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Tetrahedron Letters 46 (2005) 6931–6935

Tetrahedron Letters

Modified porphyrinoids from carbazates and hydrazones and the first crystal structure of a di-iminoporphodimethene

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Received 31 May 2005; revised 29 July 2005; accepted 1 August 2005

Abstract—Novel porphyrinoids with interrupted conjugation (di-iminoporphodimethenes) result from the Pd-catalyzed coupling of *meso*-bromo porphyrins and their metal complexes with carbazates and hydrazones, followed by aerial oxidation. X-ray crystallography revealed a saddle shape for molecules of the nickel(II) complex of a di-iminoporphodimethene.

In recent years, palladium-catalyzed couplings have been used extensively to prepare many novel mono- and oligoporphyrins for a variety of applications.[1] Most of these have involved carbon–carbon couplings, but recently couplings with softer nucleophiles have been achieved, for example, C–N, C–O and C–S bond formation to the porphyrin periphery.[2] These reactions afford a wide range of new functionalized porphyrins with possible biological activity that is yet to be investigated. We have now extended these aminations by using protected hydrazines as nucleophiles, and discovered unique reactivity apparently due to the presence of the second nitrogen atom attached to the amino substituent.

Excess *tert*-butyl carbazate was reacted with 5-bromo-10,20-diphenylporphyrinatonickel(II) **Ni·1a** (Scheme 1) under reaction conditions similar to those described by Suda and co-workers for amination and amidation.[2a] The reaction, however, did not proceed as expected, and three novel products were isolated after extraction and column chromatography. The structures of these products were elucidated spectroscopically and the least polar, bright green product was found to be **Ni·2a**, a mono-*meso*-substituted azocarboxylate. Anderson and co-workers have synthesized mono-*meso*-substituted arylazo compounds,[3] however, we believe, that this is the first reported synthesis of *meso*-substituted azo compounds using palladium catalysis.

More interestingly, the major product of the reaction was found to be the very polar blue-green **Ni·3a**, a structure closely related to 5,15-dioxoporphyrins (or dioxoporphodimethenes), which have been known for some time.[4] Other 'deconjugated porphyrinoids' include the dialkylidene quinoidal porphyrins of Anderson and co-workers.[5] The Ni(II) complex of 5-imino-15-oxooctaethylporphyrin, prepared by $FeCl_3$ oxidation of the 5-amino complex, was recently reported by Balch and co-workers.[6] The analogous Zn(II) complex was mentioned in 1970.[7] However, porphyrinoids with two exocyclic imine bonds, displaying the general structure **3**, are previously unreported. It is noteworthy that a bis-amination occurred, despite the presence of only one bromo substituent. This double activation of an opposite *meso* position may be a general phenomenon in the presence of suitable substituents, and is worthy of study in its own right. The unsubstituted NiDPP was subjected to the usual coupling conditions, but addition of carbazates did not occur. It appears that the presence of the first azo (or hydrazo) substituent is necessary for the activation of the opposite *meso* carbon to the second addition. We are currently investigating the mechanisms of these reactions in detail.

The third product is the (expected) red porphyrinylcarbazate **Ni·4a**, which was shown by TLC to convert to

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Keywords: Porphyrinoid; Hydrazines; Di-iminoporphodimethenes; Palladium; Crystal structure.

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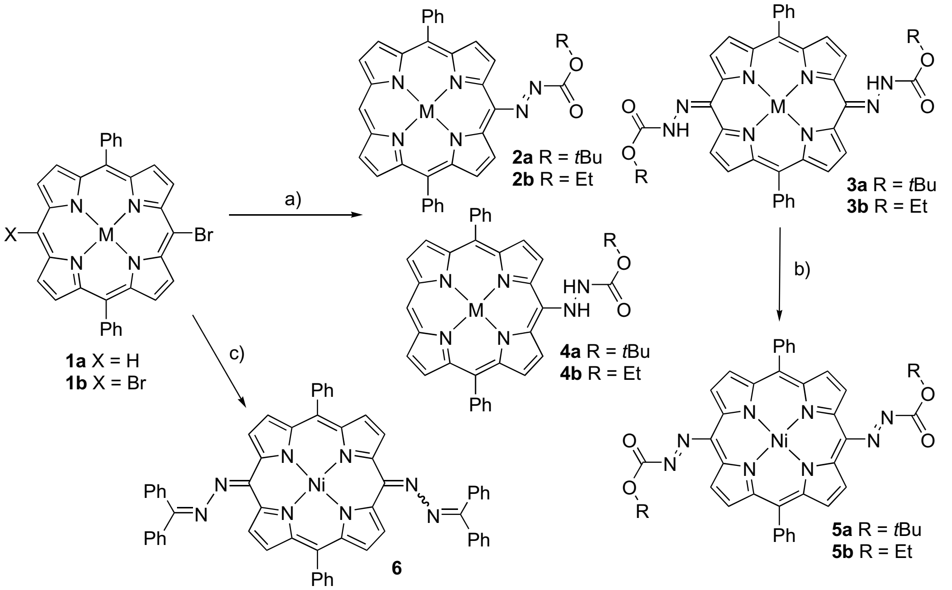
doi:10.1016/j.tetlet.2005.08.004



