β-Imino-*meso*-tetraphenylporphyrin Derivatives in Hetero-Diels−Alder Reactions

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Dedicated to Prof. Peter Stanetty, Vienna University of Technology, on the occasion of his 60th birthday

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Two types of β-imino-*meso*-tetraphenylporphyrin derivatives were used as heterodienes in Diels–Alder reactions with electron-rich dienophiles. These reactions were catalysed by lanthanum triflate. Depending on the starting imine derivative, the products of these reactions are pyrido[2,3-*b*]porphyrins or β-tetrahydroquinoline-substituted porphyrins.

Introduction

Certain porphyrin derivatives are finding important applications in various fields, of which the industrial and medicinal ones seem to be highly promising. Several research groups are studying the use of porphyrins as photosensitizers[1] in cancer treatment and detection and also of their metal complexes as catalysts[2] in oxidative transformations. The search for new functionalization procedures, leading to new macrocyclic derivatives, therefore plays a key role in finding other promising compounds. In recent years we have devoted a considerable effort to the search for new procedures for the functionalisation of the porphyrin nucleus.[3] Recently, we have shown that β-iminoporphyrin derivatives **1** can act as heterodienes in Diels−Alder reactions with electron-rich dienophiles.[4] In these transformations, two π-electrons of the porphyrin macrocycle are involved in the diene system and participate in the reaction. Pyrido[2,3-*b*]porphyrins of type **3** (and their corresponding dehydro derivatives) are obtained (Scheme 1, path 1B). We therefore decided to investigate the reactivity of the isomeric imines **2** as heterodienes in Diels−Alder reactions. These imines also react with electron-rich dienophiles but, in this case, the π-electron system of the porphyrin macrocycle is not involved in the reaction and the isolated Diels−Alder adducts are β-substituted porphyrins of type **4** (Scheme 1, path 2A). These results are in agreement with reported data for different compounds showing that an aromatic ring linked to a nitrogen atom is the one involved in the cycloaddition and therefore the heterodiene system always reacts as a 2-azadiene.[5] Since both imines **1** and **2** are easily obtained from the reaction of β-amino- or β-formyl-*meso*-tetraphenylporphyrin, respectively, with the corresponding benzaldehydes or anilines, their use in Diels−Alder reactions is certainly an interesting approach to new porphyrinic macrocycles.

A full account of the results obtained in the studies carried out with imines **1** and **2** as heterodienes in Diels−Alder reactions with 3,4-dihydro-2*H*-pyran and 2,3-dihydrofuran is given in this publication.

Results and Discussion

Imines from β-Amino-*meso*-tetraphenylporphyrin and Benzaldehydes

The synthesis of β-iminoporphyrins **1** and the corresponding Diels−Alder reactions were carried out as one-pot procedures. Imines **1** were obtained from the reaction of the nickel complex of β-amino-*meso*-tetraphenylporphyrin with benzaldehyde and *p*-nitrobenzaldehyde in refluxing toluene and in the presence of La(OTf)$_3$. The reaction mixtures were allowed to reach room temperature and a large excess of dienophile was then added. After stirring at room temperature for four days, washing with water, drying and purification by preparative TLC, the new products were obtained; they were fully characterised by NMR [^{1}H, ^{13}C, DEPT, COSY, HETCOR, HMBC and NOESY], MS and UV/Vis spectroscopic techniques.

In the reactions of imines **1a** and **1b** with 3,4-dihydro-2*H*-pyran the products with higher R_f were identified as the expected tetrahydropyridine-fused derivatives **5a** and **5b**; the products with lower R_f were identified as the pyridoporphyrins **6a** and **6b** (Scheme 2). The *trans* configuration of com-

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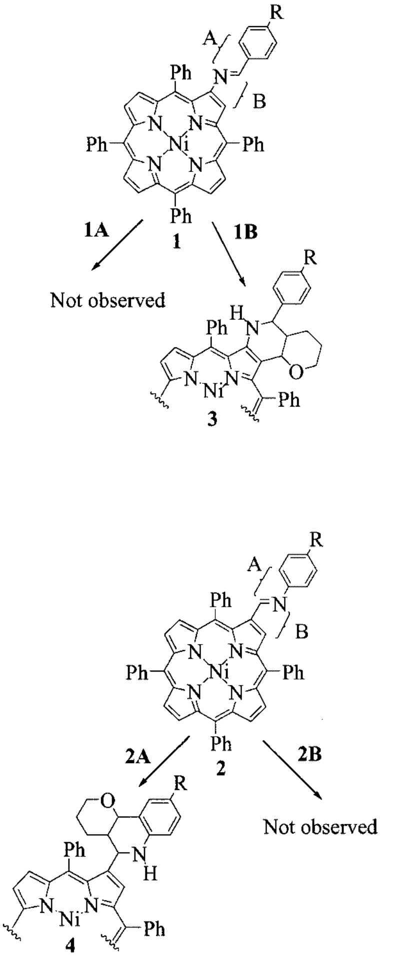
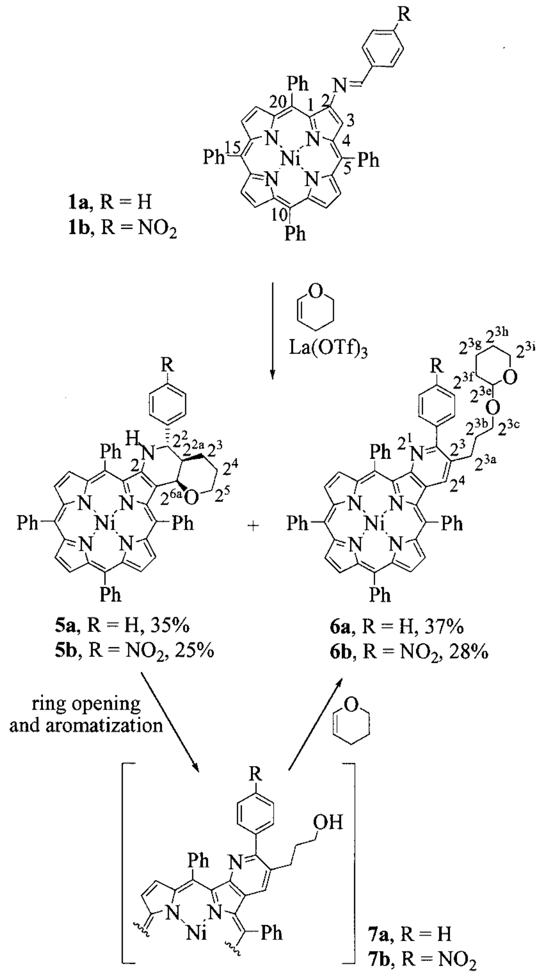


Scheme 1



Scheme 2

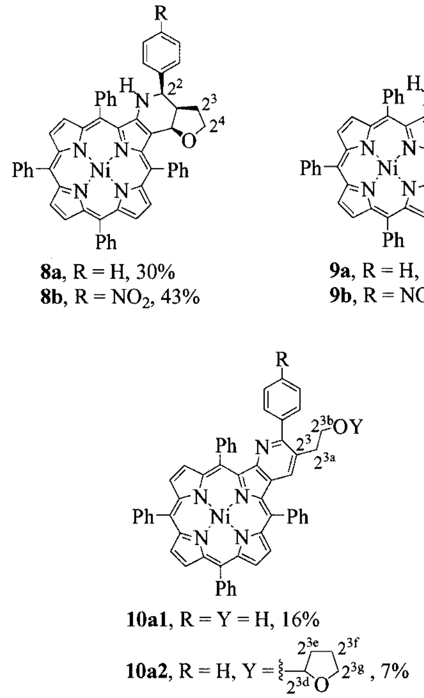
pounds **5a** and **5b** was confirmed by NOE studies: i) a close proximity was observed between H-2^2 and NH; ii) a close proximity was also observed between H-2^{2a} and H-2^{6a} but not with H-2^2.

