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Reaction of β-Formylporphyrins with Organometallic Reagents - A Facile Method for the Preparation of Porphyrins with Exocyclic Double Bonds

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Abstract: 5,10,15,20-Tetralkyl-2-formylporphyrins were treated with various organolithium reagents to form porphyrins with exocyclic double bonds. The reaction involved conversion with LiR to the respective alcohol. Subsequence dehydratization of the alcohols yielded olefinic systems in which the double bond formed was located in the meso substituent neighboring the β position, i.e., the result of a 1,5-hydride shift. Depending on the organolithium reagent used various olefinic porphyrins are accessible, provided the stability of the intermediary carbenium ion is high enough. Furthermore, use of a Peterson olefination allowed the facile synthesis of 2-vinyl-5,10,15,20-tetralkylporphyrins and use of an organodilithium reagent gave convenient access to functionalized bisporphyrins.

INTRODUCTION

The stepwise synthesis of asymmetrical porphyrins starting from aldehydes, pyrroles and/or dipyrromethanes is a tedious process requiring complex multi-step syntheses, laborious chromatographic work-up, and often can be accomplished only in very low yields. Nevertheless, the synthesis of porphyrins with asymmetric substituent pattern is required when attempts are made to construct biomimetic systems for the various *in vivo* functions of porphyrins. As nature has made use of only certain substituent pattern derived from uroporphyrinogen I or III, another approach towards asymmetrically substituted porphyrins consists of functionalizing existing porphyrin systems. Thus, the development of appropriate functionalization reactions is an ongoing effort in porphyrin chemistry and numerous attempts have been made to transfer results from the large area of functionalization of simple aromatic systems to porphyrins. Significant progress has been made in using such reactions with 5,10,15,20-tetraarylporphyrins and 2,3,7,8,12,13,17,18-octaalkylporphyrins.[1-5]

Due to their relevance for conformational studies and applications in catalysis 5,10,15,20-tetraalkylporphyrins have recently again attracted interest.[6-8] This is due to the observation of often highly ruffled macrocycle conformations[8b] that would allow the use of such porphyrins as conformationally distorted donors in donor-acceptor electron transfer model compounds. Our studies have shown that synthetic methods developed for tetraarylporphyrins are not easily applicable to tetraalkylporphyrins.[6-8] One of our target

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compounds are covalently linked porphyrin quinones with nonplanar macrocycle systems to study the influence of the macrocycle properties on the electron transfer.[9] As attempts to synthesize 5,10,15-trialkyl-20-quinonyl-porphyrins *via* standard cross condensation reactions yielded only porphyrin-quinones with moderately nonplanar macrocycles[10] we anticipated that the use of suitable C-C coupling reactions might yield β-linked porphyrin quinones with more steric hindrance and thus more nonplanar macrocycles.

As shown below, the use of organolithium reagents for the modification of 2-formylporphyrins resulted in the observation of several new reactions involving the porphyrin periphery. For example, a hydride shift from β to meso positions was found and several methods for the functionalization of 5,10,15,20-tetraalkyl-2-formylporphyrins were developed that ultimately were applied to the simple synthesis of a substituted bisporphyrin.

RESULTS AND DISSCUSION

In order to allow multiple conversions and a wide variety in the applicable reactions the starting porphyrin should be accessible in good yields, reasonably stable, undergo peripheral transformations in high yield, and, with respect to our continuing interest in conformationally distorted porphyrins,[8a,b] should possess a moderate degree of nonplanarity. 5,10,5,20-Tetrakis(1-ethylpropyl)porphyrin can be synthesized in acceptable yields and fulfills all the criteria listed above.[8] Using a Vilsmeier formylation the respective nickel complex can easily be monofunctionalized,[7] yielding a 2-formylporphyrin which was used for various coupling reactions. In contrast to (meso) 2,3,7,8,12,13,17,18-octaethyl-5-formylporphyrin[11] and (ß) 2-formyl-5,10,15,20-tetraphenylporphyrin,[3,12] the formyl group in {2-formyl-5,10,15,20-tetra-(1-ethylpropyl)-porphyrinato}nickel(II) was found to be remarkably stable against acids and bases.[13]

The molecular structure of **1** in the crystal shows a highly nonplanar macrocycle with an average deviation from planarity for the 24 macrocycle atoms (Δ24) of 0.41 Å (Figure 1).

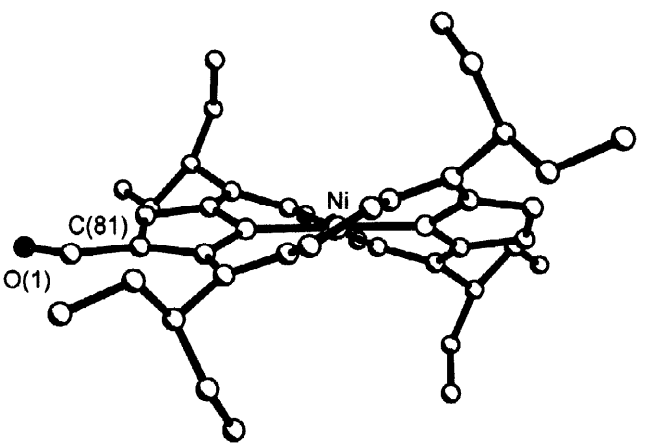
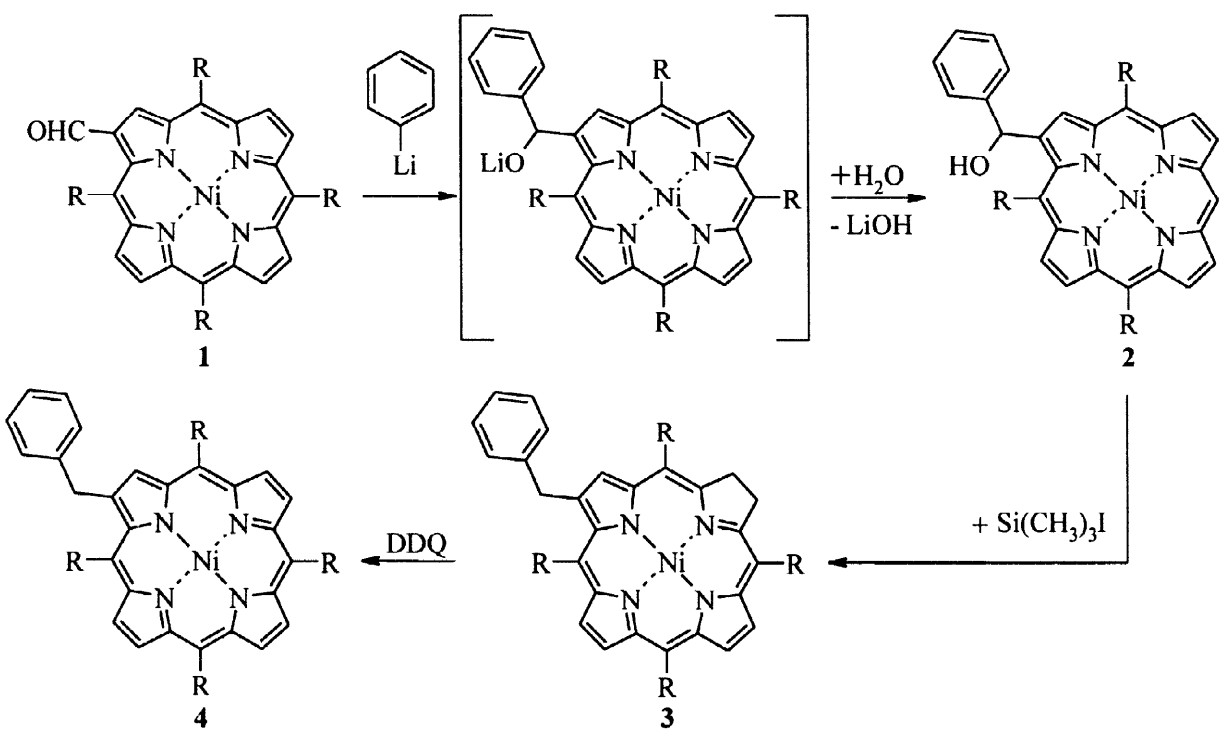


Figure 1. Computer generated view of the molecular structure of **1** in the crystal. Hydrogen atoms and disordered positions have been omitted for clarity.

