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Improved syntheses of *meso*-tetraarylbenziporphyrins and observations of substituent effects on the diatropic characteristics of these formally nonaromatic carbaporphyrinoids☆

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ABSTRACT

Carbaporphyrinoid systems are widely investigated but improved routes to these systems are needed. A fairly direct route to tetraphenylbenziporphyrin has been reported previously starting from isophthalaldehyde and this approach has been adapted to make use of more easily accessible isophthalic acids. Isophthalic acid and 5-*tert*-butylisophthalic acid were converted into the related diacyl chlorides and reacted with excess benzene or chlorobenzene to give a series of diketones. These were reduced with sodium borohydride to give the corresponding dialcohols in virtually quantitative yields and this route allows the synthesis of >10 g quantities of these key intermediates. Reaction of these dicarbinols with pyrrole and benzaldehyde or 4-chlorobenzaldehyde in the presence of $BF_3 \cdot Et_2O$ in dichloromethane, followed by oxidation with DDQ, gave a series of eight-different tetraarylbenziporphyrins in up to 32% yield. Although benziporphyrins are generally considered to be nonaromatic, they may exhibit trace amounts of global diatropic character and this appears to be enhanced by the presence of a *tert*-butyl group on the benzene moiety or the introduction of 4-chlorophenyl substituents. Addition of TFA to the NMR solutions generated dications that exhibit an unambiguous ring current effect where the internal CH proton NMR resonances appear upfield in the range of 5.05–5.65 ppm, while the external pyrrolic resonances show concomitant downfield shifts to give values between 7.08 and 7.86 ppm. A *tert*-butyl substituent again increased the diatropic character of the macrocycle, although replacement of *meso*-phenyl groups with more electron-withdrawing 4-chlorophenyl units had the opposite effect in this case. These results are consistent with the aromatic characteristics deriving from canonical forms that have [18]annulene substructures. Two examples of palladium(II) benziporphyrin complexes were prepared and these results demonstrate that the presence of 4-chlorophenyl or *tert*-butyl groupings do not have a negative impact on the formation of organometallic derivatives. The improved yields for the reported synthetic methodology and the new information that can be obtained by systematically altering the substitution patterns around the macrocyclic periphery will facilitate further development of the chemistry of benziporphyrins.

1. Introduction

Carbaporphyrinoid systems (e.g., **1**), porphyrin analogues with one or more of the pyrrole subunits replaced by carbocyclic rings, have been intensively investigated over the past 15 years.[1–3] These investigations, together with studies on the related *N*-confused porphyrins **2**,[4–7] have led to the discovery of many unusual organometallic derivatives as well as revealing intriguing chemical reactivity. In addition, these systems provide significant insights into the macrocyclic aromatic properties of porphyrins and related conjugated macrocycles.[1–3,8] Carbaporphyrins **1**[9] and *N*-confused porphyrins **2**[4–7] show highly diatropic characteristics, but other carbaporphyrinoid structures exhibit a wide range of aromatic properties.[1–3] Although tropiporphyrins **3**[10] and oxybenziporphyrins **4**,[11–14] like **1** and **2**, give proton NMR spectra where the internal CH resonance shows up near −7 ppm, azuliporphyrins **5** show much reduced diatropicity with the internal CH giving rise to a singlet near +3 ppm,[15–19] and benziporphyrins **6a** and **7a** are generally considered to have no overall macrocyclic aromaticity.[11–13,20,21] Nevertheless, dimethoxybenziporphyrins **6b** and **7b** do show some diatropic character, that is greatly enhanced upon protonation and even the dications derived from **6a** and **7a** show a small but significant upfield shift to the internal CH

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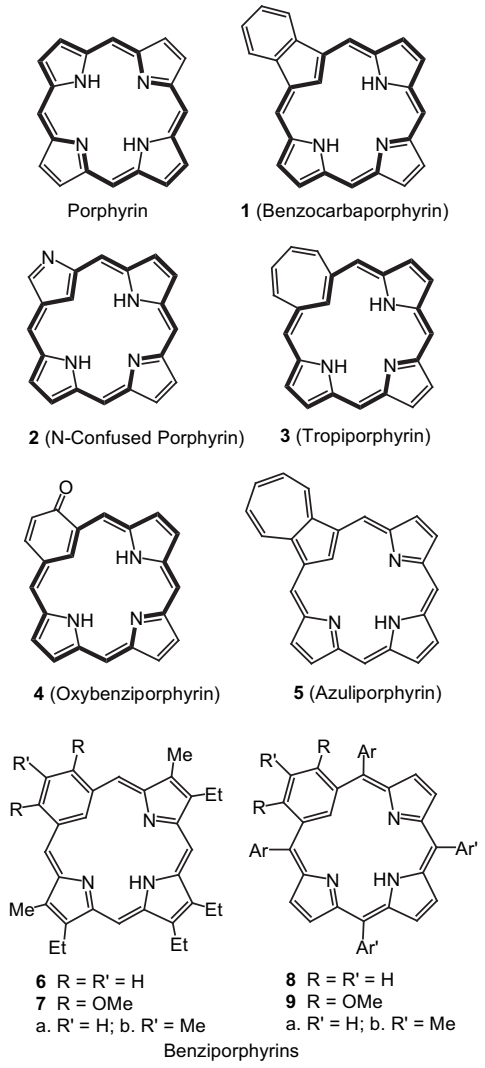
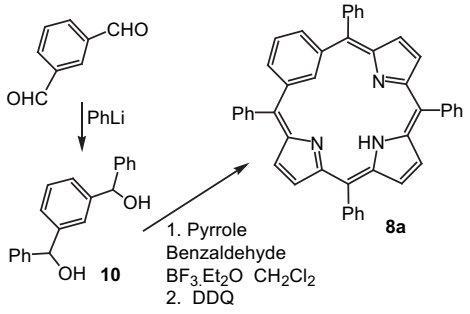


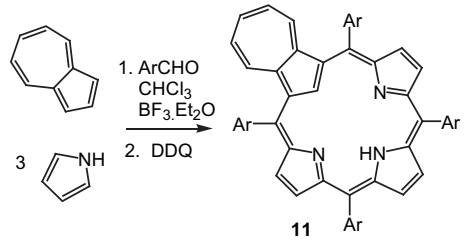
resonance.[13,22,23] Although the [18]annulene model for porphyrinoid aromaticity[1,24] can be considered to be naïve,[8,25] this interpretation still provides the best explanations for the results obtained for these macrocyclic structures.[3] In this work, we examined the spectroscopic properties of a series of *meso*-tetraaryl substituted benziporphyrins to see whether substituent effects could reveal the presence of residual macrocyclic diatropicity. In addition, an efficient and more versatile route to tetraarylbenziporphyrins has been developed.[26,27]

2. Results and discussion

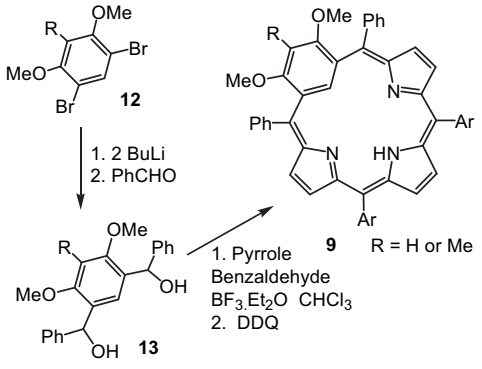
The first syntheses of benziporphyrins[11,12,20] were carried out using the '3+1' variant on the MacDonald condensation[28] where isophthalaldehydes were condensed with tripyrranes in the presence of an acid catalyst, followed by oxidation. Although this approach gave good yields of *meso*-unsubstituted benziporphyrins **6** and **7**, the methodology requires the use of tripyrranes that must be prepared by multistep procedures. Stepien and Latos-Grazynski subsequently reported a more direct route to *meso*-tetraarylbenziporphyrins **8** by reacting dicarbinol **10a** with pyrrole and benzaldehyde in the presence of $BF_3.Et_2O$ in dichloromethane, followed by oxidation with DDQ (Scheme 1).[21] This route complemented our investigations into the synthesis of *meso*-tetraarylazuliporphyrins **11** from azulenes and aryl aldehydes, again using one-pot Lindsey reaction conditions (Scheme 2).[18,19] The same approach was also used to prepare dimethoxybenziporphyrins **9** (Scheme 3).[22,23] Dibromodimethoxybenzenes **12** were metalated with *n*-butyllithium and further treated with benzaldehyde to give the dicarbinols **13**.[22,23] Further Lindsey-type condensation[29] with pyrrole and benzaldehydes gave good yields of the corresponding tetraarylbenziporphyrins **9**.[22,23] The synthesis of dicarbinols **13** relies on the ability of the methoxy substituents to direct metal–halogen exchange and other substituted benziporphyrins could not be easily prepared by this approach. The related dialcohol **10a** was originally prepared in moderate yield by reacting a deficiency of phenyllithium with isophthalaldehyde,[21] although these yields can be increased by using an excess of the organometallic reagent.[23] However, dicarboxylic acids **14** are far more readily accessible than the corresponding dialdehydes and are therefore more versatile precursors to benziporphyrins. In addition, a series of dialcohols **10a–d** (Scheme 4) can be synthesized without resorting to the use of organolithium reagents.



