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Exploration of *meso*-Substituted Formylporphyrins and Their Grignard and Wittig Reactions

Katja Dahms,[a] Mathias O. Senge,*[a] and M. Bakri Bakar[a]

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Formylporphyrins were prepared by using either the 1,3-dithian-2-yl residue as a precursor for the CHO group or by the Vilsmeier reaction. Two synthetic routes for the introduction of the 1,2-dithian-2-yl group were explored. Furthermore, reactions of the 1,3,5-trithian-2-yl group with porphyrins were examined as well as spirobisdithiane derivatives as precursors for the ultimate assembly of porphyrin spirobisdithanyl-linked bioconjugates. The obtained formylporphyrins were reacted with organomagnesium or organophosphorus compounds. A series of hydroxyporphyrins resulting from the Grignard reaction of 5,15-substituted porphyrins were synthesised in high yields. Several porphyrins with unsaturated residues introduced by the Wittig reaction were obtained in moderate yields. The less sterically hindered 5,15-substituted porphyrins show increased reactivity and give higher yields; their reaction products are higher in stability relative to other porphyrin systems.

Introduction

Porphyrins are an essential class of natural compounds that are ubiquitous in nature. They play an important role in biological processes such as oxygen transport, electron transfer and photosynthesis.[1] Their properties also make them useful in applications ranging from catalysis,[2] drug delivery,[3] nonlinear optics,[4] photodynamic therapy,[5] and the fundamental studies and generation of novel macrocycles.[6] As a result of these properties, they are some of the most important fine chemicals that are available in industry, and they are utilised in an ever-expanding array of applications. Hence, methods to improve the synthesis of functionalised porphyrins are of fundamental importance. One functional group, which allows asymmetric modification and is widely used in porphyrin chemistry, is the formyl group.[7] The formyl fragment can be used to build up alkenyl and alkyl chains, cyano groups, carbonic acids, alcohols and ethers, or they can be use to construct bisporphyrins. These compounds can then be used for further reactions.

Formylporphyrins have been explored extensively in general.[8,9] However, few reactions using *meso*-substituted formylporphyrins for the purpose of functionalising the porphyrins have been reported. Arnold et al. reported the reaction of 2,3,7,8,12,13,17,18-octaethyl-5-formylporphyrin with methylmagnesium iodide to yield the *meso*-(1-hydroxyethyl) derivative only as a crude product as decomposition to the *meso*-vinyl compound occurred rapidly.[10] Smith and co-workers continued these studies by using several Grignard reagents such as methylmagnesium bromide, ethylmagnesium bromide and benzylmagnesium chloride and an acid.[11] Surprisingly, they did not obtain the expected carbinol compounds but observed direct *meso* alkylation at the 15-position opposite to the formyl group. We earlier studied reactions of β-substituted formylporphyrins with organometallic reagents and found comparable yields and products for reactions with RLi and RMgX.[12] For β-substituted porphyrins, the Wittig reaction has been investigated in some detail. Callot reported the reactions of (2,3,7,8,12,13,17,18-octaethyl-5-formylporphyrinato)nickel(II) as well as (2-formyl-5,10,15,20-tetraphenylporphyrinato)nickel(II) with several Wittig reagents in yields ranging from 29 to 93%.[13a] Further Wittig condensations were reported by Arnold et al. who prepared various *meso*-vinyl derivatives of nickel porphyrins in yields ranging from 44 to 70%.[13b] Similarly, McMurry coupling reactions have been investigated in detail.[13c]

The porphyrins studied so far in these reactions possess either *meso* or β substituents adjacent to the formyl group that can cause *peri* interactions, which would result in deformation of the macrocycle[14] or facilitate complex rearrangement reactions.[9,15] To further develop the use of these core intermediates in porphyrin chemistry, we decided to investigate the synthesis of β-unsubstituted *meso*-formylporphyrins and their reactions with Grignard and Wittig reagents. In light of the increasing use of asymmetrically substituted porphyrins and the need to develop syntheses

[a] School of Chemistry, SFI Tetrapyrrole Laboratory, Trinity College Dublin,
Dublin 2, Ireland
Fax: +353-1-8968537
E-mail: sengem@tcd.ie

for multichromophore nanomaterials,[16] we chose 5,15-diaryl- and alkylporphyrins as starting material, as they can be prepared in high yields and purities.[17]

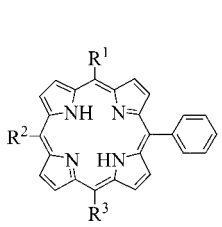
Results and Discussion

Dithian-2-ylporphyrins

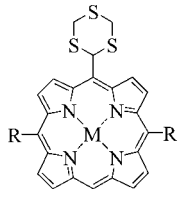
An effective method for the C–C coupling of different residues with the porphyrin moiety is the use of organolithium reagents.[18] This technique can be applied for a number of different porphyrins with various residues because of the mild reaction conditions. It can be utilised both for free-base porphyrins and metalloporphyrins, and the reaction typically gives products in good-to-excellent yields. Another approach is the reaction of an organolithium compound with an organosulfur compound. For example, the reaction of *n*-butyllithium with 1,3-dithiane at –30 °C in THF under an atmosphere of argon gives the classical umpolung synthon for a formyl group, 1,3-dithian-2-yl, which was developed by Seebach and Corey.[19] This reaction allows entry into formylporphyrins under nucleophilic conditions.[20,21]

Investigation of this reaction was carried out with 5,15-disubstituted porphyrins **1a**–**f** at –78 °C in THF under an atmosphere of argon. The substitution reaction was promoted by TMEDA, quenched with water and oxidised by DDQ to the corresponding mono-1,3-dithian-2-yl-substituted porphyrins **2a**–**f** in 4–53% yield (Scheme 1). Ni^{II} porphyrins generally showed higher yields than the free-base porphyrins, and because of the steric hindrance of the bulky dithian-2-yl residue, the yields are comparable to those of *i*PrLi or *s*BuLi reactions.[22a] Subsequent treatment with DDQ and $BF_3{\cdot}OEt_2$ led to deprotection of **2** to the respective formylporphyrins **3a**–**c** in varying yields ranging from 39–94%.

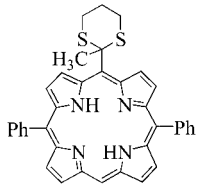
To test the reactivity with more asymmetrical porphyrins, porphyrin **4** was prepared by standard 2+2 condensation and then treated with 1,3-dithian-2-yl; workup of this unoptimised reaction yielded a small amount of the deprotected formyl porphyrin **5a**. We also attempted to trap the in situ generated "porphyrin anion" with electrophiles, akin to the reactions with standard RLi reagents.[22b] Reaction of free base **1a** with 1,3-dithian-2-yllithium and pentyl iodide followed by standard workup yielded the double substituted formylporphyrin **5b** in low yield (11%). These reactions already indicated that the stability of the dithian-2-yl residue is limited under the reaction conditions necessary for porphyrin substitution.



$R^1 = R^3 = H$, R^2 = Hexyl (**4**)
R^1 = CHO, R^2 = Hexyl, R^3 = H (**5a**)
R^1 = CHO, R^2 = Ph, R^3 = Pentyl (**5b**)



R = Ph, M = 2H (**6a**)
R = Ph, M = Ni^{II} (**6b**)
R = 3-$MeOC_6H_4$, M = Ni^{II} (**6c**)
R = Hexyl, M = Ni^{II} (**6d**)



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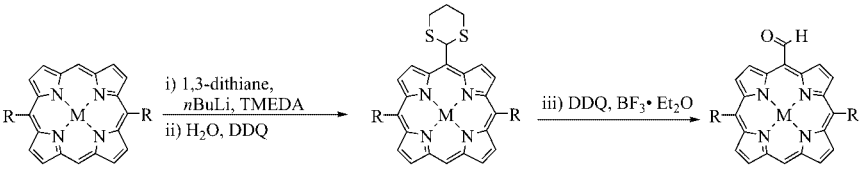
The 1,3,5-trithian-2-yl group could be used in a similar manner, and the reaction of the lithio derivative, the 1,3,5-trithian-2-ylporphyrins **6a**–**d** could be obtained from the respective free base and nickel(II) porphyrins in moderate yields from 18–38%. The yields were lower than those of the related dithian-2-yl reactions. Reaction with the sterically more hindered 2-methyl-1,3-dithiane to yield putative compound **7** was problematic. Spectroscopic evidence indicates the formation of β adducts in low yields.[23]

The initial success in using the 1,3-dithiane residue for porphyrin substitution reactions prompted us to investigate the utility of spirobisdithiane derivatives[24] for the ultimate construction of porphyrin spirobisdithanyl-linked bioconjugates. Such systems would have significant potential in biomedical applications as a drug delivery system owing to the cleavable spirobisdithiane linker. Spirobisdithiane **8** was prepared as described by Kutateladze et al.,[24a] and its reaction with *n*-butyllithium and DMF gave bisaldehyde **9** in 56% yield. As outlined in Scheme 2, the reaction of disub-



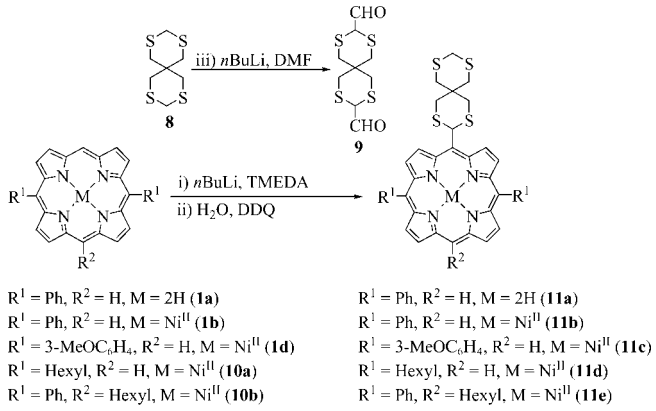
R = Ph, M = 2H (**1a**)
R = Ph, M = Ni^{II} (**1b**)
R = 3-$MeOC_6H_4$, M = 2H (**1c**)
R = 3-$MeOC_6H_4$, M = Ni^{II} (**1d**)
R = *i*Bu, M = 2H (**1e**)
R = *i*Bu, M = Ni^{II} (**1f**)

R = Ph, M = 2H (**2a**, 47%)
R = Ph, M = Ni^{II} (**2b**, 53%)
R = 3-$MeOC_6H_4$, M = 2H (**2c**, 10%)
R = 3-$MeOC_6H_4$, M = Ni^{II} (**2d**, 49%)
R = *i*Bu, M = 2H (**2e**, 4%)
R = *i*Bu, M = Ni^{II} (**2f**, 53%)

R = Ph, M = 2H (**3a**, 44%)
R = Ph, M = Ni^{II} (**3b**, 39%)
R = 3-$MeOC_6H_4$, M = Ni^{II} (**3c**, 94%)

Scheme 1. Formylation of porphyrins by the 1,3-dithian-2-yl synthon.

stituted porphyrins with the in situ generated spirobisdithianyllithium gave the respective spirobisdithianylporphyrins **11a**–**e** in yields ranging from 19 to 40%.

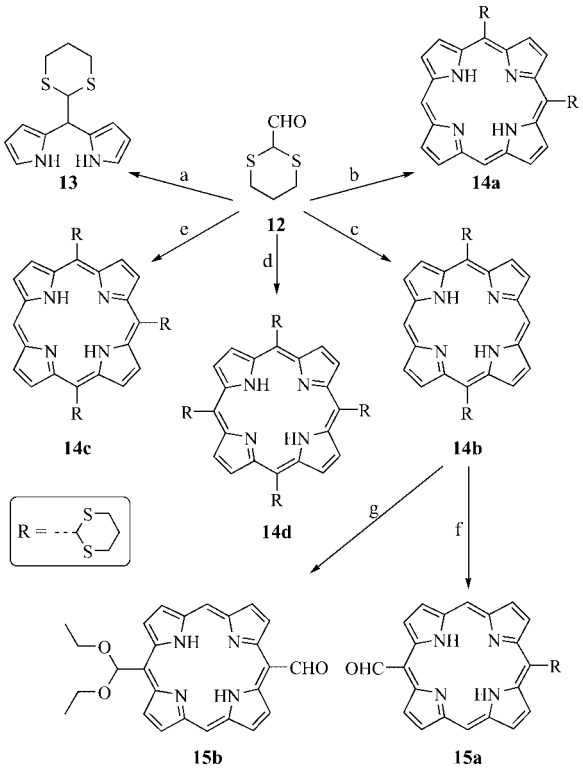


Scheme 2. Synthesis of spirobisdithiane derivatives.

Unfortunately all attempts to use the spirobisdithianyl dianion for double substitution reactions failed or gave alternative products. For example, reaction of **1a** with the dilithio derivative of **8** gave 71% of the respective 5-butyl-substituted porphyrin and 6% of **11b**.

More successful were the attempts to use the 2-formyl-1,3-dithiane **12**[25] in classic porphyrin condensation reactions (Scheme 3). Reaction with pyrrole generated the 1,3-dithian-2-yldipyrromethane **13** as a key building block in almost quantitative yield (96%). Depending on the reaction conditions, equivalents of reactants and acid, porphyrins **14a**–**d** with two to four *meso*-dithian-2-yl residues could be prepared in low-to-moderate yields that are typical for porphyrin condensation reactions. Like all dithian-2-yl porphyrins, this series showed that the introduction of each dithian-2-yl residue shifts the absorption maxima bathochromically by about 10 nm. All dithian-2-yl porphyrins exhibited very broad signals in the ^{1}H NMR spectra for the β protons flanking the dithian-2-yl residues. Variable temperature NMR showed that these signal became sharper (ca. 58 °C) with increasing temperature, which indicates that intramolecular hydrogen bonds between the β protons and the sulfur atoms prevent the free rotation of the dithian-2-yl residues at lower temperatures.[26]

Nevertheless, the oxidative dethioacetylation proved to be difficult owing to the low stability and solubility of the dithian-2-ylporphyrins with more then two dithian-2-yl residues or with dithian-2-yl residues in a 5,10 regiochemical arrangement. Porphyrins with one or two dithian-2-yl residues in a 5,15 orientation are stable, the 5,10 derivative **14a** and the tri- **14c** and tetrasubstituted porphyrins **14d** were increasingly unstable especially towards traces of acid. The latter had to be stored under an atmosphere of argon at –20 °C. The instability of these compounds is a result of both increased steric strain in such systems[27] and the reactivity of the dithian-2-yl residues. For example, formation of **14c** under the conditions given can only be explained



Scheme 3. Condensation reactions involving dithian-2-carbaldehyde. Conditions: (a) pyrrole, $BF_3{\cdot}OEt_2$, room temp., 40 min, then NaOH, 96%. (b) CH_2Cl_2, tripyrrane, pyrrole, 45 min, room temp.; then TFA, room temp., 16 h; then DDQ; then NEt_3, 3%. (c) CH_2Cl_2, dipyrromethane, TFA, 14 h, room temp.; then DDQ, 10 min, reflux, 16%. (d) CH_2Cl_2, pyrrole, $BF_3{\cdot}OEt_2$, 1 h, room temp.; then NEt_3, DDQ, 4 min, 15%. (e) CH_2Cl_2, pyrrole, $BF_3{\cdot}OEt_2$, 1 h, room temp.; then excess DDQ, 1 h, 46%. (f) $CHCl_3$, 8 equiv. bis(trifluoroacetoxy)iodobenzene (BTIB), 45 °C, 30 min, 62%. (g) $CHCl_3$, 4 equiv. BTIB, room temp., 30 min, 30%.

through the initial formation of the porphyrinogen related to **14d** followed by acid-catalysed cleavage of one dithian-2-yl residue and subsequent oxidation to the porphyrin.[28,29]

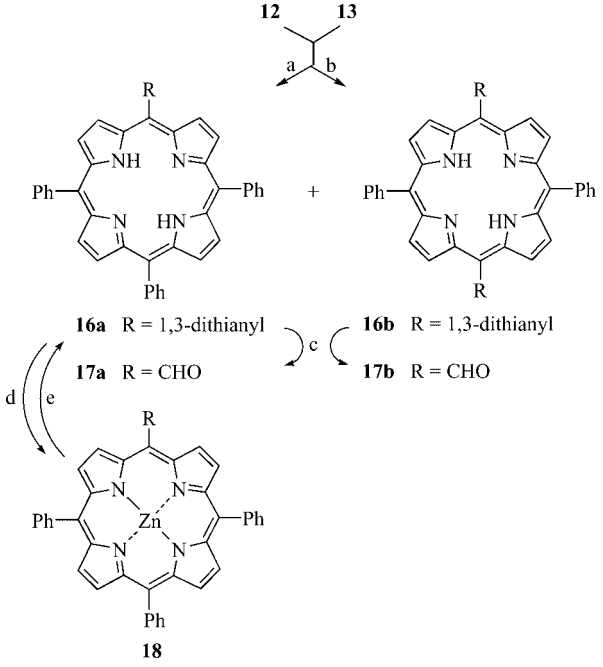
Despite testing many different reagents for the dethioacetylation, only porphyrins with one or two dithian-2-yl residues could be converted into the formylporphyrins with ease. By using bis(trifluoroacetoxy)iodobenzene (BTIB), porphyrin **14b** was converted into either the mono-formylporphyrin **15a**[30] or the acetal **15b**.[31] Porphyrins such as **14c** or **14d** always resulted in the formation of complex mixtures with partially deprotected groups and the loss of individual *meso* substituents. Thus, our initial hopes to use the dithian-2-yl group as a synthon for polyformylporphyrins, which cannot be prepared by Vilsmeier formylation because of the deactivation of the aromatic system, have not yet been realised. Nevertheless, this group allows the preparation of free-base formylporphyrins without prior activation through conversion to the copper(II) or nickel(II) complex, as is required for classic porphyrin formylation reactions.