The largest deviations from planarity are observed for the meso carbon atoms, which show an average deviation from the 4N-plane of 0.87 Å. Thus, the macrocycle exhibits a ruffled conformation with a degree of distortion significantly exceeding that of either (5,10,15,20-tetraphenylporphyrinato)nickel(II) or (2,3,7,8,12,13,17,18-octaethylporphyrin-ato)nickel(II). For comparison, the related Ni(II) porphyrin without the formyl group has a slightly less distorted macrocycle with a Δ24 of 0.39 Å and average deviations from planarity for the meso positions of 0.81 Å.[8] The structural study clearly shows that the starting material chosen for the subsequent transformations indeed has a significant degree of nonplanarity and can serve as a test case for the chemical reactivity of ruffled porphyrins.

As known coupling reactions (Wittig,[14,15] McMurry[16-18]) proved to be either too laborious with respect to starting materials and reagents or could not be applied to 5,10,15,20-tetraalkylporphyrin an investigation of reactions using organometallic reagents was performed. The observation that Grignard compounds react easily with 2,3,7,8,12,13,17,18-octaethyl-5-formylporphyrin[19,20] raised our interest to test whether the more easily accessible organolithium reagents can react under mild conditions with 2-formylporphyrins. In addition, our recent experiences with LiR reagents for the functionalization of porphyrins have shown that these reactions generally proceed efficiently and reproducible.[21]

To test this approach, {5,10,15,20-tetrakis(1-ethylpropyl)-2-formylporphyrinato}nickel(II) **1** was treated at –80 °C with phenyllithium in absolute THF and the reaction quenched with water.



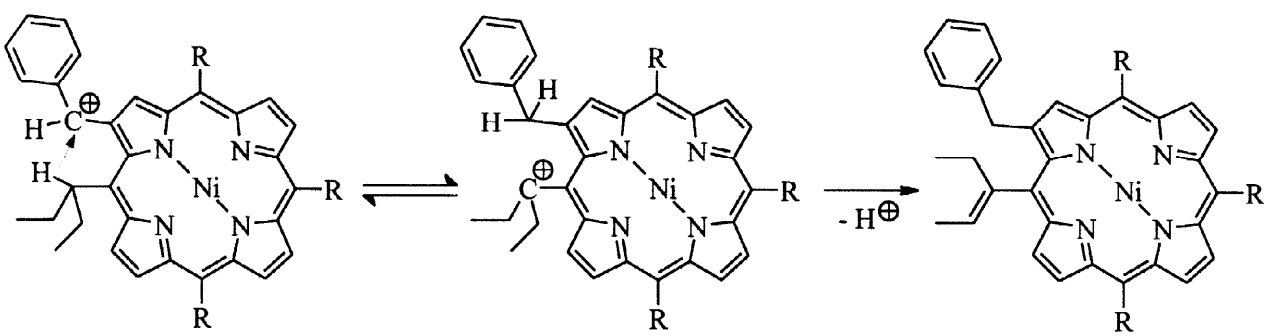
R = 1-ethylpropyl

Scheme 1

To remove the hydroxyl group the resulting racemic phenylcarbinol **2** was reduced with trimethylsilyl iodide.[22,23] Although this reaction had not been applied before to porphyrins we were quite surprised to observe the formation of the chlorin (hydroporphyrin) **3** under these conditions. Unfortunately, it proved to be very unstable and could not be isolated in pure form. Thus, the reaction mixture was oxidized with DDQ yielding the porphyrin **4** as the sole reaction product (Scheme 1).

To circumvent the intermediary formation of chlorin the removal of the hydroxyl group was attempted under acidic and milder conditions.[24] Again, the reaction product formed did not completely conform to our expectations. While the hydroxyl group was cleaved off, simultaneously, two protons were lost and formation of an olefinic double bond was observed. The ^{1}H NMR spectrum confirmed the formation of {2-benzyl-5,10,15-tris(1-ethylpropyl)-20-(1-ethenylpropyl)porphyrinato}nickel(II) **5** as the main product. The spectrum showed a splitting of the benzylic protons into a AB-system (4.85-5.18 ppm, J_{AB} =17 Hz) and signals for the protons from the opposing methylene group at 1.98-2.15 ppm and 2.27-2.58 ppm.

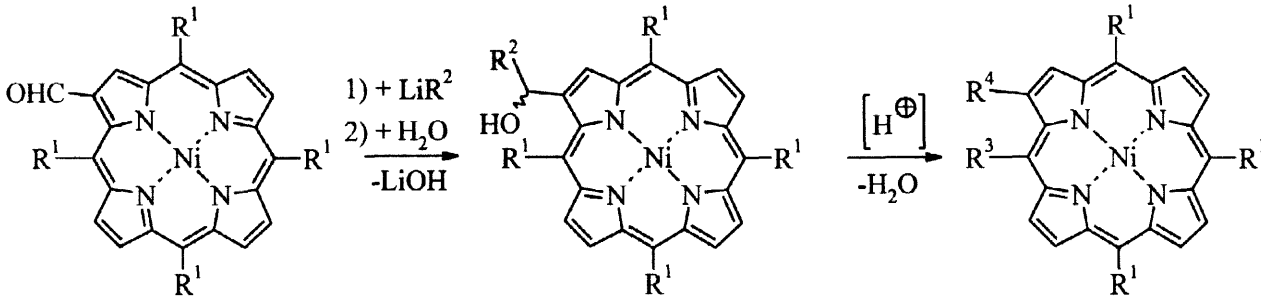
This is a consequence of the restricted free rotation of the individual substituents resulting in a chemically equivalent but magnetically inequivalent environment. Formation of this porphyrin can only be explained with a 1,5-hydride shift from the 1-ethylpropyl group in position 20 to the neighboring methylene carbon atom in the β position. The intermediary formed carbenium ion is stabilized by an equilibrium reaction and can only form a double bond involving a tertiary carbon atom (Scheme 2).



R = 1-ethylpropyl **5**

Scheme 2

This reaction proceeds quite easily, requires only catalytic amounts of acid, and is irreversible. A similar reaction was observed by Johnson and coworkers during the reaction of meso formyl-octaethylporphyrin with phenylmagnesium bromide.[19] To investigate this β → meso H shift in more detail a variety of reactions using different β and meso substituents were performed (Scheme 3).



1, 6 - 8 **2, 9 - 16** **5, 17 - 20**

No.	R^1	R^2	R^3	R^4
1	1-ethylpropyl	-	-	-
2	1-ethylpropyl	phenyl	-	-
5	1-ethylpropyl		1-ethenylpropyl	benzyl
6	n-butyl	-	-	-
7	2-methylpropyl	-	-	-
8	1-methylethyl	-	-	-
9	n-butyl	phenyl	-	-
10	2-methylpropyl	phenyl	-	-
11	1-methylethyl	phenyl	-	-
12	1-ethylpropyl	n-butyl	-	-
13	1-ethylpropyl	2,2-dimethylpropyl	-	-
14	1-ethylpropyl	4-bromo-2-methoxyphenyl	-	-
15	1-ethylpropyl	diphenylmethyl	-	-
16	1-ethylpropyl	2,5-dimethoxyphenyl	-	-
17	1-methylethyl	-	1-methylethenyl	benzyl
18	1-ethylpropyl	-	1-ethylpropyl	1-pentenyl
19	1-ethylpropyl	-	1-ethenylpropyl	5-bromo-2-methoxybenzyl
20	1-ethylpropyl	-	1-ethylpropyl	2,2-diphenylethenyl

Scheme 3

These studies allowed the conclusion that the 1,5-hydride shift proceeds only from a tertiary carbon atom involving an activated carbenium ion. For example, this reaction yielded porphyrins with a substituted benzyl residue in 2 position **19** and a meso-vinyl-trialkylporphyrin **17**. Treatment of **1** with *tert*-butyllithium gave the stable carbinol **13** that could not be converted into the respective β-2,2-dimethylporphyrin.