A probable pathway leading to the formation of compounds **6** is outlined in Scheme 2. The opening of the pyran ring, supported by the vinylogous nitrogen, leads to dihydropyridines, which are then oxidized to the aromatic intermediates **7**; the addition of **7** to another molecule of 3,4-dihydro-2*H*-pyran yields the final products **6**. In support of this mechanism we have found that derivative **5b**, when stirred with 3,4-dihydro-2*H*-pyran in the presence of La-$(OTf)_3$, is converted into compound **6b**. We also verified that compounds **6**, when treated with trifluoroacetic acid, afford the metal-free derivatives **7**. Under these conditions the demetallation of the macrocycle and deprotection of the hydroxyl group occurs.

Imines **1a** and **1b** also react with 2,3-dihydrofuran, under the conditions described above, to yield the corresponding pyridine-fused derivatives **8**−**10** (Scheme 3). However, contrary to the reaction with 3,4-dihydro-2*H*-pyran, which gave only *trans*-tetrahydropyridine-fused derivatives **5**, in this case mixtures of *cis* (**8**) and *trans* (**9**) products were obtained. With imine **1a** minor amounts of the alcohol **10a1** and the corresponding tetrahydrofuranyl derivative **10a2** were also obtained.[6] The configuration of compounds **8** and **9** was confirmed by NOE studies: i) for compounds **8** a close proximity was observed between H-2^{2a} and H-2^2 and H-2^{5a}; ii) for compounds **9** a close proximity was observed between H-2^{2a} and H-2^{5a} but not with H-2^2.

Imines from β-Formyl-*meso*-tetraphenylporphyrin and Anilines

The synthesis of the β-iminoporphyrin derivatives **2** and the corresponding Diels−Alder reactions were also carried out as one-pot procedures. Imines **2a** and **2b** were prepared by reaction of the nickel complex of β-formyl-*meso*-tetraphenylporphyrin with the corresponding anilines in refluxing toluene in the presence of $La(OTf)_3$. After having verified by TLC that the starting porphyrin had been converted into the imine (ca. 6 h), the reaction mixtures were allowed to reach room temperature and an excess of the dienophile was added. The resulting mixtures were stirred at room temperature until TLC revealed no further progress of the reaction (1 to 7 days). After the usual work-up and separation by preparative TLC the new compounds were

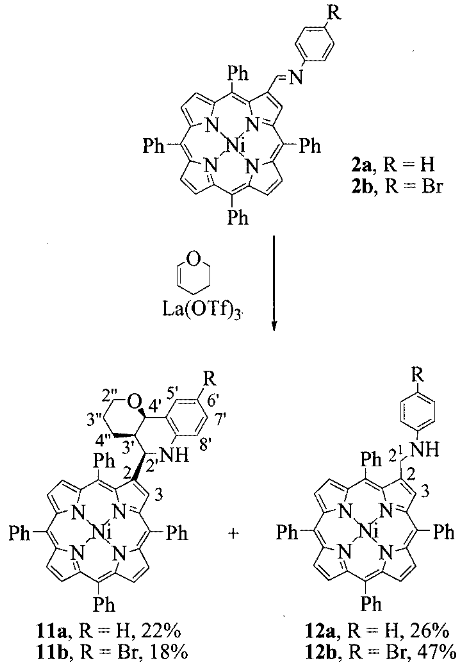


8a, R = H, 30%
8b, R = NO_2, 43%

9a, R = H, 22%
9b, R = NO_2, 42%

10a1, R = Y = H, 16%
10a2, R = H, Y = , 7%

Scheme 3



11a, R = H, 22%
11b, R = Br, 18%

12a, R = H, 26%
12b, R = Br, 47%

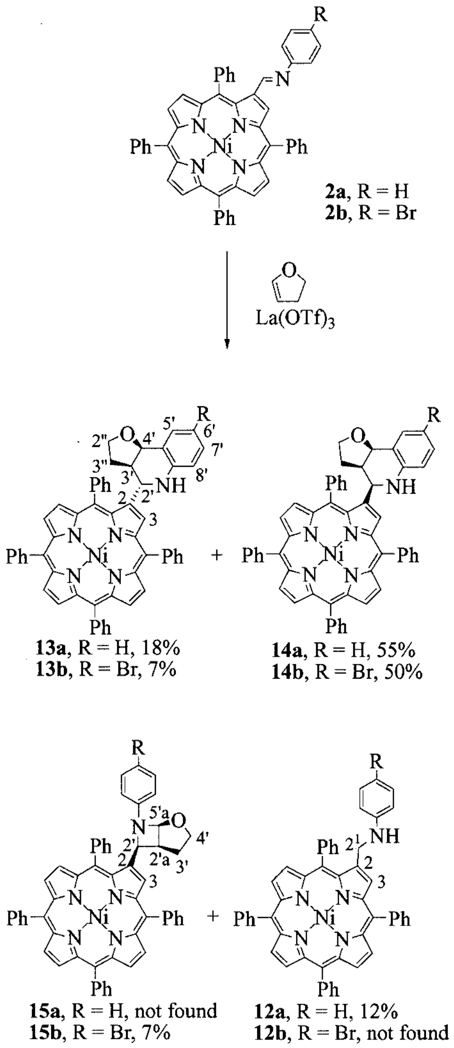
Scheme 4

fully characterized by NMR [^{1}H, ^{13}C, DEPT, COSY, HSQC, HMBC and NOESY], MS and UV/Vis spectroscopic techniques.

When 3,4-dihydro-2*H*-pyran was used as dienophile each imino derivative **2a** and **2b** afforded two main products. Careful structural analysis of the compounds with lower R_f showed that they were the expected 2-quinolyl derivatives **11a** and **11b** (Scheme 4). The *cis* configuration of both compounds was confirmed by NOE studies; a close proximity between H-2′, H-3′ and H-4′ was observed. Surprisingly, the major products were identified as the β-anilinomethyl derivatives **12a** and **12b**. These two compounds show very simple NMR spectra: in the ^{1}H NMR spectra the signals at δ = 4.16/4.17 ppm (br. s, NH), δ = 4.30−4.37 ppm (m, 2^1-CH_2), and δ = 8.70/8.65 ppm (s, H-3) clearly support the structure depicted in Scheme 4. The ^{13}C NMR spectra also confirm the presence of only one sp^3 carbon (signals at δ = 44.3/44.2 ppm).