Scheme 1. Synthesis of azocarboxylates and di-iminoporphodimethenes. Reagents and conditions: (a) *t*Bu or Et carbazate, $Pd(OAc)_2$, *rac*-BINAP, Cs_2CO_3, THF, 68 °C, 18 h (**Ni·2b**, X = H, M = Ni, 1 equiv carbazate: 63%; **Ni·3b**, X = Br, M = Ni, 2.2 equiv carbazate: 61%); (b) DDQ, CH_2Cl_2, 5 min (**5b**: 89%); (c) benzophenone hydrazone, $Pd(OAc)_2$, *rac*-BINAP, Cs_2CO_3, THF, 68 °C, 18 h (66%).

Ni·3a during the coupling reaction, and to **Ni·2a** spontaneously by aerial oxidation. This product may be by-passed by continuing the coupling reaction for 26 h and working-up the reaction by stirring the THF/water mixture in air for at least an hour, a procedure that gives the highest yields of **3** and the cleanest chromatographic separations. By changing the reaction conditions, the Ni(II) complexes **Ni·2a,b** and **Ni·3a,b** can be prepared selectively, utilizing one equivalent of *tert*-butyl or ethyl carbazate and the monobromoporphyrin for the former and the 5,15-dibromo Ni(II) complex **Ni·1b** and excess carbazate for the latter.[8,9]

The imino compounds display interesting characteristics, including markedly increased solubility in polar solvents such as methanol, compared with diphenylporphyrin precursors. This increase in solubility has also been previously noted for dioxoporphyrins.[10] The absorption spectrum of **Ni·3a** is similar to that of the latter compounds (Fig. 1), the porphodimethene system giving rise to two major bands at 437 and 606 nm. The higher energy band is much reduced in intensity compared to the Soret band of its porphyrin precursor. A third absorption band at 334 nm appears to be characteristic of this type of porphodimethene, but its origin is unknown as yet. The ^1H NMR spectrum of **Ni·3a** shows the loss of ring current with the resonances of the β-pyrrolic protons shifted upfield to <7 ppm. The carbamate-like NH signal appears at 8.72 ppm as a broad singlet that is readily eliminated by treatment with D_2O. The Ni(II) di-iminoporphodimethenes can be quantitatively oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to reconjugate the porphyrin macrocycle, forming the blue-green bis(azocarboxylates) **5**.[11] The absorption spectra of **Ni·3a** and its derivative **5a** are compared in Figure 1, the latter showing a strongly red-shifted porphyrinic spectrum.

The crystal structure[12] of **Ni·3a** (Fig. 2a) shows that the coordination sphere is very close to square planar. Minimal tetrahedral distortion is indicated by the small deviations of the coordinated N atoms from their least

