FULL PAPER

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Synthesis and Reactivity of Allenylporphyrins

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Several different methods have been utilized in an effort to allow for the effective the effective synthesis of a new class of porphyrins, bearing the synthetically intriguing propadienyl (or allenyl) functional group. Of these, successive HWE couplings proved impossible, but Pd-catalyzed cross couplings enabled quick and easy synthetic access to allenylporphyrins. Suzuki-Miyaura cross coupling conditions of bromoporphyrins with allenylboronic acid pinacol ester were optimized and represent the first successful use of this boronic acid in a Suzuki-type coupling. While this routine proved successful for the synthesis of porphyrins possessing aromatic substituents a more robust method involving Sonogashira coupling of a bromoporphyrin with *N,N*-diisopropylprop-2-yn-1-amine followed by Pd catalyzed rearrangement was developed to give allenylporphyrins in high yields. The applicable metalation states of the porphyrin core were also investigated in both routes with mixed results. The utility of the addition of the allenyl functional group was then probed using both directly linked allenylporphyrins and those bearing a phenyl “spacer”.

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Introduction

The synthesis and functionalization of porphyrins with novel and synthetically useful functional groups is an on-going challenge for synthetic porphyrin chemists.[1] 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. As a result, functional group interconversion and synthetic transformations spanning the field of porphyrin chemistry are constantly being explored and improved.[2] 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 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] While cumulenic porphyrin dimers linked by two carbons have been explored for their impressive optical properties, these dimers are quinoidal in nature and arise from modification of an internal alkyne, which results in exceptionally perturbed electronic absorption spectra.[4] Thus, we undertook a synthetic program aimed at the utilization and subsequent transformation of terminal cumulative double bonds in porphyrinoid systems.[1]

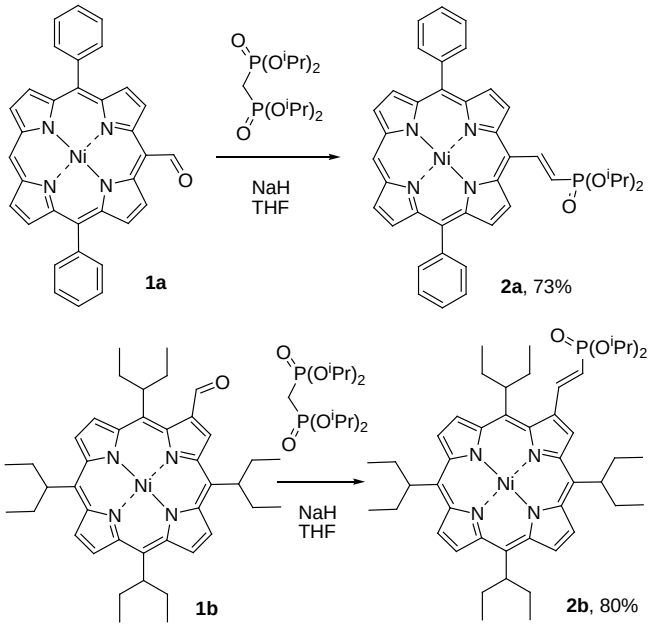
Allenes were seen as a synthetically interesting and useful functional group to introduce, as the orthogonal double bonds should provide a facile route towards further functionalizations as well as creating structurally interesting compounds possessing both the interesting physiochemical, biological and catalytic properties of porphyrins[5] and the optical properties of allenic systems observed previously.[6] Our research thus focused on initially installing a free allene onto the porphyrin core to be followed by investigations of reactivity.

Results and Discussion

Allene synthesis *via* HWE Reactions

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[7] and to its need for a formylporphyrin precursor. Formylporphyrins are commonly used precursors, the utility of which has recently been expanded successfully from solely metalloporphyrins to include their metal-free analogues.[8]

Applying the one-pot double olefination procedure designed by Tomioka and co-workers[9] to formylporphyrins **1a** and **1b** (Scheme 1), the first HWE reaction using tetraisopropyl methylenebisphosphonate and NaH worked well and the extremely polar intermediates **2a** and **2b** could both be isolated by simple chromatography in very good yield.



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

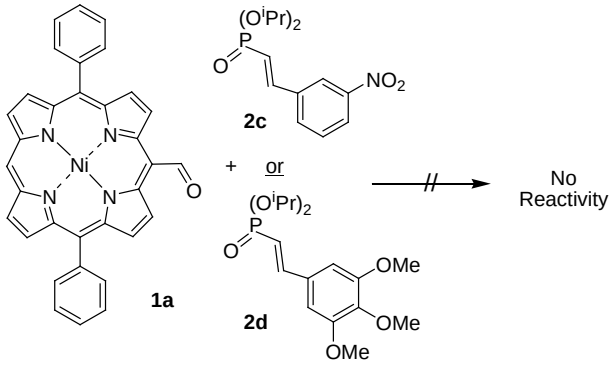
Interestingly though, both in the one-pot procedure, and using the isolated intermediates **2a** and **2b**, the second olefination reaction could not be realized under a variety of conditions. This olefination reaction occurs through direct deprotonation of the alkenylphosphonate with LDA and then treatment with an aldehyde to afford an hydroxyalkenylphosphonate, which is then converted into the corresponding allene by a subsequent HWE olefination reaction with another aldehyde.[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. Reaction of diisopropylamine with **2a** occurred seemingly regardless of the temperature used (-80 °C to 60 °C). Porphyrin **2b** exhibited no reactivity with LDA. Use of ^{t}BuLi as base resulted in degradation of the porphyrin.

To test the reverse reaction, two novel alkenylphosphonates, **2c** and **2d**, were synthesized. These were treated with LDA followed by addition of formylporphyrin **1a**. Again, however, the desired second HWE reaction could not be achieved (Scheme 2). A plausible reason for the reactive reticence may be steric hindrance caused by the bulky *iso*-propoxy residues attached to the phosphorous atom.

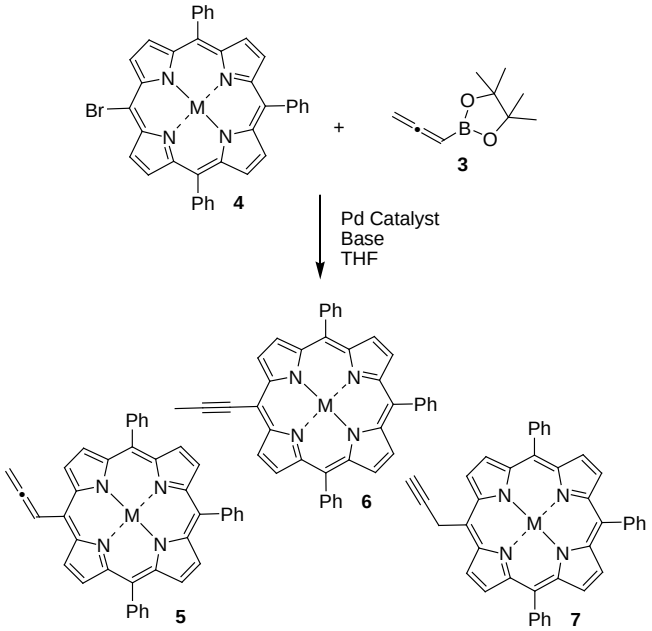
Allene synthesis *via* Palladium catalyzed cross coupling

Due to the failure of the double HWE reaction to yield any allenic products our attention turned to the commercially available allenylboronic acid pinnacol ester (**3**). Previously, **3** had been used mainly 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] Pd-catalyzed coupling between **3** and triphenylbromoporphyrin **4** was seen as being a convenient way both to test the utility of **3** in such coupling reactions while providing a facile entry to triphenylallenylporphyrin **5**.

Using a variety of conditions to couple the allenylboronate to the bromoporphyrin as per Scheme 3, 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 allenyl, **5**, 1-propynyl, **6**, or 2-propynylporphyrin, **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.



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



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

Except for when K_3PO_4 was used as base, standard 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 (**4a**), and the use of this with a strong base resulted in rearrangement of the allene (**5a**) to the more stable 1-propynylporphyrin **6a**, along with the formation of unidentifiable side products. Our first successful attempt at isolating the allenylporphyrin **5a** came from heating in THF to 80 °C in a sealed Schlenk tube and using a 20-fold excess of K_3PO_4 (9% yield). Interestingly, using the same conditions, but in 1,4-dioxane at 80 °C, 100 °C and 120 °C, no allenyl or propynylporphyrin was isolated.

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

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

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, **5a** was isolated in up to 50% yield when K_2CO_3 was used as the base in 10-fold excess. Interestingly, while $PdCl_2$(dppe) and $PdCl_2$(dppp) were found to be equally effective in coupling, when a twofold 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 optimization experiments. It should be noted that 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 twofold excess of Cs_2CO_3 resulted in **5a** solely being isolated from the reaction, while a 10-fold excess resulted in **6a** being the only Suzuki product in 61% yield. 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 10-fold excess led to **5a** again being isolated as the only product, while quite surprisingly, the kinetically rearranged **7** was the only product isolated from the reaction of Zn(II)bromoporphyrin **4j.** Free-base bromoporphyrin **4l** gave no identifiable products under any conditions.

This optimization work exclusively used triphenylporphyrins as the bromo partners. This is due to the ready availability and known reactivity of porphyrins possessing phenyl substituents. Having successfully achieved the first synthesis of an allenylporphyrin (**5a**) we decided to probe the versatility of the above reaction in installing allenyl functional groups to generate a library of allenyl porphyrins, bearing different substituents, and then to test the reactivity of the allenic double bonds.

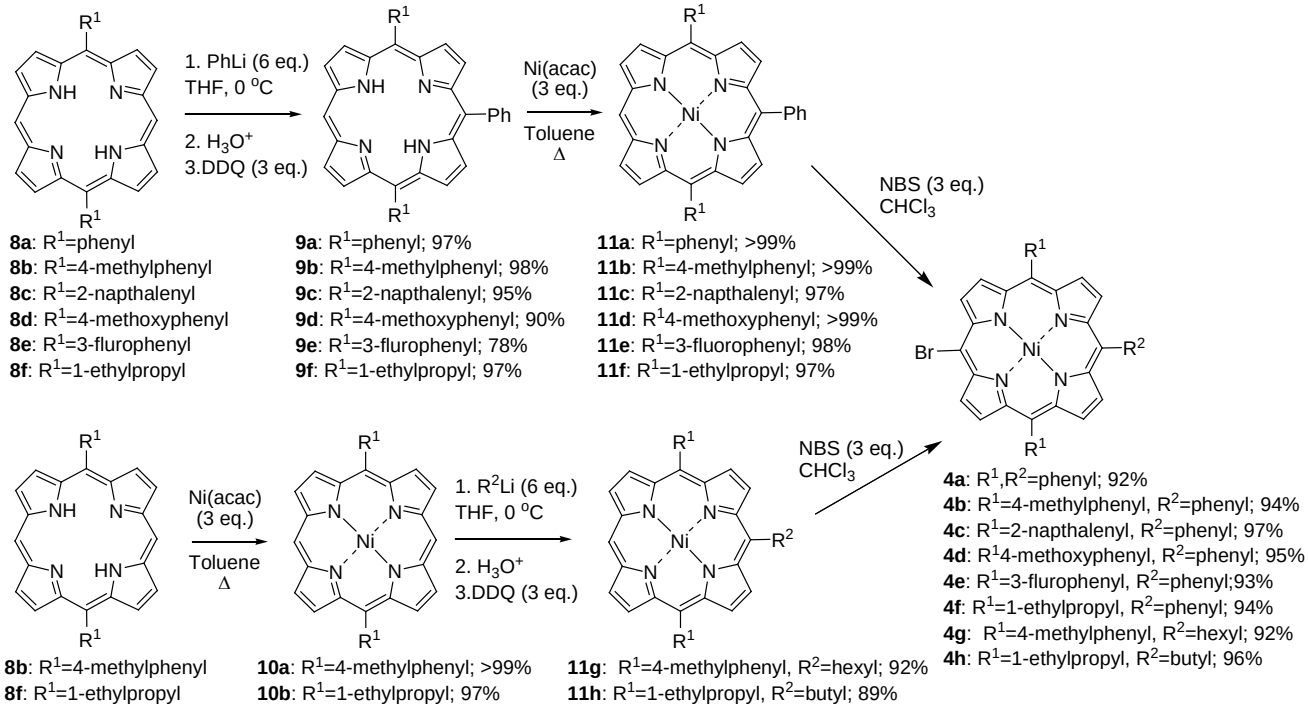
Synthesis of Nickel(II)bromoporphyrins

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 *via* the Lindsey method[15]) and an appropriate aldehyde. The second step involves methodology developed by us[16] and used the nucleophilic addition of an aryl or alkyl lithium to one of the free meso positions followed by quenching of the generated anion with acid and subsequent oxidation to the substituted porphyrin product. For the addition of aromatic lithiating agents the reaction works best with free base porphyrins so this step must take place to give **9a-f** before metalation with nickel acetylacetonate, yielding **11a-f**. However, when alkyl substituents are being installed in this manner the reaction proceeds much more smoothly with nickel(II)porphyrins **10a/b**, yielding trisubstituted porphyrins **11g/h**. The desired target functionality thus dictated the synthetic route followed. With trisubstituted nickel(II)porphyrins **11a-h** in hand, bromination with *N*-bromosuccinimide (NBS) to give **4a-h** becomes particularly facile as there is only one reactive meso position remaining.[17]

Suzuki/Miyaura cross-coupling reactions

Following on from the success using **4a**, aromatically substituted porphyrins were seen as the favored initial starting point to test the general applicability of the synthetic methodology. The optimized conditions were employed (Table 1; Entry 10) using **4b** as a substrate. A small degree of conversion was observed after 24 hours but most of the starting material had not been consumed. The reaction time was thus extended and it was observed that after 72 hours all of the starting material had been converted, either to allenylporphyrin **4b**, or to debrominated starting material **11b** as well as trace propynylporphyrins. It was initially assumed that, within the Suzuki cycle, protodemetalation to give debrominated starting material and transmetalation leading to allenylporphyrins, were competitive but later tests with **4c** showed that after 36 hours the products in the flask were allenylporphyrin **5c** and unreacted starting material **4c**. The yield of **5c** after 36 hours could be increased with longer reaction time, at which stage protodemetalation does begin to occur. Separation of the target allenyl porphyrins **5** from porphyrins of type **11** proved much easier than separation from **4** so the time scale was extended to 72 hours for all 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 hours all of the C-Br bonds have been cleaved.



Scheme 4: Synthesis of nickel(II)bromoporphyrins **4**.

Table 2 illustrates the results of the various Suzuki/Miyaura cross-coupling reactions attempted and shows some quite interesting results, the first of which is that the successful yields are all greater than the 50% seen with the synthesis of **5a** after 24 hours. From the aromatic residues tested it seems that this procedure is somewhat limited in scope and, while it works incredibly well for standard aromatic residues (**5a-c**), disturbances to the aromaticity lead to significantly reduced yields (**5d** and **5e**). As well as expanding the allenic library using purely aromatic substituents, it was decided to attempt to also introduce different alkyl substituents onto the porphyrin periphery in order to further probe the versatility of the reaction conditions and yield even more structurally interesting porphyrins. Unfortunately, these efforts proved quite disappointing. None of the porphyrins bearing alkyl substituents **4f-h** yielded an allenylporphyrin in high enough yields to be characterized. This is most likely due to the known reduced reactivity of alkyl-substituted porphyrins towards standard transformations.[18] In terms of general trends in reactivity it is obvious that as the number of aliphatic substituents increases the yield of **5** decreases sharply. Porphyrins bearing just one aliphatic substituent could still be converted to **5** in very low yields (**5g**) while those bearing two or three were only converted in trace amounts, if at all (**5f/h**).

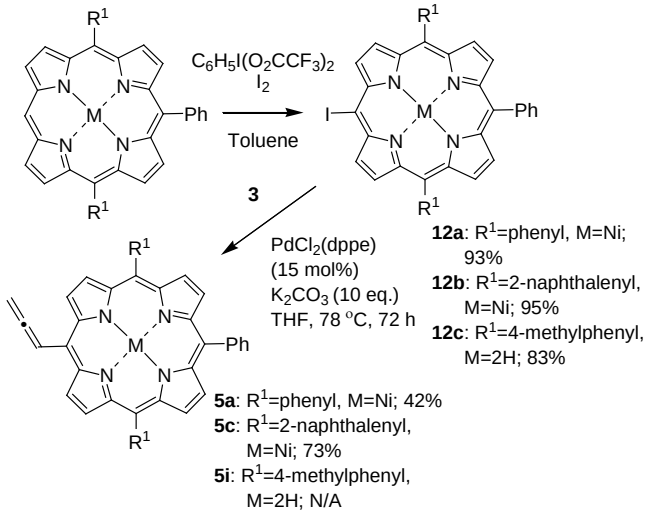
As a final optimization effort for the Suzuki/Miyaura conditions, three iodoporphyrins, **12a-c**, were synthesized using [bis(trifluroacetoxy)]iodobenzene, iodine and the appropriate trisubstituted porphyrin (**9b**,**11a/c**). These were then subjected to the optimized coupling conditions as per Scheme 5. While aromatic iodides are expected to be significantly more activated than analogous bromides towards metal catalyzed couplings with boronic esters, this proved to not be the case in this situation as the yields obtained from these reactions are all lower than those involving bromoporphyrins **4a** and **4c**. Furthermore, the free base iodoporphyrin **12c** was as unreactive under these conditions as the free base bromoporphyrin tested previously.

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

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-flurophenyl	phenyl	**5e**	64
4f	1-ethylpropyl	phenyl	**5f**	Trace
4g	4-methylphenyl	hexyl	**5g**	8%
4h	1-ethylpropyl	butyl	**5h**	N/A

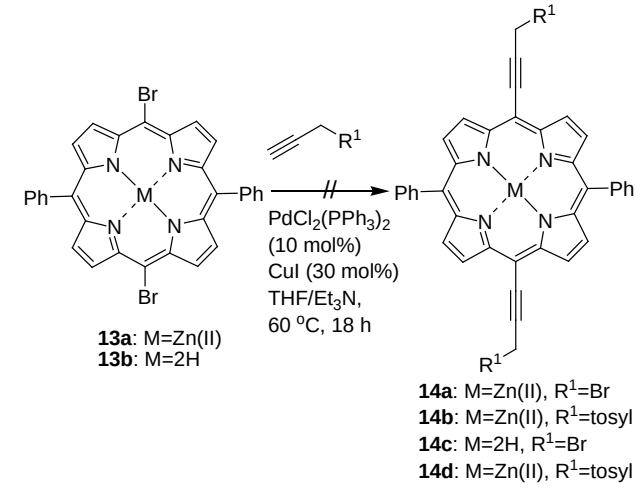
Allene synthesis *via* rearrangements of propargyl substituted porphyrins

While the Suzuki-Miyaura cross coupling reactions proved to be moderately successful for specific functional groups the scope of the reaction is quite narrow so attention turned to other applicable methods to introduce allenyl functionality. One of the most commonly employed syntheses for terminal allenes begins with propargyl electrophiles that bear a terminal leaving group.[19] Sonogashira cross-coupling is employed to introduce the desired propargyl residues to the precursor molecule.[20] Pd-catalyzed rearrangement and loss of the leaving group at the propargyl substituent then affords the terminal allene. The dibromoporphyrins **13a** and **13b** were dissolved in THF and treated with triethylamine, $PdCl_2(PPh_3)_2$, copper(I)iodide and the respective propargyl compound under reflux and an argon atmosphere (Scheme 6), analogous to the procedure reported for the preparation of arylethynylporphyrins and trimethylsilylethynylporphyrins.[21]



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

The dipropargylporphyrins **14a-d** could not be isolated, however, and only starting material and an insoluble polymer were obtained. Increasing the equivalents of CuI and triethylamine or decreasing the amount of porphyrin used did not lead to the desired products. A plausible explanation for this behavior is that the propargyl compounds necessarily carry good leaving groups and may react with themselves under the conditions employed. It is also possible that the desired porphyrins are formed, but react again with either the propargyl compound or starting dibromoporphyrin.

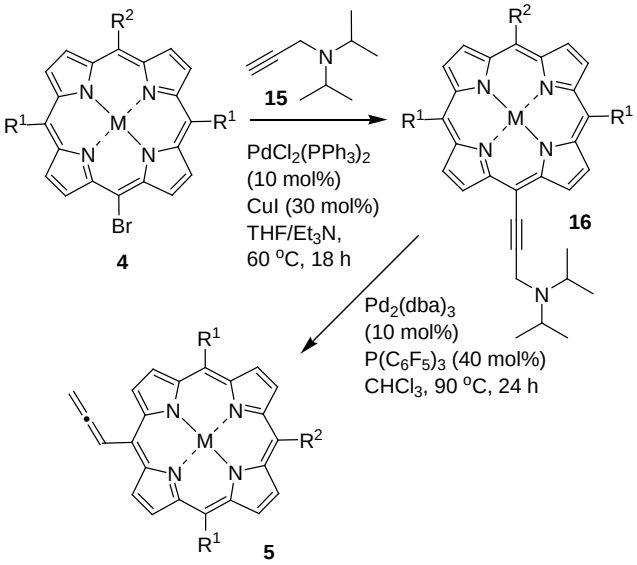


Scheme 6: Attempted Sonogashira cross-coupling reactions with dibromoporphyrins.

Attention then turned to less reactive propargyl groups that could be successfully coupled to the porphyrin core yet still retain reactivity to undergo the desired rearrangement to give allenylporphyrins. Work by Nakamura et al. utilizing propargyl amines followed by Pd-catalyzed hydrogen transfer is one of the more recent advances in this area which seemed to offer the best potential for success.[22] The first step of this synthesis involved a Sonogashira reaction analogous to that described in Scheme 5, using *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 heated to reflux in the presence of $Pd_2(dba)_3$ as the precatalyst and $P(C_6F_5)_3$ as the ligand source. This methodology was applied to a number of monobromonickel(II)porphyrins 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 tested using the Suzuki conditions previously (**4a-c**) proved to be similarly reactive under these Sonogashira/hydrogen transfer conditions. Residues such as 4-methoxyphenyl (**4d**) and 3-flurophenyl (**4e**) which showed diminished reactivity with relation to the more standard aromatic residues previously, showed practically equal reactivity under these conditions.

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



Starting Material	M	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-flurophenyl	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	2H	2-naphthalenyl	phenyl	**5l**	N/A
4l	2H	phenyl	phenyl	**5m**	N/A

The synthesis of allenylporphyrins bearing aliphatic residues, which could not be synthesized at all *via* Suzuki methodology, can easily be affected under these conditions. This is a particularly important strength of this methodology as it shows it to be a much more robust and versatile synthetic method than any described previously. This allows for the facile introduction of a terminal allene group to virtually any bromoporphyrin *via* 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 novel porphyrins incorporating the known nonplanar

properties of alkylporphyrins with the impressive optical properties of allenes.

In terms of the metalation state of the porphyrin, while the Suzuki/Miyaura conditions could only be employed with nickel(II)porphyrins, Cu(II) was successfully incorporated into an allenylporphyrin (**5j**) under these conditions, starting from the appropriately metalated bromoporphyrin **4i**. Successful synthesis of a Zn(II) or free base allenylporphyrin (**5k/l/m**), starting from the appropriate bromoporphyrin **4j/k/l**, could still not be achieved, however, as the reactions yielded a complex mixture of polymeric material. Zn(II)allenylporphyrin (**5k**) could be identified in trace amounts from this material but could not be isolated.

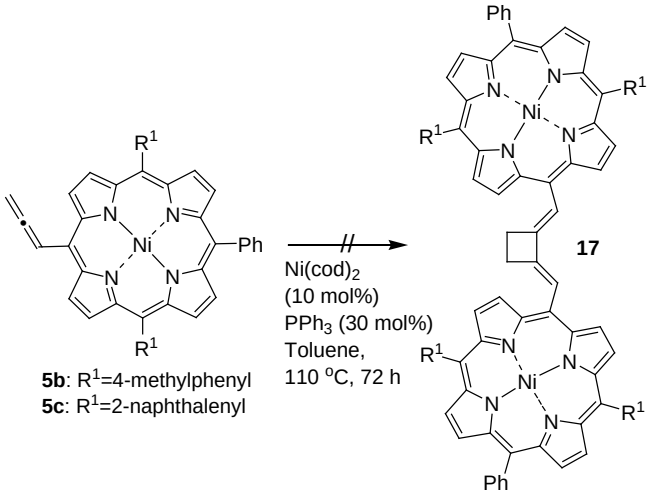
The solubility of the propargylporphyrins **16** posed one of the few issues with this synthesis. These porphyrins proved quite difficult to purify as the R_f on silica using chlorinated solvents was practically zero whereas, while using ethyl acetate, the target porphyrins co-eluted with the unreacted propargyl amines. This proved to be of only minor inconvenience as filtration through silica using dichloromethane as eluent served to remove any undesired porphyrin by-products. Changing the eluent to ethyl acetate yielded the crude target porphyrin in high enough purity to be subjected to the $Pd_2(dba)_3$ catalyzed rearrangement. The resultant allenyl porphyrin could then be easily purified via standard methods. As a result porphyrins of type **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 spectroscopic analysis become evident. First, in the ^{1}H NMR spectra the three allenic protons appear as a distinct doublet at 5.28 ppm representing the two terminal protons and a triplet at 8.26 ppm for the internal hydrogen atom. These signals possess a significant $^4J_{H\text{-}H}$ coupling constant of 6.9 Hz. In terms of the ^{13}C NMR spectra, the terminal carbon appears at 76.0 ppm, the porphyrin-adjacent carbon at 92.5 ppm and the highly deshielded internal carbon atom at 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 around 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 all shared across the library of allenylporphyrins synthesized and allow for quick and easy determination of the presence of the allenyl group.

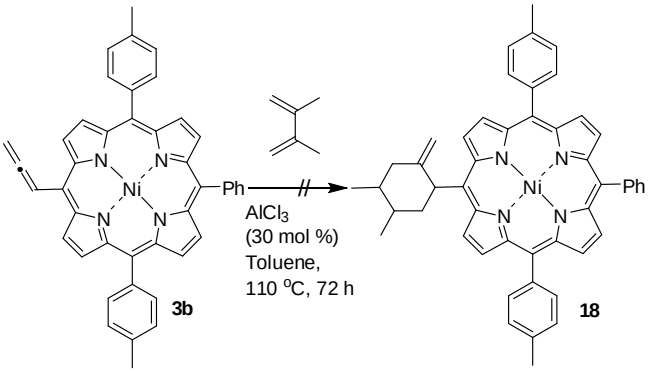
Reactivity of allenylporphyrins

With a library of allenylporphyrins at hand some exploratory reactions of the allenyl group were attempted and we focused on straightforward cyclizations reactions.[19a,23] It has long been known that allenes 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.* into the use of Ni(II) catalysts which promote regioselective dimerization of terminal allenes bonded to electron withdrawing groups[25] appealed to us, both as a simple method of testing the reactivity of the installed group as well as potentially making a rather interesting porphyrin dimer **17**. Scheme 7 illustrates the reaction conditions employed but regardless of porphyrin residues **5b** or **5c** employed, the best outcome after three days refluxing was only a crude HRMS spectrum showing trace product formation. While disappointing, this is not a thoroughly unexpected result, as the steric hindrance invoked by the porphyrin core, coupled with its electronic impact, obviously makes orientating both porphyrins for this cyclisation to occur highly demanding.



