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Highly substituted 2,3,7,8,12,13,17,18-octaethylporphyrins with *meso* aryl residues

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ABSTRACT

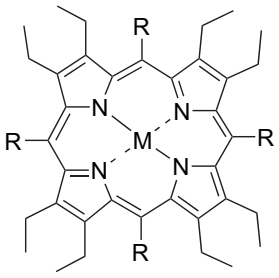
Highly substituted porphyrin-bearing *meso* aryl groups are useful compounds for optical applications and for studies on the interrelationship between the substituent pattern, macrocycle conformation and physical properties. They serve as biomimetic models for the function of tetrapyrroles in nature and help to elucidate modulation of cofactor properties through conformational effects. Using a sequence of lithium organic substitution reactions the synthesis of novel free base 5,10-A_2- and 5,10-AB-2,3,7,8,12,13,17,18-octaethylporphyrins bearing donating groups such as –OMe and –NMe_2 on the aryl-substituent was achieved. Larger aromatic residues (1-naphthyl, 9-anthracenyl and 9-phenanthrenyl) could be introduced into the macrocycle system as well, and these systems were used for the preparation of highly substituted porphyrins with a mixed substituent pattern. Using phenanthrenyl derivatives, the complete series of *meso* phenanthrenyl substituted octaethylporphyrins was successfully synthesized and the palladium complexes were prepared for photophysical investigations. Structural studies clearly showed the influence of individual substituents on the conformation of the tetrapyrrole macrocycle and conformational analyses revealed the variation of the underlying distortion modes depending on the type and arrangement of the *meso* substituents.

1. Introduction

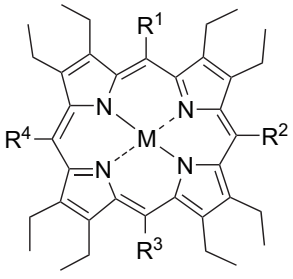
Unsymmetrically *meso* substituted porphyrins are of interest for a wide range of potential applications including nonlinear optics (NLO), photodynamic therapy (PDT), and sensor and device applications.[1] Based on both condensation[2] and C–C coupling reactions[3] the array of methods suitable for these so-called ABCD-type porphyrins is continuously expanding for β-unsubstituted porphyrins. However, applying similar methods to β-substituted porphyrins, e.g., 2,3,7,8,12,13,17,18-octaethylporphyrin (H_2OEP) **1** to yield systems of type **5**, remains a challenge.

The controlled access to halogenated derivatives such as *meso* mono- and dibromosubstituted OEP remains especially difficult, and thus prevents the use of straightforward Heck– or Suzuki–type coupling reactions.[4] Indeed, many syntheses actually first construct a purely *meso* substituted porphyrin, followed by β-bromination and then subsequent C–C couplings to construct porphyrins with both *meso* and β substituents.[5]

Due to their excellent solubility, well established photophysics and the potential to fine-tune their physicochemical properties via conformational control,[6] OEP derivatives are of considerable interest. Even more so, many potential technical applications use the



1 R = H, M = 2H
2 R = H, M = Ni(II)
3 R = H, M = Pd(II)
4 R = H, M = Pt(II)



5

easily available Pd(II) (**3**) or Pt(II) complexes of OEP (**4**),[7] or π-extended S_4 symmetric porphyrins.[8]

Further optimization of these systems requires a fine–tuning of the porphyrin properties via modification of either the β[8]or *meso* positions, and the latter requires the synthesis of multiply *meso*-substituted OEP derivatives. Many approaches for symmetric *meso*-substituted OEP-derivatives have been published, primarily in the context of highly substituted porphyrins or the synthesis of benzoporphyrins.[6,9,10] Nevertheless, approaches to unsymmetric derivatives primarily involved the use of mixed condensation with necessary tedious chromatographic work-up.

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A different approach developed by us involved the use of organolithium reagents for the direct substitution of porphyrins.[11,12] This approach showed that it was feasible to introduce up to four different *meso* substituents at the *meso* positions into a porphyrin. However, most of the developmental work for this reaction was done with simple 5,15-disubstituted porphyrins and we here turn our attention back to the functionalization of OEP derivatives.[12,13]

2. Results and discussion

2.1. *meso* Monosubstituted porphyrins

First we studied the reaction of OEP with various organolithium reagents to yield *meso* monosubstituted porphyrins. In line with earlier results,[11a–c,14] OEP reacts only sluggishly with sterically hindered reagents, such as *s*BuLi, while the alkenylporphyrin **8** could be prepared in acceptable yields (Scheme 1). However, primarily we were interested in extending the scope of this reaction for aryl residues. We had shown that PhLi reacts in quantitative yield with H_2OEP **1** and in good yield with the related Ni^{II} complex **2**.[11a,b] Accordingly, we used various aryl lithium reagents for reaction with H_2OEP all of which gave the desired products, shown in Scheme 1, in low to excellent yields. Reactions with aryl residues carrying –OH, –OMe or $–NMe_2$ groups typically gave the lowest yields while no reaction was observed with lithiated anthracene derivatives. In several reactions formation of multiply substituted products was observed when using a large excess of RLi reagent.

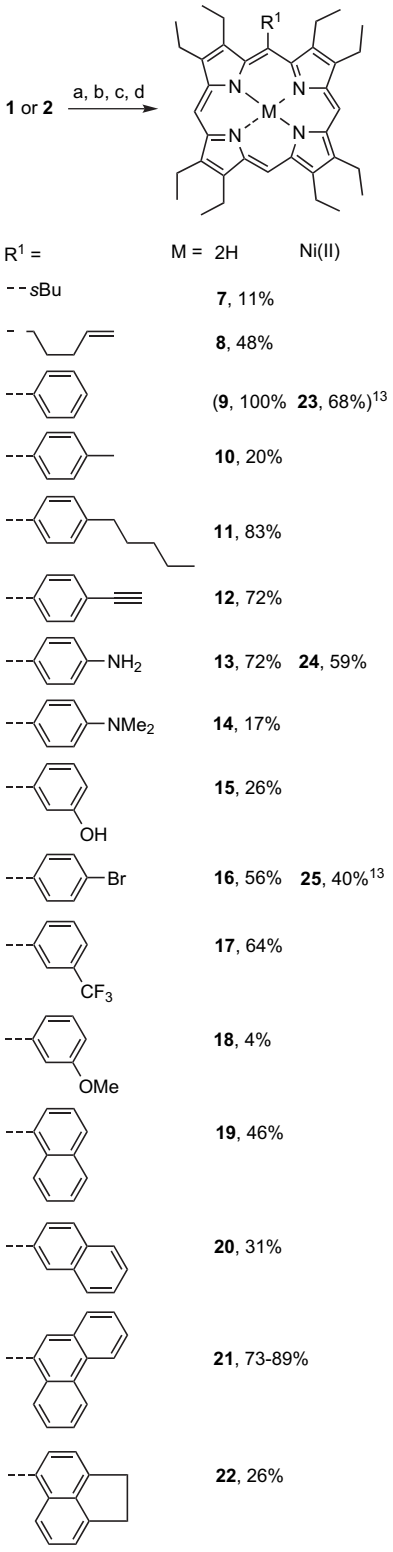
Most of these reactions were performed and optimized for free base OEP to allow for the later introduction of various metals without any demetallation/metalation sequences. Overall, use of 15–20 equiv of the respective bromides and an excess of 30–40 equiv of BuLi for the generation of the lithiated species was used. This allowed the preparation of various *meso* monosubstituted porphyrins carrying functional groups suitable for subsequent modification. For example, the 4-aminophenyl residues could be introduced in both the free base and Ni^{II} complex in good yields (**13** and **24** in 72 and 59% yield, respectively). The yields observed in these reactions are slightly lower when compared to similar reactions with 5,15-disubstituted porphyrins without β-substituents.[11f,14] However, most of those reactions were performed with the more reactive Ni^{II} complexes.

2.2. *meso* Disubstituted porphyrins

Next we turned our attention to the preparation of *meso* disubstituted porphyrins. Initial reactions were performed with free base 5-Ph-OEP **9**. As shown in Scheme 2 this porphyrin reacted readily with various ArLi reagents in good to excellent yields, including the naphthyl-, anthryl- and phenanthryl derivatives. Again, 3-methoxyphenyllithium gave only very unsatisfactory yields.

As expected the 5,10-regioisomer is the only regioisomer formed in these reactions. In distinction to earlier studies with alkyl lithium reagents, in most cases no formation of the 5,15-regioisomers was observed. This confirms our earlier assumptions about the reaction mechanism.[11c]

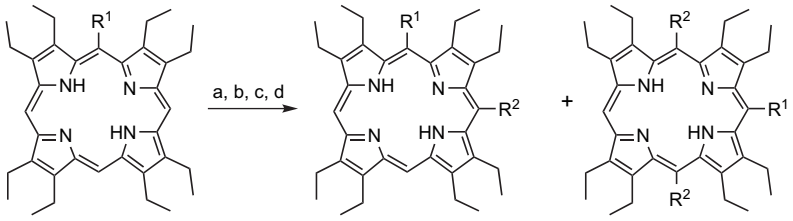
However, in several cases, the formation of *meso* trisubstituted porphyrins, i.e., products of a diarylation reaction were observed. For example, reaction of **9** with 9-anthracenyl lithium gave the products **33** and **34** in a 2:1 ratio. In the case of reaction of **11** with 9-phenanthrenyl lithium the higher arylated species **40** was the main product. Formation of these products is the result of the necessity to use an excess of RLi reagents to drive the reaction. This is clearly evidenced by reaction of **9** with 9-phenanthrenyl lithium. As shown in Scheme 2, this reaction can be adjusted in such a way as to give either the *meso* disubstituted product **35** in almost quantitative yield or the *meso* trisubstituted product **36** in 33% yield by adjusting the



Scheme 1. Synthesis and yields of *meso* substituted 2,3,7,8,12,13,17,18-octaethylporphyrins. (a) LiR[1], THF, −40 to −80 °C; (b) 1 h, rt; (c) H_2O, 15 min; (d) DDQ, 1 h.

number of equivalents of reagents used. Likewise, reaction of **21** with 9-phenanthrenyl lithium resulted in formation of the *meso* di- **48**, tri- **49**, and tetrasubstituted **66** porphyrins. Similar multiple arylation were observed for reactions of benzoporphyrins.[11e,13]

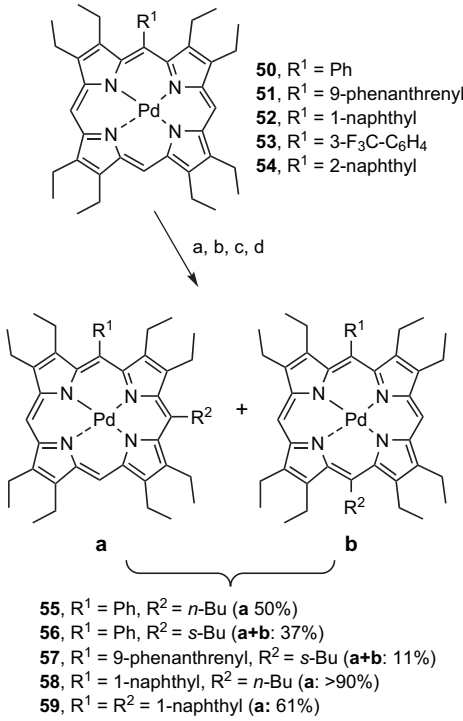
In order to further test the reactivity of OEP metal complexes we prepared the palladium complexes[15] of some of the *meso* monosubstituted porphyrins. Pd(II)OEP **3** did not react with *n*BuLi or



			R^1 =	R^2 =
9	**26**, 45%	---	Ph	4-pentylphenyl
9	**27**, 46%	---	Ph	4-bromophenyl
9	**28**, 4%	**29**, 3%	Ph	3-methoxyphenyl
9	**30**, 79%	---	Ph	4-dimethylaminophenyl
9	**31**, 61%	---	Ph	4-ethynylphenyl
9	**32**, 48%	---	Ph	1-naphthyl
9	**33**, 16%	**34**, 7%	Ph	9-anthracenyl
9	**35**, 92%	---	Ph	9-phenanthrenyl
9	---	**36**, 33%	Ph	9-phenanthrenyl
11	**37**, 47%	---	Ph	
11	**38**, 38%	---		
11	**39**, 16%	**40**, 25%	4-pentylphenyl	4-pentylphenyl
12	**41**, 65%	---	4-pentylphenyl	9-anthracenyl
17	**42**, 48%	---	4-pentylphenyl	9-phenanthrenyl
19	**43**, 47%	---	4-ethynylphenyl	4-ethynylphenyl
19	**44**, 44%	---	3-trifluoromethylphenyl	4-dimethylaminophenyl
19	**45**, 46%	**46**, 14%	1-naphthyl	4-pentylphenyl
21	**47**, 71%	---	1-naphthyl	1-naphthyl
21	**48**, 43%	**49**, 25%	1-naphthyl	9-phenanthrenyl
			9-phenanthrenyl	4-dimethylaminophenyl
			9-phenanthrenyl	9-phenanthrenyl

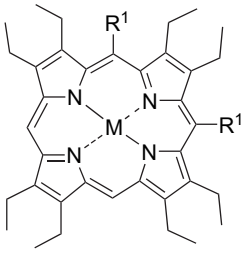
Scheme 2. Synthesis and yields of *meso* di- and trisubstituted 2,3,7,8,12,13,17,18-octaethylporphyrins. (a) LiR^2, THF, −40 to −80 °C; (b) 1 h, rt; (c) H_2O, 15 min; (d) DDQ, 1 h.

*s*BuLi. Reaction with PhLi gave a pink product in small amounts that could not be isolated. The only example reported in the literature was the reaction with an electrophile when Grigg et al. serendipitously prepared (2,3,7,8,12,13,17,18-octaethyl-5-methylporphy-rinato)palladium from **3** by reaction with trifluoromethyl sulfonate.[16] The *meso* monosubstituted Pd(II)OEP complexes showed an increased reactivity toward RLi reagents (Scheme 3).



Scheme 3. Reactions of *meso* monosubstituted palladium porphyrins. (a) LiR^2, THF, −40 to −80 °C; (b) 1 h, rt; (c) H_2O, 15 min; (d) DDQ, 1 h.

Reaction of Pd(II)(5-*n*Bu-OEP) with *n*BuLi gave an inseparable mixture of the 5,10- and 5,15-regioisomers in a 3:1 ratio and 82% overall yield (not shown). Similar results were obtained with the Pd(II) complex **51**. Reaction with *s*BuLi gave an inseparable 1:1 mixture of the two regioisomers **57a** and **57b** (combined yield approx. 11%). NMR spectroscopy indicated that **57a** occurred as a mixture of two atropoisomers. Reaction of **52** with *n*BuLi gave the respective 5,10-regioisomer **58a** based on NMR spectroscopy in high yield. However, all attempts to purify the material failed. Reaction of the same starting material **52** with naphthyl lithium was a bit more promising and gave the desired 5,10-regioisomer **59a** as the sole product in good yield (61%).



60 R^1 = Ph, M = 2H
61 R^1 = 4-ethynylphenyl, M = Ni(II)

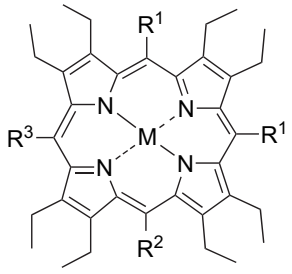
In practical terms, the use of the Pd(II) complexes in substitution reactions was a disappointment. While the reactions proceeded reasonably well, in many cases the products could not be separated chromatographically. Thus it appeared likely that use of free base porphyrins in the substitution reactions followed by insertion of Pd(II) is the better route to Pd(II) complexes of highly substituted porphyrins. In addition, we prepared the metal complex **61** in 85% yield via metalation of **41** for comparative analyses and coupling experiments.

2.3. *meso* Tri- and tetrasubstituted porphyrins

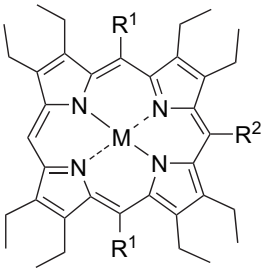
The synthesis of *meso* tri- and tetrasubstituted porphyrins proceeded similarly to the syntheses for mono- or disubstitution. As described above, *meso* trisubstituted OEPs were accessible to some extent as side products of the disubstitution reaction. A more logical approach is their synthesis through reaction of the disubstituted porphyrins with another RLi sequence. For example, reaction of **60** with 4-dimethylaminophenyl lithium gave the porphyrin **62** in 69% yield, while the *meso* tetrasubstituted porphyrin **66** could be prepared in 42% yield directly from **21**. In contrast to our earlier results with alkyl lithium reagents[11a,b,17] no thermodynamically and sterically controlled formation of porphodimethenes was observed for the highly substituted phenanthrenylporphyrins. Again, for spectroscopic analyses, several Pd(II) complexes (**67**–**70**) were prepared through standard reactions.

2.4. Spectroscopic studies

The NMR spectra of the porphyrins prepared here show typical features for highly substituted porphyrins. These are



62 R^1 = Ph, R^2 = 4-dimethylaminophenyl, R^3 = H, M = 2H
63 R^1 = Ph, R^2 = 4-bromophenyl, R^3 = H, M = 2H
64 R^1 = Ph, R^2 = 4-pentylphenyl, R^3 = H, M = 2H
65 R^1 = R^2 = 1-naphthyl, R^3 = H, M = 2H
66 R^1 = R^2 = R^3 = 9-phenanthrenyl, M = 2H
67 R^1 = 9-phenanthrenyl, R^2 = R^3 = H, M = Pd(II)
68 R^1 = R^2 = 9-phenanthrenyl, R^3 = H, M = Pd(II)
69 R^1 = R^2 = R^3 = 9-phenanthrenyl, M = Pd(II)



70 R^1 = 9-phenanthrenyl, R^2 = Ph, M = Pd(II)

notably upfield shifts of the signals with increasing degree of substitution,[9] NH signals shifted downfield with increasing substitution[18] and in several cases a broadening of the ^{1}H NMR proton signals at rt was observed.[10b,19] Porphyrins with larger aromatic residues, e.g., the naphthyl and phenanthrenyl derivatives occurred as mixtures of atropoisomers, due to hindered rotation of the aryl substituents. Detailed NMR spectroscopic investigations[20] were in agreement with earlier reports.[19,21]

As expected, an increasing number of *meso* substituents is accompanied by increasing bathochromic shifts of the absorption bands, which is an indication of increased macrocycle distortion.[18,22] Larger *meso* aryl residues typically gave larger red shifts, presumably due to stronger *peri* interactions. A typical example is the series of phenanthrenylporphyrins with 1–4 *meso* residues: **21**, **48**, **49**, **66**. The Soret and long wavelength Q absorption band for these porphyrins are: 406, 426; 426, sh; 445, 665; and 493, 697 nm, respectively, indicating a maximum bathochromic shift of almost 100 nm compared to H_2OEP. Similar results were observed for the related Pd(II) series: **51**, **67**, **68**, **69**. Here the relevant absorption maxima are: 400, 550; 414, 562; 429, 575; and 443, 590 nm, respectively. The *meso* 5,10-disubstituted OEPs with larger residues often exhibited split Soret bands. Similar trends were found for the Pd(II) complexes. Depending on higher polarity on unsymmetrically substituted nonplanar porphyrins, a solvent dependency of the absorption spectra has also been shown.[23]

2.5. Conformational and structural studies

In order to gain some insight into the structural and conformational effects of the *meso* substitution, crystal structure analyses were performed for several compounds. Based on earlier data, H_2OEP derivatives with one *meso* substituent were expected to show evidence for localized C_m displacements at the substituted position and in-plane distortion through core elongation.[24,25]

In line with these results compound **8** (Fig. 1) exhibits a relatively flat macrocycle with an average deviation of the 24 macrocycle atoms from their least-squares plane of 0.04 Å (Table 1). The local steric effect of the 5-*meso* substituent is evidenced by the larger out-of-plane displacement of the substituted C_m atom compared to the others. Similar to other octa-β-*meso*-monosubstituted free base porphyrins the compound shows in-plane distortion through core elongation of the macrocycle. The double bond character of the terminal C54–C55 bond is clearly indicated by the bond length of 1.350(3) Å.

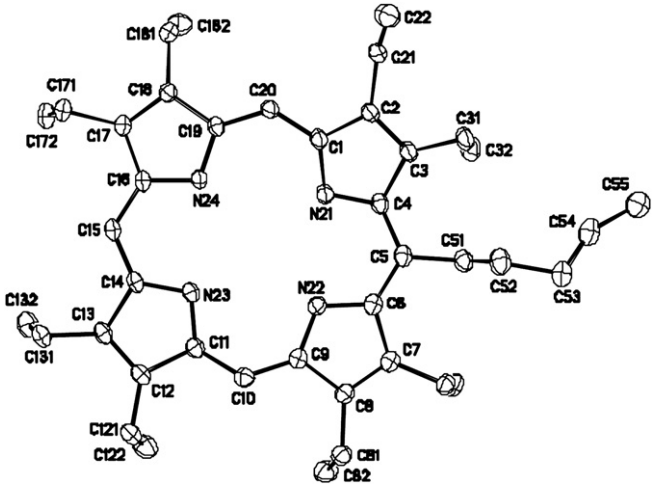


Figure 1. View of the molecular structure of **8** in the crystal. Hydrogen atoms and disordered positions have been omitted for clarity; thermal ellipsoids are drawn for 50% occupancy.

