Nickel Hemiporphyrazines as Bisdienes and Bisdienophiles: Synthesis and Characterization

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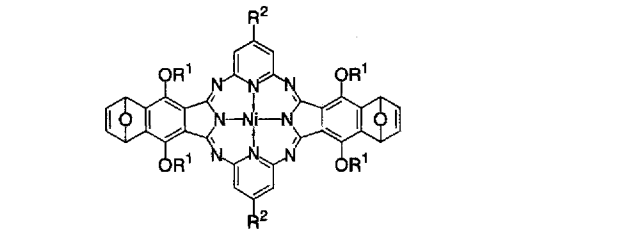
The bisdienophilic (hemiporphyrazinato)nickel complexes **1a–d** bearing various alkoxy groups were synthesized from diiminoisoindoles **9a–d**, diaminopyridines **10a, d**, and nickel acetate. Reaction of **1a–d** with an excess of pentaene **3** delivered the macrocyclic bisdienes **2a–d**. The hemiporphyrazines were characterized by ^{1}H- and ^{13}C-NMR spectroscopy. The NMR spectra of the 1,6,16,21-tetrabutoxy-substituted compounds **1b** and **2b** are discussed with respect to the presence of *syn/anti* isomers.

Recently, we reported on the (hemiporphyrazinato)nickel(II) complexes (HpNi) **1**, **2**[1] and the pentaene **3**[2] as building blocks for the synthesis of ladder oligomers and polymers, e.g. the conversion of equimolar amounts of **1** and **2** (with $R^1 = C_4H_9$, $R^2 = H$) in a repetitive Diels-Alder reaction delivered the polymer **4**. The compounds **1** and **2** can be classified as macrocyclic bisdienes and bisdienophiles.



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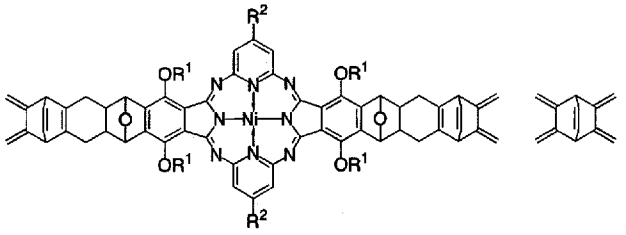

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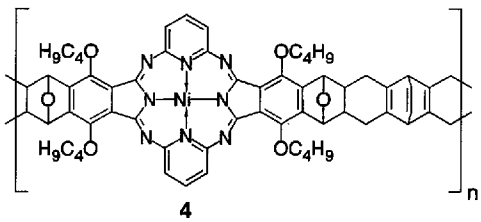

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We now describe the synthesis of the nickel hemiporphyrazines **1** and **2** bearing various peripheral alkoxy groups. The 1,6:16,21-tetrasubstituted HpNi as **1** are superior to the related 2,5:17,20-tetrasubstituted compounds concerning their reactivity in Diels-Alder reactions[3]. This fact may be due to steric reasons.

The synthetic route started with tetrabromohydroquinone (**5**)[4], which was obtained from hydroquinone and bromine in acetic acid. Treatment of the disodium salt of **5** with alkyl halides[5] [RX = CH_3I (**a**); C_4H_9Br (**b**); $C_6H_{13}Br$ (**c**)] led to the corresponding tetrabromohydroquinone bisalkyl ethers **6a–c**. Compounds **6a–c** were subsequently converted at −50 °C with a 1.2 molar amount of *n*BuLi to the corresponding monoarynes, which in situ underwent with furan a Diels-Alder reaction[6] with formation of 5,8-dialkoxy-6,7-dibromo-1,4-dihydro-1,4-epoxynaphthalenes **7a–c**. A Rosenmund-von Braun reaction[7] of **7a–c** using CuCN in DMF afforded 6,7-dicyanonaphthalenes **8a–c**. The reaction of **8a–c** with NH_3 in MeOH (catalyzed by CH_3O^-, 7 days) delivered the corresponding diiminoisoindoles **9a–c**. To synthesize the hemiporphyrazines **1a–d**[8], the isoindoles **9a–c** were stirred in *n*-butanol at 100 °C with 2,6-diaminopyridine or 2,6-diamino-4-butoxypyridine, respectively. The subsequent addition of $Ni(OAc)_2 \cdot 4\,H_2O$ at 100 °C led to a strong evolution of ammonia. The metalation was finished after an additional heating at 120 °C for 2 hours. The products were purified by column chromatography (alumina and silica gel). The yields of the macrocycles **1a–d** increase with increasing chain length of the peripheral alkoxy substituents.

The excellent solubility of the HpNi **1a–d** in solvents like chloroform, dichloromethane, or toluene allows their characterization by ^{1}H- and ^{13}C-NMR spectroscopy. Figure 1 shows as an example the ^{1}H-NMR spectrum of **1b**.

Characteristic of the ^{1}H-NMR spectra of hemiporphyrazines are the signals resulting from 9-H (triplet, δ = 7.37) and 8-H (doublet, δ = 6.47) of the pyridine fragment. The resonances of 1-H and 2-H appear as singlets at δ = 7.00 and 5.90, respectively. The HpNi **1a–d** are present as a mixture of *syn/anti* isomers due to the relative orientation of the oxygen bridges. Therefore, the absorptions at δ = 7.37