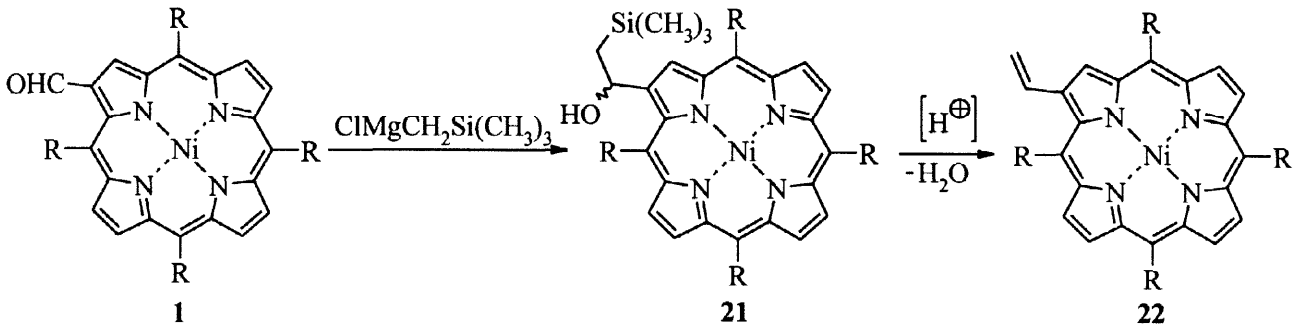
Similarly, the carbinols **9** and **10** resulting from the reaction of **6** and **7** with phenyllithium, even under extreme conditions (heating to reflux in TFA/toluene), underwent no hydride shift. This shows that the general statements about the relative stability of carbenium ions are equally applicable to porphyrins.

In contrast, when porphyrin **1** was treated with alkyllithium reagents containing hydrogen atoms in the α position, dehydration occurred in the ß position resulting in the porphyrins **18** and **20**. Compound **20** carries a 2,2-diphenylethenyl substituent conjugated over all rings and thus should exhibit interesting optical properties. For example, **20** has a Soret band at 432 nm, the most bathochromically shifted of all compounds

discussed here. Here, further optimization of the synthesis and a variation of the diphenyl systems are required for other studies, e.g., the rational construction of push-pull porphyrins.

Generally, these reactions showed that the use of 5,10,15,20-tetraalkylporphyrins with sterically undemanding substituents (**6**,**7**) as well as the employment of highly reactive lithium reagents resulted in an increase in side reactions that could not be prevented by using very mild conditions. The higher meso reactivity of these compounds (and potentially phlorin formation) is the main reason for the large variety in the yields observed in different reactions.

Due to their importance in natural porphyrin systems the synthesis of vinyl porphyrins is of principal interest. Up to now only one synthesis, involving a traditional Wittig reaction, was known to generate a 2-vinylporphyrin from a 2-formylporphyrin.[25] Other reactions to form a formyl group in ß position are known, but involve more complex starting materials.[26] Expecting numerous side reactions when using methyl lithium, a more modern Grignard reagent was used for reaction with **1**. Treatment of **1** with (trimethylsilyl)methylmagnesium chloride results in formation of the very acid labile alcohol **21** that immediately converts into the respective 2-vinylporphyrin (Scheme 4).



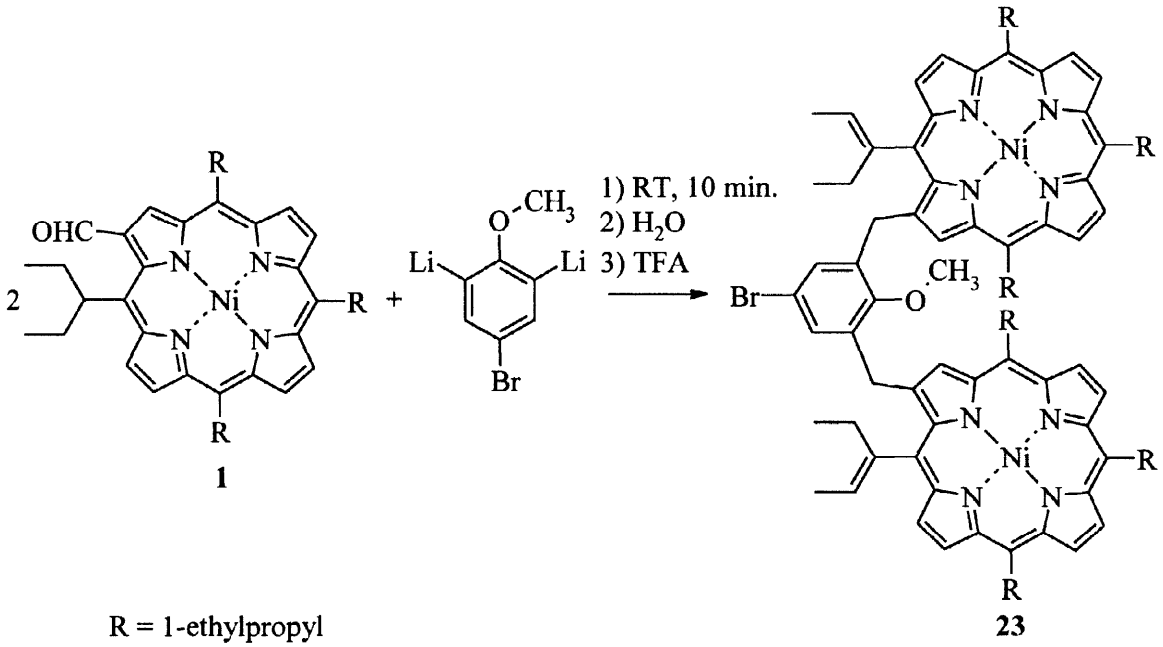
1 **21** **22**

R = 1-ethylpropyl

Scheme 4

Thus, for the first time a Peterson olefination was applied to the β position to generate vinyl functionalities in porphyrins. As this reactions proceeds with excellent yield (80 %) 5,10,15,20-tetraalkyl-2-vinylporphyrins are now accessible for further transformations. The synthesis of more complex multicomponent porphyrin systems for modeling various biological processes[27] often requires an initial dimerization step to yield bisporphyrins.[16,28-30] The easier this dimerization can be performed, preferably with very simple starting materials, in high yield and resulting in highly soluble bisporphyrins, the more complex systems can ultimately be constructed. As shown above, **1** reacts readily with various organometallic reagents. Thus, use of an easily accessible dilithium compound would be a simple avenue to covalently linked bisporphyrins. 2,4,6-Tribromoanisole was found to be such a molecule that can easily be converted with butyl lithium into the respective 4-bromo-2,6-dilithiumanisole.[31]

Reaction of **1** with this dilithium compound in THF, followed by acidic work-up resulted in the porphyrin dimer **23** which is bridged *via* a *m*-xylene ring (Scheme 5).

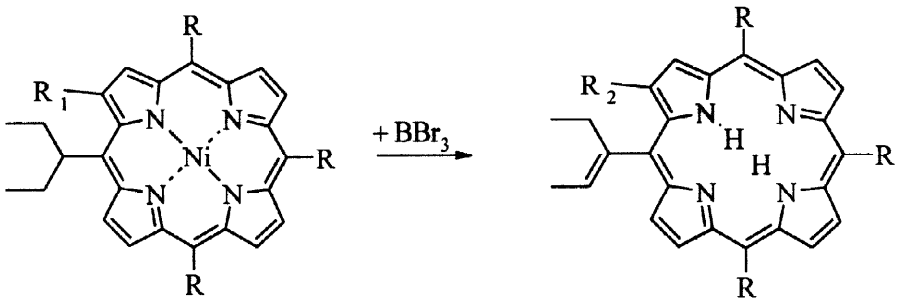


R = 1-ethylpropyl

Scheme 5

In addition, this dimer bears two olefinic double bonds in the 20 and 20' positions and carries a halogen and methyl ether functionality at the bridge. Thus, various further transformations involving these residues are possible. Going back to our original aim, the synthesis of ß linked porphyrin quinones, bromo-2,5-dimethoxybenzene was converted with butyllithium into the respective lithium compound and used for conversion of **1** into the carbinol **16**. As the two methyl ester residues can be deprotected most easily with boron tribromide,[10] a strong Lewis acid that should also promote the described 1,5-hydride shift, both deprotection and double bond formation should proceeded in one step (Scheme 6).