A similar situation is found in the structure of **12** (Fig. 2). However, here the conformation is clearly nonplanar (Fig. 3) with significant up and down out-of-plane displacements for all C_m positions, i.e., *ruf* distortion. This is the result of closer crystal packing. Both **8** and **12** form π-stacked aggregates, with a closer intermacrocycle separation in the latter. The triple bond on the aryl ring is clearly indicated by a bond length of 1.181(5) Å for C57–C58.

Table 1
Selected structural and conformation parameters [Å]

Compd	8	12	16	55
M-N(21)	—	—	—	1.996(2)
M-N(22)	—	—	—	2.008(2)
M-N(23)	—	—	—	2.010(2)
M-N(24)	—	—	—	2.011(2)
M-N_{av}	—	—	—	2.006(2)
⊕[a]	2.074	2.023	2.069	2.006
Ξ[b]	0.337	0.356	0.296	0.016
Δ24[c]	0.04	0.132	0.141	0.286
ΔC_m[d]	0.04	0.22	0.22	0.369
δC_5[e]	0.10	0.24	0.26	0.545
δC_{10}[e]	0	0.24	0.20	0.307
δC_{15}[e]	0.03	0.31	0.30	0.289
δC_{20}[e]	0.02	0.08	0.13	0.339

[a] Core size, average vector length from the geometric center of the four nitrogen atoms to the nitrogen atoms.
[b] Core elongation parameter defined as the difference between the vector lengths (|N21-N22|+|N23-N24|)/2-(|N22-N23|+|N21-N24|)/2.
[c] Average deviation of the 24 macrocycle atoms from their least-squares plane.
[d] Average deviation of the C_m carbon atoms from the 4*N*-plane.
[e] Average deviation of the C_m carbon atom from the 4*N*-plane.

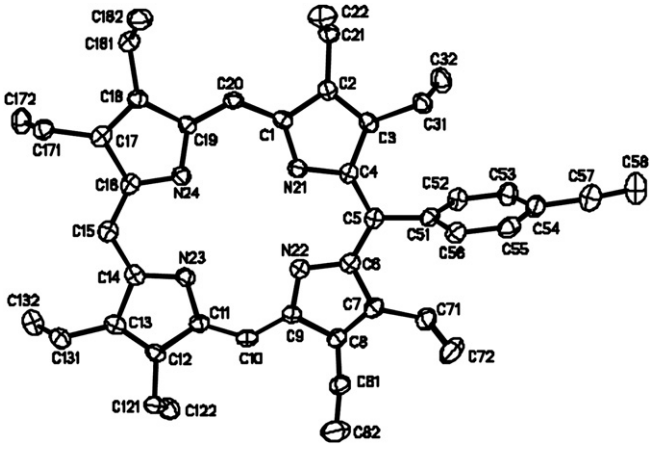


Figure 2. View of the molecular structure of **12** in the crystal. Hydrogen atoms have been omitted for clarity; thermal ellipsoids are drawn for 50% occupancy.

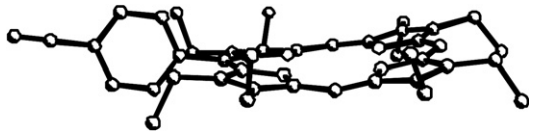


Figure 3. Side view of the molecular structure of **12** in the crystal. Hydrogen atoms have been omitted for clarity.

As shown in Table 1 the conformation of **16** (Fig. 4) is similar to that of **12**. Both in-plane and C_m out-of-plane distortions are present; which is typical for these 'nonasubstituted' porphyrins.[26]

The structure of the palladium(II) porphyrin **55** with two different *meso* substituents is the first example of such a Pd(II) compound (Fig. 5). The conformation of the porphyrin is clearly nonplanar, which is best seen in the skeletal deviation plot (Fig. 6). As evidenced by a normal structural decomposition (NSD) analysis[27] (Fig. 7) the main contributors to the conformation are the out-of-plane *sad* and *ruf* distortion modes. Thus, a significant mixing of distortion modes occurs in this type of compound. The average Pd–N bond length is slightly shorter then those of the planar Pd(II)OEP[28a] or the ruffled (5,10,15,20-tetraisopropylporphyrinato)palladium(II).[28b]

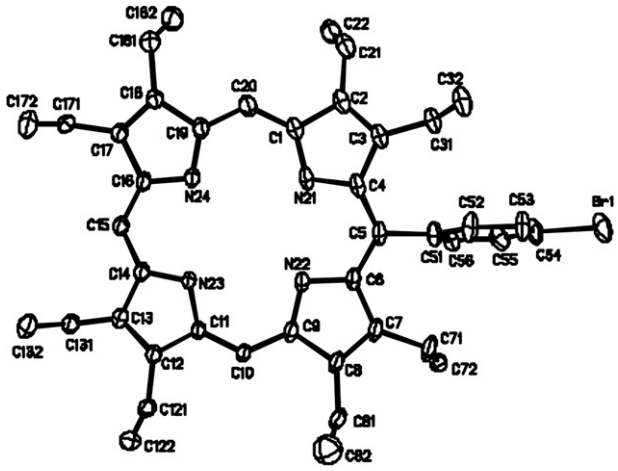


Figure 4. View of the molecular structure of **16** in the crystal. Hydrogen atoms and disordered positions have been omitted for clarity; thermal ellipsoids are drawn for 50% occupancy.

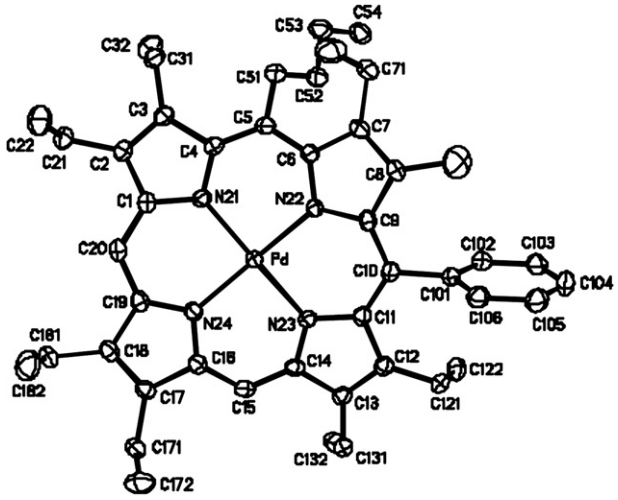


Figure 5. View of the molecular structure of **55** in the crystal. Hydrogen atoms have been omitted for clarity; thermal ellipsoids are drawn for 50% occupancy.

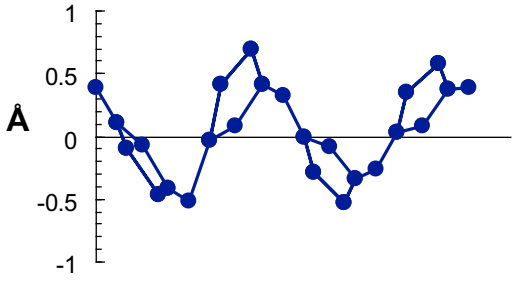


Figure 6. View of the skeletal deviations in **55**. The sequence of *meso* carbon atoms is C20, C5, C10, C15, C20 from left to right.

3. Experimental

3.1. General methods

^{1}H NMR spectra were recorded on a Bruker DPX 400 (400 MHz for ^{1}H NMR) or a Bruker AV 600 instrument (600 MHz for ^{1}H NMR; 100 MHz for ^{13}C NMR). High resolution mass spectrometry was carried out on Micromass/Waters Corp. USA liquid chromatography time-of-flight spectrometer equipped with electrospray source. Low resolution mass spectra were recorded on Micromass/Waters

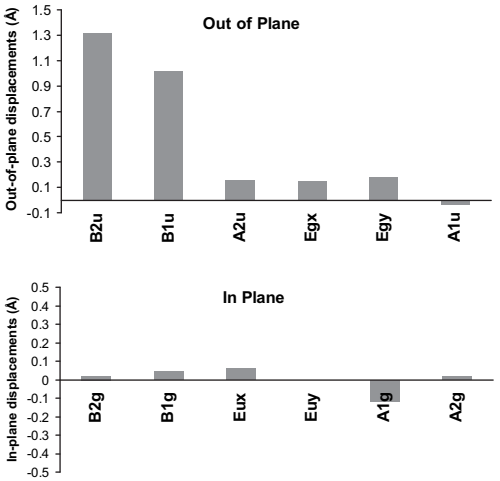


Figure 7. NSD analysis of Pd(II) porphyrin **55**. Top panel gives out-of-plane distortions, lower panel in-plane distortions.

Corp. Quattro *micro*™ LC-MS/MS instrument. UV/vis measurements were performed using a Shimadzu MultiSpec-1501 instrument. Melting points were determined using a Stuart SMP10 melting point apparatus and are uncorrected. Thin layer chromatography (TLC) was performed on silica gel 60F_{254} (Merck) precoated aluminum sheets. Column chromatography was performed using a forced flow of the indicated solvent system on Fluka silica gel 60 (230–400 mesh) or aluminum oxide. Diethylether and THF were distilled from sodium/benzophenone under argon. *n*-Butyl lithium, 1-bromonaphthalene, 2-bromonaphthalene, 1,4-dibromobenzene, and 3-bromobenzotrifluoride were purchased from Aldrich Chem. Co., 1-bromo-4-pentylbenzene was supplied from Maybridge, 9-bromophenanthrene, 3-bromoanisol, and 9-bromoanthracene from Acros, and 4-bromo-dimethylanilin from Fluka. All named chemicals were used without further purification. Other techniques were as described earlier.[1b]

3.2. Starting materials

2,3,7,8,12,13,17,18-Octaethylporphyrin **1**,[29] and its nickel(II) complex **2** were synthesized according to standard procedures. The synthesis of the Pd(II) complex **50**–**52** will be given elsewhere.[30]

3.3. General procedures

3.3.1. General procedure A—preparation of meso mono-, di-, and tri-substituted free base 2,3,7,8,12,13,17,18-octaethylporphyrins. For the preparation of in situ generated organolithium reagents the corresponding bromide (optimized equivalents) was dissolved in ether (15 mL) and an excess of *n*-BuLi (optimized equivalents, 2.5 M in *n*-hexane) was added during 5–10 min at 0 to −50 °C depending on the bromide under an argon atmosphere. The reaction mixture was stirred for an hour at rt and the corresponding octaethylporphyrin dissolved in 50 mL THF (rt to −50 °C) was added at rt to −75 °C. Stirring was continued for one hour or until TLC monitoring indicated the formation of the product (red and slightly more polar than OEP for *meso* monosubstituted compounds; green-brown, polar spot for di- and higher substituted octaethylporphyrins on silica gel, *n*-hexane/CH_2Cl_2, v/v, 1/1). The reaction was quenched with 1–2 mL of water at rt to −50 °C (color change from brown-red to dark green for *meso* monosubstituted compounds) and 5 min later a solution of DDQ (150–300 mg) in 15-mL CH_2Cl_2 was added quickly for oxidation at the same temperature (color change to dark red for *meso* monosubstituted OEPs) and stirred for 15–30 min at rt. Monosubstituted products were filtered through a frit with silica gel, eluting with *n*-hexane/CH_2Cl_2, v/v, 1/1 to 1/2 and for complete elution with CH_2Cl_2. For more polar *meso* di- and higher substituted products it was filtered through aluminum oxide with CH_2Cl_2 and for complete elution ethylacetate was added. The solvent was evaporated and the crude product purified by column chromatography on silica gel (elution with *n*-hexane/CH_2Cl_2, v/v, 4/1 to 2/1, and after elution of yellow impurities addition of 20 mL acetone to 200 mL eluent for elution of disubstituted products and addition of 20 mL ethylacetate to 200 ml eluent or 5 mL of EtOH to 100 mL eluent for elution of tri- and tetrasubstituted products). *meso* Monosubstituted compounds were recrystallized from CH_2Cl_2/CH_3OH. Fractions of *meso* di- (brown-orange solution, purple solid), tri- or tetra-substituted products (green-brown to green solutions, purple and green solids) were, if necessary, purified or separated again by column chromatography on aluminum oxide with *n*-hexane/CH_2Cl_2, v/v, from 7/1 to 2/1 to neat CH_2Cl_2 and by addition of acetone or ethylacetate to the eluent (20–200 mL CH_2Cl_2) for complete elution or elution of the tetrasubstituted product. Further purification by passing through aluminum oxide also deprotonated the inner NH groups due to its basic character, as indicated by a color change from clear green to dirty brown-green and which is necessary for the palladium(II) insertion. Compounds were precipitated from CH_2Cl_2/MeOH.

3.3.2. General procedure B—palladium(II) insertion. The respective free base porphyrin was dissolved in chloroform (c=0.002 mol L^{-1}) and two equivalents of palladium acetate in methanol (c=0.015 mol L^{-1}) was added. For sterically hindered porphyrins, the free base in solution was passed through a short column of alox to assure formation of the unprotonated form. The reaction mixture was stirred under an air atmosphere for 4 h to two days at rt under TLC monitoring (silica gel, *n*-hexane/CH_2Cl_2, v/v, 1/1). A color change from brown-green to red or dark pink was observed. The solvent was evaporated under reduced pressure and the red residue dissolved in a small amount of CH_2Cl_2 and purified using column chromatography (silica gel, *n*-hexane/CH_2Cl_2, v/v, 4/1). For further purification the compounds were precipitated from CH_2Cl_2 with *n*-hexane or methanol.

3.4. Syntheses

*3.4.1. 2,3,7,8,12,13,17,18-Octaethyl-5-(1-methylpropyl) porphyrin (**7**).* General procedure A: H_2OEP (150 mg, 0.28 mmol) was dissolved at rt in THF (50 mL) under an Ar atmosphere. Over 15 min of *s*BuLi (3.2 mL, 4.2 mmol, 15 equiv, 1.3 M in cyclohexane) was added slowly at −75 °C. The reaction mixture turned from red to green and stirring was continued for 30 min at −50 °C followed by 25 min at rt. The mixture was quenched with water (1 mL) and after 5 min DDQ in dichloromethane was added. Stirring was continued for 10 min at −40 °C and 20 min at rt. The crude mixture was filtered through alumina eluting with *n*-hexane/CH_2Cl_2 (1:1, v/v) followed by column chromatography on silica gel with *n*-hexane/CH_2Cl_2 (1:1, v/v). First a yellow and brown fraction eluted, then, after addition of 2 mL ethanol to 200 mL of the eluent a red product fraction was obtained to yield 19 mg (0.03 mmol, 11%). Mp 278 °C; R_f=0.80 (SiO_2, *n*-hexane/CH_2Cl_2/MeOH, 3:3:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ=10.08 (s, 2H, H_{meso}), 9.74 (s, 1H, H_{meso}), 5.11 (m, 1H, *s*Bu–C*H*), 4.03 (m, 16H, CH_2), 2.62 (d, 3H, J=7.64 Hz, *s*Bu–CH_3), 2.48 (m, 2H, *s*Bu–CH_2), 2.2 (m, 1H, C*H*), 1.95 (m, 18H, CH_3), 1.81 (t, 3H, J=7.09 Hz, CH_3), 0.51 (t, 3H, J=7.28 Hz, *s*Bu–CH_3); −2.30 ppm (s, 2H, N*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.7, 17.4, 17.8, 18.4, 19.7, 20.0, 22.4, 24.4, 29.7, 33.7, 40.1, 95.1, 96.6, 124.4, 140.0, 140.6, 140.7, 141.9, 142.1, 144.4, 145.7, 146.1 ppm; MS (ES^+), m/z (%): 591 (100) $[M+H]^+$; HRMS (ES^+) [$C_{40}H_{54}N_4$]: calcd 591.4425, found 591.4425.

*3.4.2. 2,3,7,8,12,13,17,18-Octaethyl-5-(5-pentenyl)-porphyrin (**8**).* For the synthesis of the organolithium reagent of 5-bromo-1-

pentene (1.2 mL, 8 mmol) was treated with Li^{t}Bu (9 mL, 15 mmol) in abs diethylether (30 mL) at −78 °C and stirred for 10 min. A solution of **1** (100 mg, 0.19 mmol) in THF (50 mL) was cooled to −78 °C and added to the organolithium reagent over the course of 1 h. Further conditions were as described for **11**. Column chromatographic workup on silica gel (dichloromethane/*n*-hexane, 1:1, v/v) gave two red fractions. The first one was identified as starting material (42%) and the second one yielded 54 mg (0.09 mmol, 48%) of **8** as purple crystals after recrystallization from CH_2Cl_2/MeOH, mp 262 °C; R_f=0.44 (dichloromethane, silica gel, 6×3 cm); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=9.96 (s, 2H, 10,20-*H*), 9.73 (s, 1H, 15-*H*), 5.77 (m, 1H, $CH_2CH_2CH_2CH$=CH_2), 4.90, 4.98 (each m, 4H, $CH_2CH_2CH_2CH$=CH_2, $CH_2CH_2CH_2CH$=CH_2), 3.97 (m, 16H, 8×CH_2CH_3), 2.15 (m, 2H, $CH_2CH_2CH_2CH$=CH_2), 1.80 (m, 26H, 8×CH_2CH_3, $CH_2CH_2CH_2CH$=CH_2), −2.96, −2.90 (each s (br), 2H, N*H*),; MS (EI, 80 eV); *m*/*z* (%): 602 (100) [M$^+$], 547 (21) [M$^+$−C_4H_7], 533 (9) [M$^+$−C_5H_9], 301 (6) [M^{2+}]; UV/vis (CH_2Cl_2) λ_{max} (log ε)=406 (5.19), 507 (4.03), 541 (3.62), 576 nm (3.58); HRMS [$C_{41}H_{54}N_4$]: calcd 602.4348, found 602.4385.

*3.4.3. 2,3,7,8,12,13,17,18-Octaethyl-5-(4-methylphenyl)-porphyrin (**10**).* Porphyrin **1** (150 mg, 0.28 mmol) was reacted with 20 equiv 4-bromotoluene (0.957 g, 5.6 mmol) and 40 equiv of *n*BuLi (4.48 mL, 11.8 mmol) according to general procedure A at −10 to 0 °C. The purple title compound **10** (35 mg, 0.056 mmol, 20%) was obtained after two column chromatographic purification steps on silica gel (first with *n*-hexane/CH_2Cl_2, 2/1, v/v and a second time with *n*-hexane/CH_2Cl_2, 4/1, v/v,). In addition, 23 mg of starting material were recovered as a first fraction (0.042 mmol, 15%). Mp 220 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=10.23 (s, 2H, H_{meso}), 9.98 (s, 1H, H_{meso}), 8.14 (d, 2H, *J*=8.8 Hz, H_{Ph}), 7.52 (d, 2H, *J*=7.8 Hz, H_{Ph}), 4.12 (m, 12H, CH_2CH_3), 2.85 (q, 4H, *J*=7.4 Hz, CH_2CH_3), 2.77 (s, 3H, Ph–CH_3), 1.98 (t, 12H, *J*=6.6 Hz, CH_2CH_3), 1.88 (t, 6H, *J*=7.6 Hz, CH_2CH_3), 1.21 (t, 6H, *J*=7.4 Hz, CH_2CH_3), −2.94 ppm (s, 2H, N*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=11.4, 13.7, 14.1, 18.0, 18.4, 18.5, 19.1, 19.7, 19.8, 20.7, 20.8, 21.7, 22.6, 24.9, 25.2, 26.9, 29.0, 30.7, 31.6, 34.3, 34.6, 36.0, 41.3, 95.2, 96.6, 119.1, 133.2, 138.0, 138.9, 140.8, 141.8, 142.1, 142.6, 142.8, 143.7, 144.0, 145.6, 173.9 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=406 (5.09), 505 (3.95), 538 (3.67), 571 (3.66), 624 nm (3.16); MS (ES$^+$), *m*/*z* (%): 625 (80) [M+H]$^+$; HRMS [$C_{43}H_{52}N_4$]: calcd 625.4270, found 625.4272.