Scheme 1.

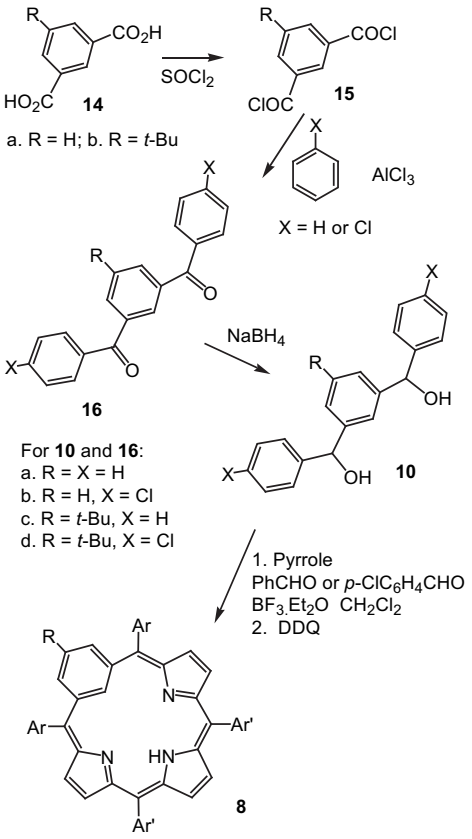


Scheme 2.



Scheme 3.

Dicarboxylic acids **14a** and **14b** can easily be converted into the corresponding diacyl chlorides **15** in quantitative yields by treatment with thionyl chloride. In addition, phthaloyl chloride is commercially available. These diacyl chlorides can be used to prepare diketones under standard Friedel–Crafts acylation conditions (Scheme 4).[30] Reaction with excess benzene readily gave the diphenyl diketones **16a** and **16c**, while good yields of the 1,3-bis(4-



14 a. R = H; b. R = *t*-Bu

15

16

10

For **10** and **16**:
a. R = X = H
b. R = H, X = Cl
c. R = *t*-Bu, X = H
d. R = *t*-Bu, X = Cl

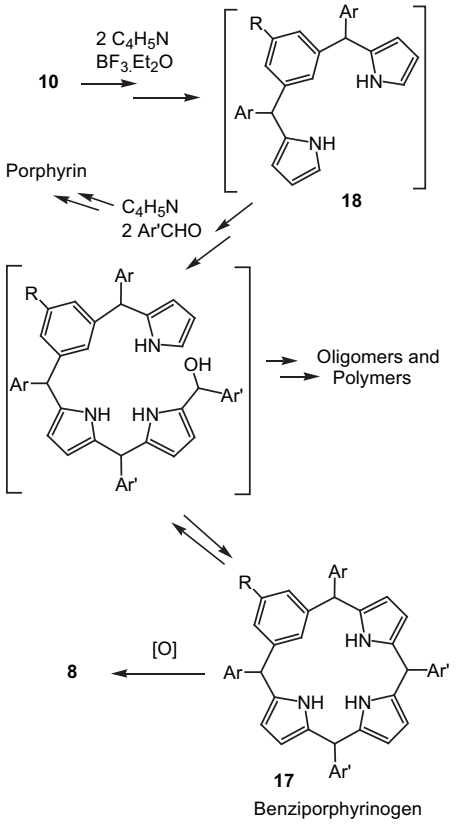
8

a. R = H, Ar = Ar' = Ph (13%)
b. R = H, Ar = Ph, Ar' = 4-ClC$_6$H$_4$ (22%)
c. R = H, Ar = 4-ClC$_6$H$_4$, Ar' = Ph (12%)
d. R = H, Ar = Ar' = 4-ClC$_6$H$_4$ (24%)
e. R = *t*-Bu, Ar = Ar' = Ph (12%)
f. R = *t*-Bu, Ar = Ph, Ar' = 4-ClC$_6$H$_4$ (19%)
g. R = *t*-Bu, Ar = 4-ClC$_6$H$_4$, Ar' = Ph (5.4%)
h. R = *t*-Bu, Ar = Ar' = 4-ClC$_6$H$_4$ (32%)

Scheme 4.

chlorobenzoyl)benzenes **16b** and **16d** can be obtained using chlorobenzene.[30] These diketones were then reduced with sodium borohydride in ethanol to give the related dicarbinols **10** in ca. 95% isolated yield. In this way, a series of dicarbinols is easily generated and this allows the systematic introduction of varying combinations of substituent groups.

In earlier studies on the synthesis of tetraarylazuliporphyrins **11** and dimethoxybenziporphyrins **9**,[18,19,22,23] significantly improved yields were obtained when 4-chlorobenzaldehyde was used as a precursor to the porphyrinoid systems instead of benzaldehyde. In the preparation of azuliporphyrins **11**, 4-bromo- and 4-iodobenzaldehyde also gave superior results.[19] In our studies on the preparation of benziporphyrins **8a**–**h** (Scheme 4), we sought to address whether the presence of 4-chloro groups had a beneficial effect on the reactions of the carbinol precursor **10**, as well as for the benzaldehyde reactant. The four available dicarbinols **10** were individually reacted with pyrrole and benzaldehyde, or 4-chlorobenzaldehyde, under the previously developed conditions.[21,23] Although we have found chloroform to be a superior solvent for the formation of tetraarylazuliporphyrins **11** or dimethoxybenziporphyrins **9**,[18,19,22,23] this gave poor results for benziporphyrins **8a**–**h**. However, when the reactions are catalyzed with boron trifluoride diethyl etherate in dichloromethane, followed by oxidation with DDQ, moderate to good yields of the targeted benziporphyrins **8** could be obtained. There are eight combinations of the reactants and the yields varied from 5–32%, although the isolated yield only drops below 12% in one case. Tetraphenylbenziporphyrin **8a** has been synthesized previously but the remaining macrocyclic products are all new examples of this class of benziporphyrins. The reaction conditions used in this work are based upon the methods developed by Lindsey's group for the synthesis of *meso*-tetraarylporphyrins.[29] A total of six carbon–carbon bonds must be generated between the original dialcohol **10**, the three pyrrole units and the two aromatic aldehydes. The initially generated reduced form of the macrocycle (**17**; benziporphyrinogen) is then dehydrogenated to give the fully conjugated system (Scheme 5). Clearly, many different products could result in these reactions, including the formation of open-chain structures such as **18**, macrocyclic by-products such as *meso*-tetraphenylporphyrin, and oligomeric or polymeric materials (Scheme 5). The products are purified by column chromatography on grade 3 basic alumina, but only a small amount of porphyrin is observed as a by-product in these reactions. However, unidentified dark materials possibly corresponding to oligomers or polymers are retained by these columns. The isolated product fractions were then recrystallized from chloroform–ligroin and the quoted yields correspond to the samples obtained after recrystallization and drying in vacuo. Useful trends could be seen in these studies. The presence of *tert*-butyl substituents in **10c** and **10d** had no significant effect on the yields and this enabled the synthesis of four *tert*-butylbenziporphyrins **8e**–**h**. Chlorophenylcarbinols **10b** and **10d** gave inferior yields of benziporphyrins **8** when reacted with pyrrole and benzaldehyde. However, phenylcarbinols **10a** and **10c** gave substantially better yields of the isomeric benziporphyrins when reacted with pyrrole and 4-chlorobenzaldehyde and again the chlorobenzaldehyde gave better results than benzaldehyde in these reactions. Although the chlorophenylcarbinols **10b** and **10d** gave the worst results when reacted with benzaldehyde, they gave excellent yields when reacted with pyrrole and 4-chlorobenzaldehyde. The latter combination gave tetrakis(4-chlorophenyl)benziporphyrins **8d** and **8h** in 24% and 32% yields, respectively. Clearly, the judicious



Scheme 5.

selection of reactants allows great improvements in the yields for these important porphyrin analogues. However, a full assessment of the origins of these differences in the yield of macrocycle is more difficult to ascertain. There are a large number of intermediary steps between the reactants and the final macrocyclic products and any one of these steps would affect the outcome of these reactions (Scheme 5). In addition, many of the condensation steps prior to oxidation are reversible and the outcome will depend on the equilibria between the many open-chain (e.g., **18**) and macrocyclic species (e.g., **17**) in the reaction solutions. However, the 4-chloro group will increase the reactivity of the arylaldehyde and this is likely to be responsible for the increased yields. On the other hand, the dicarbinols would need to generate carbocation intermediates and the chlorophenyl unit would not be effective in stabilizing this electrophilic species. These factors rationalize the results for **8a**–**c** and **8e**–**g**, but do not explain why a combination of chlorophenyl units in both reactants gives the best yields of all. However, the chlorophenyl groups would be expected to stabilize the benziporphyrinogen structures **17** and may thereby decrease back reactions (acidolysis) to open-chain species.