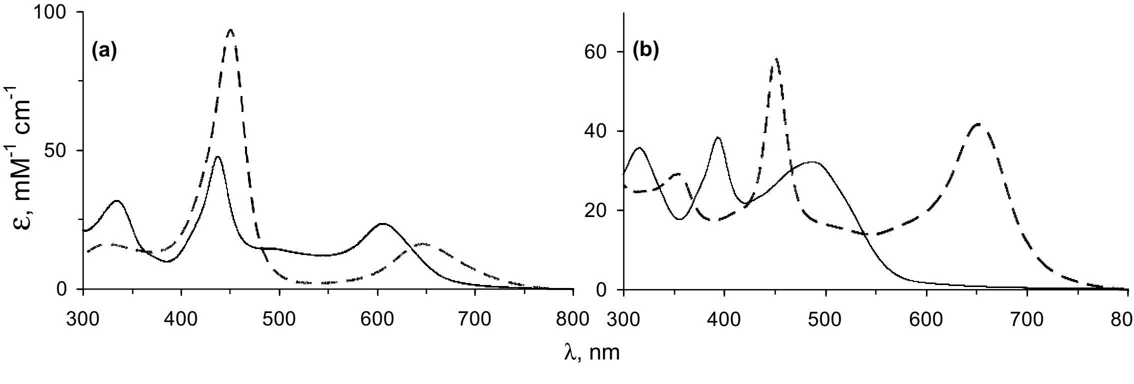


Figure 1. Absorption spectra of (a) **Ni·3a** (solid) and **Ni·5a** (dashed) and (b) $\mathbf{H_23a}$ (solid) and **6** (dashed) in CH_2Cl_2.

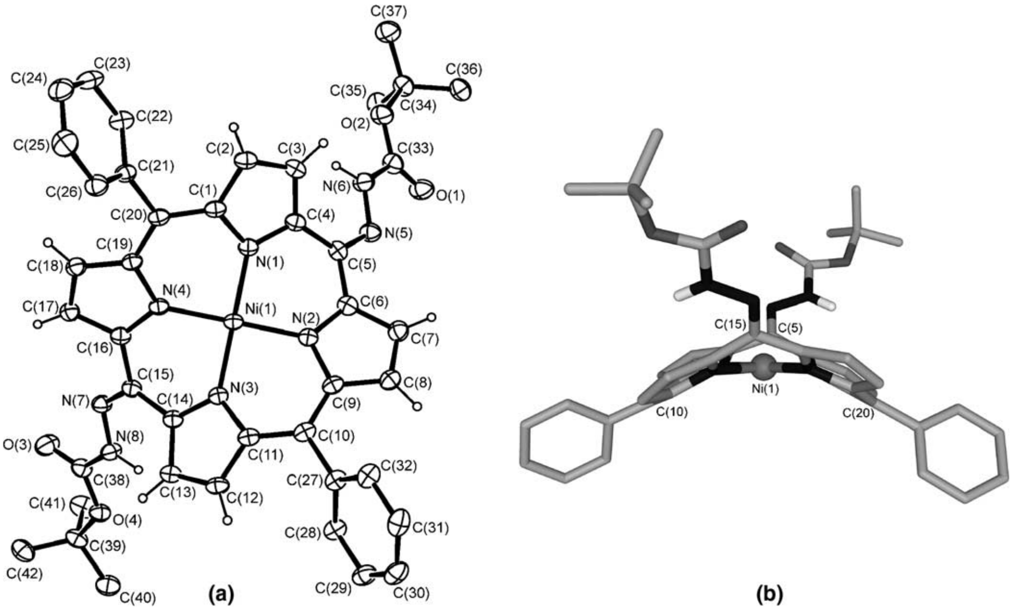


Figure 2. (a) ORTEP depiction of **Ni·3a**·1.5(dioxane)·H_2O with ellipsoids drawn at the 35% probability level. Water and dioxane molecules and H atoms attached to phenyl and *tert*-butyl carbon atoms have been omitted for clarity. Selected bond lengths: Ni(1)–N(1) 1.893(2), Ni(1)–N(2) 1.893(2), Ni(1)–N(3) 1.886(2), Ni(1)–N(4) 1.892(2) Å; imino N=C$_{meso}$, N(5)=C(5) 1.299(4), N(7)=C(15) 1.297(4) Å; hydrazino N–NH, N(7)–N(8) 1.349(4), N(5)–N(6) 1.349(3) Å. (b) Representation of **Ni·3a** viewed approximately parallel to the least squares plane of the macrocycle illustrating the saddle shape of the complex (C—light grey, O—medium grey, N—black, H atoms not shown except those attached to N atoms—white). The *meso*-carbon atoms (labelled) protrude farthest from the least squares plane of the 24 atoms of the porphyrinoid macrocycle.

