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Tetraaryldimethoxybenziporphyrins. At the Edge of Carbaporphyrinoid Aromaticity†

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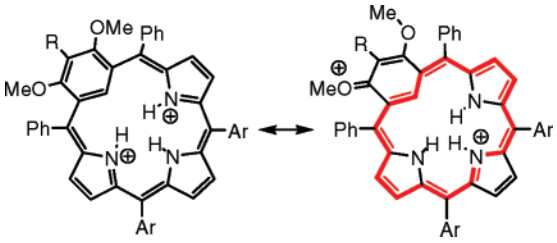

A series of eight dimethoxybenziporphyrins were prepared in three steps from 1,3-dimethoxybenzene or 2,6-dimethoxytoluene. Dibromination, followed by lithium−halogen exchange and reaction with benzaldehyde gave dicarbinol intermediates. These reacted with pyrrole and aryl aldehydes in the presence of BF_3•Et_2O in chloroform, followed by oxidation with DDQ, to give the benziporphyrins in 15−25% yield. These compounds readily gave nickel(II) and palladium(II) organometallic derivatives and could be selectively reduced with sodium borohydride to give unstable benziphlorins. Regioselective oxidation with silver acetate afforded the related 22-acetoxybenziporphyrins in 52−64% yield. The dimethoxybenziporphyrins showed chemical shifts by proton NMR spectroscopy that were consistent with weakly diatropic macrocycles. However, addition of TFA gave dications that showed far more significant shifts that are attributed to the presence of a more substantial diatropic ring current. The internal CH for **11**H_2^{2+} was observed at 3.5 ppm, but this effect was diminished for the 3-methylbenziporphyrins **12**H_2^{2+} where this resonance appears at 4.7 ppm. Even in the absence of the methoxy substituents, the dication derived from tetraphenylbenziporphyrin **8**H_2^{2+} shows an upfield shift for this resonance to 5.5 ppm. The dications of the 22-acetoxybenziporphyrins also show similar effects despite the presence of an internal ester moiety. These results demonstrate that a spectrum of diatropic character can manifest even in highly crowded benziporphyrin derivatives.

Introduction

Replacement of one or two isoindole moieties in phthalocyanines with benzene units gives rise to macrocycles such as **1**,[1] while a similar substitution of a pyrrole group in the porphyrin macrocycle leads to benziporphyrins such as **2a** (Chart 1).[2−4] The presence of these benzene units give rise to cross-conjugated systems that show no indication of any overall aromatic character.[5] However, the presence of electron-donating methoxy groups in **2b**, and to a lesser extent in **2c**, leads to weakly diatropic species, particularly for the protonated porphyrinoids.[6] Furthermore, addition of a hydroxyl substituent at C-2 facilitates a keto−enol-like tautomerization that results in the fully aromatic carbaporphyrinoid system oxybenziporphyrin **3**.[3,4,7] Benziporphyrins **2** and **3**, as well as related carbaporphyrinoids such as the azuliporphyrins **4**,[8] can easily be prepared using a '3 + 1' version of the MacDonald condensation.[9] Although this strategy has been very successful, it relies on the

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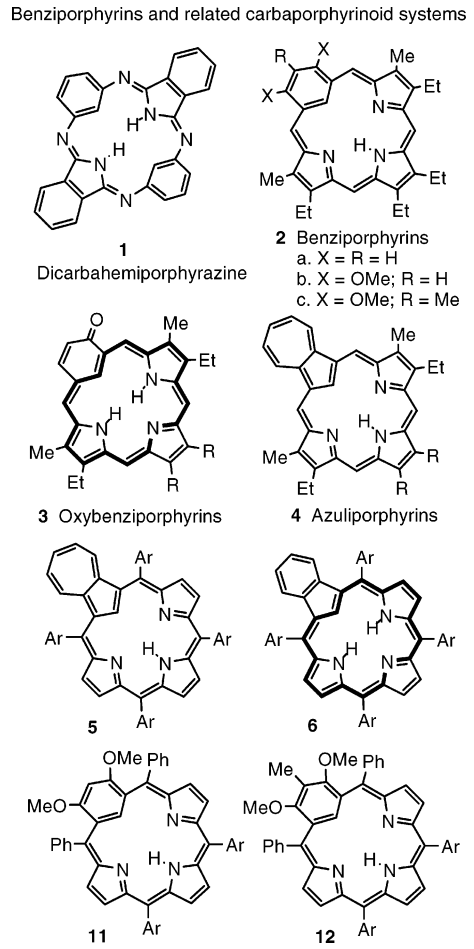
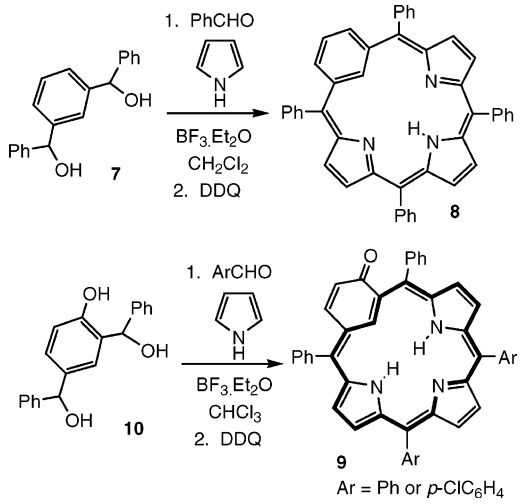
CHART 1



availability of tripyrrane intermediates that must be prepared by a multistep approach.[10] This limits the quantities of material available for further study. In addition, *meso*-unsubstituted porphyrin analogues are often less soluble in organic solvents and may be less stable than their *meso*-tetrasubstituted counterparts.[11] These considerations led us to develop a one-step route to tetraarylazuliporphyrins **5** using Lindsey−Rothemund conditions, and oxidative ring contraction allows access to the related benzocarbaporphyrins **6**.[11,12] In independent work, Stepien and Latos−Grazynski demonstrated that dicarbinol **7** condensed with pyrrole and aryl aldehydes under similar reaction conditions to give nonaromatic tetraarylbenziporphyrins **8** (Scheme 1A).[13] This approach was also successfully used in the synthesis of the aromatic porphyrin analogue tetraphenyloxybenziporphyrin **9** from the phenolic dicarbinol **10** (Scheme 1B).[14] These systems have been used to prepare interesting coordination complexes and some organometallic derivatives.[15−17]

SCHEME 1



We have been exploring the limits of aromatic character in carbaporphyrinoids and for this reason wanted to prepare the analogous dimethoxybenziporphyrins **11** and **12**. In this paper, efficient syntheses of these porphyrin analogues are reported, and their reactivity and spectroscopic characteristics are contrasted to benziporphyrins **8**.[18,19]

Results and Discussion

The synthesis of *meso*-tetraarylbenziporphyrins requires the availability of dicarbinols such as **7** (Scheme 1). Stepien and Latos-Grazynski prepared **7** in 56% yield by reacting a deficiency of phenylmagnesium bromide with isophthalaldehyde.[13] Although this approach could be used to prepare the related dimethoxy derivatives **13a** and **13b**, we speculated that a more efficient synthesis could be accomplished by using the readily available dibromodimethoxybenzenes **14**[20] (Scheme 2). Treatment of 4,6-dibromo-1,3-dimethoxybenzene (**14a**) with n-butyllithium afforded the dilithiated species **15a**, and this was directly reacted with benzaldehyde to give the dicarbinol **13a** in 71% yield. Similarly, the dimethoxytoluene derivative **14b** afforded the related dicarbinol **13b** in 62% yield. In both cases, the proton and carbon-13 NMR spectra indicated that the products had been isolated as a mixture of two diastereomers, but this was not important, as the stereochemistry is not retained in the final tetraarylbenziporphyrins. The synthesis of **11a** was

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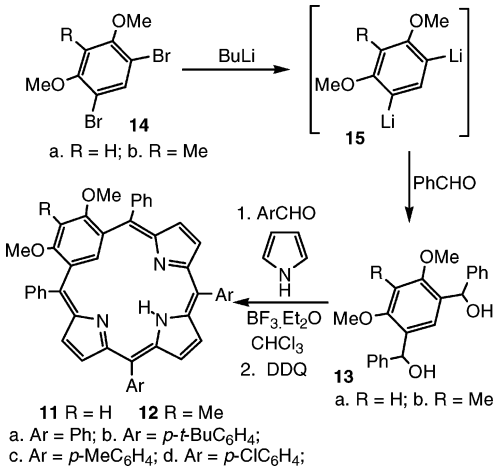
(19) These results were presented, in part, at the following meetings: (a) Szymanski, J. T.; Lash, T. D. *Program and Abstracts*, 35th Great Lakes Regional American Chemical Society Meeting, Loyola University, Chicago, IL, June 2003; American Chemical Society: Washington, DC, 2003; Abstract No. 216. (b) Szymanski, J. T.; Lash, T. D. *Book of Abstracts*, 227th National ACS Meeting, Anaheim, CA, March 28−April 1, 2004; American Chemical Society: Washington, DC, 2004; ORGN 147. (c) Szymanski, J. T.; Lash, T. D. *Program and Abstracts*, 36th Great Lakes Regional American Chemical Society Meeting, Peoria, IL, October 2004; American Chemical Society: Washington, DC, 2004; Abstract No. 315.

(20) Worden, L. R.; Kaufman, K. D.; Smith, P. J.; Widiger, G. N. *J. Chem. Soc. (C)* **1969**, 227−230.

SCHEME 2



initially attempted by mixing a dichloromethane solution of **13a** with 2 equiv of benzaldehyde and 3 equiv of pyrrole in the presence of $BF_3 \cdot Et_2O$. Following oxidation with DDQ, chromatography on silica and recrystallization from chloroform−methanol, the *meso*-tetraphenyldimethoxybenziporphyrin **11a** was isolated in 5% yield. Previously, it has been observed that the yields for many sterically hindered porphyrins,[21,22] as well as tetraarylazuliporphyrins,[11,12] are greatly improved when chloroform is used as the solvent for this chemistry. This appears to be because of the presence of ethanol as a stabilizer which modifies the reactivity of the Lewis acid catalyst. Under optimized conditions using chloroform, the yield of **11a** was raised to 15%. Significantly, under the same conditions, **13b** reacted with pyrrole and benzaldehyde to give the related porphyrinoid **12a** in 25% yield.

The superior yields obtained in these studies, and the small number of steps involved, allows the synthesis of significant quantities of dimethoxybenziporphyrins. In the synthesis of tetraphenylporphyrins, all of the carbon−carbon bond forming steps are potentially reversible, and this can lead to the scrambling of the *meso*-substituents.[23] This issue arises because the electron-rich pyrrole units can easily protonate and eliminate and because a second pyrrole group can stabilize the resulting carbocation. The electron-donating methoxy groups might facilitate acidolytic cleavage reactions, and the use of other aryl aldehydes were investigated to see whether dicarbinols **13a** and **13b** gave single benziporphyrin products. Hence, **13a** and **13b** were treated with 4-*tert*-butylbenzaldehyde, *p*-tolualdehyde, or 4-chlorobenzaldehede under the same reaction conditions. Following workup, column chromatography, and recrystallization, only one isomerically pure benziporphyrin product was obtained in each case. Yields in these reactions varied from 15 to 25%, but the methyl-substituted dicarbinol consistently gave superior yields, and 4-chlorobenzaldehyde also gave slightly better results in these investigations. Hence, this methodology allows for the regiospecific introduction of two different aryl substituents without any problems arising due to scrambling.