*3.4.4. 2,3,7,8,12,13,17,18-Octaethyl-5-(4-pentylphenyl)-porphyrin (**11**).* Porphyrin **1** (150 mg, 0.28 mmol) was reacted with 20 equiv of 1-bromo-4-pentylbenzene (1 mL, 5.6 mmol) and 40 equiv of *n*BuLi (4.48 mL, 11.2 mmol) at 0 °C following general procedure A and yielded purple crystals after precipitation (160 mg, 0.22 mmol, 82%). Mp 200 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=10.16 (s, 2H, *meso*-*H*), 9.92 (s, 1H, *meso*-*H*), 8.10 (d, 2H, *J*=7.8 Hz, H_{Ph}), 7.47 (d, 2H, *J*=7.8 Hz, H_{Ph}), 4.06 (m, 12H, CH_2CH_3), 2.98 (t, 2H, *J*=7.35 Hz, pentyl-CH_2), 2.79 (m, 4H, CH_2CH_3), 1.91 (t, 12H, *J*=7.7 Hz, CH_2CH_3), 1.85 (t, 6H, *J*=7.7 Hz, CH_2CH_3), 1.51 (m, 6H, pentyl-CH_2), 1.15 (t, 6H, *J*=7.7 Hz, CH_2CH_3), 1.04, (t, 3H, *J*=7.3 Hz, pentyl-CH_3), −3.02 (s, 1H, N*H*), −3.15 ppm (s, 1H, N*H*); ^{13}C NMR (400 MHz, $CDCl_3$): δ=14.2, 18.0, 18.4, 18.5, 19.8, 20.7, 22.7, 31.7, 31.5, 72.7, 80.5, 96.6, 153.6, 155.0, 184.9, 191.6 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=404 (5.12), 503 (4.99), 537 (4.69), 571 nm (4.64); MS (ES$^+$), *m*/*z* (%): 681 (13) [M+H]$^+$; HRMS (ES$^+$) [$C_{47}H_{60}N_4$]: calcd 681.4896, found 681.4871.

*3.4.5. 2,3,7,8,12,13,17,18-Octaethyl-5-(4-ethynyl-phenyl)porphyrin (**12**).* 1-Bromo-4-ethynylbenzene (0.5 g, 2.7 mmol) was dissolved in abs diethylether (15 ml) in a 250 ml Schlenk tube. Butyl lithium (2.2 ml of a 2.5 M solution in hexane, 5.5 mmol) was added dropwise over 30 min under argon at −70 °C. The reaction mixture was warmed to −40 °C and THF (abs) was added dropwise until the aryl lithium compound formed a light white suspension. After removal of the cold bath the mixture was stirred for 15 min under argon. A solution of 2,3,7,8,12,13,17,18-octaethylporphyrin **1** (150 mg, 0.29 mmol) in abs THF (60 mL) was cooled to −20 °C and then added under argon to the vigorously stirred reaction mixture. The cold bath was removed and the mixture stirred for 60 min, followed by addition of water (5 mL) in THF (5 ml). After stirring for an additional 30 min 10–15 equiv of DDQ (ca. 0.06 M as a solution in THF) were added. After 60 min the reaction mixture was filtered through neutral alumina, washed with dichloromethane and concentrated in vacuo. Column chromatographic work-up on alumina eluting with dichloromethane/*n*-hexane (1:20, v/v) gave three fractions. The starting material (10 mg, 7%) eluted first, followed by porphyrin **12** (128 mg, 0.2 mmol, 72%) and the disubstituted compound **41** (21 mg, 0.029 mmol, 10%). Compound **12** crystallized as purple crystals from CH_2Cl_2/MeOH, mp 260 °C; R_f=0.42 (dichloromethane/*n*-hexane=1:10, v/v, alumina, 6×3 cm); ^{1}H NMR (500 MHz, $CDCl_3$, $SiMe_4$): δ=10.18 (s, 2H, H_{meso}), 9.93 (s, 1H, H_{meso}), 7.85, 8.20 (each d, 4H, *J*=4.7, H_{Ph}), 3.95–4.15 (m, 12H, 6×CH_2CH_3), 3.35 (s, 1H, C≡C*H*), 2.75 (m, 4H, 2×CH_2CH_3), 1.90 (m, 12H, 4×CH_2CH_3), 1.85 (t, 6H, ^3J=7.5 Hz, 2×CH_2CH_3), 1.15, (t, 6H, *J*=7.5 Hz, CH_2CH_3), −3.20, −3.05 (s (br.), 2H, N*H*), ppm; MS (EI, 80 eV, 250 °C), *m*/*z* (%): 634 (100) [M$^+$], 619 (3) [M$^+$−CH_3], 534 (14) [(M+H)$^+$−C_8H_5], 317 (9) [M^{2+}]; UV/vis (CH_2Cl_2): λ_{max} (log ε)=405 (5.21), 504 (4.27), 539 (4.08), 573 (4.06), 625 nm (3.91); HRMS [$C_{44}H_{50}N_4$]: calcd 634.4036, found 634.4032.

*3.4.6. 5-(4-Aminophenyl)-2,3,7,8,12,13,17,18-octaethyl-porphyrin (**13**).* For preparation of the organolithium reagent 1 g *p*-bromoaniline (5 mmol) were dissolved in diethylether (15 mL) in a 250 ml Schlenk tube. Within 1 h Li^{n}Bu (6 mL, 2.5 M in *n*-hexane, 15 mmol) were added dropwise at 0 °C (Ar) to the reaction mixture. The cold bath was removed and the yellow mixture stirred for 1 h at room temperature. Porphyrin **1** (100 mg, 0.19 mmol) was dissolved in THF (60 mL) and cooled to −40 °C. The cold solution of the porphyrin was added under Ar to the organo-lithium reagent and stirred for 1 h at room temperature. The cold bath was removed and the mixture stirred for 60 min, followed by addition of 5 ml water in 5 ml THF. After stirring for an additional 30 min 10–15 equiv of DDQ (ca. 0.06 M as a solution in THF) were added. After 60 min the reaction mixture was filtered through neutral alumina, washed with dichloromethane, and concentrated in vacuo. Column chromatography on neutral alumina (Brockmann grade III) eluting with *n*-hexane/dichloromethane (6:1, v/v) yielded three fractions. The most polar one was identified as the main product **13** and gave 85 mg (0.14 mmol, 72%) of purple crystals after recrystallization from dichloromethane/methanol. The two remaining fractions were further purified with a second chromatography column eluting with *n*-hexane/CH_2Cl_2 (9:1, v/v). The first fraction was identified as starting material (~5%) **1** and the second fraction as a minor fraction of 2,3,7,8,12,13,17,18-octaethyl-5-phenyl-porphyrin **9**. Analytical data for **13**: mp 259 °C; R_f=0.24 (*n*-hexane/dichloromethane, 4:1, v/v, alumina, 6×3 cm); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=10.19 (s, 2H, 10,20-H) 9.95 (s, 1H, 15-H), 7.95 (d, 2H, ^3J=3.8 Hz, H_{Ph}), 6.96 (d, 2H, ^3J=3.8 Hz, H_{Ph}), 4.08 (m, 12H, 6×CH_2CH_3), 3.95 (s, 2H, phenyl–NH_2), 2.94 (q, 4H, ^3J=7.4 Hz, 2×CH_2CH_3), 1.95 (t, 12H, ^3J=7.5 Hz, 4×CH_2CH_3), 1.89 (t, 6H, ^3J=7.4 Hz, 2×CH_2CH_3), 1.19 (t, 6H, ^3J=7.3 Hz, 2×CH_2CH_3), −3.05, 2.99 (each s, 2H, N*H*) ppm; MS (EI, 80 eV), *m*/*z* (%): 625 (100) [M$^+$], 610 (6) [M$^+$−CH_3], 596 (4) [M$^+$−C_2H_5], 313 (11) [M^{2+}]; UV/vis (CH_2Cl_2+1% NEt_3): λ_{max} (log ε)=406 (5.45), 505 (4.39), 537 (4.07), 573 (3.99), 625 nm (3.49); HRMS [$C_{42}H_{51}N_5$]: calcd 625.4144, found 625.4172.

*3.4.7. 2,3,7,8,12,13,17,18-Octaethyl-5-(4-dimethyl-aminophenyl)porphyrin (**14**).* Free base **1** (150 mg, 0.28 mmol) was reacted following general procedure A with 20 equiv of

4-dimethylaniline (1.12 g, 5.6 mmol) and 40 equiv of *n*-BuLi (4.48 mL, 11.2 mmol) at −70 to −40 °C to yield 33 mg of purple crystals (0.050 mmol, 17%). Mp >300 °C; R_f=0.03 (CH_2Cl_2/*n*-hexane, v/v, 2/1, silica gel, 3.5×6 cm), 0.62 (CH_2Cl_2/*n*-hexane/MeOH, v/v, 3/3/1, silica gel, 3.5×6 cm); ^{1}H NMR (400 MHz, $CDCl_3$): δ=10.20 (s, 2H, H_{meso}), 9.95 (s, 1H, H_{meso}), 8.04 (d, 1H, J=8.7 Hz, H_{Ph}), 7.49 (d, 1H, J=9.0 Hz, H_{Ph}), 7.04 (d, 1H, J=8.7 Hz, H_{Ph}), 6.83 (d, 1H, J=8.8 Hz, H_{Ph}), 4.09 (m, 12H, CH_2CH_3), 3.24 (s, 6H, N(CH_3)$_2$), 2.94 (m, 4H, CH_2CH_3), 1.96 (t, 12H, J=7.7 Hz, CH_2CH_3), 1.90 (t, 6H, J=7.6 Hz, CH_2CH_3), 1.20 ppm (t, 6H, J=7.3 Hz, CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=18.1, 18.4, 19.7, 19.8, 20.8, 40.7, 40.9, 96.5, 110.4, 113.7, 119.7, 126.5, 133.9, 140.7, 142.0, 143.0, 143.7, 145.5, 150.8, 162.8, 170.5 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=406 (5.26), 505 (4.33), 538 (3.97), 572 nm (3.97), 624 (1.25); MS (ES$^+$), *m*/*z* (%): 654 (100) [M+H]$^+$; HRMS [$C_{44}H_{55}N_5$]: calcd 654.4536, found 654.4537.

*3.4.8. 2,3,7,8,12,13,17,18-Octaethyl-5-(3-hydroxy-phenyl)porphyrin (**15**).* The free base **1** (150 mg, 0.28 mmol) was reacted with 20 equiv of 3-bromophenol (0.968 g, 5.6 mmol) and 60 equiv of *n*BuLi (6.72 mL, 16.8 mmol) at −70 to −40 °C following general procedure A. Column chromatography eluted first 33 mg (0.061 mmol, 21%) of starting material and then a fraction that gave red-purple crystals of the title compound after precipitation (46 mg, 0.073 mmol, 26%). Mp >300 °C; R_f=0.65 (CH_2Cl_2/*n*-hexane/MeOH, 3/3/1, v/v, 3.5×6 cm, silica gel); ^{1}H NMR (400 MHz, $CDCl_3$): δ=10.16 (s, 2H, H_{meso}), 9.92 (s, 1H, H_{meso}), 7.78, 7.59 (each m, each 1H, H_{Ph}), 7.49 (t, 1H, J=7.95 Hz, H_{Ph}), 7.22 (m, 1H, H_{Ph}), 4.06 (m, 12H, CH_2CH_3), 2.83 (q, 4H, J=7.48 Hz, CH_2CH_3), 1.91 (t, 12H, J=7.57 Hz, CH_2CH_3), 1.85 (t, 6H, J=7.57 Hz, CH_2CH_3), 1.18 ppm (t, 6H, J=7.48 Hz, CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.2, 104.3, 105.4, 107.9, 109.1, 114.1, 115.9, 151.7, 152.5, 155.5, 159.8, 162.4, 172.5, 176.9, 182.5, 183.9, 184.6, 188.1, 195.6, 199.3, 208.5, 212.2 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=404 (5.03), 503 (4.02), 537 (3.79), 571 (3.76), 623 (3.45) nm; MS (ES$^+$), *m*/*z* (%): 627 (100) [M+H]$^+$; HRMS [$C_{42}H_{50}N_4O$]: calcd 627.4063, found 627.4036.

*3.4.9. 5-(4-Bromophenyl)-2,3,7,8,12,13,17,18-octaethyl-porphyrin (**16**).* For preparation of *p*-bromophenyl lithium 1 g (4.24 mmol) 1,4-dibromobenzene were dissolved in 20 ml abs THF and cooled to −80 °C. After a course of 30 min Li^{n}Bu (2.12 mL, 2 M solution, 4.24 mmol) was added to the cold solution. The cold bath was removed and the reaction mixture stirred for 1 h. In the meantime a solution of **1** (100 mg, 0.19 mmol) in THF (50 mL) was prepared and cooled to 0 °C. The solution of the porphyrin was added to the organolithium reagent under argon and stirred for 30 min at room temperature. Subsequent steps followed the procedure given for **12**. The crude mixture was purified using silica gel (dichloromethane/*n*-hexane, 1:1, v/v) and gave two red fractions. The first fraction contained starting material **1** (28%) and the second fraction gave 73 mg (0.11 mmol, 56%) of purple crystals of **16** after recrystallization from CH_2Cl_2/*n*-hexane, mp 248 °C; R_f=0.37 (dichloromethane, silica gel, 6×3 cm); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=10.10 (s, 2H, 10–20-H) 9.85 (s, 1H, 15-H), 8.01 (d, 2H, ^3J=4.3 Hz, H_{Ph}), 7.72 (d, 2H, ^3J=4.3 Hz, H_{Ph}), 3.98 (m, 12H, 6×CH_2CH_3), 2.72 (m, 4H, 2×CH_2CH_3), 1.80 (m, 18H, 6×CH_2CH_3), 1.09 (m, 6H, 2×CH_2CH_3,), −3.24, −3.11 (each s, br, 2H, N*H*) ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=424 (5.15), 520 (4.12), 592 nm (3.79); MS (EI, 80 eV), *m*/*z* (%): 690 (100) [$C_{42}H_{49}N_4{}^{81}Br^+$], 688 (80) [$C_{42}H_{49}N_4{}^{79}Br^+$], 611 (21) [$M^+-{}^{81}Br$, $M^+-{}^{79}Br$], 591 (13) [$M^+-C_6H_5Br$], 534 (69) [$M^+-C_5H_9$], 345 (10) [$C_{42}H_{49}N_4{}^{81}Br^{2+}$], 344 (10) [$C_{42}H_{49}N_4{}^{79}Br^{2+}$]; HRMS [$C_{42}H_{49}N_4{}^{79}Br$]: calcd 688.3141, found 688.3168; HRMS [$C_{42}H_{49}N_4{}^{81}Br$]: calcd 690.3120, found 690.3165.

*3.4.10. 2,3,7,8,12,13,17,18-Octaethyl-5-(3-trifluoromethyl-phenyl)-porphyrin (**17**).* The free base **1** (150 mg, 0.28 mmol) was reacted with 20 equiv of 3-bromobenzotrifluoride (0.77 mL, 5.6 mmol) and 40 equiv of *n*-BuLi (4.48 mL, 11.2 mmol) according to general procedure A at −30 °C and yielded purple crystals (125 mg, 0.179 mmol, 64%). Mp 212 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=10.20 (s, 2H, H_{meso}), 9.67 (s, 1H, H_{meso}), 8.61 (s, 1H, H_{Ph}), 8.36 (d, 1H, J=7.5 Hz, H_{Ph}), 8.11 (d, 1H, J=7.9 Hz, H_{Ph}), 7.81 (t, 1H, J=7.6 Hz, H_{Ph}), 4.09 (m, 12H, CH_2CH_3), 2.81 (m, 2H, CH_2CH_3), 2.61 (m, 2H, CH_2CH_3), 1.93 (t, 12H, J=7.4 Hz, CH_2CH_3), 1.85 (t, 6H, J=7.5 Hz, CH_2CH_3), 1.15 (t, 6H, J=7.4 Hz, CH_2CH_3), −3.02 (s, 1H, N*H*), −3.17 ppm (s, 1H, N*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=17.7, 18.4, 18.50, 18.53, 19.7, 20.7, 95.7, 96.1, 116.5, 125.1, 127.0, 129.5, 136.5, 141.1, 142.0, 142.3, 142.9, 144.5, 145.8 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=404 (6.68), 503 (5.44), 537 (4.93), 571 nm (4.76); MS (ES$^+$), *m*/*z* (%): 679 (100%) {M+H}$^+$; HRMS [$C_{43}H_{49}F_3N_4$]: calcd 679.3988, found 679.3958.

*3.4.11. 2,3,7,8,12,13,17,18-Octaethyl-5-(3-methoxy-phenyl)porphyrin (**18**).* The free base **1** (150 mg, 0.28 mmol) was reacted with 10 equiv of 3-bromoanisol (0.523 g, 2.8 mmol) and 20 equiv of *n*-BuLi (2.24 mL, 5,6 mmol) according to general procedure A at −75 °C. The mixture was stirred at rt and OEP was added after 1 h. Workup after 24 h yielded purple crystals (7 mg, 0.011 mmol, 4%). Mp 217 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=10.17 (s, 2H, H_{meso}), 9.92 (s, 1H, H_{meso}), 7.82 (d, 1H, J=7.25 Hz, H_{Ph}), 7.77 (br s, 1H, H_{Ph}), 7.56 (t, 1H, J=7.26 Hz, H_{Ph}), 7.36 (m, 1H, H_{Ph}); 4.07 (m, 12H, CH_2), 3.96 (s, 3H, OCH_3), 2.82 (m, 4H, CH_2), 1.91 (m, 18H, CH_3), 1.21 (m, 6H, CH_3), −3.07 ppm (s, 2H, N*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=18.0, 18.4, 19.7, 20.7, 55.4, 95.3, 96.6, 114.5, 118.6, 119.0, 126.5, 127.3, 140.9, 141.3, 141.8, 142.2, 142.7, 143.3, 144.2, 145.6, 157.6 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=405 (5.32), 503 (4.26), 537 (3.95), 571 (3.92), 623 nm (3.41); MS (ES$^+$), *m*/*z* (%): 641 (100%) {M+H}$^+$; HRMS [$C_{43}H_{53}N_4O$]: calcd 641.4219, found 641.4244.

*3.4.12. 2,3,7,8,12,13,17,18-Octaethyl-5-(1-naphtyl)-porphyrin (**19**).* The free base **1** (150 mg, 0.28 mmol) was reacted with 31 equiv of 1-bromonaphthalene (1.2 mL, 8.68 mmol) and 40 equiv of *n*-BuLi (4.48 mL, 11.2 mmol) according to general procedure A at −30 °C. The mixture was stirred at rt and OEP was added after 1 h at −30 °C. Workup after 24 h yielded purple crystals (91 mg, 0.128 mmol, 46%). Mp 200 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=10.20 (s, 2H, H_{meso}), 9.98 (s, 1H, H_{meso}), 8.40 (d, 1H, J=5.8 Hz, $H_{naphthyl}$), 8.30 (d, 1H, J=7.7 Hz, $H_{naphthyl}$), 8.12 (d, 1H, J=8.3 Hz, $H_{naphthyl}$), 7.84 (t, 1H, J=6.9 Hz, $H_{naphthyl}$), 7.47 (m, 1H, $H_{naphthyl}$), 7.01 (m, 2H, $H_{naphthyl}$), 4.12 (m, 8H, CH_2), 3.97 (m, 4H, CH_2), 2.64 (m, 2H, CH_2), 2.29 (m, 2H, CH_2), 1.95 (t, 12H, J=7.8 Hz, CH_3), 1.87 (t, 6H, J=7.6 Hz, CH_3), 0.87 (t, 6H, J=7.6 Hz, CH_3), −2.79 ppm (s, 2H, N*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=16.6, 18.4 m 19.7, 19.8, 20.7, 95.4, 96.6, 116.4, 124.3, 125.9, 127.7, 128.4, 128.8, 131.7, 132.6 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=406 (4.13), 504 (4.02), 538 (3.84), 572 (3.85), 625 nm (3.41); MS (ES$^+$), *m*/*z* (%): 661 (100%) {M+H}$^+$; HRMS [$C_{46}H_{52}N_4$]: calcd 661.4270, found 661.4265.

*3.4.13. 2,3,7,8,12,13,17,18-Octaethyl-5-(2-naphthyl)-porphyrin (**20**).* Free base **1** (100 mg, 0.18 mmol) was reacted with 20 equiv 2-bromonaphthalene (0.7449 g, 3.6 mmol) and 60 equiv of *n*-BuLi (4.5 mL, 10.8 mmol) at −50 °C according to general procedure A to yield purple crystals (45 mg, 0.055 mmol, 31%). Mp 198 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=10.22 (s, 2H, H_{meso}), 9.98 (s, 1H, H_{meso}), 8.72 (s, 1H, $H_{naphthyl}$), 8.39 (d, 1H, J=8.1 Hz, $H_{naphthyl}$), 8.21 (d, 1H, J=7.6 Hz, $H_{naphthyl}$), 8.16 (d, 1H, J=8.1 Hz, $H_{naphthyl}$), 8.04 (d, 1H, J=7.2 Hz, $H_{naphthyl}$), 7.03 (m, 2H, $H_{naphthyl}$), 4.12 (m, 8H, CH_2CH_3), 4.03 (m, 4H, CH_2CH_3), 2.77 (m, 2H, CH_2CH_3), 2.57 (m, 2H, CH_2CH_3), 1.59 (t, 12H, J=7.6 Hz, CH_2CH_3), 1.86 (t, 6H, J=7.5 Hz, CH_2CH_3), 1.08 (t, 6H, J=7.2 Hz, CH_2CH_3), −2.92 (s, 1H, N*H*), −3.09 ppm (s, 1H, N*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=17.7, 18.4, 18.5, 19.7, 19.8, 20.8, 95.3, 96.7, 118.7, 125.5, 126.4, 126.8, 131.6, 132.1, 133.1, 139.2, 140.9, 141.8, 142.2, 142.6, 142.7, 143.6, 144.2, 145.7 ppm; UV/vis (CH_2Cl_2): λ_{max}

($\log \varepsilon$)=406 (5.61), 505 (4.48), 538 (4.20), 572 (4.20), 624 nm (3.71); MS (ES^+), *m*/*z* (%): 661 (100) $[M+H]^+$; HRMS [$C_{46}H_{52}N_4$]: calcd 661.4270, found 661.4290.