In order to understand the formation of these unexpected aniline derivatives, two complementary experiments were carried out: i) a toluene solution of β-iminoporphyrin **2b** and 3,4-dihydro-2*H*-pyran, in the absence of La(OTf)$_3$, was left at room temperature for one week. None of the products (**11b** or **12b**) were formed under these conditions; ii) a toluene solution of β-iminoporphyrin **2b** and La(OTf)$_3$, in the absence of 3,4-dihydro-2*H*-pyran, was left at room temperature for one week. Compound **12b** was not formed under these conditions. When the missing catalyst or reagent was added to these mixtures, the compounds **11b** and **12b** were formed in both cases. This means that the simultaneous presence of La(OTf)$_3$ and the electron-rich dienophile is necessary for the formation of amines **12**. It is worth pointing out that the mechanism of the reaction leading to these amines remains unclear. A similar reduction product has been observed during the cycloaddition reaction of *N*-benzylideneaniline with 2-methoxypropene in the presence of lanthanide salts.[5c] The authors postulated that the aromatization of the resulting tetrahydroquinoline to quinoline is the source of the hydrogen atom for the reduction. In our case the reduction of the imines **2a** and **2b** into the corresponding β-anilinomethyl derivatives **12a** and **12b** probably occurs by dehydrogenation of 3,4-dihydro-2*H*-pyran and 2,3-dihydrofuran (vide infra).

In the reaction of **2a** and **2b** with 2,3-dihydrofuran three major products were formed in both cases (Scheme 5). In both reactions the products with lower R_f showed, in their mass spectra (FAB$^+$), *m/z* values corresponding to the expected 2-quinolyl derivatives — 843 [$M^{+\cdot}$] for **13a** and **14a** and 922 ($[M + H]^+$) for **13b** and **14b**. The compounds with higher R_f were identified as the β-anilinomethyl derivative **12a** (12%) and the azetidine **15b** (7%). From detailed NMR analysis of such compounds we were able to assign their structures. The relative configurations of compounds **13** and **14** were deduced mainly from the resonance of H-2′. In the case of compounds **13** it appears as a doublet in each case ($^3J_{H\text{-}2',H\text{-}3'}$ = 10.3 Hz in **13a** and 10.4 Hz in **13b**), whereas in the case of compounds **14** it appears as a broad singlet in each case; this suggests a *trans* configuration in **13a**,**b** and a *cis* configuration in **14a**,**b**. In the NOESY spectra of compounds **13** and **14** NOE cross peaks are observed between H-3′ and H-4′. However NOE cross peaks between H-2′ and one of the H-3′′ protons are only observed in the case of the *trans* isomers (**13a** and **13b**). All these data support the structures depicted in Scheme 5.



Scheme 5

The structure of the unexpected azetidine **15b** was confirmed by NMR spectroscopy: i) the doublets at δ = 6.54 and 7.20 ppm were assigned to the proton resonances of the *p*-bromophenyl ring; ii) the signal of H-2′ appears at δ = 5.20 ppm as a doublet of doublets due to coupling with H-2′a (^{3}J = 6.9 Hz) and H-3 (^{4}J = 0.9 Hz); iii) the resonance of H-5′a appears at δ = 5.41 ppm as a doublet due to coupling with H-2′a, and the latter resonates as a multiplet at δ = 2.47−2.54 ppm; iv) the resonance of the β-pyrrolic proton H-3 appears at δ = 8.76 ppm as a doublet due to coupling with H-2′ (^{4}J = 0.9 Hz). The COSY spectrum of **15b** allowed us to identify all these couplings and the NOESY spectra the spatial proximity between H-2′, H-2′a and H-5′a.

It is worth noting that the formation of [2+2] and [2+4] cycloadducts in the reaction of *N*-benzylideneaniline with 2,3-dihydrofuran and 3,4-dihydro-*2H*-pyran has been reported by Laszlo and co-workers.[7] Later, the same authors[8] and another group[9] corrected the proposed structure for the [2+2] cycloadducts. In the new proposal the products were identified as isomeric tetrahydroquinolines resulting from [4+2] cycloadditions. In our studies we have found not only the [4+2] stereoisomeric adducts **13** and **14**, but also the [2+2] cycloadduct **15b**.

Conclusion

In conclusion, the present work points out the versatility of β-iminoporphyrin derivatives in hetero-Diels−Alder reactions with electron-rich dienophiles. Pyridoporphyrins and β-tetrahydroquinoline-substituted porphyrins can be obtained in good yields from these reactions. One aspect of these reactions which requires further studies is the great difference observed in the reaction of imines **2** with 3,4-dihydro-2*H*-pyran and 2,3-dihydrofuran, both in terms of chemoselectivity and diastereoselectivity.

Experimental Section

General: ^{1}H and ^{13}C 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 using 2D COSY and NOESY spectra (mixing time of 800 ms), while ^{13}C assignments were made on the basis of 2D HETCOR (or HSQC) and HMBC experiments (delay for long-range J C/H couplings were optimized for 7 Hz). Mass spectra and HRMS were recorded on VG AutoSpec Q and M mass spectrometers using $CHCl_3$ as solvent and 3-nitrobenzyl alcohol (NBA) as matrix. Elemental analysis were performed with a Carlo Erba 1108 analyzer. The UV/Vis spectra were recorded on a Uvikon spectrophotometer using $CHCl_3$ as solvent. Melting points were measured on a Reichert Thermovar apparatus fitted with a microscope and are uncorrected. 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).

Reaction of Imines 1 with Electron-Rich Dienophiles. Typical Procedure: The nickel(II) complex of β-amino-*meso*-tetraphenylporphyrin (12 mg, 1.75×10^{-5} mol) was dissolved in dry toluene (2 mL) and then lanthanum triflate (2 mg, 0.2 equiv.) and the corresponding aldehyde (3 equiv. for *p*-nitrobenzaldehyde; 50 equiv. for benzaldehyde) were added. The resulting mixture was refluxed under a nitrogen atmosphere until complete conversion of the starting porphyrin into the β-imino derivative **1** was observed (3 hours). The reaction mixture was allowed to reach room temperature and then the electron-rich dienophile (60 equiv.) was added. The reaction was stirred at room temperature under a nitrogen atmosphere until total consumption of the β-imino derivative (4 days). After this period, each organic layer was washed with water, extracted with dichloromethane and dried over sodium sulfate. Evaporation of the solvent under reduced pressure gave a residue which was dissolved in toluene and chromatographed by preparative thin-layer chromatography using toluene as eluent.

Compound 5a: Yield: 5.2 mg (35%); m.p. > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.15−1.28 (m, 1 H, H-2^{4}), 1.42−1.45 (m, 2 H, H-2^{3}), 1.79−1.86 (m, 1 H, H-2^{4}); 2.05−2.08 (m, 1 H, H-2^{2a}), 2.86 (dd, J = 4.3, 11.2 Hz, 1 H, H-2^{5}), 3.84 (dd, J = 10.3, 11.2 Hz, 1 H, H-2^{5}), 4.03 (d, J = 2.2 Hz, 1 H, H-2^{6a}), 4.19 (s, 1 H, NH), 4.84 (d, J = 11.5 Hz, 1 H, H-2^{2}), 7.21−7.25 (m, 2 H, H-*o*−Ph-2^{2}), 7.32−7.34 (m, 3 H, H-*m,p*-Ph-2^{2}), 7.52−7.65 (m, 12 H, H-*m,p*-Ph), 7.95−7.98 (m, 6 H, H-*o*-Ph), 8.04 (d, J = 6.7 Hz, 2 H, H-*o*-Ph), 8.46 (d, J = 5.0 Hz, 1 H, H-β), 8.57 (d, J = 5.0 Hz, 1 H, H-β), 8.59 (d, J = 5.0 Hz, 1 H, H-β), 8.60 (s, 2 H, H-12,13), 8.62 (d, J = 5.0 Hz, 1 H, H-β) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 21.6 (C-2^{4}), 24.6 (C-2^{3}), 38.9 (C-2^{2a}), 55.3 (C-2^{2}), 68.5 (C-2^{5}), 70.2 (C-2^{6a}), 113.6, 114.8, 115.6, 118.0, 120.0, 126.2, 126.8, 126.9, 127.4, 127.5, 127.6, 127.7, 128.1, 128.2, 129.5 (C-β), 130.4, 130.8 (C-β), 131.3 (C-β), 131.4 (C-β), 131.5, 132.1 (C-β), 132.4 (C-*o*-Ph), 133.5 (C-*o*-Ph), 133.6 (C-*o*-Ph), 139.4, 140.2, 140.8, 140.9, 141.2, 141.3, 141.7, 142.3, 142.6, 144.2, 152.5 (C-2) ppm. UV/Vis (CHCl$_3$): λ_{max} (log ε) = 415 (5.16), 537 (3.94), 579 (3.90) nm. HRMS (FAB): *m/z* calcd. for $C_{56}H_{42}N_5NiO$ [M + H]$^{+}$ 858.2743; found 858.2760.