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

Perhaps the most straightforward cyclization reaction that allenes undergo is the classic Diels-Alder reaction.[26] Here one of the double bonds in the allenyl functional unit acts as the dienophile and readily reacts with an appropriate diene. Tailoring the electronics of the group attached to the terminal allene dictates which of the two possible double bonds is most amenable to act as the dienophile. Scheme 8 depicts the Diels-Alder attempt using **5b** as the allenylporphyrin together with 2,3-dimethyl-1,3-butadiene. However, no conversion to **18** was witnessed after 72 hours refluxing, with **5b** being completely recovered from the reaction. Again, steric encumbrance by the porphyrin core seems to be the most likely reason for the failure of **5b** to undergo any noticeable reactivity. The problem is doubly compounded here by the fact that the electronic withdrawing effect of the porphyrin is expected to activate the first, and therefore most sterically shielded, of the double bonds.



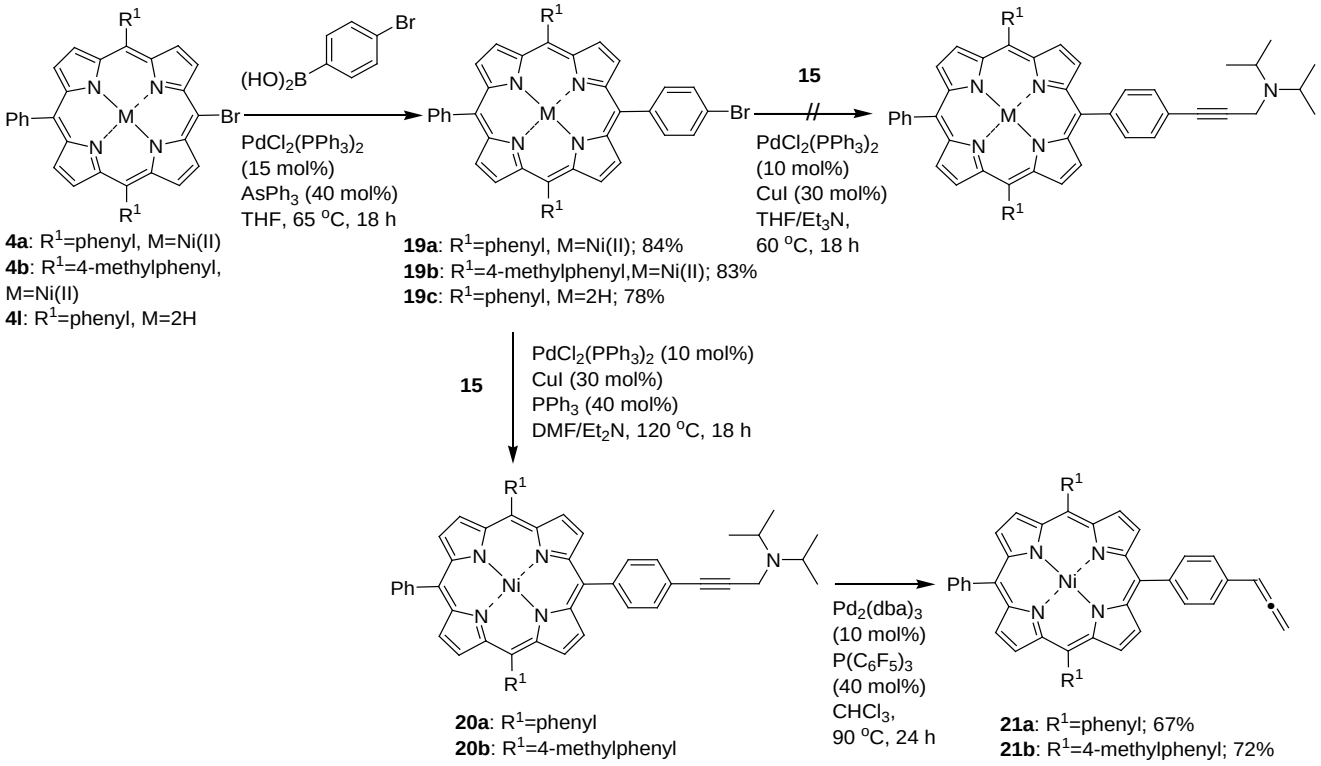
Scheme 8: Attempted Diels-Alder reaction using **5b** as the dienophile.

Due to this failure of the directly linked allenylporphyrins to display any further reactivity, we then looked towards installing a phenyl 'spacer' between the porphyrin core and the allene group. While theoretically a very simple proposition this proved to be somewhat more complicated an endeavor then initially expected. The first step of this synthesis involved taking the previously formed bromoporphyrin **4a** and performing a Suzuki/Miyaura cross coupling reaction with 4-bromophenylboronic acid (Scheme 9*)*. The target reaction proceeded quite readily, in spite of the obvious complications posed by the multiple aromatic bromides present, with the target porphyrin **19a** obtained in 84% yield. Compound **19a** was then subjected to standard Sonogashira coupling conditions, which had worked perfectly with bromoporphyrin **4a**. Interestingly, **19a** showed no reactivity under these conditions. This was quite an unusual result as on paper the more aromatic bromide in **19a** is expected to be more activated towards coupling reactions than the bromide in **4a**. The lowered reactivity of **19a** under these conditions may also help explain the high yield of the monobromophenyl product from the Suzuki reaction in lieu of any further-coupled derivatives.

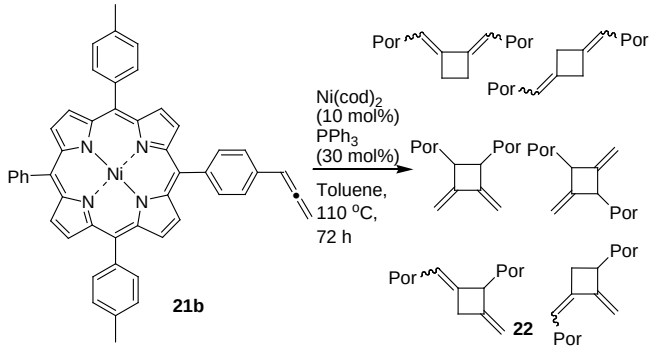
Initially the lack of reactivity of **19a** towards standard Sonogashira couplings was assumed to be a product of the known insolubility of nickel(II)tetraphenylporphyrin (NiTPP), which is obviously an intermediate in any catalytic coupling cycle of **19a**. However, installing different residues, 4-methylphenyl (**19b**), or changing the metalation of the porphyrin (**19c**) showed no increase in reactivity. As a result, much more forcing Sonogashira conditions were attempted. It was found that, by both increasing the catalyst turnover rate by changing the base to the less sterically hindered diethylamine and adding more ligand in the form of triphenylphosphine as well as increasing the reaction temperature by refluxing in DMF, almost quantitative coupling of **19a** and **19b** could be obtained after 24 hours. With the coupled products **20a/b** in hand the standard allene forming reaction proceeded readily to give **21a/b** in reasonable yield (Scheme 9).

With allenylporphyrins **21a/b** in hand we returned to probing the reactivity of the installed allenyl group. The first reaction attempted was the head to head dimerization described previously (c.f. Scheme 7). While the directly linked allenylporphyrins **5b** and **5c** exhibited only minimal activity the reactions with both **21a** and **21b** proceeded readily, with complete consumption of starting material after just 18 hours refluxing. Unfortunately, this reaction displayed none of the expected selectivity with regards to which of the allenic bonds reacts.[25] A complex mixture of poorly soluble dimers was the result of this synthesis, which could not be separated by column chromatography (Scheme 10). UV analysis showed negligible changes with respect to the starting material, which is to be 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 proved unsatisfactory in analyzing the cyclobutane region due to significant broadening of the NMR signals.

The next reaction performed was a Diels-Alder reaction using 1,3-cyclohexadiene as the diene and **21b** as the dienophile. Even after 3 days refluxing in toluene, no consumption of starting materials was observed. Literature examples quote Rh(I) salts as helping promote Diels-Alder reactions of allenes[23c,27] so $Cl_2Rh_2(cod)_2$ was added to help effect the desired reaction. **21b** was entirely consumed after 18 hours but the Diels-Alder product was obtained only in trace amounts as the dimerization reaction described in Scheme 10 proved to be the dominant reaction. This is an unsurprising result in certain regards as Rh(I) salts are also known to promote [2+2] additions of allenes. Nevertheless the [4+2] product was expected to be more favoured than the disallowed [2+2] addition.



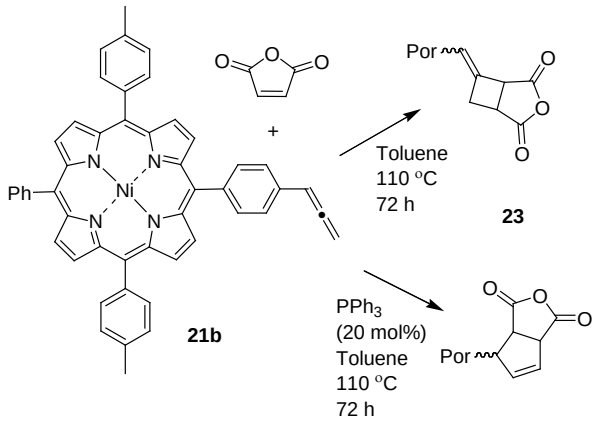
Scheme 9: Incorporation of a phenyl spacer into an allenylporphyrin.



Scheme 10: Ni(II) promoted dimerization of **21b** showing potential isomerisation patterns of cylcoadduct **22** which could not be isolated and resolved. (Por = Porphyrinoid core of **21b**).

This apparent preference for [2+2] cycloadditions led us to attempt a more straightforward reaction using the strongly electron deficient maleic anhydride. Here, in the absence of any additives, the [2+2] addition could be effected between **21b** and maleic anhydride after 3 days refluxing in toluene (Scheme 11). The resultant porphyrin exhibited extremely poor solubility and could not be purified by column chromatography. Both TLC and HRMS analysis indicate complete consumption of **21b** and formation of a [2+2] cycloadduct. Similarly, the IR spectrum of the product shows 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}. The regiochemistry of the addition could again not be determined as a clean ^1H NMR spectra could not be obtained.

Some very interesting research by Lu et al into the use of PPh_3 to effect the [3+2] addition of allenes[28] greatly interested us as a method to manufacture diverse ring systems from the allenic system. The reaction again took 3 days to go to completion with TLC and HRMS analysis indicating quantitative formation of a cycloadduct. Disappointingly, ^1H NMR analysis proved impossible so the method and regioselectivity of the addition still elude us. Solubility again is the major issue as the product of this reaction proved similarly impossible to column or to recrystallize cleanly. As a result we are unable to determine whether or not the desired [3+2] cycloaddition occurred or if the product is simply the [2+2] adducted formed previously.



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**).

Conclusions

The synthesis of allenylporphyrins has been thoroughly investigated with two high yielding methods allowing for their successful synthesis. Of these, 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 yield novel porphyrins bearing interesting structural, electronic and optical properties, further proving the synthetic utility of this porphyrin functional group.

Experimental Section

General Methods: All chemicals used were of analytical grade and purified before use. CH_2Cl_2 was dried with phosphorus pentoxide followed by distillation; THF was dried with sodium, followed by distillation. 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 are uncorrected and were measured with a Reichert Thermovar instrument. NMR spectra were recorded using Bruker DPX 400 (400.13 MHz for ^1H NMR and 100.61 MHz for ^{13}C NMR), Bruker AV 600 (600.13 MHz for ^1H NMR and 150.90 MHz for ^{13}C NMR) or Agilent MR400 (400.13 MHz for ^1H NMR and 100.61 MHz for ^{13}C NMR) instruments. Chemical shifts are given in ppm and referenced to $CDCl_3$. The assignment of the signals was confirmed by 2D spectra (COSY, HMBC, heteronuclear multiple quantum coherence) except for those porphyrins with low solubility. Mass spectra were recorded using 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 using a Micromass TOF instrument fitted with an EI probe. IR spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer.

Starting Materials: Formylporphyrins **1a**,[29] **1b**;[30] bromoporphyrins **4a,**[31] **4j,**[32] **4l**;[31] dipyrromethane[15], 5,15-disubstituted porphyrins: **8a**,[33] **8b**,[14b] **8c**,[34] **8d**,[14b] **8e**,[35] **8f**,[36] **10a**,[37] 5,10,15-triphenylporphyrin **9a** and the nickel(II) complex **11a**,[39] and 5,15-bis(4-methylphenyl)-10-phenylporphyrin **(9b)**[40] were prepared using standard methodologies and had analytical data consistent with that in the literature.

General Procedure A. Reaction with Phenyllithium: The free-base porphyrin was dissolved in THF in a Schlenk flask and degassed under high vacuum. The reaction vessel was then purged with argon before the drop-wise addition of PhLi (6 eq.) over 10 minutes. The solution was stirred at room temperature for two hours and then quenched by adding a solution of water in THF (1:4 v/v). 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 3 eq.) was added in CH_2Cl_2 (10 mL) and the solution left to oxidize for 30 minutes. Solvents were removed *in vacuo* and the crude product was then filtered through silica gel using CH_2Cl_2 as eluent. Removal of the solvents followed by recrystallization from $CHCl_3$/MeOH typically gave pure material.

General Procedure B. Nickel(II) Insertion: Free-base porphyrin and $Ni(acac)_2$ (3 eq.) were dissolved in toluene and heated to reflux. The reaction process was monitored by TLC and once all the starting material was consumed the reaction flask was allowed to cool and filtered through silica gel using CH_2Cl_2 as eluent. Removal of the solvents was followed by recrystallization from $CHCl_3$/MeOH.

General Procedure C. Reaction with Alkyllithium reagents: A nickel(II) porphyrin was dissolved in THF in a Schlenk flask and degassed under high vacuum. The reaction vessel was then purged with argon and cooled to -78 °C. The appropriate alkyllithium reagent (6 eq.) was added drop-wise over 10 minutes and the solution was stirred at -78 °C for 30 minutes and then quenched by adding a solution of water in THF (1:4 v/v). 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 3 eq.) was added in CH_2Cl_2 (10 mL) and the solution left to warm to room temperature. Solvents were removed *in vacuo* and the crude product was then filtered through silica gel using CH_2Cl_2 as eluent. Removal of the solvents was followed by recrystallization from $CHCl_3$/MeOH.

General Procedure D. Bromination of Porphyrins: This procedure was adapted from Boyle and co-workers.[17] The porphyrin was dissolved in $CHCl_3$ and NBS (3 eq.) and pyridine (0.3 mL) were added. The progress of the reaction was monitored by TLC and once all starting material had been consumed the reaction was filtered through silica gel. The solvents were then removed and the crude product purified by recrystallization from $CHCl_3$/MeOH.

General Procedure E. Synthesis of Allenylporphyrins *via* Suzuki/Miyaura Reactions with Allenylboronic Acid Pinnacol Ester: The appropriate bromoporphyrin, $PdCl_2$(dppe) (15 mol%) and K_2CO_3 (10 eq.) were added to an oven dried Schlenk flask equipped with a magnetic stirrer bar. The contents of the flask were heated under vacuum. Anhydrous THF was added and the solution frozen and thawed under vacuum three times before being released to argon. The contents of the flask were then heated to reflux for 72 hours. The crude material was purified by filtration through a short silica plug using CH_2Cl_2 as eluent followed by column chromatography.

General Procedure F. Synthesis of Allenylporphyrins *via* 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 equipped with a magnetic stirrer bar. The contents of the flask were heated under vacuum. Anhydrous THF and triethylamine (4:1, v/v) were added and the solution frozen and thawed under vacuum three times before being released to argon. *N*,*N*-diisopropylprop-2-yn-1-amine (**11**) (5 eq.) was added and the contents of the flask were heated to 60 °C for 24 hours. The crude material was purified by filtration through a short silica plug using CH_2Cl_2 as eluent to remove any unreacted starting material. The eluent was then changed to EtOAc to yield crude alkyne-coupled porphyrin, which was typically used without any further purification. This intermediate was dried *in vacuo* and transferred to a small RBF. Dry $CHCl_3$, $Pd_2(dba)_3$ (10 mol%) and $P(C_6F_5)_3$ (40 mol%) were added and the solution degassed with argon over 10 minutes before being heated to 90 °C for 24 hours. The crude material was purified by filtration through silica gel using $CHCl_3$ as eluent. Column chromatography and recrystallization were performed as required.

General procedure G. Synthesis of Phosphonates: Tetra(isopropyl) methylenebisphosphonate (1 eq.) was added to a suspension of sodium hydride (1.5 eq.) in dry THF at 0 °C. The mixture was stirred for 30 min before the respective aldehyde was added. The solution was stirred overnight at room temperature. Subsequently, the reaction mixture was quenched with saturated NH_4Cl-solution, 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 by reaction of **1a** (300 mg, 0.55 mmol) following General Procedure G. The first fraction of column chromatography on silica gel eluting with ethyl acetate: *n*-hexane (4:1, v/v) gave the pure product as purple crystals after recrystallization from dichloromethane/methanol (284.9 mg, 0.4 mmol, 73%). M.p. 183 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.47 (d, $^3J_{H\text{-}H}$ = 6.0 Hz, 6H, CH_3), 1.50, (d, $^3J_{H\text{-}H}$ = 6.3 Hz, 6H, CH_3), 4.95 (m, 2H, CH(CH_3)$_2$), 6.24 (t, $^3J_{HHP}$ = 17.9 Hz, 2H, CH=CH-P), 7.74 (m, 6H, Ar$_H$), 8.02 (m, 4H, Ar$_H$), 8.83 (d, $^3J_{H\text{-}H}$ = 4.8 Hz, 2H, H_β), 8.90 (d, $^3J_{H\text{-}H}$ =5.0 Hz, 2H, H_β), 9.08 (d, $^3J_{H\text{-}H}$ =4.5 Hz, 2H, H_β), 9.43 (d, $^3J_{H\text{-}H}$ =4.8 Hz, 2H, H_β), 9.72 (s, 1H, H_{meso}), 9.79 ppm (dd, $^3J_{HHP}$=17.1 Hz, $^2J_{HP}$=22.1 Hz, 1H, CH=CH-P); ^{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 and 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) = 415 (5.17), 529 (4.17), 566 nm (3.87); HRMS (ES$^+$) [$C_{40}H_{35}N_4NiO_3P$+H]: calcd 709.1879, found 709.1862.

[2-(*E*)-Di(isopropyl)ethenylphosphono-5,10,15,20-tetrakis(1-ethylpropyl)porphyrinato]nickel(II) (2b): Prepared by reaction of **1b** (300mg, 0.46 mmol) following General Procedure G. The first fraction of column chromatography on silica gel eluting with ethyl acetate : *n*-hexane (4:1, v/v) gave the pure product as purple crystals after recrystallization from 1,4-dioxane/water (312.3 mg, 0.37 mmol, 80%): M.p. 144 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.88 (t, $^3J_{H\text{-}H}$ = 7.3 Hz, 6H, CH_2CH_3), 1.01 (t, $^3J_{H\text{-}H}$ = 7.3 Hz, 18H, CH_2CH_3), 1.59 (d, $^3J_{H\text{-}H}$ = 6.4 Hz, 6H, (CH_3)$_2$CH), 1.61 (d, $^3J_{H\text{-}H}$ = 6.4 Hz, 6H, (CH_3)$_2$CH), 2.68 (m, 16H, CH_2CH_3), 4.14 (t, $^3J_{H\text{-}H}$ = 7.0 Hz, 1H, CHCH$_2$), 4.23 (m, 3H, CHCH$_2$), 4.94 (m, 2H, CHCH$_3$), 6.24 (dd, $^3J_{H\text{-}H}$ = 16.9 Hz, $^3J_{H\text{-}H}$ = 20.5 Hz, 1H, CH=CH-P), 8.80 (dd, $^3J_{HHP}$ = 16.9 Hz, $^2J_{HP}$ = 20.5 Hz, 1H, CH=CH-P), 9.16 (d, $^3J_{H\text{-}H}$ = 4.7 Hz, 1H, H_β), 9.19 (s, 4H, H_β), 9.23 (s, 1H, H_β), 9.26 ppm (d, $^3J_{H\text{-}H}$ = 5.3 Hz, 1H, H_β); ^{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 and 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) = 431 (4.70), 556 (3.91), 593 nm (3.54); HRMS (ES$^+$) [$C_{48}H_{67}N_4NiO_3P$+H]: calcd 837.4383, found 837.4377.

(*E*)-Diisopropyl-3-nitrostyrylphosphonate (2c): Prepared by reaction of 3-nitrobenzaldehyde (1g, 6.6 mmol) following General Procedure G. The first fraction of column chromatography on silica gel eluting with ethyl acetate: *n*-hexane (4:1, v/v) gave the pure product as yellow crystals after recrystallization from dichloromethane/methanol (1.71 g, 5.6 mmol) in 85 % yield: M.p. 64 °C. Compound had data consistent with that in the literature.[38]

(*E*)-Diisopropyl-3,4,5-trimethoxystyrylphosphonate (2d): Prepared by reaction of 3,4,5-trimethoxbenzaldehyde (1g, 5 mmol) following General Procedure G. The first fraction of column chromatography on silica gel eluting with ethyl acetate : *n*-hexane (4:1, v/v) gave the pure product as white crystals after recrystallization from dichloromethane/methanol (1.74 g, 5.0 mmol) in 99 % yield: M.p. 77 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.34 (d, $^3J_{H\text{-}H}$ = 6.0 Hz, 6H, CH_3), 1.38 (d, $^3J_{H\text{-}H}$ = 6.3 Hz, 6H, CH_3), 3.88 (s, 3H, 4-OCH_3), 3.89 (s, 6H, 3,5-OCH_3), 4.72 (m, 2H, CH(CH$_3$)$_2$); 6.17 (t, $^3J_{HHP}$ = 17.2 Hz, 1H, CH), 6.73 (s, 2H, Ar$_H$), 7.40 ppm (dd, $^3J_{HHP}$ = 17.3 Hz, $^2J_{HP}$ = 22.3 Hz, 1H, CH), ^{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: ν = 1120 cm^{-1} (P-O-alkyl), 1232 (P=O), 1377 (d, C(CH$_3$)$_2$); HRMS (ES$^+$) [2×$C_{17}H_{27}O_6P$]: calcd 739.2988, found 739.2980.

[5-Bromo-10,20-bis(4-methylphenyl)-15-phenylporphyrinato]nickel(II) (4b): Synthesized *via* General Procedure D from **11b** (500 mg, 0.79 mmol) and NBS (420 mg, 2.4 mmol) in $CHCl_3$ (200 mL). Yield: purple crystals (0.74 mmol, 521 mg, 94%); M.p. >223 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.65 (s, 6H, tolyl-CH_3), 7.48 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 4H, tolyl-*o*-CH), 7.65-7.69 (m, 3H, Ph-*o*/*p*-CH), 7.85 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 4H, tolyl-*m*-CH), 7.96-7.98 (m, 2H, Ph-*m*-CH), 8.67 (d, $^3J_{H\text{-}H}$ = 5.0 Hz, 2 H, H_β), 8.70 (d, $^3J_{H\text{-}H}$

= 5.0 Hz, 2H, H_β), 8.80 (d, $^3J_{H\text{-}H}$ = 5.0 Hz, 2H, H_β), 9.49 ppm (d, $^3J_{H\text{-}H}$ = 5.0 Hz, 2H, H_β); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 21.5, 102.1, 119.4, 119.5, 126.9, 127.1, 127.7, 127.8, 128.7, 132.4, 132.6, 133.0, 133.3, 133.55, 133.6, 137.5, 140.6, 142.3, 142.9 and 143.2 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 427 (5.10), 545 nm (3.99); HRMS (Maldi) *m/z* calcd. for $C_{40}H_{27}BrN_4Ni$ $[M]^+$: 700.0773, found 700.0748.

[5-Bromo-10,20-bis(2-naphthalenyl)-15-phenylporphyrinato]nickel(II) (4c): Synthesized *via* General Procedure D from **11c** (500 mg, 0.72 mmol) and NBS (380 mg, 2.15 mmol) in $CHCl_3$ (200 mL). Yield: purple crystals (0.70 mmol, 542 mg, 97%); M.p. 255 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.65-7.70 (m, 7H, Ar-C*H*), 7.97-7.99 (m, 2H, Naph-C*H*), 8.01-8.03 (m, 2H, Naph-C*H*), 8.13-8.17 (m, 6H, Ar-C*H*), 8.43 (s, 2H, Naph-C*H*), 8.67 (s, 4H, H_β), 8.80 (d, $^3J_{H\text{-}H}$ = 5.0 Hz, 2H, H_β), 8.95 ppm (d, $^3J_{H\text{-}H}$ = 5.0 Hz, 2H, H_β); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 102.4, 119.4, 119.7, 126.2, 126.7, 126.8, 126.9, 126.95, 127.9, 131.7, 132.2, 132.6, 132.7, 132.8, 133.3, 133.4, 133.6, 137.9, 140.5, 142.5, 143.0, 143.1 and 143.3 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 420 (5.38), 533 nm (4.28); HRMS (Maldi) *m/z* calcd. for $C_{46}H_{27}BrN_4Ni$ $[M]^+$: 772.0773, found 772.0739.

[5-Bromo-10,20-bis(4-methoxyphenyl)-15-phenylporphyrinato]nickel(II) (4d): Synthesized *via* General Procedure D from **11d** (500 mg, 0.76 mmol) and NBS (407 mg, 2.29 mmol) in $CHCl_3$ (200 mL). Yield: purple crystals (0.72 mmol, 530 mg, 95%); M.p. 210 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.04 (s, 6H, OC*H*$_3$), 7.21 (d, $^3J_{H\text{-}H}$ = 8.6 Hz, 4H, C_6H_4OMe-*o*-C*H*), 7.65-7.67 (m, 3H, Ph-*o/p*-C*H*), 7.88 (d, $^3J_{H\text{-}H}$ = 8.6 Hz, 4H, C_6H_4OMe-*m*-C*H*), 7.96 (m, 2H, Ph-*m*-C*H*), 8.67 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 8.70 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 8.80 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.48 ppm (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 55.5, 112.5, 112.6, 119.2, 119.4, 126.9, 127.8, 132.4, 132.6, 132.8, 133.0, 133.3, 133.5, 133.6, 134.6, 134.7, 142.3, 142.9, 143.2, 143.4 and 159.5 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 421 (5.33), 536 nm (4.21); HRMS (Maldi) *m/z* calcd. for $C_{40}H_{27}BrN_4NiO_2$ $[M]^+$: 732.0671, found 732.0667.

[5-Bromo-10,20-bis(3-fluorophenyl)-15-phenylporphyrinato]nickel(II) (4e): Synthesized *via* General Procedure D from **11e** (590 mg, 0.93 mmol) and NBS (496 mg, 2.79 mmol) in $CHCl_3$ (250 mL). Yield purple crystals (0.86 mmol, 614 mg, 93%); M.p. 186 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 7.41-7.45 (m, 2H, Ar-C*H*), 7.59-7.73 (m, 9H, Ar-C*H*), 7.96 (m, 2H, Ar-C*H*), 8.66 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 8.71 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 8.72 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.45 ppm (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β); ^{19}F NMR (400 MHz, $CDCl_3$, 25 °C): -114.55 ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 102.5, 114.9, 115.1, 117.9, 119.9, 120.6, 120.9, 126.9, 127.9, 128.3, 128.4, 129.6, 132.3, 132.9, 133.0, 133.4, 133.5, 133.6, 140.3, 142.4, 142.5, 142.7, 143.2, 160.2 and 162.7 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 417 (5.36), 532 nm (4.23); HRMS (Maldi) *m/z* calcd. for $C_{38}H_{21}BrF_2N_4Ni$ $[M]^+$: 708.0271, found 708.0255.