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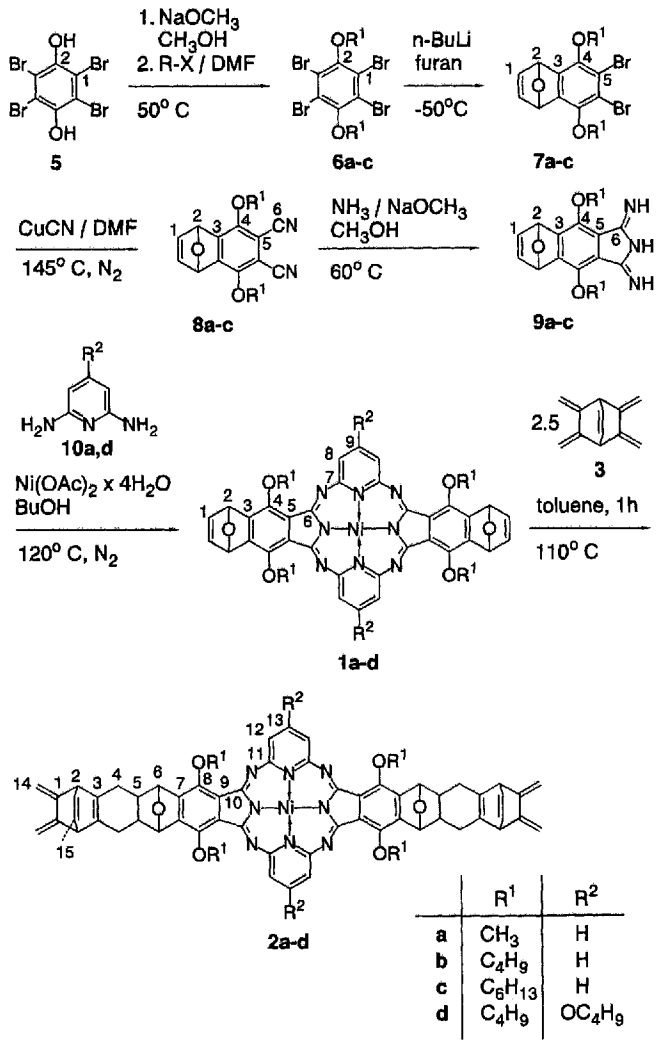
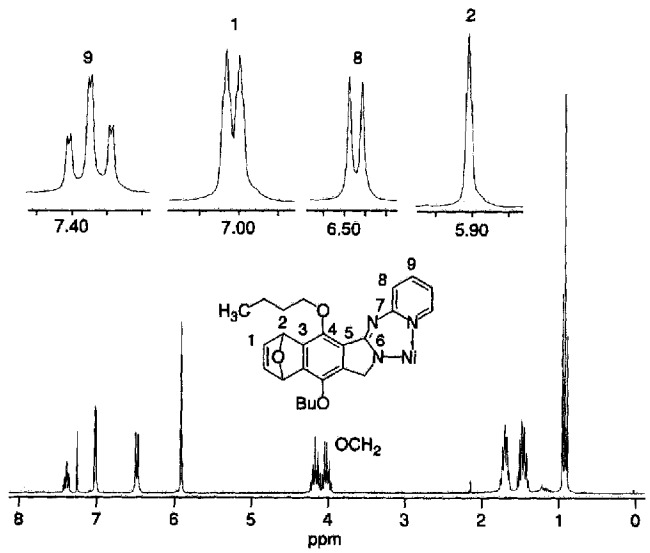
Scheme 1. Syntheses of the (hemiporphyrazinato)nickel complexes **1a–d** and **2a–d**



	R^1	R^2
a	CH_3	H
b	C_4H_9	H
c	C_6H_{13}	H
d	C_4H_9	OC_4H_9

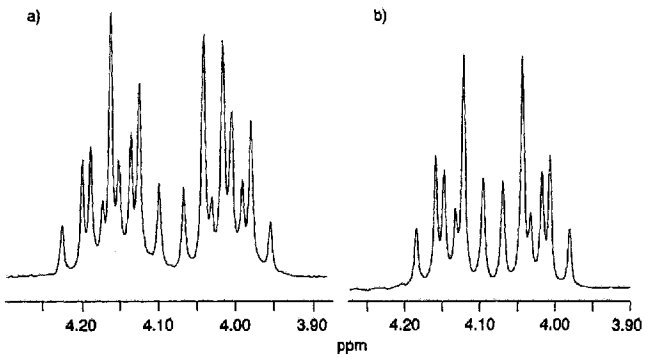
Figure 1. ^{1}H-NMR spectrum of *syn,anti*-**1b** (250 MHz, $CDCl_3$)



(9-H) and at δ = 7.00 (1-H) are doubled. The signals of the OCH_2 groups of the side chains form a multiplet at δ = 3.95–4.23. This multiplet can be explained by the diastereotopy of the OCH_2 protons and additionally by the existence of two isomers. The ^{1}H chemical shifts of **1a, c, d** show only minor deviations compared with those of compound **1b**. A difference is observed in the case of **1d**, where the signal of 8-H appears as a singlet. This is due to the additional butoxy substituent on the pyridine fragment of this compound.

In order to analyze the configuration of the *syn/anti* isomers of **1b**, they were separated by column chromatography and by TLC (alumina). The two isomers (*syn/anti*) of **1b** are present in a 1:1 ratio. The configuration of the isomers cannot be determined by ^{1}H-NMR spectroscopy, although the spectra are not exactly the same. The chemical shifts of 9-H and 1-H are slightly different (see Figure 1). Moreover, the multiplets formed by the OCH_2 proton signals (δ = 3.95–4.23) show a different shape for each isomer. The diastereotopic protons of the OCH_2 groups are magnetically nonequivalent and form an ABX_2 spin system with the adjacent CH_2 protons. In Figure 2, the resulting multiplets are shown for the isomeric mixture and for the pure *anti* isomer of **1b**.

Figure 2. Multiplets in the ^{1}H-NMR spectra of **1b** (OCH_2 protons, 250 MHz). – a) *syn,anti*-**1b**. – b) Pure *anti*-**1b**



The configuration was determined unequivocally by crystal structure analysis of the bispyridinium complex of *anti*-**1b**[1]. The ^{13}C-NMR signals of **1a–d** were assigned by a comparison with those of other hemiporphyrazines[8b,c] and in addition by *J*-modulated spin-echo and DEPT experiments.

The reaction of the bisdienophilic hemiporphyrazines **1a–d** with pentaene **3**[2] (molar ratio 1:2.5) in boiling toluene led to the bisdienes **2a–d** in yields of 38, 57, 40, and 69%. The remainders of the products were not furthermore investigated, but we believe that also oligomeric molecules have been formed. However, the Diels-Alder reaction of **2b** with excess **1b** afforded a HpNi trimer while a polymeric material was formed if **2b** and **1b** were converted in equimolar amounts[1].

By using the *syn/anti* isomers of **1a–d** as starting materials, we obtained as expected an isomeric mixture of the HpNi **2a–d**. The purification of the compounds **2a–d** by column chromatography (Al_2O_3) delivered two clearly sep-

arated fractions from which the *syn/anti* isomers (*syn/anti* refers here also to the position of the oxygen bridges) were isolated.

