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Synthesis and Reactivity of Allenylporphyrins

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Several different methods have been utilized for the effective synthesis of a new class of porphyrins that contains the synthetically intriguing propadienyl (or allenyl) functional group. Of these approaches, successive Horner–Wadsworth–Emmons couplings proved impossible, but Pd-catalyzed cross-coupling reactions enabled quick and easy synthetic access to allenylporphyrins. The conditions for the Suzuki–Miyaura cross-coupling reaction of bromoporphyrins with allenylboronic acid pinacol ester were optimized. This reaction represents the first successful use of this boronic acid in a Suzuki-type coupling. Although this routine was successful for the syntheses of porphyrins that contain aromatic substituents, a more robust method was also developed that involves a Sonogashira coupling of a bromoporphyrin with *N*,*N*-diisopropylprop-2-yn-1-amine followed by a Pd-catalyzed rearrangement to give allenylporphyrins in high yields. For both routes, the applicable metalation states of the porphyrin core were investigated with mixed results. The utility of the addition of the allenyl functional group was then probed with both directly linked allenylporphyrins and those containing a phenyl "spacer".

Introduction

Tetrapyrroles play pivotal and diverse roles in nature, and there is a continuing desire to exploit their properties for applications in medicine, catalysis, and nanomaterials. The synthesis and functionalization of porphyrins with new and synthetically useful functional groups is an ongoing challenge for synthetic porphyrin chemists.[1] As a result, functional group interconversion and synthetic transformations that span the field of porphyrin chemistry are constantly being explored and improved.[2] One niche in the area of synthetic transformations, which has received little to no attention with regard to porphyrins, is the utilization of 1,2-propadiene (i.e., allene).

Allenes are a highly versatile functional group that can be utilized as a building block in a variety of synthetic transformations. 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.[3] Although cumulenic porphyrin dimers that are linked by two carbons have been explored for their impressive optical properties, these dimers are quinoidal in nature and arise from modification of the internal alkyne, which results in significantly perturbed electronic absorption spectra.[4] Thus, we undertook a synthetic program aimed at the utilization and subsequent transformation of the terminal cumulative double bonds in porphyrinoid systems.[1]

Allenes are a synthetically interesting and useful functional group to introduce into porphyrins, as the orthogonal double bonds of the allene moiety should provide a facile route towards further functionalizations and create structurally interesting compounds that possess both the interesting physiochemical, biological, and catalytic properties of porphyrins[5] as well as the optical properties of allenic systems that were observed previously.[6] Thus, our research focused on the initial installation of a free allene into the porphyrin core, which was followed by an investigation of the reactivity of the resulting allenylporphyrin.

Results and Discussion

Allene Synthesis through Horner–Wadworth–Emmons Reaction

Of the methods we envisaged for the installation of allene onto the macrocycle periphery, the Horner–Wadsworth–Emmons (HWE) reaction had the most appeal because of its versatility in allene generation[7] and its need for a formylporphyrin precursor. Formylporphyrins are commonly used precursors in diverse functionalization reactions, and recently their utility has been successfully expanded from metalloporphyrins to include also their metal-free analogues.[8]

By applying the one-pot double olefination procedure, designed by Tomioka and co-workers,[9] to formylporphyrins **1a** and **1b** (see Scheme 1), the first HWE reaction

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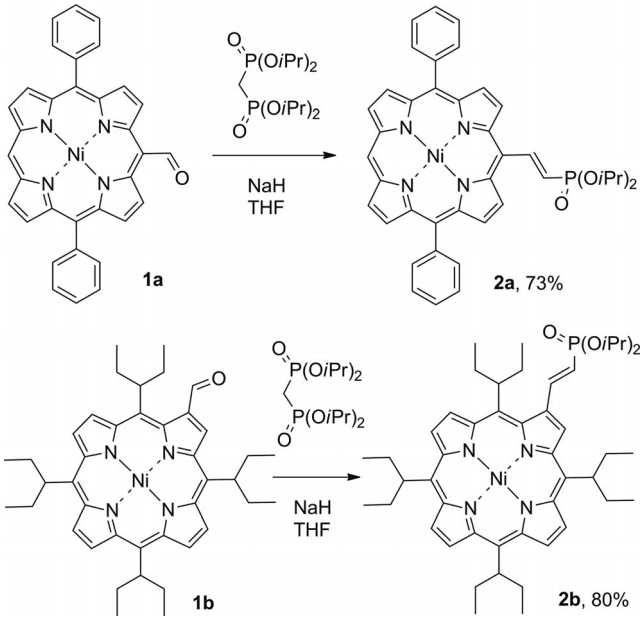
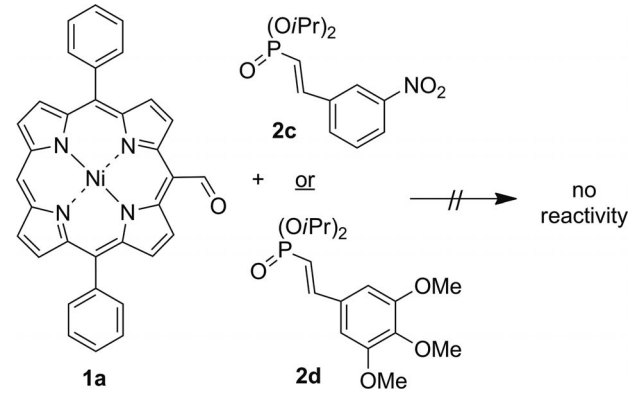
using tetraisopropyl methylenebis(phosphonate) and NaH worked well, and the extremely polar intermediates **2a** and **2b** were isolated by simple chromatography in very good yields.



Scheme 1. Synthesis of alkenylphosphonate porphyrins **2a** and **2b**.

Interestingly, both in the one-pot procedure and in using the isolated intermediates **2a** and **2b**, the second olefination reaction could not be realized under a variety of conditions. This olefination reaction occurs through direct deprotonation of the alkenylphosphonate with lithium diisopropylamide (LDA), which is followed by treatment with an aldehyde to afford a hydroxyalkenylphosphonate. Conversion of the hydroxyalkenylphosphonate into the corresponding allene then takes place by a subsequent HWE olefination reaction.[9] However, in our case, when using either benzaldehyde or hexanal in conjunction with LDA and **2a**, the result was the unexpected substitution of diisopropylamine from the base onto the alkenephosphonate. Regardless of the temperature (–80 to 60 °C), the reaction of diisopropylamine with **2a** seemingly occurred, whereas porphyrin **2b** exhibited no reactivity with LDA. The use of *t*BuLi as the base resulted in degradation of the porphyrin.

To test the reverse reaction, two new alkenylphosphonates **2c** and **2d** were synthesized. These were treated with LDA, which was followed by the addition of formylporphyrin **1a**. Again, the desired second HWE reaction could not be achieved (see Scheme 2). A plausible reason for this reactive reticence may be because of the steric hindrance caused by the bulky isopropoxy residues that are attached to the phosphorus atom.

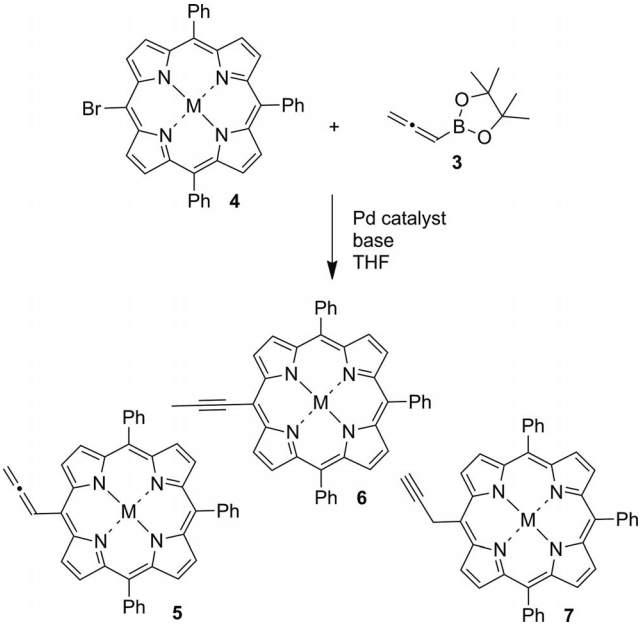


Scheme 2. Attempted reaction of alkenylphosphonates **2c** and **2d** with **1a**.

Allene Synthesis through Palladium-Catalyzed Cross-Coupling Reaction

Because of the failure of the double HWE reaction to yield any allenic products, our attention turned to commercially available allenylboronic acid pinnacol ester (**3**). Previously, **3** had been primarily used to take advantage of the allene in three- and four-component reactions[10] and in Ru^{II} catalysis to generate alkenylboronates.[11] Although **3** had never previously been used in a Suzuki–Miyaura cross-coupling reaction,[12] the Pd-catalyzed coupling between **3** and triphenylbromoporphyrin **4** appeared a convenient way to test the utility of **3** in such coupling reactions and to provide a facile entry to triphenylallenylporphyrin **5**.

Using a variety of conditions to couple the allenylboronate to the bromoporphyrin (see Scheme 3), we discovered that very few conditions resulted in the consumption of the bromo starting material. However, when reactions occurred depending on the base and metalloporphyrin used, either the allenylporphyrin **5**, 1-propynylporphyrin **6**, or 2-prop-



Scheme 3. Reaction scheme for Suzuki coupling of bromoporphyrins with **3**.

Table 1. Results of the optimization efforts of the reaction between bromoporphyrin **4** and allenyl boronate **3**.

Entry	M^{II}	Catalyst	Cat. conc. [mol-%]	Time [h]	Base [equiv.]	Temp. [°C]	Yield of **5** [%]	Yield of **6** [%]	Yield of **7** [%]
1	Ni^{II}	$Pd(PPh_3)_4$	15	18	Cs_2CO_3 (2)	80	2	–	–
2	Ni^{II}	$Pd(PPh_3)_4$	15	18	K_3PO_4 (2)	67	–	25	–
3	Ni^{II}	$Pd(PPh_3)_4$	15	18	K_3PO_4 (20)	80	9	14	–
4	Ni^{II}	$PdCl_2(PPh_3)_2/AsPh_3$	25	18	Cs_2CO_3 (2)	80	8	–	–
5	Ni^{II}	$PdCl_2(PPh_3)_2/AsPh_3$	15	5	Cs_2CO_3 (2)	80	10	–	–
6	Ni^{II}	$Pd_2(dba)_3/AsPh_3$	15	18	Cs_2CO_3 (2)	80	10	–	–
7	Ni^{II}	$PdCl_2$(dppp)	15	18	Cs_2CO_3 (2)	80	37	9	–
8	Ni^{II}	$PdCl_2$(dppe)	15	18	Cs_2CO_3 (2)	80	41	–	–
9	Ni^{II}	$PdCl_2$(dppe)	15	18	Cs_2CO_3 (10)	80	–	61	–
10	Ni^{II}	$PdCl_2$(dppe)	15	18	K_2CO_3 (10)	80	50	–	–
11	Zn^{II}	$PdCl_2$(dppe)	15	18	K_2CO_3 (10)	80	–	–	46

ynylporphyrin **7** could be isolated after column chromatography. The results of the preliminary investigations to find the optimum conditions for attaching the allene to the porphyrin are shown in Table 1.

With the exception of using K_3PO_4 as the base, the standard Suzuki coupling was relatively unsuccessful when carried out at reflux in tetrahydrofuran (THF). When K_3PO_4 was used, coupling only occurred with the Ni^{II} bromoporphyrin **4a**, and this resulted in the rearrangement of allene **5a** to the more stable 1-propynylporphyrin **6a** along with the formation of unidentifiable side products. Our first successful attempt at isolating allenylporphyrin **5a** came from heating the reaction mixture in THF to 80 °C in a sealed Schlenk tube and using a 20-fold excess amount of K_3PO_4 (9% yield). Interestingly, by using the same conditions, but in 1,4-dioxane at 80, 100, and 120 °C, no allenyl or propynylporphyrin was isolated.

Upon varying the Pd catalyst, we achieved the best coupling results by using Pd^{II} salts with the bidentate ligands 1,2-bis(diphenylphosphanyl)ethane (dppe) and 1,3-bis(diphenylphosphanyl)propane (dppp). In particular, when the base K_2CO_3 was used in a 10-fold excess amount, **5a** was isolated in up to 50% yield. Interestingly, although $PdCl_2$(dppe) and $PdCl_2$(dppp) were found to be equally effective in coupling, when a twofold excess amount of Cs_2CO_3 was used, the $PdCl_2$(dppp) resulted in a 25% rearrangement from the allene to the 1-propynylporphyrin (see Table 1, Entry 7). The use of $PdCl_2$(dppe) gave no such rearrangement, so it was considered the catalyst of choice for the remaining optimization experiments. It should be noted that these reactions represent new applications for the catalysts $PdCl_2$(dppe) and $PdCl_2$(dppp).