[5-Bromo-10,20-bis(1-ethylpropyl)-15-phenylporphyrinato]nickel(II) (4f): Synthesized *via* General Procedure D from **11f** (500 mg, 0.86 mmol) and NBS (457 mg, 2.57 mmol) in $CHCl_3$ (250 mL). Yield: purple crystals (0.81 mmol, 487 mg, 94%); M.p. 232 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.89 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 12H, alkyl-C*H*$_3$), 2.55-2.67 (m, 8H, alkyl-C*H*$_2$), 4.31 (m, 2H, alkyl-C*H*), 7.64-7.66 (m, 3H, Ph-*o/p*-C*H*), 7.93-7.95 (m, 2H, Ph-*m*-C*H*), 8.65 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.26 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.36 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.43 ppm (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 13.9, 33.6, 49.4, 100.9, 118.1, 121.7, 126.9, 127.7, 131.0, 131.8, 132.5, 133.2, 133.4 and 140.4 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 424 (5.22), 548 (4.14), 589 nm (3.60); HRMS (Maldi) *m/z* calcd. for $C_{36}H_{35}BrN_4Ni$ $[M]^+$: 660.1399, found 660.1421.

[5-Bromo-10,20-bis(4-methylphenyl)-15-hexylporphyrinato]nickel(II) (4g): Synthesized *via* General Procedure D from **11g** (500 mg, 0.79 mmol) and NBS (423 mg, 2.37 mmol) in $CHCl_3$ (250 mL). Yield: purple crystals (0.73 mmol, 516 mg, 92%); M.p. 237 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.88 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 3H, hexyl-C*H*$_3$), 1.28-1.41 (m, 6H, hexyl-C*H*$_2$), 2.25 (m, 2H, hexyl-C*H*$_2$), 2.65 (s, 3H, tolyl-C*H*$_3$), 4.46 (m, 2H, hexyl-C*H*$_2$), 7.45 (d, $^3J_{H\text{-}H}$ = 7.6 Hz, 4H, tolyl-*o*-C*H*), 7.79 (d, $^3J_{H\text{-}H}$ = 7.6 Hz, 4H, tolyl-*m*-C*H*), 8.70 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 4H, H_β), 9.18 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.38 ppm (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.1, 21.5, 22.6, 30.0, 31.7, 34.2, 37.4, 118.8, 119.4, 127.6, 127.7, 129.7, 132.8, 133.2, 133.4, 133.5, 137.5, 142.1, 142.2 and 142.5 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 422 (5.28), 538 nm (4.17); HRMS (Maldi) *m/z* calcd. for $C_{40}H_{35}BrN_4Ni$ $[M]^+$: 708.1399, found 708.1406.

[5-Bromo-10,20-bis(1-ethylpropyl)-15-(*n*-butyl)porphyrinato]nickel(II) (4h): Synthesized *via* General Procedure D from **11h** (500 mg, 0.89 mmol) and NBS (475 mg, 2.67 mmol) in $CHCl_3$ (250 mL). Yield purple: crystals (0.79 mmol, 508 mg, 89%); M.p. 190 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.89 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 12H, alkyl-C*H*$_3$), 1.01 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 3H, butyl-C*H*$_3$), 1.54 (m, 2H, butyl-C*H*$_2$), 2.20 (m, 2H, butyl-C*H*$_2$), 2.54-2.68 (m, 8H, alkyl-C*H*$_2$), 4.25 (m, 2H, alkyl-C*H*), 4.40 (t, $^3J_{H\text{-}H}$ = 8.0 Hz, 2H, butyl-C*H*$_2$), 9.18 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.28 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2 H, H_β), 9.30 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.35 ppm (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 13.9, 14.0, 23.4, 33.5, 39.2, 49.3, 100.1, 118.2, 121.2, 130.0, 131.2, 131.8, 132.9, 140.2 and 140.5 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 423 (5.30), 546 (4.14), 588 nm (3.52); HRMS (Maldi) *m/z* calcd. for $C_{34}H_{39}BrN_4Ni$ $[M]^+$: 640.1712, found 640.1696.

[5-Bromo-10,20-bis(2-naphthalenyl)-15-phenylporphyrinato]copper(II) (4i): Porphyrin **4k** (270 mg, 0.38 mmol) and copper(II)acetylacetonate (306 mg, 1.1 mmol) were dissolved in toluene and brought to reflux. Reaction progress was monitored by TLC and once all the starting material had been consumed the reaction was stopped by filtration through silica. Product was recrystallized form $CHCl_3$/MeOH. Yield: purple crystals (0.35 mmol, 273 mg, 92%); M.p. >300 °C; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 422 (5.86), 546 (4.63), 583 nm (3.99); HRMS (Maldi) *m/z* calcd. for $C_{46}H_{27}BrN_4Cu$ $[M]^+$: 777.0715, found 777.0717.

[5,10,15-Triphenyl-20-propadienylporphyrinato]nickel(II) (5a): *Method 1*: Synthesized *via* General Procedure E 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). Product purified by column chromatography (*n*-hexane: CH_2Cl_2, 3:1, v/v). Yield: purple crystals (91 mg, 143 µmol, 88%). *Method 2*: Synthesized *via* General Procedure E 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). Product purified by column chromatography (*n*-hexane: CH_2Cl_2, 3:1, v/v). Yield: purple crystals (22 mg, 35 µmol, 42%). *Method 3*: Synthesized *via* General Procedure F 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). 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). Product purified by column chromatography (*n*-hexane:CH_2Cl_2, 3:1, v/v) to yield purple crystals (157 mg, 0.24 mmol, 79%). M.p. >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): 5.32 (d, $^4J_{H\text{-}H}$ = 6.8 Hz, 2H, allene–C*H*$_2$), 7.70 (m, 9H, Ph-*m/p*-C*H*), 8.01 (m, 6H, Ph-*o*–C*H*), 8.31 (t, $^4J_{H\text{-}H}$ = 6.8 Hz, 1H, allene–C*H*), 8.67 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 8.69 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 8.80 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.46 ppm (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): 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 and 216.6 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 421 (5.41), 535 (4.31), 575 (3.81); HRMS (Maldi) *m/z* 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 *via*

General Procedure E 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). Product purified by column chromatography (*n*-hexane:CH_2Cl_2, 6:1, v/v). Yield: purple crystals (41 mg, 61 µmol, 78%). *Method 2*: Synthesized *via* General Procedure F 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). 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). Product purified by column chromatography (*n*-hexane: CH_2Cl_2, 6:1, v/v) to yield purple crystals (155 mg, 0.24 mmol, 84%); M.p. >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.64 (s, 6H, tolyl-CH_3), 5.28 (d, $^4J_{H\text{-}H}$ = 6.9 Hz, 2H, allene-CH_2), 7.47 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 4H, tolyl-*o*-C*H*), 7.65-7.67 (m, 3H, Ph-*o/p*-C*H*), 7.86 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 4H, tolyl-*m*-C*H*), 7.96-7.97 (m, 2H, Ph-*m*-C*H*), 8.26 (t, $^4J_{H\text{-}H}$ = 6.9 Hz, 1H, allene-C*H*), 8.65 (d, $^3J_{H\text{-}H}$ = 5.0 Hz, 2H, H_β), 8.68 (d, $^3J_{H\text{-}H}$ = 5.0 Hz, 2H, H_β), 8.80 (d, $^3J_{H\text{-}H}$ = 5.0 Hz, 2H, H_β), 9.41 ppm (d, $^3J_{H\text{-}H}$=5.0 Hz, 2H, 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 and 215.9 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 422 (5.10), 536 (4.07), 623 nm (3.42); IR (neat): ν = 2962.6, 2918.4, 1939.4 cm^{-1}; HRMS (Maldi) *m/z* calcd. for $C_{43}H_{30}N_4Ni$ $[M]^+$: 660.1824, found 660.1848; LRMS (ESI+, 150V): 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 *via* General Procedure E 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). Product purified by column chromatography (*n*-hexane: CH_2Cl_2, 6:1, v/v). Yield: purple crystals (87 mg, 124 µmol, 91%). *Method 2*: Synthesized *via* General Procedure E 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). Product purified by column chromatography (*n*-hexane: CH_2Cl_2, 6:1, v/v). Yield: purple crystals (70 mg, 100 µmol, 73%). *Method 3*: Synthesized *via* General Procedure F 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). 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). Product purified by column chromatography (*n*-hexane:CH_2Cl_2, 6:1, v/v) to yield purple crystals (180 mg, 0.25 mmol, 82%); M.p. >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 5.27 (d, $^4J_{H\text{-}H}$ = 6.9 Hz, 2H, allene-CH_2), 740-7.42 (m, 2H, naph-C*H*), 7.65-7.70 (m, 7 H, Ar-C*H*), 7.97-8.01 (m, 2H, naph-C*H*), 8.08-8.17 (m, 6H, Ar-C*H*), 8.23 (t, $^4J_{H\text{-}H}$ = 6.9 Hz, 1H, allene-C*H*), 8.42 (s, 2H, naph-C*H*), 8.69 (s, 4H, H_β), 8.78 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.39 ppm (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β); ^{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 and 216.0 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 423 (5.19), 536 nm (4.14); IR (neat): 3051.3, 2962.9, 1939.1 cm^{-1}; HRMS (Maldi) *m/z* calcd. for $C_{49}H_{30}N_4Ni$ $[M]^+$: 732.1824, found 732.1810; LRMS (ESI+, 150V): 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 *via* General Procedure F 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). 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). Product purified by column chromatography (*n*-hexane:CH_2Cl_2, 4:1, v/v) to yield purple crystals (0.27 mmol, 189 mg, 68%); M.p. 248 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.03 (s, 6H, OCH_3), 5.28 (d, $^4J_{H\text{-}H}$ = 6.8 Hz, 2H, allene-CH_2), 7.19 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 4H, C_6H_4OMe-*o*-C*H*), 7.63-7.65 (m, 3H, Ph-*o/p*-C*H*), 7.87 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 4H, C_6H_4OMe-*m*-C*H*), 7.94-7.96 (m, 2H, Ph-*m*-C*H*), 8.27 (t, $^4J_{H\text{-}H}$ = 6.8 Hz, 1H, allene-C*H*), 8.63 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 8.67 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 8.78 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.40 ppm (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β); ^{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 and 206.9 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 424 (5.19), 538 nm (4.09); IR (neat): ν = 2961.0, 2928.0, 2831.3, 1944.3 cm^{-1}; HRMS (Maldi) *m/z* calcd. for $C_{43}H_{30}N_4NiO_2$ $[M]^+$: 692.1722, found 692.1722; LRMS (ESI+, 200V): 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 *via* General Procedure E 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). Product purified by column chromatography (*n*-hexane:CH_2Cl_2, 5:1, v/v). Yield: purple crystals (30 mg, 45 µmol, 64%). *Method 2*: Synthesized *via* General Procedure F 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). 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). Product purified by column chromatography (*n*-hexane: CH_2Cl_2, 5:1, v/v) to yield purple crystals (137 mg, 0.20 mmol, 73%); M.p. 285 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 5.30 (d, $^4J_{H\text{-}H}$ = 6.9 Hz, 2H, allene-CH_2), 7.40-7.44 (m, 2H, Ar-C*H*), 7.61-7.76 (m, 9H, Ar-C*H*), 7.96 (m, 2H, Ar-C*H*), 8.27 (t, $^4J_{H\text{-}H}$ = 6.9 Hz, 1H, allene-C*H*), 8.63 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 8.68 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 8.75 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.43 ppm (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β); ^{19}F NMR (400 MHz, $CDCl_3$, 25 °C): -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 and 216.1 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 420 (5.18), 536 (4.15), 673 nm (3.34); IR (neat): ν = 2922.3, 2851.5, 1938.5 cm^{-1}; HRMS (Maldi) *m/z* calcd. for $C_{41}H_{24}F_2N_4Ni$ $[M]^+$: 668.1323, found 668.1305; LRMS (ESI+, 150V): 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 *via* General Procedure F 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). 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). Product purified by column chromatography (*n*-hexane:CH_2Cl_2, 7:1, v/v). Yield: purple crystals (0.18 mmol, 112 mg, 45%); M.p. >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.88 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 12H, alkyl-CH_3), 2.54-2.69 (m, 8H, alkyl-CH_2), 4.24-4.32 (m, 2H, alkyl-C*H*), 5.25 (d, $^4J_{H\text{-}H}$ = 6.9 Hz, 2H, allene-CH_2), 7.63-7.66 (m, 3H, Ph-*o/p*-C*H*), 7.91-7.93 (m, 2H, Ph-*m*-C*H*), 8.16 (t, $^4J_{H\text{-}H}$ = 6.9 Hz, 1H, allene-C*H*), 8.60 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.21 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.32 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.36 ppm (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β); ^{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 and 215.9 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 428 (5.20), 549 (4.14), 595 nm (3.79); IR (neat): ν = 2958.9, 2921.9, 2851.5,

1938.2 cm^{-1}; HRMS (Maldi) *m/z* calcd. for $C_{39}H_{38}N_4Ni$ $[M]^+$: 620.245, found 620.2434; LRMS (ESI+, 200V): 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 *via* General Procedure F 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). 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). Product purified by column chromatography (*n*-hexane:CH_2Cl_2, 8:1, v/v) to yield purple crystals (0.15 mmol, 105 mg, 53%); M.p. > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.92 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 3H, hexyl-CH_3), 1.28-1.40 (m, 6H, hexyl-CH_2), 2.22-2.28 (m, 2H, hexyl-CH_2), 2.64 (s, 3H, tolyl-CH_3), 4.49-4.54 (m, 2H, hexyl-CH_2), 5.25 (d, $^4J_{H\text{-}H}$ = 6.9 Hz, 2H, allene-CH_2), 7.46 (d, $^3J_{H\text{-}H}$ = 7.7 Hz, 4H, tolyl-*o*-C*H*), 7.83 (d, $^3J_{H\text{-}H}$ = 7.7 Hz, 4H, tolyl-*m*-C*H*), 8.21 (t, $^4J_{H\text{-}H}$ = 6.9 Hz, 1H, allene-C*H*), 8.71 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 8.73 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.21 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.35 ppm (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β); ^{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 and 215.9 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 424 (5.15), 541 (4.01), 587 nm (3.47); IR (neat): ν = 2858.2, 2919.1, 2850.4, 1939.6 cm^{-1}; HRMS (Maldi) *m/z* 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 *via* General Procedure F 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). 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). Product purified by column chromatography (*n*-hexane: CH_2Cl_2, 8:1, v/v) to yield purple crystals (74 mg, 0.12 mmol, 44%); M.p. 164 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.88 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 12H, alkyl-CH_3), 0.99 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 3H, butyl-CH_3), 1.51 (m, 2H, butyl-CH_2), 2.17 (m, 2H, butyl-CH_2), 2.53-2.68 (m, 8H, alkyl-CH_2), 4.23 (m, 2H, alkyl-C*H*), 4.40 (t, $^3J_{H\text{-}H}$ = 8.0 Hz, 2H, butyl-CH_2), 5.22 (d, $^4J_{H\text{-}H}$ = 6.9 Hz, 2H, allene-CH_2), 8.11 (t, $^4J_{H\text{-}H}$ = 6.9 Hz, 1H, allene-C*H*), 9.14 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.26 (m, 4H, H_β), 9.30 ppm (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β); ^{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 and 215.8 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 429 (5.24), 552 (4.17), 594 nm (3.82); IR (neat): ν = 2956.6, 2924.2, 2866.9, 1938.3, 1641.3 cm^{-1}; HRMS (Maldi) *m/z* calcd. for $C_{37}H_{42}N_4Ni$ $[M]^+$: 600.2763, found 600.2755; LRMS (ESI+, 200V): 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 *via* General Procedure F 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). 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). Product purified by column chromatography (*n*-hexane:CH_2Cl_2, 6:1, v/v) to yield red/purple crystals (104 mg, 0.14 mmol, 47%); M.p. > 300 °C; λ_{max} (log ε) = 427 (5.95), 549 (4.76), 585 nm (4.31); HRMS (Maldi) *m/z* calcd. for $C_{49}H_{30}N_4Cu$ $[M]^+$: 737.1766, found 737.1743; LRMS (ESI+, 150V): 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-$C_{33}H_{11}CuN$).

5,15-Bis(2-naphthalenyl)-10-phenylporphyrin (9c): Synthesized *via* General Procedure A from **8c** (560 mg, 1.0 mmol) and PhLi (1.8M, 6 mmol, 3.3 mL) in THF (300 mL). Yield purple solid (607 mg, 0.95 mmol, 95%); M.p. >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = -2.87 (s, 2H, N*H*), 7.76-7.79 (m, 7H, Ar-C*H*), 8.14-8.16 (m, 2H, naph-C*H*), 8.23-8.26 (m, 6H, Ar-C*H*), 8.46 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, 2H, naph-C*H*), 8.74 (s, 2H, naph-C*H*), 8.91 (d, $^3J_{H\text{-}H}$ = 4.8 Hz, 2H, H_β), 8.95 (d, $^3J_{H\text{-}H}$ = 4.8 Hz, 2H, H_β), 9.06 (d, $^3J_{H\text{-}H}$ = 4.8 Hz, 2H, H_β), 9.37 (d, $^3J_{H\text{-}H}$ = 4.8 Hz, 2H, H_β), 10.28 ppm (s, 1 H, meso-C*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 104.9, 119.5, 126.0, 126.6, 126.7, 127.0, 127.8, 128.0, 131.5, 132.3, 132.8, 133.9, 134.5, 139.3 and 142.5 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 416 (5.86), 511 (4.59), 546 (4.30), 584 (4.20), 642 nm (4.06); HRMS (ESI+) *m/z* calcd. for $C_{46}H_{31}N_4$ [M+H]: 639.2544, found 639.2549.

5,15-Bis(4-methoxyphenyl)-10-phenylporphyrin (9d): Synthesized *via* General Procedure A from **8d** (500 mg, 0.96 mmol) and PhLi (1.8M, 5.7 mmol, 3.3 mL) in THF (300 mL) to yield purple solid (517 mg, 0.86 mmol, 90%); M.p. 292 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = -2.95 (s, 2H, N*H*), 4.10 (s, 6H, OCH_3), 7.31 (d, $^3J_{H\text{-}H}$ = 8.6 Hz, 4H, C_6H_4OMe-*o*-C*H*), 7.74-7.78 (m, 3H, Ph-*o*/*p*-C*H*), 8.15 (d, $^3J_{H\text{-}H}$ = 8.6 Hz, 4H, C_6H_4OMe-*m*-C*H*), 8.20-8.23 (m, 2H, Ph-*m*-C*H*), 8.86 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 8.93 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.05 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.31 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 10.19 ppm (s, 1 H, meso-C*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 55.6, 104.7, 112.4, 119.4, 120.4, 126.5, 127.7, 131.4, 134.1, 134.5, 135.7, 142.7 and 159.4 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 415 (5.47), 452 (4.31), 511 (4.22), 547(3.89), 586 nm (3.78); HRMS (Maldi) *m/z* calcd. for $C_{40}H_{30}N_4O_2$ $[M]^+$: 598.2369, found 598.2385.

5,15-Bis(3-fluorophenyl)-10-phenylporphyrin (9e): Synthesized *via* General Procedure A from **8e** (650 mg, 1.3 mmol) and PhLi (1.8M, 7.8 mmol, 4.4 mL) in THF (300 mL). Purified by column chromatography (*n*-hexane:CH_2Cl_2, 4:1, v/v). Yield: purple solid (582 mg, 1 mmol, 78%); M.p. 190 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = -3.02 (s, 2H, N*H*), 7.51-7.56 (m, 2H, Ar-C*H*), 7.72-7.81 (m, 5H, Ar-C*H*), 7.98-8.05 (m, 4H, Ar-C*H*), 8.21-8.24 (m, 2H, Ar-C*H*), 8.92 (s, 4H, H_β), 9.02 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.33 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 10.21 ppm (s, 1H, meso-C*H*); ^{19}F NMR (400 MHz, $CDCl_3$, 25 °C): -115.02 ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 105.0, 112.4, 114.8, 115.0, 118.0, 121.6, 121.8, 125.6, 126.6, 127.4, 127.5, 127.8, 128.1, 128.2, 129.0, 130.6, 130.7, 134.5, 134.6, 135.2, 142.4, 142.8, 142.9, 160.3 and 162.7 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 413 (5.48), 508 (4.21), 543 (3.76), 584 (3.76), 639 nm (3.46); HRMS (Maldi) *m/z* calcd. for $C_{38}H_{24}F_2N_4$ $[M]^+$: 574.1968, found 574.1974.

5,15-Bis(1-ethylpropyl)-10-phenylporphyrin (9f): Synthesized *via* General Procedure A from **8f** (500 mg, 1.1 mmol) and PhLi (1.8M, 6.6 mmol, 3.7 mL) in THF (300 mL) to yield a purple solid (561 mg, 1.07 mmol, 97%); M.p. >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = -2.47 (s, 2H, N*H*), 0.94 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 12H, alkyl-CH_3), 2.77-2.94 (m, 8H, alkyl-CH_2), 4.99-5.04 (m, 2H, alkyl-C*H*), 7.72-7.80 (m, 3H, Ph-*o*/*p*-C*H*), 8.18-8.20 (m, 2H, Ph-*m*-C*H*), 8.85 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.37 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.55 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.68 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 10.12 ppm (s, 1 H, meso-C*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.1, 30.9, 34.5, 49.9, 126.2, 127.6, 131.7, 131.8 and 134.2 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 411 (5.62), 511 (4.36), 544 (3.88), 586 (3.88), 640 nm (3.65); HRMS (Maldi) *m/z* calcd. for $C_{36}H_{38}N_4$ $[M]^+$: 526.3096, found 526.3085.

[5,15-Bis(1-ethylpropyl)porphyrinato]nickel(II) (10b): Synthesized via General Procedure B from **8f** (500 mg, 1.11 mmol) and $Ni(acac)_2$ (0.86 g, 3.33 mmol) in toluene (250 mL). Yield: purple crystals (546 mg, 1.07 mmol, 97%). M.p. >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.89 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 12H, alkyl-CH_3), 2.62-2.79 (m, 8H, alkyl-CH_2), 4.48 (m, 2H, alkyl-C*H*), 9.09 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 4H, H_β), 9.49 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 4H, H_β), 9.57 ppm (s, 2H, meso-C*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 13.9, 33.6, 49.4, 103.4, 120.0, 130.9 and 131.9 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 405 (5.42), 525 (4.22), 560 nm (3.71); HRMS (Maldi) *m/z* calcd. for $C_{30}H_{32}N_4Ni$ $[M]^+$: 506.1980, found 506.1958.

[5,15-Bis(4-methylphenyl)-10-phenylporphyrinato]nickel(II) (11b): Synthesized *via* General Procedure B from **9b** (650 mg, 1.14 mmol) and

$Ni(acac)_2$ (0.88 g, 3.44 mmol) in toluene (250 mL). Yield: purple solid (710 mg, 1.14 mmol, >99%); M.p. >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.66 (s, 6H, tolyl-CH_3), 7.49 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 4H, tolyl-*o*-C*H*), 7.66-7.68 (m, 3H, Ph-*o*/*p*-C*H*), 7.91 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 4H, tolyl-*m*-C*H*), 8.00-8.02 (m, 2H, Ph-*m*-C*H*), 8.75 (d, $^3J_{H\text{-}H}$ = 5.0 Hz, 2H, H_β), 8.79 (d, $^3J_{H\text{-}H}$ = 5.0 Hz, 2H, H_β), 8.91 (d, $^3J_{H\text{-}H}$ = 5.0 Hz, 2H, H_β), 9.12 (d, $^3J_{H\text{-}H}$ = 5.0 Hz, 2H, H_β), 9.82 ppm (s, 1H, meso-C*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 21.5, 104.5, 118.7, 119.3, 126.8, 127.6, 131.9, 132.0, 132.1, 132.6, 133.7, 137.4, 138.0, 142.3, 142.7, 142.8 and 142.9 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 409 (5.70), 522 (4.56), 552 (4.02) nm; HRMS (Maldi) *m/z* calcd. for $C_{40}H_{28}N_4Ni$ $[M]^+$: 622.1667, found 622.1664.

[5,15-Bis(2-naphthalenyl)-10-phenylporphyrinato]nickel(II) (11c): Synthesized *via* General Procedure B from **9c** (550 mg, 0.86 mmol) and $Ni(acac)_2$ (0.66 g, 2.58 mmol) in toluene (250 mL). Yield: purple solid (580 mg, 0.83 mmol, 97%); M.p. >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.69-7.74 (m, 7H, Ar-C*H*), 8.05-8.08 (m, 4H, Ar-C*H*), 8.17-8.19 (m, 4H, naph-C*H*), 8.25-8.27 (m, 2H, naph-C*H*), 8.52 (s, 2H, naph-C*H*), 8.81 (d, $^3J_{H\text{-}H}$ = 4.8 Hz, 2H, H_β), 8.83 (d, $^3J_{H\text{-}H}$ = 4.8 Hz, 2H, H_β), 8.93 (d, $^3J_{H\text{-}H}$ = 4.8 Hz, 2H, H_β), 9.16 (d, $^3J_{H\text{-}H}$ = 4.8 Hz, 2H, H_β), 9.88 ppm (s, 1 H, meso-C*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 104.8, 118.6, 119.6, 126.1, 126.6, 126.8, 126.9, 127.8, 128.0, 128.4, 131.9, 132.2, 132.3, 132.7, 132.8, 132.9, 133.7, 138.5, 142.5, 142.9 and 143.0 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 411 (5.69), 523 (4.58), 554 nm (4.10); HRMS (Maldi) *m/z* calcd. for $C_{46}H_{28}N_4Ni$ $[M]^+$: 694.1667, found 694.1678.

[5,15-Bis(4-methoxyphenyl)-10-phenylporphyrinato]nickel(II) (11d): Synthesized *via* General Procedure B from **9d** (500 mg, 0.84 mmol) and $Ni(acac)_2$ (0.64 g, 2.5 mmol) in toluene (250 mL). Yield: purple solid (550 mg, 0.84 mmol, >99%); M.p. 270 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.05 (s, 6H, OCH_3), 7.22 (d, $^3J_{H\text{-}H}$ = 8.6 Hz, 4H, C_6H_4OMe-*o*-C*H*), 7.66-7.68 (m, 3H, Ph-*o*/*p*-C*H*), 7.94 (d, $^3J_{H\text{-}H}$ = 8.6 Hz, 4H, C_6H_4OMe-*m*-C*H*), 8.00-8.02 (m, 2H, Ph-*m*-C*H*), 8.76 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 8.80 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 8.91 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.11 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.80 ppm (s, 1H, meso-C*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ =55.5, 104.5, 112.4, 118.3, 119.3, 126.8, 127.7, 131.9, 132.0, 132.5, 133.3, 133.7, 134.8, 141.2, 142.3, 142.7, 143.1, 143.2 and 159.4 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 410 (5.36), 523 (4.25), 553 nm (3.77); HRMS (Maldi) *m/z* calcd. for $C_{40}H_{28}N_4NiO_2$ $[M]^+$: 654.1566, found 654.1586.

