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5,10-A₂B₂-type meso Substituted Porphyrins – A Unique Class of Porphyrins with Realigned Dipole Moment

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Abstract: Current applications in porphyrin chemistry require the use of unsymmetrically substituted porphyrins. Many current industrial interests in optics and biomedicine require systems with either push-pull (electron donating and withdrawing groups) or amphiphilic systems (hydrophobic and hydrophilic groups). In this context we present the class of 5,10-A₂B₂-type porphyrins where two different substituents are positioned in diagonally opposite meso positions.

Thus, the intramolecular dipole moment in these tetrapyrroles is positioned along a β–β vector passing through two pyrrole rings. This is opposite to the situation of the frequently used 5,15-A₂BC porphyrins where the dipole moment is oriented along a meso-meso axis. We have elaborated syntheses of the 5,10-A₂B₂ porphyrins using transition metal catalyzed transformations of 5,10-A₂ porphyrins or direct substitutions reactions thereof which give the target

molecules in 22–77 % overall yield. The compounds exhibit interesting structural, spectroscopic and optical features and can serve as building blocks for new porphyrin arrays and applications.

Keywords: porphyrinoids • nonlinear optics • tetrapyrroles • macrocycles • nitrogen heterocycles

Introduction

Porphyrins are important natural products and industrially relevant dyes. Although their basic structure and chemistry has been known now for almost a century, research into their chemistry and technical and biomedical uses continues apace. Indeed, the last quarter of a century has seen an almost explosive growth of new porphyrinoid, pyrrole-based chromophores. After the landmark discovery of porphycene as a C-skeleton isomer of porphyrin by Vogel^[1] and the calixphyrins^[2] related to Baeyer's "Azetopyrrol"^[2b] a whole cornucopia of expanded, contracted and isomeric porphyrins, and cyclopyrroles have been - and continue to be - discovered.^[2c,2d] In light of this quest for ever more elaborate porphyrinoid systems it might come as a surprise to the nonspecialist that many important classes of the chemically simpler, "true" porphyrins, i.e., 18π-aromatic tetrapyrrolic systems have remained elusive until recently.

Figure 1. Selected A_x- and ABCD-type porphyrins.

Especially the group of the so-called A_x- and ABCD-type porphyrins contained several missing links. This terminology relates to the various regioisomers of meso substituted porphyrins with different residues at the methine bridges.^[3] Figure 1 illustrates the constitution of selected members of the porphyrin "alphabet soup".^[4] Going back only about a decade, most of the less symmetrical compounds in this series were either unknown or had been prepared merely through mixed condensations in minuscule yields. In practical terms only the symmetric 5,15-A₂- **4** and 5,10,15,20-A₄-type **6** systems could be prepared with ease. Especially the A- **2** and 5,10-A₂-type **3** porphyrins remained almost unexplored white specks on the porphyrin landscape. The underlying problem is the propensity of pyrrole compounds to undergo acid-catalyzed scrambling reactions.^[5] This negated many total synthesis approaches and even made it problematic to use preformed building blocks such as dipyrromethanes for [2+2] or [3+1] condensation reactions. The only alternative at that time was the use of mixed (aldehyde + pyrrole) condensation reactions. Nevertheless, the required chromatographic work-up and acid instability of certain groups made this prohibitive for, e. g., the ABCD-type systems **10**.

In the meantime flexible total synthesis routes have been developed for many of these systems by Lindsey's group and judicious choice of the ABCD residues, their kinetic stability, steric hindrance, and the sequence of use of the individual building blocks allows the large scale preparation of many but not all desired compounds.^[6] In parallel we developed porphyrin syntheses based

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on the step-wise introduction of functional groups into preformed macrocycles, i.e. through functionalization reactions. This goes back to our initial observation that porphyrins can be substituted in high yield at the meso positions with organolithium reagents,^[7] and by now has evolved to a strategy which utilized various organometallic reactions for the step-wise transformation of unsubstituted porphyrin ($2, A = H$) $\rightarrow A- \rightarrow AB- \rightarrow ABC- \rightarrow ABCD$ -type porphyrins.^[4,8]

Next to access to porphine,^[9] this strategy required access to the monosubstituted porphyrins **2** and appropriate synthetic routes were developed by us based on condensation and substitution reactions.^[10] Logical construction of the ABCD-type systems **10** via step-wise functionalization also required a means to introduce a second meso substituent in a neighboring meso position, i.e. a way to generate the 5,10-regioisomers. Of the two possibilities, use of an appropriate precursor, e. g., reaction of tripyrrane^[11a] with pyrrole and aldehyde, or exploitation of the regioselectivity of S_NAr reactions in porphyrins,^[11b] both could be used to develop an entry into the 5,10- A_2 -type systems **3**.^[10b,12] Thus, only the 5,10- A_2B_2 porphyrins remained an unexplored entity in the world of meso substituted porphyrins. Here, we present general synthetic routes for the preparation of these A_2B_2 -type porphyrins and discuss some of their properties.^[13]

Results and Discussion

Synthetic rational and brief review of the literature: Current application developments indicate a considerable demand for unsymmetrically substituted porphyrins. Examples for this are amphiphilic porphyrins in photodynamic cancer therapy (PDT),^[14a] synthons for crystal engineering and supramolecular chemistry,^[14b] push-pull systems for biomimetic studies on electron transfer,^[14c] and uses in optics, esp. in nonlinear optics (NLO).^[14d] Unsymmetrical substitution is used to either position donor/acceptor residues in a manner suitable for the desired interaction or to yield systems with a strong intermolecular dipole moment to enhance optical effects. Thus, contemporary studies habitually employ 5,15- A_2BC porphyrins **8**, where B and C are used for macrocycle diversification.

Porphyrins of type **8** require a step-wise functionalization or a total synthesis.^[8] While the precursor 5,15- A_2 porphyrins **4** are easily obtained in high yield^[15] introduction of the two different meso substituents B and C requires first an appropriate monofunctionalization for the introduction of B (e. g., monobromination and then C–C coupling) and then introduction of C; alternatively for a one-pot reaction with R^1Li/R^2I is possible.^[7b,7f] In a fundamental sense this yields porphyrins with an intramolecular dipole moment aligned along a 5,15 meso-meso axis (Fig. 2, **8**). The 5,10- A_2B_2 type systems are accessible more easily. They require no selective monofunctionalization, rather a double substitution of the "free" 15,20-positions (e. g., unspecific dibromination and then C–C coupling; see Scheme 2). Here, only two different substituents (A and B) are required to construct unsymmetrical systems. Thus, in the case of electron withdrawing/donating groups porphyrins will be obtained where the dipole moment passes through the middle of two opposing β – β units ($N \cdots N$) (Fig. 2, **9**).

Figure 2. Orientation of the intramolecular dipole moment in 5,15- A_2BC - and 5,10- A_2B_2 -type porphyrins.

5,10-Disubstituted porphyrins were first reported by Longo but not characterized.^[16a] In the early 21st century examples for condensation reactions,^[16b] total syntheses^[16c] and N-confused derivatives^[16d] were reported. This was then followed by the more general methods described above for porphyrins^[10b,12] and calixphyrins.^[16e] This opened the possibility to use the 5,10- A_2 porphyrins as simple starting materials for the synthesis of 5,10- A_2B_2 systems as outlined above. A few 5,10- A_2B_2 compounds have been reported before; however, all were prepared in low yields through statistical condensation methods using pyrroles, dipyrromethanes or tripyrranes with the usual attendant problems of tedious chromatographic separation, scrambling and other limitations.^[17] The only exception is Lindsey's elegant study on the development of total syntheses using diacyldipyrromethanes. This method was successfully used to prepare some compounds with aryl substituents.^[6a]

Based on the current state of the art in porphyrin functionalization reactions there are several methods for the introduction of the B residue into an A_2 porphyrin. The majorities of them employs organometallic reagents and are discussed in subsequent sections.

Synthesis via RLi reactions: Based on our earlier experience with the use of organolithium reagents for the meso functionalization of porphyrins,^[7] it was logical to apply these for the current problem as well. For initial experiments we used the nickel(II)porphyrin **11**, which typically shows good reactivity with RLi. In order to achieve "full" substitution of both 15,20 meso positions we used 6 equivalents of hexyllithium. Indeed, the target compound **17** was obtained in 58 %. The different reactivity of free base and metallo porphyrins became evident when a similar experiment was performed with **12**. Here, a low yield of the monosubstituted porphyrin **18**, i.e. an 5,10- A_2B system, was obtained. Full, disubstitution to **19** was only achieved when the number of hexyllithium equivalents was raised to 10. A similar reactivity was found for **13** which could be transformed into **20** in 26 %. Use of *n*-BuLi and reaction with **12** to give **21** did not improve the yield significantly, while the use of 20 equiv. of *n*-BuLi with **14** in the presence of TMEDA only gave the A_2B porphyrin **22**.

Scheme 1. Synthesis of 5,10- A_2B_2 -porphyrins using organolithium reagents. i) 1. R_2Li , THF, 2. H_2O , 3. DDQ.

Next we tried to introduce residues with functional groups using the same methodology *via in situ* generation of organolithium reagents. For example, reaction of **12** with 4-(*N,N*-dimethylamino)phenyllithium gave **23** in 71 % yield. However, the reaction is somewhat inefficient as it required 100 equivalents of RLi. Likewise the *p*-hydroxyphenyl derivative **24** could be prepared in good yield. Reaction of the methoxyphenylporphyrin **15** gave **25**, accompanied by a small amount of **26**. Likewise, the *p*-phenylethynyl group could be introduced into the tolylporphyrin **12** to yield **27**. Finally, the free base porphyrin **16** was prepared through a condensation approach in 5 % yield and reacted with *p*-phenylethynyllithium to **28**. We also attempted the introduction of stronger electron withdrawing groups through similar reactions. However, a reaction of **12** using *n*-BuLi/*p*-bromobenzonitrile (–100 °C) only gave only the butylated product **21**. No reaction was observed with 1-bromo-4-nitrobenzene/*n*-BuLi and only starting material was recovered.

Synthesis via Heck reactions: In order to expand the scope of these compounds we next turned our attention to the use of Pd-catalyzed reactions. Many of these have now been applied to porphyrin chemistry.^[4] The Heck reaction^[18a] was initially applied for the β -substitution of porphyrins^[18b] and we were interested in preparing meso vinyl acceptor substituted porphyrins.

The Heck reaction requires a bromo-substituted coupling partner and thus preparation of bromoporphyrins was the first step. DiMaggio *et al.*^[19] had shown that 5,15- A_2 porphyrins can easily be brominated with NBS in both meso positions and the same conditions could be applied straightforwardly to the 5,10- A_2 -type systems. Using the ditolylporphyrin for exploration of this reaction it was brominated to **29**. In order to prevent the incorporation of Pd from the catalysts we transformed it into the respective zinc(II) **30** and nickel(II)porphyrin **31**. First we reacted the zinc(II) porphyrin **30** with butyl acrylate. Heating at 120 °C for 24 h gave the desired $\{(all-E)-5,10-bis(4-(2-butoxycarbonyl)ethenyl)-15,20-di(p-tolyl)porphyrinato\}zinc(II)$ **32** the sole product in 64 %. Similarly, reaction with a methyl vinylketone gave **33**. The *E*-configuration is clearly evidenced by the respective NMR coupling constant of 16 Hz. Reaction of the zinc(II) complex **30** with nitrostyrene gave the analogous porphyrin **34** in good yield. The nickel(II) complex **31** is less reactive and reaction with nitrostyrene gave **35** in much lower yield (Scheme 2).

Scheme 2. Synthesis of 5,10- A_2B_2 -porphyrins using Heck reactions. i) NBS, pyridine, $CHCl_3$; ii) ZnO, CH_2Cl_2 , TFA or Ni(acac)₂, toluene, Δ ; iii) Pd(OAc)₂, NaOAc, PPh₃, DMF, Δ .

Synthesis via Suzuki reactions: Next we focused on applications of the Suzuki reaction for the task at hand. Suzuki reactions have been very fruitfully applied to porphyrins and offer the advantage that no prior metallation is necessary.^[20] Again, bromoporphyrins are required as coupling partners and, in addition to the ones mentioned above, a few more (**36-40**) were synthesized to gain access to a broader range of A/B substituent systems. Likewise, two new 5,10- A_2 porphyrins (**41,42**) were prepared using condensations reactions.

By now optimized catalyst/base systems have been established for Suzuki reactions with 5,15- A_2 systems.^[20d] These could be easily applied for the modification of 5,10- A_2 porphyrins. As shown in Scheme 3 a large set of compounds could be prepared using Pd(PPh₃)₄ as palladium catalyst and K₃PO₄ as a base. Yields varied from 22 to 59 %, both aryl- and alkylhalogenoporphyrins could be used, and reaction times from 7 to 13 h. For example, the bromotolylporphyrin **29** was reacted with 4-methoxycarbonylphenyl boronic acid for 7 h and gave **43** in 52 % yield. The best yield for this reagent was obtained for the pentylporphyrin derivative **57**. The reactivity of 4-cyanophenyl boronic acid towards aryl and alkyl haloporphyrins was investigated as well. The best results of 47 % each were obtained for **44** and the (3-methoxyphenyl)porphyrin **52**. Alkyl haloporphyrins, e.g., 5,10-dibromo-15,20-dipentylporphyrin or 5,10-dibromo-15,20-dihexylporphyrin gave the corresponding products **58** and **61** in 40 % yield, respectively. Even lower yields were obtained for porphyrins **48** and **49**, materials synthesized from 5,10-dibromo-15,20-diphenylporphyrin **70**.

Introduction of the nitrophenyl residue proceed well with good yields, e.g. for compounds **45**, **50**, **53** and the alkylporphyrins **59** and **62**. The 3-nitrophenyl boronic acid required longer reaction times than the 4-nitrophenyl boronic acid and gave lower yield. This was no the case for the 3-cyanophenyl versus 4-cyanophenyl

reagent. Reactions with the electron poor 2,3-difluorophenylporphyrins proceeded poorly with yield ranging from 22 to 30 %. Clearly, the Suzuki reaction provides convenient access to various 5,10- A_2B_2 -type porphyrins. Still, some scope for optimization exists. A number of the free base porphyrins prepared from the reactions described above, were converted into the respective zinc(II) porphyrins for comparative photophysical analyses. The metalloporphyrins **63-68** were obtained through standard reactions in good yield.

Scheme 3. Synthesis of 5,10- A_2B_2 -porphyrins using Suzuki reactions. i) boronic acid or ester, K₃PO₄, Pd(PPh₃)₄, THF, Δ .

Functionalization reactions: The target systems can also be prepared through simple functionalization reactions. Examples for this are the partial reduction of nitro groups in, e.g., a tetra-nitrophenylporphyrin.^[21a] Perhaps not elegant in synthetic chemistry terms such strategies offer a quick entry into various systems and have recently been used to generate 5,10-type precursors for Huisgen Cu(I) coupling chemistry.^[21b]

Other, "simple" reactions may be performed as well. For example, the Vilsmeier formylation^[22a] has been used often for the modification of porphyrins.^[22b-d] Using "excess" conditions it can be used to diformylate metallo octaethylporphyrins^[22c] and 5,15- A_2 -type porphyrins,^[22d] but mostly gives mixtures of the mono- and diformyl product. In the case of the 5,10- A_2 porphyrin **69** standard Vilsmeier-Haack formylation gave the respective 5,10- A_2 (CHO)₂-porphyrin **70** in very good yield (77 %) and as the sole product (Scheme 4). Other possibilities for selective functionalizations are the use of (e.g., **41**) organotin reactions.^[23]

Scheme 4. Synthesis of the diformylporphyrin **64**. i) DMF, POCl₃, dichloroethane, 50–90 °C.

Structural studies: In order to establish some basic structural features of the 5,10- A_2B_2 -type porphyrins a X-ray crystallographic analysis of compound **29** was performed. The molecular structure in the crystal is shown in Figure 3. Overall, the structural properties are similar to those of 5,15- A_2B_2 - and A_4 -type porphyrins. There is no evidence for core elongation or other changes to the core structure. For example, the core size (average N...Ct distance) is 2.064 Å and similar to that of 5,10,15,20-tetraphenylporphyrin (TPP).^[24] Similarly, the bond lengths and angles of the tetrapyrrole framework are in line with "normal" porphyrin systems.^[25] The packing of the molecules (not shown) is characterized by the formation of weak π - π aggregates in a head-to-tail fashion.^[25]

Figure 3. View of the molecular structure of **29** in the crystal. Hydrogen atoms have been removed for clarity and thermal ellipsoids show 50 % occupancy.

The conformation of the molecule is nonplanar.^[25a,b] The average deviation of the 24 macrocycle atoms from their least-squares-plane (Δ_{24}) is 0.159 Å, slightly less than the tetragonal form of TPP.^[26] The macrocycle exhibits a ruffled distortion mode, with alternate C_m displacements of 0.15–0.34 Å from the 24-macrocycle atom plane. A detailed normal structural decomposition analysis (NSD)^[27] reveals a more complex situation. The conformation is characterized by almost similarly strong out-of-plane contributions from *sad* and *ruf* distortions (B_{1u} and B_{2u}), a moderate contribution from *doming* (A_{2u}), and a minor one from *wave* (E_{gx}). With regard to in-plane distortion modes, the most significant contributor is *macrocycle-breathing* (A_{1g}). In a first approximation this is similar to

the structure of 5,10-diphenylporphyrin,^[28] which exhibits less *sad* distortion and more *wave* contribution.

NLO properties: Understanding the nonlinear absorption (NLA) properties of macrocyclic dyes is important for the development of related applications. Besides instantaneous two-photon absorption (TPA) arising at nonresonant frequencies, which has potential for 3D-microfabrication and multiphoton microscopy, porphyrins exhibit sequential TPA, i.e. reverse saturable absorption (RSA) and saturable absorption (SA) at resonant or close to resonant wavelengths. The latter two processes occur when the absorption arising from higher excited state is higher and lower respectively to that of the ground state. RSA has potential for use in pulse sensors and in optical limiting devices that protect sensitive optical components or the human eye from laser-induced damage. SA finds application for mode locking, laser pulse compression and laser amplification.

Our open aperture Z-scan studies at close to resonant wavelength revealed that 5,10-A₂B₂ compounds exhibit an interesting NLO effect, which has not been observed for porphyrins in the ns regime before. The compounds exhibit pure RSA response when low laser energies inputs were used, which is a standard response commonly observed for macrocyclic dyes under such experimental conditions. However, when the input energy was increased with the onfocus intensity I_{00} reaching approximately 0.4 GW cm⁻², the RSA response was observed to switch to SA in the tight focal regime. When the input energy was increased further on, with I_{00} being on the order of ~0.5 GW cm⁻², a similar RSA/SA signal was detected, though with a much more pronounced SA peak. The SA response within an RSA remained highly symmetrical for all of the measurements (not shown^[29]).

Interestingly, compounds with similar substituents but in a 5,15-A₂B₂ substitution pattern, exhibit a pure RSA response both at lower and higher inputs.^[30] This clearly demonstrates that the RSA/SA switch is intrinsic to 5,10-A₂B₂ compounds. The origin of the behavior is not understood at this stage. Most likely the RSA/SA switch is the result of absorption arising from higher excited states. Further studies are necessary in order to understand the observed switch.

Conclusion

We here present a conceptionally new class of *push-pull* porphyrins i.e., 5,10-A₂B₂ porphyrins with the intramolecular dipole moment positioned along the β - β vector passing through two pyrrole rings. Starting from 5,10-A₂ precursors, numerous 5,10-A₂B₂ compounds with varied push-pull character can be obtained using organolithium, palladium catalyzed cross coupling or other functionalization reactions. These approaches allow the synthesis in moderate to good yields and open an avenue for further studies on these yet poorly explored compounds.

In the past push-pull molecules with a similar orientation of the intramolecular dipole moment, i.e. along the β - β vector passing through two pyrrole rings were obtained through the functionalization of the β position of the porphyrin ring, e.g., in TTP derivatives.^[31] In the well studied 5,15-A₂BC compounds the push-pull character is tuned through the B and C substituents. Here, the dipole moment is aligned along the 5,15 meso-meso axis. Nevertheless, access to these 5,15-A₂BC compounds is more

complex in comparison to 5,10-A₂B₂ as it involves firstly an appropriate monofunctionalization of the 5,15-A₂ precursor and secondly further additional steps for the incorporation of the third functional group C. In case of 5,10-A₂B₂ compounds only two substituent are needed to introduce dipole moment, which consequently involves less steps and omits the troublesome monofunctionalization.

The 5,10-A₂B₂ compounds are candidates for many potential applications. Inequivalent substituents can be used to bring in about an amphiphilic character of the molecule which turns those compounds into drug candidates for PDT applications. The push-pull character can be tuned via A and B substituents and makes 5,10-A₂B₂ porphyrins an interesting group of compounds for ET studies and optics, especially NLO. Our preliminary NLO studies indeed revealed that those compounds exhibit interesting properties in this area. 5,10-A₂B₂ type systems can also be used as crystal engineering synthons to access new supramolecular structures. For example, Maeda *et al.* reported recently on L-shaped porphyrin trimers which assemblies exhibited efficient ET. Those compounds were prepared via functionalization of 5,10-A₂B₂ dibrominated precursor with appropriate 5,15-A₂BC porphyrins.^[32] 5,10-A₂B₂ porphyrins may also serve as new ligand systems, as was shown recently for the related calixporphyrins.^[33]

Experimental Section

General methods: Instrumentation and standard techniques used were as described elsewhere.^[9] NLO studies were carried out with open aperture Z-scan technique.^[34] Experimental set-up and sample preparation details can be found elsewhere.^[13]

Starting materials: Tripyrrane,^[35] and various 5,10-di(alkyl/aryl)porphyrins^[10b] were prepared according to published procedures.

General procedure A – Condensation method for 5,10-A₂ porphyrins: A three-necked flask was charged with a solution of tripyrrane (1 equiv.), pyrrole (1equiv.), and the corresponding aldehyde (2.1 equiv.) in dry CH₂Cl₂ (1 L). The mixture was shielded from light and stirred under argon for 30 min. TFA (100 %) was added and stirring was continued at RT for 16 h. This was followed by oxidation with DDQ (4 eq.), stirring for 60 min, and addition of triethylamine (1 mL). Typically, the reaction mixture was filtered through a short silica-gel column, eluting with CH₂Cl₂, then the solution was concentrated *in vacuo* and the residue purified by column chromatography on silica gel.

General procedure B – Reactions with organolithium compounds: A 250 mL Schlenk flask was charged with the porphyrin (1 equiv.) in 50 mL THF under argon. The solution was cooled to -70 °C for alkyl lithium reagents or 0 °C for aryl lithium reagents. The respective LiR compound was added drop wise over 15 min and the color changed from red to brown-green. The cold bath was removed and the solution was stirred for 30 min at RT. A mixture of 1 mL water in 5 mL THF was added and the color changed to green. The mixture was stirred for 15 min and, unless noted otherwise, oxidized with DDQ (5.5 equiv.) followed by stirring for 30 min. This was accompanied by a color change to red. The solution was filtered through silica gel (CH₂Cl₂) and the solvent removed under reduced pressure. For *in situ* preparation of RLi reagents *n*-butyllithium (2 equiv.) was slowly added (ca. 1 h) under an argon atmosphere to a 100 mL Schlenk flask charged with a solution of the bromine (1 equiv.) in 10 mL dry diethyl ether at -78 °C. The reaction mixture was then warmed up to -40 °C and THF was added drop wise until the aryllithium was formed as a bright pink suspension. To this vigorously stirred mixture was added rapidly a solution of the porphyrin (0.9 equiv.) in 80 mL dry THF under an argon atmosphere. The color of the reaction mixture changed from purple to brown within 30 min, subsequently 5 mL water in 5 mL dry THF was added for hydrolysis. After stirring the mixture for 10 min, a solution of 10-15 equiv. of DDQ in CH₂Cl₂ was added and the reaction mixture was stirred for another 60 min at RT.

General procedure C – Bromination of 5,10-A₂ porphyrins: A 100 mL round bottom flask was charged with the porphyrin (1 equiv.) dissolved in chloroform (50 mL) and pyridine (0.2 mL) and was cooled to 0 °C. Next *N*-bromosuccinimide (NBS) (2.5 equiv.) was added and the solution stirred for 10 min. The color changed from red to brown-red. The reaction was then quenched via addition of 4 mL acetone. The solvent was removed under reduced pressure, the residue dissolved in CH₂Cl₂ and filtered through silica gel (CH₂Cl₂). The solvent was removed under reduced pressure and the residue was washed with MeOH and dried.

General procedure D – Insertion of zinc(II): The free base porphyrin (1 equiv.) and zinc oxide (2–3 equiv.) were dissolved in CH_2Cl_2 (50 mL) and treated with three to five drops of TFA. After stirring for 10 min the color changed from green to purple-red. The reaction was followed by TLC control and the solution filtered through silica gel (CH_2Cl_2) and the solvent removed under reduced pressure.

General procedure E – Heck reactions: A 50 mL three-necked flask equipped with condenser was charged with the zinc(II)porphyrin (10 equiv.), sodium acetate (56 equiv.), palladium acetate (1 equiv.) and triphenylphosphine (4 equiv.) in 15 mL dry DMF under argon. Next, the respective olefin was added and the solution heated at 120 °C for 24 h. The reaction was followed by TLC control. After completion of the reaction the solution was cooled to RT mixed with CH_2Cl_2 , washed with water (50 mL) and dried over Na_2SO_4 . The solvent was removed under reduced pressure and the residue was dissolved in CH_2Cl_2 . The solution was filtered through alumina (Brockmann grade III) (eluent: CH_2Cl_2 , 1 % triethylamine) and the solvent was removed under reduced pressure. Final purification involved recrystallization from $\text{CH}_2\text{Cl}_2/n$ -hexane.

General procedure F – Suzuki reactions: A Schlenk flask was charged with K_2PO_4 (20 equiv.) and anhydrous THF (60 mL) under an argon atmosphere, then porphyrin (1 equiv.), arylboronic acid or arylboronic ester (10 equiv.) and $\text{Pd}(\text{PPh}_3)_4$ (0.1 equiv.) were added. The reaction was heated at reflux for 7–10 h (TLC control) and protected from light. After completion, the solvent was evaporated and the residue was dissolved in CH_2Cl_2 . The mixture was washed with saturated NaHCO_3 , water, and brine and then dried over Na_2SO_4 . The organic solvent was evaporated and the crude product was purified by flash chromatography followed by recrystallization.

General procedure G – Insertion of nickel(II): Porphyrin (1 equiv.) and $\text{Ni}(\text{acac})_2$ (1.1 equiv.) were dissolved in toluene (20 mL) and heated to reflux. The progress of the reaction was monitored by TLC. Upon completion, the solvent was removed *in vacuo* and the product was isolated after passage through a plug of silica gel using CH_2Cl_2 as the eluent.

5,10-Bis(2,6-difluorophenyl)porphyrin 16: Following the general procedure A, tripyrrane (0.500 g, 2.22 mmol), pyrrole (0.154 mL, 2.22 mmol) and 2,6-difluorobenzaldehyde (0.788 g, 5.55 mmol) were added to a dry CH_2Cl_2 solution (1 L). After stirring for 30 min, TFA (0.15 mL) was added and stirring was continued for 16 h. DDQ (2.015 g, 8.88 mmol) was added and the crude product was purified by column chromatography ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:2, v/v) to give 50 mg (0.093 mmol, 5 %) of a purple powder after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. R_f = 0.3 ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v); m.p. >300 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = -3.42 (s, 2H, H_f), 7.49 (t, 4H, 3J = 8.2 Hz, Ar- H), 7.91 (m, 2H, Ar- H), 9.08 (d, 4H, 3J = 4.7 Hz, H_b), 9.53 (d, 4H, 3J = 4.7 Hz, H_b), 10.41 ppm (s, 2H, H_{meso}); compound too insoluble for ^{13}C NMR; UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 418 (5.07), 516 (3.68), 550 (3.29), 593 (3.14), 649 nm (2.99); HRMS: m/z calcd for $[\text{C}_{32}\text{H}_{19}\text{N}_4\text{F}_4] [\text{M}+\text{H}]^+$: 535.1546, found: 535.1536.