For benziporphyrins, the presence of a benzene ring introduces an element of cross-conjugation and does not allow for

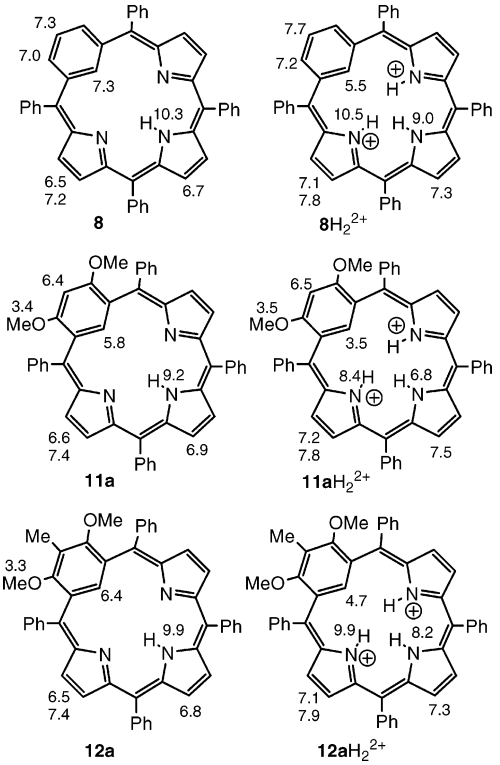


FIGURE 1. Proton NMR chemical shifts for selected protons on tetraphenylbenziporphyrins in $CDCl_3$ and the related dications in TFA−$CDCl_3$ at 25 °C.

an 18π electron delocalization pathway. For this reason, these macrocycles would not be expected to exhibit diatropic ring currents in their proton NMR spectra.[5] In addition, *meso*-aryl substituents generally decrease the planarity of porphyrins, and in the case of **11** and **12** this effect would be further exacerbated because of the presence of adjacent methoxy units that are oriented toward two of the phenyl moieties. Although the proton NMR chemical shifts for aromatic systems can be misleading,[24] the diatropic character of porphyrinoid systems is generally accepted as a reliable guide to macrocyclic aromaticity.[24−26] It was intriguing, therefore, that the internal CH of **11a** resonates at 5.84 ppm. This suggests the presence of a small diamagnetic ring current, as tetraphenylbenziporphyrin **8** shows this resonance at 7.3 ppm (Figure 1). In addition, the NH for **11a** gives rise to a broad peak at 9.2 ppm compared to 10.3 for **8**. In the proton NMR spectrum for **12a**, these resonances show up at 6.42 and 9.9 ppm, respectively, indicating that **11a** is more aromatic than **12a**. Although these shifts are relatively small, the corresponding dications **11**H_2^{2+} or **12**H_2^{2+} that are formed by addition of TFA to solutions of **11** or **12** in $CDCl_3$ showed far more pronounced effects (Figure 2). In the proton NMR spectrum of **11a**H_2^{2+} in TFA−$CDCl_3$, the internal CH shifts upfield to 3.5 ppm, while the NHs give rise to two resonances at 8.4 (2H) and 6.8 ppm (1H). The external pyrrolic protons also shift downfield by ca. 0.5 ppm. This effect is much reduced for the 2-methylbenziporphyrin dication **12a**H_2^{2+}, where the interior CH was observed at 4.7 ppm and the NH resonances

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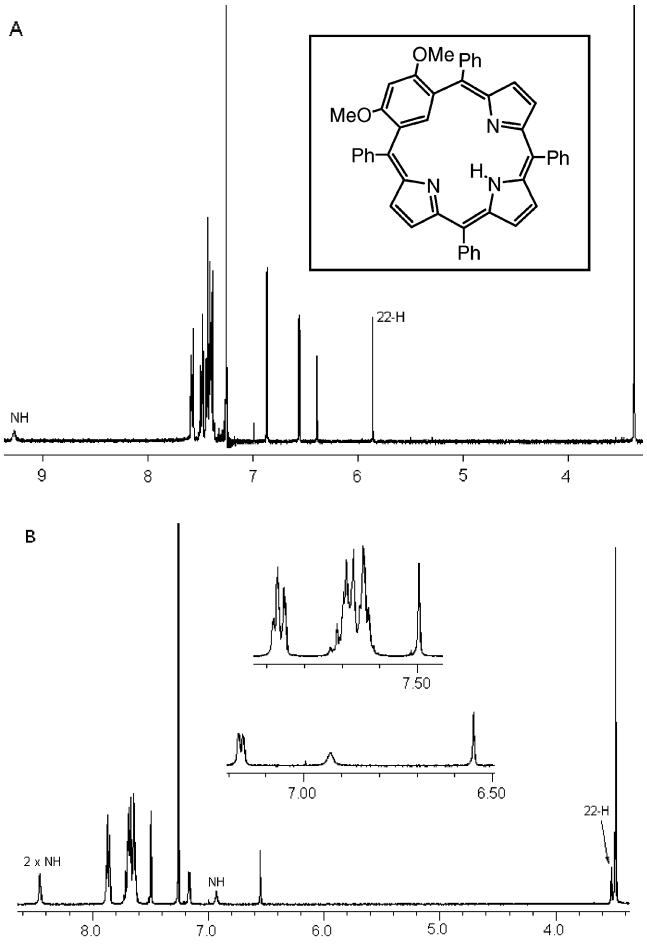
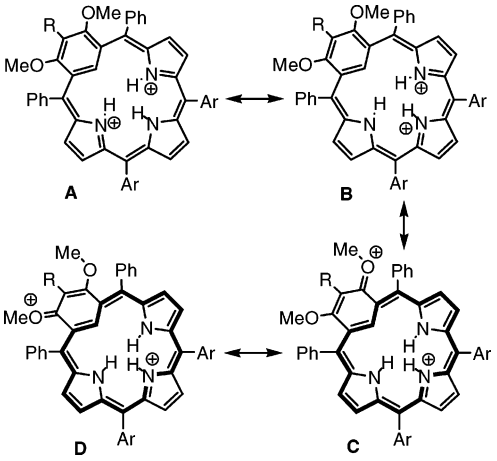


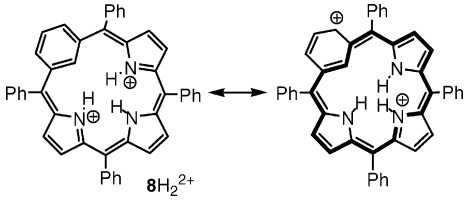
FIGURE 2. 400 MHz proton NMR spectra of dimethoxybenziporphyrin **11a** in $CDCl_3$ (A, free base) and TFA−$CDCl_3$ (B, dication **11a**H_2^{2+}). The internal CH (position 22) shows a pronounced upfield shift from 5.8 to 3.5 ppm due to increased macrocyclic diatropicity.

appeared at 8.2 and 9.9 ppm. Even so, these shifts clearly point to the presence of a diamagnetic ring current for **12a**H_2^{2+} as well as for **11a**H_2^{2+}. Similar results were obtained for the mixed tetraaarylbenziporphyrins **11b**−**d** and **12b**−**d**, although the more electron-donating *p*-tolyl- or 4-*tert*-butylphenyl-substituted porphyrinoids **11**/**12b**,**c** showed a slight increase in the diatropic shifts. The origin of the observed diatropic character for the dimethoxybenziporphyrins most likely derives from the electron-donating influence of the methoxy groupings. These effects allow for better charge delocalization in the protonated species **11**H_2^{2+} and **12**H_2^{2+} (Scheme 3). A series of canonical forms (e.g., **A**−**D**) can be used to describe these dications, and in contributors such as **C** and **D**, electron-donation leads to the presence of an 18π-electron delocalization pathway. These electronic interactions require the oxygen atoms to take on sp^2 hydrid character, and this requires the methoxy groups to lie in the same plane as the macrocycle. The methyl-substituted system is too sterically crowded to easily allow the methoxy units to take on the required geometry, although the associated electronic interaction must still occur to a limited extent. The electron-donating groups also provide more stabilization to the delocalized dicationic species. The free-base molecules **11** and **12** can have similar dipolar resonance contributors, but these are less favored because of the associated need for charge separation. Hence, dimethoxytetraphenylbenziporphyrins are intriguing

SCHEME 3



SCHEME 4



systems that have properties that are intermediary between tetraphenylbenziporphyrin **8** and tetraphenylazuliporphyrin **5**.[11,12] It is noteworthy that the free base and dicationic forms for these macrocycles show increasing aromatic character going from **8** to **12** to **11** to **5**. However, tetraphenyloxybenziporphyrin **9** shows the greatest aromatic character for the free base but reverts to a nonaromatic phenolic species upon diprotonation.[14] For instance, the proton NMR spectra for the free base forms in $CDCl_3$ show the internal CHs of **8**, **12a**, **11a**, **5** and **9** at 7.33, 6.42, 5.84, 3.35 and −3.0 ppm, respectively. These differences cannot be simply due to electron-donating effects, and are paralleled by a downfield shift of the external pyrrolic protons. The dications for **12a**, **11a**, and azuliporphyrin **5** show a more pronounced trend for the inner CH, giving resonances at 4.73, 3.5, and −0.33 ppm,[12] respectively. However, this proton is shifted downfield for **9**H_2^{2+}, showing up at 4.25 ppm.[14] The upfield shifts for the internal CHs is paralleled by a downfield shift for the external pyrrolic protons, with **9**H_2^{2+} again showing the opposite trend. Perhaps most surprising of all is that the dication **8**H_2^{2+} of tetraphenylbenziporphyrin shows an upfield shift for the internal CH to 5.5 ppm (Figure 1). Although the shift is small, this result suggests that resonance contributors of the type shown in Scheme 4 allow for a small diatropic ring current in this case as well.

The UV−vis spectra for the free base forms of **11a**, **12a**, and **8** are similar to one another, showing a weak Soret-like band slightly above 400 nm, and a broad absorption near 700 nm (Figure 3). However, there is a bathochromic shift for the shorter wavelength band going from **8** to **12a** to **11a**, giving λ_{max} values of 437, 422, and 411 nm, respectively. The dications of **12a**, **11a**, and **5** in 1% TFA−chloroform all show a strong broad absorption in the far red, although in this case there is a hypsochromic shift for the series with the λ_{max} values at 889, 876, and 850 nm, respectively. The dication of **8** gives data that are in agreement with this trend, showing the equivalent absorption at >900 nm.[13]

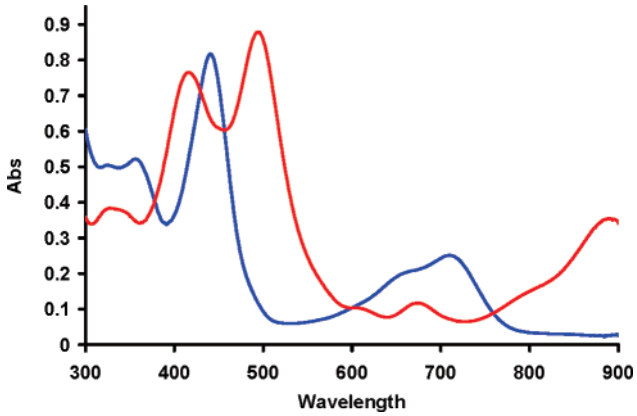
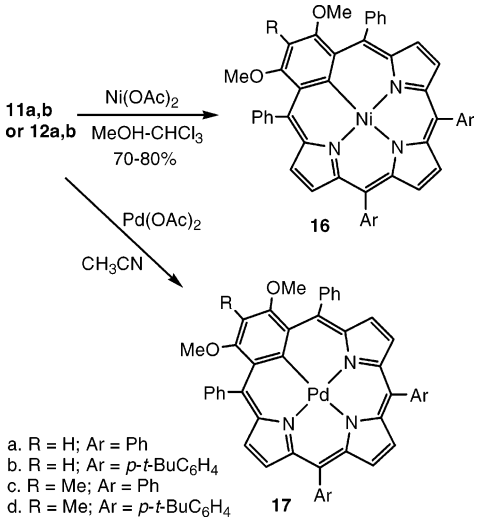


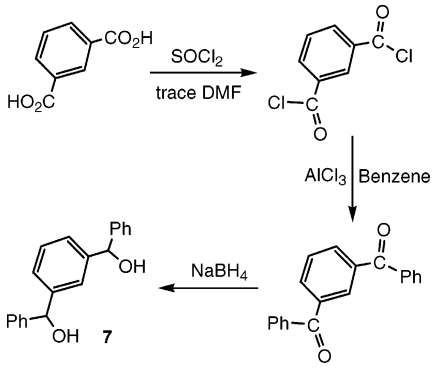
FIGURE 3. UV−vis spectra of dimethoxybenziporphyrin **11a** in 1% Et_3N−chloroform (blue line, free base) and 1% TFA-chloroform (red line, dication **11a**H_2^{2+}).

SCHEME 5



Azuliporphyrins and benziporphyrins undergo metalation with nickel(II) or palladium(II) salts,[15−17,27] and it was of some interest to see whether it is also possible to synthesize organometallic derivatives of this type for **11** and **12**. These studies were conducted on **11a**,**b** and **12a**,**b** so that four different metallo-derivatives were available. Nickel(II) acetate in chloroform−methanol was found to cleanly react with **11** and **12** to afford the related organometallic derivatives **16** in 70−80% yield (Scheme 5). When these initial studies were conducted,[18] the nickel(II) derivative of tetraphenylbenziporphyrin **8** had not been reported and this metalloporphyrinoid was prepared so that comparisons could be made to the dimethoxy metallo-derivatives **16**. The synthesis of **8** requires dicarbinol **7** as a precursor, and this was previously obtained by reacting a Grignard reagent with isophthalaldehyde.[13] Yields could be substantially improved by using an excess of phenylmagnesium bromide or phenyllithium. However, we considered dicarboxylic acids to be far more convenient precursors to the required dicarbinols. Isophthalic acid is easily converted into 1,3-dibenzoylbenzene (Scheme 6),[28] and reduction with sodium borohydride in ethanol gives **7** in

SCHEME 6



virtually quantitative yield. Tetraphenylbenziporphyrin **8** was generated in 13% yield using the previously reported procedure (Scheme 1A).[13] Interestingly, this reaction only gave good results when dichloromethane was used as the reaction solvent and, in contrast to our other results, virtually no benziporphyrin was formed when the reaction was carried out in chloroform. Benziporphyrin afforded the nickel(II) complex Ni**8** in good yields when using excess nickel(II) acetate in refluxing chloroform−methanol. The nickel(II) complex of **8** was subsequently reported by Stepien et al. using somewhat different metalation conditions as part of a far more detailed report on the metallo-derivatives of benziporphyrins.[15] In our original communication,[18] we noted that palladium(II) acetate failed to react with **11a** or **12a** to give palladium(II) benziporphyrins **17**, and considerable decomposition was noted for prolonged reaction times under the conditions used to prepare **16**. However, when the reactions were carried out in refluxing acetonitrile the palladium(II) derivatives **17** could be isolated in 73−81% yield (Scheme 5).