[5,15-Bis(3-fluorophenyl)-10-phenylporphyrinato]nickel(II) (11e): Synthesized *via* General Procedure B from **9e** (550 mg, 0.96 mmol) and $Ni(acac)_2$ (0.74 g, 2.87 mmol) in toluene (250 mL). Yield: purple solid (594 mg, 0.94 mmol, 98%); M.p. 206 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.44-7.49 (m, 2H, Ar-C*H*), 7.61-7.73 (m, 5H, Ar-C*H*), 7.78-7.82 (m, 4H, Ar-C*H*), 8.04-8.06 (m, 2H, Ar-C*H*), 8.79 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 8.83 (m, 4H, H_β), 9.01 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.66 ppm (s, 1H, meso-C*H*); ^{19}F NMR (400 MHz, $CDCl_3$, 25 °C): -115.38 ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 104.8, 114.8, 115.0, 117.1, 119.8, 120.8, 121.0, 126.9, 127.9, 128.2, 128.3, 129.8, 131.8, 132.2, 132.4, 133.7, 140.9, 142.3, 142.5, 142.6, 142.9, 143.0, 143.1, 160.3 and 162.7 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 406 (5.31), 521 (4.16), 551 nm (3.74); HRMS (Maldi) *m/z* calcd. for $C_{38}H_{22}F_2N_4Ni$ $[M]^+$: 630.1166, found 630.1143.

[5,15-Bis(1-ethylpropyl)-10-phenylporphyrinato]nickel(II) (11f): Synthesized *via* General Procedure B from **9f** (500 mg, 0.95 mmol) and $Ni(acac)_2$ (0.73 g, 2.85 mmol) in toluene (250 mL). Yield: purple solid (561 mg, 0.92 mmol, 97%); M.p. >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.89 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 12H, alkyl-CH_3), 2.59-2.74 (m, 8H, alkyl-CH_2), 4.40-4.44 (m, 2H, alkyl-C*H*), 7.65-7.67 (m, 3H, Ph-*o*/*p*-C*H*), 7.96-7.98 (m, 2H, Ph-*m*-C*H*), 8.71 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.05 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.36 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.44 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.48 ppm (s, 1H, meso-C*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.0, 33.6, 49.4, 102.9, 117.7, 120.5, 126.8, 127.2, 128.7, 130.5, 131.1, 132.0, 133.5 and 140.1 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 413 (5.14), 532 nm (4.00); HRMS (Maldi) *m/z* calcd. for $C_{36}H_{36}N_4Ni$ $[M]^+$: 582.2293, found 582.2286.

[5-Hexyl-10,20-bis(4-methylphenyl)porphyrinato]nickel(II) (11g): Synthesized *via* General Procedure C from **10a** (500 mg, 0.91 mmol) and *n*-hexyl lithium (2.5 M, 5.5 mmol, 2.2 mL) in THF (250 mL). Yield: purple crystals (0.84 mmol, 530 mg, 92%); M.p. 258 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.90 (t, $^3J_{H\text{-}H}$ = 7.3 Hz, 3H, hexyl-CH_3), 1.30-1.36 (m, 2H, hexyl-CH_2), 1.38-1.44 (m, 2H, hexyl-CH_2), 1.61-1.64 (m, 2H, hexyl-CH_2), 2.32-2.36 (m, 2H, hexyl-CH_2), 2.67 (s, 3H, tolyl-CH_3), 4.63 (m, 2H, hexyl-CH_2), 7.49 (d, $^3J_{H\text{-}H}$ = 7.6 Hz, 4H, tolyl-*o*-C*H*), 7.90 (d, $^3J_{H\text{-}H}$ = 7.6 Hz, 4H, tolyl-*m*-C*H*), 8.84 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 8.86 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.03 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.34 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.66 ppm (s, 1 H, meso-C*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.1, 21.5, 22.7, 30.1, 31.8, 34.5, 37.7, 103.7, 118.0, 119.2, 127.6, 129.2, 131.8, 132.3, 132.5, 133.7, 137.3, 138.0, 141.9, 142.2, 142.3 and 142.7 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 410 (5.08), 525 (3.95), 555 nm (3.57); HRMS (Maldi) *m/z* calcd. for $C_{40}H_{36}N_4Ni$ $[M]^+$: 630.2293, found 630.2289.

[5-(*n*-Butyl)-10,20-bis(1-ethylpropylporphyrinato]nickel(II) (11h): Synthesized *via* General Procedure C from **10b** (500 mg, 0.99 mmol) and *n*-butyl lithium in THF (250 mL). Yield: purple crystals (0.87 mmol, 494 mg, 89%); M.p. 143 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.90 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 12H, alkyl-CH_3), 1.03 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 3H, butyl-CH_3), 1.57 (m, 2H, butyl-CH_2), 2.27 (m, 2H, butyl-CH_2), 2.58-2.75 (m, 8H, alkyl-CH_2), 4.34-4.38 (m, 2H, alkyl-C*H*), 4.52 (t, $^3J_{H\text{-}H}$ = 8.0 Hz, 2H, butyl-CH_2), 8.98 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.28 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.36 (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β), 9.38 (s, 1 H, meso-C*H*), 9.40 ppm (d, $^3J_{H\text{-}H}$ = 4.9 Hz, 2H, H_β); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 13.9, 14.0, 23.4, 33.5, 33.8, 39.5, 49.3, 102.2, 117.8, 120.0, 129.5, 130.7, 131.0 and 131.8 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 414 (5.47), 534 nm (4.30); HRMS (Maldi) *m/z* calcd. for $C_{34}H_{40}N_4Ni$ $[M]^+$: 562.2606, found 562.2596.

General Procedure H: Iodination of porphyrins: Following the procedure of Boyle and co-workers[17,41] the porphyrin was dissolved in $CHCl_3$ and purged with argon. Iodine (1.5 eq.) and bis(trifluroacetoxy)iodobenzene (1.1 eq.) were added and the flask shielded from light. The reaction was left to stir at R.T. until consumption of the starting material was complete (approx. 48 hrs.). The solution was then filtered through silica gel using CH_2Cl_2 as eluent, solvents were removed and the product was recrystallized from $CHCl_3$/MeOH.

(5-Iodo-10,15,20-triphenylporphyrinato)nickel(II) (12a): Synthesized *via* General Procedure H 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). Yield: purple crystals (0.32 mmol, 228 mg, 93%); M.p. 265 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.65-7.71 (m, 9H, Ph-*o*/*p*-C*H*), 7.95-7.97 (m, 6H, Ph-*o*-C*H*), 8.66-8.70 (m, 4H, H_β), 8.73 (d, $^3J_{H\text{-}H}$ = 5.0 Hz, 2H, H_β), 9.47 ppm (d, $^3J_{H\text{-}H}$ = 5.0 Hz, 2H, H_β); ^{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 and 144.5 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 419 (5.54), 533 nm (4.40); HRMS (Maldi) *m/z* 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): General Procedure H 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). Yield: purple crystals (0.41 mmol, 333 mg, 95%); M.p. 291 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.68-7.73 (m, 7H, Ar-C*H*), 8.00 (m, 2H, naph-C*H*), 8.05 (m, 2H, naph-C*H*), 8.15-8.20 (m, 6H, Ar-C*H*), 8.44 (s, 2H, naph-C*H*), 8.71 (s, 4H, H_β), 8.78 (d, $^3J_{H\text{-}H}$ = 5.0 Hz, 2H, H_β), 9.53 ppm (d, $^3J_{H\text{-}H}$ = 5.0 Hz, 2H, H_β); ^{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 and 144.6 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 422 (5.37), 535 nm (4.25); HRMS (Maldi) *m/z* 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 *via* General Procedure H 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). Yield: purple crystals (0.39 mmol, 270 mg, 83%); M.p. >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = -2.72 (s, 2H, N*H*), 2.70 (s, 6H, tolyl-C*H*$_3$), 7.55 (d, $^3J_{H\text{-}H}$ = 7.7 Hz, 4H, tolyl-*o*-C*H*), 7.72-7.74 (m, 3H, Ph-*o/p*-C*H*), 8.05 (d, $^3J_{H\text{-}H}$ = 7.7 Hz, 4H, tolyl-*m*-C*H*), 8.15-8.17 (m, 2H, Ph-*m*-C*H*), 8.78 (m, 4H, H_β), 8.87 (d, $^3J_{H\text{-}H}$ = 4.8 Hz, 2H, H_β), 9.65 ppm (d, $^3J_{H\text{-}H}$ = 4.8 Hz, 2H, H_β); ^{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 and 141.8 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 423 (5.48), 522 (4.07), 558 (3.85), 598 (3.51), 655 nm (3.64); HRMS (Maldi) *m/z* calcd. for $C_{40}H_{29}IN_4$ $[M]^+$: 692.1437, found 692.1431.

General Procedure I. Suzuki reaction with 4-bromophenylboronic acid: The appropriate bromoporphyrin was dissolved in dry THF in an oven dried Schlenk flask and subjected to 3 freeze-pump-thaw cycles before being released to argon. 4-bromophenylboronic acid (5 eq.), $PdCl_2(PPh_3)_2$ (20 mol%), triphenylarsine (40 mol%) and K_3PO_4 (5 eq.) were added and the solution heated to 60 °C for 18 hr. The product was filtered through silica gel using CH_2Cl_2 as eluent and then purified by column chromatography.

[5-(4-Bromophenyl)-10,15,20-triphenylporphyrinato]nickel(II) (19a): Synthesized *via* General Procedure I from **4a** (200 mg, 0.33 mmol), 4-bromophenylboronic 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). Product purified by column chromatography on silica gel using *n*-hexane/CH_2Cl_2 (6:1, v/v) as eluent followed by crystallization from $CHCl_3$/MeOH. Yield purple crystals (0.28 mmol, 208 mg, 84%); M.p. >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.66-7.73 (m, 9H, Ph-*o/p*-C*H*), 7.81 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, 2H, *o*-C_6H_4Br), 7.89 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, 2H, *m*-C_6H_4Br), 8.01-8.03 (m, 6H, Ph-*o*-C*H*), 8.73 (d, $^3J_{H\text{-}H}$ = 5.0 Hz, 2H, H_β), 8.77-8.78 ppm (m, 6H, H_β); ^{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) = 414 (5.40), 528 nm (4.27); HRMS (Maldi) *m/z* 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 *via* General Procedure I from **4b** (230 mg, 0.33 mmol), 4-bromophenylboronic 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). Product purified by column chromatography on silica gel using *n*-hexane/CH_2Cl_2 (6:1, v/v) as eluent followed by crystallization from $CHCl_3$/MeOH. Yield: purple crystals (0.27 mmol, 213 mg, 83%); M.p. >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.64 (s, 6H, tolyl-C*H*$_3$), 7.47 (d, $^3J_{H\text{-}H}$ = 7.7 Hz, 4H, tolyl-*o*-C*H*), 7.66-7.67 (m, 3H, Ph-*o/p*-C*H*), 7.79 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, 2H, *o*-C_6H_4Br), 7.86-7.89 (m, 6H, tolyl-*m*-C*H*, *m*-C_6H_4Br), 7.99-8.02 (m, 2H, Ph-*m*-C*H*), 8.70 (d, $^3J_{H\text{-}H}$ = 5.0 Hz, 2H, H_β), 8.73 (d, $^3J_{H\text{-}H}$ = 5.0 Hz, 2H, H_β), 8.78 (d, $^3J_{H\text{-}H}$ = 5.0 Hz, 2H, H_β), 8.79 ppm (d, $^3J_{H\text{-}H}$ = 5.0 Hz, 2H, H_β); ^{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 and 142.9 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 416 (5.23), 529 (4.09) nm; HRMS (Maldi) *m/z* calcd. for $C_{46}H_{31}BrN_4Ni$ $[M]^+$: 776.1086, found 776.1096.

5-(4-Bromophenyl)-10,15,20-triphenylporphyrin (19c): Synthesized *via* General Procedure I from **4l** (200 mg, 0.31 mmol), 4-bromophenylboronic 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). Product purified by column chromatography on silica gel using *n*-hexane/CH_2Cl_2 (4:1, v/v) as eluent followed by crystallization from $CHCl_3$/MeOH. Yield: purple crystals (0.24 mmol, 173 mg, 78%). Product had analytical data consistent with the literature.[42]

[5,10,15-Triphenyl-20-(4-propadienylphenyl)porphyrinato]nickel(II) (21a): Synthesized *via* a modified General Procedure F 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 and washed five times with water to remove residual DMF before filtration through silica gel using EtOAc as eluent. 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). Product purified by column chromatography (*n*-hexane:CH_2Cl_2, 4:1, v/v). Yield: purple crystals (252 mg, 0.36 mmol, 67%). M.p. >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): 5.25 (d, $^4J_{H\text{-}H}$ = 6.8 Hz, 2H, allene–C*H*$_2$), 6.38 (t, $^4J_{H\text{-}H}$ = 6.8 Hz, 1H, allene–C*H*), 7.55 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 2H, *o*-C_6H_4), 7.59-7.64 (m, 9H, Ph-*m/p*-C*H*), 7.90 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 2H, *m*-C_6H_4), 7.94-7.97 (m, 6H, Ph-*o*–C*H*), 8.69-8.73 ppm (m, 8H, H_β); ^{13}C NMR (150 MHz, $CDCl_3$): 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 and 210.2 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 416 (5.39), 529 nm (4.30); IR (neat): ν = 2923.8, 2850.2, 1939.1 cm^{-1}; HRMS (Maldi) *m/z* calcd, for $C_{47}H_{30}N_4Ni$ $[M]^+$: 708.1824, found 708.1811; LRMS (ESI+, 200V): 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 *via* a modified General Procedure F 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 and washed five times with water to remove residual DMF before filtration through silica gel using EtOAc as eluent. 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). Product purified by column chromatography (*n*-hexane:CH_2Cl_2, 5:1, v/v). Yield: purple crystals (207 mg, 0.28 mmol, 72%); M.p. >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.63 (s, 6H, tolyl-C*H*$_3$), 5.29 (d, $^4J_{H\text{-}H}$ = 6.9 Hz, 2H, allene-C*H*$_2$), 6.43 (t, $^4J_{H\text{-}H}$ = 6.9 Hz, 1H, allene-C*H*), 7.46 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 4H, tolyl-*o*-C*H*), 7.60 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 2H, *o*-C_6H_4), 7.65-7.69 (m, 3H, Ph-*o/p*-C*H*), 7.89 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 4H, tolyl-*m*-C*H*), 7.95 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 2H, *m*-C_6H_4), 7.99-8.01 (m, 2H, Ph-*m*-C*H*), 8.73 (d, $^3J_{H\text{-}H}$ = 5.0 Hz, 2H, H_β), 8.76-8.77 ppm (m, 6H, H_β); ^{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 and 210.2 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 417 (5.27), 529 nm (4.13) nm; IR (neat): ν = 2921.4, 2853.7, 1940.2 cm^{-1}; HRMS (Maldi) *m/z* calcd. for $C_{49}H_{34}N_4Ni$ $[M]^+$: 736.2137, found 736.2130; LRMS (ESI+, 200V): 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 Copies of ^{1}H NMR and ^{13}C NMR spectra of all haloporphyrins and allenylporphyrins are available in the Supporting Information.

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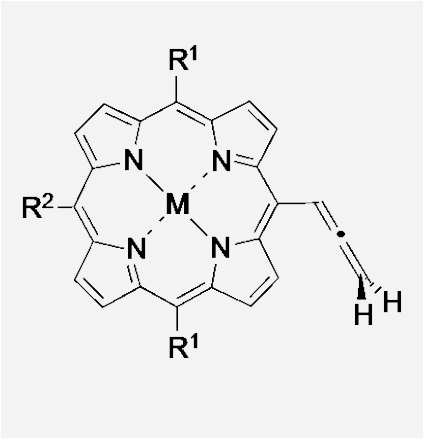
((Allenylporphyrins))

The synthesis of a diverse library of allenylporphyrins *via* two distinct metal catalyzed pathways is described. The reactivity of both directly linked allenylporphyrins and those possessing a phenyl “spacer” has been investigated with promising results.



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Synthesis and Reactivity of Allenylporphyrins

Keywords: Porphyrins / Allenes / Synthetic Methods / Cross-couplings / Cyclizations