The resulting porphyrin hydroquinone **24** showed that not only these two reactions had occurred but that simultaneously the porphyrin was demetallated. Thus, three reactions were performed in one step. This interesting demetallation reaction can be applied to other nickel(II) porphyrins as well. For example, reaction of **8** with BBr_3 gave the free base **25** in 72 %. Studies in our and other laboratories appear to indicate that this is a generally applicable demetallation reaction.[32] So far, demetallation of porphyrins was performed under extreme conditions (heating under reflux in DMF, conc. H_2SO_4; stirring in conc. H_2SO_4 at 50°; etc.[1,3]) often accompanied by a significant loss of material. Use of BBr_3 now allows demetallation under much milder conditions in good yields.



16 R = 1-ethylpropyl
R_1 = 2,5-dimethoxyphenyl-hydroxymethyl

8 R = 1-ethylpropyl
R_1 = 1-hydroxybenzyl

24 R = 1-ethylpropyl
R_1 = 2,5-hydroxybenzyl

25 R = 1-ethylpropyl
R_1 = benzyl

Scheme 6

Unfortunately, the hydroquinone **24** was found to be very resistant towards oxidation with either silver(I) or lead(II) oxide and could not be converted to the desired quinone. Nevertheless, the present results indicate the feasibility of using organolithium compounds for the functionalization of various β-formylporphyrins. The largest potential lies in the convenient access to porphyrins with divers meso and/or β olefinic systems. In addition, utilization of this synthetic methodology with simultaneous occurrence of organometallic coupling, dehydratization and hydride shift in one step allows the facile preparation of more complex tetrapyrrole systems, e.g., bisporphyrins. The products described herein have further applications and synthetic potential, for example, *via* olefinic coupling reactions to yield even more complex systems.

EXPERIMENTAL

General

All chemicals used were of analytical and purified before use by distillation. THF and n-hexane was dried before use by filtration through basic aluminum oxide (grade I, neutral). All reactions with organolithium reagents were performed under a purified argon atmosphere. Melting points were measured on a Büchi melting point apparatus and are uncorrected. Silica gel 60 (Merck) or basic alumina (Alfa) (usually Brockmann Grade III, i.e. deactivated with 7% water) were used for column chromatography. Analytical thin-layer chromatography (TLC) was carried out using Merck silica gel 60 plates or alumina 60 (neutral, fluorescence indicator F_{254}) plates (precoated sheets, 0.2 mm thick). ^{1}H NMR spectra were recorded at frequency of 250 MHz (AC 250) or 500 MHz (Bruker, AMX 500). All chemical shifts are given in ppm, referenced on the δ scale downfield from the TMS signal as internal standard. Electronic absorption spectra were recorded with a Specord S10 (Carl Zeiss) spectrophotometer using dichloromethane as solvent. Mass

spectra were recorded with Varian MAT 711 mass spectrometer using EI technique with a direct insertion probe and an excitation energy of 80 eV. Elemental Analyses were performed with a Perkin-Elmer 240 Analyzer.

Synthesis of the 5,10,15,20-tetraalkyl-2-formylporphyrins and the commercially not available lithium reagents, and the cleavage of the methyl groups from protected hydroquinones were performed using literature procedures.[8,10,31,33]

General procedure for the reaction of 2-formylporphyrins with organolithium reagents

A Schlenk flask was charged with 0.3 mmol of the porphyrin (ca. 200 mg) dissolved in 30 ml THF. After purging with Ar, four equivalents of the organolithium reagent were added dropwise through a septum under stirring at -80 °C. After 15-30 min the color of the reaction changed from green to red. The reaction was quenched *via* addition of 2-3 ml water and the reaction mixture warmed to room temperature. The mixture was filtered through alumina (neutral, Brockmann grade I) and purified by column chromatography on silica gel (hexane/CH_2Cl_2, 1:1, v/v). The first green fraction contained unreacted starting material and the second, red fraction the desired product.

General procedure for the synthesis of porphyrins with exocyclic double bonds

The respective porphyrin was dissolved in dichloromethane and stirred with a few drops of TFA at room temperature for 10 min. The reaction mixture was neutralized with sodium hydrogen carbonate, dried over Na_2SO_4, and purified by column chromatography (silica gel, hexane/CH_2Cl_2, 1:1, v/v).

{2-(1-Hydroxybenzyl)-5,10,15,20-tetrakis(1-ethylpropyl)porphyrinato}nickel(II) **(2)**. Prepared using the general method given above. Yield: 170 mg (0.225 mmol, 76 %) red crystals from CH_2Cl_2/MeOH; m. p. 105-110 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0-0.06 (t, J = 7.3 Hz, 3H, $CH(CH_2C\underline{H}_3)_2$), 0.71-0.99 (m, 18H, $CH(CH_2C\underline{H}_3)_2$), 1.06-1.12 (t, J = 7.3 Hz, 3H, $CH(CH_2C\underline{H}_3)_2$), 1.98-2.15 (m, 2H, $CH(C\underline{H}_2CH_3)_2$), 2.42-2.69 (m, 12H, $CH(C\underline{H}_2CH_3)_2$), 2.74-2.76 (d, J = 4.3 Hz, 1H, C<u>H</u>OH), 2.79-2.89 (m, 2H, $CH(C\underline{H}_2CH_3)_2$), 3.97-4.21 (m, 4H, $C\underline{H}(CH_2CH_3)2$), 7.33-7.41 (m, 3H, $H_{p,m\text{-}ph}$), 7.58-7.62 (m, 2H, $H_{o\text{-}ph}$), 9.14-9.22 (m, 7H, $H_{\beta\text{-}pyrrole}$); UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 242 nm (4.22), 343 (3.90), 427 (5.08), 551 (3.97), 589 (3.24); MS (40 eV); *m/z* (%): 752 (100) [M^+], 723 (21) [M^+-C_2H_5]; HRMS [$C_{47}H_{58}N_4ONi$]: calcd. 752.39641, found 752.39227.

{2-Benzyl-5,10,15,20-tetrakis(1-ethylpropyl)porphyrinato}nickel(II) **(4)**. A mixture of 0.51 ml (4 mmol) trimethyl silyl chloride, 0.6 g (4 mmol) sodium iodide and 0.2 ml (4 mmol) acetonitrile was treated dropwise under stirring with a solution of 200 mg (0.3 mmol) **2** in 75 ml methylene chloride followed by stirring for 24 h. After washing with water the organic phase was dried with sodium sulfate and stirred for 30 min with 53 mg (0.3 mmol) DDQ. Standard chromatographic work up yielded 13 mg (0.018 mmol, 6 %) red

crystals from CH_2Cl_2/MeOH; m. p. 285-295 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.51-0.57 (t, J = 7.3 Hz, 6H, $CH(CH_2C\underline{H}_3)2$), 0.78-0.95 (m, 18H, $CH(CH_2C\underline{H}_3)_2$), 2.34-2.67 (m, 16H, $CH(C\underline{H}_2CH_3)_2$), 3.90-4.03 (sext, 2H, $C\underline{H}(CH_2CH_3)_2$), 4.06-4.15 (sext, 2H, $C\underline{H}(CH_2CH_3)_2$), 5.22 (s, 2H, $C\underline{H}_2C_6H_5$), 7.26-7.34 (m, 5H, H_{ph}), 8.76 (s, 1H, $H_{\beta\text{-pyrrole}}$), 9.10-9.20 (m, 6H, $H_{\beta\text{-pyrrole}}$); UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 344 nm (4.15), 427 (5.21), 551 (4.19), 590 (3.63); MS (40 eV); *m/z* (%): 736 (100) [M^+], 707 (63) [M^+-C_2H_5]; HRMS [$C_{47}H_{58}N_4Ni$]: calcd. 736.4015, found 736.4042; [$C_{47}H_{58}N_4Ni$, 737.69 g mol^{-1}]: anal. calcd. C 76.52, H 7.92, N 7.59, found C 75.71, H 7.85, N 7.48.