The proton NMR spectra for the nickel(II) and palladium(II) complexes were consistent with the proposed diamagnetic organometallic species **16** and **17**. The proton NMR spectra for nickel(II) benziporphyrins **16a** and **16b** in $CDCl_3$ gave resonances for the pyrrolic protons that were ca. 0.6 ppm further downfield than the corresponding free bases **16a** and **16b**, and similar, albeit smaller, shifts were noted for the 2-methylbenziporphyrin complexes **16c** and **16d** as well. In addition, the external pyrrolic protons for Ni**8** gave peaks that were between 0.3 and 0.5 ppm upfield from those for **16a** and **16b** while the 2-methyl metalloporphyrinoids **16c** and **16d** gave intermediary values. For instance, the 13,14-pyrrolic protons for Ni**8**, **16c**, and **16a** were 7.3, 7.4, and 7.6 ppm, respectively. Similar trends were noted for the palladium(II) complexes **17** as well. These results imply that the metallo-derivatives **16** and **17** have significantly higher diatropic character than the corresponding free base dimethoxybenziporphyrins, a feature that may be due in part to a conformational change associated with binding to metal cations. Both the nickel(II) and palladium derivatives also show a clear trend of increased diatropic character due to the presence of the methoxy groups with the 2-methyl versions again showing smaller shifts due to the disruptive steric interactions previously discussed. The UV−vis spectra for **16** and **17** showed multiple bands with weak Soret-like absorptions between 400 and 500 nm. However, the UV−vis spectra for the nickel complexes **16** did not give reproducible results, apparently because of irreversible degradation processes in the dilute solutions. No problems were encountered running the NMR spectra of **16**, and the palladium(II) derivatives **17** did not show

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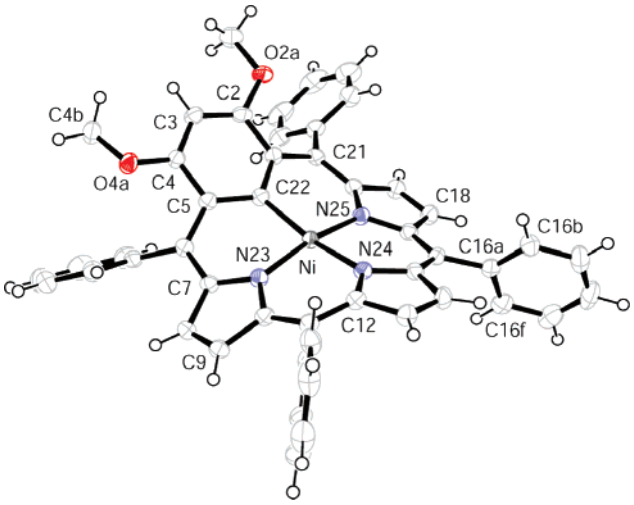


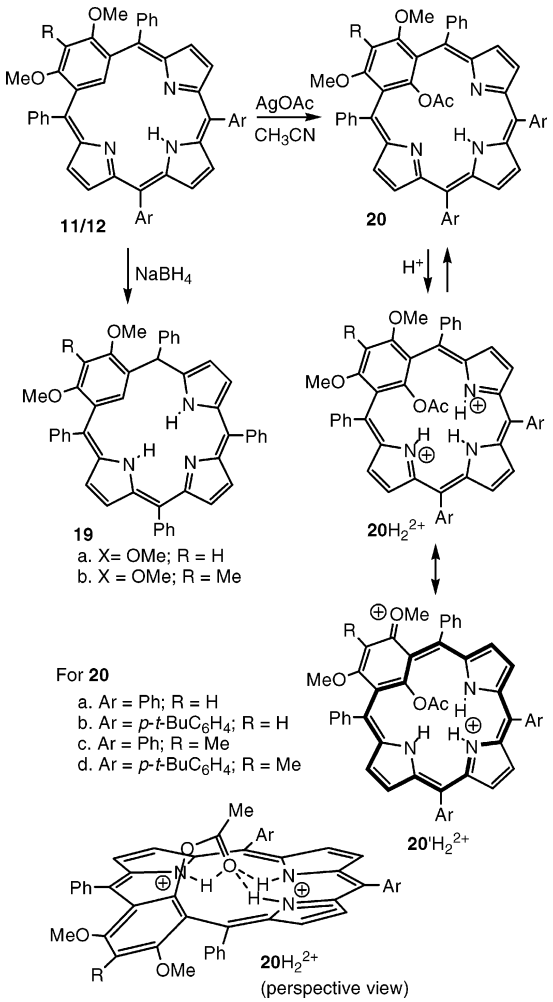
FIGURE 4. ORTEP III drawing (35% probability level, hydrogen atoms drawn arbitrarily small) of nickel complex **16a** showing the twisted geometry of the benzene subunit. Selected bond lengths (Å): Ni−C(22) 1.969(3), Ni−N(23) 1.922(3), Ni−N(24) 1.967(3), Ni−N(25) 1.915(3), C(1)−C(22) 1.424(5), C(5)−C(22) 1.436(4). Selected bond angles (deg): C(22)−Ni−N(24) 166.2(1), N(23)−Ni−N(25) 166.5-(1), C(22)−Ni−N(23) 91.6(1), C(22)−Ni−N(25) 92.1(1), N(23)−Ni−N(24) 89.5(1), N(24)−Ni−N(25) 89.9(1), C(1)−C(22)−C(5) 114.6(3).

any significant variations in their spectra. Stepien et al. have noted that the C−Ni bond of Ni**8** can be cleaved with HCl to generate a paramagnetic nickel(II) complex,[15] but we have not pursued this line of investigation.

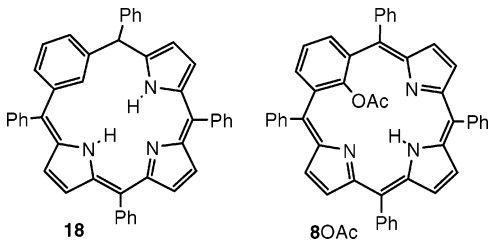
Despite these observations, slow growth of X-ray quality crystals for **16a** was accomplished (Figure 4). Black single-crystal blocks of **16a** were grown by vapor diffusion of hexanes into a dichloroethane solution followed by slow evaporation. The nickel(II) ion coordinates to the three tripyrrane nitrogen atoms and C(22) and is best described as having a distorted square planar coordination geometry. The macrocycle adopts a saddle geometry with the dimethoxyphenyl ring bent nearly 40° out of the NiN_3 plane. Close examination of the structure indicates this striking feature is attributable to contact between the alkoxy oxygen atoms and the adjacent phenyl ipso carbon atoms. The 2.587(4) Å O(2a)−C(21a) and 2.599(4) Å O(4a)−C(6a) bond separations are substantially smaller than the 2.95 Å sum of the Pauling Van der Waal radii. The 1.969(3) Å Ni−C bond length is well within the typical range of four coordinate divalent nickel(II) complexes;[29] however, it is more than 60 pm longer than the corresponding parameter in other nickel(II) carbaporphyrinoid examples.[17,30−32] That the steric strain imposed by the C(22) metal coordination coupled with the crowding imposed by the methoxy groups is substantial is shown by the significant dimethoxyphenyl ring distortion from planarity demonstrated by the more than 15° C(1)−C(22)−C(5)−C(4) and C(5)−C(22)−C(1)−C(2) torsion angles.

In order to further contrast the dimethoxy macrocycles **11** and **12** with **8**, additional reactivity studies were carried out. Benziporphyrin **8** has been shown to undergo regioselective

SCHEME 7



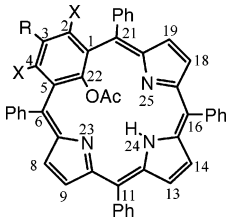
reduction with sodium borohydride to give benziphlorin **18**, while oxidation with silver acetate afforded the 22-acetoxy derivative **8**OAc.[13] Dimethoxybenziporphyrin **11a** was reacted with $NaBH_4$ in ethanol−chloroform for 16 h and gave blue-green solutions of the dihydrobenziporphyrin **19a** (Scheme 7). This compound was not very stable but could be recrystallized to give a reasonably pure product. The same chemistry could be performed on **12a**, but the resulting phlorin **19b** was significantly less stable and could not be fully purified. Nevertheless, **11a** and **12a** show similar reactivity toward $NaBH_4$ as **8**.



Dimethoxybenziporphyrin **11a** was reacted with silver acetate in refluxing acetonitrile−chloroform for 2 h, and following column chromatography on basic alumina and recrystallization from chloroform−methanol, the related acetoxy compound **20a** was isolated in 60% yield (Scheme 7). Benziporphyrins **11b** and **12a** were found to react similarly to give the 22-acetoxy

(29) Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380−388; Cambridge Structural Database, version 5.28 (Nov 2006).
(30) Pawlicki, M.; Latos-Grazynski, L. *Chem. Eur. J.* **2003**, *9*, 4650−4660.
(31) Xiao, Z.; Patrick, B. O.; Dolphin, D. *Chem. Commun.* **2002**, 1816−1817.
(32) Schmidt, I.; Chmielewski, P. J.; Ciunik, Z. *J. Org. Chem.* **2002**, *67*, 8917−8927.

TABLE 1. Selected ^{1}H NMR Chemical Shifts for 22-acetoxybenziporphyrins



	OAc	OMe	3	8,19	9,18	13,14	24	23,25
8OAc (R = X = H)								
in $CDCl_3$	1.33	-	7.19	7.32	6.54	6.86	9.50	-
in TFA−$CDCl_3$	1.03	-	7.6	7.93	7.21	7.41	6.1	10.3
20a (R = H; X = OMe)								
in $CDCl_3$	1.12	3.4	6.35	7.4	6.5	6.9	8.9	-
in TFA−$CDCl_3$	0.51	3.5	6.51	8.0	7.3	7.7	4.2	8.4
20c (R = Me; X = OMe)								
in $CDCl_3$	1.29	3.21	-	7.4	6.5	6.8	9.4	-
in TFA−$CDCl_3$	0.93	3.16	-	7.9	7.2	7.5	5.7	10.0

derivatives **20b** and **20c**, respectively, in 52−64% yield. The same chemistry was performed on **12b**, but in this case poor results were obtained and the product **20d** could not be isolated in pure form. Clearly, **11** and **12** have similar reactivity to **8**, and the silver acetate reaction provides a convenient method for derivatization of the internal carbon. On the basis of steric considerations, it initially seemed somewhat implausible that acetates **20** would exhibit any diatropic character. However, the acetate group gives a 3H singlet at 1.12 ppm for **20a** and at 1.29 ppm for **20c**, indicating that this moiety is shielded by the π-system (Table 1). More significantly, addition of TFA gives dications **20**H_2^{2+} where the acetate resonance for **20a** shifts upfield to 0.51 ppm (Figure 5), while in the case of **20c** this unit gives a peak at 0.93 ppm. These shifts are consistent with a significant diatropic ring current for the acetate dications, and once again the effect is reduced by the presence of a methyl group at position 3. Further evidence for the diatropic character

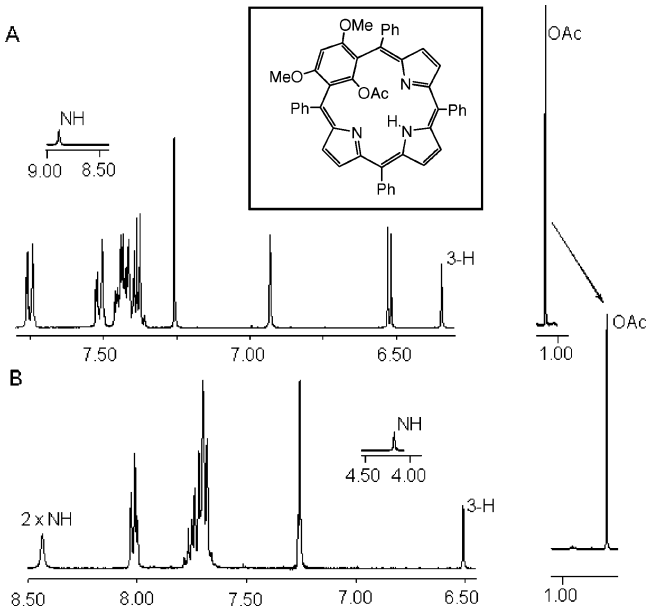


FIGURE 5. Partial 400 MHz proton NMR spectra for 22-acetoxybenziporphyrin **20a** in $CDCl_3$ (A, free base) and TFA−$CDCl_3$ (B, dication **20a**H_2^{2+}). The acetate resonance shifts upfield from 1.1 to 0.5 ppm while the 24-NH shifts from 8.9 to 4.2 ppm.