The availability of eight-different benziporphyrins allows us to contrast the properties of these porphyrinoids and assess trends due to substituent effects. The UV–vis spectra for **8a**–**h** were all very similar, showing a moderate Soret-like band between 413 and 420 nm and a broad peak in the far red region (Fig. 1). The presence of chlorophenyl units or a *tert*-butyl moiety gave rise to minor bathochromic shifts. The Soret-like band of tetraphenylbenziporphyrin **8a** in chloroform gave a λ_{max} value of 413 nm, while the *tert*-butylbenziporphyrin **8e** gave this band at 418 nm (Table 1). Comparisons of **8b** to **8f**, **8c** to **8g**, and **8d** to **8h**, each of which differ by having an H or a *t*-Bu group at position 3, showed a consistent 4–5 nm red shift when the *tert*-butyl group was present. The chlorophenyl groups exerted a smaller effect but nevertheless consistently gave higher λ_{max} values as the number of these units was increased. Addition of TFA to solutions of benziporphyrins **8** produces the corresponding dications $\mathbf{8}H_2^{2+}$ (Scheme 6). These give stronger Soret-like bands in the range of 459–469 nm and a broad absorption that extends beyond 900 nm (Fig. 1). The dication also shows substituent effects that lead to bathochromic shifts. The presence of a *tert*-butyl group leads

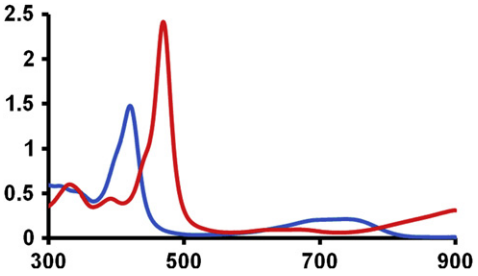
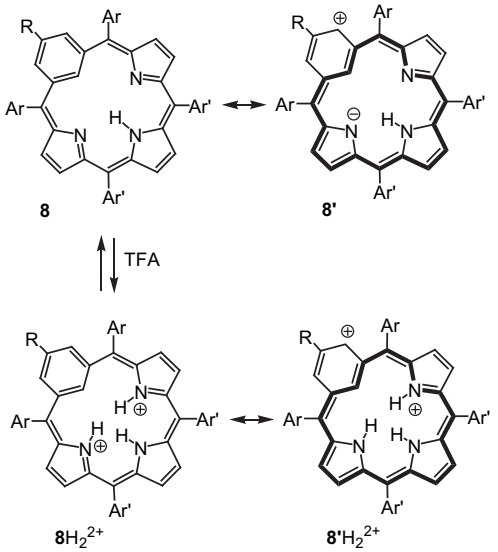


Figure 1. UV–vis spectra of benziporphyrin **8h**. Blue line: free base in chloroform. Red line: dictation $\mathbf{8h}H_2^{2+}$ in 1% TFA–chloroform.

Table 1
Wavelength values of the Soret-like bands for free base benziporphyrins **8a**–**h** in chloroform and dications $\mathbf{8}H_2^{2+}$ in 1% TFA–chloroform

Benziporphyrin	λ_{max} Free base	λ_{max} Dictation $\mathbf{8}H_2^{2+}$
8a	413 nm	459 nm
8b	415 nm	461 nm
8c	415 nm	465 nm
8d	416 nm	466 nm
8e	418 nm	462 nm
8f	419 nm	464 nm
8g	419 nm	467 nm
8h	420 nm	469 nm



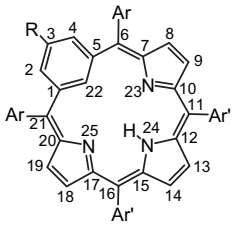
Scheme 6.

to a 2–3 nm red shift, while the presence of chlorophenyl units gave up to a 7 nm shift to longer wavelength (Table 1). In this series, the chlorophenyl units had a significantly larger effect at the 6,21-positions rather than the 11,16-positions (5–6 nm vs 2 nm).

Although benziporphyrins have generally been considered to be nonaromatic porphyrinoids,[12] diatropic properties can be ascribed to the NMR data, particularly in the case of the diprotonated dications $\mathbf{8}H_2^{2+}$. The aromatic properties of porphyrins and related macrocycles can be considered to be due to [18]annulene substructures.[1] While the precise nature of aromaticity in these systems is still being assessed, the [18]annulene model has provided a self-consistent framework that appears to explain the observed properties of these systems. Benziporphyrins are cross-conjugated and would of necessity have to loose the 6π arene identity of their benzene rings to become fully aromatic porphyrinoids. However, electron donating effects can favor resonance contributors that can take on the required [18]annulene characteristics.[1,13] In the case of free base benziporphyrins, canonical forms like **8′** would fit the criteria, but this type of structure would be expected to be a minor contributor due to the formal loss of the benzene subunit and the requirement for charge separation. Nevertheless, this may facilitate a small amount of diatropic character that could be enhanced by the presence of suitable substitution patterns. Although strongly electron-donating groups such as methoxy have been shown to greatly increase the aromatic character of the benziporphyrin system,[13,22,23] little is known about the effects that would result from more subtle electronic interactions. The proton NMR data for benziporphyrins **8a**–**h** provide important information that gives insights into these issues.

If a porphyrinoid system has diatropic properties, the internal protons (22-H and NH) should be shifted upfield while the external protons will be shifted downfield. The three types of external protons on the pyrrole units (positions 13,14 (2H, s), 9,18 (2H, d) and 8,19 (2H, d), respectively) provide the best data for comparison as they are well removed from local inductive effects. The external benzene protons at positions 2 and 4 can potentially give some information but they are aligned above the adjacent phenyl substituents and this leads to a shielding factor that must also be taken into account. Proton NMR spectra were run on benziporphyrins **8a**–**h** at approximately the same concentrations in $CDCl_3$ on a Bruker 500 MHz instrument and the chemical shifts for selected resonances are shown in Table 2. The three types of pyrrole protons gave resonances near 6.5, 6.8, and 7.0 ppm, while the internal CH appeared between 6.94 and 7.35 ppm and the NH was observed

Table 2
Selected proton NMR chemical shifts for benziporphyrins **8** in $CDCl_3$ at 296 K



	22-H	NH	2,4-H	13,14-H	9,18-H	8,19-H
8a	7.35	10.30	7.01	6.76	6.54	7.21
8b	7.30	10.25	7.00	6.74	6.52	7.23
8c	7.29	10.26	6.99	6.77	6.56	7.17
8d	7.24	10.21	6.99	6.75	6.54	7.19
8e	7.05	10.14	7.04	6.78	6.56	7.24
8f	7.00	10.10	7.03	6.77	6.54	7.26
8g	6.98	10.12	7.03	6.79	6.57	7.19
8h	6.94	10.07	7.03	6.77	6.56	7.22

slightly downfield from 10 ppm (Fig. 2 and Table 2). Coupling could also be seen between the external benzene protons (2,4-H) and the internal 22-CH, and this is illustrated for the 500 MHz NMR spectrum of **8h**, which shows a ^4J coupled triplet and doublet at 6.94 and 7.03 ppm, respectively (Fig. 2). An analysis of the data for all eight benziporphyrins shows that both the 22-H and NH resonances are significantly shielded when a *tert*-butyl moiety is introduced (upfield shifts of 0.14–0.31 ppm). Small upfield shifts for these resonances can also be seen as the number of chlorophenyl substituents is increased. However, the chemical shifts of the pyrrolic resonances are not significantly influenced by these structural changes. The results appear to indicate that the free base porphyrins possess a very weak global ring current that is enhanced when the *tert*-butyl or chlorophenyl units are present. These data are consistent with our suggestion that the weak macrocyclic ring current is due to dipolar resonance contributors like **8′**.[23] The contributor would be stabilized by the electron donating *tert*-butyl group on the benzene ring, and the more electron-withdrawing

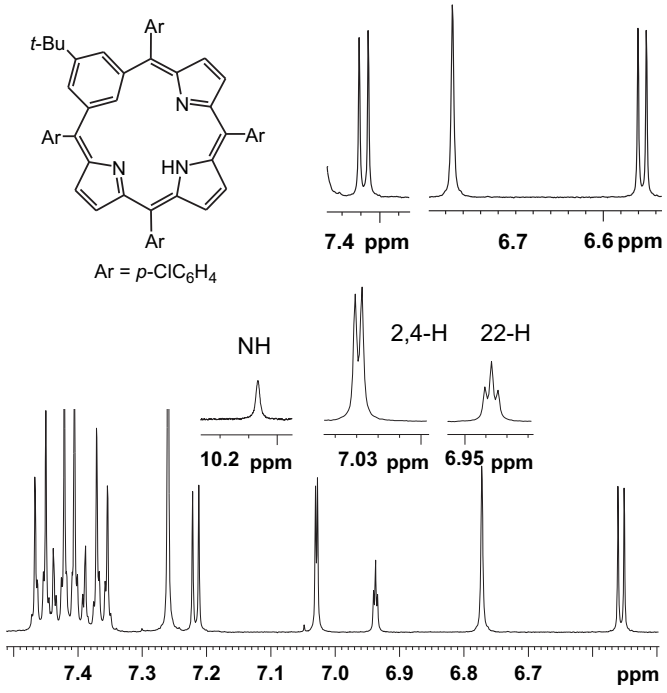


Figure 2. Partial 500 MHz proton NMR spectrum of benziporphyrin **8h** in $CDCl_3$.

