Synthesis of New β-Substituted *meso*-Tetraphenylporphyrins via 1,3-Dipolar Cycloaddition Reactions. 1

Ana M. G. Silva, Augusto C. Tomé, Maria G. P. M. S. Neves, Artur M. S. Silva, and José A. S. Cavaleiro*

Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

Received July 2, 2001

The azomethine ylide generated from the reaction of (β-formyl-*meso*-tetraphenylporphyrinato)nickel(II) with *N*-methylglycine reacts with a range of dipolarophiles, yielding new β-substituted-*meso*-tetraphenylporphyrins. The regio- and stereochemistry of the new compounds was established using one- and two-dimensional NMR techniques.

Introduction

Porphyrins demonstrate promising applications in various scientific fields such as supramolecular chemistry, biomimetic models for photosynthesis, catalysis, and medicinal applications such as photodynamic therapy.[1] Knowing that all those processes are strongly dependent on the structure of the tetrapyrrolic system, the chemical functionalization of porphyrins with different types of substituents at the β- and *meso*-positions is an active and exciting field in organic chemistry.

Recently we have shown that peripheral double bond(s) of the porphyrin macrocycle can participate in Diels−Alder[2] reactions and in 1,3-dipolar cycloadditions,[3] yielding novel chlorins, bacteriochlorins, and isobacteriochlorins. Now, as a complement of our work on the addition of azomethine ylides to porphyrins,[3a] we report the generation of the porphyrinic azomethine ylide **2** and its reactions with several dipolarophiles to yield new β-substituted *meso*-tetraphenylporphyrins of type **3** (Scheme 1).

Results and Discussion

The azomethine ylide **2** was generated in situ from the reaction of (β-formyl-*meso*-tetraphenylporphyrinato)-nickel(II) (**1**) with *N*-methylglycine.[4] The reactions were carried out in refluxing toluene, under nitrogen, in the presence of different dipolarophiles: *N*-phenylmaleimide, dimethyl fumarate, dimethyl acetylenedicarboxylate, *trans*-β-nitrostyrene, 1,4-benzoquinone, and 1,4-naphthoquinone.

When the cycloaddition reactions were carried out with *N*-phenylmaleimide or dimethyl fumarate, TLC revealed that in both cases porphyrin **1** was completely consumed after 5 h and two new products (with lower R_f) were formed (Scheme 2). After the workup and purification by chromatography the new compounds were fully characterized by spectroscopic techniques, namely, ^{1}H, ^{13}C, COSY, NOESY, HETCOR (or HSQC), and HMBC NMR and MS.

In the case of *N*-phenylmaleimide both compounds showed the same molecular ion [$(M + H)^+ = 899$]; the analysis of the NMR spectra allowed us to identify the compound with the higher R_f (61%) as the diastereoisomer **4a** and the other as **4b** (35%) (vide infra).

The reaction with dimethyl fumarate also afforded two new diastereoisomeric β-pyrrolidine derivatives of TPP, and we were able to establish structure **5b** for the main product (68%, lower R_f) and structure **5a** for the minor one (28%) (vide infra).

Two new products were also obtained when the cycloaddition reaction was carried out with dimethyl acetylenedicarboxylate. After separation by preparative TLC, the new compounds were identified as the expected adduct **6a** (38%) and the dehydrogenated adduct **7a** (4%)-(Scheme 2). This last compound showed a parent ion at $m/z = 866$ (two hydrogen atoms less than **6a**), and analysis of the ^{1}H NMR spectrum confirmed the presence of the pyrrole ring.

When these studies were extended to the asymmetric dipolarophile *trans*-β-nitrostyrene, two new compounds were also obtained (see Scheme 2). Both compounds showed the same parent ion [$(M + H)^+ = 875$], and the detailed analysis of the ^{1}H, ^{13}C, COSY, NOESY, HSQC, and HMBC spectra allowed us to establish the structure of the main product as **8b** (60%, lower R_f) and the structure of the minor one as **8a** (36%).

When the cycloaddition reactions were carried out with 1,4-benzoquinone or 1,4-naphthoquinone, the isolated products were the dehydrogenated adducts **9** and **10a**/**11a**, respectively (Scheme 3). While the reaction of ylide **2** with 1,4-benzoquinone afforded only compound **9** (in 94% yield, after column chromatography), the reaction with 1,4-naphthoquinone yielded two products. On the basis of their mass and NMR spectra, the one with higher R_f was identified as **10a** (36%) [$(M + H)^+ = 880$] and the other as **11a** (60%) [$(M + H)^+ = 882$]. These two compounds were formed by dehydrogenation of the expected adduct.

* To whom correspondence should be addressed. E-mail: jcavaleiro@dq.ua.pt. Phone: +351 234 370 717 (direct line) or 370 200, ext 3533. Fax: + 351 234 370 084.

(1) (a) *The Porphyrin Handbook*; Kadish, K. M., Smith K. M., Guilard, R., Eds.; Academic Press: San Diego, 2000; Vol. 6. (b) Meunier, B. *Chem. Rev.* **1992**, *92*, 1411. (c) Bonnett, R. *Chem. Soc. Rev.* **1995**, *24*, 19. (d) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435.

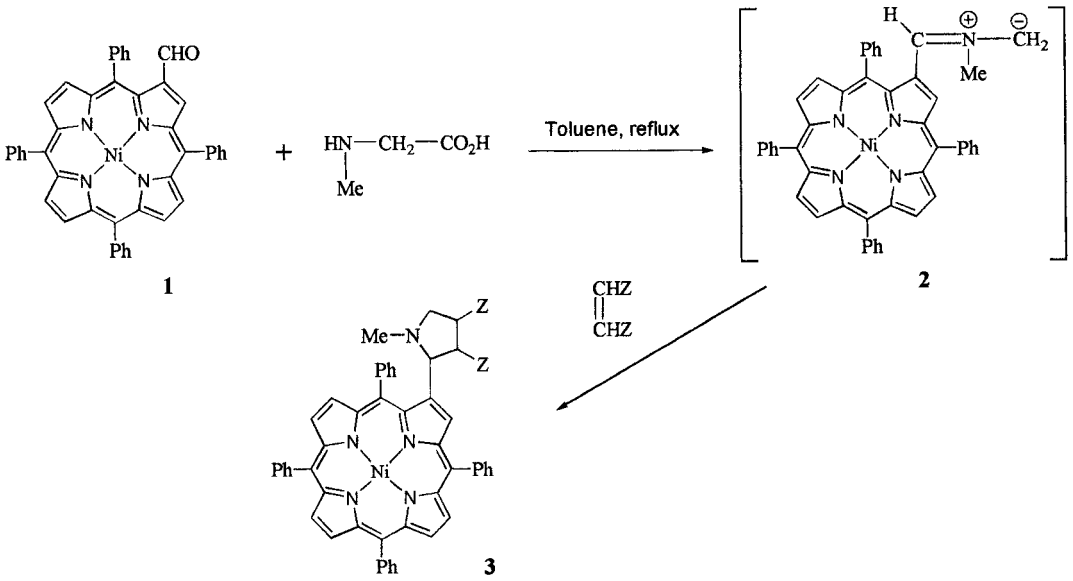
(2) (a) Tomé, A. C.; Lacerda, P. S. S.; Neves, M. G. P. M. S.; Cavaleiro, J. A. S. *Chem. Commun.* **1997**, 1199. (b) Silva, A. M. G.; Tomé, A. C.; Neves, M. G. P. M. S.; Cavaleiro, J. A. S. *Tetrahedron Lett.* **2000**, *41*, 3065. (c) Cavaleiro, J. A. S.; Neves, M. G. P. M. S.; Tomé, A. C.; Silva, A. M. S.; Faustino, M. A. F.; Lacerda, P. S. S.; Silva, A. M. G. *J. Heterocycl. Chem.* **2000**, *37*, 527.

(3) (a) Silva, A. M. G.; Tomé, A. C.; Neves, M. G. P. M. S.; Silva, A. M. S.; Cavaleiro, J. A. S. *Chem. Commun.* **1999**, 1767. (b) Tomé, A. C.; Lacerda, P. S. S.; Silva, A. M. G.; Neves, M. G. P. M. S.; Cavaleiro, J. A. S. *J. Porphyrins Phthalocyanines* **2000**, *4*, 532.