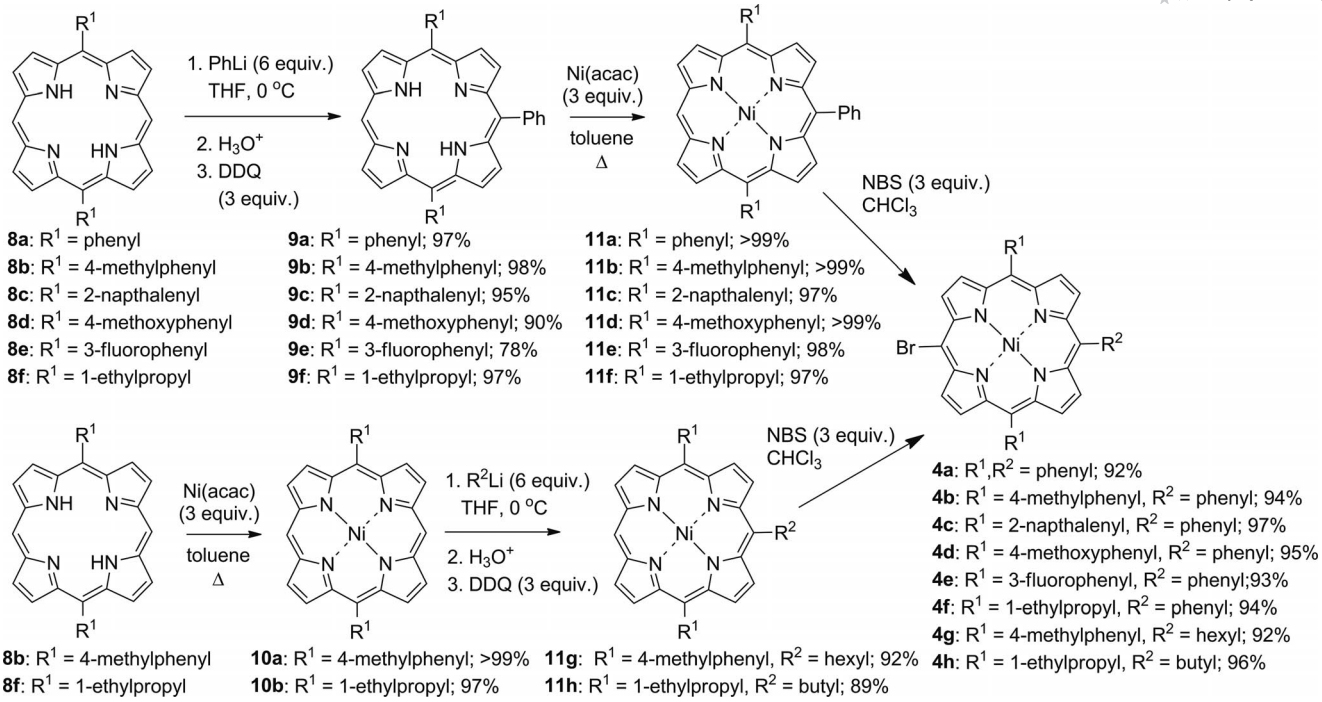
The amount and strength of base and the type of metalloporphyrin used in the coupling reactions also had a profound effect on the outcome of the reaction. Using a twofold excess amount of Cs_2CO_3 resulted in only **5a** being isolated from the reaction, whereas a 10-fold excess amount resulted in **6a** as the only Suzuki product in a 61% yield. When either a Zn^{II} porphyrin or a free-base porphyrin was used, Cs_2CO_3 was an inappropriate base, and the reactions resulted in unidentifiable products. Using a 10-fold excess of the less labile alkali base K_2CO_3 led to the isolation of **5a** as the only product. Surprisingly, the only product isolated from the reaction of Zn^{II} bromoporphyrin **4j** was the kinetically rearranged 2-propynylporphyrin **7**. This may be a result of the coordination of the base to the vacant sites on the Zn^{II} center, which facilitates the base-promoted isomerization of the allenyl functional group. Free-base bromoporphyrin **4l** gave no identifiable products under any conditions.

This optimization work exclusively used triphenylporphyrins as the bromo partners, as they are readily available and their reactivity is known. Having successfully achieved the first synthesis of allenylporphyrin **5a**, we decided to probe the versatility of the above reaction to install allenyl functional groups, to generate a library of allenylporphyrins that contain different substituents, and then to test the reactivity of the allenic double bonds.

Synthesis of Nickel(II) Bromoporphyrins

The synthetic route chosen to create the requisite bromoporphyrin library is shown in Scheme 4 and uses optimized, high yielding synthetic transformations.[5,13]

The first step involves a simple MacDonald [2+2] condensation[14] between dipyrromethane (DPM, synthesized by the Lindsey method[15]) and an appropriate aldehyde. The second step involves methodology that we developed[16] and uses a nucleophilic addition of an aryl or alkyllithium to one of the free *meso* positions to generate an anion, which is then quenched with acid. A subsequent oxidation gives the substituted porphyrin product. The addition of the aromatic lithiating agents works best with free-base porphyrins. Therefore, the preparation of **9a**–**9f** takes place first and is then followed by a metalation with nickel acetylacetonate to yield **11a**–**11f**. However, the installation of alkyl substituents in this manner proceeds much more smoothly by using nickel(II) porphyrins **10a** and **10b** to yield trisubstituted porphyrins **11g** and **11h**. Thus, the desired target functionality dictated the synthetic route followed. With trisubstituted nickel(II) porphyrins **11a**–**11h** in hand, the bromination with *N*-bromosuccinimide (NBS) to give **4a**–**4h** becomes particularly facile, as there is only one reactive *meso* position remaining.[17]



Scheme 4. Synthesis of nickel(II) bromoporphyrins **4** (DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone).

Suzuki–Miyaura Cross-Coupling Reactions

Following the success with **4a**, aromatically substituted porphyrins were favored as the initial starting point to test the general applicability of the synthetic methodology. The optimized conditions were employed (see Table 1, Entry 10) with **4b** as the substrate. A small degree of conversion was observed after 24 h, but most of the starting material had not been consumed. Therefore, the reaction time was extended, and after 72 h, all of the starting material was converted either into allenylporphyrin **5b** or into the debrominated starting material **11b** as well as into a trace amount of the propynylporphyrins. It was initially assumed that, within the Suzuki cycle, protodemetalation to give the debrominated starting material and transmetalation to give the allenylporphyrins were competitive, but later tests with **4c** showed that after 36 h, the products were allenylporphyrin **5c** and unreacted starting material **4c**. After 36 h, the yield of **5c** could be increased with a longer reaction time, but at this stage, protodemetalation does begin to occur. Separating the target allenylporphyrins **5** from debrominated porphyrins **11** proved to be much easier than the separation of **5** from **4**, so the time scale was extended to 72 h for all of the subsequent syntheses. The main drawback of modifying the procedure in this manner is that no starting material can be recovered from the reaction, as after 72 h, all of the C–Br bonds have been cleaved.

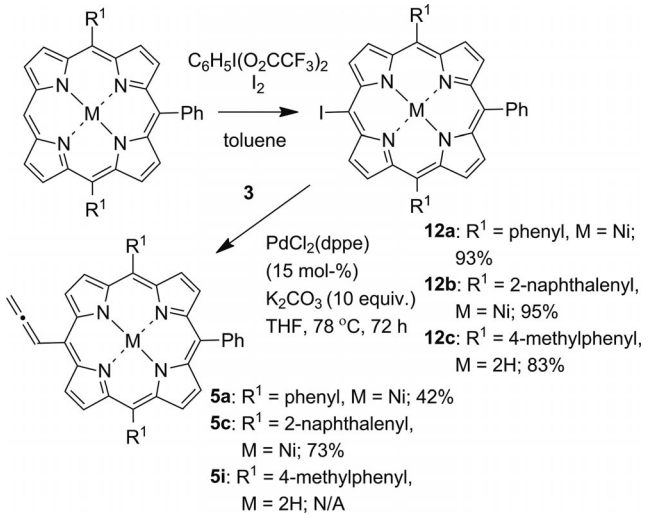
Table 2 illustrates the results of the various Suzuki–Miyaura cross-coupling reactions attempted and shows some interesting results. The first is that all of the successful reactions gave yields that were greater than the 50% yield that was observed with the synthesis of **5a** after 24 h. From the results of aromatic residues examined, this procedure appears somewhat limited in scope. Although it worked incredibly well with standard aromatic residues (i.e., **5a**–**5c**), disturbances to the aromaticity led to significantly reduced yields (i.e., **5d** and **5e**). In addition to expanding the allenic library by using purely aromatic substituents, we decided to also introduce different alkyl substituents onto the porphyrin periphery to probe the versatility of the reaction conditions further and yield more structurally interesting porphyrins. Unfortunately, these efforts proved quite disappointing. Porphyrins **4f**–**4h**, which contained alkyl substituents, did not yield any allenylporphyrin in high enough yields to be characterized. Most likely, this is due to the known reduced reactivity of alkyl-substituted porphyrins towards standard transformations.[18] In terms of general trends in reactivity, as the number of aliphatic substituents increases, the yield of **5** sharply decreases. Porphyrins containing only one aliphatic substituent could be converted into **5** in very low yields (i.e., **5g**), but those containing two or three aliphatic substituents only gave trace amounts or no product at all (i.e., **5f** and **5h**).

As a final effort to optimize the Suzuki–Miyaura reaction conditions, the three iodoporphyrins **12a**–**12c** were synthesized using [bis(trifluoroacetoxy)]iodobenzene, iodine, and the appropriate trisubstituted porphyrin (i.e., **11a**, **11c**, and **9b**, respectively). These were then subjected to the optimized coupling conditions as shown in Scheme 5. Although aromatic iodides are expected to be significantly more active than the analogous bromides towards metal-catalyzed coupling reactions with boronic esters, this proved not to be the case. In this situation, the yields that were obtained were lower than those involving bromoporphyrins **4a**

Table 2. Results of Suzuki–Miyaura cross-coupling reactions performed on **4a**–**4h**.

Starting material	R^1	R^2	Product	Yield [%]
4a	phenyl	phenyl	**5a**	88
4b	4-methylphenyl	phenyl	**5b**	78
4c	2-naphthalenyl	phenyl	**5c**	91
4d	4-methoxyphenyl	phenyl	**5d**	trace
4e	3-fluorophenyl	phenyl	**5e**	64
4f	1-ethylpropyl	phenyl	**5f**	trace
4g	4-methylphenyl	hexyl	**5g**	8%
4h	1-ethylpropyl	butyl	**5h**	N/A

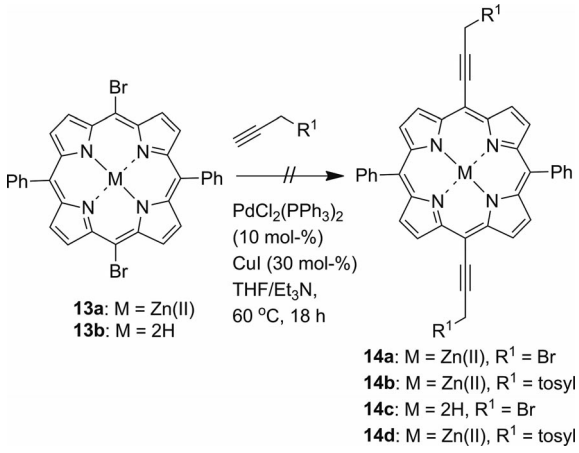
and **4c**. Furthermore, the free-base iodoporphyrin **12c** was as unreactive under these conditions as the free-base bromoporphyrin tested previously.



Scheme 5. Synthesis and use of iodoporphyrins as Suzuki–Miyaura partners.