Table 3
Selected proton NMR chemical shifts for benziporphyrins **8** in trace TFA–$CDCl_3$ at 296 K

	22-H	NHs	2,4-H	13,14-H	9,18-H	8,19-H
8aH_2^{2+}	5.65	9.54, 10.75	7.19	7.24	7.08	7.79
8bH_2^{2+}	5.51	9.05, 10.46	7.20	7.25	7.09	7.84
8cH_2^{2+}	5.43	8.98, 10.39	7.19	7.28	7.12	7.81
8dH_2^{2+}	5.47	9.11, 10.45	7.19	7.26	7.11	7.81
8eH_2^{2+}	5.05	8.47, 10.14	7.21	7.29	7.12	7.86
8fH_2^{2+}	5.18	8.95, 10.38	7.20	7.25	7.10	7.84
8gH_2^{2+}	5.13	8.95, 10.36	7.20	7.27	7.11	7.80
8hH_2^{2+}	5.16	9.09, 10.42	7.20	7.26	7.11	7.81

chlorophenyl units would be expected to stabilize the increased electron density on the macrocycle. Nevertheless, these shifts are relatively small and show only a pale ghost of porphyrinoid aromaticity. This system is at the lower limit for where we can see effects of this type, but they do mirror the shifts observed for more aromatic porphyrinoids such as **9** and **11**.[18,19,23]

Addition of TFA to these NMR solutions generates dicationic species **8**H_2^{2+} that show increased diatropic character (Table 3 and Fig. 3). The internal CH gives rise to weakly coupled resonances between 5.05 and 5.65 ppm, an upfield shift of 1.7–2.0 ppm compared to the corresponding free base benziporphyrins, and two types of NH protons can now be seen at 8.47–9.54 ppm (1H) and 10.14–10.75 ppm (2H). The dications show weak long range coupling between the NHs and the external pyrrolic protons. The pyrrole resonances are all shifted downfield by 0.48–0.64 ppm, while the external benzene protons at positions 2 and 4 are deshielded by 0.17–0.20 ppm. Although the downfield shifts can be partly attributed to the 2+ charge on the system, these data are consistent with an increased macrocyclic ring current for the dications **8a**–**h**. Resonance contributors with [18]annulene substructures (e.g., **8′**H_2^{2+}) now aid in charge delocalization and for this reason would be expected to be far more favored for the dications than was the case for the free base benziporphyrins. For these diprotonated benziporphyrins, the presence of a *tert*-butyl moiety causes the 22-H to shift upfield by 0.31–0.60 ppm and upfield shifts can also be seen for the NH resonances, particularly when the tetraphenylbenziporphyrins **8a** and **8e** are compared. The presence of the 3-*tert*-butyl group is also associated with a small downfield shift for the external proton

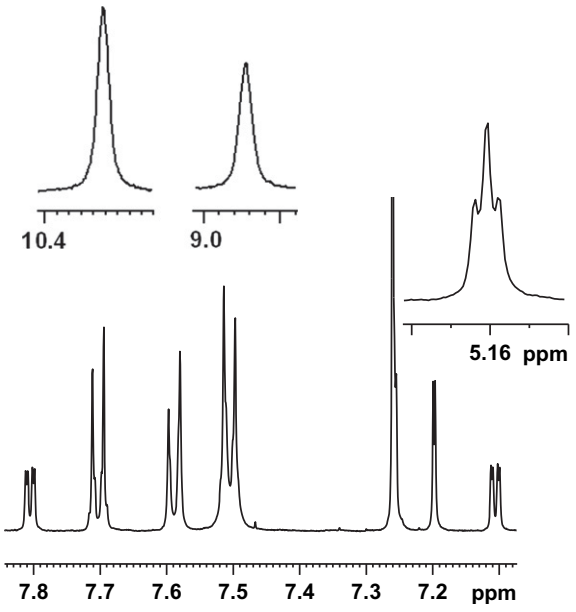


Figure 3. Partial 500 MHz proton NMR spectrum of benziporphyrin dictation **8h**H_2^{2+} in TFA–$CDCl_3$ showing the internal CH as a long range coupled triplet at 5.16 ppm.

resonances. These results are consistent with the electron-donating substituent stabilizing resonance contributors like **8′**H_2^{2+}. The introduction of chlorophenyl groups has the opposite effect leading to downfield shifts to the internal protons (22-H, NHs) and small upfield shifts to the pyrrolic protons. This is the opposite trend to the one observed for the free base benziporphyrins, but the increased electron-withdrawing effects due to the chlorophenyl substituents would destabilize the delocalized positive charges in **8′**H_2^{2+} whereas they would exert a beneficial effect in canonical form **8′**. This inverted trend was also seen for the more diatropic dimethoxybenziporphyrins **9**.[23] Interestingly, these effects appear to be much larger for the 11,16-bis(4-chlorophenyl)benziporphyrins **8b** and **8f** than for the 6,21-versions **8c** and **8g**, implying that the electron-density at *meso*-positions 11 and 16 is lower than at positions 6 and 21. The benziporphyrins were also characterized by carbon-13 NMR spectroscopy, mass spectrometry and combustion analysis. The carbon-13 data for the dications **8**H_2^{2+} in TFA–$CDCl_3$ is worthy of further note. In these spectra, the 22-CH was observed at the unusual values of 93.6–94.5 ppm for **8a–d** and the even lower value of 91.1–92.3 ppm for the *tert*-butyl versions **8e–h** (Fig. 4). This assignment was confirmed by running HSQS spectra to show the ^1H–^{13}C correlations, but the origin of this effect is not clear. The EIMS data showed strong M+2H peaks, a feature of these compounds that had been noted previously.[12,20]

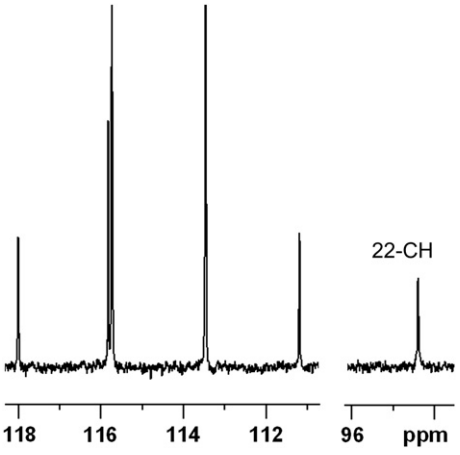
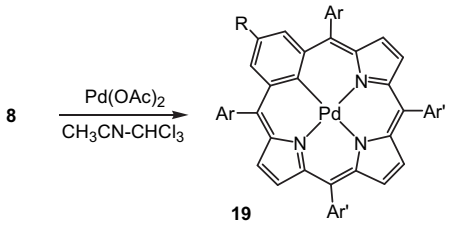


Figure 4. Partial carbon-13 NMR spectrum of **8d**H_2^{2+} in TFA–$CDCl_3$ showing the abnormally upfield resonance for the 22-CH. A resonance at 116 ppm falls very close to one of the lines for the CF_3 quartet produced by the TFA.

Benziporphyrins can easily be converted into organometallic derivatives[31–36] and the palladium(II) derivatives of *tert*-butylbenziporphyrins **8e** and **8h** were also investigated. Reaction of **8e** and **8h** with palladium(II) acetate in refluxing chloroform–acetonitrile gave good yields of the palladium derivatives **19a** and **19b**, respectively (Scheme 7). The UV–vis spectrum **19a** showed a Soret-like band at 438 nm (Fig. 5), slightly red shifted compared to the previously described palladium(II) complex **19c** of tetraphenylbenziporphyrin,[21] and a series of broad absorptions between 500 and 900 nm. The tetrakis(4-chlorophenyl)benziporphyrin derivative **19b** gave a similar UV–Vis spectrum but in this case a split Soret band was observed at 419 and 439 nm (Fig. 5). The pyrrole protons in **19a** and **19b** showed up in the range of 7.00–7.21 ppm, values that are slightly downfield compared to the data reported for **19c**. The results are consistent with the palladium(II) derivatives having slightly increased diatropic character compared to the free base benziporphyrins and indicate that the *tert*-butyl group enhances this characteristic, as was the case for the free base and dicationic forms of **8a–h**, although the presence of chlorophenyl substituents did not result in significant changes.



a. R = *t*-Bu, Ar = Ar' = Ph
b. R = *t*-Bu, Ar = Ar' = *p*-ClC_6H_4
c. R = H, Ar = Ar' = Ph

Scheme 7.

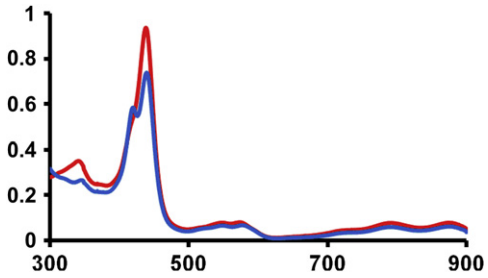


Figure 5. UV–vis spectra of palladium(II) benziporphyrins in chloroform. Red line: Tetraphenylbenziporphyrin complex **19a**. Blue line: Tetrakis(4-chlorophenyl)benziporphyrin derivative **19b** showing a split Soret-type absorption.

