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Synthesis and Reactivity of 2^3-*tert*-Butyl- and 2^3-Phenyltetraarylazuliporphyrins: an Analysis of the Effect of Bulky Substituents on Oxidative Ring Contractions to Benzocarbaporphyrins[‡]

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6-*tert*-Butyl- and 6-phenylazulene reacted with pyrrole and benzaldehyde in a molar ratio of 1:3:4 in the presence of BF_3·Et_2O in chloroform, followed by oxidation with DDQ, to give 2^3-substituted tetraphenylazuliporphyrins in 15–20 % yield. Slightly higher yields of the related *meso*-tetrakis(4-chlorophenyl)azuliporphyrins were obtained using 4-chlorobenzaldehyde. The presence of an electron-donating *tert*-butyl substituent increased the diatropic character of the azuliporphyrin system as determined by the proton NMR chemical shifts for the internal CH resonance, while intermediary results were noted for 2^3-phenylazuliporphyrins. Addition of TFA afforded dications with increased aromatic ring currents, but electron-donating substituents (*t*Bu > Ph) again produced a larger upfield shift for the internal CH signal due to stabilization of the tropylium character that is required so that the system can attain carbaporphyrin-type aromaticity. The substituted azuliporphyrins reacted with nickel(II) acetate or palladium(II) acetate to give the corresponding organometallic derivatives. In addition, oxidations with *t*BuOOH and KOH afforded benzocarbaporphyrin products in approximately 50 % yield. The presence of *tert*-butyl or phenyl substituents did not block these oxidative ring contraction processes, and the rate of reaction was slightly increased compared to 2^3-unsubstituted azuliporphyrins. The major products were 2^2-*tert*-butyl or phenyl-substituted benzocarbaporphyrins and minor products with an additional formyl substituent were also isolated. These products are consistent with an initial nucleophilic addition occurring at the position adjacent to the R group on the azulene ring. Detailed mechanisms are proposed to explain these observations.
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Introduction

Azuliporphyrins **1** are an intriguing family of carbaporphyrinoids where an azulene unit has replaced one of the usual pyrrole moieties in the porphyrin macrocycle.[1] The first synthesis of an azuliporphyrin **2** (Figure 1), reported in 1997,[2] was carried out using the "3 + 1" condensation[3] of 1,3-azulenedicarbaldehyde with a tripyrrane in the presence of TFA, followed by oxidation with DDQ. An alternative "3 + 1" route to azuliporphyrins was subsequently reported,[4] and this methodology was adapted to the synthesis of hetero-analogues and a related dicarbaporphyrinoid system.[1,4,5] In these reactions, benzocarbaporphyrin by-products **3** were commonly observed.[1–4,6] These aromatic carbaporphyrins appear to arise by an oxidative ring contraction of the azulene subunit.[7]

Azuliporphyrins themselves have significant diatropic character,[1,2] although the free base forms of the etio-series azuliporphyrins **2** are poorly soluble in organic solvents and the internal CH resonance is not easily identified.[1,2] Nevertheless, the external *meso* protons are shifted downfield to give two 2 H singlets at 8 and 9 ppm, and the internal CH was tentatively identified near 2 ppm.[1] Subsequently, a one pot synthesis of tetraarylazuliporphyrins **4** was developed and this system was shown to have similar properties where the internal CH resonated at 3 ppm.[8,9] The diatropic character of azuliporphyrins appears to be due to dipolar canonical forms such as **4′** (Scheme 1), which simultaneously imbues the system with carbaporphyrin and tropylium characteristics.[1,2,10] However, this contribution is limited by the need for charge separation.[1,2] Addition of TFA affords dications **5** that have greatly increased aromatic ring currents due to the resonance contributors **5′** now facilitating charge delocalization. When nucleophiles such as pyrrolidine are added to azuliporphyrins **2** or **4**, carbaporphyrin adducts (e.g., **6**) are generated which show full carbaporphyrinoid aromaticity and the internal CH resonance shifts upfield to –5.6 or –6.9 ppm for **4** or **2**, respectively.[1,7–9] These additions are reversible and removal of excess nucleophile afforded the original azuliporphyrin. The data also indicates that the nucleophilic addition occurs regioselectively at the 2^3-position (Figure 1) to give symmetrical adducts such as **6**.[1,7–9]

[‡] Conjugated Macrocycles Related to the Porphyrins, 44. Part 43: T. D. Lash, K. Pokharel, J. M. Serling, V. R. Yant, G. M. Ferrence, *Org. Lett.* **2007**, *9*, 2863–2866.

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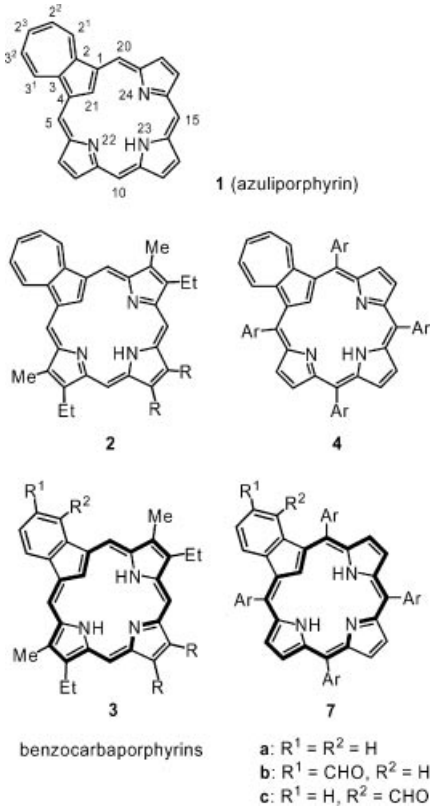
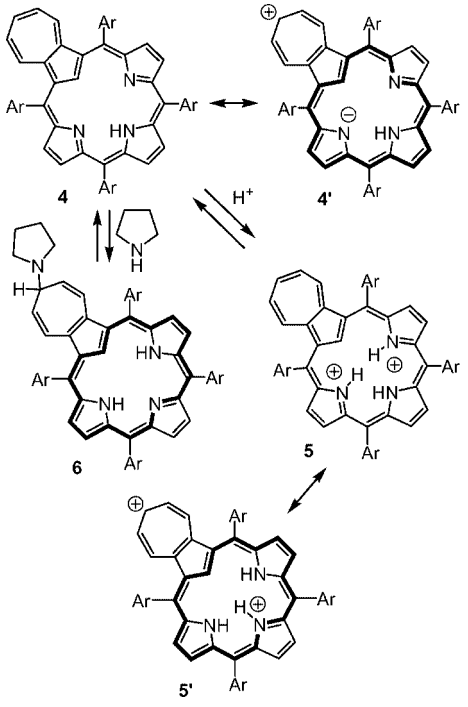


Figure 1. Azuliporphyrins and carbaporphyrins derived therefrom.



Scheme 1. Protonation and nucleophilic addition reactions of azuliporphyrins.

Azuliporphyrins show unusual reactivity and undergo selective oxidation reactions[11] as well as the formation of stable organometallic derivatives.[12,13] Addition of *tert*-butyl hydroperoxide to azuliporphyrins **2** under basic conditions afforded mixtures of benzocarbaporphyrins **3**,[1,7] while tetraarylazuliporphyrins **4** gave the related carbaporphyrins **7** (Figure 1).[8,9] We proposed that these ring contraction reactions involve initial nucleophilic attack by the *tert*-butyl peroxide anion, followed by a Cope rearrangement and elimination of *tert*-butyl alcohol.[1,7–9] In order to further investigate this chemistry, azuliporphyrins with bulky substituents at the 2^3-position (Figure 1) were synthesized from 6-*tert*-butyl- and 6-phenylazulene.[14,15] The symmetry of the precursors allows the azuliporphyrins to retain a plane of symmetry, while the placement of large substituents at the 6-position of azulene would be expected to have little effect on macrocycle formation as these groups are orientated away from the 1,3-positions where the carbon–carbon bond-forming reactions take place.[16]