squares plane [maximum displacement from the mean plane is 0.0285 Å for N(3)]. In contrast, the porphyrinoid ring displays a strongly puckered geometry with three-dimensional curvature of the macrocyclic ring. The least squares plane for the 24 atoms of the porphyrinoid ring is almost coincident with the least squares plane of the four metal-coordinated nitrogen atoms N(1)–N(4) [dihedral angle 0.47° with Ni(1) displaced by 0.15 Å]. However, there are severe displacements of the *meso*-carbon atoms from the 24-atom mean plane (Fig. 2b) [C(5) 1.064, C(10) −0.821, C(15) 1.085, C(20) −0.836 Å] and so the distortion is of the type described in the literature as 'ruffled'.[13] The coordination geometry at nickel and overall porphyrinoid shape are similar to those of the oxo-quinoidal Ni complex recently reported by Osuka's group.[14]

The corresponding Zn(II) complexes **Zn·3a**,**b** were prepared in high yield from **Zn·1b**, but the free bases **H_2·3a**,**b** were more difficult to isolate in pure form. The inner N–H protons of **H_2·3a** resonate at 12.42 ppm in contrast to those of **H_2·1a** at −2.99 ppm. This shift is similar to that for a free base dioxoporphodimethene.[10] The absorption spectrum of **H_2·3a** shows a broad, blue-shifted band in comparison to that of **Ni·3a** (Fig. 1).

In order to examine the generality of this hydrazination/oxidation and to see whether the porphodimethene conjugation could be further extended, benzophenone hydrazone was reacted with **Ni·1b**. It was found that **6** could be readily prepared using the same catalytic onditions as for **3**.[15] The absorption spectrum of **6**, comprising two major bands (Fig. 1), is similar to that of linearly extended systems with interrupted porphyrin conjugation, such as Anderson's 5,15-dialkylideneporphyrins.[5]

We expect these compounds to open the door to a range of new functionalized porphyrinoids. Carbazates and azoesters are known to be biologically active[16] and their combination with the well known photosensitizing and tumour-localizing abilities of porphyrins may lead to new candidate drugs. The long wavelength absorptions of molecules such as **6** indicate the possibility of tailoring the absorption characteristics by further extension of the conjugation. Linearly extended porphyrinoids have potential for non-linear optics and molecular electronics. Moreover, investigation of the redox chemistry of these compounds should be interesting, given the unusual propensity for the part-oxidation with loss of macrocyclic conjugation. Studies of all these aspects are in progress, and will be facilitated by the solubilities of these new compounds in a wide variety of solvents.

Acknowledgements

We thank the Faculty of Science and the Synthesis and Molecular Recognition Program, Queensland University of Technology, for a Scholarship for L.J.E.