Allene Synthesis through Rearrangements of Propargyl-Substituted Porphyrins

Although the Suzuki–Miyaura cross-coupling reactions proved to be moderately successful for specific functional groups, the scope of the reaction is quite narrow, and, therefore, we turned to other applicable methods to introduce the allenyl functionality. One of the most commonly employed syntheses for terminal allenes begins with propargyl electrophiles that contain a terminal leaving group.[19] The Sonogashira cross-coupling reaction is employed to introduce the desired propargyl residues into the precursor molecule.[20] The Pd-catalyzed rearrangement and the loss of the leaving group at the propargyl substituent then affords the terminal allene. Dibromoporphyrins **13a** and **13b** were dissolved in THF and then treated with triethylamine, $PdCl_2(PPh_3)_2$, copper(I) iodide, and the respective propargyl compound. The reaction mixture was heated at reflux under argon (see Scheme 6), which is analogous to the procedure reported for the preparation of (2-arylethynyl)porphyrins and [2-(trimethylsilyl)ethynyl]porphyrins.[21]



Scheme 6. Attempted Sonogashira cross-coupling reactions with dibromoporphyrins.

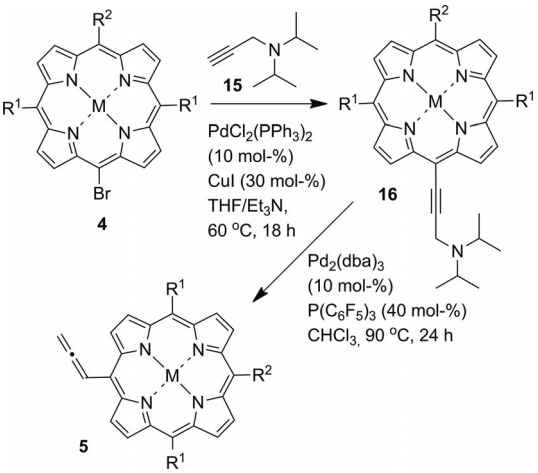
However, dipropargylporphyrins **14a**–**14d** could not be isolated, and only the starting material and an insoluble polymer were obtained. Increasing the equivalents of CuI and triethylamine or decreasing the amount of porphyrin did not give the desired products. A plausible explanation is that the necessary propargyl compounds have good leaving groups and may undergo a reaction with themselves under the conditions. It is also possible that the desired porphyrins are formed, but undergo another reaction with either the propargyl compound or the starting dibromoporphyrin.

We then turned to less reactive propargyl compounds that could successfully couple to the porphyrin core and still retain the reactivity to undergo the desired rearrangement to give the allenylporphyrins. One of the more recent advances in this area, which offered the best potential for success, was work by Nakamura et al. that utilized propargylamines followed by a Pd-catalyzed hydrogen transfer.[22] Analogous to the pathway described in Scheme 5, the first step of this synthesis involved a Sonogashira reaction that used *N*,*N*-diisopropylprop-2-yn-1-amine (**15**) as the alkyne partner. The resultant propargylporphyrin **16** was then dissolved in a minimum amount of chloroform, and the solution was heated to reflux in the presence of $Pd_2(dba)_3$ (dba = dibenzylideneacetone) as the precatalyst and $P(C_6F_5)_3$ as the ligand source. This methodology was applied to a number of nickel(II) monobromoporphyrins with gratifying results as shown in Table 3.

The results of this study show this method to be highly robust and tolerant of a wide degree of variation around the porphyrin core. The standard aromatic residues previously tested by the Suzuki conditions (i.e., **4a**–**4c**) proved to be similarly reactive under these Sonogashira/hydrogen transfer conditions. Residues with groups such as 4-methoxyphenyl (i.e., **4d**) and 3-fluorophenyl (i.e., **4e**), which previously showed diminished reactivity in relation to the more standard aromatic residues, showed practically equal reactivity under these conditions.

The synthesis of allenylporphyrins that contain aliphatic residues, which could not be synthesized by the Suzuki methodology, could easily be prepared under these condi-

Table 3. Results of the synthesis of allenylporphyrins (**5**) through Sonogashira couplings of **4** followed by Pd-catalyzed hydrogen transfer.



Starting material	M^{II}	R^1	R^2	Product	Yield [%]
4a	Ni^{II}	phenyl	phenyl	**5a**	79
4b	Ni^{II}	4-methylphenyl	phenyl	**5b**	84
4c	Ni^{II}	2-naphthalenyl	phenyl	**5c**	82
4d	Ni^{II}	4-methoxyphenyl	phenyl	**5d**	68
4e	Ni^{II}	3-fluorophenyl	phenyl	**5e**	73
4f	Ni^{II}	1-ethylpropyl	phenyl	**5f**	45
4g	Ni^{II}	4-methylphenyl	hexyl	**5g**	53
4h	Ni^{II}	1-ethylpropyl	butyl	**5h**	44
4i	Cu^{II}	2-naphthalenyl	phenyl	**5j**	47
4j	Zn^{II}	phenyl	phenyl	**5k**	N/A
4k	2 H	2-naphthalenyl	phenyl	**5l**	N/A
4l	2 H	phenyl	phenyl	**5m**	N/A

tions. This is a particularly important strength of this methodology, as it is a more robust and versatile synthetic method in comparison to any described previously. This allows for the facile introduction of a terminal allene group to virtually any bromoporphyrin through an easy two-step process. The ability to introduce aliphatic substituents provides the ability to fine tune the periphery of the porphyrin and could lead to many new porphyrins that incorporate the known nonplanar properties of alkylporphyrins with the impressive optical properties of allenes.

In terms of the metalation state of the porphyrin, the Suzuki–Miyaura conditions could only be employed with nickel(II) porphyrins. However, Cu^{II} was successfully incorporated into allenylporphyrin **5j** under these conditions by starting from the appropriately metalated bromoporphyrin **4i**. By starting from the appropriate bromoporphyrin **4j**, **4k**, and **4l**, the successful synthesis of Zn^{II} allenylporphyrin **5k** or free-base allenylporphyrins **5l** and **5m** could still not be achieved, as the reactions yielded complex mixtures of polymeric material. Zn^{II} allenylporphyrin **5k** was identified in trace amounts from this material, but could not be isolated. Theoretically, the free-base allenylporphyrin could be obtained by the demetalation of the appropriate Ni^{II} porphyrin, and subsequent metalation could give access to the Zn^{II} allenylporphyrin. However, considering the very harsh conditions (concentrated H_2SO_4 or a strong Lewis acid such as BBr_3) involved in removing nickel(II) from the porphyrin core, we did not expect the chemically labile allene group to survive a demetalation, and, as such, it was not attempted.

The solubility of the propargylporphyrins **16** presented one of the few issues with this synthesis. These porphyrins were quite difficult to purify, as the R_f values by eluting with chlorinated solvents on silica were practically zero. Moreover, when using ethyl acetate, the target porphyrins coeluted with the unreacted propargylamines. This was only a minor inconvenience, as filtration through silica with dichloromethane as the eluent removed any undesired porphyrin byproducts. Changing the eluent to ethyl acetate yielded the crude target porphyrin in a high enough purity to be subjected to the $Pd_2(dba)_3$-catalyzed rearrangement. The resultant allenylporphyrin was then easily purified by standard methods. As a result, porphyrins **16** were not isolated and characterized.

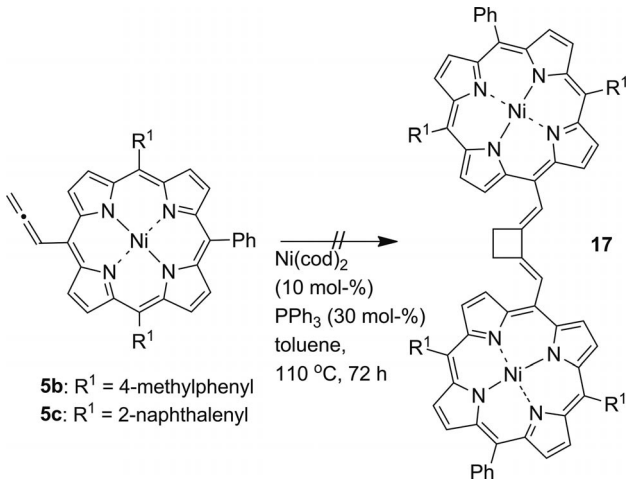
Spectroscopic Analysis of Allenylporphyrins

The presence of the allenyl functional group was readily assigned by various spectroscopic methods. Using the values obtained for **5b**, as a model, certain general trends in the spectroscopic analyses became evident. First, in the ^1H NMR spectra, the three allenic protons appear as a distinct doublet at δ = 5.28 ppm, which represents the two terminal protons, and a triplet at δ = 8.26 ppm for the internal hydrogen atom. These signals possess a significant $^4J_{H,H}$ coupling constant of 6.9 Hz. In terms of the ^{13}C NMR spectra, the terminal carbon appears at δ = 76.0 ppm, the carbon adjacent to the porphyrin appears at δ = 92.5 ppm, and the highly deshielded internal carbon atom appears at δ = 215.9 ppm. The analysis of all of these signals can be confirmed by H-H, C-H, and long-range C-H coupling experiments. In the IR spectrum, the fingerprint region for the allenic bond appears as a series of sharp signals at approximately 2900 cm^{-1} as well as a strong absorption at 1939 cm^{-1}. Any other allenic absorption frequencies are largely obscured by the many porphyrinoid signals below 1900 cm^{-1}. These spectroscopic traits are shared across the library of allenylporphyrins that were synthesized and allow for a quick and easy determination of the presence of the allenyl group.

Reactivity of Allenylporphyrins

With a library of allenylporphyrins at hand, we attempted some exploratory reactions that involve the allenyl group and focused on straightforward cyclization reactions.[19a,23] Allenes can self-dimerize upon heating to give cyclobutane derivatives, which are usually obtained as a complex mixture of isomers.[24] Recent work by Saito et al. on the use of Ni^{II} catalysts that promote the regioselective dimerization of terminal allenes bonded to electron-withdrawing groups[25] appealed to us, as it is both a simple

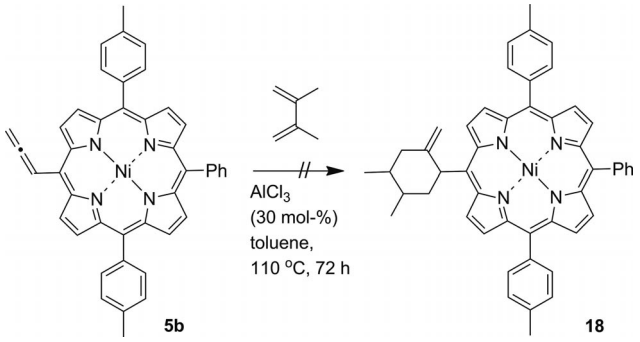
method for testing the reactivity of the installed group as well as for potentially making the interesting porphyrin dimer **17**. Scheme 7 illustrates the reaction conditions employed. Regardless of which porphyrin residue (i.e., **5b** or **5c**) was used, the best outcome after heating at reflux for three days was only a crude HRMS spectrum that showed a trace amount of product formation. Although this is disappointing, it is not a thoroughly unexpected result. The steric hindrance invoked by the porphyrin core, coupled with its electronic impact, makes it very difficult to orient both porphyrins for the cyclization.



Scheme 7. Attempted dimerization of allenylporphyrins **5b** and **5c**.

Perhaps the most straightforward cyclization reaction that allenes can undergo is the classic Diels–Alder reaction.[26] Here, one of the double bonds of the allenyl functional unit acts as the dienophile and readily undergoes reaction with an appropriate diene. Tailoring the electronics of the group attached to the terminal allene determines which of the two possible double bonds is more amenable as the dienophile. Scheme 8 depicts the Diels–Alder attempt with **5b** as the allenylporphyrin together with 2,3-dimethyl-1,3-butadiene. Unfortunately, no conversion to **18** was observed after heating at reflux for 72 h, and **5b** was completely recovered from the reaction mixture. Again, the steric encumbrance by the porphyrin core seems the most likely reason for the failure of **5b** to undergo any noticeable reaction. The problem is compounded by the electron-withdrawing effect of the porphyrin that is expected to activate the first, and thus the most sterically hindered, of the double bonds.