Results and Discussion

6-*tert*-Butylazulene (**8a**) and 6-phenylazulene (**8b**) are easily synthesized from the related 4-substituted pyridines using a literature method (Scheme 2).[14] Azulene had been previously shown to react with aromatic aldehydes, pyrrole and boron trifluoride–diethyl ether in chloroform to give, following oxidation with DDQ, the corresponding azuliporphyrins **4**.[8,9] The method was based upon the conditions used by Lindsey and co-workers to prepare *meso*-tetraarylporphyrins,[17] but only gave satisfactory results when chloroform was used as a solvent. The reactions were usually carried out in approximately 400 mL of chloroform for every 1 mmol of azulene, although slightly higher yields could be obtained under more dilute conditions. Reaction of 6-*tert*-butylazulene with 3 equiv. of pyrrole and 4 equiv. benzaldehyde in the presence of a catalytic amount of $BF_3{\cdot}Et_2O$ for 16 h, followed by oxidation with DDQ, gave 2^3-the *tert*-butylazuliporphyrin **9a** in 20% yield. When the reaction was carried out with a four-fold increase in the amount of solvent, the yields increased to nearly 30%. However, the large amounts of solvents needed for those conditions were considered to be impractical, and the chemistry was generally carried out under the more concentrated reaction conditions. In order to simplify the spectroscopic analyses, a [D_{20}]-labeled tetraphenylazuliporphyrin **9b** was prepared from [D_6]benzaldehyde and 6-*tert*-butylazulene. In addition, 6-phenylazulene was found to react similarly to give the pentaphenylazuliporphyrin **9c** in 15% yield.[18] As had been found to be the case for reactions with unsubstituted azulene, the initial condensation required prolonged reaction times (ca. 16 h) and this presumably results in the accumulation of an azuliporphyrinogen intermediate **10**. This species only affords the azuliporphyrin chromophore on oxidation with DDQ. The azulenes **8a** and **8b** were also reacted with pyrrole and 4-chlorobenzaldehyde to give the tetrakis(4-chlorophenyl)azuliporphyrins **9d** and **9e**, respectively. As had been observed for other carbaporphyrinoid syntheses of this type,[9,19,20] yields were significantly im-

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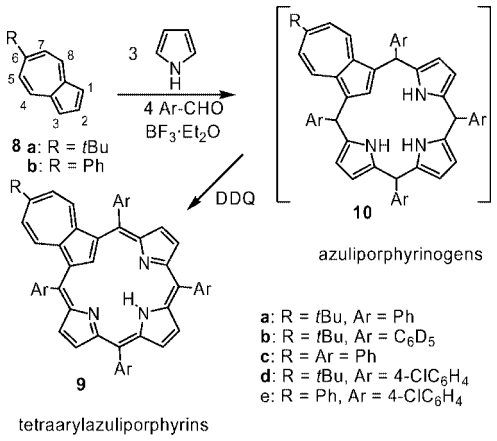
proved (23–26%) using 4-chlorobenzaldehyde. Initially, difficulties were encountered in the purification of **9d** and **9e**, but column chromatography on grade 2 basic alumina eluting with 5% ethyl acetate/toluene was found to be a straightforward method for obtaining pure azuliporphyrin products.



Scheme 2. Synthesis of tetraarylazuliporphyrins from 6-*tert*-butyl- and 6-phenylazulene.

The proton NMR spectra for the azuliporphyrins **9** were complex due to the large number of aromatic protons that are overlapped in the 7–9 ppm region. The [D_{20}]tetraphenyl *tert*-butylazuliporphyrin (**9b**) gave greatly simplified proton NMR spectroscopic data (Figure 2) and showed the pyrrolic protons as two 2 H doublets at δ = 7.38 and 7.98 ppm (J = ca. 5 Hz), and a 2 H singlet at δ = 7.68 ppm. The azulene protons gave rise to two 2 H doublets at δ = 7.12 and 7.62 ppm (J = ca. 11 Hz), while the NH gave rise to a broad peak at 4.6 ppm and the internal CH resonated at δ = 2.88 ppm. The substituents produced small but significant shifts in the proton NMR spectra that indicated that the diatropic character was affected. Specifically, the internal CH resonances for **4** (Ar = Ph), **9c** and **9a**, where the 2^3 substituent is H, Ph or *t*Bu, respectively, were observed at δ = 3.35, 3.24 and 2.88 ppm. This trend indicates that the electron-donating *tert*-butyl substituent stabilizes the tropylium character of canonical form **4′** to such an extent that the 21-H resonance shifts upfield by approximately 0.5 ppm. As would be expected, the decreased electron-donating ability of the phenyl group gives intermediary results. The same trend can be seen for azuliporphyrins **4** (Ar = 4-ClC_6H_4), **9d** and **9e** when *meso*-(4-chlorophenyl) substituents are present. However, the 21-H resonances are shifted ca. 0.2 ppm further upfield for this series. This observation indicates that the anionic character required for the carbaporphyrin components of the dipolar resonance contributors are stabilized by the slightly electron-withdrawing 4-chlorophenyl substituents. The proton and carbon-13 NMR spectroscopic data for azuliporphyrins **9a**–**e** also demonstrated the presence of a plane of symmetry and the identity of these products were further confirmed by mass spectrometry. The UV/Vis spectra for the new azuliporphyrins were similar to those previously reported for azuliporphyrins **4**,[8,9] showing several medium intensity bands between 400 and 500 nm, and weaker absorptions at higher wavelengths.

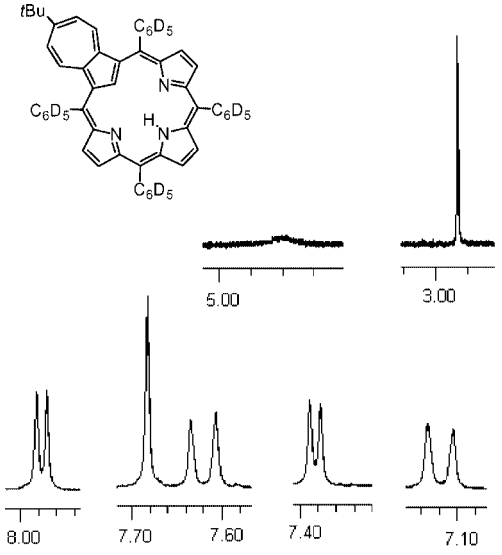


Figure 2. 400 MHz proton NMR spectrum of [D_{20}]tetraphenyl *tert*-butylazuliporphyrin (**9b**) in $CDCl_3$ showing the external pyrrole and azulene protons and the comparatively upfield resonances for the 21-H and NH units.

Addition of TFA to solutions of azuliporphyrins **9** gave the corresponding dications. The UV/Vis spectrum of **9a**H_2^{2+} showed a strong Soret-like band at 516 nm, and several Q-type bands at 611, 672 and 837 nm. The protonated azuliporphyrins show greatly increased diatropic ring currents, but steric crowding leads to broadened resonances in the downfield region. The broadened peaks show better resolution at higher temperatures. For tetraphenylazuliporphyrin **4** (Ar = Ph) in TFA/$CDCl_3$, the internal CH appeared at –0.50 ppm at 20 °C but the resonance shifted downfield to –0.33 ppm at 55 °C.[8] The *tert*-butylazuliporphyrin **9a** in TFA/$CDCl_3$ gave the resonance at –1.13 ppm at 25 °C but this again shifted upfield to –0.82 ppm at 50 °C. The remaining data was collected at 25 °C so that meaningful comparisons could be made. The pentaphenylazuliporphyrin **9c** in TFA/$CDCl_3$ gave the 21-H resonance at –1.00 ppm, an intermediary value between the *tert*-butyl- and 2^3-unsubstituted azuliporphyrins. However, this resonance shifted downfield by 0.09 to 0.14 ppm for the corresponding series of azuliporphyrins bearing *meso*-(4-chlorophenyl) substituents. The data confirm that electron-donating substituents on the azulene unit stabilize the aromatic tropylium/carbaporphyrin resonance contributors and this leads to enhanced diatropicity. However, the electron-withdrawing 4-chlorophenyl substituents no longer exert a beneficial effect as they destabilize the dication and this leads to the decreased ring current. The downfield region for the dications could not be completely assigned because of the presence of broadened peaks due to the aryl substituents. However, the external hydrogens for [D_{20}]tetraphenyl *tert*-butylazuliporphyrin **9b** in TFA/$CDCl_3$ were

