Cyclohexylene-Bridged Porphyrin Quinones with Variable Acceptor Strength as Biomimetic Models for Photosynthesis: Evidence for Twist-Boat Conformation

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Rigidly and covalently linked porphyrin quinones are well-suited as biomimetic model compounds for studying the photoinduced electron transfer (PET) reaction occurring in primary processes of photosynthesis. In this context, the synthesis of new porphyrin quinones with a *cis*- or *trans*-1,4-disubstituted cyclohexylene bridge linking the electron donor and the electron acceptor is reported. To study the dependence of the PET rate of the difference of the free enthalpy of the PET reaction, four quinones with different structures and therefore redox potentials were used as electron acceptor components. As a whole, two series of each four new *cis*- and *trans*-1,4-cyclohexylene-bridged porphyrin quinones with variable acceptor strength were synthesized. The most important synthetic steps comprised the free radical addition of the ester functionalized cyclohexylene bridge to the quinone, reduction of the ester to the alcohol group with lithium borohydride or DIBALH, oxidation of the alcohol to the corresponding aldehyde with PCC or TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl)/NaOCl, and condensation of these aldehydes with pyrrole and 4-methylbenzaldehyde under equilibrium conditions. Analysis of the ^{1}H NMR spectra unambiguously indicated the chair conformation for the cyclohexane ring of all porphyrin precursors and *trans*-cyclohexane-bridged porphyrin quinones, whereas the *cis*-cyclohexane-bridged porphyrin quinones had the cyclohexane ring in the unusual twist-boat conformation. This was additionally confirmed by an X-ray crystal structure of one of the *cis*-porphyrin quinones and the corresponding *trans*-porphyrin quinone. NOE experiments gave information about the spatial arrangement of the diastereomeric target compounds in solution.

Introduction

Photosynthetic reaction centers (RC) consist of the protein matrix and the donor−acceptor redox active pigments. In RC photoinduced electron transfer (PET) takes place within about 3 ps after singlet state excitation and the initial energy conversion act proceeds with a quantum yield of nearly unity. The unpaired electron moves energetically downhill from (bacterio)chlorophylls or their corresponding dimers to (bacterio)pheophytins and quinone acceptors Q_A and Q_B.

To gain a better insight into the dependencies of PET rate constants on donor−acceptor distance, relative orientation, free energy of reaction, and electronic coupling, numerous porphyrin quinone (P−Q) models have been prepared and studied by different optical and magnetic resonance spectroscopic techniques. Recent reviews report on synthesis and investigations of covalently linked donors and acceptors extending even to so-called pentads connecting five different PET active moieties.[1] One of the requirements to define a "good" model compound is a fairly rigid structure of the aggregate, since flexible spacers result in some uncertainty in the geometrical relationship between donor and acceptor. Well-defined geometrical parameters are a prerequisite for a sound theoretical interpretation of the spectroscopic data.

The aliphatic cyclohexylene spacer, linking porphyrin and quinone either in 1,4-*cis* or -*trans* conformation, respectively, has proved useful in this context.[2−4] In the present paper we take advantage of this system and report on synthesis and characterization of a variety of P−Q's which have in common the donor 10,15,20-tris(4-methylphenylene)porphyrin-5-yl residue, abbreviated as P and the cyclohexylene spacer, whereas the quinone acceptors (Q) are different (Figure 1). The underlying idea was to essentially keep the basic molecular frame constant and to modify only one parameter (the driving force $\Delta G°$ of PET). According to Marcus theory this free energy of reaction significantly influences the PET rate constants.[5] The Marcus theory predicts at first an increase in the PET rate constant with increasing exergonicity in the "normal region" of the PET reaction, i.e., with more negative values for $\Delta G°$. Subsequently, the PET rate passes through a maximum value and finally will decrease with further increasing exergonicity in the "inverted region".

Hence, the goal was to obtain a series of compounds with gradually increasing exergonicity. Therefore, the

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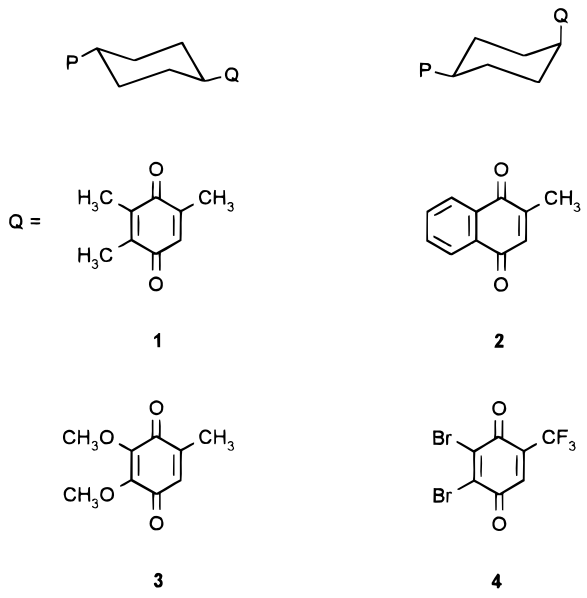

Figure 1. Target molecules with the same electron donor (10,15,20-tris(4-methylphenylene)porphyrin-5-yl residue, abbreviated as P) for all compounds, a *cis*- or *trans*-cyclohexylene spacer, and different quinones (Q) as electron acceptors.

quinones **1**−**4** were chosen as acceptors. They span different redox potentials ranging from −0.70 V (**1**) to +0.08 V (**4**) (measured vs SCE in dichloromethane with ferrocene as standard) which results in different driving forces $\Delta G°$.[6] Due to the electron-withdrawing substituents of **4**, this quinone is the strongest oxidizing agent of all electron acceptors used in our model compounds. Thus, the most exergonic PET reaction is to be expected which should give rise to observe a PET reaction in the "Marcus inverted region".

To introduce some rigidity and to retain similar geometrical arrangements between quinone and bridge, the quinones bear a methyl or trifluoromethyl group, respectively, next to the linking position. Detailed structural information could be obtained by X-ray crystallography of two diastereomeric target P−Q's. Only the synthesis of the ubiquinone derivatives has already been outlined previously in a short communication.[7] Optical and electron paramagnetic resonance spectroscopic studies on some of these systems have already been[8] or will be published elsewhere.

Results and Discussion

Synthesis of 2,3-dibromo-5-(trifluoromethyl)-1,4-benzoquinone. Whereas syntheses for three of the four electron acceptors, i.e., for the quinones **1**,[31] **2**,[27] and **3**,[28] have already been described in the literature, the synthetic pathway for the preparation of the hitherto unknown quinone **4** is depicted in Scheme 1.

Starting from 3-(trifluoromethyl)phenol (**5**), 3-(trifluoromethyl)-1,4-benzoquinone (**9**) was obtained following a literature procedure,[9] which, however, was simplified and improved. The bromination of **9**, which generally proceeds rapidly with 1,4-benzoquinones,[10] yielded the dibromo adduct **10**. The acid-induced 2-fold tautomerization[11] of such quinone dibromides yielded the hydroquinone **11**, which after oxidation with DDQ gave 2,3-dibromo-5-(trifluoromethyl)-1,4-benzoquinone (**4**) in 79% yield.

Syntheses of the Porphyrin Quinones. The reaction pathways for the different porphyrin quinones are shown in Schemes 2−4. The free radical alkylation of the quinones in order to link the cyclohexylene bridge to the quinone (Scheme 2) followed a procedure originally described by Jacobsen *et al.*[12] A *cis*/*trans* mixture of **12a**/**b** and the quinones **1**−**4** were reacted at 40 °C in a two-phase system of dichloromethane/water with ammonium peroxodisulfate as oxidant and silver nitrate as catalyst. The products **13a**/**b**−**16a**/**b** were obtained in 30−50% yield with a *cis*/*trans* ratio of 3:2. Due to poor separability of the alkylated quinones with HPLC on a preparative scale, only small amounts were separated for analytical purposes.

In the next step the alkylated quinones **13a**/**b**−**16a**/**b** were reduced with sodium hyposulfite[13] or by catalytic hydrogenation[13] to the corresponding hydroquinones **17a**/**b**−**20a**/**b** without isolation. The subsequent reduction of the methyl ester group to the alcohol group was performed with lithium borohydride[14] or DIBALH[15] (Scheme 2). Only the diastereomeric acceptor-substituted hydroquinones **24a**/**b** are stable and could be isolated (total yield 93%) and separated by HPLC. An attempted isolation of the other hydroquinones **21a**/**b**−**23b** led to their decomposition. Hence, **21a**/**b**−**23a**/**b** were immediately oxidized with iron(III) chloride or ammonium cerium(IV) nitrate to the corresponding quinones **25a**/**b**−**27a**/**b** in 57−75% overall yield. With the exception of **27a**/**b**, all product mixtures of the diastereomeric alcohols could be separated by HPLC. The method of choice for the conversion of the alcohols to the corresponding aldehydes (Scheme 3) in the case of **25a**, **25b**, **26a** and **26b** proved to be the oxidation with TEMPO as catalyst and sodium hypochlorite as oxidizing agent.[16] The products were obtained in high yield (85−90%) and are isomerically pure. Unfortunately, this method failed in the case of **24a**, **24b**, and **27a**/**b** due to rapid decomposition of the educts. These aldehydes could be obtained only with PCC[17] (pyridinium chlorochromate) as oxidant in ca. 75% yield. Due to the acidic character of PCC,[17] isomerization reactions of the products—most probable via a keto−enol tautomerization—were observed result-

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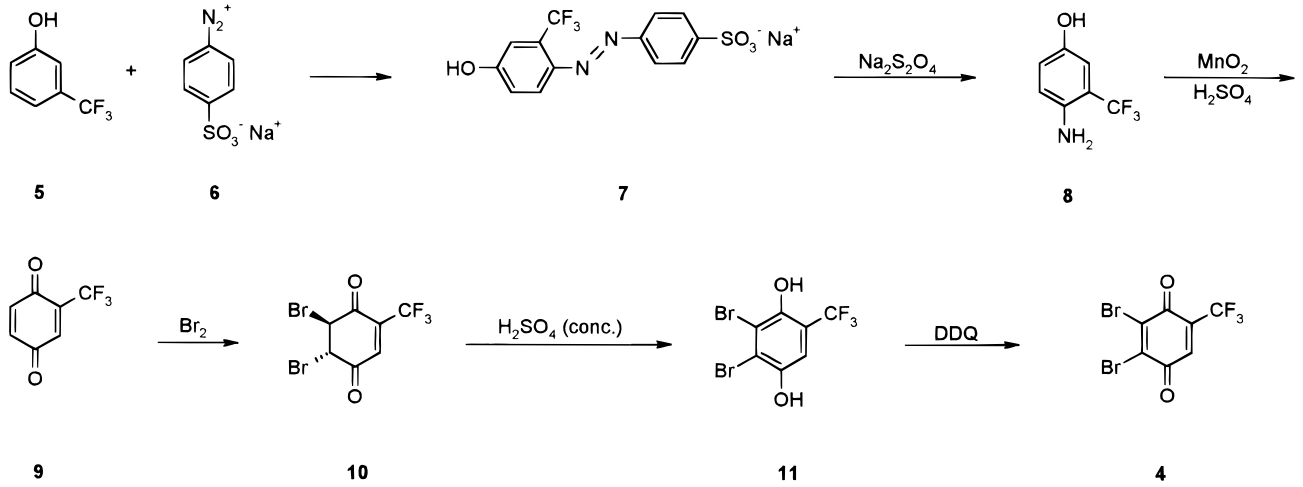
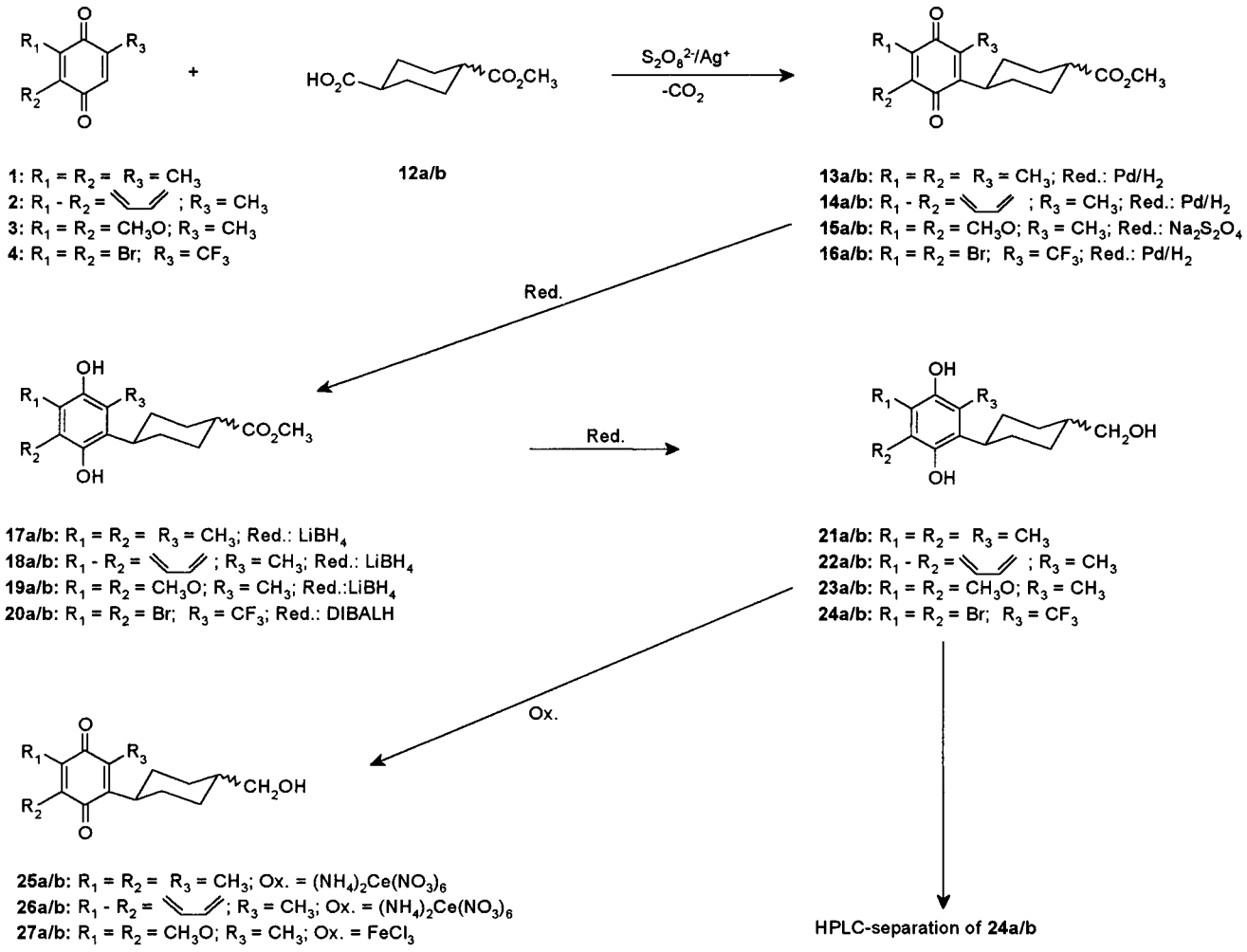
Scheme 1. Synthesis of 2,3-Dibromo-5-(trifluoromethyl)-1,4-benzoquinone (4)



Scheme 2. Free Radical Alkylation of the Quinones and Reduction of the Esters to the Alcohol Groups



ing in *cis*/*trans* mixtures of the products **28a** (*cis*/*trans* ratio 9:1) and **28b** (*cis*/*trans* ratio 5:95) despite starting with the isomerically pure educts **24a** and **24b**, respectively. Likewise, oxidation of **27a**/**b** resulted in a change of the *cis*/*trans* ratio of 3:2 (educts) to 1:1 (products **31a**/**b**).

The synthesis of the target compounds (Scheme 4) followed the method originally described by Lindsey et al. for symmetric porphyrins, which was successfully applied also for the preparation of unsymmetrical *meso*-substituted porphyrins.[18] The aldehydes from the preceding step were reacted with 4-methylbenzaldehyde (**33**) and pyrrole (**34**) in a ratio of 1:3:4 in the presence of trifluoroacetic acid as catalyst. **28a** and **28b** were reduced via catalytic hydrogenation in quantitative yield to their corresponding hydroquinones **32a** and **32b**, respectively, due to a rapid decomposition of the quinone moieties in the presence of pyrrole and trifluoroacetic acid yielding a black, tarry product. In a similar case, the chemical instability of tetrachloro-1,4-benzoquinone in

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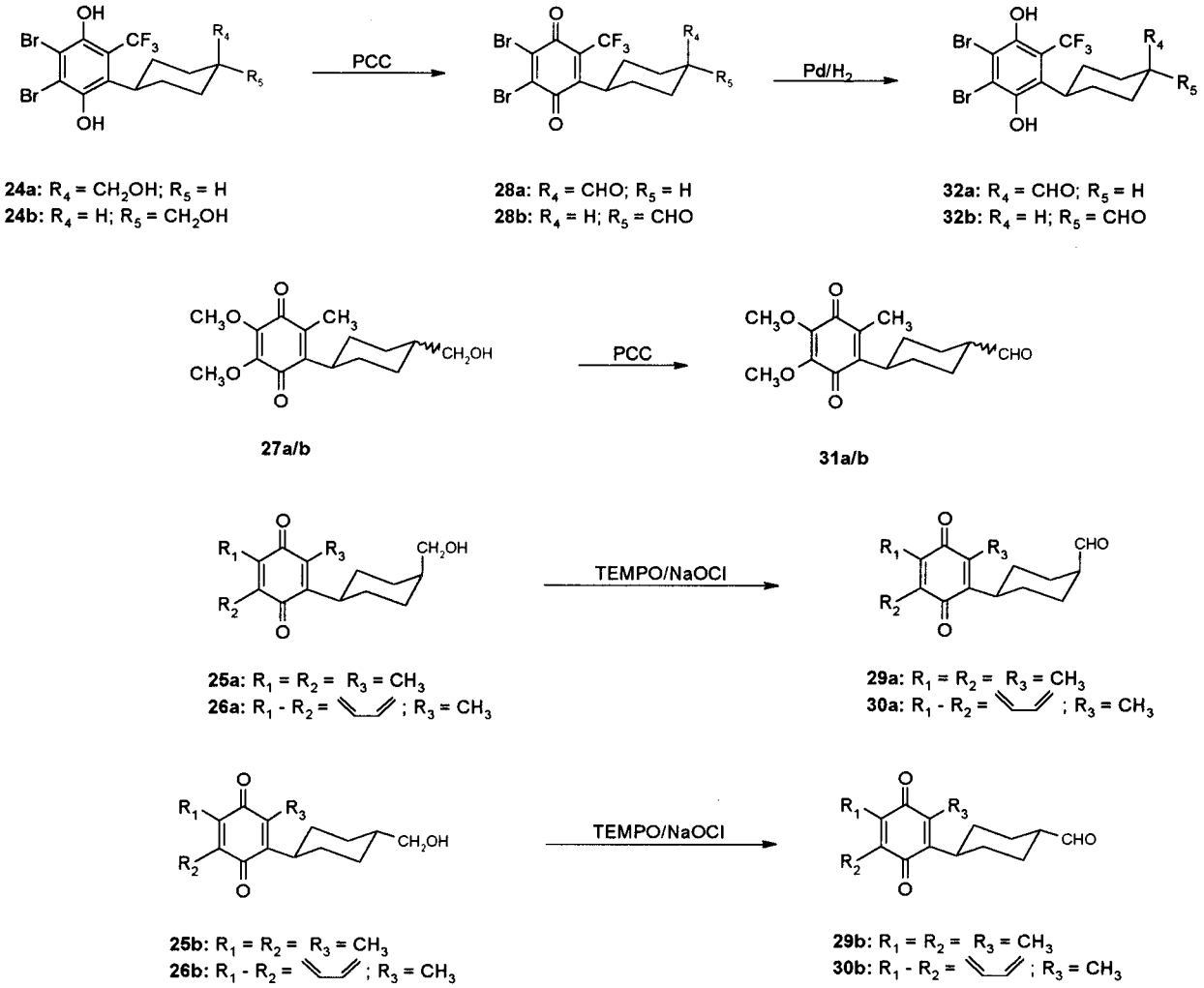
Scheme 3. Oxidation of the Alcohols to the Corresponding Aldehydes



the presence of pyrrole and acid was reported earlier.[19] The porphyrin quinones were obtained in 5−13% yield after repeated purification by column chromatography and HPLC. No *cis*−*trans* isomerization of the acid-sensitive *cis*-aldehydes **29a** and **30a** took place, since both *cis*-porphyrin quinones **35a** and **36a** were formed isomerically pure. The separation of the diastereomers **37a** and **37b** was achieved by HPLC.