of the dications comes from the large downfield shifts for the pyrrolic hydrogens ($\Delta\delta$ = 0.6−0.8 ppm for **20a** and $\Delta\delta$ = 0.5−0.7 ppm for **20c**). In addition, the NH resonances for the protonated species are upfield from the values expected for a dication and in **20a**H_2^{2+} show up at 4.2 (1H) and 8.4 (2H) ppm (Table 1). The shifts suggest that these dications have comparable diatropicity to the parent benziporphyrin dications **11**H_2^{2+} and **12**H_2^{2+}. This property is presumably still due to resonance contributors such as **20′**H_2^{2+} which facilitate charge delocalization, and the results imply that the system must retain sufficient planarity to allow π-conjugation over the macrocycle. The internal acetate unit can hydrogen bond to the NHs, and this presumably holds the ring system in a favorable geometry for π-electron delocalization. In addition, this intramolecular hydrogen bonding interaction would further stabilize this system. It is possible that this is also a factor for the free base 22-acetate derivatives **20**, but it is worth noting that the free base form of **8**OAc has been characterized by X-ray crystallography and does not show this type of interaction. Instead, **16** showed hydrogen bonding between the imine nitrogens and a cocrystallized water molecule, and the acetate carbonyl was orientated away from the central cavity.[13] In order to compare our data with **8**OAc, a sample of this compound was also prepared and proton NMR spectra were obtained in $CDCl_3$ and TFA−$CDCl_3$ (the former spectrum was virtually identical to the spectrum reported by Stepien and Latos-Grazynski[13]). This compound again showed significant shifts upon protonation that were consistent with a small diatropic ring current (Table 1). The acetate methyl resonance shifted upfield by 0.3 ppm for **8**OAcH_2^{2+}, and one of the internal NH resonances was present at 6.11 ppm. The results indicate that the diatropic character is largest for **20a**H_2^{2+} and smallest for **8**OAcH_2^{2+}, but even when no methoxy substituents are present there are still significant shifts that support the presence of a small diatropic ring current.[33] The UV−vis spectra for the dications gave broad absorptions at 849

(33) As a counterpoint to our observations, it is worth noting that 22-hydroxytetraphenylbenziporphyrin tautomerizes to give an antiaromatic ketone that affords paratropic proton NMR chemical shifts: Stepien, M.; Latos-Grazynski, L.; Szterenberg, L. *J. Org. Chem.* **2007**, *72*, 2259−2270. For a related azuliporphyrin derivative, see: Colby, D. A.; Ferrence, G. M.; Lash, T. D. *Angew. Chem., Int. Ed.* **2004**, *43*, 1346−1349.

nm for **20a** and 873 nm for **20c**, and in this respect these spectra resembled those obtained for the parent benziporphyrins **11a** and **12a**.

Conclusions

A straightforward three-step route to electron-rich tetraphenylbenziporphyrins **11** and **12** from dimethoxybenzenes has been developed. These novel porphyrin analogues show enhanced diatropic character under acidic conditions that is similar to the results obtained for azuliporphyrins.[8,11,12] While these shifts are not as large as those observed for the azuliporphyrins, a small diatropic ring current can even be observed for the tetraphenylbenziporphyrin dication $\mathbf{8}H_2^{2+}$. The new macrocycles readily form nickel(II) and palladium(II) complexes and can be selectively reduced with sodium borohydride to give benziphlorins. Reaction with silver acetate gives 22-acetoxy derivatives, but the internal acetate group does not disrupt the diatropicity of the related dications $\mathbf{20}H_2^{2+}$ relative to the 22-unsubstituted versions to any significant extent. These studies make far more diverse tetraarylbenziporphyrin structures available for study and demonstrate that these porphyrin analogues may have varying degrees of aromatic character even when a high degree of steric crowding is present.

Experimental Section

4,6-Bis(α-hydroxyphenylmethyl)-1,3-dimethoxybenzene (**13a**). A solution of n-butyllithium in hexanes (2.5 M; 40 mL; 64 mmol) was added via a syringe to a stirred solution of 4,6-dibromo-1,3-dimethoxybenzene (8.30 g; 28.0 mmol) in sodium-dried ether (450 mL) under a nitrogen atmosphere. The resulting cloudy white mixture was stirred for 15 min at room temperature. After this time, benzaldehyde (8.10 g; 76 mmol) was added dropwise via a pressure-equalized addition funnel over a period of approximately 5 min and a thick white precipitate was formed. After the mixture had stirred for a further 10 min, 200 mL of aqueous 10% ammonium chloride solution was added. The ether layer was separated and dried over sodium sulfate, and the solvent was evaporated under reduced pressure. The residue was recrystallized from chloroform−petroleum ether (60−90°) to give the dicarbinol (6.98 g; 19.9 mmol; 71%) as small white crystals, mp 114−116 °C; ^{1}H NMR ($CDCl_3$): δ 2.86−2.90 (2H, m), 3.80 (6H, s), 5.95 (2H, d, J = 5.2 Hz), 6.45 (1H, s), 7.13 and 7.18 (2 singlets for diastereomers, 1H), 7.22−7.34 (10H, m); ^{13}C NMR ($CDCl_3$): δ 55.9, 72.3, 95.9, 124.4, 126.6, 127.2, 127.7, 127.8, 128.0, 128.3 (2 peaks), 143.8, 157.4. Anal. Calcd for $C_{22}H_{22}O_4$: C, 75.41; H, 6.33. Found: C, 74.85; H, 6.53.

3,5-Bis(α-hydroxyphenylmethyl)-2,6-dimethoxytoluene (**13b**). The title compound was prepared by the foregoing procedure from 3,5-dibromo-2,6-dimethoxytoluene (8.00 g; 25.8 mmol), 32.3 mL of n-butyllithium (2.5 M solution in hexanes; 51.7 mmol) and benzaldehyde (5.49 g; 51.7 mmol). Recrystallization was performed by first dissolving the crude product in methanol, heating the solution on a hot water bath, and adding water until the solution remained slightly turbid even at elevated temperatures. The mixture was allowed to stand at room temperature for 5 days in order to allow crystal formation. The white precipitate was suction filtered, dried *in vacuo* overnight, and further recrystallized from chloroform−ether to give the dialcohol (5.88 g; 16.1 mmol; 62%) as a white powder, mp 89−91 °C; ^{1}H NMR ($CDCl_3$): δ 2.18 (3H, s), 2.9−3.0 (2H, br m), 3.47 and 3.48 (2 singlets for the diastereomers, 6H), 5.96 (1H), 7.23−7.38 (10H, m); ^{13}C NMR ($CDCl_3$): δ 10.2, 60.9 (2 peaks for diastereomers), 72.3 and 72.4 (2 peaks for diastereomers), 125.0 (2 peaks for diastereomers), 125.2 (2 peaks for diastereomers), 126.7 (2 peaks for diastereomers), 127.5 (2 peaks for diastereomers), 128.5 (2 peaks), 132.8, 144.2 (2 peaks for diastereomers), 156.9 (2 peaks for diastereomers). Anal. Calcd for $C_{23}H_{24}O_4$: C, 75.80; H, 6.64. Found: C, 75.44; H, 6.64.

1,3-Bis(α-hydroxyphenylmethyl)benzene (**7**). 1,3-Dibenzoylbenzene (10.00 g; 35.0 mmol) and ethanol (100 mL) were placed in a 500 mL Erlenmeyer flask and stirred with gentle heating on a hot plate until the diketone had completely dissolved. Sodium borohydride was added over 5 min in four portions to the hot solution and the mixture stirred at room temperature for 15 min. Water (100 mL) was added, and the mixture was heated to gentle boiling and stirred for 30 min. The mixture was diluted with water (200 mL) and cooled in an ice bath, and the resulting white precipitate was suction filtered and washed well with water. The sample was dried *in vacuo* to give the dicarbinol (9.74 g; 33.6 mmol; 96%) as a white powder, mp 129−132 °C. As expected, the NMR data showed the presence of two diastereomers. ^{1}H NMR ($CDCl_3$): δ 2.28 (2H, d, J = 3.5 Hz), 5.81 (2H, d, J = 3.5 Hz), 7.23−7.37 (13H, m), 7.45−7.48 (1H, m); ^{13}C NMR ($CDCl_3$): δ 76.5, 125.0, 126.0, 126.1, 126.8, 126.9, 127.8, 128.7, 128.9, 144.0, 144.4.

2,4-Dimethoxy-6,11,16,21-tetraphenylbenziporphyrin (**11a**). Nitrogen was slowly bubbled through a stirred solution of 4,6-bis(α-hydroxyphenylmethyl)-1,3-dimethoxybenzene (0.70 g; 2.0 mmol) in 900 mL of chloroform in a 1 L round-bottom flask that had been covered with aluminum foil to protect the reaction from ambient light. A septum was placed in the neck of the flask, and a nitrogen-filled balloon was attached to maintain the inert atmosphere. Next, freshly distilled pyrrole (420 μL; 6.0 mmol) and benzaldehyde (400 μL; 4.0 mmol) were added via syringe, followed by 0.20 mL of boron trifluoride etherate. The resulting mixture was stirred for 2 h at room temperature. The initially colorless solution turned orange and then became a deep red color. DDQ (1.40 g; 98%; 6.0 mmol) was added and the mixture stirred for an additional 10 min. The dark solution was evaporated under reduced pressure and the residue purified on a Grade 3 basic alumina column eluting with dichloromethane. Tetraphenylporphyrin and unidentified brown byproducts eluted initially, followed by a dark emerald green band corresponding to the title benziporphyrin. Recrystallization from chloroform−methanol gave the dimethoxybenziporphyrin (210 mg; 0.306 mmol; 15%) as a green powder, mp 282−284 °C, dec; UV−vis (1% Et_3N−$CHCl_3$): λ_{max} (log ϵ) 354 (4.59), 437 (4.75), 657 (sh, 4.15), 699 nm (4.23); UV−vis (1% TFA−$CHCl_3$): λ_{max} (log ϵ) 322 (4.46), 404 (4.71), 488 (4.76), 601 (3.80), 664 (3.80), 876 nm (4.41); ^{1}H NMR ($CDCl_3$): δ 3.37 (6H, s), 5.84 (1H, s), 6.40 (1H, s), 6.56 (2H, d, J = 4.8 Hz), 6.88 (2H, s), 7.38−7.45 (14H, m), 7.48−7.52 (4H, m), 7.56−7.60 (4H, m), 9.23 (1H, br s); ^{1}H NMR (TFA−$CDCl_3$): δ 3.49 (6H, s), 3.52 (1H, s), 6.55 (1H, s), 6.93 (1H, br s), 7.17 (2H, dd, J = 1,2 4.8 Hz), 7.50 (2H, s), 7.62−7.730 (16H, m), 7.85−7.89 (6H, m), 8.45 (2H, br s); ^{13}C NMR (TFA−$CDCl_3$): δ 56.3, 97.0, 99.6, 115.9, 122.3, 128.3, 128.9, 129.0, 130.3, 131.9, 132.9, 133.5, 134.1, 136.6, 136.9, 140.0, 144.1, 147.0, 150.6, 158.8, 163.9; EI MS (70 eV): *m*/*z* (% rel int) 690.4 (4.5), 689.4 (11), 688.4 (15), 687.4 (27), 686.4 (2), 685.4 (2, M^+), 344.9 (3.3), 343.9 (9.6, M^{2+}), 91.0 (100); HR MS: Calcd for $C_{48}H_{35}N_3O_2$ + 2H: 687.2886. Found: 687.2877. Anal. Calcd for $C_{48}H_{35}N_3O_2 \cdot {}^1/_8CHCl_3$: C, 82.49; H, 5.05; N, 6.00. Found: C, 82.49; H, 5.06; N, 6.08.

2,4-Dimethoxy-11,16-bis(4-*tert*-butylphenyl)-6,21-diphenylbenziporphyrin (**11b**). The bis(*tert*-butylphenyl) derivative was prepared by the same procedure from dicarbinol **13a** (0.70 g; 2.0 mmol), pyrrole (415 μL; 6.0 mmol), 4-*tert*-butylbenzaldehyde (0.65 g; 4.0 mmol), and 200 μL of $BF_3 \cdot Et_2O$. Recrystallization from chloroform−methanol gave **11b** (255 mg; 0.320 mmol; 16%) as very dark green crystals, mp 242−244 °C; UV−vis (1% Et_3N−$CHCl_3$): λ_{max} (log ϵ) 325 (sh, 4.55), 356 (4.56), 440 (4.75), 674 (sh, 4.16), 711 nm (4.24); UV−vis (1% TFA−$CHCl_3$): λ_{max} (log ϵ) 327 (4.43), 416 (4.73), 494 (4.79), 674 (3.91), 895 nm (4.39); ^{1}H NMR ($CDCl_3$): δ 1.40 (18H, s), 3.37 (6H, s), 5.86 (1H, s), 6.40 (1H, s), 6.60 (2H, d, J = 4.8 Hz), 6.95 (2H, s), 7.39 (2H, d, J = 4.8 Hz), 7.37−7.46 (14H, m), 7.57−7.60 (4H, m), 9.26 (1H,

br s); ^{1}H NMR (TFA−$CDCl_3$; 30 °C): δ 1.46 (18H, s), 3.36 (1H, s), 3.48 (6H, s), 6.56 (1H, s), 6.59 (1H, br s), 7.22 (2H, dd, J = 1.6, 5.2 Hz), 7.55 (2H, d, J = 1.2 Hz), 7.60−7.73 (16H, m), 7.85−7.90 (6H, m), 8.26 (2H, br s); ^{13}C NMR ($CDCl_3$): δ 31.7, 34.8, 55.6, 98.4, 109.8, 114.5, 122.1, 124.8, 127.3, 127.7, 129.7, 130.8, 131.6, 132.4, 135.2, 137.3, 142.0, 143.6, 147.3, 150.3, 156.6, 160.0, 170.6; ^{13}C NMR (TFA−$CDCl_3$): δ 31.4, 35.2, 56.3, 95.7, 99.8, 116.3, 122.3, 126.1, 128.7, 129.0, 132.0, 132.9, 133.6, 134.0, 136.6, 139.9, 144.1, 146.7, 150.1, 154.2, 158.7, 163.9; HR FAB MS: Calcd for $C_{56}H_{51}N_3O_2$ + H: 798.4059. Found: 798.4071. Anal. Calcd for $C_{56}H_{51}N_3O_2 \cdot {}^1/_{10}CHCl_3$: C, 83.19; H, 6.36; N, 5.19. Found: C, 83.01; H, 6.13; N, 5.08.