To increase the stability and solubility of the dithian-2-ylporphyrins, we attempted to use **12** or **13** in mixed condensation reactions.[32] Indeed, either 2-formyl-1,3-dithiane **12** and 5-phenyldipyrromethane or 1,3-dithian-2-yldipyrro-

methane **13** and benzaldehyde could be used as starting materials (Scheme 4). Depending on the reaction conditions, porphyrins **16a** and **16b** could be isolated in yields of 2–4 and 2–3%, respectively. The appearance of compound **16a** is due to scrambling during the condensation process.[33] Porphyrins **16a** and **16b** were both converted into the respective formylporphyrins **17a** and **17b** in quantitative yield.

Dithian-2-ylporphyrins such as **16** are stable enough to withstand metallation–demetallation sequences. For example, **16a** could be converted into zinc(II) porphyrin **18** under standard metallation conditions[34] with zinc acetate and methanol in dichloromethane in 53% yield. Demetallation was found to be possible, although problematic. For example, nickel(II) porphyrin **2b** could be demetallated with BBr_3, albeit in 24% yield only.

An exemplary molecular structure of a dithian-2-ylporphyrin is given in Figure 1. Single-crystal X-ray structure determination of **16b** shows that the S–S vector in each dithian-2-yl residue is orthogonal to the mean plane of the macrocycle (∠ 91.3°). The contact between the sulfur atoms and the neighbouring β hydrogen atoms is 2.971 Å. Although overall planar, the macrocycle exhibits a minor *wav* distortion and some core elongation.[14e–14g]



Scheme 4. *meso*-Substituted dithian-2-ylporphyrins. Conditions: (a) CH_2Cl_2, 5-phenyldipyrromethane, cat. TFA, 16 h, room temp.; then DDQ, 45 min, **16a** 3%, **16b** 2%. (b) CH_2Cl_2, benzaldehyde, cat. TFA, 16 h, room temp., then DDQ, 45 min, **16a** 2%, **16b** 4%. (c) CH_2Cl_2, DDQ, $BF_3{\cdot}OEt_2$, room temp., 10 min, 97%. (d) CH_2Cl_2, ZnOAc, CH_3OH, room temp., 30 min, 53%. (e) H_2SO_4.

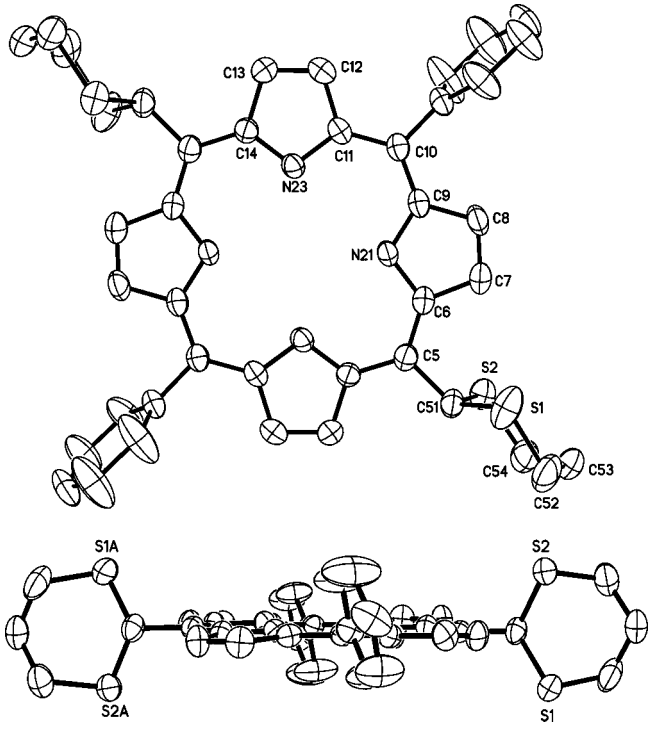
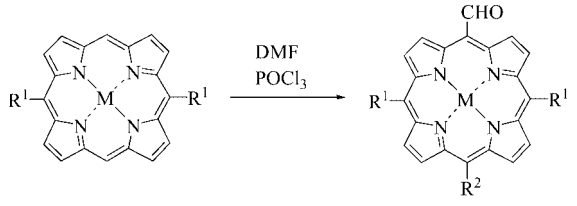


Figure 1. Top and side view of the molecular structure of **16b** in the crystal. Thermal ellipsoids are drawn for 50% occupancy; hydrogen atoms are omitted for clarity.

Vilsmeier Formylation

Whereas the dithian-2-yl synthon offered some new possibilities for the synthesis of formylporphyrins, the classic Vilsmeier formylation still has some benefits due to the unproblematic experimental procedure. To gain more material for subsequent reactivity studies, we thus prepared a variety of formyl derivatives of 5,15-disubstituted porphyrins. Metallation was achieved by standard conditions with nickel(II) acetate in DMF under reflux conditions and copper(II) acetate in dichloromethane at room temp. respectively.[34] The experimental procedure used for the Vilsmeier formylation was adapted from the one developed by Johnson and Oldfield.[35] The yield was between 13 (for **20a**) and 97% (for **20h**), as summarised in Scheme 5. The low yield



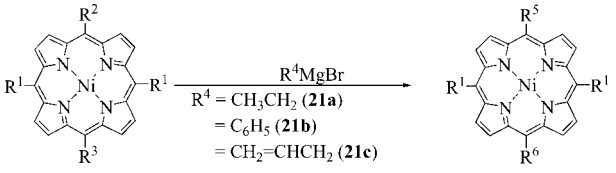
Compound	M	R^1	R^2	Yield [%]
3b	Ni^{II}	Ph	H	59
20a	Cu^{II}	3-$MeOC_6H_4$	H	13
20b	Cu^{II}	3-$MeOC_6H_4$	CHO	20
20c	Ni^{II}	3-$MeOC_6H_4$	CHO	48
20d	Ni^{II}	Hexyl	H	60
20e	Ni^{II}	Hexyl	CHO	42
20f	Cu^{II}	Hexyl	CHO	18
20g	Cu^{II}	*i*Bu	H	47
20h	Cu^{II}	1-Ethylpropyl	H	97

Scheme 5. Vilsmeier formylations. Conditions: 1,2-dichloroethane, 90 °C, 3–16 h.

for compound **20a** was a result of problems in separating the mono- from the diformylated porphyrin. Compounds **3b**, **20d** and **20e** were used as starting material for further reactions.

Grignard and Wittig Reactions

One reaction type that can be carried out with the formyl group on the porphyrin is the Grignard reaction.[10,36] Formylporphyrins **3b**, **20d** and **20e** were treated with ethylmagnesium bromide (**21a**), phenylmagnesium bromide (**21b**) and allylmagnesium bromide (**21c**) to obtain compounds **22a**–**h**. The reactions were performed in dry THF under an atmosphere of argon at room temp. for the reaction between porphyrins and phenyl- and allylmagnesium bromide and at 75 °C for the reaction with ethylmagnesium bromide as reported by Arnold et al.[10] An excess amount of the Grignard reagent (10 equiv.) was used for monoformylated porphyrins **3b** and **20d** and 20 equiv. for the reaction with (5,15-diformyl-10,20-dihexylporphyrinato)nickel(II) **20e**. The yields are given in Scheme 6.



3b / 20d,e **22a–h**

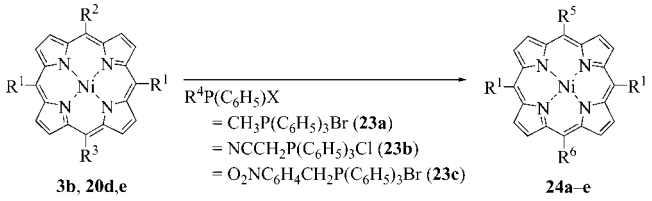
22	R^1	R^2	R^3	R^5	R^6	Yield [%]
a	Ph	CHO	H	$CH(OH)(C_2H_5)$	H	68
b	Hexyl	CHO	H	$CH(OH)(C_2H_5)$	H	54
c	Hexyl	CHO	CHO	$CH(OH)(C_2H_5)$	$CH(OH)(C_2H_5)$	35
d	Ph	CHO	H	$CH(OH)(C_6H_5)$	H	93
e	Hexyl	CHO	H	$CH(OH)(C_6H_5)$	H	85
f	Hexyl	CHO	CHO	$CH(OH)(C_6H_5)$	$CH(OH)(C_6H_5)$	68
g	Ph	CHO	H	$CH(OH)(CH_2CH=CH_2)$	H	80
h	Hexyl	CHO	CHO	$CH(OH)(CH_2CH=CH_2)$	$CH(OH)(CH_2CH=CH_2)$	9

Scheme 6. Grignard reactions.

Interestingly, when the diformylated porphyrin **20e** was treated with **21a** and **21c** the resulting (1-hydroxypropyl)- and (1-hydroxybut-3-enyl)porphyrins were found to be unstable. The disubstituted (1-hydroxypropyl)porphyrin **22c** could be isolated by column chromatography in 35% yield and (1-hydroxybut-3-enyl)porphyrin **22h** in 9% yield. Both porphyrins were characterised by ^{1}H NMR spectroscopy but no further characterisation could be accomplished because of the decomposition of the porphyrins. Similar problems were found by Arnold et al. for the reaction of *meso*-formyloctaethylporphyrin with methylmagnesium bromide and phenylmagnesium bromide.[10] In contrast, the products of the reactions of ethylmagnesium bromide or allylmagnesium bromide with the monoformylated porphyrins **3b** and **20d** or phenylmagnesium bromide with **3b**, **20d** or **20e** were found to be stable. Porphyrins **22a**,**b** and **22d**–**g** were synthesised in good yields, ranging from 68% for the disubstituted porphyrin up to 93% for **22d**. Though, Smith and coworkers observed the direct *meso* alkylation of zinc or metal-free 5-formyloctaethylporphyrin by using Grignard reagents. A regioselective attack at the *meso* position diametrically opposite to the formyl group of the porphyrin macrocycle was reported and the unexpected 5-formyl-15-alkylporphyrin was obtained.[11] No reaction with the formyl group was observed.

Compound **22g** resulting from the reaction of formylporphyrin **3b** with allylmagnesium bromide is particularly interesting as the starting material for further reactions involving the double bond, such as metathesis, to investigate the activating or deactivating influence of the adjacent hydroxy group.

An additional reaction type that can be performed on formylporphyrins is the Wittig reaction.[37] Reactions between methyltriphenylphosphonium bromide (**23a**), (cyanomethyl)triphenylphosphonium chloride (**23b**) and (4-nitrophenyl)triphenylphosphonium bromide (**23c**) and compounds **3b**, **20d** and **20e** were investigated (Scheme 7).



3b, 20d,e **24a–e**

24	R^1	R^2	R^3	R^5	R^6	Yield [%]
a	Ph	CHO	H	CH=CHCN	H	81
b	Hexyl	CHO	CHO	CH=CHCN	CH=CHCN	10
c	Hexyl	CHO	CHO	$CH=CH(C_6H_4NO_2)$	$CH=CH(C_6H_4NO_2)$	11
d	Hexyl	CHO	H	$CH=CH_2$	H	61
e	Hexyl	CHO	CHO	$CH=CH_2$	$CH=CH_2$	41

Scheme 7. Wittig reactions.

An excess of the phosphonium salt was suspended in dry THF and *n*-butyllithium was added dropwise at room temp. The suspension was stirred for 5 min to form the ylide in situ before adding the respective formylporphyrin. The best yield was achieved for compound **24a** with 81% after heating at reflux overnight. Moderate yields from 41 to 61% were obtained for the vinyl compounds. However, only 10% of compound **24b** and 11% of compound **24c** could be isolated mainly as a result of problems associated with the separation of the side products.

In comparison, Callot obtained the (5-vinyl-2,3,7,8,12,13,17,18-octaethylporphyrinato)nickel(II) for example in 27% yield. For reactions with different residues adjacent to the double bond he obtained yields from 69 to 93%.[13a] Likewise, Arnold et al. investigated different Wittig reactions of (5-formyloctaethylporphyrinato)nickel(II) and (5-formyletioporphyrinato)nickel(II).[13b] Various *meso*-vinyl derivatives of nickel porphyrins were prepared in yields ranging from 44% to 70%. Thus, the yields of Wittig reactions of *meso*-substituted porphyrins are comparable to the results for β-substituted porphyrins.

The expected products bearing unsaturated substituents can furthermore be applied as precursors for metathesis[38] or Diels–Alder reactions[39] and offer potential use for photodynamic therapy[17c,40] or in the field of nanoscience.[41] Cyanoethenylporphyrin **24a** is interesting for further hetero-Diels–Alder reactions.[42] Another synthetic approach for cyanoethenylporphyrins was reported by Locos and Arnold in 2006.[43] They described the Heck coupling of bromoporphyrins with acrylonitrile. The mono- as well as the disubstituted alkenylporphyrins were isolated as an inseparable mixture of the *cis* and *trans* isomers. In our case, by employing the Wittig reaction, cyanoethenylporphyrin **24a** was isolated as the *trans* isomer only in a very good yield of 81%.

Conclusions

Umpolung reactions were used to synthesise six 1,3-dithian-2-yl porphyrins **2a**–**f** in moderate yields. Porphyrins **2a**, **2b** and **2d** were deprotected to the corresponding formylporphyrins **3a**–**c**. This shows that this method offers a new pathway for the preparation of formylporphyrins in their free base form as well as metalloporphyrins under milder reaction conditions with yields comparable to the Vilsmeier reaction. Owing to the low stability of polydithianylporphyrins, access to *meso*-polyformylporphyrins could not be realised with the use of this method. Nonetheless, the Vilsmeier reaction is still the most common way for introducing the formyl group into the porphyrin moiety. Porphyrins **3b** and **20a**–**h** were synthesised by using this method.

To demonstrate the wide range of applications for the formyl group to yield functionalised porphyrins, studies of Grignard and Wittig reactions of 5,15-disubstituted porphyrins were performed. The yields of porphyrins **22a**–**f** and **24a**–**e** ranged from 54 to 93% and from 10 to 81%, respectively. These yields are much better then those from similar reactions with 5-formyl-2,3,7,8,12,13,17,18-octaethylporphyrins. Hence, the lower steric hindrance present in the 5,15-substituted porphyrins facilitates their reactivity and, as a result, the yields and stability of the resulting porphyrins.

Experimental Section

Instrumentation and General Considerations: ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DPX 400 (400.13 MHz for ^{1}H NMR; 100.61 MHz for ^{13}C NMR) and/or a Bruker AV 600 (600.13 MHz for ^{1}H NMR; 150.90 MHz for ^{13}C NMR). Chemical shifts are reported in ppm referenced to tetramethylsilane (δ = 0.00 ppm). High-resolution mass spectra and low-resolution mass spectra were recorded with Micromass/Waters Corp. USA Quattro *micro* LC–MS/MS and with a Finnigan SSQ 710 GC–MS, GC–TOF and ESI/APCI-Q-TOF$_{micro}$. UV/Vis measurements were performed with a Shimadzu Multispec-1501. Melting points were acquired with a Stuart SMP10 melting point apparatus and are uncorrected. Thin-layer chromatography (TLC) was performed on silica gel 60F$_{254}$ (Merck) precoated aluminium sheets. Chromatography on silica gel was carried out by using a forced flow of the indicated solvent system on either Fluka Silica Gel 60 (230–400 mesh) or Fluka Alox (basic). Tetrahydrofuran (THF) was distilled from sodium/benzophenone under an atmosphere of argon. All commercial chemicals were supplied by Aldrich and used without further purification. Other conditions were as described before.[44]

Synthesis of Dithian-2-ylporphyrins

General Procedure A: A dried out, septum-equipped Schlenk flask under an atmosphere of argon was charged with 1,3-dithiane (1.16, 9.64 mmol). The flask was evacuated under vacuum for 30 min, and freshly distilled THF (25 mL) was added. The solution was cooled to –40 °C, and *n*-butyllithium (2.5 M, 3.84 mL, 9.6 mmol) was added dropwise by syringe through the septum. The reaction mixture was stirred for 2 h at –30 to –40 °C. The solution of the organometallic compound was cooled to –78 °C and mixed with a suspension (–78 °C) of the porphyrin (0.45 mmol) in absolute THF (20 mL). After transfer of the porphyrin suspension, *N*,*N*,*N*,*N*-tetramethylethylenediamine (0.25 mL, 1.6 mmol) was added, and the reaction mixture turned dark brown. After stirring for 1 min, the cold bath was removed, and the reaction mixture was stirred for 15 min. Water (6 mL) was added by syringe, which resulted in an immediate colour change to dark green. The mixture was stirred for 15 min at room temp., followed by the addition of a solution of DDQ (0.6 g, ca. 0.75 mmol) in THF (10 mL), and the colour of the solution changed to purple. Stirring was continued for 15 min, followed by filtration of the reaction mixture through silica (200 mL) and washing with CH_2Cl_2. The eluted porphyrin fractions were evaporated to dryness and washed with *n*-hexane (2 × 10 mL). The residue was purified by column chromatography (silica, CH_2Cl_2/C_6H_{14}, 3:1), and the target compounds were obtained as the second fraction.