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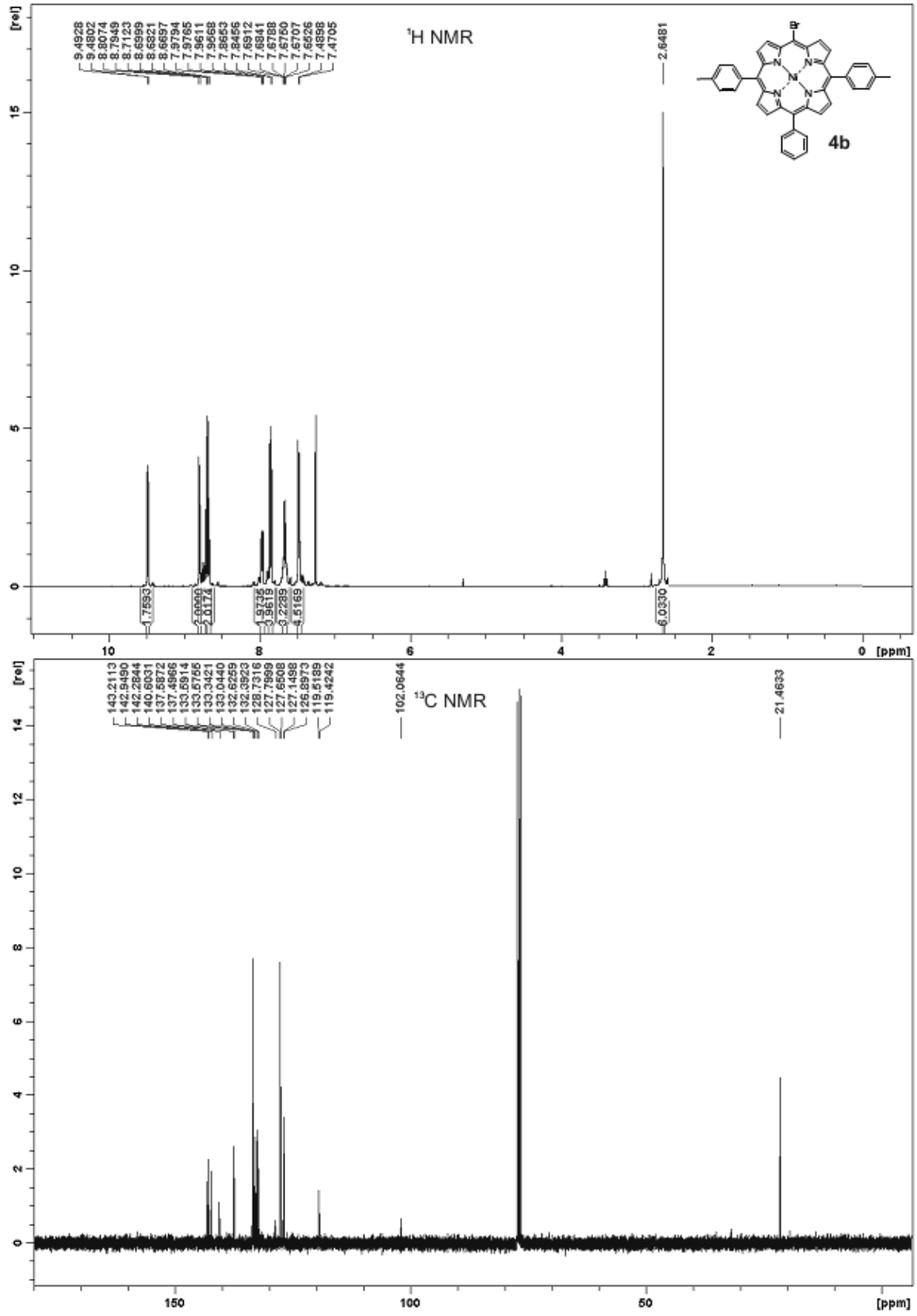
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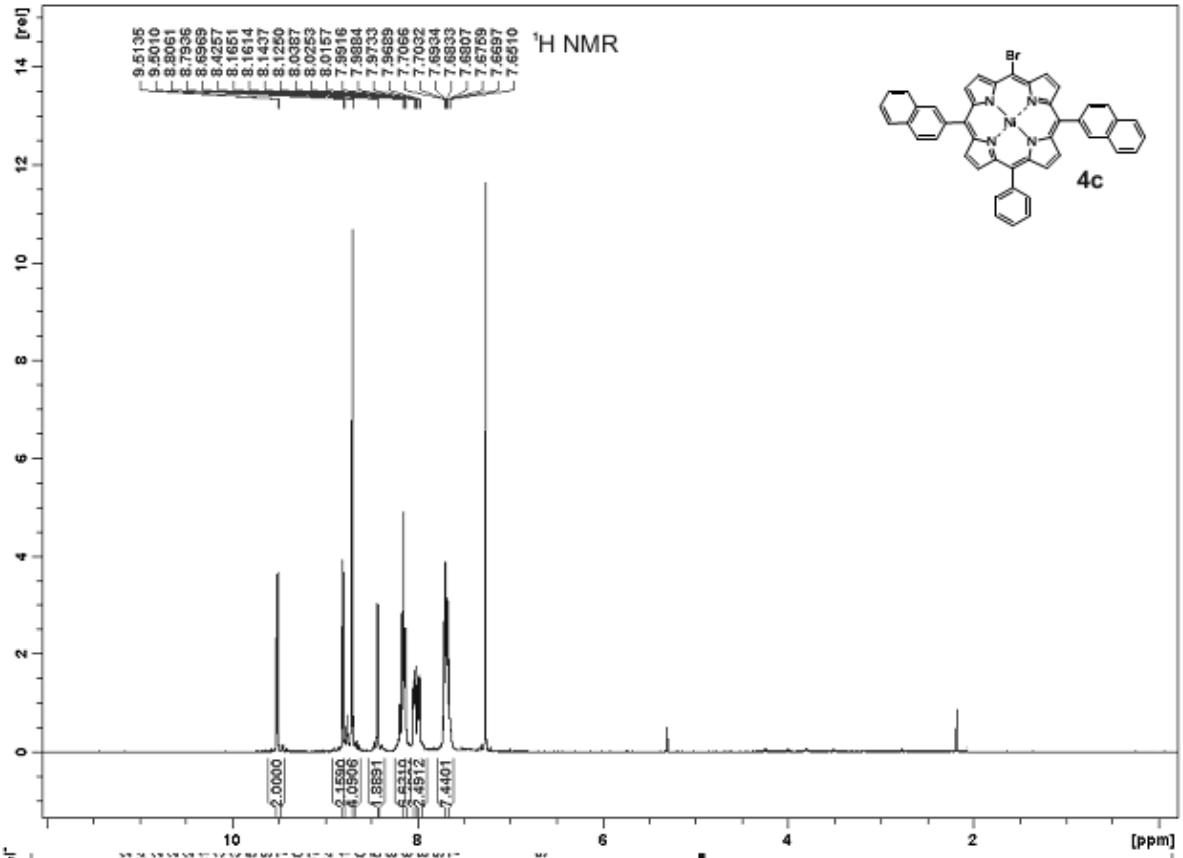
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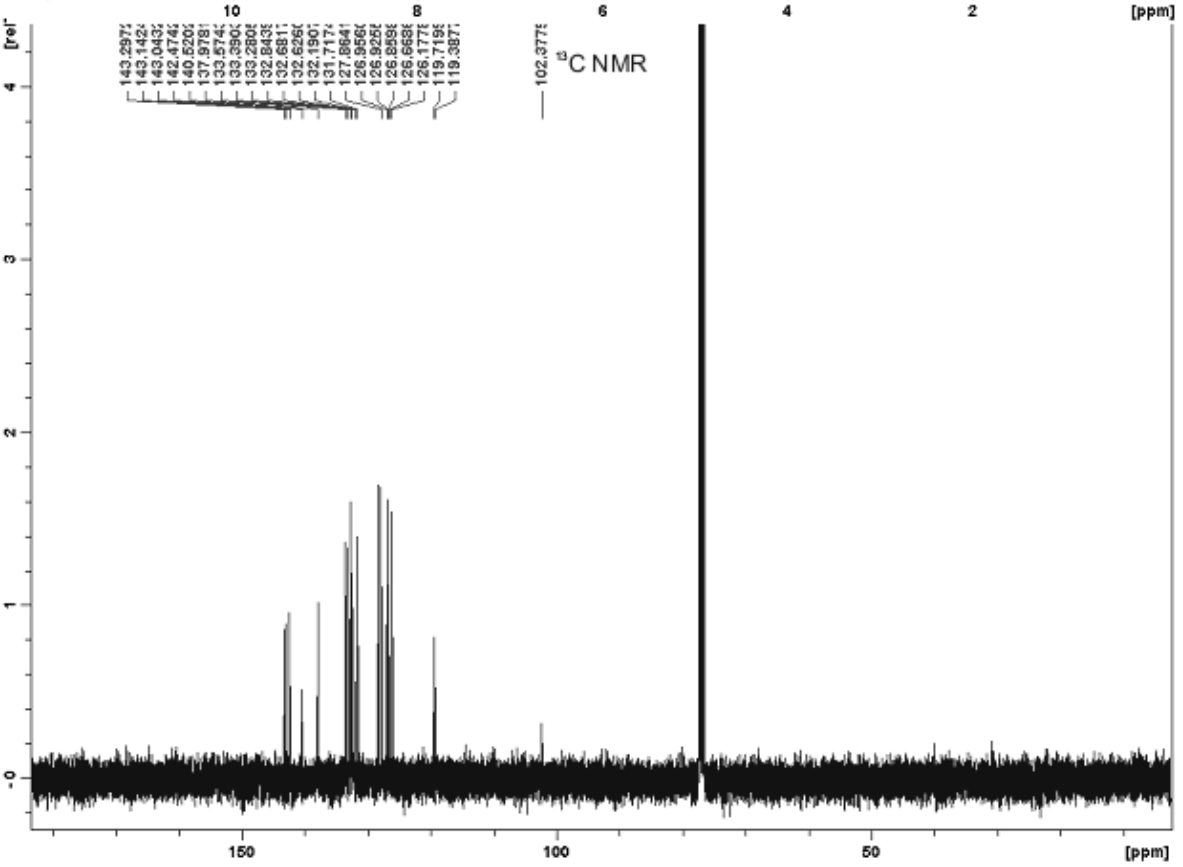
^{13}C NMR
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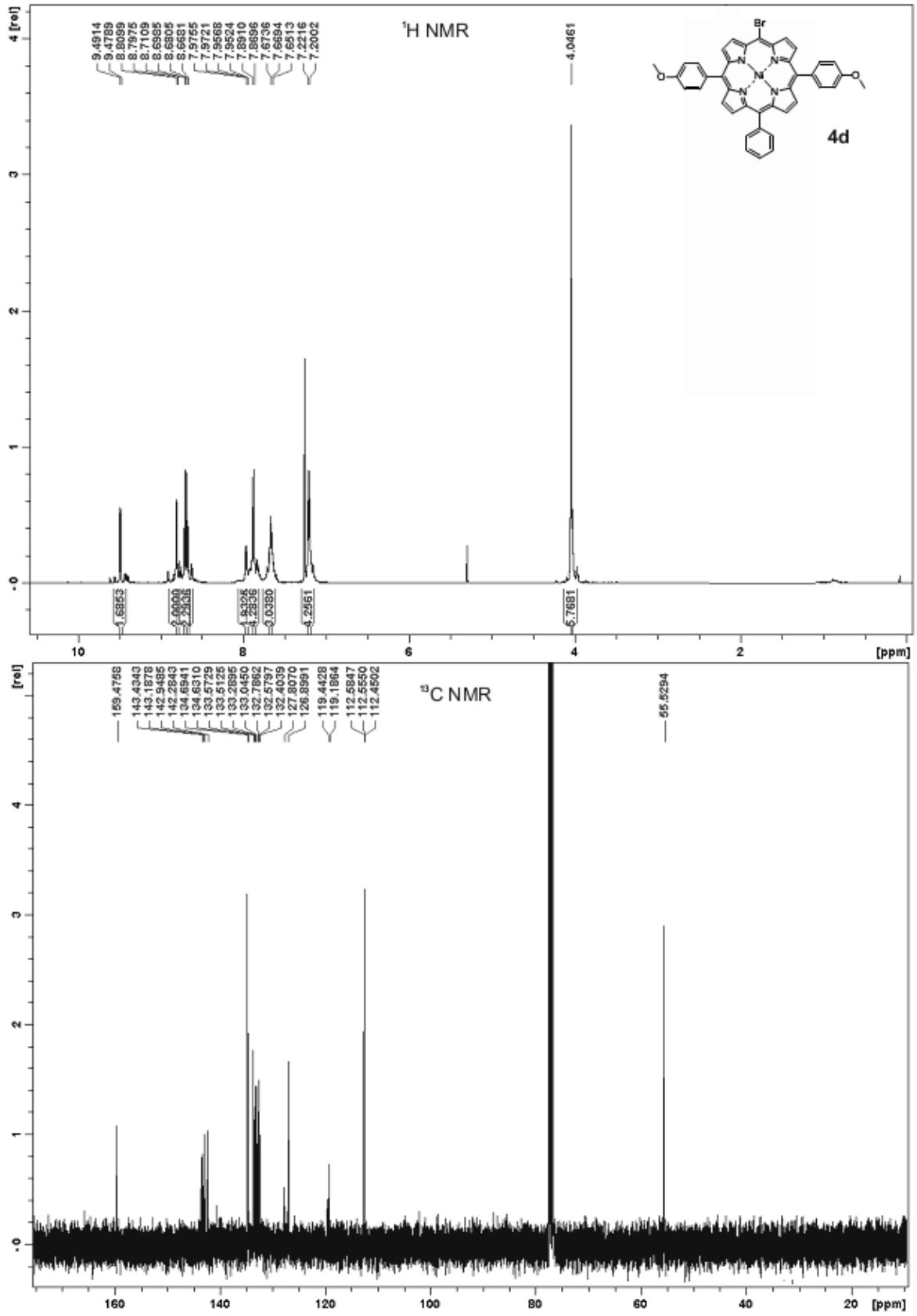
[ppm]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8.7975
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8.6985
8.6805
8.6681
7.9755
7.9721
7.9568
7.9524
7.8910
7.8896
7.6736
7.6694
7.6613
7.2216
7.2002
4.0461
1.6853
2.0000
2.2836
1.9206
2.2836
3.0380
6.2961
6.7681
[rel]
[ppm]
Br
N
Ni
O
4d
^{13}C NMR
159.4758
143.4343
143.1678
142.9485
142.2843
134.6941
134.6310
133.5729
133.5125
133.2695
133.0450
132.7862
132.5797
132.4039
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119.4428
119.1864
112.5847
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112.4502
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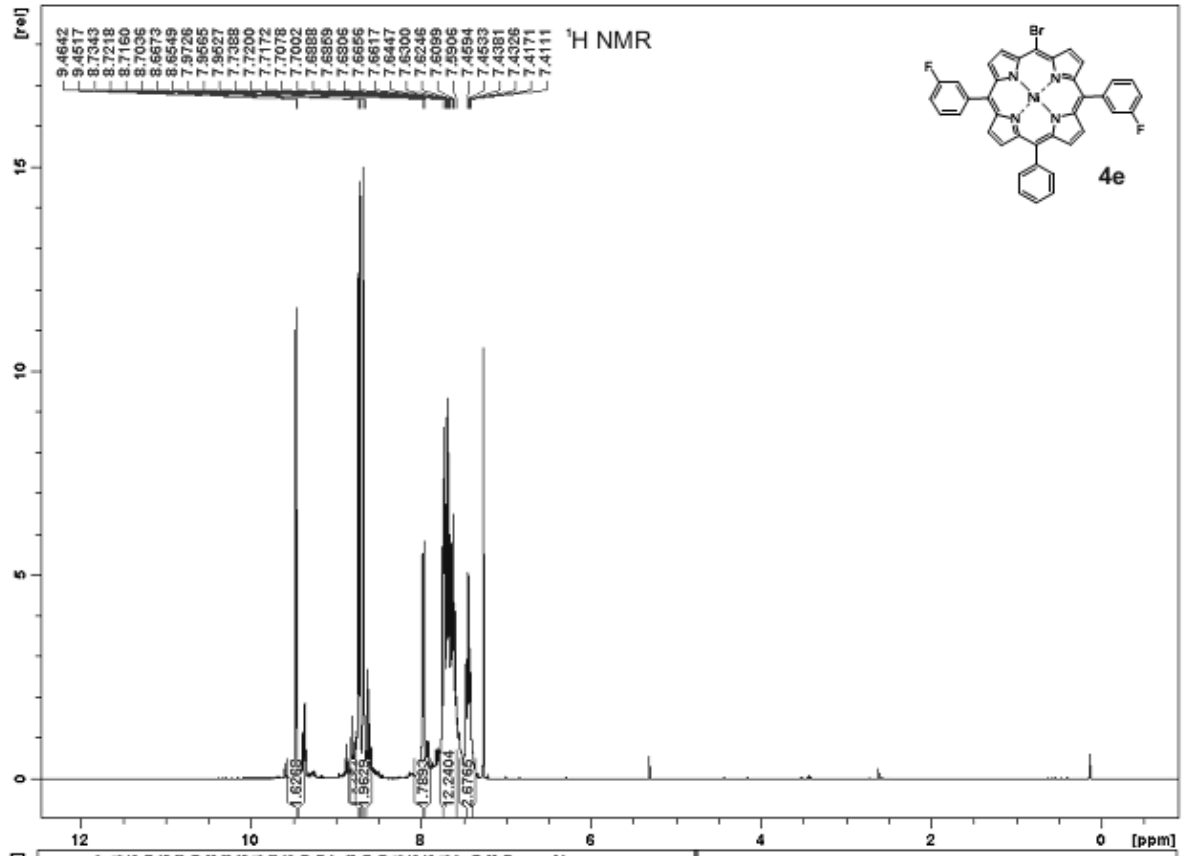
[rel]
[ppm]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8.6549
7.9726
7.9585
7.9527
7.7388
7.7200
7.7172
7.7078
7.7002
7.6888
7.6859
7.6806
7.6656
7.6617
7.6447
7.6300
7.6246
7.6099
7.5906
7.4594
7.4533
7.4381
7.4328
7.4171
7.4111
1.6268
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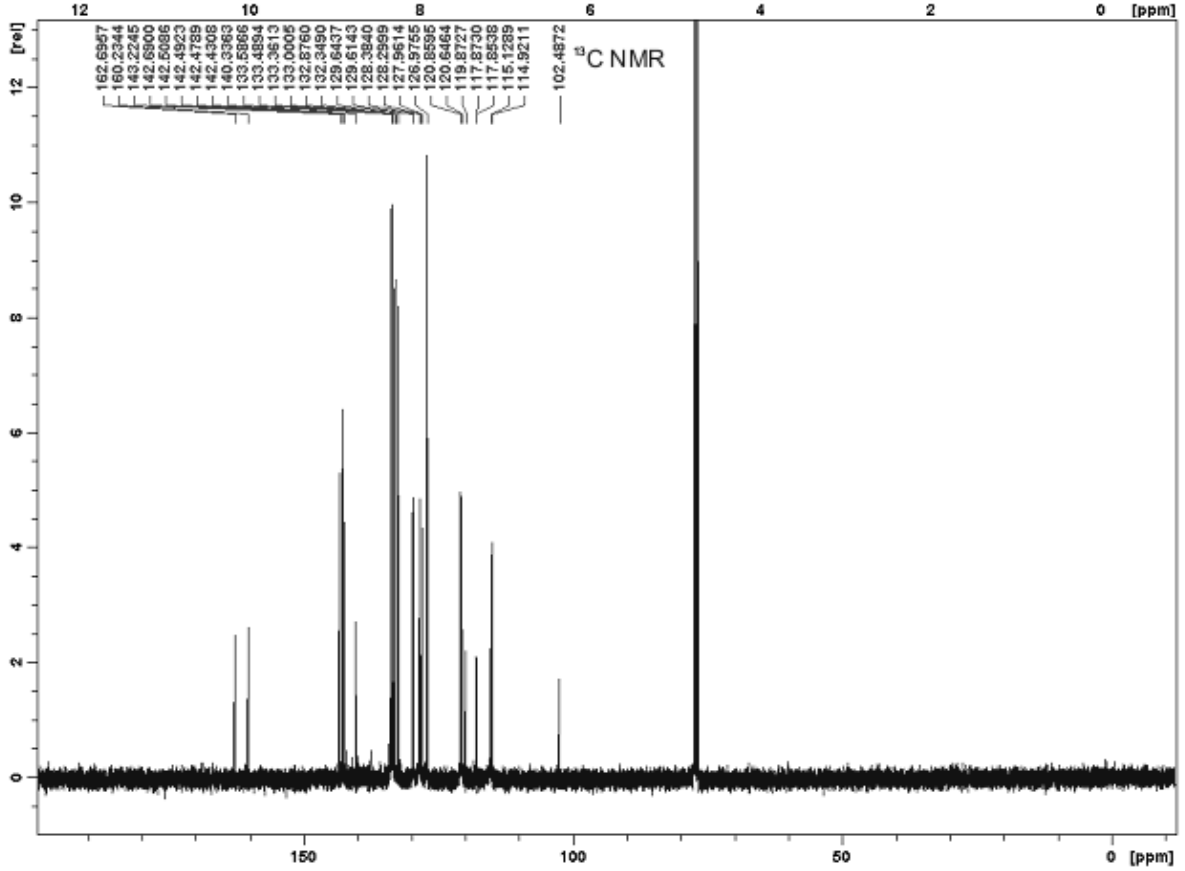
12.2404
2.6765
Br
F
F
N
N
N
N
Ni
4e
[ppm]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133.5866
133.4894
133.3813
133.0005
132.8760
132.3490
129.6437
129.6143
128.3840
128.2999
127.9614
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120.6464
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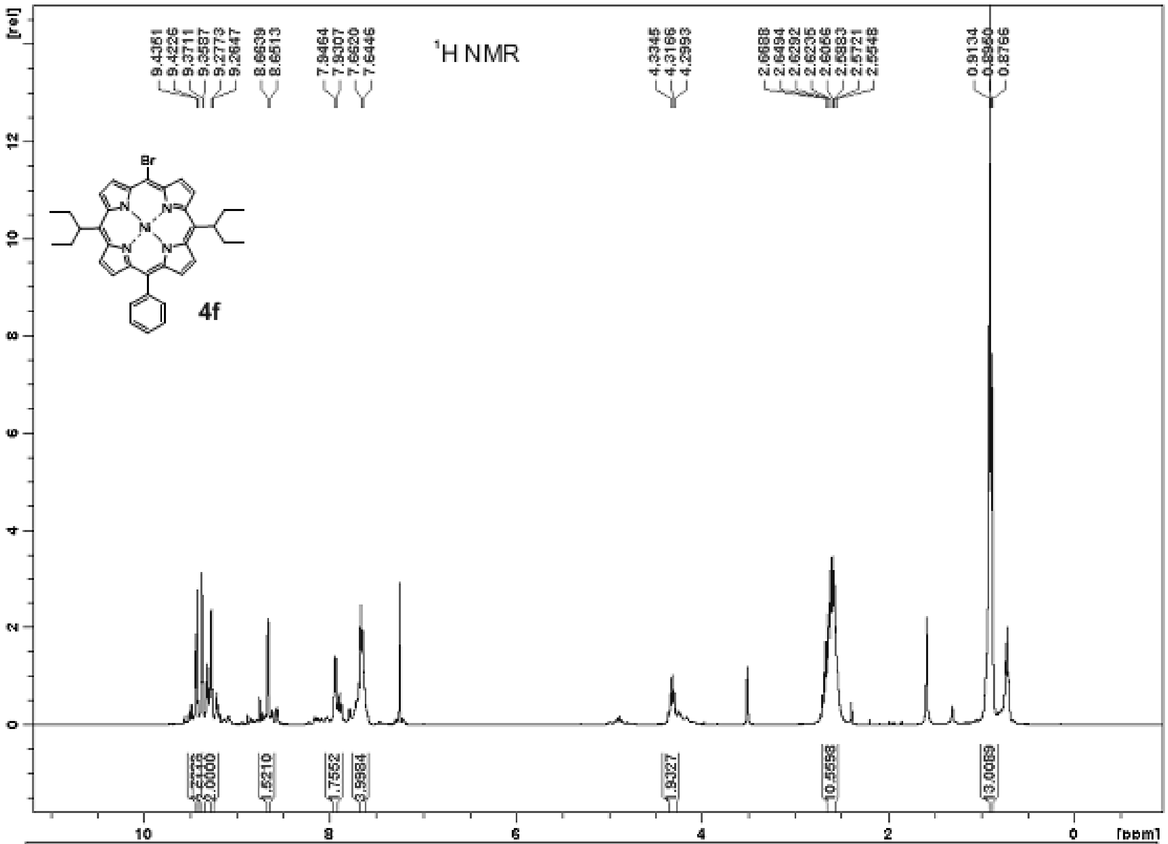
117.8730
117.8538
115.1289
114.9211
102.4872
[ppm]



¹H NMR
4f
Br
Ni
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9.4226
9.3711
9.3587
9.2773
9.2647
8.6639
8.6513
7.9464
7.9307
7.6620
7.6446
4.3345
4.3166
4.2993
2.6688
2.6494
2.6292
2.6235
2.6056
2.5883
2.5721
2.5548
0.9134
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1.7552
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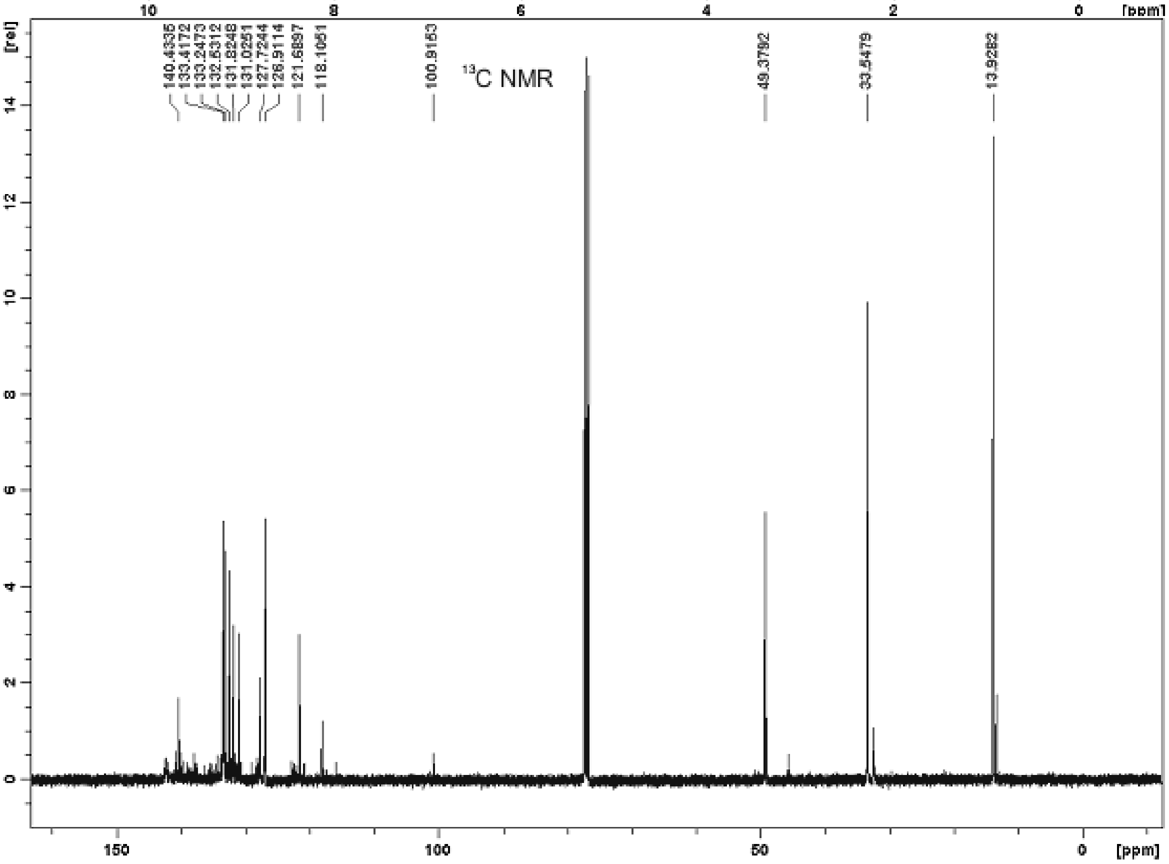
[ppm]



