3-Cyclobutenyl-1,2-dione-Substituted Porphyrins. A General and Efficient Entry to Porphyrin−Quinone and Quinone−Porphyrin−Quinone Architectures

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A new and efficient synthesis of *meso*-linked porphyrin−quinone dyads and quinone−porphyrin−quinone triads has been developed via the intermediacy of porphyrins bearing 3-cyclobutenyl-1,2-dione and 3-(1-ethenyl)cyclobutenyl-1,2-dione substituents at one or two nonadjacent *meso*-positions. The free-base porphyrins 5-bromo-10,20-diphenylporphyrin and 5,15-dibromo-10,20-diphenylporphyrin undergo facile palladium-catalyzed Stille coupling with 3-isopropoxy-2-tri-*n*-butylstannylcyclobutene-1,2-dione to produce the corresponding mono- and bis(3-cyclobutenyl-1,2-dione)-substituted porphyrins in good yields. In contrast, the zinc bromoporphyrins reacted with the same tin reagent only slowly and with the formation of side products. The free-base bromoporphyrins also were coupled with tri-*n*-butylvinyltin to afford vinylporphyrins in very good yields. 5,15-Diphenyl-10-vinylporphyrin was converted into *trans*-bromovinylporphyrin, which underwent facile Stille coupling with 3-isopropoxy-2-tri-*n*-butylstannylcyclobutene-1,2-dione to afford the vinylogous 3-cyclobutenyl-1,2-dione-substituted porphyrin. The molecular structure of 5,15-bis(3-cyclobutenyl-1,2-dione)-10,20-diphenylporphyrin(Zn) was determined by X-ray crystallography. Although the data revealed a fairly large dihedral angle between the cyclobutenedione and the porphyrin rings (57°), the UV−vis spectra of both the mono- and bis(3-cyclobutenyl-1,2-dione)-substituted porphyrins showed B- and Q-band red shifts indicative of strong electronic coupling between the porphyrin and cyclobutenedione chromophores in solution. Introduction of a double bond between the cyclobutenedione and porphyrin rings resulted in a significant red shift of both the B- and Q-bands compared to those of the nonvinylogous system. All porphyrinic cyclobutenediones were metalated with zinc and then, using established cyclobutenedione chemistry, converted into a variety of porphyrin−quinones in excellent yields with aryllithium and vinylic Grignard reagents. From the mono(3-cyclobutenyl-1,2-dione)-substituted porphyrin, **7**, a variety of directly linked monoquinone−porphyrin dyads were easily synthesized. Substituents could also be introduced at the free *meso*-position of **7** by bromination followed by palladium-catalyzed cross-coupling reactions, and additional porphyrinic monoquinones were then prepared from these starting materials. The vinylogous squarylporphyrin was converted into a double bond linked porphyrin−quinone via reaction with phenyllithium followed by thermal rearrangement and oxidation. As a result of the hindered rotation around the C−C bond between the porphyrin and the quinone, pairs of stable, separable, and thermally interconvertable atropisomers of porphyrin−quinones were obtained from 5,15-bis(3-cyclobutenyl-1,2-dione)-10,20-diphenylporphyrin(Zn). The structure of one of the atropisomers was determined by X-ray crystallography.

Introduction

Because of their great potential in health-related[1−6] and advanced materials applications,[7−9] and as models for naturally occurring processes,[10−14] there is much interest in novel and efficient routes to substituted porphyrins.[15−18] Of particular interest are synthetic porphyrins bearing moieties that impart unusual biological,[19] photophysical,[20] or electronic properties[21] to the system.

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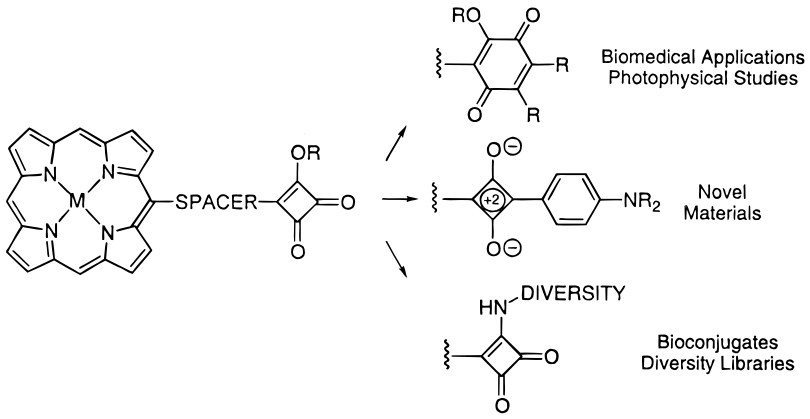
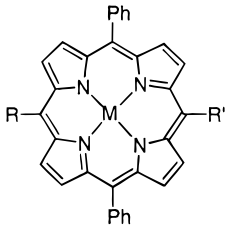


Figure 1.

Cyclobutenediones are exceptionally versatile precursors to a broad array of molecular systems.[22−27] By attaching a 3-cyclobutenyl-1,2-dione fragment to a readily available porphyrin core, the wealth of chemistry emanating from the cyclobutenedione functionality can be easily brought to porphyrinic molecules, as suggested in Figure 1. As a specific case in point, porphyrinic cyclobutenediones should be effective precursors to structurally diverse porphyrin−quinone architectures. In addition to the importance of these molecules as model systems for photosynthetic[28,29] electron-transfer studies,[12−14,30] some porphyrin−quinone compounds have shown potential as anticancer agents,[31] and others might function as unique bimodal catalysts for redox reactions of small molecules.[32] Herein is described an efficient method for generating 3-cyclobutenyl-1,2-dione substituted porphyrins and the high-yield conversion of these into a variety of porphyrinic quinones.

Results and Discussion

General and efficient synthetic methods that allow the easy preparation of structurally diverse porphyrinic quinones are rare.[29,33,34] If a 3-cyclobutenyl-1,2-dione unit could be attached to the porphyrin core, these molecules could be readily available from simple porphyrins, such as 5,15-diphenylporphyrin, using cyclobutenedione chemistry.[35] Palladium-catalyzed carbon−carbon cross-coupling technology offers a convenient solution to the task, since it has proven highly effective for the construction of substituted porphyrinic systems[15−17,33,34,36−43] as well as substituted cyclobutenediones.[44−47] Porphyrinic quinones with considerable variation in substitution pattern and structure should be preparable with this strategy when coupled with known methods for the selective bromination and iodination of porphyrins.[16,37,48,49]



1 M = 2H, R = R' = H
2 M = 2H, R = H, R' = Br
3 M = Zn, R = H, R' = Br
4 M = 2H, R = R' = Br
5 M = Zn, R = R' = Br

Figure 2.

The readily available 5,15-diphenylporphyrin (**1**) was selected for initial studies.[16,35] 5,15-Dibromo-10,20-diphenylporphyrin (**4**) has been described in the literature: using 2.2 equiv of NBS, **4** was obtained from **1** as the exclusive product in 85% yield.[16] Bromination of **1** with 1.1 equiv of NBS led to 5-bromo-10,20-diphenylporphyrin

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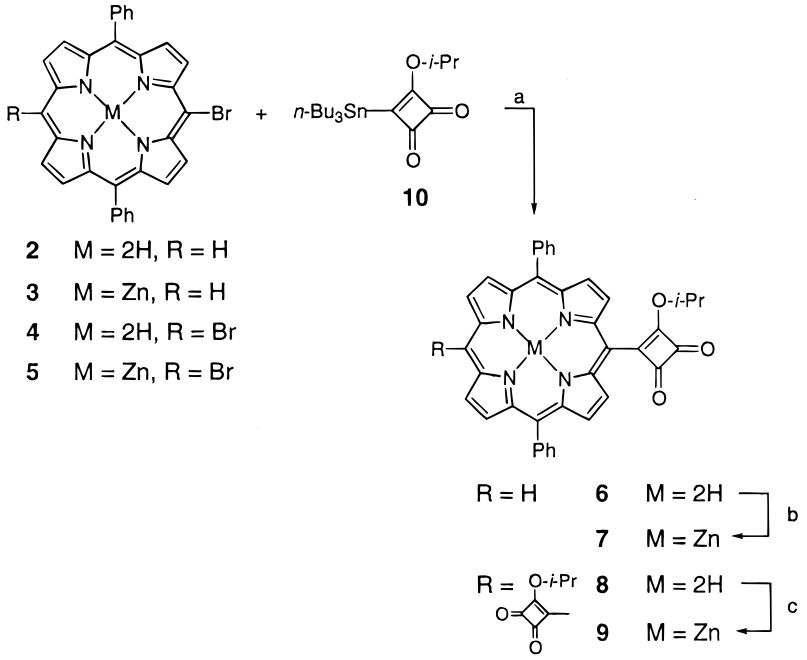
Scheme 1[a]



[a] (a) $Pd_2(dba)_3$, $AsPh_3$, THF, 55 °C: 85% for **6**, 76% for **8**. b or c CH_2Cl_2, $Zn(OAc)_2$ in MeOH, reflux, 98% for **7**, 86% for **9**.

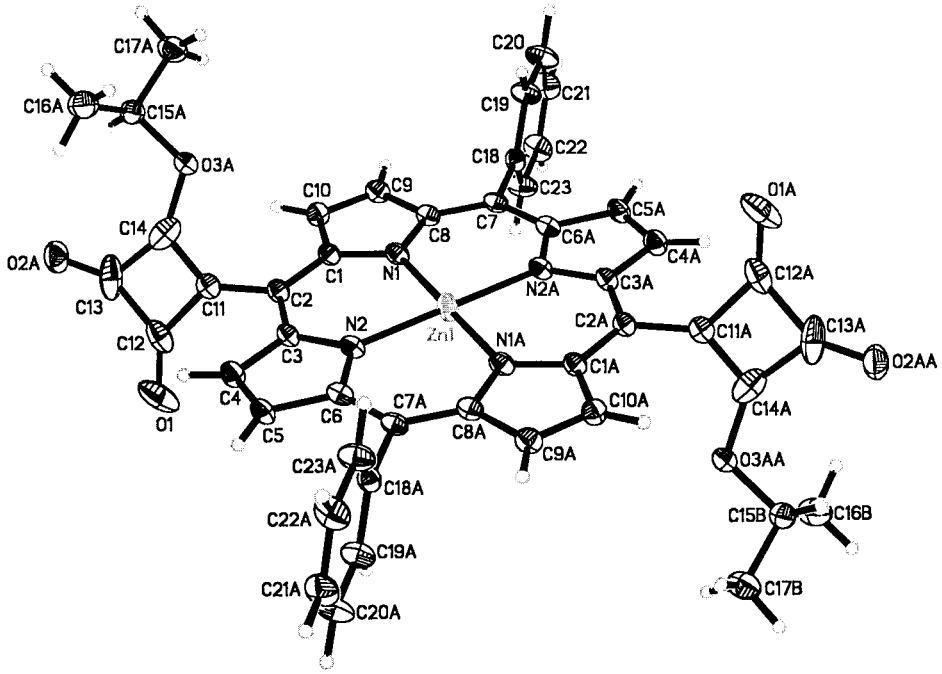


Figure 3. X-ray Structure of compound **9** ($C_{46}H_{32}N_4O_6Zn{\cdot}2CH_3CO_2C_2H_5$). Coordinated solvent molecules are omitted for clarity.

(**2**; 57%) and 5,15-dibromo-10,20-diphenylporphyrin (**4**; 11%) (Figure 2).

Synthesis of *meso*-Linked Squarylporphyrins. Following the lead of DiMagno, Lin and Therien,[16] who suggested that free base porphyrins would be problematic in palladium-catalyzed Stille cross-couplings, the zinc porphyrins **3** and **5** were treated with 3-isopropoxy-2-tri-*n*-butylstannylcyclobutenedione (**10**) using $Pd(PPh_3)_4$ as the catalyst. Unfortunately, the reaction was slow and accompanied by the formation of unwanted side products, and separation of the desired product required careful chromatography. Although modification of the palladium precatalyst from $Pd(PPh_3)_4$ to $Pd_2(dba)_3/AsPh_3$ allowed an efficient coupling of zinc porphyrin **3** with **10**, this catalytic system did not prove useful for the coupling of **5** with **10**.

Since electron-withdrawing groups tend to accelerate many palladium-catalyzed cross-coupling reactions,[50−52] free-base porphyrins should undergo palladium-catalyzed cross-coupling reactions with greater facility than the more electron-rich metalloporphyrins, at least at the *meso*-positions.[53] Indeed, compound **4** reacted smoothly

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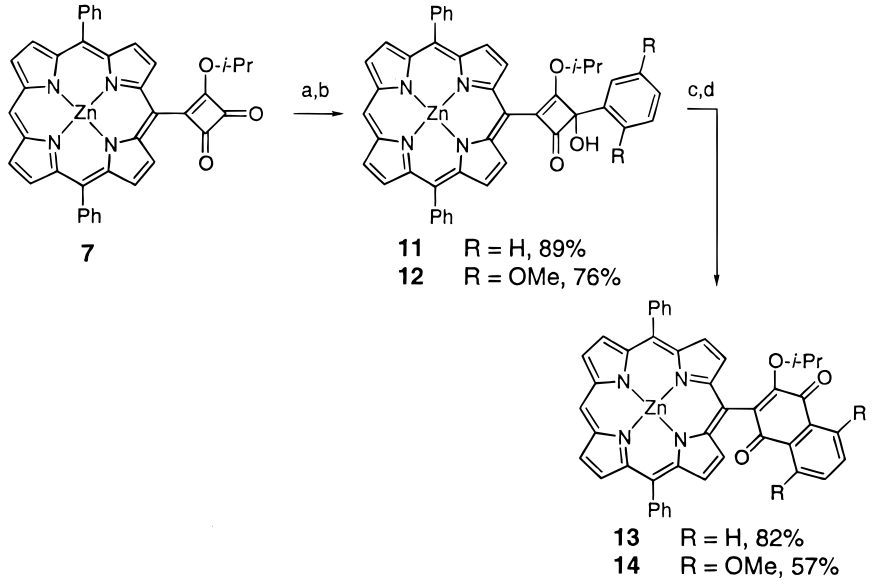
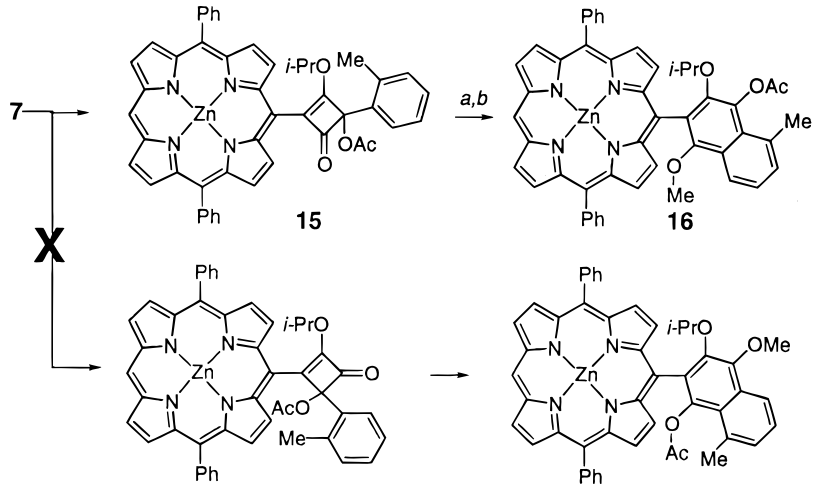
Scheme 2[a]



[a] (a) Phenyllithium for **11**; 2,5-Dimethoxyphenyllithium for **12**, THF, −78 °C; (b) NH_4Cl-H_2O; (c) xylene, reflux; (d) air, room temperature.