5-(1,3-Dithian-2-yl)-10,20-diphenylporphyrin (2a): Procedure A, yield: 120 mg (0.207 mmol, 47%) of purple crystals. M.p. 290 °C. R_f = 0.2 (CH_2Cl_2/C_6H_{14}, 3:1). ^{1}H NMR (250 MHz, $CDCl_3$, 20 °C): δ = –3.03 (br. s, 2 H, N*H*), 2.53 (m, 2 H, 5^4-CH_2), 3.31 (m, 2 H, S–CH_2), 3.63 (m, 2 H, S–CH_2), 7.78 (m, 6 H, Ar$_{o,p\text{-}H}$), 7.87 (s, 1 H, 5^1-C*H*), 8.21 (m, 4 H, Ar$_{m\text{-}H}$), 8.92 (AB/AB, ^3J = 8.1 Hz, ^4J = 4.7 Hz, 4 H, 12,13,17,18-H_β), 9.25 (AB, ^3J = 4.6 Hz, 2 H, 2,8-H_β), 9.71 (br. s, 1 H, 3- or 7-H_β), 10.12 (s, 1 H, 15-H_{meso}), 10.71 (br. s, 1 H, 3- or 7-H_β) ppm. ^{13}C NMR (60 MHz, $CDCl_3$, 20 °C): δ = 26.21, 35.87, 54.51, 105.74, 114.53, 126.74, 127.77, ≈132, 134.60, 141.90 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 416 (5.49), 512 (4.02), 544 (3.23), 586 (3.45), 640 (2.72) nm. MS (EI, 80 eV, 200 °C): *m*/*z* (%) = 580 (100) [M]$^+$, 519 (33) [M – C_2H_5S]$^+$, 506 (62) [M – C_3H_6S]$^+$, 476 (86) [M – $C_3H_4S_2$]$^+$, 462 (17) [M – $C_4H_6S_2$]$^+$, 290 (8) [M]$^{2+}$. HRMS (EI): calcd. for $C_{36}H_{28}N_4S_2$ 580.1755; found 580.1772.

[5-(1,3-Dithian-2-yl)-10,20-diphenylporphyrinato]nickel(II) (2b): Procedure A, yield: 140 mg (0.22 mmol, 53%) of purple crystals. M.p. >300 °C. R_f = 0.60 (CH_2Cl_2/C_6H_{14}, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 2.45 (m, 2 H, CH_2–CH_2–CH_2) 3.22 (m, 2 H, S–CH_2), 3.45 (m, 2 H, S–CH_2), 7.24 (s, 1 H, S–C*H*–S), 7.69 (m, 6 H, Ar$_{o,p\text{-}H}$), 7.99 (m, 4 H, Ar$_{m\text{-}H}$), 8.78 (m, 4 H, 12,13,17,18-H_β), 9.02 (AB, ^3J = 4.8 Hz, 2 H, 2,8-H_β), 9.65 (s, 1 H, 15-H_{meso}), 9.88 (br. s, 2 H, 3,7-H_β) ppm. ^{13}C NMR (63 MHz, $CDCl_3$, 20 °C): δ = 26.00, 35.20, 52.77, 104.99, 112.55, 118.37, 126.87, 127.73, 132.32, 132.37, 133.66, 140.54, 141.88, 142.14, 142.55 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 413 (5.09), 529 (4.07), 560 (3.71) nm. MS (70 eV): *m*/*z* (%) = 636 (4) [M]$^{\cdot+}$, 575 (7) [M – C_2H_5S]$^+$, 562 (10) [M – C_3H_6S]$^+$, 532 (2.5) [M – $C_3H_4S_2$]$^+$, 518 (4)

$[M - C_4H_6S_2]^+$, 318 (2) $[M]^{2+}$. HRMS (EI): calcd. for $C_{36}H_{26}N_4NiS_2$ 636.0952; found 636.0956.

5-(1,3-Dithian-2-yl)-10,20-bis(3-methoxyphenyl)porphyrin (2c): Procedure A, yield: 15 mg (0.0234 mmol, 4%) of purple crystals. M.p. 268 °C. R_f = 0.09 (CH_2Cl_2/C_6H_{14}, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = –3.03 (br. s, 2 H, N*H*), 2.55 (m, 2 H, CH_2–C*H*$_2$–CH_2), 3.33 (m, 2 H, S–C*H*$_2$), 3.64 (m, 2 H, S–C*H*$_2$), 4.00 (s, 6 H, OC*H*$_3$), 7.37 (m, 2 H, Ar$_H$), 7.69 (m, 2 H, Ar$_H$), 7.82 (m, 5 H, Ar$_H$, S–C*H*–S, Ar$_{m\text{-}H}$), 8.98 (m, 4 H, 12,13,17,18-H_β), 9.27 (AB, ^3J = 4.5 Hz, 2 H, 2,8-H_β), 9.65 (br. s, 1 H, H_β), 10.14 (s, 1 H, 15-H_{meso}),10.63 (br., 1 H, H_β) ppm. ^{13}C NMR (63 MHz, $CDCl_3$, 20 °C): δ = 35.88, 55.54, 113.71, 120.47, 127.55, 127.71, 127.80, 143.21, 158.02 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 417 (5.29), 513 (3.81), 557 (3.38), 588 (3.41), 648 (3.25) nm. MS (EI, 80 eV, 200 °C): *m*/*z* (%) = 640 (2) $[M]^{\cdot+}$, 580 (5) $[M - C_2H_4S]^+$, 522 (7) $[M - C_4H_6S_2]^+$. HRMS (EI): calcd. for $C_{38}H_{32}N_4O_2S_2$ 640.1967; found 640.1979. – Alternatively this compound was prepared by demetallation of **2d**. Ni^{II} complex **2d** (70 mg, 0.1 mmol) was dissolved under an atmosphere of Ar in dry CH_2Cl_2 (15 mL) and cooled to –70 °C. BBr_3 (4 mL) was added dropwise, and the red solution turned green. After removal of the cold bath, the mixture was stirred for 12 h at room temp. Water was then added slowly for hydrolysis, and the mixture was extracted with water (2 × 20 mL) and a saturated $NaHCO_3$ solution (20 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure and recrystallisation from CH_2Cl_2/CH_3OH gave 15 mg (0.02 mmol, 24%) of the title compound.

[5-(1,3-Dithian-2-yl)-10,20-bis(3-methoxyphenyl)porphyrinato]nickel-(II) (2d): Procedure A, yield: 167 mg (0.239 mmol, 53%) of purple crystals. M.p. >300 °C. R_f = 0.10 (CH_2Cl_2/C_6H_{14}, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 2.44 (m, 2 H, CH_2–C*H*$_2$–CH_2), 3.22 (m, 2 H, S–C*H*$_2$), 3.49 (m, 2 H, S–C*H*$_2$), 3.94 (s, 6 H, OC*H*$_3$), 7.25 (m, 4 H, Ar$_{o,p\text{-}H}$), 7.60 (m, 5 H, Ar$_{m\text{-}H}$, S–C*H*–S), 8.82 (m, 4 H, 12,13,17,18-H_β), 9.02 (AB, ^3J = 4.8 Hz, 2 H, 2,8-H_β), 9.65 (s, 1 H, 15-H_{meso}), 9.87 (br. s, 2 H, 3,7-H_β) ppm. ^{13}C NMR (60 MHz, $CDCl_3$, 20 °C): δ = 25.99, 35.20, 52.75, 55.42, 105.02, 112.58, 113.58, 118.14, 119.57, 126.68, 127.75, 132.44, 132.64, 141.17, 141.76, 141.83, 142.19, 142.44, 158.13 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 413 (5.13), 529 (4.16), 560 (3.80) nm. MS (EI, 70 eV): *m*/*z* (%) = 698 (2) $[M]^{\cdot+}$, 537 (2.5) $[M - C_2H_5S]^+$, 624 (2) $[M - C_3H_6S]^+$, 349 (1) $[M]^{2+}$. HRMS (EI): calcd. for $C_{38}H_{30}N_4NiO_2S_2$ 696.1164; found 696.1138.

5,15-Diisobutyl-10-(1,3-dithian-2-yl)porphyrin (2e): Procedure A, yield: 24 mg (0.044 mmol, 10.1%) of purple crystals. M.p. 268 °C. R_f = 0.30 (CH_2Cl_2/C_6H_{14}, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = –2.91 (s, 2 H, N*H*), 1.19 [d, ^3J = 6.6 Hz, 12 H, CH-(C*H*$_3$)$_2$], 2.57 [m, 2 H, C*H*(CH$_3$)$_2$], 2.76 (m, 2 H, –C*H*$_2$CH– 3.35 (m, 2 H, S–C*H*$_2$), 3.66 (m, 2 H, S–C*H*$_2$), 4.81 (d, ^3J = 7.2 Hz, 4 H, C*H*$_2$–CH), 7.89 (s, 1 H, S–C*H*–S), 9.27 (AB, ^3J = 5.0 Hz, 2 H, H_β), 9.45 (AB, ^3J = 4.6 Hz, 2 H, H_β), 9.52 (AB, ^3J = 5.0 Hz, 2 H, H_β), 9.77 (br. s, 1 H, H_β), 9.98 (s, 1 H, 20-H_{meso}), 10.78 (br. s, 1 H, H_β) ppm. ^{13}C NMR (63 MHz, $CDCl_3$, 20 °C): δ = 23.32, 26.32, 35.95, 36.65, 36.71, 43.41, 54.98, 104.93, 113.18, 120.99 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 416 (5.57), 514 (4.17), 547 (3.58), 590 (3.63), 646 (3.45) nm. MS (EI, 70 eV): *m*/*z* (%) = 540 (1) $[M]^{\cdot+}$, 423 (2) $[M - C_2H_4S]^+$, 407 (40) $[M - C_5H_9S_2]^+$. HRMS (EI): calcd. for $C_{32}H_{36}N_4S_2$ 540.2381; found 540.2381.

[5,15-Diisobutyl-10-(1,3-dithian-2-yl)porphyrinato]nickel(II) (2f): Procedure A, yield: 128 mg (0.214 mmol, 49%) of purple crystals. M.p. 250 °C. R_f = 0.30 (CH_2Cl_2/C_6H_{14}, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 0.84 [d, ^3J = 6.6 Hz, 12 H, CH(C*H*$_3$)$_2$], 2.22 [m, 2 H, C*H*(CH$_3$)$_2$], 2.46 (m, 2 H, –C*H*$_2$CH–), 3.24 (m, 2 H, S–C*H*$_2$), 3.49 (m, 2 H, S–C*H*$_2$), 4.52 (d, ^3J = 7.2 Hz, 4 H, CH–CH$_2$), 7.14 (s, 1 H, –S–C*H*–S–), 9.03 (AB, ^3J = 5.2 Hz, 2 H, H_β), 9.30 (AB/AB, ^3J = 6.0 Hz, ^4J = 5.0 Hz, 4 H, 2,3,17,18-H_β), 9.47 (s, 1 H, 20-H_{meso}), 9.86 (br. s, 2 H, 8,12-H_β) ppm. ^{13}C NMR (63 MHz, $CDCl_3$, 20 °C): δ = 22.99, 26.09, 34.38, 35.19, 42.14, 52.65, 104.05, 111.22, 116.46, 130.41, 132.46, 139.87, 141.02, 142.00, 142.87 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 416 (5.45), 534 (4.11), 568 (3.59) nm. MS (EI, 70 eV): *m*/*z* (%) = 596 (5) $[M]^{\cdot+}$, 553 (6) $[M - C_2H_5S]^+$, 535 (7) $[M - C_3H_7]^+$, 522 (11) $[M - C_3H_6S]^+$, 492 (4) $[M - C_3H_4S_2]^+$, 481 (17.5) $[M - C_8H_{18}]^+$, 298 (2) $[M]^{2+}$. HRMS (EI): calcd. for $C_{32}H_{34}N_4S_2$ 596.1578; found 596.1576.

Deprotection of the Dithian-2-ylporphyrins

General Procedure B: To a solution of dithian-2-ylporphyrin (0.06 mmol) in CH_2Cl_2 (60 mL) was added DDQ (500 mg, 2.20 mmol) and $BF_3{\cdot}Et_2O$ (0.5 mL, 9.95 mmol), and the colour of the red solution changed over yellow to green. After stirring for 45 min, the reaction was quenched by the addition of aqueous sodium hydrogen carbonate. The organic phase was washed with a saturated solution of sodium hydrogen carbonate several times, followed by drying over anhydrous sodium sulfate and evaporation of the solvent in vacuo. After filtration through silica gel and recrystallisation from CH_2Cl_2/MeOH the pure product could be obtained.

5-Formyl-10,20-diphenylporphyrin (3a): Procedure B, yield: 13 mg (0.03 mmol, 44%) of purple crystals. M.p. >310 °C. R_f = 0.53 (CH_2Cl_2/C_6H_{14}, 2:1). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = –2.54 (br. s, 2 H, N*H*), 7.81 (m, 6 H, Ar$_{o,p\text{-}H}$), 8.18 (dd, ^3J = 6.0 Hz, ^4J = 1.5 Hz, 4 H, Ar$_{m\text{-}H}$), 8.85 (AB, ^3J = 4.5 Hz, 2 H, H_β), 9.02 (AB, ^3J = 4.9 Hz, 2 H, 2,8-H_β), 9.22 (AB, ^3J = 4.5 Hz, 2 H, H_β), 10.11 (AB, ^3J = 4.7 Hz, 2 H, 3,7-H_β), 10.18 (s, 1 H, 15-H_{meso}), 12.52 (s, 1 H, C*H*O) ppm. ^{13}C NMR (63 MHz, $CDCl_3$, 20 °C): δ = 108.08, 109.87, 122.13, 124.92, 126.94, 127.80, 128.10, 128.64, 130.19, 131.18, 133.86, 134.42, 141.18, 195.15 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 411 (5.49), 508 (3.95), 561 (3.47), 581 (3.56), 647 (3.30) nm. MS (70 eV): *m*/*z* (%) = 490 (23) $[M]^{\cdot+}$, 462 (6) $[M - CO]^+$, 245 (16) $[M]^{2+}$. HRMS (EI): calcd. for $C_{33}H_{22}N_4O$ 490.1794; found 490.1777.

(5-Formyl-10,20-diphenylporphyrinato)nickel(II) (3b): Procedure B, yield: 13 mg (0.02 mmol, 39%) of purple crystals. M.p. 215 °C. R_f = 0.59 (CH_2Cl_2/C_6H_{14}, 2:1). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 7.72 (m, 6 H, Ar$_{o,p\text{-}H}$), 7.98 (dd, ^3J = 5.8 Hz, ^4J = 1.5 Hz, 4 H, Ar$_{m\text{-}H}$), 8.74 (AB, ^3J = 4.8 Hz, 2 H, H_β), 8.89 (AB, ^3J = 5.2 Hz, 2 H, 2,8-H_β), 9.05 (AB, ^3J = 4.8 Hz, 2 H, H_β), 9.75 (s, 1 H, 15-H_{meso}), 9.86 (AB, ^3J = 5.2 Hz, 2 H, 3,7-H_β), 12.13 (s, 1 H, C*H*O) ppm. ^{13}C NMR (63 MHz, $CDCl_3$, 20 °C): δ = 106.49, 108.59, 111.61, 127.04, 128.08, 130.53, 132.38, 133.19, 133.53, 135.29, 141.80, 144.26, 173.52 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 417 (5.31), 545 (3.75), 589 (3.94) nm. MS (EI, 70 eV): *m*/*z* = 546 (18) $[M]^{\cdot+}$, 517 (16) $[M - CHO]^+$, 440 (52) $[M - C_7H_6O]^+$. HRMS (EI): calcd. for $C_{33}H_{20}N_4NiO$ 546.0991; found 546.0989.