Insertion of zinc into the porphyrin core was performed using the "acetate method" with zinc(II) acetate in a mixture of dichloromethane and methanol with nearly quantitative yields.[20,34] Under these conditions **38a** and **38b** decomposed, presumably due to addition of methanol or acetate ions to the electron-deficient double bonds of the quinone. After modification of the reaction conditions these zinc porphyrin quinones were obtained in about 90% yield by reacting the porphyrin quinones **38a** or **38b** with an excess of zinc oxide in the presence of a catalytic amount of trifluoroacetic acid.

Structures and Conformations. The *cis* and *trans* stereochemistry of the diastereomers was investigated with ^{1}H NMR spectroscopy. The assignments were confirmed by ^{1}H−^{1}H COSY and selective decoupling experiments. The results for **15a**, **15b**, **24a**, **24b**, **37a**, and **37b** are compiled in Table 1.

In particular, the different magnitudes of vicinal and geminal couplings[21] between two axial (9−13 Hz), an axial and an equatorial (3−5 Hz), two equatorial (2−4 Hz), and two geminally grouped protons (11−15 Hz), respectively, gave rise to characteristic coupling patterns that enabled us to discriminate unambiguously between the *cis* and *trans* diastereomers. The most characteristic coupling patterns were observed for the protons connected to the cyclohexane ring carbons bearing the substituents, i.e., to C-1 and C-4, respectively. If both protons bound to C-1 and C-4 are in an axial position (designated as H_a-1 and H_a-4, respectively), which is true for all *trans* isomers, a well-resolved triplet of triplets due to a large coupling constant of ca. 12 Hz with the axial neighbor protons and a smaller one of ca. 3.5 Hz with the equatorial protons bound to the adjacent ring carbons appears in the ^{1}H NMR spectrum both for H_a-1 and H_a-4. In the corresponding *cis* isomers (apart from **37a**, see below) the proton bound to C-1 is in an axial position (H_a-1), whereas the proton connected to C-4 is equatorially bound (H_e-4). The signal assigned to H_a-1 is a triplet of triplets, for the same reason as it is in the case of the corresponding *trans* isomer. On the contrary, however, the coupling pattern of H_e-4 results in a broad multiplet due to vicinal couplings with the axial and equatorial neighbor protons which are of nearly equal magnitude and cannot be resolved.

The different coupling patterns show clearly, as expected, the chair conformation for **15a**, **15b**, **24a**, and **24b**. The larger (hydro)quinone substituent bound to the

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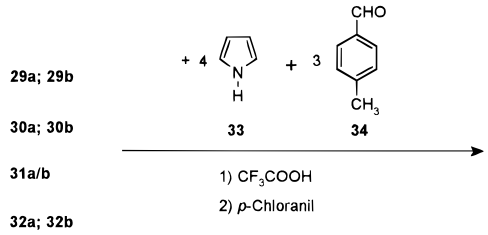
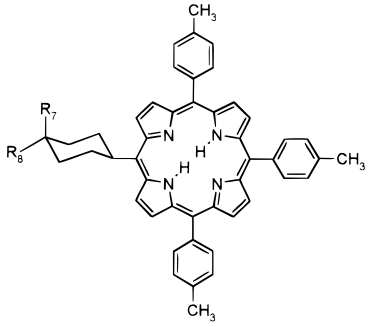
Table 1. δ_H Values (ppm) and Coupling Constants (Hz) of the Cyclohexylene Protons from 15a, 15b, 24a, 24b, 37a, and 37b

proton(s)	15a	15b	24a	24b	37a	37b
H_a-1	2.82 (tt) $^3J_{aa} = 12.5$ $^3J_{ae} = 3.3$	2.65 (tt) $^3J_{aa} = 12.5$ $^3J_{ae} = 3.3$	3.06 (tt) $^3J_{aa} = 12.5$ $^3J_{ae} = 3.6$	2.98 (tt) $^3J_{aa} \approx 12$ $^3J_{ae} \approx 3$	5.47 (tt) $^3J_1 = 11.0$ $^3J_2 = 7.2$	5.38 (tt) $^3J_{aa} = 12.5$ $^3J_{ae} = 3.4$
H_a-2, H_a-6	2.01 (qd) $^2J_{ae} = {}^3J_{aa} = 13.2$ $^3J_{ae} = 3.5$	1.97 (qd) $^2J_{ae} = {}^3J_{aa} = 13.1$ $^3J_{ae} = 3.7$	2.34 (qd) $^2J_{ae} = {}^3J_{aa} = 13.0$ $^3J_{ae} = 3.6$	2.30 (qd) $^2J_{ae} = {}^3J_{aa} = 12.5$ $^3J_{ae} = 3.6$	3.50 (m)	3.24 (qd) $^2J_{ae} = {}^3J_{aa} = 12.8$ $^3J_{ae} = 3.4$
H_e-2, H_e-6	1.38 (br d) $^2J_{ae} = 13.4$	1.59 (br d) $^2J_{ae} = 13.2$	1.40 (dq) $^2J_{ae} = 13.4$ $^3J_{ae} = {}^3J_{ee} = 3.2$	1.63 (dq) $^2J_{ae} = 13.0$ $^3J_{ae} = {}^3J_{ee} = 3.6$	2.71 (m)	2.88 (br d) $^2J_{ae} = 13.6$
H_a-3, H_a-5	1.48 (tt) $^2J_{ae} = {}^3J_{aa} = 13.5$ $^3J_{ae} = 4.3$	1.44 (qd) $^2J_{ae} = {}^3J_{aa} = 12.9$ $^3J_{ae} = 3.3$	1.58 (tt) $^2J_{ae} = {}^3J_{aa} = 13.8$ $^3J_{ae} = 3.9$	1.07 (qd) $^2J_{ae} = {}^3J_{aa} = 12.5$ $^3J_{ae} = 3.6$	2.66 (m)	2.72 (qd) $^2J_{ae} \approx 14$
H_e-3, H_e-5	2.21 (br d) $^2J_{ae} = 14.0$	2.04 (br d) $^2J_{ae} \approx 14$	1.86 (dq) $^2J_{ae} = 13.8$ $^3J_{ae} = {}^3J_{ee} = 3.5$	1.90 (dq) $^2J_{ae} = 13.9$ $^3J_{ae} = {}^3J_{ee} = 3.2$	2.10 (m)	2.10 (br d) $^2J_{ae} = 13.5$
H_a-4		2.37 (tt) $^3J_{aa} = 12.3$ $^3J_{ae} = 3.4$		1.60 (m)		3.44 (tt) $^3J_{aa} = 12.0$ $^3J_{ae} \approx 3$
H_e4[a]	2.66 (m)		1.92 (m)		3.61 (tt) $^3J_1 = 9.6$ $^3J_2 = 7.2$	

[a] Pseudoaxially positioned in the case of **37a**.

Scheme 4. Synthesis of the Porphyrin Quinones. Aldehydes 31a and 31b Were Reacted as a Mixture of Both Diastereomers. The Resulting Porphyrin Quinones, 37a and 37b, Were Separated by HPLC





R_7 = H; R_8 =	1	2	3	4
cis-PQ	**35a**	**36a**	**37a**	**38a**

R_8 = H; R_7 =	1	2	3	4
trans-PQ	**35b**	**36b**	**37b**	**38b**

ring carbon C-1 resides in the equatorial position in each compound, whereas the smaller ester and hydroxymethyl group bound to the ring carbon C-4 takes the axial position in **15a** and **24a** (*cis* diastereomers) and the equatorial position in **15b** and **24b** (*trans* diastereomers), respectively. Likewise, both the bulky porphyrin (bound to C-1) and the quinone substituents (bound to C-4) are arranged in the energetically favored equatorial positions of the *trans*-porphyrin quinone **37b**.

The molecular structure of **36b**, determined by X-ray crystallography, is shown in Figure 2. **36b** is a *trans*-porphyrin quinone with similar structure compared to **37b**, but with a different quinone moiety. The cyclohexane ring adopts the chair conformation as was also deduced from ^{1}H NMR spectroscopy. This is also apparent as well from the size and the alternating sign of the torsion angles, which are typical of cyclohexane derivatives in a chair conformation (Figure 3). The average value of 52° deviates from the corresponding value of 56° for unsubstituted cyclohexane, thus indicating a slightly flattened ring. The least-squares plane of the cyclohexane ring is orientated perpendicular to the N_4-plane of the porphyrin (dihedral angle 88.2°) and to the quinone (dihedral angle 89.5°). Both chromophores are positioned nearly in the same plane (dihedral angle 5.8°). The center-to-center distance between the porphyrin and quinone rings amounts to 10.80 Å.

A completely different situation was observed for the *cis*-porphyrin quinone **37a**. Here, the magnitude of the coupling constants deviates strongly from the corresponding ones of the *cis*-substituted precursor **15a** (see Table 1). Especially, the vicinal couplings of the protons H_a-1 and H_e-4 at the positions connecting the porphyrin and quinone substituents (C-1 and C-4) are of equal order of magnitude (H_a-1, 11.0 and 7.2 Hz; H_e-4, 9.6 and 7.2 Hz) and thus incompatible with a chair conformation of the cyclohexylene bridge. Similar couplings were observed in the ^{1}H NMR spectrum of *cis*-1,4-di-*tert*-butylcyclohexane indicating a twist-boat conformation of the cyclohexane ring.[22] Force-field calculations[23] corroborated these spectroscopic results.

The molecular structure of **36a**, a *cis*-porphyrin quinone with a different quinone moiety than that of **37a**, is shown in Figure 4. The magnitude and the order of signs of the torsion angles of unsubstituted cyclohexane in a twist-boat conformation compared to the corresponding torsion angles of **36a** (Figure 5) show unequivocally that both the porphyrin and quinone take pseudoequatorial positions[24] of the cyclohexane ring in a twist-boat conformation. Obviously, the quinone is too bulky for an axial position in the chair conformation of the cyclohexane ring. Thus, the *cis*-porphyrin quinones exist in the energetically more favored twist-boat conformation, which

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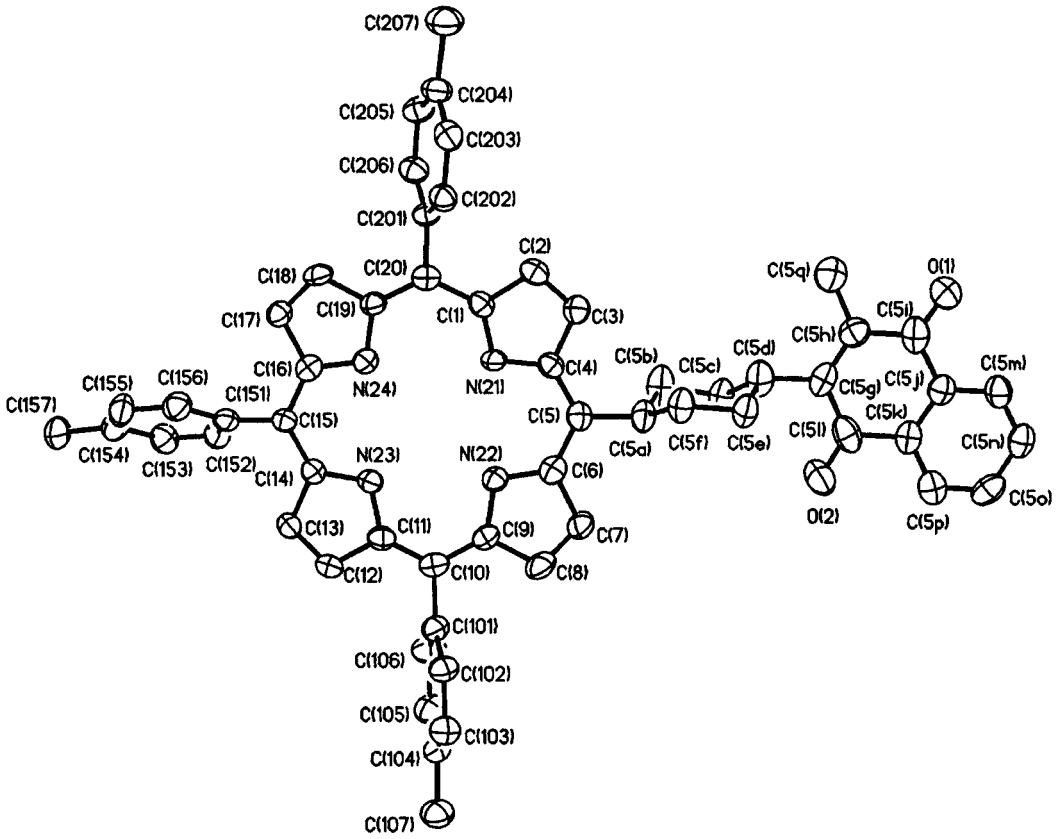

Figure 2. View of the molecular structure of the porphyrin quinone **36b**. Hydrogens have been omitted for clarity.

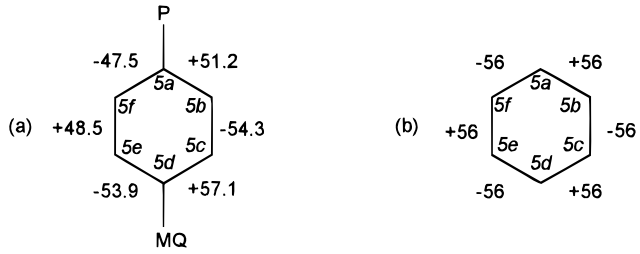

Figure 3. (a) Torsion angles of the cyclohexane ring of **36b** (P = porphyrin; MQ = 2-methyl-1,4-naphthoquinone). (b) For comparison, the torsion angles[24] of cyclohexane in the chair conformation.

could account for the unexpected NMR spectroscopic results. Whereas the conformation of the cyclohexane ring is totally different for both diastereomers, the remaining conformational properties resemble those of the *trans* isomer. The least-squares plane of the cyclohexane ring is nearly perpendicularly orientated to the plane of the porphyrin (N_4-plane) *and* to the quinone (dihedral angles 83.9° and 84.5°, respectively). Both chromophores are nearly coplanar (dihedral angle 6.7°) with a center-to-center separation of 10.72 Å; this is nearly the same value as found for the *trans* isomer.

As far as we are aware, the molecular structure of **36a** is the only example for a *cis*-1,4-disubstituted cyclohexane existing in a twist-boat conformation, whereas crystal structures of 1,2,3,4-tetrasubstituted cyclohexanes in a twist-boat conformation are known.[25] Results similar to those from the crystal structures were obtained with a MNDO (MOPAC 6.0) calculation[35] for the structure of **Zn-37a**, which revealed a twist-boat conformation as the minimum of energy.

Since the PET properties are governed not only by parameters such as the driving force of the PET reaction and distance of donor and acceptor etc. but also by the mutual orientation of the electron donor and acceptor,[1] information about their relative spatial arrangement are of utmost importance. Thus, NOE experiments were undertaken with **37a** and **37b** to gain insight into the conformation of the target molecules in solution.

NOE measurements with **37b** showed NOEs of 15−20% for the signals of the spatially neighboring protons (Figure 6) from the porphyrin ring and that of the cyclohexylene bridge confirming a perpendicular orientation of the cyclohexane ring relative to porphyrin plain. This arrangement was also found in the molecular structure of the structurally related compound **36b** (see above). Additionally, NOEs of 5 and 12%, respectively, were observed for the signal of the quinoid methyl group when the signal of the axial cyclohexane protons H_a-4 and H_a-3/H_a-5 was irradiated. These results indicate the

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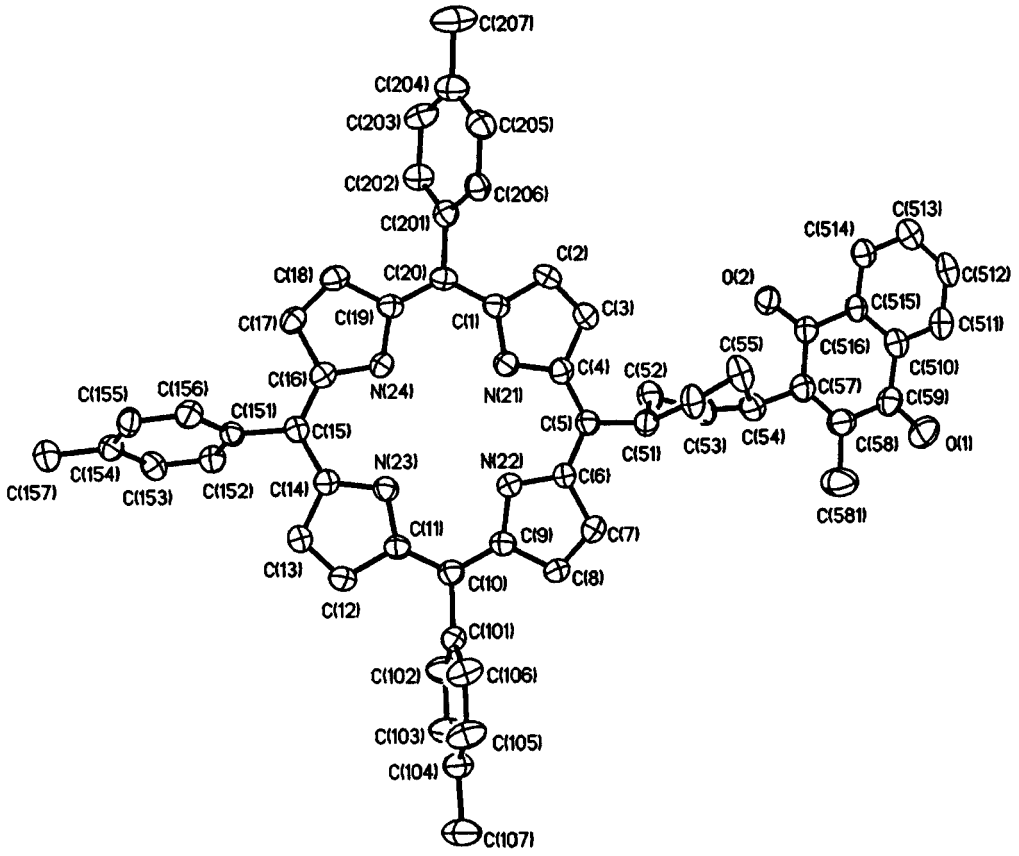

Figure 4. View of the molecular structure of the porphyrin quinone **36a**. Hydrogens have been omitted for clarity.