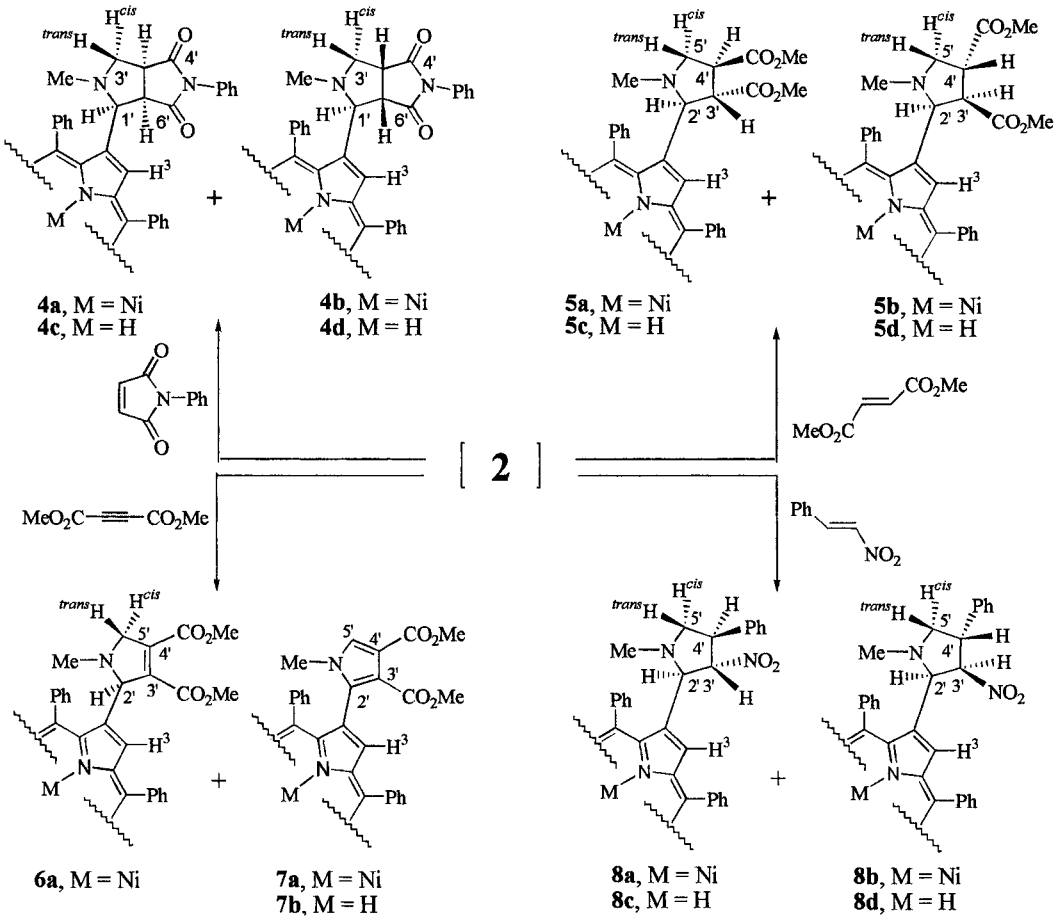
(4) Drovetskaya, T.; Reed, C. A.; Boyd, P. *Tetrahedron Lett.* **1995**, *36*, 7971.

10.1021/jo0106703 CCC: $22.00
Published on Web 01/15/2002

Scheme 1



Scheme 2

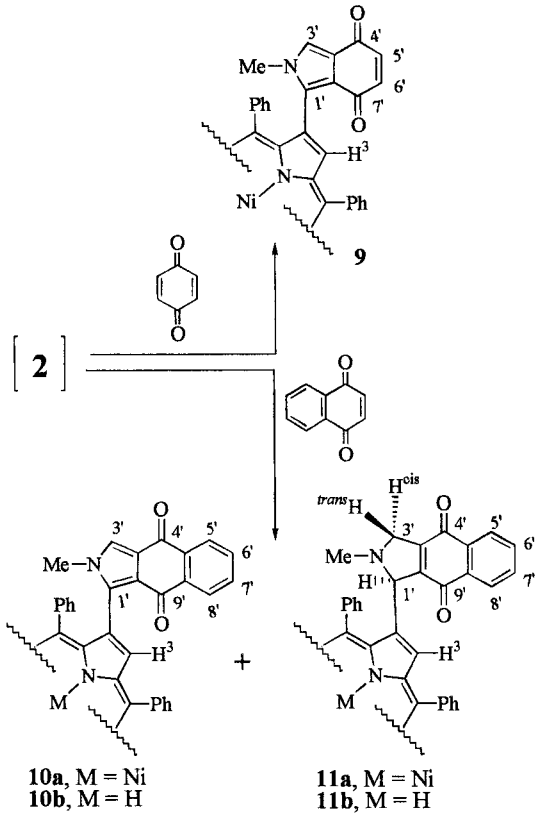


The demetalation of the nickel complexes with a mixture of sulfuric acid in chloroform afforded the corresponding metal-free porphyrins in high yields except in the cases of compound **9**, which gave only decomposition products, and compound **6a**, which aromatizes to pyrrole **7b**. The demetaled adducts can also be prepared in good yields if β-formyl-*meso*-tetraphenylporphyrin (free form) is used instead of **1**. For instance, the reaction of β-formyl-*meso*-tetraphenylporphyrin with *N*-methylglycine and *N*-phenylmaleimide gives compounds **4c** (65%) and **4d** (35%). The metal-free porphyrins were characterized by UV−vis, mass spectrometry, ^{1}H NMR, and elemental analysis.

Characterization of the New Compounds

The presence of the substituted pyrrolo[3,4-*c*]pyrrole fused ring system as β-substituent in porphyrins **4a** and **4b** was confirmed by the presence, in their ^{13}C NMR spectra, of the carbon resonances of two carbonyl groups,

Scheme 3



four aliphatic carbons, and that of the *N*-methyl group. The unequivocal assignment of the resonances of each carbonyl group was made by the analysis of the HMBC spectra of **4a** and **4b**. The resonances of H-1′ and H-3′$_{cis}$ correlate with those at, respectively, 174.8−174.9 and 177.4−178.5 ppm, proving the assignment of the former to C-6′ and the latter to C-4′. In these spectra the resonance of H-1′ also correlates with those of C-3 and with one appearing at 142.9 ppm for **4a** and 144.3 ppm for **4b** and which were then attributed to the resonance of C-2.

The NOESY studies were particularly important for the assignment of structure **4a** to the more abundant isomer (the one with higher R_f) and structure **4b** to the other diastereomer. The cross-peaks that were observed in these spectra allowed the establishment of the stereochemistry of **4a** and **4b** as depicted in Scheme 2; the most important results are indicated in Figure 1. These data indicate that in compound **4a** the protons H-1′ and H-6a′ have a *cis* configuration whereas in isomer **4b** these protons have a *trans* configuration.

The analysis of the COSY and NOESY NMR spectra of compounds **5a** and **5b** allowed the assignment of all the proton resonances and the configuration of the pyrrolidine rings to be established as depicted in Scheme 2. The most important cross-peaks found in the NOESY spectra of these compounds are shown in Figure 2; they allowed the conclusion that H-2′ and H-3′ have a *trans* configuration in the case of **5a** and a *cis* configuration in **5b** (Scheme 2).

The unequivocal assignment of the carbon resonances of the two carbonyl groups of cycloadducts **5a** and **5b** was made by the analysis of their HMBC spectra. In the case of **5a** there are correlations between the proton resonances of H-5′$_{cis}$ and 4′-CO_2CH_3 and that at 174.0 ppm and also between those of H-3′, H-4′, and 3′-CO_2CH_3 and that at 172.7 ppm. These results allow the attribution of the former resonance to the carbonyl carbon of 4′-CO_2CH_3 and the latter to 3′-CO_2CH_3. The correlations (H-2′, H-3′, 3′-CO_2CH_3 → 172.5 ppm; 4′-CO_2CH_3 → 173.2 ppm) observed in the HMBC spectrum of **5b** allowed the assignments of these two carbon resonances to the carbonyl groups of 3′-CO_2CH_3 and 4′-CO_2CH_3, respectively. The correlation of the signal of H-3′ and those at 146.7 ppm for **5a** and 143.3 ppm for **5b** in the HMBC spectra allowed the assignment of these resonances to C-2.