¹³C NMR
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132.5312
131.8248
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121.6897
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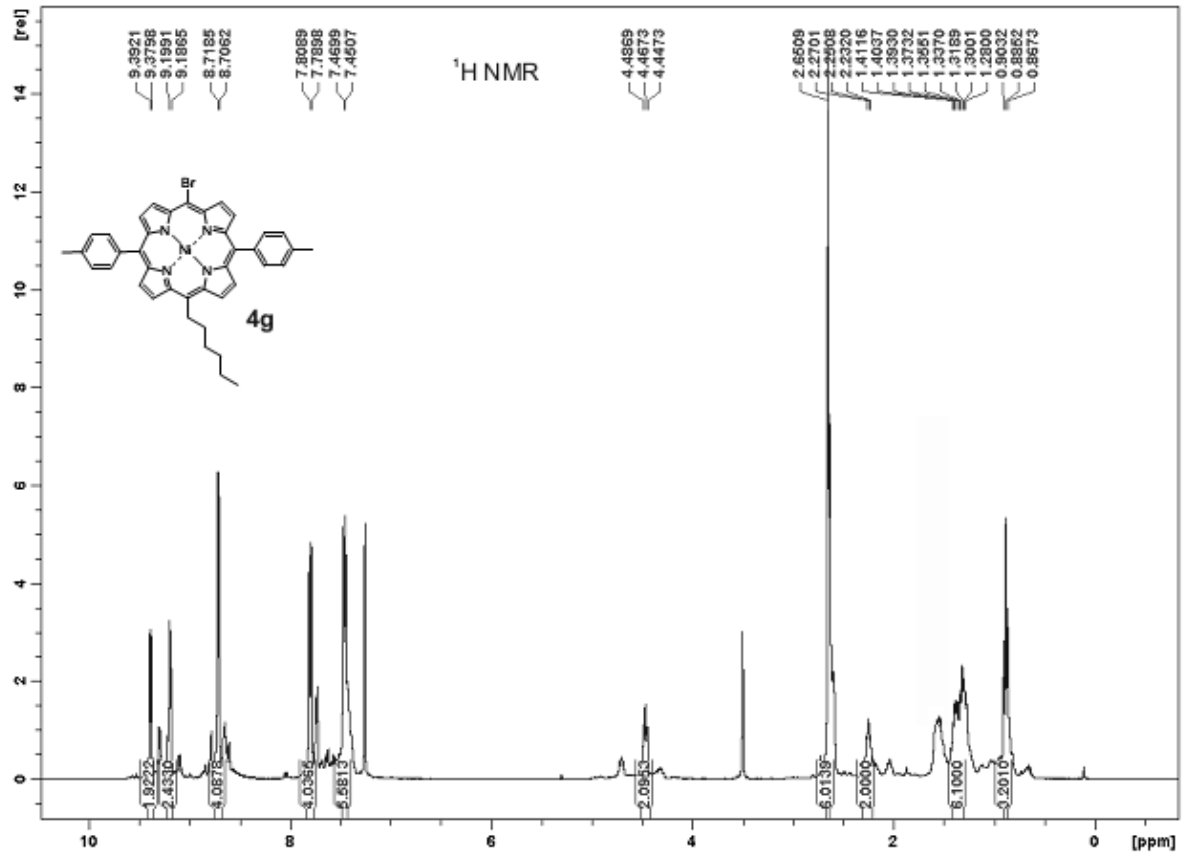
[ppm]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9.1991
9.1865
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7.4699
7.4507
4.4869
4.4673
4.4473
2.6509
2.2701
2.2508
2.2320
1.4116
1.4037
1.3930
1.3732
1.3651
1.3370
1.3189
1.3001
1.2800
0.9032
0.8852
0.8573
1H NMR
Br
N
Ni
4g
1.9222
2.4310
4.0878
4.0356
5.5813
2.0953
6.0139
2.0000
6.1000
3.2010
10
8
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4
2
0
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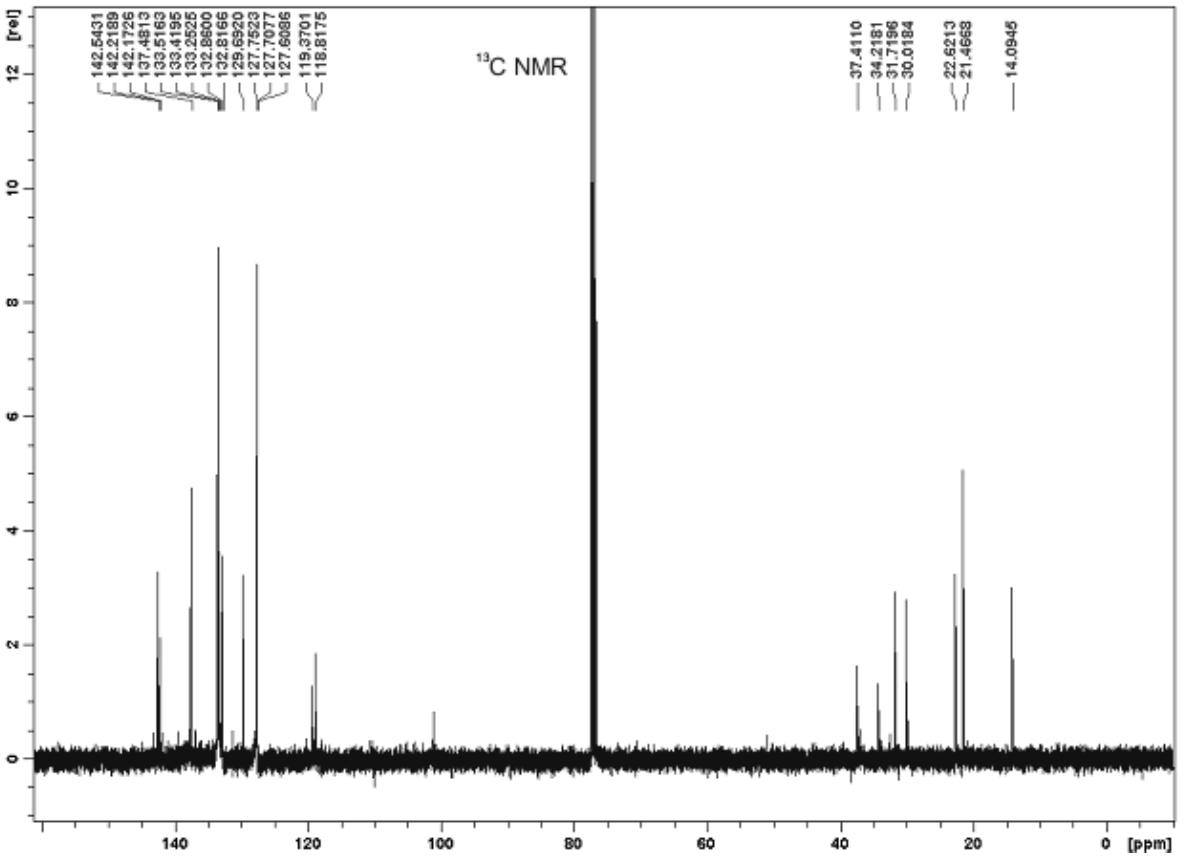
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142.1726
137.4813
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132.8800
132.8166
129.6920
127.7523
127.7077
127.6086
119.3701
118.8175
13C NMR
37.4110
34.2181
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14.0945
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120
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60
40
20
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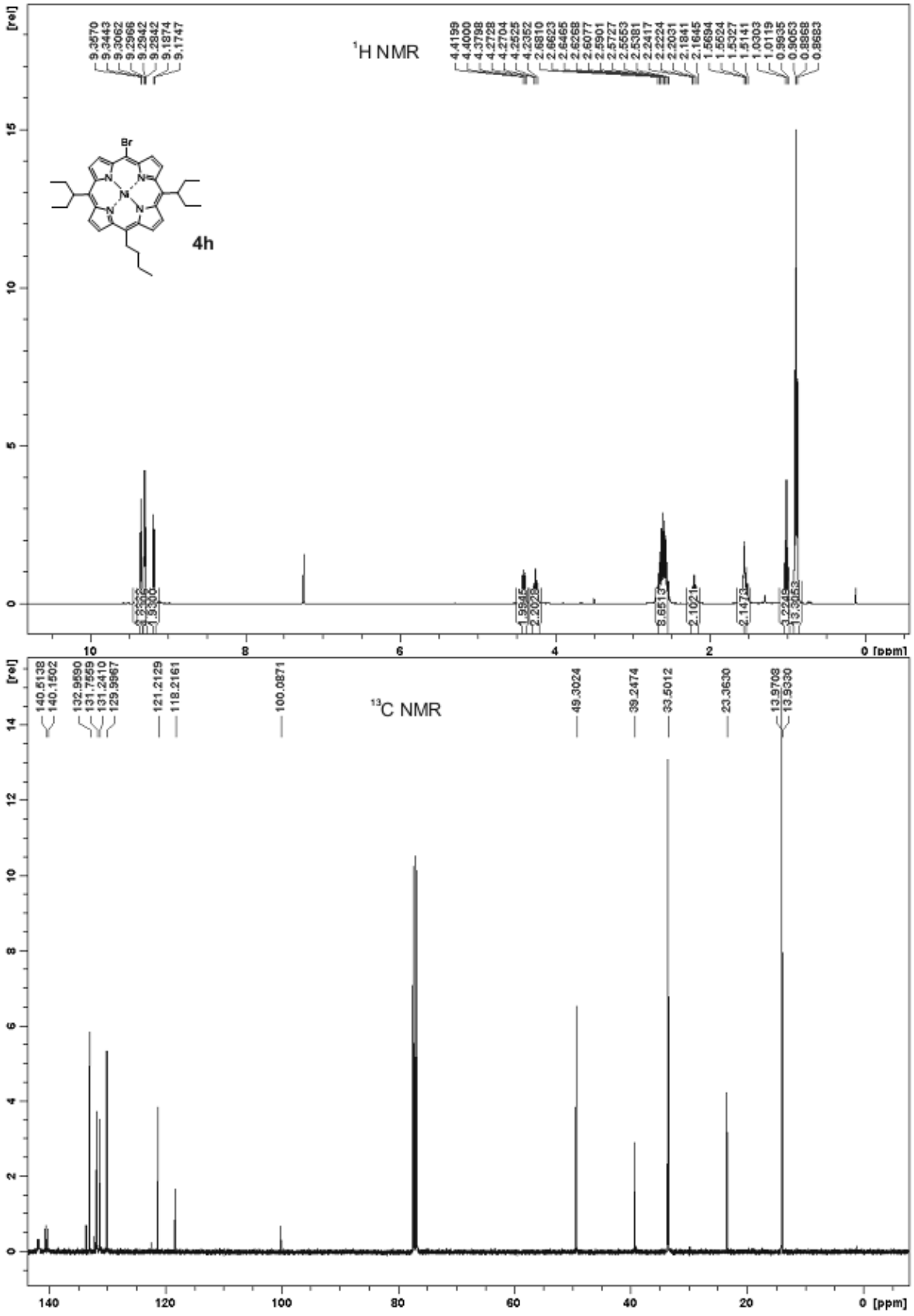
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9.1747
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4.4000
4.3798
4.2728
4.2704
4.2525
4.2352
2.6810
2.6623
2.6465
2.6268
2.6077
2.5901
2.5727
2.5553
2.5381
2.2417
2.2224
2.2031
2.1841
2.1645
1.5694
1.5524
1.5327
1.5141
1.0303
1.0119
0.9935
0.9063
0.8868
0.8683
Br
4h
1.9300
1.9545
2.2028
8.6513
2.1021
2.1473
3.2245
13.3053
10
8
6
4
2
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131.2410
129.9967
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100.0871
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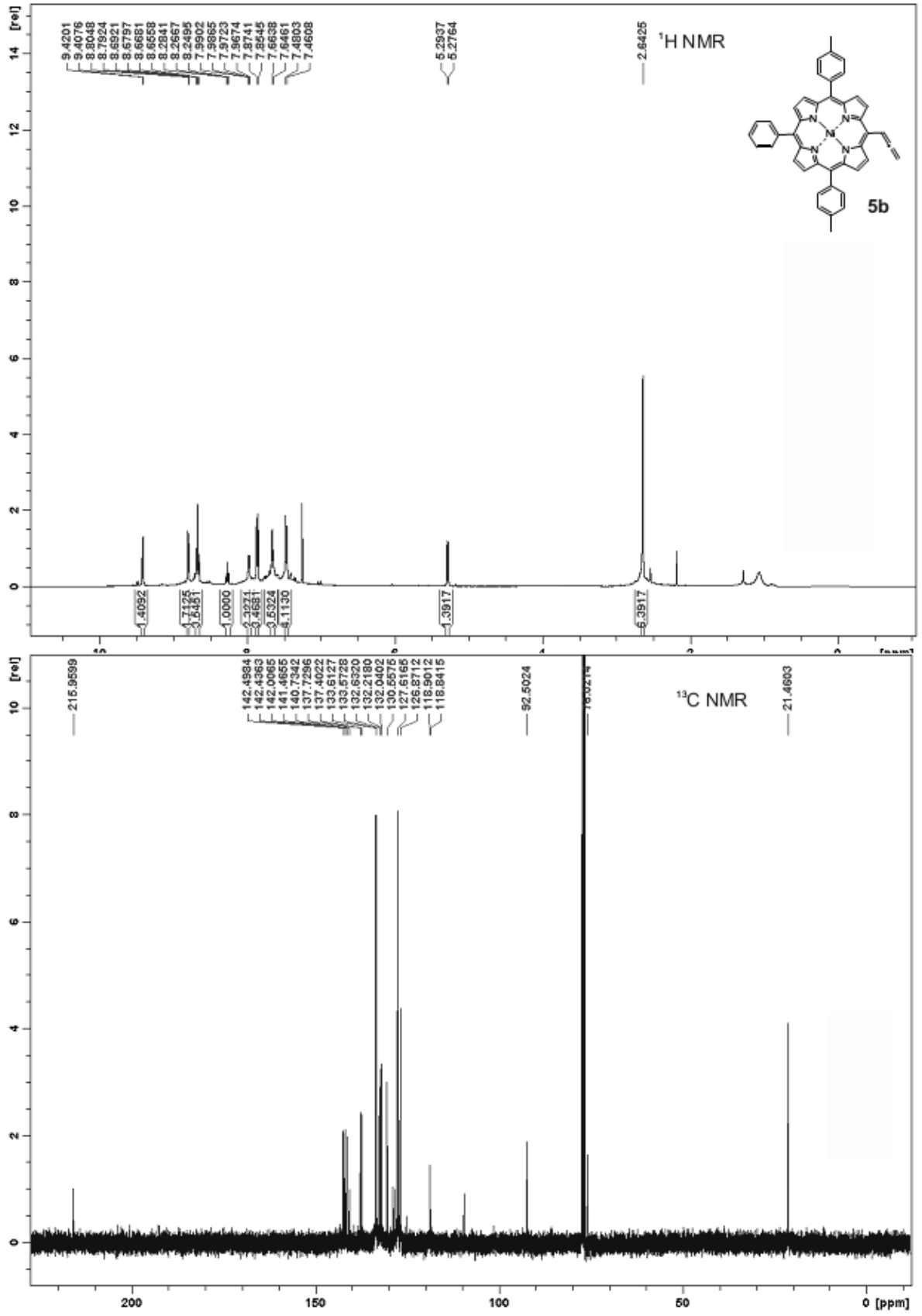
23.3630
13.9708
13.9330
140
120
100
80
60
40
20
0 [ppm]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8.6681
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8.2841
8.2667
8.2495
7.9902
7.9865
7.9723
7.9674
7.8741
7.8545
7.6638
7.6461
7.4803
7.4608
5.2937
5.2764
2.6425
1H NMR
5b
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1.3817
6.3917
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137.4022
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133.5728
132.6320
132.2180
132.0402
130.5576
127.6166
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76.9214
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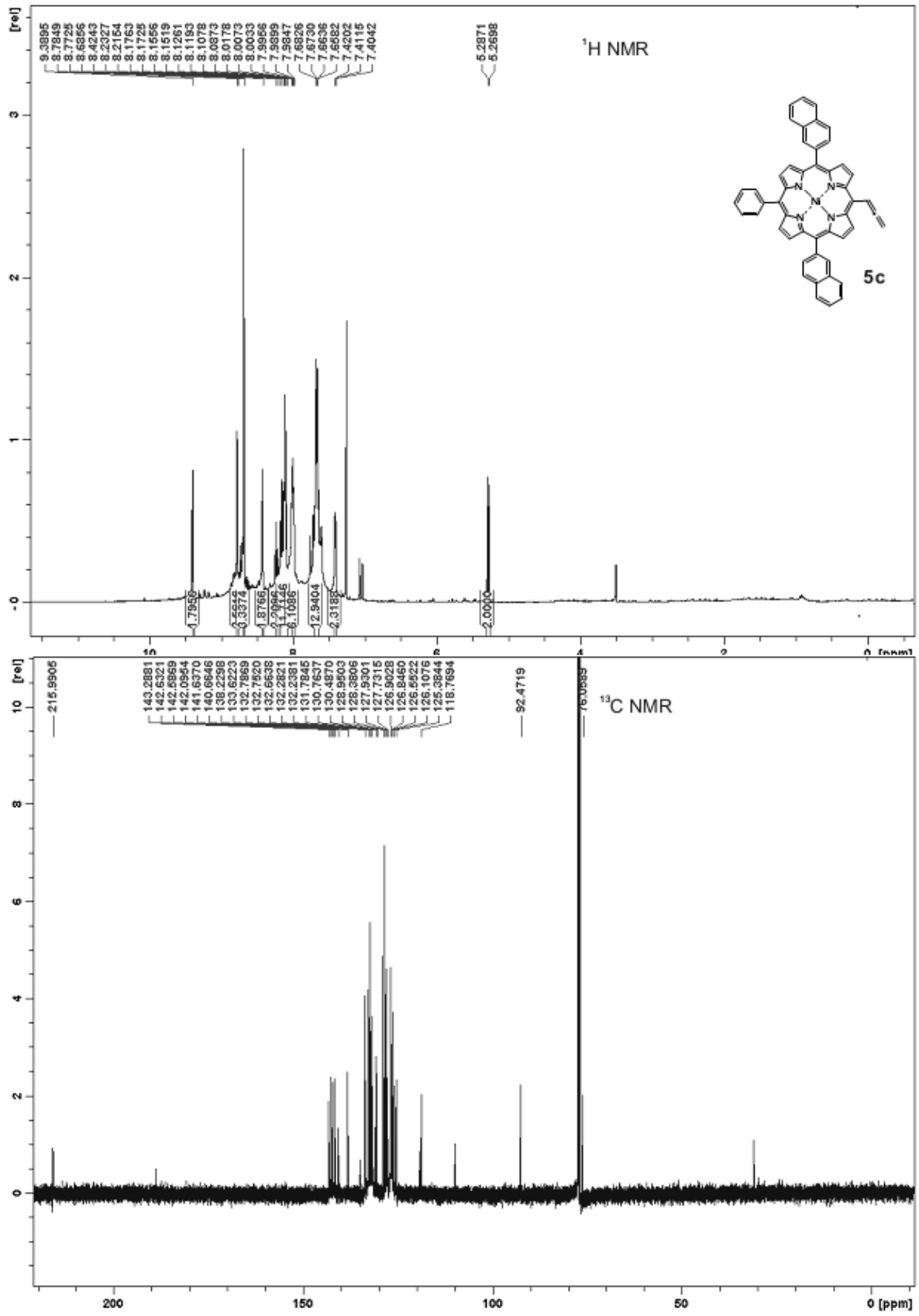
150
100
50
0 [ppm]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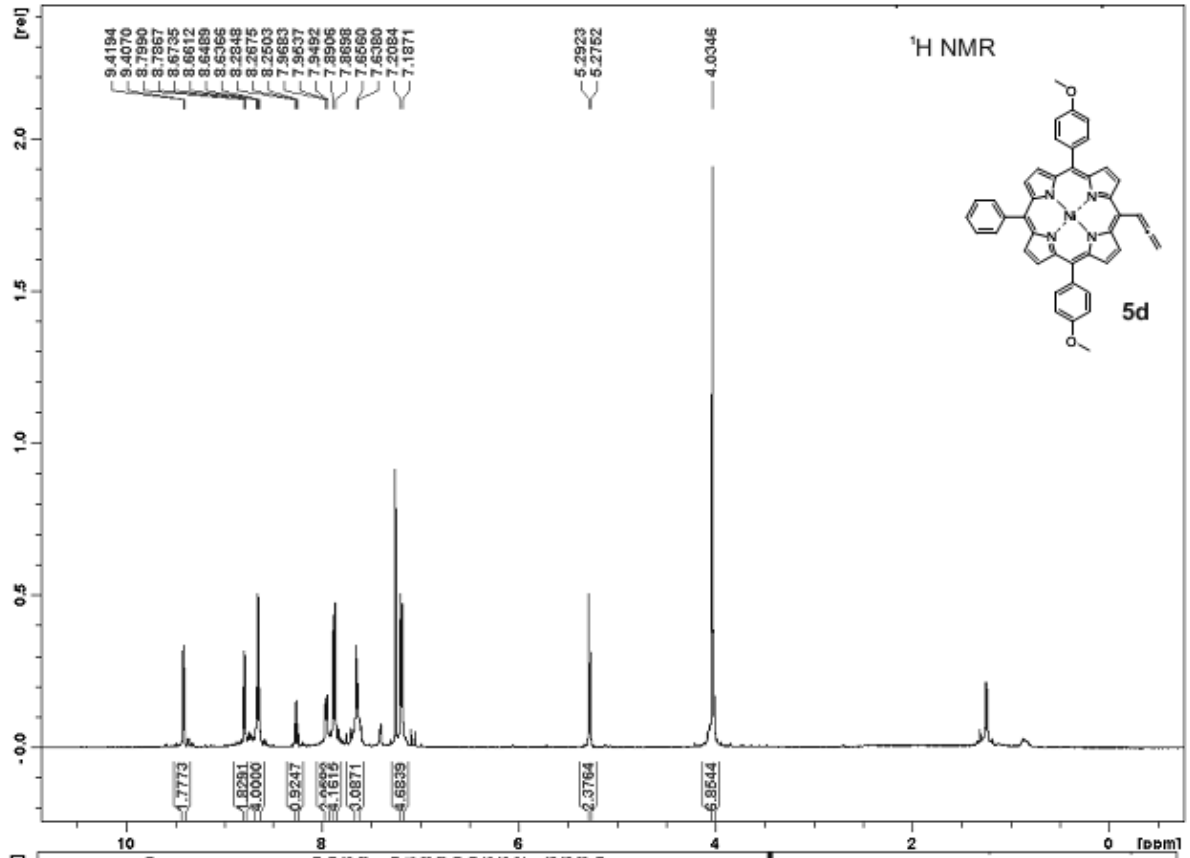
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8.2848
8.2675
8.2503
7.9683
7.9537
7.9492
7.8906
7.8858
7.8660
7.8380
7.2084
7.1871
5.2923
5.2752
4.0346
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6.8544
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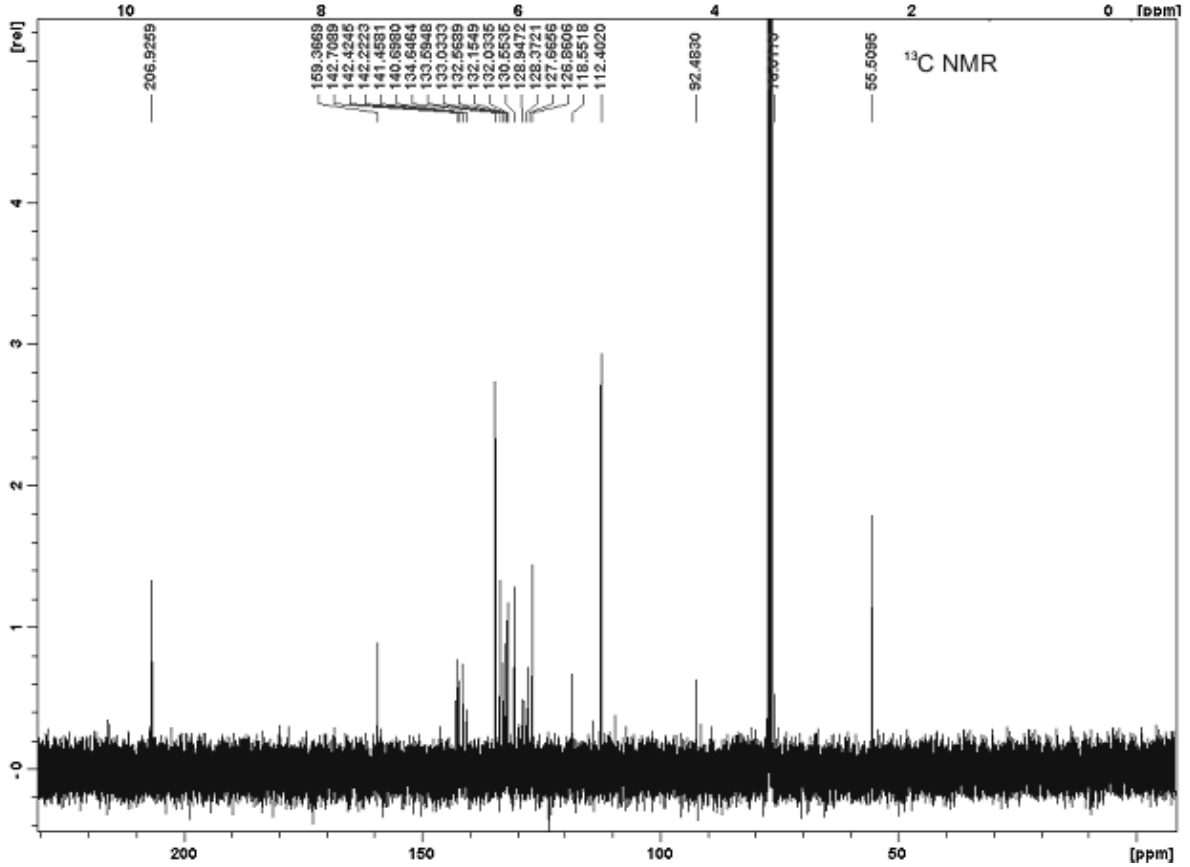
5d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132.1549
132.0335
130.5535
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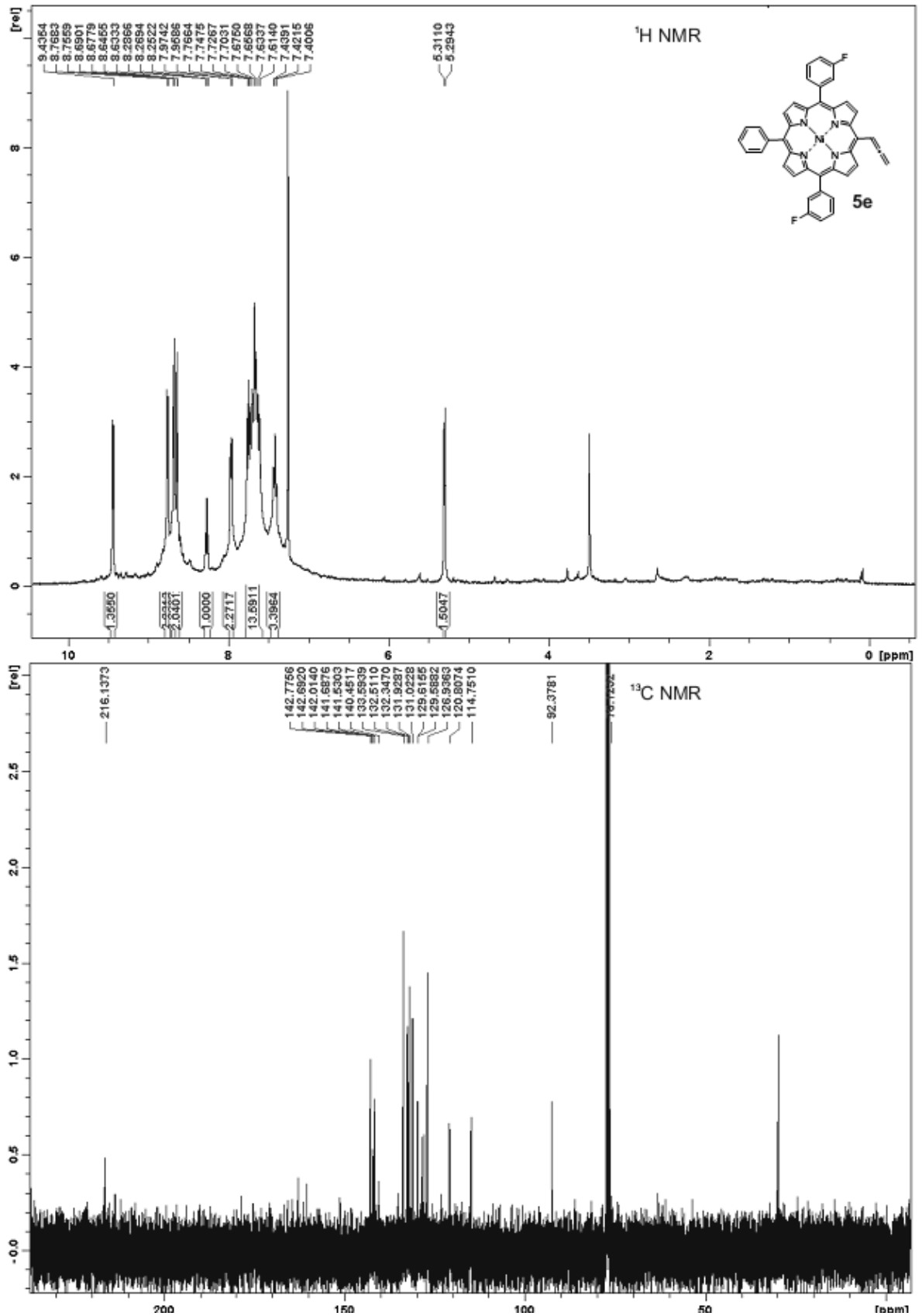
[ppm]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8.2522
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7.9686
7.7664
7.7475
7.7267
7.7031
7.6750
7.6568
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7.6140
7.4391
7.4215
7.4006
5.3110
5.2943
1H NMR
5e
F
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1.0000
2.2717
13.6911
3.3964
1.5047
10
8
6
4
2
0 [ppm]
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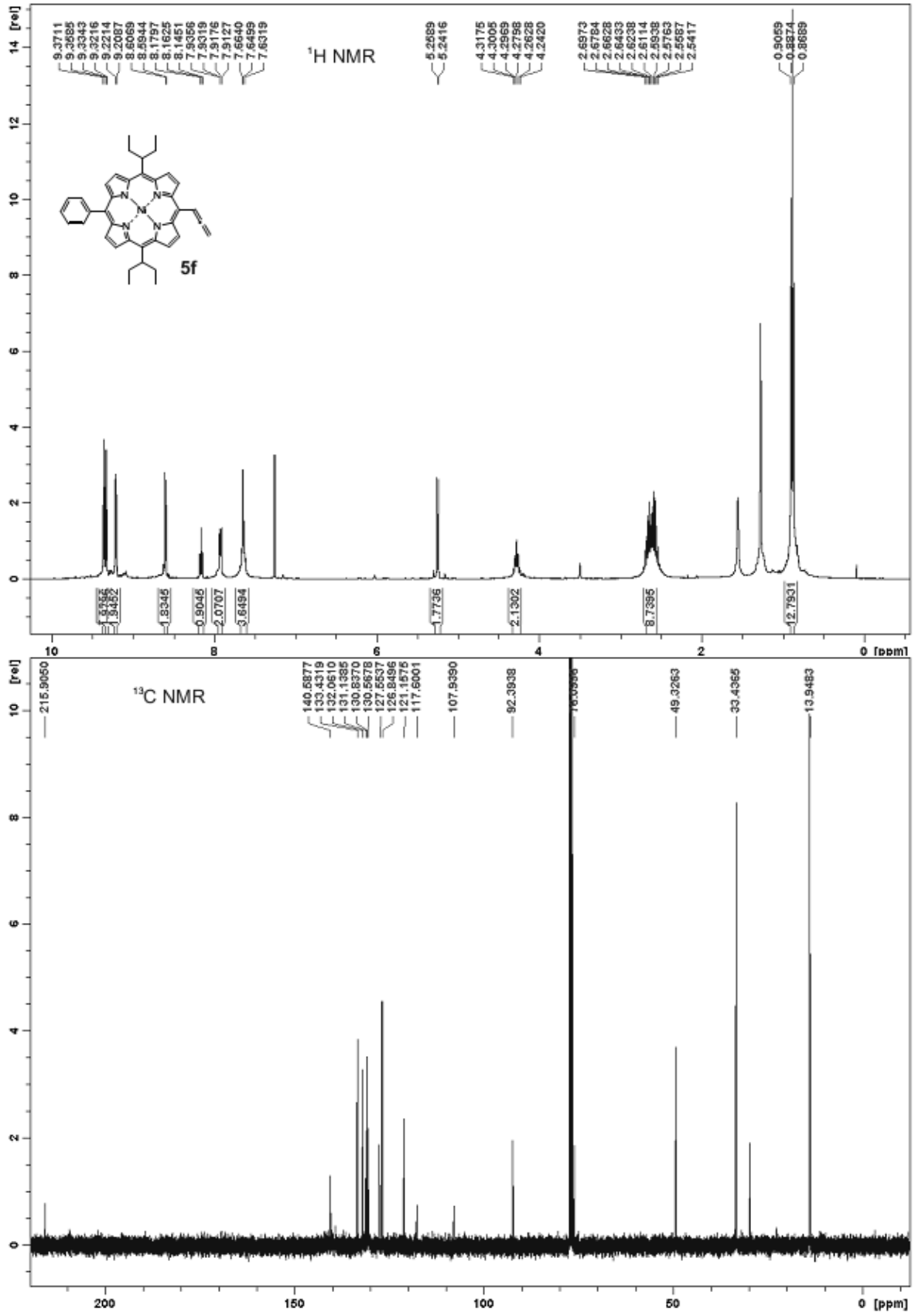
[ppm]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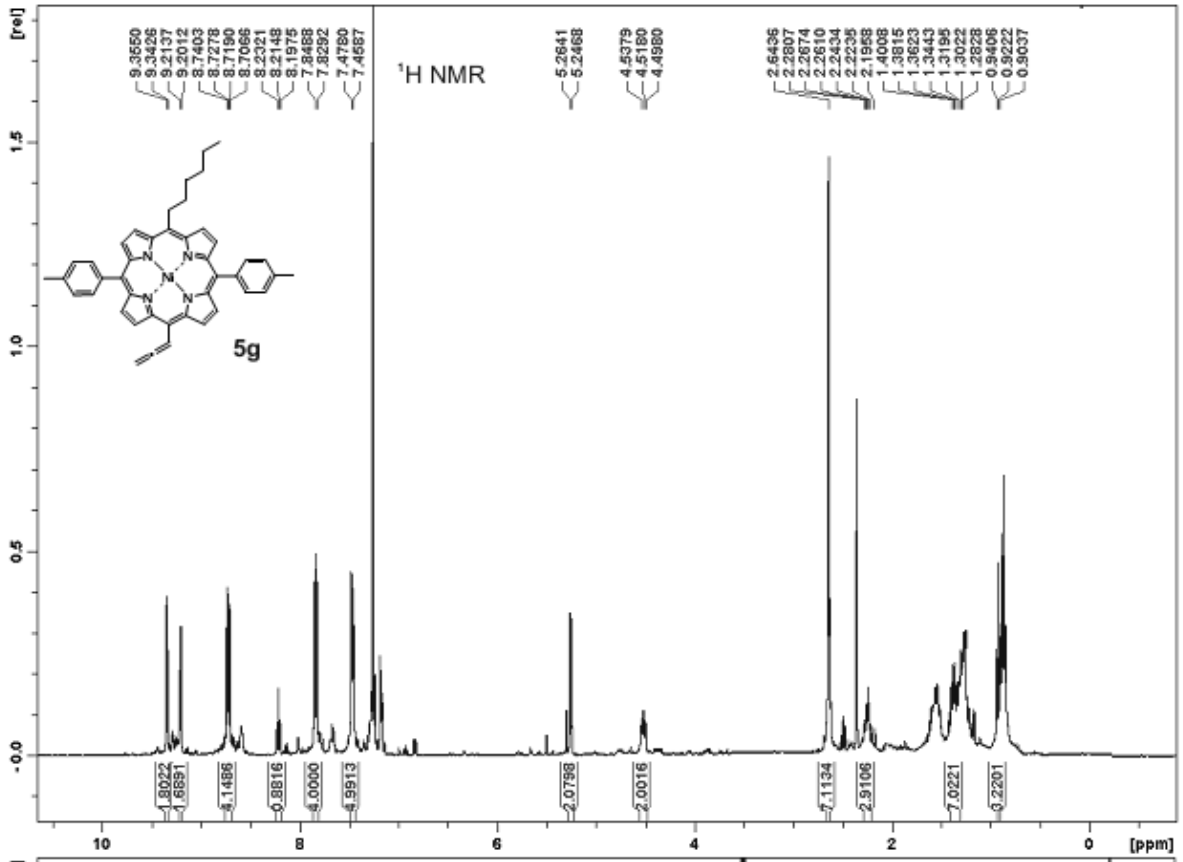
5f
^{13}C NMR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7.8292
7.4780
7.4587
^{1}H NMR
5.2641
5.2468
4.5379
4.5180
4.4980
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2.2807
2.2674
2.2610
2.2434
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2.1958
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1.3815
1.3623
1.3443
1.3195
1.3022
1.2828
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5g
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1.6891
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2.9106
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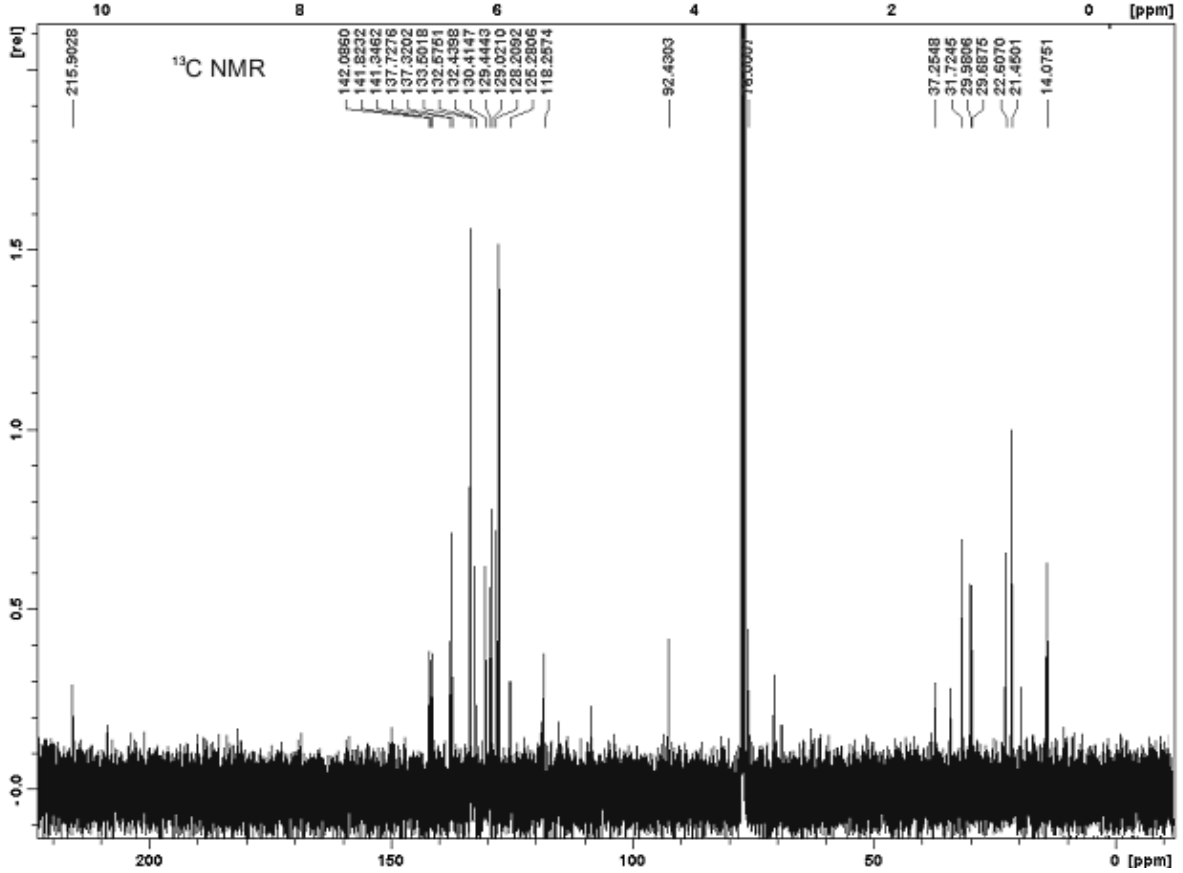
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128.2692
125.2806
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37.2548
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29.9806
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22.6070
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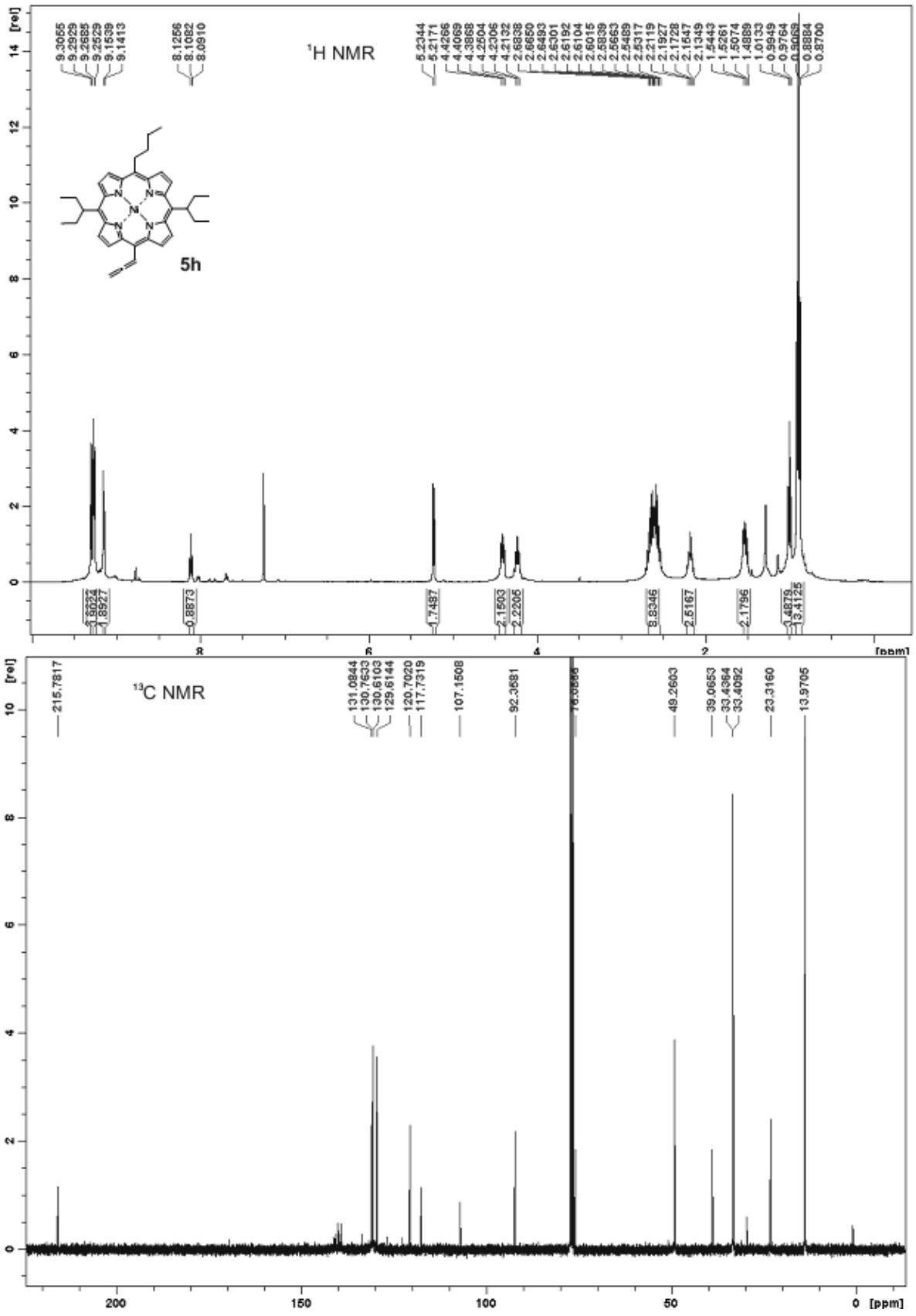
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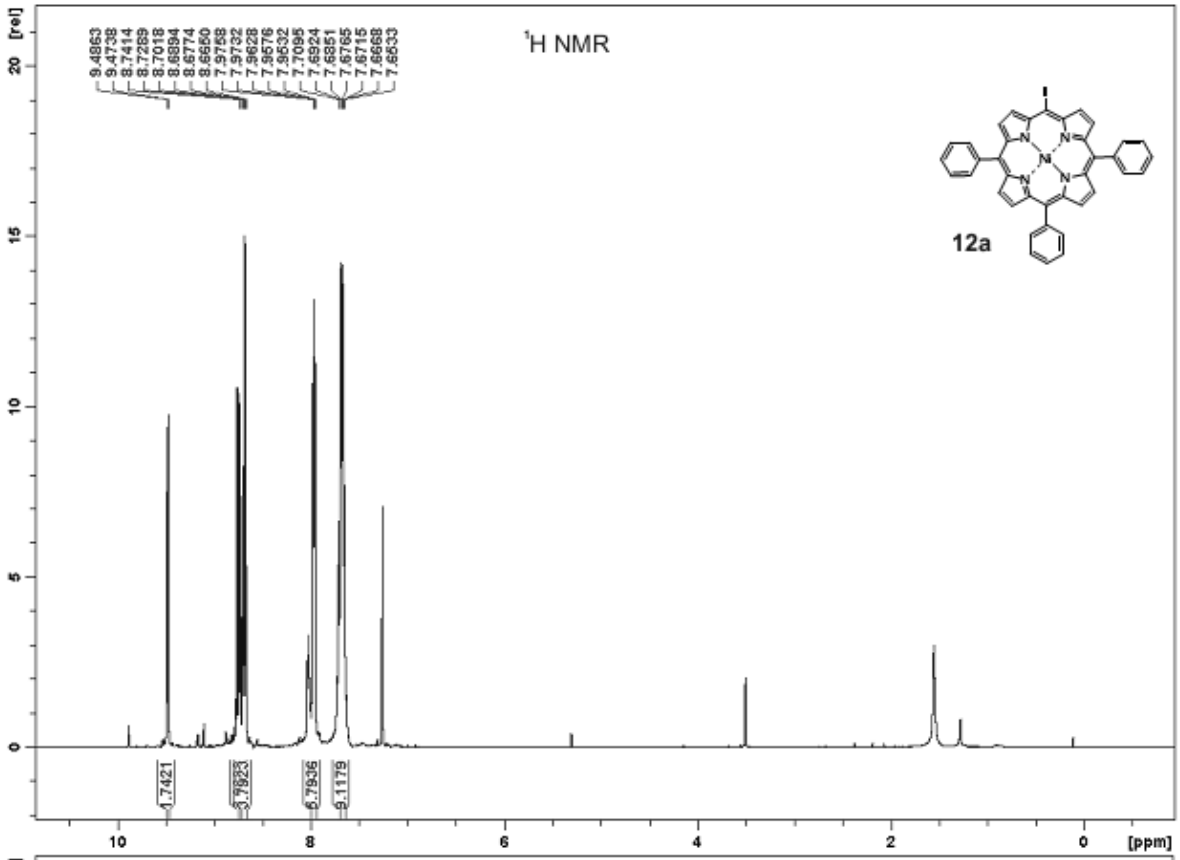
5h
^{13}C NMR
[ppm]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8.6894
8.6774
8.6550
7.9758
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7.6924
7.6851
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7.6533
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5.7936
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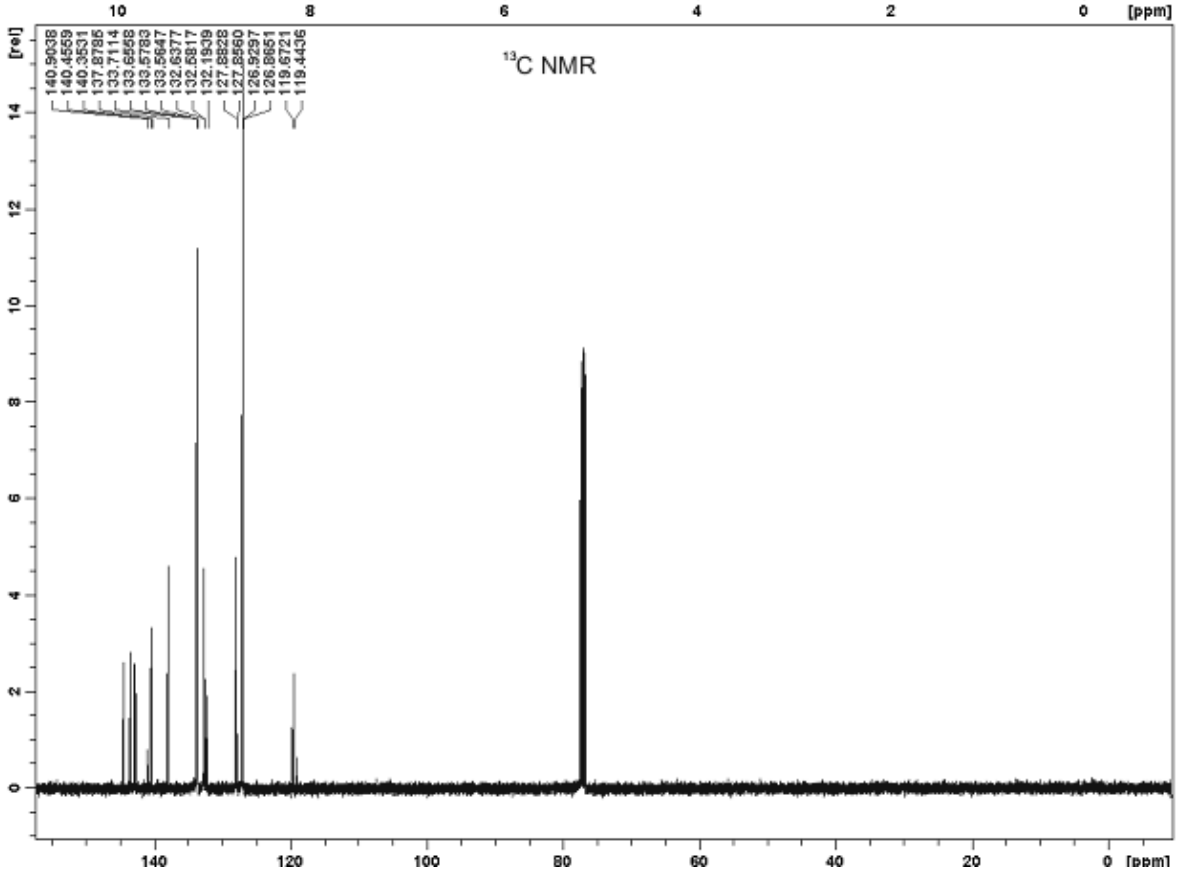
[ppm]