2,4-Dimethoxy-11,16-bis(4-methylphenyl)-6,21-diphenylbenziporphyrin (**11c**). The tetraarylporphyrinoid was prepared by the earlier procedure from dicarbinol **13a** (0.700 g; 2.00 mmol), pyrrole (415 μL; 6.0 mmol), *p*-tolualdehyde (0.480 g; 4.0 mmol), and 200 μL of $BF_3 \cdot Et_2O$. Recrystallization from chloroform−methanol gave **11c** (0.22 g; 0.31 mmol; 15%) as bright green crystals, mp 278−279 °C; UV−vis (1% Et_3N−$CHCl_3$): λ_{max} (logϵ) 326 (4.53), 355 (4.55), 440 (4.74), 670 (sh, 4.16), 707 nm (4.23); UV−vis (1% TFA−$CHCl_3$): λ_{max} (logϵ) 325 (4.42), 416 (4.71), 493 (4.77), 673 (3.89), 888 nm (4.39); ^{1}H NMR ($CDCl_3$): δ 2.44 (6H, s), 3.37 (6H, s), 5.84 (1H, s), 6.40 (1H, s), 6.58 (2H, d, J = 4.4 Hz), 6.89 (2H, s), 7.24 (4H, d, J = 8 Hz), 7.36−7.45 (12H, m), 7.58 (4H, d, J = 7 Hz), 9.24 (1H, br s); ^{1}H NMR (TFA−$CDCl_3$): δ 2.55 (6H, s), 3.27 (1H, s), 3.48 (6H, s), 6.34 (1H, br s), 6.57 (1H, s), 7.20 (2H, dd, J = 1.2, 5.2 Hz), 7.45 (4H, d, J = 8 Hz), 7.52 (2H, d, J = 1.2 Hz), 7.56 (4H, d, J = 8 Hz), 7.66−7.73 (6H, m), 7.85−7.89 (4H, m), 7.90 (2H, dd, J = 1.4, 5.0 Hz), 8.17 (2H, br s); ^{13}C NMR ($CDCl_3$): δ 21.4, 55.6, 98.5, 109.7, 114.4, 122.1, 127.3, 127.7, 128.7, 129.6, 130.7, 131.6, 132.6, 135.3, 137.0, 137.3, 142.1, 143.6, 147.3, 156.6, 159.7, 170.5; ^{13}C NMR (TFA−$CDCl_3$): δ 21.5, 56.3, 95.9, 99.8, 116.2, 122.4, 128.5, 128.9, 129.8, 131.9, 132.8, 133.5, 134.0, 136.6, 140.0, 141.0, 144.1, 146.6, 150.3, 158.8, 163.9; EI MS (70 eV): *m*/*z* (% rel int) 719 (1.8), 718 (3.9), 717 (8.9), 716 (10), 715 (18), 358 (3.4), 91 (100); HR EI MS: Calcd for $C_{50}H_{39}N_3O_2$ + 2H: 715.3199. Found: 715.3202. Anal. Calcd for $C_{50}H_{39}N_3O_2 \cdot {}^1/_3CHCl_3$: C, 80.21; H, 5.26; N, 5.57. Found: C, 79.88; H, 5.17; N, 5.53.

2,4-Dimethoxy-11,16-bis(4-chlorophenyl)-6,21-diphenylbenziporphyrin (**11d**). The benziporphyrin was prepared by the foregoing procedure from dicarbinol **13a** (1.40 g; 4.00 mmol), pyrrole (830 μL; 6.0 mmol), 4-chlorobenzaldehyde (1.12 g; 8.0 mmol), and 400 μL of $BF_3 \cdot Et_2O$ in chloroform (900 mL). Recrystallization from chloroform−methanol gave **11d** (0.58 g; 0.77 mmol; 19%) as dark green crystals, mp 277−278 °C; UV−vis (1% Et_3N−$CHCl_3$): λ_{max} (logϵ) 357 (4.59), 438 (4.72), 661 (sh, 4.17), 697 nm (4.23); UV−vis (1% TFA−$CHCl_3$): λ_{max} (logϵ) 322 (4.49), 411 (4.73), 493 (4.77), 601 (3.89), 663 (3.89), 871 nm (4.42); ^{1}H NMR ($CDCl_3$; 30 °C): δ 3.37 (6H, s), 5.82 (1H, s), 6.39 (1H, s), 6.55 (2H, d, J = 4.8 Hz), 6.86 (2H, s), 7.40−7.47 (16H, m), 7.56−7.60 (4H, m), 9.22 (1H, br s); ^{1}H NMR (TFA−$CDCl_3$): δ 3.45 (1H, s), 3.49 (6H, s), 6.56 (1H, s), 6.71 (1H, s), 7.17 (2H, dd, J = 1.6, 5.2 Hz), 7.49 (2H, d, J = 1.6 Hz), 7.60−7.64 (8H, m), 7.66−7.76 (6H, m), 7.84−7.87 (4H, m), 7.89 (2H, dd, J = 2.0, 5.2 Hz), 8.34 (2H, br s); ^{13}C NMR ($CDCl_3$): δ 55.6, 98.4, 110.4, 113.3, 122.0, 127.4, 127.9, 128.3, 129.6, 130.1, 131.6, 133.6, 133.9, 135.7, 138.7, 143.2, 143.4, 147.1, 156.5, 160.0, 169.8; ^{13}C NMR (TFA−$CDCl_3$): δ 56.3, 97.9, 99.6, 114.6, 122.4, 128.0, 128.9, 129.4, 132.1, 132.7, 133.6, 135.1, 135.3, 136.8, 137.1, 139.9, 144.1, 147.7, 150.4, 158.5, 164.1; EI MS (70 eV): *m*/*z* (% rel int) 760 (1.6), 759 (3.7), 758 (4.7), 757 (9.5), 756 (5.9), 755 (10), 377 (2.0), 91 (100); HR EI MS: Calcd for $C_{48}H_{33}Cl_2N_3O_2$ + 2H: 755.2106. Found: 755.2088. Anal. Calcd for $C_{48}H_{33}Cl_2N_3O_2 \cdot {}^1/_3CHCl_3$: C, 73.07; H, 4.23; N, 5.29. Found: C, 73.05; H, 4.09; N, 5.16.

2,4-Dimethoxy-3-methyl-6,11,16,21-tetraphenylbenziporphyrin (**12a**). The porphyrin analogue was prepared by the foregoing procedure from 3,5-bis(α-hydroxyphenylmethyl)-2,6-dimethoxytoluene (0.700 g; 1.92 mmol), pyrrole (410 μL; 5.9 mmol), benzaldehyde (405 μL; 4.0 mmol), boron trifluoride etherate (200 μL), and DDQ (1.40 g). The crude product was purified on Grade 3 basic alumina eluting with dichloromethane, and following a forerun of tetraphenylporphyrin and unidentified brown byproducts, **12a** was collected as a dark emerald green band. The porphyrin analogue was rechromatographed on Grade 3 basic alumina, eluting with dichloromethane, and the product fraction recrystallized from chloroform−methanol to give benziporphyrin **12a** (340 mg; 0.486 mmol; 25%) as a navy-blue powder, mp 286−288 °C. In some batches, the product was obtained as lustrous dark blue-green flakes. UV−vis (1% Et_3N−$CHCl_3$): λ_{max} (logϵ) 321 (4.50), 368 (4.40), 422 (4.82), 699 nm (4.17); UV−vis (1% TFA−$CHCl_3$): λ_{max} (logϵ) 324 (4.44), 404 (sh, 4.56), 472 (4.90), 658 (3.72), 889 nm (4.29); ^{1}H NMR ($CDCl_3$): δ 2.01 (3H, s), 3.27 (6H, s), 6.42 (1H, s), 6.51 (2H, d, J = 4.8 Hz), 6.77 (2H, s), 7.38−7.48 (14H, m), 7.54−7.58 (8H, m), 9.93 (1H, br s); ^{1}H NMR (TFA−$CDCl_3$): δ 2.03 (3H, s), 3.19 (6H, s), 4.73 (1H, s), 7.07 (2H, dd, J = 4.8, 0.8 Hz), 7.33 (2H, s), 7.54−7.64 (10H, m), 7.68−7.76 (10H, m), 7.87 (2H, dd, J = 5.2, 1.2 Hz), 8.21 (1H, br s), 9.96 (2H, br s); ^{13}C NMR ($CDCl_3$): δ 10.4, 61.4, 107.7, 114.7, 127.0, 127.5, 127.8, 128.1, 128.5, 129.3, 131.1, 131.3, 132.5, 135.4, 140.0, 142.7, 142.8, 147.8, 157.2, 158.0, 171.3; ^{13}C NMR (TFA−$CDCl_3$): δ 11.1, 62.7, 92.6, 116.4, 128.6, 129.1, 129.2, 129.4, 130.0, 130.5, 132.5, 132.9, 133.6, 136.3, 137.7, 139.7, 144.7, 148.7, 151.7, 161.1, 162.3; EI MS (70 eV): *m*/*z* (% rel int) 704.4 (9), 703.4 (27), 702.4 (53), 701.4 (100), 700.4 (17), 699.4 (26, M^+), 350.9 (26), 349.9 (7.6, M^{2+}), 91.0 (81); HR MS: Calcd for $C_{49}H_{37}N_3O_2$ + 2H: 701.3042. Found: 701.3041. Anal. Calcd for $C_{49}H_{37}N_3O_2 \cdot 0.4CHCl_3$: C, 79.37; H, 5.04; N, 5.62. Found: C, 79.62; H, 5.02; N, 5.81.

2,4-Dimethoxy-3-methyl-11,16-bis(4-*tert*-butylphenyl)-6,21-diphenylbenziporphyrin (**12b**). The porphyrin analogue was prepared similarly from dicarbinol **13b** (0.700 g; 1.92 mmol), pyrrole (410 μL; 5.9 mmol), 4-*tert*-butylbenzaldehyde (0.65 g; 4.0 mmol), and 200 μL of $BF_3 \cdot Et_2O$. Recrystallization from chloroform−methanol gave **12b** (0.32 g; 0.40 mmol; 21%) as lustrous navy blue crystals, mp 260−262 °C; UV−vis (1% Et_3N−$CHCl_3$): λ_{max} (logϵ) 424 (4.83), 712 nm (4.19); UV−vis (1% TFA−$CHCl_3$): λ_{max} (logϵ) 343 (4.47), 411 (sh, 4.61), 477 (4.92), 670 (3.80), 900 nm (4.24); ^{1}H NMR ($CDCl_3$): δ 1.39 (18H, s), 2.01 (3H, s), 3.27 (6H, s), 6.42 (1H, s), 6.54 (2H, d, J = 4.8 Hz), 6.82 (2H, s), 7.36 (4H, d, J = 7.6 Hz), 7.38 (2H, d, J = 4.4 Hz), 7.42−7.48 (10H, m), 7.53−7.58 (4H, m), 9.94 (1H, br s); ^{1}H NMR (TFA−$CDCl_3$): δ 1.43 (18H, s), 2.03 (3H, s), 3.21 (6H, s), 4.68 (1H, s), 7.11 (2H, dd, J = 1.6, 5.2 Hz), 7.36 (2H, d, J = 1.6 Hz), 7.48 (4H, d, J = 8.4 Hz), 7.60 (4H, d, J = 8.4 Hz), 7.66−7.75 (10H, m), 7.85 (2H, dd, J = 1.2, 5.2 Hz), 8.22 (1H, br s), 9.92 (2H, br s); ^{13}C NMR ($CDCl_3$): δ 10.3, 31.6, 34.8, 61.3, 107.5, 114.6, 124.9, 126.9, 127.7, 128.3, 129.3, 130.0, 131.3, 131.4, 132.1, 135.2, 137.0, 142.4, 142.8, 147.8, 150.4, 157.2, 157.9, 171.5; ^{13}C NMR (TFA−$CDCl_3$): δ 11.1, 31.4, 35.2, 62.7, 91.3, 116.7, 126.1, 128.7, 129.1, 129.7, 130.0, 132.4, 132.9, 133.5, 137.4, 139.8, 144.7, 147.9, 151.5, 154.3, 161.0, 162.1; FAB MS: *m*/*z* (% rel int) 816 (3.9), 815 (14), 814 (40), 813 (85), 812 (100), 811 (7.2, M^+), 810 (3.9); HR FAB MS: Calcd for $C_{57}H_{53}N_3O_2$ + H: 812.4216. Found: 812.4202. Anal. Calcd for $C_{57}H_{53}N_3O_2$: C, 84.31; H, 6.58; N, 5.17. Found: C, 83.81; H, 6.45; N, 5.27.