*3.4.14. 2,3,7,8,12,13,17,18-Octaethyl-5-(9-phenanthren-yl)porphyrin (**21**).* Free base **1** (150 mg, 0.28 mmol) was reacted at −20 °C with 31 equiv 9-bromophenanthrene (2.23 g, 8.86 mmol) and 40 equiv of *n*-BuLi (4.5 mL, 11.2 mmol, −30 °C) according to general procedure A to yield purple crystals (147 mg, 0.207 mmol, 89%). Mp >300 °C; R_f=0.86 (CH_2Cl_2/*n*-hexane/MeOH, v/v, 3/3/1, silica gel); ^1H NMR (400 MHz, $CDCl_3$): δ=10.20 (s, 2H, H_{meso}), 9.98 (s, 1H, H_{meso}), 9.04 (d, 1H, *J*=8.56 Hz, $H_{phenanthrenyl}$), 9.00 (d, 1H, *J*=7.54 Hz, $H_{phenanthrenyl}$), 8.71 (m, 1H, $H_{phenanthrenyl}$), 8.08 (d, 1H, *J*=7.89 Hz, $H_{phenanthrenyl}$), 7.92 (t, 1H, *J*=8.20 Hz, $H_{phenanthrenyl}$), 7.81 (t, 1H, *J*=7.27 Hz, $H_{phenanthrenyl}$), 7.65 (m, 1H, $H_{phenanthrenyl}$), 7.27 (m, 1H, $H_{phenanthrenyl}$), 7.14 (m, 1H, $H_{phenanthrenyl}$), 4.13 (m, 8H, CH_2), 3.96 (m, 4H, CH_2), 2.79 (m, 2H, CH_2), 2.36 (m, 2H, CH_2), 1.94 (t, 12H, *J*=7.20 Hz, CH_3), 1.82 (t, 6H, *J*=7.61 Hz, CH_3), 0.85 (t, 6H, *J*=7.42 Hz, CH_3), −2.73 (s, 1H, N*H*), −3.00 ppm (s, 1H, N*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=17.0, 18.6, 18.7, 20.0, 21.1, 21.3, 96.1, 97.1, 116.4, 123.4, 126.9, 127.8, 129.4, 131.2, 137.7, 141.8, 142.9, 143.0, 145.4 ppm; UV/vis (CH_2Cl_2): λ_{max} ($\log \varepsilon$)=406 (5.13), 504 (4.13), 538 (3.86), 571 (3.83), 624 nm (3.52); MS (ES^+), *m*/*z* (%): 711 (49) $[M+H]^+$; HRMS [$C_{50}H_{54}N_4$]: calcd 711.4427, found 711.4426.

*3.4.15. 5-Acenaphthyl-2,3,7,8,12,13,17,18-octaethylporphyrin (**22**).* Free base **1** (150 mg, 0.28 mmol) was reacted at −20 °C with 31 equiv 1-bromoacenaphtene (2.021 g, 8.68 mmol) and 40 equiv of *n*-BuLi (4.5 mL, 11.2 mmol, −60 °C) according to general procedure A to yield purple crystals (51 mg, 0.074 mmol, 26%). Mp 190 °C; ^1H NMR (400 MHz, $CDCl_3$): δ=10.21 (s, 2H, H_{meso}), 9.98 (s, 1H, H_{meso}), 8.36 (d, 1H, *J*=6.6 Hz, $H_{acenaphthyl}$), 7.64 (d, 1H, *J*=6.8 Hz, $H_{acenaphthyl}$), 7.32 (d, 1H, *J*=6.6 Hz, $H_{acenaphthyl}$), 7.05 (t, 1H, *J*=8.4 Hz, $H_{acenaphthyl}$), 6.66 (d, 1H, *J*=8.2 Hz, $H_{acenaphthyl}$), 4.12 (m, 8H, CH_2), 3.99 (m, 4H, CH_2), 3.79 (m, 2H, $CH_{2acenaphthyl}$), 3.72 (m, 2H, $CH_{2acenaphthyl}$), 2.73 (m, 2H, CH_2), 2.35 (m, 2H, CH_2), 1.95 (t, 12H, *J*=8.5 Hz, CH_3), 1.85 (t, 6H, *J*=7.5 Hz, CH_3), 0.91 (t, 6H, *J*=7.3 Hz, CH_3), −2.8 (s, 1H, N*H*), −3.04 ppm (s, 1H, N*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=17.1, 18.4, 18.5, 19.73, 19.78, 19.83, 20.8, 95.3, 96.5, 116.3, 117.8, 119.2, 123.0, 127.9, 133.1, 135.5, 138.3, 140.8, 141.8, 142.5, 144.4, 144.3, 145.3, 145.5, 146.8 ppm; UV/vis (CH_2Cl_2): λ_{max} ($\log \varepsilon$)=407 (5.02), 505 (3.92), 538 (3.66), 574 (3.64), 625 nm (3.26); MS (ES^+), *m*/*z* (%): 687 (42) $[M+H]^+$; HRMS [$C_{48}H_{54}N_4$]: calcd 687.4427, found 687.4450.

*3.4.16. {5-(4-Aminophenyl)-2,3,7,8,12,13,17,18-octa-ethylporphyrinato}nickel(II) (**24**).* Preparation of the organo-lithium reagent and the general synthetic procedure was performed as described for the free base. Use of **2** (100 mg, 0.17 mmol) and chromatographic work-up with neutral alumina (Brockmann grade III, *n*-hexane/dichloromethane, 4:1, v/v) yielded two fractions. The first, red band was starting material **2** followed by a major second, red fraction. After recrystallization from dichloromethane/methanol 68 mg (59%, 0.10 mmol) of purple crystals were obtained. Mp 263 °C. R_f=0.35 (*n*-hexane/dichloromethane, 4:1, v/v, alumina, 6×3 cm); ^1H NMR (500 MHz, $CDCl_3$, TMS): δ=0.83 (t, 6H, ^3J=7.3 Hz, 2×CH_2CH_3), 1.60 (t, 6H, ^3J=7.3 Hz, 2×CH_2CH_3), 1.69 (t, 12H, ^3J=7.4 Hz, 4×CH_2CH_3), 2.67 (q, 4H, ^3J=7.4 Hz, 2×CH_2CH_3), 3.67 (m, 4H, 2×CH_2CH_3), 3.70 (m, 8H, 4×CH_2CH_3), 6.79 (d, 2H, ^3J=4.0 Hz, H_{Ph}), 7.62 (d, 2H, ^3J=4.0 Hz, H_{Ph}), 9.41 (s, 1H, 15-H), 9.46 ppm (s, 2H, 10,20-H); UV/vis (CH_2Cl_2): λ_{max} ($\log \varepsilon$)=403 (5.21), 525 (4.02), 559 nm (4.28); MS (EI, 80 eV), *m*/*z* (%): 681 (100) $[M^+]$, 666 (6) $[M^+-CH_3]$, 638 (4) $[M^+-C_3H_7]$, 341 (10) $[M^{2+}]$; HRMS [$C_{42}H_{49}N_5Ni$]: calcd 681.3341, found 681.3372.

*3.4.17. 2,3,7,8,12,13,17,18-Octaethyl-5-(4-pentylphenyl)-10-phenylporphyrin (**26**).* The reaction was performed following general procedure A using 40 equiv of 1-bromo-4-pentylbenzene (0.93 mL, 5.24 mmol) and 50 equiv of *n*-BuLi (2.62 mL, 6.55 mmol) at 0 °C to rt. Porphyrin **9** (80 mg, 0.131 mmol) in THF was added after 80 min at −0 °C. After 30 min at rt the mixture was cooled to −0 °C and quenched. Standard work-up yielded 46 mg (0.060 mmol, 45%) of a purple solid of the title compound. Mp 110 °C; ^1H NMR (400 MHz, $CDCl_3$): δ=9.68 (s, 2H, H_{meso}), 8.37 (d, 2H, *J*=7.02 Hz, $H_{pentylPh}$), 8.25 (d, 2H, *J*=7.78 Hz, $H_{pentylPh}$), 7.80 (t, 1H, *J*=7.40 Hz, *para* H_{Ph}), 7.72 (t, 2H, *J*=7.42 Hz, *meta* H_{Ph}), 7.53 (t, 2H, *J*=7.79 Hz, *ortho* H_{Ph}), 3.98 (m, 4H, CH_2CH_3), 3.79 (m, 4H, CH_2CH_3), 2.99 (t, 2H, *J*=7.41 Hz, pentyl-CH_2), 2.73 (m, 4H, CH_2CH_3), 2.32 (m, 4H, CH_2CH_3), 1.86 (t, 6H, *J*=7.54 Hz, CH_2CH_3), 1.62 (t, 6H, *J*=7.52 Hz, CH_2CH_3), 1.52 (m, 6H, pentyl-CH_2), 1.04 (t, 3H, *J*=6.81 Hz, pentyl-CH_3), 0.69 (m, 6H, CH_2CH_3), 0.50 (m, 6H, CH_2CH_3), −2.70 ppm (s, 2H, N*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.0, 14.1, 17.3, 17.9, 18.1, 19.3, 19.5, 20.5, 22.5, 22.6, 31.2, 31.4, 35.9, 94.7, 94.8, 119.2, 119.5, 125.7, 126.6, 126.8, 128.2, 135.1, 135.3, 138.7, 141.4, 143.1 ppm; UV/vis (CH_2Cl_2): λ_{max} ($\log \varepsilon$)=425 (5.50), 521 (4.29), 592 nm (4.13); MS (ES^+), *m*/*z* (%): 556 (39), 757 (38) $[M^+]$; HRMS [$C_{53}H_{64}N_4$]: calcd 757.5209, found 757.5180.

*3.4.18. 5-(4-Bromophenyl)-2,3,7,8,12,13,17,18-octaethyl-10-phenylporphyrin (**27**).* The reaction was performed following the general procedure A using 40 equiv of 1,4-dibromobenzene (1.236 g, 5.24 mmol) and 50 equiv of *n*-BuLi (2.6 mL, 6.55 mol) at −30 °C to rt. Porphyrin **9** (80 mg, 0.131 mmol) in THF was added after 100 min at −30 °C and after stirring for 30 min at rt it was quenched at −30 °C with water. Work-up yielded 47 mg (0.061 mmol, 46%) of the title compound as a purple solid. Mp 119 °C; ^1H NMR (500 MHz, $CDCl_3$): δ=9.66, 9.65 (each s, each 1H, H_{meso}), 8.33 (m, 2H, $H_{4\text{-}Br\text{-}Ph}$), 8.23 (d, 2H, *J*=8.18 Hz, H_{Ph}), 7.86 (d, 2H, *J*=8.16 Hz, $H_{4\text{-}Br\text{-}Ph}$), 7.77 (t, 1H, *J*=7.43 Hz, H_{Ph}), 7.69 (t, 2H, *J*=7.44 Hz, H_{Ph}), 3.95 (q, 4H, *J*=7.45 Hz, CH_2CH_3), 3.82 (m, 4H, CH_2CH_3), 2.71 (m, 4H, CH_2CH_3), 2.29 (m, 4H, CH_2CH_3), 1.84 (t, 6H, *J*=7.59 Hz, CH_2CH_3), 1.59 (t, 6H, *J*=7.41 Hz, CH_2CH_3), 0.66 (t, 6H, *J*=7.26 Hz, CH_2CH_3), 0.47 (m, 6H, CH_2CH_3), −2.72 ppm (s, 2H, N*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=11.2, 13.9, 17.0, 17.8, 18.0, 20.2, 20.4, 22.4, 25.0, 26.7, 28.8, 30.7, 31.4, 34.3, 34.4, 94.8, 94.9, 117.3, 119.3, 122.7, 126.4, 128.1, 129.6, 135.0, 136.5, 140.0, 141.1 ppm; UV/vis (CH_2Cl_2): λ_{max} ($\log \varepsilon$)=425 (3.99), 521 (3.81), 592 nm (3.61); MS (ES^+), *m*/*z* (%): 765.3538 (48) $[M^+]$; HRMS [$C_{48}H_{53}N_4Br$]: calcd 765.3532, found 765.3538.

*3.4.19. 2,3,7,8,12,13,17,18-Octaethyl-5-(3-methoxy-phenyl)-10-phenylporphyrin (**28**).* The reaction was performed following general procedure A using 40 equiv of 3-bromoanisol (0.66 mL, 5.24 mmol) and 50 equiv of *n*-BuLi (2.62 mL, 6.55 mmol) at −60 °C to rt. Free base **9** (80 mg, 0.131 mmol) in 50 mL THF was added after 90 min at −50 °C. The reaction was kept at low temperature for 15 min and then stirred for 35 min at rt. It was quenched at −20 °C, followed by standard work-up to yield 4 mg (0.0054 mmol, 4%) of the title compound (first fraction) as a purple solid accompanied by 3% of **29** (second fraction). Data for **28**: Mp 133 °C; ^1H NMR (500 MHz, $CDCl_3$): δ=9.63 (s, 2H, H_{meso}), 8.31 (d, 2H, *J*=6.63 Hz, H_{Ph}), 7.92 (d, 1H, *J*=7.44 Hz, $H_{MeO\text{–}Ph}$), 7.87 (m, 1H, $H_{MeO\text{–}Ph}$), 7.76 (t, 1H, *J*=7.41 Hz, H_{Ph}), 7.67 (t, 2H, *J*=7.50 Hz, H_{Ph}), 7.57 (t, 1H, *J*=8.02 Hz, $H_{MeO\text{–}Ph}$), 7.33–7.31 (m, 1H, $H_{MeO\text{–}Ph}$), 3.95 (s, 3H, OCH_3), 3.92 (q, 4H, *J*=7.40 Hz, CH_2CH_3), 3.81 (m, 4H, CH_2CH_3), 2.69–2.63 (m, 4H, CH_2CH_3), 2.34–2.25 (m, 4H, CH_2CH_3), 1.80 (t, 6H, *J*=7.59 Hz, CH_2CH_3), 0.88 (m, 6H, CH_2CH_3), 0.70 (t, 3H, *J*=7.38 Hz, CH_2CH_3), 0.62 (t, 3H, *J*=7.38 Hz, CH_2CH_3), 0.51 (t, 3H, *J*=7.01 Hz, CH_2CH_3), 0.44 (t, 3H, *J*=6.93 Hz, CH_2CH_3), −2.74 ppm (s, 2H, N*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.1, 17.35, 17.39, 17.4, 18.0, 18.2, 19.3, 19.5, 20.5, 22.6, 29.6, 55.5, 60.4, 94.9, 114.3, 118.9, 119.2, 120.8, 126.6, 127.5, 128.2, 135.2, 141.3, 142.6 ppm; UV/vis (CH_2Cl_2): λ_{max} ($\log \varepsilon$)=425 (4.59), 448 (4.36), 521 (3.48), 592 (3.37), 636 nm (0.035); MS (ES^+), *m*/*z* (%):

730 (100) $[M+H]^+$; HRMS $[C_{49}H_{56}N_4O]$: calcd 730.4849, found 730.4867.

*3.4.20. 2,3,7,8,12,13,17,18-Octaethyl-5,15-bis(3-methoxyphenyl)-10-phenylporphyrin (**29**).* The compound was isolated from the reaction described in Section 3.4.19. Yield: 4 mg, (0.0048 mmol, 3%) of a green solid. Mp 168 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.38–9.24 (br s, 1H, H_{meso}), 8.60–8.40 (m, 2H, H_{Ph}), 8.05 (m, 2H, H_{MeO-Ph}), 7.84 (m, 1H, H_{Ph}, 2H, H_{MeO-Ph}), 7.68 (m, 2H, H_{Ph}), 7.50 (m, 2H, H_{MeO-Ph}), 7.37 (m, 2H, H_{MeO-Ph}), 4.1 (s, 6H, 2×OCH_3), 3.66 (m, 4H, CH_2CH$_3$), 2.73–2.67 (m, 12H, CH_2CH$_3$), 1.53 (m, 6H, CH$_2$CH_3), 0.68–0.2 (m, 18H, CH$_2$CH_3), −0.08 ppm (s, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=15.3, 16.4, 18.1, 19.9, 55.9, 116.0, 121.0, 121.9, 29.1, 129.3, 130.8, 137.3, 139.2, 142.7 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=465 (5.23), 569 (3.56), 608 (3.86), 663 nm (4.01); MS (ES$^+$), m/z (%): 578 (29), 823 (22) $[M+H]^+$; HRMS $[C_{56}H_{62}N_4O_2]$: calcd 823.4951, found 823.4958.

*3.4.21. 5-(4-Dimethylaminophenyl)-2,3,7,8,12,13,17,18-octaethyl-10-phenylporphyrin (**30**).* The reaction was performed following the general procedure A using 40 equiv of 1-bromo-4-dimethylaminobenzene (1.048 g, 5.24 mmol) and 50 equiv of *n*-BuLi (2.62 mL, 6.55 mmol) at −45 °C to rt. Free base **9** (80 mg, 0.131 mmol) in THF was added after 1 h at −20 °C and after 30 min stirring at rt the reaction was quenched at the same temperature to yield 76 mg (0.104 mmol, 79%) of a purple solid. Mp 151 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.61 (s, 1H, H_{meso}), 9.60 (s, 1H, H_{meso}), 8.33 (d, 2H, J=6.94 Hz, H_{Ph}), 8.12 (d, 2H, J=8.54 Hz, $H_{Me2N-Ph}$), 7.87 (d, 1H, J=9.04 Hz, H_{Ph}), 7.67 (t, 2H, J=7.43 Hz, H_{Ph}), 7.03 (d, 2H, J=8.60 Hz, $H_{Me2N-Ph}$), 3.92 (q, 4H, J=7.50 Hz, CH_2CH$_3$), 3.81 (m, 4H, CH_2CH$_3$), 3.23 (s, 6H, N(CH_3)$_2$), 2.83 (m, 2H, CH_2CH$_3$), 2.69 (m, 2H, CH_2CH$_3$), 2.35 (m, 2H, CH_2CH$_3$), 2.23 (m, 2H, CH_2CH$_3$), 1.80 (t, 6H, J=7.59 Hz, CH$_2$CH_3), 1.63 (m, 6H, CH$_2$CH_3), 0.63 (m, 6H, CH$_2$CH_3), 0.42 (m, 6H, CH$_2$CH_3), −2.64 ppm (br s, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.9, 17.3, 17.8, 19.2, 19.5, 24.6, 31.5, 40.6, 40.7, 74.1, 74.2, 94.3, 94.6, 110.5, 112.5, 112.9, 125.2, 126.6, 126.9, 130.0, 130.5, 132.7, 135.3, 136.2, 150.1, 155.5 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=427 (4.40), 593 (3.27), 667 nm (3.30); MS (ES$^+$), m/z (%): 730.4867 (100) $[M+H]^+$; HRMS $[C_{50}H_{59}N_5]$: calcd 730.4867, found 730.4849.

*3.4.22. 2,3,7,8,12,13,17,18-Octaethyl-5-(4-ethynyl-phenyl)-10-phenylporphyrin (**31**).* The organo-lithium reagent was prepared as described in Section 3.4.5 for **12** using 1 g 1-bromo-4-ethynylbenzene (5.4 mmol) and reacted with 100 mg **9** (0.19 mmol) in 40 ml THF at −20 °C. Column chromatography on neutral alumina eluting with dichloromethane/*n*-hexane (1:1, v/v) resolved first a yellow fraction. The polarity of the solvent was slowly increased and elution with neat dichloromethane gave a red fraction containing starting material **9** (35%). Subsequent development of the column with dichloromethane/methanol (99:1, v/v) eluted the target compound and gave purple crystals after recrystallization from CH_2Cl_2/CH_3OH (82 mg, 0.12 mmol, 61%), mp 265 °C; R_f=0.25 (dichloromethane/*n*-hexane: 3:1, v/v, alumina, 6×3 cm); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=9.64, 9.65 (each s, 2H, 15–20-H) 8.27 (d, 4H, ^3J=4.3 Hz, H_{Ph}), 7.83 (d, 2H, ^3J=4.3 Hz, H_{Ph}), 7.77 (m, 1H, H_{Ph}), 7.67 (m, 2H, H_{Ph}), 3.91 (m, 4H, 2×CH_2CH$_3$), 3.80 (m, 4H, 2×CH$_2$CH_3), 3.37 (s, 1H, C≡CH), 2.64–2.76 (m, 8H, 4×CH_2CH$_3$), 1.79 (t, 6H, ^3J=7.3 Hz, 2×CH$_2$CH_3), 1.57 (t, 6H, ^3J=7.3 Hz, 2×CH$_2$CH_3), 1.11 (t, 12H, ^3J=7.5 Hz, 4×CH$_2$CH_3), −2.82 (s, 2H, NH); UV/vis (CH_2Cl_2+1% NEt_3): λ_{max} (log ε)=424 (5.15), 520 (4.12), 592 nm (3.79); MS (EI, 80 eV), m/z (%): 710 (100) $[M^+]$, 681 (4) $[M^+-C_2H_5]$, 355 (10) $[M^{2+}]$; HRMS $[C_{50}H_{54}N_4]$: calcd 710.4348, found 710.4384.