3. Conclusions

Efficient syntheses of tetraarylbenziporphyrins have been developed starting with isophthalic acids. This has allowed the preparation of a series of benziporphyrins with varying number of chlorophenyl substituents and with *tert*-butyl substituted benzene subunits. These substituents exert subtle effects on the UV–vis and NMR spectra for these porphyrinoids. The proton NMR data for the free base porphyrins suggest that there is a trace of global aromatic character in these formally nonaromatic macrocycles that is increased by the presence of an electron-donating *tert*-butyl group and the introduction of electron-withdrawing chlorophenyl substituents. Protonation gave dications, which exhibited increased diatropic character that was again enhanced by the presence of a *tert*-butyl moiety. However, chlorophenyl substituents slightly decreased the diatropic character for these diprotonated species. Two examples of palladium(II) complexes were prepared and these results indicated that the presence of *tert*-butyl or chlorophenyl substituents did not interfere with the formation of these stable organometallic derivatives. The improved yields for this synthetic approach, and the wealth of information that can be obtained by systematically altering the substitution patterns around the macrocyclic periphery, will allow further development of the chemistry of these important porphyrin analogues.

4. Experimental

4.1. General

Boron trifluoride etherate, aluminum chloride, 4-chlorobenzaldehyde, phthaloyl chloride, 5-*tert*-butylphthalic acid, palladium(II) acetate, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), thionyl chloride and sodium borohydride were purchased from Aldrich or Acros and were used without further purification. Commercially available pyrrole and benzaldehyde were distilled prior to use. Chromatography was performed using grade 3 basic alumina or 70–230 mesh silica gel. Melting points were determined in open

capillary tubes on a Mel-Temp apparatus and are uncorrected. Proton and carbon-13 NMR data were obtained on a Varian Gemini 400 MHz FT NMR spectrometer or a 500 MHz Bruker Avance III NMR spectrometer; funding for the latter instrument was provided by the National Science Foundation under grant no. CHE-0722385. Mass spectral determinations were conducted at the Mass Spectral Laboratory, School of Chemical Sciences, University of Illinois at Urbana-Champaign, and elemental analyses were obtained from the School of Chemical Sciences Microanalysis Laboratory at the University of Illinois.

4.2. Synthetic procedures

*4.2.1. 1,3-Dibenzoyl-5-tert-butylbenzene (**16c**).* Several drops of DMF were added to a stirred mixture of 5-*tert*-butylisophthalic acid (10.01 g, 45.5 mmol) and thionyl chloride (50 mL) and the mixture was refluxed for 1 h. The excess thionyl chloride was removed on a rotary evaporator and the residual diacyl chloride was taken up in benzene (400 mL) and cooled in an ice water bath. Anhydrous aluminum chloride (15 g) was added, and the resulting mixture was stirred at room temperature for 16 h and then at 60 °C for 4 h. The cooled reaction mixture was poured into a beaker of ice water (300 g) and concentrated hydrochloric acid (45 mL). The pale yellow organic layer was separated and washed sequentially with water, 5% aqueous sodium bicarbonate solution, and water. The organic layer was dried over sodium sulfate and the solvent removed under reduced pressure. Recrystallization from chloroform–ligroin gave the diketone (10.52 g, 30.8 mmol, 68%) as off-white crystals, mp 77.5–79 °C (lit. mp[30] 80.5–82.5 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.39 (9H, s), 7.47–7.51 (4H, m), 7.60 (2H, tt, J=1.3, 7.4 Hz), 7.80–7.84 (2H, m), 7.93 (1H, t, J=1.6 Hz), 8.08 (2H, d, J=1.6 Hz); ^{13}C NMR ($CDCl_3$): δ 31.4, 35.3, 128.6, 129.1, 130.3, 130.8, 133.0, 137.4, 137.7, 152.4, 196.5.

*4.2.2. 1,3-Bis(phenylhydroxymethyl)-5-tert-butylbenzene (**10c**).* 1,3-Dibenzoyl-5-*tert*-butylbenzene (9.10 g, 26.6 mmol) was dissolved in ethanol (100 mL) while gentle heating. The flask was cooled to room temperature, sodium borohydride (1.12 g) was added, and the mixture was stirred for a further 20 min. Water (100 mL) was added, and the solution was heated on a boiling water bath for 20 min. The solution was diluted with water (200 mL) and cooled in an ice bath. The resulting precipitate was suction filtered and dried in vacuo overnight to give the dialcohol (8.776 g, 25.4 mmol, 96%) as a white solid, mp 109–112 °C. An analytical sample was obtained by recrystallization from ethanol–water as small white needles, mp 109–112 °C. The proton NMR data for the dicarbinols **10** were consistent with the presence of two diastereoisomers. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.30 (9H, s), 2.23–2.26 (2H, 2 overlapping doublets), 5.82–5.85 (2H, br m), 7.22–7.25 (1H, m), 7.26–7.31 (3H, m), 7.33–7.40 (9H, m); ^{13}C NMR ($CDCl_3$): δ 31.6, 35.0, 76.7 (2), 122.3, 123.1, 123.2, 126.7, 126.8, 127.7 (2), 128.7, 143.8, 143.9, 144.0 (2), 152.0. Anal. calcd for $C_{24}H_{26}O_2$: C, 83.20; H, 7.56. Found: C, 83.21; H, 7.79.

*4.2.3. 1,3-Bis(4-chlorophenylhydroxymethyl)benzene (**10b**).* Using the foregoing procedure, diketone **16b**[30] (2.02 g, 5.69 mmol) gave the dialcohol (1.945 g, 5.42 mmol, 95%) as a white solid, mp 124–128 °C. An analytical sample was obtained by recrystallization from ethanol–water as a white powder, mp 125–127.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.31 (2H, br s), 5.82 (2H, br s), 7.22–7.25 (2H, m), 7.26–7.32 (9H, m), 7.38–7.41 (1H, m); ^{13}C NMR ($CDCl_3$): δ 75.7, 124.8, 126.2 (2), 128.1 (2), 128.9, 129.2, 133.6 (2), 142.2, 144.1 (2). Anal. calcd for $C_{20}H_{16}Cl_2O_2$: C, 66.87; H, 4.49. Found: C, 66.76; H, 4.34.

*4.2.4. 1,3-Bis(4-chlorophenylhydroxymethyl)-5-tert-butylbenzene (**10d**).* Diketone **16d**[30] (6.06 g, 14.7 mmol) was reduced with sodium borohydride (1.12 g) as described in the foregoing procedure and gave the dicarbinol (5.88 g, 14.2 mmol, 96%) as a white solid, mp 162–164 °C. An analytical sample was obtained by recrystallization from ethanol–water as fluffy white crystals, mp 163–165 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.27 (9H, s), 2.23–2.25 (2H, 2 overlapping doublets), 5.77 (2H, br d), 7.12–7.14 (1H, m), 7.28–7.31 (10H, m); ^{13}C NMR ($CDCl_3$): δ 31.5, 35.1, 76.0, 122.1, 123.3 (2), 128.1 (2), 128.8, 133.5, 142.3, 143.7 (2), 152.4. Anal. calcd for $C_{24}H_{24}Cl_2O_2$: C, 69.40; H, 5.82. Found: C, 69.23; H, 5.86.

*4.2.5. 6,11,16,21-Tetraphenylbenziporphyrin (**8a**).* Prepared in 13% yield as reported previously.[23] UV–vis (1% Et_3N-$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 413 (4.82), 692 (sh, 3.99), 729 nm (4.00); UV–vis (1% TFA–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 329 (4.46), 377 (4.39), 459 (5.04), 609 (3.67), 665 (3.59), 900 nm (4.18); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.54 (2H, d, J=4.7 Hz), 6.76 (2H, s), 7.01 (2H, dd, J=1.8, 7.8 Hz), 7.21 (2H, d, J=4.7 Hz), 7.32 (1H, t, J=7.8 Hz), 7.35 (1H, br t, J=1.6 Hz), 7.40–7.49 (20H, m), 10.30 (1H, br s); ^{1}H NMR (500 MHz, TFA–$CDCl_3$): δ 5.65 (1H, br t, J=1.6 Hz), 7.08 (2H, d, J=5.0 Hz), 7.19 (2H, dd, J=1.7, 7.8 Hz), 7.24 (2H, br d, J=1.0 Hz), 7.55–7.63 (14H, m), 7.69 (4H, t, J=7.7 Hz), 7.74–7.80 (5H, m), 9.54 (1H, br s), 10.75 (2H, br s); ^{13}C NMR (TFA–$CDCl_3$): δ 94.1, 116.7, 128.9, 129.1, 129.5, 130.5, 132.9, 133.6, 133.9, 135.4, 135.9, 136.4, 138.1, 138.3, 139.9, 144.3, 151.6, 152.3, 161.7.