The identification of compounds **6a** and **7a** was based mainly on their ^{1}H NMR spectra. Compound **6a** shows the following features in the aliphatic region: three singlets at 2.16, 3.28, and 3.77 ppm corresponding, respectively, to the methyl and methoxyl protons and two double doublets at 3.37 and 4.06 ppm and a multiplet at 4.70−4.74 ppm, which were assigned, respectively, to the CH_2 and C*H* protons. The ^{1}H NMR spectrum of compound **7a** shows a less complex aliphatic region, with only three singlets at 2.99, 3.49, and 3.86 ppm due to the methyl and the two methoxyl groups. However, the aromatic region of the spectrum reveals, in addition to the protons in the porphyrinic ring, the presence of one singlet at 6.83 ppm, which was assigned to the resonance of the α-proton of the exocyclic pyrrole.

A detailed analysis of the ^{1}H and COSY spectra of compounds **8a** and **8b** allowed the assignment of all the proton resonances of the pyrrolidine rings. The regiospecific cycloaddition of *trans*-*β*-nitrostyrene was confirmed by the multiplicity observed on the signals assigned to H-2′ (a doublet at 3.76 ppm, *J* 7.0 Hz) and to H-3′ (a double doublet at 4.93 ppm, *J* 7.0 and 4.4 Hz) in compound **8a** and on the signals of H-2′ (a doublet at 4.09 ppm, *J* 8.4 Hz) and H-3′ (a double doublet at 5.02 ppm; *J* 8.4 and 5.6 Hz) in compound **8b.**

The NOESY studies (Figure 3) confirmed the *cis* configuration in compound **8b** since intense NOE cross-peaks were observed between H-2′ and H-3′. The absence of NOE cross-peaks between these two protons in **8a** indicates a *trans* configuration in this isomer.

The correlations between the proton resonances of H-3′ and H-2′ and those at 144.9 ppm, for **8a**, and at 139.4 ppm, for **8b**, observed in the HMBC spectra allowed the assignment of these resonances to C-2 and also the regioselectivity of the reaction of **2** with *β*-nitrostyrene to be confirmed.

The ^{1}H NMR spectrum of compound **9** shows, in the aromatic region, in addition to the porphyrin protons, a singlet at 7.06 ppm due to the resonance of the α-proton (H-3′) of the exocyclic pyrrole ring and two doublets at 6.60 and 6.50 ppm (*J* 10.4 Hz) corresponding to H-5′ and H-6′; the aliphatic region revealed only a singlet at 3.29 ppm due to the *N*-methyl proton resonance. The analysis of the 2D NMR spectra (COSY, HETCOR, NOESY, and HMBC) of compound **9** confirms its structure. Its HMBC spectrum presents correlations between the proton resonances of *N*-CH_3 and those at 134.7 ppm and of C-3′. This carbon resonance was then assigned to C-1′. The resonance of H-3′ correlates with that of C-1′ and with those at 118.7 and 121.2 ppm, which were then assigned to C-3a′ and C-7a′.

The ^{1}H NMR spectrum of compound **10a** is also in agreement with the oxidized form, showing only a singlet in the aliphatic region, which is due to the *N*-CH_3 protons;

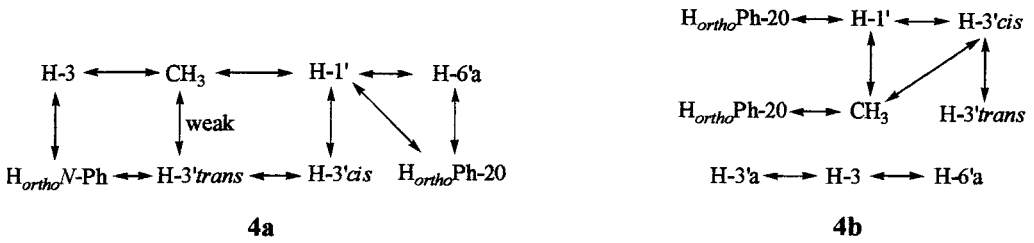


Figure 1. Important NOE cross-peaks observed in the NOESY spectra of compounds **4a** and **4b**.

Figure 2. Important NOE cross-peaks observed in the NOESY spectra of compounds **5a** and **5b**.

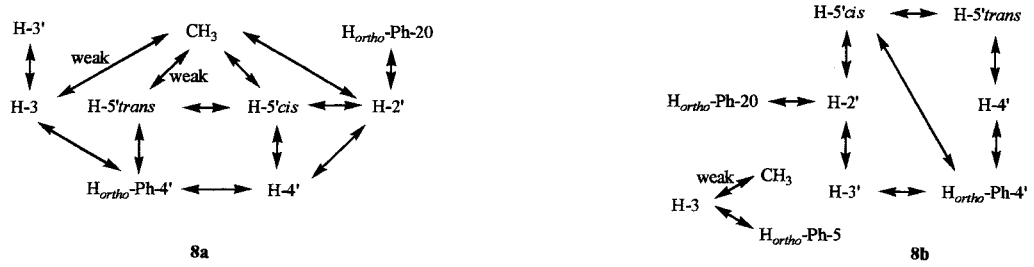


Figure 3. Important NOE cross-peaks observed in the NOESY spectra of compounds **8a** and **8b**.

N-C*H*$_3$ → C-3' and 135.0 ppm (C-1')

H-3' → δ 120.8 and 122.6 ppm (C-3a' and C-9a'), 180.4 ppm (C-4')

H-3 → δ 132.4 ppm (C-2)

Figure 4. Main correlations observed in the HMBC spectrum of compound **10a**.

the signals corresponding to the naphthyl protons fall in the aromatic region along with the protons of the porphyrin phenyl rings. The cross-peaks observed in the HMBC spectrum of **10a** (Figure 4) allow the assignment of the carbon resonances of C-1′, C-2, and C-4′ (C=O). The carbon resonance of the other carbonyl group (C-9′) was then assigned to the signal appearing at 179.2 ppm.

The ^{1}H NMR spectrum of compound **11a** displays a singlet due to *N*-C*H*$_3$ protons (2.34 ppm), two double doublets at 3.63 ppm (*J* 16.4 and 5.8 Hz) and 4.35 ppm (*J* 16.4 and 4.8 Hz) corresponding to the C*H*$_2$ protons, and a broad singlet at 4.86 ppm corresponding to the C*H* proton of the pyrroline ring. The naphthyl protons also fall in the aromatic region along with the protons of the porphyrin phenyl rings. The stereochemistry of **11a**, as depicted in Scheme 3, was established by considering the NOE cross-peaks observed in its NOESY spectrum (H-1′ → H-3′$_{cis}$ and one H$_{ortho}$-Ph-20; *N*-C*H*$_3$ → H-3′$_{cis}$, H-3′$_{trans}$, H-1′ and weakly with H-3).

Conclusions

New β-substituted *meso*-tetraphenylporphyrins can be obtained, in high yield, via 1,3-dipolar cycloaddition reactions of the porphyrinic azomethine ylide **2** with several dipolarophiles. The cycloaddition reactions with *N*-phenylmaleimide, dimethyl fumarate, and *trans*-β-nitrostyrene afforded the *cis* isomer in higher yield than the *trans* isomer. The reaction with *trans*-β-nitrostyrene is regioselective, yielding only one pair of diasteriomers. The reaction with dimethyl acetylenedicarboxylate affords the expected adduct and, in a minor amount, the corresponding oxidized form. With quinones only didehydro and tetradehydro adducts are isolated.