[5,10-Di(*n*-hexyl)-15,20-diphenylporphyrinato]nickel(II) 17: (5,10-Diphenylporphyrinato)nickel(II) **11** (37 mg, 0.07 mmol) was reacted with a 2.5 M solution of *n*-hexyllithium in *n*-hexane (0.17 mL, 0.43 mmol, 6 equiv.) following procedure B. Purification on silica gel ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v) and recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ gave purple crystals (28 mg, 0.04 mmol, 58 %). R_f = 0.69 ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v); m.p. 167 °C; ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): δ = 0.90 (t, 6H, 3J = 2J = 7.3 Hz, $\text{C}_3\text{H}_7(\text{CH}_2)_3$), 1.35 (m, 8H, $\text{C}_3\text{H}_7(\text{CH}_2)_2\text{CH}_3$), 1.59 (m, 4H, $\text{C}_2\text{H}_4\text{CH}_2\text{C}_3\text{H}_7$), 2.29 (m, 4H, $\text{CH}_2\text{CH}_2\text{C}_4\text{H}_9$), 4.54 (t, 4H, 3J = 7.8 Hz, $\text{CH}_2\text{C}_5\text{H}_{11}$), 7.66 (m, 6H, Ar- H_m , Ar- H_p), 7.97 (m, 4H, Ar- H_o), 8.63 (br s, 2H, $H_{b(7,8)}$), 8.73 (AB, 2H, $^3J_{H12,H13} = ^3J_{H13,H17} = ^3J_{H12,H17} = 5.1$ Hz, $H_{b(2,13)}$), 9.24 (AB, 2H, $^3J_{H12,H13} = ^3J_{H13,H17} = 5.1$ Hz, $H_{b(12,13)}$), 9.34 ppm (br s, 2H, $H_{b(17,18)}$); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, TMS): δ = 14.10, 22.65, 30.05, 31.77, 34.20, 37.41, 117.58, 118.20, 126.83, 127.57, 129.51, 129.81, 131.94, 132.22, 133.62, 140.92, 141.66, 141.74, 141.97, 142.03 ppm; UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 416 (5.21), 532 nm (4.06); MS (70 eV, EI, 350 °C): m/z (%) = 686 (100%), $[\text{M}]^+$, 615 (89%), $[\text{M} - \text{C}_3\text{H}_7]^+$, 544 (50%), $[\text{M} - 2\text{C}_3\text{H}_7]^+$; HRMS: m/z calcd for $[\text{C}_{44}\text{H}_{54}\text{N}_4\text{Ni}] [\text{M}+\text{H}]^+$: 687.2998, found: 687.2936.

5-(*n*-Hexyl)-10,15-bis(4-methylphenyl)porphyrin 18: 5,10-Bis(4-methylphenyl)porphyrin **12** (32 mg, 0.07 mmol) was reacted with a 2.5 M solution of *n*-hexyllithium in *n*-hexane (0.22 mL, 0.39 mmol, 6 equiv.) following procedure B. Purification on silica gel ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v) and recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ gave purple crystals (12 mg, 0.02 mmol, 18 %). R_f = 0.49 ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v); m.p. 168 °C; ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): δ = -2.93 (br s, 2H, NH), 0.92 (t, 3H, 3J = 7.2 Hz, $\text{C}_3\text{H}_7(\text{CH}_2)_3$), 1.52 (m, 4H, $\text{C}_3\text{H}_7(\text{CH}_2)_2\text{CH}_3$), 1.81 (m, 2H, $\text{C}_2\text{H}_4\text{CH}_2\text{C}_3\text{H}_7$), 2.55 (m, 2H, $\text{CH}_2\text{CH}_2\text{C}_4\text{H}_9$), 2.70 (s, 6H, Ar- CH_3), 5.01 (t, 2H, 3J = 8.2 Hz, $\text{CH}_2\text{C}_5\text{H}_{11}$), 7.54 (m, 4H, Ar- H_m), 8.07 (m, 4H, Ar- H_o), 8.81, 8.85 (AB, 2H, $^3J_{H12,H13} = ^3J_{H13,H17} = 4.7$ Hz, $H_{b(12,13)}$), 8.93 (AB, 1H, $^3J_{H18,H7} = 4.9$ Hz, $H_{b(8)}$), 8.97 (AB, 1H, $^3J_{H17,H18} = 4.7$ Hz, $H_{b(7)}$), 9.27 (AB, 1H, $^3J_{H18,H17} = 4.7$ Hz, $H_{b(18)}$), 9.37 (AB, 1H, $^3J_{H12,H13} = 4.7$ Hz, $H_{b(2)}$), 9.47 (AB, 1H, $^3J_{H17,H7} = 4.9$ Hz, $H_{b(7)}$), 9.58 (AB, 1H, $^3J_{H13,H12} = 4.7$ Hz, $H_{b(3)}$), 10.10 ppm (s, 1H, 20- H_{meso}); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, TMS): δ = 14.12, 21.53, 22.73, 29.70, 30.28, 31.93, 38.78, 104.11, 118.95, 120.02, 120.11, 127.19, 127.58, ~131, 134.38, 134.60, 137.26, 138.81 ppm; UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 413 (4.99), 510 (4.19), 545 (3.79), 585 (3.71), 641 nm (3.56); MS (70 eV, EI): m/z (%) = 574 (100%), $[\text{M}]^+$, 503 (63%), $[\text{M} - \text{C}_3\text{H}_7]^+$, 413 (89%), $[\text{M} - \text{C}_3\text{H}_7 - \text{C}_3\text{H}_7 + \text{H}]^+$, 287 (4%), $[\text{M}]^+$, 252 (2%), $[\text{M} - \text{C}_3\text{H}_7]^+$; HRMS: m/z calcd for $[\text{C}_{36}\text{H}_{38}\text{N}_4] [\text{M}]^+$: 574.3096, found: 574.3094.

5,10-(*n*-Dihexyl)-15,20-bis(4-methylphenyl)porphyrin 19: 5,10-Bis(4-methylphenyl)porphyrin **12** (79 mg, 0.16 mmol) was reacted with a 2.5 M solution of *n*-hexyllithium in *n*-hexane (0.65 mL, 1.61 mmol, 10 equiv.) following procedure B.

Purification on silica gel ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v) and recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ gave purple crystals (23 mg, 0.03 mmol, 22 %). R_f = 0.55 ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v); m.p. 172 °C; ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): δ = -2.64 (br s, 2H, NH), 0.99 (t, 6H, 3J = 2J = 7.2 Hz, $\text{C}_3\text{H}_7(\text{CH}_2)_3$), 1.44 (m, 4H, $\text{C}_2\text{H}_4\text{CH}_2\text{C}_3\text{H}_7$), 1.54 (m, 4H, $\text{C}_3\text{H}_7(\text{CH}_2)_2\text{CH}_3$), 1.83 (m, 4H, $\text{C}_2\text{H}_4\text{CH}_2\text{C}_3\text{H}_7$), 2.56 (m, 4H, $\text{CH}_2\text{CH}_2\text{C}_4\text{H}_9$), 2.73 (s, 6H, Ar- CH_3), 4.97 (t, 4H, 3J = 2J = 7.9 Hz, $\text{CH}_2\text{C}_5\text{H}_{11}$), 7.56 (AB, 4H, 3J = 2J = 3J = 7.9 Hz, Ar- H_m), 8.10 (AB, 4H, 3J = 2J = 3J = 7.9 Hz, Ar- H_o), 8.81 (s, 2H, $H_{b(17,18)}$), 8.92 (AB, 2H, 3J = 4.9 Hz, $H_{b(2,13)}$), 9.44 (AB, 2H, $^3J_{H13,H12} = ^3J_{H12,H13} = 4.9$ Hz, $H_{b(3,12)}$), 9.53 ppm (s, 2H, $H_{b(7,8)}$); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, TMS): δ = 14.16, 21.50, 22.75, 30.28, 31.93, 35.65, 38.81, 118.81, 119.81, 127.38, ~128, ~131, 134.42, 139.47 ppm; UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 419 (4.92), 517 (3.82), 554 (3.61), 595 (3.34), 651 nm (3.45); MS (70 eV, EI): m/z (%) = 658 (16%), $[\text{M}]^+$, 587 (67%), $[\text{M} - \text{C}_3\text{H}_7]^+$, 516 (27%), $[\text{M} - 2\text{C}_3\text{H}_7]^+$, 425 (4%), $[\text{M} - 2\text{C}_3\text{H}_7 - \text{C}_3\text{H}_7]^+$, 334 (4%), $[\text{M} - 2\text{C}_3\text{H}_7 - 2\text{C}_3\text{H}_7]^+$, 329 (37%), $[\text{M}]^+$, 294 (18%), $[\text{M} - \text{C}_3\text{H}_7]^+$, 259 (43%), $[\text{M} - 2\text{C}_3\text{H}_7]^+$; HRMS: m/z calcd for $[\text{C}_{46}\text{H}_{58}\text{N}_4] [\text{M}]^+$: 658.4035, found: 658.4014.

5,10-Di(*n*-hexyl)-15,20-di(*iso*-butyl)porphyrin 20: 5,10-Di(*iso*-butyl)porphyrin **13** (30 mg, 0.07 mmol) was reacted with a 2.5 M solution of *n*-hexyllithium in *n*-hexane (0.29 mL, 0.71 mmol, 10 equiv.) following procedure B. Purification on silica gel (*n*-hexane/ethyl acetate = 5:1, v/v) and recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ gave purple crystals (11 mg, 0.02 mmol, 26 %). R_f = 0.67 ($\text{CH}_2\text{Cl}_2/n$ -hexane = 2:3, v/v); m.p. 97 °C; ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): δ = -2.65 (br s, 2H, NH), 0.95 (t, 6H, 3J = 2J = 7.2 Hz, $\text{C}_3\text{H}_7(\text{CH}_2)_3$), 1.19 (d, 12H, 3J = 2J = 3J = 6.7 Hz, $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 1.47 (m, 8H, $\text{C}_3\text{H}_7(\text{CH}_2)_2\text{CH}_3$), 1.82 (m, 4H, $\text{C}_2\text{H}_4\text{CH}_2\text{C}_3\text{H}_7$), 2.52 (m, 4H, $\text{CH}_2\text{CH}_2\text{C}_4\text{H}_9$), 2.75 (m, 2H, $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 4.82 (d, 4H, 3J = 2J = 7.3 Hz, $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 4.93 (t, 4H, 3J = 2J = 8.0 Hz, $\text{CH}_2\text{C}_5\text{H}_{11}$), 9.46 ppm (m, 8H, H_b); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, TMS): δ = 14.16, 22.77, 23.33, 30.29, 31.94, 35.58, 36.68, 38.66, 43.76, 117.17, 118.51, ~129 ppm; UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 418 (4.97), 520 (4.12), 554 (3.99), 599 (3.74), 659 nm (3.83); MS (70 eV, EI): m/z (%) = 590 (100%), $[\text{M}]^+$, 547 (69%), $[\text{M} - \text{C}_3\text{H}_7]^+$, 519 (11%), $[\text{M} - \text{C}_3\text{H}_7]^+$, 295 (4%), $[\text{M}]^+$; HRMS: m/z calcd for $[\text{C}_{40}\text{H}_{54}\text{N}_4] [\text{M}]^+$: 590.4348, found: 590.4346.

5,10-Di(*n*-butyl)-15,20-bis(4-methylphenyl)porphyrin 21: Following procedure B and the details given for **27** reaction of *n*-butyllithium (4 mL of 2.5 M solution in *n*-hexane, 10 mmol), a solution of *p*-bromobenzonitrile (0.72 g, 4.0 mmol) in 15 mL of dry diethyl ether at -100 °C and 5,10-bis(4-methylphenyl)porphyrin **12** (50 mg, 0.110 mmol) gave 24 mg (0.034 mmol, 31 %), of the title compound. m.p. >300 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = -2.67 (s, 2H, NH), 1.17 (t, 6H, 3J = 7., 7.6 Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.34 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.57 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.76 (s, 6H, Ar- CH_3), 5.04 (t, 4H, 3J = 7.6, 8.2 Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 7.57 (d, 4H, 3J = 7.6 Hz, Ar- H), 8.08 (d, 4H, 3J = 7.6 Hz, Ar- H), 8.78 (s, 2H, H_b), 8.91 (d, 2H, 3J = 4.7 Hz, H_b), 9.46 (d, 2H, 3J = 4.7 Hz, H_b), 9.6 ppm (s, 2H, H_b); ^{13}C NMR (63 MHz, CDCl_3 , 25 °C, TMS): δ = 14.06 21.36, 23.54, 29.55, 35.23, 40.77, 118.66, 119.63, 127.19, 127.27, 134.25 137.02, 139.28 ppm; UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 418 (4.92), 518 (3.56), 555 (3.36), 637 (3.05), 647 nm (3.02); HRMS: m/z calcd for $[\text{C}_{42}\text{H}_{48}\text{N}_4] [\text{M}+\text{H}]^+$: 603.3488, found: 604.3472.

5-(*n*-Butyl)-10,15-diphenylporphyrin 22: 5,10-Diphenylporphyrin **14** (1 eq.) was placed in a Schlenk flask and dissolved in dry THF under argon. The solution was cooled down -78 °C. Then *n*-butyllithium (20 eq., 2.5 M solution in *n*-hexane) and *N,N,N',N'*-tetramethylethylenediamine (3.3 eq.) were added drop wise. The mixture was allowed to warm up to RT and was stirred for 30 additional min. The reaction was quenched with 3 mL water and stirred for another 15 min. DDQ (5.5 eq.) was added. Stirring was continued for 15 min followed by filtration of the reaction mixture through 200 mL silica gel and washing with CH_2Cl_2 . The eluted porphyrin fractions were evaporated to dryness. The residue was dissolved in CH_2Cl_2 and purified *via* column chromatography on silica gel with $\text{CH}_2\text{Cl}_2/n$ -hexane (1:1, v/v, h = 44 cm, ϕ = 3 cm). The product was obtained as purple crystals after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (31.7 mg, 0.06 mmol, 26 %). R_f = 0.6 ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v); m.p. 155 °C; ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): δ = -2.90 (s, 2H, NH), 1.15 (t, 3H, 3J = 7.3 Hz, CH_2CH_3), 1.84 (m, 2H, CH_2CH_3), 2.56 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 5.04 (t, 2H, 3J = 7.9 Hz, $\text{CH}_2\text{CH}_2\text{CH}_3$), 7.78 (m, 6H, Ar- H), 8.23 (m, 4H, Ar- H), 8.84 (dd, 2H, 3J = 4.8 Hz, H_b), 8.94 (d, 1H, 3J = 4.8 Hz, H_b), 8.98 (d, 1H, 3J = 4.6 Hz, H_b), 9.30 (d, 1H, 3J = 4.7 Hz, H_b), 9.40 (d, 1H, 3J = 4.7 Hz, H_b), 9.50 (d, 1H, 3J = 4.9 Hz, H_b), 9.60 (d, 1H, 3J = 4.7 Hz, H_b), 10.14 ppm (s, 1H, H_{meso}); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, TMS): δ = 14.2, 23.7, 34.9, 40.9, 104.3, 118.8, 119.9, 120.2, 126.5, 126.8, 127.6, 128.4, 130.4, 131.0, 131.3, 131.6, 131.8, 134.4, 134.7, 141.7, 142.8 ppm; UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 412 (5.33), 509 (4.23), 543 (3.68), 585 (3.26), 641 nm (3.06); MS (EI, 70 eV): m/z (%) = 518 (98 %), $[\text{M}]^+$, 475 (100 %), $[\text{M} - \text{C}_3\text{H}_7]^+$, 259 (4 %), $[\text{M}]^+$; HRMS (ES+): m/z calcd for $[\text{C}_{36}\text{H}_{31}\text{N}_4] [\text{M}+\text{H}]^+$: 519.2549, found 519.2579.

5,10-Bis(4-(*N,N*-dimethylamino)phenyl)-15,20-bis(4-methylphenyl)porphyrin 23: 5,10-Bis(4-methylphenyl)porphyrin **12** (63 mg, 0.13 mmol) was reacted with 4-(*N,N*-dimethylamino)phenyllithium following procedure B. Purification on silica gel (CH_2Cl_2) and recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ gave purple crystals (67 mg, 0.09 mmol, 71 %). R_f = 0.67 ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ = 95:5, v/v); m.p. >300 °C; ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): δ = -2.68 (br s, 2H, NH), 2.69 (s, 6H, Ar- CH_3), 3.22 (s, 12H, $\text{N}(\text{CH}_3)_2$), 7.09 (AB, 4H, 3J = 2J = 3J = 8.8 Hz, 5,10-Ar- H_m), 7.53 (AB, 4H, 3J = 2J = 3J = 7.7 Hz, 15,20-Ar- H_m), 8.07 (AB, 4H, 3J = 2J = 3J = 8.8 Hz, 5,10-Ar- H_o), 8.09 (AB, 4H, 3J = 2J = 3J = 7.7 Hz, 15,20-Ar- H_o), 8.81 ppm (m, 8H, H_b); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, TMS): δ = 21.52, 40.74, 110.67, 119.46, 120.89, 127.35, 130.46, 134.51, 135.74, 137.15, 139.49, 149.90 ppm; UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 425 (4.86), 522 (4.13), 565 (4.15), 598 (sh), 656 nm (3.90); MS (TOF, MS, ES+, 70 eV): m/z (%) = 728 (100 %), $[\text{M}]^+$; HRMS: m/z calcd for $[\text{C}_{50}\text{H}_{46}\text{N}_6] [\text{M}]^+$: 728.3627, found: 728.3624.

5,10-Bis(4-hydroxyphenyl)-15,20-bis(4-methylphenyl)porphyrin 24: 5,10-Bis(4-methylphenyl)porphyrin **12** (52 mg, 0.11 mmol) was reacted with 4-hydroxyphenyllithium following procedure B. Purification on silica gel (CH₂Cl₂) and recrystallization from CH₂Cl₂/MeOH gave purple crystals (41 mg, 0.06 mmol, 57 %). *R*_f = 0.36 (CH₂Cl₂), m.p. 102 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 2.67 (s, 6H, Ar-CH₃), 7.01 (AB, 4H, ³J = ³J = ³J = 8.2 Hz, 5,10-Ar-H_m), 7.52 (AB, 4H, ³J = ³J = ³J = 7.6 Hz, 15,20-Ar-H_m), 7.98 (AB, 4H, ³J = ³J = ³J = 8.2 Hz, 5,10-Ar-H_o), 8.07 (AB, 4H, ³J = ³J = ³J = 7.6 Hz, 15,20-Ar-H_o), 8.84 ppm (m, 8H, H_p); UV/VIS (CH₂Cl₂): λ_{max} (lg ε) = 420 (4.88), 517 (3.83), 553 (3.64), 592 (3.42), 648 nm (3.43); MS (TOF, MS, ES⁺, 70 eV): *m/z* (%): 674 (27 %, [M]⁺), 337 (2 %, [M]²⁺); HRMS: *m/z* calcd for [C₂₈H₂₄N₄O₂] [M]⁺: 674.2682, found: 674.2645.

5,10-Bis[4-(*N,N*-dimethylamino)phenyl]-15,20-bis(3-methoxyphenyl)porphyrin 25: 5,10-Bis(3-methoxyphenyl)porphyrin **15** (79 mg, 0.16 mmol) was reacted with 4-(*N,N*-dimethylamino)phenyllithium following procedure B. Purification on silica gel (CH₂Cl₂/MeOH = 98 : 2, v/v) gave two fractions. The first contained the monarylated species **26** and the second the title compound. Recrystallization from CH₂Cl₂/*n*-hexane gave purple crystals (28 mg, 0.04 mmol, 32 %). *R*_f = 0.67 (CH₂Cl₂/MeOH = 95:5, v/v); m.p. 236 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = -2.62 (br s, 2H, NH), 3.22 (s, 12H, N(CH₃)₂), 3.99 (s, 6H, OCH₃), 7.10 (AB, 4H, ³J = ³J = ³J = 8.6 Hz, 5,10-Ar-H_m), 7.33 (m, 2H, 15,20-Ar-H_p), 7.64 (m, 2H, 15,20-Ar-H_m), 7.84 (m, 4H, 15,20-Ar-H_o), 8.11 (AB, 4H, ³J = ³J = ³J = 8.6 Hz, 5,10-Ar-H_o), 8.88 (m, 4H, H_{p2,7,8,13}), 8.97 ppm (m, 4H, H_{p3,12,17,18}); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 40.69, 55.47, 110.68, 113.48, 119.02, 120.45, 127.42, 127.69, 130.38, 135.73, 143.77, 149.95, 157.95 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ε) = 425 (5.00), 522 (4.17), 565 (4.16), 596 (sh), 656 nm (3.90); MS (EI, 70 eV): *m/z* (%): 760 (7 %, [M]⁺), 380 (100 %, [M]²⁺); HRMS: *m/z* calcd for [C₃₀H₃₄N₄O₂] [M]⁺: 760.3526, found: 760.3500.

5-[4-(*N,N*-Dimethylamino)phenyl]-10,15-bis(3-methoxyphenyl)porphyrin 26: Obtained from the synthesis of **25** as purple crystals (5 mg, 0.01 mmol, 5 %). *R*_f = 0.4 (CH₂Cl₂/MeOH = 95:5, v/v); m.p. 98 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = -2.97 (br s, 2H, NH), 3.23 (s, 6H, N(CH₃)₂), 3.99 (s, 6H, OCH₃), 7.09 (AB, 2H, ³J = ³J = 8.8 Hz, 5-Ar-H_p), 7.33 (m, 2H, 10,15-Ar-H_p), 7.65 (m, 2H, 10,15-Ar-H_m), 7.82 (m, 2H, 10,15-Ar-H_o), 8.06 (AB, 2H, ³J = ³J = 8.8 Hz, 5-Ar-H_o), 8.91, 8.97 (AB, 4H, ³J_{H7,H8} = ³J_{H8,H7} = ³J_{H12,H13} = ³J_{H13,H12} = 4.7 Hz, H_{p7,8,12,13}), 9.03 (AB, 2H, ³J_{H3,H2} = ³J_{H17,H18} = 4.7 Hz, H_{p3,17}), 9.29 (AB, 2H, ³J_{H2,H3} = ³J_{H18,H17} = 4.7 Hz, H_{p2,18}), 10.15 ppm (s, 1H, H_{meso}); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 40.73, 55.52, 104.27, 110.60, 113.52, 119.14, 120.59, 127.56, 127.79, 135.68, 143.28, 149.27, 158.08 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ε) = 413 (4.66), 512 (4.27), 550 (4.06), 585 (3.99), 642 nm (3.90); MS (EI, 70 eV): *m/z* (%): 641 (48 %, [M]⁺), 321 (100 %, [M]²⁺); HRMS: *m/z* calcd for [C₂₈H₃₀N₄O₂] [M]⁺: 641.2791, found: 641.2771.

5,10-Bis(4-ethynylphenyl)-15,20-bis(4-methylphenyl)porphyrin 27: Following procedure B, *n*-butyllithium (4 mL of 2.5M solution in *n*-hexane, 10 mmol) was slowly added (ca. 1h) under an argon atmosphere to a 100 mL Schlenk flask charged with a solution of *p*-bromophenylethyne (0.91 g, 5.0 mmol) in 15 mL of dry diethyl ether at -70 °C. The reaction mixture was then warmed to -40 °C and THF was added drop wise until the aryllithium was formed as a white/pink suspension. To this vigorously stirred mixture was added rapidly a solution of 5,10-bis(4-methylphenyl)porphyrin **12** (56 mg, 0.125 mmol) in 50 mL of dry THF. The color of the mixture changed from deep purple to brown within 30 min, subsequently a mixture of 5 mL water in 5 mL of THF was added for hydrolysis. After stirring of the mixture for 20 min, a solution of DDQ (283 mg, 1.25 mmol) in CH₂Cl₂ was added and the reaction mixture was stirred for another 60 min at RT. The crude product was subjected to column chromatography using CH₂Cl₂/*n*-hexane (1:1, v/v) to give 24 mg (0.034 mmol, 31 %), of a purple solid after recrystallization from CH₂Cl₂/MeOH. *R*_f = 0.73 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.78 (s, 2H, NH), 2.73 (s, 6H, Ar-CH₃), 3.34 (s, 2H, -C≡CH), 7.58 (d, 4H, ³J = 7.6 Hz, Ar-H), 7.92 (d, 4H, ³J = 8.2 Hz, Ar-H), 8.11 (d, 4H, ³J = 7.6 Hz, Ar-H), 8.20 (d, 4H, ³J = 7.6 Hz, Ar-H), 8.84 (m, 4H, H_p), 8.90 ppm (m, 4H, H_p); ¹³C NMR (63 MHz, CDCl₃, 25 °C, TMS): δ = 21.09, 77.84, 83.22, 118.42, 120.29, 121.14, 127.01, 130.17, 134.06, 134.19, 137.03, 138.61, 142.37; UV/VIS (DMF): λ_{max} (lg ε) = 420 (4.92), 516 (3.61), 551 (3.38), 592 (3.20), 655 nm (3.19); HRMS: *m/z* calcd for [C₃₀H₂₂N₄] [M+H]⁺: 691.2862, found: 691.2858.

5,10-Bis(4-ethynylphenyl)-15,20-bis(2,6-difluorophenyl)porphyrin 28: Following procedure B and the details given for **27** reaction of *p*-bromophenylethyne (0.55 g, 3.0 mmol) and 5,10-bis(2,6-difluorophenyl)porphyrin **16** (40 mg, 0.075 mmol) gave 14 mg (0.019 mmol, 25 %) of the title compound. *R*_f = 0.6 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.71 (s, 2H, NH), 3.51 (s, 2H, -C≡CH), 7.43 (t, 4H, ³J = 8.2 Hz, Ar-H), 7.81 (m, 2H, Ar-H), 7.96 (t, 4H, ³J = 8.2 Hz, Ar-H), 8.23 (t, 4H, ³J = 7.6 Hz, Ar-H), 8.92 (m, 4H, H_p), 9.02 ppm (m, 4H, H_p); UV/VIS (DMF): λ_{max} (lg ε) = 414 (5.09), 508 (3.83), 543 (3.18), 585 (3.30), 637 nm (2.89); HRMS: *m/z* calcd for [C₂₈H₁₂F₄N₄] [M+H]⁺: 735.2172, found: 735.2197.

5,10-Dibromo-15,20-bis(4-methylphenyl)porphyrin 29: 5,10-Bis(4-methylphenyl)porphyrin **12** (93 mg, 0.19 mmol) was reacted with NBS (84 mg, 0.47 mmol) following procedure C to yield purple crystals (102 mg, 0.16 mmol, 83 %). *R*_f = 0.59 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. 285 °C (dec.); ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = -2.91 (br s, 2H, NH), 2.69 (s, 6H, Ar-CH₃), 7.54 (AB, 4H, ³J = ³J = ³J = 7.9 Hz, Ar-H_m), 8.01 (AB, 4H, ³J = ³J = ³J = 7.9 Hz, Ar-H_o), 8.74 (s, 2H, H_{p17,18}), 8.82 (AB, 2H, ³J = ³J = 4.8 Hz, H_{p2,13}), 9.52 (AB, 2H, ³J = ³J = 4.8 Hz, H_{p3,12}), 9.54 ppm (s, 2H, H_{p7,8}); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 21.53, 103.15, 121.75, 127.55, ~131, 134.40, 137.73, 138.57 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ε) = 423 (5.03), 523 (4.21), 558 (4.07), 602 (3.77), 659 nm (3.81); MS (TOF, MS, ES⁺, 70 eV): *m/z* (%): 646 (49 %, [M]⁺); HRMS: *m/z* calcd for [C₂₄H₂₂N₄Br₂] [M]⁺: 646.0368, found: 646.0347.