Compound 5b: Yield: 3.9 mg (25%); m.p. > 300 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.21−1.33 (m, 2 H, H-2^{3} and H-2^{4}), 1.42−1.53 (m, 1 H, H-2^{3}), 1.77−1.82 (m, 1 H, H-2^{4}), 2.05−2.09 (m, 1 H, H-2^{2a}), 2.89 (br. t, J = 11.1 Hz, 1 H, H-2^{5}), 3.86 (dd, J = 3.9, 11.1 Hz, 1 H, H-2^{5}), 4.03 (d, J = 2.2 Hz, 1 H, H-2^{6a}), 4.16 (s, 1 H, NH), 4.97 (d, J = 11.5 Hz, 1 H, H-2^{2}), 7.35−7.39, 7.58−7.65 and 7.95−8.09 (3 m, 20 H, H-*o,m,p*-Ph), 7.44 (br. d, J = 8.5 Hz, 2 H, H-*o*-Ph-2^{2}), 8.22 (br. d, J = 8.5 Hz, 2 H, H-*m*-Ph-2^{2}), 8.48 (d, J = 4.8 Hz, 1 H, H-β), 8.59 (d, J = 4.8 Hz, 1 H, H-β), 8.62 (d, J = 4.8 Hz, 1 H, H-β), 8.63 (s, 2 H, H-12,13), 8.63 (d, J = 4.8 Hz, 1 H, H-β) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 21.5 (C-2^{4}), 24.4 (C-2^{3}), 39.3 (C-2^{2a}), 54.9 (C-2^{2}), 68.5 (C-2^{5}), 70.0 (C-2^{6a}), 113.9, 115.5, 115.7, 118.3, 120.2, 123.5 (C-*m*-Ph-2^{2}), 126.3, 126.9, 127.5, 127.6, 127.7, 128.1, 128.4, 128.6 (C-*o*-Ph-2^{2}), 129.7 (C-β), 130.1, 131.1 (C-β), 131.5, 131.6 (C-β), 132.2 (C-β), 132.5 (C-β), 133.5, 133.6, 134.2, 139.5, 140.1, 140.5, 140.7, 141.1, 141.4, 142.4, 142.5, 144.1, 147.6, 149.6, 151.7 ppm. UV/Vis (CHCl$_3$): λ_{max} (log ε) = 416 (5.18), 538 (3.99) nm. HRMS (FAB): *m/z* calcd. for $C_{56}H_{41}N_6NiO_3$ [M + H]$^{+}$ 903.2594; found 903.2588.

Compound 6a: Yield: 6.1 mg (37%); m.p. 261−263 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.52−1.76 (m, 8 H, H-2^{3b}, 2^{3f}, 2^{3g}, 2^{3h}), 2.86−2.98 (m, 2 H, H-2^{3a}), 3.28−3.35 and 3.63−3.70 (2 m, 2 H, H-2^{3c}), 3.44−3.48 and 3.74−3.81 (2 m, 2 H, H-2^{3i}), 4.50−4.52 (m, 1 H, H-2^{3e}), 7.12 (s, 1 H, H-2^{4}), 7.35−7.37 (m, 3 H, H-*m,p*-Ph-2^{2}), 7.42−7.45 (m, 2 H, H-*o*-Ph-2^{2}), 7.56−7.60, 7.64−7.68 and 7.76−7.81 (3 m, 12 H, H-*m,p*-Ph), 7.87 (dd, J = 7.8, 1.8 Hz, 2 H, H-*o*-Ph), 7.96−8.01 (2 m, 6 H, H-*o*-Ph), 8.64−8.75 (m, 6 H, H-β) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 19.4 (C-2^{3g}), 25.5, 29.9 (C-2^{3a}), 30.6, 30.7 (C-2^{3b}), 62.0 (C-2^{3i}), 66.5 (C-2^{3c}), 98.4 (C-2^{3e}), 115.6, 115.8, 120.1, 120.2, 126.8, 126.9, 127.0, 127.4, 127.8, 128.0, 128.4, 130.2, 130.8, 131.4. 131.5, 131.6, 131.8, 132.1, 132.5 (C-2^{4}), 132.6, 132.8, 132.9, 133.5, 135.1, 136.3, 140.4, 140.5, 140.6, 140.7, 140.8, 141.0, 141.6, 141.8, 143.1, 144.5, 155.1, 156.3 ppm. UV/Vis (CHCl$_3$): λ_{max} (log ε) = 427 (5.41), 541 (4.22), 579 (3.99) nm. HRMS (FAB): *m/z* calcd. for $C_{61}H_{48}N_5NiO_2$ [M + H]$^{+}$ 940.3161; found 940.3118. $C_{61}H_{47}N_5NiO_2$: calcd. C 77.88, H 5.04, N 7.44; found C 77.79, H 5.10, N 7.40.

Compound 6b: Yield: 4.8 mg (28%); m.p. > 300 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.50−1.77 (m, 8 H, H-2^{3b}, 2^{3f}, 2^{3g}, 2^{3h}), 2.82−2.99 (m, 2 H, H-2^{3a}), 3.28−3.36 and 3.61−3.70 (2 m, 2 H, H-2^{3c}), 3.44−3.53 and 3.72−3.80 (2 m, 2 H, H-2^{3i}), 4.50−4.52 (m, 1 H, H-2^{3e}), 7.15 (s, 1 H, H-2^{4}), 7.61 (d, J = 8.9 Hz, 2 H, H-*o*-Ph-2^{2}), 7.64−7.69 and 7.76−7.82 (2 m, 12 H, H-*m,p*-Ph), 7.85−7.88 and 7.95−8.01 (2 m, 8 H, H-*o*-Ph), 8.22 (d, J = 8.9 Hz, 2 H, H-*m*-Ph-2^{2}), 8.66−8.75 (m, 6 H, H-β) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 19.5 (C-2^{3g}), 25.4, 29.8 (C-2^{3a}), 30.6, 30.7 (C-2^{3b}), 62.2 (C-2^{3i}), 66.3 (C-2^{3c}), 98.6 (C-2^{3e}), 115.7, 115.9, 120.4, 122.7 (C-*m*-Ph-2^{2}), 126.9, 127.0, 127.2, 127.9, 128.0, 128.5, 130.9 (C-β), 131.1 (C-*o*-Ph-2^{2}), 131.6, 131.7 (C-β), 131.8, 132.3, 132.5 (C-2^{4}), 132.8, 132.9 (C-β), 133.5, 134.5, 135.9, 140.3, 140.6, 140.9, 141.1, 141.8, 142.0, 143.1, 144.4. 146.9, 147.3, 153.5 (C-2^{2}), 155.0 ppm. UV/Vis (CHCl$_3$): λ_{max} (log ε) = 431 (5.61), 543 (4.56), 579 (4.30) nm. HRMS (FAB): *m/z* calcd. for $C_{61}H_{47}N_6NiO_4$ [M + H]$^{+}$ 985.3012; found 985.2966. $C_{61}H_{46}N_6NiO_4$: calcd. C 74.32, H 4.70, N 8.53; found C 74.12, H 4.72, N 8.54.