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8. Compound **Ni·2b**: 5-Bromo-10,20-diphenylporphyrinatonickel(II) **Ni·1a** (20.0 mg, 0.0334 mmol), ethyl carbazate (3.5 mg, 0.0334 mmol), Cs_2CO_3 (7.1 equiv, 77.3 mg, 0.237 mmol), $Pd(OAc)_2$ (7 mol%, 0.5 mg, 0.0023 mmol) and *rac*-BINAP (20 mol%, 4.2 mg, 0.0067 mmol) were dried under vacuum in a Schlenk flask for 30 min and freshly distilled anhydrous THF (5 cm^3) was added. The mixture was stirred at 68 °C for 18 h and was then quenched with water (10 cm^3). The mixture was stirred at room temperature, exposed to air for 1 h and the products were then extracted into DCM. The solvent was removed and the product was purified using flash chromatography in DCM. The green product **Ni·2b** (13.0 mg, 63%) was recrystallized from dioxane/water (ca. 1 cm^3+5 cm^3) at 4 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 9.67 (d, $J = 5.1$ Hz, 2H; βH), 9.50 (s, 1H; *meso H*), 8.87 (d, $J = 4.7$ Hz, 2H; βH), 8.78 (d, $J = 5.1$ Hz, 2H; βH), 8.59 (d, $J = 4.7$ Hz, 2H; βH), 7.94–7.91 (m, 4H; phenyl *H*), 7.70–7.68 (m, 6H; phenyl *H*), 4.69 (q, $J = 7.1$ Hz, 2H; CH_2), 1.61 (t, $J = 7.1$ Hz, 3H; CH_3); UV/vis: λ_{max} (ε) 443 (79.5), 534 (5.4), 612 nm (10.7×10^3 M^{-1} cm^{-1}); MALDI-TOF-MS: *m*/*z* 619.14 (MH^+, $[C_{35}H_{24}N_6NiO_2+H]$ calcd 619.14).
9. Compound **Ni·3b**: Prepared similarly using 5,15-dibromo-10,20-diphenylporphyrinatonickel(II) **Ni·1b** (20.0 mg, 0.0295 mmol), ethyl carbazate (2.2 equiv, 6.8 mg, 0.065 mmol), Cs_2CO_3 (7.1 equiv, 68.2 mg, 0.209 mmol), $Pd(OAc)_2$ (7 mol%, 0.5 mg, 0.002 mmol) and *rac*-BINAP (20 mol%, 3.7 mg, 0.0059 mmol) in THF (5 cm^3), heating for 22 h at 68 °C. The product was purified using flash chromatography [DCM then DCM/MeOH (95.5:0.5)]. The dark green major product **Ni·3b** (13.0 mg, 61%) was recrystallized from dioxane/water (ca. 1 cm^3+5 cm^3) at 4 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 8.80 (br s, 2H; NH), 7.52–7.41 (m, 10H; phenyl H), 6.96 (d, $J = 4.9$ Hz, 2H; βH), 6.84 (d, $J = 4.4$ Hz, 2H; βH), 6.71 (d, $J = 4.9$ Hz, 2H; βH), 6.68 (d, $J = 4.4$ Hz, 2H; βH), 4.33 (q, $J = 7.1$ Hz, 4H; CH_2), 1.34 (t, $J = 7.1$ Hz, 6H; CH_3); UV/vis: λ_{max} (ε) 335 (33.4), 438 (48.7), 605 nm (23.0×10^3 M^{-1} cm^{-1}); MALDI-TOF-MS: *m*/*z* 721.15 (MH^+, $[C_{38}H_{30}N_8NiO_4+H]$ calcd 721.18).
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11. Compound **5b**: **Ni·3b** (12.0 mg, 0.0154 mmol) was dissolved in DCM (3 cm^3), DDQ (7.0 mg, 0.31 mmol) was added and the mixture was stirred for 5 min. The product was purified using flash chromatography in DCM and recrystallized from DCM/MeOH (ca. 1 cm^3+5 cm^3) to give the blue-green crystalline product **5b** (10.6 mg, 89%). ^1H NMR (400 MHz, $CDCl_3$) δ: 9.48 (d, *J* 5.0 Hz, 4H; βH), 8.66 (d, *J* 5.0 Hz, 4H; βH), 7.91–7.89 (m, 4H; phenyl H), 7.72–7.66 (m, 6H; phenyl H), 4.68 (q, $J = 7.1$ Hz, 4H; CH_2), 1.59 (t, $J = 7.1$ Hz, 6H; CH_3); UV/vis: λ_{max} (ε) 329 (19.9), 452 (90.5), 653 nm (16.8×10^3 M^{-1} cm^{-1}); MALDI-TOF-MS: *m*/*z* 719.12 (MH^+, $[C_{38}H_{28}N_8NiO_4+H]$ calcd 719.17).
12. Crystals of **Ni·3a** were grown from dioxane–water at RT. Data were collected at 150(2) K with ω and ϕ scans to approximately 56° 2θ using an APEX II-FR591 diffractometer employing graphite-monochromated Mo-Kα radiation generated from a rotating anode (0.71073 Å). Data integration and reduction were undertaken with SAINT and XPREP [Bruker–Nonius (2003); APEX, SAINT and XPREP. Area detector control and data integration and reduction software. Bruker–Nonius Analytical X-ray Instruments Inc., Madison, WI, USA] and subsequent computations were carried out using the WinGX-32 [Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837] graphical user interface. Scaling and a multi-scan empirical absorption correction were applied to the data using the program SADABS. [G. M. Sheldrick, SADABS. Empirical absorption correction program for area detector data. University of Göttingen, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1999]. The structure was solved by direct methods using SIR97 [Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giocavazzo, C.; Guagliardi, A.; Moliterni, A. G. C.; Polidori, G.; Spagna, S. *J. Appl. Crystallogr.* **1999**, *32*, 115] then refined and extended with SHELXL-97 [Sheldrick, G. M. SHELX-97. Programs for crystal structure analysis, University of Göttingen, Institut für Anorganische Chemie der Universität, Tammanstrasse