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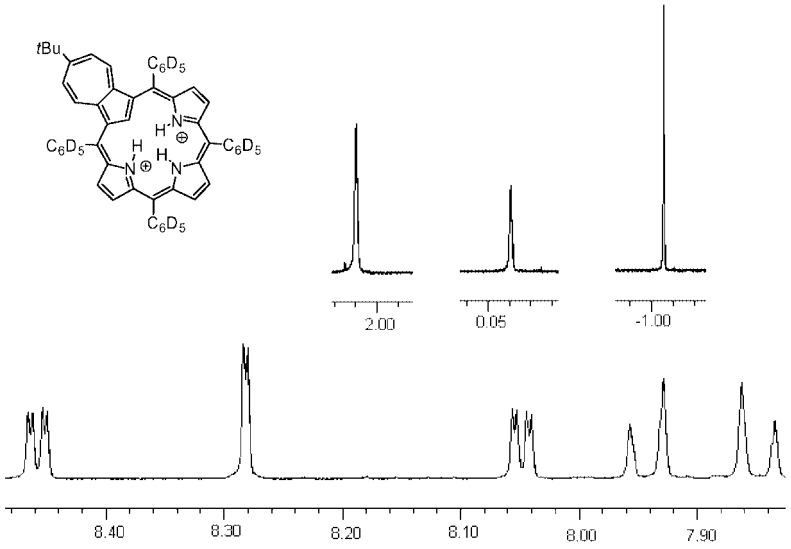

Figure 3. 400 MHz proton NMR spectrum of the [D_{20}]-tetraphenyl *tert*-butylazuliporphyrin dication **9b**H_2^{2+} in TFA/$CDCl_3$ showing the external pyrrole protons between 9.0 and 8.5 ppm and the azulene protons near 7.9 ppm. The internal CH is shifted upfield to –1.1 ppm.

well resolved (Figure 3) and the azulene protons showed up as two doublets at δ = 7.12 and 7.62 ppm ($J \approx 11$ Hz). The pyrrolic protons showed coupling to the internal NHs and gave a 2 H doublet (J = 1.2 Hz) at δ = 8.28 ppm and two 2 H doublets of doublets ($J \approx 1.5$ and 5 Hz) at δ = 8.05 and 8.45 ppm.

Azuliporphyrins are dianionic organometallic ligands and we took the opportunity to synthesize the nickel(II) and palladium(II) derivatives of azuliporphyrins **9a** and **9c**. The deuteriated azuliporphyrin **9b** was also metalated to simplify the spectroscopic analyses. Azuliporphyrins **9a**–**c** reacted with nickel(II) acetate in refluxing DMF to give the nickel(II) derivatives **11** in 68–73% yield. The palladium(II) complexes **12** were prepared similarly in 59–74% yield from **9a**–**c** and palladium(II) acetate. These complexes were characterized by UV/Vis, proton NMR and carbon-13 NMR spectroscopy, and the results were similar to those previously reported for the 2^3-unsubstituted azuliporphyrins **4**. The proton NMR spectra in $CDCl_3$ for the deuteriated azuliporphyrin complexes gave well resolved peaks for the pyrrolic and azulene protons (Figure 4). The azulene protons for the nickel(II) complex **11b** showed additional second-order coupling that was consistent with an AA′XX′ system (Figure 4, A). This could be seen to a lesser extent for the palladium(II) complex **12b** (Figure 4, B) but the spectra for azuliporphyrins **9a**–**e** showed the azulene resonances as an A_2X_2 system. This may be due to minor changes in the bond angles facilitating ^4J coupling interactions. The chemical shifts for the pyrrolic protons of nickel(II) and palladium(II) complexes **11** and **12** were similar, indicating that the macrocyclic diatropicity was also similar. This contrasts to the 2^3-unsubstituted complexes where these resonances were significantly shifted downfield for the palladium(II) complexes compared to the nickel(II) derivatives.

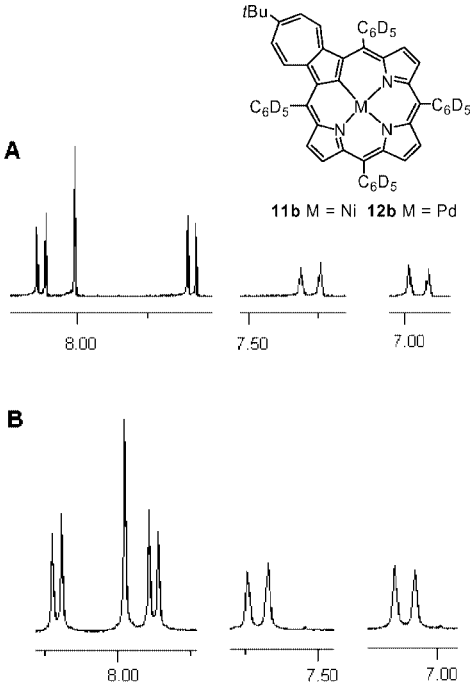

Figure 4. 400 MHz proton NMR spectra showing the downfield region for [D_{20}]-labeled tetraphenyl *tert*-butylazuliporphyrin metal complexes **11b** (A) and **12b** (B).

Addition of pyrrolidine to solutions of the azuliporphyrins **4** gave aromatic carbaporphyrin adducts that showed porphyrin-like UV/Vis spectra and highly diatropic ring currents by proton NMR spectroscopy (Scheme 1).[8,9] The proton NMR spectra of the pyrrolidine adducts showed that a single species **6** was favored and that nucleophilic addition occurred selectively at position 2^3 on the azulene ring.[8,9] When similar studies were carried out on the 2^3-

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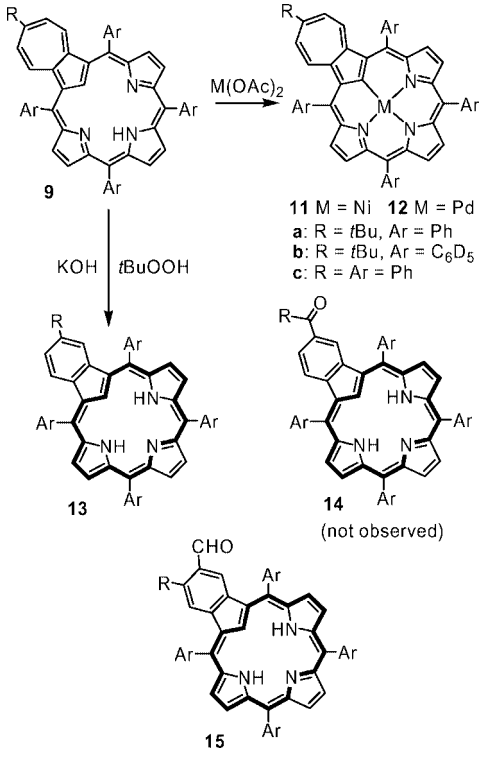
substituted azuliporphyrins, complex results were obtained. The proton NMR spectra showed the presence peaks near –6 ppm that would be expected for carbaporphyrin species, but complex mixtures appeared to be present. For **4**, one drop of pyrrolidine was sufficient to completely shift the equilibrium to the adduct **6**. However, larger amounts of pyrrolidine were needed for the azuliporphyrins **9** to give significant adduct formation. These data show that the substituents inhibit nucleophilic attack and/or the stability of the carbaporphyrin adduct. This interpretation is supported by the UV/Vis data for solutions of **9a**, **9c**, **9d** or **9e** with 1%, 5% and 10% pyrrolidine in chloroform, which in contrast to **4** showed highly variable results although strong Soret-like bands near 440 nm were noted. As nucleophilic attack onto the azulene ring is thought to be the first step in the oxidative ring contraction of azuliporphyrins to give benzocarbaporphyrins, the results lead to an expectation that these rearrangements would also be inhibited.

In order to investigate the oxidative rearrangements, the *tert*-butylazuliporphyrin **9a** was treated with *t*BuOOH and KOH in methanol/dichloromethane at room temperature (Scheme 3). Initially, poor results were obtained due to degradation after longer reaction times. However, when the reaction was monitored by TLC, we observed that the starting material was consumed after 45 min and the rate of reaction appeared to be slightly increased compared to the 2^3-unsubstituted case.[21] Excess reagents and longer reaction times did not appear to be detrimental for reactions of **4** with *t*BuOOH/KOH but this factor was crucial in the reactions of 2^3-substituted azuliporphyrins. The carbaporphyrin products were purified by column chromatography on grade 3 alumina. A major brown fraction was collected and following recrystallization from chloroform/methanol, a substituted benzocarbaporphyrin **13a** was isolated in nearly 50% yield. If initial nucleophilic attack occurred at the 2^3-position, the ketone **14a** would be generated. However, although the proton NMR spectrum demonstrated that the *tert*-butyl group had been retained, the IR spectrum showed the absence of a C=O stretch and HRMS gave the molecular formula $C_{53}H_{41}N_3$. The reaction was repeated with **9b** and this gave the [D_{20}]-product **13b**. The proton NMR spectrum for **13b** showed the benzo protons as a 1 H doublet at 6.68 (J = 8 Hz), a 1 H doublet at 6.98 (J = 1.6 Hz) and a 1 H doublet of doublets at δ = 7.03 ppm (J = 2, 8.4 Hz), confirming the presence of a 1,2,4-trisubsubstituted benzene unit. The six pyrrolic protons were present in the downfield region from 8.5–8.8 ppm, while the internal CH gave a singlet upfield at –5.37 ppm. These data conclusively



Scheme 3. Reactions of substituted azuliporphyrins.