2,4-Dimethoxy-3-methyl-11,16-bis(4-methylphenyl)-6,21-diphenylbenziporphyrin (**12c**). Porphyrinoid **12c** was prepared from dicarbinol **13b** (0.700 g; 1.92 mmol), pyrrole (420 μL; 6.0 mmol), *p*-tolualdehyde (0.480 g; 4.00 mmol), and 200 μL of $BF_3 \cdot Et_2O$. Recrystallization from chloroform−methanol gave **6c** (267 mg; 0.367 mmol; 19%) as small shiny purple needles, mp 280−281 °C; UV−vis (1% Et_3N−$CHCl_3$): λ_{max} (logϵ) 425 (4.81), 712 nm (4.16); UV−vis (1% TFA−$CHCl_3$): λ_{max} (logϵ) 328 (4.44), 410 (sh, 4.58), 477 (4.90), 673 (3.76), 900 nm (4.22); ^{1}H NMR ($CDCl_3$): δ 2.01 (3H, s), 2.43 (6H, s), 3.27 (6H, s), 6.41 (1H, s), 6.52 (2H, d, J = 4.4 Hz), 6.77 (2H, s), 7.22 (4H, d, J = 8.4 Hz), 7.32 (2H, d, J = 8.0 Hz), 7.38 (2H, d, J = 4.4 Hz), 7.41−7.48

(6H, m), 7.53−7.56 (4H, m), 9.93 (1H, br s); ^{1}H NMR (TFA−$CDCl_3$): δ 2.02 (3H, s), 2.52 (6H, s), 3.21 (6H, s), 4.64 (1H, s), 7.09 (2H, dd, J = 1.6, 5.2 Hz), 7.33 (2H, d, J = 1.2 Hz), 7.38−7.45 (8H, AB quartet, J = 8 Hz), 7.60 (4H, d, J = 8.4 Hz), 7.67−7.75 (10H, m), 7.86 (2H, dd, J = 2.0, 5.2 Hz), 8.20 (1H, br s), 9.86 (2H, br s); ^{13}C NMR ($CDCl_3$): δ 10.3, 21.4, 61.3, 107.5, 114.5, 126.9, 127.7, 128.4, 128.8, 129.3, 129.9, 131.2, 132.3, 135.2, 137.0, 137.2, 142.5, 142.7, 147.8, 157.2, 157.9, 171.4; ^{13}C NMR (TFA−$CDCl_3$): δ 11.0, 21.5, 62.7, 91.2, 116.7, 128.7, 129.1, 129.6, 129.9, 132.4, 132.9, 133.4, 133.6, 137.5, 139.4, 141.3, 144.7, 148.0, 151.5, 161.0, 162.1; EI MS (70 eV): *m*/*z* (% rel int) 730 (1.9), 729 (3.7), 91 (100); FAB MS: *m*/*z* (% rel int) 732 (3.7), 731 (13), 730 (40), 729 (82), 728 (100), 727 (7.2, M^+), 726 (2.6); HR FAB MS: Calcd for $C_{51}H_{41}N_3O_2$ + H: 728.3277. Found: 728.3291. Anal. Calcd for $C_{51}H_{41}N_3O_2 \cdot 0.3CHCl_3$: C, 80.68; H, 5.45; N, 5.50. Found: C, 80.78; H, 5.40; N, 5.62.

2,4-Dimethoxy-3-methyl-11,16-bis(4-chlorophenyl)-6,21-diphenylbenziporphyrin (**12d**). The porphyrin analogue was prepared similarly from dicarbinol **13b** (1.40 g; 3.84 mmol), pyrrole (840 μL; 12 mmol), 4-chlorobenzaldehyde (1.20 g; 8.5 mmol), and 400 μL of $BF_3 \cdot Et_2O$ in chloroform (900 mL). Recrystallization from chloroform−methanol gave **12d** (0.70 g; 0.91 mmol; 24%) as dark bluish purple crystals, mp 282−283 °C; UV−vis (1% Et_3N−$CHCl_3$): λ_{max} (logϵ) 345 (4.49), 424 (4.81), 695 nm (4.17); UV−vis (1% TFA−$CHCl_3$): λ_{max} (logϵ) 325 (4.46), 407 (sh, 4.59), 475 (4.90), 660 (3.73), 876 nm (4.31); ^{1}H NMR ($CDCl_3$): δ 2.01 (3H, s), 3.25 (6H, s), 6.39 (1H, s), 6.48 (2H, d, J = 4.8 Hz), 6.74 (2H, s), 7.35−7.42 (8H, AB quartet, J = 8 Hz), 7.39 (2H, d, partially obscured), 7.44−7.50 (6H, m), 7.53−7.57 (4H, m), 9.90 (1H, br s); ^{1}H NMR (TFA−$CDCl_3$): δ 2.03 (3H, s), 3.20 (6H, s), 4.75 (1H, s), 7.06 (2H, dd, J = 1.4, 5.0 Hz), 7.31 (2H, d, J = 1.2 Hz), 7.49 (4H, d, J = 8.4 Hz), 7.58 (4H, d, J = 8.4 Hz), 7.68−7.76 (10H, m), 7.87 (2H, dd, J = 1.6, 5.2 Hz), 8.32 (1H, br s), 10.00 (2H, br s); ^{13}C NMR ($CDCl_3$): δ 10.4, 61.3, 108.0, 113.4, 127.0, 127.8, 128.4, 128.6, 129.2, 129.8, 130.7, 131.3, 133.6, 133.7, 135.7, 138.4, 142.6, 143.6, 147.6, 157.0, 158.2, 170.7; ^{13}C NMR (TFA−$CDCl_3$): δ 11.1, 62.7, 93.4, 115.0, 128.6, 129.0, 129.2, 129.5, 129.9, 132.7, 133.0, 133.4, 134.6, 134.7, 137.3, 137.9, 139.7, 144.7, 149.5, 151.5, 160.7, 162.6; EI MS (70 eV): *m*/*z* (% rel int) 774 (2.3), 773 (6.0), 772 (9.0), 771 (18), 770 (13), 769 (23), 768 (3.0), 767 (4.4, M^+), 385 (3.0), 91 (100); HR EI MS: Calcd for $C_{49}H_{35}Cl_2N_3O_2$ + 2H: 769.2263. Found: 769.2265. Anal. Calcd for $C_{49}H_{35}Cl_2N_3O_2 \cdot 0.4CHCl_3$: C, 72.67; H, 4.37; N, 5.15. Found: C, 72.74; H, 4.50; N, 5.15.

6,11,16,21-Tetraphenylbenziporphyrin (**8**).[13] Nitrogen was slowly bubbled through a stirred solution of 1,3-bis(α-hydroxyphenylmethyl)benzene (0.290 g; 1.00 mmol) in 900 mL of dichloromethane in a 1 L round-bottom flask that had been covered with aluminum foil to protect the reaction from ambient light. A septum was placed in the neck of the flask, and a nitrogen-filled balloon was attached to maintain the inert atmosphere. Next, freshly distilled pyrrole (0.208 mL; 3.00 mmol) and benzaldehyde (0.205 mL; 2.02 mmol) were added via syringe, followed by 0.20 mL of boron trifluoride etherate. The resulting mixture was stirred for 2 h at room temperature. The initially colorless solution turned orange and then became a deep red color. DDQ (750 mg) was added and the mixture stirred for an additional 10 min. The dark solution was evaporated under reduced pressure and the residue purified on a Grade 3 basic alumina column eluting with dichloromethane. Tetraphenylporphyrin and unidentified brown byproducts eluted initially, followed by a dark green band corresponding to the title benziporphyrin. Recrystallization from chloroform−methanol gave the benziporphyrin (83 mg; 0.13 mmol; 13%) as a green powder, mp >280 °C; ^{1}H NMR ($CDCl_3$): δ 6.54 (2H, d, J = 4.8 Hz), 6.76 (2H, s), 7.00 (2H, dd, J = 1.6, 8 Hz), 7.21 (2H, d, J = 5.2 Hz), 7.31 (1H, t, J = 8 Hz), 7.35 (1H, br t, J = 1 Hz), 7.40−7.49 (20H, m), 10.30 (2H, br s); ^{1}H NMR (TFA−$CDCl_3$): δ 5.52 (1H, s), 7.10 (2H, dd, J = 1, 4.8 Hz), 7.20 (2H, dd, J = 1.2, 8.0 Hz), 7.26 (2H, s), 7.55−7.63 (14H, m), 7.70 (4H, t, J = 7.6 Hz), 7.80−7.85 (3H, m), 7.89 (2H, dd, J = 1.6, 5.2 Hz), 9.04 (1H, br s), 10.48 (2H, br s). Ni**8**:[15] ^{1}H NMR ($CDCl_3$): δ 6.88 (2H, d, J = 5.2 Hz), 7.11 (1H, t, J = 7.6 Hz), 7.16 (2H, d, J = 5.2 Hz), 7.32 (2H, s), 7.42−7.55 (20H, m), 7.83 (2H, d, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$): δ 117.4, 125.0, 126.9, 127.7, 127.9, 130.1, 132.3, 132.5, 133.8, 135.9, 137.9, 139.1, 140.6, 141.0, 143.0; HR MS (FAB): Calcd for $C_{46}H_{29}N_3Ni$ + H: 682.1793. Found: 682.1793. Anal. Calcd for $C_{46}H_{29}N_3Ni \cdot {}^1/_4CHCl_3$: C, 77.99; H, 4.14; N, 5.90. Found: C, 77.89; H, 3.98; N, 5.97. **8**OAc:[13] ^{1}H NMR ($CDCl_3$): δ 1.33 (3H, s), 6.54 (2H, d, J = 5.2 Hz), 6.86 (2H, s), 7.09 (2H, d, J = 8 Hz), 7.19 (1H, t, J = 7.6 Hz), 7.32 (2H, d, J = 4.8 Hz), 7.40−7.51 (16H, m), 7.56−7.59 (4H, m), 9.50 (1H, br s); ^{1}H NMR (TFA−$CDCl_3$): δ 1.03 (3H, s), 6.11 (1H, br s), 7.20 (2H, d, J = 5.2 Hz), 7.21 (2H, d, J = 7.6 Hz), 7.41 (2H, s), 7.58−7.68 (11H, m), 7.72−7.74 (6H, m), 7.78−7.84 (4H, m), 7.93 (2H, d, J = 5.2 Hz), 10.31 (2H, br s).

[2,4-Dimethoxy-6,11,16,21-tetraphenylbenziporphyrinato]-nickel(II) (**16a**). A solution of **11a** (50 mg; 0.0730 mmol) in chloroform (50 mL) was placed in a 100 mL round-bottom flask that was covered with foil to protect the reaction from light. A saturated solution of nickel(II) acetate in methanol (40 mL) was added and the mixture stirred at room temperature under nitrogen for 2 h. During the course of the reaction, the solution turned from a deep green to a brown color. The solution was washed with water, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified on a grade 3 basic alumina column eluting with chloroform. The organometallic derivative was collected as a brownish-green band. Recrystallization from chloroform−hexanes, and then from chloroform−methanol, gave the nickel(II) complex (44 mg; 0.0594 mmol; 81%) as lustrous black needles, mp 302−304 °C; UV−vis ($CHCl_3$): λ_{max} (logϵ) 350 (4.28), 458 (4.43), 766 nm (4.00); ^{1}H NMR ($CDCl_3$): δ 3.36 (6H, s), 6.17 (1H, s), 7.24 (2H, d, J = 4.8 Hz), 7.35−7.39 (2H, dt), 7.42−7.46 (4H, m), 7.48−7.54 (6H, m), 7.56−7.59 (4H, m), 7.59 (2H, s), 7.66 (2H, d, J = 4.8 Hz), 7.67−7.71 (4H, m); ^{13}C NMR ($CDCl_3$): δ 55.7, 94.6, 116.6, 125.8, 126.4, 126.8, 127.5, 127.6, 128.6, 131.4, 132.7, 133.3, 134.4, 135.0, 140.1, 144.3, 146.4, 150.7, 154.8, 155.8, 173.5; EI MS (70 eV): *m*/*z* (% rel int) 746.3 (1.5), 745.3 (2.8), 744.3 (1.8), 743.3 (2.9), 742 (<1), 741 (<1), 91.2 (100); HR MS: Calcd for $C_{48}H_{33}N_3O_2Ni$: 741.1926. Found: 741.1921. Anal. Calcd for $C_{48}H_{33}N_3NiO_2 \cdot {}^3/_5CHCl_3$: C, 71.70; H, 4.16; N, 5.16. Found: C, 71.87; H, 4.05; N, 5.25.