Scheme 3[a]



[a] (a) Xylene reflux; (b) MeI, K_2CO_3, acetone, room temperature.

with the tri-*n*-butylstannylcyclobutenedione **10** to give the desired product **8** in 76% yield (Scheme 1). Porphyrin **8** was easily purified by trituration with hexanes to remove all tin-containing compounds, followed by filtration through a silica gel plug. Metalation of **8** then gave the desired zinc complex **9**. Using the same procedure, **2** was coupled with **10** to give **6** in 84% yield, which was easily converted into the zinc complex **7** in 98% yield.

An X-ray crystal structure of **9** obtained from a single crystal grown from hexanes−ethyl acetate showed that the two squaryl rings are tilted 57.5° from the plane of the porphyrin ring (Figure 3). Nevertheless, in solution the B-band and Q-bands of the UV−vis spectra of both **7** and especially **9** are red-shifted compared to 5,15-diphenylporphyrin, suggesting a fair degree of conjugation between the squaryl ring and the porphyrin unit.

Porphyrin−Quinone Dyads from Squarylporphyrins. As anticipated, the squarylporphyrins proved to be excellent precursors to porphyrin−quinone dyads. Reaction of **7** with phenyllithium in THF at −78 °C was complete within a few minutes and gave the 1,2-adduct **11** in 89% yield after aqueous workup and chromatography. Thermal rearrangement of **11** followed by air oxidation of the intermediate hydroquinone gave the anticipated porphyrin−quinone **13** in 82% yield (Scheme 2). In a similar manner, **12** was isolated in 76% yield from the reaction of **7** with 2,5-dimethoxyphenyllithium. Rearrangement of **12** followed by air oxidation afforded **14** in 57% isolated yield.

For unsymmetrically substituted alkoxy(or amino)-cyclobutenediones, it is known that nucleophilic reagents add selectively to the carbonyl group adjacent to the heteroatom substituent.[22,23] This precedent notwithstanding, the unknown effect of the porphyrin substituent made assignment of the regiochemistry of nucleophilic addition to the porphyrinic cyclobutenedione tenuous. In an effort to determine the regiochemistry of the 1,2-adduct unambiguously, compound **16** was synthesized

(53) Fuhrhop, J.-H. In *Irreversible Reaction on the Porphyrin Periphery*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. II, p 134.

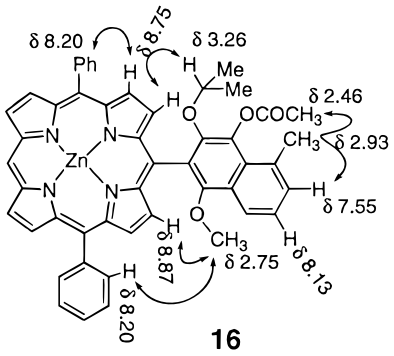


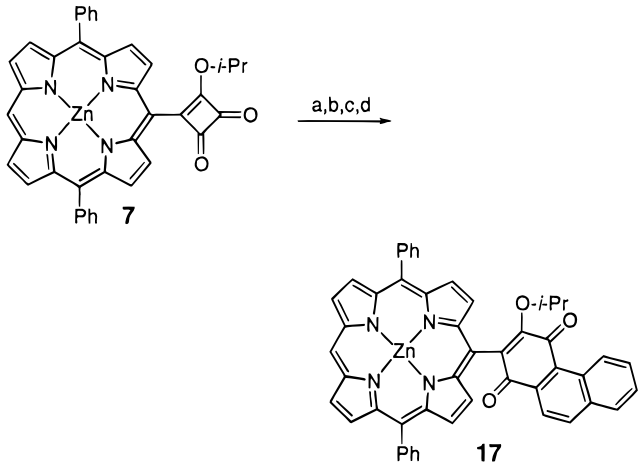
Figure 4. NOE connections obtained from the NOESY spectrum (taken in DMSO-d_6 at rt).

and subjected to NMR studies. Scheme 3 illustrates the two possible regioisomers resulting from addition to the different carbonyl groups to **7**. After addition of *o*-tolyllithium to **7**, the reaction mixture was quenched with Ac_2O to afford **15**. Thermal rearrangement of **15** led to an intermediate hydroquinone monoacetate that was unstable in air. Therefore, **15** was thermally rearranged in carefully degassed xylene, and the intermediate hydroquinone monoacetate was immediately transformed into the air-stable methyl ether **16** by direct treatment with K_2CO_3/MeI.

The analysis of the ^{1}H NMR spectrum of **16** taken at 400 MHz was not routine. The signal from the methine of the isopropyl group was clearly observable as a heptet at 3.27 ppm, but a signal for the isopropyl methyl groups was not found, presumably because of slowed rotation leading to coalescence of the isopropyl methyl groups on the 400 MHz NMR time scale.[54,55] In contrast, the ^{1}H NMR spectrum taken at 300 MHz showed a very broad peak at 0.0 ppm. In addition, the acetoxy, methoxy, and naphthylmethyl signals could not be unambiguously assigned, since they all appeared in the same region of the spectrum (2.46, 2.75, and 2.93 ppm, respectively). HETCOR, NOESY, and COSY NMR experiments were needed to assign these signals and determine the structure of **16**.

First, the methoxy protons were easily assigned using a carbon−proton chemical shift correlation experiment (HETCOR), which showed a clear cross-peak between the proton signal at 2.75 ppm and the CH_3O− carbon signal

Scheme 4[a]



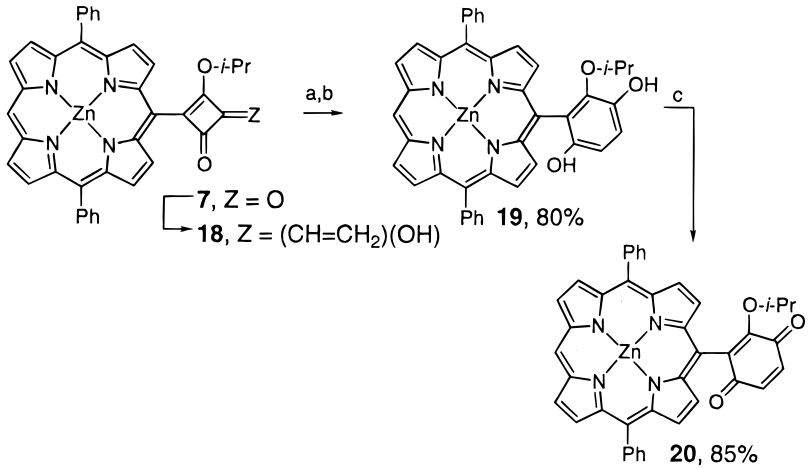
[a] (a) 1-Naphthyllithium, THF, −78 °C; (b) NH_4CL-H_2O, −78 °C; (c) xylene, reflux; (d) air, room temperature.

at 60.5 ppm. The unusual upfield displacement to 2.75 ppm of this methoxy group suggests that it sits in the shielding area of the porphyrin ring, as would be expected for structure **16**. With this signal assigned, NOE experiments then revealed the structure of **16**, the results of which are shown in Figure 4.

A NOE between the singlet at 2.93 ppm and a doublet from the naphthalene ring at 7.55 ppm indicates that the signal at 2.93 ppm originates from the naphthylmethyl substituent. This assignment was confirmed by a COSY experiment using a modified pulse sequence to enhance long-range couplings. Cross-peaks between the singlet at 2.93 ppm and both the doublet at 7.55 ppm and a triplet at 8.13 ppm (protons on the naphthalene ring) clearly demonstrate that the singlet at 2.93 ppm is the naphthylmethyl group. The unusual downfield chemical shift of the methyl might be due to the deshielding effect of the adjacent carbonyl group. Even with all the methyl groups now assigned, the lack of a NOE between the isopropoxy methine and the acetyl or methoxy groups prevented regiochemical assignment without further analysis.

The NOESY spectrum of **16** showed clear NOE connections between naphthyl ring substituents and protons on the porphyrin ring and on the *meso*-phenyl substituents. These connections, in conjunction with the COSY

Scheme 5[a]



[a] Conditions: (a) vinylMgBr, THF, −78 °C to rt; (b) aqueous NH_4Cl, −78 °C to rt; (c) DDQ, THF, rt, 5 min.

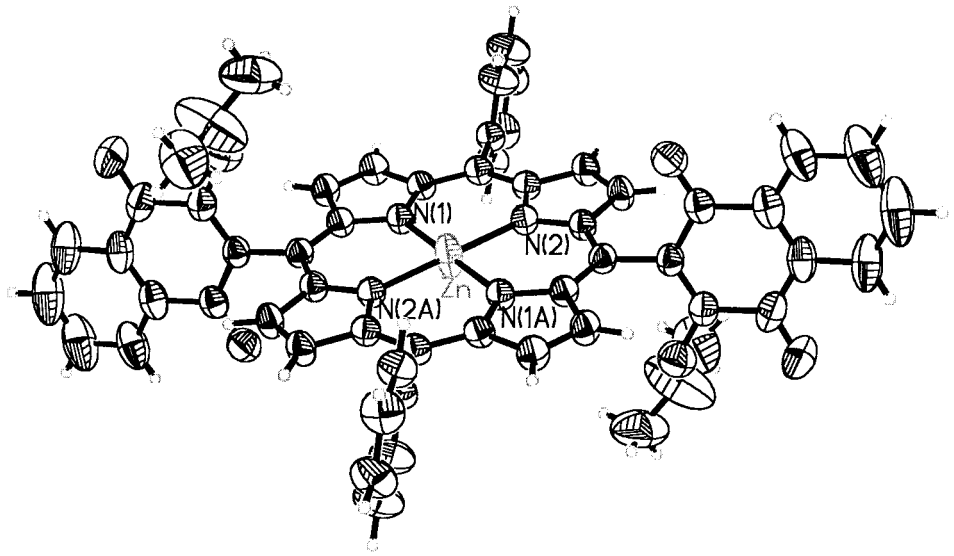
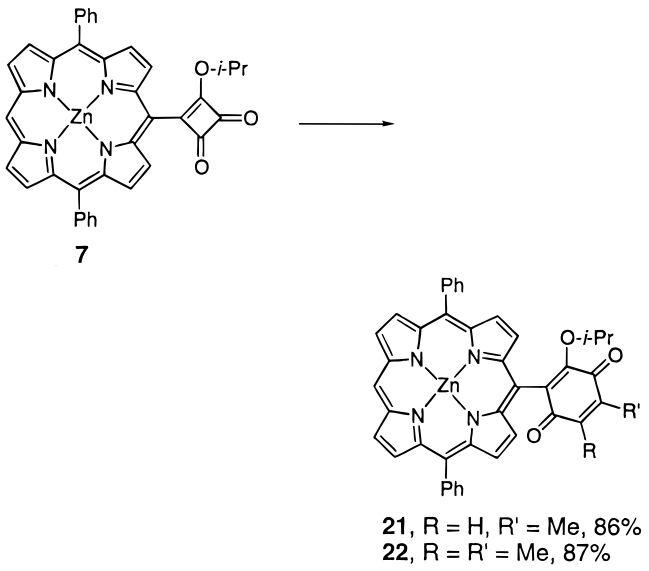


Figure 5. X-ray structure of compound **24** ($C_{58}H_{40}N_4O_6Zn \cdot 2Et_2O$. Coordinated solvent molecules are omitted for clarity.

Scheme 6



spectrum, allowed unambiguous assignments of all the proton signals. The regiochemical arrangement of the naphthyl substituents was then determined by three NOE connections: (1) between the methine proton on the isopropoxy and the β-proton on the porphyrin, (2) between the methoxy group and the β-proton of the porphyrin, and (3) between the methoxy group and the α-protons of the *meso*-phenyls. These connections verify the proximity of the isopropoxy and the methoxy groups, but not the acetoxy, to the porphyrin and securely establish the structure of compound **16** as shown in Figure 4. Therefore, these results unambiguously establish the regiochemistry of the cyclobutenedione addition reactions (Schemes 2 and Scheme 3). The lack of NOE between the methine proton on the isopropyl and the acetyl methyl is probably due to noncovalent interaction of the isopropoxy and acetyl that makes the two groups orient away from each other.[55]

Isolation and purification of the intermediate 1,2-adducts produced from addition of aryllithium reagents to **7** was not necessary for the synthesis of porphyrin−quinones. For example, **13** was synthesized in 93% isolated yield following the sequence shown in Scheme 2, but without purification of the adduct **11**. Similarly, addition of 1-naphthyllithium to **7** at −78 °C followed by quenching with NH_4Cl-H_2O at the same temperature gave a 1,2-adduct. The crude adduct was heated at reflux in xylene and then oxidized by air to afford **17** in 78% isolated yield based on **7** (Scheme 4).

Analogous reactions of monosquarylporphyrin **7** with alkenyl Grignard reagents provided a route to benzoquinone−substituted porphyrins. In contrast to the aryllithium examples described above, where the intermediate 1,2-adducts were observed, addition of 1.5 equiv of vinylmagnesium bromide to a THF solution of **7** directly generated porphyrin−hydroquinone **19** along with traces of the porphyrin−quinone **20** (Scheme 5). The porphyrinic hydroquinone was efficiently oxidized to the corresponding porphyrinic quinone with DDQ.

This overall reaction sequence was successfully extended to the addition of isopropenylmagnesium bromide and 1-methyl-1-propenylmagnesium bromide to squarylporphyrin **7**. Without isolation, the resulting mixtures of hydroquinone and quinone were subjected to DDQ oxidation to produce the porphyrin−quinones **21** and **22** in excellent yields (Scheme 6).