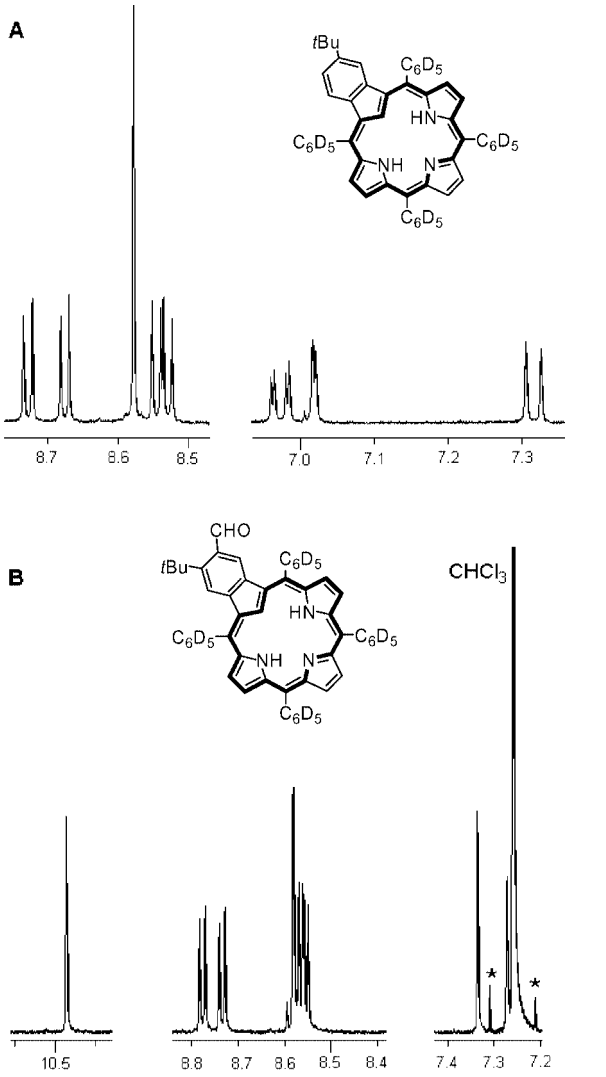


Figure 5. Downfield region of the 400-MHz ^{1}H NMR spectra for the major (A) and minor (B) ring contraction products obtained by reacting *tert*-butylazuliporphyrin **9b** with *t*BuOOH and KOH. The peaks labeled with an asterisk are spinning side bands for the chloroform signal.

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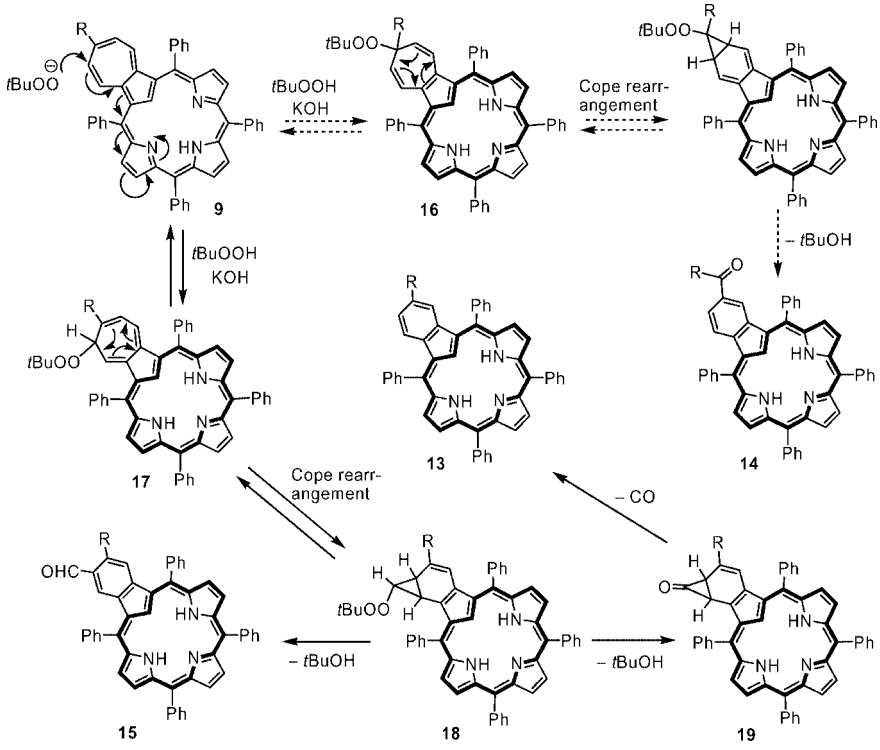
demonstrate that the major product is benzocarbaporphyrin **13**. However, a second minor fraction **15** was also collected in these reactions (ca. 5%). This carbaporphyrin product showed an aldehyde resonance at δ = 10.5 ppm, but the presence of the *tert*-butyl group was also clearly evident. In the [D_{20}]-labeled product **15b**, two 1 H singlets were observed for the benzo unit at δ = 7.27 and 7.33 ppm (Figure 5, B). The pyrrolic protons gave a series of doublets for 6 H between 8.5 and 8.8 ppm, while the internal CH resonated at –5.18 ppm. These data, together with the HRMS results, demonstrated that the minor product was **15** and none of the ketone product **14** was observed. Pentaphenylazuliporphyrin **9c** also reacted under these conditions to give carbaporphyrin products. The major product was the pentaphenylbenzocarbaporphyrin **13c** and a minor side product was also isolated in < 5% yield. Careful examination of the proton NMR spectroscopic data showed that this product was an aldehyde, where the benzo unit has only two attached hydrogen atoms and the fifth phenyl unit was also still present. On the basis of these results and the MS data, the minor carbaporphyrin product was assigned as structure **15c**. Again, the ketone product **14c** was not observed, although trace amounts of other carbaporphyrin products may have been generated. The yields of carbaporphyrins obtained in these reactions were comparable to the results reported for 2^3-unsubstituted azuliporphyrins.[8,9] However, in reactions of **4** with *t*BuOOH/KOH, two major benzocarbaporphyrin products are formed in a total yield of approximately 50%. Although the yields are similar for **9a**–**c**, only one major product is formed from the substituted azuliporphyrins. As this is the only route currently available for preparing *meso*-tetrasubstituted benzocarbaporphyrins,[22] the formation of one major product may make larger quantities of this system available for further study.[23]

The mechanism for oxidative rearrangement is likely to involve an initial nucleophilic attack, but this cannot be a rate-limiting step because the rate of reaction appears to be slightly enhanced compared to the reactions of 2^3-unsubstituted azuliporphyrins. As nucleophilic additions to azuliporphyrins are reversible, this step would involve an equilibrium and would therefore not be governed by sterically controlled kinetic factors. Nucleophilic attack at position 2^3 would lead to adducts **16** and following a Cope rearrangement and elimination of *tert*-butyl alcohol the carbaporphyrin ketone **14** would be formed (Scheme 4). As this species was not isolated, this pathway must be disfavored presumably due to steric factors. However, nucleophilic attack at the adjacent position would give adducts **17** and subsequent Cope rearrangement would then afford the dihydrobenzocyclopropane structures **18**. Elimination of *t*BuOH could produce cyclopropanones **19** and subsequent extrusion of CO would then generate the observed major carbaporphyrin products **13**. Alternatively, elimination of *t*BuOH from **18** could give the aldehydes **15** which are observed as minor by-products. Hence, this mechanistic Scheme allows the structural data to be completely explained. Nevertheless, the observation that the reaction rates are slightly increased merits further discussion. As the equilibria between **9** and **18** are likely to not be rate determining processes, the overall reaction rate is presumably controlled by the subsequent elimination step. This process would relieve strain due to



Scheme 4. Mechanism for the formation of benzocarbaporphyrins from azuliporphyrins.