Because of the failure of the directly linked allenylporphyrins to display any further reactivity, we looked to install a phenyl "spacer" between the porphyrin core and the allene group. Although this was theoretically a very simple proposition, it proved to be a more complicated endeavor than initially expected. The first step of this synthesis involved the previously formed bromoporphyrin **4a**, which underwent a Suzuki–Miyaura cross-coupling reaction with (4-bromophenyl)boronic acid (see Scheme 9). The target reaction proceeded readily, in spite of the complications pre-

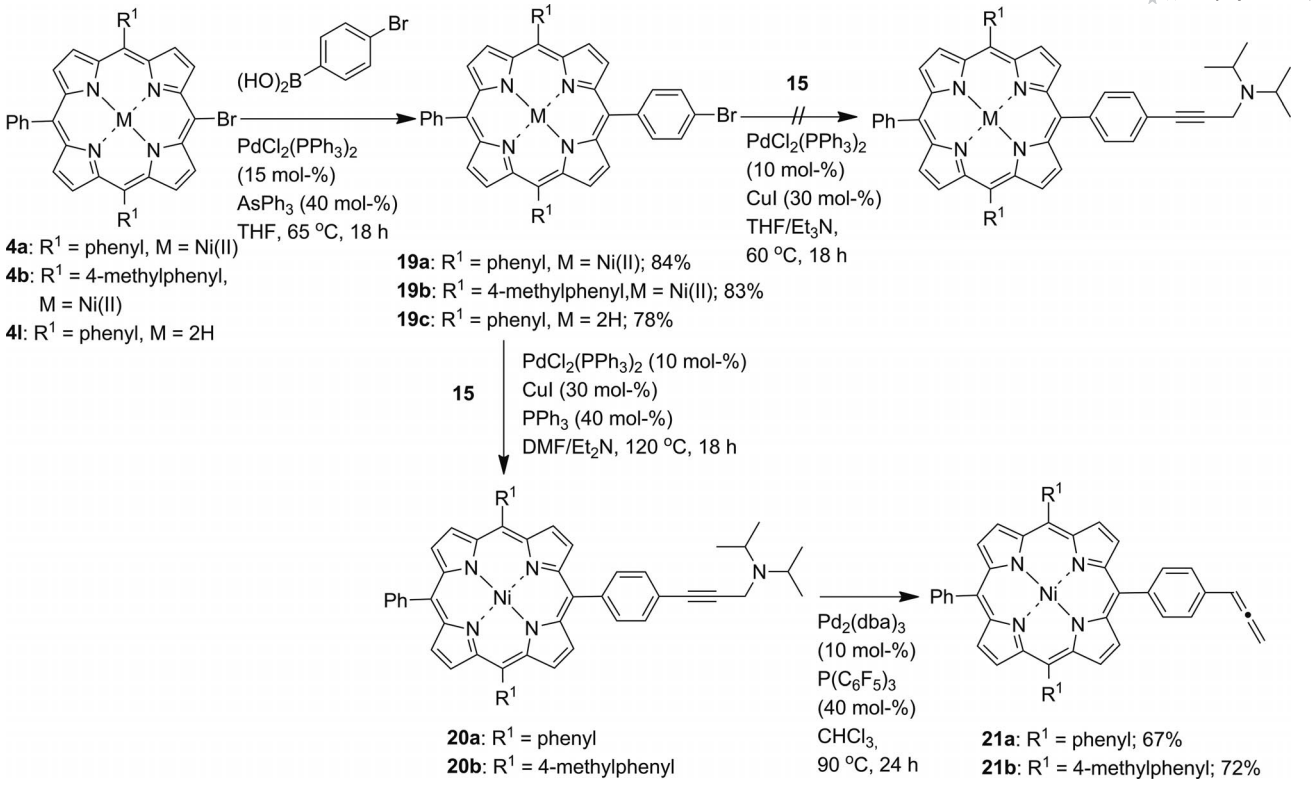


Scheme 8. Attempted Diels–Alder reaction with **5b** as the dienophile.

sented by the multiple aromatic bromides, and the target porphyrin **19a** was obtained in 84% yield. Compound **19a** was then subjected to standard Sonogashira coupling conditions, which were successful with bromoporphyrin **4a**. Interestingly, **19a** showed no reactivity under these conditions. This was an unusual result, as the aromatic bromide in **19a** is expected to be more active towards coupling reactions than the bromide in **4a**. The lowered reactivity of **19a** under these conditions may also explain the high yield of the monobromophenyl product from the Suzuki reaction in lieu of any further coupled derivatives.

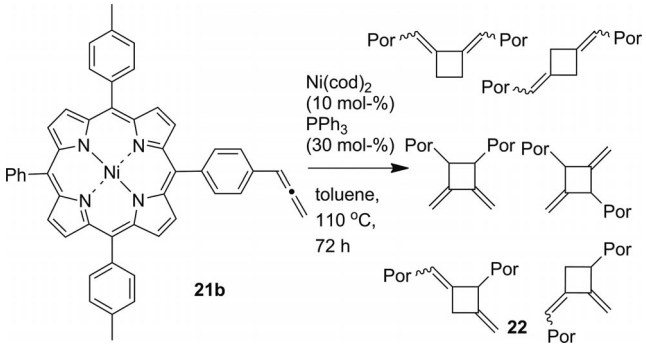
Initially, the lack of reactivity of **19a** towards the standard Sonogashira couplings was assumed to be a result of the known insolubility of nickel(II) tetraphenylporphyrin (NiTPP), which is an intermediate in the catalytic coupling cycle of **19a**. However, neither installing different residues such as the 4-methylphenyl group in **19b** or changing the metalation of the porphyrin as in **19c** resulted in an increase in the reactivity. As a consequence, more forcing Sonogashira conditions were attempted. The catalyst turnover rate was increased by changing the base to the less sterically hindered diethylamine (DEA), more ligand was added in the form of triphenylphosphane, and the reaction temperature was increased by heating to reflux in *N*,*N*-dimethylformamide (DMF). When **19a** and **19b** were subjected to the coupling reaction under these conditions, products were formed in an almost quantitative yield after 24 h. With the coupled products **20a** and **20b** in hand, the standard allene forming reaction proceeded readily to give **21a** and **21b** in reasonable yields (see Scheme 9).

With allenylporphyrins **21a** and **21b**, we returned to probe the reactivity of the installed allenyl group. The first reaction that we attempted was the head-to-head dimerization, as previously described (cf. Scheme 7). Although the directly linked allenylporphyrins **5b** and **5c** exhibited only minimal activity, the reactions with both **21a** and **21b** proceeded readily, and there was complete consumption of the starting material after heating at reflux for just 18 h. Unfortunately, this reaction displayed none of the expected selectivity with regards to which of the allenic bonds underwent reaction.[25] A complex mixture of poorly soluble dimers, which could not be separated by column chromatography, was the result (see Scheme 10). UV analysis showed negligi-



Scheme 9. Incorporation of a phenyl spacer into an allenylporphyrin.

ble changes with respect to the starting material, which was expected considering the lack of conjugation between the distal allenic bond and the porphyrinoid system. HRMS (MALDI) indicated the presence of the target compound, but NMR spectroscopy was unsatisfactory for analyzing the cyclobutane region because of the significant broadening of the NMR signals.

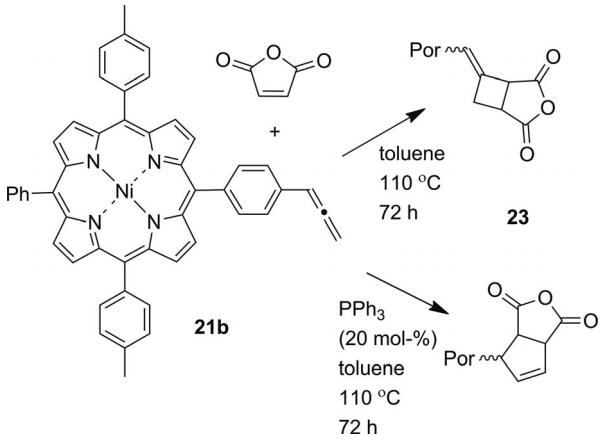


Scheme 10. Ni^{II}-promoted dimerization of **21b** with the potential isomerization patterns of cycloadduct **22**, which could not be isolated and resolved (Por = porphyrinoid core of **21b**).

The next reaction performed was a Diels–Alder reaction with 1,3-cyclohexadiene as the diene and **21b** as the dienophile. Even after heating at reflux in toluene for three days, no consumption of the starting materials was observed. Examples in the literature report that Rh^{I} salts can help to promote Diels–Alder reactions of allenes.[23c,27] Therefore, $Cl_2Rh_2(cod)_2$ (cod = 1,5-cyclooctadiene) was added to help effect the desired reaction. After 18 h, **21b** was entirely consumed, but the Diels–Alder product was obtained in only trace amounts. Here, the dimerization reaction described in Scheme 10 was the dominant reaction. This is not surprising, as Rh^{I} salts are also known to promote [2+2] additions of allenes. Nevertheless, the [4+2] product was expected to be more favored than the disallowed [2+2] addition.

The apparent preference for [2+2] cycloadditions led us to attempt a more straightforward reaction that involves the strongly electron-deficient maleic anhydride. Here, in the absence of any additives, the [2+2] addition was effected between **21b** and maleic anhydride, after heating at reflux in toluene for three days (see Scheme 11). The resultant porphyrin exhibited extremely poor solubility and could not be purified by column chromatography. Both TLC and HRMS analysis indicated the complete consumption of **21b** and the formation of the [2+2] cycloadduct. Similarly, the IR spectrum of the product showed the expected carbonyl stretching frequency at 1623.9 cm^{-1} with a shoulder at 1768.7 cm^{-1} as well as a broad peak at 3256.4 cm^{-1}. Again, the regiochemistry of the addition could not be determined, as a clean ^1H NMR spectrum could not be obtained.

Some interesting research by Lu et al. on the use of PPh_3 to effect the [3+2] addition of allenes[28] could be employed as a method to manufacture diverse ring systems from the allenic system. This reaction took three days to reach completion, and TLC as well as HRMS analysis indicate the quantitative formation of a cycloadduct. Disappointingly, the ^1H NMR analysis was impossible, and, therefore, the method and regioselectivity of the addition still elude us.



Scheme 11. Reaction of **21b** with maleic anhydride in either [2+2] or [3+2] manner. Isomeric porphyrins **23** could not be characterized completely (Por = porphyrinoid core of **21b**).

Again, solubility was a major issue, as the product was impossible to purify cleanly by column chromatography or recrystallization. As a result, we were unable to determine whether the desired [3+2] or the previously realized [2+2] cycloaddition occurred.

Conclusions

The synthesis of allenylporphyrins has been thoroughly investigated with two high yielding methods for their successful preparation. Of these approaches, Pd-catalyzed transformations of propargyl-substituted porphyrins proved to be a highly robust method for the synthesis of a wide range of allenylporphyrins in high yield. Preliminary studies on the reactivity of this installed allenyl functional group have been promising, but an in-depth analysis of their reactivity remains to be performed to prove further the synthetic utility of this porphyrin functional group and yield new porphyrins with interesting structural, electronic, and optical properties. Further investigations will focus on the applicability of these methods to *β*-functionalized porphyrins as well as physicochemical studies on the properties of allenylporphyrin systems.

Experimental Section

General Methods: All chemicals were analytical grade and purified before use. CH_2Cl_2 was dried with phosphorus pentoxide and then distilled. THF was dried with sodium and then distilled. Silica gel 60 (Merck) was used for column chromatography unless otherwise noted. Analytical TLC was carried out with silica gel 60 plates (fluorescence indicator F_{254}, Merck). Melting points were measured with a Reichert Thermovar instrument. NMR spectroscopic data were recorded with a Bruker DPX 400 (400.13 MHz for ^{1}H NMR and 100.61 MHz for ^{13}C NMR), a Bruker AV 600 (600.13 MHz for ^{1}H NMR and 150.90 MHz for ^{13}C NMR), and an Agilent MR400 (400.13 MHz for ^{1}H NMR and 100.61 MHz for ^{13}C NMR) instrument. Chemical shifts are given in ppm and referenced to $CDCl_3$. The assignment of the signals was confirmed by 2D spectroscopic data (COSY, HMBC, heteronuclear multiple quantum coherence) except for those porphyrins with low solubility. Mass spectra were recorded with a Varian MAT 711 or MAT 112 S mass spectrometer using the EI technique with a direct insertion probe and an excitation energy of 80 eV. FAB spectra were recorded with a CH-5 DF instrument from Varian. HRMS data were determined with a Micromass TOF instrument fitted with an EI probe. IR spectra were recorded with a Perkin–Elmer Spectrum 100 FTIR spectrometer.

Starting Materials: Formylporphyrins **1a**,[29] and **1b**,[30] bromoporphyrins **4a**,[31] **4j**,[32] and **4l**,[31] dipyrromethane,[15] 5,15-disubstituted porphyrins **8a**,[33] **8b**,[14b] **8c**,[34] **8d**,[14b] **8e**,[35] **8f**,[36] and **10a**,[37] 5,10,15-triphenylporphyrin (**9a**), nickel(II) complex **11a**,[38] and 5,15-bis(4-methylphenyl)-10-phenylporphyrin (**9b**)[39] were prepared using standard methodologies and had analytical data consistent with that in the literature.