[5,10-Dibromo-15,20-bis(4-methylphenyl)porphyrinato]zinc(II) 30: 5,10-Dibromo-15,20-bis(4-methylphenyl)porphyrin **29** (83 mg, 0.13 mmol) was reacted following procedure D. Column chromatography on silica gel (CH₂Cl₂) gave a single product. Recrystallization from CH₂Cl₂/MeOH/H₂O gave purple crystals (66 mg, 0.09 mmol, 72 %). *R*_f = 0.42 (CH₂Cl₂/*n*-hexane = 2:1, v/v); m.p. >310 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 2.75 (s, 6H, Ar-CH₃), 7.61 (AB, 4H, ³J = ³J = ³J = 7.7 Hz, Ar-H_m), 8.06 (AB, 4H, ³J = ³J = ³J = 7.7 Hz, Ar-H_o), 8.76 (s, 2H, H_{p7,8}), 8.77 (AB, 2H, ³J = ³J = 4.7 Hz, H_{p2,13}), 8.86 (s, 2H, H_{p17,18}), 9.29 ppm (AB, 2H, ³J = ³J = 4.7 Hz, H_{p3,12}); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 21.32, 103.73, 122.44, 127.44, 132.29, 132.50, 132.65, 133.20, 134.52, 137.60, 139.29, 148.43, 149.07, 150.92, 151.08 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ε) = 424 (5.09), 557 (4.21), 597 nm (3.83); MS (TOF, MS, ES⁺, 70 eV): *m/z* (%): 708 (39 %, [M]⁺); HRMS: *m/z* calcd for [C₂₄H₂₂N₄Br₂Zn] [M]⁺: 707.9503, found: 707.9469.

[5,10-Dibromo-15,20-bis(4-methylphenyl)porphyrinato]nickel(II) 31: Following the general procedure G, 5,10-dibromo-15,20-bis(4-methylphenyl)porphyrin **29** (100 mg, 0.154 mmol) and Ni(acac)₂ (43.5 mg, 0.169 mmol) were dissolved in toluene (20 mL) and heated to reflux for 6 h to give 80 mg (0.113 mmol, 80 %) after recrystallization from CH₂Cl₂/MeOH. *R*_f = 0.7 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, 25 °C, CDCl₃): δ = 2.66 ppm (s, 6H, CH₃), 7.49 (d, 4H, ³J = 7.6 Hz, Ar-H), 7.82 (d, 4H, ³J = 8.2 Hz, Ar-H), 8.66 (s, 2H, H_p), 8.74 (d, 2H, ³J = 5.3 Hz, H_p), 9.39 (d, 2H, ³J = 5.3 Hz, H_p), 9.46 ppm (s, 2H, H_p); UV/VIS (CH₂Cl₂): λ_{max} (lg ε) = 421 (5.08), 538 (3.92), 589 nm (3.38); HRMS: *m/z* calcd for [C₂₄H₂₂N₄Br₂Ni] [M]⁺: 701.9565, found 701.9681; elemental analysis calcd (%) for C₂₄H₂₂N₄Br₂Ni (705.07): C 57.91, H 3.15, N 7.95, found: C 57.65, H 3.40, N 8.01.

{(all-*E*)-5,10-Bis[4-(2-butoxycarbonylethenyl)-15,20-bis(4-methylphenyl)porphyrinato]zinc(II) 32: [5,10-Dibromo-15,20-bis(4-methylphenyl)porphyrinato]zinc(II) **30** (77.7 mg, 0.11 mmol) was reacted with butyl acrylate (1.00 mL, 7.01 mmol) following procedure E to yield purple crystals (60 mg, 0.07 mmol, 64 %). *R*_f = 0.34 (CH₂Cl₂, 1 % triethylamine, v/v, alumina); m.p. 176 °C; ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS): δ = 1.08 (t, 6H, ³J = ³J = 7.4 Hz, C₂H₅CH₂), 1.60 (m, 4H, C₂H₅CH₂CH₂), 1.88 (m, 4H, CH₂CH₂C₂H₅), 2.70 (s, 6H, Ar-CH₃), 4.43 (t, 4H, ³J = ³J = 6.8 Hz, CH₂C₃H₇), 6.73 (d, 2H, ³J = ³J = 15.7 Hz, CH=CH-CO), 7.54 (d, 4H, ³J = ³J = ³J = 7.5 Hz, Ar-H_m), 7.99 (d, 4H, ³J = ³J = ³J = 7.5 Hz, Ar-H_o), 8.70 (s, 2H, H_{p17,18}), 8.84 (AB, 2H, ³J = ³J = 4.7 Hz, H_{p2,13}), 9.39 (AB, 2H, ³J = ³J = 4.7 Hz, H_{p3,12}), 9.52 (s, 2H, H_{p7,8}), 10.23 ppm (d, 2H, ³J = ³J = 15.7 Hz, CH=CH-CO); ¹³C NMR (126 MHz, CDCl₃, 25 °C, TMS): δ = 13.74, 19.46, 21.26, 31.06, 64.66, 112.98, 123.51, 127.19, 128.77, 129.80, 130.09, 131.80, 132.78, 134.44, 137.21, 140.03, 146.86, 148.97, 149.41, 149.67, 150.31, 166.38 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ε) = 438 (5.14), 572 (4.00), 616 nm (3.92); MS (TOF, MS, ES⁺, 70 eV): *m/z* (%): 805 (100 %, [M+H]⁺); HRMS: *m/z* calcd for [C₃₈H₄₈N₄O₄Zn] [M+H]⁺: 805.2732, found: 805.2706.

{(all-*E*)-5,10-Bis(4-methylphenyl)-15,20-bis[4-(3-oxobut-1-enyl)porphyrinato]zinc(II) 33: [5,10-Dibromo-15,20-bis(4-methylphenyl)porphyrinato]zinc(II) **30** (77.7 mg, 0.11 mmol) was reacted with methyl vinyl ketone (0.57 mL, 7.02 mmol) following procedure E to yield purple crystals (35 mg, 0.05 mmol, 50 %). *R*_f = 0.5 (CH₂Cl₂, 5 % MeOH, v/v); m.p. 215 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 2.50 (s, 6H, CO-CH₃), 2.71 (s, 6H, Ar-CH₃), 6.58 (d, 2H, ³J = ³J = 15.7 Hz, CH=CH-CO), 7.55 (AB, 4H, ³J = ³J = ³J = 7.5 Hz, Ar-H_m), 8.00 (d, 4H, ³J = ³J = ³J = 7.5 Hz, Ar-H_o), 8.80 (s, 2H, H_{p17,18}), 8.89 (AB, 2H, ³J = ³J = 4.7 Hz, H_{p2,13}), 9.22 (s, 2H, H_{p7,8}), 9.28 (AB, 2H, ³J = ³J = 4.7 Hz, H_{p3,12}), 9.80 ppm (d, 2H, ³J = ³J = 15.7 Hz, CH=CH-CO); ¹³C NMR (63 MHz, CDCl₃, 25 °C, TMS): δ = 20.78, 27.29, 112.81, 123.21, 126.81, 128.53, 129.33, 131.04, 131.61, 132.49, 133.88, 136.96, 139.20, 144.93, 148.25, 148.83, 149.32, 149.98, 196.33 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ε) = 443 (4.44), 577 (4.18), 621 nm (4.14); MS (TOF, MS, ES⁺, 70 eV): *m/z* (%): 689 (100 %, [M+H]⁺); HRMS: *m/z* calcd for [C₂₆H₂₈N₄O₂Zn] [M]⁺: 689.1895, found: 689.1889.

{(all-*E*)-5,10-Bis(4-methylphenyl)-15,20-bis[2-(3-nitrophenyl)vinyl]porphyrinato]zinc(II) 34: Following the general procedure E, [5,10-Dibromo-15,20-bis(4-methylphenyl)porphyrinato]zinc(II) **30** (100 mg, 0.140 mmol), was dissolved in DMF (50 mL) under a nitrogen atmosphere. The 3-nitrostyrene (1.36 mL, 9.8 mmol), sodium acetate (65 mg, 0.784 mmol), palladium acetate (3.1 mg, 0.014 mmol) and triphenylphosphine (14.7 mg, 0.056 mmol) were added and the temperature was raised to 120 °C for 16 h (TLC control). The crude product was extracted with CH₂Cl₂ and washed with water. The product was purified by silica gel column chromatography using CH₂Cl₂/*n*-hexane (1:1, v/v) and gave 70 mg (0.082 mmol, 60 %) of the desired compound after recrystallization from CH₂Cl₂/MeOH. *R*_f = 0.12 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. > 300 °C; ¹H NMR (600 MHz, CD₂Cl₂, 25 °C, TMS): δ = 2.76 (s, 6H, CH₃), 6.58 (d, 2H, ³J = 16 Hz, vinyl), 7.49 (d, 4H, ³J = 7.7 Hz, Ar-H), 7.69 (t, 4H, ³J = 7.7 Hz, Ar-H), 7.91 (d, 4H, ³J = 7.7 Hz, Ar-H), 7.93 (d, 2H, ³J = 7.7 Hz, Ar-H), 8.29 (d, 2H, ³J = 8.2 Hz, Ar-H), 8.65 (s, 2H, H_p), 8.71 (d, 2H, ³J = 16 Hz, vinyl), 8.88 (s, 2H, H_p), 8.93 (d, 2H, ³J = 4.4 Hz, H_p), 9.23 ppm (d, 2H, ³J = 4.4 Hz, H_p); ¹³C NMR (125 MHz, CD₂Cl₂, 25 °C, TMS): δ = 138.67, 139.29, 146.90, 148.53, 148.92, 149.72, 150.38 ppm; UV/VIS (DMF): λ_{max} (lg ε) = 445 (5.12), 584 (3.98), 630 nm (3.80).

{(all-*E*)-5,10-Bis(4-methylphenyl)-15,20-[2-(3-nitrophenyl)vinyl]porphyrinato]nickel(II) 35: Following the general procedure E, [5,10-dibromo-15,20-bis(4-methylphenyl)porphyrinato]nickel(II) **31** (25 mg, 0.140 mmol), 3-nitrostyrene (0.35 mL, 2.48 mmol), sodium acetate (16 mg, 0.196 mmol), palladium acetate (0.8 mg, 0.003 mmol) and triphenylphosphine (3.7 mg, 0.014 mmol) in DMF (50 mL) gave 5 mg (0.006 mmol, 34 %) of a purple compound after recrystallization from CH₂Cl₂/MeOH. *R*_f = 0.47 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 2.66 (s, 6H, CH₃), 6.71 (d, 2H, ³J = 15.8 Hz, alkene-H), 7.49 (d, 4H,

$^3J = 7.6$ Hz, Ar-*H*), 7.64 (t, 2H, $^3J = 7.6$ Hz, Ar-*H*), 7.82 (d, 4H, $^3J = 7.6$ Hz, Ar-*H*), 7.93 (d, 2H, $^3J = 7.7$ Hz, Ar-*H*), 8.22 (d, 2H, $^3J = 7.6$ Hz, Ar-*H*), 8.59 (s, 2H, Ar-*H*), 8.61 (s, 2H, *H_β*), 8.73 (d, 2H, $^3J = 4.7$ Hz, *H_β*), 9.14 (d, 2H, $^3J = 4.7$ Hz, *H_β*), 9.18 (d, 2H, $^3J = 15.8$ Hz, alkene-*H*), 9.23 ppm (s, 2H, *H_β*); ^{13}C NMR (150 MHz, CDCl_3 , 25 °C, TMS): $\delta = 21.44, 29.34, 112.65, 120.79, 122.47, 127.78, 129.56, 129.84, 130.91, 132.22, 133.38, 137.61, 138.51, 139.87, 141.39, 142.31, 148.63$ ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 444 (4.87), 563 (3.83), 614 nm (3.75).

5,10-Dibromo-15,20-diphenylporphyrin 36: Following the general procedure C, 5,10-diphenylporphyrin **14** (90 mg, 0.19 mmol) and NBS (87 mg, 0.48 mmol) gave 84 mg (0.14 mmol, 70 %) of a purple solid after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. $R_f = 0.59$ ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 1:1$, v/v); m.p. > 300 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = -2.88$ (s, 2H, *NH*), 7.78 (m, 4H, Ar-*H*), 8.17 (m, 4H, Ar-*H*), 8.78 (m, 4H, *H_β*), 9.57 (m, 4H, *H_β*); UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 421 (4.98), 522 (3.57), 557 (3.33), 600 (2.89), 663 nm (2.86).

5,10-Dibromo-15,20-bis(3-methoxyphenyl)porphyrin 37: 5,10-Bis(3-methoxyphenyl)porphyrin **15** (77 mg, 0.15 mmol) was reacted with NBS (66 mg, 0.37 mmol) following procedure C to yield red crystals (74 mg, 0.11 mmol, 74 %). $R_f = 0.43$ ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 2:1$, v/v); m.p. 198 °C; ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): $\delta = -2.82$ (br s, 2H, *NH*), 3.97 (s, 6H, Ar-*OCCH₃*), 7.33 (m, 2H, Ar-*H_β*), 7.63 (m, 2H, Ar-*H_α*), 7.72 (m, 4H, Ar-*H_α*), 8.77 (s, 2H, *H_{β17,18}*), 8.87 (AB, 2H, $^3J = ^3J = 4.8$ Hz, *H_{β2,13}*), 9.56 (AB, 2H, $^3J = ^3J = 4.8$ Hz, *H_{β3,12}*), 9.63 ppm (s, 2H, s, *H_{β7,8}*); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, TMS): $\delta = 55.51, 103.44, 113.71, 120.50, 121.19, 127.52, 127.65, \sim 131, 142.76, 158.03$ ppm; UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 423 (5.01), 521 (3.44), 556 (3.12), 600 (3.56), 658 nm (3.55); MS (TOF, MS, ES⁺, 70 eV): m/z (%): 678 (52 %, [M]⁺); HRMS: m/z calcd for [$\text{C}_{34}\text{H}_{34}\text{N}_4\text{Br}_2\text{O}_2$] [M]⁺: 678.0266, found: 678.0243.

5,10-Dibromo-15,20-bis(2,6-difluorophenyl)porphyrin 38: Following the general procedure C, 5,10-bis(2,6-difluorophenyl)porphyrin **16** (200 mg, 0.374 mmol) and NBS (166 mg, 0.94 mmol) gave 150 mg (0.21 mmol, 58 %) of a purple solid after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$; $R_f = 0.48$ ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 1:1$, v/v). m.p. >300 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = -2.92$ (s, 2H, *NH*), 7.43 (t, 4H, $^3J = 7.8$ Hz, Ar-*H*), 7.83 (m, 2H, Ar-*H*), 8.83 (s, 4H, *H_β*), 9.36 (d, 2H, $^3J = 4.7$ Hz, *H_β*), 9.59 ppm (d, 2H, $^3J = 4.7$ Hz, *H_β*); UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 419 (4.94), 516 (3.73), 555 (3.18), 596 (3.11), 649 nm (2.49); HRMS (MS ES⁺): m/z calcd for [$\text{C}_{32}\text{H}_{16}\text{N}_4\text{Br}_2\text{F}_4$] [M]⁺: calcd 689.9678 found 689.9372.

5,10-Dibromo-15,20-di(*n*-pentyl)porphyrin 39: Following the general procedure C, 5,10-di(*n*-pentyl)porphyrin (90 mg, 0.2 mmol) and NBS (89 mg, 0.5 mmol) gave 73 mg (0.12 mmol, 60 %) of a purple solid after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. $R_f = 0.62$ ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 2:1$, v/v); m.p. >198 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = -3.15$ (s, 2H, *NH*), 1.00 (t, 6H, $^3J = 7.3$, 7.0 Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.56 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.77 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.44 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 4.77 (t, 4H, $^3J = 7.7$, 8 Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 9.20 (m, 4H, *H_β*), 9.49 ppm (m, 4H, *H_β*); ^{13}C NMR (150 MHz, 25 °C, CDCl_3): $\delta = 13.86, 22.71, 29.40, 32.40, 35.24, 38.25, 101.90, 121.45$ ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 422 (4.48), 524 (3.48), 559 (3.25), 605 (2.78), 664 nm (3.14); HRMS (MS ES⁺): m/z calcd for [$\text{C}_{30}\text{H}_{33}\text{N}_4\text{Br}_2$] [M+H]⁺: 607.1072, found: 607.1097.

5,10-Dibromo-15,20-di(*n*-hexyl)porphyrin 40: Following the general procedure C, 5,10-di(*n*-hexyl)porphyrin (70 mg, 0.14 mmol) and NBS (65 mg, 0.36 mmol) gave 47 mg (0.07 mmol, 50 %) of a purple solid after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. m.p. >300 °C; $R_f = 0.6$ ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 1:1$, v/v); ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = -2.81$ (s, 2H, *NH*), 0.97 (t, 6H, $^3J = 7.6, 7.01$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.42 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.45 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.82 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.49 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 4.87 (t, 4H, $^3J = 8.2, 7.6$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 9.52 (m, 4H, *H_β*), 9.62 ppm (m, 4H, *H_β*); ^{13}C NMR (150 MHz, CDCl_3 , 25 °C, TMS): $\delta = 14.15, 22.73, 30.25, 31.86, 35.66, 38.83, 102.06, 121.72$ ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 420 (4.88), 522 (3.63), 558 (3.51), 603 (3.26), 663 nm (3.18); HRMS (MS ES⁺): m/z calcd for [$\text{C}_{32}\text{H}_{37}\text{N}_4\text{Br}_2$] [M+H]⁺: calcd: 637.1364, found 637.1379.

5,10-Bis(4-bromophenyl)porphyrin 41: 4-Bromobenzaldehyde (0.74 g, 4 mmol) was reacted according to a procedure given before.^[12] Column chromatography on silica gel ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 1:4$, v/v) gave the 5,10,15-tris(4-bromophenyl)porphyrin **71** as the first fraction, followed by the title compound and then traces of (4-bromophenyl)porphyrin. Recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ gave 46 mg (0.07 mmol, 4 %) of purple crystals. $R_f = 0.38$ ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 1:1$, v/v); m.p. >300 °C; ^1H NMR (500 MHz, CDCl_3 , 25 °C, TMS): $\delta = -3.45$ (br s, 2H, *NH*), 7.89 (AB, 4H, $^3J = ^3J = ^3J = ^3J = 8.1$ Hz, Ar-*H_α*), 8.05 (AB, 4H, $^3J = ^3J = ^3J = ^3J = 8.1$ Hz, Ar-*H_α*), 8.89 (s, 2H, *H_{β7,8}*), 8.96 (AB, 2H, $^3J = 4.7$ Hz, *H_{β2,13}*), 9.30 (AB, 2H, $^3J = ^3J = 4.7$ Hz, *H_{β3,12}*), 9.38 (s, 2H, *H_{β17,18}*), 10.17 ppm (s, 2H, *H_{meso}*); ^{13}C NMR (63 MHz, CDCl_3 , 25 °C, TMS): $\delta = 104.53, 118.41, 122.52, 129.90, \sim 131, 135.89, 140.98$, ppm; UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 407 (5.36), 502 (4.33), 534 (3.67), 575 (3.87), 629 nm (3.38); MS (70 eV, EI): m/z (%): 620 (9 %, [M]⁺), 540 (4 %, [M – Br]⁺), 464 (3 %, [M – C₆H₄Br + Br]⁺), 310 (14 %, [M]²⁺); HRMS: m/z calcd for [$\text{C}_{28}\text{H}_{20}\text{N}_4\text{Br}_2$] [M]⁺: 618.0055, found: 618.0061.

5,10-Bis(3,4,5-trifluorophenyl)porphyrin 42: 3,4,5-Trifluorobenzaldehyde (0.64 g, 4 mmol) was reacted according to a procedure given before.^[12] Column chromatography on silica gel ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 1:1$, v/v) gave the 5,10,15-tris(3,4,5-trifluorophenyl)porphyrin **72** as the first fraction, followed by the title compound and then traces of (3,4,5-trifluorophenyl)porphyrin. Recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ gave 10 mg (0.02 mmol, 1 %) of purple crystals. $R_f = 0.47$ ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 1:1$,

v/v); m.p. 285 °C; ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): $\delta = -3.52$ (br s, 2H, *NH*), 7.85 (m, 4H, Ar-*H_α*), 8.92 (s, 2H, *H_{β2,13}*), 8.98 (AB, 2H, $^3J = ^3J = 4.4$ Hz, *H_{β3,12}*), 9.39 (AB, 2H, $^3J = ^3J = 4.6$ Hz, *H_{β7,8}*), 9.45 (AB, 2H, $^3J = ^3J = 4.6$ Hz, *H_{β17,18}*), 10.27 ppm (s, 2H, *H_{meso}*); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, TMS): $\delta = 105.27, 119.16, 130.96, 131.41, 132.32, 138.26, 148.31, 151.67$ ppm; UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 405 (5.03), 500 (4.09), 532 (3.47), 573 (3.73), 627 nm (3.06); MS (70 eV, EI, 350 °C): m/z (%): 570 (100 %, [M]⁺), 439 (11 %, [M – C₆H₃F₃]⁺), 285 (50 %, [M]²⁺), 251 (6 %, [M – C₆H₃F₃]²⁺); HRMS: m/z calcd for [$\text{C}_{32}\text{H}_6\text{F}_6\text{N}_4$] [M]⁺: 570.1279, found: 570.1259.

5,10-Bis(4-methoxycarbonylphenyl)-15,20-bis(4-methylphenyl)porphyrin 43: Following the general procedure F, 5,10-dibromo-15,20-bis(4-methylphenyl)porphyrin **29** (33 mg, 0.05 mmol), 4-methoxycarbonylphenyl boronic acid (90 mg, 0.5 mmol), Pd(PPh₃)₄ (5.8 mg, 0.005 mmol) and K₃PO₄ (212 mg, 1 mmol) in THF (60 mL) gave 20 mg (0.02 mmol, 52 %) of a purple solid after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. $R_f = 0.28$ ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 1:1$, v/v); m.p. >300 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = -2.76$ (s, 2H, *NH*), 2.70 (s, 6H, *CH₃*), 4.13 (s, 6H, *OCCH₃*), 7.59 (d, 4H, $^3J = 7.6$ Hz, Ar-*H*), 8.12 (d, 4H, $^3J = 7.6$ Hz, Ar-*H*), 8.32 (d, 4H, $^3J = 8.2$ Hz, Ar-*H*), 8.46 (d, 4H, $^3J = 8.2$ Hz, Ar-*H*), 8.80 (d, 2H, $^3J = 4.7$ Hz, *H_β*), 8.82 (s, 2H, *H_β*), 8.90 (s, 2H, *H_β*), 8.92 ppm (d, 2H, $^3J = 4.7$ Hz, *H_β*); ^{13}C NMR (125 MHz, CDCl_3 , 25 °C, TMS): $\delta = 21.46, 52.37, 118.09, 120.85, 126.80, 127.03, 127.48, 129.12, 129.76, 134.10, 137.09, 138.54, 146.66, 166.89$ ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 420 (4.92), 516 (4.27), 551 (4.08), 581 (3.87), 655 nm (3.97); HRMS (MS ES⁺): m/z calcd for [$\text{C}_{50}\text{H}_{39}\text{N}_4\text{O}_4$] [M+H]⁺: 759.2971, found 759.2941.

5,10-Bis(4-cyanophenyl)-15,20-bis(4-methylphenyl)porphyrin 44: Following the general procedure F, 5,10-dibromo-15,20-bis(4-methylphenyl)porphyrin **29** (30 mg, 0.046 mmol), 4-cyanophenyl boronic acid (68 mg, 0.46 mmol), Pd(PPh₃)₄ (5.3 mg, 0.0046 mmol) and K₃PO₄ (196 mg, 0.925 mmol) in THF (50 mL) gave 15 mg (0.021 mmol, 47 %) of a purple solid after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. $R_f = 0.34$ ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 1:1$, v/v); m.p. >300 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = -2.79$ (s, 2H, *NH*), 2.74 (s, 6H, *CH₃*), 7.60 (d, 4H, $^3J = 8.2$ Hz, Ar-*H*), 8.10 (m, 8H, Ar-*H*), 8.36 (d, 4H, $^3J = 8.2$ Hz, Ar-*H*), 8.75 (d, 2H, $^3J = 4.7$ Hz, *H_β*), 8.78 (s, 2H, *H_β*), 8.92 (s, 2H, *H_β*), 8.95 ppm (d, 2H, $^3J = 4.7$ Hz, *H_β*); ^{13}C NMR (125 MHz, CDCl_3 , 25 °C, TMS): $\delta = 21.10, 111.51, 118.57, 121.13, 130.13, 134.29, 137.11, 137.28, 138.30, 146.55$, ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 420 (4.94), 515 (3.79), 551 (3.62), 584 (3.44), 655 nm (3.68); HRMS (MS ES⁺): m/z calcd for [$\text{C}_{48}\text{H}_{33}\text{N}_4$] [M+H]⁺: 693.2767, found 693.2734.

5,10-Bis(4-methylphenyl)-15,20-bis(4-nitrophenyl)porphyrin 45: Following the general procedure F, 5,10-dibromo-15,20-bis(4-methylphenyl)porphyrin **29** (30 mg, 0.0462 mmol), 4-nitrophenylboronic acid pinacol ester (116 mg, 0.462 mmol), Pd(PPh₃)₄ (5.3 mg, 0.0046 mmol) and K₃PO₄ (196 mg, 0.925 mmol) in THF (50 mL) gave 16 mg (0.021 mmol, 47 %) of a purple solid after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. $R_f = 0.5$ ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 1:1$, v/v); m.p. > 300 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = -2.76$ (s, 2H, *NH*), 2.74 (s, 6H, *CH₃*), 7.60 (d, 4H, $^3J = 7.6$ Hz, Ar-*H*), 8.11 (d, 4H, $^3J = 7.6$ Hz, Ar-*H*), 8.42 (d, 4H, $^3J = 8.2$ Hz, Ar-*H*), 8.67 (d, 4H, $^3J = 8.2$ Hz, Ar-*H*), 8.76 (d, 2H, $^3J = 4.7$ Hz, *H_β*), 8.80 (s, 2H, *H_β*), 8.92 (s, 2H, *H_β*), 8.96 ppm (d, 2H, $^3J = 4.7$ Hz, *H_β*); ^{13}C NMR (125 MHz, CDCl_3 , 25 °C, TMS): $\delta = 21.09, 116.47, 121.48, 127.12, 134.66, 137.33, 138.25, 147.31, 148.53$ ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 421 (4.90), 516 (3.64), 552 (3.46), 584 (3.34), 655 nm (3.60); HRMS (MS ES⁺): m/z calcd for [$\text{C}_{46}\text{H}_{32}\text{N}_6\text{O}_4$] [M+H]⁺: 733.2563, found 733.2573.