Experimental Section

General Remarks. Melting points were measured on a Reichert Thermovar apparatus fitted with a microscope and are uncorrected. ^{1}H and ^{13}C solution NMR spectra were recorded on a Bruker AMX 300 spectrometer at 300.13 and 75.47 MHz, respectively. $CDCl_3$ was used as solvent and TMS as internal reference; the chemical shifts are expressed in δ (ppm) and the coupling constants (*J*) in hertz (Hz). Unequivocal ^{1}H assignments were made with the aid of 2D COSY (^{1}H/^{1}H) and NOESY spectra (mixing time of 800 ms), while ^{13}C assignments were made on the basis of 2D HETCOR (^{1}H/^{13}C) (or HSQC) and HMBC (delays for long-range *J* C/H couplings were optimized for 7 Hz) experiments. Mass spectra and HRMS spectra were recorded on VG AutoSpec Q and M mass spectrometers using $CHCl_3$ as solvent and NBA as matrix. Elemental analyses were performed in a Leco 999 CHN analyzer. The UV−vis spectra were recorded on a Uvikon spectrophotometer using CH_2Cl_2 or $CHCl_3$ as solvent. Column chromatography was carried out using silica gel (Merck, 35−70 mesh). Preparative thin-layer chromatography was carried out on 20 × 20 cm glass plates coated with Merck 60 silica gel (1 mm thick). Analytical TLC was carried out on precoated sheets with silica gel (Merck 60, 0.2 mm thick).

Chemistry. (β-Formyl-*meso*-tetraphenylporphyrinato)nickel(II) (**1**) was prepared by Vilsmeier formylation of the nickel-

(II) complex of *meso*-tetraphenylporphyrin.[5] All the other chemicals and solvents used herein were obtained from commercial sources and were used as received or distilled and dried using standard procedures. Light petroleum was the fraction of bp 40−60 °C.

General Procedure for the 1,3-Dipolar Cycloadditions. A toluene (5 mL) solution of **1** (0.01 mmol), *N*-methylglycine (0.07 mmol), and the dipolarophile (0.02 mmol, except with dimethyl acetylenedicarboxylate and with 1,4-benzoquinone, where 0.12 mmol was used instead) was refluxed for 5−7 h under a nitrogen atmosphere. After the solution was cooled to room temperature, the toluene was evaporated. The resulting residue was purified by column chromatography (silica gel) using a mixture of chloroform/light petroleum (3:2) as eluent. Some products were further purified by preparative chromatography using the following eluents: chloroform/light petroleum (3:1) for compounds **5**, light petroleum/ethyl acetate (8:2) for compounds **6** and **7**, and dichloromethane/light petroleum (3:7) for compounds **8**. The isolated compounds were then crystallized from dichloromethane/hexane, yielding purple crystals.

Data for {2-(2-Methyl-4,6-dioxo-5-phenyl-1,3,3a,4,6,6a-hexahydropyrrolo[3,4-*c*]pyrrol-1-yl)-5,10,15,20-tetraphenylporphyrinato}nickel(II) (4a and 4b). 4a: yield 61%; mp 242−244 °C; ^{1}H NMR δ 2.23 (s, 3 H, CH_3), 2.32−2.40 (m, 1 H, H-3′$_{cis}$), 3.15−3.22 (m, 2 H, H-3a′ and H-6a′), 3.65 (d, 1 H, *J* 9.6, H-3′$_{trans}$), 3.78−3.80 (m, 1 H, H-1′), 7.02 (d, 2 H, *J* 6.9, H$_{ortho}$-*N*-Ph), 7.28−7.39 (m, 3 H, H$_{meta,para}$-*N*-Ph), 7.55−7.76 (m, 12 H, H$_{meta,para}$-Ph), 7.86 (d, 2 H, *J* 7.2, H$_{ortho}$-Ph), 7.97−8.08 (m, 6 H, H$_{ortho}$-Ph), 8.59 (d, 1 H, *J* 4.8, H-β), 8.64 (s, 2 H, H-12 and H-13), 8.67 (d, 1 H, *J* 4.8, H-β), 8.69−8.72 (m, 2 H, H-β), 8.70 (s, 1 H, H-3); ^{13}C NMR δ 40.4 (*C*H$_3$), 44.4 (C-3a′), 50.2 (C-6a′), 58.0 (C-3′), 68.4 (C-1′), 117.4, 118.4, 118.7, 119.0, 126.4 (*N*-Ph), 126.8, 126.87, 126.9, 127.7, 128.2 (*N*-Ph), 128.5, 128.8 (*N*-Ph), 131.7 (C-12,13), 132.0 (*N*-Ph), 132.10 (C-β), 132.12 (C-β), 132.3 (C-β), 132.5 (C-β), 132.9, 133.6, 133.7, 134.10, 134.13 (C-3), 139.9, 140.6, 140.7, 140.8, 141.1, 142.2, 142.3, 142.5, 142.6, 142.9 (C-2), 143.3, 174.9 (C-6′), 178.5 (C-4′); MS (LSIMS) 899 (M + H)$^+$, 898 (M)$^{\bullet+}$.

4b: yield 35%; mp 296−298 °C; ^{1}H NMR δ 1.95 (s, 3 H, CH_3), 2.52 (dd, 1 H, *J* 9.8 and 6.0, H-3′$_{cis}$), 3.44 (dd, 1 H, *J* 9.8 and 9.0, H-3′$_{trans}$), 3.58−3.66 (dt, 1 H, *J* 9.0 and 6.0, H-3a′), 3.75 (dd, 1 H, *J* 9.0 and 6.0, H-6a′), 3.84 (d, 1 H, *J* 6.0, H-1′), 7.32−7.56 (m, 5 H, *N*-Ph and 1 H, H$_{meta}$-Ph-20), 7.60−7.71 (m, 9 H, H$_{meta,para}$-Ph-5,10,15 and 2 H, H$_{meta,para}$-Ph-20), 7.81 (d, 1 H, *J* 7.5, H$_{ortho}$-Ph-20), 7.94 (d, 1 H, *J* 7.6, H$_{ortho}$-Ph-20), 7.93−8.02 (m, 6 H, H$_{ortho}$-Ph-5,10,15 and 1 H, H$_{ortho}$-Ph-20), 8.61 (d, 1 H, *J* 5.1, H-β), 8.63 (d, 1 H, *J* 5.1, H-β), 8.68 (d, 1 H, *J* 5.0, H-β), 8.71 (d, 1 H, *J* 5.0, H-β), 8.71 (s, 2 H, H-12 and H-13), 8.80 (s, 1 H, H-3); ^{13}C NMR δ 38.4 (*C*H$_3$), 44.2 (C-3a′), 55.5 (C-6a′), 56.9 (C-3′), 64.4 (C-1′), 118.4, 118.6, 118.7, 119.1, 126.5 (*N*-Ph), 126.9, 127.0, 127.4, 127.78, 127.83, 128.2, 128.5 (*N*-Ph), 129.1 (*N*-Ph), 131.8 (C-β), 131.9 (*N*-Ph), 132.3 (C-β), 132.4 (C-β), 132.58 (C-β), 132.60 (C-β), 133.0, 133.4 (C-3), 133.7, 134.5, 133.9, 140.1, 140.2, 140.4, 140.5, 140.7, 142.2, 142.5, 142.6, 142.8, 143.6, 144.3 (C-2), 174.8 (C-6′), 177.4 (C-4′); MS (LSIMS) 899 (M + H)$^+$, 898 (M)$^{\bullet+}$.

Data for {2-[3,4-Bis(methoxycarbonyl)-1-methyl-2,3,4,5-tetrahydropyrrol-2-yl]-5,10,15,20-tetraphenylporphyrinato}nickel(II) (5a and 5b). 5a: yield 28%, mp 178−180 °C; ^{1}H NMR δ 2.14 (s, 3 H, CH_3), 2.43 (dd, 1 H, *J* 9.7 and 9.0, H-5′$_{cis}$), 3.23 (s, 3 H, 3′-CO$_2$CH_3), 3.30 (ddd, 1 H, *J* 9.0, 8.8 and 2.2, H-4′), 3.37 (d, 1 H, *J* 8.6, H-2′), 3.45 (dd, 1 H, *J* 9.7 and *J* 2.2, H-5′$_{trans}$), 3.58 (dd, 1 H, *J* 8.6 and 6.4, H-3′), 3.68 (s, 3 H, 4′-CO$_2$CH_3), 7.57−7.71 (m, 13 H, 1 H$_{ortho}$-Ph-20, 12 H$_{meta,para}$-Ph-5,10,15,20), 7.84 (d, 1 H, *J* 7.5, H$_{ortho}$-Ph-20), 7.97−8.04 (m, 6 H, H$_{ortho}$-Ph-5,10,15), 8.64 (s, 2 H, H-β), 8.65 (d, 1 H, *J* 4.8, H-β), 8.70 (d, 1 H, *J* 4.8, H-β), 8.70 (s, 2 H, H-12,13), 9.03 (s, 1 H, H-3); ^{13}C RMN δ 39.7 (*C*H$_3$), 44.5 (C-4′), 51.5 (3′-OCH_3), 52.3 (4′-OCH_3), 57.0 (C-3′), 58.0 (C-5′), 66.2 (C-2′), 118.0, 118.6, 118.7, 118.9, 126.7, 126.95, 126.99, 127.70, 127.8, 128.2, 131.1, 132.2 (C-β), 132.3 (C-β), 132.5 (C-β), 132.7 (C-β), 132.8 (C-β), 133.7, 133.9, 134.3 (C-3), 134.4, 140.3, 140.5, 140.56, 140.63, 140.9, 142.2, 142.37, 142.44, 142.55, 142.63, 143.3, 146.7 (C-2), 172.7 (3′-*C*O$_2$CH$_3$), 174.0 (4′-*C*O$_2$CH$_3$); MS (LSIMS) 870 (M + H)$^+$, 869 (M)$^{\bullet+}$, 810 (M − CO$_2$Me)$^{\bullet+}$.