General Procedure A. Synthesis of Phosphonates: Tetra(isopropyl)-methylenebis(phosphonate) (1 equiv.) was added to a suspension of sodium hydride (1.5 equiv.) in dry THF at 0 °C. The mixture was stirred for 30 min, and then the respective aldehyde was added. The solution was stirred overnight at room temperature. Subsequently, the reaction mixture was quenched with saturated NH_4Cl solution, and the resulting mixture was extracted with ethyl acetate and washed with brine. The residue was purified by column chromatography on silica gel.

[5-(*E*)-Di(isopropyl)ethenylphosphono-10,20-diphenylporphyrinato]-nickel(II) (2a): Prepared from formylporphyrin **1a** (300 mg, 0.55 mmol) by following General Procedure A. The first fraction from column chromatography on silica gel (ethyl acetate/*n*-hexane, 4:1, v/v) gave the product, which was recrystallized (dichloromethane/methanol) to give the pure product (284.9 mg, 0.4 mmol, 73%) as purple crystals; m.p. 183 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.47 (d, $^3J_{H,H}$ = 6.0 Hz, 6 H, CH_3), 1.50, (d, $^3J_{H,H}$ = 6.3 Hz, 6 H, CH_3), 4.95 [m, 2 H, CH(CH$_3$)$_2$], 6.24 (t, $^3J_{HHP}$ = 17.9 Hz, 2 H, CH=CH-P), 7.74 (m, 6 H, Ar), 8.02 (m, 4 H, Ar), 8.83 (d, $^3J_{H,H}$ = 4.8 Hz, 2 H, H_β), 8.90 (d, $^3J_{H,H}$ = 5.0 Hz, 2 H, H_β), 9.08 (d, $^3J_{H,H}$ = 4.5 Hz, 2 H, H_β), 9.43 (d, $^3J_{H,H}$ = 4.8 Hz, 2 H, H_β), 9.72 (s, 1 H, H_{meso}), 9.79 (dd, $^3J_{HHP}$ = 17.1 Hz, $^2J_{H,P}$ = 22.1 Hz, 1 H, CH=CH-P) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 24.3, 70.8, 70.9, 105.48, 111.6, 111.8, 118.9, 127.0, 127.9, 130.4, 130.9, 132.3, 132.6, 132.7, 133.4, 133.7, 140.4, 140.8, 141.9, 142.4, 142.8 ppm. ^{31}P NMR (162 MHz, $CDCl_3$, 20 °C): δ = 14.73 ppm. UV/Vis (CH_2Cl_2): λ_{max} [log(ε/M^{-1}cm^{-1})] = 415 [5.17], 529 [4.17], 566 [3.87] nm. HRMS (ES+): calcd. for [$C_{40}H_{35}N_4NiO_3P$ + H] 709.1879; found 709.1862.

[2-(*E*)-Di(isopropyl)ethenylphosphono-5,10,15,20-tetrakis(1-ethylpropyl)porphyrinato]nickel(II) (2b): Prepared from formylporphyrin **1b** (300 mg, 0.46 mmol) by following General Procedure A. The first fraction from column chromatography on silica gel (ethyl acetate/*n*-hexane, 4:1, v/v) gave the product, which was recrystallized (1,4-dioxane/water) to give the pure product (312.3 mg, 0.37 mmol, 80%) as purple crystals; m.p. 144 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.88 (t, $^3J_{H,H}$ = 7.3 Hz, 6 H, CH_2CH_3), 1.01 (t, $^3J_{H,H}$ = 7.3 Hz, 18 H, CH_2CH_3), 1.59 [d, $^3J_{H,H}$ = 6.4 Hz, 6 H, (CH_3)$_2$-CH], 1.61 [d, $^3J_{H,H}$ = 6.4 Hz, 6 H, (CH_3)$_2$CH], 2.68 (m, 16 H, CH_2CH$_3$), 4.14 (t, $^3J_{H,H}$ = 7.0 Hz, 1 H, CHCH$_2$), 4.23 (m, 3 H, CHCH$_2$), 4.94 (m, 2 H, CHCH$_3$), 6.24 (dd, $^3J_{H,H}$ = 16.9 Hz, $^3J_{H,H}$ = 20.5 Hz, 1 H, CH=CH-P), 8.80 (dd, $^3J_{HHP}$ = 16.9 Hz, $^2J_{H,P}$ = 20.5 Hz, 1 H, CH=CH-P), 9.16 (d, $^3J_{H,H}$ = 4.7 Hz, 1 H, H_β), 9.19 (s, 4 H, H_β), 9.23 (s, 1 H, H_β), 9.26 (d, $^3J_{H,H}$ = 5.3 Hz, 1 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 13.6, 14.0, 14.1,

24.1, 24.2, 24.25, 24.3, 32.5, 33.4, 33.5, 48.8, 49.2, 49.3, 67.1, 70.5, 70.6, 117.5, 119.3, 120.5, 120.8, 120.9, 121.6, 130.5, 130.6, 130.7, 130.9, 131.1, 132.4, 132.6, 137.8, 139.7, 140.4, 142.4, 145.6 ppm. ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = 17.82 ppm. UV/Vis (CH_2Cl_2): λ_{max} [log(ε/M^{-1} cm^{-1})] = 431 [4.70], 556 [3.91], 593 [3.54] nm. HRMS (ES+): calcd. for [$C_{48}H_{67}N_4NiO_3P$ + H] 837.4383; found 837.4377.

(*E*)-Diisopropyl-3-nitrostyrylphosphonate (2c): Prepared from 3-nitrobenzaldehyde (1 g, 6.6 mmol) by following General Procedure A. The first fraction from column chromatography on silica gel (ethyl acetate/*n*-hexane, 4:1, v/v) gave the product, which was recrystallized (dichloromethane/methanol) to give the pure product (1.71 g, 5.6 mmol, 85%) as yellow crystals; m.p. 64 °C. Compound had data consistent with that in the literature.[40]

(*E*)-Diisopropyl-3,4,5-trimethoxystyrylphosphonate (2d): Prepared from 3,4,5-trimethoxbenzaldehyde (1 g, 5 mmol) by following General Procedure A. The first fraction from column chromatography on silica gel (ethyl acetate/*n*-hexane, 4:1, v/v) gave the product, which was recrystallized (dichloromethane/methanol) to give the pure product (1.74 g, 5.0 mmol, 99%) as white crystals; m.p. 77 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.34 (d, $^3J_{H,H}$ = 6.0 Hz, 6 H, CH_3), 1.38 (d, $^3J_{H,H}$ = 6.3 Hz, 6 H, CH_3), 3.88 (s, 3 H, 4-OCH_3), 3.89 (s, 6 H, 3,5-OCH_3), 4.72 [m, 2 H, CH(CH$_3$)$_2$], 6.17 (t, $^3J_{HHP}$ = 17.2 Hz, 1 H, CH), 6.73 (s, 2 H, Ar), 7.40 ppm (dd, $^3J_{HHP}$ = 17.3 Hz, $^2J_{H,P}$ = 22.3 Hz, 1 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 24.05, 24.10, 29.70, 56.14, 60.96, 70.43, 70.48, 104.76, 113.83, 115.75, 130.49, 130.73, 139.79, 147.65, 147.72, 153.40 ppm. ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = 17.46 ppm. IR: $\tilde{\nu}$ = 1120 (P–O–alkyl), 1232 (P=O), 1377 [d, C(CH$_3$)$_2$] cm^{-1}. HRMS (ES+): calcd. for [2 $C_{17}H_{27}O_6P$] 739.2988; found 739.2980.

General Procedure B. Synthesis of Allenylporphyrins through Suzuki–Miyaura Reactions with Allenylboronic Acid Pinacol Ester: The appropriate bromoporphyrin, $PdCl_2$(dppe) (15 mol-%), and K_2CO_3 (10 equiv.) were added to an oven-dried Schlenk flask that was equipped with a magnetic stir bar. The contents of the flask were heated under vacuum. Anhydrous THF was added, and the solution was frozen and thawed under vacuum (3×), before being released to argon. The contents of the flask were then heated at reflux for 72 h. The crude material was purified by filtration through a short silica plug (CH_2Cl_2) and then by column chromatography.

General Procedure C. Synthesis of Allenylporphyrins through Sequential Sonogashira and Hydrogen Transfer Reactions: The appropriate bromoporphyrin, $PdCl_2(PPh_3)_2$ (10 mol-%), and CuI (30 mol-%) were added to an oven-dried Schlenk flask that was equipped with a magnetic stir bar. The contents of the flask were heated under vacuum. Anhydrous THF/triethylamine (TEA, 4:1, v/v) were added, and the solution was frozen and thawed under vacuum (3×), before being released to argon. *N*,*N*-diisopropylprop-2-yn-1-amine (**11**, 5 equiv.) was added, and the contents of the flask were heated to 60 °C for 24 h. The crude material was purified by filtration through a short silica plug (CH_2Cl_2) to remove any unreacted starting material. The eluent was then changed to EtOAc to yield the crude alkyne-coupled porphyrin, which was typically used without any further purification. This intermediate was dried in vacuo and then transferred to a small round-bottom flask. Dry $CHCl_3$, $Pd_2(dba)_3$ (10 mol-%), and $P(C_6F_5)_3$ (40 mol-%) were added, and the solution was degassed with argon over 10 min, before being heated to 90 °C for 24 h. The crude material was purified by filtration through silica gel ($CHCl_3$). Column chromatography and recrystallization were performed as required.

[5,10,15-Triphenyl-20-propadienylporphyrinato]nickel(II) (5a)

Method 1: Synthesized by using General Procedure B from **4a** (100 mg, 163 μmol), $PdCl_2$(dppe) (14 mg, 25 μmol), K_2CO_3 (225 mg, 1.6 mmol), and **3** (0.29 mL, 1.6 mmol) in THF (15 mL). The product was purified by column chromatography (*n*-hexane/CH_2Cl_2, 3:1, v/v) to yield **5a** (91 mg, 143 μmol, 88%) as purple crystals.

Method 2: Synthesized by using General Procedure B from **12a** (60 mg, 83 μmol), $PdCl_2$(dppe) (7 mg, 13 μmol), K_2CO_3 (110 mg, 0.83 mmol), and **3** (0.15 mL, 0.83 mmol) in THF (15 mL). The product was purified by column chromatography (*n*-hexane/CH_2Cl_2, 3:1, v/v) to yield **5a** (22 mg, 35 μmol, 42%) as purple crystals.

Method 3: Synthesized by using General Procedure C from **4a** (185 mg, 0.3 mmol), $PdCl_2(PPh_3)_2$ (21 mg, 30 μmol), CuI (17 mg, 90 μmol), and **15** (208 mg, 1.5 mmol) in THF/TEA (40 mL, 4:1, v/v). The title compound was obtained from crude **16a** with $Pd_2(dba)_3$ (27 mg, 30 μmol) and $P(C_6F_5)_3$ (64 mg, 0.12 mmol) in $CHCl_3$ (5 mL). Purification by column chromatography (*n*-hexane/CH_2Cl_2, 3:1, v/v) gave **5a** (157 mg, 0.24 mmol, 79%) as purple crystals; m.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 5.32 (d, $^4J_{H,H}$ = 6.8 Hz, 2 H, allene-CH_2), 7.70 (m, 9 H, Ph-*m*/*p*-CH), 8.01 (m, 6 H, Ph-*o*-CH), 8.31 (t, $^4J_{H,H}$ = 6.8 Hz, 1 H, allene-CH), 8.67 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, H_β), 8.69 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, H_β), 8.80 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, H_β), 9.46 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 92.1, 109.3, 118.6, 125.5, 126.5, 128.2, 130.3, 131.7, 131.8, 132.0, 132.2, 140.2, 140.5, 141.1, 141.4, 141.9, 142.1, 216.6 ppm. UV/Vis (CH_2Cl_2): λ_{max} [log(ε/M^{-1} cm^{-1})] = 421 [5.41], 535 [4.31], 575 [3.81] nm. HRMS (MALDI): calcd. for $C_{41}H_{26}N_4Ni$ [M]$^+$ 632.1511; found 632.1530.

[5,15-Bis(4-methylphenyl)-10-phenyl-20-propadienylporphyrinato]-nickel(II) (5b)

Method 1: Synthesized by using General Procedure B from **4b** (55 mg, 78 μmol), $PdCl_2$(dppe) (7 mg, 12 μmol), K_2CO_3 (106 mg, 7.8 mmol), and **3** (0.14 mL, 0.78 mmol) in THF (10 mL). The product was purified by column chromatography (*n*-hexane/CH_2Cl_2, 6:1, v/v) to yield **5b** (41 mg, 61 μmol, 78%) as purple crystals.