{2-Benzyl-20-(1-ethenylpropyl)-5,10,15-tris(1-ethylpropyl)porphyrinato}nickel(II) **(5).** Prepared using the general method given above. Yield: 160 mg (0.22 mmol, 82 %) red crystals from CH_2Cl_2/MeOH; m.p. 105-110 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.44-0.52 (m, 3H, CH_3CH=C-$CH_2C\underline{H}_3$), 0.77-0.95 (m, 18H, $CH(CH_2C\underline{H}_3)_2$), 1.94-2.05 (sext, J = 7.3 Hz, 1H, CH_3CH=C-$C\underline{H}_2CH_3$), 2.15-2.18 (d, J = 6.9 Hz, 3H, $C\underline{H}_3CH$=C-CH_2CH_3), 2.27-2.58 (m, 12H, $CH(C\underline{H}_2CH_3)_2$), 2.82-2.91 (sext, J = 7.3 Hz, 1H, CH_3CH=C-$C\underline{H}_2CH_3$), 3.92-3.98 (quint, 1H, $C\underline{H}(CH_2CH_3)_2$), 4.09-4.21 (quint, J = 7.3 Hz, 2H, $C\underline{H}(CH_2CH_3)_2$), 4.85-4.91 (d, J = 17.2 Hz, 1H, $C\underline{H}_2C_6H_5$), 5.12-5.18 (d, J = 17.2 Hz, 1H, $C\underline{H}_2C_6H_5$), 6.58-6.66 (quart, J = 6.9 Hz, 1H, $CH_3C\underline{H}$=C-CH_2CH_3), 7.34-7.48 (m, 5H, H_{ph}), 8.56 (s, 1H, $H_{\beta\text{-pyrrole}}$), 9.04-9.07 (d, J = 5.2 Hz, 1H, $H_{\beta\text{-pyrrole}}$), 9.15-9.25 (m, 5H, $H_{\beta\text{-pyrrole}}$); UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 423 nm (5.28), 547 (3.90); MS (40 eV); *m/z* (%): 734 (100) [M^+], 705 (16) [M^+-C_2H_5], 643 (96) [M^+-C_7H_7]; HRMS [$C_{47}H_{56}N_4Ni$]: calcd. 734.3858, found 734.3871

{2-(1-Hydroxybenzyl)-5,10,15,20-tetrabutylporphyrinato}nickel(II) **(9).** Prepared using the general method given above. Yield: 90 mg (0.13 mmol, 21 %) red crystals from CH_2Cl_2/MeOH; m. p. > 300 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.74-0.80 (t, J = 7.3 Hz, 3H, $CH_2CH_2CH_2C\underline{H}_3$), 0.93-1.06 (m, 9H, $CH_2CH_2CH_2C\underline{H}_3$), 1.09-1.26 (hept, J = 7.4 Hz, 2H, $CH_2C\underline{H}_2C\underline{H}_2CH_3$), 1.43-1.64 (hept, J = 7.4 Hz, 8H, $CH_2CH_2C\underline{H}_2CH_3$), 2.10-2.27 (m, 6H, $CH_2C\underline{H}_2CH_2CH_3$), 2.88 (br. s, OH), 4.29-4.48 (t, J = 8.2 Hz, 4H, $C\underline{H}_2CH_2CH_2CH_3$), 4.39-4.48 (m, 4H, $C\underline{H}_2CH_2CH_2CH_3$), 7.31 (s, C<u>H</u>OH), 7.41-7.49 (m, 3H, $H_{m,p\text{-ph}}$), 7.61-7.62 (d, J = 2.0 Hz, 1H, $H_{o\text{-ph}}$), 7.64-7.65 (d, J = 2.0 Hz, 1H, $H_{o\text{-ph}}$), 9.15-9.23 (m, 7H, $H_{\beta\text{-pyrrole}}$); UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 231 nm (4.13), 299 (3.85) 345 (3.85), 423 (4.83), 544 (3.78), 584 (3.27); MS (40 eV); *m/z* (%): 696 (100) [M^+], 679 (81) [M^+-OH], 587 (13) [M^+-OH-C_7H_8]; HRMS [$C_{43}H_{50}N_4ONi$]: calcd. 696.3338, found 696.3382.

{2-(1-Hydroxybenzyl)-5,10,15,20-tetrakis(2-methylpropyl)porphyrinato}nickel(II) **(10).** Prepared using the general method given above but with 250 mg of porphyrin **7**. Yield: 60 mg (0.086 mmol, 24 %) red crystals from CH_2Cl_2/MeOH; m. p. 210-215 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.04-0.07 (d, J = 6.2 Hz, 3H, $CH_2CH(C\underline{H}_3)_2$), 0.44-0.46 (d, J = 5.9 Hz, 3H, $CH_2CH(C\underline{H}_3)_2$), 0.73-0.77 (m, 18H, $CH_2CH(C\underline{H}_3)_2$), 1.17-

1.28 (m, 1H, $CH_2C\underline{H}(CH_3)_2$), 2.04-2.19 (m, 2H, $CH_2C\underline{H}(CH_3)_2$), 2.45-2.51 (m, 1H, $CH_2C\underline{H}(CH_3)_2$), 4.12-4.21 (m, 1H, $C\underline{H}_2CH(CH_3)_2$), 4.33-4.36 (m, 3H, $CH_2C\underline{H}(CH_3)_2$), 4.38-4.45 (m, 4H, $C\underline{H}_2CH(CH_3)_2$), 7.28-7.31 (m, 1H, C<u>H</u>OH), 7.41-7.49 (m, 3H, $H_{m,p\text{-}ph}$), 7.69-7.73 (dd, J = 2.0 Hz, J = 8.3 Hz, 2H, $H_{o\text{-}ph}$), 9.11-9.22 (m, 7H, $H_{\beta\text{-}pyrrole}$); UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 233 nm (4.29), 289 (3.94), 424 (5.05), 546 (3.86), 582 (2.44); MS (40 eV); *m/z* (%): 696 (80) [M^+], 680 (88) [M^+-H_2O], 653 (44) [M^+ C_3H_7], 637 (100) [M^+-Ni], 590 (19) [M^+-C_7H_5O]; HRMS [$C_{43}H_{52}N_4ONi$]: calcd. 696.3338, found 696.3307.

{2-(1-Hydroxybenzyl)-5,10,15,20-tetrakis(1-methylethyl)porphyrinato}nickel(II) **(11).** Prepared using the general method given above. As this porphyrin is unstable it was characterized by NMR only. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.58-1.61 (d, J = 6.9 Hz, 3H, $CH(C\underline{H}_3)_2$), 2.04-2.10 (d, J = 7.7 Hz, 3H, $CH(C\underline{H}_3)_2$), 2.17-2.23 (m, 18H, $CH(C\underline{H}_3)_2$), 2.81-2.83 (d, J = 4.3 Hz, 1H, C<u>H</u>OH), 4.53-4.80 (m, 4H, $C\underline{H}(CH_3)_2$), 7.35-7.48 (m, 3H, $H_{p,m\text{-}ph}$), 7.68-7.72 (m, 2H, $H_{o\text{-}ph}$), 9.19-9.34 (m, 7H, $H_{\beta\text{-}pyrrole}$).