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steric interactions between the cyclopropane ring and the R group, and this factor provides a plausible explanation for the results.

Conclusions

Reaction of 6-phenyl- or 6-*tert*-butylazulene with pyrrole and aromatic aldehydes in the presence of $BF_3{\cdot}Et_2O$ in chloroform, followed by oxidation with DDQ, gives good yields of 2^3-substituted azuliporphyrins. The electron-donating substituents (*t*Bu > Ph) slightly increase the diatropic character for the free base and the related dications due to the stabilization of tropylium character that is required for macrocyclic aromaticity. In addition, these substituted azuliporphyrins readily form nickel(II) and palladium(II) complexes. Reactions of 2^3-substituted azuliporphyrins with *t*BuOOH and KOH afforded a major decarbonylated carbaporphyrin product and a minor aldehyde by-product that would be expected if nucleophilic attack occurred at the position adjacent to the azulene substituent. The presence of these bulky substituents slightly increases the rates for these reactions and oxidative ring contractions are not sterically inhibited as had been anticipated. The results obtained for these substituted azuliporphyrins provides valuable insights into the reactivity of this important organometallic ligand system.

Experimental Section

General Remarks: 6-*tert*-Butyl- and 6-phenylazulene were prepared from 4-*tert*-butyl- and 4-phenylpyridine, respectively, via *N*-butylpyridinium bromide intermediates using a literature procedure.[14] Pyrrole, 4-*tert*-butylpyridine, 4-phenylpyridine, 1-bromobutane, *tert*-butyl hydroperoxide (5–6 M in decane), benzaldehyde, [D_6]-benzaldehyde, 4-chlorobenzaldehyde, boron trifluoride–diethyl ether, DDQ, palladium(II) acetate, nickel(II) acetate and pyrrolidine were purchased from Aldrich or Acros. UV/Vis spectra were obtained on a Cary 1 Bio spectrophotometer. NMR spectra were recorded with a Varian Gemini-400 MHz NMR spectrometer at 25 °C, unless otherwise indicated, and recorded in ppm relative to $CDCl_3$ (residual chloroform at δ = 7.26 ppm) in proton NMR and the $CDCl_3$ triplet at δ = 77.23 ppm in carbon-13 NMR spectra. Mass spectrometry data were obtained from 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.

2^3-*tert*-Butyl-5,10,15,20-tetraphenylazuliporphyrin (9a): 6-*tert*-Butylazulene (72.0 mg, 0.391 mmol), benzaldehyde (158 μL, 166 mg, 1.57 mmol) and pyrrole (81 μL, 79 mg, 1.18 mmol) were dissolved in chloroform (160 mL) and the resulting solution was purged with nitrogen for 10 min. A 10% solution of boron trifluoride–diethyl ether in chloroform (40 μL) was then added and the reaction stirred for 16 h under nitrogen in the dark. DDQ (98%, 267 mg, 1.15 mmol) was added and the solution stirred for an additional 1 h. The mixture was then washed with water and a saturated sodium hydrogen carbonate solution, back extracting with chloroform at each stage, and the combined organic solutions dried with sodium sulfate, filtered and evaporated under reduced pressure. The residue was purified by column chromatography on grade 2 basic alumina, eluting with 5% ethyl acetate/toluene. Tetraphenylporphyrin eluted initially, followed by trace amounts of carbaporphyrins, and then a deep reddish-brown fraction corresponding to the azuliporphyrin product was collected. Recrystallization from chloroform/methanol afforded the tetraphenylporphyrinoid (59 mg, 0.079 mmol, 20%) as dark green crystals, m.p. 240 °C (dec.). UV/Vis (1% $Et_3N/CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 399 (4.68), 499 (4.75), 669 nm (4.01). UV/Vis (1% TFA/$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 403 (4.65), 463 (4.72), 516 (5.01), 611 (4.09), 672 (3.99), 837 nm (4.21). UV/Vis (1% pyrrolidine/$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 437 (4.77), 497 nm (4.63). UV/Vis (5% pyrrolidine/$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 438 (4.94), 741 nm (3.80). UV/Vis (10% pyrrolidine/$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 449 nm (4.84). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (s, 9 H), 2.88 (s, 1 H), 4.56 (br. s, 1 H), 7.12 (t, *J* = 11.2 Hz, 2 H), 7.38 (d, *J* = 4.4 Hz, 1 H), 7.54–7.60 (m, 6 H), 7.62 (d, *J* = 11.2 Hz, 2 H), 7.65–7.68 (m, 8 H), 7.83–7.86 (m, 4 H), 7.90–7.94 (m, 6 H) ppm. ^{1}H NMR (400 MHz, TFA/$CDCl_3$, 50 °C, dication): δ = –0.82 (s, 1 H), 0.84 (s, 1 H), 1.34 (s, 9 H), 2.39 (br. s, 2 H), 7.79–7.87 (m, 8 H), 7.92–7.98 (m, 8 H), 8.01 (d, *J* = 4.8 Hz, 2 H), 8.16–8.19 (m, 4 H), 8.22 (s, 2 H), 8.32–8.39 (br. m, 4 H), 8.42 (d, *J* = 4.8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.6, 38.5, 115.5, 123.4, 126.8, 127.3, 127.5 (2), 128.2, 129.1, 129.3, 130.1, 133.9, 135.1, 135.3, 138.3, 139.2, 141.8, 143.1, 143.7, 155.4, 164.4, 164.9 ppm. ^{13}C NMR (100 MHz, TFA/$CDCl_3$, 25 °C): δ = 31.3, 114.5, 117.4, 127.4, 128.8, 129.4, 130.1, 130.4, 131.2, 132.0, 132.2, 135.9, 136.4, 137.7, 138.8, 138.9, 140.8, 142.0, 143.9, 146.4, 150.6, 172.2 ppm. HRMS (EI): calcd. for $C_{54}H_{41}N_3$ + 2 H: *m*/*z* = 733.3457; found 733.3445. $C_{54}H_{41}N_3{\cdot}0.3CHCl_3$ (767.75): calcd. C 84.95, H 5.41, N 5.47; found C 85.02, H 5.56, N 5.72.

[D_{20}]-2^3-*tert*-Butyl-5,10,15,20-tetraphenylazuliporphyrin (9b): Prepared under the foregoing conditions from 6-*tert*-butylazulene and [D_6]benzaldehyde. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (s, 9 H), 2.87 (s, 1 H), 4.6 (br. s, 1 H), 7.12 (t, *J* = 11.2 Hz, 2 H), 7.38 (d, *J* = 4.8 Hz, 2 H), 7.62 (d, *J* = 11.2 Hz, 2 H), 7.68 (s, 2 H), 7.98 (d, *J* = 4.4 Hz, 2 H) ppm. ^{1}H NMR (400 MHz, TFA/$CDCl_3$, dication): δ = –1.06 (s, 1 H), 0.39 (br. s, 1 H), 1.34 (s, 9 H), 2.10 (br. s, 2 H), 7.85 (d, *J* = 11.2 Hz, 2 H), 7.94 (d, *J* = 11.2 Hz, 2 H), 8.05 (dd, *J* = 1.6, 4.8 Hz, 2 H), 8.28 (d, *J* = 1.2 Hz, 2 H), 8.45 (dd, *J* = 1.4, 5.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.6, 38.5, 115.4, 123.3, 126.8, 129.1, 129.3, 130.1, 135.1, 135.3, 138.3, 139.1, 141.6, 142.8, 143.7, 155.4, 164.4, 164.9 ppm. HRMS (EI): calcd. for $C_{54}H_{21}D_{20}N_3$ + H: *m*/*z* = 752.4634; found 752.4636.