Compound 8a: Yield: 4.4 mg (30%); m.p. >300 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.25−1.31 and 1.92−1.98 (2 m, 2 H, H-2^{3}), 2.76−2.84 (m, 1 H, H-2^{2a}), 3.17−3.24 and 3.30−3.37 (2 m, 2 H, H-2^{4}), 4.24 (s, 1 H, NH), 4.79 (d, J = 2.3 Hz, 1 H, H-2^{2}), 5.08 (d, J = 8.1 Hz, 1 H, H-2^{5a}), 7.12−7.14 (m, 2 H, H-*o*-Ph-2^{2}), 7.30−7.36 (m, 3 H, H-*m,p*-Ph-2^{2}), 7.47−7.67 (m, 12 H, H-*m,p*-Ph), 7.85−7.90, 7.95−8.10, 8.27−8.30 (3 m, 8 H, H-*o*-Ph), 8.51−8.66 (m, 6 H, H-β) ppm. UV/Vis (CHCl$_3$): λ_{max} (log ε) = 417 (5.42), 531 (4.27) nm. HRMS (FAB): *m/z* calcd. for $C_{55}H_{40}N_5NiO$ [M + H]$^{+}$ 844.2586; found 844.2567.

Compound 8b: Yield: 6.7 mg (43%); m.p. 238−240 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.26−1.32 and 1.83−1.94 (2 m, 2 H, H-2^{3}), 2.65−2.73 (m, 1 H, H-2^{2a}), 3.15−3.22 and 3.29−3.37 (2 m, 2 H, H-2^{4}), 4.18 (s, 1 H, NH), 4.86 (d, J = 2.9 Hz, 1 H, H-2^{2}), 5.08 (d, J = 8.0 Hz, 1 H, H-2^{5a}), 7.32 (br. d, J = 8.7 Hz, 2 H, H-*o*-Ph-2^{2}), 7.47 (br. t, J = 7.1 Hz, 1 H, H-*m*-Ph or H-*p*-Ph), 7.57−7.69 (m, 11 H, H-*o,m,p*-Ph), 7.88 (dt, J = 1.2, 7.6 Hz, 1 H, H-*m*-Ph or H-*p*-Ph), 7.98−8.01 (m, 6 H, H-*o*-Ph), 8.19 (br. d, J = 8.7 Hz, 2 H, H-*m*-Ph-2^{2}), 8.29 (br. d, J = 7.6 Hz, 1 H, H-*o*-Ph), 8.54 (d, J = 5.0 Hz, 1 H, H-β), 8.54 (d, J = 5.0 Hz, 1 H, H-β), 8.62 (d, J = 5.0 Hz, 1 H, H-β), 8.62 (d, J = 5.0 Hz, 1 H, H-β), 8.63 (s, 2 H, H-12,13), 8.64 (d, J = 5.0 Hz, 1 H, H-β), 8.66 (d, J = 5.0 Hz, 1 H, H-β) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 24.7 (C-2^{3}), 45.8 (C-2^{2a}), 58.5 (C-2^{2}), 65.4 (C-2^{4}), 73.4 (C-2^{5a}), 115.2, 115.5, 118.7, 118.9, 120.0, 123.7 (C-*m*-Ph-2^{2}), 124.2, 126.0, 127.0 (C-*o*-Ph-2^{2}), 127.7, 127.6, 127.7, 128.2, 128.3, 128.7, 130.2, 130.3, 130.4, 131.2, 131.5, 131.7, 132.2, 132.4, 133.3, 133.5, 133.7, 139.7, 140.3, 140.6, 140.9, 141.2, 141.4, 141.7, 142.5, 142.6, 144.3, 147.2, 149.0, 152.3 ppm. UV/Vis (CHCl$_3$): λ_{max} (log ε) = 415 (5.25), 539 (4.08) nm. HRMS (FAB): *m/z* calcd. for $C_{55}H_{39}N_6NiO_3$ [M + H]$^{+}$ 889.2437; found 889.2408.

Compound 9a: Yield: 3.2 mg (22%); m.p. 290−292 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.42−1.50 and 1.74−1.76 (2 m, 2 H, H-2^{3}), 2.17−2.25 (m, 1 H, H-2^{2a}), 3.12−3.20 and 3.77−3.84 (2 m, 2 H, H-2^{4}), 3.89 (d, J = 11.2 Hz, 1 H, H-2^{2}), 4.17 (d, J = 4.0 Hz, 1 H, H-2^{5a}), 4.35 (s, 1 H, NH), 7.21−7.23 (m, 2 H, H-*o*-Ph-2^{2}), 7.32−7.34 (m, 3 H, H-*m,p*-Ph-2^{2}), 7.36−7.65 (m, 12 H, H-*m,p*-Ph), 7.73−7.74, 7.88−7.91 and 7.96−7.98 (3 m, 8 H, H-*o*-Ph), 8.47−8.68 (m, 6 H, H-β) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 27.7 (C-2^{3}), 41.3 (C-2^{2a}), 58.0 (C-2^{2}), 64.0 (C-2^{4}), 72.3 (C-2^{5a}), 113.7, 114.1, 115.6, 118.1, 120.0, 126.0, 126.8, 126.9, 127.4, 127.5, 127.6, 127.9, 128.0, 128.1, 128.3, 128.3, 129.6, 130.5, 130.9, 131.4, 131.4, 132.2, 132.4, 132.7, 133.5, 133.6, 139.3, 139.7, 140.4, 140.8, 140.8, 140.9, 141.0, 141.4, 142.1, 142.4, 142.6, 144.2 ppm. UV/Vis (CHCl$_3$): λ_{max} (log ε) = 413 (5.19), 535 (3.97) nm. HRMS (FAB): *m/z* calcd. for $C_{55}H_{40}N_5NiO$ [M + H]$^{+}$ 844.2586; found 844.2569.

