyrin **Ni7**, along with the formation of unidentifiable side products. Our first successful attempt at isolating the allenylporphyrin **Ni8** came from heating in THF to 80 °C in a sealed Schlenk tube and using a twenty-fold excess of K_3PO_4 (9% yield). Porphyrin **Ni7** was also isolated from this reaction in 14% yield along with unidentifiable side products. Interestingly, using the same conditions, but in 1,4-dioxane at 80 °C, 100 °C and 120 °C, no allenyl- or propynyl-porphyrin was isolated.

On varying the Pd catalyst, the best coupling results were achieved with Pd^{II} salts with the bidentate ligands 1,2-(diphenylphosphino)ethane and 1,3-(diphenylphosphino)propane. In particular, the allenyl-porphyrin **Ni8** was isolated in up to 50% yield when K_2CO_3 was used as the base in ten-fold excess.[14] Interestingly, while $PdCl_2$(dppe) and $PdCl_2$(dppp) were found to be equally effective in coupling, when a two-fold excess of Cs_2CO_3 was used, the $PdCl_2$(dppp) caused ~25% rearrangement from the allene to the 1-propynylporphyrin (entry 7). The use of $PdCl_2$(dppe) gave no such rearrangement, so it was considered the catalyst of choice for the remaining optimisation experiments. It should be noted that the Pd^{II} catalysts were synthesised according to the procedure of Miyaura and Suzuki,[15] and these represent new applications for the catalysts $PdCl_2$(dppe) and $PdCl_2$(dppp).

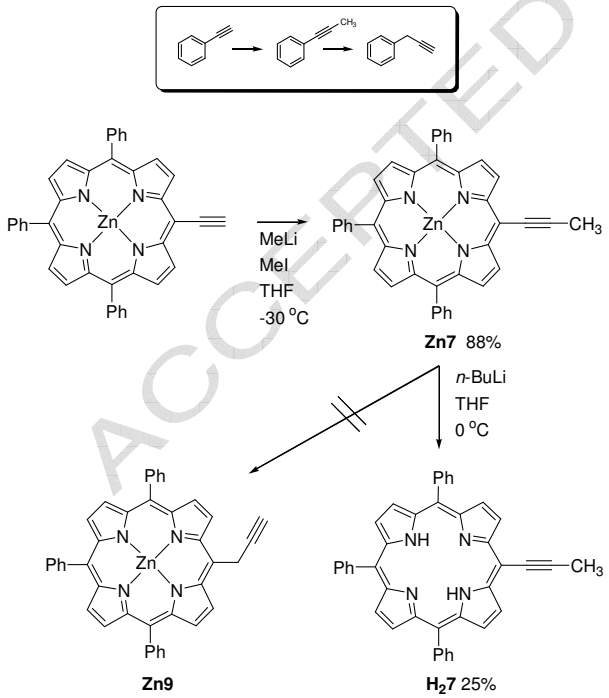
The amount of base, strength of base and type of metalloporphyrin used in the coupling reactions were also found to have a profound effect on the outcome of the reaction. Using a two-fold excess of Cs_2CO_3 resulted in **Ni8** solely being isolated from the reaction, while a ten-fold excess resulted in **Ni7** being the only Suzuki product in 61% yield.[14b] Cs_2CO_3 was found to be an inappropriate base when either a Zn^{II} or free-base porphyrin was used, the result being unidentifiable products. Using the less labile alkali base, K_2CO_3 in ten-fold excess led to **Ni8** again being isolated as the only product from **Ni5**, while quite surprisingly, the kinetically rearranged **Zn9** was the only product isolated from the reaction of **Zn5**.[14c] K_2CO_3 was ineffective for porphyrin $\mathbf{H_2 5}$, while Na_2CO_3 did not aid in Suzuki coupling for any of the metalloporphyrins.

Table 1. Yields of the Suzuki-Miyaura coupling reaction between **5** and allenylboronate in THF.