*4.2.6. 11,16-Bis(4-chlorophenyl)-6,21-diphenylbenziporphyrin (**8b**).* Nitrogen was bubbled through a solution of 1,3-bis(phenylhydroxymethyl)benzene[23] (290 mg, 1.00 mmol) in dichloromethane (900 mL) and the 1 L round bottom flask was covered with aluminum foil to protect the solution from ambient light. Freshly distilled pyrrole (208 μL, 3.00 mmol) was added to the stirred solution via a syringe, followed by 4-chlorobenzaldehyde (281.2 mg, 2.00 mmol) and 2 mL of a 10% v/v solution of boron trifluoride etherate in dichloromethane. The mixture was stirred for 2 h and the initially clear yellow solution turned orange and then red. DDQ (0.750 g) was added and the resulting dark brown solution was stirred for 1 h. The solvent was evaporated under reduced pressure and the residue was purified on a grade 3 basic alumina column eluting with 50% dichloromethane–hexanes. Trace amounts of 5,10,15,20-tetrakis(4-chlorophenyl)porphyrin and unidentified brown by-products eluted initially, followed by an emerald green band that corresponded to the title benziporphyrin. Recrystallization from chloroform–ligroin gave the macrocyclic product (155.6 mg, 0.224 mmol, 22%) as dark green crystals, mp 295–297 °C, dec; UV–vis (1% Et_3N–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 415 (4.92), 692 (sh, 4.08), 729 nm (4.10); UV–vis (1% TFA–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 338 (4.54), 383 (4.48), 461 (5.15), 619 (3.72), 662 (3.72), 900 nm (4.30); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.52 (2H, d, J=4.8 Hz), 6.74 (2H, s), 7.00 (2H, dd, J=1.7, 7.8 Hz), 7.23 (2H, d, J=4.8 Hz), 7.30 (1H, t, J=1.6 Hz), 7.32 (1H, t, J=7.8 Hz), 7.39–7.49 (18H, m), 10.25 (1H, br s); ^{1}H NMR (500 MHz, TFA–$CDCl_3$): δ 5.51 (1H, t, J=1.6 Hz), 7.09 (2H, dd, J=1.5, 5.1 Hz), 7.20 (2H, dd, J=1.6, 7.8 Hz), 7.25 (2H, d, J=1.4 Hz), 7.50 (4H, br d, J=7.8 Hz), 7.55–7.60 (8H, m), 7.71 (4H, t, J=7.7 Hz), 7.77–7.83 (3H, m), 7.84 (2H, dd, J=1.6, 5.1 Hz), 9.05 (1H, br s), 10.46 (2H, br s); ^{13}C NMR (TFA–$CDCl_3$): δ 94.5, 115.5, 129.2, 129.6, 133.3, 133.6, 133.9, 134.6, 135.6, 136.5, 137.5, 138.3, 138.7, 139.5, 144.3, 151.8, 153.1, 161.3; HRMS (EI), m/z calcd for $C_{46}H_{29}Cl_2N_3$+2H: 695.1895. Found: 695.1902. Anal. calcd for $C_{46}H_{29}Cl_2N_3.{}^1/_{10}CHCl_3$: C, 78.36; H, 4.15; N, 5.95. Found: C, 78.73; H, 4.01; N, 5.94.

*4.2.7. 6,21-Bis(4-chlorophenyl)-11,16-diphenylbenziporphyrin (**8c**).* Prepared by the foregoing procedure from dicarbinol **10b** (359 mg, 1.00 mmol), benzaldehyde (205 μL, 2.00 mmol) and pyrrole (208 μL, 3.00 mmol). Recrystallization from chloroform–ligroin gave the benziporphyrin (83.7 mg, 0.121 mmol, 12%) as dark green crystals, mp >300 °C; UV–vis (1% Et_3N–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 415 (4.85), 693 (sh, 4.03), 738 nm (4.06); UV–vis (1% TFA–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 333 (4.50), 381 (4.40), 465 (5.15), 620 (3.69), 674 (3.65), 900 nm (4.17); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.56 (2H, d, J=4.8 Hz),

6.77 (2H, s), 6.99 (2H, dd, J=1.7, 7.7 Hz), 7.17 (2H, d, J=4.8 Hz), 7.29 (1H, t, J=1.6 Hz), 734–7.37 (5H, m), 7.40–7.48 (12H, m), 10.26 (1H, br s); ^{1}H NMR (500 MHz, TFA–$CDCl_3$): δ 5.43 (1H, t, J=1.6 Hz), 7.12 (2H, dd, J=1.5, 5.0 Hz), 7.19 (2H, dd, J=1.6, 7.8 Hz), 7.28 (2H, d, J=1.4 Hz), 7.50 (4H, d, J=8.5 Hz), 7.54 (4H, br s, J=7.0 Hz), 7.58–7.66 (6H, m), 7.68 (4H, d, J=8.5 Hz), 7.79–7.83 (3H, m), 8.98 (1H, br s), 10.39 (2H, br s); ^{13}C NMR (TFA–$CDCl_3$): δ 93.6, 117.2, 129.2, 129.5, 129.9, 130.8, 133.3, 133.6, 134.1, 135.9, 136.1, 136.3, 137.8, 137.95, 138.02, 140.4, 144.4, 150.0, 152.3, 161.8; HRMS (EI), m/z calcd for $C_{46}H_{29}Cl_2N_3$+2H: 695.1895. Found: 695.1884. Anal. calcd for $C_{46}H_{29}Cl_2N_3 \cdot {}^1/_{10}CHCl_3$: C, 78.36; H, 4.15; N, 5.95. Found: C, 78.29; H, 4.06; N, 5.86.

*4.2.8. 6,11,16,21-Tetrakis(chlorophenyl)benziporphyrin (**8d**).* Prepared by the foregoing procedure from dicarbinol **10b** (359 mg, 1.00 mmol), 4-chlorobenzaldehyde (281.2 mg, 2.00 mmol) and pyrrole (208 μL, 3.00 mmol). Recrystallization from chloroform–ligroin gave the benziporphyrin (183.5 mg, 0.240 mmol, 24%) as dark green crystals, mp >300 °C; UV–vis (1% Et_3N–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 416 (4.92), 690 (sh, 4.12), 730 nm (4.14); UV–vis (1% TFA–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 336 (4.57), 387 (4.45), 466 (5.14), 627 (3.75), 670 (3.75), 900 nm (4.26); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.54 (2H, d, J=4.8 Hz), 6.75 (2H, s), 6.99 (2H, dd, J=1.7, 7.8 Hz), 7.19 (2H, d, J=4.8 Hz), 7.24 (1H, br t, J=1.6 Hz), 7.33–7.46 (16H, m), 10.21 (1H, br s); ^{1}H NMR (500 MHz, TFA–$CDCl_3$): δ 5.47 (1H, t, J=1.6 Hz), 7.11 (2H, dd, J=1.5, 5.0 Hz), 7.19 (2H, dd, J=1.7, 7.8 Hz), 7.26 (2H, d, J=1.5 Hz, obscured by solvent peak), 7.47–7.50 (8H, m), 7.58–7.60 (4H, m), 7.68–7.71 (4H, m), 7.80–7.83 (3H, m), 9.11 (1H, br s), 10.45 (2H, br s); ^{13}C NMR (TFA–$CDCl_3$): δ 94.4, 115.8, 129.5, 129.60, 129.62, 133.4, 133.9, 134.5, 134.6, 136.2, 136.4, 137.5, 137.9, 138.00, 138.05, 140.7, 144.3, 150.7, 152.1, 161.5; HRMS (EI), m/z calcd for $C_{46}H_{27}Cl_4N_3$+2H: 763.1115. Found: 763.1120. Anal. calcd for $C_{46}H_{27}Cl_4N_3 \cdot {}^1/_6CHCl_3$: C, 70.78; H, 3.49; N, 5.36. Found: C, 70.80; H, 3.36; N, 5.41.

*4.2.9. 3-tert-Butyl-6,11,16,21-tetraphenylbenziporphyrin (**8e**).* Prepared by the foregoing procedure from dicarbinol **10c** (346 mg, 1.00 mmol), benzaldehyde (205 μL, 2.00 mmol) and pyrrole (208 μL, 3.00 mmol). Recrystallization from chloroform–ligroin gave the benziporphyrin (82.8 mg, 0.121 mmol, 12%) as green crystals, mp >300 °C; UV–vis (1% Et_3N–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 418 (4.83), 690 (sh, 3.96), 729 nm (3.96); UV–vis (1% TFA–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 329 (4.52), 380 (4.46), 462 (5.04), 610 (3.88), 668 (3.82), 900 nm (4.19); ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.99 (9H, s), 6.56 (2H, d, J=4.8 Hz), 6.78 (2H, s), 7.04 (2H, d, J=1.5 Hz), 7.05 (1H, t, J=1.5 Hz), 7.24 (2H, d, J=4.8 Hz), 7.39–7.50 (20H, m), 10.14 (1H, br s); ^{1}H NMR (500 MHz, TFA–$CDCl_3$): δ 1.09 (9H, s), 5.05 (1H, t, J=1.6 Hz), 7.12 (2H, dd, J=1.5, 5.0 Hz), 7.21 (2H, d, J=1.5 Hz), 7.29 (2H, d, J=1.4 Hz), 7.55–7.65 (14H, m), 7.72 (4H, t, J=7.7 Hz), 7.82 (2H, tt, J=1.1, 7.4 Hz), 7.86 (2H, dd, J=1.6, 5.0 Hz), 8.47 (1H, br s), 10.14 (2H, br s); ^{13}C NMR ($CDCl_3$): δ 31.0, 34.7, 107.4, 115.0, 127.2, 127.5, 128.1, 128.4, 130.0, 130.5, 131.4, 132.5, 133.4, 136.5, 137.8, 140.0, 143.2, 145.4, 147.8, 151.1, 156.6, 171.8; ^{13}C NMR (TFA–$CDCl_3$): δ 30.6, 35.4, 91.3, 116.6, 129.0, 129.1, 129.3, 130.5, 133.2, 133.4, 133.6, 133.8, 135.6, 136.4, 138.0, 138.1, 139.8, 144.2, 151.8, 152.5, 156.8, 161.3; HRMS (EI), m/z calcd for $C_{50}H_{39}N_3$+2H: 683.3300. Found: 683.3302. Anal. calcd for $C_{50}H_{39}N_3 \cdot {}^1/_5CHCl_3$: C, 85.43; H, 5.60; N, 5.95. Found: C, 85.60; H, 5.67; N, 5.97.