Compound 9b: Yield: 6.5 mg (42%); m.p. 277−279 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.33−1.48 and 1.73−1.85 (2 m, 2 H, H-2^{3}), 2.17−2.24 (m, 1 H, H-2^{2a}), 3.13−3.21 and 3.79−3.86 (2m, 2 H, H-2^{4}), 4.00 (d, J = 11.1 Hz, 1 H, H-2^{2}), 4.14 (d, J = 4.0 Hz, 1 H, H-2^{5a}), 4.32 (s, 1 H, NH), 7.42 (br. d, J = 8.6 Hz, 2 H, H-*o*-Ph-2^{2}), 7.54−7.74 and 7.93−7.98 (2 m, 20 H, H-*o,m,p*-Ph), 8.21 (br. d, J = 8.6 Hz, 2 H, H-*m*-Ph-2^{2}), 8.50 (d, J = 5.0 Hz, 1 H, H-β), 8.61 (d, *J* = 5.0 Hz, 1 H, H-β), 8.63 (d, *J* = 5.0 Hz, 1 H, H-β), 8.64 (s, 2 H, H-12,13), 8.68 (d, *J* = 5.0 Hz, 1 H, H-β) ppm.^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.5 (C-2^{3}), 41.8 (C-2^{2a}), 57.7 (C-2^{2}), 64.0 (C-2^{4}), 72.1 (C-2^{5a}), 114.3, 114.4, 115.5, 118.4, 120.2, 123.6 (C-*m*-Ph-2^{2}), 126.0, 126.9, 127.5, 127.6, 127.7, 128.0, 128.1, 128.5, 129.0 (C-*o*-Ph-2^{2}), 129.8, 130.2, 131.2, 131.4, 131.6, 131.7, 132.3, 132.5, 132.9, 133.5, 133.6, 139.4, 139.5, 140.7, 141.2, 141.5, 141.5, 142.2, 142.5, 144.1, 147.7, 148.7, 152.1 ppm. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 414 (5.26), 537 (4.08) nm. HRMS (FAB): *m*/*z* calcd. for $C_{55}H_{39}N_6NiO_3$ [M + H]$^{+}$ 889.2235; found 889.2395. $C_{55}H_{38}N_6NiO_3$: calcd. C 74.25, H 4.31, N 9.45; found C 73.89, H 4.18, N 9.07.

Compound 10a1: Yield: 2.3 mg (16%); m.p. 142−144 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.11 (t, *J* = 6.8 Hz, 2 H, H-2^{3a}), 3.69−3.73 (m, 2 H, H-2^{3b}), 6.91 (s, 1 H, H-2^{4}), 7.37−7.45, 7.55−7.61, 7.64−7.70, 7.76−7.89 (4 m, 20 H, H-*o,m,p*-Ph, H-Ph-2^{2} and OH), 7.96−8.02 (m, 6 H, H-*o*-Ph), 8.66−8.74 (m, 6 H, H-β) ppm. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 426 (5.44), 540 (4.27), 578 (4.04) nm. HRMS (FAB): *m*/*z* calcd. for $C_{55}H_{38}N_5NiO_4$ [M + H]$^{+}$ 842.2430; found 842.2400.

Compound 10a2: Yield: 1.1 mg (7%); m.p. 190−192 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.74−1.91 (m, 4 H, H-2^{3e}, 2^{3f}), 3.07 (t, *J* = 7.3 Hz, 2 H, H-2^{3a}), 3.42−3.50 and 3.79−3.84 (2 m, 2 H, H-2^{3g}), 3.69−3.77 (m, 2 H H-2^{3b}), 5.03 (d, *J* = 3.5 Hz, 1 H, H-2^{3d}), 7.10 (s, 1 H, H-2^{4}), 7.36−7.39 (m, 3 H, H-*m,p*-Ph-2^{2}), 7.45−7.48 (m, 2 H, H-*o*-Ph-2^{2}), 7.56−7.70, 7.78−7.88 and 7.97−8.02 (3 m, 20 H, H-*o,m,p*-Ph), 8.64−8.74 (m, 6 H, H-β) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.3, 32.2, 33.4, 66.7, 67.0, 103.6, 115.6, 115.9, 120.1, 120.2, 126.8, 127.0, 127.1, 127.4, 127.8, 128.0, 128.5, 128.5, 130.4, 130.8, 131.5, 131.6, 131.6, 131.6, 132.5, 132.6, 132.8, 132.9. 133.5, 135.1, 136.2, 140.3, 140.4, 140.6, 140.7, 140.8, 141.0, 141.7, 141.8, 143.1, 144.5, 155.3, 156.6 ppm. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 426 (5.54), 540 (4.36), 578 (4.13) nm. HRMS (FAB): *m*/*z* calcd. for $C_{59}H_{44}N_5NiO_2$ [M + H]$^{+}$ 912.2848; found 912.2832.

Reaction of Imines 2 with Electron-Rich Dienophiles. Typical Procedure: Lanthanum triflate (2 mg, 0.2 equiv.) and the corresponding aniline (3 equiv. for *p*-bromoaniline; 50 equiv. for aniline) were added to a stirred solution of β-formyl-*meso*-tetraphenylporphyrinatonickel(II) (12 mg, 1.72 × 10^{-5} mol) in toluene (2 mL). The reaction was refluxed under a nitrogen atmosphere until no further consumption of the starting porphyrin was observed (6 h). After this period the reaction mixture was allowed to reach room temperature and the electron-rich dienophile (60 equiv.) was added. The reaction was maintained at this temperature and under nitrogen atmosphere until total consumption of the β-imino derivatives **2** (1 day for the formation of compounds **13b**, **14b** and **15b**, 4 days for compounds **13a** and **14a** and 7 days for compounds **11a,b** and **12a,b**). After this time the organic layer was washed with water, extracted with dichloromethane and dried over sodium sulfate. After solvent evaporation under reduced pressure the remaining residue was dissolved in toluene and chromatographed by preparative thin layer chromatography using a mixture of toluene and light petroleum (9:1) as eluent.

Compound 11a: Yield: 3.2 mg (22%); m.p. 262−264 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08−1.14 and 1.26−1.34 (2 m, 4 H, H-3′′,4′′), 2.32−2.35 (m, 1 H, H-3′), 3.47−3.52 and 3.70−3.73 (2 m, 2 H, H-2′′), 4.28 (d, *J* = 3.5 Hz, 1 H, H-4′), 4.37 (br. s, 1 H, NH), 4.57 (d, *J* = 8.1 Hz, 1 H, H-2′), 6.49 (dd, *J* = 7.6, 0.7 Hz, 1 H, H-8′), 6.72 (dt, *J* = 7.6, 0.7 Hz, 1 H, H-6′), 7.09 (dt, *J* = 7.6, 1.2 Hz), 1 H, H-7′, 7.19 (dd, *J* = 7.6, 1.2 Hz, 1 H, H-5′), 7.51−7.68 (m, 12 H, H-*m,p*-Ph), 7.83−8.13 (m, 8 H, H-*o*-Ph), 8.62−8.70 (m, 4 H, H-β), 8.71 (s, 2 H, H-12,13), 8.76 (s, 1 H, H-3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.1 (C-3′′), 24.4 (C-4′′), 38.0 (C-3′), 50.4 (C-2′), 65.9 (C-2′′), 72.8 (C-4′), 113.5, 117.4, 118.1, 118.3, 118.7, 119.2, 120.3, 126.8, 126.9, 127.6, 127.8, 128.7, 128.8, 129.7, 131.8, 132.3, 132.5, 132.6, 132.7, 133.3, 133.6, 133.7, 135.8, 139.2, 140.2, 140.4, 140.5, 140.6, 142.3, 142.4, 142.5, 142.6, 142.7, 143.5, 144.4, 147.6 ppm. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 417 (5.40), 531 (4.24) nm. HRMS (FAB): *m*/*z* calcd. for $C_{56}H_{42}N_5NiO$ [M + H]$^{+}$ 858.2743; found 858.2714.