[5-Formyl-10,20-bis(3-methoxyphenyl)porphyrinato]nickel(II) (3c): Procedure B, yield: 34 mg (0.05 mmol, 94%) of dark purple crystals. M.p. >300 °C. R_f = 0.26 (CH_2Cl_2/C_6H_{14}, 2:1). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 3.95 (s, 6 H, OC*H*$_3$), 7.58 (m, 8 H, Ar$_{o,m,p\text{-}H}$), 8.77 (AB, ^3J = 4.8 Hz, 2 H, H_β), 8.93 (AB, ^3J = 5.2 Hz, 2 H, 2,8-H_β), 9.03 (AB, ^3J = 4.8 Hz, 2 H, H_β), 9.72 (s, 1 H, 15-H_{meso}), 9.84 (AB, ^3J = 5.2 Hz, 2 H, 3,7-H_β), 12.11 (s, 1 H, C*H*O) ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 419 (4.69), 545 (3.47), 592 (3.56) nm. MS (ESI): *m*/*z* (%) = 606 (100) $[M]^{\cdot+}$. HRMS (EI): calcd. for $C_{35}H_{24}N_4NiO_3$ 606.1202; found 606.1190.

5-Hexyl-15-phenylporphyrin (4): Dry CH_2Cl_2 (2 L) was placed in a three-necked flask equipped with magnetic stirrer, gas inlet (argon)

and a reflux condenser. Dipyrromethane (1.2 g, 8.2 mmol), benzaldehyde (0.46 mL, 4.6 mmol), and heptanal (0.64 mL, 4.6 mmol) were added. The flask was shielded from ambient light and then TFA (140 μL, 1.8 mmol) was added, and the reaction mixture was stirred for 18 h at room temp. After this time, DDQ (2.77 g, 12.2 mmol) suspended in dry CH_2Cl_2 (100 mL) was added, and the mixture was stirred for 1 h. Triethylamine (6 mL) was then added, and the reaction mixture was concentrated in vacuo to about 200 mL. The reaction mixture was filtered through silica (500 mL, column diameter 5 cm), washing with CH_2Cl_2. The eluted porphyrin fractions were evaporated to dryness. The porphyrins were separated by column chromatography (silica, CH_2Cl_2/C_6H_{14}, 1:1). The first fraction was 5,15-dihexylporphyrin (45 mg, 0.09 mmol, 4%), the second fraction, 5-phenyl-15-hexylporphyrin (189 mg, 0.40 mmol, 14%) and the third fraction 5,15-diphenylporphyrin (65 mg, 0.14 mmol, 6%). The porphyrins were recrystallised from CH_2Cl_2/MeOH. The suspension was filtered through a D3 frit leaving behind purple crystals of the title compound. M.p. >310 °C. R_f = 0.86 (CH_2Cl_2/C_6H_{14}, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = –3.08 (s, 2 H, N*H*), 1.05 (t, J = 7.6 Hz, 3 H, 5^6-CH_3), 1.48 (m, 2 H, 5^5-CH_2), 1.51 (m, 2 H, 5^4-CH_2), 1.86 (m, 2 H, 5^3-CH_2), 2.58 (m, 2 H, 5^2-CH_2), 4.96 (t, J = 8.0 Hz, 2 H, 5^1-CH_2), 7.89 (m, 3 H, Ar$_H$), 8.33 (m, 2 H, Ar$_H$), 9.12 (d, J = 4.5 Hz, 2 H, H_β), 9.38 (d, J = 4.5 Hz, 4 H, H_β), 9.56 (d, J = 7.6 Hz, 2 H, H_β), 10.19 (s, 2 H, H_{meso}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 13.8, 22.4, 29.9, 31.5, 34.3, 38.4, 104.3, 117.9, 126.6, 127.5, 130.3, 131.3, 134.5, 141.0, 144.3, 147.0 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 408 (4.55), 427 (4.74), 503 (2.90), 539 (3.13), 573 (3.39), 620 (3.33) nm. HRMS (ES+): calcd. for $C_{32}H_{30}N_4$ [M + H]$^+$ 471.2549; found 471.2553.

5-Formyl-10-hexyl-20-phenylporphyrin (5a): 1,3-Dithiane (0.56 g, 4.67 mmol) was placed in a dried, septum-equipped Schlenk flask under an atmosphere of argon. The flask was evacuated for 30 min, then backfilled with argon and charged with freshly distilled THF (25 mL). The solution was cooled to –40 °C and *n*-butyllithium (2.5 M, 1.87 mL, 4.67 mmol) was added dropwise by syringe through the septum. The reaction mixture was stirred for 30–40 min at –30 to –40 °C. The solution of the organometallic compound was cooled to –78 °C and mixed with a suspension (–30 °C) of 5-hexyl-15-phenylporphyrin **4** (100 mg, 0.21 mmol) in THF (20 mL). After transfer of the porphyrin suspension, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.2 mL, 1.6 mmol) was added, and the reaction mixture turned dark-brown. After stirring for 15 min, the cold bath was removed, and the reaction mixture was stirred for 1 h at room temp. The solution was then treated with *n*-propyl iodide (0.7 mL, 0.42 mmol) and heated at reflux for an additional day. Water (3 mL) was added by syringe, resulting in an immediate colour change of the solution to dark green. The mixture was stirred for 15 min at room temp, followed by the addition of a solution of DDQ (0.3 g of DDQ, ca. 0.75 mmol) in THF (10 mL), and the colour of the solution changed from green to purple. Stirring was continued for 15 min, followed by filtration of the mixture through silica (200 mL) washing with CH_2Cl_2. The eluted porphyrins were evaporated to dryness and further purified by column chromatography (silica, CH_2Cl_2/C_6H_{14}, 2:1) to yield the compound as a side product (2.2 mg, 0.02 mmol, 2.1%) as a purple solid. M.p. >310 °C. R_f = 0.71 (CH_2Cl_2/C_6H_{14}, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = –2.50 (s, 2 H, N*H*), 0.97 (t, J = 7.3 Hz, 3 H, 5^6-CH_3), 1.44 (m, 2 H, 5^5-CH_2), 1.54 (m, 2 H, 5^4-CH_2), 1.83 (m, 2 H, 5^3-CH_2), 2.52 (m, 2 H, 5^2-CH_2), 4.90 (t, J = 7.7 Hz, 2 H, 5^1-CH_2), 7.83 (m, 6 H, Ar$_H$), 8.19 (d, J = 7.16 Hz, 4 H, Ar$_H$), 8.85 (d, J = 4.7 Hz, 1 H, H_β), 9.00 (d, J = 4.7 Hz, 1 H, H_β), 9.24 (d, J = 4.7 Hz, 1 H, H_β), 9.32 (d, J = 4.1 Hz, 1 H, H_β), 9.43 (d, J = 4.7 Hz, 1 H, H_β), 9.59 (d, J = 5.3 Hz, 1 H, H_β), 9.99 (d, J = 4.7 Hz, 1 H, H_β), 10.12 (d, J = 5.3 Hz, 1 H, H_β), 10.15 (s, 1 H, H_{meso}), 12.55 (s, 1 H, C*H*O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 13.7, 22.3, 28.9, 31.5, 35.0, 38.3, 107.1, 109.2, 126.6, 127.6, 133.9, 140.6, 194.9 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 423 (4.02), 458 (3.99), 502 (2.78), 572 (2.78), 601 (2.90), 655 (3.18) nm. HRMS (ES+): calcd. for $C_{38}H_{33}N_4O$ [M + H]$^+$ 499.2514; found 499.2498.

5-Formyl-15-pentyl-10,20-diphenylporphyrin (5b): 1,3-Dithiane (0.58 g, 4.82 mmol) was placed in a dried, septum-equipped Schlenk flask under an atmosphere of argon. The flask was evacuated for 30 min, then backfilled with argon and charged with freshly distilled THF (25 mL). The solution was cooled to –40 °C and *n*-butyllithium (2.5 M, 1.92 mL, 4.8 mmol) was added dropwise by syringe through the septum. The reaction mixture was stirred for 30–40 min at –30 to –40 °C. The solution of the organometallic compound was cooled to –78 °C and mixed with a suspension (–30 °C) of 5,15-diphenylporphyrin **1a** (100 mg, 0.22 mmol) in THF (20 mL). After transfer of the porphyrin suspension, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.2 mL, 1.6 mmol) was added, and the reaction mixture turned dark brown. After stirring for 15 min, the cold bath was removed, and the reaction mixture was stirred for 1 h at room temp. The solution was treated with *n*-pentyl iodide (0.7 mL, 0.42 mmol) and stirred for 2 d. Water (3 mL) was added by syringe, resulting in an immediate colour change of the solution to dark green. The mixture was stirred for 15 min at room temp, followed by the addition of a solution of DDQ (0.3 g, ca. 0.75 mmol) in THF (10 mL), and the colour of the solution changed from green to purple. Stirring was to continue for 15 min, followed by filtration of the mixture through silica (200 mL) washing with CH_2Cl_2. The eluted porphyrins were evaporated to dryness and further purified by column chromatography (silica, CH_2Cl_2/C_6H_{14}, 2:1) to yield the compound as a side product (13.55 mg, 0.02 mmol, 11%) as a purple solid. M.p. >310 °C. R_f = 0.87 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = –1.81 (s, 2 H, N*H*), 0.98 (t, J = 7.6 Hz, 3 H, 5^5-CH_3), 1.55 (m, 2 H, 5^4-CH_2), 1.77 (m, 2 H, 5^3-CH_2), 2.50 (m, 2 H, 5^2-CH_2), 4.88 (t, J = 8.2 Hz, 2 H, 5^1-CH_2), 7.79 (m, 6 H, Ar$_H$), 8.16 (d, J = 7.0 Hz, 4 H, Ar$_H$), 8.75 (d, J = 4.7 Hz, 2 H, H_β), 8.90 (d, J = 4.7 Hz, 2 H, H_β), 9.37 (d, J = 4.7 Hz, 2 H, H_β), 9.94 (d, J = 5.2 Hz, 2 H, H_β), 12.41 (s, 1 H, C*H*O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 13.7, 22.3, 29.3, 31.5, 38.0, 126.3, 127.4, 129.8, 133.7, 141.3, 194.0 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 422 (4.91), 441 (4.99), 523 (4.12), 563 (4.13), 592 (4.13), 652 (4.15) nm. HRMS (ES+): calcd. for $C_{38}H_{33}N_4O$ [M + H]$^+$ 561.2665; found 561.2654.

5,15-Diphenyl-10-(1,3,5-trithian-2-yl)porphyrin (6a): *n*-Butyllithium (2.5 M, 1.92 mL, 4.8 mmol) was added under an atmosphere of argon to a 100-mL Schlenk flask charged with a solution of 1,3,5-trithiane (0.67, 4.84 mmol) in dry THF (20 mL) at –40 °C. The reaction mixture was then stirred for 2.5 h at 20 °C. The solution of the organometallic compound was cooled to –78 °C and mixed with a suspension (–30 °C) of 5,15-diphenylporphyrin **1a** (100 mg, 0.22 mmol) in THF (20 mL). After transferring the porphyrin suspension, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.2 mL, 1.6 mmol) was added, and the reaction mixture turned dark brown. After stirring for 15 min, the cold bath was removed, and the reaction mixture was stirred for 1 h at room temp. Subsequently, water (3 mL) was added for hydrolysis. The mixture was stirred for another 15 min at room temp, followed by the addition of a solution of DDQ (0.3 g, ca. 0.75 mmol) in THF (10 mL), and the colour of the solution changed to purple. Stirring was continued for another 15 min, and the organic solvent was removed under vacuum. Final purification was achieved by column chromatography (EtOAc/C_6H_{14}, 1:20) under dark conditions to yield title compound **6a** (24 mg, 0.04 mmol, 18%) as a purple solid. M.p. >310 °C. R_f =

0.83 (CH_2Cl_2/C_6H_{14}, 3:1). ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = –3.06 (s, 2 H, N*H*), 4.36 (d, J = 14.6 Hz, 2 H, S–CH_2–S), 5.06 (d, J = 14.6 Hz, 2 H, S–CH_2), 7.78 (m, 6 H, Ar$_H$), 7.94 (s, 1 H, S–C*H*–S), 8.18 (d, J = 7.0 Hz, 4 H, Ar$_H$), 8.91 (d, J = 15.2 Hz, 4 H, H_β), 9.25 (s, 2 H, H_β), 9.52 (s, 1 H, H_β), 10.13 (s, 1 H, H_{meso}), 10.50 (s, 1 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 30.5, 40.9, 57.7, 105.6, 113.3, 126.4, 127.4, 134.2, 141.3 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 415 (4.25), 512 (3.52), 548 (3.42), 587 (3.43), 640 (3.39) nm. HRMS (ES+): calcd. for $C_{39}H_{32}N_4S_4$ [M + H]$^+$ 599.1398; found 599.1411.

[5,15-Diphenyl-10-(1,3,5-trithian-2-yl)porphyrinato]nickel(II) (6b): The reaction was performed with the use of the same conditions as for free base **6a** by using 1,3,5-trithiane (0.55 g, 4.01 mmol), *n*-butyllithium (2.5 M, 1.60 mL, 4.0 mmol) and (5,15-diphenylporphyrinato)nickel(II) **1b** (100 mg, 0.18 mmol). Elution with CH_2Cl_2/C_6H_{14} (1:1) yielded the title compound (46 mg, 0.07 mmol, 38%) as a purple solid. M.p. >310 °C. R_f = 0.89 (CH_2Cl_2/C_6H_{14}, 2:1). ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 4.27 (d, J = 15.2 Hz, 2 H, S–CH_2–S), 4.92 (d, J = 14.6 Hz, 2 H, S–CH_2–S), 7.30 (s, 1 H, S–C*H*–S), 7.68 (m, 6 H, Ar$_H$), 7.95 (d, J = 6.4 Hz, 4 H, Ar$_H$), 8.77 (m, J = 4.7 Hz, 4 H, H_β), 9.02 (d, J = 4.7 Hz, 2 H, H_β), 9.67 (s, 1 H, H_{meso}), 9.72 (s, 2 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 35.0, 40.3, 56.0, 102.6, 104.9, 126.5, 127.4, 132.1, 132.2, 133.2, 139.9, 141.6, 141.8, 142.3 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 413 (5.73), 530 (4.54), 565(4.11) nm.

{5,15-Bis[3-methoxyphenyl-10-(1,3,5-trithian-2-yl)]porphyrinato}-nickel(II) (6c): The reaction was performed wit the use of the same conditions as for free base **6a** by using 1,3,5-trithiane (0.53 g, 3.80 mmol), *n*-butyllithium (2.5 M, 1.51 mL, 3.80 mmol) and [5,15-bis(3-methoxyphenyl)porphyrinato]nickel(II) **1d** (100 mg, 0.17 mmol). Elution with CH_2Cl_2/C_6H_{14} (1:1) yielded the title compound as a red solid (42 mg, 0.06 mmol, 34%). M.p. >310 °C. R_f = 0.74 (CH_2Cl_2/C_6H_{14}, 3:1). ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 3.92 (s, 6 H, OCH_3), 4.29 (d, J = 15.2 Hz, 2 H, S–CH_2–S), 4.90 (d, J = 14.6 Hz, 2 H, S–CH_2–S), 7.29 (s, 1 H, S–C*H*–S), 7.50 (s, 2 H, Ar$_H$), 7.57 (d, J = 5.3 Hz, 6 H, Ar$_H$), 8.81 (m, 4 H, H_β), 9.00 (d, J = 4.6 Hz, 2 H, H_β), 9.63 (s, 1 H, H_{meso}), 9.74 (s, 2 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 26.67, 29.28, 30.61, 40.31, 55.00, 55.90, 61.60, 104.87, 111.41, 113.15, 117.94, 119.15, 123.44, 126.23, 127.39, 132.15, 141.24, 141.87, 157.69 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 413 (5.05), 531 (4.23), 574 (4.17) nm.

[5,15-Dihexyl-10-(1,3,5-trithian-2-yl)porphyrinato]nickel(II) (6d): The reaction was performed with the use of the same conditions as for free base **6a by** using 1,3,5-trithiane (0.57 g, 4.11 mmol), *n*-butyllithium (2.5 M, 1.63 mL, 4.11 mmol) and (5,15-dihexylporphyrinato)nickel(II) (100 mg, 0.19 mmol). Elution with CH_2Cl_2/C_6H_{14} (1:1) gave the title compound as a red solid (31 mg, 0.05 mmol, 24%). M.p. >310 °C. R_f = 0.88 (CH_2Cl_2/C_6H_{14}, 3:1). ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.88 (t, J = 7.0 Hz, 3 H, 5^6-CH_3), 1.30 (m, 2 H, 5^5-CH_2), 1.51 (m, 2 H, 5^4-CH_2), 2.12 (m, 2 H, 5^3-CH_2), 2.20 (m, 2 H, 5^2-CH_2), 4.38 (t, J = 14.6 Hz, 2 H, S–CH_2–S), 4.26 (t, J = 7.6 Hz, 2 H, 5^1-CH_2), 4.80 (t, J = 14.6 Hz, 2 H, S–CH_2–S), 7.10 (s, 1 H, S–C*H*–S), 9.08 (d, J = 4.7 Hz, 2 H, H_β), 9.15 (m, 4 H, H_β), 9.36 (s, 1 H, H_{meso}), 9.52 (s, 2 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 13.71, 19.00, 22.22, 29.57, 31.31, 33.45, 36.96, 40.23, 55.71, 103.78, 108.93, 110.03, 112.84, 117.46, 128.98, 129.29, 132.18, 140.35, 141.12, 142.00 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 418 (5.53), 539 (4.65), 576 (4.52) nm.