The hemiporphyrazines **2a–d** are soluble in common solvents like dichloromethane, chloroform, toluene, and acetone. For compounds **2a–d**, the ^{1}H-NMR spectrum of **2b** will be discussed as an example in detail: In analogy to compounds **1a–d**, the signals of the pyridine fragment protons of **2b** show the expected triplet (δ = 7.33, 13-H) and doublet (δ = 6.46, 12-H) structure. The ethylene bridge and the bridgehead protons 15-H and 2-H form an AA'XX' spin system. The corresponding signal groups are found at δ = 6.33 (15-H) and δ = 3.83 (2-H). The signals of the methylene protons (14-H) appear as singlets at δ = 4.91 (*cis*) and δ = 4.70 (*trans*) and those of protons of the "cyclohexene" ring at δ = 2.56 (4-H), 2.10 (4-H), and 1.97 (5-H). The OCH_2 group proton signals of the *anti* isomer of **2b** exhibit a triplet (δ = 4.05) and those of the *syn* isomer a multiplet (δ = 4.05). The relative orientation of the oxygen bridges can be determined by reaction of pure *anti*-**1b** with 2.5 equiv. of pentaene **3** in boiling toluene. The ^{1}H-NMR spectrum of the obtained product is identical with that of the above-mentioned *anti*-**2b**. The distinction between the *endo* and *exo* configuration is feasible by considering the coupling constant between 6-H and 5-H[9]. The signal of 6-H appears as singlet in the ^{1}H-NMR spectra of *syn*-**2b** and *anti*-**2b**. Therefore, only *exo* addition occurs in the described Diels-Alder reaction.

The structure can be proven exactly only by a crystal structure analysis. Attempts to crystallize *anti*-**2b** without axial ligands or a bisaxially coordinated bis(pyridine), bis(4-picoline), and bis(*tert*-butyl isocyanide) complex failed. The ^{13}C-NMR spectrum of *syn/anti*-**2b** shows characteristic signals of the ethylene bridge carbon atoms at δ = 133.6, the ethylene bridgehead carbon atoms at δ = 53.5, and of the CH_2 groups of the "cyclohexene" ring at δ = 30.5. The resonances of the methylene carbon atoms appear at δ = 101.4. The signals of the hemiporphyrazine frame do not shift substantially compared with the signals of the starting compound.

The comparison of the IR spectra of the hemiporphyrazines **1a–d** with those of **2a–d** shows an additional absorption in the fingerprint region between 670–650 cm^{-1} for the bisdienes **2a–d**. By addition of the pentaene **3** to the macrocycles **1a–d**, new olefinic bonds are introduced. The absorption at 650 cm^{-1} could therefore be due to the C–H deformation vibration of the ethylene bridge.

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Experimental

Commercially available 2,6-diaminopyridine (**10a**) was purified by sublimation before use. The following compounds were prepared as described in the literature: 2,3,5,6-tetrakis(methylene)bicyclo[2.2.2]oct-2-ene (**3**)[2], tetrabromohydroquinone (**5**)[4], 2,6-diamino-4-butoxypyridine (**10d**)[10]. – All melting points are uncorrected. – FT-IR: Bruker IFS 48. – NMR: Bruker AC 250 (^{1}H: 250.1 MHz, ^{13}C: 62.9 MHz), Bruker AMX 400 (^{1}H: 400.1 MHz; ^{13}C: 100.6 MHz). – MS: Finnigan MAT ISQ 70 (EI, 70 eV), Finnigan MAT 711A (modified) (FD). – Elemental analyses: Carlo Erba Elemental Analyser 1106.

1,2,4,5-Tetrabromo-3,6-dimethoxybenzene[11] (**6a**): A suspension of tetrabromohydroquinone **5** (60.0 g, 0.141 mol) and sodium methoxide (15.25 g, 0.282 mol) in 150 ml of dry MeOH was stirred under nitrogen for 15 min. The solvent was removed in vacuo. After addition of dry DMF (200 ml) and CH_3I (40.0 g, 0.282 mol) to the residue the mixture was stirred under N_2 at 40°C for 3 h. It was then poured into water (600 ml). The precipitate was collected by suction filtration, washed with water, and dried in vacuo at 50°C. The product was recrystallized from methanol. Yield of **6a** 33.6 g (53%), m.p. 230–231°C. – IR (KBr): $\tilde{\nu}$ = 2984 cm^{-1}, 2854, 1460, 1371, 1340, 991, 795, 604. – ^{1}H NMR ($CDCl_3$): δ = 3.85 (s, 6H, OCH_3). – ^{13}C NMR ($CDCl_3$): δ = 152.9 (C-2), 121.3 (C-1), 60.6 (OCH_3). – MS (70 eV), *m/z* (%): 458, 456, 454, 452, 450 [M$^+$]. – $C_8H_6Br_4O_2$ (453.7): calcd. C 21.17, H 1.33, Br 70.44; found C 20.98, H 1.16, Br 70.38.

1,2,4,5-Tetrabromo-3,6-dibutoxybenzene (**6b**): Compound **6b** was prepared in analogy to **6a**. Tetrabromohydroquinone **5** (10.0 g, 23.5 mmol), sodium methoxide (2.54 g, 47 mmol), and *n*-butyl bromide (6.44 g, 47 mmol) were allowed to react in dry methanol (25 ml) and dry DMF (40 ml). Yield 7.6 g (60.2%), m.p. 92–93°C (acetone). – IR (KBr): $\tilde{\nu}$ = 2970 cm^{-1}, 2951, 2905, 1464, 1425, 1371, 1358, 1059, 1020, 951, 887, 806. – ^{1}H NMR ($CDCl_3$): δ = 3.97 (t, J = 6.5 Hz, 4H, OCH_2), 1.85 (m, 4H, CH_2), 1.58 (m, 4H, CH_2), 0.97 (t, J = 7.3 Hz, 6H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 151.9 (C-2), 121.4 (C-1), 73.3 (OCH_2), 31.9 (CH_2), 19.1 (CH_2), 13.9 (CH_3). – MS (70 eV), *m/z* (%): 542, 540, 538, 536, 534 (10) [M$^+$], 482 (8) [M$^+$ – C_4H_8], 426 (100) [M$^+$ – 2 × C_4H_8]. – $C_{14}H_{18}Br_4O_2$ (537.9): calcd. C 31.26, H 3.37, Br 59.42; found C 30.80, H 3.18, Br 59.33.