5,10-Bis(4-methylphenyl)-15,20-bis(3-nitrophenyl)porphyrin 46: Following the general procedure F, 5,10-dibromo-15,20-bis(4-methylphenyl)porphyrin **29** (33 mg, 0.05 mmol), 4-methoxycarbonylphenyl boronic acid (90 mg, 0.5 mmol), Pd(PPh₃)₄ (5.8 mg, 0.005 mmol), K₃PO₄ (212 mg, 1 mmol) in THF (60 mL) gave 10 mg (0.013 mmol, 30 %) of a purple solid after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. $R_f = 0.3$ ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 1:1$, v/v); m.p. >300 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = -2.77$ (s, 2H, *NH*), 2.74 (s, 6H, *CH₃*), 7.60 (d, 4H, $^3J = 7.6$ Hz, Ar-*H*), 7.99 (t, 2H, $^3J = 7.6$ Hz, Ar-*H*), 8.13 (d, 2H, $^3J = 7\text{Hz}$, Ar-*H*), 8.57 (m, 2H, Ar-*H*), 8.72 (d, 4H, $^3J = 8.2$ Hz, Ar-*H*), 8.79 (d, 2H, $^3J = 4.7$ Hz, *H_β*), 8.93 (s, 2H, *H_β*), 8.96 (d, 2H, $^3J = 4.7$ Hz, *H_β*), 9.11 ppm (s, 2H, *H_β*); ^{13}C NMR (125 MHz, CDCl_3 , 25 °C, TMS): $\delta = 29.59, 116.46, 121.52, 122.88, 127.44, 127.66, 128.20, 134.38, 137.61, 138.62, 139.69, 143.64, 146.84$ ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 421 (4.90), 516 (3.64), 551 (3.46), 589 (3.34), 646 nm (3.16); HRMS (MS ES⁺): m/z calcd for [$\text{C}_{44}\text{H}_{32}\text{N}_4\text{O}_4$] [M+H]⁺: 733.2563, found 733.2540.

5,10-Bis(3-Cyanophenyl)-15,20-bis(4-methylphenyl)porphyrin (47): Following the general procedure F, 5,10-dibromo-15,20-bis(4-methylphenyl)porphyrin **29** (20 mg, 0.0308 mmol), 4-cyanophenyl boronic acid (46 mg, 0.308 mmol) and Pd(PPh₃)₄ (3.6 mg, 0.003 mmol), K₃PO₄ (131 mg, 0.617 mmol) in THF (60 mL) gave 10 mg (0.014 mmol, 47 %). m.p. >300 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = -2.79$ (s, 2H, *NH*), 2.74 (s, 6H, *-CH₃*), 7.61 (d, 4H, $^3J = 7\text{Hz}$, Ar-*H*), 7.92 (m, 2H, Ar-*H*), 8.14 (m, 6H, Ar-*H*), 8.49 (t, 2H, $^3J = 7, 6.4\text{Hz}$, Ar-*H*), 8.55 (m, 2H, Ar-*H*), 8.74 (d, 2H, $^3J = 4.7$ Hz, *H_β*), 8.78 (s, 2H, *H_β*), 8.93 (s, 2H, *H_β*), 8.96 ppm (d, 2H, $^3J = 4.7$ Hz, *H_β*); ^{13}C NMR (150 MHz, CDCl_3 , 25 °C, TMS): $\delta = 21.10, 110.92, 116.32, 118.48, 121.10, 127.25, 131.16, 134.10, 136.62, 137.26, 137.84, 138.32, 142.99$ ppm; UV/VIS (DMF):

λ_{max} (log ϵ) = 419 (4.88), 514 (3.61), 548 (3.44), 589 (3.31), 646 nm (3.38); HRMS (MS ES+): m/z calcd for $[\text{C}_{48}\text{H}_{32}\text{N}_6] [\text{M}+\text{H}]^+$: 693.2767, found 693.2743.

5,10-Bis(4-methoxycarbonylphenyl)-15,20-diphenylporphyrin 48: Following the general procedure F 5,10-dibromo-15,20-diphenylporphyrin **36** (30 mg, 0.048 mmol), 4-methoxycarbonylphenylboronic acid (86 mg, 0.48 mmol), $\text{Pd}(\text{PPh}_3)_4$ (5.5 mg, 0.005 mmol) and K_3PO_4 (205 mg, 0.967 mmol) in THF (50 mL) gave 10 mg (0.013 mmol, 30 %) of a purple solid after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. $R_f = 0.5$ ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v); m.p. > 300 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = -2.76 (s, 2H, *NH*), 4.14 (s, 6H, CH_3), 7.79 (d, 4H, $^3J = 7.6$ Hz, *Ar-H*), 8.24 (d, 4H, $^3J = 8.2$ Hz, *Ar-H*), 8.33 (d, 4H, $^3J = 8.2$ Hz, *Ar-H*), 8.47 (d, 4H, $^3J = 8.2$ Hz, *Ar-H*), 8.82 (m, 4H, H_β), 8.90 ppm (m, 4H, H_β); ^{13}C NMR (125 MHz, CDCl_3 , 25 °C, TMS): δ = 45.57, 51.99, 118.30, 126.29, 127.44, 129.19, 134.07, 141.47, 146.45, 166.85 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 418 (4.94), 514 (3.80), 548 (3.61), 588 (3.34), 646 nm (3.32); HRMS (MS ES+): m/z calcd for $[\text{C}_{48}\text{H}_{35}\text{N}_6\text{O}_4] [\text{M}+\text{H}]^+$: 731.2658, found 731.2625.

5,10-Bis(4-cyanophenyl)-15,20-diphenylporphyrin 49: Following the general procedure F 5,10-dibromo-15,20-diphenylporphyrin **36** (20 mg, 0.032 mmol), 4-cyanophenylboronic acid (47 mg, 0.32 mol), $\text{Pd}(\text{PPh}_3)_4$ (3.7 mg, 0.003 mmol), K_3PO_4 (136 mg, 0.644 mmol) in THF (50 mL) gave 6 mg (0.009 mmol, 29 %) of a purple solid after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. $R_f = 0.3$ ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v); m.p. >300 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = -2.80 (s, 2H, *NH*), 7.80 (m, 4H, *Ar-H*), 8.11 (d, 4H, $^3J = 7.6$ Hz, *Ar-H*), 8.23 (d, 4H, $^3J = 7.6$ Hz, *Ar-H*), 8.37 (d, 4H, $^3J = 8.2$ Hz, *Ar-H*), 8.76 (d, 2H, $^3J = 4.7$ Hz, H_β), 8.80 (s, 2H, H_β), 8.90 (s, 2H, H_β), 8.93 ppm (d, 2H, $^3J = 4.7$ Hz, H_β); ^{13}C NMR (150 MHz, CDCl_3 , 25 °C, TMS): δ = 29.26, 111.58, 117.12, 118.54, 120.94, 126.37, 127.56, 130.14, 130.23, 134.08, 134.52, 141.22, 146.48 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 418 (4.98), 514 (3.64), 548 (3.26), 588 (2.87), 645 nm (2.56); HRMS (MS ES+): m/z calcd for $[\text{C}_{46}\text{H}_{29}\text{N}_6] [\text{M}+\text{H}]^+$: 665.2454, found 665.2468.

5,10-Bis(4-nitrophenyl)-15,20-diphenylporphyrin 50: Following the general procedure F 5,10-dibromo-15,20-diphenylporphyrin **36** (20 mg, 0.032 mmol), 4-nitrophenyl boronic pinacol ester (80 mg, 0.32 mmol), $\text{Pd}(\text{PPh}_3)_4$ (3.7 mg, 0.003 mmol), K_3PO_4 (135 mg, 0.64 mmol) in THF (60 mL) gave 10 mg (0.014 mmol, 43 %) of the title compound. $R_f = 0.3$ ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v); m.p. >300 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = -2.77 (s, 2H, *NH*), 7.82 (m, 4H, *Ar-H*), 8.23 (d, 4H, $^3J = 6.4$ Hz, *Ar-H*), 8.42 (d, 4H, $^3J = 8.8$ Hz, *Ar-H*), 8.67 (d, 4H, $^3J = 8.8$ Hz, *Ar-H*), 8.78 (d, 2H, $^3J = 4.7$ Hz, H_β), 8.82 (s, 2H, H_β), 8.90 (s, 2H, H_β), 8.94 ppm (d, 2H, $^3J = 4.7$ Hz, H_β); UV/VIS (DMF): λ_{max} (lg ϵ) = 421 (4.95), 516 (3.69), 552 (3.58), 592 (3.29), 646 nm (3.45); HRMS (MS ES+): m/z calcd for $[\text{C}_{44}\text{H}_{29}\text{N}_6\text{O}_4] [\text{M}+\text{H}]^+$: 705.2250, found 705.2278.

5,10-Bis(4-methoxycarbonylphenyl)-15,20-bis(3-methoxyphenyl)porphyrin 51: Following the general procedure F 5,10-dibromo-15,20-bis(3-methoxyphenyl)porphyrin **37** (20 mg, 0.029 mmol), 4-methoxycarbonylphenylboronic acid (52 mg, 0.293 mmol), $\text{Pd}(\text{PPh}_3)_4$ (3.3 mg, 0.0029 mmol), K_3PO_4 (124 mg, 0.587 mmol) in THF (50 mL) gave 9 mg (0.011 mmol, 32 %) of a purple solid after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. $R_f = 0.3$ ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v); m.p. > 300 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = -2.78 (s, 2H, *NH*), 4.01 (s, 6H, OCH_3), 4.14 (s, 6H, OCH_3), 7.37 (d, 2H, $^3J = 8.2$ Hz, *Ar-H*), 7.67 (t, 2H, $^3J = 8.2$ Hz, *Ar-H*), 7.82 (d, 4H, $^3J = 7.6$ Hz, *Ar-H*), 8.33 (d, 4H, $^3J = 7.6$ Hz, *Ar-H*), 8.47 (d, 4H, $^3J = 7.6$ Hz, *Ar-H*), 8.82 ppm (m, 4H, H_β), 8.93 (m, 4H, H_β); ^{13}C NMR (125 MHz, CDCl_3 , 25 °C, TMS): δ = 52.33, 55.37, 113.46, 118.79, 120.35, 127.81, 129.48, 134.40, 143.06, 146.74, 157.80, 167.18 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 419 (4.96), 514 (3.74), 549 (3.47), 588 (3.34), 646 nm (3.36); HRMS (MS ES+): m/z calcd for $[\text{C}_{50}\text{H}_{39}\text{N}_4\text{O}_6] [\text{M}+\text{H}]^+$: 791.2870, found 791.2865.

5,10-Bis(4-cyanophenyl)-15,20-bis(3-methoxyphenyl)porphyrin 52: Following the general procedure F 5,10-dibromo-15,20-bis(3-methoxyphenyl)porphyrin **37** (30 mg, 0.044 mmol), 4-cyanophenyl boronic acid (64 mg, 0.44 mmol), $\text{Pd}(\text{PPh}_3)_4$ (5 mg, 0.004 mmol) and K_3PO_4 (186 mg, 0.88 mmol) in THF (60 mL) gave 15 mg (0.020 mmol, 47 %) of a purple solid after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. $R_f = 0.3$ ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v); m.p. > 300 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = -2.82 (s, 2H, *NH*), 4.02 (s, 6H, OCH_3), 7.38 (m, 2H, *Ar-H*), 7.69 (t, 4H, $^3J = 8.2$ Hz, *Ar-H*), 7.81 (m, 4H, *Ar-H*), 8.10 (d, 4H, $^3J = 8.2$ Hz, *Ar-H*), 8.36 (d, 4H, $^3J = 7.6$ Hz, *Ar-H*), 8.77 (d, 2H, $^3J = 4.7$ Hz, H_β), 8.79 (s, 2H, H_β), 8.94 (s, 2H, H_β), 8.97 ppm (d, 2H, $^3J = 4.68$ Hz, H_β); ^{13}C NMR (125 MHz, CDCl_3 , 25 °C, TMS): δ = 55.07, 111.58, 113.19, 115.85, 117.18, 118.53, 120.56, 127.19, 130.14, 134.51, 142.51, 146.47, 157.55 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 419 (4.90), 513 (3.56), 547 (3.25), 592 (3.16), 643 nm (3.18); HRMS (MS ES+): m/z calcd for $[\text{C}_{48}\text{H}_{33}\text{N}_6\text{O}_2] [\text{M}+\text{H}]^+$: 725.2655, found 725.2641.

5,10-Bis(3-methoxyphenyl)-15,20-bis(4-nitrophenyl)porphyrin 53: Following the general procedure F 5,10-dibromo-15,20-bis(3-methoxyphenyl)porphyrin **37** (20 mg, 0.03 mmol), 4-nitrophenylboronic acid pinacol ester (74 mg, 0.3 mmol), $\text{Pd}(\text{PPh}_3)_4$ (3.4 mg, 0.003 mmol), K_3PO_4 (125 mg, 0.59 mmol) in THF gave 13 mg (0.017 mmol, 56 %) of the title compound. $R_f = 0.3$ ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v); m.p. >300 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = -2.78 (s, 2H, *NH*), 4.02 (s, 6H, OCH_3), 7.69 (t, 2H, $^3J = 8.2$, 7.6 Hz, *Ar-H*), 7.82 (t, 4H, $^3J = 7.6$ Hz, *Ar-H*), 8.42 (d, 4H, $^3J = 8.8$ Hz, *Ar-H*), 8.67 (d, 4H, $^3J = 8.2$ Hz, *Ar-H*), 8.77 (d, 2H, $^3J = 4.7$ Hz, H_β), 8.81 (s, 2H, H_β), 8.94 (s, 2H, H_β), 8.98 ppm (d, 2H, $^3J = 4.7$ Hz, H_β); ^{13}C NMR (150 MHz, CDCl_3 , 25 °C, TMS): δ = 55.08, 113.20, 116.74, 120.75, 121.73, 126.97, 127.47, 134.64, 142.46, 147.34, 148.43, 157.56 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 421 (4.89), 516 (3.58), 551 (3.36), 592 (3.28), 655 nm (3.48); HRMS (MS ES+): m/z calcd for $[\text{C}_{46}\text{H}_{33}\text{N}_6\text{O}_6] [\text{M}+\text{H}]^+$: 765.2462, found 765.2495.

5,10-Bis(2,6-difluorophenyl)-15,20-bis(4-methoxycarbonylphenyl)porphyrin 54: Following the general procedure F, 5,10-dibromo-15,20-bis(2,6-difluorophenyl)porphyrin **38** (20 mg, 0.028 mmol), 4-methoxycarbonylphenylboronic acid (63 mg, 0.35 mmol), $\text{Pd}(\text{PPh}_3)_4$ (3.2 mg, 0.003 mmol) and K_3PO_4 (154 mg, 0.722 mmol) in THF (30 mL) gave 7 mg (0.008 mmol, 30 %) of purple solid after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. $R_f = 0.5$ ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v); m.p. >300 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = -2.72 (s, 2H, *NH*), 4.15 (s, 6H, CH_3), 7.42 (t, 4H, $^3J = 6.4$ Hz, *Ar-H*), 7.83 (m, 2H, *Ar-H*), 8.34 (d, 4H, $^3J = 8.2$ Hz, *Ar-H*), 8.38 (d, 4H, $^3J = 8.2$ Hz, *Ar-H*), 8.93 ppm (m, 8H, H_β); UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 416 (4.98), 511 (3.77), 547 (3.30), 590 (3.27), 647 nm (2.95); HRMS (MS ES+): m/z calcd for $[\text{C}_{48}\text{H}_{31}\text{N}_4\text{O}_4\text{F}_4] [\text{M}+\text{H}]^+$: 803.2281, found 803.2261.

5,10-Bis(4-cyanophenyl)-15,20-bis(2,6-difluorophenyl)porphyrin 55: Following the general procedure F, 5,10-dibromo-15,20-bis(2,6-difluorophenyl)porphyrin **38** (20 mg, 0.028 mmol), 4-cyanophenylboronic acid (52 mg, 0.35 mol), $\text{Pd}(\text{PPh}_3)_4$ (3.2 mg, 0.003 mmol), K_3PO_4 (154 mg, 0.722 mmol) in THF (30 mL) gave 6 mg (0.008 mmol, 28 %) of purple solid after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. $R_f = 0.5$ ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v); m.p. > 300 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = -2.78 (s, 2H, *NH*), 7.42 (t, 4H, $^3J = 8.7$, 7.6 Hz, *Ar-H*), 7.85 (m, 2H, *Ar-H*), 8.10 (d, 4H, $^3J = 8.2$ Hz, *Ar-H*), 8.35 (d, 4H, $^3J = 8.2$ Hz, *Ar-H*), 8.78 (s, 2H, H_β), 8.81 (d, 2H, $^3J = 4.7$ Hz, H_β), 8.91 (d, 2H, $^3J = 4.7$ Hz, H_β), 8.93 ppm (s, 2H, H_β); UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 417 (5.06), 511 (3.81), 548 (3.26), 585 (3.31), 645 nm (2.96); HRMS (MS ES+): m/z calcd for $[\text{C}_{46}\text{H}_{25}\text{N}_4\text{F}_4] [\text{M}+\text{H}]^+$: 737.2077, found 737.2088.

5,10-Bis(2,6-difluorophenyl)-15,20-bis(4-nitrophenyl)porphyrin 56: Following the general procedure F, 5,10-dibromo-15,20-bis(2,6-difluorophenyl)porphyrin **38** (20 mg, 0.028 mmol), 4-nitrophenyl boronic pinacol ester (91 mg, 0.364 mmol), $\text{Pd}(\text{PPh}_3)_4$ (3.2 mg, 0.003 mmol), K_3PO_4 (154 mg, 0.722 mmol) in THF (30 mL) gave 5 mg (0.006 mmol, 22 %) of the title compound. $R_f = 0.5$ ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v); m.p. >300 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = -2.75 (s, 2H, *NH*), 7.44 (t, 4H, $^3J = 8.2$ Hz, *Ar-H*), 7.85 (m, 2H, *Ar-H*), 8.42 (d, 4H, $^3J = 8.7$ Hz, *Ar-H*), 8.68 (d, 4H, $^3J = 8.2$ Hz, *Ar-H*), 8.81 (s, 2H, H_β), 8.83 (d, 2H, $^3J = 4.7$ Hz, H_β), 8.92 (d, 2H, $^3J = 4.7$ Hz, H_β), 8.94 ppm (s, 2H, H_β); UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 418 (5.11), 512 (3.96), 550 (3.32), 591 (3.39), 646 nm (2.43); HRMS (MS ES+): m/z calcd for $[\text{C}_{44}\text{H}_{25}\text{N}_6\text{O}_4\text{F}_4] [\text{M}+\text{H}]^+$: 777.1873, found 777.1884.

5,10-Bis(4-methoxycarbonylphenyl)-15,20-di(*n*-pentyl)porphyrin 57: Following the general procedure F 5,10-dibromo-15,20-di(*n*-pentyl)porphyrin **39** (30 mg, 0.049 mmol), 4-methoxycarbonylphenylboronic acid (88 mg, 0.49 mmol), $\text{Pd}(\text{PPh}_3)_4$ (5.7 mg, 0.005 mmol), K_3PO_4 (209 mg, 0.986 mmol) in THF (50 mL) gave 20 mg (0.026 mmol, 57 %) of the title compound. $R_f = 0.35$ ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v); m.p. >300 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = -2.68 (s, 2H, *NH*), 1.02 (t, 6H, $^3J = 7.6$, 7.0 Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.68 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.85 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.58 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 4.14 (s, 6H, OCH_3), 5.03 (t, 4H, $^3J = 8.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 8.28 (d, 4H, $^3J = 8.2$ Hz, *Ar-H*), 8.45 (d, 4H, $^3J = 8.2$ Hz, *Ar-H*), 8.71 (s, 2H, H_β), 8.83 (d, 2H, $^3J = 4.7$ Hz, H_β), 9.49 (d, 2H, $^3J = 4.7$ Hz, H_β), 9.61 ppm (s, 2H, H_β); ^{13}C NMR (150 MHz, CDCl_3 , 25 °C, TMS): δ = 13.35, 29.63, 32.33, 35.25, 38.21, 51.80, 116.90, 120.40, 126.79, 127.69, 129.01, 129.75, 134.04, 146.67, 166.92 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 418 (4.93), 518 (4.03), 550 (3.95), 592 (3.85), 651 nm (3.88); HRMS (MS ES+): m/z calcd for $[\text{C}_{46}\text{H}_{47}\text{N}_4\text{O}_4] [\text{M}+\text{H}]^+$: 719.3597, found 719.3620.

5,10-Bis(4-cyanophenyl)-15,20-di(*n*-pentyl)porphyrin 58: Following the general procedure F, 5,10-dibromo-15,20-di(*n*-pentyl)porphyrin **39** (40 mg, 0.065 mmol), 4-cyanophenyl boronic acid (95.5 mg, 0.65 mmol), $\text{Pd}(\text{PPh}_3)_4$ (7.5 mg, 0.007 mmol), K_3PO_4 (279 mg, 1.31 mmol) in THF (60 mL) gave 17 mg (0.026 mmol, 40 %) of the title compound. $R_f = 0.4$ ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v); m.p. >300 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = -2.70 (s, 2H, *NH*), 1.01 (t, 6H, $^3J = 7\text{ Hz}$, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.28 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.83 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.58 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 5.03 (t, 4H, $^3J = 8.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 8.08 (d, 4H, $^3J = 8.2$ Hz, *Ar-H*), 8.31 (d, 4H, $^3J = 8.2$ Hz, *Ar-H*), 8.67 (s, 2H, H_β), 8.77 (d, 2H, $^3J = 4.7$ Hz, H_β), 9.52 (d, 2H, $^3J = 4.7$ Hz, H_β), 9.62 ppm (s, 2H, H_β); ^{13}C NMR (150 MHz, CDCl_3 , 25 °C, TMS): δ = 13.71, 22.33, 29.27, 32.30, 35.29, 38.28, 111.37, 115.77, 118.62, 121.10, 130.09, 134.64, 146.69 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 419 (4.97), 517 (3.75), 552 (3.58), 592 (3.27), 650 nm (3.41); HRMS (MS ES+): m/z calcd for $[\text{C}_{44}\text{H}_{41}\text{N}_6] [\text{M}+\text{H}]^+$: 653.3393, found 653.3382.

5,10-Bis(4-nitrophenyl)-15,20-di(*n*-pentyl)porphyrin 59: Following the general procedure F, 5,10-dibromo-15,20-di(*n*-pentyl)porphyrin **39** (40 mg, 0.065 mmol), 4-nitrophenyl boronic pinacol ester (161 mg, 0.65 mmol), $\text{Pd}(\text{PPh}_3)_4$ (7.5 mg, 0.007 mmol), K_3PO_4 (279 mg, 1.31 mmol) in THF (60 mL) gave 22 mg (0.031 mmol, 47 %), $R_f = 0.59$ ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v); m.p. >300 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = -2.67 (s, 2H, *NH*), 1.02 (t, 6H, $^3J = 7.6$, 7 Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.30 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.83 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.58 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 5.03 (t, 4H, $^3J = 8.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 8.36 (d, 4H, $^3J = 8.7$ Hz, *Ar-H*), 8.65 (d, 4H, $^3J = 8.2$ Hz, *Ar-H*), 8.69 (s, 2H, H_β), 8.78 (d, 2H, $^3J = 4.7$ Hz, H_β), 9.53 (d, 2H, $^3J = 4.7$ Hz, H_β), 9.62 ppm (s, 2H, H_β); ^{13}C NMR (150 MHz, CDCl_3 , 25 °C, TMS): δ = 13.71, 29.1, 32.31, 35.31, 38.30, 115.33, 121.44, 134.59, 147.23, 148.66 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 420 (4.90), 517 (3.73), 554 (3.45), 594 (3.15), 651 nm (3.33); HRMS (MS ES+): m/z calcd for $[\text{C}_{42}\text{H}_{41}\text{N}_6\text{O}_4] [\text{M}+\text{H}]^+$: 693.3189, found 693.3160.

5,10-Di(*n*-hexyl)-15,20-bis(4-methoxycarbonylphenyl)porphyrin 60: Following the general procedure F, 5,10-dibromo-15,20-di(*n*-hexyl)porphyrin **40** (25 mg, 0.04 mmol), 4-methoxycarbonylphenylboronic acid (72 mg, 0.4 mmol), $\text{Pd}(\text{PPh}_3)_4$ (4.6 mg, 0.004 mmol), K_3PO_4 (169 mg, 0.8 mmol) in THF gave 10 mg (0.013 mmol, 34 %) of the title

compound. $R_f = 0.54$ ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 1:1$, v/v); m.p. $>300^\circ\text{C}$; $^1\text{H NMR}$ (400 MHz, CDCl_3 , 25°C , TMS) $\delta = -2.68$ (s, 2H, NH), 0.96 (t, 6H, $^3J = 7.6$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.42 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.54 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.85 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.56 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 4.14 (s, 6H, OCH_3), 5.03 (t, 4H, $^3J = 8.9$, 7.6 Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 8.28 (d, 4H, $^3J = 8.2$ Hz, Ar-H), 8.45 (d, 4H, $^3J = 8.2$ Hz, Ar-H), 8.71 (s, 2H, H_{β}), 8.83 (d, 2H, $^3J = 4.7$ Hz, H_{β}), 9.49 (d, 2H, $^3J = 4.7$ Hz, H_{β}), 9.61 ppm (s, 2H, H_{β}); $^{13}\text{C NMR}$ (150 MHz, CDCl_3 , 25°C , TMS): $\delta = 13.68$, 22.27, 24.91, 28.90, 29.62, 31.46, 35.41, 38.46, 51.93, 119.47, 127.49, 134 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 416 (4.96), 518 (3.86), 552 (3.66), 598 (3.47), 655 nm (3.56); HRMS (MS ES+): m/z calcd for $[\text{C}_{48}\text{H}_{51}\text{N}_4\text{O}_4] [\text{M}+\text{H}]^+$: 747.3910, found 747.3907.

5,10-Bis(4-cyanophenyl)-15,20-di(*n*-hexyl)porphyrin 61: Following the general procedure F 5,10-dibromo-15,20-di(*n*-hexyl)porphyrin **40** (30 mg, 0.047 mmol), 4-cyanophenylboronic acid (69 mg, 0.47 mmol), $\text{Pd}(\text{PPh}_3)_4$ (5.4 mg, 0.005 mmol), K_3PO_4 (200 mg, 0.942 mmol) in THF gave 13 mg (0.019 mmol, 40 %) of the title compound. $R_f = 0.2$ ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 1:1$, v/v); m.p. $>300^\circ\text{C}$; $^1\text{H NMR}$ (400 MHz, CDCl_3 , 25°C , TMS): $\delta = -2.66$ (s, 2H, NH), 0.96 (t, 6H, $^3J = 7.6$, 7 Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.43 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.54 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.85 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.55 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 5.04 (t, 4H, $^3J = 8.2$, 7.6 Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 8.09 (d, 4H, $^3J = 8.2$ Hz, Ar-H), 8.32 (d, 4H, $^3J = 8.2$ Hz, Ar-H), 8.67 (s, 2H, H_{β}), 8.77 (d, 2H, $^3J = 4.7$ Hz, H_{β}), 9.52 (d, 2H, $^3J = 4.7$ Hz, H_{β}), 9.63 ppm (s, 2H, H_{β}); $^{13}\text{C NMR}$ (150 MHz, CDCl_3 , 25°C , TMS): $\delta = 14.06$, 22.66, 31.91, 35.70, 39.09, 112.11, 115.83, 119.11, 121.64, 130.59, 134.89, 147.13, 148.08 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 418 (4.87), 517 (4.53), 551 (3.43), 592 (3.13), 650 nm (3.31); HRMS (MS ES+): m/z calcd for $[\text{C}_{46}\text{H}_{45}\text{N}_6] [\text{M}+\text{H}]^+$: 681.3706, found 681.3710.