*3.4.23. 2,3,7,8,12,13,17,18-Octaethyl-5-(1-naphthyl)-10-phenylporphyrin (**32**).* The reaction was performed as described in Section 3.3.1 using 40 equiv of 1-bromonaphthalene (0.71 mL, 5.24 mmol) and 50 equiv of *n*-BuLi (2.62 ml, 6.55 mmol) at −40 °C to rt. Free base **9** (80 mg, 0.131 mmol) in 50 mL THF was added after 1 h at −10 °C. After 30 min at rt the reaction was quenched at rt to yield 46 mg (0.062 mmol, 47%) of a purple solid. Mp 155 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.69 (s, 1H, H_{meso}), 9.67 (s, 1H, H_{meso}), 8.42 (d, 1H, J=6.87 Hz, $H_{naphthyl}$), 8.33 (d, 2H, J=7.09 Hz, H_{Ph}), 8.29 (d, 1H, J=8.25 Hz, $H_{naphthyl}$), 8.11 (d, 1H, J=8.07 Hz, $H_{naphthyl}$), 7.90 (t, 1H, J=9.37 Hz, H_{Ph}), 7.83 (d, 1H, J=8.04 Hz, $H_{naphthyl}$), 7.82–7.75 (m, 1H, $H_{naphthyl}$), 7.68 (t, 2H, J=7.42 Hz, H_{Ph}),7.53 (d, 1H, J=7.82 Hz, $H_{naphthyl}$), 7.22 (t, 1H, J=7.62 Hz, $H_{naphthyl}$), 3.97 (m, 4H, CH_2CH$_3$), 3.84 (m, 2H, CH_2CH$_3$), 3.74 (m, 2H, CH_2CH$_3$), 2.69 (br m, 2H, CH_2CH$_3$), 2.42 (br m, 2H, CH_2CH$_3$), 2.39–2.24 (m, 4H, CH_2CH$_3$), 1.84 (t, 6H, J=7.50 CH$_2$CH_3), 1.60 (t, 3H, J=7.51 CH$_2$CH_3), 1.53 (t, 3H, J=7.43 CH$_2$CH_3), 0.67 (t, 3H, J=7.36, CH$_2$CH_3), 0.46 (t, 3H, J=7.41 Hz, CH$_2$CH_3), 0.41 (t, 3H, J=7.36 Hz, CH$_2$CH_3), 0.34 (t, 3H, J=7.17 Hz, CH$_2$CH_3), −2.60 ppm (s, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=16.6, 16.9, 17.3, 17.4, 18.0, 18.2, 19.2, 19.4, 19.5, 20.4, 20.5, 94.9, 95.0, 116.2, 118.9, 124.4, 125.8, 126.0, 126.6, 127.7, 128.1, 128.2, 128.9, 132.2, 133.4, 135.2, 137.1, 139.1, 141.3 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=425 (3.22), 520 (3.01), 592 (sh), 650 nm (sh); MS (ES$^+$), m/z (%): 737 (32) $[M+H]^+$; HRMS $[C_{52}H_{56}N_4]$: calcd 737.4583, found 737.4572.

*3.4.24. 5-(9-Anthracenyl)-2,3,7,8,12,13,17,18-octaethyl-10-(4-phenyl)porphyrin (**33**).* The reaction was performed following the procedure in Section 3.3.1 using 50 equiv of 9-bromoanthracene (1.2403 g, 4.90 mmol) and 60 equiv of *n*-BuLi (2.35 mL, 5.88 mmol) at −40 °C to rt. Free base **9** (60 mg, 0.098 mmol) in 50 mL THF was added after 80 min at −20 °C, followed by stirring for 80 min at rt. After quenching with water −0 °C the reaction yieled 13 mg (0.0165 mmol, 16%) of a purple solid of the title compound as the first green-brown fraction and 7 mg of **34** as the second green fraction. Mp 110 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.70 (s, 1H, H_{meso}), 9.67 (s, 1H, H_{meso}), 8.88 (s, 1H, $H_{anthracenyl}$), 8.30 (d, 2H, J=6.6 Hz, H_{Ph}), 8.21 (d, 2H, J=8.6 Hz, $H_{anthracenyl}$), 7.73 (t, 1H, J=7.41 Hz, H_{Ph}), 7.61 (t, 2H, J=7.43 Hz, H_{Ph}), 7.59 (m, 1H, $H_{anthracenyl}$), 7.47 (m, 3H, $H_{anthracenyl}$), 7.10 (m, 2H, $H_{anthracenyl}$), 3.96 (m, 4H, CH_2CH$_3$), 3.83 (m, 2H, CH_2CH$_3$), 3.63 (m, 2H, CH_2CH$_3$), 2.66 (m, 2H, CH_2CH$_3$), 2.11 (m, 2H, CH_2CH$_3$), 1.84 (m, 4H, CH_2CH$_3$), 1.59 (m, 6H, CH$_2$CH_3), 1.45 (t, 3H, J=7.52 Hz, CH$_2$CH_3), 0.89 (m, 3H, CH$_2$CH_3), 0.68 (t, 3H, J=7.37 Hz, CH$_2$CH_3), 0.33 (t, 3H, J=7.19 Hz, CH$_2$CH_3), 0.01 (m, 3H, CH$_2$CH_3), −0.08 (t, 3H, J=7.30 Hz, CH$_2$CH_3), −2.50 ppm (br s, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=15.3, 15.9, 17.4, 18.0, 18.2, 19.2, 19.3, 19.6, 20.5, 31.8, 94.9, 95.2, 113.8, 125.3, 126.5, 127.1, 127.9, 128.0, 128.1, 128.6, 130.9, 135.2, 135.4 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=425 (4.54), 520 (3.50), 592 nm (sh, 3.92); MS (ES$^+$), m/z (%): 787 (20) {M+H]$^+$; HRMS $[C_{56}H_{58}N_4]$: calcd 787.4740, found 787.4703.

*3.4.25. 5,15-bis(9-Anthracenyl)-2,3,7,8,12,13,17,18-octa-ethyl-10-phenylporphyrin (**34**).* The compound was obtained from the reaction described in Section 3.4.24 and was isolated as a green solid (7 mg, 0.0072 mmol, 7%). NMR spectroscopy indicated the formation of atropoisomers due to hindered anthracenyl rotation. Mp 145 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=9.52 (s, 1H, H_{meso}), 8.90 (s, 2H, $H_{anthracenyl}$), 8.35 (d, 2H, J=6.58 Hz, H_{Ph}), 8.26 (d, 4H, J=8.52 Hz, $H_{anthracenyl}$), 7.69 (m, 1H, H_{Ph}), 7.62 (m, 2H, H_{Ph}, 4H, $H_{anthracenyl}$), 7.52 (m, 4H, $H_{anthracenyl}$), 7.21 (m, 4H, $H_{anthracenyl}$), 3.56 (m, 6H, CH_2), 3.40 (m, 2H, CH_2), 2.09–1.88 (m, 8H, CH_2), 2.28–2.01 (m, 8H, CH_2), 1.56 (t, 6H, J=7.48 Hz, CH_3), 0.25 (t, 6H, J=7.10 Hz, CH_3), 0.08 (t, 6H, J=7.30 Hz, CH_3), −0.06 (t, 6H, J=7.24 Hz, CH_3), −0.25 ppm (s, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=11.4, 14.1, 15.3, 19.3, 20.4, 20.6, 22.65, 22.69, 25.2, 26.9, 29.0, 29.6, 31.5, 31.9, 34.6, 41.3, 112.4, 125.3, 128.2, 128.4, 131.0, 135.3 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=446 (4.59), 538 (3.59), 609 (3.42), 666 (3.31) nm; MS (ES$^+$), m/z 578 (80),

963 (15) $[M+H]^+$; HRMS $[C_{70}H_{66}N_4]$: calcd 963.5375, found 963.5366.

*3.4.26. 2,3,7,8,12,13,17,18-Octaethyl-5-(9-phenanthre-nyl)-10-phenylporphyrin (**35**).* The reaction was performed using the general procedure A using 34 equiv of 9-bromophenanthrene (1.708 g, 6.64 mmol) and 43 equiv of *n*-BuLi (3.37 mL, 8.425 mmol) at −30 °C to rt. Free base **9** (120 mg, 0.196 mmol) in 50 mL THF was added after 1 h at rt. After 40 min at the same temperature the reaction was quenched with water to yield 125 mg (0.181 mmol, 92%) of a purple solid after work-up as the main fraction. When the reaction was performed with 30 equiv of 9-bromoanthracene, 30 equiv of BuLi and 150 mg of **9** gave 26 mg (0.032 mmol, 13%) of the title compound as the second fraction, followed by 25 mg (0.025 mmol, 10%) of the trisubstituted compound **36** accompanied by 22% recovered starting material as the first fraction. Mp 168 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.69 (s, 1H, H_{meso}), 9.67 (s, 1H, H_{meso}), 9.00 (m 2H, $H_{phenanthrenyl}$), 8.66 (s, 1H, $H_{phenanthrenyl}$), 8.33 (d, 2H, J=6.09 Hz, H_{Ph}), 8.09 (d, 1H, J=7.63 Hz, $H_{phenanthrenyl}$), 7.87 (t, 1H, J=7.11 Hz, $H_{phenanthrenyl}$), 7.65–7.80 (m, 2H, H_{Ph}; 3H, $H_{phenanthrenyl}$), 7.59 (d, 1H, J=7.95 Hz, H_{Ph}), 7.29 (t, 1H, J=7.21 Hz, $H_{phenanthrenyl}$), 3.96 (m, 4H, CH_2CH_3), 3.84 (m, 2H, CH_2CH_3), 3.70 (m, 2H, CH_2CH_3), 2.72–2.53 (m, 4H, CH_2CH_3), 2.27–2.09 (m, 4H, CH_2CH_3), 1.83 (t, 6H, J=7.47 Hz, CH_2CH_3), 1.59 (t, 6H, J=7.47 Hz, CH_2CH_3), 0.67 (t, 3H, J=7.33 Hz, CH_2CH_3), 0.45 (t, J=7.35 Hz, 3H, CH_2CH_3), 0.37 (t, 6H, J=6.31 Hz, CH_2CH_3), −2.58 ppm (s, 2H, N*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=16.4, 16.7, 17.3, 18.0, 18.2, 19.2, 19.3, 19.4, 19.5, 19.8, 20.2, 20.6, 29.6, 94.9, 95.1, 116.0, 118.9, 122.5, 122.9, 126.4, 126.6, 127.1, 127.2, 128.2, 129.1, 129.2, 129.4, 130.7, 130.9, 134.1, 135.2, 136.4, 137.3, 141.3 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=430 (sh), 454 (4.76), 587 (3.63), 541 (4.07), 638 nm (3.42); MS (ES^+), m/z (%): 681 (13) $[M+H]^+$.

*3.4.27. 2,3,7,8,12,13,17,18-Octaethyl-5,15-bis(9-phenan-threnyl)-10-phenylporphyrin (**36**).* The title compound could be obtained from the reaction described in Section 3.4.26. Alternatively, reaction of **9** with 24 equiv of 9-bromophenanthrene and 37 equiv. BuLi afforded exclusively the title compound (39 mg, 0.0404 mmol, 33%). Mp 148 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.52 (s, 1H, H_{meso}), 8.98 (m, 4H, $H_{phenanthrenyl}$), 8.68 (s, 1H, $H_{phenanthrenyl}$), 8.67 (s, 1H, $H_{phenanthrenyl}$), 8.34–8.43 (m, 3H, H_{Ph}), 8.08 (d, 2H, J=7.73 Hz, $H_{phenanthrenyl}$), 7.85 (t, 2H, J=7.54 Hz, $H_{phenanthrenyl}$), 7.76 (t, 2H, J=7.35 Hz, H_{Ph}), 7.75–7.64 (m, 6H, $H_{phenanthrenyl}$), 7.36 (m, 2H, $H_{phenanthrenyl}$), 3.67 (m, 4H, CH_2CH_3), 2.59 (m, 2H, CH_2CH_3), 2.37 (m, 2H, CH_2CH_3), 2.28–2.01 (m, 8H, CH_2CH_3), 1.52 (m, 6H, CH_2CH_3), 0.54 (t, 6H, J=7.26 Hz, CH_2CH_3), 0.40 (t, 6H, J=7.29, CH_2CH_3), 0.27 (m, 6H, CH_2CH_3), −1.78 ppm (br s, 2H, N*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=16.2, 16.6, 17.1, 17.8, 19.3, 19.5, 20.4, 20.5, 114.6, 122.8, 126.4, 126.6, 127.1, 127.4, 128.1, 128.9, 129.1, 130.9, 131.0 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=472 (5.14), 564 (sh), 608 (3.38), 663 nm (3.70); MS (ES^+), m/z (%): 963 (15) $[M+H]^+$, 964 (10) $[M+2H]^+$; HRMS $[C_{70}H_{66}N_4]$: calcd 963.5366, found 963.5388.

*3.4.28. 2,3,7,8,12,13,17,18-Octaethyl-5,10-bis(4-pentyl-phenyl)-porphyrin (**37**).* The reaction was performed following the procedure given in Section 3.3.1 using 40 equiv of 1-bromo-4-pentylbenzene (0.83 mL, 4.68 mmol) and 50 equiv of *n*-BuLi (2.34 mL, 5.87 mmol) at −20 °C to rt. Free base **11** (80 mg, 0.117 mmol) in THF (50 mL) was added after 80 min at rt, followed by stirring for 1 h at the same temperature. Then the reaction was quenched with water at 0 °C to yield 46 mg (0.055 mmol, 47%) of a purple solid after work-up. Mp 68 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.62 (s, 2H, H_{meso}), 8.19 (d, 4H, J=7.45 Hz, H_{Ar}), 7.48 (d, 4H, J=7.45 Hz, H_{Ar}), 3.83 (q, 4H, J=7.44 Hz, CH_2CH_3), 3.81 (m, 4H, CH_2CH_3), 2.95 (t, 4H, J=7.45 Hz, pentyl-CH_2), 2.70 (br m, 4H, CH_2CH_3), 2.28 (br m, 4H, CH_2CH_3), 1.88 (m, 4H, pentyl-CH_2), 1.81 (t, 6H, J=7.45 Hz, CH_2CH_3), 1.57 (t, 6H, J=7.51 Hz, CH_2CH_3), 1.49 (m, 8H, pentyl-CH_2), 1.00 (t, 6H, J=6.80 Hz, pentyl-CH_3), 0.64 (t, 6H, J=7.35 Hz, CH_2CH_3), 0.45 (t, 6H, J=6.75 Hz, CH_2CH_3), −2.71 ppm (s, 2H, N*H*); ^{13}C NMR (100 MHz $CDCl_3$): δ=14.2, 17.3, 18.0, 18.1, 19.5, 19.6, 20.5, 22.6, 29.7, 31.3, 31.4, 35.9, 94.7, 119.4, 135.2, 138.7, 143.1 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=425 (5.17), 521 (4.00), 592 nm (3.78); MS (ES^+), m/z (%): 827 (100) $[M+H]^+$; HRMS $[C_{58}H_{74}N_4]$: calcd 827.5992, found 827.5952.

*3.4.29. 5-(9-Anthracenyl)-2,3,7,8,12,13,17,18-octaethyl-10-(4-pentylphenyl)porphyrin (**38**).* The reaction was performed as described in Section 3.3.1 using 60 equiv of 9-bromoanthracene (1.3668 g, 5.40 mmol) and 75 equiv of *n*-BuLi (2.7 mL, 6.75 mmol) at −30 °C to rt. The free base **11** (62 mg, 0.090 mmol) in THF was added after 1 h at −10 °C and the mixture was stirred for 4 h at rt. This was followed by quenching with water −0 °C to yield 30 mg (0.035 mmol, 38%) of the title compound as a purple solid. Mp 72 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.70 (s, 1H, H_{meso}), 9.68 (s, 1H, H_{meso}), 8.90 (s, 1H, $H_{anthracenyl}$), 8.25 (d, 2H, J=8.1 Hz, H_{Ar}), 8.19 (d, 2H, J=7.8 Hz, H_{Ar}), 7.86 (m, 2H, $H_{anthracenyl}$), 7.51 (m, 5H, $H_{anthracenyl}$), 7.13 (m, 2H, $H_{anthracenyl}$), 3.98 (m, 4H, CH_2CH_3), 3.85 (m, 2H, CH_2CH_3), 3.65 (m, 2H, CH_2CH_3), 2.93 (t, 2H, J=7.41 Hz, pentyl-CH_2), 2.70 (m, 2H, CH_2CH_3), 2.16 (m, 2H, CH_2CH_3), 1.86 (m, 6H, CH_2CH_3, 2H, CH_2CH_3), 1.72 (m, 2H, CH_2CH_3), 1.60 (t, 3H, J=7.55 Hz, CH_2CH_3), 1.47 (m, 6H, pentyl-CH_2; 3H, CH_2CH_3), 1.00 (m, 3H, CH_2CH_3), 0.71 (t, 3H, J=7.40 Hz, CH_2CH_3), 0.36 (t, 3H, J=7.17 Hz, pentyl-CH_3), 0.3 (t, 3H, J=7.39 Hz, CH_2CH_3), −0.07 (t, 3H, J=7.34 Hz, CH_2CH_3), −2.48 (s, 2H, N*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.1, 15.2, 15.8, 17.3, 17.8, 18.1, 19.3, 19.7, 20.3, 20.8, 22.5, 26.9, 29.0, 31.2, 31.6, 34.6, 35.9, 94.1, 95.1, 113.6, 125.4, 125.8, 126.7, 127.8, 128.0, 128.8, 130.9, 135.1, 135.6 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=425 (4.68), 520 (3.63), 592 (3.34), 644 nm (2.78); MS (ES^+), m/z (%): 857 (20) $[M+H]^+$, 578 (60); HRMS $[C_{61}H_{68}N_4]$: calcd 857.5522, found 857.5541.

*3.4.30. 2,3,7,8,12,13,17,18-Octaethyl-5-(4-pentylphenyl)-10-phenanthrenyl-porphyrin (**39**).* The reaction was performed as described in Section 3.3.1 using 40 equiv of 1-bromophenanthrene (2.263 g, 8.80 mmol) and 40 equiv of *n*-BuLi (3.52 mL, 8.80 mmol) at −50 °C to rt. The porphyrin **11** (150 mg, 0.220 mmol) in 50 mL THF was added after 90 min at −30 °C. After stirring for 40 min at rt the reaction mixture was quenched at −30 °C to yield 32 mg (0.037 mmol, 16%) of purple crystals of **39** from MeOH/CH_2Cl_2 as the first green-brown fraction, followed by a second, light green fraction upon addition of EtOH that contained **40** (58 mg, 0.056 mmol, 25%). Data for **39**: mp 165 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.71 (s, 1H, H_{meso}), 9.70 (s, 1H, H_{meso}), 9.01 (d, 1H, J=8.48 Hz, $H_{phenanthrenyl}$), 9.00 (d, 1H, J=8.40 Hz, $H_{phenanthrenyl}$), 8.70 (s, 1H, $H_{phenanthrenyl}$), 8.23 (d, 2H, J=6.21 Hz, H_{Ar}), 8.12 (d, 1H, J=7.68 Hz, $H_{phenanthrenyl}$), 7.89 (t, 1H, J=7.65 Hz, $H_{phenanthrenyl}$), 7.80 (t, 1H, J=7.46 Hz, $H_{phenanthrenyl}$), 7.72 (t, 1H, J=7.51 Hz, $H_{phenanthrenyl}$), 7.63 (d, 1H, J=8.21 Hz, $H_{phenanthrenyl}$), 7.50 (d, 2H, J=7.45 Hz, H_{Ar}), 7.32 (t, 1H, J=7.71 Hz, $H_{phenanthrenyl}$), 3.99 (m, 4H, CH_2CH_3), 3.87 (m, 2H, CH_2CH_3), 3.74 (m, 2H, CH_2CH_3), 2.97 (t, 2H, J=7.29 Hz, pentyl-CH_2), 2.74 (m, 2H, CH_2CH_3), 2.61 (m, 2H, CH_2CH_3), 2.25 (m, 4H, CH_2CH_3), 1.86 (t, 6H, J=7.25 Hz, CH_2CH_3), 1.62 (t, 3H, J=7.35 Hz, CH_2CH_3), 1.52 (m, 3H, CH_2CH_3; 6H, pentyl-CH_2), 1.01 (m, 3H, CH_2CH_3), 0.70 (t, 3H, J=7.21 Hz, CH_2CH_3), 0.42 (t, 3H, J=7.23 Hz, pentyl-CH_3), 0.40 (m, 6H, CH_2CH_3), −2.53 ppm (br s, 2H, N*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.1, 16.4, 16.7, 17.3, 18.0, 18.1, 19.3, 19.4, 19.6, 19.7, 20.6, 20.5, 22.6, 31.2, 31.4, 35.8, 94.8, 95.1, 116.0, 119.2, 119.8, 122.5, 122.9, 126.4, 126.6, 126.7, 127.1, 127.2, 129.1, 129.5, 130.7, 131.0, 134.1, 135.1, 136.5, 137.4, 138.7, 143.1 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=460 (5.25), 589 (4.19), 639 nm (4.07); MS (ES^+), m/z (%): 857 (48) $[M+H]^+$; HRMS $[C_{61}H_{68}N_4]$: calcd 857.5522, found 857.5526.