1,2,4,5-Tetrabromo-3,6-dihexyloxybenzene (**6c**): Compound **6c** was prepared in analogy to **6a**. Tetrabromohydroquinone **5** (60.0 g, 0.141 mmol), sodium methylate (15.25 g, 0.282 mol), and *n*-hexyl bromide (46.5 g, 0.282 mol) were allowed to react in 150 ml of MeOH and 200 ml of DMF. Yield 39.2 g (46.8%), m.p. 54–55°C (acetone). – IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1}, 2926, 2856, 1475, 1466, 1429, 1359, 1342, 1011, 981. – ^{1}H NMR ($CDCl_3$): δ = 3.89 (t, J = 6.6 Hz, 4H, OCH_2), 1.80 (m, 4H, CH_2), 1.43 (m, 4H, CH_2), 1.26 (m, 8H, 2 × CH_2), 0.84 (t, J = 6.9 Hz, 6H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 152.0 (C-2), 121.4 (C-1), 73.6 (OCH_2), 31.6 (CH_2), 29.9 (CH_2), 25.5 (CH_2), 22.6 (CH_2), 14.1 (CH_3). – MS (70 eV), *m/z* (%): 598, 596, 594, 592, 590 (50) [M$^+$], 426 (80) [M$^+$ – 2 × C_6H_{12}]. – $C_{18}H_{26}Br_4O_2$ (594.0): calcd. C 36.39, H 4.41, Br 53.81; found C 36.62, H 4.59, Br 51.17.

6,7-Dibromo-1,4-dihydro-5,8-dimethoxy-1,4-diepoxynaphthalene (**7a**): *n*BuLi (53.8 ml, 86 mmol) (1.6 M solution in hexane) diluted with dry hexane (500 ml) was added to a suspension of **6a** (32.5 g, 71.6 mmol) in dry toluene (750 ml) and furan (60 ml) under nitrogen at –50°C over 5 h. The reaction mixture was maintained at this temperature for 1 h. The reaction was quenched with 3 ml of methanol. The mixture was allowed to reach room temp., washed with water (3 × 500 ml), dried with $MgSO_4$, and concentrated to give a yellow oil. This was recrystallized from methanol and dried in vacuo at 60°C. Yield of **7a** 14.6 g (65%), m.p. 94–95°C. – IR (KBr): $\tilde{\nu}$ = 3007 cm^{-1}, 2945, 2927, 2852, 1571, 1452, 1373, 1245, 1058, 1039, 1014, 883, 842. – ^{1}H NMR ($CDCl_3$): δ = 7.04 (s, 2H, 1-H), 5.98 (s, 2H, 2-H), 3.86 (s, 6H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 147.4 (C-4), 142.5 (C-1), 139.1 (C-3), 117.9 (C-5), 81.1 (C-2), 61.5 (CH_3). – MS (70 eV), *m/z* (%): 361.9 (24) [M$^+$], 346.9 (11)

$[M^+ - CH_3]$. – $C_{12}H_{10}Br_2O_3$ (362.0): calcd. C 39.81, H 2.78, Br 44.14; found C 39.75, H 2.84, Br 44.08.

6,7-Dibromo-5,8-dibutoxy-1,4-dihydro-1,4-diepoxynaphthalene (**7b**): Compound **7b** was prepared in analogy to **7a**. **6b** (10.0 g, 18.6 mmol) and furan (15 ml) in dry toluene (250 ml) were treated with *n*BuLi (14.0 ml, 22.3 mmol) (1.6 M solution in hexane) diluted with hexane (200 ml). Yield 5.6 g (70%), m.p. 72–73°C (methanol). – IR (KBr): $\tilde{\nu}$ = 3022 cm^{-1}, 2959, 2892, 1456, 1416, 1362, 1281, 1236, 1065, 879. – ^1H NMR ($CDCl_3$): δ = 7.03 (s, 2H, 1-H), 5.97 (s, 2H, 2-H), 3.95 (m, 4H, OCH_2), 1.75 (m, 4H, CH_2), 1.54 (m, 4H, CH_2), 0.95 (t, *J* = 7.3 Hz, 6H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 146.6 (C-4), 142.5 (C-1), 139.6 (C-3), 118.3 (C-5), 81.1 (C-2), 74.3 (OCH_2), 32.1 (CH_2), 19.2 (CH_2), 13.9 (CH_3). – MS (70 eV), *m/z* (%): 445.8 (12) $[M^+]$, 366.0 (16) $[M^+ - Br]$, 333.8 (10) $[M^+ - 2 \times C_4H_8]$, 174 (10) $[M^+ - 2 \times C_4H_8 - 2 \times Br]$. – $C_{18}H_{22}Br_2O_3$ (446.2): calcd. C 48.45, H 4.97; found C 48.68, H 5.18.

6,7-Dibromo-5,8-dihexyloxy-1,4-dihydro-1,4-diepoxynaphthalene (**7c**): Compound **7c** was prepared in analogy to **7a**. **6c** (30.0 g, 50.5 mmol) and furan (40 ml) in dry toluene (750 ml) were treated with *n*BuLi (37.9 ml, 60.6 mmol) (1.6 M solution in hexane) diluted with hexane (500 ml). Yield 15.8 g (62.3%), m.p. 105–106°C (methanol). – IR (KBr): $\tilde{\nu}$ = 3051 cm^{-1}, 3024, 2870, 1489, 1468, 1393, 1283, 1277, 1067, 1013, 997, 868. – ^1H NMR ($CDCl_3$): δ = 7.02 (s, 2H, 1-H), 5.91 (s, 2H, 2-H), 3.95 (m, 4H, OCH_2), 1.77 (m, 4H, CH_2), 1.50 (m, 4H, CH_2), 1.34 (m, 8H, $2 \times CH_2$), 0.91 (t, *J* = 6.8 Hz, 6H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 146.6 (C-4), 142.5 (C-1), 139.6 (C-3), 118.3 (C-5), 81.1 (C-2), 73.7 (OCH_2), 31.6 (CH_2), 22.9 (CH_2), 25.6 (CH_2), 22.6 (CH_2), 13.9 (CH_3). – MS (70 eV), *m/z* (%): 502.0 (19) $[M^+]$, 422.1 (17) $[M^+ - Br]$. – $C_{22}H_{30}Br_2O_3$ (502.3): calcd. C 52.61, H 6.02, Br 31.82; found C 56.71, H 6.02, Br 25.05.