5b: yield 68%; mp 183−185 °C; ^{1}H NMR δ 2.11 (s, 3 H, 3′-CO$_2$CH_3), 2.13−2.20 (m, 1 H, H-5′$_{cis}$), 2.20 (s, 3 H, CH_3), 3.38 (dd, 1 H, *J* 9.6 and *J* 6.5, H-3′), 3.48 (dd, 1 H, *J* 8.9 and 8.2, H-5′$_{trans}$), 3.52 (d, 1H, *J* 9.6, H-2′), 3.71 (s, 3 H, 4′-CO$_2$CH_3), 3.73−3.78 (m, 1 H, H-4′), 7.62−7.73 (m, 12 H, H$_{meta,para}$-Ph), 7.93−8.07 (m, 8 H, H$_{ortho}$-Ph), 8.62 (d, 1 H, *J* 4.8, H-β), 8.67−8.73 (m, 5 H, H-β), 8.78 (s, 1 H, H-3); ^{13}C RMN δ 40.5 (*C*H$_3$), 43.8 (C-4′), 50.7 (3′-OCH_3), 52.0 (4′-OCH_3), 52.8 (C-3′), 58.4 (C-5′), 67.7 (C-2′), 117.8, 118.4, 118.7, 119.0, 126.9, 127.0, 127.1, 127.8, 128.5, 131.7 (C-β), 132.2 (C-12,13), 132.4 (C-β), 132.5 (C-β), 132.7 (C-β), 133.1, 133.4, 133.6, 133.7, 134.1 (C-3), 140.2, 140.6, 140.8, 142.1, 142.3, 142.4, 142.6, 143.3 (C-2), 172.5 (3′-*C*O$_2$CH$_3$), 173.2 (4′-*C*O$_2$CH$_3$); MS (LSIMS) 870 (M + H)$^+$, 869 (M)$^{\bullet+}$.

Data for {2-[3,4-Bis(methoxycarbonyl)-1-methyl-2,5-dihydropyrrol-2-yl]-5,10,15,20-tetraphenylporphyrinato}nickel(II) (6a): yield 38%; mp 88−90 °C; ^{1}H NMR δ 2.16 (s, 3 H, CH_3), 3.28 (s, 3 H, 3′-OCH_3), 3.38 (dd, 1 H, *J* 14.5 and *J* 5.9, H-5′$_{cis}$), 3.77 (s, 3 H, 4′-OCH_3), 4.07 (dd, 1 H, *J* 14.5 and *J* 4.7, H-5′$_{trans}$), 4.73 (m, 1 H, H-2′), 7.61−7.73 (m, 12 H, H$_{meta,para}$-Ph-5,10,15,20), 7.90−7.92 (m, 2 H, H$_{ortho}$-Ph-20), 7.95−8.00 (m, 6 H, H$_{ortho}$-Ph-5,10,15), 8.64 (d, 1 H, *J* 2.2, H-β), 8.65 (d, 1 H, *J* 2.2, H-β), 8.69−8.72 (m, 4 H, H-β), 8.91 (s, 1 H, H-3); ^{13}C NMR δ 39.8 (*C*H$_3$), 51.7 (3′-OCH_3), 52.1 (4′-OCH_3), 60.4 (C-5′), 69.4 (C-2′), 118.1, 118.6, 118.9, 119.0, 126.7, 126.9, 127.3, 127.69, 127.75, 128.4, 131.7 (C-β), 132.2 (C-β), 132.4 (C-β), 132.6 (C-β), 132.8 (C-β), 133.1 (C-β), 133.5 (C-3′), 133.7, 134.0, 134.1, 135.9 (C-3), 139.7, 140.1, 140.50, 140.53, 142.4, 142.5, 142.6, 142.7, 143.3, 144.4 (C-4′), 163.5 (4′-*C*O$_2$CH$_3$), 164.5 (3′-*C*O$_2$CH$_3$); MS (LSIMS) 868 (M + H)$^+$, 867 (M)$^{\bullet+}$, 808 [M − CO$_2$CH$_3$]$^{\bullet+}$.

Data for {2-[3,4-Bis(methoxycarbonyl)-1-methylpyrrol-2-yl]-5,10,15,20-tetraphenylporphyrinato}nickel(II) (7a): yield 4%; mp 284−286 °C; ^{1}H NMR δ 2.99, 3.49 and 3.86 (3s, 9 H, CH_3 and 2 x CO$_2$CH_3), 6.83 (s, 1 H, H-5′), 7.33−7.38 (m, 3 H, H$_{meta,para}$-Ph-20), 7.63−7.70 (m, 11 H, H$_{meta,para}$-Ph-5,-10,15 and H$_{ortho}$-Ph-20), 7.95−8.02 (m, 6 H, H$_{ortho}$-Ph-5,10,15), 8.41 (d, 1 H, *J* 5.0, H-β), 8.62 (d, 1 H, *J* 5.0, H-β), 8.70 (d, 1 H, *J* 5.0, H-β), 8.72 (d, 1 H, *J* 5.2, H-β), 8.72 (s, 1 H, H-3), 8.73 (d, 1 H, *J* 5.2, H-β), 8.75 (d, 1 H, *J* 5.0, H-β); MS (LSIMS) 866 (M + H)$^+$, 865 (M)$^{\bullet+}$.

Data for {2-[1-Methyl-3-nitro-4-phenyl-2,3,4,5-tetrahydropyrrol-2-yl]-5,10,15,20-tetraphenylporphyrinato}nickel(II) (8a and 8b). 8a: yield 36%; mp 191−193 °C; ^{1}H NMR δ: 2.31 (s, 3 H, CH_3), 2.94 (t, 1 H, *J* 9.3, H-5′$_{cis}$), 3.32 (dd, 1 H, *J* 9.3 and *J* 1.7, H-5′$_{trans}$), 3.76 (d, 1 H, *J* 7.0, H-2′), 3.80−3.84 (m, 1 H, H-4′), 4.93 (dd, 1 H, *J* 7.0 and *J* 4.4, H-3′), 7.28−7.31 (m, 3 H, H$_{meta,para}$-Ph-4′), 7.41−7.44 (m, 2 H, H$_{ortho}$-Ph-4′), 7.62−7.78 (m, 12 H, H$_{meta,para}$-Ph-5,10,15,20), 7.78−7.87 (m, 2 H, H$_{ortho}$-Ph-20), 7.94−7.99 (m, 6 H, H$_{ortho}$-Ph-5,10,15), 8.62 (d, 1 H, *J* 5.1, H-β), 8.64 (d, 1 H, *J* 5.1, H-β), 8.66 (d, 1 H, *J* 5.1, H-β), 8.70 (d, 1 H, *J* 5.1, H-β), 8.71 (s, 2 H, H-12,13), 9.02 (s, 1 H, H-3); ^{13}C NMR δ 40.1 (*C*H$_3$), 47.5 (C-4′), 62.1 (C-5′), 68.8 (C-2′), 101.9 (C-3′), 118.3, 118.6, 119.1, 126.5, 126.9, 127.2, 127.5, 127.7, 127.76, 127.84, 128.2, 128.9, 131.8 (C-β), 132.4 (C-β), 132.6 (C-β), 132.7 (C-β), 133.0 (C-β), 133.1, 133.6, 133.8, 134.0, 134.1 (C-3), 139.8, 139.9, 140.4, 140.5, 140.6, 142.1, 142.5, 142.77, 142.79, 143.0, 143.3, 144.9 (C-2); MS (LSIMS) 875 (M + H)$^+$, 874 (M)$^{\bullet+}$, 828 [(M + H)$^+$ − HNO$_2$]$^+$.