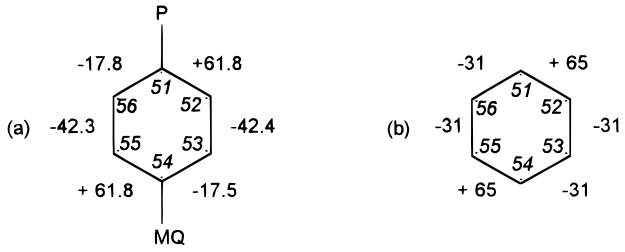

Figure 5. (a) Torsion angles of the cyclohexane ring of **36a** (P = porphyrin; MQ = 2-methyl-1,4-naphthoquinone). (b) For comparison, the torsion angles of cyclohexane[24] in the twist-boat conformation.

existence of two conformers differing only in the orientation of the quinone ring relative to the cyclohexane moiety. A rapid interconversion of the rotamers takes place in solution. Such conformers were also detected in solution (2-propanol) by our ESR, electron nuclear double resonance (ENDOR), and ENDOR-induced EPR spectroscopical experiments of paramagnetic species (semiquinone-anion radicals) which were derived from *cis*- and *trans*-porphyrin quinones and some of their precursors.[7,26]

NOE experiments with the *cis* isomer **37a** (Figure 7) gave NOEs of 5 and 2% for the signal of the porphyrin proton H-3 and for the pseudoaxial proton H_a-4, respectively, revealing a close vicinity of H_a-1 and the porphyrin ring and of H_a-4 and the quinoid methyl group. Two different orientations of the quinone ring relative to the cyclohexylene bridge, as was established for the corresponding *trans* isomer with NOE experiments, could not be found. However, the existence of such rotamers could be deduced not only from the results of MNDO (MOPAC 6.0) calculations[35] but also from ESR and ENDOR measurements as was already mentioned before. The

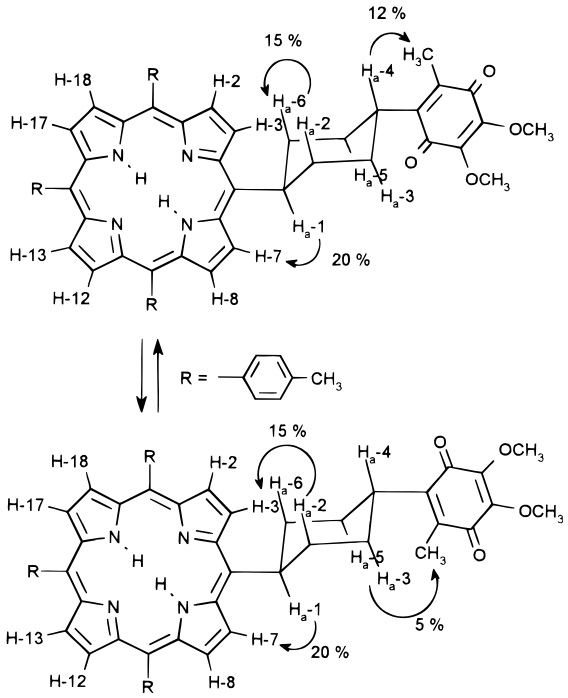

Figure 6. NOE experiments with **37b**.

NOE of 3% for the signal of H_a-4 irradiating the signal of H_a-1 is indicative of a twist-boat conformation, since the distance of both protons would be too great in a chair conformation for an NOE to be observable.

In conclusion, the synthesis of new 1,4-cyclohexylene-bridged *cis*- and *trans*-porphyrin quinones with variable acceptor strengths and their characterization by ^{1}H NMR spectroscopy and single-crystal X-ray crystallography has been described. These compounds are valuable objects

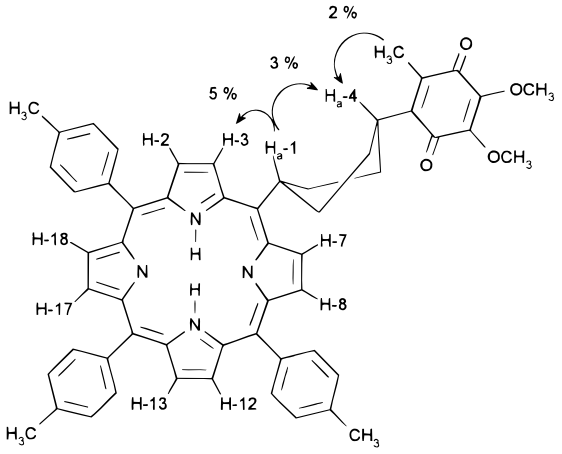

Figure 7. NOE experiments with **37a**.

for several interesting spectroscopical investigations concerning the kinetics of the PET reaction, e.g. formation and decay of the charge-separated biradical state with time-resolved picosecond fluorescence and time-resolved EPR or transient absorption spectroscopy. Work in this field is already proceeding.

Experimental Section

Instrumentation. Conditions and instruments for ^{1}H NMR, ^{13}C NMR, UV, and mass spectra, elemental analysis, and melting points were described in a previous publication.[3] ^{19}F NMR spectra, JEOL FX 90 Q-spectrometer, internal standard, fluorotrichloromethane. Chromatography: TLC, glass plates with silica gel 60 coating (0.25 mm) and fluorescence indicator (Merck). Flash-column chromatography: silica gel 60 (Merck, 0.040−0.063 mm, 230−400 mesh). Preparative HPLC: Waters Delta Preparative Chromatography System 3000 or Knauer modul systems (HPLC Pump 64, MPLC Pump; variable wavelength detector Nr. A0293). Analytical HPLC for purity control: modul systems with Gynkotek SP-6-detector and Waters 510-HPLC Pump or Knauer Pump 64 and Knauer variable wavelength detector Nr. A0293. Mobile and stationary phases are specified below in the individual experimental descriptions.

Educts. 2-methyl-1,4-naphthoquinone (**2**),[27] 2,3-dimethoxy-5-methyl-1,4-benzoquinone (**3**),[28] and 1,4-cyclohexanedicarbonic acid monomethyl ester (**12a**/**b**) (4:1 *cis*/*trans* mixture)[29] were prepared according to established procedures. All other educts were purchased from Aldrich, Fluka, or Merck and, if necessary, purified applying standard methods.

Crystal Structure Determinations. 36a: $C_{58}H_{48}N_4O_2 \cdot 2CH_2Cl_2$, at 125 K (Cu Kα radiation $\lambda = 1.54178$ Å, $2\theta_{max} = 112.12°$), triclinic, space group $P\bar{1}$, $a = 10.652(3)$, $b = 14.558(5)$, and $c = 16.561(5)$ Å, $\alpha = 94.01(3)°$, $\beta = 91.76(2)°$, $\gamma = 103.15(2)°$, $V = 2491.8(14)$ Å^3, $Z = 2$, refined against $|F^2|$ using all data, R1 = 0.120, wR = 0.27, $S = 1.082$ for 6496 reflections and 629 parameters. **36b**: $C_{58}H_{48}N_4O_2 \cdot CH_2Cl_2$ at 126 K (Cu Kα radiation $\lambda = 1.54178$ Å, $2\theta_{max} = 114°$), monoclinic, space group $P2_1/n$, $a = 10.388(3)$, $b = 15.525(4)$, and $c = 28.804(6)$ Å, $\beta = 98.8(2)°$, $V = 4887(2)$ Å^3, $Z = 4$, refined against $|F^2|$ using all data, R1 = 0.129, wR2 = 0.322, $S = 1.077$ for 6438 reflections and 604 parameters. Full details of the crystallographic studies will be given elsewhere.[30]

Trimethyl-1,4-benzoquinone (1). Iron(III) chloride (40 g, 145 mmol) was dissolved in 150 mL of water and mixed with 10 g (65.7 mmol) of trimethylhydroquinone in 100 mL of ether. After the mixture was stirred for 2 h the organic phase was separated and the aqueous phase extracted with 2 × 50 mL of ether. After drying (Na_2SO_4) and filtering of the combined organic phases, the solvent was evaporated and the residue was dissolved in dichloromethane and run through a small column of dry silica gel. After drying 9.2 g (93.5%) of a yellow solid was obtained, mp 29−30 °C (lit.[31] mp 29−30 °C). ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.94 (s, 3H), 1.96 (s, 3H), 1.97 (d, $J = 1.6$ Hz, 3H), 6.40 (q, $J = 1.6$ Hz, 1H).

Sodium 4-[4-Hydroxy-2-(trifluoromethyl)phenylazo]-benzenesulfonate (7). A precooled (15 °C) solution of 79.0 g (0.46 mol) of 4-aminobenzene sulfonic acid, 24.4 g (0.23 mol) of sodium carbonate, and 35 g (0.5 mol) of sodium nitrite in 450 mL of water was added to a mixture of 550 g of ice and 96 mL (1.15 mol) of hydrochloric acid (37%, w/w). After 30 min of standing in an ice bath, the suspension of **6** was gradually added at 0−5 °C to a solution of 67 g (0.41 mol) of 3-(trifluoromethyl)phenol (**5**) and 32.8 g sodium hydroxide in 300 mL of water. After addition of sodium chloride the reddish brown product was filtered off, dried, and used for the next step without further purification. An analytical sample was obtained after 2-fold recrystallization from water, mp > 350 °C. ^{1}H NMR (250 MHz, DMSO-d_6): δ 7.16 (dd, $J = 7.5$ Hz, 2.5 Hz, 1H), 7.26 (d, $J = 2.5$ Hz, 1H), 7.80 (s, 4H), 7.84 (d, $J = 7.5$ Hz, 1H). ^{19}F NMR (DMSO-d_6): δ −55.9 (s). UV (water): λ_{max} (log ϵ) 234 (4.17), 350 (4.54), 430 (sh) (3.54) nm. FABMS: *m*/*z* (%) 391 (20) ([M + Na]$^+$), 367 (35) ([M − H]$^-$), 345 (100) ([M − Na]$^-$). Anal. Calcd for $C_{13}H_8F_3N_2NaO_4S \cdot 2.5H_2O$: C, 37.78; H, 3.17; N, 6.78. Found: C, 37.82; H, 3.04; N, 6.66.

4-Amino-3-(trifluoromethyl)phenol (8). A vigorously stirred suspension of the azo dye **7** in 1000 mL of water was warmed to 50 °C, and 300 g (1.7 mol) of sodium hyposulfite was added in portions. After the solution was cooled to 20 °C, the product was filtered off, washed with cold water, and dried. After sublimation (0.1 mbar/85 °C bath temperature) 47.2 g of the product (65% corresponding to **5**) was obtained, mp 158 °C (lit.[32] mp 158 °C). ^{1}H NMR (250 MHz, DMSO-d_6): δ 4.88 (br s, 2H), 6.78 (m, 3H), 8.94 (s, 1H). ^{19}F NMR (DMSO-d_6): δ −60.9 (s).

2-(Trifluoromethyl)-1,4-benzoquinone (9). A solution of 11.6 g (65.2 mmol) of 4-amino-3-(trifluoromethyl)phenol (**8**) in 120 mL of 2.5 M sulfuric acid was added at 5 °C to a suspension of 13.0 g (150 mmol) of manganese(IV) oxide in 120 mL of 2.5 M sulfuric acid over the course of 3 h. After 2 h of stirring at 5 °C and filtration, the residue was extracted five times with 200 mL of hexane each. The combined hexane fractions were cooled to −95 °C and allowed to stand for 1 h. After filtration and drying 4.2 g (35%) of the product was obtained which was sufficiently pure for the next step. Hint: The product is very volatile and should be kept at −30 °C. For analytical purposes 200 mg was sublimed at 15 mbar/40 °C bath temperature and 15 mbar/rt, mp 54−55 °C (lit.[9] mp 54−55 °C), R_f (TLC, dichloromethane) = 0.8. ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.94 (m, 2H), 7.14 (m, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 120.41 (q, $J_{C-F} = 277$ Hz), 134.60 (q, $J_{C-F} = 4.8$ Hz), 135.30 (q, $J_{C-F} = 31.4$ Hz), 136.47 (s), 137.02 (s), 181.42 (s), 185.55 (s). ^{19}F NMR ($CDCl_3$): δ −66.4 (s).

(±)-*trans*-5,6-Dibromo-2-(trifluoromethyl)cyclohex-2-ene-1,4-dione (10). Bromine (4 g, 25 mmol, 1.3 mL) was added to a solution of 4.05 g (23 mmol) **9** in 50 mL of dichloromethane. After the solution was stirred for 2.5 h at rt, the solvent was evaporated and the colorless residue dried. Yield: 7.7 g (quantitative yield). The product is sufficiently pure for the next step. For analysis 100 mg of the crude product was sublimed at 0.1 mbar/65 °C bath temperature and 0.1 mbar/rt, mp 89−90 °C, R_f (TLC, dichloromethane) = 0.8. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.86 (dd, $J = 3.0$, 1.90 Hz, 1H), 4.88 (d, $J = 3.0$ Hz, 1H), 7.05 (m, $J = 1.90$ Hz, 0.95 Hz, 1H). ^{19}F NMR ($CDCl_3$): δ −67.0 (s). EIMS: *m*/*z* (%) 334 (6) [M$^+$(^{79}Br)], 255 (100) [M$^+$(^{79}Br) − ^{79}Br]. HRMS: calcd for $C_7H_3Br_2F_3O_2$ 333.84522, found 333.84554. Anal. Calcd for $C_7H_3Br_2F_3O_2$: C, 25.03; H, 0.90. Found: C, 24.94; H, 0.95.

2,3-Dibromo-5-(trifluoromethyl)-1,4-dihydroxybenzene (11). A total of 50 mL of precooled (0 °C) concentrated sulfuric acid (98% w/w, $\rho = 1.84$ g/mL) was added to 6.05 g (18 mmol) of the dibromo adduct **10**. After being stirred at the same temperature for 2.5 h, the reaction mixture was poured on ice and filtered and the residue was thoroughly washed with water. After drying and sublimation at 0.1 mbar/80 °C, 5.3 g (87.7%) product was obtained, mp 145−147 °C, R_f (TLC, dichloromethane) = 0.5. ^{1}H NMR (250 MHz, DMSO-d_6): δ 7.14 (s, 1H), 9.66 (s, 1H), 10.60 (s, 1H). ^{19}F−NMR (DMSO-d_6): δ −62.0 (s). EIMS: *m*/*z* (%) 334 (22) [M$^+$(^{79}Br)], 314 (53) [M$^+$(^{79}Br) − HF], 286 (19) [M$^+$(^{79}Br) − CO − HF], 235 (35) [M$^+$(^{79}Br) − ^{79}Br − HF]. HRMS: calcd for $C_7H_3Br_2F_3O_2$

333.84522, found 333.84504. Anal. Calcd for $C_7H_3Br_2F_3O_2$: C, 25.03; H, 0.90. Found: C, 25.25; H, 0.97.

2,3-Dibromo-5-(trifluoromethyl)-1,4-benzoquinone (4). DDQ (4.1 g, 18 mmol) dissolved in 60 mL of toluene was added to 5.36 g (16 mmol) of **11** dissolved in 50 mL of ether within 1.5 h. After further stirring for 2 h at rt, the solvent was removed by distillation, and the residue was dissolved in dichloromethane and filtered through a short silica gel column. After evaporation of dichloromethane and sublimation at 0.1 mbar/85 °C bath temperature, **4** was obtained in 90% yield (4.8 g), mp 162−164 °C, R_f (TLC, toluene/hexane 1:1) = 0.5. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.38 (q, J = 1.0 Hz, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 119.99 (q, J_{C-F} = 275 Hz), 134.58 (q, J_{C-F} = 4.8 Hz), 134.97 (q, J_{C-F} = 31 Hz), 139.78 (s), 140.33 (s), 172.07 (s), 175.89 (s). ^{19}F NMR ($CDCl_3$): δ −66.1 (s). UV (dichloromethane): λ_{max} (log ϵ) 251 (4.01), 373 (3.34) nm. EIMS: m/z (%) 332 (26) [M^+(^{79}Br)], 253 (55) [M^+(^{79}Br) − ^{79}Br], 225 (61) [M^+(^{79}Br) − ^{79}Br − CO], 131 (100) [M^+(^{79}Br) − ^{79}Br − C_3HF_3 − CO]. HRMS: calcd for $C_7HBr_2F_3O_2$ 331.82957, found 331.82938. Anal. Calcd for $C_7HBr_2F_3O_2$: C, 25.18; H, 0.30. Found: C, 25.25; H, 0.44.

General Procedure for the Radical Alkylation of the Quinones. The quinone, **12a**/**b**, and silver nitrate were dissolved in a mixture of equal volumes of water and dichloromethane and heated to reflux. An aqueous solution of ammonium peroxodisulfate was added within 3−5 h and heating was continued for 1 h. The organic phase was separated, the aqueous one was extracted with dichloromethane, and the combined organic phases were dried over sodium sulfate. After filtration and evaporation of the solvent the crude product was purified by column chromatography. In all cases the *cis*/*trans* ratio was 3:2. Separation of the isomers for analytical purposes was achieved by preparative HPLC.