6,7-Dicyano-1,4-dihydro-5,8-dimethoxy-1,4-diepoxynaphthalene (**8a**): A mixture of **7a** (8.0 g, 22 mmol) and copper(I) cyanide (11.9 g, 132 mmol) in dry DMF (20 ml) was stirred for 18 h at 145°C under nitrogen. After cooling to room temp. the mixture was poured into a concentrated ammonia solution. A stream of air was bubbled through the suspension for 12 h. The solid material was collected and washed with water. It was then extracted with CH_2Cl_2 in a Soxhlet apparatus for 24 h. The precipitate was collected by suction filtration and dried in vacuo at 50°C. Yield of **8a** 3.2 g (56.2%), m.p. 155–157°C. – IR (KBr): $\tilde{\nu}$ = 2979 cm^{-1}, 2948, 2230, 1472, 1410, 1288, 1055, 1030. – ^1H NMR ($CDCl_3$): δ = 7.11 (s, 2H, 1-H), 6.10 (s, 2H, 2-H), 4.03 (s, 6H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 150.4 (C-4), 145.2 (C-3), 142.5 (C-1), 113.1 (C-6), 107.9 (C-5), 81.1 (C-2), 61.4 (CH_3). – MS (70 eV), *m/z* (%): 254.0 (33) $[M^+]$, 239.1 (3) $[M^+ - CH_3]$, 228.0 (51) $[M^+ - CN]$. – $C_{14}H_{10}N_2O_3$ (254.2): calcd. C 66.14, H 3.96, N 11.02; found C 66.14, H 3.95, N 10.98.

5,8-Dibutoxy-6,7-dicyano-1,4-dihydro-1,4-diepoxynaphthalene (**8b**): Compound **8b** was prepared as described for **8a**. **7b** (7.2 g, 16 mmol) and copper(I) cyanide (8.6 g, 96 mmol) were allowed to react in dry DMF (20 ml). Yield 3.59 g (66%), m.p. 105–106°C (hexane). – IR (KBr): $\tilde{\nu}$ = 2961 cm^{-1}, 2874, 2232, 1582, 1447, 1377, 1288, 1072. – ^1H NMR ($CDCl_3$): δ = 7.09 (s, 2H, 1-H), 6.01 (s, 2H, 2-H), 4.13 (m, 4H, OCH_2), 1.78 (m, 4H, CH_2), 1.52 (m, 4H, CH_2), 0.98 (t, *J* = 7.3 Hz, 6H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 149.8 (C-4), 145.8 (C-3), 142.5 (C-1), 113.2 (C-6), 108.5 (C-5), 81.1 (C-2), 74.7 (OCH_2), 31.8 (CH_2), 18.9 (CH_2), 13.7 (CH_3). – MS (70 eV), *m/z* (%): 338.1 (9) $[M^+]$, 282.1 (8) $[M^+ - C_4H_8]$, 226.0 (32), $[M^+ - 2 \times C_4H_8]$. – $C_{20}H_{22}N_2O_3$ (338.4): calcd. C 70.98, H 6.55, N 8.28; found C 71.01, H 6.69, N 8.27.

6,7-Dicyano-5,8-dihexyloxy-1,4-dihydro-1,4-diepoxynaphthalene (**8c**): Compound **8c** was prepared as described for **8a**. **7c** (5.0 g, 9.9 mmol) and copper(I) cyanide (5.4 g, 59.7 mmol) were allowed to react in dry DMF (15 ml). Yield 2.1 g (54%), m.p. 73–74°C. – IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1}, 2930, 2232, 1578, 1448, 1377, 1286, 1032, 891, 864. – ^1H NMR ($CDCl_3$): δ = 7.09 (s, 2H, 1-H), 6.00 (s, 2H, 2-H), 4.10 (m, 4H, OCH_2), 1.75 (m, 4H, CH_2), 1.47 (m, 4H, CH_2), 1.30 (m, 8H, $2 \times CH_2$), 0.89 (t, *J* = 7.0 Hz, 6H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 149.8 (C-4), 145.8 (C-3), 142.5 (C-1), 113.3 (C-6), 108.4 (C-5), 81.1 (C-2), 74.9 (OCH_2), 31.4 (CH_2), 29.7 (CH_2), 25.4 (CH_2), 22.5 (CH_2), 13.9 (CH_3). – MS (70 eV), *m/z* (%): 394.2 (4) $[M^+]$, 310.1 (6) $[M^+ - C_6H_{12}]$, 226.0 (23) $[M^+ - 2 \times C_6H_{12}]$. – $C_{24}H_{30}N_2O_3$ (394.5): calcd. C 73.07, H 7.66, N 7.10; found C 72.32, H 7.51, N 6.93.

2,3,5,8-Tetrahydro-1,3-diimino-4,9-dimethoxy-1H-5,8-epoxybenz[f]isoindole (**9a**): Sodium (0.1 g, 4.3 mmol) was dissolved in dry methanol (20 ml) at room temp. A stream of dry ammonia was bubbled through the mixture for 1 h. Then **8a** (4.8 g, 18.9 mmol) was added and the mixture was stirred at 60°C for 7 d, while bubbling of ammonia was continued. After cooling to room temp. the product was filtered and washed with cold methanol. It was then dried in vacuo at 70°C. Yield of **9a** 1.73 g (34%), m.p. 175–177°C. – IR (KBr): $\tilde{\nu}$ = 3443 cm^{-1}, 3321, 3248, 2941, 2837, 1653, 1572, 1283, 1150, 1055, 872. Since the product is poorly soluble in common organic solvents, NMR spectra provide no valuable information. The substance shows no analytical purity.

4,9-Dibutoxy-2,3,5,8-tetrahydro-1,3-diimino-1H-5,8-epoxybenz[f]isoindole (**9b**): Compound **9b** was prepared as described for **9a**. **8b** (5.4 g, 16 mmol) was allowed to react in dry methanol (10 ml). Yield 4.37 g (77%), m.p. 175–176°C. – IR (KBr): $\tilde{\nu}$ = 3460 cm^{-1}, 3323, 3122, 2958, 2935, 1728, 1647, 1537, 1145, 872. – ^1H NMR ($CDCl_3$): δ = 8.10 (s, 3H, NH), 7.06 (s, 2H, 1-H), 5.98 (s, 2H, 2-H), 4.10 (m, 4H, OCH_2), 1.78 (m, 4H, CH_2), 1.48 (m, 4H, CH_2), 0.98 (t, *J* = 7.3 Hz, 6H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 166.0 (C-6), 144.3 (C-4), 142.3 (C-1), 122.5 (C-5), 81.1 (C-2), 73.4 (OCH_2), 31.9 (CH_2), 19.1 (CH_2), 13.7 (CH_3). – MS (70 eV), *m/z* (%): 357 (8) $[M^+ + 2H]$, 338 (20) $[M^+ - NH_3]$, 313 (85). – $C_{20}H_{25}N_3O_3$ (355.4): calcd. C 67.58, H 7.09, N 11.82; found C 68.16, H 7.40, N 11.83.