Entry	M	Catalyst	Cat. Conc. (% mol)	Time (h)	Base (excess)	Temp °C	Yield **7** (%)[a]	Yield **8** (%)[a]	Yield **9** (%)[a]
1	Ni	$Pd(PPh_3)_4$	15	15	Cs_2CO_3 (2-fold)	80	-	2	-
2[b]	Ni	$Pd(PPh_3)_4$	15	15	K_3PO_4 (2-fold)	67	25	-	-
3[b]	Ni	$Pd(PPh_3)_4$	15	15	K_3PO_4 (20-fold)	80	14	9	-
4	Ni	$PdCl_2(PPh_3)_2/AsPh_3$	25	15	Cs_2CO_3 (2-fold)	80	-	8	-
5	Ni	$PdCl_2(PPh_3)_2/AsPh_3$	15	5	Cs_2CO_3 (2-fold)	80	-	10	-
6	Ni	$Pd_2(dba)_3/AsPh_3$	15	15	Cs_2CO_3 (2-fold)	80	-	10	-
7	Ni	$PdCl_2$(dppp)	15	15	Cs_2CO_3 (2-fold)	80	9	37	-
8	Ni	$PdCl_2$(dppe)	15	15	Cs_2CO_3 (2-fold)	80	-	41	-
9	Ni	$PdCl_2$(dppe)	15	15	Cs_2CO_3 (10-fold)	80	61	-	-
10	Ni	$PdCl_2$(dppe)	15	15	K_2CO_3 (10-fold)	80	-	50	-
11	Zn	$PdCl_2$(dppe)	15	15	K_2CO_3 (10-fold)	80	-	-	46

[a]Isolated yield; [b] the strength of the base resulted in another porphyrin product that was not identifiable by ^{1}H NMR and MS analysis.

Inspired by the base-catalysed kinetic rearrangement of the allene in the Zn^{II} porphyrin to form **Zn9**, the same rearrangement was attempted for **Zn7** (Scheme 3). **Zn7** was prepared by a method adapted from Newman-Evans *et al*. for phenylprop-2-yne from phenylacetylene,[16] which subjects the alkyne to a strong base with subsequent trapping of the anion intermediate with MeI. However, only starting material and the demetallated $\mathbf{H_2}$**7** were retrieved from the reaction mixture after column chromatography when subjecting 2-propynylporphyrin **Zn7** to 2-equiv of *n*-BuLi in THF at 0 °C. This preliminary investigation is ongoing in our laboratory with Ni^{II} derivatives.



Scheme 3.

In conclusion, for the first time, unsubstituted allenes and propargyl substituents have been attached to the porphyrin periphery by Suzuki coupling and trapping of an alkyne anion with MeI. The phenomenon of allene rearrangement on the porphyrin periphery is still being investigated. However, as allenes are particularly reactive functional groups, especially toward metal catalysis,[7c,17,18] we have also begun exploring their reactivity on the macrocycle.