2-[4-(Methoxycarbonyl)cyclohexyl]-3,5,6-trimethyl-1,4-benzoquinone (*Cis*/*Trans* Mixture 13a/b). Ammonium peroxodisulfate (11.5 g, 50.4 mmol), dissolved in 100 mL of water and 5 g (33.3 mmol) of the quinone **1**, 9.3 g (50 mmol) **12a**/**b**, 1.72 g (10 mmol) of silver nitrate in 50 mL of water, and dichloromethane each were reacted according to the general procedure. After column chromatography (eluant: dichloromethane) 5.0 g (51.5%) of a dark yellow oil was obtained. Separation of the diastereomers by preparative HPLC: column, 32 × 125 mm; stationary phase, Nucleosil 50, 5 μm; mobile phase, hexane/ethyl acetate 40:1; t_R = 14.4 min (**13a**); t_R = 16.0 min (**13b**); flow rate, 64 mL/min. Analytical HPLC: column, 4 × 250 mm; stationary phase, Nucleosil 50, 5 μm; mobile phase, hexane/ethyl acetate 40:1; t_R = 19.4 min (**13a**); t_R = 21.4 min; (**13b**); flow rate, 1.5 mL/min.

2-[4(a)-(Methoxycarbonyl)cyclohex-(e)-yl]-3,5,6-trimethyl-1,4-benzoquinone (13a): mp 92−93 °C, R_f (TLC, dichloromethane) = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.40 (br d, J = 13.5 Hz, 2H), 1.50 (tt, J = 13.0, 4.2 Hz, 2H), 1.90 (s, 6H), 2.00 (s, 3H), 2.04 (qd, J = 13.0 Hz, 3.3 Hz, 2H), 2.22 (br d, J = 13.8 Hz, 2H), 2.68 (m, 1H), 2.80 (tt, J = 12.5, 3.1 Hz, 1H), 3.70 (s, 3H). EIMS: m/z (%) 290 (100) [M^+], 230 (70) [M^+ − CH_3OH − CO]. Anal. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.63. Found: C, 70.24; H, 7.63.

2-[4(e)-(Methoxycarbonyl)cyclohex-(e)-yl]-3,5,6-trimethyl-1,4-benzoquinone (13b): mp 77−78 °C, R_f (TLC, dichloromethane) = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.46 (qd, J = 12.6, 3.7 Hz, 2H), 1.58 (br d, J = 14.0 Hz, 2H), 1.91 (s, 3H), 1.92 (s, 3H), 1.98 (m, 4H), 1.98 (s, 3H), 2.38 (tt, J = 12.2, 3.6 Hz, 1H), 2.64 (tt, J = 12.5 Hz, 3.5 Hz, 1H), 3.64 (s, 3H). UV (dichloromethane): λ_{max} (log ϵ) 264 (4.27), 271 (4.26), 344 (2.47) nm. EIMS: m/z (%) 290 (85) [M^+], 230 (100) [M^+ − CH_3OH − CO]. Anal. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.63. Found: C, 70.24; H, 7.59.

2-[4(a)-(Methoxycarbonyl)cyclohex-(e)-yl]-3-methyl-1,4-naphthoquinone (*Cis*/*Trans* Mixture 14a/b). Ammonium peroxodisulfate (10.3 g, 45 mmol) dissolved in 100 mL water, and 5 g (29.1 mmol) of the quinone **2**, 8.4 g (45 mmol) **12a**/**b**, 1.0 g (5.9 mmol) silver nitrate, each dissolved in 50 mL water and dichloromethane, were reacted according to the general procedure. After column chromatography (dichloromethane) 4.6 g (50.7%) of a yellow solid was obtained. Separation of the diastereomers by preparative HPLC: column, 32 × 125 mm; stationary phase, Nucleosil 50, 5 μm; mobile phase, hexane/ethyl acetate 25:1; t_R = 12.6 min (**14a**); t_R = 13.6 min (**14b**); flow rate, 64 mL/min. Analytical HPLC: column, 4 × 300 mm; stationary phase, Nucleosil 50, 5 μm, mobile phase, hexane/ethyl acetate 25:1; t_R = 18.7 min (**14a**); t_R = 19.7 min; (**14b**); flow rate, 1.5 mL/min.

2-[4(a)-(Methoxycarbonyl)cyclohex-(e)-yl]-3-methyl-1,4-naphthoquinone (14a): mp 117 °C, R_f (TLC, dichloromethane) = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.53 (br d, J = 13.5 Hz, 2H), 1.61 (tt, J = 13.5, 3.8 Hz, 2H), 2.22 (qd, J = 13.1, 3.4 Hz, 2H), 2.23 (s, 3H), 2.31 (br d, J = 14.1 Hz, 2H), 2.77 (m, 1H), 2.82 (tt, J = 12.5, 3.2 Hz, 1H), 3.80 (s, 3H), 7.69 (m, 2H), 8.03 (m, 2H). EIMS: m/z (%) 312 (100) [M^+], 252 (72) [M^+ − CH_3OH − CO]. Anal. Calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 72.93; H, 6.41.

2-[4(e)-(Methoxycarbonyl)cyclohex-(e)-yl]-3-methyl-1,4-naphthoquinone (14b): mp 114 °C, R_f (TLC, dichloromethane) = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.53 (qd, J = 13.0, 3.3 Hz, 2H), 1.68 (br d, J = 13.5 Hz, 2H), 2.11 (br d, J = 13.4 Hz, 2H), 2.18 (qd, J = 13.2, 3.6 Hz, 2H), 2.22 (s, 3H), 2.45 (tt, J = 12.5, 3.3 Hz, 1H), 2.82 (tt, J = 12.3, 3.2 Hz, 1H), 3.72 (s, 3H), 7.69 (m, 2H), 8.03 (m, 2H). UV (dichloromethane): λ_{max} (log ϵ) 242 (4.20), 248 (4.20), 268 (4.20), 274 (4.20), 329 (3.44), 420 (1.87) nm. EIMS: m/z (%) 312 (100) [M^+], 252 (96) [M^+ − CH_3OH − CO]. Anal. Calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 72.81; H, 6.36.

2-[4-(Methoxycarbonyl)cyclohexyl]-5,6-dimethoxy-3-methyl-1,4-benzoquinone (*Cis*/*Trans* Mixture 15a/b). Reaction of 10 g (43.8 mmol) of ammonium peroxodisulfate dissolved in 100 mL of water, 5 g (27.4 mmol) of the quinone **3**, 8 g (43 mmol) of **12a**/**b**, and 1.5 g (8.8 mmol) of silver nitrate, each dissolved in 50 mL of water and dichloromethane, under standard conditions gave 3.2 g (35.6%) of a dark red oil after column chromatography (dichloromethane/ethyl acetate 20:1). Separation of the diastereomers by preparative HPLC: column, 32 × 250 mm; stationary phase, Nucleosil 50, 7 μm; mobile phase, dichloromethane; t_R = 7.06 min (**15b**); t_R = 8.62 min (**15a**); flow rate, 64 mL/min. Analytical HPLC: column, 4 × 120 mm; stationary phase, Eurospher 80, 5 μm; mobile phase, dichloromethane/water 99.9:0.1; t_R = 1.46 min (**15b**); t_R = 1.74 min (**15a**); flow rate, 2 mL/min.

2-[4(a)-(Methoxycarbonyl)cyclohex-(e)-yl]-5,6-dimethoxy-3-methyl-1,4-benzoquinone (15a): mp 77−78 °C, R_f (TLC, dichloromethane/ether 20:1) = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.38 (br d, $^2J_{2a2e}$ = 13.4 Hz, 2H, H_e-2, H_e-6), 1.48 (tt, $^2J_{3a3e} \approx J_{2a3a} \approx$ 13.5 Hz, $J_{2e3a} \approx J_{3a4e} \approx$ 4.3 Hz, 2H, H_a-3, H_a-5), 2.01 (s, 3H, CH_3-quinone), 2.01 (qd, $^2J_{2a2e} \approx J_{1a2a} \approx J_{2a3a} \approx$ 13.2 Hz, J_{2a3e} = 3.5 Hz, 2H, H_a-2, H_a-6), 2.21 (br d, $^2J_{3a3e}$ = 14.0 Hz, 2H, H_e-3, H_e-5), 2.66 (m, 1H, H_e-4), 2.82 (tt, $J_{1a2a} = J_{1a6a}$ = 12.5 Hz, $J_{1a2e} = J_{1a6e}$ = 3.3 Hz, 1H, H_a-1), 3.76 (s, 3H, CH_3OCO), 3.91 (s, 3H, CH_3O), 3.92 (s, 3H, CH_3O). EIMS: m/z (%) 322 (100) [M^+], 262 (47) [M^+ − CH_3OH − CO]. Anal. Calcd for $C_{17}H_{22}O_6$: C, 63.34; H, 6.88. Found: C, 63.32; H, 6.60.

2-[4(e)-(Methoxycarbonyl)cyclohex-(e)-yl]-5,6-dimethoxy-3-methyl-1,4-benzoquinone (15b): mp 65−66 °C, R_f (TLC, dichloromethane/ether 20:1) = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.44 (qd, $^2J_{3a3e} \approx J_{2a3a} \approx J_{3a4a} \approx$ 12.9 Hz, J_{2e3a} = 3.3 Hz, 2H, H_a-3, H_a-5), 1.59 (br d, $^2J_{2a2e}$ = 13.2 Hz, 2H, H_e-2, H_e-6), 1.97 (qd, $^2J_{2a2e} \approx J_{1a2a} \approx J_{2a3a} \approx$ 13.1 Hz, J_{2a3e} = 3.7 Hz, 2H, H_a-2, H_a-6), 2.03 (s, 3H, CH_3-quinone), 2.04 (br d, 2H, H_e-3, H_e-5), 2.37 (tt, $J_{3a4a} = J_{4a5a}$ = 12.3 Hz, $J_{3e4a} = J_{4a5e}$ = 3.4 Hz, 1H, H_a-4), 2.65 (tt, $J_{1a2a} = J_{1a6a}$ = 12.5 Hz, $J_{1a2e} = J_{1a6e}$ = 3.3 Hz, 1H, H_a-1), 3.64 (s, 3H, CH_3OCO), 3.93 (s, 3H, CH_3O), 3.94 (s, 3H, CH_3O). UV (dichloromethane): λ_{max} (log ϵ) 280 (4.18), 408 (2.67) nm. EIMS: m/z (%) 322 (100) [M^+], 262 (42) [M^+ − CH_3OH − CO]. Anal. Calcd for $C_{17}H_{22}O_6$: C, 63.34; H, 6.88. Found: C, 63.13; H, 6.70.

2,3-Dibromo-5-[4(a)-(methoxycarbonyl)cyclohex-(e)-yl]-6-(trifluoromethyl)-1,4-benzoquinone (*Cis*/*Trans* Mixture 16a/b). Reaction of 15.0 g (65.7 mmol) of ammonium peroxodisulfate, dissolved in 100 mL of water, 3 g (8.9 mmol) of quinone **4**, 2.5 g (13.4 mmol) of **12a**/**b**, and 0.5 g (2.9 mmol) of silver nitrate, each dissolved in 50 mL of water and dichloromethane following the standard procedure, gave 1.3 g (30%) of a dark yellow oil after column chromatography (dichloromethane). Separation of the diastereomers by pre-

parative HPLC: column, 32 × 125 mm; stationary phase, Nucleosil 50, 5 μm; mobile phase, hexane/dichloromethane 2:1; t_R = 21 min (**16a**); t_R = 23 min (**16b**); flow rate, 64 mL/min. Analytical HPLC: column, 4 × 250 mm; stationary phase, Nucleosil 50, 5 μm; mobile phase, hexane/dichloromethane 3:2; t_R = 21.4 min (**16a**); t_R = 23.4 min (**16b**); flow rate, 1.5 mL/min.

2,3-Dibromo-5-[4(a)-(methoxycarbonyl)cyclohex-(e)-yl]-6-(trifluoromethyl)-1,4-benzoquinone) (16a): mp 116−118 °C, R_f (TLC, dichloromethane) = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.56 (m, 4H), 2.12 (qd, J = 13.3, 3.7 Hz, 2H), 2.33 (br d, J = 14.0 Hz, 2H), 2.75 (m, 1H), 3.10 (tt, J = 12.5, 3.3 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 26.98 (s), 27.24 (s), 38.10 (s), 41.55 (s), 51.88 (s), 121.50 (q, J_{C-F} = 279 Hz), 131.90 (q, J_{C-F} = 30 Hz), 139.15 (q, J_{C-F} = 2 Hz), 139.56 (s), 155.02 (s), 173.39 (s), 174.71 (s), 176.54 (s). ^{19}F NMR ($CDCl_3$): δ −56.7 (s). EIMS: *m/z* (%) 472 (11) [M^+(^{79}Br)], 412 (47) [M^+(^{79}Br) − CH_3OH − CO]. HRMS: calcd for $C_{15}H_{13}Br_2F_3O_4$ 471.91330, found 471.91341. Anal. Calcd for $C_{15}H_{13}Br_2F_3O_4$: C, 38.00; H, 2.76. Found: C, 38.07; H, 2.75.

2,3-Dibromo-5-[4(e)-(methoxycarbonyl)cyclohex-(e)-yl]-6-(trifluoromethyl)-1,4-benzoquinone (16b): mp 102−103 °C, R_f (TLC, dichloromethane) = 0.6. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.52 (qd, J = 13.1, 3.4 Hz, 2H), 1.74 (dq, J = 13.4, 3.2 Hz, 2H), 2.05 (qd, J = 13.0, 3.7 Hz, 2H), 2.12 (dq, J = 13.4, 3.1 Hz, 2H), 2.44 (tt, J = 12.5, 3.8 Hz, 1H), 3.02 (tt, J = 12.3, 3.4 Hz, 1H), 3.70 (s, 3H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 28.84 (s), 29.33 (s), 41.19 (s), 42.11 (s), 51.71 (s), 121.41 (q, J_{C-F} = 279 Hz), 132.22 (q, J_{C-F} = 30 Hz), 139.31 (q, J_{C-F} = 2 Hz), 139.45 (s), 154.79 (s), 173.24 (s), 175.70 (s), 176.81 (s). ^{19}F NMR ($CDCl_3$): δ −57.2 (s). UV (dichloromethane): λ_{max} (log ϵ) 278 (3.91), 366 (2.99) nm. EIMS: *m/z* (%) 472 (1) [M^+(^{79}Br)], 412 (33) [M^+(^{79}Br) − CH_3OH − CO], 372 (53) [M^+(^{79}Br) − CH_3OH − CO − 2HF]. HRMS: calcd for $C_{15}H_{13}Br_2F_3O_4$ 471.91330, found 471.91341. Anal. Calcd for $C_{15}H_{13}Br_2F_3O_4$: C, 38.00; H, 2.76. Found: C, 37.93; H, 2.77.

2,3-Dibromo-5-[4-(methoxycarbonyl)cyclohexyl]-6-(trifluoromethyl)-1,4-dihydroxybenzene (*Cis*/*Trans* Mixture 20a/b). *Cis*/*Trans* mixture **16a**/**b** (5 g, 10.5 mmol), dissolved in 100 mL of toluene, was hydrogenated with 50 mg of palladium catalyst (Pd−C; 10% Pd). After uptake of hydrogen had ceased, the solution was filtered, the solvent distilled off, and the remaining colorless oil dried yielding quantitatively the *cis*/*trans* mixture of **20a**/**b**. For analytical purposes, small amounts of isomerically pure samples of **20a** and **20b**, respectively, were reduced to the corresponding hydroquinones under the same conditions as described for the *cis*/*trans* mixture of **20a**/**b**.

2,3-Dibromo-5-[4(a)-(methoxycarbonyl)cyclohex-(e)-yl]-6-(trifluoromethyl)-1,4-dihydroxybenzene (20a). Ester **16a** (50 mg, 0.1 mmol), dissolved in 10 mL of toluene, was hydrogenated with 5 mg of palladium catalyst in quantitative yield and worked up as described above. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.50 (br d, J = 13.2 Hz, 2H), 1.58 (tt, J = 13.4, 4.1 Hz, 2H), 2.28 (br d, J = 14.0 Hz, 2H), 2.40 (qd, J = 13.0, 4.1 Hz, 2H), 2.74 (m, 1H), 3.08 (tt, J = 12.5, 3.5 Hz, 1H), 3.76 (s, 3H), 5.86 (s, 1H), 6.00 (s, 1H). ^{19}F NMR ($CDCl_3$): δ −52.2 (s). EIMS: *m/z* (%) 474 (22) [M^+(^{79}Br)], 414 (57) [M^+(^{79}Br) − CH_3OH − CO]. HRMS: calcd for $C_{15}H_{15}Br_2F_3O_4$ 473.92895, found 473.92905.

2,3-Dibromo-5-[4(e)-(methoxycarbonyl)cyclohex-(e)-yl]-6-(trifluoromethyl)-1,4-dihydroxybenzene (20b). Ester **16b** (50 mg, 0.1 mmol), dissolved in 10 mL of toluene, was hydrogenated with 5 mg of palladium catalyst in quantitative yield and worked up as described above. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.54 (qd, J = 13.3, 3.5 Hz, 2H), 1.66 (br d, J = 13.2 Hz, 2H), 2.08 (br d, J = 14.0 Hz, 2H), 2.30 (qd, J = 13.0, 3.6 Hz, 2H), 2.40 (tt, J = 12.5, 3.2 Hz, 1H), 3.01 (tt, J = 12.5, 3.2 Hz, 1H), 3.68 (s, 3H), 5.60 (s, 1H), 5.96 (s, 1H). ^{19}F NMR ($CDCl_3$): δ −52.2 (s). EIMS: *m/z* (%) 474 (21) [M^+(^{79}Br)], 414 (43) [M^+(^{79}Br) − CH_3OH − CO]. HRMS: calcd for $C_{15}H_{15}Br_2F_3O_4$ 473.92895, found 473.92882.

2-[4-(Hydroxymethyl)cyclohexyl]-3,5,6-trimethyl-1,4-benzoquinone (*Cis*/*Trans* Mixture 25a/b). 13a/**b** (5 g, 17.2 mmol), was dissolved in 60 mL of THF, and 100 mg of catalyst for hydrogenation (Pd−C, 10% Pd) was added. After cessation of hydrogen uptake, the catalyst was removed and 1.6 g (73.5 mmol) of lithium borohydride added. After being heated under reflux for 20 h, the reaction mixture was cautiously hydrolyzed with water and hydrochloric acid. Subsequently, 100 mL of ether and within 20 min 100 mL of an aqueous solution of ammonium cerium(IV) nitrate (23.6 g, 43 mmol) were added. The ether layer was separated, the aqueous one was extracted three times with 50 mL of ether, and the combined organic phases were dried over Na_2SO_4. After filtration and evaporation of the solvent the yellow residue was purified by column chromatography (dichloromethane/acetone 10:1) yielding 3.3 g (72%) of product. Separation of the diastereomers with preparative HPLC: column, 32 × 125 mm; stationary phase, Nucleosil 50, 5 μm; mobile phase, dichloromethane/ethyl acetate 97:3; t_R = 12.8 min (**25b**); t_R = 15 min (**25a**); flow rate, 64 mL/min. Analytical HPLC: column, 4 × 250 mm; stationary phase, Nucleosil 50, 5 μm; mobile phase, dichloromethane/ethyl acetate 20:1; t_R = 17.2 min (**25b**); t_R = 19.8 min (**25a**); flow rate, 1.5 mL/min.