8b: yield 60%; mp 179−180 °C; ^{1}H NMR δ 2.21 (dt, 1 H, *J* 10.2 and 9.5, H-5′$_{cis}$), 2.21 (s, 3 H, CH_3), 3.64 (dd, 1 H, *J* 9.5 and 8.0, H-5′$_{trans}$), 4.09 (d, 1 H, *J* 8.4, H-2′), 4.32−4.40 (m, 1 H, H-4′), 5.02 (dd, 1 H, *J* 8.4 and 5.6, H-3′), 7.08 (d, 2 H, *J* 8.3, H$_{ortho}$-Ph-4′), 7.31−7.41 (m, 3 H, H$_{meta,para}$-Ph-4′), 7.56−7.70 (m, 10 H, H$_{meta,para}$-Ph-5,10,15 and H$_{meta}$-Ph-20), 7.80−7.83 (m, 2 H, H$_{meta,para}$-Ph-20), 7.89−7.92 (m, 1 H, H$_{ortho}$-Ph-20), 7.99 (m, 6 H, H$_{ortho}$-Ph-5,10,15), 8.24−8.27 (m, 1 H, H$_{ortho}$-Ph-20), 8.62 (d, 1 H, *J* 5.0, H-β), 8.65 (d, 1 H, *J* 5.1, H-β), 8.67 (d, 1 H, *J* 5.1, H-β), 8.69 (d, 2 H, *J* 5.2, H-β), 8.72 (d, 1 H, *J* 5.0, H-β),

(5) (a) Inhofen, H. H.; Fuhrhop, J.-H.; Voigt, H.; Brockmann, H., Jr. *Liebigs Ann. Chem.* **1966**, *695*, 133. (b) Callot, H. J. *Tetrahedron* **1973**, *29*, 899. (c) Barloy, L.; Dolphin, D.; Dupré, D.; Wijesekera, T. P. *J. Org. Chem.* **1994**, *59*, 7976.

8.91 (s, 1 H, H-3); ^{13}C NMR δ 40.7 (*C*H$_3$), 47.7 (C-4′), 63.4 (C-5′), 70.4 (C-2′), 97.7 (C-3′), 117.1, 118.8, 119.0, 119.2, 126.9, 127.0, 127.2, 127.48, 127.54, 127.8, 127.9, 128.6, 128.8, 131.8 (C-β), 132.3 (C-β), 132.5 (C-β), 132.6 (C-β), 132.8 (C-β), 133.2, 133.66, 133.68, 134.0, 134.1, 135.5 (C-3), 139.36 (C-2), 139.43, 140.51, 140.54, 141.3, 142.35, 142.43, 142.7, 143.2; MS (LSIMS) 875 (M + H)$^+$, 874 (M)$^{\bullet+}$, 828 [(M + H)$^+$ − HNO$_2$]$^+$.

Data for {2-(4,7-Dihydro-2-methyl-4,7-dioxobenzo[*c*]-pyrrol-1-yl)-5,10,15,20-tetraphenylporphyrinato}nickel-(II) (9): yield 94%; mp >300 °C; ^{1}H NMR δ 3.29 (s, 3 H, C*H*$_3$), 6.50 and 6.60 (2d, 2 H, *J* 10.4, H-5′ and H-6′), 7.06 (s, 1 H, H-3′), 7.15−7.33 (m, 3 H, H$_{meta,para}$-Ph-20), 7.62−7.71 (m, 11 H, H$_{meta,para}$-Ph-5,10,15 and H$_{ortho}$-Ph-20), 7.97−8.03 (m, 6 H, H$_{ortho}$-Ph-5,10,15), 8.45 (d, 1 H, *J* 5.0, H-β), 8.63 (d, 1 H, *J* 5.0, H-β), 8.70−8.75 (m, 4 H, H-β), 8.75 (s, 1 H, H-3); ^{13}C NMR δ 35.0 (*C*H$_3$), 118.7 and 121.2 (C-3a′ and C-7a′), 119.1, 119.2, 119.25, 119.30, 124.4 (C-3′), 125.9, 127.0, 127.9, 128.1, 132.0 (C-β), 132.4 (C-2), 132.5 (C-β), 132.6 (C-β), 132.7 (C-β), 132.8 (C-β), 133.1 (C-β), 133.7, 133.9, 134.7 (C-1′), 136.4 (C-3), 138.6 and 140.5 (C-5′ and C-6′), 139.0, 140.3, 140.4, 140.45, 140.52, 142.3, 143.0, 143.1, 143.2, 143.7, 181.1 and 182.2 (C-4′ and C-7′); UV−vis (CHCl$_3$) λ$_{max}$/nm (log ε) 419 (5.36), 535 (4.30); MS (LSIMS) 830 (M + H)$^+$, 829 (M)$^{\bullet+}$; MS-HRFAB exact mass *m*/*z* for C$_{53}$H$_{34}$O$_2$N$_5$Ni (M + H)$^+$ calcd 830.2066, found 830.2080.

Data for {2-(4,9-Dihydro-2-methyl-4,9-dioxonaphtho-[2,3-*c*]pyrrol-1-yl)-5,10,15,20-tetraphenylporphyrinato}-nickel(II) (10a): yield 36%; mp > 300 °C; ^{1}H NMR δ 3.43 (s, 3 H, C*H*$_3$), 6.78−6.85 (m, 1 H, H$_{meta}$-Ph-20), 7.14 (t, 1 H, *J* 7.4, H$_{para}$-Ph-20), 7.21−7.27 (m, 1 H, H$_{meta}$-Ph-20), 7.25 (s, 1 H, H-3′), 7.57−7.73 (m, 13 H, H$_{meta,para}$-Ph-5,10,15; H$_{ortho}$-Ph-20; H-6′ and H-7′), 7.96−8.11 (m, 7 H, H$_{ortho}$-Ph and H-5′ or H-8′), 8.23 (dd, 1 H, *J* 1.3 and 7.6, H-5′ or H-8′), 8.43 (d, 1 H, *J* 5.0, H-β), 8.60 (d, 1 H, *J* 5.0, H-β), 8.72 (s, 2 H, H-12,13), 8.71 (d, 1 H, *J* 5.2, H-β), 8.74 (d, 1 H, *J* 5.2, H-β), 8.80 (s, 1 H, H-3); ^{13}C NMR δ 35.2 (*C*H$_3$), 118.8, 119.0, 119.1, 119.2, 120.8 and 122.6 (C-3a′ and C-9a′), 124.9 (C-3′), 125.9, 126.6 and 126.7 (C-5′ and C-8′), 126.9, 127.8, 132.0 (C-β), 132.56 (C-β), 132.59 (C-β), 132.4 (C-2), 132.5 and 132.9 (C-6′ and C-7′), 132.7 (C-β), 133.1 (C-β), 133.7, 133.9, 135.0, 135.1, 136.0, 136.2 (C-3), 138.9, 139.1, 140.4, 140.5, 142.3, 142.9, 143.0, 143.1, 143.7, 179.2 (C-9′), 180.4 (C-4′); MS (LSIMS) 880 (M + H)$^+$, 879 (M)$^{\bullet+}$.