2,8-Diformylspirobisdithiane (9): Spirobisdithiane **8** (1.00 g, 4.40 mmol) was dried in vacuo in a septum-equipped Schlenk flask for 30 min. Dry THF (25 mL) was then added under an atmosphere of argon, and the suspension was cooled to –78 °C. *n*-Butyllithium (2.5 M, 9.9 mL, 15.99 mmol) was added dropwise by syringe through the septum, and the reaction mixture was stirred for 2 h at –25 °C. The solution of the organometallic compound was cooled to –78 °C and mixed with a suspension (–10 °C) of DMF (10 mL). The solution was stirred for 2 h at –10 °C and the colour of the solution turned to light yellow. The solution was then stored in the freezer overnight. For workup, the solution was poured into ice, and the aqueous phase was extract with hexane. The aqueous phase was then neutralised with HCL (1 M) before extraction with CH_2Cl_2 for the second time. The organic phase was dried with $MgSO_4$, and the organic solvent was removed under vacuum. The remaining yellow oil was recrystallised from C_6H_{14}/CH_2Cl_2 and gave the title compound (0.70 g, 2.49 mmol, 56%) as a yellow solid. M.p. 165 °C. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 2.86 (s, 4 H, –S–CH_2–), 2.94 (s, 4 H, –S–CH_2–), 4.03 (s, 2 H, –S–C*H*–S–), 9.39 (s, 2 H, -CHO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.72, 30.99, 36.06, 46.63, 186.86 ppm.

5,15-Diphenyl-10-(spirobis-1,3-dithian-2-yl)porphyrin (11a): Spirobisdithiane (1.08 g, 4.84 mmol) was dried in vacuo in a septum-equipped Schlenk flask for 30 min. Dry THF (20 mL) was then added under an atmosphere of argon, and the suspension was cooled to –40 °C. *n*-Butyllithium (2.5 M, 1.92 mL, 4.84 mmol) was added dropwise by syringe through the septum, and the reaction mixture was stirred for 2 h at –25 °C. The solution of the organometallic compound was cooled to –78 °C and mixed with a suspension (–30 °C) of 5,15-diphenylporphyrin **1a** (100 mg, 0.22 mmol) in dry THF (20 mL). After transfer of the porphyrin suspension, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.2 mL, 1.6 mmol) was added, and the reaction mixture turned dark brown. After stirring for 15 min, the cold bath was removed, and the reaction mixture was stirred for 1 h at room temp. Upon the addition of water (3 mL), the reaction mixture changed its colour to dark green. The mixture was stirred for 15 min at room temp., followed by the addition of a solution of DDQ (0.3 g, ca. 0.75 mmol) in THF (10 mL), and the colour of the solution changed from green to purple. Stirring was continued for a further 15 min, and the organic solvent was removed under reduced pressure. Final purification was achieved by column chromatography ($EtOAc/C_6H_{14}$, 1:20) in the dark to yield the title compound (33 mg, 0.05 mmol, 22%) as a purple solid. M.p. >310 °C. R_f = 0.76 (CH_2Cl_2/C_6H_{14}, 2:1). ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = –3.04 (s, 2 H, N*H*), 3.38 (d, J = 14.7 Hz, 2 H, S–CH_2–S), 3.65 (m, 8 H, S–CH_2), 7.71 (s, 1 H, S–C*H*–S), 7.76 (m, 6 H, Ar$_H$), 8.18 (d, J = 6.4 Hz, 4 H, Ar$_H$), 8.92 (dd, J = 4.7 Hz, 4 H, H_β), 9.25 (d, J = 4.7 Hz, 2 H, H_β), 9.53 (s, 1 H, H_β), 10.13 (s, 1 H, H_{meso}), 10.55 (s, 1 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 24.0, 31.8, 35.1, 41.5, 55.0, 105.5, 112.7, 126.3, 127.4, 134.2, 141.4 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 415 (4.42), 511 (3.54), 549 (3.39), 586 (3.42), 638 (3.34) nm. HRMS (ES+): calcd. for $C_{39}H_{32}N_4S_4$ [M + H]$^+$ 685.1588; found 685.1578.

[5,15-Diphenyl-10-(spirobis-1,3-dithian-2-yl)porphyrinato]nickel(II) (11b): The reaction was performed with the use of the same conditions as given for free base **11a by** using spirobisdithiane (0.89 g, 4.01 mmol), *n*-butyllithium (2.5 M, 1.59 mL, 4.0 mmol) and (5,15-diphenylporphyrinato)nickel(II) **1b** (100 mg, 0.18 mmol). The mixture was purified by column chromatography (CH_2Cl_2/C_6H_{14}, 1:1) and yielded the title compound (45 mg, 0.06 mmol, 33%) as a red solid. M.p. >310 °C. R_f = 0.82 (CH_2Cl_2/C_6H_{14}, 3:1). ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 3.31 (d, J = 14.0 Hz, 2 H, S–CH_2–S), 3.67 (m, 8 H, S–CH_2), 7.08 (s, 1 H, S–C*H*–S), 7.68 (m, 6 H, Ar$_H$), 7.95 (d, J = 6.4 Hz, 4 H, Ar$_H$), 8.77 (m, J = 4.7 Hz, 4 H, H_β), 9.02 (d, J = 4.7 Hz, 2 H, H_β), 9.66 (s, 1 H, H_{meso}), 9.77 (s, 2 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 22.3, 27.4,

29.3, 36.7, 52.8, 104.8, 126.7, 127.4, 132.1, 132.4, 133.2, 140.0, 141.5, 141.8, 142.2 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 413 (5.52), 530 (4.34), 569 (3.84) nm.

[5,15-Bis(3-methoxyphenyl)-10-(spirobis-1,3-dithian-2-yl)porphyrinato]nickel(II) (11c): The reaction was performed with the use of the same conditions as given for the free base **11a by** using spirobisdithiane (0.85 g, 3.81 mmol), *n*-butyllithium (2.5 M, 1.51 mL, 3.81 mmol) and [5,15-bis(3-methoxyphenyl)porphyrinato]nickel(II) **1d** (100 mg, 0.17 mmol). The mixture was purified by column chromatography (CH_2Cl_2/C_6H_{14}, 1:1) and yielded the title compound (47 mg, 0.06 mmol, 34%) as a red solid. M.p. >310 °C. R_f = 0.45 (CH_2Cl_2/C_6H_{14}, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 3.33 (d, J = 14.0 Hz, 2 H, S–C*H*$_2$–S), 3.74 (m, 8 H, S–CH_2), 3.92 (s, 6 H, OCH_3), 7.09 (s, 1 H, S–C*H*–S), 7.57 (m, 8 H, Ar$_H$), 8.82 (m, 4 H, H_β), 9.03 (d, J = 4.1 Hz, 2 H, H_β), 9.67 (s, 1 H, H_{meso}), 9.77 (s, 2 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 22.27, 29.27, 31.62, 38.07, 55.00, 104.76, 113.15, 119.14, 126.24, 127.37, 130.46, 132.10, 140.49, 141.28, 141.31, 141.85, 157.68 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 414 (4.96), 530 (3.78), 567 (3.48) nm.

[5,15-Dihexyl-10-(spirobis-1,3-dithian-2-yl)porphyrinato]nickel(II) (11d): The reaction was performed with the use of the same conditions as given for free base **11a by** using spirobisdithiane (0.92 g, 4.11 mmol), *n*-butyllithium (2.5 M, 1.63 mL, 4.11 mmol) and (5,15-dihexylporphyrinato)nickel(II) (100 mg, 0.19 mmol). The mixture was purified by column chromatography (CH_2Cl_2/C_6H_{14}, 1:1) and yielded the title compound (28 mg, 0.02 mmol, 19%) as a red solid. M.p. >310 °C. R_f = 0.67 (CH_2Cl_2/C_6H_{14}, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.91 (t, J = 7.0 Hz, 3 H, 5^6-CH_3), 1.32 (m, 2 H, 5^5-CH_2), 1.34 (m, 2 H, 5^4-CH_2), 1.58 (m, 2 H, 5^3-CH_2), 2.27 (m, 2 H, 5^2-CH_2), 3.26 (d, J = 14.0 Hz, 2 H, S–CH_2–S), 4.49 (t, J = 7.6 Hz, 2 H, 5^1-CH_2), 4.80 (m, 8 H, S–CH_2), 6.95 (s, 1 H, S–C*H*–S), 9.03 (d, J = 4.7 Hz, 2 H, H_β), 9.26 (dd, J = 5.28 Hz, 4 H, H_β), 9.45 (s, 1 H, H_{meso}), 9.75 (s, 2 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 13.79, 22.28, 23.83, 24.31, 29.66, 31.34, 33.56, 35.11, 37.14, 38.80, 41.51, 43.39, 53.14, 103.77, 117.51, 120.92, 129.40, 129.70, 132.24, 139.28, 140.64, 141.04, 141.95 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 416 (4.98), 535 (3.70), 568 (3.48) nm.

[5-Hexyl-10,20-diphenyl-15-(spirobis-1,3-dithian-2-yl)porphyrinato]-nickel(II) (11e): The reaction was performed with the use of the same conditions as given for free base **11a by** using spirobisdithiane (0.82 g, 3.65 mmol), *n*-butyllithium (2.5 M, 1.45 mL, 3.65 mmol) and (5-hexyl-10,20-diphenylporphyrinato)nickel(II)[17c,34] (100 mg, 0.17 mmol). The mixture was purified by column chromatography (CH_2Cl_2/C_6H_{14}, 2:1) and yielded the title compound (54 mg, 0.06 mmol, 40%) as a red solid. M.p. >310 °C. R_f = 0.78 (CH_2Cl_2/C_6H_{14}, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.85 (t, J = 7.6 Hz, 3 H, 5^6-CH_3), 1.36 (m, 2 H, 5^5-CH_2), 1.55 (m, 2 H, 5^4-CH_2), 2.39 (m, 2 H, 5^3-CH_2), 2.61 (m, 2 H, 5^2-CH_2), 3.14 (d, J = 14.6 Hz, 2 H, S–CH_2–S), 3.59 (m, 8 H, S–CH_2), 4.46 (t, J = 7.6 Hz, 2 H, 5^1-CH_2), 6.88 (s, 1 H, S–C*H*–S), 7.65 (m, 6 H, Ar$_H$), 7.91 (d, J = 6.4 Hz, 4 H, Ar$_H$), 8.67 (dd, J = 4.7 Hz, 4 H, H_β), 9.18 (d, J = 4.7 Hz, 2 H, H_β), 9.62 (s, 2 H, H_β) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 13.70, 22.19, 23.76, 24.29, 29.29, 31.60, 33.64, 36.94, 38.00, 52.85, 109.62, 118.01, 119.57, 126.49, 127.33, 129.58, 132.00, 132.47, 133.14, 139.92, 140.66, 140.77, 141.3917, 141.5077 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 421 (4.95), 539 (4.01), 577 (3.79) nm.

5-(1,3-Dithian-2-yl)dipyrromethane (13): A mixture of 2-formyl-1,3-dithiane **12** (1.48 g, 10 mmol) and pyrrole (400 mL) was purged with argon for 10 min, followed by the addition of $BF_3{\cdot}Et_2O$ (500 μL). After 20 min, the same amount of acid was added again. After 40 min, the reaction was terminated by the addition of NaOH (0.1 M, 16.7 mL). The solution was washed several times with water, and the solvent was removed under reduced pressure to yield a yellow oil as the crude product. Column chromatography (silica, C_6H_{14}/CH_2Cl_2, 1:2, 1% NEt_3) followed by recrystallisation from C_6H_{14} yielded a white solid (2.54 g, 9.62 mmol, 96%). M.p. 51 °C. ^{1}H NMR (270 MHz, $CDCl_3$, 47 °C): δ = 1.86 (m, 1 H, CH_2–CH_{2eq}–CH_2), 2.10 (m, 1 H, CH_2–CH_{2ax}–CH_2), 2.90 (m, 4 H, S–CH_2), 4.52 (d, ^3J = 4.41 Hz, 1 H, C–C*H*–C), 4.66 (d, ^3J = 4.41 Hz, 1 H, S–C*H*–S), 6.11 (m, 2 H, CH–CH=C*H*), 6.19 (m, 2 H, N–C*H*), 6.71 (m, 2 H, N–CH=C*H*), 8.49 (br. s, 2 H, N*H*) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 320 K): δ = 25.49, 31.15, 43.24, 53.37, 107.92, 108.18, 117.40, 129.52 ppm. MS (200 °C, 80 eV): *m*/*z* (%) = 264 (77) $[M]^{\cdot+}$, 145 (100) $[M - C_4H_7S_2]^+$, 119 (80) $[M - C_9H_9N_2]^{\cdot+}$. HRMS: calcd. for $C_{13}H_{16}N_2S_2$ 264.07549; found 264.077553. $C_{13}H_{16}N_2S_2$ (264.40): calcd. C 59.05, H 6.10, N 10.59; found C 59.35, H 6.27, N 10.32.

5,10-Bis(1,3-dithian-2-yl)porphyrin (14a): A solution of tripyrrane (464 mg, 2.06 mmol), pyrrole (143 μL, 2.06 mmol) and 2-formyl-1,3-dithiane **12** (611 mg, 4.12 mmol) in CH_2Cl_2 (100 mL) was stirred under an atmosphere of argon with exclusion from light for 45 min followed by the addition of TFA (100 μL). After 16 h of stirring at room temp., DDQ (1.5 g) was added, and the solution was stirred for 1 h. The solution was filtered through a plug of silica gel with CH_2Cl_2 containing 1% NEt_3. The residue was purified by column chromatography on (silica, CH_2Cl_2/C_6H_{14}, 2:1, 1% NEt_3). Three fractions were collected; the first one was not characterised because of the small amount. The second fraction contained porphin, and the desired compound was collected as last fraction as a mixture of 5,10- **14a** and 5,15-bis(1,3-dithian-2-yl)-porphyrin **14b**. The separation was carried out by a second column chromatography on alumina. The desired product was obtained as the second fraction as purple crystals (22.5 mg, 41.2 μmol, 3.0%). M.p. >297 °C. ^{1}H NMR (270 MHz, $CDCl_3$, 20 °C): δ = –3.52 (br. s, 2 H, N*H*), 2.53 (m, 4 H, CH_2–CH_2–CH_2), 3.34 (m, 4 H, S–CH_{2eq}), 3.70 (m, 4 H, S–CH_{2ax}), 7.87 (s, 2 H, S–C*H*–S), 9.40 (m, 4 H, 2,13,17,18-H_β), 9.74 (br. s, 2 H, 3,12-H_β), 10.10 (s, 2 H, 15,20-H_{meso}), 10.70 (br. s, 2 H, 7,8-H_β) ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 413 (5.34), 510 (4.23), 546 (3.79), 582 (3.82), 633 (3.43) nm. MS (FAB+, 3 KV): *m*/*z* (%) = 547.0 (10) $[M + H]^{\cdot+}$, 427.0 (2) $[M - C_4H_7S_2+H]^+$.

5,15-Bis(1,3-dithian-2-yl)porphyrin (14b): 2-Formyl-1,3-dithiane **12** (100 mg, 0.67 mmol) and dipyrromethane (100 mg, 0.67 mmol) were dissolved in CH_2Cl_2 (170 mL). After purging with argon TFA (10 μL) was added, and the mixture was stirred for 14 h. Then, DDQ (390 mg, 1.7 mmol) was added, and the mixture was heated for 10 min under reflux. The crude mixture was filtered through silica gel, concentrated under reduced pressure and subjected to column chromatography (silica, CH_2Cl_2/C_6H_{14},1:2) to yield the title compound as a purple solid (300 mg, 0.55 mmol, 16.0%). M.p. >320 °C. ^{1}H NMR (270 MHz, $CDCl_3$, 20 °C): δ = –2.75 (br. s, 2 H, N*H*), 2.45 (*m*, 4 H, CH_2–CH_2–CH_2), 3.38 (m, 4 H, S–CH_{2eq}), 3.67 (m, 4 H, S–CH_{2ax}), 7.76 (s, 2 H, S–C*H*-S), 9.37 (AB, ^3J = 4.41 Hz, 4 H, 2,8,12,18-H_β), 10.20 (s, 2 H, 10,20-H_{meso}), 9.71 + 10.55 (2 br. s, 4 H, 3,7,13,17-H_β) ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 410 (4.95), 509 (3.82), 545 (3.65), 578 (3.46), 638 (3.30) nm. MS (305 °C, 80 eV): *m*/*z* (%) = 546 (100) $[M]^{\cdot+}$, 442 (30) $[M - C_3H_7S_2+H]^+$, 273 (5) $[M]^{2+}$. HRMS: calcd. for $C_{28}H_{26}N_4S_4$ 546.10403; found 546.10500. $C_{28}H_{26}N_4S_4$ (546.78): calcd. C 61.51, H 4.79, N 10.25; found C 61.31, H 5.01, N 10.23. – Reaction of **13** with trimethylorthoformate and trichloroacetic acid gave the same product in 3% yield.