2-[4(a)-(Hydroxymethyl)cyclohex-(e)-yl]-3,5,6-trimethyl-1,4-benzoquinone (25a): mp 91−92 °C, R_f (TLC, dichloromethane/acetone 10:1) = 0.4. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.36 (dq, J = 13.4, 3.5 Hz, 2H), 1.48 (s, 1H), 1.54 (tt, J = 13.5, 4.2 Hz, 2H), 1.90 (dq, J = 14.0, 3.4 Hz, 2H), 1.92 (m, 1H), 1.98 (q, J = 2.0 Hz, 3H), 1.99 (q, J = 2.0 Hz, 3H), 2.04 (qd, J = 13.3, 3.6 Hz, 2H), 2.08 (s, 3H), 2.74 (tt, J = 12.5, 3.4 Hz, 1H), 3.86 (d, J = 7,5 Hz, 2H). EIMS: *m/z* (%) 262 (100) [M^+], 244 (42) [M^+ − H_2O]; 229 (42) [M^+ − CH_3 − H_2O]. Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.24; H, 8.33.

2-[4(e)-(Hydroxymethyl)cyclohex-(e)-yl]-3,5,6-trimethyl-1,4-benzoquinone (25b): mp 73−74 °C, R_f (TLC, dichloromethane/acetone 10:1) = 0.4. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.06 (qd, J = 12.7, 3.7 Hz, 2H), 1.58 (s, 1H), 1.61 (m, 3H), 1.90 (dq, J = 14.0, 3.2 Hz, 2H), 1.98 (q, J = 2 Hz, 3H), 1.99 (q, J = 2 Hz, 3H), 3H), 2.01 (qd, J = 13.0, 3.5 Hz, 2H), 2.08 (s, 3H), 2.70 (tt, J = 12.5, 3.5 Hz, 1H), 3.50 (d, J = 7.5 Hz, 2H). EIMS: *m/z* (%) 262 (100) [M^+], 244 (45) [M^+ − H_2O]; 229 (39) [M^+ − CH_3 − H_2O]. Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.15; H, 8.35.

2-[4-(Hydroxymethyl)cyclohexyl]-3-methyl-1,4-naphthoquinone (*Cis*/*Trans* Mixture 26a/b). Esters **14a**/**b** (5 g, 16 mmol) were converted to the corresponding alcohols via catalytical hydrogenation, reduction of the ester group with lithium borohydride (1.5 g, 69 mmol), and oxidation of the hydroquinone with ammonium cerium(IV) nitrate (22 g, 40 mmol) as described for **13a**/**b**. After column chromatography (dichloromethane/acetone 10:1) 3.4 g (74.7%) of product were obtained. Separation of the diastereomers with preparative HPLC: column, 32 × 125 mm; stationary phase, Nucleosil 50, 5 μm; mobile phase, dichloromethane/ethyl acetate 98:2; t_R = 9.3 min (**26b**); t_R = 10.3 min (**26a**); flow rate, 64 mL/min. Analytical HPLC: column, 4 × 250 mm; stationary phase, Nucleosil 50, 5 μm; mobile phase, dichloromethane/ethyl acetate 10:1; t_R = 11.8 min (**26b**); t_R = 12.9 min (**26a**); flow rate, 1.5 mL/min.

2-[4(a)-(Hydroxymethyl)cyclohex-(e)-yl]-3-methyl-1,4-naphthoquinone (26a): mp 152 °C, R_f (TLC, dichloromethane/acetone 10:1) = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.41 (dq, J = 13.9, 3.2 Hz, 2H), 1.50 (s, 1H), 1.58 (tt, J = 13.7, 4.0 Hz, 2H), 1.92 (dq, J = 14.0, 3.9 Hz, 2H), 1.99 (m, 1H), 2.21 (qd, J =13.6, 3.4 Hz, 2H), 2.24 (s, 3H), 2.85 (tt, J = 12.5, 3.4 Hz, 1H), 3.91 (d, J = 7.5 Hz, 2H), 7.67 (m, 2H), 8.03 (m, 2H). EIMS: *m/z* (%) 284 (100) [M^+], 266 (73) [M^+ − H_2O]; 251 (51) [M^+ − CH_3 − H_2O]. Anal. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 75.79; H, 6.98.

2-[4(e)-(Hydroxymethyl)cyclohex-(e)-yl]-3-methyl-1,4-naphthoquinone (26b): mp 124 °C, R_f (TLC, dichloromethane/acetone 10:1) = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.11 (qd, J = 12.5, 3.8 Hz, 2H), 1.40 (s, 1H), 1.63 (m, 3H), 1.96 (dq, J = 14.0, 3.3 Hz, 2H), 2.14 (qd, J = 13.3, 3.8 Hz, 2H), 2.22 (s, 3H), 2.84 (tt, J = 12.5, 3.2 Hz, 1H), 3.52 (d, J = 7.0 Hz, 2H), 7.70 (m, 2H), 8.06 (m, 2H). EIMS: *m/z* (%) 284 (100) [M^+], 266 (62) [M^+ − H_2O]; 251 (42) [M^+ − CH_3 − H_2O]. Anal. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 75.82; H, 7.00.

2-[4-(Hydroxymethyl)cyclohexyl]-5,6-dimethoxy-3-methyl-1,4-benzoquinone (*Cis*/*Trans* Mixture 27a/b). An aqueous solution (150 mL) of 25 g (144 mmol) of sodium hyposulfite

was added to a solution of 100 mL of 5 g (15.5 mmol) of **15a**/**b** in dichloromethane and stirring was continued until the organic phase had turned colorless. The organic phase was separated, and the aqueous one was extracted three times with 30 mL of dichloromethane. The combined organic phases were dried over Na_2SO_4 under an argon atmosphere. After filtration the solvent was removed, the remaining oil was dissolved in 100 mL of THF, lithium borohydride was added in two portions of 510 mg each (total 1.02 g, 46.8 mmol), and the solution was heated under reflux for 20 h. Water, hydrochloric acid (25% w/w), and 100 mL of ether were added cautiously under cooling with ice. An aqueous solution (120 mL) of iron(III) chloride (12.2 g, 45 mmol) was added within 20 min and stirring was continued for 1 h. The ether phase was separated, the aqueous one was extracted three times with 30 mL of ether each. After drying (Na_2SO_4), filtration, and evaporation of the solvent, the dark red residue was purified by column chromatography (dichloromethane/acetone 10:1) yielding 2.6 g (57%) product. Attempted separation of the diastereomers with preparative HPLC was unsuccessful. For characterization of **27a** and **27b**, the isomerically pure esters **15a** and **15b** were reduced, respectively.

2-[4(a)-(Hydroxymethyl)cyclohex-(e)-yl]-5,6-dimethoxy-3-methyl-1,4-benzoquinone (27a). With one-tenth of the reaction scale as described above for the *cis*/*trans* mixture, **15a** was reduced to **27a**. Yield: 260 mg (56.9%), mp 89−90 °C, R_f (TLC, dichloromethane/acetone 10:1) = 0.4. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.35 (br d, J = 13.2, 2H), 1.55 (tt, J = 13.5, 3.6 Hz, 2H), 1.59 (s, 1H), 1.88 (br d, J = 14.0 Hz, 2H), 1.95 (m, 1H), 2.05 (qd, J = 12.9, 3.6 Hz, 2H), 2.06 (s, 3H), 2.71 (tt, J = 12.5, 3.2 Hz, 1H), 3.84 (d, J = 7.5 Hz, 2H), 3.98 (s, 3H), 3.99 (s, 3H). EIMS: *m*/*z* (%) 294 (100) [M^+]. Anal. Calcd for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53. Found: C, 65.29; H, 7.49.

2-[4(e)-(Hydroxymethyl)cyclohex-(e)-yl]-5,6-dimethoxy-3-methyl-1,4-benzoquinone (27b). With one-tenth the reaction scale as described above for **15a**/**b**, **15b** was reduced to **27b**. Yield: 270 mg (59.1%), mp 100−101 °C, R_f (TLC, dichloromethane/acetone 10:1) = 0.4. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.04 (qd, J = 12.8, 3.7 Hz, 2H), 1.48 (s, 1H), 1.61 (m, 3H), 1.90 (dq, J = 13.8, 3.2 Hz, 2H), 1.99 (qd, J = 12.8, 3.7 Hz, 2H), 2.06 (s, 3H), 2.70 (tt, J = 12.5, 3.5 Hz, 1H), 3.50 (d, J = 7.5 Hz, 2H), 3.98 (s, 3H), 3.99 (s, 3H). EIMS: *m*/*z* (%) 294 (100) [M^+]. Anal. Calcd for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53. Found: C, 65.17; H, 7.44.

2,3-Dibromo-5-[4-(hydroxymethyl)cyclohexyl]-6-(trifluoromethyl)-1,4-dihydroxybenzene (*Cis*/*Trans* Mixture 24a/b). A 1 M DIBALH solution (110 mL, 110 mmol) was added to a solution of 7.5 g (15.8 mmol) of **20a**/**b** in 100 mL of THF at −50 °C over the course of 40 min. Stirring was continued for 1 h at the same temperature, and 100 mL of 2 M hydrochloric acid was added. Subsequently the reaction mixture was warmed to rt, 150 mL of ether was added, and the organic phase was separated. The aqueous phase was extracted with five portions of 30 mL of ether each. The combined organic phases were dried (Na_2SO_4) and filtered, and the solvent was removed by distillation yielding 6.6 g (92.7%). Separation of the diastereomers by preparative HPLC: column, 32 × 125 mm; stationary phase, Nucleosil 50, 5 μm; mobile phase, dichloromethane/ethyl acetate 94:6; t_R = 11.2 min (**24b**); t_R = 13.4 min (**24a**); flow rate, 64 mL/min. Analytical HPLC: column, 4 × 250 mm; stationary phase, Nucleosil 50, 5 μm; mobile phase, dichloromethane/ethyl acetate 10:1; t_R = 6.9 min (**24b**); t_R = 9.0 min (**24a**); flow rate, 1.5 mL/min.

2,3-Dibromo-5-[4(a)-(hydroxymethyl)cyclohex-(e)-yl]-6-(trifluoromethyl)-1,4-dihydroxybenzene (24a): mp 122−123 °C, R_f (TLC, dichloromethane/acetone 10:1) = 0.4. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.37 (s, 1H, CH_2OH), 1.40 (dq, $^2J_{2a2e}$ = 13.4 Hz, $J_{1a2e} \approx J_{2e3a} \approx J_{2e3e} \approx$ 3.2 Hz, 2H, H_e-2, H_e-6), 1.58 (tt, $^2J_{3a3e} \approx J_{2a3a} \approx$ 13.8 Hz, $J_{2e3a} \approx J_{3a4e} \approx$ 3.9 Hz, 2H, H_a-3, H_a-5), 1.86 (dq, $^2J_{3a3e}$ = 13.8 Hz, $J_{2a3e} \approx J_{2e3e} \approx J_{3e4e} \approx$ 3.5 Hz, 2H, H_e-3, H_e-5), 1.92 (m, 1H, H_e-4), 2.34 (qd, $^2J_{2a2e} \approx J_{1a2a} \approx J_{2a3a} \approx$ 13.0 Hz, J_{2a3e} = 3.6 Hz, 2H, H_a-2, H_a-6), 3.06 (tt, $J_{1a2a} = J_{1a6a}$ = 12.5 Hz, $J_{1a2e} = J_{1a6e}$ = 3.6 Hz, 1H, H_a-1), 3.85 (d, J = 7.5 Hz, 2H, CH_2OH), 5.78 (s, 1H, OH), 5.98 (s, 1H, OH). ^{19}F NMR ($CDCl_3$): δ −52.1 (s). EIMS: *m*/*z* (%) 446 (13) [M^+(^{79}Br)], 428 (32) [M^+(^{79}Br) − H_2O], 360 (50) [M^+(^{79}Br) − C_5H_8 − H_2O]. HRMS: calcd for $C_{14}H_{15}Br_2F_3O_3$ 445.93403, found 445.93415. Anal. Calcd for $C_{14}H_{15}Br_2F_3O_3$: C, 37.52; H, 3.37. Found: C, 37.55; H, 3.34.

2,3-Dibromo-5-[4(e)-(hydroxymethyl)cyclohex-(e)-yl]-6-(trifluoromethyl)-1,4-dihydroxybenzene (24b): mp 139−140 °C, R_f (TLC, dichloromethane/acetone 10:1) = 0.4. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.07 (qd, $^2J_{3a3e} \approx J_{2a3a} \approx J_{3a4a} \approx$ 12.5 Hz, J_{2e3a} = 3.6 Hz, 2H, H_a-3, H_a-5), 1.38 (s, 1H, CH_2OH), 1.60 (m, 1H, H_a-4), 1.63 (dq, $^2J_{2a2e}$ = 13.0 Hz, $J_{1a2e} \approx J_{2e3a} \approx J_{2e3e} \approx$ 3.6 Hz, 2H, H_e-2, H_e-6), 1.90 (dq, $^2J_{3a3e}$ = 13.9 Hz, $J_{2a3e} \approx J_{2e3e} \approx J_{3e4a} \approx$ 3.2 Hz, 2H, H_e-3, H_e-5), 2.30 (qd, $^2J_{2a2e} \approx J_{1a2a} \approx J_{2a3a} \approx$ 12.5 Hz; J_{2a3e} = 3.6 Hz, 2H, H_a-2, H_a-6), 2.98 (tt, $J_{1a2a} = J_{1a6a} \approx$ 12 Hz, $J_{1a2e} = J_{1a6e} \approx$ 3 Hz, 1H, H_a-1), 3.51 (d, J = 7.0 Hz, CH_2OH), 5.60 (s, 1H, OH), 5.94 (s, 1H, OH). ^{19}F−NMR ($CDCl_3$): δ −52.2 (s). EIMS: *m*/*z* (%) 446 (49) [M^+(^{79}Br)], 428 (18) [M^+(^{79}Br) − H_2O], 360 (35) [M^+(^{79}Br) − C_5H_8 − H_2O]. HRMS: calcd for $C_{14}H_{15}Br_2F_3O_3$ 445.93403, found 445.93415. Anal. Calcd for $C_{14}H_{15}Br_2F_3O_3$: C, 37.52; H, 3.37. Found: C, 37.43; H, 3.29.

2-[4(a)-Formylcyclohex-(e)-yl]-3,5,6-trimethyl-1,4-benzoquinone (29a). 25a (0.71 g, 2.7 mmol), 0.014 g (0.09 mmol) of TEMPO, and 0.35 g (3 mmol) of potassium bromide were dissolved in a two-phase system of 8 mL of dichloromethane and 4 mL of water. After the solution was cooled to 0 °C, 3.5 mL of a sodium hypochlorite solution was added within 20 min in several portions under vigorous stirring. The pH of the sodium hypochlorite solution was adjusted with sodium hydrogencarbonate to 8.5 prior to addition. Potassium iodide (2 g) (in 3 mL of water) and subsequently 2.5 g of sodium thiosulfate (in 5 mL of water) were added. The organic phase was separated, and the aqueous one was extracted with 5 mL of dichloromethane. After drying over sodium sulfate, filtration, and removal of the solvent, 0.7 g (98.7%) of the aldehyde was obtained as a yellow oil. A pure sample of the aldehyde for elemental analysis could not be obtained, since attempted purification by chromatography or by recrystallization from hexane yielded a partially *cis*/*trans* isomerized or an oily product, respectively. However, the crude product was sufficiently pure for the reaction in the next step: R_f (TLC, dichloromethane/ether 50:1) = 0.5. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.50 (br d, 2H), 1.68 (tt, 2H), 1.98 (s, 3H), 1.99 (s, 3H), 2.00 (qd, 2H), 2.04 (s, 3H), 2.38 (br d, 2H), 2.56 (m, 1H), 2.82 (tt, 1H), 9.84 (s, 1H). EIMS: *m*/*z* (%) 260 (100) [M^+], 242 (13) [M^+ − H_2O]. HRMS: calcd for $C_{16}H_{20}O_3$ 260.14125, found 260.14120.

2-[4(e)-Formylcyclohex-(e)-yl]-3,5,6-trimethyl-1,4-benzoquinone (29b). Using the conditions described for **29a**, 0.85 g (3.23 mmol) of **25b**, 0.017 g (0.11 mmol) of TEMPO, and 0.39 g (3.25 mmol) of potassium bromide in a two-phase system of 10 mL of dichloromethane and 5 mL of water were treated with 4.5 mL of sodium hypochlorite (12%). Workup as described above gave 0.73 g (86%) of **29b** as a yellow oil. A pure sample of the aldehyde for elemental analysis could not be obtained, since attempted purification by chromatography or by recrystallization from hexane yielded a partially *cis*/*trans* isomerized or an oily product, respectively. However, the crude product was sufficiently pure for the reaction in the next step: R_f (TLC, dichloromethane/ether 50:1) = 0.5. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.34 (qd, 2H), 1.58 (br d, 2H), 1.98 (s, 3H), 1.99 (s, 3H), 2.04 (m, 4H), 2.08 (s, 3H), 2.36 (tt, 1H), 2.70 (tt, 1H), 9.68 (s, 1H). EIMS: *m*/*z* (%) 260 (100) [M^+], 242 (60) [M^+ − H_2O], 230 (78) [M^+ − CHO − H]. HRMS: calcd for $C_{16}H_{20}O_3$ 260.14125, found 260.14120.

2-[4(a)-Formylcyclohex-(e)-yl]-3-methyl-1,4-naphthoquinone (30a). Analogous to the synthesis of **29a**, 1.0 g (3.5 mmol) of **26a**, 0.013 g (0.08 mmol) of TEMPO, and 0.03 g (0.25 mmol) of potassium bromide in a two-phase system of 10 mL of dichloromethane and 5 mL of water were treated with 3.5 mL of sodium hypochlorite (12%). Workup as described for **29a** yielded 0.84 g (85%) of **30a**, which was recrystallized from hexane, mp 144 °C, R_f (TLC, dichloromethane/ether 50:1) = 0.5. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.54 (br d, 2H), 1.68 (tt, 2H), 2.08 (qd, 2H), 2.20 (s, 3H), 2.36 (br d, 2H), 2.56 (m, 1H), 2.96 (tt, 1H), 7.64 (m, 2H), 8.00 (m, 2H), 9.84 (s, 1H). EIMS: *m*/*z* (%) 282 (100) [M^+]. Anal. Calcd for $C_{18}H_{18}0_3$: C, 76.57; H, 6.43. Found: C, 76.46; H, 6.44.