5,10-Di(*n*-hexyl)-15,20-bis(4-nitrophenyl)porphyrin 62: Following the general procedure F, 5,10-dibromo-15,20-di(*n*-hexyl)porphyrin **40** (33 mg, 0.047 mmol), 4-nitrophenyl boronic pinacol ester (117 mg, 0.47 mmol), $\text{Pd}(\text{PPh}_3)_4$ (5.4 mg, 0.005 mmol), K_3PO_4 (200 mg, 0.942 mmol) in THF (60 mL) gave 20 mg (0.027 mmol, 59 %) of the title compound. $R_f = 0.6$ ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 1:1$, v/v); m.p. $>300^\circ\text{C}$; $^1\text{H NMR}$ (600 MHz, CDCl_3 , 25°C , TMS): $\delta = -2.66$ (s, 2H, NH), 0.98 (t, 6H, $^3J = 7.3$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.44 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.56 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.85 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.58 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 5.02 (t, 4H, $^3J = 8.1$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 8.36 (d, 4H, $^3J = 8.1$ Hz, Ar-H), 8.65 (d, 4H, $^3J = 8.1$ Hz, Ar-H), 8.69 (s, 2H, H_{β}), 8.78 (d, 2H, $^3J = 4.7$ Hz, H_{β}), 9.52 (d, 2H, $^3J = 4.7$ Hz, H_{β}), 9.62 ppm (s, 2H, H_{β}); $^{13}\text{C NMR}$ (150 MHz, CDCl_3 , 25°C , TMS): $\delta = 22.63$, 30.22, 31.81, 35.73, 38.95, 115.72, 121.70, 122.07, 134.88, 135.02, 147.77, 149.37 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 421 (5.02), 519 (3.89), 554 (3.76), 595 (3.47), 652 nm (3.55); HRMS (MS ES+): m/z calcd for $[\text{C}_{44}\text{H}_{43}\text{N}_6\text{O}_4] [\text{M}+\text{H}]^+$: 721.3502, found 721.3520.

[5,10-Bis(4-ethynylphenyl)-15,20-bis(4-methylphenyl)porphyrinato]zinc (II) 63: Following the general procedure D, 5,10-bis(4-ethynylphenyl)-15,20-bis(4-methylphenyl)porphyrin **27** (15 mg, 0.022 mmol) was treated with 300 mg of zinc oxide to give 13 mg (0.017 mmol, 81 %) of the desired product after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. $R_f = 0.4$ ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 1:1$, v/v); m.p. $>300^\circ\text{C}$; $^1\text{H NMR}$ (600 MHz, CDCl_3 , 25°C , TMS): $\delta = 2.77$ (s, 6H, CH_3), 3.34 (s, 2H, $\text{C}\equiv\text{CH}$), 7.59 (d, 4H, $^3J = 7.7$ Hz, Ar-H), 7.92 (d, 4H, $^3J = 7.7$ Hz, Ar-H), 8.13 (d, 4H, $^3J = 7.7$ Hz, Ar-H), 8.22 (d, 4H, $^3J = 7.7$ Hz, Ar-H), 8.95 (m, 4H, H_{β}), 9.02 ppm (m, 4H, H_{β}); $^{13}\text{C NMR}$ (150 MHz, CDCl_3 , 25°C , TMS): $\delta = 14.02$, 21.38, 29.52, 77.97, 83.62, 119.79, 121.26, 127.19, 130.26, 131.43, 132.03, 134.19, 134.32, 137.09, 139.56, 143.37, 149.62, 150.27 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 427 (4.94), 560 (3.64), 601 nm (3.40); HRMS: m/z calcd for $[\text{C}_{50}\text{H}_{32}\text{N}_4\text{Zn}] [\text{M}]^+$: 752.1918, found 752.1916.

[5,10-Bis(4-methoxycarbonylphenyl)-15,20-bis(4-methylphenyl)porphyrinato]zinc(II) 64: Following the general procedure D, 5,10-bis(4-methoxycarbonylphenyl)-15,20-bis(4-methylphenyl)porphyrin **43** (15 mg, 0.019 mmol) was treated with 300 mg of zinc oxide to give 13 mg (0.015 mmol, 81 %) of the title compound after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. $R_f = 0.1$ ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 1:1$, v/v); m.p. $>300^\circ\text{C}$; $^1\text{H NMR}$ (600 MHz, CDCl_3 , 25°C , TMS): $\delta = 2.75$ (s, 6H, CH_3), 4.13 (s, 6H, OCH_3), 7.59 (d, 4H, $^3J = 7.2$ Hz, Ar-H), 8.13 (d, 4H, $^3J = 7.5$ Hz, Ar-H), 8.33 (d, 4H, $^3J = 7.9$ Hz, Ar-H), 8.46 (d, 4H, $^3J = 7.5$ Hz, Ar-H), 8.91 (m, 4H, H_{β}), 8.97 ppm (m, 4H, H_{β}); $^{13}\text{C NMR}$ (150 MHz, CDCl_3 , 25°C , TMS): $\delta = 13.95$, 29.21, 52.22, 119.46, 121.76, 127.09, 129.26, 130.05, 131.32, 132.12, 137.13, 139.50, 147.56, 149.39, 150.29, 150.48, 166.64, 167.23 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 428 (5.02), 560 (3.72), 601 nm (3.35); HRMS (MS ES+): m/z calcd for $[\text{C}_{50}\text{H}_{37}\text{N}_4\text{O}_6\text{Zn}] [\text{M}+\text{H}]^+$: 821.2106, found 821.2146.

[5,10-Bis(4-cyanophenyl)-15,20-bis(4-methylphenyl)porphyrinato]zinc(II) 65: Following the general procedure D, 5,10-bis(4-cyanophenyl)-15,20-bis(4-methylphenyl)porphyrin **44** (10 mg, 0.014 mmol) was treated with 300 mg of zinc oxide to yield 8 mg (0.010 mmol, 72 %) of the desired product after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. $R_f = 0.27$ ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 1:1$, v/v); m.p. $>300^\circ\text{C}$; $^1\text{H NMR}$ (600 MHz, CDCl_3 , 25°C , TMS): $\delta = 2.76$ (s, 6H, CH_3), 7.61 (d, 4H, $^3J = 7.2$ Hz, Ar-H), 8.11 (m, 8H, Ar-H), 8.37 (d, 4H, $^3J = 7.7$ Hz, Ar-H), 8.86 (d, 2H, $^3J = 4.4$ Hz, H_{β}), 8.89 (s, 2H, H_{β}), 9.03 (s, 2H, H_{β}), 9.06 ppm (d, 2H, $^3J = 4.4$ Hz, H_{β}); $^{13}\text{C NMR}$ (150 MHz, CDCl_3 , 25°C , TMS): $\delta = 13.95$, 21.38, 29.55, 111.63, 127.27, 130.28, 131.01, 132.42, 132.84, 134.22, 134.71, 137.31, 150.40 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 421 (4.94), 548 (3.74), 628 nm (3.52); HRMS: m/z calcd for $[\text{C}_{48}\text{H}_{30}\text{N}_6\text{Zn}] [\text{M}]^+$: 754.1823, found 754.1875.

[5,10-Dibromo-15,20-bis(3-methoxyphenyl)porphyrinato]zinc(II) 66: 5,10-Dibromo-15,20-bis(3-methoxyphenyl)porphyrin **37** (50 mg, 0.07 mmol) was reacted

following procedure D. Column chromatography on silica gel (CH_2Cl_2) gave a single product. Recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{H}_2\text{O}$ gave purple crystals (49 mg, 0.07 mmol, 90 %). $R_f = 0.27$ ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 3:1$, v/v); m.p. 187°C ; $^1\text{H NMR}$ (500 MHz, CDCl_3 , 25°C , TMS): $\delta = 3.91$ (s, 6H, Ar-OCH_3), 7.29 (m, 2H, Ar-H_{β}), 7.68 (m, 4H, Ar-H_{α} , Ar-H_{β}), 7.79 (m, 2H, Ar-H_{α}), 8.43 (s, 2H, H_{β}), 8.76 (AB, 2H, $^3J = ^3J = 4.6$ Hz, H_{β}), 8.89 (s, 2H, H_{β}), 9.21 ppm (AB, 2H, $^3J = ^3J = 4.6$ Hz, H_{β}); $^{13}\text{C NMR}$ (126 MHz, CDCl_3 , 25°C , TMS): $\delta = 55.55$, 103.95, 113.35, 120.70, 121.90, 127.50, 127.63, 132.30, 132.67, 132.70, 133.18, 143.57, 148.41, 149.13, 150.79, 150.94, 158.03 ppm; UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 424 (5.26), 556 (4.26), 595 nm (3.83); MS (TOF, MS, ES+, 70 eV): m/z (%): 740 (39 %, $[\text{M}]^+$); HRMS: m/z calcd for $[\text{C}_{34}\text{H}_{22}\text{N}_4\text{Br}_2\text{O}_2\text{Zn}] [\text{M}]^+$: 739.9401, found: 739.9391.

[5,10-Bis(4-cyanophenyl)-15,20-bis(3-methoxyphenyl)porphyrinato]zinc(II) 67: Following the general procedure D, 5,10-bis(4-cyanophenyl)-15,20-bis(3-methoxyphenyl)porphyrin **52** (0.013 mmol) was treated with 300 mg of zinc oxide to give 8 mg (0.009 mmol, 72 %) of the title compound after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. $R_f = 0.3$ ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 1:1$, v/v); m.p. $>300^\circ\text{C}$; $^1\text{H NMR}$ (400 MHz, CDCl_3 , 25°C , TMS): $\delta = 3.99$ (s, 6H, OCH_3), 7.36 (d, 2H, $^3J = 8.2$ Hz, Ar-H), 7.67 (t, 2H, $^3J = 8.2$, 7.6 Hz, Ar-H), 7.78 (s, 2H, Ar-H), 7.82 (d, 2H, $^3J = 7.6$ Hz, Ar-H), 8.09 (d, 4H, $^3J = 8.2$ Hz, Ar-H), 8.36 (d, 4H, $^3J = 8.2$ Hz, Ar-H), 8.85 (d, 2H, $^3J = 4.7$ Hz, H_{β}), 8.88 (s, 2H, H_{β}), 9.03 (s, 2H, H_{β}), 9.06 ppm (d, 2H, $^3J = 4.7$ Hz, H_{β}); $^{13}\text{C NMR}$ (150 MHz, CDCl_3 , 25°C , TMS): $\delta = 29.54$, 55.35, 111.66, 113.34, 118.89, 120.38, 121.76, 127.31, 130.28, 131.17, 132.41, 134.70, 143.52, 147.54, 149.07, 149.38, 150.18, 150.50, 157.78 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 428 (5.06), 560 (3.69), 599 nm (3.45); HRMS: m/z calcd for $[\text{C}_{48}\text{H}_{30}\text{N}_6\text{O}_2\text{Zn}] [\text{M}]^+$: 786.1722, found 786.1625.

[5,10-Bis(3-methoxyphenyl)-15,20-bis(4-nitrophenyl)porphyrinato]zinc(II) 68: Following the general procedure D, 5,10-bis(3-methoxyphenyl)-15,20-bis(4-nitrophenyl)porphyrin **53** (10 mg, 0.013 mmol) was treated with 300 mg of zinc oxide to give 8 mg (0.009 mmol, 81 %) of the desired product after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. $R_f = (\text{CH}_2\text{Cl}_2/n\text{-hexane} = 1:1$, v/v); m.p. $>300^\circ\text{C}$; $^1\text{H NMR}$ (600 MHz, CDCl_3 , 25°C , TMS): $\delta = 3.98$ (s, 6H, OCH_3), 7.35 (d, 2H, $^3J = 8.2$ Hz, Ar-H), 7.67 (t, 2H, $^3J = 7.7$, 8.07 Hz, Ar-H), 7.77 (s, 2H, Ar-H), 7.82 (d, 2H, $^3J = 7.0$ Hz, Ar-H), 8.42 (d, 4H, $^3J = 7.7$ Hz, Ar-H), 8.65 (d, 4H, $^3J = 7.7$ Hz, Ar-H), 8.86 (d, 2H, $^3J = 4\text{ Hz}$, H_{β}), 8.89 (s, 2H, H_{β}), 9.03 (s, 2H, H_{β}), 9.07 ppm (d, 2H, $^3J = 4$ Hz, H_{β}); $^{13}\text{C NMR}$ (150 MHz, CDCl_3 , 25°C , TMS): $\delta = 13.89$, 22.54, 29.55, 55.35, 113.32, 118.05, 120.43, 121.90, 127.43, 131.11, 132.47, 134.83, 143.51, 147.55, 148.99, 149.57, 150.21, 150.56, 157.77 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 421 (5.13), 550 (3.97), 592 nm (3.29); HRMS: m/z calcd for $[\text{C}_{46}\text{H}_{30}\text{N}_6\text{O}_6\text{Zn}]$: 826.1518, found 826.1584.

(5,10-Diformyl-15,20-diphenylporphyrinato)copper(II) 70: A 100 ml three-necked flask equipped with a reflux condenser containing anhydrous DMF (75 eq.) was charged drop wise and slowly with POCl_3 (74 eq.) at $0-2^\circ\text{C}$ under an argon atmosphere. After 20 min the POCl_3 -DMF complex solidified. After removal of the ice-bath, 1,2-dichloroethane (5 mL) was added and the solution was heated gently to 50°C . (5,10-Diphenylporphyrinato)copper(II) **69** was added slowly at 50°C as a solution in 1,2-dichloroethane (25 mL). After complete addition the mixture was heated to 90°C for 12 h. After cooling with an ice-bath a saturated aqueous sodium acetate solution was added very carefully and then the mixture was heated to 80°C for 3 h for completion of the hydrolysis. After cooling to RT the porphyrin was extracted into CH_2Cl_2 (3 $\times$), followed by washing once with water, twice with aqueous NaHCO_3 , and then finally twice with brine. Finally, the organic phase was dried with anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. After column chromatography on silica gel ($h = 46$ cm, $\phi = 3$ cm) with CH_2Cl_2 the first fraction containing pure product was obtained as dark green crystals after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (45.1 mg, 0.077 mmol, 77 %). $R_f = 0.4$ ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 3:1$, v/v); m.p. 220°C ; UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 432 (4.45), 562 (3.50), 602 nm (3.43); MS (EI, 70 eV): m/z (%): 581 (4 %, $[\text{M}]^+$), 552 (1 %, $[\text{M} - \text{CHO}]^+$), 523 (2 %, $[\text{M} - \text{C}_2\text{H}_2\text{O}_2]^+$), 445 (2 %, $[\text{M} - \text{C}_2\text{H}_2\text{O}_2 - \text{C}_6\text{H}_6]^+$); HRMS: m/z calcd for $[\text{C}_{34}\text{H}_{22}\text{N}_4\text{O}_2\text{Cu}] [\text{M}+2\text{H}]^{2+}$: 581.1039, found 581.1042.

5,10,15-Tris(3,4,5-trifluorophenyl)porphyrin 71: Obtained from the synthesis of **42** (5 mg, 7 μmol , $<1\%$). $R_f = 0.6$ ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 1:1$, v/v); m.p. 290°C ; $^1\text{H NMR}$ (300 MHz, CDCl_3 , 25°C , TMS): $\delta = -3.21$ (br s, 1H, NH), 7.85 (m, 6H, Ar-H_{α}), 8.91, 8.87 (AB, 4H, $^3J = ^3J = ^3J = 4.9$ Hz, H_{β}), 8.99 (AB, 2H, $^3J = ^3J = 4.6$ Hz, H_{β}), 9.40 (AB, 2H, $^3J = ^3J = 4.6$ Hz, H_{β}), 10.30 ppm (s, 1H, H_{meso}); $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , 25°C , TMS): $\delta = 106.70$, 119.19, ~ 131 , 132.86, 137.62, 148.50, 151.83, , ppm; UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 410 (4.98), 506 (4.02), 538 (3.46), 581 (3.58), 634 nm (3.20); MS (70 eV, EI) m/z (%): 700 (16 %, $[\text{M}]^+$), 570 (14 %, $[\text{M} - \text{C}_6\text{H}_4\text{F}_3 + \text{H}]^+$), 350 (100 %, $[\text{M}]^{2+}$), 285 (20 %, $[\text{M} - \text{C}_6\text{H}_4\text{F}_3 + \text{H}]^{2+}$); HRMS: m/z calcd for $[\text{C}_{38}\text{H}_7\text{F}_9\text{N}_4] [\text{M}]^+$: 700.1310, found: 700.1280.

5,10,15-Tris(4-bromophenyl)porphyrin 72: Obtained from the synthesis of **41** (12 mg, 0.02 mmol, $<1\%$). $R_f = 0.48$ ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 1:1$, v/v); m.p. $>300^\circ\text{C}$; $^1\text{H NMR}$ (500 MHz, CDCl_3 , 25°C , TMS): $\delta = -3.09$ (br s, 1H, NH), 7.88 (AB, 6H, $^3J = ^3J = ^3J = 8.1$ Hz, Ar-H_{α}), 8.85 (m, 4H, H_{β}), 8.97 (AB, 2H, $^3J = ^3J = 4.7$ Hz, H_{β}), 9.32 (AB, 2H, $^3J = ^3J = 4.7$ Hz, H_{β}), 10.20 ppm (s, 1H, H_{meso}); $^{13}\text{C NMR}$ (63 MHz, CDCl_3 , 25°C , TMS): $\delta = 105.33$, 118.30, 118.99, 122.62, 129.98, 130.08, ~ 131 , 135.81, 135.95, 140.54 ppm; UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 413 (5.09), 508 (4.32), 542 (3.95), 583 (3.90), 637 nm (3.68); MS (TOF, MS, ES+, 70 eV) m/z (%): 772 (32 %, $[\text{M}]^+$); HRMS: m/z calcd for $[\text{C}_{38}\text{H}_{23}\text{N}_4\text{Br}_3] [\text{M}]^+$: 771.9473, found: 771.9454.

X-ray single crystal structure determination of 29: Growth and handling of crystals followed the protocol developed by Hope.^[36] Intensity data were collected at 118 K with a Rigaku CCD system utilizing Mo-K α radiation ($\lambda = 0.71073$ Å). The intensities were

corrected for Lorentz, polarization and extinction effects. The structure was solved with Direct Methods using the SHELXTL PLUS program system and refined against $|F^2|$ with the program XL from SHELX-97 using all data.^[37] Nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed into geometrically calculated positions and refined using a riding model. The N-H hydrogen atoms were refined as disordered over all four positions with occupancies of 50 % each. CCDC-829928 contains 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. Crystal data: C₃₄H₂₄Br₂N₄, $FW = 648.39$, red parallelepiped from CH₂Cl₂/CH₃OH, crystal size 0.5 x 0.3 x 0.2 mm, monoclinic, $C2/c$, $a = 30.27(2)$ Å, $b = 12.148(7)$ Å, $c = 15.884(10)$ Å, $\beta = 111.123(14)^\circ$, $V = 5448(6)$ Å³, $Z = 8$, $d_{\text{calc}} = 1.581$ Mg.m⁻³, $\mu(\text{Mo K}\alpha) = 3.008$ mm⁻¹, $T_{\text{min}} = 0.315$, $T_{\text{max}} = 0.585$, $\theta_{\text{max}} = 31.24^\circ$, 21370 reflections collected, 4765 independent reflections, $R_{\text{int}} = 0.1081$, 3368 reflections with $I > 2.0\sigma(I)$, 364 parameters, RI ($I > 2.0\sigma(I)$) = 0.0757, RI (all data) = 0.1092, $wR2$ (all data) = 0.2168, $S = 1.042$, $\rho_{\text{max}} = 1.744$ e.Å⁻³ (near Br atoms).

Acknowledgements

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**5,10-A₂B₂-type meso Substituted
Porphyrins – A Unique Class of
Porphyrins with Realigned Dipole
Moment**

Transition metal catalyzed transformation or direct substitution of 5,10-A₂ porphyrins is an efficient way of generating push-pull 5,10-A₂B₂ porphyrins. Those compounds exhibit interesting structural, spectroscopic and optical features and offer potential for various applications.

Supplementary Material for

5,10-A₂B₂-type meso Substituted Porphyrins – A Unique Class of Porphyrins with Realigned Dipole Moment

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Supporting information for this article is available on the WWW under <http://www.chemeurj.org/> or from the author.

Experimental data for all compounds:

General methods: Instrumentation and standard techniques used were as described elsewhere.^[8] NLO studies were carried out with open aperture Z-scan technique.^[34] Experimental set-up and sample preparation details can be found elsewhere.^[13]

Starting materials: Tripyrrane,^[35] and various 5,10-di(alkyl/aryl)porphyrins^[10b] were prepared according to published procedures.

General procedure A – Condensation method for 5,10-A₂ porphyrins: A three-necked flask was charged with a solution of tripyrrane (1 equiv.), pyrrole (1equiv.), and the corresponding aldehyde (2.1 equiv.) in dry CH₂Cl₂ (1 L). The mixture was shielded from light and stirred under argon for 30 min. TFA (100 %) was added and stirring was continued at RT for 16 h. This was followed by oxidation with DDQ (4 eq.), stirring for 60 min, and addition of triethylamine (1 mL). Typically, the reaction mixture was filtered through a short silica-gel column, eluting with CH₂Cl₂, then the solution was concentrated *in vacuo* and the residue purified by column chromatography on silica gel.

General procedure B – Reactions with organolithium compounds: A 250 mL Schlenk flask was charged with the porphyrin (1 equiv.) in 50 mL THF under argon. The solution was cooled to –70 °C for alkyl lithium reagents or 0 °C for aryl lithium reagents. The respective LiR compound was added drop wise over 15 min and the color changed from red to brown-green. The cold bath was removed and the solution was stirred for 30 min at RT. A mixture of 1 mL water in 5 mL THF was added and the color changed to green. The mixture was stirred for 15 min and, unless noted otherwise, oxidized with DDQ (5.5 equiv.) followed by stirring for 30 min. This was accompanied by a color change to red.

The solution was filtered through silica gel (CH_2Cl_2) and the solvent removed under reduced pressure. For *in situ* preparation of RLi reagents *n*-butyllithium (2 equiv.) was slowly added (ca. 1 h) under an argon atmosphere to a 100 mL Schlenk flask charged with a solution of the bromine (1 equiv.) in 10 mL dry diethyl ether at $-78\text{ }^\circ\text{C}$. The reaction mixture was then warmed up to $-40\text{ }^\circ\text{C}$ and THF was added drop wise until the aryllithium was formed as a bright pink suspension. To this vigorously stirred mixture was added rapidly a solution of the porphyrin (0.9 equiv.) in 80 mL dry THF under an argon atmosphere. The color of the reaction mixture changed from purple to brown within 30 min, subsequently 5 mL water in 5 mL dry THF was added for hydrolysis. After stirring the mixture for 10 min, a solution of 10-15 equiv. of DDQ in CH_2Cl_2 was added and the reaction mixture was stirred for another 60 min at RT.

General procedure C – Bromination of 5,10- A_2 porphyrins: A 100 mL round bottom flask was charged with the porphyrin (1 equiv.) dissolved in chloroform (50 mL) and pyridine (0.2 mL) and was cooled to $0\text{ }^\circ\text{C}$. Next *N*-bromosuccinimide (NBS) (2.5 equiv.) was added and the solution stirred for 10 min. The color changed from red to brown-red. The reaction was then quenched via addition of 4 mL acetone. The solvent was removed under reduced pressure, the residue dissolved in CH_2Cl_2 and filtered through silica gel (CH_2Cl_2). The solvent was removed under reduced pressure and the residue was washed with MeOH and dried.

General procedure D – Insertion of zinc(II): The free base porphyrin (1 equiv.) and zinc oxide (2–3 equiv.) were dissolved in CH_2Cl_2 (50 mL) and treated with three to five drops of TFA. After stirring for 10 min the color changed from green to purple-red. The reaction was followed by TLC control and the solution filtered through silica gel (CH_2Cl_2) and the solvent removed under reduced pressure.

General procedure E – Heck reactions: A 50 mL three-necked flask equipped with condenser was charged with the zinc(II)porphyrin (10 equiv.), sodium acetate (56 equiv.), palladium acetate (1 equiv.) and triphenylphosphine (4 equiv.) in 15 mL dry DMF under argon. Next, the respective olefin was added and the solution heated at $120\text{ }^\circ\text{C}$ for 24 h. The reaction was followed by TLC control. After completion of the reaction the solution was cooled to RT mixed with CH_2Cl_2 , washed with water (50 mL) and dried over Na_2SO_4 . The solvent was removed under reduced pressure and the residue was dissolved in CH_2Cl_2 . The solution was filtered through alumina (Brockmann grade III) (eluent: CH_2Cl_2 , 1 % triethylamine) and the solvent was removed under reduced pressure. Final purification involved recrystallization from CH_2Cl_2 /*n*-hexane.

General procedure F – Suzuki reactions: A Schlenk flask was charged with K_3PO_4 (20 equiv.) and anhydrous THF (60 mL) under an argon atmosphere, then porphyrin (1 equiv.), arylboronic acid or arylboronic ester (10 equiv.) and $\text{Pd}(\text{PPh}_3)_4$ (0.1 equiv.) were added. The reaction was heated at reflux for 7-10 h (TLC control) and protected from light. After completion, the solvent was evaporated and the residue was dissolved in CH_2Cl_2 . The mixture was washed with saturated NaHCO_3 , water, and brine and then dried over Na_2SO_4 . The organic solvent was evaporated and the crude product was purified by flash chromatography followed by recrystallization.

General procedure G – Insertion of nickel(II): Porphyrin (1 equiv.) and Ni(acac)₂ (1.1 equiv.) were dissolved in toluene (20 mL) and heated to reflux. The progress of the reaction was monitored by TLC. Upon completion, the solvent was removed *in vacuo* and the product was isolated after passage through a plug of silica gel using CH₂Cl₂ as the eluent.

5,10-Bis(2,6-difluorophenyl)porphyrin 16: Following the general procedure A, tripyrrane (0.500 g, 2.22 mmol), pyrrole (0.154 mL, 2.22 mmol) and 2,6-difluorobenzaldehyde (0.788 g, 5.55 mmol) were added to a dry CH₂Cl₂ solution (1 L). After stirring for 30 min, TFA (0.15 mL) was added and stirring was continued for 16 h. DDQ (2.015 g, 8.88 mmol) was added and the crude product was purified by column chromatography (CH₂Cl₂/*n*-hexane = 1:2, v/v) to give 50 mg (0.093 mmol, 5 %) of a purple powder after recrystallization from CH₂Cl₂/MeOH. *R*_f = 0.3 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -3.42 (s, 2H, NH), 7.49 (t, 4H, ³*J* = 8.2 Hz, Ar-*H*), 7.91 (m, 2H, Ar-*H*), 9.08 (d, 4H, ³*J* = 4.7 Hz, *H*_β), 9.53 (d, 4H, ³*J* = 4.7 Hz, *H*_β), 10.41 ppm (s, 2H, *H*_{meso}); compound too insoluble for ¹³C NMR; UV/VIS (CH₂Cl₂): λ_{max} (lg ε) = 418 (5.07), 516 (3.68), 550 (3.29), 593 (3.14), 649 nm (2.99); HRMS: *m/z* calcd for [C₃₂H₁₉N₄F₄] [M+H]⁺: 535.1546, found: 535.1536.

[5,10-Di(*n*-hexyl)-15,20-diphenylporphyrinato]nickel(II) 17: (5,10-Diphenylporphyrinato)nickel(II) **11** (37 mg, 0.07 mmol) was reacted with a 2.5 M solution of *n*-hexyllithium in *n*-hexane (0.17 mL, 0.43 mmol, 6 equiv.) following procedure B. Purification on silica gel (CH₂Cl₂/*n*-hexane = 1:1, v/v) and recrystallization from CH₂Cl₂/MeOH gave purple crystals (28 mg, 0.04 mmol, 58 %). *R*_f = 0.69 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. 167 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 0.90 (t, 6H, ³*J* = ³*J* = 7.3 Hz, C₅H₁₀CH₃), 1.35 (m, 8H, C₃H₆(CH₂)₂CH₃), 1.59 (m, 4H, C₂H₄CH₂C₃H₇), 2.29 (m, 4H, CH₂CH₂C₄H₉), 4.54 (t, 4H, ³*J* = ³*J* = 7.8 Hz, CH₂C₅H₁₁), 7.66 (m, 6H, Ar-*H*_m, Ar-*H*_p), 7.97 (m, 4H, Ar-*H*_o), 8.63 (br s, 2H, *H*_{β7,8}), 8.73 (AB, 2H, ³*J*_{H2,H3} = ³*J*_{H13,H17} = ³*J*_{H12,H13} = ³*J*_{H18,H17} = 5.1 Hz, *H*_{β2,13}), 9.24 (AB, 2H, ³*J*_{H3,H2} = ³*J*_{H12,H13} = 5.1 Hz, *H*_{β3,12}), 9.34 ppm (br s, 2H, *H*_{β17,18}); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 14.10, 22.65, 30.05, 31.77, 34.20, 37.41, 117.58, 118.20, 126.83, 127.57, 129.51, 129.81, 131.94, 132.22, 133.62, 140.92, 141.66, 141.74, 141.97, 142.03, ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ε) = 416 (5.21), 532 nm (4.06); MS (70 eV, EI, 350 °C): *m/z* (%): 686 (100 %, [M]⁺), 615 (89 %, [M – C₅H₁₁]⁺), 544 (50 %, [M – 2 C₅H₁₁]⁺); HRMS: *m/z* calcd for [C₄₄H₄₅N₄Ni] [M+H]⁺: 687.2998, found: 687.2936.