4,9-Dihexyloxy-2,3,5,8-tetrahydro-1,3-diimino-1H-5,8-epoxybenz[f]isoindole (**9c**): Compound **9c** was prepared as described for **9a**. **8c** (7.0 g, 18 mmol) was allowed to react in dry methanol (20 ml). Yield 5.9 g (81%), m.p. 97–99°C. – IR (KBr): $\tilde{\nu}$ = 3454 cm^{-1}, 3321, 2947, 1666, 1643, 1537, 1469, 1448, 1101, 1047, 866. – ^1H NMR ($CDCl_3$): δ = 7.96 (s, 3H, NH), 7.21 (s, 2H, 1-H), 5.94 (s, 2H, 2-H), 4.05 (m, 4H, OCH_2), 1.75 (m, 4H, CH_2), 1.40 (m, 4H, CH_2), 1.26 (m, 8H, $2 \times CH_2$), 0.83 (t, *J* = 6.9 Hz, 6H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 166.3 (C-6), 144.3 (C-4), 142.4 (C-1), 122.5 (C-5), 81.2 (C-2), 73.9 (OCH_2), 31.5 (CH_2), 30.0 (CH_2), 25.6 (CH_2), 22.5 (CH_2), 13.9 (CH_3). – MS (70 eV), *m/z* (%): 412 (3) $[M^+ + H]$, 394 (15) $[M^+ - NH_3]$, 340 (30). – $C_{24}H_{33}N_3O_3$ (411.5): calcd. C 70.04, H 8.08, N 10.21; found C 69.93, H 8.47, N 10.20.

[2,5,17,20-Tetrahydro-1,6,16,21-tetramethoxy-2,5:17,20-diepoxyheminaphthoporphyrazinato]nickel(II) (**1a**): **9a** (0.7 g, 2.6 mmol) and 2,6-diaminopyridine **10a** (0.28 g, 2.6 mmol) were suspended in *n*-butanol (20 ml) and stirred in a permanent, slight stream of nitrogen at 100°C, until no more ammonia evolution was observed. After addition of $Ni(OAc)_2 \cdot 4\ H_2O$ (0.4 g, 1.6 mmol) the reaction mixture was stirred at 100°C for 1 h and for additional 2 h at 120°C. The solvent was removed in vacuo and the residue was chromatographed on a short column (silica gel; eluent: CH_2Cl_2) to remove insoluble components. Purification by column chromatography (neutral alumina, deactivated with 4% H_2O; eluent: CH_2Cl_2/

MeOH, 5:1, R_f = 0.63) afforded 70 mg (7%) of **1a**. – IR (KBr): $\tilde{\nu}$ = 2933 cm^{-1}, 2829, 1662, 1616, 1576, 1539, 1491, 1431, 1392, 1336, 1286, 1205, 1155. – ^1H NMR ($CDCl_3$): δ = 7.30 (t, *J* = 7.5 Hz, 2H, 9-H), 6.97 (s, 4H, 1-H), 6.47 (d, *J* = 7.5 Hz, 4H, 8-H), 5.94 (s, 4H, 2-H), 3.90 (s, 6H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 158.5 (C-7), 155.9 (C-6), 145.1 (C-3), 144.8 (C-4), 142.6 (C-1), 139.3 (C-9), 129.0 (C-5), 120.7 (C-8), 80.8 (C-2), 61.8 (CH_3). – MS (FD), *m/z*: 749.1 [M^+]. – $C_{38}H_{26}N_8NiO_6$ (749.3): calcd. C 60.90, H 3.49, N 14.95; found C 60.47, H 3.26, N 14.03.

[1,6,16,21-Tetrabutoxy-2,5,17,20-tetrahydro-2,5:17,20-diepoxyheminaphthoporphyrazinato]nickel(II) (**1b**): Compound **1b** was synthesized as described for **1a**. **9b** (1 g, 2.82 mmol), **10a** (0.3 g, 2.82 mmol) and $Ni(OAc)_2 \cdot 4\ H_2O$ (0.42 g, 1.7 mmol) were allowed to react in *n*-butanol (20 ml). Purification by column chromatography (neutral alumina, deactivated with 4% H_2O; eluent: hexane/ethyl acetate, 1:1, R_f = 0.66 and silica gel, eluent: hexane/ethyl acetate, 1:1, R_f = 0.50) yielded 404 mg (31%) of **1b**. – IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1}, 2932, 2870, 1662, 1614, 1578, 1537, 1489, 1464, 1391, 1335, 1205, 1155, 867. – ^1H NMR ($CDCl_3$): δ = 7.37 (t, *J* = 7.6 Hz, 2H, 9-H), 7.00 (s, 4H, 1-H), 6.47 (d, *J* = 7.6 Hz, 4H, 8-H), 5.90 (s, 4H, 2-H), 4.09 (m, 8H, OCH_2), 1.71 (m, 8H, CH_2), 1.47 (m, 8H, CH_2), 0.93 (t, *J* = 7.3 Hz, 12H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 158.5 (C-7), 155.7 (C-6), 145.6 (C-3), 144.3 (C-4), 142.4 (C-1), 139.2 (C-9), 129.2 (C-5), 120.3 (C-8), 80.7 (C-2), 74.5 (OCH_2), 32.1 (CH_2), 19.1 (CH_2), 13.9 (CH_3). – MS (FD), *m/z*: 916.6 [M^+ – 1]. – $C_{50}H_{50}N_8NiO_6$ (917.7): calcd. C 65.44, H 5.49, N 12.21; found C 65.58, H 5.45, N 12.05.

Separation of the syn/anti isomers of **1b**: 200 mg of **1b** was separated by column chromatography during 12 h (neutral alumina, deactivated with 4% H_2O; eluent: CH_2Cl_2/MeOH, 500:1). Removal of the solvent and drying in vacuo yielded 53 mg of the *anti* (first fraction) and 62 mg of the *syn* isomer (second fraction). Separation by preparative TLC (alumina; eluent CH_2Cl_2/MeOH, 250:1) is also possible.