2-[4(e)-Formylcyclohex-(e)-yl]-3-methyl-1,4-naphthoquinone (30b). Reaction scale and workup was as described for **30a**. Yield: 0.82 g (83%) of **30b**, R_f (TLC, dichloromethane/ether 50:1) = 0.5. A pure sample of the aldehyde for elemental analysis could not be obtained, since attempted purification by chromatography or by recrystallization from hexane yielded a partially *cis*/*trans* isomerized or an oily product, respectively. However, the crude product was sufficiently pure for the reaction in the next step. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.24 (qd, 2H), 1.64 (br d, 2H), 2.08 (m, 4H), 2.12 (s, 3H), 2.32 (tt, 1H), 2.74 (tt, 1H), 7.52 (m, 2H), 8.84 (m, 2H), 9.56 (s, 1H). EIMS: *m*/*z* (%) 282 (100) [M^+]. HRMS: calcd 282.12560, found 282.12529.

2-[4-Formylcyclohexyl]-5,6-dimethoxy-3-methyl-1,4-benzoquinone (*Cis*/*Trans* Mixture 31a/b). Pyridinium chlorochromate (PCC) (3.0 g, 16.6 mmol) was added to 1.8 g (6.1 mmol) of **27a**/**b** in 20 mL of dichloromethane, and the solution was stirred for 2.5 h. After dilution with 20 mL of ether, the reaction mixture was filtered over Florisil, the solvent was evaporated, and the oily residue was dried in vacuo. Yield: 1.4 g (75%). *Cis*/*trans* ratio: 1:1 (from ^{1}H NMR spectrum). For characterization of **31a** and **31b**, small amounts of **27a** and **27b** were oxidized, respectively.

2-[4(a)-Formylcyclohex-(e)-yl]-5,6-dimethoxy-3-methyl-1,4-benzoquinone (31a). **27a** (60 mg, 0.2 mmol) was dissolved in 5 mL of dichloromethane, and 90 mg (0.4 mmol) of PCC was added. After workup as described above, 50 mg (85%) of the aldehyde was obtained as an orange oil. A pure sample of the aldehyde for elemental analysis could not be obtained, since attempted purification by chromatography or by recrystallization from hexane yielded no analytically pure product. *Cis*/*trans* ratio (from ^{1}H NMR spectrum): 15:85. R_f (TLC, toluene/acetone 10:1) = 0.5. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.50 (br d, 2H), 1.64 (tt, 2H), 1.84 (qd, 2H), 2.04 (s, 3H), 2.36 (br d, 2H), 2.51 (m, 1H), 2.80 (tt, 1H), 3.99 (s, 6H), 9.80 (s, 1H). EIMS: *m*/*z* (%) 292 (100) [M^+], 264 (13) [$M^+ -$ CO]. HRMS: calcd for $C_{16}H_{20}O_5$ 292.13108, found 292.13102.

2-[4(e)-Formylcyclohex-(e)-yl]-5,6-dimethoxy-3-methyl-1,4-benzoquinone (31b). **27b** was oxidized as described for **27a** yielding 47 mg (81.3%) of aldehyde as an orange oil. A pure sample of the aldehyde for elemental analysis could not be obtained, since attempted purification by chromatography or by recrystallization from hexane yielded no analytically pure product. However, the crude product was sufficiently pure for the reaction in the next step. *Cis*/*trans* ratio (from ^{1}H NMR spectrum): 5:95. R_f (TLC, toluene/acetone 10:1) = 0.5. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.32 (qd, 2H), 1.58 (br d, 2H), 2.04 (s, 3H), 2.08 (m, 4H), 2.36 (tt, 1H), 2.66 (tt, 1H), 3.99 (s, 3H), 4.00 (s, 3H), 9.64 (s, 1H). EIMS: *m*/*z* (%) 292 (100) [M^+], 263 (10) [$M^+ -$ CHO]. HRMS: calcd for $C_{16}H_{20}O_5$ 292.13108, found 292.13099.

2,3-Dibromo-5-[4(a)-formylcyclohex-(e)-yl]-6-(trifluoromethyl)-1,4-benzoquinone (28a). PCC (3.4 g, 15.7 mmol) was added to 1.4 g (3.1 mmol) of **24a** in 20 mL of dichloromethane, and the solution was reacted for 2 h. After dilution with 20 mL of ether, filtration over Florisil, and drying in vacuo, 1.1 g (75%) of the aldehyde was obtained as a dark yellow oil. A pure sample of the aldehyde for elemental analysis could not be obtained, since attempted purification by chromatography or by recrystallization from hexane yielded no analytically pure product. *Cis*/*trans* ratio (from ^{1}H NMR spectrum): 9:1. R_f (TLC, dichloromethane/ether 50:1) = 0.7. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.56 (m, 4H), 2.00 (qd, 2H), 2.36 (br d, 2H), 2.54 (m, 1H), 2.80 (tt, 1H), 9.80 (s, 1H). ^{19}F NMR ($CDCl_3$): δ −57.2 (s). EIMS: *m*/*z* (%) 442 (43) [M^+(^{79}Br)], 424 (24) [M^+(^{79}Br) − H_2O]. HRMS: calcd for $C_{14}H_{11}Br_2F_3O_3$ 441.90273, found 441.0279.

2,3-Dibromo-5-[4(a)-formylcyclohex-(e)-yl]-6-(trifluoromethyl)-1,4-dihydroxybenzene (32a). **28a** (1.1 g, 2.5 mmol) was dissolved in 25 mL of toluene, and 50 mg of hydrogenation catalyst (Pd−C; 10% Pd) was added. After cessation of hydrogen uptake, the catalyst was removed by filtration through sodium sulfate. After evaporation of the solvent and drying in vacuo the hydroquinone **32a** was obtained in quantitative yield as a colorless oil. A pure sample of the aldehyde for elemental analysis could not be obtained, since attempted purification by chromatography or by recrystallization from hexane yielded no analytically pure product. However, the crude product was sufficiently pure for the reaction in the next step. R_f (TLC, dichloromethane/ether 50:1) = 0.6. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.52 (br d, 2H), 1.68 (tt, 2H), 2.32 (m, 4H), 2.52 (m, 1H), 3.04 (tt, 1H), 5.70 (s, 1H), 6.04 (s, 1H), 9.80 (s, 1H). ^{19}F NMR ($CDCl_3$): δ −52.2 (s). EIMS: *m*/*z* (%) 444 (50) [M^+(^{79}Br)], 426 (47) [M^+(^{79}Br) − H_2O]. HRMS: calcd for $C_{14}H_{13}Br_2F_3O_3$ 443.91838, found 443.91845.

2,3-Dibromo-5-[4(e)-formylcyclohex-(e)-yl]-6-(trifluoromethyl)-1,4-benzoquinone (28b). **24b** (1.5 g, 3.4 mmol) was oxidized with 3.6 g of (16.9 mmol) PCC as described for **24a**. The aldehyde (1.1 g, 73%) was obtained as a yellow oil. *Cis*/*trans* ratio (from ^{1}H NMR spectrum): 5:95. R_f (TLC, dichloromethane/ether 50:1) = 0.7. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.36 (qd, 2H), 1.82 (br d, 2H), 2.12 (m, 4H), 2.44 (tt, 1H), 3.04 (tt, 1H), 9.54 (s, 1H). ^{19}F NMR ($CDCl_3$): δ −57.2 (s). EIMS: *m*/*z* (%) 442 (29) [M^+(^{79}Br)], 424 (17) [M^+(^{79}Br) − H_2O]. HRMS: calcd for $C_{14}H_{11}Br_2F_3O_3$ 441.90273, found 441.90279.

2,3-Dibromo-5-[4(e)-formylcyclohex-(e)-yl]-6-(trifluoromethyl)-1,4-dihydroxybenzene (32b). **28b** was hydrogenated in the same manner as described for **28a** to yield **32b** in quantitative yield. R_f (TLC, dichloromethane/ether 50:1) = 0.6. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.38 (qd, 2H), 1.76 (dq, 2H), 2.08 (br d, 2H), 2.34 (m, 3H), 3.01 (tt, 1H), 5.70 (s, 1H), 6.06 (s, 1H), 9.64 (s, 1H). ^{19}F NMR ($CDCl_3$): δ −52.5 (s). EIMS: *m*/*z* (%) 444 (51) [M^+(^{79}Br)], 426 (36) [M^+(^{79}Br) − H_2O]. HRMS: calcd for $C_{14}H_{13}Br_2F_3O_3$ 443.91838, found 443.91823.

General Procedure for Synthesis of the Porphyrin Quinones. Pyrrole (**33**), 4-methylbenzaldehyde (**34**), and one of the cyclohexyl carbaldehydes bearing a (hydro)quinone substituent (i.e. **29a**, **29b**, **30a**, **30b**, **31a**/**b**, **32a**, or **32b**) were mixed in an adequate volume of dry dichloromethane in the ratio 4:3:1, so that the concentration of pyrrole and of *both* aldehydes was 0.01 mol L^{-1}. Argon was bubbled through the solution for 20 min, and an adequate amount of trifluoroacetic acid was added subsequently, so that the acid concentration was also 0.01 mol L^{-1}. During the reaction a slight stream of argon was bubbled through the solution. The reaction mixture changed its color from yellow to dark red. After 4 h 0.75 equiv (referring to amount of pyrrole) of tetrachloro-1,4-benzoquinone (TCQ) was added all at once and stirring at rt was continued for 18 h. The volume of the reaction mixture was then reduced to 150−200 mL, and the solution was deacidified with 50 mL of a 5% solution of sodium hydrogen carbonate. The product was purified by filtration over a short and dry column of silica gel and with repeated column chromatography. The porphyrin quinone contained about 10% chlorins, which were converted to the porphyrin via oxidation with DDQ as described in the literature.[33] Other impurities were separated with HPLC. The product was crystallized from dichloromethane/methanol or dichloromethane/hexane at −30 °C and dried in vacuo for several days at 40−50 °C.

5-[4(a)-(2,3,5-Trimethyl-1,4-benzoquinon-6-yl)cyclohex-(e)-yl]-10,15,20-tris(4-methylphenylene)porphyrin (35a). Reaction of 0.7 g (2.68 mmol) of the aldehyde **29a**, 0.97 g (8.06 mmol, 0.95 mL) of 4-methylbenzaldehyde with 0.72 g (10.74 mmol, 0.75 mL) of pyrrole, and 1.22 g (10.74 mmol, 0.83 mL) of trifluoroacetic acid in 1.1 L dichloromethane, followed by oxidation with 2.0 g (8.05 mmol) of TCQ, proceeded according to the general procedure. Repetitive column chromatography (dichloromethane) and oxidation of chlorins with 10 mg (0.044 mmol) of DDQ gave **35a**, which was further purified with preparative HPLC: column, 32 × 125 mm; stationary phase, Nucleosil 50, 5 μm; mobile phase, dichloromethane/ethyl acetate 99:1; t_R = 6.3 min; flow, 64 mL/min. Analytical HPLC: column, 4 × 250 mm; stationary phase, Nucleosil 50, 5 μm; mobile phase, dichloromethane/water 99.88:0.12; t_R = 6.1 min; flow rate, 1.5 mL/min. Yield: 250 mg (11.5%), mp 318−320 °C, R_f (TLC, dichloromethane) = 0.7. ^{1}H NMR (500 MHz, $CDCl_3$): δ −2.65 (br s, 2H), 2.08 (s, 3H), 2.10 (m, 2H), 2.12 (s, 3H), 2.30 (s, 3H), 2.67 (s, 3H), 2.71 (s, 6H), 2.71 (m, 4H), 3.51 (m, 2H), 3.61 (tt, J = 9.7, 7.2 Hz, 1H), 5.48 (tt, J = 11.0, 7.2 Hz, 1H), 7.54 (AA′BB′ signal, 2H), 7.56 (AA′BB′ signal, 4H), 8.08 (AA′BB′ signal, 2H), 8.11 (AA′BB′ signal, 4H), 8.82 (AB signal, J = 4.8 Hz, 4H), 8.92 (d, J = 5.0 Hz, 2H), 9.61 (d, J = 5.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 12.48,

12.51, 21.50, 21.54, 27.17, 33.11, 34.52, 40.20, 119.50, 119.53, 126.12, 127.27, 127.49, 127.93 (br), 130.58 (br), 131.51 (br), 134.40, 134.50, 137.22, 137.25, 138.89, 139.69, 140.11, 140.29, 141.20, 148.53, 187.73, 188.01. UV (dichloromethane): λ_{max} (log ϵ) 266 (4.51), 272 (4.51), 373 (4.36), 303 (4.16), 400 (sh) (4.90), 419 (5.65), 486 (3.54), 517 (4.23), 553 (3.98), 594 (3.71), 649 (3.72) nm. EIMS: *m/z* (%) 812 (5) [$M^+ + 2H$], 811 (13) [$M^+ + H$], 810 (21) [M^+], 581 (14) [tris(4-methylphenylene)-porphyrin$^+$ + H], 580 (8) [tris(4-methylphenylene)porphyrin$^+$]. HRMS: calcd for $C_{56}H_{50}N_4O_2$ 810.39338, found 810.39301. Anal. Calcd for $C_{56}H_{50}N_4O_2$: C, 82.93; H, 6.21; N, 6.90. Found: C, 82.92; H, 6.18; N, 7.06.

5-[4(e)-(2,3,5-Trimethyl-1,4-benzoquinon-6-yl)cyclohex-(e)-yl]-10,15,20-tris(4-methylphenylene)porphyrin (35b). Reaction of 0.68 g (2.61 mmol) of the aldehyde **29b**, 0.94 g (7.83 mmol, 0.92 mL) of 4-methylbenzaldehyde with 0.70 g (10.45 mmol, 0.73 mL) of pyrrole, and 1.2 g (10.45 mmol, 0.80 mL) of trifluoroacetic acid in 1050 mL of dichloromethane, followed by oxidation with 1.93 g (7.83 mmol) of TCQ, proceeded according to the general procedure. Repetitive column chromatography (dichloromethane) and oxidation of chlorins with 10 mg (0.044 mmol) of DDQ gave **35b**, which was further purified with preparative HPLC: column, 32 × 125 mm; stationary phase, Nucleosil 50, 5 μm; mobile phase, dichloromethane/ethyl acetate 99:1; t_R = 6.3 min; flow, 64 mL/min. Analytical HPLC: column, 4 × 250 mm; stationary phase, Nucleosil 50, 5 μm; mobile phase, dichloromethane/water 99.88:0.12; t_R = 7.0 min; flow rate, 1.5 mL/min. Yield: 280 mg (13.2%), mp >350 °C, R_f (TLC, dichloromethane) = 0.7. ^{1}H NMR (500 MHz, $CDCl_3$): δ −2.63 (s, 2H), 2.08 (s, 3H), 2.10 (br d, 2H), 2.13 (s, 3H), 2.38 (s, 3H), 2.68 (s, 3H), 2.71 (s, 6H), 2.73 (qd, J = 12.7, 3.3 Hz, 2H), 2.89 (br d, J = 13.6 Hz, 2H), 3.25 (qd, J = 12.9, 3.2 Hz, 2H), 3.47 (tt, J = 12.0, 3.0 Hz, 1H), 5.39 (tt, J = 12.5, 3.2 Hz, 1H), 7.53 (AA′BB′ signal, 2H), 7.55 (AA′BB′ signal, 4H), 8.06 (AA′BB′ signal, 2H), 8.08 (AA′BB′ signal, 4H), 8.78 (AB signal, J = 5.0 Hz, 4H), 8.92 (d, J = 5.0 Hz, 2H), 9.70 (d, J = 5.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 12.40, 12.48, 21.51, 21.56, 31.99, 38.89, 40.41, 46.17, 119.55, 119.58, 124.39, 127.28, 127.51, 130.56 (br), 131.39 (br), 134.42, 134.52, 137.25, 137.28, 138.83, 139.72, 140.00, 140.54, 141.20, 147.31, 187.94, 187.98. UV (dichloromethane): λ_{max} (log ϵ) 266 (4.28), 272 (4.27), 307 (3.97), 372 (sh) (4.23), 400 (sh) (4.77), 419 (5.51), 485 (sh) (3.41), 517 (4.10), 552 (3.84), 593 (3.57), 649 (3.58) nm. EIMS: *m/z* (%) 812 (13) [$M^+ + 2H$], 811 (37) [$M^+ + H$], 810 (58) [M^+], 581 (71) [tris(4-methylphenylene)-porphyrin$^+$ + H], 580 (12) [tris(4-methylphenylene)-porphyrin$^+$]. HRMS: calcd for $C_{56}H_{50}N_4O_2$ 810.39338, found 810.39317. Anal. Calcd for $C_{56}H_{50}N_4O_2$: C, 82.93; H, 6.21; N, 6.90. Found: C, 82.97; H, 6.35; N, 6.68.