*4.2.10. 3-tert-Butyl-11,16-bis(4-chlorophenyl)-6,21-diphenylbenziporphyrin (**8f**).* Prepared by the foregoing procedure from dicarbinol **10c** (346 mg, 1.00 mmol), 4-chlorobenzaldehyde (281.2 mg, 2.00 mmol) and pyrrole (208 μL, 3.00 mmol). Recrystallization from chloroform–ligroin gave the benziporphyrin (142.7 mg, 0.190 mmol, 19%) as dark green crystals, mp >300 °C; UV–vis (1% Et_3N–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 419 (4.97), 685 (4.11), 729 nm (4.12); UV–vis (1% TFA–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 327 (4.55), 386 (4.49), 464 (5.17), 619 (3.75), 663 (3.75), 900 nm (4.31); ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.99 (9H, s), 6.54 (2H, d, J=4.8 Hz), 6.77 (2H, s), 7.00 (1H, t, J=1.6 Hz), 7.03 (2H, d, J=1.6 Hz), 7.26 (2H, d, J=4.8 Hz, partially obscured by solvent peak), 7.40–7.49 (18H, m), 10.10 (1H, br s); ^{1}H NMR (500 MHz, TFA–$CDCl_3$): δ 1.09 (9H, s), 5.18 (1H, t, J=1.6 Hz), 7.10 (2H, dd, J=1.5, 5.0 Hz), 7.20 (2H, d, J=1.5 Hz), 7.25 (2H, d, J=1.4 Hz), 7.52 (4H, br d, J=7.9 Hz), 7.56–7.60 (8H, m), 7.72 (4H, t, J=7.9 Hz), 7.80–7.83 (2H, m), 7.84 (2H, dd, J=1.5, 5.0 Hz), 8.95 (1H, br s), 10.38 (2H, br s); ^{13}C NMR (TFA–$CDCl_3$): δ 30.6, 35.4, 92.3, 115.1, 128.89, 128.94, 129.4, 133.1, 133.3, 133.5, 134.7, 135.0, 135.5, 137.0, 137.9, 138.1, 139.9, 144.2, 152.0, 152.8, 156.5, 161.0; HRMS (EI), m/z calcd for $C_{50}H_{37}Cl_2N_3$+2H: 751.2521. Found: 751.2524. Anal. calcd for $C_{50}H_{37}Cl_2N_3$: C, 79.99; H, 4.97; N, 5.60. Found: C, 79.97; H, 4.80; N, 5.56.

*4.2.11. 3-tert-Butyl-6,21-bis(4-chlorophenyl)-11,16-diphenylbenziporphyrin (**8g**).* Prepared by the foregoing procedure from dicarbinol **10d** (415 mg, 1.00 mmol), benzaldehyde (205 μL, 2.00 mmol) and pyrrole (208 μL, 3.00 mmol). Recrystallization from chloroform–ligroin gave the benziporphyrin (40.9 mg, 0.054 mmol, 5.4%) as dark green crystals, mp >300 °C; UV–vis (1% Et_3N–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 419 (4.96), 698 (sh, 4.11), 746 nm (4.14); UV–vis (1% TFA–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 329 (4.57), 385 (4.42), 467 (5.19), 629 (3.72), 672 (3.71), 900 nm (4.29); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.03 (9H, s), 6.57 (2H, d, J=4.8 Hz), 6.79 (2H, s), 6.98 (1H, t, J=1.6 Hz), 7.03 (2H, d, J=1.6 Hz), 7.19 (2H, d, J=4.8 Hz), 7.37 (4H, d, J=8.4 Hz), 7.41–7.49 (14H, m), 10.12 (1H, br s); ^{1}H NMR (500 MHz, TFA–$CDCl_3$): δ 1.12 (9H, s), 5.13 (1H, t, J=1.5 Hz), 7.11 (2H, dd, J=1.5, 5.0 Hz), 7.20 (2H, d, J=1.6 Hz), 7.27 (2H, d, J=1.4 Hz), 7.51 (4H, d, J=8.5 Hz), 7.56 (4H, br d, J=6.8 Hz), 7.58–7.65 (6H, m), 7.69 (4H, d, J=8.5 Hz), 7.80 (2H, dd, J=1.5, 5.0 Hz), 8.95 (1H, br s), 10.36 (2H, br s); ^{13}C NMR (TFA–$CDCl_3$): δ 30.7, 35.5, 91.1, 116.9, 129.1, 129.3, 129.6, 130.5, 132.8, 133.7, 133.8, 136.3, 136.5, 137.2, 137.9, 138.2, 139.9, 144.3, 150.1, 152.3, 156.9, 161.5; HRMS (EI), m/z calcd for $C_{50}H_{37}Cl_2N_3$+2H: 751.2521. Found: 751.2526. Anal. calcd for $C_{50}H_{37}Cl_2N_3$: C, 79.99; H, 4.97; N, 5.60. Found: C, 80.03; H, 4.75; N, 5.57.

*4.2.12. 3-tert-Butyl-6,11,16,21-tetrakis(4-chlorophenyl)benziporphyrin (**8h**).* Prepared by the foregoing procedure from dicarbinol **10d** (415 mg, 1.00 mmol), 4-chlorobenzaldehyde (281.2 mg, 2.00 mmol) and pyrrole (208 μL, 3.00 mmol). Recrystallization from chloroform–ligroin gave the benziporphyrin (261.2 mg, 0.318 mmol, 32%) as dark green crystals, mp >300 °C; UV–vis (1% Et_3N–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 420 (4.98), 691 (sh, 4.11), 738 nm (4.14); UV–vis (1% TFA–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 331 (4.59), 391 (4.46), 469 (5.19), 627 (3.80), 668 (3.81), 900 nm (4.31); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.03 (9H, s), 6.56 (2H, d, J=4.8 Hz), 6.77 (2H, s), 6.94 (1H, t, J=1.6 Hz), 7.03 (2H, d, J=1.6 Hz), 7.22 (2H, d, J=4.8 Hz), 7.35–7.47 (16H, m), 10.07 (1H, br s); ^{1}H NMR (500 MHz, TFA–$CDCl_3$): δ 1.12 (9H, s), 5.16 (1H, t, J=1.6 Hz), 7.11 (2H, dd, J=1.5, 5.0 Hz), 7.20 (2H, d, J=1.5 Hz), 7.26 (2H, d, J=1.5 Hz, partially obscured by solvent peak), 7.50 (8H, d, J=8.5 Hz), 7.59 (4H, d, J=8.6 Hz), 7.70 (4H, d, J=8.5 Hz), 7.81 (2H, dd, J=1.5, 5.0 Hz), 9.09 (1H, br s), 10.42 (2H, br s); ^{13}C NMR (TFA–$CDCl_3$): δ 30.6, 35.5, 91.8, 115.6, 129.3, 129.5, 133.2, 133.7, 134.7, 134.8, 136.4, 137.3, 137.5, 137.9, 138.0, 140.4, 144.3, 151.0, 152.1, 157.1, 161.2; HRMS (EI), m/z calcd for $C_{50}H_{35}Cl_4N_3$+2H: 819.1741. Found: 819.1743. Anal. calcd for $C_{50}H_{35}Cl_4N_3$: C, 73.27; H, 4.30; N, 5.13. Found: C, 73.48; H, 4.18; N, 5.16.

*4.2.13. [3-tert-Butyl-6,11,16,21-tetraphenylbenziporphyrinato]-palladium(II) (**19a**).* Palladium(II) acetate (8.0 mg) and acetonitrile (10 mL) were added to a solution of benziporphyrin **8e** (20.0 mg, 0.029 mmol) in chloroform (10 mL), and the mixture was stirred under reflux for 2 h. The solution was cooled, washed with water and evaporated under reduced pressure. The residue was chromatographed on grade 3 basic alumina, eluting with 50% dichloromethane–hexanes, and recrystallized from chloroform–methanol to give the palladium complex (14.7 mg, 0.019 mmol, 65%) as deep purple crystals, mp >300 °C; UV–vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 341

(4.48), 415 (sh, 4.64), 438 (4.91), 545 (3.83), 573 (3.84), 721 (sh, 3.59), 791 (3.83), 872 nm (3.83); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.02 (9H, s), 7.01 (2H, d, J=5.2 Hz), 7.14 (2H, d, J=5.2 Hz), 7.21 (2H, s), 7.44–7.53 (12H, m), 7.58–7.63 (8H, m), 7.85 (2H, s); ^{13}C NMR ($CDCl_3$): δ 30.6, 34.1, 117.9, 126.4, 127.7, 127.8, 129.9, 132.7, 132.8, 133.7, 134.2, 135.5, 140.3, 140.9, 142.4, 142.5, 144.5, 145.6, 146.5, 152.5, 157.4; HRMS (EI), m/z calcd for $C_{50}H_{37}N_3Pd$: 785.2022. Found: 785.2023.