{2-(1-Hydroxy-2,2-dimethylpropyl)-5,10,15,20-tetrakis(1-ethylpropyl)porphyrino}nickel(II) **(13).** Prepared using the general method given above. Yield: 65 mg (0.091 mmol, 31 %) red crystals from CH_2Cl_2/MeOH; m. p. 215-220 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ =-0.09--0.03 (t, J = 7.3 Hz, 3H, $CH(CH_2C\underline{H}_3)_2$), 0.83-0.97 (m, 18H, $CH(CH_2C\underline{H}_3)_2$), 1.34 (s, 9H, $C(C\underline{H}_3)_3$), 1.39-1.46 (t, J = 7.0 Hz, 3H, $CH(CH_2C\underline{H}_3)_2$), 1.84-1.95 (m, 2H, $CH(C\underline{H}_2CH_3)_2$), 2.13-2.24 (m, 2H, $CH(C\underline{H}_2CH_3)_2$), 2.50-2.65 (m, 10H, $CH(C\underline{H}_2CH_3)_2$), 2.96-3.19 (m, 2H, $CH(C\underline{H}_2CH_3)_2$), 4.01-4.12 (m, 3H, $C\underline{H}(CH_2CH_3)_2$), 4.15-4.25 (m, 1H, $C\underline{H}(CH_2CH_3)_2$), 6.18 (s, 1H, $C\underline{H}C(CH_3)_3$), 9.09-9.11 (d, J = 5.3 Hz, 2H, $H_{\beta\text{-}pyrrole}$), 9.12-9.19 (m, 4H, $H_{\beta\text{-}pyrrole}$), 9.21-9.23 (d, J = 5.3 Hz, 1H, $H_{\beta\text{-}pyrrole}$), 9.39 (s, 1H, $H_{\beta\text{-}pyrrole}$); UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 236 nm (4.02), 316 (3.90), 344 (3.91), 428 (5.05), 552 (3.97), 590 (3.44); MS (40 eV); *m/z* (%): 732 (100) [M^+], 714 (72) [M^+-H_2O], 703 (38) [M^+-C_2H_5], 675 (27) [M^+-C_4H_9], 645 (24) [M^+-$C_5H_{11}O$]; HRMS [$C_{45}H_{62}N_4ONi$]: calcd. 732.4277, found 732.4228.

{2-[(2,5-Dimethoxyphenyl)hydroxymethyl]-5,10,15,20-tetrakis(1-ethylpropyl)porphyrinato}nickel(II) **(16).** Prepared using the general method given above. Yield: 210 g (0.26 mmol, 87 %) red crystals from CH_2Cl_2/MeOH; m. p. 180-185 °C; ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ = 0.10-0.16 (t, J = 7.3 Hz, 3H, $CH(CH_2C\underline{H}_3)_2$), 0.79-1.02 (m, 21H, $CH(CH_2C\underline{H}_3)_2$), 2.04-2.24 (sext, J = 7.0 Hz, 2H, $CH(C\underline{H}_2CH_3)_2$), 2.40-2.68 (m, 12 H, $CH(C\underline{H}_2CH_3)_2$), 2.70-2.84 (sext, J = 7.0 Hz, 2H, $CH(C\underline{H}_2CH_3)_2$), 3.52 (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 3.92-4.20 (m, 4H, $C\underline{H}(CH_2CH_3)_2$), 6.71-6.72 (d, J = 3.4 Hz, 1H, C<u>H</u>OH), 6.83-6.85 (d, J = 8.6 Hz, 1H, $H_{p\text{-}ph}$), 6.97-7.00 (d, J = 8.6 Hz, 1H, $H_{m\text{-}ph}$), 7.51 (s, 1H, $H_{o\text{-}ph}$), 9.12-9.22 (m, 7H, $H_{\beta\text{-}pyrrole}$); UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 233 nm (4.48), 301 (4.20), 345 (3.89), 427 (5.04), 551 (3.98), 593 (3.16)-MS (40 eV); *m/z* (%): 812 (3) [M^+], 794 (12) [M^+-H_2O], 643 (41) [M^+-$C_9H_{11}O_3$]; [$C_{49}H_{62}N_4O_3Ni$, 813.74 g mol^{-1}]: anal. calcd. C 72.32, H 7.67, N 6.88; found C 72.16, H 7.55, N 6.34.

{2-Benzyl-5,10,15,20-tetrakis(1-methylethenyl)porphyrinato}nickel(II) **(17).** Prepared using the general method given above, but with 540 mg of porphyrin **11**. Yield: 400 mg (0.641 mmol, 76 %) red crystals from CH_2Cl_2/MeOH; m. p. 110-115 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.98-2.01 (d, J = 6.9 Hz, 6H, $CH(C\underline{H}_3)_2$), 2.14-2.18 (2x d, J = 7.0 Hz, 12H, $CH(C\underline{H}_3)_2$), 2.40 (s, 3H, $CH_2{=}CC\underline{H}_3$), 4.51-4.62 (sext, J = 7.4 Hz, 1H, $C\underline{H}(CH_3)_2$), 4.69-4.83 (sext, 2H, $C\underline{H}(CH_3)_2$), 5.13 (m, 2H, $C\underline{H}_2{=}CCH_3$), 5.73 (s, 1H, $C\underline{H}_2C_6H_5$), 6.02 (s, 1H, $C\underline{H}_2C_6H_5$), 7.28-7.7.38 (m, 2H, $H_{o\text{-}ph}$), 7.40-7.45 (m, 3H, $H_{m,p\text{-}ph}$), 8.66 (s, 1H, $H_{\beta\text{-}pyrrole}$), 9.10-9.12 (d, J = 5.2 Hz, 1H, $H_{\beta\text{-}pyrrole}$), 9.17-9.19 (d, J = 5.2 Hz, 1H, $H_{\beta\text{-}pyrrole}$), 9.22-9.27 (m, 4H, $H_{\beta\text{-}pyrrole}$); UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 241 nm (4.24), 287 (4.15), 338 (4.11) 423 (4.93), 546 (4.01), 580 (3.71); MS (40 eV); *m/z* (%): 622 (25) [M^+], 531 (100) [M^+-C_7H_7], 430 (6) [M^+-C_7H_7-7xCH_3]; HRMS [$C_{39}H_{40}N_4Ni$]: calcd. 622.2606, found 622.2653.

2-(Penten-1-yl)-5,10,15,20-tetrakis(1-ethylpropyl)porphyrin **(18).** Prepared using the general method given above. As the hydroxy compound **12** readily reacts even with traces of acid, it was immediately treated with TFA and the yield is given with respect to the starting formylporphyrin. Yield: 60 mg (0.084 mmol, 28 %) red-purple crystals from CH_2Cl_2/MeOH; m. p. > 300 °C; ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ = 0.65-0.71 (t, J = 7.3 Hz, 6H, $CH(CH_2C\underline{H}_3)_2$), 0.83-0.90 (m, 21H, $CH{=}CHCH_2CH_2C\underline{H}_3$, $CH(CH_2C\underline{H}_3)_2$), 1.08-1.14 (t, J = 7.31 Hz, 2H, $CH{=}CHCH_2C\underline{H}_2CH_3$), 1.68-1.79 (sext, J = 7.0 Hz, 2H, $CH{=}CHC\underline{H}_2CH_2CH_3$), 2.46-2.66 (m, 16H, $CH(C\underline{H}_2CH_3)_2$), 4.02-4.14 (m, 3H, $C\underline{H}(CH_2CH_3)_2$), 4.19-4.28 (quint, J = 6.88 Hz, 1H, $C\underline{H}(CH_2CH_3)_2$), 6.30-6.42 (td, J_{trans} = 15.5 Hz, J = 7.31 Hz, 1H, $CH{=}C\underline{H}CH_2CH_2CH_3$), 7.56-7.62 (d, J_{trans} = 15.5 Hz, 1H, $C\underline{H}{=}CHCH_2CH_2CH_3$), 8.96 (s, 1H, $H_{\beta\text{-}pyrrole}$), 9.10-9.22 (m, 6H, $H_{\beta\text{-}pyrrole}$); UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 236 nm (4.26), 316 (4.11), 341 (4.13), 428 (4.96), 552 (4.03), 586 (3.7); MS (40 eV); *m/z* (%): 714 (100) [M^+], 685 (41) [M^+-C_2H_5], 643 (9) [M^+ C_5H_{11}]; HRMS [$C_{45}H_{60}N_4Ni$]: calcd. 714.41715, found 714.4129.