5-[4(a)-(2-Methyl-1,4-naphthoquinon-3-yl)cyclohex-(e)-yl]-10,15,20-tris(4-methylphenylene)porphyrin (36a). Reaction of 0.7 g (2.5 mmol) of the aldehyde **30a**, 0.90 g (7.5 mmol, 0.88 mL) of 4-methylbenzaldehyde with 0.67 g (10.0 mmol, 0.69 mL) of pyrrole, and 1.14 g (10.0 mmol, 0.77 mL) of trifluoroacetic acid in 1000 mL of dichloromethane, followed by oxidation with 1.85 g (7.5 mmol) of TCQ, proceeded according to the general procedure. Repetitive column chromatography (dichloromethane) and oxidation of chlorins with 10 mg (0.044 mmol) of DDQ gave **36a**, which was further purified with preparative HPLC: column, 32 × 125 mm; stationary phase, Nucleosil 50, 5 μm; mobile phase, dichloromethane/hexane 2:1; t_R = 4.0 min; flow: 64 mL/min. Analytical HPLC: column, 4 × 250 mm; stationary phase, Nucleosil 50, 5 μm; mobile phase, dichloromethane/hexane 7:3; t_R = 10.2 min; flow rate, 1.5 mL/min. Yield: 113 mg (5.4%), mp 320−322 °C, R_f (TLC, dichloromethane) = 0.7. ^{1}H NMR (500 MHz, $CDCl_3$): δ −2.66 (s, 2H), 2.20 (m, 2H), 2.48 (s, 3H), 2.66 (s, 3H), 2.70 (s, 6H), 2.78 (m, 4H), 3.54 (m, 2H), 3.76 (tt, 1H), 5.52 (tt, 1H), 7.54 (AA′BB′ signal, 2H), 7.56 (AA′BB′ signal, 4H), 7.74 (m, 2H), 8.06 (AA′BB′ signal, 2H), 8.10 (AA′BB′ signal, 4H), 8.14 (m, 1H), 8.22 (m, 1H), 8.80 (AB signal, J = 4.8 Hz, 4H), 8.93 (d, J = 5.0 Hz, 2H), 9.68 (d, J = 5.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.11, 21.52, 21.57, 27.06, 33.69, 34.52, 40.16, 119.54, 126.09, 126.21, 126.35, 127.28, 127.49, 131.33 (br), 131.89, 132.82, 133.33, 133.54, 134.41, 134.51, 137.26, 138.86, 139.65, 143.35, 151.51, 185.23, 185.65. UV (dichloromethane): λ_{max} (log ϵ) 244 (4.46), 249 (4.46), 269 (sh) (4.44), 275 (4.45), 302 (4.19), 371 (4.35), 400 (4.87), 418 (5.61), 485 (3.56), 517 (4.23), 552 (3.97), 593 (3.70), 649 (3.72) nm. EIMS: *m/z* (%) 833 (1) [$M^+ + H$], 832 (1) [M^+], 581 (11) [tris(4-methylphenylene)porphyrin$^+$ + H], 580 (17) [tris(4-methylphenylene)porphyrin$^+$]. HRMS: calcd for $C_{58}H_{48}N_4O_2$ 832.37773, found 832.37747. Anal. Calcd for $C_{58}H_{48}N_4O_2 \cdot 0.5H_2O$: C, 82.73; H, 5.87; N, 6.65. Found: C, 82.61; H, 5.89; N, 6.70.

5-[4(e)-(2-Methyl-1,4-naphthoquinon-3-yl)cyclohex-(e)-yl]-10,15,20-tris(4-methylphenylene)porphyrin (36b). 36b was synthesized using the same reaction scale as described for **36a** using aldehyde **30b** instead of **30a** and was further purified with preparative HPLC: column, 32 × 125 mm; stationary phase, Nucleosil 50, 5 μm; mobile phase, dichloromethane/hexane 2:1; t_R = 4.8 min; flow rate, 64 mL/min. Analytical HPLC: column, 4 × 250 mm; stationary phase, Nucleosil 50, 5 μm; mobile phase, dichloromethane/hexane 7:3; t_R = 8.0 min; flow, 1.5 mL/min. Yield: 202 mg (9.7%), mp >350 °C, R_f (TLC, dichloromethane) = 0.7. ^{1}H NMR (500 MHz, $CDCl_3$): δ −2.60 (s, 2H), 2.16 (br d, J = 13.0 Hz, 2H), 2.52 (s, 3H), 2.66 (s, 3H), 2.70 (s, 6H), 2.89 (m, 4H), 3.30 (qd, J = 12.6, 3.2 Hz, 2H), 3.58 (tt, J = 12, 3 Hz, 1H), 5.44 (tt, J = 12.5, 3.3 Hz, 1H), 7.54 (AA′BB′ signal, 2H), 7.56 (AA′BB′ signal, 4H), 7.72 (td, J = 7.5, J = 2.0 Hz, 1H), 7.76 (td, J = 7.2, 2.0 Hz, 1H), 8.06 (AA′BB′ signal, 2H), 8.10 (AA′BB′ signal, 4H), 8.14 (dd, J = 7.2, 2.0 Hz, 1H), 8.18 (dd, J = 7.5, 2.0 Hz, 1H) 8.79 (AB signal, J = 4.8 Hz, 4H), 8.94 (d, J = 4.8 Hz, 2H), 9.74 (d, J = 4.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 12.95, 21.51, 21.56, 31.81, 38.85, 41.07, 46.10, 119.58, 124.32, 126.16, 126.28, 127.27, 127.50, 130.59 (br), 131.37 (br), 131.78, 132.80, 133.28, 133.54, 134.41, 134.51, 137.24, 137.27, 138.77, 139.67, 143.59, 150.25, 185.43, 185.59. UV (dichloromethane): λ_{max} (log ϵ) 244 (4.46), 249 (4.46), 268 (sh) (4.45), 275 (4.46), 303 (4.19), 371 (4.36), 400 (4.90), 418 (5.63), 485 (3.55), 516 (4.23), 552 (3.97), 593 (3.70), 648 (3.72) nm. EIMS: *m/z* (%) 833 (5) [$M^+ + H$], 832 (7) [M^+], 581 (45) [tris(4-methylphenylene)-porphyrin$^+$ + H], 580 (21) [tris(4-methylphenylene)porphyrin$^+$]. HRMS: calcd for $C_{58}H_{48}N_4O_2$ 832.37773, found 832.37707. Anal. Calcd for $C_{58}H_{48}N_4O_2$: C, 83.63; H, 5.81; N, 6.73. Found: C, 83.61; H, 5.81; N, 6.75.

5-[4-(2,3-Dimethoxy-5-methyl-1,4-benzoquinon-6-yl)cyclohexyl]-10,15,20-tris(4-methylphenylene)porphyrin (*Cis*/*Trans* Mixture 37a/b). Reaction of 1.35 g (4.6 mmol) of the 1:1 *cis*/*trans* mixture of aldehydes **31a**/**b**, 1.66 g (13.9 mmol, 1.63 mL) of 4-methylbenzaldehyde with 1.23 g (18.5 mmol, 1.28 mL) of pyrrole, and 2.1 g (18.5 mmol, 1.42 mL) of trifluoroacetic acid in 1800 mL of dichloromethane followed by oxidation with 3.4 g (13.9 mmol) of TCQ proceeded according to the general procedure. Repetitive column chromatography (dichloromethane/2-propanol 100:1) and oxidation of chlorins with 10 mg (0.044 mmol) of DDQ gave a 2:3 *cis*/*trans* mixture (from ^{1}H NMR spectrum) of the porphyrin quinones **37a** and **37b**. Separation of the diastereomers was carried out with preparative HPLC: column, 16 × 250 mm; stationary phase, Nucleosil 50, 5 μm; mobile phase, dichloromethane/water 99.92:0.08; t_R = 6.5 min (**37a**); t_R = 7.5 min (**37b**); flow rate, 16 mL/min. Analytical HPLC: column, 4 × 250 mm; stationary phase, Nucleosil 50, 5 μm; mobile phase, dichloromethane/water 99.88:0.12; t_R = 4.9 min (**37a**); t_R = 5.4 min (**37b**); flow rate, 1.0 mL/min.

5-[4(a)-(2,3-Dimethoxy-5-methyl-1,4-benzoquinon-6-yl)cyclohex-(e)-yl]-10,15,20-tris(4-methylphenylene)porphyrin (37a). Yield: 140 mg (7.2%), mp 315−317 °C, R_f (TLC, dichloromethane/2-propanol 99:1) = 0.4. ^{1}H NMR (500 MHz, $CDCl_3$): δ −2.65 (s, 2H, NH), 2.10 (m, 2H, H_e-3, H_e-5), 2.31 (s, 3H, quinone-3-CH_3), 2.66 (m, 2H, H_a-3, H_a-5), 2.68 (s, 3H, 15-*p*-phenyl-CH_3), 2.71 (m, 2H, H_e-2, H_e-6), 2.71 (s, 6H, 10- and 20-*p*-phenyl-CH_3), 3.50 (m, 2H, H_a-2, H_a-6), 3.61 (tt, J_1 = 9.6 Hz, J_2 = 7.2 Hz, 1H, H_a-4), 4.06 (s, 3H, CH_3O), 4.12 (s, 3H, CH_3O), 5.47 (tt, J_1 = 11.0 Hz, J_2 = 7.2 Hz, 1H, H_a-1), 7.54 (AA′BB′, 2H, *m*-H 15-*p*-phenyl-CH_3), 7.55 (AA′BB′, 4H, *m*-H 10- and 20-*p*-phenyl-CH_3), 8.07 (AA′BB′, 2H, *o*-H 15-*p*-phenyl-CH_3), 8.08 (AA′BB′, 4H, *o*-H 10- and 20-*p*-phenyl-CH_3), 8.80 (AB, J_{AB} = 4.7 Hz, 4H, porphyrin-H-12,13,17,18), 8.92 (d, J = 4.8 Hz, 2H, porphyrin-H-2,8), 9.61 (d, J = 4.8 Hz, 2H, porphyrin-H-3,7). ^{13}C NMR ($CDCl_3$): δ 12.25, 21.45, 27.08, 32.98, 34.34, 40.12, 61.10, 61.18, 119.46, 125.85, 127.19,

127.40, 127.80 (br), 130.48 (br), 131.21 (br), 134.33, 134.42, 137.18, 138.87, 139.64, 143.74, 144.46, 146.98, 184.44, 184.79. UV (dichloromethane): λ_{max} (log ϵ) 284 (4.44), 368 (sh) (4.33), 400 (sh) (4.88), 419 (5.64), 486 (3.55), 518 (4.22), 553 (3.96), 594 (3.69), 650 (3.70) nm. EIMS: *m*/*z* (%) 844 (17) [$M^+ + 2H$], 843 (23) [$M^+ + H$], 842 (33) [M^+], 581 (9) [tris(4-methylphenylene)porphyrin$^+ + H$], 580 (16) [tris(4-methylphenylene)porphyrin$^+$]. HRMS: calcd for $C_{56}H_{50}N_4O_4$ 842.38321, found 842.38302. Anal. Calcd for $C_{56}H_{50}N_4O_4$: C, 79.78; H, 5.98; N, 6.64. Found: C, 79.45; H, 5.98; N, 6.49.

5-[4(e)-(2,3-Dimethoxy-5-methyl-1,4-benzoquinon-6-yl)cyclohex-(e)-yl]-10,15,20-tris(4-methylphenylene)porphyrin (37b). Yield: 170 mg (8.7%), mp >350 °C, R_f (TLC, dichloromethane/2-propanol 99:1) = 0.4. ^{1}H NMR (500 MHz, $CDCl_3$): δ −2.65 (s, 2H, NH), 2.10 (br d, $^2J_{3a3e}$ = 13.5 Hz, 2H, H_e-3, H_e-5), 2.34 (s, 3H, quinone-3-CH_3), 2.68 (s, 3H, 15-*p*-phenyl-CH_3), 2.72 (s, 6H, 10- and 20-*p*-phenyl-CH_3), 2.72 (qd, 2H, H_a-3, H_a-5), 2.88 (br d, $^2J_{2a2e}$ = 13.6 Hz, 2H, H_e-2, H_e-6), 3.24 (qd, $^2J_{2a2e} \approx J_{1a2a} \approx J_{2a3a} \approx$ 12.8 Hz, J_{2a3e} = 3.4 Hz, 2H, H_a-2, H_a-6), 3.44 (tt, $J_{3a4a} = J_{4a5a}$ = 12.0 Hz, $J_{3e4a} = J_{4a5e} \approx$ 3 Hz, 1H, H_a-4), 4.06 (s, 3H, CH_3O), 4.12 (s, 3H, CH_3O), 5.38 (tt, $J_{1a2a} = J_{1a6a}$ = 12.5 Hz, $J_{1a2e} = J_{1a6e}$ = 3.4 Hz, 1H, H_a-1), 7.53 (AA′BB′, 2H, *m*-H 15-*p*-phenyl-CH_3), 7.55 (AA′BB′, 4H, *m*-H 10- and 20-*p*-phenyl-CH_3), 8.06 (AA′BB′, 2H, *o*-H 15-*p*-phenyl-CH_3), 8.08 (AA′BB′, 4H, *o*-H 10- and 20-*p*-phenyl-CH_3), 8.80 (AB, J_{AB} = 4.8 Hz, 4H, porphyrin-H-12,13,17,18), 8.92 (d, *J* = 4.8 Hz, 2H, porphyrin-H-2,8), 9.70 (d, *J* = 4.8 Hz, 2H, porphyrin-H-3,7). ^{13}C NMR (125 MHz, $CDCl_3$): δ 12.28, 21.50, 21.55, 31.87, 38.77, 40.21, 46.07, 61.18, 61.28, 119.59, 124.21, 127.27, 127.50, 130.55 (br), 131.88 (br), 134.41, 134.50, 137.24, 137.27, 138.79, 139.20, 143.74, 144.46, 145.76, 184.60, 184.85. UV (dichloromethane): λ_{max} (log ϵ) 283 (4.43), 368 (sh) (4.33), 400 (sh) (4.88), 419 (5.62), 485 (sh) (3.54), 517 (4.22), 552 (3.95), 593 (3.68), 649 (3.69) nm. EIMS: *m*/*z* (%) 844 (67) [$M^+ + 2H$], 843 (67) [$M^+ + H$], 842 (97) [M^+], 581 (65) [tris(4-methylphenylene)-porphyrin$^+ + H$], 580 (100) [tris(4-methylphenylene)-porphyrin$^+$]. HRMS: calcd for $C_{56}H_{50}N_4O_4$ 842.38321, found 842.38369. Anal. Calcd for $C_{56}H_{50}N_4O_4$: C, 79.78; H, 5.98; N, 6.64. Found: C, 79.50; H, 5.98; N, 6.36.

5-[4(a)-(2,3-Dibromo-5-(trifluoromethyl)-1,4-benzoquinon-6-yl)cyclohex-(e)-yl]-10,15,20-tris(4-methylphenylene)porphyrin (38a). Reaction of 1.13 g (2.5 mmol) of the 9:1 *cis*/*trans* mixture of aldehydes **32a**/**b**, 0.90 g (7.5 mmol, 0.88 mL) of 4-methyl benzaldehyde with 0.67 g (10 mmol, 0.69 mL) of pyrrole, and 1.14 g (10.0 mmol, 0.77 mL) of trifluoroacetic acid in 1000 mL of dichloromethane followed by oxidation with 2.45 g (10.0 mmol) of TCQ proceeded according to the general procedure. Repetitive column chromatography (trichloromethane) and oxidation of chlorins with 10 mg (0.044 mmol) of DDQ gave a 8:2 *cis*/*trans* mixture of the porphyrin quinones **38a** and **38b** (from ^{1}H NMR spectrum). Separation of the diastereomers with preparative HPLC: column, 32 × 125 mm; stationary phase, Nucleosil 50, 5 μm; mobile phase, dichloromethane/hexane 3:2; t_R = 8.6 min (**38a**); flow, 64 mL/min. Analytical HPLC: column, 4 × 250 mm; stationary phase, Nucleosil 50, 5 μm; mobile phase, dichloromethane/hexane 1:1; t_R = 10.5 min (**38a**); flow rate, 1.5 mL/min. Yield: 120 mg (4.8%), mp >350 °C, R_f (TLC, trichloromethane) = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$): δ −2.63 (s, 2H), 2.20 (m, 2H), 2.69 (s, 3H), 2.72 (s, 6H), 2.73 (m, 4H), 3.54 (m, 2H), 3.92 (tt, *J* = 9.6, 7.2 Hz, 1H), 5.49 (tt, *J* = 11.0, 7.2 Hz, 1H), 7.54 (AA′BB′ signal, 2H), 7.55 (AA′BB′ signal, 4H), 8.07 (AA′BB′ signal, 2H), 8.08 (AA′BB′ signal, 4H), 8.81 (AB signal, *J* = 5.0 Hz, 4H), 8.94 (d, *J* = 5.0 Hz, 2H), 9.57 (d, *J* = 5.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.51, 21.55, 27.66, 33.82, 35.33, 39.50, 119.66, 119.73, 123.99 (q, J_{C-F} = 279 Hz), 125.16, 127.30, 127.51, 127.30, 127.51, 131.31 (br), 131.88 (q, J_{C-F} = 30 Hz), 132.00, 134.41, 134.51, 137.28, 137.32, 138.83, 139.60, 139.70, 139.77, 139.78, 156.27, 173.39, 177.10. ^{19}F NMR ($CDCl_3$): δ −55.1 (s). UV (dichloromethane): λ_{max} (log ϵ) 257 (sh) (4.27), 284 (4.31), 371 (4.36), 400 (sh) (4.89), 419 (5.63), 486 (3.55), 517 (4.22), 553 (3.95), 594 (3.70), 650 (3.67) nm. EIMS: *m*/*z* (%) 992 (1) [M^+(^{79}Br)], 581 (1) [tris(4-methylphenylene)-porphyrin$^+ + H$], 580 (1) [tris(4-methylphenylene)porphyrin$^+$]. HRMS: calcd for $C_{54}H_{41}Br_2F_3N_4O_2$ 992.15486, found 992.15469. Anal. Calcd for $C_{54}H_{41}Br_2F_3N_4O_2$: C, 65.20; H, 4.15; N, 5.63. Found: C, 65.35; H, 4.20; N, 5.43.

5-[4(e)-(2,3-Dibromo-5-(trifluoromethyl)-1,4-benzoquinon-6-yl)cyclohex-(e)-yl]-10,15,20-tris(4-methylphenylene)porphyrin (38b). Reaction of 1.10 g (2.45 mmol) of the 5:95 *cis*/*trans* mixture of aldehydes **32a**/**b**, 0.88 g (7.35 mmol, 0.86 mL) of 4-methylbenzaldehyde with 0.66 g (9.8 mmol, 0.67 mL) of pyrrole, and 1.11 g (9.8 mmol, 0.76 mL) of trifluoroacetic acid in 1000 mL of dichloromethane followed by oxidation with 2.4 g (9.8 mmol) of TCQ proceeded according to the general procedure. Repetitive column chromatography (trichloromethane) and oxidation of chlorins with 10 mg (0.044 mmol) of DDQ gave the isomerically pure porphyrin quinone **38b** (from ^{1}H NMR spectrum), which was further purified by preparative HPLC: column, 32 × 125 mm; stationary phase, Nucleosil 50, 5 μm; mobile phase, dichloromethane/hexane 3:2; t_R = 9.8 min; flow rate, 64 mL/min. Analytical HPLC: column, 4 × 250 mm; stationary phase, Nucleosil 50, 5 μm; mobile phase, dichloromethane/hexane 1:1; t_R = 8.4 min; flow rate, 1.5 mL/min. Yield: 224 mg (9.2%), mp >350 °C, R_f (TLC, trichloromethane) = 0.5. ^{1}H NMR (500 MHz, $CDCl_3$): δ −2.63 (s, 2H), 2.23 (br d, *J* = 12.6 Hz, 2H), 2.68 (s, 3H), 2.72 (s, 6H), 2.78 (qd, *J* = 12.7 Hz, 3.2 Hz, 2H), 2.93 (br d, *J* = 13.6 Hz, 2H), 3.28 (qd, *J* = 12.5, 3.3 Hz, 2H), 3.78 (tt, *J* = 12,0, 3.2 Hz, 1H), 5.41 (tt, *J* = 12.5, 3.2 Hz, 1H), 7.54 (AA′BB′ signal, 2H), 7.56 (AA′BB′ signal, 4H), 8.06 (AA′BB′ signal, 2H), 8.08 (AA′BB′ signal, 4H), 8.80 (AB signal, *J* = 4.9 Hz, 4H), 8.93 (d, *J* = 4.9 Hz, 2H), 9.65 (d, *J* = 4.9 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.51, 21.55, 32.40, 38.16, 42.32, 45.62), 119.70, 119.77, 120.66, 121.77 (q, J_{C-F} = 278 Hz), 122.88, 123.28, 127.29, 127.52, 130.66 (br), 131.42 (br), 132.16, 132.28 (q, J_{C-F} = 30 Hz), 132.39, 134.41, 134.52, 137.29, 137.34, 138.76, 139.52, 139.54, 139.63, 139.68, 155.61, 173.43, 177.26. ^{19}F NMR ($CDCl_3$): δ −55.1 (s). UV (dichloromethane): λ_{max} (log ϵ) 255 (sh) (4.27), 283 (4.32), 374 (4.36), 399 (sh) (4.88), 418 (5.63), 485 (sh) (3.54), 517 (4.22), 552 (3.94), 593 (3.70), 649 (3.69) nm. EIMS: *m*/*z* (%) 992 (1) [M^+(^{79}Br)], 581 (2) [tris(4-methylphenylene)porphyrin$^+ + H$], 580 (1) [tris(4-methylphenylene)porphyrin$^+$]. HRMS: calcd for $C_{54}H_{41}Br_2F_3N_4O_2$ 992.15486, found 992.15421. Anal. Calcd for $C_{54}H_{41}Br_2F_3N_4O_2$: C, 65.20; H, 4.15; N, 5.63. Found: C, 65.07; H, 4.20; N, 5.45.