*3.4.31. 2,3,7,8,12,13,17,18-Octaethyl-5-(4-pentylphenyl)-10,20-bis(9-phenanthrenyl)porphyrin (**40**).* The title compound was isolated

from reaction in Section 3.4.30 as a green solid. NMR spectroscopy indicated the formation of atropoisomers due to hindered phenanthrenyl rotation. Mp 136 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.50, (br s, 1H, H_{meso}), 8.98 (t, 4H, J=8.80 Hz, $H_{phenanthrenyl}$), 8.67, 8.68 (each s, each 1H, $H_{phenanthrenyl}$), 8.32–8.15 (br s, 1H, $H_{phenanthrenyl}$), 8.28 (d, 1H, J=7.82 Hz, $H_{phenanthrenyl}$), 8.12 (d, 2H, J=7.73 Hz, $H_{phenanthrenyl}$), 7.87 (t, 2H, J=7.50 Hz, $H_{phenanthrenyl}$), 7.80 (t, 2H, J=7.31 Hz, $H_{phenanthrenyl}$), 7.72 (m, 4H, H_{Ar}), 7.46 (d, 2H, J=7.76 Hz, $H_{phenanthrenyl}$), 7.34 (m, 2H, $H_{phenanthrenyl}$), 3.67 (m, 4H, CH_2CH_3), 2.90 (t, 2H, J=7.29 Hz, pentyl-CH_2), 2.59 (m, 2H, CH_2CH_3), 2.22 (m, 10H, CH_2CH_3), 1.84 (m, 2H, pentyl-CH_2), 1.51 (m, 4H, pentyl-CH_2; 6H, CH_2CH_3), 0.94 (m, 3H, pentyl-CH_3), 0.53 (t, 6H, J=0.53 Hz, CH_2CH_3), 0.37 (m, 6H, CH_2CH_3), 0.29 (m, 6H, CH_2CH_3), −1.73 ppm (s, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.1, 16.3, 16.7, 17.1, 17.9, 19.2, 19.4, 19.5, 20.4, 20.6, 22.5, 29.2, 31.2, 31.3, 31.7, 35.8, 53.7, 114.6, 122.6, 122.9, 126.7, 126.8, 126.5, 127.1, 129.0, 129.1, 129.6, 131.0, 133.6, 133.8, 135.9, 136.2, 136.6, 138.7, 140.2, 142.5, 142.1, 143.0 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=442 (5.06), 470 (4.76), 537 (3.95), 609 (3.75), 665 nm (3.72); MS (ES$^+$), m/z (%): 1034 (100) [M+H]$^+$; HRMS [$C_{75}H_{76}N_4$]: calcd 1033.6148, found 1033.6157.

*3.4.32. 2,3,7,8,12,13,17,18-Octaethyl-5,10-bis(4-ethynyl-phenyl)-porphyrin (**41**).* A solution of porphyrin **12** (150 mg, 0.24 mmol) in 60 ml THF was cooled to −20 °C added to a vigorously stirred solution of 4-lithioethynylphenyl lithium. Subsequent steps followed the procedure given in Section 3.3.1. TLC of the crude reaction mixture showed several red, brown-green, and blue bands, which could not be separated completely. Column chromatography on alumina gel eluting with dichloromethane/n-hexane (1:20, v/v) eluted first recovered starting material **12** (35 mg, 0.05 mmol, 20%) followed by the product. Recrystallization from CH_2Cl_2/MeOH gave purple crystals (128 mg, 0.16 mmol, 65%). Note, this compound was also obtained as a side product during the synthesis of **12** (see Section 3.4.5). Mp 220 °C; (CH_2Cl_2/CH_3OH); R_f=0.22 (dichloromethane/n-hexane 1:10, v/v, alumina, 6×3 cm); ^{1}H NMR (500 MHz, $CDCl_3$, $SiMe_4$): δ= −2.85 (s (br), 2H, NH), 0.35, 0.55, 1.50, 1.79 (each t, 24H, ^3J=7.5 Hz, CH_2CH_3), 2.20, 2.63 (each m, 8H, CH_2CH_3), 3.27 (s, 2H, C≡CH), 3.75, 3.85 (each q, 8H, ^3J=7.5 Hz, CH_2CH_3), 7.59 (each d, 4H, J=4.7, H_{Ph}), 7.64 (each d, 4H, J=4.7, H_{Ph}), 9.60 ppm (s, 2H, H_{meso}); MS (EI, 80 eV, 200 °C), m/z (%): 734 (100) [M$^+$], 706 (5) [M$^+$−CH_2CH_2], 633 (3) [M$^+$−C_8H_5], 367 (25) [M^{2+}]; UV/vis (CH_2Cl_2): λ_{max} (log ε)=426 (5.17), 523 (4.01), 559 (3.49), 597 nm (3.54); HRMS [$C_{52}H_{54}N_4$]: calcd 734.4349, found 734.4346.

*3.4.33. 5-(4-|Dimethylaminophenyl-2,3,7,8,12,13,17,18-octaethyl-10-(3-trifluoromethylphenyl))porphyrin (**42**).* The reaction was performed as described in Section 3.3.1. using 60 equiv of 1-bromodimethylaniline (1.0088 g, 5.04 mmol) and 75 equiv of n-BuLi (2.52 mL, 6.30 mmol) at −20 °C to rt. Free base **17** (57 mg, 0.084 mmol) in 50 mL THF (low solubility) was added after 40 min at rt and after stirring for 25 min it was quenched at the same temperature with water to yield 33 mg of a purple solid (0.041 mmol, 48%). Mp 125 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.64, 9.61 (each s, each 1H, H_{meso}), 8.66 (s, 1H, H_{F3C-Ph}), 8.50 (d, 1H, J=7.49 Hz, H_{F3C-Ph}), 8.11 (d, 2H, J=7.99 Hz, $H_{Me2N-Ph}$), 8.05 (d, 1H, J=7.87 Hz, H_{F3C-Ph}), 7.82 (t, 1H, J=7.72 Hz, H_{F3C-Ph}), 7.04 (d, 2H, J=8.48 Hz, $H_{Me2N-Ph}$), 3.93 (q, 4H, J=7.32 Hz, CH_2CH_3), 3.81 (m, 4H, CH_2CH_3), 3.23 (s, 6H, N(CH_3)$_2$), 2.62 (m, 4H, CH_2CH_3), 2.35 (m, 4H, CH_2CH_3), 1.81 (t, 6H, J=7.84 Hz, CH_2CH_3), 0.89 (m, 6H, CH_2CH_3), 0.63 (m, 6H, CH_2CH_3), 0.45 (t, 3H, J=6.33 Hz, CH_2CH_3), 0.39 (t, 3H, J=6.71 Hz, CH_2CH_3), −2.68 ppm (s, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.0, 14.7, 17.2, 17.3, 17.9, 18.1, 18.3, 19.2, 19.3, 19.4, 19.5, 20.3, 20.4, 20.6, 22.6, 25.2, 26.8, 28.9, 29.6, 31.5, 34.6, 39.8, 40.6, 74.1, 94.5, 95.1, 110.4, 110.5, 110.9, 112.4, 116.7, 120.6, 124.7, 125.0, 126.8, 127.1, 130.1, 136.1, 138.3, 142.1, 150.5, 153.1 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=429 (4.72), 513 (sh), 595 (3.67), 663 nm (3.74); MS (ES$^+$), m/z (%): 798 (40) [M+H]$^+$; HRMS [$C_{51}H_{58}N_5F_3$]: calcd 798.4723, found 798.4743.

*3.4.34. 2,3,7,8,12,13,17,18-Octaethyl-5-(1-naphthyl)-10-(4-pentylphenyl)porphyrin (**43**).* The reaction was performed as described in Section 3.3.1 using 40 equiv of 1-bromo-4-pentylphenyl (0.85 mL, 4.84 mmol) and 50 equiv of n-BuLi (2.42 mL, 6.05 mmol) at −30 °C to rt. The free base **19** (80 mg, 0.121 mmol) in 50 mL THF was added after 80 min at −0 °C. After 30 min at rt the reaction was quenched at −0 °C with water to yield 46 mg (0.057 mmol, 47%) of a purple solid. Mp 133 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.67 (s, 1H, H_{meso}), 9.66 (s, 1H, H_{meso}), 8.41 (d, 1H, J=6.87 Hz, $H_{naphthyl}$), 8.28 (d, 1H, J=8.26 Hz, $H_{naphthyl}$), 8.20 (d, 2H, J=7.84 Hz, H_{Ar}), 8.11 (d, 1H, J=7.94 Hz, $H_{naphthyl}$), 7.81 (t, 2H, J=8.10 Hz, $H_{naphthyl}$), 7.52 (t, 1H, J=6.85, $H_{naphthyl}$), 7.47 (d, 2H, J=7.80 Hz, H_{Ar}), 7.20 (t, 1H, J=7.65 Hz, $H_{naphthyl}$), 3.95 (q, 4H, J=7.08 Hz, CH_2CH_3), 3.83 (m, 2H, CH_2CH_3), 3.73 (m, 2H, CH_2CH_3), 2.95 (t, 2H, J=7.41 Hz, pentyl-CH_2), 2.70 (m, 2H, CH_2CH_3), 2.40 (m, 2H, CH_2CH_3), 2.25 (m, 2H, CH_2CH_3), 2.11 (m, 2H, CH_2CH_3), 1.83 (m, 6H, CH_2CH_3), 1.59 (t, 3H, J=7.52 Hz, CH_2CH_3), 1.53 (m, 6H, pentyl-CH_2; 3H, CH_2CH_3), 0.99 (m, 3H, pentyl-CH_3), 0.67 (t, 3H, J=7.38 Hz, CH_2CH_3), 0.45 (m, 6H, CH_2CH_3), 0.33 (t, 3H, J=7.15 Hz, CH_2CH_3), −2.61 ppm (s, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.1, 16.5, 16.9, 17.3, 17.9, 18.1, 19.4, 19.5, 19.6, 20.4, 20.5, 22.6, 26.9, 31.2, 31.4, 35.8, 94.8, 95.0, 116.2, 124.4, 125.8, 126.0, 126.7, 127.7, 128.1, 128.9, 132.7, 133.4, 135.1, 137.2, 139.2, 143.1 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=426 (4.88), 519 (3.74), 555 (3.61), 592 (3.72), 643 nm (3.48); MS (ES$^+$), m/z (%): 807 (100) [M+H]$^+$; HRMS [$C_{57}H_{66}N_4$]: calcd 807.5366, found 807.5374.

*3.4.35. 2,3,7,8,12,13,17,18-Octaethyl-5,10-bis(1-naphth-yl)porphyrin (**44**).* The reaction was performed as described in Section 3.3.1 using 60 equiv of 1-bromonaphthalene (1.08 mL, 8.00 mmol) and 75 equiv of n-BuLi (3.99 mL, 9.97 mmol) at −20 °C to rt. The free base **19** (88 mg, 0.133 mmol) in THF was added after 45 min at rt and after stirring for 25 min the reaction was quenched at rt with water to yield 46 mg (0.060 mmol, 44%) of a purple solid. Mp 178 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.69 (s, 1H, H_{meso}), 9.67 (s, 1H, H_{meso}), 8.47 (d, 1H, J=6.87 Hz, $H_{naphthyl}$), 8.40 (d, 1H, J=6.89 Hz, $H_{naphthyl}$), 8.27 (d, 2H, J=8.20 Hz, $H_{naphthyl}$), 8.09 (t, 2H, J=7.19 Hz, $H_{naphtyl}$), 7.81 (m, 2H, $H_{naphthyl}$), 7.50 (m, 4H, $H_{naphthyl}$), 7.20 (m, 2H, $H_{naphthyl}$), 3.98 (m, 4H, CH_2CH_3), 3.75 (m, 4H, CH_2CH_3), 2.60 (m, 2H, CH_2CH_3), 2.42 (m, 2H, CH_2CH_3), 2.23–2.00 (m, 4H, CH_2CH_3), 1.84 (m, 6H, CH_2CH_3), 0.89 (m, 6H, CH_2CH_3), 0.45 (m, 6H, CH_2CH_3), 0.26 (m, 6H, CH_2CH_3), −2.44 (s, 1H, NH), −2.52 ppm (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.9, 14.0, 14.1, 16.6, 16.7, 16.93, 16.95, 18.01, 18.02, 18.6, 19.4, 19.6, 20.5, 22.4, 22.5, 22.6, 31.2, 31.5, 33.7, 35.2, 35.5, 95.0, 95.1, 116.0, 124.3, 124.4, 125.9, 126.2, 127.7, 127.9, 128.0, 128.2, 129.0, 132.6, 132.7, 133.2, 133.3, 137.2, 137.3, 138.8, 139.1 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=426 (4.89), 521 (3.79), 592 nm (3.53); MS (ES$^+$), m/z (%): 787 (90) [M+H]$^+$; HRMS [$C_{56}H_{58}N_4$]: calcd 787.4740, found 787.4733.

*3.4.36. 2,3,7,8,12,13,17,18-Octaethyl-5-(1-naphthyl)-10-(9-phenanthrenyl)porphyrin (**45**).* The reaction was performed as described in Section 3.3.1 using 40 equiv of 9-bromophenanthrene (1.2427 g, 4.84 mmol) and 50 equiv of n-BuLi (2.42 mL, 6.05 mmol) at −30 °C to rt. Free base **19** (80 mg, 0.121 mmol) in 50 mL THF was added after 1 h at −10 °C. After stirring for 30 min at rt it was quenched at −0 °C to yield 47 mg (0.056 mmol, 46%) of a purple solid as a red-green fraction. Addition of ethylacetate eluted a second fraction to yield 14% (22 mg, 0.0217 mmol) of **46**. Data for **45**: NMR spectroscopy indicated the formation of atropoisomers due to hindered phenanthrenyl rotation. Mp 140 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.71 (s, 1H, H_{meso}), 9.68 (s, 1H, H_{meso}), 8.99–8.93 (m, 2H, $H_{phenanthrenyl}$), 8.72–8.67 (br s, 1H, $H_{phenanthrenyl}$), 8.49–8.39 (d, 1H, J=7.02 Hz, $H_{naphthyl}$ H), 8.26 (d, 1H, J=8.24 Hz, $H_{naphthyl}$), 8.09 (m,

2H, $H_{phenanthrenyl}$), 7.88–7.77 (m, 3H, $H_{phenanthrenyl}$), 7.69 (t, 1H, J=6.87 Hz, $H_{phenanthrenyl}$), 7.59–7.48 (m, 4H, $H_{naphthyl}$), 7.20 (m, 1H, $H_{naphthyl}$), 3.97 (m, 4H, CH_2CH_3), 3.75 (m, 4H, CH_2CH_3), 2.57–2.00 (br m, 8H, CH_2CH_3), 1.85 (m, 6H, CH_2CH_3), 0.89 (m, 6H, CH_2CH_3), 0.47 (m, 6H, CH_2CH_3), 0.31–0.22 (m, 6H, CH_2CH_3), −2.42 (s, 1H, N*H*), −2.50 ppm (s, 1H, N*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=11.0, 11.4, 14.1, 16.5, 16.9, 18.0, 18.3, 19.4, 19.5, 19.6, 20.4, 20.6, 20.7, 22.7, 25.2, 26.8, 27.6, 29.0, 31.5, 34.7, 35.9, 41.4, 95.3, 116.0, 122.4, 122.9, 124.4, 125.9, 126.5, 127.0, 127.6, 128.8, 129.1, 129.6, 130.8, 132.5, 133.3, 133.9, 136.5, 137.4 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=430 (5.01), 455 (5.01), 519 (3.90), 591 (4.04), 643 nm (3.81); MS (ES^+), m/z (%): 837 (19) $[M+H]^+$; HRMS $[C_{60}H_{60}N_4]$: calcd 837.4896, found 837.4871.

*3.4.37. 2,3,7,8,12,13,17,18-Octaethyl-5-(1-naphthyl)-10,20-bis(9-phenanthrenyl)porphyrin (**46**).* The compound was obtained from the reaction described in Section 3.4.36. NMR spectroscopy indicated the formation of atropoisomers due to hindered phenanthrenyl/naphthyl rotation in about a 1:1 ratio. Mp 132 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.54–9.49 (s, 1H H_{meso}), 8.98 (m, 4H, $H_{phenanthrenyl}$), 8.76–8.74 (s, 1H, $H_{phenanthrenyl}$), 8.67, 8.64 (each s, each 0.5H, $H_{phenanthrenyl}$), 8.58, 8.48 (each d, each 0.5H, J=7.23 Hz, $H_{naphthyl}$), 8.36–8.27 (m, 1H, $H_{naphthyl}$), 8.22 (m, 1H, $H_{naphthyl}$), 8.12 (m, 2H, $H_{naphthyl/phenanthryl}$), 8.05 (m, 1H, $H_{phenanthrenyl}$), 7.87 (m, 2H, $H_{phenanthrenyl}$), 7.81–7.71 (m, 7H, $H_{phenanthrenyl/naphthyl}$), 7.53 (m, 2H, $H_{naphthyl}$), 7.39 (m, 2H, $H_{phenanthrenyl}$), 7.30 (m, 1H, $H_{naphthyl}$), 3.69 (m, 4H, CH_2CH_3), 2.71–2.13 (m, 6H, CH_2CH_3), 1.88 (m, 6H, CH_2CH_3), 1.51 (m, 6H, CH_2CH_3), 0.88 (m, 6H, CH_2CH_3), 0.53 (m, 6H, CH_2CH_3), 0.30 ppm (m, 6H, CH_2CH_3); −1.51 ppm (s, 2H, N*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.1, 16.2, 16.7, 18.7, 19.2, 19.3, 19.4, 22.6, 29.3, 29.6, 31.9, 122.5, 122.9, 125.9, 126.5, 126.9, 127.1, 128.8, 129.2, 130.7, 130.9 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=445 (4.89), 472 (3.65), 538 (3.78), 611 (3.64), 665 nm (3.51); MS (ES^+), m/z (%): 1013 (50) $[M+H]^+$; HRMS $[C_{74}H_{68}N_4]$: calcd 1013.5522, found 1013.5505.

*3.4.38. 5-(4-Dimethylaminophenyl)-2,3,7,8,12,13,17,18-octaethyl-10-(9-phenanthrenyl)porphyrin (**47**).* The reaction was performed as described in Section 3.3.1 using 40 equiv of bromo 4-dimethylaminophenyl (0.942 g, 4.71 mmol) and 50 equiv of *n*-BuLi (2.35 mL, 5.88 mmol) at −30 °C to rt. The free base **21** (80 mg, 0.117 mmol) in 50 mL THF was added after 1 h at 0 °C and after 30 min stirring at rt it was quenched at the same temperature to yield 70 mg (0.084 mmol, 71%) of a purple solid. Mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.64 (s, 1H, H_{meso}), 9.61 (s, 1H, H_{meso}), 8.96 (m, 2H, $H_{phenanthrenyl}$), 8.66 (s, 1H, $H_{phenanthrenyl}$), 8.09 (t, 3H, J=7.9 Hz, $H_{phenanthrenyl}$), 7.85 (m, 2H, $H_{phenanthrenyl}$), 7.76 (t, 1H, J=8.1 Hz, $H_{phenanthrenyl}$), 7.61 (d, 1H, J=7.8 Hz, phenyl H), 7.28 (d, 1H, J=7.1 Hz, H_{Ar}), 7.00 (d, 2H, J=8.6 Hz, $|H_{Ar}$), 3.93 (m, 4H, CH_2CH_3), 3.81 (m, 2H, CH_2CH_3), 3.70 (m, 2H, CH_2CH_3), 3.19 (s, 6H, $N(CH_3)_2$), 2.83 (m, 2H, CH_2CH_3), 2.55 (m, 2H, CH_2CH_3), 2.22 (m, 4H, CH_2CH_3), 1.80 (m, 6H, CH_2CH_3), 1.55 (t, 3H, J=7.6 Hz, CH_2CH_3), 1.48 (m, 3H, CH_2CH_3), 0.63 (t, 3H, J=7.3 Hz, CH_2CH_3), 0.44 (t, 3H, J=7.3 Hz, CH_2CH_3), 0.32 (m, 6H, CH_2CH_3), −2.55 ppm (s, 2H, N*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=16.3, 16.6, 17.1, 17.4, 17.9, 18.2, 19.2, 19.4, 19.6, 19.8, 20.5, 26.8, 40.1, 40.8, 94.3, 94.9, 110.6, 115.8, 120.2, 122.2, 122.9, 126.7, 127.1, 129.1, 129.6, 130.2, 130.7, 131.0, 134.2, 136.3, 136.3, 137.4, 150.6 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=433 (4.93), 521 (4.04), 596 (3.63), 664 (3.45) nm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=433 (4.93), 521 (4.04), 596 (3.63), 664 nm (3.45); MS (ES^+), m/z (%): 830 (60) $[M+H]^+$; HRMS $[C_{58}H_{63}N_5]$: calcd 830.5162, found 830.5185.