[2,4-Dimethoxy-11,16-bis(4-*tert*-butylphenyl)-6,21-diphenylbenziporphyrinato]nickel(II) (**16b**). Compound **16b** was prepared from benziporphyrin **11b** (20 mg; 0.025 mmol) and nickel(II) acetate using the previous procedure. Recrystallization from chloroform−methanol gave the nickel complex (15.9 mg; 0.0186 mmol; 75%) as purple flakes, mp 275−276 °C; UV−vis ($CHCl_3$): λ_{max} (logϵ) 460 (4.59), 772 nm (4.14); ^{1}H NMR ($CDCl_3$): δ 1.45 (18H, s), 3.35 (6H, s), 6.17 (1H, s), 7.26 (2H, d, partially obscured by $CHCl_3$), 7.34−7.39 (2H, dt), 7.41−7.46 (4H, m), 7.53 (4H, d, J = 8 Hz), 7.56−7.59 (4H, m), 7.60−7.63 (6H, m), 7.65 (2H, d, J = 5.2 Hz); ^{13}C NMR ($CDCl_3$): δ 31.7, 34.9, 55.7, 94.6, 116.7, 124.5, 125.9, 126.3, 126.8, 128.8, 131.5, 132.7, 133.0, 134.3, 134.8, 137.0, 144.4, 146.6, 150.3, 151.0, 154.9, 156.2, 173.0; EI MS (70 eV): *m*/*z* (% rel int) 858 (3.5), 857 (8.4), 856 (11), 855 (17), 854 (10), 853 (15), 778 (4.1); HR MS: Calcd for $C_{56}H_{49}N_3NiO_2$: 853.3178. Found: 853.3182. Anal. Calcd for $C_{56}H_{49}N_3NiO_2 \cdot {}^1/_4CHCl_3$: C, 76.38; H, 5.61; N, 4.75. Found: C, 76.08; H, 5.43; N, 4.76.

[2,4-Dimethoxy-3-methyl-6,11,16,21-tetraphenylbenziporphyrinato]nickel(II) (**16c**). The metallo-derivative was prepared from **12a** (20.0 mg; 0.0286 mmol) by the procedure described above. The crude product was purified on a Grade 3 basic alumina column eluting with chloroform. The initial brownish-green fraction corresponded to the required complex. Recrystallization from chloroform−methanol afforded the nickel(II) porphyrinoid (16.0 mg; 0.0212 mmol; 74%) as a bronze powder, mp 288−290 °C; UV−vis ($CHCl_3$): λ_{max} (logϵ) 443 (4.67), 792 nm (4.11); ^{1}H NMR

($CDCl_3$): δ 1.95 (3H, s), 3.21 (6H, s), 6.99 (2H, d, J = 5.2 Hz), 7.37 (2H, s), 7.38−7.54 (16H, m), 7.55 (2H, d, J = 5.2 Hz), 7.59−7.63 (4H, m); ^{13}C NMR ($CDCl_3$): δ 10.6, 62.8, 117.0, 120.3, 127.0, 127.1, 127.6, 127.8, 128.9, 131.1, 131.3, 133.0, 133.1, 134.9, 136.2, 139.5, 143.1, 148.5, 152.6, 158.9, 170.2; EI MS (70 eV): *m*/*z* (% rel int) 760.3 (3.5), 759.3 (8.3), 758.4 (6.4), 757.4 (10), 756.4 (2.8), 755.4 (2.7), 91.2 (100); HR MS: Calcd for $C_{49}H_{35}N_3NiO_2$ + 2H: 757.2239. Found: 757.2233. Anal. Calcd for $C_{49}H_{35}N_3NiO_2 \cdot {}^1/_2CHCl_3$: C, 72.84; H, 4.38; N, 5.15. Found: C, 72.99; H, 4.63; N, 5.18.

[2,4-Dimethoxy-3-methyl-11,16-bis(4-*tert*-butylphenyl)-6,21-diphenylbenziporphyrinato]nickel(II) (**16d**). The nickel complex was prepared from **12b** (20.0 mg; 0.0246 mmol) by the procedure described above. Recrystallization from chloroform−methanol afforded the nickel(II) porphyrinoid (16.0 mg; 0.0185 mmol; 75%) as dark purple crystals, mp 272−273 °C; UV−vis ($CHCl_3$): λ_{max} (logϵ) 445 (4.65), 800 nm (4.08); ^{1}H NMR ($CDCl_3$): δ 1.43 (18H, s), 1.95 (3H, s), 3.21 (6H, s), 7.02 (2H, d, J = 5.2 Hz), 7.42 (2H, s), 7.37−7.47 (6H, m), 7.49−7.55 (14H, m); ^{13}C NMR ($CDCl_3$): δ 10.6, 31.7, 34.9, 62.8, 117.1, 120.3, 124.7, 127.0, 127.1, 129.2, 131.1, 131.3, 132.7, 133.1, 134.8, 135.9, 136.5, 143.2, 148.6, 150.5, 152.7, 153.6, 159.2, 169.9; EI MS (70 eV): *m*/*z* (% rel int) 873 (3.7), 872 (7.9), 871 (15), 870 (19), 869 (27), 868 (8.5), 867 (8.5), 792 (4.2); HR MS: Calcd for $C_{57}H_{51}N_3NiO_2$: 867.3335. Found: 867.3336. Anal. Calcd for $C_{57}H_{51}N_3NiO_2 \cdot {}^1/_3CHCl_3$: C, 75.79; H, 5.69; N, 4.62. Found: C, 75.73; H, 5.51; N, 4.72.

[2,4-Dimethoxy-6,11,16,21-tetraphenylbenziporphyrinato]-palladium(II) (**17a**). A solution of **11a** (20.3 mg; 0.0292 mmol) and palladium(II) acetate (8.3 mg) in acetonitrile (20 mL) was stirred under reflux for 2 h. During the course of the reaction, the solution turned from a deep green to a brown color. The solution was diluted with chloroform, washed with water, dried over sodium sulfate, and evaporated under reduced pressure. The residue was purified on a grade 3 basic alumina column eluting with chloroform, and the organometallic derivative was collected as a brown band. Recrystallization from chloroform−methanol gave the palladium-(II) complex (19.0 mg; 0.0241 mmol; 82%) as dark purple crystals, mp > 300 °C; UV−vis ($CHCl_3$): λ_{max} (logϵ) 349 (4.65), 408 (4.67), 463 (4.89), 556 (4.09), 599 (4.27), 736 (3.97), 812 nm (4.11); ^{1}H NMR ($CDCl_3$): δ 3.35 (6H, s), 6.17 (1H, s), 7.30 (2H, d, J = 5.2 Hz), 7.37−7.42 (2H, dt), 7.45−7.50 (4H, m), 7.52 (2H, s), 7.52−7.57 (6H, m), 7.69−7.77 (8H, m), 7.74 (2H, d, J = 4.8 Hz); ^{13}C NMR ($CDCl_3$): δ 55.8, 95.1, 117.9, 124.1, 126.3, 126.7, 127.5, 127.6, 129.0, 131.8, 132.7, 133.6, 134.0, 139.6, 140.9, 145.4, 145.7, 150.8, 154.8, 154.9, 171.7; EI MS (70 eV): *m*/*z* (% rel int) 795 (2.1), 794 (2.5), 793 (4.8), 792 (3.7), 791 (6.4), 790 (4.8), 789 (4.2), 788 (2.0), 716 (2.3), 714 (2.8, $M^+ - C_6H_5$), 713 (2.0), 207 (100); HR MS: Calcd for $C_{48}H_{33}N_3O_2Pd$: 789.1608. Found: 789.1614. Anal. Calcd for $C_{48}H_{33}N_3O_2Pd$: C, 72.96; H, 4.21; N, 5.32. Found: C, 72.50; H, 4.05; N, 5.17.

[2,4-Dimethoxy-11,16-bis(4-*tert*-butylphenyl)-6,21-diphenylbenziporphyrinato]palladium(II) (**17b**). Compound **17b** was prepared from **11b** (50 mg; 0.0627 mmol) and palladium(II) acetate (28.2 mg; 0.126 mmol) in acetonitrile (50 mL) under the conditions described above. Recrystallization from chloroform−methanol gave the palladium(II) complex (43.5 mg; 0.0483 mmol; 77%) as dark purple crystals, mp 274−275 °C; UV−vis ($CHCl_3$): λ_{max} (logϵ) 355 (4.60), 410 (4.64), 465 (4.86), 556 (4.12), 599 (4.22), 740 (4.02), 815 nm (4.12); ^{1}H NMR ($CDCl_3$): δ 1.45 (18H, s), 3.35 (6H, s), 6.17 (1H, s), 7.34 (2H, d, J = 4.8 Hz), 7.39 (2H, t, J = 7.4 Hz), 7.48 (4H, t, J = 7.6 Hz), 7.76 (4H, d), 7.58 (2H, s, overlapped with previous signal), 7.67−7.74 (10H, m); ^{13}C NMR ($CDCl_3$): δ 31.7, 34.9, 55.8, 95.1, 118.0, 124.1, 124.4, 126.3, 126.7, 129.3, 131.8, 132.8, 133.4, 133.9, 137.9, 139.4, 145.5, 145.8, 150.4, 151.0, 155.1, 171.5; HR EI MS: Calcd for $C_{56}H_{49}N_3O_2Pd$: 901.2860. Found: 901.2870. Anal. Calcd for $C_{56}H_{49}N_3O_2Pd \cdot {}^1/_{10}CHCl_3$: C, 73.69; H, 5.41; N, 4.59. Found: C, 73.69; H, 5.24; N, 4.53.

[2,4-Dimethoxy-3-methyl-6,11,16,21-tetraphenylbenziporphyrinato]palladium(II) (**17c**). The complex was prepared from **12a** (50 mg; 0.0715 mmol) and palladium(II) acetate (20 mg; 0.089 mmol) under the conditions described above. Recrystallization from chloroform−methanol gave the palladium(II) complex (41.9 mg; 0.0522 mmol; 73%) as dark purple crystals, mp >300 °C; UV−vis ($CHCl_3$): λ_{max} (logϵ) 349 (4.51), 454 (4.77), 557 (4.00), 859 nm (3.88); ^{1}H NMR ($CDCl_3$): δ 1.92 (3H, s), 3.22 (6H, s), 7.06 (2H, d, J = 5.2 Hz), 7.28 (2H, s), 7.38−7.43 (2H, dt), 7.46−54 (10H, m), 7.58 (2H, d, J = 5.2 Hz), 7.60−7.67 (8H, m); ^{13}C NMR ($CDCl_3$): δ 11.0, 63.2, 118.0, 120.9, 127.0, 127.6, 127.7, 129.3, 129.5, 131.3, 133.1, 133.2, 134.5, 140.3, 141.2, 144.3, 147.4, 152.3, 153.9, 157.5, 169.5; EI MS (70 eV): *m*/*z* (% rel int) 808 (3.1), 807 (6.8), 806 (5.7), 805 (11), 804 (7.9), 803 (10); HR MS: Calcd for $C_{49}H_{35}N_3O_2{}^{106}Pd$: 803.1764. Found: 803.1771. Anal. Calcd for $C_{49}H_{35}N_3O_2Pd \cdot {}^1/_{10}CHCl_3$: C, 72.25; H, 4.33; N, 5.15. Found: C, 72.32; H, 4.08; N, 4.80.

[2,4-Dimethoxy-3-methyl-11,16-bis(4-*tert*-butylphenyl)-6,21-diphenylbenziporphyrinato]palladium(II) (**17d**). The palladium complex was prepared under the foregoing conditions from **12b** (44.0 mg; 0.0542 mmol) and palladium(II) acetate (24.0 mg; 0.107 mmol). Recrystallization from dichloromethane-methanol gave the palladium(II) complex (36.4 mg; 0.040 mmol; 74%) as dark purple crystals, mp 248−250 °C; UV−vis ($CHCl_3$): λ_{max} (logϵ) 355 (4.47), 420 (4.68), 453 (4.78), 869 (3.88); ^{1}H NMR ($CDCl_3$): δ 1.45 (18H, s), 1.92 (3H, s), 3.23 (6H, s), 7.10 (2H, d, J = 5.2 Hz), 7.34 (2H, s), 7.39−7.43 (2H, dt), 7.46−7.50 (4H, m), 7.53 (4H, d, J = 8 Hz), 7.56 (2H, d, J = 5.2 Hz), 7.59 (4H, d, J = 8 Hz), 7.59−7.64 (4H, m); ^{13}C NMR ($CDCl_3$): δ 11.0, 31.7, 34.9, 63.2, 118.1, 121.0, 124.6, 127.0, 129.3, 129.8, 131.3, 133.0, 133.2, 134.4, 137.3, 140.9, 144.3, 147.4, 150.6, 152.5, 154.1, 157.8, 169.4; HR EI MS: Calcd for $C_{57}H_{51}N_3O_2{}^{106}Pd$: 913.3021. Found: 913.3016. Anal. Calcd for $C_{57}H_{51}N_3O_2Pd \cdot {}^1/_{10}CHCl_3$: C, 73.87; H, 5.55; N, 4.53. Found: C, 74.03; H, 5.47; N, 4.55.