Compound 11b: Yield: 2.9 mg (18%); m.p. >300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.15−1.23 (m, 1 H, H-4′′), 1.25−1.30 (m, 2 H, H-3′′), 1.42−1.48 (m, 1 H, H-4′′), 2.06−2.11 (m, 1 H, H-3′), 3.27−3.35 and 3.46−3.59 (2 m, 2 H, H-2′′), 4.16 (br. s, 1 H, NH), 4.46 (d, *J* = 5.3 Hz, 1 H, H-2′), 4.63 (br. s, 1 H, H-4′), 6.51 (d, *J* = 8.5 Hz, 1 H, H-8′), 7.15 (dd, *J* = 2.2, 8.5 Hz, 1 H, H-7′), 7.45 (d, *J* = 2.2 Hz, 1 H, H-5′), 7.66−7.68 (m, 12 H, H-*m,p*-Ph), 7.88−7.97 (m, 8 H, H-*o*-Ph), 8.62−8.74 (m, 6 H, H-β), 8.88 (s, 1 H, H-3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.9 (C-3′′), 25.3 (C-4′′), 36.4 (C-3′), 54.2 (C-2′), 60.7 (C-2′′), 72.2 (C-4′), 109.8, 116.1 (C-8′), 117.7, 118.0, 118.9, 119.4, 122.3, 126.9, 127.0, 127.1, 127.5, 127.8, 128.6, 130.2 (C-5′), 130.5 (C-7′), 131.9 (C-β), 132.3 (C-β), 132.5 (C-β), 132.6, 132.7 (C-β), 133.0 (C-3), 133.6, 133.7, 138.1, 140.1, 140.3, 140.5, 140.7, 142.2, 142.4, 142.5, 142.6, 142.7, 143.4, 144.4, 145.2 ppm. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 418 (5.41), 533 (4.28) nm. HRMS (FAB): *m*/*z* calcd. for $C_{56}H_{41}BrN_5NiO$ [M + H]$^{+}$ 936.1848; found 936.1810. $C_{56}H_{40}BrN_5NiO$: calcd. C 71.74, H 4.30, N 7.47; found C 71.70, H 4.44, N 7.36.

Compound 12a: Yield: 3.5 mg (26%); m.p. 224−226 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.16 (br. s, 1 H, NH), 4.36−4.37 (m, 2 H, H-2^{1}), 6.50 (d, *J* = 7.7 Hz, 2 H, H-Ph-*o*-2^{2}), 6.71 (t, *J* = 7.3 Hz, 1 H, H-*p*-Ph-2^{2}), 7.10−7.16 (m, 2 H, H-*m*-Ph-2^{2}), 7.58−7.69 (m, 12 H, H-*m,p*-Ph), 7.85−8.00 (m, 8 H, H-*o*-Ph), 8.70 (s, 1 H, H-3), 8.63−8.74 (m, 6 H, H-β) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 44.3 (C-2^{1}), 92.3, 113.2, 117.4, 117.9, 118.0, 118.8, 119.2, 126.9, 127.5, 127.6, 127.7, 128.4, 129.0, 131.9, 132.1, 132.2, 132.3, 132.5, 132.9, 133.6, 133.8, 138.9, 140.5, 140.6, 140.7, 142.0, 142.1, 142.3, 142.5, 143.2, 144.8, 148.0 ppm. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 416 (5.36), 529 (4.19) nm. HRMS (FAB): *m*/*z* calcd. for $C_{51}H_{35}N_5Ni$ [M^{+}] 775.2246; found 775.2269. $C_{51}H_{34}N_5Ni$: calcd. C 78.88, H 4.54, N 9.02; found C 78.67, H 4.70, N 8.72.

Compound 12b: Yield: 6.9 mg (47%); m.p. 175−177 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.17 (br. s, 1 H, NH), 4.30−4.33 (m, 2 H, H-2^{1}), 6.35 (d, *J* = 8.8 Hz, 2 H, H-*o*-Ph-2^{2}), 7.19 (d, *J* = 8.8 Hz, 2 H, H-*m*-Ph-2^{2}), 7.56−7.69 (m, 12 H, H-*m,p*-Ph), 7.84−7.91 and 7.97−8.00 (2 m, 8 H, H-*o*-Ph), 8.65 (s, 1 H, H-3), 8.63−8.74 (m, 6 H, H-β) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 44.2 (C-2^{1}), 109.0, 114.8, 117.9, 118.0, 118.9, 119.3, 126.9, 127.4, 127.7, 127.8, 128.5, 131.7, 131.9, 132.2, 132.3, 132.5, 132.6, 133.1, 133.6, 133.8, 138.8, 140.6, 142.2, 142.3, 142.4, 142.6, 142.7, 143.2, 143.8, 146.9 ppm. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 417 (5.38), 537 (4.23) nm. HRMS (FAB): *m*/*z* calcd. for $C_{51}H_{34}BrN_5Ni$ [M^{+}] 855.1331; found 855.1362. $C_{51}H_{34}BrN_5Ni$: calcd. C 71.61, H 4.01, N 8.19; found C 71.66, H 3.99, N 8.15.

Compound 13a: Yield: 2.6 mg (18%); m.p. 245−247 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.50−1.54 and 1.92−2.04 (2 m, 2 H, H-3′′), 2.82−2.91 (m, 1 H, H-3′), 3.64−3.79 (m, 2 H, H-2′′), 3.76 (d, *J* = 10.4 Hz, 1 H, H-2′), 4.25 (br. s, 1 H, NH), 4.55 (d, *J* = 5.4 Hz, 1 H, H-4′), 6.52 (d, *J* = 7.6 Hz, 1 H, H-8′), 6.79 (dt, *J* = 0.6, 7.6 Hz, 1 H, H-6′), 7.11 (dt, *J* = 1.4, 7.6 Hz, 1 H, H-7′), 7.31 (dd, *J* = 1.4, 7.6 Hz, 1 H, H-5′), 7.37−7.48 and 7.61−7.68 (2 m, 12 H, H-*m,p*-Ph), 7.80−7.83 and 7.94−8.00 (2 m, 8 H, H-*o*-Ph), 8.66−8.72 (m, 4 H, H-β), 8.74 (s, 2 H, H-12, 13), 8.89 (s, 1 H, H-3) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 29.8 (C-3′′), 43.3 (C-3′), 50.7 (C-2′), 65.3 (C-2′′), 76.0 (C-4′), 114.5 (C-8′), 118.0 (C-6′), 118.4, 118.5, 118.8, 119.2, 120.8, 126.6, 126.9, 127.1, 127.8, 128.3 (C-7′), 128.4, 130.8 (C-5′), 131.9, 132.0, 132.3, 132.4, 132.6, 132.7, 132.8, 133.7 (C-3), 139.7, 139.9, 140.4, 140.5, 140.5, 140.6, 142.3, 142.4, 142.5, 142.7, 142.8, 143.3, 145.1, 146.3 ppm. UV/Vis (CHCl$_3$): $\lambda_{\max}$ (log ε) = 417 (5.35), 531 (4.20) nm. HRMS (FAB): *m*/*z* calcd. for C$_{55}$H$_{39}$N$_5$NiO [M$^+$] 843.2508; found 843.2507.