Data for {2-(1,3,4,9-Tetrahydro-2-methyl-4,9-dioxo-naphtho[2,3-*c*]pyrrol-1-yl)-5,10,15,20-tetraphenyl-porphyrinato}nickel(II) (11a): yield 60%; mp 280−282 °C; ^{1}H NMR δ 2.34 (s, 3 H, C*H*$_3$), 3.63 (dd, 1 H, *J* 16.4 and *J* 5.8, H-3′$_{trans}$), 4.35 (dd, 1 H, *J* 16.4 and *J* 4.8, H-3′$_{cis}$), 4.86 (s broad, 1 H, H-1′), 7.50−7.69 (m, 16 H, H−Ph; H-6′, H-7′ and H-5′ or H-8′), 7.88−8.06 (m, 7 H, H$_{ortho}$-Ph; H-5′ or H-8′), 8.27 (d, 1 H, *J* 7.2, H$_{ortho}$-Ph), 8.58 (d, 1 H, *J* 5.0, H-β), 8.66 (d, 1 H, *J* 5.0, H-β), 8.68−8.73 (m, 4 H, H-β), 8.78 (s, 1 H, H-3); ^{13}C NMR δ 39.6 (*C*H$_3$), 57.9 (C-3′), 67.2 (C-1′), 118.41, 118.38, 118.5, 118.9, 125.9 and 126.9 (C-5′ and C-8′), 126.3, 126.6, 126.75, 126.80, 126.9, 127.6, 127.70, 127.73, 127.8, 128.3, 131.8 (C-β), 132.2 (C-β), 132.4 (C-β), 132.5 (C-β), 132.9 (C-β), 132.6 (C-2), 133.1 and 133.2 (C-6′ and C-7′), 133.7, 133.8, 134.2, 134.6, 134.9 (C-3), 139.9, 140.4, 140.65, 140.68, 140.71, 140.8, 142.3, 142.4, 142.5, 142.6, 143.6, 146.0, 146.7 and 150.3 (C-3a′ and C-9a′), 181.0 and 183.1 (C-4′ and C-9′); MS (LSIMS) 882 (M + H)$^+$, 881 (M)$^{\bullet+}$.

Demetalation of the Porphyrin Derivatives. Each nickel complex was treated with a mixture of 10% H$_2$SO$_4$ in chloroform. The reaction mixture was stirred at room temperature for 10 min and then neutralized with a saturated solution of Na$_2$CO$_3$. The aqueous phase was extracted with chloroform, and the organic phase was dried over Na$_2$SO$_4$ and evaporated in a vacuum to dryness. The resulting residue was crystallized in dichloromethane/hexane. With compound **9** only decomposition products were obtained.

Data for 2-(2-Methyl-4,6-dioxo-5-phenyl-1,3,3a,4,6,6a-hexahydropyrrolo[3,4-*c*]pyrrol-1-yl)-5,10,15,20-tetra-phenylporphyrin (4c and 4d). 4c: yield 98%; mp > 300 °C; ^{1}H NMR δ − 2.71 (s, 2 H, N*H*), 2.25 (s, 3 H, C*H*$_3$), 2.42 (dd, 1 H, *J* 9.7 and 6.8, H-3′$_{cis}$), 3.22 (dd, 1 H, *J* 6.8 and 8.2, H-3a′), 3.36 (dd, 1 H, *J* 8.2 and 8.7, H-6a′), 3.70 (d, 1 H, *J* 9.7, H-3′$_{trans}$), 3.87 (d, 1 H, *J* 8.7, H-1′), 7.01 (d, 2 H, *J* 7.7, H$_{ortho}$-*N*-Ph), 7.27−7.37 (m, 3 H, H$_{meta,para}$-*N*-Ph), 7.61−7.84 (m, 12 H, H$_{meta,para}$-Ph), 8.10−8.22 (m, 7 H, H$_{ortho}$-Ph), 8.41 (d, 1 H, *J* 7.6, H$_{ortho}$-Ph), 8.55 (d, 1 H, *J* 4.7, H-β), 8.70 (d, 1 H, *J* 4.7, H-β), 8.73 (d, 1 H, *J* 4.9, H-β), 8.76 (d, 1 H, *J* 4.9, H-β), 8.83 (s, 1 H, H-3), 8.81−8.84 (m, 2 H, H-β); UV−vis (CHCl$_3$) λ$_{max}$/nm (log ε) 419 (5.75), 515 (4.37), 551 (3.89), 591 (3.83), 646 (3.54). Anal. Calcd for C$_{57}$H$_{42}$N$_6$O$_2$: C, 81.20; N, 9.97; H, 5.03. Found: C, 81.52; N, 9.57; H, 4.89.

4d: yield 94%; mp 231−232 °C; ^{1}H NMR δ −2.66 (s, 2 H, N*H*), 1.93 (s, 3 H, C*H*$_3$), 2.57 (dd, 1 H, *J* 9.8 and 5.9, H-3′$_{cis}$), 3.45 (dd, 1 H, *J* 9.8 and 9.3, H-3′$_{trans}$), 3.64−3.73 (m, 1 H, H-3a′), 3.86−3.93 (m, 2 H, H-6a′ and H-1′), 7.36−7.58 (m, 5 H, *N*-Ph and 1 H, H$_{meta}$-Ph-20), 7.71−7.79 (m, 9 H, H$_{meta,para}$-Ph-5,10,15 and 2 H, H$_{meta,para}$-Ph-20), 8.08−8.23 (m, 8 H, H$_{ortho}$-Ph), 8.64 (d, 1 H, *J* 4.8, H-β), 8.72 (d, 1 H, *J* 4.8, H-β), 8.77 (d, 1 H, *J* 4.9, H-β), 8.81 (d, 1 H, *J* 4.9, H-β), 8.82 (d, 1 H, *J* 4.9, H-β), 8.85 (d, 1 H, *J* 4.9, H-β), 8.90 (s, 1 H, H-3); UV−vis (CHCl$_3$) λ$_{max}$/nm (log ε) 420 (5.73), 517 (4.34), 552 (3.96), 593 (3.81), 649 (3.54). Anal. Calcd for C$_{57}$H$_{42}$N$_6$O$_2$·H$_2$O: C, 79.50; N, 9.77; H, 5.15. Found: C, 79.63; N, 9.35; H, 5.02.

Data for 2-[3,4-Bis(methoxycarbonyl)-1-methyl-2,3,4,5-tetrahydropyrrol-2-yl]-5,10,1 5,20-tetraphenylporphyrin (5c and 5d). 5c: yield 93%; mp 81−83 °C; ^{1}H NMR δ −2.68 (s, 2 H, N*H*), 2.18 (s, 3 H, C*H*$_3$), 3.18 (s, 3 H, 3′-CO$_2$C*H*$_3$), 3.39−3.77 (m, 5 H, H-2′, H-3′, H-4′, H-5′$_{cis}$ and H-5′$_{trans}$), 3.74 (s, 3 H, 4′-CO$_2$C*H*$_3$), 7.66−8.27 (m, 20 H, H−Ph), 8.60−8.86 (m, 7 H, H-β); UV−vis (CH$_2$Cl$_2$) λ$_{max}$/nm (log ε) 419 (5.71), 517 (4.24), 552 (3.83), 592 (3.71), 648 (3.43). Anal. Calcd for C$_{53}$H$_{43}$N$_5$O$_4$·2H$_2$O: C, 74.88; N, 8.24; H, 5.58. Found: C, 74.81; N, 7.72; H, 5.56.

5d: yield 98%; mp 271−273 °C; ^{1}H NMR δ −2.75 (s, 2 H, N*H*), 2.15 and 2.17 (2s, 6 H, C*H*$_3$ and 3′-CO$_2$C*H*$_3$), 2.17−2.22 (m, 1 H, H-5′$_{cis}$), 3.53−3.75 (m, 4 H, H-2′, H-3′, H-4′ and H-5′$_{trans}$), 3.75 (s, 3H, 4′-CO$_2$C*H*$_3$), 7.69−7.86 (m, 12 H, H$_{meta,para}$-Ph), 8.03 (d, 1 H, *J* 7.2, H$_{ortho}$-Ph), 8.11−8.25 (m, 6 H, H$_{ortho}$-Ph), 8.41 (d, 1 H, *J* 7.2, H$_{ortho}$-Ph), 8.63 (d, 1 H, *J* 4.8, H-β), 8.72 (d, 1 H, *J* 4.7, H-β), 8.76 (d, 1 H, *J* 4.8, H-β), 8.79 (d, 1 H, *J* 4.7, H-β), 8.83−8.87 (m, 2 H, H-12 and H-13), 8.92 (s, 1 H, H-3); UV−vis (CH$_2$Cl$_2$) λ$_{max}$/nm (log ε) 418 (5.74), 515 (4.33), 550 (3.85), 590 (3.79), 646 (3.51). Anal. Calcd for C$_{53}$H$_{43}$N$_5$O$_4$: C, 78.20; N, 8.61; H, 5.33. Found: C, 78.58; N, 8.21; H, 5.34.