22-Acetoxy-2,4-dimethoxy-6,11,16,21-tetraphenylbenziporphyrin (**20a**). Tetraphenyldimethoxybenziporphyrin **11a** (100 mg; 0.146 mmol) was refluxed with silver(I) acetate (73 mg; 0.44 mmol) in a 50/50 v/v mixture of chloroform and acetonitrile (100 mL) for 2 h. The solvent was evaporated and the residue purified on a grade 3 basic alumina column eluting with chloroform. The product eluted as the first green fraction. Recrystallization from chloroform−methanol gave the acetoxy derivative (84 mg; 0.113 mmol; 77%) as turquoise flakes, mp >280 °C; UV−vis (1% Et_3N−$CHCl_3$): λ_{max} (logϵ) 351 (4.54), 434 (4.72), 644 (sh, 4.19), 686 nm (4.30); UV−vis (1% TFA−$CHCl_3$): λ_{max} (logϵ) 317 (4.42), 464 (4.77), 786 (sh, 4.04), 849 nm (4.38); ^{1}H NMR ($CDCl_3$): δ 1.12 (3H, s), 3.40 (6H, s), 6.35 (1H, s), 6.52 (2H, d, J = 4.8 Hz), 6.93 (2H, s), 7.37−7.46 (14H, m), 7.50−7.53 (4H, m), 7.74−7.77 (4H, m), 8.89 (1H, br s); ^{1}H NMR (TFA−$CDCl_3$): δ 0.51 (3H, s), 3.50 (6H, s), 4.18 (1H, br s), 6.51 (1H, s), 7.25−7.27 (2H, dd, obscured by $CHCl_3$), 7.68−7.78 (18H, m), 8.00−8.04 (6H, m), 8.44 (1H, br s); ^{13}C NMR ($CDCl_3$): δ 20.2, 55.9, 96.3, 114.6, 117.5, 127.4, 127.6, 127.9, 128.0, 130.1, 130.8, 132.4, 132.8, 134.5, 137.8, 140.2, 142.4, 147.5, 157.3, 158.6, 169.2, 169.4; ^{13}C NMR (TFA−$CDCl_3$): δ 18.6, 56.8, 98.1, 109.7, 116.8, 118.0, 129.1, 129.3, 129.4, 131.0, 132.8, 133.6, 134.2, 134.5, 136.2, 136.8, 139.0, 142.6, 145.1, 149.7, 158.2, 162.7, 167.4; HR EI MS: Calcd for $C_{50}H_{37}N_3O_4$: 743.2784. Found: 743.2787. Anal. Calcd for $C_{50}H_{37}N_3O_4 \cdot 0.6CHCl_3$: C, 74.53; H, 4.64; N, 5.15. Found: C, 74.76; H, 4.36; N, 5.08.

22-Acetoxy-2,4-dimethoxy-11,16-bis(4-*tert*-butylphenyl)-6,21-diphenylbenziporphyrin (**20b**). Compound **20b** was prepared from **11b** (34.2 mg; 0.0428 mmol) and silver(I) acetate (23 mg; 0.15 mmol) in acetonitrile (80 mL) under the conditions described above. Recrystallization from dichloromethane-methanol gave the acetoxybenziporphyrin (23.4 mg; 0.0273 mmol; 64%) as dark purple crystals, mp 215−216 °C; UV−vis (1% Et_3N−$CHCl_3$): λ_{max} (logϵ) 353 (4.53), 438 (4.73), 653 (sh, 4.18), 699 nm (4.31); UV−vis (1% TFA−$CHCl_3$): λ_{max} (logϵ) 320 (4.37), 359 (4.36), 449 (4.73), 489 (4.73), 677 (3.81), 881 nm (4.42); ^{1}H NMR ($CDCl_3$): δ 1.10 (3H, s), 1.45 (18H, s), 3.40 (6H, s), 6.34 (1H, s), 6.55 (2H, d, J = 4.8 Hz), 7.00 (2H, s), 7.35−7.45 (16H, m), 7.75 (4H, d, J =

7 Hz), 8.85 (1H, br s); ^{1}H NMR (TFA−$CDCl_3$): δ 0.48 (3H, s), 1.47 (18H, s), 3.49 (6H, s), 4.11 (1H, br s), 6.51 (1H, s), 7.30 (2H, dd, J = 1.2, 5.2 Hz), 7.65 (4H, d, J = 8 Hz), 7.69 (2H, s), 7.70−7.78 (10H, m), 8.00 (2H, dd, J = 1.6, 5.2 Hz), 8.01−8.04 (4H, m), 8.32 (1H, br s); ^{13}C NMR ($CDCl_3$): δ 20.2, 31.7, 34.8, 55.9, 96.3, 114.5, 117.5, 124.8, 127.5, 127.8, 130.1, 131.1, 132.47, 132.52, 134.4, 137.3, 137.4, 142.5, 147.6, 150.3, 157.35, 158.5, 169.46, 169.50; ^{13}C NMR (TFA−$CDCl_3$): δ 18.6, 31.4, 35.3, 56.8, 98.1, 108.6, 117.0, 117.9, 126.4, 129.2, 129.4, 132.7, 133.5, 133.6, 134.2, 134.5, 136.5, 139.0, 141.9, 145.1, 149.5, 154.9, 158.2, 162.7, 167.3; EI MS (70 eV): *m*/*z* (% rel int) 860 (3.3), 859 (13), 858 (40), 857 (63), 856 (4.9), 855 (M^+, 5.3), 815 (10), 281 (100); HR EI MS: Calcd for $C_{58}H_{53}N_3O_4$ + 2H: 857.4192. Found: 857.4186. Anal. Calcd for $C_{58}H_{53}N_3O_4 \cdot 0.3CHCl_3$: C, 78.51; H, 6.02; N, 4.71. Found: C, 78.36; H, 6.08; N, 4.74.

22-Acetoxy-2,4-dimethoxy-3-methyl-6,11,16,21-tetraphenylbenziporphyrin (**20c**). Acetoxy derivative **20c** was prepared from **12a** (100 mg; 0.143 mmol) and silver(I) acetate (70 mg; 0.42 mmol) in acetonitrile (60 mL) and chloroform (30 mL) under the conditions described above. Recrystallization from chloroform−methanol gave the acetoxybenziporphyrin (69.4 mg; 0.0917 mmol; 64%) as purple flakes, mp 242−243 °C; UV−vis (1% Et_3N−$CHCl_3$): λ_{max} (logϵ) 334 (4.43), 422 (4.78), 650 (sh, 4.17), 693 nm (4.27); UV−vis (1% TFA−$CHCl_3$): λ_{max} (logϵ) 474 (4.91), 662 (3.69), 873 nm (4.37); ^{1}H NMR ($CDCl_3$): δ 1.29 (3H, s), 2.01 (3H, s), 3.21 (6H, s), 6.49 (2H, d, J = 4.8 Hz), 6.84 (2H, s), 7.38 (2H, d, J = 4.4 Hz), 7.40−7.49 (16H, m), 7.73−7.76 (4H, m), 9.39 (1H, br s); ^{1}H NMR (TFA−$CDCl_3$): δ 0.93 (3H, s), 2.00 (3H, s), 3.16 (6H, s), 5.72 (1H, br s), 7.16 (2H, d, J = 5.2 Hz), 7.46 (2H, d, J = 1.6 Hz), 7.58−7.67 (10H, m), 7.71−7.77 (6H, m), 7.91−7.96 (6H, m), 10.00 (1H, br s); ^{13}C NMR ($CDCl_3$): δ 10.5, 20.3, 60.9, 114.6, 119.7, 124.67, 124.69, 127.5, 127.9, 128.1, 128.5, 130.3, 131.3, 132.3, 132.6, 134.5, 138.1, 140.0, 141.8, 147.9, 157.2, 157.7, 169.9, 170.0; ^{13}C NMR (TFA−$CDCl_3$): δ 11.4, 19.0, 62.6, 107.1, 117.1, 124.1, 127.9, 129.3, 129.5, 130.1, 130.9, 133.0, 133.8, 134.01, 134.04, 135.9, 137.3, 139.1, 143.7, 145.6, 151.0, 160.4, 161.6; EI MS (70 eV): *m*/*z* (% rel int) 762 (2.4), 761 (8.7), 760 (31), 759 (57), 745 (13); HR EI MS: Calcd for $C_{51}H_{39}N_3O_4$: 757.2940. Found: 757.2938. Anal. Calcd for $C_{51}H_{39}N_3O_4 \cdot {}^2/_3CHCl_3$: C, 74.10; H, 4.77; N, 5.02. Found: C, 74.23; H, 4.56; N, 4.81.

6,23-Dihydro-2,4-dimethoxy-6,11,16,21-tetraphenylbenziporphyrin (**19a**). A solution of sodium borohydride (50 mg) in ethanol (15 mL) was added to a stirred solution of benziporphyrin **11a** (20.3 mg; 0.0296 mmol) in chloroform (25 mL) and the mixture stirred at room temperature overnight. The mixture was washed with water, back extracted with chloroform, and evaporated under reduced pressure. The residue was chromatographed with dichloromethane on a grade 3 basic alumina column, and the product was collected as a blue-green fraction that eluted before a green band corresponding to residual starting material. Recrystallization from chloroform−methanol gave the dihydrobenziporphyrin (13.8 mg; 0.0201 mmol; 68%) as dark purple crystals, mp 218 °C, dec; UV−vis (1% Et_3N−$CHCl_3$): λ_{max} (log ϵ) 414 (4.51), 630 (sh, 4.23), 672 nm (4.37); UV−vis (1% TFA−$CHCl_3$): λ_{max} (log ϵ) 324 (4.32), 408 (4.63), 487 (4.66), 665 (3.80), 885 nm (4.16); ^{1}H NMR ($CDCl_3$): δ 3.37 (3H, s), 3.89 (3H, s), 5.30 (1H, s), 6.07 (1H, s), 6.33 (1H, d, J = 4.4 Hz), 6.42 (1H, s), 6.44 (1H, d, J = 3.6 Hz), 6.50 (1H, d, J = 3.6 Hz), 6.59−6.61 (2H, m), 6.73 (1H, d, J = 4.4 Hz), 7.02 (1H, d, J = 5.6 Hz), 7.10 (2H, d, J = 7.6 Hz), 7.15 (1H, t, J = 7 Hz), 7.21−7.42 (16H, m) 7.82 (1H, br s), 9.86 (1H, br s); ^{1}H NMR (TFA−$CDCl_3$): δ 0.93 (3H, s), 2.00 (3H, s), 3.16 (6H, s), 5.72 (1H, br s), 7.16 (2H, d, J = 5.2 Hz), 7.46 (2H, d, J = 1.6 Hz), 7.58−7.67 (10H, m), 7.71−7.77 (6H, m), 7.91−7.96 (6H, m), 10.00 (1H, br s); ^{13}C NMR ($CDCl_3$): δ 42.6, 56.2, 56.4, 97.3, 108.3, 112.3, 118.9, 119.9, 121.3, 121.5, 122.8, 126.4, 126.5, 126.9, 127.4, 127.7, 128.0, 128.2, 128.5, 128.6, 128.7, 129.1, 130.2, 131.6, 132.3, 132.6, 134.2, 135.1, 139.7, 140.4, 140.9, 142.0, 142.6, 142.7, 147.3, 151.4, 156.6, 158.2, 167.1; HR EI MS: Calcd for $C_{48}H_{37}N_3O_2$: 687.2886. Found: 687.2899.

Crystal Structure Determination of 16a. X-ray quality crystals of **16a** were obtained by vapor diffusion of hexanes into a 1,2-dichloroethane solution followed by slow evaporation. A black block thereby obtained of approximate dimensions 0.38 × 0.28 × 0.25 mm^3 was affixed to a glass fiber using Paratone-N oil and transferred to a Bruker P4/R4/SMART 1000 CCD diffractometer. The X-ray diffraction data were collected at −80 °C using Mo−K_a (λ = 0.71073 Å) radiation. Data collection and cell refinement were performed using SMART.[34] The unit cell parameters were obtained from a least-squares refinement of 4308 centered reflections. The nickel complex **16a** was found to crystallize in the monoclinic crystal system with the following unit cell parameters: a = 9.968(1) Å, b = 18.833(3) Å, c = 18.415(3) Å, β = 95.555(3)°, Z = 4. The systematic absences indicated the space group to be $P2_1/c$ (no. 14).[35] A total of 20720 reflections were collected, of which 7013 were unique, and 5478 were observed $F_o^2 > 2s(F_o^2)$. Limiting indicies were as follows: $-12 \le h \le 12$, $-23 \le k \le 20$, $-22 \le l \le 22$. Data reduction were accomplished using SAINT.[34b] The data were corrected for absorption through use a face-indexing procedure.

Solution and data analysis were performed using the WinGX software package.[36] The structure of **16a** was solved by direct methods using the program SIR2004[37] and the refinement was completed using the program SHELX-97.[38] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned positions based on the geometries of their attached carbon atoms. Hydrogen atoms were given thermal parameters of 20% greater than those of the attached atoms. Full-matrix least-squares refinement on F^2 led to convergence, $(\Delta/\sigma)_{max}$ = 0.001, $(\Delta/\sigma)_{mean}$ = 0.0000, with R_1 = 0.0676 and wR_2 = 0.1895 for 5478 data with $F_o^2 > 2s(F_o^2)$ using 0 restraints and 487 parameters. A final difference Fourier synthesis showed features in the range of $\Delta\rho_{max}$ = 1.86 e$^-$/Å^3 (0.87 Å from Ni) to $\Delta\rho_{min}$ = −1.31 e$^-$/Å^3 (0.88 Å from Ni) which were deemed of no chemical significance. Molecular diagrams were generated using ORTEP-3.[39] X-ray structural data has been deposited with the CCDC.[40]

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Supporting Information Available: Crystallographic data for **16a** in CIF format and copies of the UV−vis, ^{1}H NMR, and ^{13}C NMR spectra for selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(40) Crystallographic data (excluding structure factors) for **16a** has been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC 645634. Copies of this data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK [fax: +44 (0)12233 336033 or e-mail: deposit@ccdc.cam.ac.uk].