Quinone-Porphyrin-Quinone Triads from Bissquarylporphyrins. Following the chemistry developed above for the synthesis of **17**, quinone−porphyrin−quinone triads were synthesized from bissquarylporphyrin **9** (Scheme 7). Due to hindered rotation around the porphyrin−quinone bond, a pair of atropisomeric porphyrin−bisquinones was obtained in each case (**23**/**24** and **25**/**26**). These stereoisomers were stable at room temperature, allowing each pair to be readily separated by flash chromatography.[56−58]

(54) Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy. A Guide for Chemists*, 2nd ed.; Oxford University Press: Oxford, 1993.
(55) Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy. A Guide for Chemists*, 2nd ed.; Oxford University Press: Oxford, 1993.
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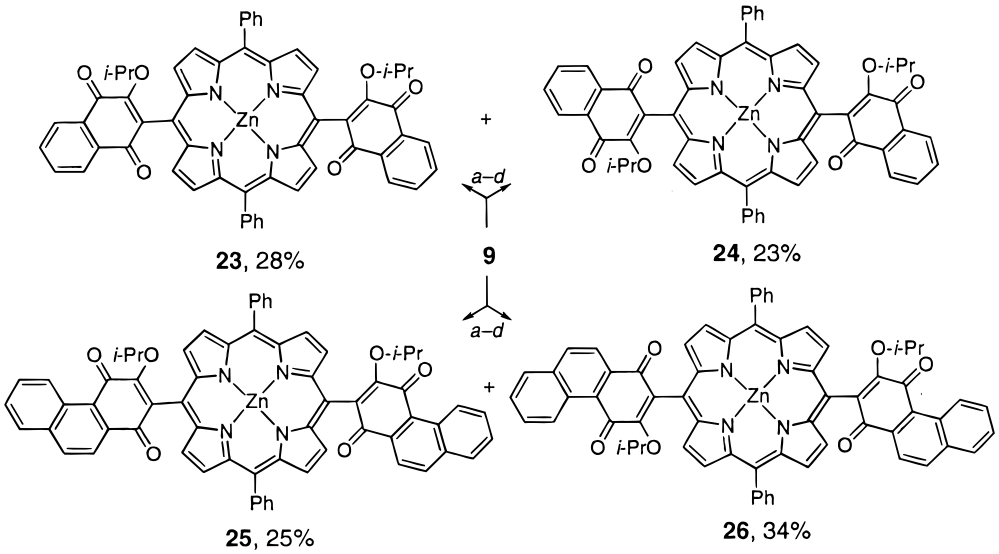
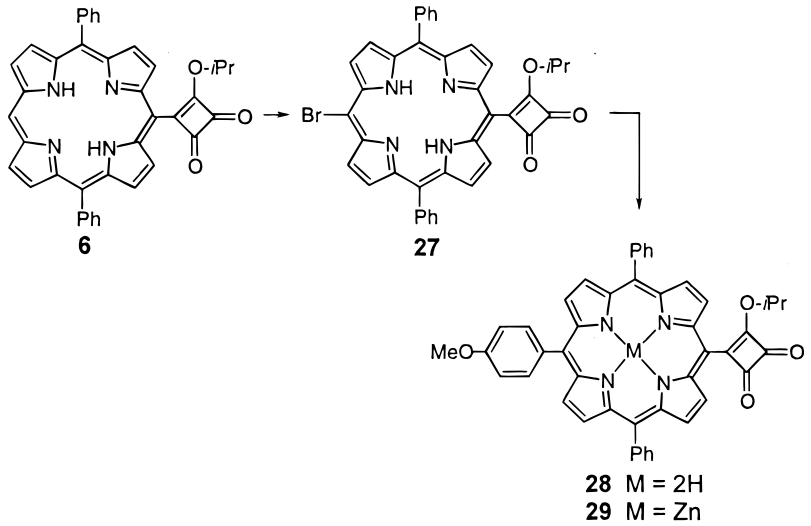
(57) Gottwald, L. K.; Ullman, E. F. *Tetrahedron Lett.* **1968**, *36*, 3071−3074.
(58) Collman, J. P.; Gagne, R. R.; Reed, C.; Halbert, T. R.; Lang, G.; Robinson, W. *J. Am. Chem. Soc.* **1975**, *97*, 1427−1439.

Scheme 7[a]



[a] a. Phenyllithium for **23** and **24**, 1-naphthyllithium for **25** and **26**, THF, −78 °C; b. NH_4Cl-H_2O, −78 °C; c. cylene, reflux; d. air, room temperature.

Scheme 8

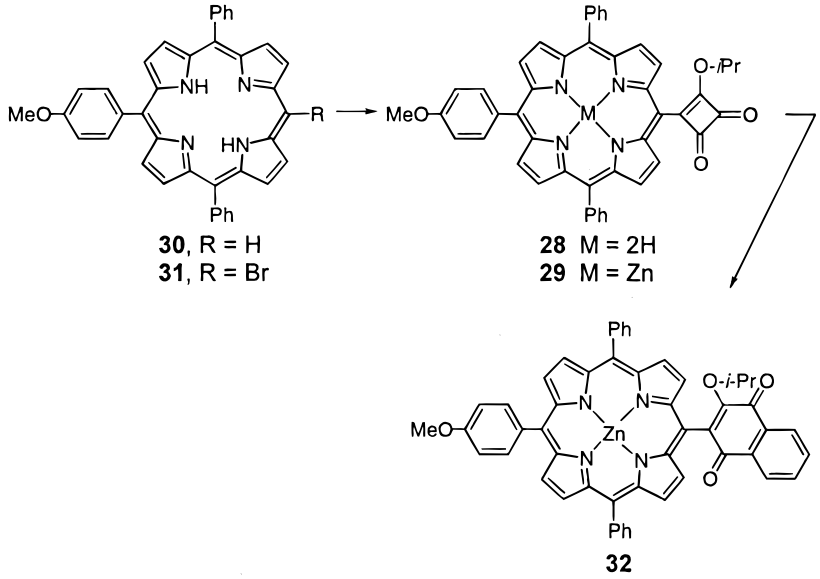


An X-ray crystal structure determination of the *anti*-isomer **24** was carried out, the ORTEP of which is shown in Figure 5. Differentiation of the two atropisomers was readily accomplished using the ^{1}H NMR spectrum: the two α-protons of the *meso*-phenyl substituents of the *anti*-isomer **24** had the same chemical shift, which is in agreement with its C2 symmetry property. However, due to the lower symmetry of the *syn*-atropisomer **23**, these two protons displayed different chemical shifts. A similar pair of atropisomers, **25** and **26**, was obtained from the reaction of 1-naphthyllithium and **9** (Scheme 7), and their structures were determined from the ^{1}H NMR spectra using the same symmetry arguments made above. Although all of these atropisomers were stable at room temperature, purified compounds **24** and **26** were readily converted into an equilibrated *anti*/*syn* mixture in an NMR tube heated at 110 °C in DMSO-d_6 for 5 min.

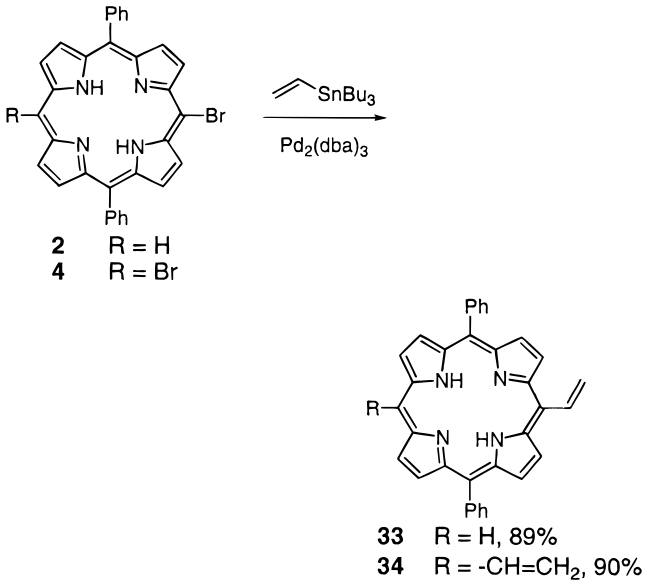
Additional Functionalization of Porphyrin−Quinone Dyads. The above reactions demonstrate a general principle for achieving structural diversity in the synthesis of porphyrinic quinones via squarylporphyrins **7** and **9**. In fact, the unsubstituted *meso*-position of porphyrinic cyclobutenedione derivatives such as **6** can be further manipulated to introduce functionality at this position and further modify the structure of the porphyrin ring. For example, bromination of monosquarylporphyrin **6** gave **27**. Free-base porphyrin **27** underwent efficient Suzuki coupling with 4-methoxyphenylboronic acid to furnish **28**, which was then easily converted into **29**, a precursor to other porphyrin−quinones (Scheme 8).

As a demonstration of the versatility of this chemistry, **29** was also synthesized by changing the order of attachment of the *p*-anisyl and the squaryl moieties (Scheme 9). Suzuki coupling of free-base porphyrin **2** with 4-methoxyphenylboronic acid gave **30**. Bromination of **30** afforded **31**, which was transformed into **28** by Stille coupling with tri-*n*-butylstannylcyclobutenedione **10**. The overall yield from **2** is 70%, compared to 44% for the procedure depicted in Scheme 8. Metalation of **28** gave **29**, which was successfully converted into porphyrinic quinone **32** in 57% yield. These transformations further demonstrate that porphyrinic cyclobutenediones are

Scheme 9



Scheme 10



readily accessible and versatile precursors to a variety of porphyrinic quinones.

Vinylogous Squarylporphyrins and Porphyrin−Quinones. Porphyrinic quinones with aromatic spacers between the porphyrin and quinone rings are relatively easy to synthesize, and many of these compounds are already known.[14,30] An intervening π-system between the porphyrin and quinone moieties allows their relative orientation and electronic communication to be tailored, factors that have recently proven vital for electron-transfer studies.[59] For the current study, 5-vinyl-10,20-diphenylporphyrins were targeted as precursors to double bond linked porphyrin−quinone compounds. To that effect, free-base bromoporphyrins **2** and **4** were easily coupled with vinyltri-*n*-butyltin and gave products **33** and **34** in 89% and 90% isolated yields, respectively (Scheme 10). These results reinforce the effectiveness of free-base porphyrins as substrates for Stille coupling reactions, and they complement the earlier studies of Therien and co-workers who carried out the same Stille cross-coupling using the zinc complex of 5,15-diphenylporphyrin.[16]

Bromination of 5-vinyl-10,20-diphenylporphyrin (**33**) with pyridinium perbromide in ethanol-free chloroform led exclusively to the *trans*-bromovinylporphyrin **35** in 44% yield (Scheme 11). The configuration about the double bond was determined from the coupling constant (13.6 Hz) between the two olefinic protons, which is comparable to the *J* value for *trans*-bromovinyl-OEP(Ni) olefin protons (14 Hz).[60] In addition, the coupling constants of the derived vinylogous cyclobutenediones (**36** and **37**; 15.6 Hz) and quinone (**38**; 16.0 Hz) compounds clearly show their *trans*-configurations (Scheme 11). The Stille reaction was applied to the bromovinylporphyrin **35**, giving the desired vinylogous cyclobutenedione−porphyrin **36** in 77% yield. Treatment with $Zn(OAc)_2$ then furnished the zinc complex **37** in 91% yield. Upon reaction of **37** with phenyllithium, the double bond linked porphyrin−quinone **38** was produced in 46% yield using the same protocol discussed above. Attempts to extend this chemistry to porphyrins attached to cyclobutenediones by way of a C−C triple bond linker have been unsuccessful thus far.

Spectroscopy. The visible spectroscopic data of the zinc metalated cyclobutenedione porphyrins are shown in Table 1.[61] In the solid-state geometries of various 5,-15-diphenylporphyrin derivatives,[16,17,62] as well as for compounds **9** and **24**, the large dihedral angles observed between *meso*-substitutents and the porphyrin ring would suggest weak conjugation between the porphyrin ring and the attached chromophores.[63] Nevertheless, strong B- and Q-band red shifts are observed relative to these of 5,15-diphenylporphyrin(Zn) (B-band, 411.0 nm;

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Scheme 11

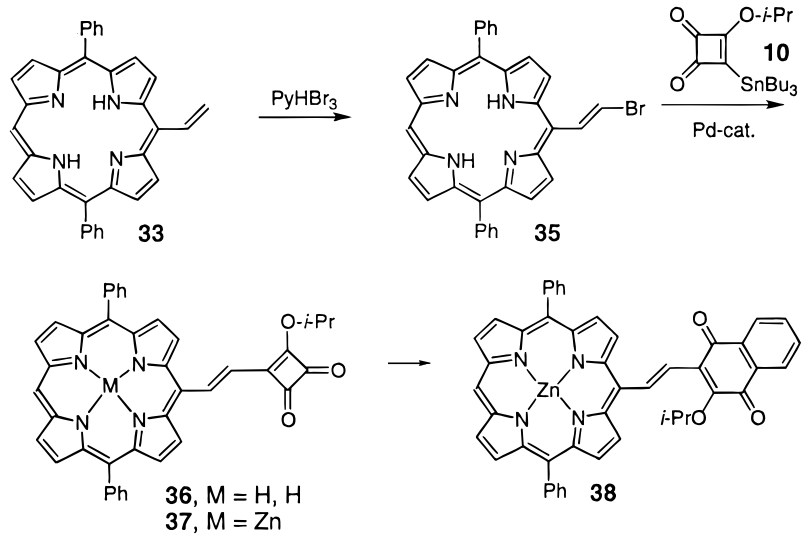

Table 1. Visible Spectra of the Porphyrinic Cyclobutenediones

	B-band		Q-bands	
compd	λ max (nm)	log ϵ	λ max (nm)	log ϵ
7	430.0	5.17	597.5	3.92
			554.5	4.00
29	438.0	5.38	617.0	4.20
			564.0	4.08
9	440.0	5.23	627.5	4.20
			570.0	3.79
37	455.5	5.23	629.0	4.36
	431.0	5.14	562.5	4.04

Q-bands, 543.0 and 579.0 nm), which suggests a reasonable degree of conjugation between the chromophores in solution.

Introduction of a double bond between the 3-cyclobutenyl-1,2-dione moiety and the porphyrin ring (**37**) produced a 31.5 and 19.5 nm red shift of the two Q-bands, relative to the absorptions of the monosquaryl porphyrin **7**. The change of the B-band of **37** is even more profound. Instead of showing a single sharp absorption, as did **7**, splitting of the band is clearly observable (Figure 6, 455.5 and 431.0 nm). Very few monomeric porphyrins show splitting of the B-band.[36,63−65] Although the B-band and Q-band absorptions of **37** were slightly blue-shifted (by 7 and 6 nm, respectively) upon a solvent change from methylene chloride to acetonitrile (Figure 6), it appears that aggregation phenomena are not responsible for the observed band splitting, since the pattern of the spectra taken in THF and methylene chloride was essentially the same.[66] B-band splitting of monomeric porphyrins which have an electron-withdrawing group at a *meso*-position (NO_2,[63] CHO,[65] and triple bonds[36]) has been attributed to charge transfer.[63,64] However, many compounds that share the above structural features do not show this split B-band absorption,[65] so it is difficult to attribute the splitting to charge transfer. Whatever the cause, these data clearly demonstrate that an intervening double bond greatly facilitates the electronic interaction between the porphyrin ring and 3-cyclobutenyl-1,2-dione, leading to significant red shifts and intensification of the longer wavelength absorption relative to the lower wavelength peak.