5,10,15-Tris(1,3-dithian-2-yl)porphyrin (14c): 2-Formyl-1,3-dithiane **12** (100 mg, 0.67 mmol) and pyrrole (50 μL) were dissolved in CH_2Cl_2 (100 mL). After purging with argon, $BF_3{\cdot}OEt_2$ (10 μL) was added, and the mixture was stirred for 1 h. The crude mixture was filtered through silica and concentrated under reduced pressure to yield a purple solid that was stored under Ar at –20 °C. Yield: 230 mg (308 mmol, 46%). M.p. 224 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 47 °C): δ = –2.76 (br. s, 2 H, N*H*), 2.53 (m, 3 H, CH_2–CH_{2eq}–CH_2), 2.89 (m, 3 H, CH_2–CH_{2ax}–CH_2), 3.29 (m, 6 H, S–CH_{2eq}), 3.59 (m, 6 H, S–CH_{2ax}), 7.66 (s, 2 H, S–C*H*–S), 7.74 (s, 1 H, S–C*H*–S), 9.24 (d, ^3J = 4.41 Hz, 2 H, 2,18-H_β), 9.98 (s, 1 H, H_{meso}), 9.34 + 10.64 (br. s, 6 H, 3,7,8,12,13,17-H_β) ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 423 (5.16), 520 (4.07), 555 (3.55), 595 (3.64), 652 (3.15) nm. MS (FAB+, 3 KV): *m/z* (%) = 665 (19) $[M + H]^+$, 664 (40) $[M]^{\cdot+}$, 663 (24) $[M - H]^+$, 590 (5) $[M - C_3H_6S]^+$. $C_{32}H_{32}N_4S_6$ (664.99): calcd. C 57.80, H 4.85, N 8.43; found C 57.41, H 4.82, N 8.32. – Alternatively, this compound could be prepared by the reaction of **12** and **13** and $BF_3{\cdot}OEt_2$ catalysis in a similar yield.

5,10,15,20-Tetrakis(1,3-dithian-2-yl)porphyrin (14d): 2-Formyl-1,3-dithiane **12** (1 g, 6.70 mmol) and pyrrole (500 μL, 6.90 mmol) were dissolved in CH_2Cl_2 (200 mL) in a 250-mL Schlenk flask and purged with argon. $BF_3{\cdot}OEt_2$ (40 μL) was added, and the mixture was stirred for 1 h under an atmosphere of Ar. After 1 h, DDQ (250 mg, 1.10 mmol) was added, which was followed by stirring for 20 min, the addition of NEt_3 (100 μL) and again stirring for 20 min. The crude mixture was concentrated to 200 mL and filtered through basic alumina, washing with CH_2Cl_2 (containing 1% NEt_3) followed by column chromatography (basic alumina, CH_2Cl_2/C_6H_{14}, 2:1 + 1% NEt_3) to yield 700 mg (0.89 mmol, 53%) of 5,10,15,20-tetrakis(1,3-dithinanyl)porphyrinogen. A solution of this porphyrinogen (50 mg) in CH_2Cl_2 (100 mL + 1 drop NEt_3) was treated with DDQ (50 mg, 0.22 mmol) over 4 min and after 5 min filtered through basic alumina with CH_2Cl_2. The solvent was evaporated, and the product was dried under high vacuum. The purple-red solid was stored under an atmosphere of argon at –20 °C. Yield: 20 mg (0.026 mmol, 30% with respect to the crude intermediate, 15% with respect to 2-formyl-1,3-dithiane). M.p. >320 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 47 °C): δ = –2.42 (br. s, 2 H, N*H*), 2.48 (m, 8 H, CH_2–CH_2–CH_2), 3.61–3.25 (m, 16 H, S–CH_2), 7.54 (s, 4 H, S–C*H*–S), 9.97 (br. s, 8 H, H_β) ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 433 (4.42), 527 (3.36), 565 (3.05), 601 (3.02), 664 (2.58) nm. MS (FAB+, 3 kV): *m/z* (%) = 783 (10) $[M + H]^+$, 665 (15) $[M - C_4H_7S_2]^+$. $C_{36}H_{38}N_4S_8$ (783.20): calcd. C 55.21, H 4.89, N 7.15; found C 55.62, H 4.97, N 7.44.

5-Formylporphyrin (15a):[30] A solution of 5,15-bis(1,3-dithian-2-yl)porphyrin **5** (40 mg, 72.0 μmol) in chloroform (30 mL) was treated with bis(trifluoracetoxy)iodobenzene (260 mg, 600 μmol). The mixture was stirred for 30 min at 45 °C. The solution was washed several times with a solution of $NaHCO_3$ and water, dried, and subjected to column chromatography (basic alumina grade III, $CHCl_3/C_6H_{14}$, 3:1). Yield: 15.0 mg (45 μmol, 61.7%) of a purple solid. M.p. >320 °C. ^{1}H NMR (270 MHz, CD_2Cl_2, 47 °C): δ = –3.27 (br. s, 2 H, N-H), 9.39 (AB, ^3J = 4.55 Hz, 2 H, H_β), 9.43 (AB, ^3J = 4.55 Hz, 2 H, H_β), 9.51 (AB, ^3J = 4.55 Hz, 2 H, H_β), 10.15 (AB, ^3J = 5.47 Hz, 2 H, H_β), 10.28 (s, 3 H, 10,15,20-H_{meso}), 12.51 (s, 1 H, C*H*O) ppm. MS (FAB+): *m/z* (%) = 339.0 (80) $[M + H]^+$.

5-Diethoxymethyl-15-formylporphyrin (15b): A solution of 5,15-bis(1,3-dithian-2-yl)porphyrin **14b** (40 mg, 72.0 μmol) in chloroform (30 mL, Merck, techn.) was treated dropwise with a solution of bis(trifluoracetoxy)iodobenzene (130 mg, 302 μmol) in chloroform (25 mL). The reaction mixture was stirred vigorously for 30 min. The organic phase was then washed with a $NaHCO_3$ solution and water. The residue was purified by column chromatography (basic alumina grade III, $CHCl_3/C_6H_{14}$, 2:1) to yield purple crystals (10.0 mg, 0.023 mmol, 30%). M.p. > 320 °C. ^{1}H NMR (270 MHz, CD_2Cl_2, 47 °C): δ = –2.92 (m, 2 H, N*H*), 1.42 (m, 6 H, CH_3), 3.92 (m, 2 H, O–CH_2), 4.33 (m, 2 H, O–CH_2), 7.77 (s, 1 H, O–C*H*–O), 9.14 (AB, ^3J = 4.55 Hz, 2 H, 13,17-H_β), 9.28 (AB, ^3J = 4.55 Hz, 2 H, 3,7-H_β), 9.75 (AB, ^3J = 4.55 Hz, 2 H, 12,18-H_β), 9.93 (AB, ^3J = 4.55 Hz, 2 H, 2,8-H_β), 9.94 (s, 2 H, 10,20-H_{meso}), 12.11 (s, 1 H, C*H*O) ppm. ^{13}C NMR (500 MHz, CD_2Cl_2, 0 °C): δ = 15.44, 64.63, 105.07, 106.61, 107.11, 119.19, 128.18, 130.28, 131.85, 134.01, 143.64, 145.38, 145.96, 148.91, 193.65 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 410 (5.10), 514 (3.71), 555 (3.94), 583 (3.62), 641 (3.82), 670 (3.40) nm. MS (FAB+): *m/z* (%) = 441 (100) $[M]^{\cdot+}$, 367 (50) $[C_4H_{10}O]^+$. HRMS: calcd. for $C_{26}H_{24}N_4O_3$ 440.18484; found 440.18500.

5-(1,3-Dithian-2-yl)-10,15,20-triphenylporphyrin (16a) and 5,15-Bis(1,3-dithian-2-yl)-10,20-diphenylporphyrin (16b): A solution of 2-formyl-1,3-dithiane **12** (1.0 g, 6.7 mmol) and 5-phenyldipyrromethane (1.49 g, 6.7 mmol) in dry CH_2Cl_2 (1.7 L) was purged with argon. After 1 h, a catalytic amount of TFA (110 μL) was added, followed by stirring at room temp. for 1 h. After the addition of DDQ (3.9 g, 17.2 mmol), the mixture was oxidised in the air for 45 min. The crude mixture was filtered through silica gel, eluting with CH_2Cl_2. Column chromatography (silica, CH_2Cl_2/C_6H_{14}, 2:1) eluted first **16a**, followed by **16b**. Analytical data for **16a**: Yield: 70 mg (0.11 mmol, 3.0%) of a purple solid. M.p. >320 °C. ^{1}H NMR (250 MHz, $CDCl_3$, 20 °C): δ = –2.65 (br. s, 2 H, N*H*), 2.50 (m, 2 H, CH_2–CH_2–CH_2), 3.28 (m, 2 H, S–CH_{2eq}), 3.61 (m, 2 H, S–CH_{2ax}), 7.72 (s, 1 H, S–C*H*–S), 7.77 (m, 9 H, Ar$_{m,p\text{-}H}$), 8.20 (m, 6 H, Ar$_{o\text{-}H}$), 8.79 (m, 4 H, 12,13,17,18-H_β), 8.92 (AB, ^3J = 4.41 Hz, 2 H, 2,8-H$_\beta$), 10.02 (m, 2 H, 3,7-H_β) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 20 °C): δ = 26.17, 35.76, 54.06, 114.05, 120.32, 121.19, 126.61, 126.74, 127.75, 131.17, 134.49, 141.73, 142.29 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 424 (5.41), 518 (4.24), 552 (3.83), 593 (3.74), 650 (3.57) nm. MS (FAB+, 3 kV): *m/z* (%) = 657 (100) $[M + H]^+$, 656 (73) $[M]^{\cdot+}$, 580 (37) $[M - C_6H_5 + H]^{\cdot+}$, 503 (28) $[M - 2C_6H_5 + H]^+$. HRMS: calcd. for $C_{42}H_{32}N_4S_2$ 656.20684; found 656.20434. $C_{42}H_{32}N_4S_2$ (656.86): calcd. C 76.80, H 4.91, N 8.53; found C 76.95, H 5.21, N 8.88. Analytical data for **16b**: Yield: 40 mg (0.057 mmol, 2%) of a purple solid. M.p. >320 °C. ^{1}H NMR (270 MHz, $CDCl_3$, 47 °C): δ = –2.59 (br. s, 2 H, N–H), 2.47 (m, 4 H, CH_2–CH_2–CH_2), 3.27 (m, 2 H, S–CH_{2eq}), 3.60 (m, 2 H, S–CH_{2ax}), 7.69 (s, 2 H, S–C*H*–S), 7.75 (m, 6 H, Ar$_{m,p\text{-}H}$), 8.14 (m, 4 H, Ar$_{o\text{-}H}$), 8.78 (AB, ^3J = 5.15 Hz, 4 H, 2,8,12,18-H_β), 9.90 (br. s, 4 H, 3,7,13,17-H_β) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 47 °C): δ = 26.17, 35.72, 53.75, 115.06, 120.42, 126.57, 127.81, 130.06, 134.43, 142.37, 146.32 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 422.76 (5.31), 521.31 (4.24), 555.70 (3.92), 598.22 (3.78), 653.70 (3.71) nm. MS (FAB+, 3 kV): *m/z* (%) = 699 (100), $[M + H]^+$, 698 (73 $[M]^{\cdot+}$. HRMS: calcd. for $C_{40}H_{34}N_4S_4$ 698.166635; found 698.16437. $C_{40}H_{34}N_4S_4$ (698.98): calcd. C 68.73, H 8.02, N 4.90; found C 68.52, H 8.25, N 4.77. Crystal data: (grown from CH_2Cl_2/MeOH by using standard techniques):[21,44,45] $C_{40}H_{34}N_4S_4$, M = 698.99, monoclinic, a = 6.6701(7) Å, b = 12.0093(16) Å, c = 21.684(3) Å, β = 92.974(9)°, V = 1734.6(4) Å^3, T = 210 K, space group $P2_1c$, Z = 2, μ(Mo-K_α) = 0.31 mm^{-1}, 10886 reflections measured, 3043 unique (R_{int} = 0.0995) which were used in all calculations. Final $R_1(F^2)$ was 0.0581 [$F > 4.0\sigma(F)$] and $wR(F^2)$ was 0.116 (all data).

5-Formyl-10,15,20-triphenylporphyrin (17a): The compound was prepared from **16a** by using procedure B described above. Yield: 33 mg of a purple solid (58 μmol, 97%). M.p. >300 °C. ^{1}H NMR

(270 MHz, $CDCl_3$, 48 °C): δ = –2.01 (br. s, 2 H, N*H*), 7.76 (m, 9 H, $Ph_{m,p\text{-}H}$), 8.15 (m, 6 H, $Ar_{o\text{-}H}$), 8.67 (AB, ^3J = 4.14 Hz, 2 H, H_β), 8.74 (AB, ^3J = 5.15 Hz, 2 H, H_β), 8.96 (AB, ^3J = 5.15 Hz, 2 H, H_β), 9.99 (AB, ^3J = 5.15 Hz, 2 H, H_β), 12.46 (s, 1 H, C*H*O) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, 48 °C): δ = 122.76, 126.8, 128.08, 128.14, 134.25, 141.44, 141.57, 153.62 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 424 (5.30), 527 (4.05), 568 (4.09), 597 (3.81), 653 (3.91) nm. MS (280 °C, 80 eV): *m*/*z* (%) = 566 (100) $[M]^{\cdot+}$, 283 (13) $[M]^{2+}$. HRMS: calcd. for $C_{39}H_{26}N_4O$ 566.2107; found 566.10.

5,15-Diformyl-10,20-diphenylporphyrin (17b): The compound was prepared from **16b** by using procedure B given above. Yield: 28.5 mg of a purple solid (55 μmol, 96%). M.p. 301 °C. ^{1}H NMR (270 MHz, $CDCl_3$, 47 °C): δ = –1.98 (br. s, 2 H, N*H*), 7.78 (m, 6 H, $Ar_{m,p\text{-}H}$), 8.17 (m, 4 H, $Ar_{o\text{-}H}$), 8.69 (AB, ^3J = 5.15 Hz, 2 H, H_β), 8.77 (AB, ^3J = 5.15 Hz, 2 H, H_β), 8.98 (AB, ^3J = 5.15 Hz, 2 H, H_β), 10.01 (AB, ^3J = 5.15 Hz, 2 H, H_β), 12.48 (s, 2 H, C*H*O) ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 424 (4.99), 527 (3.93), 568 (3.88), 597 (3.74), 654 (3.70) nm. MS (280 °C, 80 eV): *m*/*z* (%) = 518 (100) $[M]^{\cdot+}$, 259 (9) $[M]^{2+}$. HRMS: calcd. for $C_{34}H_{22}N_4O_2$ 518.17428; found 518.17431. $C_{34}H_{22}N_4O_2$ (518.57): calcd. C 78.75, H 4.28, N 10.80; found C 78.81, H 4.37, N 10.68.

[5-(1,3-Dithian-2-yl)-10,15,20-triphenyl)porphyrinato]zinc(II) (18): A solution of 5-(1,3-dithian-2-yl)-10,15,20-triphenylporphyrin **16a** (50 mg, 0.08 mmol) in CH_2Cl_2 (10 mL) was treated under an atmosphere of argon at room temp. with MeOH (0.5 mL) and zinc acetate (200 mg, 1.09 mmol). The mixture was stirred for 30 min. The organic phase was then washed with water and dried with sodium sulfate. After recrystallisation from CH_2Cl_2/MeOH purple crystals were obtained. Yield: 29 mg (1.43 mmol, 53%). M.p. >300 °C. R_f = 0.57 (CH_2Cl_2/C_6H_{14}, 2:1). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 2.25 (m, 2 H, CH_2–C*H*$_2$–CH_2), 3.10 (m, 2 H, S–C*H*$_2$), 3.58 (m, 2 H, S–C*H*$_2$), 7.75 (m, 10 H, S–C*H*–S, $Ar_{o,p\text{-}H}$), 8.15 (m, 6 H, $Ar_{m\text{-}H}$), 8.76 (AB, ^3J = 4.6 Hz, 2 H, H_β), 8.82 (AB, ^3J = 4.7 Hz, 2 H, H_β), 8.95 (AB, ^3J = 4.7 Hz, 2 H, 2,8-H_β), 9.76 (AB, ^3J = 5.0 Hz, 2 H, 3,7-H_β) ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 425 (5.86), 555 (4.30), 600 (3.82) nm. MS (ESI): *m*/*z* (%) = 718 (100) $[M]^{\cdot+}$. HRMS: calcd. for $C_{42}H_{30}N_4S_2Zn$ 718.1203; found 718.1170.