{2-(5-Bromo-2-methoxyphenyl)methyl-5,10,15-tris(1-ethylpropyl)-20-(1-ethenylpropyl)-porphyrinato}nickel(II) **(19)**: Prepared using the general method given above. See remarks for **18**. Yield: 60 mg (0.071 mmol, 24 %) red-purple crystals from CH_2Cl_2/MeOH; m. p. > 300 °C; ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ = 0.48-0.51 (t, J = 7.5 Hz, 3H, $CH(CH_2CH_3)_2$), 0.73-1.03 (m, 18H, $CH(CH_2CH_3)_2$), 2.01-2.08 (sext, J = 7.26 Hz, 1H, $CH(CH_2CH_3)_2$), 2.13-2.14 (d, J = 6.78 Hz, 3H, $CH(CH_2CH_3)_2$), 2.34-2.57 (m, 12H, $CH(CH_2CH_3)_2$), 2.84-2.92 (sext, 1H, $CH(CH_2CH_3)_2$), 3.83 (s, 3H, OCH_3), 3.96-4.02 (quint, J = 7.4 Hz, 1H, $CH(CH_2CH_3)_2$), 4.14-4.20 (quint, J = 7.5 Hz, 2H, $CH(CH_2CH_3)_2$), 4.79-4.82 (d, J = 16.9 Hz, 1H, CH_2) 5.03-5.06 (d, J = 16.9 Hz, 1H, CH_2) 6.58-6.62 (quart, J = 6.6 Hz, 1H, CH-H3), 6.92-6.94 (d, J = 8.9 Hz, 1H, $H_{o\text{-}ph}$), 7.47-7.49 (m, 2H, $H_{m,p\text{-}ph}$), 8.57 (s, 1H, $H_{\beta\text{-}pyrrole}$), 9.05-9.06 (d, J = 4.9 Hz, 1H, $H_{\beta\text{-}pyrrole}$), 9.16-9.17 (d, J = 5.1 Hz, 1H, $H_{\beta\text{-}pyrrole}$), 9.19-9.20 (d, J = 5.1 Hz, 1H, $H_{\beta\text{-}pyrrole}$), 9.22-9.25 (m, 3H, $H_{\beta\text{-}pyrrole}$) UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 232 nm (4.12), 286 (3.73), 339 (3.68), 423 (4.93), 546 (3.73), 584 (2.29); MS (40 eV); *m/z* (%): 844 (18) [M^+],

815 (4) [M^+-CHO], 764 (2) [M^+-Br], 643 (41) [M^+-Br-C_8H_9O]; HRMS [$C_{48}H_{57}N_4ONiBr$]: calcd. 842.30692, found 842.30237.

{2-(2,2-Diphenylethenyl)-5,10,15,20-tetrakis(1-ethylpropyl)porphyrinato}nickel(II) **(20)**: Prepared using the general method given above. See remarks for **18**. Yield: 35 mg (0.042 mmol, 14 %) red-purple crystals from CH_2Cl_2/MeOH; m. p. > 300 °C; ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ = 0.46-0.52 (t, J = 6.9 Hz, 6H, $CH(CH_2CH_3)_2$), 0.61-0.67 (t, J = 7.3 Hz, 6H, $CH(CH_2C\underline{H}_3)_2$), 0.87-0.93 (t, J = 6.9 Hz, 6H, $CH(CH_2C\underline{H}_3)_2$), 0.92-0.99 (t, J = 6.9 Hz, 6H, $CH(CH_2C\underline{H}_3)_2$), 2.09-2.21 (quint, J = 7.3 Hz, 4H, $CH(C\underline{H}_2CH_3)_2$), 2.49-2.69 (m, 12H, $CH(C\underline{H}_2CH_3)_2$), 3.78-3.87 (quint, J = 7.5 Hz, 1H, $C\underline{H}(CH_2CH_3)_2$, 4.06-4.21 (m, 2H, $C\underline{H}(CH_2CH_3)_2$), 4.41-4.49 (quint, J = 6.9 Hz, 1H, $C\underline{H}(CH_2CH_3)_2$), 7.30-7.32 (m, 4H, $H_{m\text{-}ph}$), 7.43-7.49 (m, 4H, $H_{o\text{-}ph}$), 7.57-7.59 (d, J = 6.9 Hz,2H, $H_{p\text{-}ph}$), 8.15 (s, 1H, $CH{=}C(C_6H_5)_2$), 8.56 (s, 1H, $H_{\beta\text{-}pyrrole}$), 9.06-9.08 (d, J = 5.2 Hz, 1H, $H_{\beta\text{-}pyrrole}$), 9.15-9.17 (d, J = 5.2 Hz, 4H, $H_{\beta\text{-}pyrrole}$), 9.25-9.27 (d, J = 5.2 Hz, 1H, $H_{\beta\text{-}pyrrolee}$); UV/vis ($CH_2Cl_2$): λ_{max} (lg ε) = 231 nm (4.42), 316 (3.98), 350 (3.88), 432 (4.89), 555 (3.86) 593 (3.37); MS (40 eV); *m/z* (%): 824 (20) [M^+], 795 (7) [M^+-C_2H_5], 754 (10) [M^+-C_5H10]; HRMS [$C_{54}H_{62}N_4Ni$]: calcd. 824.43279, found 824.43634.

2-Vinyl-5,10,15,20-tetrakis(1-ethylpropyl)porphyrin **(22)**: Porphyrin **1** (0.3 mmol, 200 mg) was dissolved under Ar in 30 ml THF. After addition of 1.2 mmol (1.2 ml of a 1M-solution in n-hexane) trimethylsilyl methylmagnesium chloride the reaction mixture was stirred for 20 min at 50 °C. After addition of 1 ml water the solution was filtered through alumina and the solvent evaporated. The residue was dissolved in 50 ml methylene chloride and stirred with a few drops of TFA. Final work-up was as given in the general procedure. Yield: 0.16 g (0.237 mmol, 80 %) red-purple crystals from CH_2Cl_2/MeOH; m. p. 283-285 °C; ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ = 0.77-0.82 (t, J = 7.0 Hz, 6H, $CH(CH_2C\underline{H}_3)_2$), 0.95-1.03 (m, 18H, $CH(CH_2C\underline{H}_3)_2$), 2.58-2.79 (m, 16H, $CH(C\underline{H}_2CH_3)_2$), 4.15-4.35 (m, 4H, $C\underline{H}(CH_2CH_3)_2$), 5.71-5.76 (dd, J_{cis} = 10.8 Hz, J_{gem} = 1.7 Hz, 1H, $CH{=}C\underline{H}_2$), 6.05-6.12 (dd, J_{trans} = 16.8 Hz, J_{gem} = 2.3Hz, 1H, $CH{=}C\underline{H}_2$), 8.04-8.15 (dd, J_{cis} = 10.3 Hz, J_{trans} = 16.9 Hz, 1H, $C\underline{H}{=}CH_2$), 9.20 (s, 1H, $H_{\beta\text{-}pyrrole}$), 9.23-9.30 (m, 6H, $H_{\beta\text{-}pyrrole}$); UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 231 nm (4.20), 312 (3.83), 343 (3.84), 427 (4.95), 553 (3.97), 594 (2.5); MS (40 eV); *m/z* (%): 672 (100) [M^+], 643 (68) [M^+-C_2H_5], 601 (45) [M^+ C_5H_{11}]; HRM [$C_{42}H_{54}N_4Ni$]: calcd. 672.37019, found 672.37433.