The visible absorption spectral data of the porphyrinic quinones are shown in Table 2. In contrast to the monosquarylporphyrins, a single *meso*-linked quinone moiety had little effect on the wavelength and intensity of the visible absorptions, compared to 5,15-diphenylporphyrin(Zn). On the other hand, the absorption of the bisquinone−porphyrins was significantly affected. The *syn*-compounds **23** and **25** gave the simplest spectra, since the longest wavelength Q-bands disappeared. The *anti*-compounds **24** and **26** displayed both Q-bands; however, they were red-shifted compared to those of 5,15-diphenylporphyrin. For compound **24** the Q-bands were red-shifted by 21.0 and 10.0 nm, whereas for **26** they were red-shifted by 14.5 and 9.5 nm.

Introduction of a double bond between the quinone and the porphyrin ring significantly changed the absorption of the porphyrin. For compound **38**, the Q-bands appeared at 633.5 and 554.5 nm, corresponding to red shifts of 54.5 and 11.5 nm, respectively, relative to the 5,15-diphenylporphyrin(Zn). As would be predicted on the basis of steric arguments, the spacer leads to better orbital interaction between the porphyrin and the quinone, compared to directly linked porphyrinic quinones.

The effects of the absorption shifts can be seen with the naked eye. All the cyclobutenedione−porphyrins are green in solution and dark green in the solid state, while the typical color of the directly linked porphyrinic quinones is red.

Conclusions

Stille coupling of 3-isopropoxy-2-tri-*n*-butylstannylcyclobutenedione with bromoporphyrins and bromovinylporphyrins produces porphyrinic cyclobutenediones. The zinc complexes of these porphyrinic cyclobutenediones proved to be excellent and versatile precursors to porphyrinic quinones. Treatment of porphyrinic cyclobutenediones with a variety of aryllithium and vinylic Grignard reagents followed by aqueous workup, thermal rearrangement, and oxidation gave the corresponding porphyrinic quinones in high yields. Therefore, a wide variety of porphyrinic quinones can now be easily syn-

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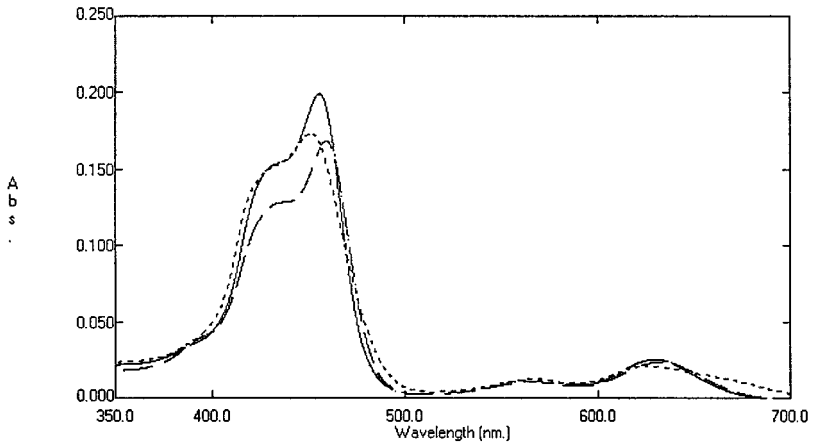

Figure 6. UV−vis spectrum of compound **37** (solid line in THF; broken line in CH_2Cl_2; dotted line in acetonitrile).

Table 2. UV−Vis Absorptions of the Porphyrin−Quinone Compounds

	B-band		Q-bands	
compd	λ max (nm)	log ϵ	λ max (nm)	log ϵ
13	414.0	5.14	584.0	4.83
			546.0	5.65
			505.0	5.11
			450.5	5.41
14	411.0	5.52	546.5	5.14
			506.5	4.97
17	414.0	5.89	546.0	5.49
			493.0	4.97
20	417.0	5.66	548.0	4.70
21	416.5	5.66	548.0	4.76
22	416.5	5.74	548.0	4.71
23	419.5	5.53	554.0	5.08
24	419.5	5.45	600.0	4.60
			553.5	5.00
25	419.0	5.38	550.0	4.95
26	420.0	5.59	593.5	4.66
			553.0	5.14
38	420.5	5.72	633.5	4.39
			554.5	4.43

thesized. Efforts are underway to use the chemistry described within this paper to synthesize novel squarylporphyrin-derived compounds, such as those depicted in Figure 1.

Experimental Section

General Methods. Tetrahydrofuran (THF) was sparged with nitrogen and then dried over 4 Å molecular sieves. The water content was ≤50 ppm as measured by a Model 447 Coulomatic K−F Titrimeter. Other solvents for reactions, extractions, and chromatography were used as received from the commercial sources. Silica gel (silica gel 60, 230−400 mesh) for flash and Baeckstrom[67] chromatography (medium pressure) was purchased from EM Science. Silica gel analytical thin-layer chromatography plates with F-254 indicator were obtained from Merck and were visualized with UV light, phosphomolybdic acid solution, or iodine. Melting points (uncorrected) were determined using a Thomas-Hoover capillary oil-immersion melting point apparatus. Phenyllithium and *tert*-butyllithium in hexanes were obtained from commercial sources and titrated with diphenyl ditelluride[68] and diphenyl acetic acid, respectively, before use. Aryllithium reagents were prepared from the corresponding aryl bromides and *tert*-butyllithium following literature procedures.[69]

Two-dimensional spectra were acquired on an INOVA-400 (400 MHz ^{1}H) spectrometer using the Varian standard microprogram at room temperature. A total of 128 t_1 increments and 1024 t_2 data points were employed. For COSY with τ (0 or 0.2 s) (pulse sequence: D1−90−D0−45−τ−FID), four scans were collected for each t_1 FID, and the spectrometer time was about 10 and 20 min, respectively. For NOESY (pulse sequence: D1−90−D0−90−mix−90−FID), 48 scans were accumulated for each t_1 FID. Two experiments with mixing times of 0.7 and 0.5 s and relaxation delays of 2 and 3 s, respectively, were performed for compound **16**. The typical spectrometer time was about 10 h. For the carbon−proton chemical shift correlation (HETCOR) spectrum of compound **16**, a total 128 t_1 increments were accumulated, and 176 scans were collected for each t_1 FID. The spectrometer time was about 12 h. DMSO-d_6 was used as the solvent for the 2D NMR experiments of **16,** and 2 drops of D_2O was added to shift the water peak away from the signal of the methine of the isopropyl group.

Starting Materials. 5,15-Diphenylporphyrin (**1**),[16] 5,15-dibromo-10,20-diphenylporphyrin (**4**),[16] 5,15-dibromo-10,20-diphenylporphyrin(Zn) (**5**),[16] and 3-isopropoxy-2-tri-*n*-butylstannylcyclobutenedione (**10**)[46] were synthesized by literature methods.

5-Bromo-10,20-diphenylporphyrin (2).[62] 5,15-Diphenylporphyrin (**1**) (3.0 g, 6.48 mmol, 1.00 equiv) and NBS (1.26 g, 7.13 mmol, 1.1 equiv) in methylene chloride (500 mL) were stirred at room temperature for 6.5 h. The volume of the solvent was reduced to 150 mL to precipitate **4**, which was filtered. The filtrate was dried, and the crude product was separated by flash chromatography (silica gel, 5 × 15 cm, hexanes−methylene chloride, gradient from 10:1 to 4:1, v/v), giving the known product **2**[62] (2.01 g, 3.72 mmol, 57%) as a brown solid of sufficient purity for subsequent reactions. Anal. Calcd for $C_{32}H_{21}N_4Br$: C, 70.99; H, 3.91; N, 10.35; Br, 14.76. Found: C, 71.06; H, 3.93; N, 10.35; Br, 14.67. In addition, dibromo compound **4** (0.47 g, 0.75 mmol, 11%) and starting material (0.22 g, 0.48 mmol, 7%) were obtained from the chromatography.

5-Bromo-10,20-diphenylporphyrin(Zn) (3).[36] 5-Bromo-10,20-diphenylporphyrin (**2**) (541 mg, 1 mmol, 1.00 equiv) in methylene chloride (200 mL) and zinc acetate (400 mg, 2.1 mmol, 2.1 equiv) in methanol (150 mL) were stirred at room temperature for 3 h and then washed three times with water to remove excess $Zn(OAc)_2$. After evaporation of the solvent, the product **3** was obtained as a red solid (592 mg, 98%) of sufficient purity for the subsequent reactions. TLC (silica gel, hexanes−methylene chloride (1:1)): R_f =0.5. Mp >250 °C (hexanes−THF). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 10.23 (s, 1 H), 9.82 (d, J = 4.5 Hz, 2 H), 9.36 (d, J = 4.8 Hz, 2 H), 9.04 (dd,

(67) Purchased from Baeckström SEPARO AB, Larsbergsvägen 24, S-181 39 Lindingö, Sweden.

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J = 4.8, 4.5 Hz, 4 H), 8.22 (d, J = 7.6 Hz, 4 H), 7.78 (m, 6 H). HRMS (FAB): calcd for $C_{32}H_{19}N_4BrZn$ 602.0084, found 602.0092.

Preparation of Squarylporphyrins 6−9. 5-(2-Isopropoxycyclobutene-3,4-dionyl)-10,20-diphenylporphyrin (6). The synthesis of this compound is representative of the preparation of other compounds by the Stille coupling reaction. To a round-bottomed flask under nitrogen were added **2** (853 mg, 1.58 mmol, 1.00 equiv), **10** (1362 mg, 3.2 mmol, 2.51 equiv), $Pd_2(dba)_3$ (72 mg, 0.079 mmol, 0.05 equiv), triphenylarsine (193 mg, 0.63 mmol, 0.40 equiv), and THF (50 mL). The mixture was stirred at 55 °C for 42 h, then solvent was removed, and the residue was triturated with hexanes three times to remove tin compounds. The crude product was initially purified by filtration through a silica gel plug (SiO_2, 3.5 × 4 cm, hexanes−methylene chloride (1:1)) to give product that was dissolved in methylene chloride and precipitated with hexanes. Filtration gave a dark brown solid (770 mg, 84%). Mp > 250 °C (hexanes−methylene chloride, diffusion). IR (KBr pellet, cm^{-1}): 3318 (m), 1785 (s),1752 (s). ^1H NMR ($CDCl_3$, 400 MHz): δ 10.22 (s, 1 H), 9.29 (d, J = 4.8 Hz, 2 H), 9.22 (d, J = 4.8 Hz, 2 H), 9.01 (d, J = 5.2 Hz, 2 H), 8.94 (d, J = 4.8 Hz, 2 H), 8.22 (dd, J = 7.2, 1.6 Hz, 4 H), 7.82 (m, 6 H), 5.86 (sept, J = 6.0 Hz, 1 H), 1.57 (d, J = 6.0 Hz, 6 H), −2.76 (s, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.2, 194.7, 194.4, 182.1, 141.2, 134.6, 132.4, 131.5, 129.3, 127.9, 126.9, 121.4, 107.8, 101.8, 80.5, 22.9. UV−vis: λ_{max} (log ϵ, CH_2Cl_2) 429.2 (5.23), 521.5 (3.99), 563.0 (4.00), 652.0 (3.36) nm. MS(FAB): m/z 601.2 (74). HRMS (FAB): calcd for $C_{39}H_{28}N_4O_3$ 600.2161, found 600.2189. The corresponding zinc complex was fully characterized, below.

Compound **7** was prepared by insertion of Zn(II) into **6** following the procedure used to prepare compound **3**, above: 5-(2-Isopropoxycyclobutene-3,4-dionyl)-10,20-diphenylporphyrin (**6**) (18 mg, 0.03 mmol), methylene chloride (5 mL), zinc acetate (16 mg, 0.088 mmol), and methanol (5 mL) yielded the product **7** (19 mg, 98%). Complete characterization is given in the following description.

5-(2-Isopropoxycyclobutene-3,4-dionyl)-10,20-diphenylporphyrin(Zn) (7). 7 was prepared by the coupling reaction of compound **3** with **10**. 5-Bromo-10,20-diphenylporphyrin(Zn) (**3**) (22 mg, 0.036 mmol, 1.00 equiv), **10** (43 mg, 0.100 mmol, 2.78 equiv), $Pd_2(dba)_3{\cdot}CHCl_3$ (7 mg, 0.007 mmol, 0.19 equiv), triphenylarsine (6 mg, 0.018 mmol, 0.50 equiv), and THF (5 mL) were heated at 60 °C with stirring for 3 d. A dark green solid (18 mg, 0.027 mmol, 75%) was obtained after chromatography (flash chromatography, silica gel, 2 × 12 cm, hexanes−ethyl acetate, gradient). TLC (silica gel, hexanes−ethyl acetate: (5:2)): R_f = 0.4. Mp > 250 °C (hexanes−ethyl acetate, diffusion). IR (KBr pellet, cm^{-1}): 1783 (s), 1750 (s), 1732 (s), 1566 (s). ^1H NMR ($(CD_3)_2CO$, 400 MHz): δ 10.37 (s, 1 H), 9.47 (d, J = 4.8 Hz, 2 H), 9.44 (d, J = 4.4 Hz, 2 H), 8.97 (d, J = 4.4 Hz, 2 H), 8.95 (d, J = 4.4 Hz, 2 H), 8.24 (dd, J = 7.2, 2.4 Hz, 4 H), 7.88−7.80 (m, 6 H), 5.89 (hept, J = 6.4 Hz, 1H), 1.57 (d, J = 6.0 Hz 6H). ^{13}C NMR ($(CD_3)_2CO$, 100 MHz): δ 199.7, 196.3, 182.6, 152.0, 151.2, 151.0, 148.7, 144.2, 135.7, 133.7, 133.7, 133.3, 131.8, 128.9, 128.0, 122.8, 109.7, 81.2, 23.6. UV−vis: λ_{max} (log ϵ, CH_2Cl_2) 430.0 (5.17), 554.5 (4.00), 597.5 (3.92) nm. MS(FAB): m/z 669.2 (8.8). HRMS (FAB): calcd for M + H^+ $C_{39}H_{26}N_4O_3Zn$ 662.1296, found M + H^+ 662.1275. Anal. Calcd for $C_{39}H_{25}N_4O_3Zn$: C, 70.65; H, 3.80; N, 8.45. Found: C, 70.46; H, 4.18; N, 8.45.

5,15-Bis(2-isopropoxycyclobutene-3,4-dionyl)-10,20-diphenylporphyrin (8). Compound **8** was prepared following the procedure used to make compound **6**, above. 5,15-Dibromo-10,20-diphenylporphyrin (**4**) (451 mg, 0.726 mmol, 1.00 equiv), **10** (1.40 g, 3.250 mmol, 4.48 equiv), $Pd_2(dba)_3{\cdot}CHCl_3$ (151 mg, 0.146 mmol, 0.20 equiv), triphenylarsine (193 mg, 0.629 mmol, 0.87 equiv), and THF (50 mL) were stirred together at 50 °C for 17 h. After removal of solvent, the crude material was triturated with hexanes and then filtered through a plug of silica gel under vacuum with 1:1 hexanes−CH_2Cl_2 to remove impurities. Elution with CH_2Cl_2 then gave the product as a dark green solid (418 mg, 0.566 mmol, 78%). TLC (silica gel, hexanes−acetone (3:1)): R_f = 0.2. Mp > 250 °C (hexanes/THF). IR (KBr pellet, cm^{-1}): 3317 (m), 1786 (s), 1754 (s). ^1H NMR ($CDCl_3$, 400 MHz): δ 9.15 (d, J = 5.2 Hz, 4 H), 8.89 (d, J = 4.8 Hz, 4 H), 8.18 (dd, J = 6.4, 1.2 Hz, 4 H), 7.81 (m, 6 H), 5.89 (sept, J = 6.0 Hz, 2 H), 1.60 (d, J = 6.0 Hz, 12 H), −2.35 (s, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.2, 194.4, 193.9, 180.7, 141.3, 134.4, 128.2, 126.9, 123.2, 104.2, 80.8, 22.9. UV−vis: λ_{max} (log ϵ, CH_2Cl_2) 441.5 (5.65), 588.0 (4.62), 679.0 (4.44) nm. MS(FAB): m/z 745 (M + Li^+) (100). HRMS (FAB): calcd for $C_{46}H_{34}O_6N_4$ Li 745.2638, found 745.2653.