12a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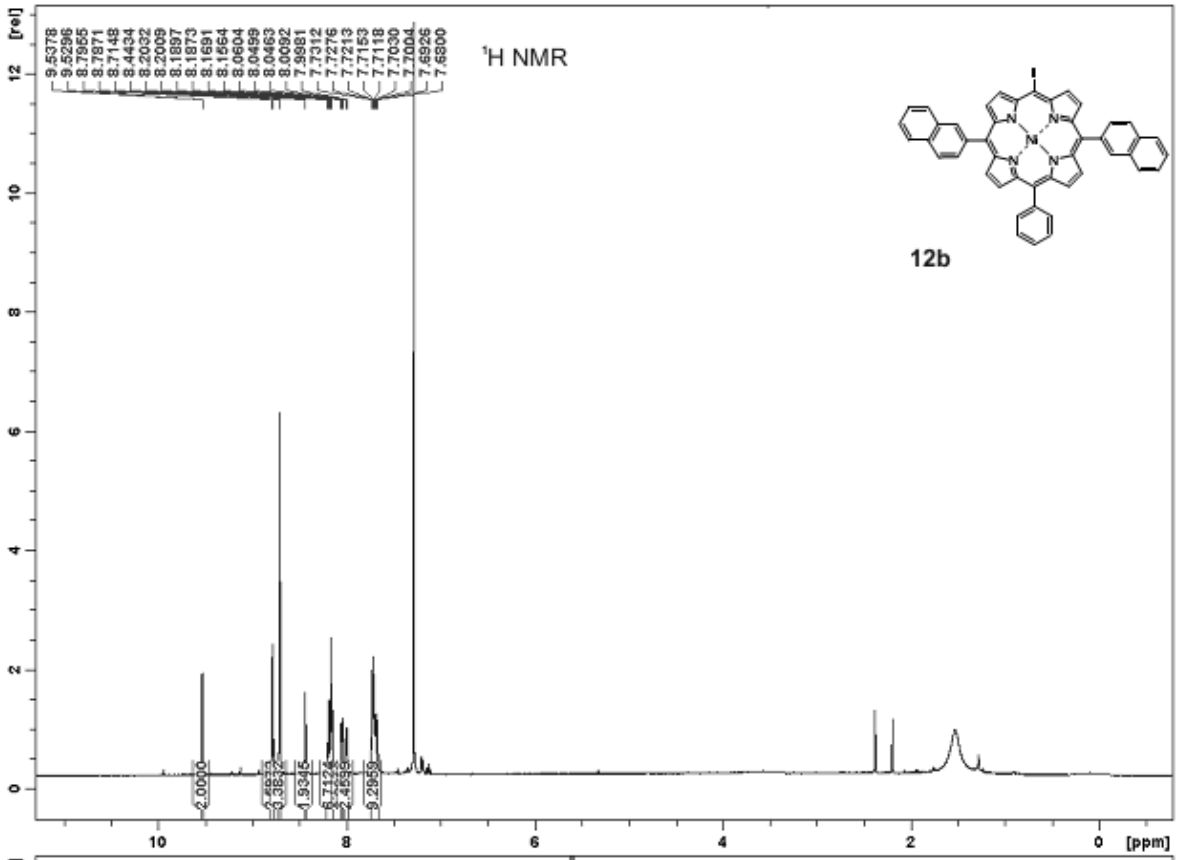
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8.0459
8.0463
8.0092
7.9981
7.7312
7.7276
7.7213
7.7153
7.7118
7.7030
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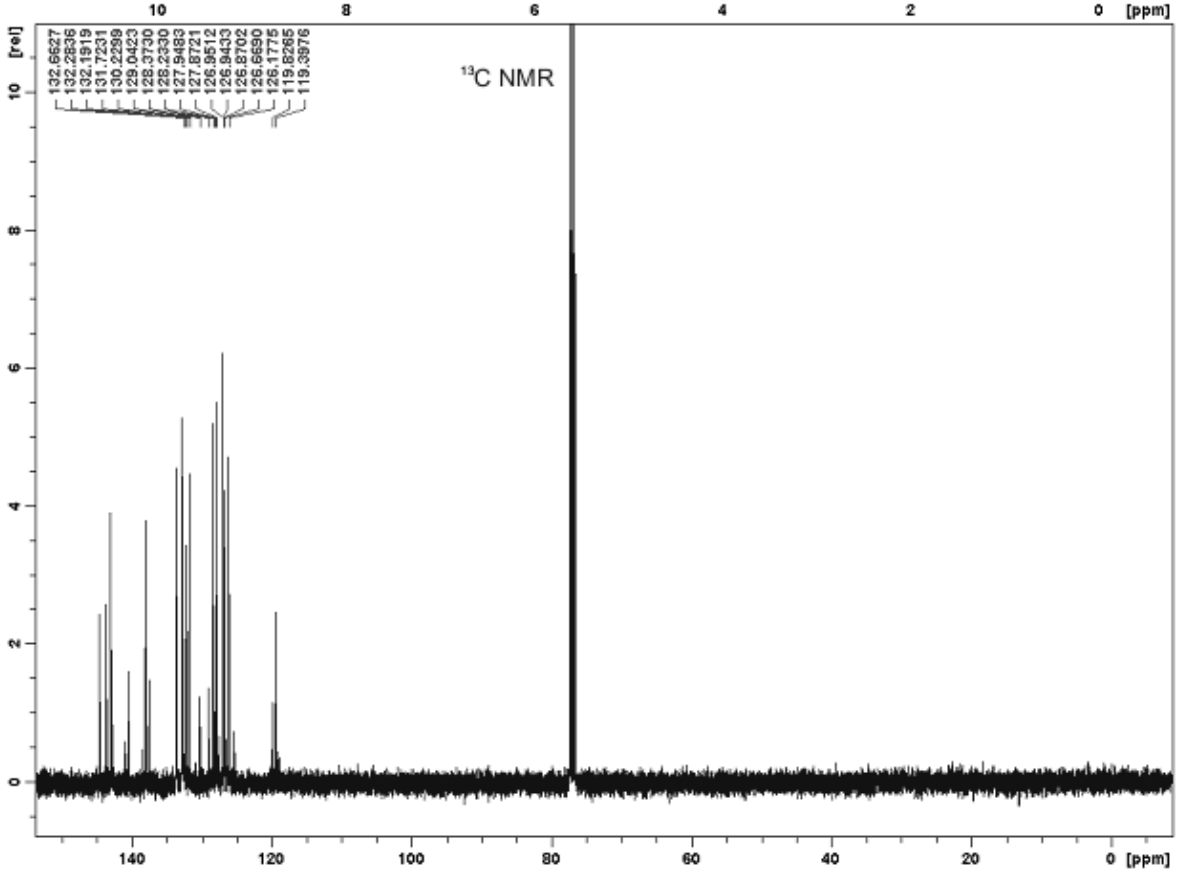
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126.9433
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119.8265
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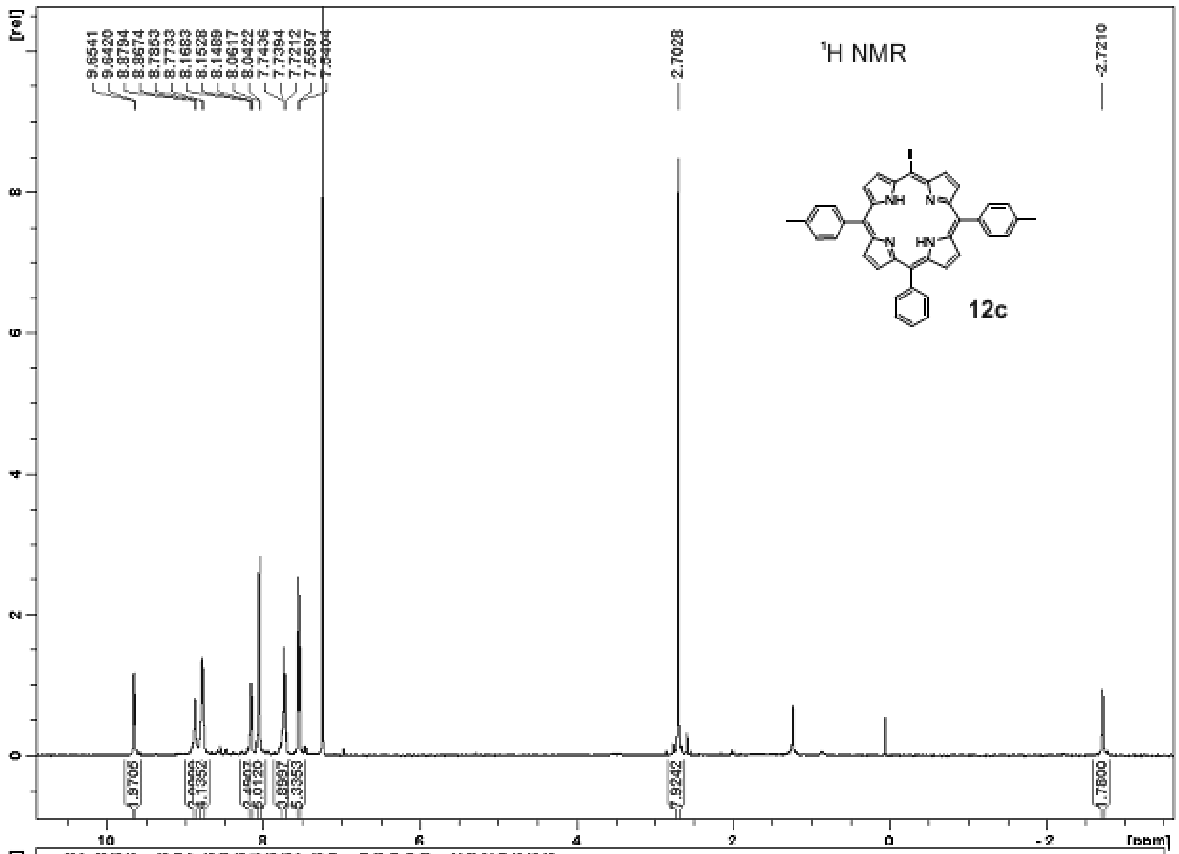
^{13}C NMR
[ppm]



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8.7853
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8.1528
8.1489
8.0617
8.0422
7.7436
7.7394
7.7212
7.5597
7.5404
2.7028
-2.7210
1H NMR
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HN
12c
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6.0120
5.3353
7.9242
1.7800
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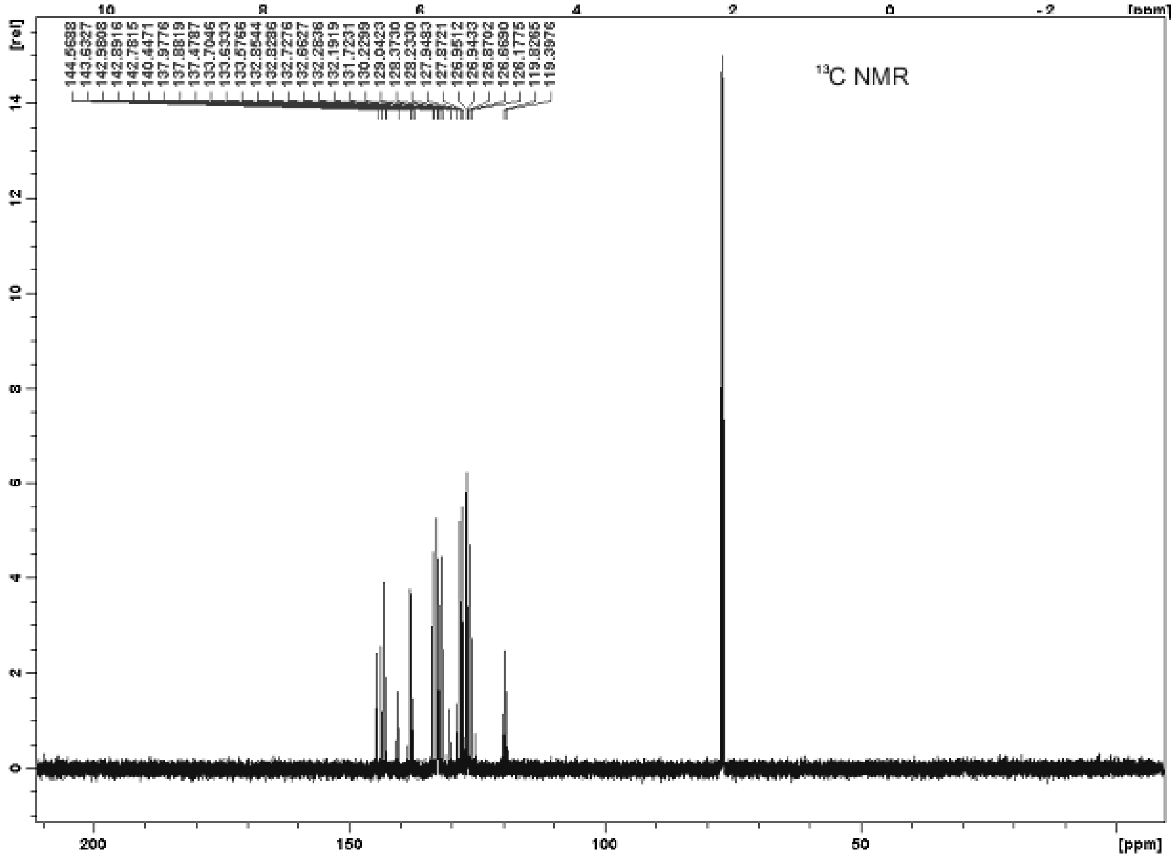
[ppm]