5-(*n*-Hexyl)-10,15-bis(4-methylphenyl)porphyrin 18: 5,10-Bis(4-methylphenyl)porphyrin **12** (32 mg, 0.07 mmol) was reacted with a 2.5 M solution of *n*-hexyllithium in *n*-hexane (0.22 mL, 0.39 mmol, 6 equiv.) following procedure B. Purification on silica gel (CH₂Cl₂/*n*-hexane = 1:1, v/v) and recrystallization from CH₂Cl₂/MeOH gave purple crystals (12 mg, 0.02 mmol, 18 %). *R*_f = 0.49 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. 168 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = -2.93 (br s, 2H, NH), 0.92 (t, 3H, ³*J* = 7.2 Hz, C₅H₁₀CH₃), 1.52 (m, 4H, C₃H₆(CH₂)₂CH₃), 1.81 (m, 2H, C₂H₄CH₂C₃H₇), 2.55 (m, 2H, CH₂CH₂C₄H₉), 2.70 (s, 6H, Ar-CH₃), 5.01 (t, 2H, ³*J* = 8.2 Hz, CH₂C₅H₁₁), 7.54 (m, 4H, Ar-*H*_m), 8.07 (m, 4H, Ar-*H*_o), 8.81, 8.85 (AB, 2H, ³*J*_{H12,H13} = ³*J*_{H13,H12} = 4.7 Hz, *H*_{β12,13}), 8.93 (AB, 1H, ³*J*_{H8,H7} = 4.9 Hz, *H*_{β8}), 8.97 (AB, 1H,

$^3J_{\text{H17,H18}} = 4.7$ Hz, $H_{\beta17}$), 9.27 (AB, 1H, $^3J_{\text{H18,H17}} = 4.7$ Hz, $H_{\beta18}$), 9.37 (AB, 1H, $^3J_{\text{H2,H3}} = 4.7$ Hz, $H_{\beta2}$), 9.47 (AB, 1H, $^3J_{\text{H7,H8}} = 4.9$ Hz, $H_{\beta7}$), 9.58 (AB, 1H, $^3J_{\text{H3,H2}} = 4.7$ Hz, $H_{\beta3}$), 10.10 ppm (s, 1H, 20- H_{meso}); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, TMS): $\delta = 14.12$, 21.53, 22.73, 29.70, 30.28, 31.93, 38.78, 104.11, 118.95, 120.02, 120.11, 127.19, 127.58, ~131, 134.38, 134.60, 137.26, 138.81 ppm; UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 413 (4.99), 510 (4.19), 545 (3.79), 585 (3.71), 641 nm (3.56); MS (70 eV, EI): m/z (%): 574 (100 %, $[\text{M}]^+$), 503 (63 %, $[\text{M} - \text{C}_5\text{H}_{11}]^+$), 413 (89 %, $[\text{M} - \text{C}_5\text{H}_{11} - \text{C}_7\text{H}_7 + \text{H}]^+$), 287 (4 %, $[\text{M}]^{2+}$), 252 (2 %, $[\text{M} - \text{C}_5\text{H}_{11}]^{2+}$); HRMS: m/z calcd for $[\text{C}_{40}\text{H}_{38}\text{N}_4] [\text{M}]^+$: 574.3096, found: 574.3094.

5,10-(*n*-Dihexyl)-15,20-bis(4-methylphenyl)porphyrin 19: 5,10-Bis(4-methylphenyl)porphyrin **12** (79 mg, 0.16 mmol) was reacted with a 2.5 M solution of *n*-hexyllithium in *n*-hexane (0.65 mL, 1.61 mmol, 10 equiv.) following procedure B. Purification on silica gel ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v) and recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ gave purple crystals (23 mg, 0.03 mmol, 22 %). $R_f = 0.55$ ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v); m.p. 172 °C; ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): $\delta = -2.64$ (br s, 2H, NH), 0.99 (t, 6H, $^3J = ^3J = 7.2$ Hz, $\text{C}_5\text{H}_{10}\text{CH}_3$), 1.44 (m, 4H, $\text{C}_4\text{H}_8\text{CH}_2\text{CH}_3$), 1.54 (m, 4H, $\text{C}_3\text{H}_6\text{CH}_2\text{C}_2\text{H}_5$), 1.83 (m, 4H, $\text{C}_2\text{H}_4\text{CH}_2\text{C}_3\text{H}_7$), 2.56 (m, 4H, $\text{CH}_2\text{CH}_2\text{C}_4\text{H}_9$), 2.73 (s, 6H, Ar- CH_3), 4.97 (t, 4H, $^3J = ^3J = 7.9$ Hz, $\text{CH}_2\text{C}_5\text{H}_{11}$), 7.56 (AB, 4H, $^3J = ^3J = ^3J = ^3J = 7.9$ Hz, Ar- H_m), 8.10 (AB, 4H, $^3J = ^3J = ^3J = ^3J = 7.9$ Hz, Ar- H_o), 8.81 (s, 2H, $H_{\beta17,18}$), 8.92 (AB, 2H, $^3J = 4.9$ Hz, $H_{\beta2,13}$), 9.44 (AB, 2H, $^3J_{\text{H3,H2}} = ^3J_{\text{H12,H13}} = 4.9$ Hz, $H_{\beta3,12}$), 9.53 ppm (s, 2H, $H_{\beta7,8}$); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, TMS): $\delta = 14.16$, 21.50, 22.75, 30.28, 31.93, 35.65, 38.81, 118.81, 119.81, 127.38, ~128, ~131, 134.42, 139.47 ppm; UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 419 (4.92), 517 (3.82), 554 (3.61), 595 (3.34), 651 nm (3.45); MS (70 eV, EI): m/z (%): 658 (16 %, $[\text{M}]^+$), 587 (67 %, $[\text{M} - \text{C}_5\text{H}_{11}]^+$), 516 (27 %, $[\text{M} - 2 \text{C}_5\text{H}_{11}]^+$), 425 (4 %, $[\text{M} - 2 \text{C}_5\text{H}_{11} - \text{C}_7\text{H}_7]^+$), 334 (4 %, $[\text{M} - 2 \text{C}_5\text{H}_{11} - 2 \text{C}_7\text{H}_7]^+$), 329 (37 %, $[\text{M}]^{2+}$), 294 (18 %, $[\text{M} - \text{C}_5\text{H}_{11}]^{2+}$), 259 (43 %, $[\text{M} - 2 \text{C}_5\text{H}_{11}]^{2+}$); HRMS: m/z calcd for $[\text{C}_{46}\text{H}_{50}\text{N}_4] [\text{M}]^+$: 658.4035, found: 658.4014.

5,10-Di(*n*-hexyl)-15,20-di(*iso*-butyl)porphyrin 20: 5,10-Di(*iso*-butyl)porphyrin **13** (30 mg, 0.07 mmol) was reacted with a 2.5 M solution of *n*-hexyllithium in *n*-hexane (0.29 mL, 0.71 mmol, 10 equiv.) following procedure B. Purification on silica gel (*n*-hexane/ethyl acetate = 5:1, v/v) and recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ gave purple crystals (11 mg, 0.02 mmol, 26 %). $R_f = 0.67$ ($\text{CH}_2\text{Cl}_2/n$ -hexane = 2:3, v/v); m.p. 97 °C; ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): $\delta = -2.65$ (br s, 2H, NH), 0.95 (t, 6H, $^3J = ^3J = 7.2$ Hz, $\text{C}_5\text{H}_{10}\text{CH}_3$), 1.19 (d, 12H, $^3J = ^3J = ^3J = 6.7$ Hz, $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 1.47 (m, 8H, $\text{C}_3\text{H}_6(\text{CH}_2)_2\text{CH}_3$), 1.82 (m, 4H, $\text{C}_2\text{H}_4\text{CH}_2\text{C}_3\text{H}_7$), 2.52 (m, 4H, $\text{CH}_2\text{CH}_2\text{C}_4\text{H}_9$), 2.75 (m, 2H, $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 4.82 (d, 4H, $^3J = ^3J = 7.3$ Hz, $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 4.93 (t, 4H, $^3J = ^3J = 8.0$ Hz, $\text{CH}_2\text{C}_5\text{H}_{11}$), 9.46 ppm (m, 8H, H_β); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, TMS): $\delta = 14.16$, 22.77, 23.33, 30.29, 31.94, 35.58, 36.68, 38.66, 43.76, 117.17, 118.51, ~129 ppm; UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 418 (4.97), 520 (4.12), 554 (3.99), 599 (3.74), 659 nm (3.83); MS (70 eV, EI): m/z (%): 590 (100 %, $[\text{M}]^+$), 547 (69 %, $[\text{M} - \text{C}_3\text{H}_7]^+$), 519 (11 %, $[\text{M} - \text{C}_5\text{H}_{11}]^+$), 295 (4 %, $[\text{M}]^{2+}$); HRMS: m/z calcd for $[\text{C}_{40}\text{H}_{54}\text{N}_4] [\text{M}]^+$: 590.4348, found: 590.4346.

5,10-Di(*n*-butyl)-15,20-bis(4-methylphenyl)porphyrin 21: Following procedure B and the details given for **27** reaction of *n*-butyllithium (4 mL of 2.5 M solution in *n*-hexane,

10 mmol), a solution of *p*-bromobenzonitrile (0.72 g, 4.0 mmol) in 15 mL of dry diethyl ether at -100 °C and 5,10-bis(4-methylphenyl)porphyrin **12** (50 mg, 0.110 mmol) gave 24 mg (0.034 mmol, 31 %), of the title compound. m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.67 (s, 2H, *NH*), 1.17 (t, 6H, ³*J* = 7., 7.6 Hz, CH₂CH₂CH₂CH₃), 2.34 (m, 4H, CH₂CH₂CH₂CH₃), 2.57 (m, 4H, CH₂CH₂CH₂CH₃), 2.76 (s, 6H, Ar-CH₃), 5.04 (t, 4H, ³*J* = 7.6, 8.2 Hz, CH₂CH₂CH₂CH₃), 7.57 (d, 4H, ³*J* = 7.6 Hz, Ar-*H*), 8.08 (d, 4H, ³*J* = 7.6 Hz, Ar-*H*), 8.78 (s, 2H, *H*_β), 8.91 (d, 2H, ³*J* = 4.7 Hz, *H*_β), 9.46 (d, 2H, ³*J* = 4.7 Hz, *H*_β), 9.6 ppm (s, 2H, *H*_β); ¹³C NMR (63 MHz, CDCl₃, 25 °C, TMS): δ = 14.06 21.36, 23.54, 29.55, 35.23, 40.77, 118.66, 119.63, 127.19, 127.27, 134.25 137.02, 139.28 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ε) = 418 (4.92), 518 (3.56), 555 (3.36), 603 (3.05), 647 nm (3.02); HRMS: *m/z* calcd for [C₄₂H₄₃N₄] [M+H]⁺: 603.3488, found: 604.3472.

5-(*n*-Butyl)-10,15-diphenylporphyrin 22: 5,10-Diphenylporphyrin **14** (1 eq.) was placed in a Schlenk flask and dissolved in dry THF under argon. The solution was cooled down -78 °C. Then *n*-butyllithium (20 eq., 2.5 M solution in *n*-hexane) and *N,N,N',N'*-tetramethylethylenediamine (3.3 eq.) were added drop wise. The mixture was allowed to warm up to RT and was stirred for 30 additional min. The reaction was quenched with 3 mL water and stirred for another 15 min. DDQ (5.5 eq.) was added. Stirring was continued for 15 min followed by filtration of the reaction mixture through 200 mL silica gel and washing with CH₂Cl₂. The eluted porphyrin fractions were evaporated to dryness. The residue was dissolved in CH₂Cl₂ and purified *via* column chromatography on silica gel with CH₂Cl₂/*n*-hexane (1:1, v/v, h = 44 cm, ø = 3 cm). The product was obtained as purple crystals after recrystallization from CH₂Cl₂/MeOH (31.7 mg, 0.06 mmol, 26 %). *R*_f = 0.6 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. 155 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = -2.90 (s, 2H, *NH*), 1.15 (t, 3H, ³*J* = 7.3 Hz, CH₂CH₃), 1.84 (m, 2H, CH₂CH₃), 2.56 (m, 2H, CH₂CH₂CH₂), 5.04 (t, 2H, ³*J* = 7.9 Hz, CH₂CH₂CH₂), 7.78 (m, 6H, Ar-*H*), 8.23 (m, 4H, Ar-*H*), 8.84 (dd, 2H, ³*J* = 4.8 Hz, *H*_β), 8.94 (d, 1H, ³*J* = 4.8 Hz, *H*_β), 8.98 (d, 1H, ³*J* = 4.6 Hz, *H*_β), 9.30 (d, 1H, ³*J* = 4.7 Hz, *H*_β), 9.40 (d, 1H, ³*J* = 4.7 Hz, *H*_β), 9.50 (d, 1H, ³*J* = 4.9 Hz, *H*_β), 9.60 (d, 1H, ³*J* = 4.7 Hz, *H*_β), 10.14 ppm (s, 1H, *H*_{meso}); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 14.2, 23.7, 34.9, 40.9, 104.3, 118.8, 119.9, 120.2, 126.5, 126.8, 127.6, 128.4, 130.4, 131.0, 131.3, 131.6, 131.8, 134.4, 134.7, 141.7, 142.8 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ε) = 412 (5.33), 509 (4.23), 543 (3.68), 585 (3.26), 641 nm (3.06); MS (EI, 70 eV): *m/z* (%): 518 (98 %, [M]⁺), 475 (100 %, [M - C₃H₇]⁺), 259 (4 %, [M]²⁺); HRMS (ES⁺): *m/z* calcd for [C₃₆H₃₁N₄] [M+H]⁺: 519.2549, found 519.2579.

5,10-Bis[4-(*N,N*-dimethylamino)phenyl]-15,20-bis(4-methylphenyl)porphyrin 23: 5,10-Bis(4-methylphenyl)porphyrin **12** (63 mg, 0.13 mmol) was reacted with 4-(*N,N*-dimethylamino)phenyllithium following procedure B. Purification on silica gel (CH₂Cl₂) and recrystallization from CH₂Cl₂/MeOH gave purple crystals (67 mg, 0.09 mmol, 71 %). *R*_f = 0.67 (CH₂Cl₂/MeOH = 95:5, v/v); m.p. >300 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = -2.68 (br s, 2H, *NH*), 2.69 (s, 6H, Ar-CH₃), 3.22 (s, 12H, N(CH₃)₂), 7.09 (AB, 4H, ³*J* = ³*J* = ³*J* = ³*J* = 8.8 Hz, 5,10-Ar-*H*_m), 7.53 (AB, 4H, ³*J* = ³*J* = ³*J* = ³*J* = 7.7 Hz, 15,20-Ar-*H*_m), 8.07 (AB, 4H, ³*J* = ³*J* = ³*J* = ³*J* = 8.8 Hz, 5,10-Ar-*H*_o), 8.09 (AB, 4H, ³*J* = ³*J* = ³*J* = ³*J* = 7.7 Hz, 15,20-Ar-*H*_o), 8.81 ppm (m, 8H, *H*_β); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 21.52, 40.74, 110.67, 119.46, 120.89, 127.35, 130.46, 134.51, 135.74,

137.15, 139.49, 149.90 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ϵ) = 425 (4.86), 522 (4.13), 565 (4.15), 598 (sh), 656 nm (3.90); MS (TOF, MS, ES⁺, 70 eV): m/z (%): 728 (100 %, [M]⁺); HRMS: m/z calcd for [C₅₀H₄₄N₆] [M]⁺: 728.3627, found: 728.3624.

5,10-Bis(4-hydroxyphenyl)-15,20-bis(4-methylphenyl)porphyrin 24: 5,10-Bis(4-methylphenyl)porphyrin **12** (52 mg, 0.11 mmol) was reacted with 4-hydroxyphenyllithium following procedure B. Purification on silica gel (CH₂Cl₂) and recrystallization from CH₂Cl₂/MeOH gave purple crystals (41 mg, 0.06 mmol, 57 %). R_f = 0.36 (CH₂Cl₂); m.p. 102 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 2.67 (s, 6H, Ar-CH₃), 7.01 (AB, 4H, ³ J = ³ J = ³ J = ³ J = 8.2 Hz, 5,10-Ar- H_m), 7.52 (AB, 4H, ³ J = ³ J = ³ J = ³ J = 7.6 Hz, 15,20-Ar- H_m), 7.98 (AB, 4H, ³ J = ³ J = ³ J = ³ J = 8.2 Hz, 5,10-Ar- H_o), 8.07 (AB, 4H, ³ J = ³ J = ³ J = ³ J = 7.6 Hz, 15,20-Ar- H_o), 8.84 ppm (m, 8H, H_β); UV/VIS (CH₂Cl₂): λ_{max} (lg ϵ) = 420 (4.88), 517 (3.83), 553 (3.64), 592 (3.42), 648 nm (3.43); MS (TOF, MS, ES⁺, 70 eV): m/z (%): 674 (27 %, [M]⁺), 337 (2 %, [M]²⁺); HRMS: m/z calcd for [C₄₆H₃₄N₄O₂] [M]⁺: 674.2682, found: 674.2645.

5,10-Bis[4-(*N,N*-dimethylamino)phenyl]-15,20-bis(3-methoxyphenyl)porphyrin 25: 5,10-Bis(3-methoxyphenyl)porphyrin **15** (79 mg, 0.16 mmol) was reacted with 4-(*N,N*-dimethylamino)phenyllithium following procedure B. Purification on silica gel (CH₂Cl₂/MeOH = 98 : 2, v/v) gave two fractions. The first contained the monarylated species **26** and the second the title compound. Recrystallization from CH₂Cl₂/*n*-hexane gave purple crystals (28 mg, 0.04 mmol, 32 %). R_f = 0.67 (CH₂Cl₂/MeOH = 95:5, v/v); m.p. 236 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = -2.62 (br s, 2H, NH), 3.22 (s, 12H, N(CH₃)₂), 3.99 (s, 6H, OCH₃), 7.10 (AB, 4H, ³ J = ³ J = ³ J = ³ J = 8.6 Hz, 5,10-Ar- H_m), 7.33 (m, 2H, 15,20-Ar- H_p), 7.64 (m, 2H, 15,20-Ar- H_m), 7.84 (m, 4H, 15,20-Ar- H_o), 8.11 (AB, 4H, ³ J = ³ J = ³ J = ³ J = 8.6 Hz, 5,10-Ar- H_o), 8.88 (m, 4H, $H_{\beta 2,7,8,13}$), 8.97 ppm (m, 4H, $H_{\beta 3,12,17,18}$); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 40.69, 55.47, 110.68, 113.48, 119.02, 120.45, 127.42, 127.69, 130.38, 135.73, 143.77, 149.95, 157.95 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ϵ) = 425 (5.00), 522 (4.17), 565 (4.16), 596 (sh), 656 nm (3.90); MS (EI, 70 eV): m/z (%): 760 (7 %, [M]⁺), 380 (100 %, [M]²⁺); HRMS: m/z calcd for [C₅₀H₄₄N₆O₂] [M]⁺: 760.3526, found: 760.3500.

5-[4-(*N,N*-Dimethylamino)phenyl]-10,15-bis(3-methoxyphenyl)porphyrin 26: Obtained from the synthesis of **25** as purple crystals (5 mg, 0.01 mmol, 5 %). R_f = 0.4 (CH₂Cl₂/MeOH = 95:5, v/v); m.p. 98 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = -2.97 (br s, 2H, NH), 3.23 (s, 6H, N(CH₃)₂), 3.99 (s, 6H, OCH₃), 7.09 (AB, 2H, ³ J = ³ J = 8.8 Hz, 5-Ar- H_m), 7.33 (m, 2H, 10,15-Ar- H_p), 7.65 (m, 2H, 10,15-Ar- H_m), 7.82 (m, 2H, 10,15-Ar- H_o), 8.06 (AB, 2H, ³ J = ³ J = 8.8 Hz, 5-Ar- H_o), 8.91, 8.97 (AB, 4H, ³ $J_{H7,H8}$ = ³ $J_{H8,H7}$ = ³ $J_{H12,H13}$ = ³ $J_{H13,H12}$ = 4.7 Hz, $H_{\beta 7,8,12,13}$), 9.03 (AB, 2H, ³ $J_{H3,H2}$ = ³ $J_{H17,H18}$ = 4.7 Hz, $H_{\beta 3,17}$), 9.29 (AB, 2H, ³ $J_{H2,H3}$ = ³ $J_{H18,H17}$ = 4.7 Hz, $H_{\beta 2,18}$), 10.15 ppm (s, 1H, H_{meso}); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 40.73, 55.52, 104.27, 110.60, 113.52, 119.14, 120.59, 127.56, 127.79, 135.68, 143.28, 149.27, 158.08 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ϵ) = 413 (4.66), 512 (4.27), 550 (4.06), 585 (3.99), 642 nm (3.90); MS (EI, 70 eV): m/z (%): 641 (48 %, [M]⁺), 321 (100 %, [M]²⁺); HRMS: m/z calcd for [C₄₂H₃₅N₅O₂] [M]⁺: 641.2791, found: 641.2771.

5,10-Bis(4-ethynylphenyl)-15,20-bis(4-methylphenyl)porphyrin 27: Following procedure B, *n*-butyllithium (4 mL of 2.5M solution in *n*-hexane, 10 mmol) was slowly added (ca. 1h) under an argon atmosphere to a 100 mL Schlenk flask charged with a solution of *p*-bromophenylethyne (0.91 g, 5.0 mmol) in 15 mL of dry diethyl ether at -70 °C. The reaction mixture was then warmed to -40 °C and THF was added drop wise until the aryllithium was formed as a white/pink suspension. To this vigorously stirred mixture was added rapidly a solution of 5,10-bis(4-methylphenyl)porphyrin **12** (56 mg, 0.125 mmol) in 50 mL of dry THF. The color of the mixture changed from deep purple to brown within 30 min, subsequently a mixture of 5 mL water in 5 mL of THF was added for hydrolysis. After stirring of the mixture for 20 min, a solution of DDQ (283 mg, 1.25 mmol) in CH₂Cl₂ was added and the reaction mixture was stirred for another 60 min at RT. The crude product was subjected to column chromatography using CH₂Cl₂/*n*-hexane (1:1, v/v) to give 24 mg (0.034 mmol, 31 %), of a purple solid after recrystallization from CH₂Cl₂/MeOH. *R*_f = 0.73 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.78 (s, 2H, *NH*), 2.73 (s, 6H, Ar-CH₃), 3.34 (s, 2H, -C≡CH), 7.58 (d, 4H, ³*J* = 7.6 Hz, Ar-*H*), 7.92 (d, 4H, ³*J* = 8.2 Hz, Ar-*H*), 8.11 (d, 4H, ³*J* = 7.6 Hz, Ar-*H*), 8.20 (d, 4H, ³*J* = 7.6 Hz, Ar-*H*), 8.84 (m, 4H, *H*_β), 8.90 ppm (m, 4H, *H*_β); ¹³C NMR (63 MHz, CDCl₃, 25 °C, TMS): δ = 21.09, 77.84, 83.22, 118.42, 120.29, 121.14, 127.01, 130.17, 134.06, 134.19, 137.03, 138.61, 142.37; UV/VIS (DMF): λ_{max} (lg ε) = 420 (4.92), 516 (3.61), 551 (3.38), 592 (3.20), 655 nm (3.19); HRMS: *m/z* calcd for [C₅₀H₃₅N₄] [M+H]⁺: 691.2862, found: 691.2858.

5,10-Bis(4-ethynylphenyl)-15,20-bis(2,6-difluorophenyl)porphyrin 28: Following procedure B and the details given for **27** reaction of *p*-bromophenylethyne (0.55 g, 3.0 mmol) and 5,10-bis(2,6-difluorophenyl)porphyrin **16** (40 mg, 0.075 mmol) gave 14 mg (0.019 mmol, 25 %) of the title compound. *R*_f = 0.6 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.71 (s, 2H, *NH*), 3.51 (s, 2H, -C≡CH), 7.43 (t, 4H, ³*J* = 8.2 Hz, Ar-*H*), 7.81 (m, 2H, Ar-*H*), 7.96 (t, 4H, ³*J* = 8.2 Hz, Ar-*H*), 8.23 (t, 4H, ³*J* = 7.6 Hz, Ar-*H*), 8.92 (m, 4H, *H*_β), 9.02 ppm (m, 4H, *H*_β); UV/VIS (DMF): λ_{max} (lg ε) = 414 (5.09), 508 (3.83), 543 (3.18), 585 (3.30), 637 nm (2.89); HRMS: *m/z* calcd for [C₄₈H₂₇F₄N₄] [M+H]⁺: 735.2172, found: 735.2197.

5,10-Dibromo-15,20-bis(4-methylphenyl)porphyrin 29: 5,10-Bis(4-methylphenyl)porphyrin **12** (93 mg, 0.19 mmol) was reacted with NBS (84 mg, 0.47 mmol) following procedure C to yield purple crystals (102 mg, 0.16 mmol, 83 %). *R*_f = 0.59 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. 285 °C (dec.); ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = -2.91 (br s, 2H, *NH*), 2.69 (s, 6H, Ar-CH₃), 7.54 (AB, 4H, ³*J* = ³*J* = ³*J* = ³*J* = 7.9 Hz, Ar-*H*_m), 8.01 (AB, 4H, ³*J* = ³*J* = ³*J* = ³*J* = 7.9 Hz, Ar-*H*_o), 8.74 (s, 2H, *H*_{β17,18}), 8.82 (AB, 2H, ³*J* = ³*J* = 4.8 Hz, *H*_{β2,13}), 9.52 (AB, 2H, ³*J* = ³*J* = 4.8 Hz, *H*_{β3,12}), 9.54 ppm (s, 2H, *H*_{β7,8}); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 21.53, 103.15, 121.75, 127.55, ~131, 134.40, 137.73, 138.57 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ε) = 423 (5.03), 523 (4.21), 558 (4.07), 602 (3.77), 659 nm (3.81); MS (TOF, MS, ES⁺, 70 eV): *m/z* (%): 646 (49 %, [M]⁺); HRMS: *m/z* calcd for [C₃₄H₂₄N₄Br₂] [M]⁺: 646.0368, found: 646.0347.