5,15-Bis(2-isopropoxycyclobutene-3,4-dionyl)-10,20-diphenylporphyrin(Zn) (9). 9 was prepared from **8** following the procedure for **7**, above. A mixture of 5,15-bis(2-isopropoxycyclobutene-3,4-dionyl)-10,20-diphenylporphyrin (**8**) (212 mg, 0.28 mmol) in methylene chloride (50 mL) and $Zn(OAc)_2$ (183 mg, 1 mmol) in methanol (40 mL) was stirred at reflux temperature for 1 h, then washed three times with water, and purified through a plug of silica gel (methylene chloride−ether (1:1)). Product **9** was obtained as a dark green solid (263 mg, 86%). TLC (silica gel, hexanes−ethyl acetate (2:1)): R_f = 0.3. Mp > 250 °C (ethyl acetate). IR (KBr pellet, cm^{-1}): 1781 (s), 1752 (s). ^1H NMR ($CDCl_3$): δ 9.47 (d, J = 4.4 Hz, 4 H), 8.90 (d, J = 4.8 Hz, 4 H), 8.23 (dd, J = 7.4, 1.6 Hz, 4 H), 7.9−7.8 (m, 6 H), 5.91 (hept, J = 6.4 Hz, 2 H), 1.58 (d, J = 6.4 Hz, 12 H). ^{13}C NMR ($(CD_3)_2CO$, 100 MHz): δ 199.9, 196.3, 196.0, 181.6, 152.2, 148.8, 144.1, 135.7, 133.8, 132.5, 129.2, 128.1, 124.4, 106.4, 81.5, 23.6, 14.0. UV−vis: λ_{max} (log ϵ, CH_2Cl_2) 444.0 (5.23), 570.0 (3.79), 627.5 (4.20) nm. HRMS (FAB): calcd for $C_{46}H_{32}O_6N_4Zn$ 800.1612, found 800.1571.

Conversion of Squarylporphyrins into Porphyrinic Quinones 13−26. Representative Procedure for Preparation of Porphyrin−Quinone Compounds. A 1.2 equiv sample of phenyllithium (0.22 M in THF, 0.81 mL) was added by a syringe at −78 °C under nitrogen to a solution of 5-(3-isopropoxycyclobutene-3,4-dionyl)-10,20-diphenylporphyrin-(Zn) (**7**) (99 mg, 0.149 mmol, 1.00 equiv) dissolved in THF (10 mL). The reaction mixture immediately turned from green to red. If the starting material was detected by TLC, additional 10% portion(s) of the lithium reagent were added until the starting material was consumed. The reaction mixture was quenched with saturated aqueous ammonium chloride solution at the same temperature, and then allowed to warm to room temperature. The mixture was extracted with ether and dried over sodium sulfate. For compound **11**, the crude product was isolated by column chromatography and characterized. In all other cases, the crude products were taken up in xylene and heated at 150 °C with stirring for 15 min to 3 h. The solution was then stirred overnight under air. Xylene was distilled off under vacuum, and the crude product was isolated by flash column chromatography to obtain the desired product.

1-Phenyl-3-(10,20-diphenylporphyrozinc)-4-onecyclobutene-1-ol (11). 5-(2-Isopropoxycyclobutene-3,4-dionyl-10,20-diphenylporphyrin(Zn) (**7**) (99 mg, 0.149 mmol, 1.00 equiv), THF (10 mL), and phenyllithium (1.2 equiv, 0.22 M, 0.75 mL) yielded a purple solid product (99 mg, 0.133 mmol, 89%). TLC (silica gel, hexanes−ethyl acetate (3:2)): R_f = 0.70. Chromatographic purification (flash column, silica gel, 2 × 12 cm, hexanes−acetone (3:1)). Mp > 250 °C (methylene chloride−hexanes, diffusion procedure). IR (KBr pellet, cm^{-1}): 3500 (s), 1742 (s), 1599 (s). ^1H NMR ($CDCl_3$, 400 MHz): δ 10.08 (s, 1 H), 9.35 (d, J = 4.0 Hz, 2 H), 9.25 (d, J = 4.4 Hz, 2 H), 8.94 (d, J = 4.4 Hz, 2 H), 8.86 (d, J = 4.4 Hz, 2 H), 8.10 (d, J = 6.8 Hz, 2 H), 7.96 (d, J = 7.2 Hz, 3 H), 7.70 (t, J = 4.0 Hz, 3 H), 7.61 (br s, 1 H), 7.55 (t, J = 8.0 Hz, 2 H), 7.45 (t, J = 7.6 Hz, 1 H), 4.80 (sept, J = 6.0 Hz, 1 H), 4.60 (br s, 1 H), 1.13 (d, J = 6.0 Hz, 3 H), 0.91 (d, J = 6.0 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.2, 149.8, 149.4, 148.9, 142.3, 137.4, 134.5, 134.3, 132.9, 132.4, 131.8, 130.3, 129.3, 129.0, 128.6, 127.4, 126.4, 126.1, 120.7, 106.8, 104.2, 93.1, 79.2, 65.6, 22.4, 22.1, 15.1. UV−vis: λ_{max} (log ϵ, THF) 422.0 (5.52), 553.8 (4.08), 593.8 (3.54) nm). MS(FAB): m/z 740. HRMS (FAB): calcd for $C_{45}H_{32}N_4O_3Zn$ 740.1766, found 740.1772. Anal. Calcd for $C_{45}H_{32}N_4O_3Zn{\cdot}H_2O$: C, 71.10; H, 4.51; N, 7.37. Found: C, 71.46; H, 4.63; N, 7.01.

5-(2-Isopropoxylnaphthoquinonyl)-10,20-diphenylporphyrin(Zn) (13). With stirring, compound **11** (37 mg, 0.050 mmol, 1.00 equiv) in xylene (10 mL) was heated at reflux for

1.5 h and then left at room temperature for 3 h under air. After the xylene was removed under vacuum, the crude product was purified by column chromatography (silica gel, hexanes−acetone (2:1)), giving a purple solid (30 mg, 0.041 mmol, 82%). TLC (silica gel, hexanes−acetone (3:1)): $R_f = 0.3$. Mp 225 °C dec (hexanes−methylene chloride, diffusion). IR (KBr pellet, cm^{-1}): 1671 (s), 1598 (s). ^1H NMR ($CDCl_3$, 400 MHz): δ 10.28 (s, 1 H), 9.40 (d, $J = 4.8$ Hz, 2 H), 9.17 (d, $J = 4.8$ Hz, 2 H), 9.08 (d, $J = 4.4$ Hz, 2 H), 9.00 (d, $J = 4.8$ Hz, 2 H), 8.43 (dd, $J = 7.6$, 1.2 Hz, 1 H), 8.32 (m, 2 H), 8.25 (dd, $J = 7.2$, 1.6 Hz, 1 H), 8.18 (br d, $J = 7.2$ Hz, 2 H), 7.91 (dt, $J = 7.2$, 1.6 Hz, 1 H), 7.88 (dt, $J = 7.2$, 1.2 Hz, 1 H), 7.80 (m, 6 H), 4.57 (hept, $J = 6.0$ Hz, 1 H), 0.55 (d, $J = 6.0$ Hz, 6 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 187.0, 182.9, 158.8, 150.3, 150.0, 149.5, 148.9, 142.7, 134.7, 134.4, 134.4, 133.6, 132.8, 132.4, 131.7, 130.2, 127.4, 127.1, 126.7, 126.6, 126.5, 120.5. 106.7, 76.5, 66.0, 65.7, 22.9. UV−vis: λ_{max} (log ϵ, Et_2O) 414.0 (5.14), 450.5 (5.41), 505.0 (5.11), 546.0 (5.65), 584.0 (4.83) nm. MS(FAB): *m*/*z* 738. HRMS (FAB): calcd for $C_{45}H_{30}N_4O_3Zn$ 738.1609, found 738.1609.

5-(2-Isopropoxylnaphthoquinonyl)-10,20-diphenylporphyrin(Zn) (13) from 7 without Purification of Intermediate 11. The crude product from the aqueous workup of the reaction of **7** (66 mg, 0.099 mmol, 1.00 equiv) in THF (10 mL) with phenyllithium (1.47 equiv, 0.21 M, 0.70 mL) was taken up by xylene and refluxed for 20 min and then stirred at room temperature overnight under air. Xylene was evaporated under vacuum, and product **13** was isolated by column chromatography (SiO_2, 2.5 × 5 cm, hexanes−ether (5:1)) as a purple solid (69 mg, 0.093 mmol, 93%).

5-(2-Isopropoxy-5,8-dimethoxynaphthoquinonyl)-10,-20-diphenylporphyrin(Zn) (14). From 5-(2-isopropoxycyclobutene-3,4-dionyl)-10,20-diphenylporphyrin(Zn) (**7**) (66 mg, 0.1 mmol), THF (6 mL), and 2,5-dimethoxyphenyllithium (0.11 mmol, 1.1 equiv, 0.31 M in THF, 0.35 mL) was obtained product **12** (61 mg, 76%), which was isolated by column chromatography (silica gel, 2 × 12 cm, solvent: hexanes−acetone (10:1 to 5:2)). This product was used directly for the following thermolysis reaction without full characterization. Compound **12** (73 mg, 0.091 mmol, 1.00 equiv) in xylene (15 mL) was heated at reflux for 3 h, and then stirred at room temperature overnight under air to give **14** as a purple solid (42 mg, 0.052 mmol, 57%), which was isolated by column chromatography (flash column, silica gel, 2 × 9 cm, hexanes−acetone gradient). TLC (silica gel, hexanes−acetone (3:1)): $R_f = 0.2$). Mp > 250 °C (methylene chloride−hexanes, diffusion). IR (KBr pellet, cm^{-1}): 1667 (s). ^1H NMR ($CDCl_3$, 400 MHz): δ 10.07 (s, 1 H), 9.26 (d, $J = 4.4$ Hz, 2 H), 9.19 (d, $J = 4.8$ Hz, 2 H), 9.02 (d, $J = 4.4$ Hz, 2 H), 8.99 (d, $J = 4.8$ Hz, 2 H), 8.30 (dd, $J = 4.4$, 2.4 Hz, 2 H), 8.17 (dd, $J = 8.0$, 1.2 Hz, 2 H), 7.78 (m, 6 H), 7.33 (s, 2 H), 4.65 (sept, $J = 6.0$ Hz, 1 H), 4.06 (s, 3 H), 3.77 (s, 3 H), 0.64 (d, $J = 6.0$ Hz, 6 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 186.5, 182.2, 158.6, 153.8, 150.1, 150.0, 149.2, 149.1, 142.7, 134.7, 134.4, 133.4, 132.7, 132.2, 131.6, 130.5, 127.4, 126.5, 126.5, 121.7, 121.6 121.3, 120.3, 119.5, 106.4, 75.8, 65.6, 57.0, 56.9, 29.7, 22.8. UV−vis: λ_{max} (log ϵ, Et_2O) 411.0 (5.52), 506.5 (4.59), 546.5 (5.14) nm. MS(FAB): *m*/*z* 799.8. HRMS (FAB): calcd for $C_{47}H_{34}N_4O_5Zn$ 798.1821, found: 798.1799.

5-(2- Isopropoxy-3- acetoxy-5-methyl-10-methoxynaphthyl)-10,20-diphenylporphyrin(Zn) (16). 2-Methylphenyllithium (0.21 M in THF, 0.57 mL, 1.2 equiv) was added dropwise under nitrogen to a 25 mL round-bottomed flask containing 5-(2-isopropoxycyclobutene-3,4-dionyl)-10,20-diphenylporphyrin(Zn) (**7**) (66 mg, 0.1 mmol) in THF (6 mL) at −78 °C. After 10 min the reaction was quenched with acetic anhydride (10 equiv) at −78 °C and then stirred at room temperature for 1 h. After removal of the solvent and chromatography (flash, SiO_2, 2 × 10 cm, hexanes−acetone (6:1)), the intermediate product **15** was obtained as a red solid (77 mg, 65%). A portion of compound **15** (6 mg, 0.076 mmol) was dissolved in xylene (5 mL) and carefully degassed using a freeze−thaw procedure and then heated at reflux under nitrogen atmosphere for 2 h. After the xylene was removed under vacuum, potassium carbonate (20 mg, 0.14 mmol) was added immediately under nitrogen. Acetone (3 mL) and iodomethane (45 mg, 0.32 mmol) were added to the mixture by a syringe, and the reaction mixture was stirred at room temperature overnight. After the reaction was complete (judged by TLC), the potassium carbonate was filtered off and the crude product was isolated by preparative TLC (SiO_2, 20 × 20 cm, 0.5 mm, hexanes−ether (3:1)), producing the desired compound **16** as a red solid (4 mg, 66%). TLC (silica gel, hexanes−acetone (3:2)): $R_f = 0.5$. Mp > 250 °C (methylene chloride−hexanes, diffusion). IR (KBr pellet, cm^{-1}): 1768 (m), 1733 (m), 1653 (m), 1635 (m). ^1H NMR ($CDCl_3$, 400 MHz): δ 10.27 (s, 1 H), 9.40 (d, $J = 4.4$ Hz, 2 H), 9.09 (d, $J = 4.4$ Hz, 4 H), 9.02 (d, $J = 4.4$ Hz, 2 H), 8.26 (m, 5 H), 7.78 (br s, 6 H), 7.49 (d, $J = 2.8$ Hz, 2 H), 3.28 (hept, $J = 6.4$ Hz, 1 H), 3.02 (s, 3 H), 2.79 (s, 3 H), 2.46 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.4, 154.7, 150.6, 150.2, 150.2, 149.3, 147.9, 142.6, 134.6, 132.9, 132.8, 132.3, 131.7, 130.7, 128.8, 128.4, 127.5, 126.5, 125.5, 121.7, 120.4, 111.1, 106.6, 75.8, 61.5, 23.7, 21.7, 21.5. UV−vis: λ_{max} (log ϵ, CH_2Cl_2) 417 (5.68), 548 (4.27), 586 (3.37) nm. MS(FAB): *m*/*z* 810 (100). HRMS (FAB): calcd for $C_{49}H_{38}N_4O_4Zn$ 810.2185, found 810.2189.