[1,6,16,21-Tetrahexyloxy-2,5,17,20-tetrahydro-2,5:17,20-diepoxyheminaphthoporphyrazinato]nickel(II) (**1c**): Compound **1c** was synthesized as described for **1a**. **9c** (0.146 g, 0.35 mmol), **10a** (38 mg, 0.35 mmol) and $Ni(OAc)_2 \cdot 4\ H_2O$ (52 mg, 0.21 mmol) were allowed to react in *n*-butanol (10 ml). Purification by column chromatography (neutral alumina, deactivated with 4% H_2O; eluent: hexane/ethyl acetate, 3:1, R_f = 0.70) yielded 139 mg (76%) of **1c**. – IR (KBr): $\tilde{\nu}$ = 2951 cm^{-1}, 2928, 2856, 1663, 1618, 1580, 1537, 1437, 1391, 1334, 1286, 1205, 1157, 868. – ^1H NMR ($CDCl_3$): δ = 7.34 (t; *J* = 7.6 Hz, 2H, 9-H), 6.96 (s, 4H, 1-H), 6.43 (d, *J* = 7.6 Hz, 4H, 8-H), 5.86 (s, 4H, 2-H), 4.04 (m, 8H, OCH_2), 1.65 (m, 8H, CH_2), 1.35 (m, 8H, CH_2), 1.25 (m, 16H, 2 × CH_2), 0.82 (t, *J* = 6.8 Hz, 12H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 158.6 (C-7), 155.8 (C-6), 145.7 (C-3), 144.4 (C-4), 142.6 (C-1), 139.2 (C-9), 129.2 (C-5), 120.3 (C-8), 80.7 (C-2), 74.9 (OCH_2), 31.7 (CH_2), 30.1 (CH_2), 25.6 (CH_2), 22.6 (CH_2), 14.0 (CH_3). – MS (FD), *m/z*: 1028.4 [M^+ – 1]. – $C_{58}H_{66}N_8NiO_6$ (1029.9): calcd. C 67.65, H 6.41, N 10.88; found C 69.00, H 7.31, N 10.46.

[1,6,11,16,21,26-Hexabutoxy-2,5,17,20-tetrahydro-2,5:17,20-diepoxyheminaphthoporphyrazinato]nickel(II) (**1d**): Compound **1d** was synthesized as described for **1a**. **9b** (0.49 g, 1.38 mmol), **10d** (0.25 g, 1.38 mmol) and $Ni(OAc)_2 \cdot 4\ H_2O$ (0.21 g, 0.83 mmol) were allowed to react in *n*-butanol (30 ml). Purification by column chromatography (neutral alumina, deactivated with 4% H_2O; eluent: hexane/ethyl acetate, 2:1, R_f = 0.37) furnished 67 mg (9%) of **1d**. – IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1}, 2934, 2872, 1668, 1628, 1582, 1529, 1489, 1433, 1385, 1335, 1285, 1207, 1196, 1136, 1067, 870. – ^1H NMR ($CDCl_3$): δ = 6.96 (s, 4H, 1-H), 6.12 (s, 4H, 8-H), 5.86 (s, 4H, 2-H), 4.07 [m, 8H, OCH_2(isoind)], 3.92 [t, *J* = 6.8 Hz, 4H, OCH_2(pyr)], 1.65 (m, 12H, CH_2), 1.45 (m, 12H, CH_2), 0.89 (t, *J* = 7.3 Hz, 18H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 167.9 (C-9), 159.3 (C-7), 156.1 (C-6), 145.6 (C-3), 144.3 (C-4), 142.6 (C-1), 129.4 (C-5), 106.1 (C-8), 80.7 (C-2), 74.5 [OCH_2(isoind)], 68.3 [OCH_2(pyr)], 32.2 (CH_2), 30.8 (CH_2), 19.2 (CH_2), 19.0 (CH_2), 13.9 (CH_3), 13.7 (CH_3). – MS (FD), *m/z*: 1062.4 [M^+]. – $C_{58}H_{66}N_8NiO_8$ (1061.9): calcd. C 65.60, H 6.26, N 10.55; found C 66.48, H 6.18, N 10.52.

HpNi **2a**: **1a** (46 mg, 0.061 mmol) was treated with **3** (24 mg, 0.15 mmol) in boiling toluene (20 ml) for 1 h. The solvent was removed in vacuo. Purification by column chromatography (neutral alumina, deactivated with 4% H_2O; eluent: CH_2Cl_2/MeOH, 3:1, R_f = 0.42) yielded 24 mg (38%) of **2a**. – IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1}, 2924, 2853, 1661, 1612, 1576, 1537, 1492, 1433, 1396, 1288, 1253, 1204, 1161, 1042, 883, 731, 658. – ^1H NMR ($CDCl_3$): δ = 7.35 (t, *J* = 7.6 Hz, 2H, 13-H), 6.49 (d, *J* = 7.6 Hz, 4H, 12-H), 6.33 (m, 4H, 15-H), 5.17 (s, 4H, 6-H), 4.90 (s, 4H, 14-H_{cis}), 4.71 (s, 4H, 14-H_{trans}), 3.90 (s, 12H, OCH_3), 3.61 (m, 4H, 2-H), 2.58 (m, 4H, 4-H), 2.11 (m, 4H, 4-H), 1.98 (m, 4H, 5-H). – ^{13}C NMR ($CDCl_3$): δ = 158.5 (C-11), 156.0 (C-10), 144.1 and 144.0 (C-1), 143.9 (C-8), 142.4 (C-7), 139.3 (C-13), 137.3 (C-3), 133.6 (C-15), 129.1 (C-9), 120.4 (C-12), 101.4 (C-14), 83.3 (C-6), 61.7 (OCH_3), 53.5 (C-2), 42.6 (C-5), 30.4 (C-4). – MS (FAB), *m/z*: 1061.3 [M^+]. – $C_{62}H_{50}N_8NiO_6$ (1061.8): calcd. C 70.13, H 7.75, N 10.55; found C 68.20, H 7.30, N 10.95.