*4.2.14. [3-tert-Butyl-6,11,16,21-tetrakis(4-chlorophenyl)benziporphyrinato]palladium(II) (**19b**).* Benziporphyrin **8h** (20.0 mg, 0.024 mmol) was reacted with palladium(II) acetate (6.8 mg) under the foregoing conditions. The crude product was purified on a silica column, eluting with dichloromethane, and recrystallized from chloroform–methanol to give the palladium derivative (15.6 mg, 0.017 mmol, 70%) as dark maroon crystals, mp >300 °C; UV–vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 419 (4.81), 439 (4.91), 522 (sh, 3.77), 548 (3.86), 577 (3.88), 723 (sh, 3.57), 791 (3.82), 878 nm (3.84); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.06 (9H, s), 7.00 (2H, d, J=5.2 Hz), 7.12 (2H, d, J=5.2 Hz), 7.20 (2H, s), 7.46–7.54 (16H, m), 7.80 (2H, s); ^{13}C NMR ($CDCl_3$): δ 30.7, 34.2, 116.8, 126.8, 128.1, 130.0, 133.8, 133.97, 133.99, 134.10, 134.12, 135.5, 138.5, 140.64, 140.67, 142.6, 143.4, 145.6, 147.0, 152.7, 157.4; HRMS (EI), m/z calcd for $C_{50}H_{33}Cl_4N_3Pd$: 921.0463. Found: 921.0457.

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Supplementary data

Supplementary data associated with this article can be found in online version, at doi:10.1016/j.tet.2009.09.060.

References and notes

1. Lash, T. D. *Synlett* **2000**, 279–295.
2. Lash, T. D. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic: San Diego, CA, 2000; Vol. 2, pp 125–199.
3. Lash, T. D. *Eur. J. Org. Chem.* **2007**, 5461–5481.
4. Latos-Grazynski, L. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic: San Diego, CA, 2000; Vol. 2, pp 361–416.
5. Srinivasan, A.; Furuta, H. *Acc. Chem. Res.* **2005**, *38*, 10–20.
6. Harvey, J. D.; Ziegler, C. J. *Coord. Chem. Rev.* **2003**, *247*, 1–19.
7. (a) Lash, T. D.; Richter, D. T.; Shiner, C. M. *J. Org. Chem.* **1999**, *64*, 7973–7982; (b) Lash, T. D.; Von Ruden, A. L. *J. Org. Chem.* **2008**, *73*, 9417–9425.
8. Aihara, J.-i. *J. Phys. Chem. A* **2008**, *112*, 5305–5311.
9. (a) Lash, T. D.; Hayes, M. J. *Angew. Chem., Int. Ed.* **1997**, *36*, 840–842; (b) Lash, T. D.; Hayes, M. J.; Spence, J. D.; Muckey, M. A.; Ferrence, G. M.; Szczepura, L. F. *J. Org. Chem.* **2002**, *67*, 4860–4874; (c) Liu, D.; Lash, T. D. *J. Org. Chem.* **2003**, *68*, 1755–1761; (d) Lash, T. D.; Muckey, M. A.; Hayes, M. J.; Liu, D.; Spence, J. D.; Ferrence, G. M. *J. Org. Chem.* **2003**, *68*, 8558–8570.
10. (a) Lash, T. D.; Chaney, S. T. *Tetrahedron Lett.* **1996**, *37*, 8825–8828; (b) Bergman, K. M.; Ferrence, G. M.; Lash, T. D. *J. Org. Chem.* **2004**, *69*, 7888–7897.
11. Lash, T. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2533–2535.
12. Lash, T. D.; Chaney, S. T.; Richter, D. T. *J. Org. Chem.* **1998**, *63*, 9076–9088.
13. Richter, D. T.; Lash, T. D. *Tetrahedron* **2001**, *57*, 3659–3673.
14. El-Beck, J. A.; Lash, T. D. *Org. Lett.* **2006**, *8*, 5263–5266.
15. For an example of an azulisapphyrin, see: Lash, T. D.; Chaney, S. T. *Angew. Chem., Int. Ed.* **1997**, *36*, 839–840; Richter, D. T.; Lash, T. D. *J. Org. Chem.* **2004**, *69*, 8842–8850.
16. (a) Lash, T. D.; Colby, D. A.; Graham, S. R.; Chaney, S. T. *J. Org. Chem.* **2004**, *69*, 8851–8864; (b) Lash, T. D.; El-Beck, J. A.; Ferrence, G. M. *J. Org. Chem.* **2007**, *72*, 8402–8415.
17. (a) Lash, T. D. *Chem. Commun.* **1998**, 1683–1684; (b) Graham, S. R.; Colby, D. A.; Lash, T. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 1371–1374; (c) Colby, D. A.; Ferrence, G. M.; Lash, T. D. *Angew. Chem., Int. Ed.* **2004**, *43*, 1346–1349.
18. Colby, D. A.; Lash, T. D. *Chem.—Eur. J.* **2002**, *8*, 5397–5402.
19. (a) Lash, T. D.; Colby, D. A.; Ferrence, G. M. *Eur. J. Org. Chem.* **2003**, 4533–4548; (b) El-Beck, J. A.; Lash, T. D. *Eur. J. Org. Chem.* **2007**, 3981–3990.
20. Berlin, K.; Breitmaier, E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1246–1247.
21. Stepien, M.; Latos-Grazynski, L. *Chem.—Eur. J.* **2001**, *7*, 5113–5117.
22. Szymanski, J. T.; Lash, T. D. *Tetrahedron Lett.* **2003**, *44*, 8613–8616.
23. Lash, T. D.; Szymanski, J. T.; Ferrence, G. M. *J. Org. Chem.* **2007**, *72*, 6481–6492.
24. Vogel, E. *J. Heterocycl. Chem.* **1996**, *33*, 1461.
25. Cyranski, M. K.; Krygowski, T. M.; Wisiorowski, M.; Hommes, N. J. R.; van, E.; Schleyer, P.; von, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 177.
26. These results were presented, in part, at the following meeting: 233rd National American Chemical Society Meeting, Chicago, Illinois, March 2007 (Yant, V.R.; Lash, T.D. Book of Abstracts, CHED 585).
27. For syntheses of related porphyrin analogues, see: (a) Sim, E.-K.; Jeong, S.-D.; Yoon, D.-W.; Hong, S.-J.; Kang, Y.; Lee, C.-H. *Org. Lett.* **2006**, *8*, 3355–3358; (b) Lash, T. D.; Pokharel, K.; Serling, J. M.; Yant, Y. R.; Ferrence, G. M. *Org. Lett.* **2007**, *9*, 2863–2866; (c) Jeong, S.-D.; Hong, S.-J.; Park, K. J.; Ham, S.; Sessler, J. L.; Lynch, V.; Lee, C.-H. *J. Org. Chem.* **2007**, *72*, 6232–6240.
28. Lash, T. D. *Chem.—Eur. J.* **1996**, *2*, 1197–1200.
29. (a) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. *J. Org. Chem.* **1987**, *52*, 827–836; (b) Lindsey, J. S.; Wagner, R. W. *J. Org. Chem.* **1989**, *54*, 828–836; (c) Geier, G. R., III; Lindsey, J. S. *J. Chem. Soc., Perkin Trans. 2* **2001**, 677–686.
30. Percec, V.; Clough, R. S.; Rinaldi, P. L.; Litman, V. E. *Macromolecules* **1994**, *27*, 1535–1547.
31. Stepien, M.; Latos-Grazynski, L.; Lash, T. D.; Szterenberg, L. *Inorg. Chem.* **2001**, *40*, 6892–6900.
32. Miyake, K.; Lash, T. D. *Chem. Commun.* **2004**, 178–179.
33. Stepien, M.; Latos-Grazynski, L.; Szterenberg, L.; Panek, J.; Latajka, Z. *J. Am. Chem. Soc.* **2004**, *126*, 4566–4580.
34. Stepien, M.; Latos-Grazynski, L. *Acc. Chem. Res.* **2005**, *38*, 88–98.
35. For other examples of organometallic derivatives of carbaporphyrinoid systems, see: (a) Graham, S. R.; Ferrence, G. M.; Lash, T. D. *Chem. Commun.* **2002**, 894–895; (b) Muckey, M. A.; Szczepura, L. F.; Ferrence, G. M.; Lash, T. D. *Inorg. Chem.* **2002**, *41*, 4840–4842; (c) Lash, T. D.; Colby, D. A.; Graham, S. R.; Ferrence, G. M.; Szczepura, L. F. *Inorg. Chem.* **2003**, *42*, 7326–7338; (d) Lash, T. D.; Rasmussen, J. M.; Bergman, K. M.; Colby, D. A. *Org. Lett.* **2004**, *6*, 549–552; (e) Lash, T. D.; Colby, D. A.; Szczepura, L. F. *Inorg. Chem.* **2004**, *43*, 5258–5267; (f) Liu, D.; Ferrence, G. M.; Lash, T. D. *J. Org. Chem.* **2004**, *69*, 6079–6093; (g) Lash, T. D.; Young, A. M.; Von Ruden, A. L.; Ferrence, G. M. *Chem. Commun.* **2008**, 6309–6311.
36. Lash, T. D. *Macroheterocycles* **2008**, *1*, 9–20.