Method 2: Synthesized by using General Procedure C from **4b** (200 mg, 0.28 mmol), $PdCl_2(PPh_3)_2$ (20 mg, 28 μmol), CuI (16 mg, 84 μmol), and **15** (234 mg, 1.68 mmol) in THF/TEA (40 mL, 4:1, v/v). The title compound was obtained from crude **16b** with $Pd_2(dba)_3$ (26 mg, 28 μmol) and $P(C_6F_5)_3$ (60 mg, 0.11 mmol) in $CHCl_3$ (5 mL). The product was purified by column chromatography (*n*-hexane/CH_2Cl_2, 6:1, v/v) to yield **5b** (155 mg, 0.24 mmol, 84%) as purple crystals; m.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.64 (s, 6 H, tolyl-CH_3), 5.28 (d, $^4J_{H,H}$ = 6.9 Hz, 2 H, allene-CH_2), 7.47 (d, $^3J_{H,H}$ = 7.8 Hz, 4 H, tolyl-*o*-CH), 7.65-7.67 (m, 3 H, Ph-*o*/*p*-CH), 7.86 (d, $^3J_{H,H}$ = 7.8 Hz, 4 H, tolyl-*m*-CH), 7.96–7.97 (m, 2 H, Ph-*m*-CH), 8.26 (t, $^4J_{H,H}$ = 6.9 Hz, 1 H, allene-CH), 8.65 (d, $^3J_{H,H}$ = 5.0 Hz, 2 H, H_β), 8.68 (d, $^3J_{H,H}$ = 5.0 Hz, 2 H, H_β), 8.80 (d, $^3J_{H,H}$ = 5.0 Hz, 2 H, H_β), 9.41 (d, $^3J_{H,H}$ = 5.0 Hz, 2 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 21.5, 76.0, 92.5, 118.8, 118.9, 126.9, 127.6, 130.6, 132.0, 132.2, 132.6, 133.6, 137.4, 137.7, 140.7, 141.5, 142.0 142.4, 142.5, 215.9 ppm. UV/Vis (CH_2Cl_2): λ_{max} [log(ε/M^{-1} cm^{-1})] = 422 [5.10], 536 [4.07, 623 [3.42] nm. IR (neat): $\tilde{\nu}$ = 2962.6, 2918.4, 1939.4 cm^{-1}. HRMS (MALDI): calcd. for $C_{43}H_{30}N_4Ni$ [M]$^+$ 660.1824; found 660.1848. LRMS (ESI+, 150 V): *m*/*z* (%) = 660.18 (30) [M]$^+$, 646.16 (38) [M – CH_3], 569.13 (57) [M – C_7H_7], 461.29 (100) [M – $C_{15}H_{17}$], 446.27 (75) [M – $C_{16}H_{20}$], 431.25 (61) [M – $C_{17}H_{23}$], 331.20 (11) [M – $C_{22}H_{21}Ni$], 243.13 (10) [M – $C_{28}H_{25}NNi$], 171.08 (8) [M – $C_{33}H_{28}N_2Ni$].

[5,15-Bis(2-naphthalenyl)-10-phenyl-20-propadienylporphyrinato]-nickel(II) (5c)

Method 1: Synthesized by using General Procedure B from **4c** (100 mg, 130 μmol), $PdCl_2$(dppe) (11 mg, 20 μmol), K_2CO_3 (180 mg, 1.3 mmol), and **3** (0.23 mL, 1.3 mmol) in THF (15 mL). The product was purified by column chromatography (*n*-hexane/CH_2Cl_2, 6:1, v/v) to yield **5c** (87 mg, 124 μmol, 91%) as purple crystals.

Method 2: Synthesized by using General Procedure B from **12b** (100 mg, 120 μmol), $PdCl_2$(dppe) (10 mg, 18 μmol), K_2CO_3 (165 mg, 1.2 mmol), and **3** (0.21 mL, 1.2 mmol) in THF (15 mL). The product was purified by column chromatography (*n*-hexane/CH_2Cl_2, 6:1, v/v) to yield **5c** (70 mg, 100 μmol, 73%) as purple crystals.

Method 3: Synthesized by using General Procedure C from **4c** (230 mg, 0.3 mmol), $PdCl_2(PPh_3)_2$ (21 mg, 30 μmol), CuI (17 mg, 90 μmol), and **15** (208 mg, 1.5 mmol) in THF/TEA (40 mL, 4:1, v/v). The title compound was obtained from crude **16c** with $Pd_2(dba)_3$ (27 mg, 30 μmol) and $P(C_6F_5)_3$ (64 mg, 0.12 mmol) in $CHCl_3$ (5 mL). The product was purified by column chromatography (*n*-hexane/CH_2Cl_2, 6:1, v/v) to yield **5c** (180 mg, 0.25 mmol, 82%) as purple crystals; m.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 5.27 (d, $^4J_{H,H}$ = 6.9 Hz, 2 H, allene-CH_2), 740–7.42 (m, 2 H, naph-C*H*), 7.65–7.70 (m, 7 H, Ar-C*H*), 7.97–8.01 (m, 2 H, naph-C*H*), 8.08–8.17 (m, 6 H, Ar-C*H*), 8.23 (t, $^4J_{H,H}$ = 6.9 Hz, 1 H, allene-C*H*), 8.42 (s, 2 H, naph-C*H*), 8.69 (s, 4 H, H_β), 8.78 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, H_β), 9.39 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 76.0, 92.5, 118.8, 125.4, 126.1, 126.6, 126.8, 126.9, 127.7, 127.9, 128.4, 128.9, 130.5, 130.8, 131.8, 132.2, 132.3, 132.7, 133.6, 138.2, 140.7, 141.6, 142.1, 142.6, 143.3, 216.0 ppm. UV/Vis (CH_2Cl_2): λ_{max} [log(ε/M^{-1} cm^{-1})] = 423 [5.19], 536 [4.14] nm. IR (neat): $\tilde{\nu}$ = 3051.3, 2962.9, 1939.1 cm^{-1}. HRMS (MALDI): calcd. for $C_{49}H_{30}N_4Ni$ [M]$^+$ 732.1824; found 732.1810. LRMS (ESI+, 150 V): *m*/*z* (%) = 731.10 (8) [M – H], 654.14 (6) [M – C_6H_5], 602.21 (10) [M – $C_{10}H_{10}$], 540.32 (8) [M – $C_{15}H_{12}$], 466.41 (4) [M – $C_{21}H_{14}$], 374.48 (17) [M – $C_{24}H_{10}Ni$], 296.55 (16) [M – $C_{30}H_{18}Ni$], 223.75 (89) [M – $C_{35}H_{17}NNi$], 214.76 (100) [M – $C_{36}H_{14}NNi$], 182.78 (24) [M – $C_{38}H_{22}NNi$].

[5,15-Bis(4-methoxyphenyl)-10-phenyl-20-propadienylporphyrinato]-nickel(II) (5d): Synthesized by by using General Procedure C from **4d** (300 mg, 0.4 mmol), $PdCl_2(PPh_3)_2$ (29 mg, 40 μmol), CuI (23 mg, 120 μmol), and **15** (334 mg, 2.4 mmol) in THF/TEA (50 mL, 4:1 v/v). The title compound was obtained from crude **16d** with $Pd_2(dba)_3$ (36 mg, 40 μmol) and $P(C_6F_5)_3$ (85 mg, 0.16 mmol) in $CHCl_3$ (7 mL). The product was purified by column chromatography (*n*-hexane/CH_2Cl_2, 4:1, v/v) to yield **5d** (0.27 mmol, 189 mg, 68%) as purple crystals; m.p. 248 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.03 (s, 6 H, OCH_3), 5.28 (d, $^4J_{H,H}$ = 6.8 Hz, 2 H, allene-CH_2), 7.19 (d, $^3J_{H,H}$ = 8.5 Hz, 4 H, C_6H_4OMe-*o*-C*H*), 7.63–7.65 (m, 3 H, Ph-*o*/*p*-C*H*), 7.87 (d, $^3J_{H,H}$ = 8.5 Hz, 4 H, C_6H_4OMe-*m*-C*H*), 7.94–7.96 (m, 2 H, Ph-*m*-C*H*), 8.27 (t, $^4J_{H,H}$ = 6.8 Hz, 1 H, allene-C*H*), 8.63 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, H_β), 8.67 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, H_β), 8.78 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, H_β), 9.40 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 55.5, 76.0, 92.5, 112.4, 118.6, 126.9, 127.7, 128.4, 128.9, 130.6, 132.0, 132.2, 132.6, 133.0, 133.6, 134.6, 140.7, 141.5, 142.2, 142.4, 142.7, 159.4, 206.9 ppm. UV/Vis (CH_2Cl_2): λ_{max} [log(ε/M^{-1} cm^{-1})] = 424 [5.19], 538 [4.09] nm. IR (neat): $\tilde{\nu}$ = 2961.0, 2928.0, 2831.3, 1944.3 cm^{-1}. HRMS (MALDI): calcd. for $C_{43}H_{30}N_4NiO_2$ [M]$^+$ 692.1722; found 692.1722. LRMS (ESI+, 200 V): *m*/*z* (%) = 692.15 (14) [M]$^+$, 603.36 (43) [M – CH_3NiO], 540.30 (80) [M – $C_9H_{12}O_2$], 440.23 (100) [M – $C_{17}H_{16}O_2$], 253.22 (56) [M – $C_{27}H_{11}NNiO_2$].

[5,15-Bis(3-fluorophenyl)-10-phenyl-20-propadienylporphyrinato]-nickel(II) (5e)

Method 1: Synthesized by using General Procedure B from **4e** (50 mg, 70 μmol), $PdCl_2$(dppe) (6 mg, 10 μmol), K_2CO_3 (10 mg, 7 mmol), and **3** (0.13 mL, 0.7 mmol) in THF (10 mL). The product was purified by column chromatography (*n*-hexane/CH_2Cl_2, 5:1, v/v) to yield **5e** (30 mg, 45 μmol, 64%) as purple crystals.

Method 2: Synthesized by using General Procedure C from **4e** (200 mg, 0.28 mmol), $PdCl_2(PPh_3)_2$ (20 mg, 28 μmol), CuI (16 mg, 84 μmol), and **15** (234 mg, 1.68 mmol) in THF/TEA (40 mL, 4:1 v/v). The title compound was obtained from crude **16e** with $Pd_2(dba)_3$ (26 mg, 28 μmol) and $P(C_6F_5)_3$ (60 mg, 0.11 mmol) in $CHCl_3$ (5 mL). The product was purified by column chromatography (*n*-hexane/CH_2Cl_2, 5:1, v/v) to yield **5e** (137 mg, 0.20 mmol, 73%) as purple crystals; m.p. 285 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 5.30 (d, $^4J_{H,H}$ = 6.9 Hz, 2 H, allene-CH_2), 7.40–7.44 (m, 2 H, Ar-C*H*), 7.61–7.76 (m, 9 H, Ar-C*H*), 7.96 (m, 2 H, Ar-C*H*), 8.27 (t, $^4J_{H,H}$ = 6.9 Hz, 1 H, allene-C*H*), 8.63 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, H_β), 8.68 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, H_β), 8.75 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, H_β), 9.43 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, H_β) ppm. ^{19}F NMR (400 MHz, $CDCl_3$, 25 °C): δ = –114.80 ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 76.1, 92.4, 114.8, 120.8, 126.9, 129.6, 131.0, 131.9, 132.3, 132.5, 133.6, 140.5, 141.5, 141.7, 142.0, 142.7, 142.8, 216.1 ppm. UV/Vis (CH_2Cl_2): λ_{max} [log(ε/M^{-1} cm^{-1})] = 420 [5.18], 536 [4.15], 673 [3.34] nm. IR (neat): $\tilde{\nu}$ = 2922.3, 2851.5, 1938.5 cm^{-1}. HRMS (MALDI): calcd. for $C_{41}H_{24}F_2N_4Ni$ [M]$^+$ 668.1323; found 668.1305. LRMS (ESI+, 150 V): *m*/*z* (%) = 667.21 (7) [M – H], 571.35 (9) [M – C_6H_6F], 518.26 (9) [M – $C_9H_4F_2$], 375.19 (15) [M – $C_{19}H_{13}F_2N$], 295.12 (15) [M – $C_{21}H_{11}F_2NNi$], 224.17 (81) [M – $C_{27}H_{10}F_2NNi$], 215.17 (100) [M – $C_{28}H_7F_2NNi$], 183.13 (25) [M – $C_{30}H_{15}F_2NNi$].