5-(2-Isopropoxy-3,10-phenanthroquinonyl)-10,20-diphenylporphyrin(Zn) (17). 1-Naphthyllithium (0.5 mL, 0.43 M in THF, 1.1 equiv) and 5-(2-isopropoxycyclobutene-3,4-dionyl)-10,20-diphenylporphyrin(Zn) (**7**) (132 mg, 0.199 mmol) in THF (12 mL) gave a 1,2-adduct, which was isolated and then heated in refluxing xylene for 30 min. After air oxidation and isolation (flash column, silica gel, 2 × 9 cm, hexanes−ether (25:7)), the product **17** was obtained (123 mg, 0.156 mmol, 78%) as a purple solid. TLC (silica gel, hexanes−ether (1:2), v/v): $R_f = 0.3$. Mp > 250 °C (methylene chloride−hexanes, diffusion). IR (KBr pellet, cm^{-1}): 1663 (s), 1599 (s). ^1H NMR ($CDCl_3$, 400 MHz): δ 10.28 (s, 1 H), 9.71 (d, $J = 8.8$ Hz, 1 H), 9.41 (d, $J = 4.4$ Hz, 2 H), 9.23 (d, $J = 4.4$ Hz, 2 H), 9.09 (d, $J = 4.4$ Hz, 2 H), 9.02 (d, $J = 4.4$ Hz, 2 H), 8.33−8.18 (m, 6 H), 7.96 (d, $J = 8.0$ Hz, 1 H), 7.86−7.68 (m, 8 H), 4.48 (hept, $J = 6.0$ Hz, 1 H), 0.65 (d, $J = 6.0$ Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 185.2, 150.3, 150.1, 149.5, 142.6, 136.4, 135.4, 134.7, 134.4, 132.9, 132.4, 131.8, 130.3, 130.2, 128.9, 128.6, 127.8, 127.5, 126.6, 126.5, 122.7, 120.6, 106.7, 76.4, 65.7, 22.7. UV−vis: λ_{max} (log ϵ, Et_2O) 414.0 (5.89), 493.3 (4.97), 546.0 (5.49) nm. MS(FAB): *m*/*z* 789; HRMS (FAB): calcd for $C_{49}H_{32}O_3N_4Zn$ 788.1765, found 788.1735.

5,15-Diphenyl-10-(2-isopropoxy-3,6-hydroxybenzene)-porphyrin(Zn) (19) and 5,15-Diphenyl-10-(2-isopropoxy-3,6-benzoquinone)porphyrin(Zn) (20). Vinylmagnesium bromide (0.22 mL, 1.0 M in THF, 0.22 mmol) was added dropwise to a solution of 5-(2-isopropoxycyclobutene-3,4-dionyl)-10,20-diphenylporphyrin(Zn) (**7**) (100 mg, 0.15 mmol) in THF (20 mL) in a 50 mL round-bottomed flask under nitrogen at −78 °C. The reaction mixture was allowed to warm to room temperature and then recooled to −78 °C, and a few drops of aqueous ammonium chloride were added. After being warmed to room temperature, the reaction mixture was partitioned between water−dichloromethane, then the organic layer was dried over anhydrous sodium sulfate, and the solvent was evaporated. Primary purification of the crude product by flash column chromatography (silica gel, 2.5 × 10 cm) using 10−20% THF−hexanes as the eluant to afford hydroquinone **19** (83 mg, 80%) and quinone **20** (18 mg, 17%), both as red solids. The hydroquinone could not be completely separated from the quinone.

Product 19. TLC (silica gel, THF−hexanes (1:3)): $R_f = 0.23$. IR (KBr pellet, cm^{-1}): 3535 (w). ^1H NMR ($CDCl_3$, 400 MHz): δ 10.28 (s, 1 H), 9.40 (d, $J = 4.8$ Hz, 2 H), 9.10 (d, $J = 4.4$ Hz, 2 H), 9.02 (s, 4 H), 8.27−8.30 (m, 2 H), 8.19−8.24 (m, 2 H), 7.75−7.84 (m, 6 H), 7.20 (d, $J = 8.8$ Hz, 1 H), 6.89 (d, $J = 8.8$ Hz, 1 H), 5.61 (s, 1 H), 4.68 (s, 1 H), 2.86 (hept, $J = 6$ Hz, 1 H), 0.14 (d, $J = 6$ Hz, 6 H). HRMS (FAB): calcd for $C_{41}H_{30}N_4O_3Zn$ 690.1609, found 690.1635.

Product 20. TLC (silica gel, THF−hexanes (1:3)): $R_f = 0.39$. Mp > 250 °C (ethyl acetate−hexanes, diffusion). IR (KBr pellet, cm^{-1}): 1673 (m), 1651 (m). ^1H NMR ($CDCl_3$, 400 MHz): δ 10.23 (s, 1 H), 9.37 (d, $J = 4.4$ Hz, 2 H), 9.11 (d, $J = 4.4$ Hz, 2 H), 9.07 (d, $J = 4.8$ Hz, 2 H), 9.02 (d, $J = 4.8$ Hz, 2 H), 8.28−8.33 (m, 2 H), 8.18−8.23 (m, 2 H), 7.75−7.84 (m, 6

H), 7.18 (d, J = 10.4 Hz, 1 H), 7.13 (d, J = 10.4 Hz, 1 H), 4.27 (hept, J = 6.0 Hz, 1 H), 0.51 (d, J = 6.0 Hz, 6 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 189.8, 184.7, 150.6, 150.3, 149.8, 149.0, 142.7, 137.2, 135.9, 134.9, 134.7, 133.2, 132.8, 132.1, 130.3, 127.7, 126.9, 126.8, 120.9, 107.1, 76.4, 22.5. UV−vis: λ_{max} (log ϵ, THF) 417.0 (5.66), 548.0 (4.70) nm. HRMS (FAB): calcd for $C_{41}H_{28}N_4O_3Zn$ 688.1453, found 688.1480.

Oxidation of 19 to 20 by DDQ. In a 25 mL round-bottomed flask hydroquinone **19** (58 mg, 0.084 mmol) in THF (10 mL) was treated with DDQ (28 mg, 0.125 mmol) under nitrogen for 5 min at room temperature. The solvent was evaporated, and the product was purified by flash column chromatography using 10−20% THF−hexanes as the eluant to provide quinone **20** (49 mg, 85%) as a red solid (data given above).

5,15-Diphenyl-10-(2-isopropoxy-4-methyl-3,6-benzoquinone)porphyrin(Zn) (21). Isopropenylmagnesium bromide (0.45 mL, 0.225 mmol, 0.5 M in THF) was added slowly to a solution of 5-(2-isopropoxycyclobutene-3,4-dionyl)-10,20-diphenylporphyrin(Zn) (**7**) (100 mg, 0.15 mmol) in THF (20 mL) at −78 °C, then the reaction mixture was allowed to warm to room temperature. After the solution was recooled to −78 °C, a few drops of aqueous ammonium chloride were added. After being warmed to room temperature, the mixture was partitioned between dichloromethane−water and dried over sodium sulfate, and the solvent was evaporated. The crude product was dissolved in THF (10 mL) and treated with DDQ (51 mg, 0.225 mmol). After the solution was stirred at room temperature for 5 min, the solvent was evaporated and the product was purified by flash column chromatography (silica gel, 2.5 × 10 cm, 10−20% THF−hexanes) to provide **21** (91 mg, 86%) as a red solid. TLC (silica gel, THF−hexanes (1:3)): R_f = 0.45. Mp > 250 °C (acetone−hexanes, diffusion). IR (KBr pellet, cm^{-1}): 1651 (w), 1588 (w). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 10.20 (s, 1 H), 9.35 (d, J = 4.5 Hz, 2 H), 9.11 (d, J = 4.8 Hz, 2 H), 9.07 (d, J = 4.5 Hz, 2 H), 9.01 (d, J = 4.5 Hz, 2 H), 8.27−8.33 (m, 2 H), 8.17−8.23 (m, 2 H), 7.76−7.84 (m, 6 H), 6.91 (s, 1 H), 4.19 (hept, J = 6.3 Hz, 1 H), 2.41 (s, 3 H), 0.50 (d, J = 6.3 Hz, 6 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 189.5, 185.1, 150.4, 150.1, 149.50, 149.0, 145.0, 142.7, 134.9, 134.6, 133.8, 133.0, 132.5, 131.9, 130.3, 127.6, 126.8, 126.7, 125.7, 120.8, 106.80, 76.3, 30.7, 22.9. UV−vis: λ_{max} (log ϵ, THF) 416.5 (5.66), 548.0 (4.76) nm. HRMS (FAB): calcd for $C_{42}H_{30}N_4O_3Zn$ 702.1609, found 702.1609.

5,15-Diphenyl-10-(2-isopropoxy-4,5-dimethyl-3,6-benzoquinone) porphyrin (Zn) (22). Following a procedure similar to that for **21**, starting from **7** (100 mg, 0.15 mmol) and 1-methyl-1-propenylmagnesium bromide (0.5 M in THF, 0.45 mL, 0.225 mmol), **22** (94 mg, 87%) was obtained as a red solid after purification (flash column, silica gel, 2.5 × 10 cm). TLC (silica gel, hexanes−THF (3:1)): R_f = 0.52. Mp >250 °C (acetone−hexanes, diffusion). IR (KBr pellet, cm^{-1}): 1656 (w), 1598 (w). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 10.20 (s, 1 H), 9.35 (d, J = 4.5 Hz, 2 H), 9.15 (d, J = 4.8 Hz, 2 H), 9.06 (d, J = 4.8 Hz, 2 H), 9.01 (d, J = 4.8 Hz, 2 H), 8.26−8.37 (m, 2 H), 8.15−8.24 (m, 2 H), 7.72−7.88 (m, 6 H), 4.26 (hept, J = 6.0 Hz, 1 H), 2.42 (s, 3 H), 2.28 (s, 3 H), 0.54 (d, J = 6.0 Hz, 6 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 189.6, 187.1, 150.3, 150.1, 149.6, 149.1, 143.0, 134.9, 134.6, 132.8, 132.5, 131.8, 130.3, 127.5, 126.7, 120.6, 106.8, 76.0, 31.9, 25.1, 22.9. UV−vis: λ_{max} (log ϵ, THF) 416.5 (5.74), 548.0 (4.71) nm. HRMS (FAB): calcd for $C_{43}H_{32}N_4O_3Zn$ 716.1766, found 716.1794.

***syn*-5,15-Bis(2-isopropoxynaphthoquinonyl)-10,20-diphenylporphyrin(Zn) (23) and *anti*-5,15-Bis(2-isopropoxynaphthoquinonyl)-10,20-diphenylporphyrin(Zn) (24).** Following the general procedure, above, 5,15-bis(2-isopropoxycyclobutene-3,4-dionyl)-10,20-diphenylporphyrin(Zn) (**9**) (120 mg, 0.149 mmol) in THF (7 mL) and phenyllithium in hexanes (1.8 mL, 0.21 M, 0.447 mmol, 3 equiv) at −78 °C gave the 1,2-adduct. This was refluxed in xylene for 30 min followed by air oxidation to afford a mixture of compounds **23** and **24**, which were separated by column chromatography (flash column, silica gel, 2.5 × 10 cm, hexanes−ether (20:3) gradient, compound **23** was eluted after compound **24**).

Product 23. Purple solid (40 mg, 0.042 mmol, 28%). TLC (silica gel, hexanes−acetone (3:1)): R_f = 0.4). Mp > 250 °C (methylene chloride−hexanes, diffusion). IR (KBr pellet, cm^{-1}): 1672 (s), 1597 (s), 1557 (w). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.14 (d, J = 4.4 Hz, 4 H), 8.95 (d, J = 4.4 Hz, 4 H), 8.42 (dd, J = 7.6, 1.2 Hz, 2 H), 8.32 (m, 2 H), 8.24 (dd, J = 7.6, 1.2 Hz, 2 H), 8.12 (d, J = 7.2 Hz, 2 H), 7.93 (dt, J = 7.6, 1.6 Hz, 2 H), 7.88 (dt, J = 7.6, 1.6 Hz, 2 H), 7.76 (m, 6 H), 4.69 (hept, J = 6.0 Hz, 2 H), 0.64 (d, J = 6.0 Hz, 12 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 186.9, 182.9, 158.9, 150.3, 149.0, 142.6, 134.4, 134.2, 133.7, 132.8, 132.2, 130.3, 127.5, 127.1, 126.7, 126.6, 126.4, 121.1, 109.6, 76.7, 22.7. UV−vis λ_{max} (log ϵ, ether) 419.0 (5.53), 554.0 (5.08) nm. MS(FAB): m/z 952. HRMS (FAB): calcd for $C_{58}H_{40}N_4O_6Zn$ 952.2239, found: 952.2238.

Product 24. Purple solid (32 mg, 0.034 mmol, 23%). TLC (silica gel, hexanes−acetone (3:1)): R_f = 0.4. Mp > 250 °C (hexanes−ether (20:3)). IR (KBr pellet, cm^{-1}): 1672 (s), 1597 (s). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.14 (d, J = 4.8 Hz, 4 H), 8.94 (d, J = 4.4 Hz, 4 H), 8.43 (dd, J = 8.0, 1.2 Hz, 2 H), 8.24 (dd, J = 7.2, 1.2 Hz, 2 H), 8.21 (dd, J = 7.6, 1.6 Hz, 4 H), 7.92 (dt, J = 7.6, 1.2 Hz, 2 H), 7.86 (dt, J = 7.6, 1.2 Hz, 2 H), 7.76 (m, 6 H), 4.51 (hept, J = 6.4 Hz, 2 H), 0.56 (d, J = 6.4 Hz, 12 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 186.9, 182.8, 158.9, 150.3, 149.0, 142.6, 134.5, 134.4, 133.9, 133.7, 132.8, 132.3, 130.3, 127.5, 127.1, 126.7, 126.5, 121.3, 109.5, 22.7. UV−vis: λ_{max} (log ϵ, Et_2O) 419.5 (5.45), 553.5 (5.00), 600.0 (4.60) nm. MS(FAB): m/z 952. HRMS (FAB): calcd for M + H^+ $C_{58}H_{41}N_4O_6Zn$ 953.2318, found: M + H^+ 953.2361. Anal. Calcd for $C_{58}H_{40}N_4O_6Zn{\cdot}2OEt_2$: C, 71.89; H, 5.49; N, 5.08. Found: C, 71.71; H, 5.48; N, 5.10. (Note: The x-ray structure also revealed that each molecule bonded with two molecules of ether).