Synthesis of Formylporphyrins by the Vilsmeier Reaction

General Procedure C: A 100-mL three-necked flask equipped with a reflux condenser containing anhydrous DMF (75 equiv.) was charged dropwise and slowly with $POCl_3$ (74 equiv.) at 0–2 °C under an atmosphere of argon. After 20 min, the $POCl_3$–DMF complex solidified. After removal of the ice bath, 1,2-dichloroethane (5 mL) was added, and the solution was heated gently to 50 °C. The metalloporphyrin (0.1–1.5 g) was added slowly at 50 °C as a solution in 1,2-dichloroethane (25 mL). After complete addition, the mixture was heated to reflux for 12 h. After cooling with an ice bath, a saturated aqueous sodium acetate solution was added very carefully, and then the mixture was heated to 80 °C for 3 h for completion of the hydrolysis. After cooling to room temp., the porphyrin was extracted into CH_2Cl_2 (3×), followed by washing with water (1×), aqueous sodium hydrogen carbonate (2×) and then with brine (2×). Finally, the organic phase was dried with anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure.

(5-Formyl-10,20-diphenylporphyrinato)nickel(II) (3b): For the Vilsmeier complex, dry DMF (2.7 mL, 34.7 mmol) and $POCl_3$ (3.06 mL, 33.4 mmol) were used for the monoformylation of (5,15-diphenylporphyrinato)nickel(II) **1b** (500 mg, 0.96 mmol) following procedure C. Yield: 308 mg (0.56 mmol, 59%). Full characterisation was described earlier by the deprotection of dithianylporphyrin **2b**.

[5-Formyl-10,20-bis(3-methoxyphenyl)porphyrinato]copper(II) (20a): Prepared by reaction of **19a** following procedure C. After column chromatography (*h* = 43 cm, *ø* = 3 cm, alumina, CH_2Cl_2), the first fraction containing product **2** as dark purple crystals (20.6 mg, 0.03 mmol, 12.9%) was obtained. M.p. 285 °C. R_f = 0.63 (CH_2Cl_2/C_6H_{14}, 2:1). UV/Vis (CH_2Cl_2): λ (log ε) = 418 (5.42), 548 (4.33), 592 (4.51) nm. MS (ES): *m*/*z* (%) = 612 (35) $[M]^{\cdot+}$, 551 (87) $[(^{63}CuM) – OCH_3 – CHO]^+$, 267 (5) $[M]^{2+}$.

[5,15-Diformyl-10,20-bis(3-methoxyphenyl)porphyrinato]copper(II) (20b): This compound was obtained as a second product from the reaction to prepare **20a**. After column chromatography (*h* = 43 cm, *ø* = 3 cm, alumina, CH_2Cl_2), the second fraction contained product **20b** as dark green crystals (32.5 mg, 0.05 mmol, 20%). M.p. >310 °C. R_f = 0.28 (CH_2Cl_2/C_6H_{14}, 2:1). UV/Vis (CH_2Cl_2): λ (log ε) = 432 (4.89), 628 (4.03) nm. MS (ES): *m*/*z* (%) = 611 (5) $[M – CHO]^+$.

[5,15-Diformyl-10,20-bis(3-methoxyphenyl)porphyrinato]nickel(II) (20c): Prepared by reaction of **1d** following procedure C. After column chromatography (*h* = 34 cm, *ø* = 3 cm, silica, CH_2Cl_2), the second fraction contained **20c** as dark green crystals (52.4 mg, 0.08 mmol, 47.7%). M.p. 254 °C. R_f = 0.3 (CH_2Cl_2/C_6H_{14}, 2:1). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 3.98 (s, 6 H, OC*H*$_3$), 7.31 (m, 2 H), 7.47 (m, 2 H), 7.52 (m, 2 H), 7.62 (m, 2 H), 8.81 (AB, ^3J = 5.11 Hz, 4 H, H_β), 9.73 (AB, ^3J = 4.68 Hz, 4 H, H_β), 11.97 (s, 2 H, C*H*O) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 20 °C): δ = 55.36, 108.27, 113.69, 119.42, 121.16, 126.23, 127.98, 131.76, 134.90, 140.22, 142.22, 142.62, 158.14, 192.47, 192.49 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 429 (7.11), 632 (3.85) nm. MS (ES+): *m*/*z* (%) = 635 (8) $[M]^{+\cdot}$, 544 (14) $[M – OCH_3 – OCH_3 – CHO]^+$, 317 (11) $[M]^{2+}$. HRMS (ES+): calcd. for $C_{36}H_{25}N_4O_4Ni$ $[M + H]^+$ 635.1229; found 635.1245.

(5-Formyl-10,20-dihexylporphyrinato)nickel(II) (20d): This compound was obtained as a second product from the reaction to prepare **20c**. After column chromatography (*h* = 34 cm, *ø* = 3 cm, silica, CH_2Cl_2), the first fraction contained product **20d** as purple crystals (275 mg, 0.49 mmol, 60%). M.p. 149 °C. R_f = 0.68 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.97 (t, ^3J = 7.04 Hz, 6 H, C*H*$_3$), 1.38 (m, 8 H, C*H*$_2$–CH_3 + C*H*$_2$–CH_2–CH_3), 1.53 (m, 4 H, C*H*$_2$–CH_2–CH_2–CH_3), 2.09 (m, 4 H, C*H*$_2$–CH_2–CH_2–CH_2–CH_3), 3.85 (t, ^3J = 8.10 Hz, 4 H, C*H*$_2$–CH_2–CH_2–CH_2–CH_2–CH_3), 8.52 (AB, ^3J = 4.52 Hz, 2 H, H_β), 8.70 (AB, ^3J = 4.65 Hz, 2 H, H_β), 8.76 (AB, ^3J = 5.18 Hz, 2 H, H_β), 8.83 (s, 1 H, H_{meso}), 9.30 (AB, ^3J = 5.18 Hz, 2 H, H_β), 11.47 (s, 1 H, C*H*O) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 20 °C): δ = 13.76, 22.28, 29.62, 31.24, 33.34, 37.14, 103.76, 106.82, 118.83, 127.86, 129.34, 130.91, 132.17, 139.32, 139.34, 142.04, 142.80, 191.88 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 421 (5.30), 550 (4.19), 594 (4.44) nm. HRMS (ES+): calcd. for $C_{33}H_{36}N_4ONi$ 562.2243; found 562.2256. $C_{33}H_{36}N_4ONi$ (563.37): calcd. C 70.36, H 6.44, N 9.95; found C 70.21, H 6.39, N 9.93.

(5,15-Diformyl-10,20-dihexylporphyrinato)nickel(II) (20e): Prepared by reaction of **10a** following procedure C. After column chromatography (*h* = 56 cm, *ø* = 3 cm, silica, CH_2Cl_2), the second fraction gave product **20e** as dark purple crystals (46.4 mg, 0.078 mmol, 41.9%). M.p. 199 °C. R_f = 0.46 (CH_2Cl_2/C_6H_{14}, 2:1). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.84 (t, ^3J = 7.04 Hz, 6 H, C*H*$_3$), 1.25 (m, 8 H, C*H*$_2$–C*H*$_2$–CH_3), 1.36 (m, 4 H, C*H*$_2$–CH_2–CH_2–CH_3), 1.86 (m, 4 H, C*H*$_2$–CH_2–CH_2–CH_2–CH_3), 4.16 (t, ^3J = 7.73 Hz, 4 H, C*H*$_2$–CH_2–CH_2–CH_2–CH_2–CH_3), 8.93 (AB, ^3J = 4.68 Hz, 4 H, H_β), 9.38 (AB, ^3J = 4.68 Hz, 4 H, H_β), 11.52 (s, 2 H, C*H*O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 13.58, 22.07, 29.29, 31.09, 33.13, 36.21, 105.97, 120.27, 131.01, 131.45, 140.15,

140.94, 191.36 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 425 (5.11), 622 (3.14) nm. MS (ES+): *m*/*z* (%) = 591 (13) $[M]^{+\cdot}$, 304 (2) $[M]^{2+}$.

(5,15-Diformyl-10,20-dihexylporphyrinato)copper(II) (20f): This compound was obtained as a second product from the reaction to prepare **20e**. The second fraction from column chromatography (silica, CH_2Cl_2/C_6H_{14}, 2:1) and recrystallisation from CH_2Cl_2/MeOH gave the product as green crystals (10 mg, 0.02 mmol, 18%). M.p. 292 °C. R_f = 0.35 (CH_2Cl_2/C_6H_{14}, 2:1). UV/Vis (CH_2Cl_2): λ (log ε) = 427 (5.16), 572 (3.56), 626 (4.12) nm. MS (EI, 70 eV): *m*/*z* = 595 (1) $[M]^{+\cdot}$, 298 (1) $[M]^{2+}$. HRMS (ES+): calcd. for $C_{34}H_{36}CuN_4O_2$ 595.2291; found 595.5298.

(5,15-Diisobutyl-10-formylporphyrinato)copper(II) (20g): Prepared by reaction of (5,15-diisobutylporphyrinato)copper(II) following procedure C. The first fraction from column chromatography (silica, CH_2Cl_2/C_6H_{14}, 2:1) followed by recrystallisation from CH_2Cl_2/MeOH gave the pure product as purple crystals (12.1 mg, 0.02 mmol) in 47% yield. M.p. >310 °C. R_f = 0.55 (CH_2Cl_2/C_6H_{14}, 2:1). UV/Vis (CH_2Cl_2): λ (log ε) = 419 (5.98), 550 (3.89), 593 (4.09) nm. MS (EI, 70 eV): *m*/*z* = 511 (13) $[M]^{+\cdot}$, 468 (2) $[M - C_3H_7]^+$. HRMS (ESI): calcd. for $C_{29}H_{29}CuN_4O$ $[M + H]^+$ 512.1637; found 512.1631.

[5,15-Bis(1-ethylpropyl)-10-formylporphyrinato]copper(II) (20h): Prepared by reaction of [5,15-bis(1-ethylpropyl)porphyrinato]copper(II) following procedure C. The second fraction of column chromatography (silica, CH_2Cl_2/C_6H_{14}, 2:1) followed by recrystallisation from CH_2Cl_2/MeOH gave the pure product as purple crystals (31 mg, 0.06 mmol) in 97% yield. M.p. 299 °C. R_f = 0.52 (CH_2Cl_2/C_6H_{14}, 2:1). UV/Vis (CH_2Cl_2): λ (log ε) = 429 (5.15), 580 (3.49), 630 (4.14) nm. MS (70 eV): *m*/*z* = 541 (2) $[M]^{+\cdot}$, 539(3) $[M]^{+\cdot}$, 396 (7) $[M - C_{11}H_{23}O]^+$, 71 (26) $[C_5H_{11}]^+$.

[5-(1-Hydroxypropyl)-10,20-diphenylporphyrinato]nickel(II) (22a): (5-Formyl-10,20-diphenylporphyrinato)nickel(II) **3b** (30 mg, 0.05 mmol) was dissolved in dry THF. A solution of ethylmagnesium bromide (3 M in Et_2O, 170 μL, 0.5 mmol) was added. The reaction mixture was stirred at room temp. for 12 h, and the reaction was quenched with aqueous saturated ammonium chloride (10 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2. The organic layer was washed with water several times. The solvent was evaporated, and the product was purified by column chromatography (*h* = 36 cm, *ø* = 3 cm, silica, CH_2Cl_2); the first fraction gave the pure product as dark red crystals (21.6 mg, 0.037 mmol, 68%). M.p. 99 °C. R_f = 0.5 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.98 (t, ^3J = 7.31 Hz, 3 H, C*H*$_3$), 2.57 (m, 1 H, C*H*$_2$), 2.84 (m, 1 H, C*H*$_2$), 3.21 (s, 1 H, O*H*), 6.68 (t, ^3J = 7.31 Hz, 1 H, C*H*), 7.71 (m, 6 H, Ar$_{o,p\text{-}H}$), 7.99 (m, 4 H, Ar$_{m\text{-}H}$), 8.83 (AB/AB, ^3J = 10.38, ^4J = 4.78 Hz, 4 H, H_β), 9.09 (AB, ^3J = 5.11 Hz, 2 H, H_β), 9.63 (AB, ^3J = 5.11 Hz, 2 H, H_β), 9.73 (s, 1 H, H_{meso}) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 20 °C): δ = 11.45, 29.29, 35.63, 104.09, 117.64, 117.99, 126.47, 127.32, 130.00, 131.90, 132.10, 132.23, 133.23, 140.22, 140.50, 141.18, 141.84 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 409 (4.84), 525 (3.84), 556 (3.43) nm. HRMS (ES+): calcd. for $C_{35}H_{26}N_4NiO$ 576.1460; found 576.1481.

[5,15-Dihexyl-10-(1-hydroxypropyl)porphyrinato]nickel(II) (22b): (5-Formyl-10,20-dihexylporphyrinato)nickel(II) **20d** (30 mg, 0.05 mmol) was dissolved in dry THF and a solution of ethylmagnesium bromide (3 M in Et_2O, 85 μL, 0.25 mmol) was added. The reaction mixture was heated to reflux at 75 °C for 12 h. The reaction was quenched with aqueous saturated ammonium chloride (10 mL). The layers were separated; the aqueous layer was extracted with CH_2Cl_2. The organic layer was washed with water several times. The solvent was evaporated, and the product was purified by column chromatography (*h* = 29 cm, *ø* = 3 cm, silica, CH_2Cl_2); the first fraction gave the product as dark red crystals (15.9 mg, 0.03 mmol, 54%). M.p. 49 °C. R_f = 0.32 (CH_2Cl_2/C_6H_{14}, 1:4). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.91 (t, ^3J = 7.27 Hz, 9 H, C*H*$_3$), 1.33 (m, 4 H, C*H*$_2$-CH$_3$), 1.41 (m, 4 H, C*H*$_2$–CH$_2$–CH$_3$), 1.57 (m, 4 H, C*H*$_2$–CH$_2$–CH$_2$–CH$_3$), 2.24 (m, 4 H, C*H*$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_3$), 4.56 (t, ^3J = 8.04 Hz, 4 H, C*H*$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_3$), 9.06 (AB, ^3J = 4.21 Hz, 2 H, H_β), 9.32 (AB/AB, ^3J = 5.40, ^4J = 2.16 Hz, 4 H, H_β), 9.36 (AB, ^3J = 4.97 Hz, 2 H, H_β), 9.48 (s, 1 H, H_{meso}) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 20 °C): δ = 8.02, 13.72, 19.52, 22.26, 29.29, 29.65, 29.88, 31.20, 31.36, 33.48, 33.59, 36.94, 37.06, 45.37, 53.01, 102.50, 114.49, 116.83, 125.11, 128.79, 129.13, 129.27, 131.025, 131.68, 135.32, 139.73, 140.25 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 415 (4.88), 532 (3.94) nm.

[5-(1-Hydroxybenzyl)-10,20-diphenylporphyrinato]nickel(II) (22c): Compound **3b** (100 mg, 0.17 mmol) was dissolved in dry THF and a solution of phenylmagnesium bromide (1 M in THF, 1.7 mL, 1.7 mmol) was added. The reaction mixture was stirred at room temp. for 12 h. The reaction was quenched with aqueous saturated ammonium chloride (10 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2. The organic layer was washed with water several times. The solvent was evaporated, and the product was purified by column chromatography (*h* = 21 cm, *ø* = 3 cm, silica, CH_2Cl_2). The first fraction gave the product as dark purple crystals (99.6 mg, 0.16 mmol, 93%). M.p. 236 °C. R_f = 0.51 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.91, 7.28 (m, 5 H, Ar$_{o\text{-}H}$ + $CDCl_3$), 7.57 (m, 2 H, Ar$_H$), 7.71 (m, 6 H, Ar$_{o,p\text{-}H}$), 8.00 (m, 4 H, Ar$_{m\text{-}H}$), 8.08 (m, 1 H, Ar$_{p\text{-}H}$), 8.79 (AB, ^3J = 5.16 Hz, 2 H, H_β), 8.85 (AB, ^3J = 4.85 Hz, 2 H, H_β), 9.12 (AB, ^3J = 4.85 Hz, 2 H, H_β), 9.37 (AB, ^3J = 5.16 Hz, 2 H, H_β), 9.78 (s, 1 H, H_{meso}) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 20 °C): δ = 74.62, 104.60, 125.88, 126.27, 126.40, 126.47, 127.36, 127.69, 130.26, 132.02, 132.16, 132.72, 133.01, 133.11, 133.22, 140.12, 141.35, 141.93, 142.19 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 409 (5.08), 525 (4.08), 554 (3.73) nm. HRMS (ES+): calcd. for $C_{39}H_{26}N_4ONi$ 624.1460; found 624.1474.