[5,15-Bis(1-ethylpropyl)-10-phenyl-20-propadienylporphyrinato]-nickel(II) (5f): Synthesized by using General Procedure C from **4f** (265 mg, 0.4 mmol), $PdCl_2(PPh_3)_2$ (29 mg, 40 μmol), CuI (23 mg, 120 μmol), and **15** (334 mg, 2.4 mmol) in THF/TEA (50 mL, 4:1, v/v). The title compound was obtained from crude **16f** with $Pd_2(dba)_3$ (36 mg, 40 μmol) and $P(C_6F_5)_3$ (85 mg, 0.16 mmol) in $CHCl_3$ (7 mL). The product was purified by column chromatography (*n*-hexane/CH_2Cl_2, 7:1, v/v) to yield **5f** (0.18 mmol, 112 mg, 45%) as purple crystals; m.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.88 (t, $^3J_{H,H}$ = 7.4 Hz, 12 H, alkyl-CH_3), 2.54–2.69 (m, 8 H, alkyl-CH_2), 4.24–4.32 (m, 2 H, alkyl-C*H*), 5.25 (d, $^4J_{H,H}$ = 6.9 Hz, 2 H, allene-CH_2), 7.63–7.66 (m, 3 H, Ph-*o*/*p*-C*H*), 7.91–7.93 (m, 2 H, Ph-*m*-C*H*), 8.16 (t, $^4J_{H,H}$ = 6.9 Hz, 1 H, allene-C*H*), 8.60 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, H_β), 9.21 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, H_β), 9.32 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, H_β), 9.36 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 13.9, 33.4, 49.3, 76.1, 92.4, 107.9, 117.6, 121.2, 126.8, 127.6, 130.6, 131.1, 132.1, 133.4, 140.6, 215.9 ppm. UV/Vis (CH_2Cl_2): λ_{max} [log(ε/M^{-1} cm^{-1})] = 428 [5.20], 549 [4.14], 595 [3.79] nm. IR (neat): $\tilde{\nu}$ = 2958.9, 2921.9, 2851.5, 1938.2 cm^{-1}. HRMS (MALDI): calcd. for $C_{39}H_{38}N_4Ni$ [M]$^+$ 620.245; found 620.2434. LRMS (ESI+, 200 V): *m*/*z* (%) = 620.25 (4) [M]$^+$, 504.13 (100) [M – C_9H_8], 427.95 (93) [M – $C_{10}H_{14}Ni$], 253.64 (5) [M – $C_{23}H_{19}NNi$].

[5-Hexyl-10,20-bis(4-methylphenyl)-15-propadienylporphyrinato]-nickel(II) (5g): Synthesized by using General Procedure C from **4g** (200 mg, 0.28 mmol), $PdCl_2(PPh_3)_2$ (20 mg, 28 μmol), CuI (16 mg, 85 μmol), and **15** (234 mg, 1.68 mmol) in THF/TEA (20 mL, 4:1, v/v). The title compound was obtained from crude **16g** with $Pd_2(dba)_3$ (26 mg, 28 μmol) and $P(C_6F_5)_3$ (60 mg, 0.112 mmol) in $CHCl_3$ (5 mL). The product was purified by column chromatography (*n*-hexane/CH_2Cl_2, 8:1, v/v) to yield **5g** (0.15 mmol, 105 mg,

53%) as purple crystals; m.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.92 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, hexyl-CH_3), 1.28–1.40 (m, 6 H, hexyl-CH_2), 2.22–2.28 (m, 2 H, hexyl-CH_2), 2.64 (s, 3 H, tolyl-CH_3), 4.49–4.54 (m, 2 H, hexyl-CH_2), 5.25 (d, $^4J_{H,H}$ = 6.9 Hz, 2 H, allene-CH_2), 7.46 (d, $^3J_{H,H}$ = 7.7 Hz, 4 H, tolyl-*o*-C*H*), 7.83 (d, $^3J_{H,H}$ = 7.7 Hz, 4 H, tolyl-*m*-C*H*), 8.21 (t, $^4J_{H,H}$ = 6.9 Hz, 1 H, allene-C*H*), 8.71 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, H_β), 8.73 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, H_β), 9.21 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, H_β), 9.35 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.1, 21.5, 22.6, 29.7, 30.0, 31.7, 37.3, 76.0, 92.4, 118.3, 125.3, 128.2, 129.0, 130.4, 132.4, 132.6, 133.5, 137.3, 137.7, 141.3, 141.8, 142.1, 215.9 ppm. UV/Vis (CH_2Cl_2): λ_{max} [log(ε/M^{-1}cm^{-1})] = 424 [5.15], 541 [4.01], 587 [3.47] nm. IR (neat): $\tilde{\nu}$ = 2858.2, 2919.1, 2850.4, 1939.6 cm^{-1}. HRMS (MALDI): calcd. for $C_{43}H_{38}N_4Ni$ $[M]^+$ 668.2450; found 668.2465.

[5-(*n*-Butyl)-10,20-bis(1-ethylpropyl)-15-propadienylporphyrinato]-nickel(II) (5h): Synthesized by using General Procedure C from **4h** (180 mg, 0.28 mmol), $PdCl_2(PPh_3)_2$ (20 mg, 28 μmol), CuI (16 mg, 84 μmol), and **15** (234 mg, 1.68 mmol) in THF/TEA (40 mL, 4:1 v/v). The title compound was obtained from crude **16h** with $Pd_2(dba)_3$ (26 mg, 28 μmol) and $P(C_6F_5)_3$ (60 mg, 0.11 mmol) in $CHCl_3$ (5 mL). The product was purified by column chromatography (*n*-hexane/CH_2Cl_2, 8:1, v/v) to yield **5h** (74 mg, 0.12 mmol, 44%) as purple crystals; m.p. 164 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.88 (t, $^3J_{H,H}$ = 7.4 Hz, 12 H, alkyl-CH_3), 0.99 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, butyl-CH_3), 1.51 (m, 2 H, butyl-CH_2), 2.17 (m, 2 H, butyl-CH_2), 2.53–2.68 (m, 8 H, alkyl-CH_2), 4.23 (m, 2 H, alkyl-C*H*), 4.40 (t, $^3J_{H,H}$ = 8.0 Hz, 2 H, butyl-CH_2), 5.22 (d, $^4J_{H,H}$ = 6.9 Hz, 2 H, allene-CH_2), 8.11 (t, $^4J_{H,H}$ = 6.9 Hz, 1 H, allene-C*H*), 9.14 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, H_β), 9.26 (m, 4 H, H_β), 9.30 (d, $^3J_{H,H}$ = 4.9 Hz, 2 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.0, 23.3, 33.4, 39.1, 49.3, 76.1, 92.4, 107.2, 117.7, 120.7, 129.6, 130.6, 130.8, 131.1, 215.8 ppm. UV/Vis (CH_2Cl_2): λ_{max} [log(ε/M^{-1}cm^{-1})] = 429 [5.24], 552 [4.17], 594 [3.82] nm. IR (neat): $\tilde{\nu}$ = 2956.6, 2924.2, 2866.9, 1938.3, 1641.3 cm^{-1}. HRMS (MALDI): calcd. for $C_{37}H_{42}N_4Ni$ $[M]^+$ 600.2763; found 600.2755. LRMS (ESI+, 200 V): *m*/*z* (%) = 600.35 (12) $[M]^+$, 440.13 (100) [M – $C_{11}H_{28}$], 253.16 (10) [M – $C_{21}H_{23}NNi$].

[5,15-Bis(2-naphthalenyl)-10-phenyl-20-propadienylporphyrinato]-copper(II) (5j): Synthesized by using General Procedure C from **4i** (233 mg, 0.3 mmol), $PdCl_2(PPh_3)_2$ (21 mg, 30 μmol), CuI (17 mg, 90 μmol), and **15** (208 mg, 1.5 mmol) in THF/TEA (40 mL, 4:1, v/v). The title compound was obtained from crude **16i** with $Pd_2(dba)_3$ (27 mg, 30 μmol) and $P(C_6F_5)_3$ (64 mg, 0.12 mmol) in $CHCl_3$ (5 mL). The product was purified by column chromatography (*n*-hexane/CH_2Cl_2, 6:1, v/v) to yield **5j** (104 mg, 0.14 mmol, 47%) as red-purple crystals; m.p. > 300 °C. UV/Vis (CH_2Cl_2): λ_{max} [log(ε/M^{-1}cm^{-1})] = 427 [5.95], 549 [4.76], 585 [4.31] nm. HRMS (MALDI): calcd. for $C_{49}H_{30}N_4Cu$ $[M]^+$ 737.1766; found 737.1743. LRMS (ESI+, 150 V): *m*/*z* (%) = 737.17 (16) $[M]^+$, 601.47 (20) [M – C_6HCu], 462.04 (37) [M – $C_{17}H_8Cu$], 387.85 (65) [M – $C_{23}H_{11}Cu$], 253.61 (100) [M – $C_{33}H_{11}CuN$].

General Procedure D. Iodination of Porphyrins: By following the procedure of Boyle and co-workers,[17,41] the porphyrin was dissolved in $CHCl_3$, and the reaction vessel was purged with argon. Iodine (1.5 equiv.) and bis(trifluroacetoxy)iodobenzene (1.1 equiv.) were added, and the flask was shielded from light. The reaction was left to stir at room temp., until there was complete consumption of the starting material (approximately 48 h). The solution was then filtered through silica gel (CH_2Cl_2), and the solvents were removed. The product was recrystallized from $CHCl_3$/MeOH.

(5-Iodo-10,15,20-triphenylporphyrinato)nickel(II) (12a): Synthesized by using General Procedure D from **11a** (200 mg, 0.34 mmol), I_2 (130 mg, 0.52 mmol), and $C_6H_5I(O_2CCF_3)_2$ (160 mg, 0.37 mmol) in $CHCl_3$ (200 mL) to yield **12a** (0.32 mmol, 228 mg, 93%) as purple crystals; m.p. 265 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.65–7.71 (m, 9 H, Ph-*o*/*p*-C*H*), 7.95–7.97 (m, 6 H, Ph-*o*-C*H*), 8.66–8.70 (m, 4 H, H_β), 8.73 (d, $^3J_{H,H}$ = 5.0 Hz, 2 H, H_β), 9.47 (d, $^3J_{H,H}$ = 5.0 Hz, 2 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 119.4, 119.7, 126.9, 127.8, 127.9, 132.2, 132.6, 133.6, 133.7, 137.9, 140.3, 140.5, 140.9, 142.7, 142.8, 142.9, 143.4, 144.5 ppm. UV/Vis (CH_2Cl_2): λ_{max} [log(ε/M^{-1}cm^{-1})] = 419 [5.54], 533 [4.40] nm. HRMS (MALDI): calcd. for $C_{38}H_{23}IN_4Ni$ $[M]^+$ 720.0331; found 720.0321.

[5-Iodo-10,20-bis(2-naphthalenyl)-15-phenylporphyrinato]nickel(II) (12b): Synthesized by using General Procedure D from **11c** (300 mg, 0.43 mmol), I_2 (150 mg, 0.60 mmol), and $C_6H_5I(O_2CCF_3)_2$ (180 mg, 0.43 mmol) in $CHCl_3$ (200 mL) to yield **12b** (0.41 mmol, 333 mg, 95%) as purple crystals; m.p. 291 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.68–7.73 (m, 7 H, Ar-C*H*), 8.00 (m, 2 H, naph-C*H*), 8.05 (m, 2 H, naph-C*H*), 8.15–8.20 (m, 6 H, Ar-C*H*), 8.44 (s, 2 H, naph-C*H*), 8.71 (s, 4 H, H_β), 8.78 (d, $^3J_{H,H}$ = 5.0 Hz, 2 H, H_β), 9.53 (d, $^3J_{H,H}$ = 5.0 Hz, 2 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 119.4, 119.8, 126.2, 126.7, 126.9, 127.9, 128.2, 128.4, 129.0, 130.2, 131.7, 132.2, 132.3, 132.7, 132.8, 133.6, 133.7, 137.5, 137.9, 140.4, 142.8, 142.9, 143.0, 143.6, 144.6 ppm. UV/Vis (CH_2Cl_2): λ_{max} [log(ε/M^{-1}cm^{-1})] = 422 [5.37], 535 [4.25] nm. HRMS (MALDI): calcd. for $C_{46}H_{27}IN_4Ni$ $[M]^+$ 820.0634; found 820.0618.