4, D-3400 Göttingen, Germany, **1998**]. Non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were included in idealized positions and refined using a riding model. Nitrogen-bound hydrogen atoms were located in the difference Fourier map and were refined with isotropic thermal parameters set at 1.2 U_{eq} of the attached nitrogen atom and with idealized bond length restraints (N–H, 0.9 Å). Hydrogen atoms attached to the water molecule were not located in the difference Fourier map and have not been included in the refinement model. The distance (2.855 Å) between the water oxygen atom, O(1w), and the carbonyl oxygen atom, O(1), is indicative of hydrogen bonding. The refinement residuals are defined as $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$ and $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_c^2)^2]\}^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (0.0362P)^2 + 2.2743P]$, $P = (F_o^2 + 2F_c^2)/3$. *Crystal data*: **Ni·3a**·1.5(1,4-dioxane)·H_2O; Formula $C_{48}H_{52}N_8NiO_8$, $M = 927.69$, triclinic, space group $P\bar{1}$ (#2), $a = 9.3327(4)$ Å, $b = 14.7511(7)$ Å, $c = 16.8029(8)$ Å, $\alpha = 85.044(2)$, $\beta = 78.268(2)$, $\gamma = 87.121(2)°$, $V = 2255.16(18)$ Å^3, $D_c = 1.366$ g cm^3, $Z = 2$, crystal size $0.160 \times 0.134 \times 0.013$ mm, dark green, habit plate, temperature 150(2) K, λ(Mo-Kα) = 0.71073, μ(Mo-Kα) 0.494 mm^1, T(Empirical)$_{min,max}$ = 0.8421, 1.000, $2\theta_{max} = 57.02$, *hkl* range −12 to 12, −19 to 19, −22 to 22, $N = 60{,}657$, $N_{ind} = 11{,}373$ ($R_{merge} = 0.0543$), $N_{obs} = 7425$ ($I > 2\sigma(I)$), $N_{var} = 598$, residuals $R1(F, 2\sigma) = 0.0600$, $wR2(F^2$, all) = 0.1859, GoF(all) = 1.052, $\Delta\rho_{min,max} = -0.603$, 1.549 e Å^{-3}. CCDC-268791 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or deposit@ ccdc.cam.ac.uk).

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15. Compound **6**: Prepared as for **Ni·3b** from 5,15-dibromo-10,20-diphenylporphyrinatonickel(II) **Ni·1b** (20.0 mg, 0.0295 mmol), benzophenone hydrazone (2.2 equiv, 12.7 mg, 0.0647 mmol), Cs_2CO_3 (7.1 equiv, 68.2 mg, 0.209 mmol), *rac*-BINAP (20 mol%, 3.7 mg, 0.0059 mmol) and $Pd(OAc)_2$ (7 mol%, 0.5 mg, 0.002 mmol) in THF (5 cm^3), heating for 18 h. The product was purified using flash chromatography in DCM. Dark blue-green product **6** was recrystallized from dioxane/water (ca. 1 cm^3+5 cm^3) at 4 °C (17.7 mg, 66%). This product comprised a mixture of two isomers in a ca. 60:40 ratio. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77–7.74 (br m, 4H), 7.43–7.40 (br m, 22H), 7.31–7.28 (br m, 4H), (phenyl H of both isomers), 6.94 (d, *J* 4.6 Hz, 2H, βH major isomer), 6.55 (s, 4H, βH major), 6.51 (d, *J* 4.4 Hz, 2H, βH major), 7.00 (d, *J* 4.6 Hz, 2H, βH minor), 6.58 (d, *J* 4.6 Hz, 2H, βH minor), 6.56 (d, *J* 4.6 Hz, 2H, βH minor), 6.49 (d, *J* 4.6 Hz, 2H, βH minor); UV/vis: λ_{max} (ε) 350 (29.2), 450 (58.5), 651 nm (41.8×10^3 M^{-1} cm^{-1}); MALDI-TOF-MS: *m*/*z* 905.12 (MH$^+$, [$C_{58}H_{38}N_8Ni$+H] calcd 905.27).
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