[5,15-Dihexyl-10-(1-hydroxybenzyl)porphyrinato]nickel(II) (22d): 5-Porphyrin **20d** (30 mg, 0.05 mmol) was dissolved in dry THF and a solution of phenylmagnesium bromide (1 M in THF, 0.5 mL, 0.5 mmol) was added. The reaction mixture was stirred at room temp. for 1 h. The reaction was quenched with aqueous saturated ammonium chloride (10 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2. The organic layer was washed with water several times. The solvent was evaporated, and the product was purified by column chromatography (*h* = 28 cm, *ø* = 3 cm, silica, CH_2Cl_2); the first fraction gave the product as purple crystals (29.1 mg, 0.045 mmol) in 85% yield. M.p. 136 °C. R_f = 0.71 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.93 (t, ^3J = 7.02 Hz, 6 H, C*H*$_3$), 1.37 (m, 8 H, C*H*$_2$–CH$_2$–CH$_3$ + C*H*$_2$–CH$_3$), 1.59 (m, 4 H, C*H*$_2$–CH$_2$–CH$_2$–CH$_3$), 2.26 (m, 4 H, C*H*$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_3$), 3.27 (br. s, 1 H, CHO*H*), 4.44 (t, ^3J = 7.64 Hz, 4 H, C*H*$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_3$), 7.29 (m, 5 H, Ar$_{o,p\text{-}H}$ + $CDCl_3$), 7.52 (m, 2 H, Ar$_{m\text{-}H}$), 7.79 (br. s, 1 H, C*H*OH), 9.07 (AB, ^3J = 4.61 Hz, 2 H, H_β), 9.16 (AB, ^3J = 5.19 Hz, 2 H, H_β), 9.20 (AB, ^3J = 5.48 Hz, 2 H, H_β), 9.28 (AB, ^3J = 4.61 Hz, 2 H, H_β), 9.51 (s, 1 H, H_{meso}) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 20 °C): δ = 13.71, 22.25, 29.64, 31.32, 33.55, 37.07, 74.36, 103.46, 115.47, 117.09, 125.89, 127.64, 129.26, 129.78, 130.39, 132.07, 140.05, 140.72, 140.88, 141.87, 146.42 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 412 (5.21), 530 (4.18), 564 (3.71) nm. HRMS (ES+): calcd. for $C_{39}H_{42}N_4ONi$ 640.2712; found 640.2741.

[5,15-Dihexyl-10,20-bis(1-hydroxybenzyl)porphyrinato]nickel(II) (22e): Diformylporphyrin **20e** (50 mg, 0.08 mmol) was dissolved in dry THF and a solution of phenylmagnesium bromide (1 M in THF, 1.6 mL, 1.6 mmol) was added. The reaction mixture was stirred at room temp. for 12 h. Subsequent workup was as described for **22d**. Yield: 40.6 mg (0.05 mmol, 68%) of purple crystals. M.p. 147 °C. R_f = 0.22 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.89 (t, ^3J = 7.53 Hz, 6 H, CH_3), 1.33 (m, 8 H, CH_2–CH$_3$ + CH_2–CH$_2$–CH$_3$), 1.54 (m, 4 H, CH_2–CH$_2$–CH$_2$–CH$_3$), 2.19 (m, 4 H, CH_2–CH$_2$–CH$_2$–CH$_2$–CH$_3$), 4.38 (t, ^3J = 7.89 Hz, 4 H, CH_2–CH$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_3$), 7.28 (m, 9 H, Ar$_{o,p\text{-}H}$ + $CDCl_3$), 7.55 (m, 4 H, Ar$_{m\text{-}H}$), 7.80 (br. s, 2 H), 9.14 (AB, ^3J = 5.26 Hz, 4 H, H_β), 9.21 (AB, ^3J = 5.26 Hz, 4 H, H_β) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 20 °C): δ = 13.69, 22.25, 29.59, 31.28, 33.45, 36.97, 125.89, 126.29, 127.69, 130.07, 130.94 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 420 (4.99), 541 (4.11), 574 (3.71) nm. HRMS (ES+): calcd. for $C_{46}H_{48}N_4O_2Ni$ 746.3131; found 746.3107.

[5-(1-Hydroxybut-3-enyl)-10,20-diphenylporphyrinato]nickel(II) (22f): Compound **3b** (30 mg, 0.05 mmol) was dissolved in dry THF and a solution of allylmagnesium bromide (1 M in Et_2O, 0.5 mL, 0.5 mmol) was added. The reaction mixture was stirred at room temp. for 6 h. The reaction mixture was stirred at room temp. for 12 h. Subsequent workup was as described for **22d**. Yield: 26 mg (0.044 mmol, 80%) of purple crystals. M.p. 96 °C. R_f = 0.42(CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 3.15–3.18 [m, 2 H, CH(OH)(CH_2)], 3.53 [m, 1 H, CH(OH)(CH'_2)], 5.04 (dd, ^3J = 10.04, ^4J = 1.00 Hz, 1 H, CH=CH_2), 5.19 (dd, ^3J = 16.06, ^4J = 1.00 Hz, 1 H, CH=CH_2), 5.88 (AB/AB, ^3J = 5.02, ^4J = 4.02 Hz, 1 H, CH =CH$_2$), 6.71 [CH(OH)(CH$_2$)], 7.63 (m, 6 H, Ar$_{o,p\text{-}H}$), 7.89 (m, 4 H, Ar$_{m\text{-}H}$), 8.71 (AB, ^3J = 5.02 Hz, 2 H, H_β), 8.74 (AB, ^3J = 5.02 Hz, 2 H, H_β), 8.98 (AB, ^3J = 5.02 Hz, 2 H, H_β), 9.51 (AB, ^3J = 5.02 Hz, 2 H, H_β), 9.60 (s, 1 H, H_{meso}) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 20 °C): δ = 47.25, 74.00, 104.16, 117.14, 117.52, 117.69, 126.46, 127.32, 129.87, 131.92, 132.10, 132.32, 133.23, 134.98, 140.18, 140.29, 141.16, 141.84, 141.87 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 408 (5.01), 524 (4.04), 556 (3.61) nm. HRMS (ES+): calcd. for $C_{36}H_{26}N_4NiO$ 588.1460; found 588.1479.

(5-Cyanoethenyl-10,20-diphenylporphyrinato)nickel(II) (24a): To a suspension of (cyanomethyl)triphenylphosphonium bromide (52 mg, 0.15 mmol) in dry THF was added *n*-butyllithium (2.5 M in hexane, 0.04 mL), and the suspension was stirred for 5 min followed by the addition of (5-formyl-10,15-diphenylporphyrinato)-nickel(II) **3b** (30 mg, 0.05 mmol). The reaction mixture was stirred at room temp. for 2 h and then heated to reflux (75 °C) for 12 h. A suspension of (cyanomethyl)triphenylphosphonium bromide (52 mg, 0.15 mmol) and *n*-butyllithium (2.5 M in hexane, 0.04 mL) in dry THF was added. The mixture was stirred for 12 h and quenched with water. CH_2Cl_2 was added and the phases were separated. The organic layer was washed with water several times. The solvent was evaporated, and the product was purified by column chromatography (h = 30 cm, $\varnothing$ = 3 cm, silica, CH_2Cl_2); the first fraction gave the title compound as purple crystals (25.5 mg, 0.044 mmol, 81%). M.p. 295 °C. R_f = 0.84 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.92 (t, ^3J = 7.15 Hz, 6 H, CH_3), 1.35 (m, 4 H, CH_2–CH$_3$), 1.42 (m, 4 H, CH_2–CH$_2$–CH$_3$), 1.59 (m, 4 H, CH_2–CH$_2$–CH$_2$–CH$_3$), 2.22 (m, 4 H, CH_2–CH$_2$–CH$_2$–CH$_2$–CH$_3$), 4.38 (t, ^3J = 8.09 Hz, 4 H, CH_2–CH$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_3$), 5.68 (d, ^3J = 15.52 Hz, 1 H, CH_3), 7.74 (m, 6 H, Ar$_{o,p\text{-}H}$), 7.99 (m, 4 H, Ar$_{m\text{-}H}$), 8.81 (AB, ^3J = 4.61 Hz, 2 H, H_β), 8.88 (AB, ^3J = 4.66 Hz, 2 H, H_β), 9.08 (AB, ^3J = 4.60 Hz, 2 H, H_β), 9.26 (AB, ^3J = 4.60 Hz, 2 H, H_β), 9.63 (d, ^3J = 15.52 Hz, 1 H, CH), 9.74 (s, 1 H, H_{meso}) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 20 °C): δ = 105.85, 107.85, 108.05, 113.64, 117.78, 119.01, 126.65, 127.61, 129.88, 132.49, 133.18, 133.49, 139.66, 139.92, 141.43, 141.96, 142.66, 149.69 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 420 (5.31), 536 (4.31), 576 (4.12) nm. HRMS (ES+): calcd. for $C_{35}H_{22}N_5Ni$ 570.1229; found 570.1230.

(5,15-Dicyanoethenyl-10,20-dihexylporphyrinato)nickel(II) (24b): To a suspension of (cyanomethyl)triphenylphosphonium chloride (340 mg, 1 mmol) in dry THF was added *n*-butyllithium (2.5 M in hexane, 0.4 mL), and the suspension was stirred for 5 min. Following the addition of (5,15-diformyl-10,15-dihexylporphyrinato)-nickel(II) **20e** (30 mg, 0.05 mmol) the reaction mixture was stirred at room temp. After 1 h, (cyanomethyl)triphenylphosphonium chloride (340 mg, 1 mmol) and *n*-butyllithium (2.5 M in hexane, 0.4 mL) were added, and the mixture was stirred for 12 h. Subsequent workup was as described for **24a**. Yield: 3.3 mg (0.005 mmol, 10%) dark green crystals. M.p. 142 °C. R_f = 0.62 (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 5.56 (d, ^3J = 16.94 Hz, 2 H, CH), 9.17 (AB, ^3J = 4.89 Hz, 4 H, H_β), 9.22 (AB, ^3J = 4.89 Hz, 4 H, H_β), 9.41 (d, ^3J = 16.94 Hz, 2 H, CH) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 20 °C): δ = 13.91, 22.45, 29.55, 29.83, 31.52, 33.71, 37.19, 67.83, 108.30, 108.75, 117.95, 120.36, 131.26, 131.39, 131.52, 139.19, 141.66, 148.83 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 440 (4.86), 571 (3.71), 625 (4.05) nm.

[5,15-Dihexyl-10,20-bis(4-nitrophenylethenyl)porphyrinato]nickel(II) (24c): To a suspension of (4-nitrophenyl)triphenylphosphonium bromide (134 mg, 0.28 mmol) in dry THF was added *n*-butyllithium (2.5 M in hexane, 0.07 mL), and the suspension was stirred for 5 min. (5,15-Diformyl-10,15-dihexylporphyrinato)nickel(II) **20e** (30 mg, 0.055 mmol) was added, and the reaction mixture was stirred for 2 d at room temp. It was quenched with water, CH_2Cl_2 was added and the phases were separated. The organic layer was washed with water several times. The solvent was evaporated, and the product was purified by column chromatography (h = 28 cm, $\varnothing$ = 3 cm, silica, CH_2Cl_2) to yield purple crystals (4.8 mg, 0.006 mmol, 11%). M.p. 296 °C. R_f = 0.44 (CH_2Cl_2/C_6H_{14}, 2:1). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.91 (t, ^3J = 7.11 Hz, 6 H, CH_3), 1.34 (m, 8 H, CH_2–CH$_3$ + CH_2–CH$_2$–CH$_3$), 1.58 (m, 4 H, CH_2–CH$_2$–CH$_2$–CH$_3$), 2.24 (m, 4 H, CH_2–CH$_2$–CH$_2$–CH$_2$–CH$_3$), 4.41 (t, ^3J = 8.01 Hz, 4 H, CH_2–CH$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_3$), 6.74 (d, ^3J = 14.85 Hz, 2 H, CH), 7.84 (d, ^3J = 8.77 Hz, 4 H, Ar$_H$), 8.35 (d, ^3J = 8.18 Hz, 4 H, Ar$_H$), 9.20 (AB, ^3J = 4.62 Hz, 4 H, H_β), 9.25 (AB, ^3J = 5.40 Hz, 4 H, H_β) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 20 °C): δ = 11.00, 13.68, 22.19, 24.83, 28.61, 29.26, 29.58, 31.29, 33.38, 34.22, 36.77, 111.92, 118.82, 123.94, 126.48, 129.99, 131.29, 139.58, 140.69, 140.93, 143.19, 146.51 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 465 (5.17), 646 (4.61) nm.

(5,15-Dihexyl-10-vinylporphyrinato)nickel(II) (24d): To a suspension of methyltriphenylphosphonium bromide (50 mg, 0.14 mmol) in dry THF was added *n*-butyllithium (2.5 M in hexane, 0.03 mL), and the suspension was stirred for 5 min. The addition of (5-formyl-10,15-dihexylporphyrinato)nickel(II) **20d** (30 mg, 0.05 mmol) was followed by stirring for 1 h at room temp. The reaction was quenched with water, CH_2Cl_2 was added and the phases were separated. The organic layer was washed with water several times. The solvent was evaporated, and the product was purified by column chromatography (h = 30 cm, $\varnothing$ = 3 cm, silica, CH_2Cl_2/C_6H_{14}, 1:1); the first fraction gave the title compound as dark red crystals (17.2 mg, 0.03 mmol, 61%). M.p. 92 °C. R_f = 0.65 (CH_2Cl_2/C_6H_{14}, 1:2). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.93 (t, ^3J = 7.12 Hz, 6 H, CH_3), 1.38 (m, 8 H, CH_2–CH$_3$ + CH_2–CH$_2$–CH$_3$), 1.62 (m, 4 H, CH_2–CH$_2$–CH$_2$–CH$_3$), 2.31 (m, 4 H, CH_2–CH$_2$–CH$_2$–CH$_2$–CH$_3$), 4.57 (t, ^3J = 8.16 Hz, 4 H, CH_2–CH$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_3$), 5.60 (dd, ^3J = 17.37, ^4J = 1.63 Hz, 1 H), 6.32 (dd, ^3J = 10.98, ^4J =

1.19 Hz, 1 H), 8.95 (dd, ^3J = 17.66, ^4J = 10.98 Hz, 1 H), 9.08 (AB, ^3J = 4.71 Hz, 2 H, H_β), 9.34 (AB/AB, ^3J = 8.69, ^4J = 4.71 Hz, 4 H, H_β), 9.41 (AB, ^3J = 5.43 Hz, 2 H, H_β), 9.51 (s, 1 H, H_{meso}) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 20 °C): δ = 13.69, 22.24, 29.28, 29.64, 29.88, 31.35, 33.63, 36.97, 102.89, 114.01, 117.00, 125.09, 127.46, 129.14, 129.32, 131.18, 131.86, 135.55, 139.44, 140.94, 141.31 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 414 (4.81), 534 (3.84), 622 (2.04) nm.

(5,15-Dihexyl-10,20-divinylporphyrinato)nickel(II) (24e): To a suspension of methyltriphenylphosphonium bromide (150 mg, 0.42 mmol) in dry THF was added *n*-butyllithium (2.5 M in hexane, 0.1 mL), and the suspension was stirred for 5 min. (5,15-Diformyl-10,15-dihexylporphyrinato)nickel(II) **20e** (30 mg, 0.05 mmol) was added, and the reaction mixture was stirred for 1.5 h at room temp. Subsequent workup was as described for **24d** and gave purple crystals (12.2 mg, 0.02 mmol, 41%). M.p. 123 °C. R_f = 0.17 ($CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.92 (t, ^3J = 7.31 Hz, 6 H, CH_3), 1.33 (m, 8 H, CH_2–CH_3 + CH_2–CH_2–CH_3), 1.58 (m, 4 H, CH_2–CH_2–CH_2–CH_3), 2.25 (m, 4 H, CH_2–CH_2–CH_2–CH_2–CH_3), 4.45 (t, ^3J = 8.16 Hz, 4 H, CH_2–CH_2–CH_2–CH_2–CH_2–CH_3), 5.53 (dd, ^3J = 17.58, ^4J = 1.75 Hz, 2 H), 6.25 (dd, ^3J = 11.10, ^4J = 1.53 Hz, 2 H), 8.83 (dd, J = 2 H, 16.85 Hz, 10.68 Hz), 9.22 (AB, ^3J = 5.06 Hz, 4 H, H_β), 9.29 (AB, ^3J = 5.22 Hz, 4 H, H_β) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 20 °C): δ = 13.72, 22.24, 29.30, 29.61, 31.34, 33.45, 36.78, 113.57, 117.27, 127.57, 128.03, 128.10, 128.29, 129.30, 129.36, 131.40, 133.22, 133.41, 135.13 ppm. UV/Vis (CH_2Cl_2): λ (log ε) = 426 (4.94), 548 (4.19), 596 (3.88) nm.

CCDC-254778 (for **16b**) contains the supplementary crystallographic data for this paper.[21] These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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