Compound 13b: Yield: 1.1 mg (7%); m.p. >300 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.41−1.52 and 1.91−2.03 (2 m, 2 H, H-3′′), 2.81−2.88 (m, 1 H, H-3′), 3.63−3.73 (m, 2 H, H-2′′), 3.76 (d, *J* = 10.3 Hz, 1 H, H-2′), 4.25 (s, 1 H, NH), 4.49 (br. d, *J* = 5.5 Hz, 1 H, H-4′), 6.40 (d, *J* = 8.5 Hz, 1 H, H-8′), 7.19 (dd, *J* = 2.1, 8.5 Hz, 1 H, H-7′), 7.43 (d, *J* = 2.1 Hz, 1 H, H-5′), 7.39−7.50, 7.62−7.69, 7.81−7.83 and 7.92−8.00 (4 m, 20 H, H-*o,m,p*-Ph), 8.67−8.72 (m, 6 H, H-β), 8.85 (s, 1 H, H-3) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 29.7 (C-3′′), 43.0 (C-3′), 50.7 (C-2′), 65.4 (C-2′′), 75.4 (C-4′), 109.9, 116.1 (C-8′), 117.9, 118.6, 118.9, 119.3, 122.9, 126.6, 127.0, 127.2, 127.8, 128.6, 131.1 (C-7′), 131.9, 132.0, 132.3, 132.5, 132.6, 132.7, 132.8, 133.3 (C-5′), 133.5 (C-3), 133.6, 139.9, 140.4, 140.4, 142.3, 142.5, 142.6, 142.8, 142.8, 143.2, 144.1, 145.8 ppm. UV/Vis (CHCl$_3$): $\lambda_{\max}$ (log ε) = 417 (5.42), 531 (4.27) nm. HRMS (FAB): *m*/*z* calcd. for C$_{55}$H$_{39}$BrN$_5$NiO [M + H]$^+$ 922.1691; found 922.1699.

Compound 14a: Yield: 8.0 mg (55%); m.p. 241−243 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.28−1.39 and 2.17−2.33 (2 m, 2 H, H-3′′), 2.74−2.82 (m, 1 H, H-3′), 3.56−3.64 and 3.67−3.74 (m, 2 H, H-2′′), 4.07 (br. s, 1 H, NH), 4.71 (d, *J* = 7.4 Hz, 1 H, H-4′), 4.72 (br. s, 1 H, H-2′), 6.38 (d, *J* = 7.6 Hz, 1 H, H-8′), 6.77 (t, *J* = 7.4 Hz, 1 H, H-6′), 7.06 (dd, *J* = 7.4, 7.6 Hz, 1 H, H-7′), 7.28 (d, *J* = 7.4 Hz, 1 H, H-5′), 7.54−7.68 (m, 12 H, H-*m,p*-Ph), 7.82−7.98 (m, 8 H, H-*o*-Ph), 8.65−8.74 (m, 6 H, H-β), 9.01 (s, 1 H, H-3) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 24.1 (C-3′′), 44.2 (C-3′), 51.5 (C-2′), 66.4 (C-2′′), 76.0 (C-4′), 114.6 (C-8′), 117.7, 118.1, 118.7 (C-6′), 118.8, 119.3, 122.5, 126.9, 126.9, 127.0, 127.4, 127.8, 127.9, 128.0 (C-7′), 128.6, 130.0 (C-5′), 131.9, 132.3, 132.4, 132.5, 132.7, 133.6, 133.6, 138.2, 140.3, 140.4, 140.5, 140.6, 142.2, 142.3, 142.5, 142.5, 142.7, 143.3, 144.9, 147.6 ppm. UV/Vis (CHCl$_3$): $\lambda_{\max}$ (log ε) = 417 (5.39), 531 (4.25) nm. HRMS (FAB): *m*/*z* calcd. for C$_{55}$H$_{40}$N$_5$NiO [M + H]$^+$ 844.2586; found 844.2611. C$_{55}$H$_{39}$N$_5$NiO: calcd. C 78.21, H 4.65, N 8.29; found C 78.04, H 4.99, N 7.99.

Compound 14b: Yield: 7.9 mg (50%); m.p. 296−298 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.34−1.44 and 2.18−2.37 (2 m, 2 H, H-3′′), 2.74−2.82 (m, 1 H, H-3′), 3.59−3.67 and 3.71−3.78 (2 m, 2 H, H-2′′), 4.11 (s, 1 H, NH), 4.66 (d, 1 H, H-4′, *J* = 7.2 Hz), 4.68 (br. s, 1 H, H-2′), 6.48 (d, *J* = 8.5 Hz, 1 H, H-8′), 7.14 (dd, *J* = 8.5, 2.1 Hz, 1 H, H-7′), 7.42 (d, *J* = 2.1 Hz, 1 H, H-5′), 7.54−7.71 (m, 12 H, H-*m,p*-Ph), 7.85−8.00 (m, 8 H, H-*o*-Ph), 8.67−8.77 (m, 4 H, H-β), 8.69 (s, 2 H, H-12,13), 8.99 (s, 1 H, H-3) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 24.0 (C-3′′), 44.0 (C-3′), 51.4 (C-2′), 66.6 (C-2′′), 75.6 (C-4′), 110.3, 116.4, 118.1, 124.7, 126.9, 127.0, 127.1, 127.4, 127.8, 127.9, 128.7, 130.8, 132.0, 132.3, 132.4, 132.5, 132.7, 132.8, 133.6, 133.7, 138.1, 140.3, 140.4, 140.4, 140.4, 140.6, 142.3, 142.4, 142.5, 142.6, 142.8, 143.3, 146.9 ppm. UV/Vis (CHCl$_3$): $\lambda_{\max}$ (log ε) = 417 (5.40), 531 (4.24) nm. HRMS (FAB): *m*/*z* calcd. for C$_{55}$H$_{39}$BrN$_5$NiO [M + H]$^+$ 922.1691; found 922.1648. C$_{55}$H$_{38}$BrN$_5$NiO: calcd. C 71.53, H 4.15, N 7.58; found C 71.38, H 4.21, N 7.52.

Compound 15b: Yield: 1.1 mg (7%); m.p. 218−220 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.47−1.51 (m, 2 H, H-3′), 2.47−2.54 (m, 1 H, H-2′a), 3.97−4.09 (m, 2 H, H-4′), 5.20 (dd, *J* = 6.9, 0.9 Hz, 1 H, H-2′), 5.41 (d, *J* = 5.1 Hz, 1 H, H-5′a), 6.54 (d, *J* = 8.8 Hz, 2 H, H-*o*-Ph-N), 7.20 (d, *J* = 8.8 Hz, 2 H, H-*m*-Ph-N), 7.51−7.72 (m, 13 H, H-*o,m,p*-Ph), 7.86 (br. d, *J* = 6.4 Hz, 2 H, H-*o*-Ph), 7.99 (br. d, *J* = 5.7 Hz, 4 H, H-*o*-Ph); 8.18 (br. d, *J* = 6.8 Hz, 1 H, H-*o*-Ph), 8.61 (d, *J* = 5.0 Hz, 1 H, H-β), 8.62 (d, *J* = 5.0 Hz, 1 H, H-β), 8.67 (d, *J* = 5.0 Hz, 1 H, H-β), 8.71−8.73 (m, 3 H, H-β), 8.76 (d, *J* = 0.9 Hz, 1 H, H-3) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 25.8 (C-3′), 43.6 (C-2′a), 60.0 (C-2′), 68.0 (C-4′), 94.9 (C-5′a), 110.8, 114.2 (C-*o*-Ph−N), 121.1, 127.0, 127.6, 127.8, 128.7, 131.6 (C-*m*-Ph-N), 132.0, 132.5, 132.7, 133.6, 133.8, 133.9, 140.5, 142.8 ppm. UV/Vis (CHCl$_3$): $\lambda_{\max}$ (log ε) = 417 (5.32), 531 (4.16) nm. HRMS (FAB): *m*/*z* calcd. for C$_{55}$H$_{39}$BrN$_5$NiO [M + H]$^+$ 922.1691; found 922.1674.

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