General Procedure for the Preparation of the Zinc Porphyrin Quinones. The zinc porphyrin quinones **Zn-35a**, **Zn-35b**, **Zn-36a**, **Zn-36b**, **Zn-37a**, and **Zn-37b** were prepared using the acetate method:[20,34] 25−50 mg of the porphyrin quinone was dissolved in 10−30 mL of dichloromethane and 5 mL of a saturated solution of zinc(II) acetate in methanol were added. After the insertion of zinc was complete (3−4 h, check with UV/vis spectroscopy), the organic phase was extracted three times with brine, dried over sodium sulfate, and filtered. The zinc porphyrin quinones were crystallized from dichloromethane/hexane or dichloromethane/methanol at −30 °C and dried in vacuo for several days at 40−50 °C.

{5-[4(a)-(2,3,5-Trimethyl-1,4-benzoquinon-6-yl)cyclohex-(e)-yl]-10,15,20-tris(4-methylphenylene)porphyrinato}-zinc(II) (Zn-35a). Zinc was inserted in 30 mg (0.037 mmol) of **35a** following the general procedure, and the product was crystallized from dichloromethane/methanol. Yield: 30 mg (92%), mp >350 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.09 (s, 3H), 2.12 (m, 2H), 2.13 (s, 3H), 2.35 (s, 3H), 2.69 (s, 3H), 2.72 (m, 4H), 2.74 (s, 6H), 3.58 (m, 2H), 3.65 (tt, 1H), 5.62 (tt, *J* = 11.0, *J* = 7.2 Hz, 1H), 7.53 (AA′BB′ signal, 2H), 7.56 (AA′BB′ signal, 4H), 8.07 (AA′BB′ signal, 2H), 8.09 (AA′BB′ signal, 4H), 8.91 (AB signal, *J* = 5.0 Hz, 4H), 9.05 (d, *J* = 5.0 Hz, 2H), 9.77 (d, *J* = 5.0 Hz, 2H). UV (dichloromethane): λ_{max} (log ϵ) 265 (4.37), 273 (4.37), 305 (4.16), 349 (3.98), 400 (4.54), 421 (5.65), 515 (sh) (3.44), 552 (4.22), 594 (3.73) nm. EIMS: *m*/*z* (%) 872 (100) [M^+(^{64}Zn)], 642 (43) [tris(4-methylphenylene)zinc porphyrin$^+$]. HRMS: calcd for $C_{56}H_{48}N_4O_2Zn$ 872.30687, found 872.30635. Anal. Calcd for $C_{56}H_{48}N_4O_2Zn$: C, 76.92; H, 5.53; N, 6.40. Found: C, 76.78; H, 5.59; N, 6.23.

{5-[4(e)-(2,3,5-Trimethyl-1,4-benzoquinon-6-yl)cyclohex-(e)-yl]-10,15,20-tris(4-methylphenylene)porphyrinato}-zinc(II) (Zn-35b). Zinc was inserted in 30 mg (0.03 mmol) of **35b** following the general procedure, and the product was crystallized from dichloromethane/methanol. Yield: 31 mg

(95%), mp 290 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.08 (s, 3H), 2.11 (br d, 2H), 2.12 (s, 3H), 2.38 (s, 3H), 2.65 (s, 3H), 2.75 (s, 6H), 2.76 (qd, J = 12.6, 3.6 Hz, 2H), 2.91 (br d, J = 13.8 Hz, 2H), 3.35 (qd, J = 13.2, 3.2 Hz, 2H), 3.49 (tt, J = 12.3, 3.3 Hz, 1H), 5.55 (tt, J = 12.5, 3.4 Hz, 1H), 7.53 (AA′BB′ signal, 2H), 7.56 (AA′BB′ signal, 4H), 8.07 (AA′BB′ signal, 2H), 8.09 (AA′BB′ signal, 4H), 8.91 (AB signal, J = 4.8 Hz, 4H), 9.05 (d, J = 5.0 Hz, 2H), 9.90 (s (br), 2H). UV (dichloromethane): λ_{max} (log ϵ) 265 (4.40), 273 (4.39), 304 (4.16), 348 (4.00), 400 (4.62), 420 (5.71), 515 (3.47), 550 (4.29), 588 (3.72) nm. EIMS: *m/z* (%) 872 (100) [M^+(^{64}Zn)], 642 (30) [tris(4-methylphenylene)zinc porphyrin$^+$]. HRMS: calcd for $C_{56}H_{48}N_4O_2Zn$ 872.30687, found 872.30610. Anal. Calcd for $C_{56}H_{48}N_4O_2Zn \cdot 0.5\ CH_3OH$: C, 76.21; H, 5.66; N, 6.29. Found: C, 76.56; H, 5.58; N, 6.07.

{5-[4(a)-(2-Methyl-1,4-naphthoquinon-3-yl)cyclohex-(e)-yl]-10,15,20-tris(4-methylphenylene)porphyrinato}-zinc(II) (Zn-36a). Zinc was inserted in 25 mg (0.03 mmol) of **36a** following the general procedure, and the product was crystallized from dichloromethane/methanol. Yield: 24 mg (91%), mp 320−322 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.20 (m, 2H), 2.44 (s, 3H), 2.70 (s, 3H), 2.74 (s, 6H), 2.80 (m, 4H), 3.62 (m, 2H), 3.78 (tt, 1H), 5.64 (tt, 1H), 7.51 (AA′BB′ signal, 2H), 7.53 (AA′BB′ signal, 4H), 7.65 (td, J = 7.5, 2.0 Hz, 1H), 7.69 (td, J = 7.5, 2.0 Hz, 1H), 7.96 (dd, J = 7.5, 2.0 Hz, 1H), 8.11 (AA′BB′ signal, 2H), 8.13 (AA′BB′ signal, 4H), 8.16 (dd, J = 7.5, 2.0 Hz, 1H), 8.94 (AB signal, J = 5.0 Hz, 4H), 9.08 (d, J = 5.0 Hz, 2H), 9.80 (d, J = 5.0 Hz. 2H). UV (dichloromethane): λ_{max} (log ϵ) 245 (sh) (4.46), 249 (4.47), 270 (sh) (4.42), 277 (4.43), 307 (4.23), 345 (sh) (4.10), 400 (sh) (4.65), 420 (5.74), 510 (3.49), 550 (4.32), 589 (3.76) nm. EIMS: *m/z* (%) 894 (17) [M^+(^{64}Zn)], 642 (85) [tris(4-methylphenylene)zinc porphyri^{n+}]. HRMS: calcd for $C_{58}H_{46}N_4O_2Zn$ 894.29122, found 894.29110. Anal. Calcd for $C_{58}H_{46}N_4O_2Zn \cdot CH_3OH$: C, 76.33; H, 5.43; N, 6.03. Found: C, 76.56; H, 5.62; N, 5.76.

{5-[4(e)-(2-Methyl-1,4-naphthoquinon-3-yl)cyclohex-(e)-yl]-10,15,20-tris(4-methylphenylene)porphyrinato}-zinc(II) (Zn-36b). Zinc was inserted in 25 mg (0.03 mmol) of **36b** following the general procedure, and the product was crystallized from dichloromethane/methanol. Yield: 25 mg (92%), mp 330−332 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.19 (br d, J = 13.0 Hz, 2H), 2.48 (s, 3H), 2.67 (s, 3H), 2.72 (s, 6H), 2.91 (m, 4H), 3.37 (qd, J = 13.1, 3.4 Hz, 2H), 3.60 (tt, J = 13.0, 3.0 Hz, 1H), 5.58 (tt, J = 12.5, 3.5 Hz, 1H), 7.53 (AA′BB′ signal, 2H), 7.56 (AA′BB′ signal, 4H), 7.70 (td, J = 7.5, 2.5 Hz, 1H), 7.73 (td, J = 7.5, 2.5 Hz, 1H), 8.04 (dd, J = 7.5, 2.5 Hz, 1H), 8.08 (AA′BB′ signal, 2H), 8.10 (AA′BB′ signal, 4H), 8.18 (dd, J = 7.5 2.0 Hz, 1H), 8.91 (AB signal, J = 4.8 Hz, 4H), 9.06 (d, J = 5.0 Hz, 2H), 9.91 (s (br), 2H). UV (dichloromethane): λ_{max} (log ϵ) 245 (sh) (4.43), 249 (4.44), 271 (sh) (4.40), 276 (4.44), 308 (4.20), 343 (sh) (4.07), 400 (sh) (4.61), 420 (5.71), 510 (sh) (3.46), 550 (4.29), 589 (3.72) nm. EIMS: *m/z* (%) 894 (4) [M^+(^{64}Zn)], 642 (28) [tris(4-methylphenylene)-zinc porphyrin$^+$]. HRMS: calcd for $C_{58}H_{46}N_4O_2Zn$ 894.29122, found 894.29101. Anal. Calcd for $C_{58}H_{46}N_4O_2Zn \cdot 2CH_3OH$: C, 75.03; H, 5.67; N, 5.83. Found: C, 75.28; H, 5.34; N, 5.89.

{5-[4(a)-(2,3-Dimethoxy-5-methyl-1,4-benzoquinon-6-yl)cyclohex-(e)-yl]-10,15,20-tris(4-methylphenylene)-porphyrinato}zinc(II) (Zn-37a). Zinc was inserted in 25 mg (0.03 mmol) of **37a** following the general procedure, and the product was crystallized from dichloromethane/methanol. Yield: 24 mg (90%), mp 310−312 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.12 (m, 2H), 2.32 (s, 3H), 2.69 (s, 3H), 2.72 (m, 4H), 2.74 (s, 6H), 3.54 (m, 3H), 4.02 (s, 3H), 4.08 (s, 3H), 5.58 (tt, 1H), 7.53 (AA′BB′ signal, 2H), 7.56 (AA′BB′ signal, 4 H), 8.07 (AA′BB′ signal, 2H), 8.09 (AA′BB′ signal, 4H), 8.90 (AB signal, J = 5 Hz, 4H), 9.05 (d, J = 5.0 Hz, 2H), 9.76 (d, J = 5.0 Hz, 2H). UV (dichloromethane): λ_{max} (log ϵ) 255 (sh) (4.24), 286 (4.44), 313 (sh) (4.16), 350 (4.02), 420 (5.74), 510 (sh) (3.48), 550 (4.32), 589 (3.75) nm. EIMS: *m/z* (%) 904 (100) [M^+(^{64}Zn)], 642 (22) [tris(4-methylphenylene)zinc porphyrin$^+$]. HRMS: calcd for $C_{56}H_{48}N_4O_4Zn$ 904.29670, found 904.29600. Anal. Calcd for $C_{56}H_{48}N_4O_4Zn \cdot CH_3OH$: C, 72.95; H, 5.59; N, 5.97. Found: C, 73.11; H, 5.59; N, 5.82.

{5-[4(e)-(2,3-Dimethoxy-5-methyl-1,4-benzoquinon-6-yl)cyclohex-(e)-yl]-10,15,20-tris(4-methylphenylene)-porphyrinato}zinc(II) (Zn-37b). Zinc was inserted in 25 mg (0.03 mmol) of **37b** following the general procedure, and the product was crystallized from dichloromethane/methanol. Yield: 24 mg (90%), mp 300 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.13 (br d, 2H), 2.35 (s, 3H), 2.65 (s, 3H), 2.75 (s, 6H), 2.75 (qd, 2H), 2.93 (br d, 2H), 3.35 (qd, 2H), 3.49 (tt, 1H), 3.95 (s, 3H), 4.00 (s, 3H), 5.51 (tt, 1H), 7.53 (AA′BB′ signal, 2H), 7.56 (AA′BB′ signal, 4H), 8.07 (AA′BB′ signal, 2H), 8.09 (AA′BB′ signal, 4H), 8.91 (AB signal, J_{AB} = 5 Hz, 4H), 9.05 (d, J = 5 Hz, 2H), 9.85 (s (br), 2H). UV (dichloromethane): λ_{max} (log ϵ) 254 (sh) (4.22), 285 (4.41), 313 (sh) (4.13), 348 (3.99), 400 (sh) (4.61), 420 (5.72), 507 (sh) (3.43), 550 (4.28), 589 (3.71) nm. EIMS *m/z* (%) 904 (100) [M^+(^{64}Zn)], 642 (12) [tris(4-methylphenylene)zinc porphyrin$^+$]. HRMS: calcd for $C_{56}H_{48}N_4O_4Zn$ 904.29670, found 904.29608. Anal. Calcd for $C_{56}H_{48}N_4O_4Zn \cdot 0.5CH_3OH$: C, 73.57; H, 5.46; N, 6.07. Found: C, 73.87; H, 5.52; N, 5.81.

{5-[4(a)-(2,3-Dibromo-5-(trifluoromethyl)-1,4-benzoquinon-6-yl)cyclohex-(e)-yl]-10,15,20-tris(4-methylphenylene)porphyrinato}zinc(II) (Zn-38a). 38a (30 mg, 0.028 mmol) was added to a suspension of 130 mg (1.6 mmol) of zinc oxide in 2.5 mL of ether and 1.5 mL of trichloromethane. Two drops of trifluoroacetic acid were added, and complexation was complete within 15 min. After dilution with 5 mL of trichloromethane, filtration over a short column (silica gel 60), crystallization from trichloromethane/hexane, and drying, 28 mg (88%) of the product was obtained, mp >350 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.21 (m, 2H), 2.69 (s, 3H), 2.72 (s, 6H), 2.74 (m, 4H), 3.60 (m, 2H), 3.97 (tt, J = 9.6, 7.2 Hz, 1H), 5.61 (tt, J = 11.0, 7.2 Hz, 1H), 7.54 (AA′BB′ signal, 2H), 7.56 (AA′BB′ signal, 4H), 8.07 (AA′BB′ signal, 2H), 8.09 (AA′BB′ signal, 4H), 8.91 (AB signal, J = 4.8 Hz, 4H), 9.06 (d, J = 5.0 Hz, 2H), 9.72 (d, J = 5.0 Hz, 2H). ^{19}F NMR ($CDCl_3$): δ −55.3 (s). UV (dichloromethane): λ_{max} (log ϵ) 253 (4.28), 290 (4.32), 308 (sh) (4.26), 349 (4.06), 401 (sh) (4.65), 420 (5.75), 483 (sh) (3.16), 515 (3.51), 550 (4.31), 589 (3.75) nm. EIMS: *m/z* (%) 1054 (1) [M^+(^{79}Br,^{64}Zn)], 642 (2) [tris(4-methylphenylene)zinc porphyrin$^+$]. HRMS: calcd for $C_{54}H_{39}Br_2F_3N_4O_2Zn$ 1054.06840, found 1054.06820. Anal. Calcd for $C_{54}H_{39}Br_2F_3N_4O_2Zn$: C, 61.30; H, 3.72; N, 5.30. Found: C, 61.21; H, 3.82; N, 5.01.

{5-[4(e)-(2,3-Dibromo-5-(trifluoromethyl)-1,4-benzoquinon-6-yl)cyclohex-(e)-yl]-10,15,20-tris(4-methylphenylene)porphyrinato}zinc(II) (Zn-38b). Insertion of zinc in **38b** followed the same manner as described for **38a**. Yield: 29 mg (91%), mp >350 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.23 (br d, J = 13.0 Hz, 2H), 2.68 (s, 3H), 2.71 (s, 6H), 2.81 (qd, J = 12.5, 3.3 Hz, 2H), 2.93 (br d, J = 14.0 Hz, 2H), 3.37 (qd, J = 13.0, 3.4 Hz, 2H), 3.81 (tt, J = 12.3, 3.2 Hz, 1H), 5.55 (tt, J = 12.5, 3.3 Hz, 1H), 7.53 (AA′BB′ signal, 2H), 7.56 (AA′BB′ signal, 4H), 8.07 (AA′BB′ signal, 2H), 8.09 (AA′BB′ signal, 4H), 8.91 (AB signal, J = 4.8 Hz, 4H), 9.06 (d, J = 5.0 Hz, 2H), 9.81 (s (br), 2H). ^{19}F NMR ($CDCl_3$): δ −55.1 (s). UV (dichloromethane): λ_{max} (log ϵ) 252 (4.27), 286 (4.31), 310 (sh) (4.23), 350 (4.05), 401 (sh) (4.64), 420 (5.74), 484 (sh) (3.17), 514 (3.51), 550 (4.31), 589 (3.73) nm. EIMS: *m/z* (%) 1054 (1) [M^+(^{79}Br,^{64}Zn)], 642 (2) [tris(4-methylphenylene)zinc porphyrin$^+$]. HRMS: calcd for $C_{54}H_{39}Br_2F_3N_4O_2Zn$ 1054.06840, found 1054.06846. Anal. Calcd for $C_{54}H_{39}Br_2F_3N_4O_2Zn$: C, 61.30; H, 3.72; N, 5.30. Found: C, 61.63; H, 3.80; N, 4.90.

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Supporting Information Available: Structures of **37a** obtained from MNDO (MOPAC 6.0) calculations and the ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **15a**, **15b**, **24a**, **24b**, **37a**, and **37b** (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of this journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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