*3.4.39. 2,3,7,8,12,13,17,18-Octaethyl-5,10-bis(9-phenan-threnyl)porphyrin (**48**).* The reaction was performed as described in Section 3.3.1 using 40 equiv of 9-bromophenanthrene (2.137 g, 8.44 mmol) and 40 equiv of *n*-BuLi (3.37 mL, 8.44 mmol) at −50 °C to rt. Free base **21** (150 mg, 0.221 mmol) in 50 mL THF was added after 1 h at −50 °C and after 45 min stirring at rt the reaction was quenched at −30 °C with water to yield 81 mg (0.093 mmol, 43%) purple crystals after crystallization from $MeOH/CH_2Cl_2$ as the first green-red fraction. Its formation was accompanied by the *meso* trisubstituted product **49** (fraction 3, light-green, 57 mg, 0.053 mmol, 25%, green solid) and the *meso* tetrasubstituted product (**66**, see Section 3.4.52) (fraction 4, dark green, 21 mg, 0.0169 mmol, 7%, green solid). Data for **48**: Mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.73, 9.70 (each s, each 1H, H_{meso}), 8.98, 8.94 (each d, each 2H, J=8.38 HZ, J=7.26 Hz, $H_{phenanthrenyl}$), 8.74, 8.65 (each s, each 1H, $H_{phenanthrenyl}$), 8.12, 8.08 (each d, each 1H, each J=7.69 Hz, $H_{phenanthrenyl}$), 7.87 (t, 2H, J=7.57, $H_{phenanthrenyl}$), 7.78 (m, 2H, $H_{phenanthrenyl}$), 7.69 (m, 2H, $H_{phenanthrenyl}$), 7.60 (t, 2H, J=8.70 Hz, $H_{phenanthrenyl}$), 7.31 (m, 2H, $H_{phenanthrenyl}$), 3.98 (m, 4H, CH_2CH_3), 3.74 (m, 4H, CH_2CH_3), 2.57 (m, 2H, CH_2CH_3), 2.28 (m, 2H, CH_2CH_3), 2.02 (m, 4H, CH_2CH_3), 1.85 (m, 6H, CH_2CH_3), 1.53 (m, 6H, CH_2CH_3), 0.49 (m, 6H, CH_2CH_3), 0.30 (m, 6H, CH_2CH_3), −2.40, −2.41 ppm (each s, each 1H, N*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=116.4, 16.7, 17.9, 18.1, 19.4, 19.5, 20.7, 29.6, 32.0, 55.3, 55.5, 95.2, 115.8, 122.3, 122.8, 123.0, 124.3, 125.8, 126.4, 126.5, 127.1, 127.5, 128.5, 128.6, 128.8, 129.0, 129.1, 129.2, 129.4, 133.9, 134.7, 136.4, 137.0, 137.3, 203.3, 205.3 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=426 (5.45), 455 (5.03), 519 (4.56), 592 nm (sh, 4.35) MS (ES^+), m/z (%): 887 (14) $[M+H]^+$; HRMS $[C_{64}H_{62}N_4]$: calcd 887.5053, found 887.5009.

*3.4.40. 2,3,7,8,12,13,17,18-Octaethyl-5,10,15-tris(9-phenanthrenyl)porphyrin (**49**).* The title compound was isolated from reaction described in Section 3.4.39. NMR spectroscopy indicated the formation of atropoisomers due to hindered phenanthrenyl rotation in about a 2:1 ratio. Mp 179 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.54–9.50 (s, 1H, H_{meso}), 8.99–8.89 (m, 6H, $H_{phenanthrenyl}$), 8.84, 8.73 (br s, 1H, atropisomers, $H_{phenanthrenyl}$), 8.77 (m, 1H, $H_{phenanthrenyl}$), 8.66–8.61 (s, 1H, atropisomers, $H_{phenanthrenyl}$), 8.15 (br d, 2H, J=8.11 Hz, $H_{phenanthrenyl}$), 8.09 (br d, 1H, J=8.09 Hz, $H_{phenanthrenyl}$), 7.90–7.67 (m, 12H, $H_{phenanthrenyl}$), 7.46–7.36 (m, 3H, $H_{phenanthrenyl}$), 3.71 (m, 4H, CH_2CH_3), 2.69–2.52 (m, 2H, CH_2CH_3), 2.42–2.29 (m, 2H, CH_2CH_3), 2.18–2.05 (m, 4H, CH_2CH_3), 1.96–1.84 (m, 4H, CH_2CH_3), 1.50 (m, 6H, CH_2CH_3), 0.88 (m, 6H, CH_2CH_3), 0.54 (m, 6H, CH_2CH_3), 0.25 (m, 3H, CH_2CH_3), 0.13 (t, 3H, J=7.67 Hz, CH_2CH_3), −1.53 ppm (br s, 2H, N*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.1, 16.3, 16.5, 16.7, 17.8, 19.3, 19.5, 20.6, 22.6., 29.3, 29.6, 31.9, 94.1, 114.6,114.7, 116.0, 116.2, 116.3, 122.5, 122.9, 126.5, 127.2, 128.8, 129.2, 129.4, 129.6, 130.7, 130.9, 133.5, 133.6, 133.8, 134.5, 134.7, 136.3, 136.5, 137.9, 137.2, 140.8, 140.9, 141.7 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=445 (4.38), 473 (4.14), 539 (3.14), 608 (3.09), 665 nm (2.95); MS (ES^+), m/z (%): 1063 (5) $[M+H]^+$; HRMS $[C_{78}H_{70}N_4]$: calcd 1063.5679, found 1063.5652.

*3.4.41. {2,3,7,8,12,13,17,18-Octaethyl-5-(3-trifluoro-methylphenyl)porphyrinato}palladium(II) (**53**).* The title compound was isolated from a reaction of the respective free base using procedure B and afforded 117 mg (0.149 mmol, 93%) of purple crystals. Mp 236 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=10.10 (s, 2H, H_{meso}), 10.03 (s, 1H, H_{meso}), 8.57 (s, 1H, H_{Ar}), 8.30 (d, 1H, J=7.6 Hz, H_{Ar}), 8.08 (d, 1H, J=7.8 Hz, H_{Ar}), 7.87 (s, 1H, H_{Ar}), 7.77 (t, 1H, J=7.6 Hz, H_{Ar}), 4.03 (q, 8H, J=7.6 Hz, CH_2), 3.95 (q, 4H, J=7.3 Hz, CH_2), 2.71 (q, 2H, J=7.3 Hz, CH_2), 2.48 (q, 2H, J=7.3 Hz, CH_2), 1.90 (m, 12H, CH_3), 1.84 (t, 6H, J=7.9 Hz, CH_3), 1.12 ppm (t, 6H, J=7.3 Hz, CH_3); UV/vis (CH_2Cl_2): λ_{max} (log ε)=400 (5.41), 516 (3.89), 550 nm (4.53).

*3.4.42. {2,3,7,8,12,13,17,18-Octaethyl-5-(2-naphthyl)-porphyrinato}palladium(II) (**54**).* The title compound was isolated from a reaction of the respective free base using procedure B and afforded 10 mg (0.013 mmol, 20%) of purple crystals. Mp 253 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=10.12 (s, 2H, H_{meso}), 10.04 (s, 1H, H_{meso}), 8.66 (s, 1H, $H_{naphthyl}$), 8.33 (d, 1H, J=8.1 Hz, $H_{naphthyl}$), 8.18 (d, 1H,

J=7.9 Hz, $H_{naphthyl}$), 8.12 (d, 1H, J=8.4 Hz, $H_{naphthyl}$), 8.01 (d, 1H, J=7.8 Hz, $H_{naphthyl}$), 7.70 (m, 2H, $H_{naphthyl}$), 4.05 (q, 8H, J=7.7 Hz, CH_2), 3.94 (q, 4H, J=7.6 Hz, CH_2), 2.68 (m, 2H, CH_2), 2.46 (m, 2H, CH_2), 1.94 (m, 12H, CH_3), 1.84 (t, 6H, J=7.7 Hz, CH_3), 1.03 ppm (t, 6H, J=7.5 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=11.4, 14.0, 17.8, 18.3, 19.8, 21.5, 22.6, 25.3, 26.9, 27.6, 28.9, 31.4, 34.7, 41.4, 53.2, 95.7, 98.7, 125.5, 126.2, 126.7, 128.2, 128.4, 131.6, 131.7, 131.8, 132.0, 133.2, 138.1, 138.4, 139.0, 139.3, 141.4, 143.4, 143.6 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=400 (4.90), 516 (3.80), 550 nm (4.14).

*3.4.43. (5-n-Butyl-2,3,7,8,12,13,17,18-octaethyl-10-phenylporphyrinato)palladium(II) (**55**).* The title compound was isolated from a reaction of **50** with 25 equiv 1-bromonaphthalene and 95 equiv. BuLi mixed at −50 °C followed by addition of the porphyrin (60 mg, 0.084 mmol) at rt, then stirring for 20 min at −20 °C and then stirring for 40 min at rt. Work-up gave a pink solid (0.0428 mmol, 50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.76 (s, 2H, H_{meso}), 7.86–7.49 (br m, 5H, H_{Ph}), 4.77 (br m, 2H, Bu–CH_2), 3.94 (m, 12H, CH_2, 2H, Bu–CH_2), 2.92–2.35 (br m, 4H, CH_2), 2.01 (t, 3H, J=7.5 Hz, CH_3), 1.86 (m,12H, CH_3, 2H, Bu-CH_2), 1.76 (t, 3H, J=7.5 Hz, CH_3), 1.12 (m, 6H, CH_3), 0.56 ppm (t, 3H, J=7.2 Hz, Bu-CH_3).

*3.4.44. (5-sec-Butyl-2,3,7,8,12,13,17,18-octaethyl-10-phenylporphyrinato)palladium(II) (**56a**).* The title compound was isolated from a reaction of **50** with 10 equiv *s*-BuLi at −60 °C with the porphyrin (80 mg, 0.112 mmol) following procedure A using a reaction time of 10 min. Work-up gave a single dark red fraction of a mixture of the two regioisomers **56a** and **56b** (35 mg 37%). Precipitation from CH_2Cl_2/MeOH gave 9 mg of red crystals of **56b** while **56a** remained in solution and was used for characterization via NMR. ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.58 (s, 1H, H_{meso}), 9.50 (s, 1H, H_{meso}), 8.19–8.08 (m, 2H, H_{Ph}), 7.74 (t, 1H, J=7.7 Hz, H_{Ph}), 7.62 (t, 2H, J=7.7 Hz, H_{Ph}), 4.49 (m, 1H, *s*Bu–C*H*), 3.97–3.73 (m, 12H, CH_2), 2.68–2.32 (m, 4H, CH_2), 2.30 (d, 3H, J=7.0 Hz, *s*Bu–CH_3), 1.79 (m, 12H, CH_3), 1.64 (t, 3H, J=7.6 Hz, CH_3), 1.52 (t, 3H, J=7.2 Hz, CH_3), 0.98 (m, 2H, *s*Bu–CH_2), 0.86 (m, 6H, CH_3), 0.48 ppm (t, 3H, J=7.3 Hz, *s*Bu–CH_3).

*3.4.45. (5-sec-Butyl-2,3,7,8,12,13,17,18-octaethyl-15-phenylporphyrinato)palladium(II) (**56b**).* The title compound was isolated from reaction described in Section 3.4.42 (9 mg, 0.011 mmol, 9%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.76 (s, 2H, H_{meso}), 8.08 (d, 2H, J=7.6 Hz, H_{Ph}), 7.43 (t, 1H, J=7.4 Hz, H_{Ph}), 7.60 (t, 2H, J=7.9 Hz, H_{Ph}), 4.51 (m, 1H, *s*Bu–C*H*), 4.16 (m, 2H, CH_2), 3.92–3.83 (m, 12H, CH_2), 2.67 (m, 4H, CH_2, *s*Bu–CH_2), 2.58 (d, 3H, J=7.74 Hz, *s*Bu–CH_3), 1.77 (t, 12H, J=7.6 Hz, CH_3), 1.64 (t, 6H, J=7.6 Hz, CH_3), 1.02 (t, 6H, J=7.2 Hz, CH_3), 0.11 ppm (t, 3H, J=7.3 Hz, *s*Bu–CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.3, 14.1, 17.9, 18.2, 19.5, 19.7, 21.1, 22.0, 24.5, 29.6, 31.5, 33.3, 40.6, 50.9, 98.6, 126.3, 133.2, 136.8, 137.6, 138.2, 141.4, 142.4, 143.4, 143.6, 144.2 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=417 (4.55), 533 (3.53), 563 nm (3.48).

*3.4.46. {2,3,7,8,12,13,17,18-Octaethyl-5,10-bis(1-naph-thyl)porphyrinato}palladium(II) (**59a**).* The reaction was performed as described in Section 3.3.1 using 60 equiv of 1-bromoaphthalene (0.80 mL, 5.96 mmol) and 75 equiv of *n*-BuLi (2.97 mL, 7.42 mmol) at −20 °C to rt. The metal complex **52** (76 mg, 0.099 mmol) in 50 mL THF was added after 1 h at rt. After stirring for 1 h at the same temperature the reaction was quenched water at −0 °C followed by standard work-up to yield 56 mg (0.060 mmol, 61%) of a pink-red solid. Alternatively, the compound was prepared via metallation of the respective free base following procedure B in 65% yield (34 mg, 0.0381 mmol). NMR spectroscopy indicated the formation of two atropoisomers in a ratio of 1:1 due to hindered naphthyl rotation. Mp 245 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.88 (s, 1H, H_{meso}), 9.87 (s, 1H, H_{meso}), 8.40 (m, 2H, $H_{naphthyl}$), 8.27 (d, 2H, J=8.28 Hz, $H_{naphthyl}$), 8.08 (m, 2H, $H_{naphthyl}$), 7.81 (m, 2H, $H_{naphthyl}$), 7.50 (m, 2H, $H_{naphthyl}$), 7.34–7.25 (m, 2H, $H_{naphthyl}$), 7.16 (m, 2H, $H_{naphthyl}$), 3.98 (m, 4H, CH_2CH_3), 3.77 (m, 4H, CH_2CH_3), 2.48–2.21 (m, 2H, CH_2CH_3), 2.21–2.20 (m, 6H, CH_2CH_3), 1.87 (t, 6H, J=7.52, CH_2CH_3), 1.65 (m, 6H, CH_2CH_3), 0.55 (t, 6H, J=7.17 Hz, CH_2CH_3), 0.39 ppm (m, 6H, CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.0, 16.8, 17.2, 18.0, 19.6, 20.2, 20.6, 21.2, 22.5, 25.2, 29.0, 29.7, 31.5, 34.6, 97.6, 117.3, 124.4, 125.9, 127.6, 127.8, 128.1, 128.8, 132.4, 132.7, 137.0, 139.0, 139.2, 140.4, 141.6, 143.3, 144.7 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=340 (3.94), 412 (4.98), 527 (3.95), 561 (4.08) nm.

*3.4.47. {2,3,7,8,12,13,17,18-Octaethyl-5,10-bis(4-ethynyl-phenyl)-porphyrinato}nickel(II) (**61**).* The free base porphyrin **41** (200 mg, 0.27 mmol) was dissolved in 60 ml DMF, 1.5 g of nickel(II)acetate was added and the mixture heated to reflux for 3 h. The solvent was removed in vacuo and the residue taken up in dichloromethane, washed three times with water, and the organic phase dried over Na_2SO_4. Chromatography on alumina (dichloromethane/*n*-hexane, 1:5, v/v) gave 183 mg (0.23 mmol, 85%) of the title compound after recrystallization from CH_2Cl_2/MeOH. Mp 280 °C; R_f=0.27 (dichloromethane/*n*-hexane, 1:10, v/v, alumina, 6×3 cm); ^{1}H NMR (500 MHz, $CDCl_3$, $SiMe_4$): δ=0.40, 0.55, 1.46, 1.67 (each t, 24H, ^3J=7.5 Hz, CH_2CH_3), 2.23, 2.47 (each m, 8H, CH_2CH_3), 3.20 (s, 2H, C≡C*H*), 3.55, 3.65 (each q, 8H, ^3J=7.5 Hz, CH_2CH_3), 7.68 (each d, 4H, J=4.7, H_{Ar}), 7.95 (each d, 4H, J=4.7, H_{Ar}), 9.25 ppm (s, 2H, H_{meso}); MS (EI, 80 eV, 270 °C), *m*/*z* (%): 790 (100) [M^+], 395 (26) [M^{2+}]; UV/vis (CH_2Cl_2): λ_{max} (log ε)=414 nm (5.19), 535 (3.97), 571 (4.10); HRMS [$C_{52}H_{52}N_4Ni$]: calcd 790.3549, found 790.3587.

*3.4.48. 5-(4-Dimethylaminophenyl)-2,3,7,8,12,13,17,18-octaethyl-10,15-diphenylporphyrin (**62**).* The reaction was performed as described in Section 3.3.1 using 60 equiv of 1-bromo-4-dimethylaniline (1.048 g, 5.24 mmol) and 75 equiv of *n*-BuLi (2.60 mL, 6.55 mmol) at −40 °C to rt. The free base **60**[12] (60 mg, 0.087 mmol) in 50 mL THF was added after 1 h at rt and after 1 h further stirring at the same temperature the reaction was quenched at 0 °C with water to yield 60 mg (0.074 mmol, 69%) of a purple solid. Mp 90 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.40 (s, 1H, H_{meso}), 8.36 (d, 2H, J=6.90 Hz, H_{Ph}), 8.25 (d, 2H, J=6.84 Hz, H_{Ph}), 8.07 (d, 2H, J=8.43 Hz, H_{NMe2Ph}), 7.73 (m, 2H, H_{Ph}), 7.65 (t, 4H, J=7.32 Hz, H_{Ph}), 7.02 (d, 2H, J=8.47 Hz, H_{NMe2Ph}), 3.72 (q, 4H, CH_2CH_3), 3.21 (s, 6H, $N(CH_3)_2$), 2.82 (m, 2H, CH_2CH_3), 2.67 (m, 2H, CH_2CH_3), 2.34 (m, 2H, CH_2CH_3), 2.26–2.17 (m, 6H, CH_2CH_3), 1.54 (m, 6H, CH_2CH_3), 0.92 (m, 6H, CH_2CH_3), 0.70 (m, 6H, CH_2CH_3), 0.43 (m, 3H, CH_2CH_3), 0.33 (m, 3H, CH_2CH_3), −2.05 ppm (br s, 2H, N*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.0, 14.1, 17.1, 17.9, 19.2, 19.5, 20.4, 22.7, 31.9, 29.7, 31.6, 31.9, 40.7, 40.8, 93.4, 110.7, 112.3, 112.5, 125.2, 126.7, 126.9, 128.1, 134.9, 135.7, 136.0, 140.2, 141.5 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=446 (4.10), 480 (4.02), 623 (3.09), 682 nm (3.47); MS (ES^+), *m*/*z* (%): 806 (15) $[M+H]^+$; HRMS [$C_{56}H_{64}N_5$]: calcd 806.5162, found 806.5122.

*3.4.49. 5-(4-Bromophenol)-2,3,7,8,12,13,17,18-octaethyl-10,15-diphenylporphyrin (**63**).* The reaction was performed as described in Section 3.3.1 using 60 equiv of 1,4-dibromobenzene (1.8823 g, 8.13 mmol) and 75 equiv of *n*-BuLi (4.05 mL, 10.125 mmol) at −30 °C to rt. Free base **60** (93 mg, 0.135 mmol) in THF (50 mL) was added after 1 h stirring at rt. The reaction mixture was quenched after another hour with water at 0 °C to yield 44 mg (0.052 mmol, 38%) of a green solid. Mp 75 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.43 (s, 1H, H_{meso}), 8.36 (d, 2H, J=7.15 Hz, H_{Ph}), 8.28 (d, 2H, J=7.02 Hz, H_{Ph}), 8.17 (d, 2H, J=8.22 Hz, H_{Br-Ph}), 7.84 (d, 2H, J=8.17 Hz, H_{Br-Ph}), 7.73 (m, 2H, H_{Ph}), 7.67 (m, 4H, H_{Ph}), 3.73 (m, 4H, CH_2CH_3), 2.67 (m, 4H, CH_2CH_3), 2.26–2.20 (m, 8H, CH_2CH_3), 1.55 (m, 6H, CH_2CH_3), 0.71 (m, 6H, CH_2CH_3), 0.44 (t, 6H, J=7.24 Hz, CH_2CH_3), 0.36 (t, 6H, J=7.29 Hz, CH_2CH_3), −2.11 ppm (s, 2H, N*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.0, 16.8, 17.2, 17.7, 19.2, 19.5, 20.5, 22.3, 22.7, 25.2, 26.8,

29.7, 34.5, 93.8, 126.7, 128.3, 130.0, 132.4, 134.9, 136.0, 136.4 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=441 (4.35), 465 (4.46), 533 (3.30), 610 (3.20), 676 (3.31) nm.