5-Iodo-10,20-bis(4-methylphenyl)-15-phenylporphyrin (12c): Synthesized by using General Procedure D from **9b** (260 mg, 0.47 mmol), I_2 (165 mg, 0.65 mmol), and $C_6H_5I(O_2CCF_3)_2$ (205 mg, 0.48 mmol) in $CHCl_3$ (300 mL) to yield **12c** (0.39 mmol, 270 mg, 83%) as purple crystals; m.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = –2.72 (s, 2 H, N*H*), 2.70 (s, 6 H, tolyl-CH_3), 7.55 (d, $^3J_{H,H}$ = 7.7 Hz, 4 H, tolyl-*o*-C*H*), 7.72–7.74 (m, 3 H, Ph-*o*/*p*-C*H*), 8.05 (d, $^3J_{H,H}$ = 7.7 Hz, 4 H, tolyl-*m*-C*H*), 8.15–8.17 (m, 2 H, Ph-*m*-C*H*), 8.78 (m, 4 H, H_β), 8.87 (d, $^3J_{H,H}$ = 4.8 Hz, 2 H, H_β), 9.65 (d, $^3J_{H,H}$ = 4.8 Hz, 2 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 21.5, 78.4, 121.0, 126.8, 127.5, 127.8, 134.4, 134.5, 137.6, 138.9, 141.8 ppm. UV/Vis (CH_2Cl_2): λ_{max} [log(ε/M^{-1}cm^{-1})] = 423 [5.48], 522 [4.07], 558 [3.85], 598 [3.51], 655 [3.64] nm. HRMS (MALDI): calcd. for $C_{40}H_{29}IN_4$ $[M]^+$ 692.1437; found 692.1431.

General Procedure E. Suzuki Reaction with (4-Bromophenyl)boronic Acid: In an oven-dried Schlenk flask, the appropriate bromoporphyrin was dissolved in dry THF, and the solution was subjected to freeze-pump-thaw cycles (3×), before being released to argon. (4-Bromophenyl)boronic acid (5 equiv.), $PdCl_2(PPh_3)_2$ (20 mol-%), triphenylarsane (40 mol-%), and K_3PO_4 (5 equiv.) were added, and the solution was heated to 60 °C for 18 h. The product was filtered through silica gel (CH_2Cl_2) and then purified by column chromatography.

[5-(4-Bromophenyl)-10,15,20-triphenylporphyrinato]nickel(II) (19a): Synthesized by using General Procedure E from **4a** (200 mg, 0.33 mmol), (4-bromophenyl)boronic acid (330 mg, 1.62 mmol), $PdCl_2(PPh_3)_2$ (46 mg, 66 μmol), $AsPh_3$ (40 mg, 0.13 mmol), and K_3PO_4 (346 mg, 1.62 mmol) in THF (50 mL). The product was purified by column chromatography on silica gel (*n*-hexane/CH_2Cl_2, 6:1, v/v) and then crystallized ($CHCl_3$/MeOH) to yield **19a** (0.28 mmol, 208 mg, 84%) as purple crystals; m.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.66–7.73 (m, 9 H, Ph-*o*/*p*-C*H*), 7.81 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, *o*-C_6H_4Br), 7.89 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, *m*-C_6H_4Br), 8.01–8.03 (m, 6 H, Ph-*o*-C*H*), 8.73 (d, $^3J_{H,H}$ = 5.0 Hz, 2 H, H_β), 8.77–8.78 (m, 6 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 117.3, 119.1, 119.2, 122.4, 126.9, 127.3, 127.7, 127.8, 128.5, 130.1, 131.8, 131.9, 132.2, 132.3, 132.4,

133.7, 134.6, 135.1, 139.9, 140.8, 142.3, 142.7 and 142.8 ppm. UV/Vis (CH_2Cl_2): λ_{max} [log(ε/M^{-1}cm^{-1})] = 414 [5.40], 528 [4.27] nm. HRMS (MALDI): calcd. for $C_{44}H_{27}BrN_4Ni$ $[M]^+$ 748.0773; found 748.0756.

[5-(4-Bromophenyl)-10,20-bis(4-methylphenyl)-15-phenylporphyrinato]nickel(II) (19b): Synthesized by using General Procedure E from **4b** (230 mg, 0.33 mmol), (4-bromophenyl)boronic acid (330 mg, 1.62 mmol), $PdCl_2(PPh_3)_2$ (46 mg, 66 μmol), $AsPh_3$ (40 mg, 0.13 mmol), and K_3PO_4 (346 mg, 1.62 mmol) in THF (50 mL). The product was purified by column chromatography on silica gel (*n*-hexane/CH_2Cl_2, 6:1, v/v) and then crystallized ($CHCl_3$/MeOH) to yield **19b** (0.27 mmol, 213 mg, 83%) as purple crystals; m.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.64 (s, 6 H, tolyl-CH_3), 7.47 (d, $^3J_{H,H}$ = 7.7 Hz, 4 H, tolyl-*o*-C*H*), 7.66–7.67 (m, 3 H, Ph-*o*/*p*-C*H*), 7.79 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, *o*-C_6H_4Br), 7.86–7.89 (m, 6 H, tolyl-*m*-C*H*, *m*-C_6H_4Br), 7.99–8.02 (m, 2 H, Ph-*m*-C*H*), 8.70 (d, $^3J_{H,H}$ = 5.0 Hz, 2 H, H_β), 8.73 (d, $^3J_{H,H}$ = 5.0 Hz, 2 H, H_β), 8.78 (d, $^3J_{H,H}$ = 5.0 Hz, 2 H, H_β), 8.79 (d, $^3J_{H,H}$ = 5.0 Hz, 2 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 21.5, 117.2, 119.0, 119.2, 121.9, 12.3, 126.8, 126.9, 127.3, 127.6, 128.4, 128.5, 130.0, 131.6, 131.9, 132.0, 132.2, 132.3, 132.4, 133.6, 133.7, 135.1, 137.5, 137.8, 138.8, 140.0, 140.9, 142.2, 142.7, 142.8, 142.9 ppm. UV/Vis (CH_2Cl_2): λ_{max} [log(ε/M^{-1}cm^{-1})] = 416 [5.23], 529 [4.09] nm. HRMS (MALDI): calcd. for $C_{46}H_{31}BrN_4Ni$ $[M]^+$ 776.1086; found 776.1096.

5-(4-Bromophenyl)-10,15,20-triphenylporphyrin (19c): Synthesized by using General Procedure E from **4l** (200 mg, 0.31 mmol), (4-bromophenyl)boronic acid (310 mg, 1.54 mmol), $PdCl_2(PPh_3)_2$ (40 mg, 60 μmol), $AsPh_3$ (30 mg, 0.10 mmol), and K_3PO_4 (328 mg, 1.54 mmol) in THF (50 mL). The product was purified by column chromatography on silica gel (*n*-hexane/CH_2Cl_2, 4:1, v/v) and then crystallized ($CHCl_3$/MeOH) to yield **19c** (0.24 mmol, 173 mg, 78%) as purple crystals. The product had analytical data consistent with the literature.[42]

[5,10,15-Triphenyl-20-(4-propadienylphenyl)porphyrinato]nickel(II) (21a): Synthesized by using a modification of General Procedure C from **19a** (400 mg, 0.53 mmol), $PdCl_2(PPh_3)_2$ (37 mg, 53 μmol), CuI (40 mg, 0.21 mmol), PPh_3 (55 mg, 0.21 mmol), and **15** (443 mg, 3.2 mmol) in DMF/DEA (40 mL, 4:1, v/v). Intermediate **20a** was extracted with CH_2Cl_2, washed with water (5×) to remove the residual DMF, and filtered through silica gel (EtOAc). The title compound was obtained from crude **20a** with $Pd_2(dba)_3$ (48 mg, 53 μmol) and $P(C_6F_5)_3$ (112 mg, 0.21 mmol) in $CHCl_3$ (8 mL). The product was purified by column chromatography (*n*-hexane/CH_2Cl_2, 4:1, v/v) to yield **21a** (252 mg, 0.36 mmol, 67%) as purple crystals; m.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 5.25 (d, $^4J_{H,H}$ = 6.8 Hz, 2 H, allene-CH_2), 6.38 (t, $^4J_{H,H}$ = 6.8 Hz, 1 H, allene-C*H*), 7.55 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, *o*-C_6H_4), 7.59–7.64 (m, 9 H, Ph-*m*/*p*-C*H*), 7.90 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, *m*-C_6H_4), 7.94–7.97 (m, 6 H, Ph-*o*-C*H*), 8.69–8.73 (m, 8 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 79.1, 93.9, 119.0, 125.2, 126.9, 127.7, 132.1, 132.2, 133.5, 133.7, 134.0, 139.5, 140.9, 142.6, 142.7, 210.2 ppm. UV/Vis (CH_2Cl_2): λ_{max} [log(ε/M^{-1}cm^{-1})] = 416 [5.39], 529 [4.30] nm. IR (neat): $\tilde{\nu}$ = 2923.8, 2850.2, 1939.1 cm^{-1}. HRMS (MALDI): calcd. for $C_{47}H_{30}N_4Ni$ $[M]^+$ 708.1824; found 708.1811. LRMS (ESI+, 200 V): *m*/*z* (%) = 708.21 (23) $[M]^+$, 631.15 (52) [M – C_6H_5], 591.36 (100) [M – C_9H_9], 515.17 (81) [M – $C_{15}H_{13}$], 412.88 (43) [M – $C_{23}H_{19}$], 253.66 (46) [M – $C_{31}H_{11}NNi$].

[5,15-Bis(4-methylphenyl)-10-phenyl-20-(4-propadienylphenyl)porphyrinato]nickel(II) (21b): Synthesized by using a modification of General Procedure C from **19b** (300 mg, 0.39 mmol), $PdCl_2(PPh_3)_2$ (27 mg, 39 μmol), CuI (29 mg, 0.15 mmol), PPh_3 (40 mg, 0.15 mmol), and **15** (230 mg, 1.54 mmol) in DMF/DEA (30 mL, 4:1, v/v). Intermediate **20b** was extracted with CH_2Cl_2, washed with water (5×) to remove residual DMF, and filtered through silica gel (EtOAc). The title compound was obtained from crude **20b** with $Pd_2(dba)_3$ (35 mg, 39 μmol) and $P(C_6F_5)_3$ (80 mg, 0.16 mmol) in $CHCl_3$ (8 mL). The product was purified by column chromatography (*n*-hexane/CH_2Cl_2, 5:1, v/v) to yield **21b** (207 mg, 0.28 mmol, 72%) as purple crystals; m.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.63 (s, 6 H, tolyl-CH_3), 5.29 (d, $^4J_{H,H}$ = 6.9 Hz, 2 H, allene-CH_2), 6.43 (t, $^4J_{H,H}$ = 6.9 Hz, 1 H, allene-C*H*), 7.46 (d, $^3J_{H,H}$ = 7.8 Hz, 4 H, tolyl-*o*-C*H*), 7.60 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, *o*-C_6H_4), 7.65–7.69 (m, 3 H, Ph-*o*/*p*-C*H*), 7.89 (d, $^3J_{H,H}$ = 7.8 Hz, 4 H, tolyl-*m*-C*H*), 7.95 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, *m*-C_6H_4), 7.99–8.01 (m, 2 H, Ph-*m*-C*H*), 8.73 (d, $^3J_{H,H}$ = 5.0 Hz, 2 H, H_β), 8.76–8.77 (m, 6 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 21.5, 79.1, 93.9, 118.6, 118.8, 119.0, 125.2, 126.8, 127.6, 131.9, 132.0, 132.2, 133.6, 134.0, 137.4, 137.9, 139.6, 140.9, 142.6, 142.8, 210.2 ppm. UV/Vis (CH_2Cl_2): λ_{max} [log(ε/M^{-1}cm^{-1})] = 417 [5.27], 529 [4.13] nm. IR (neat): $\tilde{\nu}$ = 2921.4, 2853.7, 1940.2 cm^{-1}. HRMS (MALDI): calcd. for $C_{49}H_{34}N_4Ni$ $[M]^+$ 736.2137; found 736.2130. LRMS (ESI+, 200 V): *m*/*z* (%) = 737.25 (100) [M + H], 645.51 (76) [M – C_7H_8], 605.38 (63) [M – $C_{10}H_{11}$], 531.21 (40) [M – $C_{16}H_{13}$], 440.98 (33) [M – $C_{23}H_{29}$], 215.53 (71) [M – $C_{36}H_{17}NNi$].

Supporting Information (see footnote on the first page of this article): Experimental procedures and analytical data for all other new compounds along with copies of ^{1}H and ^{13}C NMR spectra of all haloporphyrins and allenylporphyrins are available in the Supporting Information.

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