***syn*-5,15-Bis(2-isopropoxyphenanthroquinonyl)-10,20-diphenylporphyrin(Zn) (25) and *anti*-5,15-Bis(2-isopropoxyphenanthroquinonyl)-10,20-diphenylporphyrin-(Zn) (26).** Following the general procedure, above, 5,15-bis(2-isopropoxycyclobutene-3,4-dionyl)-10,20-diphenylporphyrin(Zn) (**9**) (140 mg, 0.175 mmol) in THF (14 mL) and 1-naphthyllithium (1.1 mL, 0.43 M in THF, 2.7 equiv) at −78 °C afforded the adduct. This was refluxed in xylene for 30 min followed by air oxidation to afford a mixture of compounds **25** and **26**, which were separated by column chromatography (flash column, silica gel, 2 × 8 cm, ether−methylene chloride (1:50), **26** eluted before **25**).

Product 25. Purple solid (46 mg, 0.044 mmol, 25%). TLC (silica gel, ether−methylene chloride (1:10)): R_f = 0.6. Mp > 250 °C (hexanes−methylene chloride, diffusion). IR (KBr pellet, cm^{-1}): 1663 (s), 1648 (s), 1621 (m), 1664 (s). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.71 (d, J = 8.8 Hz, 2 H), 9.20 (d, J = 4.8 Hz, 4 H), 8.96 (d, J = 4.8 Hz, 4 H), 8.36 (d, J = 8.4 Hz, 2 H), 8.32 (m, 2 H), 8.29 (d, J = 8.4 Hz, 2 H), 8.13 (br d, J = 7.2 Hz, 2 H), 8.03 (br d, J = 8.0 Hz, 2 H), 7.88 (dt, J = 7.2, 1.2 Hz, 2 H), 7.73 (m, 8 H), 4.59 (hept, J = 6.0 Hz, 2 H), 0.70 (d, J = 6.4 Hz, 14 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 187.7, 185.3, 159.8, 150.4, 149.2, 142.6, 136.5, 135.5, 134.8, 134.2, 132.9, 132.8, 130.8, 130.5, 130.3, 130.1, 129.0, 128.6, 127.9, 127.8, 127.5, 126.6, 126.4, 122.7, 121.2, 109.3, 76.4, 22.8. UV−vis: λ_{max} (log ϵ, Et_2O) 419.0 (5.38), 550.0 (4.95) nm. MS(FAB): m/z 1052 (74). HRMS (FAB): calcd for $C_{66}H_{44}N_4O_6Zn$ 1052.2552, found 1052.2546.

Product 26. Purple solid (63 mg, 0.060 mmol, 34%). TLC (silica gel, ether−methylene chloride (1:10)): R_f = 0.7. Chromatographic purification (flash column, silica gel, 2 × 8 cm, ether−methylene chloride (2:25)). Mp > 250 °C (methylene chloride−hexanes, diffusion). IR (KBr pellet, cm^{-1}): 1663 (s), 1603 (s). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.57 (d, J = 8.4 Hz, 2 H), 9.38 (d, J = 4.4 Hz, 4 H), 8.73 (d, J = 4.8 Hz, 4 H), 8.51 (d, J = 8.4 Hz, 2 H), 8.26−8.18 (m, 8 H), 7.97 (dt, J = 7.2 Hz, 2 H), 7.86 (dt, J = 7.2 Hz, 2 H), 7.80 (m, 6 H), 4.74 (hept, J = 6.0 Hz, 2 H), 0.67 (d, J = 6.0 Hz, 12 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 187.7, 185.2, 159.7, 150.3, 149.2, 142.6, 136.5, 135.5, 134.5, 132.9, 132.7, 130.4, 130.3, 130.0, 128.9, 128.6, 127.9, 127.8, 127.5, 126.5, 122.7, 121.3, 109.2, 76.5, 29.7, 22.7. UV−vis: λ_{max} (log ϵ, Et_2O) 420.0 (5.59), 553.0 (5.14), 593.0 (4.66) nm. HRMS (FAB): calcd for $C_{66}H_{44}N_4O_6Zn$ 1052.2551, found 1052.2546.

Other Transformations of Porphyrin−Quinone Dyads. 5-(2-Isopropoxycyclobutene-3,4-dionyl)-15-bromo-10,20-diphenylporphyrin (27). 5-(2-Isopropoxycyclobutene-3,4-dionyl)-10,20-diphenylporphyrin (**6**) (120 mg, 0.200 mmol) and NBS (48 mg, 0.27 mmol) in methylene chloride (50 mL) in a 100 mL round-bottomed flask were stirred at room temperature for 5 h. After removal of the solvent, the crude product was isolated by flash column chromatography (flash column, silica gel, 3.5 × 10 cm, hexanes−methylene chloride (1:3)) to give a dark green solid (114 mg, 0.168 mmol, 84%). TLC (silica gel, hexanes−methylene chloride (1:3)): $R_f = 0.35$). Mp > 250 °C(methylene chloride−hexanes, diffusion). IR (KBr pellet, cm^{-1}): 3318 (w),1785 (s), 1754 (s), 1581 (s). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.61 (d, $J = 5.2$ Hz, 2 H), 9.11 (d, $J = 4.8$ Hz, 2 H), 8.87 (d, $J = 4.8$ Hz, 2 H), 8.81 (d, $J = 4.8$ Hz, 2 H), 8.17 (dt, $J = 6.4$, 1.6 Hz, 4 H), 7.84−7.75 (m, 6 H), 5.88 (hept, $J = 6.0$ Hz, 1 H), 1.59 (d, $J = 6.0$ Hz, 6 H), −2.39 (s, 2 H). UV−vis: λ_{max} (log ϵ, CH_2Cl_2) 429 (5.48), 526 (4.22), 567 (4.42), 606 (3.95), 665 (4.16) nm. MS(FAB): *m*/*z* 679. HRMS (FAB): calcd for M + Li^+ $C_{39}H_{27}N_4O_3BrLi$ 685.1427, found: 685.1413.

5-(2-Isopropoxycyclobutene-3,4-dionyl)-15-(4-methoxyphenyl)-10,20-diphenylporphyrin (28) from Suzuki Coupling of 27 with *p*-Anisylboronic Acid. A mixture of 5-(2-isopropoxycyclobutene-3,4-dionyl)-15-bromo-10,20-diphenylporphyrin (**27**) (17 mg, 0.025 mmol), 4-methoxyphenylboronic acid (8 mg, 0.05 mmol), $Pd(Ph_3P)_4$ (4 mg, 0.0038 mmol), and potassium carbonate (28 mg, 0.20 mmol) in toluene (10 mL) was heated at 90 °C for 20 h under nitrogen. The product was purified by filtration through a plug of silica gel (2 × 2 cm) under vacuum (hexane−methylene chloride (1:1)). The product **27** was obtained as a dark green solid (11 mg, 62%). TLC (silica gel, hexanes−acetone (3:2)): $R_f = 0.34$). Mp > 240 °C (methylene chloride−hexanes, diffusion). IR (KBr pellet, cm^{-1}): 3315 (w),1785 (s), 1752 (s), 1575 (s). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.16 (d, $J = 4.8$ Hz, 2 H), 8.92 (d, $J = 4.8$ Hz, 2 H), 8.83 (d, $J = 4.8$ Hz, 2 H), 8.76 (d, $J = 4.8$ Hz, 2 H), 8.19 (dt, $J = 6.0$, 1.2 Hz, 4 H), 8.10 (d, $J = 8.4$ Hz, 2 H), 7.81−7.75 (m, 6 H), 7.29 (d, $J = 8.8$ Hz, 2 H), 5.89 (hept, $J = 6.4$ Hz, 1 H), 4.09 (s, 3 H), 1.60 (d, $J = 6.4$ Hz, 6 H), −2.35 (s, 2 H). UV−vis: λ_{max} (log ϵ, CH_2Cl_2) 431 (5.58), 525 (4.12), 568 (4.36), 598 (3.81), 660 (4.01) nm. MS(FAB): *m*/*z* 713 (100). Anal. Calcd for $C_{46}H_{34}N_4O_4$: C, 78.17; H, 4.85; N, 7.93. Found: C, 77.92; H, 4.96; N, 7.66.

5-(2-Isopropoxycyclobutene-3,4-dionyl)-15-(4-methoxyphenyl)-10,20-diphenylporphyrin (**28**) is better prepared by the Stille coupling of **31** (described below) with **10.**

5-(2-Isopropoxycyclobutene-3,4-dionyl)-15-(4-methoxyphenyl)-10,20-diphenylporphyrin (28) from Stille Coupling of 31 and 10. 5-Bromo-15-(4-methoxyphenyl)-10,20-diphenylporphyin (**31**) (90 mg, 0.15 mmol; see below), compound **10** (125 mg, 0.29 mmol), $Pd_2(dba)_3$ (7 mg, 0.0075 mmol), and triphenylarsine (13.8 mg, 0.045 mmol) in THF (10 mL) were heated at 55 °C for 21 h under nitrogen. After removal of the solvent the residue was taken up in methylene chloride and ethyl acetate (1:2). Saturated aqueous KF solution was added, and the mixture was stirred at room temperature for 30 min. The organic layer was separated, dried, concentrated, and purified by filtration through a plug of silica gel (4.2 × 2 cm) under vacuum (hexanes−methylene chloride (1:1)). The product was obtained as a dark green solid (95 mg, 0.134 mmol, 88%).

5-(2-Isopropoxycyclobutenedionyl)-15-(4-methoxyphenyl)-10,20-diphenylporphyrin(Zn) (29). A mixture of 5-(2-isopropoxycyclobutenedionyl)-15-(4-methoxyphenyl)-10,20-diphenylporphyrin (**28**) (64 mg, 0.091 mmol, 1.00 equiv) in methylene chloride (50 mL) and zinc acetate (50 mg, 0.273 mmol, 3.00 equiv) in methanol (20 mL) was stirred at room temperature for 2.5 h. The mixture was poured into water, and the organic phase was separated and washed three times with water. After removal of the solvent, a dark green solid was obtained (70 mg, 0.091 mmol, 100%). Mp > 250 °C (at 210 °C the crystals shrunk and changed color from dark green to purple) (methylene chloride−hexanes, diffusion). IR (KBr pellet, cm^{-1}): 1782 (s), 1751 (s), 1571 (s). ^{1}H NMR (acetone-d_6, 400 MHz): δ 9.44 (d, $J = 4.8$ Hz, 2 H), 8.90 (d, $J = 4.8$ Hz, 2 H), 8.87 (d, $J = 4.8$ Hz, 2 H), 8.80 (d, $J = 4.8$ Hz, 2 H), 8.22 (dt, $J = 6.0$, 1.6 Hz, 4 H), 8.10 (d, $J = 8.4$ Hz, 2 H), 7.84−7.78 (m, 6 H), 7.34 (d, $J = 8.8$ Hz, 2 H), 5.92 (hept, $J = 6.4$ Hz, 1 H), 4.08 (s, 3 H), 1.59 (d, $J = 6.0$ Hz, 6 H). UV−vis: λ_{max} (log ϵ, CH_2Cl_2) 438.0 (5.38), 564.0 (4.08), 617.0 (4.20) nm. MS(FAB): *m*/*z* 768. HRMS (FAB): calcd for $C_{46}H_{32}N_4O_4Zn$ 768.1714, found 768.1683.

5-(4-Methoxyphenyl)-10,20-diphenylporphyrin (30). A mixture of 5-bromo-10,20-diphenylporphyrin (**2**) (195 mg, 0.360 mmol, 1.00), 4-methoxyphenylboronic acid (109 mg, 0.717 mmol, 1.99 equiv), potassium carbonate (397 mg, 2.877 mmol, 7.99 equiv), $Pd(PPh_3)_4$ (62 mg, 0.054 mmol, 0.15 equiv), and toluene (25 mL) was heated at 90 °C for 20 h under nitrogen. After removal of the potassium carbonate and solvent, the residue was purified by chromatography (flash, silica gel, 2 × 12 cm, hexanes−methylene chloride (2:1)) to give the product as a red solid (169 mg, 0.297 mmol, 82%). TLC (silica gel, hexanes−acetone (3:1)): $R_f = 0.5$. Mp > 240 °C (methylene chloride−hexanes, diffusion). IR (KBr pellet, cm^{-1}): 3311 (m). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.21 (s, 1 H), 9.33 (d, $J = 4.4$ Hz, 2 H), 9.02 (d, $J = 4.8$ Hz, 2 H), 8.91 (s, 4 H), 8.25 (d, $J = 7.6$ Hz, 4 H), 8.13 (d, $J = 8.4$ Hz, 2 H), 7.80−7.78 (m, 6 H), 7.28 (d, $J = 8.4$ Hz, 2 H), 4.10 (s, 3 H), −2.99 (s, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.3, 141.8, 135.5, 134.9, 134.7, 131.5 (4C−N(br)), 127.7, 126.8, 120.5, 119.6, 112.0, 104.6, 55.5. UV−vis: λ_{max} (log ϵ, THF) 411 (5.39), 506.8 (4.11), 541.4 (3.70), 581.6 (3.63) nm. HRMS (FAB): calcd for M + Li^+ $C_{39}H_{28}N_4OLi$: 575.2423, found 575.2449. Anal. Calcd for $C_{39}H_{28}N_4O$: C, 82.37; H, 4.96; N, 9.85. Found: C, 82.37; H, 5.02; N, 9.87.

5-Bromo-15-(4-methoxyphenyl)-10,20-diphenylporphyrin (31). A mixture of 5-(4-methoxyphenyl)-10,20-diphenylporphyrin (**30**) (20 mg, 0.035 mmol, 1.00 equiv) and NBS (6 mg, 0.035 mmol, 1.00 equiv) in CH_2Cl_2 (5 mL) was stirred at room temperature for 3 h. After removal of the solvent, the residue was triturated once with boiling methanol (30 mL). The resulting purple solid (22 mg, 0.034 mmol, 97%) was pure by NMR and was not further purified. TLC (silica gel, hexanes−acetone (2:1)): $R_f = 0.6$. Mp > 250 °C. IR (KBr pellet, cm^{-1}): 3319 (w). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.66 (d, $J = 5.2$ Hz, 2 H), 8.91 (d, $J = 4.8$ Hz, 2 H), 8.83 (d, $J = 6.8$ Hz, 2 H), 8.79 (d, $J = 6.0$ Hz, 2 H), 8.19 (dd, $J = 9.6$, 1.6 Hz, 2 H), 8.18 (d, $J = 10.4$ Hz, 2 H), 8.12 (d, $J = 11.1$ Hz, 2 H), 7.81 (m, 6 H), 7.27 (d, $J = 8.8$ Hz, 2 H), 4.08 (s, 3 H), −2.73 (s, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.5, 141.8, 135.5, 134.5, 134.2, 127.8, 126.7, 120.9, 120.7, 112.2, 102.7, 55.6 (the signals from C−N were not observed due to exchange of the N−H proton). UV−vis λ_{max} (log ϵ, THF) 419.0 (5.55), 516.8 (4.17), 552.2 (3.95), 595.6 (3.64), 652.6 (3.61) nm. MS(FAB): *m*/*z* 648. HRMS (FAB): calcd for $C_{39}H_{27}N_4OBr$ 646.1368, found 646.1356.