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128.3730
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126.8702
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13C NMR
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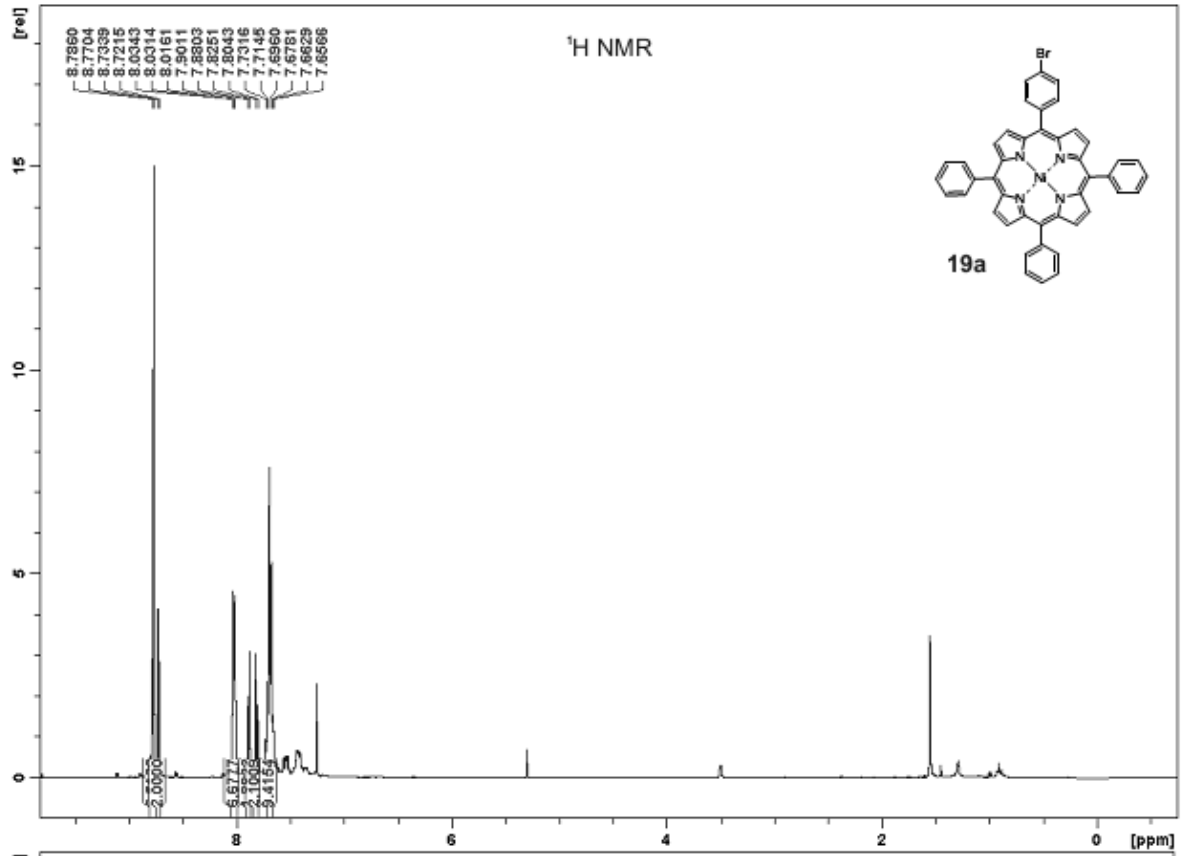
[rel]
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8.7860
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8.0314
8.0161
7.9011
7.8803
7.8251
7.8043
7.7316
7.7145
7.6960
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7.6629
7.6566
Br
19a
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6.6177
2.1008
9.4154
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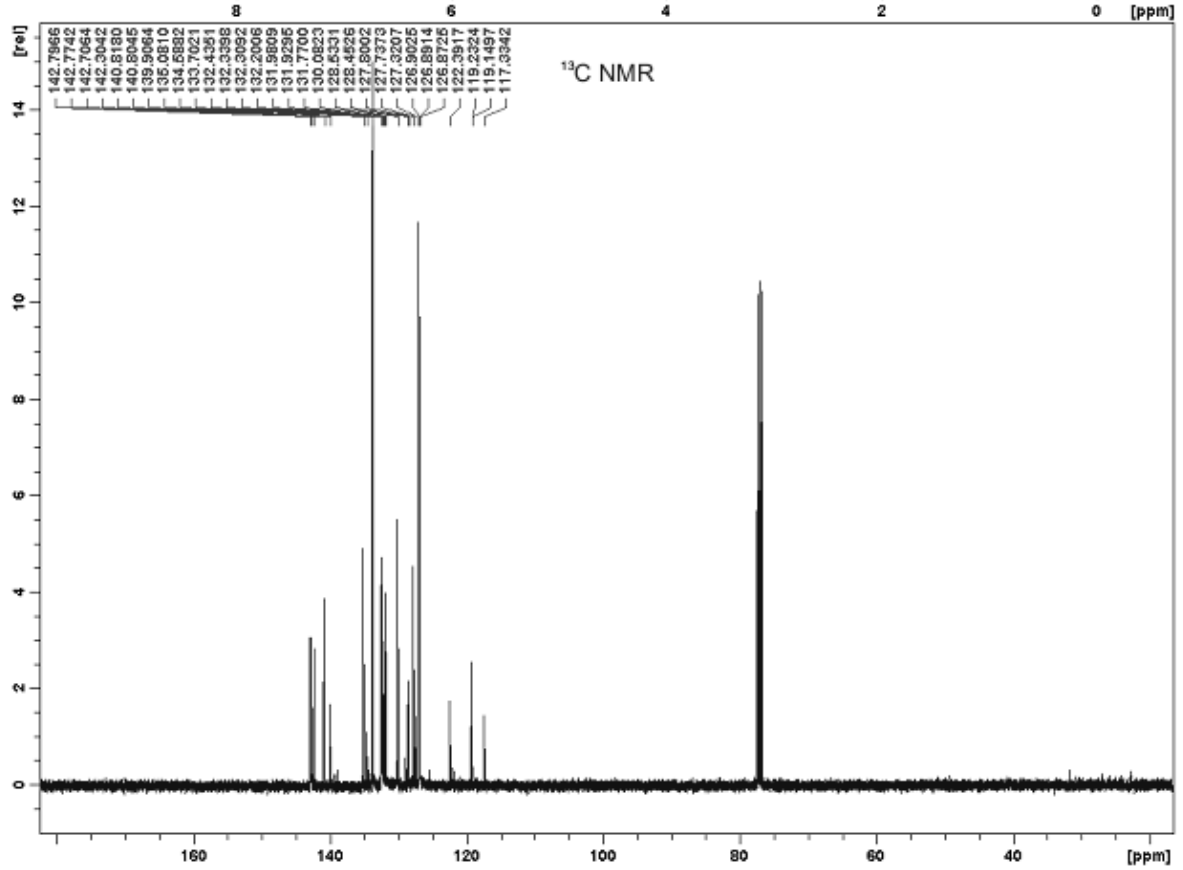
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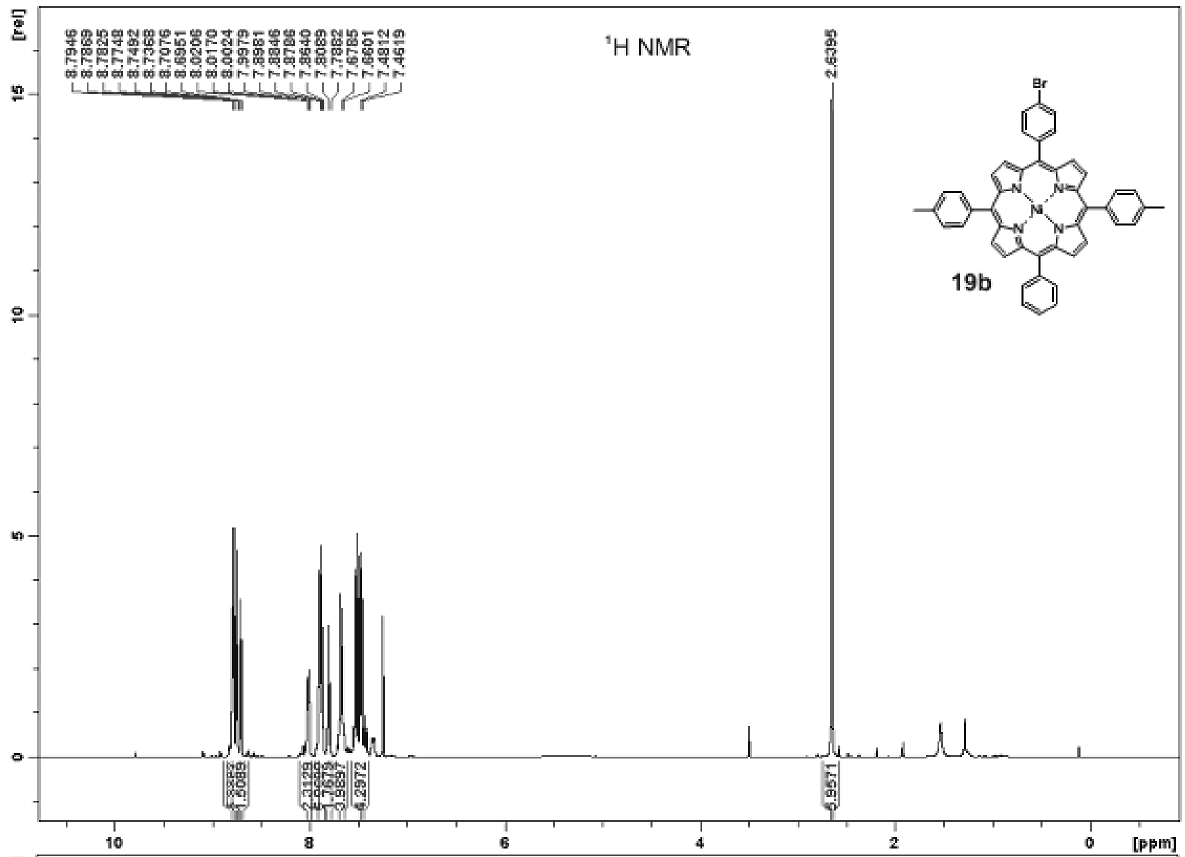
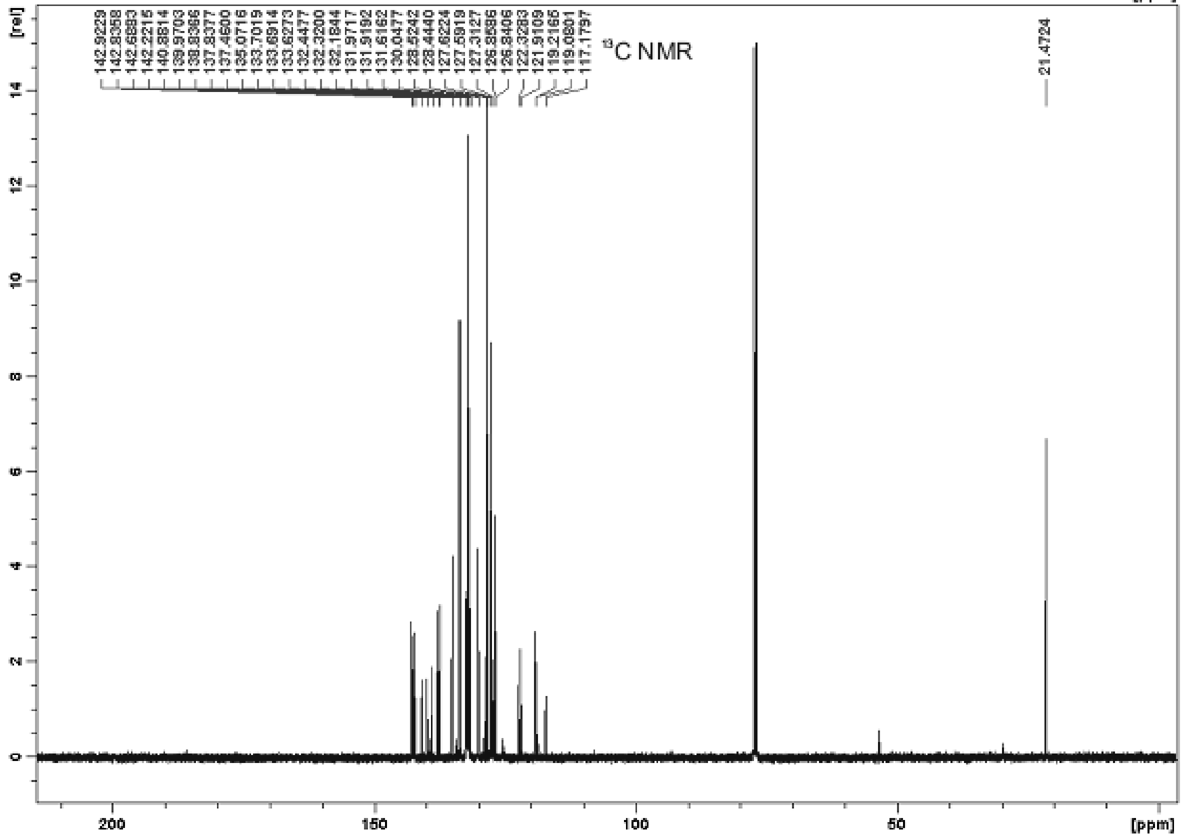
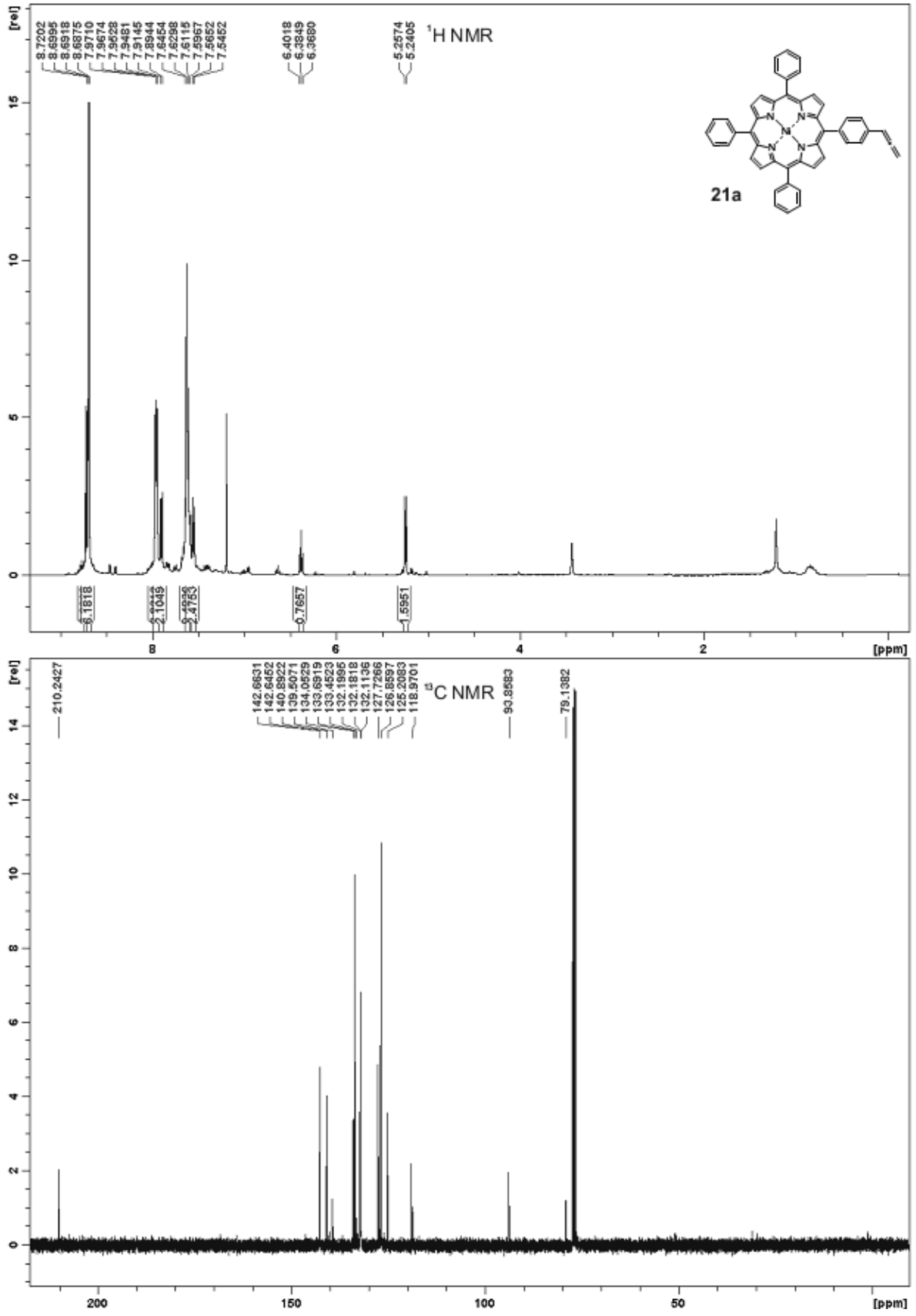
139.9964
135.0810
134.5882
133.7021
132.4351
132.3398
132.3092
132.2006
131.9809
131.9295
131.7700
130.0823
128.5331
128.4526
127.8002
127.7373
127.3207
126.9025
126.8914
126.8725
122.3917
119.2324
119.1497
117.3342
[ppm]

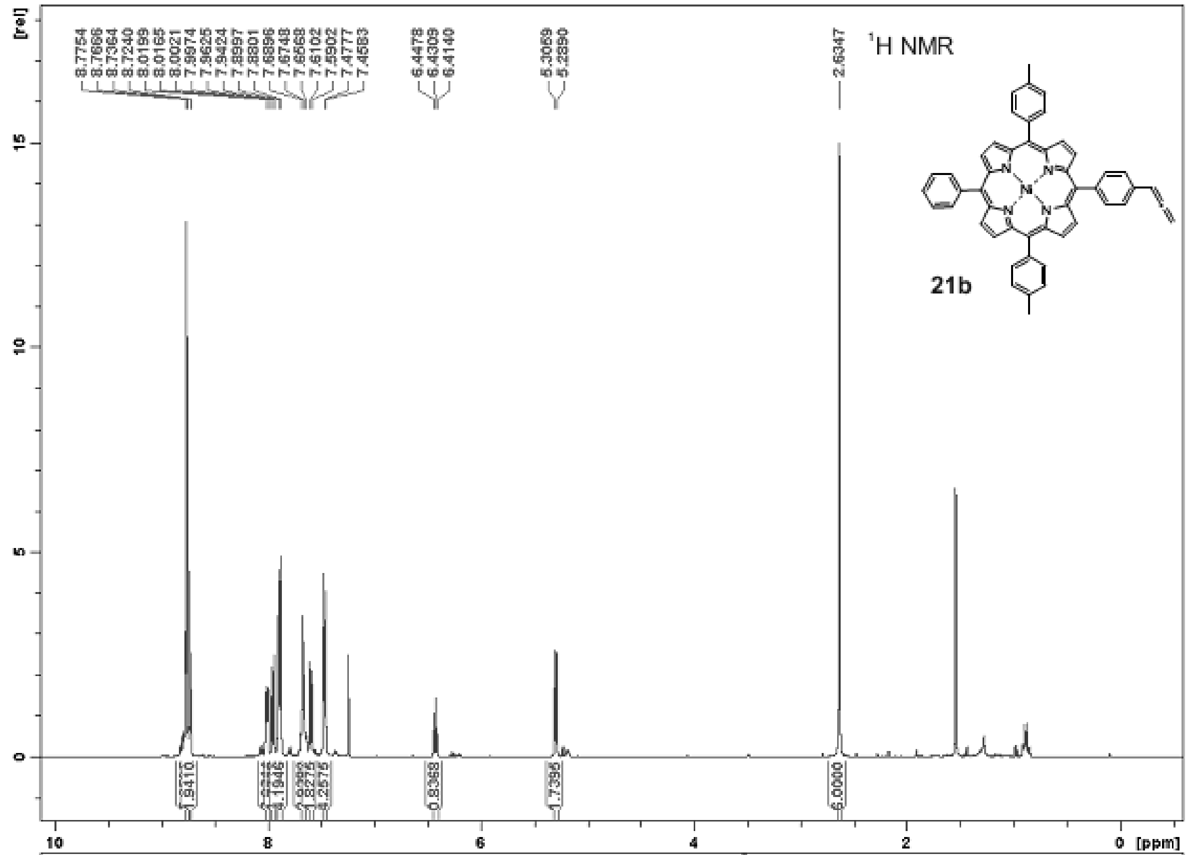


1H NMR
19b
Br
Ni
8.7946 8.7869 8.7825 8.7748 8.7492 8.7368 8.7076 8.6951 8.0206 8.0170 8.0024 7.9979 7.8981 7.8846 7.8786 7.8640 7.8089 7.7882 7.6785 7.6601 7.4812 7.4619
2.6395
[rel]
[ppm]

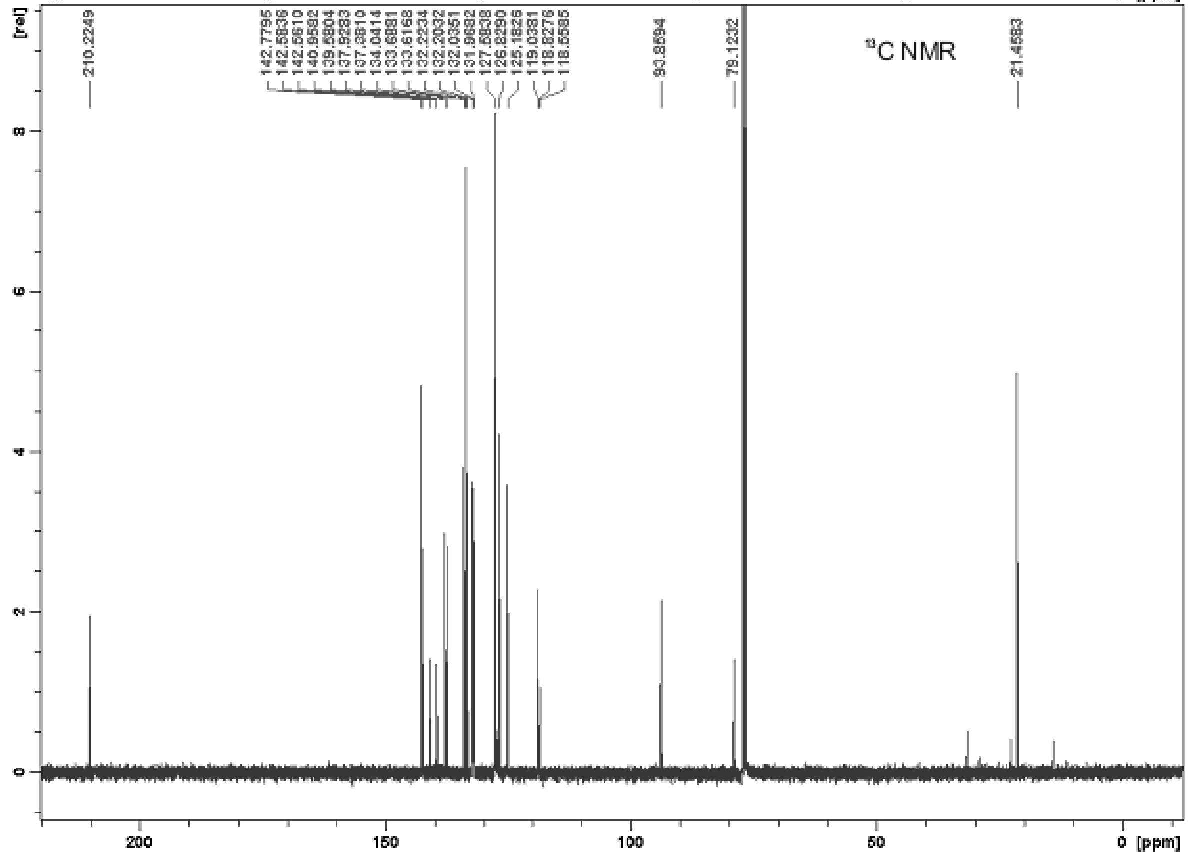


13C NMR
142.9229 142.8358 142.6883 142.2215 140.8814 139.9703 138.8366 137.8377 137.4600 135.0716 133.7019 133.6914 133.6273 132.4477 132.3200 132.1844 131.9717 131.9192 131.6162 130.0477 128.5242 128.4440 127.6224 127.5919 127.3127 126.8886 126.8406 122.3283 121.9109 119.2165 119.0801 117.1797
21.4724
[rel]
[ppm]


[rel]
8.7202
8.6995
8.6918
8.6875
7.9710
7.9674
7.9528
7.9481
7.9145
7.8944
7.6454
7.6298
7.6115
7.5967
7.5652
7.5452
6.4018
6.3849
6.3680
5.2574
5.2405
^{1}H NMR
21a
6.1818
2.1049
2.4755
0.7657
1.5951
8
6
4
2
[ppm]
[rel]
210.2427
142.6631
142.6452
140.8922
139.5071
134.0529
133.6819
133.4523
132.1996
132.1818
132.1136
127.7266
126.8597
125.2083
118.9701
^{13}C NMR
93.8583
79.1382
200
150
100
50
[ppm]



^{1}H NMR
21b
8.7754 8.7666 8.7364 8.7240 8.0199 8.0165 8.0021 7.9974 7.9625 7.9424 7.8997 7.8801 7.6896 7.6748 7.6568 7.6102 7.5902 7.4777 7.4583
6.4478 6.4309 6.4140
5.3059 5.2890
2.6347
[rel]
[ppm]



^{13}C NMR
210.2249
142.7795 142.5836 142.5610 140.9582 139.5804 137.9283 137.3810 134.0414 133.6881 133.6168 132.2234 132.2032 132.0351 131.9882 127.5838 126.8290 125.1826 119.0381 118.8276 118.5585
93.8594
78.1232
21.4583
[rel]
[ppm]