2^3,5,10,15,20-Pentaphenylazuliporphyrin (9c): The title azuliporphyrin was prepared using the foregoing conditions from 6-phenylazulene (120 mg, 0.588 mmol), benzaldehyde (238 μL, 250 mg, 2.36 mmol), pyrrole (122 μL, 119 mg, 1.78 mmol) and $BF_3{\cdot}Et_2O$ (10%, 60 μL) in chloroform (240 mL), followed by oxidation with DDQ (98%, 400 mg, 1.73 mmol). Recrystallization from chloroform/methanol gave the pentaphenylazuliporphyrin (67 mg, 0.089 mmol, 15%) as olive-green crystals, m.p. 240 °C (dec.). UV/Vis (1% $Et_3N/CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 380 (4.70), 402 (4.72), 502 (4.79), 668 nm (4.06). UV/Vis (1% TFA/$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 412 (4.70), 523 (5.04), 612 (4.20), 674 (4.06), 843 nm (4.23). UV/Vis (1% pyrrolidine/$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 439 (4.85), 499 (4.24), 665 nm (3.93). UV/Vis (5% pyrrolidine/$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 440 (4.91), 728 nm (3.84). UV/Vis (10% pyrrolidine/$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 465 nm (4.88). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.24 (s, 1 H), 4.99 (br. s, 1 H), 7.16 (d, *J* = 10.8 Hz, 2 H), 7.35 (d, *J* = 4.4 Hz, 2 H), 7.36–7.39 (m, 3 H), 7.42–7.45 (m, 2 H), 7.54–7.60 (m, 6 H), 7.63 (s, 2 H), 7.65–7.68 (m, 8 H), 7.82–7.85 (m, 4 H), 7.96–8.00 (m, 6 H) ppm. ^{1}H NMR (400 MHz, TFA/$CDCl_3$, dication): δ = –1.00 (s, 1 H), 0.34 (br. s, 1 H), 2.11 (br. s, 2 H), 7.35–7.44 (m,

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5 H), 7.76–7.78 (m, 6 H), 7.81 (d, J = 10.4 Hz, 2 H), 7.85–7.92 (m, 8 H), 7.97 (d, J = 4.8 Hz, 2 H), 8.05–8.12 (m, 4 H), 8.20 (s, 2 H), 8.3–8.4 (br. s, 4 H), 8.40 (d, J = 4.4 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 115.6, 123.8, 123.9, 127.3, 127.5, 127.6, 128.2 (2), 128.9, 129.0, 129.2, 130.3, 130.9, 133.8, 134.9, 135.2, 135.4, 138.4 (2), 141.7, 143.0, 144.1, 153.2, 155.7, 165.5 ppm. ^{13}C NMR (100 MHz, TFA/$CDCl_3$, dication): δ = 113.4, 117.6, 127.7, 128.7, 128.8, 129.5, 129.7, 130.4, 130.7, 131.1, 131.5, 132.1, 132.6, 136.2, 136.4, 137.5 (br), 138.5, 138.8, 139.3, 140.1, 140.7, 142.3, 144.0, 146.2, 150.8, 160.2 ppm. HRMS (EI): calcd. for $C_{56}H_{37}N_3$ + 2 H: m/z = 753.3144; found 753.3152; $C_{56}H_{37}N_3 \cdot {}^1/_2H_2O$ (760.94): calcd. C 88.39, H 5.03, N 5.52; found: C 87.99, H 5.17, N 5.67.

2^3-*tert*-Butyl-5,10,15,20-tetrakis(4-chlorophenyl)azuliporphyrin (9d): The tetraarylazuliporphyrin was prepared by the foregoing conditions from 6-*tert*-butylazulene (108 mg, 0.587 mmol), 4-chlorobenzaldehyde (330 mg, 2.35 mmol), pyrrole (123 μL, 120 mg, 1.79 mmol) and $BF_3 \cdot Et_2O$ (10%, 600 μL) in chloroform (240 mL), followed by oxidation with DDQ (98%, 400 mg, 1.73 mmol). Following purification by column chromatography on grade 2 basic alumina, eluting with 5% ethyl acetate/toluene, and recrystallization from chloroform/methanol, the title azuliporphyrin (115.5 mg, 0.133 mmol, 23%) was obtained as dull emerald green crystals, m.p. > 300 °C. UV/Vis (1% $Et_3N/CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 399 (4.78), 500 (4.88), 675 nm (4.16). UV/Vis (1% TFA/$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 412 (4.83), 469 (4.81), 531 (5.10), 625 (4.14), 689 (3.99), 876 nm (4.33). UV/Vis (1% pyrrolidine/$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 440 (5.08), 597 (4.05), 745 nm (3.91). UV/Vis (5% pyrrolidine/$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 447 (5.05), 597 (4.05), 647 (4.04), 729 nm (3.97). UV/Vis (10% pyrrolidine/$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 452 (5.03), 595 (4.06), 641 (4.11), 729 nm (3.96). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27 (s, 9 H), 2.68 (s, 1 H), 4.50 (br. s, 1 H), 7.24 (doublet overlapped with $CHCl_3$, 2 H), 7.37 (d, J = 4.8 Hz, 2 H), 7.55–7.58 (AA′XX′ system, 4 H), 7.65–7.70 (m, 8 H), 7.74–7.78 (AA′XX′ system, 4 H), 7.91–7.94 (m, 6 H) ppm. ^{1}H NMR (400 MHz, TFA/$CDCl_3$, dication): δ = –0.99 (s, 1 H), 0.72 (br. s, 1 H), 1.39 (s, 9 H), 2.06 (br. s, 2 H), 7.85 (br. d, J = 7 Hz, 4 H), 7.94–8.03 (m, 10 H), 8.07–8.12 (br. m, 4 H), 8.24 (s, 2 H), 8.3 (very br., 4 H), 8.41 (d, J = 4.4 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.6, 38.7, 114.4, 123.2, 126.5, 127.8, 127.9, 129.0, 129.7, 130.1, 133.8, 134.1, 134.9, 135.9, 138.1, 138.9, 140.0, 141.3, 143.7, 155.4, 164.7, 165.1 ppm. ^{13}C NMR (100 MHz, TFA/$CDCl_3$, dication): δ = 31.3, 40.3, 114.6, 116.6, 127.5, 129.3, 130.0, 130.5, 130.6, 131.2, 132.2, 135.0, 137.1, 137.2, 137.6, 138.4 (sharp peak overlapped with a broad resonance), 139.6, 140.8, 141.9, 144.1, 146.6, 150.5, 173.4 ppm. HRMS (FAB): calcd. for $C_{54}H_{37}Cl_4N_3$ + H: m/z = 868.1820; found 868.1818; $C_{54}H_{37}Cl_4N_3 \cdot {}^1/_4CHCl_3$ (899.56): calcd. C 72.43, H 4.17, N 4.67; found: C 72.43, H 4.16, N 4.67.

5,10,15,20-Tetrakis(4-chlorophenyl)-2^3-phenylazuliporphyrin (9e): Azuliporphyrin **7e** was prepared using the same conditions from 6-phenylazulene (120 mg, 0.588 mmol), 4-chlorobenzaldehyde (330 mg, 2.35 mmol), pyrrole (123 μL, 120 mg, 1.79 mmol) and $BF_3 \cdot Et_2O$ (10%, 60 μL) in chloroform (240 mL), followed by oxidation with DDQ (98%, 400 mg, 1.73 mmol). Recrystallization from chloroform/methanol gave the azuliporphyrin (138.3 mg, 0.155 mmol, 26%) as dull emerald green crystals, m.p. > 300 °C. UV/Vis (1% $Et_3N/CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 404 (4.75), 504 (4.86), 669 nm (4.11). UV/Vis (1% TFA/$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 421 (4.80), 475 (4.72), 538 (5.05), 627 (4.10), 703 (3.89), 887 nm (4.24). UV/Vis (1% pyrrolidine/$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 441 (5.04), 597 (4.01), 759 nm (3.83). UV/Vis (5% pyrrolidine/$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 444 (4.88), 481 (4.87), 597 (3.99), 647 nm (3.97). UV/Vis (10% pyrrolidine/$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 445 (4.85), 481 (4.89), 596 (4.03), 646 (4.04), 729 nm (3.92). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.02 (s, 1 H), 4.81 (br. s, 1 H), 7.29 (d, J = 11.2 Hz, 2 H), 7.34 (d, J = 5.2 Hz, 2 H), 7.40–7.44 (m, 3 H), 7.47–7.51 (m, 2 H), 7.54–7.58 (AA′XX′ system, 4 H), 7.63 (s, 2 H), 7.64–7.68 (AA′XX′ system, 4 H), 7.72 (d, J = 10 Hz, partially obscured, 2 H), 7.73–7.76 (AA′XX′ system, 4 H), 7.90–7.94 (AA′XX′ system, 4 H), 7.93 (d, J = 4.8 Hz, overlapped with previous peak, 2 H) ppm. ^{1}H NMR (400 MHz, TFA/$CDCl_3$, dication): δ = –0.87 (s, 1 H), 0.79 (br. s, 1 H), 2.20 (br. s, 2 H), 7.48–7.58 (m, 5 H), 7.86 (d, J = 8 Hz, 4 H), 7.93–8.00 (br. m, 4 H), 8.02–8.05 (m, 6 H), 8.08–8.11 (m, 4 H), 8.2–8.3 (very br., 4 H), 8.25 (d, J = 1.2 Hz, 2 H), 8.45 (dd, J = 2.0, 4.8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 114.5, 123.5, 127.0, 127.8, 127.9, 128.3, 129.1, 129.2 (2), 130.3, 131.3, 133.9, 134.3, 134.8, 135.0, 135.8, 138.3, 139.9, 141.2, 144.0, 153.8, 155.7, 165.3 ppm. ^{13}C NMR (100 MHz, TFA/$CDCl_3$, dication): δ = 114.0, 116.5, 127.5, 128.8, 129.2, 129.7, 129.9, 130.6, 131.19, 131.23, 132.2, 135.1, 136.9, 137.1, 137.5, 138.1 (br), 139.4, 139.6, 139.8, 140.6, 141.9, 143.9, 146.7, 150.7, 160.3 ppm. HRMS (FAB): calcd. for $C_{56}H_{33}Cl_4N_3$ + H: m/z = 888.1501; found 888.1504; $C_{56}H_{33}Cl_4N_3 \cdot {}^1/_2CHCl_3$ (949.40): calcd. C 71.48, H 3.56, N 4.42; found: C 71.44, H 3.58, N 4.37.