Data for 2-[3,4-Bis(methoxycarbonyl)-1-methylpyrrol-2-yl]-5,10,15,20-tetraphenylporphyrin (7b): yield 91%; mp 221−223 °C; ^{1}H NMR δ −2.64 (s, 2 H, N*H*), 3.18, 3.33, 3.88 (3s, 9 H, 2 × CO$_2$C*H*$_3$ and C*H*$_3$), 6.93 (s, 1 H, H-5′), 7.42−7.46 (m, 3 H, H$_{meta,para}$-Ph-20), 7.73−7.78 (m, 9 H, H$_{meta,para}$-Ph-5,-10,15), 7.93−8.06 (m, 2 H, H$_{ortho}$-Ph-20), 8.17−8.23 (m, 6 H, H$_{ortho}$-Ph-5,10,15), 8.64 (d, 1 H, *J* 4.9, H-β), 8.76−8.82 (m, 5 H, H-β), 8,87 (s, 1 H, H-3); UV−vis (CHCl$_3$) λ$_{max}$/nm (log ε) 422 (5.57), 519 (4.25), 554 (3.82), 592 (3.75), 651 (3.58). Anal. Calcd for C$_{53}$H$_{39}$N$_5$O$_4$·H$_2$O: C, 76.89; N, 8.46; H, 4.99. Found: C, 76.52; N, 8.37; H, 5.37.

Data for 2-[1-Methyl-3-nitro-4-phenyl-2,3,4,5-tetrahydropyrrol-2-yl]-5,10,15,20-tetraphenylporphyrin (8c and 8d). 8c: yield 63%; mp 126−128 °C; ^{1}H NMR δ −2.68 (s, 2 H, N*H*), 2.30 (s, 3 H, C*H*$_3$), 2.99 (t, 1 H, *J* 9.3, H-5′$_{cis}$), 3.35 (dd, 1 H, *J* 9.3 and *J* 1.7, H-5′$_{trans}$), 3.85 (d, 1 H, *J* 7.1, H-2′), 3.89−3.93 (m, 1 H, H-4′), 5.07 (dd, 1 H, *J* 7.1 and *J* 4.6, H-3′), 7.29−7.33 (m, 3 H, H$_{meta,para}$-Ph-4′), 7.42−7.46 (m, 2 H, H$_{ortho}$-Ph-4′), 7.64−7.86 (m, 12 H, H$_{meta,para}$-Ph-5,10,15,20; 1 H, H$_{ortho}$-Ph-20), 7.96 (d, 1 H, *J* 7.5, H$_{ortho}$-Ph-20), 8.15−8.23 (m, 6 H, H$_{ortho}$-Ph-5,10,15), 8.63 (d, 1 H, *J* 4.8, H-β), 8.73 (d, 1 H, *J* 4.8, H-β), 8.79 (s, 2 H, H-12 and H-13), 8.83 (d, 1 H, *J* 4.9, H-β), 8.85 (d, 1 H, *J* 4.9, H-β), 9.11 (s, 1 H, H-3); UV−vis (CHCl$_3$) λ$_{max}$/nm (log ε): 421 (6.00), 518 (4.63), 553 (4.25), 593 (4.70), 649 (3.83). Anal. Calcd for C$_{55}$H$_{42}$N$_6$O$_2$·^{1}/$_2$H$_2$O: C, 79.78; N, 10.15; H, 5.23. Found: C, 80.21; N, 10.13; H, 5.69.

8d: yield 97%; mp 241−243 °C; ^{1}H NMR δ −2.71 (s, 2 H, N*H*), 2.20 (s, 3 H, C*H*$_3$), 2.23−2.29 (m, 1 H, H-5′$_{cis}$), 3.67 (dd, 1 H, *J* 9.2 and 7.9, H-5′$_{trans}$), 4.14 (d, 1 H, *J* 8.5, H-2′), 4.39−4.47 (m, 1 H, H-4′), 5.22 (dd, 1 H, *J* 8.5 and *J* 5.7, H-3′); 7.12−7.18 (m, 2 H, H$_{ortho}$-Ph-4′), 7.34−7.44 (m, 3 H, H$_{meta,para}$-Ph-4′), 7.68−7.93 (m, 12 H, H$_{meta,para}$-Ph-5,10,15,20), 8.18−8.28 (m, 7 H, H$_{ortho}$-Ph-5,10,15,20), 8.40 (d, 1 H, *J* 7.6, H$_{ortho}$-Ph-20), 8.57

(d, 1 H, *J* 4.8, H-β), 8.75 (d, 1 H, *J* 4.8, H-β), 8.76−8.86 (m, 4 H, H-β), 9.01 (s, 1 H, H-3); UV−vis ($CHCl_3$) λ_{max}/nm (log ϵ) 421 (5.68), 517 (4.29), 553 (3.87), 592 (3.77), 648 (3.50). Anal. Calcd for $C_{55}H_{42}N_6O_2 \cdot H_2O$: C, 78.93; N, 10.04; H, 5.30. Found: C, 79.04; N, 9.96; H, 5.73.

Data for 2-(4,9-Dihydro-2-methyl-4,9-dioxonaphtho-[2,3-*c*]pyrrol-1-yl)-5,10,15,20-tetraphenylporphyrin (10b): yield 97%; mp > 300 °C; ^{1}H NMR δ −2.61 (s, 2 H, N*H*), 3.51 (s, 3 H, CH_3), 6.92 (t, 1 H, *J* 7.5, H−Ph), 7.20−7.35 (m, 2 H, H−Ph), 7.31 (s, 1 H, H-3′), 7.58−7.79 (m, 11 H, H−Ph), 7.88−7.98 (m, 3 H, H−Ph), 8.18−8.36 (m, 7 H, H−Ph), 8.64 (d, 1 H, *J* 4.9, H-β), 8.76−8.81 (m, 3 H, H-β), 8.82 (s, 1 H, H-3), 8.89 (s, 2 H, H-12 and H-13); UV−vis ($CHCl_3$) λ_{max}/nm (log ϵ) 423 (5.66), 519 (4.42), 555 (3.92), 596 (3.86), 652 (3.77). Anal. Calcd for $C_{57}H_{37}N_5O_2 \cdot H_2O$: C, 81.31; N, 8.32; H, 4.67. Found: C, 81.68; N, 7.91; H, 4.88.

Data for 2-(1,3,4,9-Tetrahydro-2-methyl-4,9-dioxonaphtho[2,3-*c*]pyrrol-1-yl)-5,10,15,20-tetraphenylporphyrin (11b): yield 96%; mp > 300 °C; ^{1}H NMR δ −2.65 (s, 2 H, N*H*), 2.37 (s, 3 H, CH_3), 3.68 (dd, 1 H, *J* 16.4 and 6.2, H-3′$_{trans}$), 4.40 (dd, 1 H, *J* 16.4 and 4.8, H-3′$_{cis}$), 4.96 (br s, 1H, H-1′), 7.49−7.76 (m, 15 H, H−Ph), 8.04−8.24 (m, 8 H, H−Ph), 8.49 (d, 1 H, *J* 7.8, H$_{ortho}$-Ph), 8.70 (d, 2 H, *J* 4.7, H-β), 8.76 (d, 2 H, *J* 4.7, H-β), 8.85 (s, 2 H, H-12 and H-13), 8.89 (s, 1 H, H-3); UV−vis ($CHCl_3$) λ_{max}/nm (log ϵ) 422 (5.24), 518 (3.93), 553 (3.48), 593 (3.40), 650 (3.20); Anal. Calcd for $C_{57}H_{39}N_5O_2 \cdot {}^1/_2H_2O$: C, 81.99; N, 8.39; H, 4.83. Found: C, 82.10; N, 8.52; H, 4.68.

Acknowledgment. Thanks are due to the University of Aveiro and Fundação para a Ciência e a Tecnologia (FCT) for funding this work. A.M.G.S. is also grateful to the FCT for a Ph.D. grant.

Supporting Information Available: ^{1}H NMR, COSY, NOESY, ^{13}C NMR, HSQC, HMBC spectra for **8a,b**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0106703