Bis-2,6-{[5,10,15-tris(1-ethylpropyl)-20-(1-ethenylpropyl)porphyrinato]nickel(II)}-4-bromoanisole **(23)**: Prepared using the general method given above. See remarks for **18**. Yield: 30 mg (0.019 mol, 14 %) red-purple crystals from CH_2Cl_2/MeOH; m. p. > 300 °C; ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ = 0.55-0.61 (t, J = 7.3 Hz, 6H, $CH_3CH{=}C\text{-}CH_2C\underline{H}_3$), 0.80-0.95 (m, 36H, $CH(CH_2C\underline{H}_3)_2$), 2.12-2.21 (m, 2H, $CH_3CH{=}C\text{-}C\underline{H}_2CH_3$), 2.28-2.31 (d, J = 6.9 Hz, 6H, $C\underline{H}_3CH{=}C\text{-}CH_2CH_3$), 2.30-2.65 (m, 24H, $CH(C\underline{H}_2CH_3)_2$), 2.98-3.01

(m, 2H, CH_3CH=C-C$\underline{H}_2CH_3$), 3.87 (s, 3H, OCH_3), 4.09-4.23 (m, 6H, C$\underline{H}$(CH_2CH_3)$_2$), 4.91-5.01 (dd, J = 17.2 Hz, J = 6.9 Hz, 2H, C$\underline{H}_2C_6H_5$), 5.39-5.47 (d, J = 17.2 Hz, 2H, C$\underline{H}_2C_6H_5$), 6.73-6.76 (m, 2H, $CH_3C\underline{H}$=C-CH_2CH_3), 7.64 (s, 2H, H_{ph}), 8.81 (s, 2H, $H_{\beta\text{-pyrrole}}$), 9.09-9.12 (d, J = 4.3 Hz, 2H, $H_{\beta\text{-pyrrole}}$), 9.19-9.26 (m, 10H, $H_{\beta\text{-pyrrole}}$); UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 341 nm (4.45), 425 (5.49), 546 (4.43), 589 (4.32); MS (40 eV); *m/z* (%): 1500 (2) [M^+], 1471 (0.5) [M^+-C_2H_5], 1431 (1) [M^+-C_5H_{11}], 643 (100) [$C_{40}H_{48}N_4Ni$].

5-(1-Ethenylpropyl)-10,15,20-tris(1-ethylpropyl)-2-(2,5-dihydroxybenzyl)porphyrin **(24)**: Prepared using the method in literature, see above. Yield: 25 mg (0.035 mol, 11 %) red-purple crystals from CH_2Cl_2/MeOH; m. p. 95-100 °C; ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ =-1.49 (s, 2H, NH), -0.17 - -0.11 (t, J = 7.3 Hz, 3H, CH_3CH=C-$CH_2C\underline{H}_3$), 0.88-0.93 (m, 18H, CH($CH_2C\underline{H}_3$)$_2$), 1.43-1.46 (d, J = 6.9 Hz, 3H, $C\underline{H}_3CH$=C-CH_2CH_3), 2.26-2.92 (m, 14H, CH_3CH=C-C$\underline{H}_2CH_3$, CH(C$\underline{H}_2CH_3$)$_2$), 4.45-4.47 (m, 1H, C$\underline{H}_2C_6H_5$), 4.49-4.69 (m, 3H, C$\underline{H}$(CH_2CH_3)$_2$), 4.76-4.77 (m, 1H, C$\underline{H}_2C_6H_5$), 6.48-6.52 (m, 1H, $CH_3C\underline{H}$=C-CH_2CH_3), 6.91-7.00 (m, 3H, H_{ph}), 8.92 (s, 1H, $H_{\beta\text{-pyrrole}}$), 9.21-9.36 (m, 6H, $H_{\beta\text{-pyrrole}}$); UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 279 nm (3.17), 427 (3.99), 528 (2.62), 560 (2.38), 598 (2.19), 658 (1.63); MS (40 eV); *m/z* (%): 710 (64) [M^+], 682 (12) [M^+-C_2H_5], 638 (100) [M^+-C_4H_8O]; HRMS [$C_{47}H_{58}N_4O_2$]: calcd. 710.45598, found 710.45416.

2-Benzyl-5,10,15-tris(1-ethylpropyl)-20-(1-ethenylpropyl)porphyrin **(25)**: The synthesis followed the procedure given in the literature for the methylether cleavage of protected quinones.[10] Yield: 65 mg (0.096 mmol, 72 %) purple crystals from CH_2Cl_2/MeOH; m. p. > 300 °C; ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ =-2.50 (s, 2H, NH), 0.84-0.91 (t, J = 7.3 Hz, 9H, CH_3CH=C-$CH_2C\underline{H}_3$, CH($CH_2C\underline{H}_3$)$_2$), 0.91-0.99 (m, 12H, CH($CH_2C\underline{H}_3$)$_2$), 1.37-1.40 (d, J = 6.9 Hz, 3H, $C\underline{H}_3CH$=C-CH_2CH_3), 2.53-3.04 (m, 14H, CH(C$\underline{H}_2CH_3$)$_2$, CH_3CH=C-C$\underline{H}_2CH_3$), 4.70-4.95 (m, 1H, C$\underline{H}$(CH_2CH_3)$_2$), 4.87-4.96 (m, 2H, C$\underline{H}$(CH_2CH_3)$_2$), 5.14-5.21 (d, J = 17.2 Hz, 1H, C$\underline{H}_2C_6H_5$), 5.27-5.34 (d, J = 17.2 Hz, 1H, C$\underline{H}_2C_6H_5$), 6.43-6.51 (quart, J = 6.9 Hz, 1H, $CH_3C\underline{H}$=C-CH_2CH_3), 7.29-7.39 (m, 5H, H_{ph}), 8.99 (s, 1H, $H_{\beta\text{-pyrrole}}$), 9.15-9.17 (d, J = 5.2 Hz, 1H, $H_{\beta\text{-pyrrole}}$), 9.42-9.55 (m, 5H, $H_{\beta\text{-pyrrole}}$); UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 420 nm (5.44), 521 (4.28), 554 (4.09), 599 (3.93), 654 (3.93); MS (40 eV); *m/z* (%): 678 (38) [M^+], 649 (16) [M^+-C_2H_3], 607 (6) [M^+-C_5H_{11}], 587 (100) [M^+-C_7H_7]; HRMS [$C_{47}H_{58}N_4$]: calcd. 678.46615, found 678.46124.

Crystal structure determination of **1**.

X-ray quality crystals were grown by liquid diffusion from CH_2Cl_2/CH_3OH. The crystals were removed from solution and covered with a layer of Paraton N®. A suitable crystal was selected, attached to a glass fiber and immediately placed into the low-temperature nitrogen stream as described by Hope.[34] Intensity data were collected at 130 K with a Siemens R3m/V diffractometer utilizing graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). An absorption correction was applied using the program XABS2,[35] while extinction effects were disregarded. The structure was solved via a Patterson synthesis followed by structure

expansion. Refinements were carried out by full-matrix least-squares on $|F^2|$ using the program SHELXL-97.[36] Hydrogen atoms were included at calculated positions using a riding model. The structure exhibits crystallographically required disorder for the formyl group, which was refined with 50 % occupancy. The respective hydrogen atom was refined accordingly. Disorder was also observed for the several atoms of the meso substituents. The carbon atoms C105, C52 and C54 were refined as disordered over two split positions with equal occupancy. Hydrogen atoms were treated accordingly.

Complete details on the crystal structure investigations, including atomic coordinates, thermal parameters and complete bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK).

Crystal data: $C_{41}H_{52}N_4NiO$, crystal size 0.8 x 0.16 x 0.12 mm, FW = 675.58, monoclinic, space group C2/c, a = 14.983(10) Å, 21.730(12) Å, c = 12.965(8) Å, β = 120.47(4)°, V = 3638(4) $Å^3$, Z = 4, d_{calc} = 1.233 $Mg.m^{-3}$, μ = 0.570 mm^{-1}, T_{min} = 0.66, T_{max} = 0.94, θ_{max} = 27.49°, 4453 reflection collected, 4181 independent reflections (R_{int} = 0.0421), 2788 reflections with $I > 2.0\sigma(I)$, 255 parameter, Δ/ρ_{max} = 1.004 e $Å^{-3}$, R1 [I > 2s(I)] = 0.0753, R1 (all data) = 0.1147, wR2 (all data) = 0.2320, S = 1.019.

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