5-(2-Isopropoxynaphthoquinonyl)-15-(4-methoxyphenyl)-10,20-diphenylporphyrin(Zn) (32). The reaction was carried out following procedures similar to those for previous quinone porphyrins. 5-(2-Isopropoxycyclobutene-3,4-dionyl-10,-20-diphenylporphyrin(Zn) (**29**) (38 mg, 0.049 mmol, 1.00 equiv) was treated with phenyllithium (0.4 mL, 0.23 M in THF, 0.09 mmol) to form the 1,2-adduct. The adduct was refluxed in xylene and then allowed to oxidize open to the air to give product **32** (24 mg, 0.028 mmol, 57%) as a purple solid after chromatography (flash column, silica gel, 1.5 × 12 cm, hexanes−acetone (3:1) followed by flash column, silica gel, 1.5 × 12 cm, hexanes−ether (4:1)). TLC (silica gel, hexanes−acetone (1:2)): $R_f = 0.5$. Mp > 250 °C (methylene chloride−hexanes, diffusion). IR (KBr pellet, cm^{-1}): 1671 (s), 1597 (s). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.13 (d, $J = 4.8$ Hz, 2 H), 8.98 (d, $J = 4.8$ Hz, 2 H), 8.96 (d, $J = 4.8$ Hz, 2 H), 8.93 (d, $J = 4.4$ Hz, 2 H), 8.40 (dd, $J = 7.6$, 1.6 Hz, 1 H), 8.30−8.25 (m, 3 H), 8.19−9.16 (m, 3 H), 8.05 (dd, $J = 8.0$, 2.4 Hz, 1 H), 7.89 (m, $J = 7.6$, 1.6 Hz, 2 H), 7.79−7.71 (m, 6 H), 7.22 (d, $J = 8.4$ Hz, 2 H), 4.52 (hept, $J = 6.4$ Hz, 1 H), 4.04 (s, 3 H), 0.56 (d, $J = 6.0$ Hz, 6 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 187.0, 182.8, 159.2, 158.9, 150.4, 150.3, 150.1, 149.3, 142.7, 135.4, 135.3, 135.1, 134.6, 134.4, 134.3, 134.2, 133.7, 132.3, 132.2, 131.8, 130.2, 127.5, 127.1, 126.7, 126.6, 126.5, 121.9, 121.1, 112.1, 111.9, 108.4, 76.5, 55.5, 22.6. UV−vis: λ_{max} (log ϵ, Et_2O) 402 (4.56), 421 (5.57), 455 (4.14), 554 (4.18), 592 (3.74) nm. MS(FAB): *m*/*z* 844. HRMS (FAB): calcd for $C_{52}H_{36}N_4O_4Zn$ 844.2027, found 844.2068.

5-Vinyl-10,20-diphenylporphyrin (33). A mixture of 5-bromo-10,20-diphenylporphyrin (81 mg, 0.15 mmol), vinyltri-*n*-butyltin (64 mg, 0.2 mmol), $Pd_2(dba)_3$ (7 mg, 0.0075 mmol), triphenylarsine (18 mg, 0.06 mmol), and THF (10 mL) in a 25 mL round-bottomed flask was heated at 50 °C for 2.5 h, and then the solvent was removed. The product was purified through a plug of silica gel (SiO_2, 2 × 2.5 cm, hexanes−methylene chloride (2:1)) to give a purple solid (65 mg, 0.133 mmol, 89%). TLC (silica gel, hexanes−methylene chloride (1:1)): R_f = 0.26. Mp > 250 °C (methylene chloride−hexanes, diffusion). IR (KBr, cm^{-1}): 3309 (w). ^1H NMR ($CDCl_3$, 400 MHz): δ 10.16 (s, 1 H), 9.55 (d, J = 4.8 Hz, 2 H), 9.30 (d, J = 4.4 Hz, 2 H), 9.29 (dd, J = 17.2, 10.8 Hz, 1 H), 8.99 (d, J = 4.8 Hz, 2 H), 8.97 (d, J = 4.8 Hz, 2 H), 8.26−8.23 (m, 4 H), 7.82−7.77 (m, 6 H), 6.56 (dd, J = 11.2, 2.0 Hz, 1 H), 6.12 (dd, J = 17.2, 1.6 Hz, 1 H), −2.96 (s, 2 H). UV−vis: λ_{max} (log ϵ, Et_2O) 407 (5.44), 509 (4.33), 542 (3.89), 587 (3.77), 644 (3.38) nm. Anal. Calcd for $C_{34}H_{24}N_4$: C, 83.58; H, 4.95; N, 11.47. Found: C, 83.51; H, 4.92; N, 11.51.

5,15-Divinyl-10,20-diphenylporphyrin (34). A mixture of 5,15-dibromo-10,20-diphenylporphyrin (150 mg, 0.24 mmol, 1.0 equiv), vinyltri-*n*-butyltin (603 mg, 0.6 mmol, 2.50 equiv), $Pd_2(dba)_3$ (11 mg, 0.012 mmol, 0.05 equiv), triphenylarsine (14.7 mg, 0.048 mmol, 0.20 equiv), and THF (20 mL) was stirred at 50 °C for 3 h. After workup and purification (flash column, silica gel, 3 × 12 cm, hexanes−methylene chloride (2:1)) a purple solid was obtained (112 mg, 0.217 mmol, 90%). TLC (silica gel, hexanes−methylene chloride (1:1)): R_f = 0.5. Mp > 250 °C (methylene chloride−hexanes, diffusion). IR (KBr pellet, cm^{-1}): 3317 (w). ^1H NMR ($CDCl_3$, 400 MHz): δ 9.45 (d, J = 6.4 Hz, 4 H), 9.19 (dd, J = 23.2, 14.8 Hz, 2 H), 8.86 (d, J = 6.4 Hz, 4 H), 8.22−8.19 (m, 4 H), 7.81−7.75 (m, 6H), 6.52 (dd, J = 14.8, 2.4 Hz, 2 H), 6.10 (dd, J = 22.8, 2.0 Hz, 2 H), −2.60 (s, 2 H). UV−vis: λ_{max} (log ϵ, THF) 416.8 (5.38), 515.8 (4.04), 556.0 (3.82), 596.2 (3.50), 656.8 (3.38) nm. MS(FAB): *m/z* 521. HRMS (FAB): calcd for M + Li^+ $C_{36}H_{26}N_4Li$ 521.2318, found: 521.2308. Anal. Calcd for $C_{36}H_{26}N_4$: C, 84.02; H, 5.09; N, 10.89. Found: C, 83.84; H, 5.19; N, 10.79.

5-Bromovinyl-10,20-diphenylporhyrin (35). 5-Vinyldiphenylporphyrin (220 mg, 0.45 mmol, 1.00 equiv) in ethanol-free chloroform (130 mL) was treated with pyridinium tribromide (199 mg, 0.55 mmol, 1.23 equiv) as a purple solid, and the mixture was stirred overnight. The reaction mixture was washed twice with water and then purified by filtration through a plug of silica gel to give a purple solid (110 mg, 0.20 mmol, 44%). An analytical sample was prepared by purification through flash column chromatography (flash column, silica gel, 3 × 9 cm, hexanes−methylene chloride (3:1)) and crystallization. TLC (silica gel, hexanes−methylene chloride (1:1)): R_f = 0.5. Mp > 250 °C (methylene chloride−hexanes, diffusion). IR (KBr pellet, cm^{-1}): 3308 (w). ^1H NMR ($CDCl_3$, 400 MHz): δ 10.19 (s, 1 H), 9.64 (d, J = 14.2 Hz, 1 H), 9.46 (d, J = 5.1 Hz, 2 H), 9.31 (d, J = 4.8 Hz, 2 H), 8.23 (m, 4 H), 7.80 (m, 6 H), 7.06 (d, J = 13.8 Hz, 1 H), −2.99 (s, 2 H). UV−vis: λ_{max} (log ϵ, THF) 414.0 (5.66), 511.0 (4.34), 545.5 (3.94), 588.0 (3.80), 645.0 (3.46) nm. MS(FAB): *m/z* 567 (21). HRMS (FAB): calcd for M + H^+ $C_{34}H_{24}N_4Br$ 567.1184, found 567.1165. Anal. Calcd for $C_{34}H_{23}N_4Br$: C, 71.96; H, 4.09; N, 9.88; Br, 14.08. Found: C, 71.66; H, 4.04; N, 9.84; Br, 14.35.

5-[(3-Isopropoxycyclobutene-1,2-dionyl)vinyl]-10,20-diphenylporphyrin (36). A mixture of 5-bromovinyl-10,20-diphenylporphyrin (291 mg, 0.515 mmol, 1.00 equiv), $Pd_2(dba)_3$ (21.3 mg, 0.023 mmol, 0.04 equiv), triphenylarsine (31 mg, 0.099 mmol, 0.19 equiv), **10** (400 mg, 0.928 mmol, 1.80 equiv), and THF (40 mL) was heated at 50 °C for 21 h under nitrogen. After removal of the solvent, the residue was triturated with hexanes and then purified by filtration through a plug of silica (solvent: methylene chloride−hexanes−acetone (10:30:0.25)) to give a dark green solid (248 mg, 0.396 mmol, 77%). Mp 232−235 °C (methylene chloride−hexanes, diffusion). IR (KBr pellet, cm^{-1}): 3468 (w), 3314 (w), 1778 (s), 1740 (s), 1575 (s). ^1H NMR ($CDCl_3$, 400 MHz): δ 10.58 (d, J = 15.6 Hz, 1 H), 10.16 (s, 1 H), 9.55 (d, J = 5.1 Hz, 2 H), 9.27 (d, J = 4.5 Hz, 2 H), 8.98 (d, J = 4.8 Hz, 2 H), 8.94 (d, J = 4.8 Hz, 2 H), 8.22 (m, 4 H), 7.81 (m, 6 H), 7.33 (d, J = 15.6 Hz, 1 H), 5.67 (hept, J = 6.3 Hz, 1 H), 1.62 (d, J = 6.0 Hz, 6 H), −2.64 (s, 2 H). UV−vis: λ_{max} (log ϵ, CH_2Cl_2) 440.5 (5.04), 514.0 (3.95), 573.5 (4.11), 665.0 (3.76). MS(FAB): *m/z* 627. HRMS (FAB): calcd for M + H^+ $C_{41}H_{31}N_4O_3$ 627.2396, found 627.2427. Anal. Calcd for $C_{41}H_{30}N_4O_3$: C, 78.58; H, 4.83; N, 8.94. Found: C, 78.06; H, 4.78; N, 8.84.

5-[(3-Isopropoxycyclobutene-1,2-dionyl)vinyl]-10,20-diphenylporphyrin(Zn) (37). 5-[(3-Isopropoxy-1,2-dionyl)-vinyl]-10,20-diphenylporphyrin (**36**) (64 mg, 0.102 mmol, 1.00 equiv) in methylene chloride (50 mL) and zinc acetate (36 mg, 0.196 mmol, 1.92 equiv) in methanol (20 mL) were stirred at room temperature for 1.5 h in a 100 mL round-bottomed flask. The mixture was then washed three times with water, and solvent was removed to give a dark green solid (64 mg, 0.093 mmol, 91%). Both TLC and NMR indicated the presence of pure compound, so no further purification was performed. Mp > 250 °C (methylene chloride−hexanes, diffusion). IR (KBr pellet, cm^{-1}): 1774 (s), 1741 (s), 1574 (s). ^1H NMR (DMSO-d_6, 400 MHz): δ 10.56 (d, J = 15.6 Hz, 1 H), 10.31 (s, 1 H), 9.60 (d, J = 4.8 Hz, 2 H), 9.43 (d, J = 4.4 Hz, 2 H), 8.92 (d, J = 4.8 Hz, 2 H), 8.81 (d, J = 4.4 Hz, 2 H), 8.21 (m, 4 H), 7.85 (m, 6 H), 7.30 (d, J = 15.6 Hz, 1 H), 5.57 (hept, J = 6.4 Hz, 1 H), 1.58 (d, J = 6.4 Hz, 6 H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 193.4, 192.6, 191.8, 171.1, 149.9, 149.3, 148.9, 148.6, 143.1, 142.3, 134.3, 132.7, 132.6, 131.8, 129.1, 127.7, 126.8, 125.9, 121.3, 113.2, 108.4, 79.7, 22.5. UV−vis: λ_{max} (log ϵ, THF) 431.0 (5.14), 455.5 (5.23), 562.5 (4.04), 629.0 (4.36) nm. MS(FAB): *m/z* 688.2. HRMS (FAB): calcd for $C_{31}H_{285}N_4O_3$ 688.1453, found 688.1476.

5-[(2-Isopropoxynaphthaquinonyl)vinyl]-10,20-diphenylporphyrin(Zn) (38). 5-[(3-Isopropoxy-1,2-dionyl)vinyl]-10,20-diphenylporphyrin(Zn) (**37**) (35 mg, 0.050 mmol, 1.00 equiv) in THF (8 mL) at −78 °C under nitrogen was treated dropwise with 1 equiv of phenyllithium (0.27 M in THF, 0.2 mL). Immediate monitoring of the reaction mixture by TLC showed disappearance of starting material. The reaction was quenched with aqueous ammonium chloride at the same temperature and then allowed to warm to room temperature. After aqueous workup, the crude product was dissolved in xylene, refluxed for 3 h, and then stirred at room temperature under air. The crude product was purified by column chromatography (flash column, silica gel, 1.5 × 6 cm, hexanes−acetone (10:1)), giving a brown solid (18 mg, 0.023 mmol, 46%). Mp > 250 °C (methylene chloride−hexanes, diffusion). IR (KBr pellet, cm^{-1}): 1660 (s), 1595 (s). ^1H NMR ($CDCl_3$, 400 MHz): δ 10.48 (d, J = 16.0 Hz, 1 H), 10.09 (s, 1 H), 9.64 (d, J = 4.8 Hz, 2 H), 9.27 (d, J = 4.4 Hz, 2 H), 9.03 (d, J = 4.8 Hz, 2 H), 8.99 (d, J = 4.4 Hz, 2 H), 8.23 (m, 4 H), 7.89 (d, J = 7.2 Hz, 1 H), 7.80 (m, 7 H), 7.55 (m, 2 H), 7.48 (d, J = 16.4 Hz, 1 H), 5.28 (hept, J = 5.6 Hz, 1 H), 1.48 (d, J = 6.4 Hz, 6 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.1, 149.7, 149.3, 149.1, 142.6, 141.7, 134.5, 133.6, 133.1, 132.5, 132.3, 131.7, 130.3, 127.5, 126.6, 126.3, 125.7, 120.9, 77.2, 23.4. UV−vis: λ_{max} (log ϵ, THF) 420.5 (5.72), 554.5 (5.43), 633.5 (5.39) nm. MS(FAB): *m/z* 764. HRMS (FAB): calcd for $C_{47}H_{32}N_4O_3Zn$ 764.1765, found 764.1757.

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Supporting Information Available: A complete description of the X-ray crystallographic determination of the structures of compounds **9** and **24** and photocopies of spectroscopic data (IR, ^1H, ^{13}C NMR) for those compounds not characterized by elemental analysis. This material is available free of charge via the Internet at http://pubs.acs.og.

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