[2^3-*tert*-Butyl-5,10,15,20-tetraphenylazuliporphyrinato]nickel(II) (11a): A solution of *tert*-butylazuliporphyrin **9a** (30.0 mg, 0.041 mmol) and nickel(II) acetate tetrahydrate (30 mg) in DMF (30 mL) was heated with stirring under reflux for 20 min. The solution was cooled to room temperature, diluted with chloroform, washed with water and dried with sodium sulfate. The solvent was evaporated under aspirator pressure and residual DMF was removed using an oil pump. The residue was purified by column chromatography on silica eluting with chloroform. Recrystallization from chloroform/methanol gave the nickel(II) derivative (21.8 mg, 0.028 mmol, 68%) as black crystals, m.p. 242 °C (dec.). UV/Vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 398 (4.83), 491 (4.69), 583 (4.22), 644 (4.23), 788 nm (3.73). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (s, 9 H), 6.98 (d, J = 11.2 Hz, 2 H), 7.41 (d, J = 11.2 Hz, 2 H), 7.57–7.66 (m, 12 H), 7.84 (d, J = 5.2 Hz, 2 H), 7.85–7.89 (m, 8 H), 8.01 (s, 2 H), 8.05 (d, J = 5.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.2, 38.2, 117.7, 127.1, 127.2, 127.4, 127.8, 128.8, 129.4, 130.0, 132.3, 132.7, 133.28, 133.33, 133.6, 134.6, 141.5, 142.2, 146.4, 148.0, 151.3, 156.1, 162.1 ppm. HRMS (EI): calcd. for $C_{54}H_{39}N_3Ni$: m/z = 787.2497; found 787.2511; $C_{54}H_{39}N_3Ni \cdot 0.4CHCl_3$ (836.36): calcd. C 78.12, H 4.75, N 5.02; found: C 78.02, H 4.81, N 4.94.

[[D$_{20}$]-2^3-*tert*-Butyl-5,10,15,20-tetraphenylazuliporphyrinato]nickel-(II) (11b): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (s, 9 H), 6.98 (d, J = 11.2 Hz, 2 H), 7.42 (d, J = 11.6 Hz, 2 H), 7.84 (d, J = 5.2 Hz, 2 H), 8.00 (s, 2 H), 8.05 (d, J = 4.8 Hz, 2 H) ppm.

[2^3,5,10,15,20-Pentaphenylazuliporphyrinato]nickel(II) (11c): The nickel complex was prepared from pentaphenylazuliporphyrin **9c** (11.2 mg, 0.0149 mmol) and nickel(II) acetate tetrahydrate (10 mg) in DMF (10 mL). Recrystallization from chloroform/methanol gave the metallo-derivative (8.8 mg, 0.0109 mmol, 73%) as black crystals, m.p. 240 °C (dec.). UV/Vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 401 (4.86), 493 (4.78), 598 (4.29), 646 (4.28), 805 nm (3.74). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.03 (d, J = 10.8 Hz, 2 H), 7.39–7.48 (m, 7 H), 7.57–7.63 (m, 12 H), 7.82 (d, J = 5.2 Hz, 2 H), 7.86–7.89 (m, 8 H), 7.99 (s, 2 H), 8.05 (d, J = 5.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 117.8, 127.2, 127.3, 127.5, 127.6, 127.9, 128.9, 129.1, 129.6, 130.2, 132.5, 132.9, 133.4, 133.6, 134.6, 135.0, 141.3, 142.1, 146.7, 148.3, 151.0, 155.3, 166.0 ppm. HRMS (EI): calcd. for $C_{56}H_{35}N_3Ni$: m/z = 807.2184; found 807.2177; $C_{56}H_{35}N_3Ni \cdot {}^1/_5CHCl_3$ (832.48): calcd. C 81.09, H 4.26, N 5.05; found: C 81.01, H 4.30, N 5.14.

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[2^3-*tert*-Butyl-5,10,15,20-tetraphenylazuliporphyrinato]palladium(II) (12a): The palladium complex was prepared using the same conditions from **9a** (10.7 mg, 0.0146 mmol) and palladium(II) acetate (10.2 mg). Recrystallization from chloroform/methanol gave the metalated azuliporphyrin (9.0 mg, 0.0108 mmol, 74%) as shiny black crystals, m.p. > 300 °C. UV/Vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 401 (4.78), 480 (4.72), 576 (4.29), 621 (4.25), 770 nm (3.80). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 (s, 9 H), 7.04 (d, J = 11.2 Hz, 2 H), 7.57–7.65 (m, 12 H), 7.69 (t, 2 H), 7.92–7.97 (m, 10 H), 7.99 (s, 2 H), 8.08 (d, J = 5.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.3, 38.2, 119.3, 126.7, 127.0, 127.1, 127.4, 127.8, 129.1, 131.4, 132.0, 132.1, 133.5, 133.8, 134.3, 135.8, 142.5, 143.3, 144.5, 147.3, 149.1, 156.9, 162.8 ppm. HRMS (EI): calcd. for $C_{54}H_{39}N_3Pd$: m/z = 835.2179; found 835.2177; $C_{54}H_{39}N_3Pd{\cdot}0.6CHCl_3$ (907.97): calcd. C 72.23, H 4.40, N 4.63; found: C 72.08, H 4.61, N 4.51.

[[D_{20}]-2^3-*tert*-Butyl-5,10,15,20-tetraphenylazuliporphyrinato]palladium(II) (12b): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 (s, 9 H), 7.04 (d, J = 11.6 Hz, 2 H), 7.58 (d, J = 12 Hz, 2 H), 7.95 (d, J = 5.2 Hz, 2 H), 7.99 (s, 2 H), 8.08 (d, J = 4.8 Hz, 2 H) ppm.

[2^3,5,10,15,20-Pentaphenylazuliporphyrinato]palladium(II) (12c): The title metallo-derivative was prepared from pentaphenylazuliporphyrin **9c** (11.3 mg, 0.0150 mmol) and palladium(II) acetate (10.2 mg) under the foregoing conditions. Recrystallization from chloroform/methanol gave the palladium complex (7.6 mg, 0.0089 mmol, 59%) as dull green crystals, m.p. > 300 °C. UV/Vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 404 (4.83), 480 (4.87), 600 (4.41), 625 (4.42), 789 nm (3.89). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10 (d, J = 11.6 Hz, 2 H), 7.41–7.45 (m, 3 H), 7.48–7.52 (m, 2 H), 7.61–7.69 (m, 14 H), 7.92–7.96 (m, 10 H), 7.97 (s, 2 H), 8.08 (d, J = 5.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 119.3, 126.9, 127.0, 127.1, 127.4, 127.6, 127.9, 129.2, 129.3, 131.5, 132.2, 133.5, 133.8, 135.7, 135.8, 142.3, 142.4, 143.2, 144.8, 147.6, 149.6, 151.6, 156.2 ppm. HRMS (EI): calcd. for $C_{56}H_{35}N_3Pd$: m/z = 855.1866; found 855.1862; $C_{56}H_{35}N_3Pd{\cdot}0.3CHCl_3$ (892.15): calcd. C 75.80, H 3.99, N 4.71; found: C 75.80, H 4.25, N 4.61.