HpNi **2b**: Compound **2b** was prepared in analogy to **2a**. **1b** (0.1 g, 0.11 mmol) and **3** (43 mg, 0.28 mmol) were allowed to react in toluene (10 ml). Purification by column chromatography (neutral alumina, deactivated with 4% H_2O; eluent: hexane/ethyl acetate, 3:1, R_f = 0.60 (*anti* isomer), 0.24 (*syn* isomer) furnished 76 mg (57%) of **2b**. – IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1}, 2930, 2870, 1663, 1610, 1576, 1537, 1489, 1435, 1394, 1285, 1246, 1204, 1161, 1074, 874, 808, 731, 658. – ^1H NMR ($CDCl_3$): δ = 7.33 (t, *J* = 7.6 Hz, 2H, 13-H), 6.46 (d, *J* = 7.6 Hz, 4H, 12-H), 6.33 (m, 4H, 15-H), 5.22 (s, 4H, 6-H), 4.91 (s, 4H, 14-H_{cis}), 4.70 (s, 4H, 14-H_{trans}), 4.05 [t, *J* = 6.4 Hz, 8H, OCH_2(*anti*)], 4.05 [m, 8H, OCH_2(*syn*)], 3.83 (m, 4H, 2-H), 2.56 (m, 4H, 4-H), 2.10 (m, 4H, 4-H), 1.97 (m, 4H, 5-H), 1.66 (m, 8H, CH_2), 1.44 (m, 8H, CH_2), 0.89 (t, *J* = 7.3 Hz, 12H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 158.5 (C-11), 156.0 (C-10), 144.1 and 144.0 (C-1), 143.2 (C-8), 143.0 and 142.8 (C-7), 139.2 (C-13), 137.3 (C-3), 133.6 (C-15), 129.1 (C-9), 120.2 (C-12), 101.4 (C-14), 83.5 (C-6), 74.4 (OCH_2), 53.5 (C-2), 42.5 (C-5), 32.2 (CH_2), 30.5 (C-4), 19.2 (CH_2), 14.0 (CH_3). – MS (FD), *m/z*: 1229.4 [M^+]. – $C_{74}H_{74}N_8NiO_6$ (1230.1): calcd. C 72.25, H 6.06, N 9.11; found C 72.71, H 6.55, N 8.75.

HpNi **2c**: Compound **2c** was prepared in analogy to **2a**. **1c** (0.11 g, 0.10 mmol) and **3** (40 mg, 0.26 mmol) were allowed to react in toluene (10 ml). Purification by column chromatography (neutral alumina, deactivated with 4% H_2O; eluent: hexane/ethyl acetate, 3:1, R_f = 0.51) afforded 53 mg (40%) of **2c**. – IR (KBr): $\tilde{\nu}$ = 2953 cm^{-1}, 2926, 2855, 1661, 1620, 1580, 1537, 1468, 1435, 1391, 1286, 1261, 1205, 1157, 1095, 1078, 873, 806, 729, 663. – ^1H NMR ($CDCl_3$): δ = 7.33 (t, *J* = 7.6 Hz, 2H, 13-H), 6.44 (d, *J* = 7.6 Hz, 4H, 12-H), 6.33 (m, 4H, 15-H), 5.09 (s, 4H, 6-H), 4.91 (s, 4H, 14-H_{cis}), 4.71 (s, 4H, 14-H_{trans}), 4.04 (m, 8H, OCH_2), 3.84 (m, 4H, 2-H), 2.56 (m, 4H, 4-H), 2.11 (m, 4H, 4-H), 1.95 (m, 4H, 5-H), 1.64 (m, 8H, CH_2), 1.39 (m, 8H, CH_2), 1.25 (m, 16H, 2 × CH_2), 0.84 (t, *J* = 6.2 Hz, 12H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 158.5 C-11), 155.7 (C-10), 144.0 (C-1), 143.2 (C-8), 143.0 (C-7), 139.2 (C-13), 137.3 (C-3), 133.6 (C-15), 129.1 (C-9), 120.1 (C-12), 101.4 (C-14), 83.5 (C-6), 74.7 (OCH_2), 53.5 (C-2), 42.5 (C-5), 31.7 (CH_2), 30.5 (C-4), 30.2 (CH_2), 25.7 (CH_2), 22.7 (CH_2), 14.1 (CH_3). – MS

(FD), *m/z*: 1343.0 [M^+]. – $C_{82}H_{90}N_8NiO_6$ (1342.3): calcd. C 73.37, H 6.76, N 8.35; found C 75.29, H 8.46, N 5.70.

HpNi **2d**: Compound **2d** was prepared in analogy to **2a**. **1d** (42 mg, 0.039 mmol) and **3** (15 mg, 0.097 mmol) were allowed to react in toluene (10 ml). Purification by column chromatography (neutral alumina, deactivated with 4% H_2O; eluent: hexane/ethyl acetate, 3:1, R_f = 0.70) delivered 37 mg (69%) of **2d**. – IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1}, 2932, 2870, 1664, 1626, 1578, 1528, 1489, 1433, 1387, 1283, 1204, 1190, 1138, 1067, 1030, 876, 841, 746, 654. – ^1H NMR ($CDCl_3$): δ = 6.33 (m, 4H, 15-H), 6.13 (s, 4H, 12-H), 5.10 (s, 4H, 6-H), 4.91 (s, 4H, 14-H_{cis}), 4.71 (s, 4H, 14-H_{trans}), 4.06 [t, *J* = 6.4 Hz, 8H, OCH_2(*anti*)], 4.06 [m, 8H, OCH_2(*syn*)], 3.92 [t, *J* = 6.5 Hz, 4H, OCH_2(pyr)], 3.83 (m, 4H, 2-H), 2.56 (m, 4H, 4-H), 2.13 (m, 4H, 4-H), 1.97 (m, 4H, 5-H), 1.66 (m, 12H, CH_2), 1.39 (m, 12H, CH_2), 0.90 (t, *J* = 7.3 Hz, 12H, CH_3), 0.89 (t, *J* = 7.3 Hz, 6H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 167.9 (C-13), 159.3 (C-11), 156.0 (C-10), 144.1 and 144.0 (C-1), 143.1 (C-8), 142.9 and 142.7 (C-7), 137.3 (C-3), 133.6 (C-15), 129.2 (C-9), 106.0 (C-12), 101.4 (C-14), 83.5 (C-6), 74.4 [OCH_2(isoind)], 68.3 [OCH_2(pyr)], 53.5 (C-2), 42.5 (C-5), 32.3 (CH_2), 30.8 (CH_2), 30.5 (C-4), 19.2 (CH_2), 19.0 (CH_2), 14.0 (CH_3), 13.7 (CH_3). – MS (FD), *m/z*: 1374.0 [M^+]. – $C_{82}H_{90}N_8NiO_8$ (1374.3): calcd. C 71.66, H 6.60, N 8.15; found C 71.72, H 6.84, N 7.88.

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