Acknowledgements

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14. (a) **Ni8** was synthesised in the optimum yield using the following procedure: To a 20 cm^3 Schlenk tube, **Ni5** (50 mg), $PdCl_2$(dppe) (15 mol%, 10 mg) and K_2CO_3 (107 mg) were added and dried under vacuum before the flask was charged with argon. Dry THF (10 cm^3) was added and the mixture was degassed via three freeze-pump-thaw cycles. Allenylboronic acid pinacol ester (140 µL, 10-fold excess) was subsequently added, and the flask was sealed and heated to 80 °C overnight. The progress of the reaction was monitored by TLC using CH_2Cl_2/*n*-hexane (1:2) as eluent. Upon complete consumption of the starting material, the solvent was removed *in vacuo* and the residue was chromatographed on silica gel using CH_2Cl_2/*n*-hexane (1:2). The first fraction collected was **Ni8** (24 mg, 50%). Analytical data: mp: >300 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): 9.46 (d, ^3J = 5.0 Hz, 2H, *β*-H), 8.80 (d, ^3J = 5.0 Hz, 2H, *β*-H), 8.69 (d, ^3J = 4.90 Hz, 2H, *β*-H), 8.67 (d, ^3J = 4.90 Hz, 2H, *β*-H), 8.31 (t, ^4J = 6.8 Hz, 1H, allene-CH), 8.01 (m, 6 H, *o*-Ph-H), 7.70 (m, 9 H, *m*,*p*-Ph-H), 5.32 (d, ^4J = 6.8 Hz, 2H, allene-CH_2); ^{13}C NMR (150 MHz, $CDCl_3$): 216.6, 142.1, 141.9, 141.4, 141.1, 140.5, 140.2, 133.2, 132.2, 132.0, 131.8, 131.7, 130.3, 128.2, 126.5, 125.5, 118.6, 109.3, 92.1; UV/Vis (CH_2Cl_2) λ_{max} (log ε): 421 (5.41), 535 (4.31), 575 (3.81); HRMS (MALDI) calcd. for $[M]^+$ $C_{41}H_{26}N_4Ni$ 632.1511, found 632.1530; IR cm^{-1}: *ν* = 696 (aromatic H), 737 (aromatic H), 1537 (N-H), 1947 (C=C=C), 3054 (aromatic H). (b) **Ni7** was synthesised using **Ni5** (0.074 mmol), $PdCl_2$(dppe) (10 mg, 0.018 mmol) and Cs_2CO_3 (254 mg, 0.78 mmol). The residue was chromatographed on silica gel using CH_2Cl_2/*n*-hexane (1:2). The first fraction collected was **Ni7** (29 mg, 61%). mp: >300 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): 9.63 (d, ^3J = 4.7 Hz, 2H, *β*-H), 8.99 (d, ^3J = 4.7 Hz, 2H, *β*-H), 8.85 (d, ^3J = 4.7 Hz, 2H, *β*-H), 8.84 (d, ^3J = 4.7 Hz, 2H, *β*-H), 8.20 (m, 6 H, *o*-Ph-H), 7.75 (m, 9 H, *m*,*p*-Ph-H), 5.99 (d, ^4J = 2.6 Hz, 2H, CH_2), 2.51 (t, ^4J = 2.6 Hz, 1H, acetylene-H); ^{13}C (150 MHz, $CDCl_3$): 144.8, 142.8, 142.4, 142.1, 140.6, 140.5, 133.5, 133.4, 132.5, 132.0, 131.9, 131.5, 127.6, 126.7, 119.7, 119.2, 100.1, 93.4, 79.7, 5.2; UV/Vis (CH_2Cl_2) λ_{max} (log ε): 420 (5.47), 553 (4.18); HRMS (ESI) calcd. for $[M]^+$ $C_{41}H_{26}N_4Ni$ 632.1449, found 632.1530. (c) **Zn9** was obtained using **Zn5** (0.073 mmol), $PdCl_2$(dppe) (10 mg, 0.018 mmol) and K_2CO_3 (107 mg, 0.78 mmol). The residue was chromatographed on silica gel using CH_2Cl_2/*n*-hexane (1:2). The first fraction collected gave **Zn9** (22 mg, 46%). mp: >300 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): 9.63 (d, ^3J = 4.7 Hz, 2H, *β*-H), 8.99 (d, ^3J = 4.7 Hz, 2H, *β*-H), 8.85 (d, ^3J = 4.7 Hz, 2H, *β*-H), 8.84 (d, ^3J = 4.7 Hz, 2H, *β*-H), 8.20 (m, 6 H, *o*-Ph-H), 7.75 (m, 9 H, *m*,*p*-Ph-H), 5.99 (d, ^4J = 2.6 Hz, 2H, CH_2), 2.51 (t, ^4J = 2.6 Hz, 1H, acetylene-H); ^{13}C NMR (150 MHz, $CDCl_3$): 150.1, 150.0, 149.8, 149.6, 143.5, 134.5, 132.5, 131.6, 128.5, 127.1, 126.3, 126.2, 122.9, 120.4, 86.0, 73.1, 29.7; UV/Vis (CH_2Cl_2) λ_{max} (log ε): 420 (5.47), 553 (4.18); LRMS (MALDI) calcd. for $[M]^+$ $C_{41}H_{26}N_4Zn$ 638.1449, found 638.1467.
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