Oxidative Ring Contraction of 9a: A solution of KOH (240 mg) in methanol (30 mL) was added to **9a** (30 mg, 0.041 mmol) in dichloromethane, followed by the addition of 20 μL of a solution of *tert*-butyl hydroperoxide in decane (5–6 M). The mixture was stirred at room temperature in the dark under nitrogen for 1 h. The mixture was diluted with chloroform, washed twice with water, dried with sodium sulfate, filtered and the solvents evaporated to dryness. The residue was loaded onto a grade 3 alumina chromatography column and eluted with 25% dichloromethane/hexanes. A major brown band eluted initially, followed by a minor slightly more polar brown fraction. The major fraction was recrystallized from chloroform/methanol to give **13a** (14.4 mg, 0.020 mmol, 49%) as red-brown crystals, m.p. 250 °C (dec.). The minor fraction was evaporated to give 1–1.5 mg (ca. 5%) of **15a** as a reddish-brown film.

2^2-*tert*-Butyl-5,10,15,20-tetraphenylbenzo[*b*]carbaporphyrin (13a): UV/Vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 448 (5.11), 537 (4.16), 577 (3.92), 638 (3.76), 708 nm (3.82). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –5.40 (s, 1 H), –2.6 (very br., 2 H), 1.06 (s, 9 H), 6.66 (d, J = 8.4 Hz, 1 H), 6.96 (d, J = 1.5 Hz, 1 H), 7.01 (dd, J = 1.6, 8.0 Hz, 1 H), 7.71–7.73 (m, 6 H), 7.78–7.83 (m, 6 H), 8.16–8.19 (m, 4 H), 8.28–8.30 (m, 2 H), 8.33–8.35 (m, 2 H), 8.50–8.53 (m, 2 H), 8.56 (s, 2 H), 8.65 (d, J = 4.8 Hz, 1 H), 8.70 (d, J = 4.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.4, 34.8, 108.8, 118.3, 118.6, 121.6, 122.0, 122.3, 123.2, 123.5, 125.2, 125.3, 126.6, 126.8, 127.0, 127.8, 128.0, 128.2, 128.3, 128.4, 133.6, 133.7, 134.8, 134.9, 135.1, 136.8, 138.4, 138.6, 138.9, 142.4, 149.4, 155.2 ppm. HRMS (EI): calcd. for $C_{53}H_{41}N_3$: m/z = 719.3300; found 719.3291; $C_{53}H_{41}N_3{\cdot}{}^1/_4CHCl_3$ (749.77): calcd. C 85.30, H 5.55, N 5.60; found: C 85.45, H 6.00, N 5.42.

2^2-*tert*-Butyl-3^2-formyl-5,10,15,20-tetraphenylbenzo[*b*]carbaporphyrin (15a): ^{1}H NMR (400 MHz, $CDCl_3$): δ = –5.19 (s, 1 H), 7.27 (s, 1 H), 7.34 (s, 1 H), 7.74–7.76 (m, 6 H), 7.80–7.90 (m, 6 H), 8.18–8.21 (m, 4 H), 8.32–8.39 (m, 4 H), 8.54–8.59 (m, 4 H), 8.73 (d, J = 4.8 Hz, 1 H), 8.78 (d, J = 4.8 Hz, 1 H), 10.47 (s, 1 H) ppm. HRMS (EI): calcd. for $C_{54}H_{41}N_3O$ + 2 H: m/z = 749.3400; found 749.3394.

Oxidative Ring Contraction of 9b: [D_{20}]-2^3-*tert*-Butyl-5,10,15,20-tetraphenylazuliporphyrin (**9b**) afforded the related [D_{20}]-carbaporphyrins **13b** and **15b**. **13b:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = –5.37 (s, 1 H), –2.75 (br. s, 2 H), 1.08 (s, 9 H), 6.68 (d, J = 8 Hz, 1 H), 6.98 (d, J = 1.6 Hz, 1 H), 7.03 (dd, J = 2, 8.4 Hz, 1 H), 8.53 (d, J = 4.8 Hz, 1 H), 8.55 (d, J = 4.8 Hz, 1 H), 8.58 (s, 2 H), 8.68 (d, J = 4.8 Hz, 1 H), 8.73 (d, J = 4.8 Hz, 1 H) ppm. **15b:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = –5.18 (s, 1 H), –2.7 (br. s, 2 H), 1.24 (s, 9 H), 7.27 (s, 1 H), 7.33 (s, 1 H), 8.55 (d, J = 4.8 Hz, 1 H), 8.56 (d, J = 5.2 Hz, 1 H), 8.57–8.59 (AB quartet, 2 H), 8.73 (d, J = 4.8 Hz, 1 H), 8.78 (d, J = 4.8 Hz, 1 H), 10.47 (s, 1 H) ppm.

Oxidative Ring Contraction of 9c: Pentaphenylbenzocarbaporphyrin **9c** (30 mg, 0.040 mmol) was treated with KOH/*t*BuOOH under the foregoing conditions. Column chromatography on grade 3 alumina, eluting with 25% dichloromethane, afforded a major brown fraction corresponding to **13c** and a slightly more polar minor band corresponding to **15c** (1 mg; < 5%). The major product was recrystallized from chloroform/methanol and gave **13c** (14.3 mg, 0.019 mmol, 48%) as dark blue crystals, m.p. 220 °C (dec.).

2^2,5,10,15,20-Pentaphenylbenzo[*b*]carbaporphyrin (13c): UV/Vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) = 451 (5.09), 539 (4.18), 580 (3.91), 639 (3.79), 705 nm (3.88). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –5.29 (s, 1 H), –2.70 (br. s, 2 H), 6.83 (d, J = 8 Hz, 1 H), 7.10 (d, J = 1.6 Hz, 1 H), 7.24–7.36 (m, 6 H), 7.74–7.76 (m, 6 H), 7.83–7.89 (m, 6 H), 8.19–8.22 (m, 4 H), 8.35–8.42 (m, 4 H), 8.55 (d, J = 4.8 Hz, 1 H), 8.57 (d, J = 4.8 Hz, 1 H), 8.58 (s, 2 H), 8.73 (d, J = 4.8 Hz, 1 H), 8.78 (d, J = 5.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 108.7, 118.6, 118.7, 122.3, 122.5, 123.0, 124.0, 124.9, 125.4, 125.5, 126.9, 127.0, 127.05, 127.1, 127.9, 128.2, 128.3, 128.5, 128.6, 128.7, 133.87, 133.92, 134.9, 135.2, 135.4, 138.1, 138.4, 138.5, 138.7, 139.5, 141.6, 142.3, 142.5, 155.4, 155.5 ppm. HRMS (EI): calcd. for $C_{55}H_{37}N_3$: m/z = 739.2987; found 739.2984; $C_{55}H_{37}N_3{\cdot}{}^1/_2CHCl_3$ (799.61): calcd. C 83.37, H 4.73, N 5.25; found: C 83.63, H 4.99, N 5.20.

2^2-Formyl-3^2,5,10,15,20-pentaphenylbenzo[*b*]carbaporphyrin (15c): ^{1}H NMR (400 MHz, $CDCl_3$): δ = –5.10 (s, 1 H), 6.83 (s, 1 H), 7.12–7.15 (m, 2 H), 7.35–7.38 (m, 3 H), 7.45 (s, 1 H), 7.75–7.77 (m, 8 H), 7.81–7.84 (m, 2 H), 7.88–7.93 (m, 4 H), 8.18–8.22 (m, 4 H), 8.33–8.38 (m, 4 H), 8.56–8.59 (m, 3 H), 8.80 (d, J = 4.8 Hz, 1 H), 9.86 (s, 1 H) ppm. HRMS (EI): calcd. for $C_{56}H_{37}N_3O$: m/z = 767.2937; found 767.2941.

Supporting Information (see also the footnote on the first page of this article): Selected UV/Vis, ^{1}H NMR and ^{13}C NMR spectra for **9**, **11**, **12**, **13** and **15** are provided.

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