[5,10-Dibromo-15,20-bis(4-methylphenyl)porphyrinato]zinc(II) 30: 5,10-Dibromo-15,20-bis(4-methylphenyl)porphyrin **29** (83 mg, 0.13 mmol) was reacted following

procedure D. Column chromatography on silica gel (CH_2Cl_2) gave a single product. Recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{H}_2\text{O}$ gave purple crystals (66 mg, 0.09 mmol, 72 %). $R_f = 0.42$ ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 2:1$, v/v); m.p. $>310^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3 , 25°C , TMS): $\delta = 2.75$ (s, 6H, Ar- CH_3), 7.61 (AB, 4H, $^3J = ^3J = ^3J = 7.7$ Hz, Ar- H_m), 8.06 (AB, 4H, $^3J = ^3J = ^3J = 7.7$ Hz, Ar- H_o), 8.76 (s, 2H, $H_{\beta 7,8}$), 8.77 (AB, 2H, $^3J = ^3J = 4.7$ Hz, $H_{\beta 2,13}$), 8.86 (s, 2H, $H_{\beta 17,18}$), 9.29 ppm (AB, 2H, $^3J = ^3J = 4.7$ Hz, $H_{\beta 3,12}$); ^{13}C NMR (75 MHz, CDCl_3 , 25°C , TMS): $\delta = 21.32$, 103.73, 122.44, 127.44, 132.29, 132.50, 132.65, 133.20, 134.52, 137.60, 139.29, 148.43, 149.07, 150.92, 151.08 ppm; UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 424 (5.09), 557 (4.21), 597 nm (3.83); MS (TOF, MS, ES+, 70 eV): m/z (%): 708 (39 %, $[\text{M}]^+$); HRMS: m/z calcd for $[\text{C}_{34}\text{H}_{22}\text{N}_4\text{Br}_2\text{Zn}] [\text{M}]^+$: 707.9503, found: 707.9469.

[5,10-Dibromo-15,20-bis(4-methylphenyl)porphyrinato]nickel(II) 31: Following the general procedure G, 5,10-dibromo-15,20-bis(4-methylphenyl)porphyrin **29** (100 mg, 0.154 mmol) and $\text{Ni}(\text{acac})_2$ (43.5 mg, 0.169 mmol) were dissolved in toluene (20 mL) and heated to reflux for 6 h to give 80 mg (0.113 mmol, 80 %) after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. $R_f = 0.7$ ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 1:1$, v/v); m.p. $>300^\circ\text{C}$; ^1H NMR (400 MHz, 25°C , CDCl_3): $\delta = 2.66$ ppm (s, 6H, CH_3), 7.49 (d, 4H, $^3J = 7.6$ Hz, Ar- H), 7.82 (d, 4H, $^3J = 8.2$ Hz, Ar- H), 8.66 (s, 2H, H_β), 8.74 (d, 2H, $^3J = 5.3$ Hz, H_β), 9.39 (d, 2H, $^3J = 5.3$ Hz, H_β), 9.46 ppm (s, 2H, H_β); UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 421 (5.08), 538 (3.92), 589 nm (3.38); HRMS: m/z calcd for $[\text{C}_{34}\text{H}_{22}\text{N}_4\text{Br}_2\text{Ni}] [\text{M}]^+$: 701.9565, found 701.9681; elemental analysis calcd (%) for $\text{C}_{34}\text{H}_{22}\text{N}_4\text{Br}_2\text{Ni}$ (705.07): C 57.91, H 3.15, N 7.95, found: C 57.65, H 3.40, N 8.01.

{(all-*E*)-5,10-Bis[4-(2-butoxycarbonylethenyl)]-15,20-bis(4-methylphenyl)porphyrinato}zinc(II) 32: [5,10-Dibromo-15,20-bis(4-methylphenyl)porphyrinato]zinc(II) **30** (77.7 mg, 0.11 mmol) was reacted with butyl acrylate (1.00 mL, 7.01 mmol) following procedure E to yield purple crystals (60 mg, 0.07 mmol, 64 %). $R_f = 0.34$ (CH_2Cl_2 , 1 % triethylamine, v/v, alumina); m.p. 176°C ; ^1H NMR (500 MHz, CDCl_3 , 25°C , TMS): $\delta = 1.08$ (t, 6H, $^3J = ^3J = 7.4$ Hz, $\text{C}_3\text{H}_6\text{CH}_3$), 1.60 (m, 4H, $\text{C}_2\text{H}_4\text{CH}_2\text{CH}_3$), 1.88 (m, 4H, $\text{CH}_2\text{CH}_2\text{C}_2\text{H}_5$), 2.70 (s, 6H, Ar- CH_3), 4.43 (t, 4H, $^3J = ^3J = 6.8$ Hz, $\text{CH}_2\text{C}_3\text{H}_7$), 6.73 (d, 2H, $^3J = ^3J = 15.7$ Hz, $\text{CH}=\text{CH}-\text{CO}$), 7.54 (d, 4H, $^3J = ^3J = ^3J = 7.5$ Hz, Ar- H_m), 7.99 (d, 4H, $^3J = ^3J = ^3J = 7.5$ Hz, Ar- H_o), 8.70 (s, 2H, $H_{\beta 17,18}$), 8.84 (AB, 2H, $^3J = ^3J = 4.7$ Hz, $H_{\beta 2,13}$), 9.39 (AB, 2H, $^3J = ^3J = 4.7$ Hz, $H_{\beta 3,12}$), 9.52 (s, 2H, $H_{\beta 7,8}$), 10.23 ppm (d, 2H, $^3J = ^3J = 15.7$ Hz, $\text{CH}=\text{CH}-\text{CO}$); ^{13}C NMR (126 MHz, CDCl_3 , 25°C , TMS): $\delta = 13.74$, 19.46, 21.26, 31.06, 64.66, 112.98, 123.51, 127.19, 128.77, 129.80, 130.09, 131.80, 132.78, 134.44, 137.21, 140.03, 146.86, 148.97, 149.41, 149.67, 150.31, 166.38 ppm; UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 438 (5.14), 572 (4.00), 616 nm (3.92); MS (TOF, MS, ES+, 70 eV): m/z (%): 805 (100 %, $[\text{M}+\text{H}]^+$); HRMS: m/z calcd for $[\text{C}_{48}\text{H}_{45}\text{N}_4\text{O}_4\text{Zn}] [\text{M}+\text{H}]^+$: 805.2732, found: 805.2706.

{(all-*E*)-5,10-Bis(4-methylphenyl)-15,20-bis[4-(3-oxobut-1-enyl)]porphyrinato}zinc(II) 33: [5,10-Dibromo-15,20-bis(4-methylphenyl)porphyrinato]zinc(II) **30** (77.7 mg, 0.11 mmol) was reacted with methyl vinyl ketone (0.57 mL, 7.02 mmol) following procedure E to yield purple crystals (35 mg, 0.05 mmol, 50 %). $R_f = 0.5$ (CH_2Cl_2 , 5 % MeOH, v/v); m.p. 215°C ; ^1H NMR (300 MHz,

CDCl₃, 25 °C, TMS): δ = 2.50 (s, 6H, CO-CH₃), 2.71 (s, 6H, Ar-CH₃), 6.58 (d, 2H, ³J = ³J = 15.7 Hz, CH=CH-CO), 7.55 (AB, 4H, ³J = ³J = ³J = ³J = 7.5 Hz, Ar-H_m), 8.00 (d, 4H, ³J = ³J = ³J = ³J = 7.5 Hz, Ar-H_o), 8.80 (s, 2H, H_{β17,18}), 8.89 (AB, 2H, ³J = ³J = 4.7 Hz, H_{β2,13}), 9.22 (s, 2H, H_{β7,8}), 9.28 (AB, 2H, ³J = ³J = 4.7 Hz, H_{β3,12}), 9.80 ppm (d, 2H, ³J = ³J = 15.7 Hz, CH=CH-CO); ¹³C NMR (63 MHz, CDCl₃, 25 °C, TMS): δ = 20.78, 27.29, 112.81, 123.21, 126.81, 128.53, 129.33, 131.04, 131.61, 132.49, 133.88, 136.96, 139.20, 144.93, 148.25, 148.83, 149.32, 149.98, 196.33 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ϵ) = 443 (4.44), 577 (4.18), 621 nm (4.14); MS (TOF, MS, ES⁺, 70 eV): *m/z* (%): 689 (100 %, [M+H]⁺); HRMS: *m/z* calcd for [C₄₂H₃₃N₄O₂Zn] [M]⁺: 689.1895, found: 689.1889.

{(all-E)-5,10-Bis(4-methylphenyl)-15,20-bis[2-(3-nitro-phenyl)vinyl]porphyrinato}zinc(II) 34: Following the general procedure E, [5,10-Dibromo-15,20-bis(4-methylphenyl)porphyrinato]zinc(II) **30** (100 mg, 0.140 mmol), was dissolved in DMF (50 mL) under a nitrogen atmosphere. The 3-nitrostyrene (1.36 mL, 9.8 mmol), sodium acetate (65 mg, 0.784 mmol), palladium acetate (3.1 mg, 0.014 mmol) and triphenylphosphine (14.7 mg, 0.056 mmol) were added and the temperature was raised to 120 °C for 16 h (TLC control). The crude product was extracted with CH₂Cl₂ and washed with water. The product was purified by silica gel column chromatography using CH₂Cl₂/*n*-hexane (1:1, v/v) and gave 70 mg (0.082 mmol, 60 %) of the desired compound after recrystallization from CH₂Cl₂/MeOH. *R*_f = 0.12 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. > 300 °C; ¹H NMR (600 MHz, CD₂Cl₂, 25 °C, TMS): δ = 2.76 (s, 6H, CH₃), 6.58 (d, 2H, ³J = 16 Hz, vinyl), 7.49 (d, 4H, ³J = 7.7 Hz, Ar-H), 7.69 (t, 4H, ³J = 7.7 Hz, Ar-H), 7.91 (d, 4H, ³J = 7.7 Hz, Ar-H), 7.93 (d, 2H, ³J = 7.7 Hz, Ar-H), 8.29 (d, 2H, ³J = 8.2 Hz, Ar-H), 8.65 (s, 2H, H_β), 8.71 (d, 2H, ³J = 16 Hz, vinyl), 8.88 (s, 2H, H_β), 8.93 (d, 2H, ³J = 4.4 Hz, H_β), 9.23 ppm (d, 2H, ³J = 4.4 Hz, H_β); ¹³C NMR (125 MHz, CD₂Cl₂, 25 °C, TMS): δ = 138.67, 139.29, 146.90, 148.53, 148.92, 149.72, 150.38 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 445 (5.12), 584 (3.98), 630 nm (3.80).

{(all-E)-5,10-Bis(4-methylphenyl)-15,20-[2-(3-nitrophenyl)vinyl]porphyrinato}nickel(II) 35: Following the general procedure E, [5,10-dibromo-15,20-bis(4-methylphenyl)porphyrinato]nickel(II) **31** (25 mg, 0.140 mmol), 3-nitrostyrene (0.35 mL, 2.48 mmol), sodium acetate (16 mg, 0.196 mmol), palladium acetate (0.8 mg, 0.003 mmol) and triphenylphosphine (3.7 mg, 0.014 mmol) in DMF (50 mL) gave 5 mg (0.006 mmol, 34 %) of a purple compound after recrystallization from CH₂Cl₂/MeOH. *R*_f = 0.47 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 2.66 (s, 6H, CH₃), 6.71 (d, 2H, ³J = 15.8 Hz, alkene-H), 7.49 (d, 4H, ³J = 7.6 Hz, Ar-H), 7.64 (t, 2H, ³J = 7.6 Hz, Ar-H), 7.82 (d, 4H, ³J = 7.6 Hz, Ar-H), 7.93 (d, 2H, ³J = 7.7 Hz, Ar-H), 8.22 (d, 2H, ³J = 7.6 Hz, Ar-H), 8.59 (s, 2H, Ar-H), 8.61 (s, 2H, H_β), 8.73 (d, 2H, ³J = 4.7 Hz, H_β), 9.14 (d, 2H, ³J = 4.7 Hz, H_β), 9.18 (d, 2H, ³J = 15.8 Hz, alkene-H), 9.23 ppm (s, 2H, H_β); ¹³C NMR (150 MHz, CD₂Cl₂, 25 °C, TMS): δ = 21.44, 29.34, 112.65, 120.79, 122.47, 127.78, 129.56, 129.84, 130.91, 132.22, 133.38, 137.61, 138.51, 139.87, 141.39, 142.31, 148.63 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 444 (4.87), 563 (3.83), 614 nm (3.75).

5,10-Dibromo-15,20-diphenylporphyrin 36: Following the general procedure C, 5,10-diphenylporphyrin **14** (90 mg, 0.19 mmol) and NBS (87 mg, 0.48 mmol) gave 84 mg (0.14 mmol, 70 %) of a purple solid after recrystallization from CH₂Cl₂/MeOH. R_f = 0.59 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. > 300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.88 (s, 2H, NH), 7.78 (m, 4H, Ar-*H*), 8.17 (m, 4H, Ar-*H*), 8.78 (m, 4H, *H* _{β}), 9.57 (m, 4H, *H* _{β}); UV/VIS (CH₂Cl₂): $\lambda_{\max}$ (lg ϵ) = 421 (4.98), 522 (3.57), 557 (3.33), 600 (2.89), 663 nm (2.86).

5,10-Dibromo-15,20-bis(3-methoxyphenyl)porphyrin 37: 5,10-Bis(3-methoxyphenyl)porphyrin **15** (77 mg, 0.15 mmol) was reacted with NBS (66 mg, 0.37 mmol) following procedure C to yield red crystals (74 mg, 0.11 mmol, 74 %). R_f = 0.43 (CH₂Cl₂/*n*-hexane = 2:1, v/v); m.p. 198 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = -2.82 (br s, 2H, NH), 3.97 (s, 6H, Ar-OCH₃), 7.33 (m, 2H, Ar-*H*_{*p*}), 7.63 (m, 2H, Ar-*H*_{*m*}), 7.72 (m, 4H, Ar-*H*_{*o*}), 8.77 (s, 2H, *H* _{β 17,18}), 8.87 (AB, 2H, ³*J* = ³*J* = 4.8 Hz, *H* _{β 2,13}), 9.56 (AB, 2H, ³*J* = ³*J* = 4.8 Hz, *H* _{β 3,12}), 9.63 ppm (s, 2H, s, *H* _{β 7,8}); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 55.51, 103.44, 113.71, 120.50, 121.19, 127.52, 127.65, ~131, 142.76, 158.03 ppm; UV/VIS (CH₂Cl₂): $\lambda_{\max}$ (lg ϵ) = 423 (5.01), 521 (3.44), 556 (3.82), 600 (3.56), 658 nm (3.55); MS (TOF, MS, ES+, 70 eV): *m/z* (%): 678 (52 %, [M]⁺); HRMS: *m/z* calcd for [C₃₄H₂₄N₄Br₂O₂] [M]⁺: 678.0266, found: 678.0243.

5,10-Dibromo-15,20-bis(2,6-difluorophenyl)porphyrin 38: Following the general procedure C, 5,10-bis(2,6-difluorophenyl)porphyrin **16** (200 mg, 0.374 mmol) and NBS (166 mg, 0.94 mmol) gave 150 mg (0.21 mmol, 58 %) of a purple solid after recrystallization from CH₂Cl₂/MeOH; R_f = 0.48 (CH₂Cl₂/*n*-hexane = 1:1, v/v). m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.92 (s, 2H, NH), 7.43 (t, 4H, ³*J* = 7.8 Hz, Ar-*H*), 7.83 (m, 2H, Ar-*H*), 8.83 (s, 4H, *H* _{β}), 9.36 (d, 2H, ³*J* = 4.7 Hz, *H* _{β}), 9.59 ppm (d, 2H, ³*J* = 4.7 Hz, *H* _{β}); UV/VIS (CH₂Cl₂): $\lambda_{\max}$ (lg ϵ) = 419 (4.94), 516 (3.73), 555 (3.18), 596 (3.11), 649 nm (2.49); HRMS (MS ES+): *m/z* calcd for [C₃₂H₁₆N₄Br₂F₄] [M]⁺: calcd 689.9678 found 689.9372.

5,10-Dibromo-15,20-di(*n*-pentylporphyrin 39: Following the general procedure C 5,10-di(*n*-pentyl)porphyrin (90 mg, 0.2 mmol) and NBS (89 mg, 0.5 mmol) gave 73 mg (0.12 mmol, 60 %) of a purple solid after recrystallization from CH₂Cl₂/MeOH. R_f = 0.62 (CH₂Cl₂/*n*-hexane = 2:1, v/v); m.p. >198 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -3.15 (s, 2H, NH), 1.00 (t, 6H, ³*J* = 7.3, 7.0 Hz, CH₂CH₂CH₂CH₂CH₃), 1.56 (m, 4H, CH₂CH₂CH₂CH₂CH₃), 1.77 (m, 4H, CH₂CH₂CH₂CH₂CH₃), 2.44 (m, 4H, CH₂CH₂CH₂CH₂CH₃), 4.77 (t, 4H, ³*J* = 7.7, 8 Hz, CH₂CH₂CH₂CH₂CH₃), 9.20 (m, 4H, *H* _{β}), 9.49 ppm (m, 4H, *H* _{β}); ¹³C NMR (150 MHz, 25 °C, CDCl₃): δ = 13.86, 22.71, 29.40, 32.40, 35.24, 38.25, 101.90, 121.45 ppm; UV/VIS (DMF): $\lambda_{\max}$ (lg ϵ) = 422 (4.48), 524 (3.48), 559 (3.25), 605 (2.78), 664 nm (3.14); HRMS (MS ES+): *m/z* calcd for [C₃₀H₃₃N₄Br₂] [M+H]⁺: 607.1072, found: 607.1097.

5,10-Dibromo-15,20-di(*n*-hexylporphyrin 40: Following the general procedure C 5,10-di(*n*-hexyl)porphyrin (70 mg, 0.14 mmol) and NBS (65 mg, 0.36 mmol) gave 47 mg (0.07 mmol, 50 %) of a purple solid after recrystallization from CH₂Cl₂/MeOH. m.p. >300 °C; R_f = 0.6 (CH₂Cl₂/*n*-hexane = 1:1, v/v); ¹H NMR (400 MHz, CDCl₃, 25 °C,

TMS): δ = -2.81 (s, 2H, NH), 0.97 (t, 6H, 3J = 7.6, 7.01 Hz, CH₂CH₂CH₂CH₂CH₂CH₃), 1.42 (m, 4H, CH₂CH₂CH₂CH₂CH₂CH₃), 1.45 (m, 4H, CH₂CH₂CH₂CH₂CH₂CH₃), 1.82 (m, 4H, CH₂CH₂CH₂CH₂CH₂CH₃), 2.49 (m, 4H, CH₂CH₂CH₂CH₂CH₂CH₃), 4.87 (t, 4H, 3J = 8.2, 7.6 Hz, CH₂CH₂CH₂CH₂CH₂CH₃), 9.52 (m, 4H, H_β), 9.62 ppm (m, 4H, H_β); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): δ = 14.15, 22.73, 30.25, 31.86, 35.66, 38.83, 102.06, 121.72 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 420 (4.88), 522 (3.63), 558 (3.51), 603 (3.26), 663 nm (3.18); HRMS (MS ES⁺): m/z calcd for [C₃₂H₃₇N₄Br₂]: [M+H]⁺ calcd: 637.1364, found 637.1379.

5,10-Bis(4-bromophenyl)porphyrin 41: 4-Bromobenzaldehyde (0.74 g, 4 mmol) was reacted according to a procedure given before.^[12] Column chromatography on silica gel (CH₂Cl₂/ *n*-hexane = 1:4, v/v) gave the 5,10,15-tris(4-bromophenyl)porphyrin **71** as the first fraction, followed by the title compound and then traces of (4-bromophenyl)porphyrin. Recrystallization from CH₂Cl₂/MeOH gave 46 mg (0.07 mmol, 4 %) of purple crystals. R_f = 0.38 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS): δ = -3.45 (br s, 2H, NH), 7.89 (AB, 4H, 3J = 3J = 3J = 3J = 8.1 Hz, Ar- H_m), 8.05 (AB, 4H, 3J = 3J = 3J = 3J = 8.1 Hz, Ar- H_o), 8.89 (s, 2H, $H_{\beta 7,8}$), 8.96 (AB, 2H, 3J = 3J = 4.7 Hz, $H_{\beta 2,13}$), 9.30 (AB, 2H, 3J = 3J = 4.7 Hz, $H_{\beta 3,12}$), 9.38 (s, 2H, $H_{\beta 17,18}$), 10.17 ppm (s, 2H, H_{meso}); ¹³C NMR (63 MHz, CDCl₃, 25 °C, TMS): δ = 104.53, 118.41, 122.52, 129.90, ~131, 135.89, 140.98, ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ϵ) = 407 (5.36), 502 (4.33), 534 (3.67), 575 (3.87), 629 nm (3.38); MS (70 eV, EI): m/z (%): 620 (9 %, [M]^{•+}), 540 (4 %, [M - Br]⁺), 464 (3 %, [M - C₆H₄Br + Br]^{•+}), 310 (14 %, [M]²⁺); HRMS: m/z calcd for [C₃₂H₂₀N₄Br₂] [M]⁺: 618.0055, found: 618.0061.

5,10-Bis(3,4,5-trifluorophenyl)porphyrin 42: 3,4,5-Trifluorobenzaldehyde (0.64 g, 4 mmol) was reacted according to a procedure given before.^[12] Column chromatography on silica gel (CH₂Cl₂/*n*-hexane = 1:1, v/v) gave the 5,10,15-tris(3,4,5-trifluorophenyl)porphyrin **72** as the first fraction, followed by the title compound and then traces of (3,4,5-trifluorophenyl)porphyrin. Recrystallization from CH₂Cl₂/MeOH gave 10 mg (0.02 mmol, 1 %) of purple crystals. R_f = 0.47 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. 285 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = -3.52 (br s, 2H, NH), 7.85 (m, 4H, Ar- H_o), 8.92 (s, 2H, $H_{\beta 2,13}$), 8.98 (AB, 2H, 3J = 3J = 4.4 Hz, $H_{\beta 3,12}$), 9.39 (AB, 2H, 3J = 3J = 4.6 Hz, $H_{\beta 7,8}$), 9.45 (AB, 2H, 3J = 3J = 4.6 Hz, $H_{\beta 17,18}$), 10.27 ppm (s, 2H, H_{meso}); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 105.27, 119.16, 130.96, 131.41, 132.32, 138.26, 148.31, 151.67 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ϵ) = 405 (5.03), 500 (4.09), 532 (3.47), 573 (3.73), 627 nm (3.06); MS (70 eV, EI, 350 °C): m/z (%): 570 (100 %, [M]^{•+}), 439 (11 %, [M - C₆H₂F₃]⁺), 285 (50 %, [M]²⁺), 251 (6 %, [M - C₆H₂F₃]²⁺); HRMS: m/z calcd for [C₃₂H₁₆F₆N₄] [M]⁺: 570.1279, found: 570.1259.

5,10-Bis(4-methoxycarbonylphenyl)-15,20-bis(4-methylphenyl)porphyrin 43: Following the general procedure F 5,10-dibromo-15,20-bis(4-methylphenyl)porphyrin **29** (33 mg, 0.05 mmol), 4-methoxycarbonylphenyl boronic acid (90 mg, 0.5 mmol), Pd(PPh₃)₄ (5.8 mg, 0.005 mmol) and K₃PO₄ (212 mg, 1 mmol) in THF (60 mL) gave 20 mg (0.02 mmol, 52 %) of a purple solid after recrystallization from CH₂Cl₂/MeOH. R_f = 0.28 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.76 (s, 2H, NH), 2.70 (s, 6H, CH₃), 4.13 (s, 6H, OCH₃), 7.59 (d, 4H, 3J = 7.6

Hz, Ar-*H*), 8.12 (d, 4H, $^3J = 7.6$ Hz, Ar-*H*), 8.32 (d, 4H, $^3J = 8.2$ Hz, Ar-*H*), 8.46 (d, 4H, $^3J = 8.2$ Hz, Ar-*H*), 8.80 (d, 2H, $^3J = 4.7$ Hz, H_β), 8.82 (s, 2H, H_β), 8.90 (s, 2H, H_β), 8.92 ppm (d, 2H, $^3J = 4.7$ Hz, H_β); ^{13}C NMR (125 MHz, CDCl_3 , 25 °C, TMS): $\delta = 21.46$, 52.37, 118.09, 120.85, 126.80, 127.03, 127.48, 129.12, 129.76, 134.10, 137.09, 138.54, 146.66, 166.89 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 420 (4.92), 516 (4.27), 551 (4.08), 581 (3.87), 655 nm (3.97); HRMS (MS ES⁺): m/z calcd for $[\text{C}_{50}\text{H}_{39}\text{N}_4\text{O}_4]$ $[\text{M}+\text{H}]^+$: 759.2971, found 759.2941.

5,10-Bis(4-cyanophenyl)-15,20-bis(4-methylphenyl)porphyrin 44: Following the general procedure F 5,10-dibromo-15,20-bis(4-methylphenyl)porphyrin **29** (30 mg, 0.046 mmol), 4-cyanophenyl boronic acid (68 mg, 0.46 mmol), $\text{Pd}(\text{PPh}_3)_4$ (5.3 mg, 0.0046 mmol) and K_3PO_4 (196 mg, 0.925 mmol) in THF (50 mL) gave 15 mg (0.021 mmol, 47 %) of a purple solid after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. $R_f = 0.34$ ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v); m.p. >300 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = -2.79$ (s, 2H, *NH*), 2.74 (s, 6H, CH_3), 7.60 (d, 4H, $^3J = 8.2$ Hz, Ar-*H*), 8.10 (m, 8H, Ar-*H*), 8.36 (d, 4H, $^3J = 8.2$ Hz, Ar-*H*), 8.75 (d, 2H, $^3J = 4.7$ Hz, H_β), 8.78 (s, 2H, H_β), 8.92 (s, 2H, H_β), 8.95 ppm (d, 2H, $^3J = 4.7$ Hz, H_β); ^{13}C NMR (125 MHz, CDCl_3 , 25 °C, TMS): $\delta = 21.10$, 111.51, 118.57, 121.13, 130.13, 134.29, 137.11, 137.28, 138.30, 146.55, ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 420 (4.94), 515 (3.79), 551 (3.62), 584 (3.44), 655 nm (3.68); HRMS (MS ES⁺): m/z calcd for $[\text{C}_{48}\text{H}_{33}\text{N}_6]$ $[\text{M}+\text{H}]^+$: 693.2767, found 693.2734.

5,10-Bis(4-methylphenyl)-15,20-bis(4-nitrophenyl)porphyrin 45: Following the general procedure F 5,10-dibromo-15,20-bis(4-methylphenyl)porphyrin **29** (30 mg, 0.0462 mmol), 4-nitrophenylboronic acid pinacol ester (116 mg, 0.462 mmol), $\text{Pd}(\text{PPh}_3)_4$ (5.3 mg, 0.0046 mmol) and K_3PO_4 (196 mg, 0.925 mmol) in THF (50 mL) gave 16 mg (0.021 mmol, 47 %) of a purple solid after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. $R_f = 0.5$ ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v); m.p. > 300 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = -2.76$ (s, 2H, *NH*), 2.74 (s, 6H, CH_3), 7.60 (d, 4H, $^3J = 7.6$ Hz, Ar-*H*), 8.11 (d, 4H, $^3J = 7.6$ Hz, Ar-*H*), 8.42 (d, 4H, $^3J = 8.2$ Hz, Ar-*H*), 8.67 (d, 4H, $^3J = 8.2$ Hz, Ar-*H*), 8.76 (d, 2H, $^3J = 4.7$ Hz, H_β), 8.80 (s, 2H, H_β), 8.92 (s, 2H, H_β), 8.96 ppm (d, 2H, $^3J = 4.7$ Hz, H_β); ^{13}C NMR (125 MHz, CDCl_3 , 25 °C, TMS): $\delta = 21.09$, 116.47, 121.48, 127.12, 134.66, 137.33, 138.25, 147.31, 148.53 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 421 (4.90), 516 (3.64), 552 (3.46), 584 (3.34), 655 nm (3.60); HRMS (MS ES⁺): m/z calcd for $[\text{C}_{46}\text{H}_{32}\text{N}_6\text{O}_4]$ $[\text{M}+\text{H}]^+$: 733.2563, found 733.2573.