*3.4.50. 2,3,7,8,12,13,17,18-Octaethyl-5-(4-pentylphenyl)-10,15-diphenylporphyrin (**64**).* The reaction was performed as described in Section 3.3.1 using 60 equiv of 1-bromo-4-pentylbenzene (1.63 mL, 9.22 mmol) and 75 equiv of *n*-BuLi (4.19 mL, 11.5 mmol) at −30 °C to rt. Free base **60** (106 mg, 0.1537 mmol) in THF (50 mL) was added after 1 h at rt and after stirring for 3 h at the same temperature the reaction was quenched at 0 °C with water to yield 23 mg (0.027 mmol, 17%) of a green solid. Mp 68 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.43 (s, 1H, H_{meso}), 8.35 (d, 2H, J=7.13 Hz, H_{Ph}), 8.28 (d, 2H, J=7.09 Hz, H_{Ph}), 8.17 (d, 2H, J=7.72 Hz, H_{Ph}), 7.74 (m, 2H, H_{Ph}), 7.66 (t, 2H, J=7.2 Hz, H_{Ph}), 7.64 (d, 4H, J=7.6 Hz, H_{Ph}), 3.73 (m, 4H, CH_2CH$_3$), 2.95 (m, 2H, pentyl-CH_2), 2.69 (m, 4H, CH_2CH$_3$), 2.57 (m, 4H, CH_2CH$_3$), 2.24 (m, 4H, CH_2CH$_3$), 1.86 (m, 4H, pentyl-CH_2), 1.58 (m, 6H, CH$_2$CH_3), 1.47 (m, 2H, pentyl-CH_2), 0.99 (m, 3H, pentyl-CH_3), 0.70 (t, 6H, J=7.3 Hz, CH$_2$CH_3), 0.44 (m, 6H, CH$_2$CH_3), 0.35 (m, 6H, CH$_2$CH_3), −2.12 ppm (s, 2H, NH); ^{13}C NMR (100 MHz $CDCl_3$): δ=14.0, 17.1, 17.9, 19.0, 19.2, 19.5, 20.4, 22.4, 27.9, 29.4, 29.5, 30.9, 31.5, 35.3, 35.9, 38.6, 93.4, 125.8, 126.7, 127.0, 127.7, 128.1, 128.5, 134.7, 135.8, 136.1, 140.4, 142.7 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=438 (4.65), 533 (3.72), 605 (3.43), 673 (3.24) nm; MS (ES$^+$), m/z (%): 833 (25) [M+H]$^+$], 578 (70); HRMS [$C_{59}H_{68}N_4$]: calcd 833.5514, found 833.5522.

*3.4.51. 2,3,7,8,12,13,17,18-Octaethyl-5,10,15-tris(1-naphthyl)porphyrin (**65**).* The green title compound was obtained as a minor side product (<1%) from the preparation of the respective *meso* monosubstituted compound **19** and was identified after accumulation of several reactions. NMR spectroscopy indicated the formation of atropoisomers due to hindered naphthyl rotation. Mp <75 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.46 (s, 1H, H_{meso}), 8.57 (d, 1H, J=8.63 Hz, $H_{naphthyl}$), 8.53 (d, 1H, J=7.01 Hz, $H_{naphthyl}$), 8.46 (m, 2H, $H_{naphthyl}$), 8.41–8.34 (m, 2H, $H_{naphthyl}$), 8.25 (d, 2H, J=8.31 Hz, $H_{naphthyl}$), 8.23 (d, 2H, J=8.64 Hz, $H_{naphthyl}$), 8.09–7.89 (m, 8H, $H_{naphthyl}$), 7.30 (m, 3H, $H_{naphthyl}$), 3.67 (m, 6H, CH_2CH$_3$), 2.50–1.80 (m, 10H, CH_2CH$_3$), 1.51 (t, 6H, J=7.35 Hz, CH$_2$CH_3), 0.51 (m, 6H, CH$_2$CH_3), 0.26 (m, 6H, CH$_2$CH_3), 0.12 (m, 6H, CH$_2$CH_3), −1.64 ppm (s, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.0, 14.0, 16.4, 16.7, 17.7, 19.1, 19.2, 20.5, 22.6, 25.5, 26.7, 27.4, 29.7, 31.6, 34.6, 38.9, 114.6, 124.4, 125.7, 127.9, 128.9, 132.9, 137.3, 138.3, 140.8, 141.8, 142.9 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=488 (5.08), 636 (3.56), 692 nm (4.00); MS (ES$^+$), m/z (%): 913 (10) [M+H]$^+$; HRMS [$C_{66}H_{64}N_4$]: calcd 913.5209, found 913.5180.

*3.4.52. 2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetrakis-(9-phenanthrenyl)porphyrin (**66**).* This product was obtained from the reaction described in Section 3.4.39. When free base **21** (66 mg, 0.092 mmol) were reacted with 60 equiv of 9-bromophenanthrene (1.431 mg, 5.57 mmol) and 60 equiv *n*-BuLi (2.2 mL, 5.57 mmol) an increased yield for the *meso* tetrasubstituted product **66** was observed. A crude mixture of di- and trisubstituted product (63 mg) was isolated followed by the green tetrasubstituted product (63 mg, 0.050 mmol, 54%, precipitated from *n*-hexane/MeOH by addition of perchloric acid). It was deprotonated by further purification on aluminum oxide for the subsequent palladium insertion to yield 48 mg of a green-brown solid (0.0392 mmol, 42%). Mp <86 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.96 (m, 8H, phenanthrenyl H), 8.90 (m, 1H, phenanthrenyl H), 8.86 (m, 1H, phenanthrenyl H), 8.72 (m, 1H, phenanthrenyl H), 8.61 (m, 1H, phenanthrenyl H), 8.23–8.14 (m, 4H, phenanthrenyl H), 8.02 (m, 2H, phenanthrenyl H), 7.81 (m, 14H, phenanthrenyl H), 7.62 (m, 2H, phenanthrenyl H), 7.53 (m, 2H, phenanthrenyl H), 2.18 (m, 12H, CH$_2$), 1.58 (m, 4H, CH$_2$), 1.24 (m, 24H, CH$_3$), −1.14 ppm (s, 2H, NH), NMR spectroscopy indicated the existence of several atropoisomers due to hindered phenanthrenyl rotation.; ^{13}C NMR (100 MHz, $CDCl_3$): δ=16.1, 16.4, 19.0, 19.9, 122.5, 122.9, 126.6, 127.1, 129.7, 129.8, 130.7, 136.3, 136.4 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=493 (5.37), 697 nm (4.13); MS (ES$^+$), m/z (%): 1240 (20) [M+H]$^+$; HRMS [$C_{92}H_{78}N_4$]: calcd 1240.6383, found 1240.6368.

*3.4.53. {2,3,7,8,12,13,17,18-Octaethyl-5,10-bis(9-phenan-threnyl)porphyrinato}palladium(II) (**67**).* Palladium insertion was performed with the respective free base **48** (40 mg, 0.045 mmol), following the procedure given in Section 3.3.2 and using palladium acetate (20 mg, 0.09 mmol) in a mixture of $CHCl_3$ (20 mL) and MeOH (5 mL). Red crystals were obtained (26 mg, 0.025 mmol, 55%). Mp 238 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.88 (s, 1H, H_{meso}), 9.86 (s, 1H, H_{meso}), 8.96 (d, 2H, J=8.50 Hz, $H_{phenanthrenyl}$), 8.92 (m, 2H, $H_{phenanthrenyl}$), 8.64 (s, 1H, $H_{phenanthrenyl}$), 8.58 (s, 1H, $H_{phenanthrenyl}$), 8.06 (d, 1H, J=7.86 Hz, $H_{phenanthrenyl}$), 8.03 (d, 1H, J=7.81 Hz, $H_{phenanthrenyl}$), 7.85 (m, 2H, $H_{phenanthrenyl}$), 7.75 (m, 2H, $H_{phenanthrenyl}$), 7.68 (m, 2H, $H_{phenanthrenyl}$), 7.43 (d, 1H, J=8.15 Hz, $H_{phenanthrenyl}$), 7.36 (d, 1H, J=8.07 Hz, $H_{phenanthrenyl}$), 7.28 (m, 1H, $H_{phenanthrenyl}$), 7.22 (m, 1H, $H_{phenanthrenyl}$), 3.97 (m, 4H, CH_2CH$_3$), 3.75 (m, 4H, CH_2CH$_3$), 2.59–2.49 (m, 2H, CH_2CH$_3$), 2.23–1.95 (m, 6H, CH_2CH$_3$), 1.85 (t, 6H, J=7.56 Hz, CH$_2$CH_3), 1.62 (m, 6H, CH$_2$CH_3), 0.54 (m, 6H, CH$_2$CH_3), 0.39 (t, 3H, J=7.36 Hz, CH$_2$CH_3), 0.35 ppm (t, 3H, J=7.35 Hz, CH$_2$CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=16.6, 16.9, 18.2, 18.1, 18.2, 19.5, 19.6, 20.4, 21.3, 21.9, 97.8, 117.0, 122.5, 122.9, 126.4, 127.1, 127.2, 128.9, 129.12, 129.17, 130.6, 130.82, 130.86, 136.41, 136.45, 137.2, 137.3, 140.0, 140.1. 140.3, 140.4, 141.5, 143.3, 143.4, 143.6, 144.5, 144.6 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=414 (5.15), 5.27 (4.09), 562 (4.24) nm.

*3.4.54. {2,3,7,8,12,13,17,18-Octaethyl-5,10,15-tris(9-phenanthrenyl)porphyrinato}palladium(II) (**68**).* Palladium insertion was performed following procedure B with 44 mg (0.410 mmol) of the respective free base **49**, 18 mg (0.082 mmol) palladium acetate in a mixture of 25 mL $CHCl_3$ and 8 mL MeOH and using a reaction time of 30 min at 50 °C under Ar. Red crystals (40 mg, 0.033 mmol, 80%) were obtained. NMR spectroscopy indicated a mixture of atropoisomers due to hindered phenanthrenyl rotation. Mp 268 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.70, 9.69, 9.67 (each s, 1H, H_{meso}), 8.99–8.88 (m, 6H, $H_{phenanthrenyl}$), 8.77, 8.73 (s, 1H, atropisomers, $H_{phenanthrenyl}$), 8.69, 8.65 (s, 1H, atropisomers, $H_{phenanthrenyl}$), 8.59, 8.55, 8.52 (s, 1H, atropisomers, $H_{phenanthrenyl}$), 8.14–8.03 (m, 3H, $H_{phenanthrenyl}$), 7.89–7.67 (m, 12H, $H_{phenanthrenyl}$), 7.54–7.33 (m, 3H, $H_{phenanthrenyl}$), 3.65 (m, 4H, CH_2CH$_3$), 2.56–2.49 (m, 2H, CH_2CH$_3$), 2.16 (m, 6H, CH_2CH$_3$), 1.97 (m, 4H, CH_2CH$_3$), 1.54 (m, 6H, CH$_2$CH_3), 0.51 (m, 6H, CH$_2$CH_3), 0.31 (t, 6H, J=7.43 Hz, CH$_2$CH_3), 0.24 ppm (m, 6H, CH$_2$CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=16.5, 16.6, 16.9, 17.9, 19.4, 20.0, 20.9, 29.6, 53.4, 116.2, 117.3, 117.4, 122.6, 122.9, 126.5, 127.1, 127.2, 128.2, 129.2, 129.4, 130.7, 130.9, 133.3, 136.0, 136.5, 136.7, 136.9, 141.0, 141.2, 141.4, 142.3, 142.5, 143.0, 143.8, 144.4, 144.5, 144.6 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=429 (4.11), 539 (4.04), 575 nm (4.06).

*3.4.55. {2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetra-kis(9-phenanthrenyl)porphyrinato}palladium(II) (**69**).* Palladium insertion was performed with the respective free base **66** (48 mg, 0.039 mmol) as described in Section 3.3.2. The reaction was performed with palladium acetate (17 mg, 0.078 mmol) in a mixture of $CHCl_3$ (20 mL) and MeOH (8 mL). The reaction mixture was stirred for three days at rt. Red crystals were obtained from CH_2Cl_2/MeOH (12 mg, 0.0094 mmol, 12%). NMR spectroscopy indicated a mixture of atropoisomers due to hindered phenanthrenyl rotation. Mp 290 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.95–8.91 (m, 8H, $H_{phenanthrenyl}$), 8.85, 8.79, 8.71, 8.66, 8.53, 8.50, 7.97, 7.95 (s, 6H, atropisomers, $H_{phenanthrenyl}$, $H_{phenanthrenyl}$), 8.13–7.95 (m, 6H, $H_{phenanthrenyl}$), 7.84–7.70 (m, 14H, $H_{phenanthrenyl}$), 7.62 (m, 2H, $H_{phenanthrenyl}$), 7.51 (m, 2H, $H_{phenanthrenyl}$), 7.62–7.42 (m, 6H, $H_{phenanthrenyl}$), 1.88 (m, 2H, CH_2CH$_3$), 1.72 (m, 4H, CH_2CH$_3$), 1.56 (m, 10H, CH_2CH$_3$), 1.16–1.08 (m,

Table 2
Crystal Summary of crystal data, data collection and refinement for the crystal structure determinations

Compound	8	12	12·CH_2Cl_2	16	55
Chemical formula	$C_{41}H_{54}N_4$	$C_{44}H_{50}N_4$	$C_{44}H_{50}N_4 \cdot CH_2Cl_2$	$C_{42}H_{49}BrN_4$	$C_{46}H_{56}N_4Pd$
Mol. wt.	602.88	634.88	719.81	689.76	771.37
Crystallization	CH_2Cl_2/CH_3OH	CH_2Cl_2/CH_3OH	CH_2Cl_2/*n*-hexane	CH_2Cl_2/*n*-hexane	CH_2Cl_2/CH_3OH
Color, habit	Red rhombus	Red plate	Red block	Red plate	Red plate
Crystal size (mm)	0.25×0.15×0.15	0.15×0.08×0.02	0.8×0.8×0.8	0.43×0.08×0.05	0.3×0.16×0.13
Lattice type	Triclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1	$P2_1/n$	*P*-1
a (Å)	9.5656(5)	7.118(3)	10.136(6)	7.0107(14)	10.250(2)
b (Å)	12.6775(7)	10.327(4)	14.276(7)	35.111(7)	14.531(3)
c (Å)	14.7408(8)	25.080(11)	15.195(10)	14.455(3)	14.880(3)
α (°)	93.3810(10)	86.94(3)	66.55(4)	90	64.425(3)
β (°)	103.8620(10)	87.76(4)	82.14(5)	97.17(3)	89.108(4)
γ (°)	95.7670(10)	74.66(4)	75.85(4)	90	72.679(3)
V (Å^3)	1720.35(16)	1774.9(13)	1954(2)	3530.4(12)	1892.0(7)
Z	2	2	2	4	2
d_{calcd} (Mg m^{-3})	1.164	1.188	1.223	1.298	1.354
μ (mm^{-1})	0.;068	0.527	0.203	1.200	0.529
T_{max}, T_{min}	0.99, 0.99	0.99, 0.92	0.86, 0.85	0.94, 0.63	0.93, 0.86
θ_{max} (°)	31.51	56.45		31.51	23.24
T, *K*	91	120	114	91	123
Collec. reflections	24,356	5152		34,954	12,633
Indep. reflections	10,694	4697		11,170	5356
Reflections with $F>4.0\sigma(F)$	4965	3632		7256	5009
R_{int}	0.0697	0.0437		0.0458	0.0216
No. of parameters	425	441		428	469
Δ/ρ_{max} (e Å^{-3})	1.616	0.243		2.295	0.524
S	0.891	1.017		1.157	1.038
*R*1 [$F>4.0\sigma(F)$]	0.0643	0.0647		0.0764	0.0280
*wR*2 [$F>4.0\sigma(F)$]	0.1634	0.1683		0.2001	0.0697
*R*1 (all data)	0.1423	0.0838		0.1197	0.0305
*wR*2 (all data)	0.1926	0.1853	[a]	0.2217	0.0713

[a] Unit cell data only, no refinement.

6H, CH_2CH_3), 0.29 ppm (m, 18H, CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.1, 16.5, 19.7, 22.7, 29.8, 31.6, 31.9, 53.4, 116.8, 122.7, 123.0, 126.6, 127.2, 128.3, 129.3, 129.7, 130.8, 131.1, 133.4, 133.6, 133.8, 135.9, 136.4, 136.6, 136.8, 144.1, 144.5 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=443 (4.43), 553 (3.89), 590 nm (3.75).

*3.4.56. {2,3,7,8,12,13,17,18-Octaethyl-5,15-bis(9-phenan-threnyl)-10-phenylporphyrinato}palladium(II) (**70**).* Palladium insertion was performed following procedure B with the respective free base **34** and stirring for 30 min to yield 52 mg (0.047 mmol, 54%) of the title compound as red crystals. Mp 257 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.70 (s, 1H, H_{meso}), 8.99, 8.98 (each d, 2H, J=7.8 Hz, $H_{phenanthrenyl}$), 8.64 (s, 1H, $H_{phenanthrenyl}$), 8.60 (s, 1H, $H_{phenanthrenyl}$), 8.36, 8.23 (m, 1H, H_{Ph}), 8.33 (d, 1H, J=6.9 Hz, H_{Ph}), 8.09 (m, 2H, $H_{phenanthrenyl}$), 7.88 (t, 2H, J=7.88 Hz, $H_{phenanthrenyl}$), 7.79 (each d, 2H, J=7.5 Hz, $H_{phenanthrenyl}$), 7.73 (m, 2H, $H_{phenanthrenyl}$, 1H, H_{Ph}), 7.68–7.63 (m, 2H, $H_{phenanthrenyl}$, 2H, H_{Ph}), 7.41–7.34 (m, 2H, $H_{phenanthrenyl}$), 3.67 (m, 4H, CH_2CH_3), 2.59–2.30 (m, 4H, CH_2CH_3), 2.24–2.19 (m, 4H, CH_2CH_3), 2.12–2.04 (m, 4H, CH_2CH_3), 1.56 (m, 6, CH_2CH_3), 0.51–0.40 ppm (m, 16H, CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=16.55, 16.90, 16.96, 17.41, 17.52, 17.94, 19.4, 19.7, 20.0, 20.8, 20.9, 122.6, 122.9, 126.5, 126.6, 126.7, 126.74, 127.1, 127.2, 128.2, 128.9, 129.1, 129.4, 130.9, 131.0, 133.4, 134.9, 135.0, 136.9, 141.1, 141.6, 141.9, 142.1, 142.8, 142.9, 143.5, 143.7, 143.8 ppm; UV/vis (CH_2Cl_2): λ_{max} (log ε)=427 (4.87), 539 (3.78), 573 nm (3.72).

3.5. Crystal structure determinations

3.5.1. General. Growth and handling of crystals followed the concept developed by Hope.[31] Intensity data were collected with a Siemens SMART system with Mo K_α radiation (λ=0.71073 Å) for **8**, **16**, and **55**, for **12** with a Siemens P4 rotating anode system with Cu K_α radiation (λ=1.54178 Å), and for **12·CH_2Cl_2** with a Siemens R3mV system with Mo-K_α radiation (λ=0.71073 Å). The intensities were corrected for Lorentz, polarization and extinction effects. The structures were solved with Direct Methods using the SHELXTL PLUS program system[32a] and refined against $|F^2|$ with the program XL from SHELX-97 using all data.[32b] Nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were generally placed into geometrically calculated positions and refined using a ridging model. The N–H hydrogen atoms were located in difference maps and refined using the standard riding model. Crystal data and refinement parameters are compiled in Table 2.

*3.5.2. Special comments: **8**.* One side chain ethyl group at C2 was disordered and refined with two split positions; the occupancy was refined using a free variable. Hydrogen atoms at N22 and N24 were located in a difference map and then refined using a standard riding model. The residual electron density accounts for a small amount of nickel(II)porphyrin impurity. **12·CH_2Cl_2**: The crystals exhibited low high angle diffraction and refinement converged only to about 0.13. The overall structure and conformation of the porphyrin macrocycle was very similar to that of the structure of the unsolvated compound **12**. Compound **16:** the ethyl side chain at C7 was disordered and refined with two split positions of equal occupancy for C72. Residual electron density is located in the disordered region.

3.5.3. Supplementary data. CCDC-756278 to 756281 contain the supplementary crystallographic data for this paper. 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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