5,10-Bis(4-methylphenyl)-15,20-bis(3-nitrophenyl)porphyrin 46: Following the general procedure F 5,10-dibromo-15,20-bis(4-methylphenyl)porphyrin **29** (33 mg, 0.05 mmol), 4-methoxycarbonylphenyl boronic acid (90 mg, 0.5 mmol), $\text{Pd}(\text{PPh}_3)_4$ (5.8 mg, 0.005 mmol), K_3PO_4 (212 mg, 1 mmol) in THF (60 mL) gave 10 mg (0.013 mmol, 30 %) of a purple solid after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. $R_f = 0.3$ ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v); m.p. >300 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = -2.77$ (s, 2H, *NH*), 2.74 (s, 6H, CH_3), 7.60 (d, 4H, $^3J = 7.6$ Hz, Ar-*H*), 7.99 (t, 2H, $^3J = 7.6$ Hz, Ar-*H*), 8.13 (d, 2H, $^3J = 7\text{ Hz}$, Ar-*H*), 8.57 (m, 2H, Ar-*H*), 8.72 (d, 4H, $^3J = 8.2$ Hz, Ar-*H*), 8.79 (d, 2H, $^3J = 4.7$ Hz, H_β), 8.93 (s, 2H, H_β), 8.96 (d, 2H, $^3J = 4.7$ Hz, H_β), 9.11 ppm (s, 2H, H_β); ^{13}C NMR (125 MHz, CDCl_3 , 25 °C, TMS): $\delta = 29.59$, 116.46, 121.52, 122.88, 127.44, 127.66, 128.20, 134.38, 137.61, 138.62, 139.69, 143.64, 146.84 ppm; UV/VIS

(DMF): $\lambda_{\max}$ (lg ϵ) = 421 (4.90), 516 (3.64), 551 (3.46), 589 (3.34), 646 nm (3.16); HRMS (MS ES⁺): m/z calcd for [C₄₄H₃₂N₄O₄] [M+H]⁺: 733.2563, found 733.2540.

5,10-Bis(3-Cyanophenyl)-15,20-bis(4-methylphenyl)porphyrin (47): Following the general procedure F, 5,10-dibromo-15,20-bis(4-methylphenyl)porphyrin **29** (20 mg, 0.0308 mmol), 4-cyanophenyl boronic acid (46 mg, 0.308 mmol), and Pd(PPh₃)₄ (3.6 mg, 0.003 mmol), K₃PO₄ (131 mg, 0.617 mmol) in THF (60 mL) gave 10 mg (0.014 mmol, 47 %). m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.79 (s, 2H, NH), 2.74 (s, 6H, -CH₃), 7.61 (d, 4H, ³J = 7 Hz, Ar-H), 7.92 (m, 2H, Ar-H), 8.14 (m, 6H, Ar-H), 8.49 (t, 2H, ³J = 7, 6.4 Hz, Ar-H), 8.55 (m, 2H, Ar-H), 8.74 (d, 2H, ³J = 4.7 Hz, H _{β}), 8.78 (s, 2H, H _{β}), 8.93 (s, 2H, H _{β}), 8.96 ppm (d, 2H, ³J = 4.7 Hz, H _{β}); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): δ = 21.10, 110.92, 116.32, 118.48, 121.10, 127.25, 131.16, 134.10, 136.62, 137.26, 137.84, 138.32, 142.99 ppm; UV/VIS (DMF): $\lambda_{\max}$ (log ϵ) = 419 (4.88), 514 (3.61), 548 (3.44), 589 (3.31), 646 nm (3.38); HRMS (MS ES⁺): m/z calcd for [C₄₈H₃₂N₆] [M+H]⁺: 693.2767, found 693.2743.

5,10-Bis(4-methoxycarbonylphenyl)-15,20-diphenylporphyrin 48: Following the general procedure F 5,10-dibromo-15,20-diphenylporphyrin **36** (30 mg, 0.048 mmol), 4-methoxycarbonylphenylboronic acid (86 mg, 0.48 mmol), Pd(PPh₃)₄ (5.5 mg, 0.005 mmol) and K₃PO₄ (205 mg, 0.967 mmol) in THF (50 mL) gave 10 mg (0.013 mmol, 30 %) of a purple solid after recrystallization from CH₂Cl₂/MeOH. R_f = 0.5 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. > 300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.76 (s, 2H, NH), 4.14 (s, 6H, CH₃), 7.79 (d, 4H, ³J = 7.6 Hz, Ar-H), 8.24 (d, 4H, ³J = 8.2 Hz, Ar-H), 8.33 (d, 4H, ³J = 8.2 Hz, Ar-H), 8.47 (d, 4H, ³J = 8.2 Hz, Ar-H), 8.82 (m, 4H, H _{β}), 8.90 ppm (m, 4H, H _{β}); ¹³C NMR (125 MHz, CDCl₃, 25 °C, TMS): δ = 45.57, 51.99, 118.30, 126.29, 127.44, 129.19, 134.07, 141.47, 146.45, 166.85 ppm; UV/VIS (DMF): $\lambda_{\max}$ (lg ϵ) = 418 (4.94), 514 (3.80), 548(3.61), 588 (3.34), 646 nm (3.32); HRMS (MS ES⁺): m/z calcd for [C₄₈H₃₅N₄O₄] [M+H]⁺: 731.2658, found 731.2625.

5,10-Bis(4-cyanophenyl)-15,20-diphenylporphyrin 49: Following the general procedure F 5,10-dibromo-15,20-diphenylporphyrin **36** (20 mg, 0.032 mmol), 4-cyanophenylboronic acid (47 mg, 0.32 mol), Pd(PPh₃)₄ (3.7 mg, 0.003 mmol), K₃PO₄ (136 mg, 0.644 mmol) in THF (50 mL) gave 6 mg (0.009 mmol, 29 %) of a purple solid after recrystallization from CH₂Cl₂/MeOH. R_f = 0.3 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.80 (s, 2H, NH), 7.80 (m, 4H, Ar-H), 8.11 (d, 4H, ³J = 7.6 Hz, Ar-H), 8.23 (d, 4H, ³J = 7.6 Hz, Ar-H), 8.37 (d, 4H, ³J = 8.2 Hz, Ar-H), 8.76 (d, 2H, ³J = 4.7 Hz, H _{β}), 8.80 (s, 2H, H _{β}), 8.90 (s, 2H, H _{β}), 8.93 ppm (d, 2H, ³J = 4.7 Hz, H _{β}); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): δ = 29.26, 111.58, 117.12, 118.54, 120.94, 126.37, 127.56, 130.14, 130.23, 134.08, 134.52, 141.22, 146.48 ppm; UV/VIS (DMF): $\lambda_{\max}$ (lg ϵ) = 418 (4.98), 514 (3.64), 548 (3.26), 588 (2.87), 645 nm (2.56); HRMS (MS ES⁺): m/z calcd for [C₄₆H₂₉N₆][M+H]⁺: 665.2454, found 665.2468.

5,10-Bis(4-nitrophenyl)-15,20-diphenylporphyrin 50: Following the general procedure F 5,10-dibromo-15,20-diphenylporphyrin **36** (20 mg, 0.032 mmol), 4-nitrophenyl boronic pinacol ester (80 mg, 0.32 mmol), Pd(PPh₃)₄ (3.7 mg, 0.003 mmol), K₃PO₄ (135 mg, 0.64 mmol) in THF (60 mL) gave 10 mg (0.014 mmol, 43 %) of the title compound. R_f = 0.3 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS):

δ = -2.77 (s, 2H, NH), 7.82 (m, 4H, Ar-*H*), 8.23 (d, 4H, 3J = 6.4 Hz, Ar-*H*), 8.42 (d, 4H, 3J = 8.8 Hz, Ar-*H*), 8.67 (d, 4H, 3J = 8.8 Hz, Ar-*H*), 8.78 (d, 2H, 3J = 4.7 Hz, H_β), 8.82 (s, 2H, H_β), 8.90 (s, 2H, H_β), 8.94 ppm (d, 2H, 3J = 4.7 Hz, H_β); UV/VIS (DMF): $\lambda_{\max}$ (lg ϵ) = 421 (4.95), 516 (3.69), 552 (3.58), 592 (3.29), 646 nm (3.45); HRMS (MS ES+) m/z calcd for [C₄₄H₂₉N₆O₄] [M+H]⁺: 705.2250, found 705.2278.

5,10-Bis(4-methoxycarbonylphenyl)-15,20-bis(3-methoxyphenyl)porphyrin 51:

Following the general procedure F 5,10-dibromo-15,20-bis(3-methoxyphenyl)porphyrin **37** (20 mg, 0.029 mmol), 4-methoxycarbonylphenylboronic acid (52 mg, 0.293 mmol), Pd(PPh₃)₄ (3.3 mg, 0.0029 mmol), K₃PO₄ (124 mg, 0.587 mmol) in THF (50 mL) gave 9 mg (0.011 mmol, 32 %) of a purple solid after recrystallization from CH₂Cl₂/MeOH. R_f = 0.3 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. > 300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.78 (s, 2H, NH), 4.01 (s, 6H, OCH₃), 4.14 (s, 6H, OCH₃), 7.37 (d, 2H, 3J = 8.2 Hz, Ar-*H*), 7.67 (t, 2H, 3J = 8.2 Hz, Ar-*H*), 7.82 (d, 4H, 3J = 7.6 Hz, Ar-*H*), 8.33 (d, 4H, 3J = 7.6 Hz, Ar-*H*), 8.47 (d, 4H, 3J = 7.6 Hz, Ar-*H*), 8.82 ppm (m, 4H, H_β), 8.93 (m, 4H, H_β); ¹³C NMR (125 MHz, CDCl₃, 25 °C, TMS): δ = 52.33, 55.37, 113.46, 118.79, 120.35, 127.81, 129.48, 134.40, 143.06, 146.74, 157.80, 167.18 ppm; UV/VIS (DMF): $\lambda_{\max}$ (lg ϵ) = 419 (4.96), 514 (3.74), 549 (3.47), 588 (3.34), 646 nm (3.36); HRMS (MS ES+): m/z calcd for [C₅₀H₃₉N₄O₆] [M+H]⁺: 791.2870, found 791.2865.

5,10-Bis(4-cyanophenyl)-15,20-bis(3-methoxyphenyl)porphyrin 52: Following the general procedure F 5,10-dibromo-15,20-bis(3-methoxyphenyl)porphyrin **37** (30 mg, 0.044 mmol), 4-cyanophenyl boronic acid (64 mg, 0.44 mmol), Pd(PPh₃)₄ (5 mg, 0.004 mmol) and K₃PO₄ (186 mg, 0.88 mmol) in THF (60 mL) gave 15 mg (0.020 mmol, 47 %) of a purple solid after recrystallization from CH₂Cl₂/MeOH. R_f = 0.3 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. > 300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.82 (s, 2H, NH), 4.02 (s, 6H, OCH₃), 7.38 (m, 2H, Ar-*H*), 7.69 (t, 4H, 3J = 8.2 Hz, Ar-*H*), 7.81 (m, 4H, Ar-*H*), 8.10 (d, 4H, 3J = 8.2 Hz, Ar-*H*), 8.36 (d, 4H, 3J = 7.6 Hz, Ar-*H*), 8.77 (d, 2H, 3J = 4.7 Hz, H_β), 8.79 (s, 2H, H_β), 8.94 (s, 2H, H_β), 8.97 ppm (d, 2H, 3J = 4.68 Hz, H_β); ¹³C NMR (125 MHz, CDCl₃, 25 °C, TMS): δ = 55.07, 111.58, 113.19, 115.85, 117.18, 118.53, 120.56, 127.19, 130.14, 134.51, 142.51, 146.47, 157.55 ppm; UV/VIS (DMF): $\lambda_{\max}$ (lg ϵ) = 419 (4.90), 513 (3.56), 547 (3.25), 592 (3.16), 643 nm (3.18); HRMS (MS ES+): m/z calcd for [C₄₈H₃₃N₆O₂] [M+H]⁺: 725.2655, found 725.2641.

5,10-Bis(3-methoxyphenyl)-15,20-bis(4-nitrophenyl)porphyrin 53: Following the general procedure F, 5,10-dibromo-15,20-bis(3-methoxyphenyl)porphyrin **37** (20 mg, 0.03 mmol), 4-nitrophenylboronic acid pinacol ester (74 mg, 0.3 mmol), Pd(PPh₃)₄ (3.4 mg, 0.003 mmol), K₃PO₄ (125 mg, 0.59 mmol) in THF gave 13 mg (0.017 mmol, 56 %) of the title compound. R_f = (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.78 (s, 2H, NH), 4.02 (s, 6H, OCH₃), 7.69 (t, 2H, 3J = 8.2, 7.6 Hz, Ar-*H*), 7.82 (t, 4H, 3J = 7.6 Hz, Ar-*H*), 8.42 (d, 4H, 3J = 8.8 Hz, Ar-*H*), 8.67 (d, 4H, 3J = 8.2 Hz, Ar-*H*), 8.77 (d, 2H, 3J = 4.7 Hz, H_β), 8.81 (s, 2H, H_β), 8.94 (s, 2H, H_β), 8.98 ppm (d, 2H, 3J = 4.7 Hz, H_β); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): δ = 55.08, 113.20, 116.74, 120.75, 121.73, 126.97, 127.47, 134.64, 142.46, 147.34, 148.43, 157.56 ppm; UV/VIS (DMF): $\lambda_{\max}$ (lg ϵ) = 421 (4.89), 516 (3.58), 551 (3.36), 592 (3.28),

655 nm (3.48); HRMS (MS ES⁺): m/z calcd for [C₄₆H₃₃N₆O₆] [M+H]⁺: 765.2462, found 765.2495.

5,10-Bis(2,6-difluorophenyl)-15,20-bis(4-methoxycarbonylphenyl)porphyrin 54:

Following the general procedure F, 5,10-dibromo-15,20-bis(2,6-difluorophenyl)porphyrin **38** (20 mg, 0.028 mmol), 4-methoxycarbonylphenylboronic acid (63 mg, 0.35 mmol), Pd(PPh₃)₄ (3.2 mg, 0.003 mmol) and K₃PO₄ (154 mg, 0.722 mmol) in THF (30 mL) gave 7 mg (0.008 mmol, 30 %) of purple solid after recrystallization from CH₂Cl₂/MeOH. R_f = 0.5 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.72 (s, 2H, NH), 4.15 (s, 6H, CH₃), 7.42 (t, 4H, ³ J = 6.4 Hz, Ar-*H*), 7.83 (m, 2H, Ar-*H*), 8.34 (d, 4H, ³ J = 8.2 Hz, Ar-*H*), 8.38 (d, 4H, ³ J = 8.2 Hz, Ar-*H*), 8.93 ppm (m, 8H, *H*_β); UV/VIS (CH₂Cl₂): $\lambda_{\max}$ (lg ϵ) = 416 (4.98), 511 (3.77), 547 (3.30), 590 (3.27), 647 nm (2.95); HRMS (MS ES⁺): m/z calcd for [C₄₈H₃₁N₄O₄F₄] [M+H]⁺: 803.2281, found 803.2261.

5,10-Bis(4-cyanophenyl)-15,20-bis(2,6-difluorophenyl)porphyrin 55: Following the general procedure F, 5,10-dibromo-15,20-bis(2,6-difluorophenyl)porphyrin **38** (20 mg, 0.028 mmol), 4-cyanophenylboronic acid (52 mg, 0.35 mol), Pd(PPh₃)₄ (3.2 mg, 0.003 mmol), K₃PO₄ (154 mg, 0.722 mmol) in THF (30 mL) gave 6 mg (0.008 mmol, 28 %) of purple solid after recrystallization from CH₂Cl₂/MeOH. R_f = 0.5 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. > 300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.78 (s, 2H, NH), 7.42 (t, 4H, ³ J = 8.7, 7.6 Hz, Ar-*H*), 7.85 (m, 2H, Ar-*H*), 8.10 (d, 4H, ³ J = 8.2 Hz, Ar-*H*), 8.35 (d, 4H, ³ J = 8.2 Hz, Ar-*H*), 8.78 (s, 2H, *H*_β), 8.81 (d, 2H, ³ J = 4.7 Hz, *H*_β), 8.91 (d, 2H, ³ J = 4.7 Hz, *H*_β), 8.93 ppm (s, 2H, *H*_β); UV/VIS (CH₂Cl₂): $\lambda_{\max}$ (lg ϵ) = 417 (5.06), 511 (3.81), 548 (3.26), 585 (3.31), 645 nm (2.96); HRMS (MS ES⁺): m/z calcd for [C₄₆H₂₅N₆F₄] [M+H]⁺: 737.2077, found 737.2088.

5,10-Bis(2,6-difluorophenyl)-15,20-bis(4-nitrophenyl)porphyrin 56: Following the general procedure F, 5,10-dibromo-15,20-bis(2,6-difluorophenyl)porphyrin **38** (20 mg, 0.028 mmol), 4-nitrophenyl boronic pinacol ester (91 mg, 0.364 mmol), Pd(PPh₃)₄ (3.2 mg, 0.003 mmol), K₃PO₄ (154 mg, 0.722 mmol) in THF (30 mL) gave 5 mg (0.006 mmol, 22 %) of the title compound. R_f = 0.5 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.75 (s, 2H, NH), 7.44 (t, 4H, ³ J = 8.2 Hz, Ar-*H*), 7.85 (m, 2H, Ar-*H*), 8.42 (d, 4H, ³ J = 8.7 Hz, Ar-*H*), 8.68 (d, 4H, ³ J = 8.2 Hz, Ar-*H*), 8.81 (s, 2H, *H*_β), 8.83 (d, 2H, ³ J = 4.7 Hz, *H*_β), 8.92 (d, 2H, ³ J = 4.7 Hz, *H*_β), 8.94 ppm (s, 2H, *H*_β); UV/VIS (CH₂Cl₂): $\lambda_{\max}$ (lg ϵ) = 418 (5.11), 512 (3.96), 550 (3.32), 591 (3.39), 646 nm (2.43); HRMS (MS ES⁺): m/z calcd for [C₄₄H₂₅N₆O₄F₄] [M+H]⁺: 777.1873, found 777.1884.

5,10-Bis(4-methoxycarbonylphenyl)-15,20-di(*n*-pentyl)porphyrin 57: Following the general procedure F, 5,10-dibromo-15,20-di(*n*-pentyl)porphyrin **39** (30 mg, 0.049 mmol), 4-methoxycarbonylphenylboronic acid (88 mg, 0.49 mmol), Pd(PPh₃)₄ (5.7 mg, 0.005 mmol), K₃PO₄ (209 mg, 0.986 mmol) in THF (50 mL) gave 20 mg (0.026 mmol, 57 %) of the title compound. R_f = 0.35 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.68 (s, 2H, NH), 1.02 (t, 6H, ³ J = 7.6, 7.0 Hz, CH₂CH₂CH₂CH₂CH₃), 1.68 (m, 4H, CH₂CH₂CH₂CH₂CH₃), 1.85 (m, 4H, CH₂CH₂CH₂CH₂CH₃), 2.58 (m, 4H, CH₂CH₂CH₂CH₂CH₃), 4.14 (s, 6H, OCH₃), 5.03 (t,

4H, $^3J = 8.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 8.28 (d, 4H, $^3J = 8.2$ Hz, Ar-*H*), 8.45 (d, 4H, $^3J = 8.2$ Hz, Ar-*H*), 8.71 (s, 2H, H_β), 8.83 (d, 2H, $^3J = 4.7$ Hz, H_β), 9.49 (d, 2H, $^3J = 4.7$ Hz, H_β), 9.61 ppm (s, 2H, H_β); ^{13}C NMR (150 MHz, CDCl_3 , 25 °C, TMS): $\delta = 13.35$, 29.63, 32.33, 35.25, 38.21, 51.80, 116.90, 120.40, 126.79, 127.69, 129.01, 129.75, 134.04, 146.67, 166.92 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 418 (4.93), 518 (4.03), 550 (3.95), 592 (3.85), 651 nm (3.88); HRMS (MS ES+): m/z calcd for $[\text{C}_{46}\text{H}_{47}\text{N}_4\text{O}_4]$ $[\text{M}+\text{H}]^+$: 719.3597, found 719.3620.

5,10-Bis(4-cyanophenyl)-15,20-di(*n*-pentyl)porphyrin 58: Following the general procedure F, 5,10-dibromo-15,20-di(*n*-pentyl)porphyrin **39** (40 mg, 0.065 mmol), 4-cyanophenyl boronic acid (95.5 mg, 0.65 mmol), $\text{Pd}(\text{PPh}_3)_4$ (7.5 mg, 0.007 mmol), K_3PO_4 (279 mg, 1.31 mmol) in THF (60 mL) gave 17 mg (0.026 mmol, 40 %) of the title compound. $R_f = 0.4$ ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v); m.p. >300 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = -2.70$ (s, 2H, 2 NH), 1.01 (t, 6H, $^3J = 7$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.28 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.83 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.58 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 5.03 (t, 4H, $^3J = 8.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 8.08 (d, 4H, $^3J = 8.2$ Hz, Ar-*H*), 8.31 (d, 4H, $^3J = 8.2$ Hz, Ar-*H*), 8.67 (s, 2H, H_β), 8.77 (d, 2H, $^3J = 4.7$ Hz, H_β), 9.52 (d, 2H, $^3J = 4.7$ Hz, H_β), 9.62 ppm (s, 2H, H_β); ^{13}C NMR (150 MHz, CDCl_3 , 25 °C, TMS): $\delta = 13.71$, 22.33, 29.27, 32.30, 35.29, 38.28, 111.37, 115.77, 118.62, 121.10, 130.09, 134.46, 146.69 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 419 (4.97), 517 (3.75), 552 (3.58), 592 (3.27), 650 nm (3.41); HRMS (MS ES+): m/z calcd for $[\text{C}_{44}\text{H}_{41}\text{N}_6]$ $[\text{M}+\text{H}]^+$: 653.3393, found 653.3382.

5,10-Bis(4-nitrophenyl)-15,20-di(*n*-pentyl)porphyrin 59: Following the general procedure F, 5,10-dibromo-15,20-di(*n*-pentyl)porphyrin **39** (40 mg, 0.065 mmol), 4-nitrophenyl boronic pinacol ester (161 mg, 0.65 mmol), $\text{Pd}(\text{PPh}_3)_4$ (7.5 mg, 0.007 mmol), K_3PO_4 (279 mg, 1.31 mmol) in THF (60 mL) gave 22 mg (0.031 mmol, 47 %). $R_f = 0.59$ ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v); m.p. >300 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = -2.67$ (s, 2H, NH), 1.02 (t, 6H, $^3J = 7.6$, 7 Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.30 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.83 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.58 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 5.03 (t, 4H, $^3J = 8.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 8.36 (d, 4H, $^3J = 8.7$ Hz, Ar-*H*), 8.65 (d, 4H, $^3J = 8.2$ Hz, Ar-*H*), 8.69 (s, 2H, H_β), 8.78 (d, 2H, $^3J = 4.7$ Hz, H_β), 9.53 (d, 2H, $^3J = 4.7$ Hz, H_β), 9.62 ppm (s, 2H, H_β); ^{13}C NMR (150 MHz, CDCl_3 , 25 °C, TMS): $\delta = 13.71$, 29.1, 32.31, 35.31, 38.30, 115.33, 121.44, 134.59, 147.23, 148.66 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 420 (4.90), 517 (3.73), 554 (3.45), 594 (3.15), 651 nm (3.33); HRMS (MS ES+): m/z calcd for $[\text{C}_{42}\text{H}_{41}\text{N}_6\text{O}_4]$ $[\text{M}+\text{H}]^+$: 693.3189, found 693.3160.

5,10-Di(*n*-hexyl)-15,20-bis(4-methoxycarbonylphenyl)porphyrin 60: Following the general procedure F, 5,10-dibromo-15,20-di(*n*-hexyl)porphyrin **40** (25 mg, 0.04 mmol), 4-methoxyphenylboronic acid (72 mg, 0.4 mmol), $\text{Pd}(\text{Ph}_3)_4$ (4.6 mg, 0.004 mmol), K_3PO_4 (169 mg, 0.8 mmol) in THF gave 10 mg (0.013 mmol, 34 %) of the title compound. $R_f = 0.54$ ($\text{CH}_2\text{Cl}_2/n$ -hexane = 1:1, v/v); m.p. >300 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS) $\delta = -2.68$ (s, 2H, NH), 0.96 (t, 6H, $^3J = 7.6$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.42 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.54 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.85 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.56 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 4.14 (s, 6H,

OCH₃), 5.03 (t, 4H, ³J = 8.9, 7.6 Hz, CH₂CH₂CH₂CH₂CH₂CH₃), 8.28 (d, 4H, ³J = 8.2 Hz, Ar-H), 8.45 (d, 4H, ³J = 8.2 Hz, Ar-H), 8.71 (s, 2H, H_β), 8.83 (d, 2H, ³J = 4.7 Hz, H_β), 9.49 (d, 2H, ³J = 4.7 Hz, H_β), 9.61 ppm (s, 2H, H_β); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): δ = 13.68, 22.27, 24.91, 28.90, 29.62, 31.46, 35.41, 38.46, 51.93, 119.47, 127.49, 134 ppm; UV/VIS (DMF): λ_{max} (lg ε) = 416 (4.96), 518 (3.86), 552 (3.66), 598 (3.47), 655 nm (3.56); HRMS (MS ES⁺): *m/z* calcd for [C₄₈H₅₁N₄O₄] [M+H]⁺: 747.3910, found 747.3907.

5,10-Bis(4-cyanophenyl)-15,20-di(*n*-hexyl)porphyrin 61: Following the general procedure F 5,10-dibromo-15,20-di(*n*-hexyl)porphyrin **40** (30 mg, 0.047 mmol), 4-cyanophenylboronic acid (69 mg, 0.47 mmol), Pd(PPh₃)₄ (5.4 mg, 0.005 mmol), K₃PO₄ (200 mg, 0.942 mmol) in THF gave 13 mg (0.019 mmol, 40 %) of the title compound. *R*_f = 0.2 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.66 (s, 2H, NH), 0.96 (t, 6H, ³J = 7.6, 7 Hz, CH₂CH₂CH₂CH₂CH₂CH₃), 1.43 (m, 4H, CH₂CH₂CH₂CH₂CH₂CH₃), 1.54 (m, 4H, CH₂CH₂CH₂CH₂CH₂CH₃), 1.85 (m, 4H, CH₂CH₂CH₂CH₂CH₂CH₃), 2.55 (m, 4H, CH₂CH₂CH₂CH₂CH₂CH₃), 5.04 (t, 4H, ³J = 8.2, 7.6 Hz, CH₂CH₂CH₂CH₂CH₂CH₃), 8.09 (d, 4H, ³J = 8.2 Hz, Ar-H), 8.32 (d, 4H, ³J = 8.2 Hz, Ar-H), 8.67 (s, 2H, H_β), 8.77 (d, 2H, ³J = 4.7 Hz, H_β), 9.52 (d, 2H, ³J = 4.7 Hz, H_β), 9.63 ppm (s, 2H, H_β); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): δ = 14.06, 22.66, 31.91, 35.70, 39.09, 112.11, 115.83, 119.11, 121.64, 130.59, 134.89, 147.13, 148.08 ppm; UV/VIS (DMF): λ_{max} (lg ε) = 418 (4.87), 517 (4.53), 551 (3.43), 592 (3.13), 650 nm (3.31); HRMS (MS ES⁺): *m/z* calcd for [C₄₆H₄₅N₆] [M+H]⁺: 681.3706, found 681.3710.

5,10-Di(*n*-hexyl)-15,20-bis(4-nitrophenyl)porphyrin 62: Following the general procedure F, 5,10-dibromo-15,20-di(*n*-hexyl)porphyrin **40** (33 mg, 0.047 mmol), 4-nitrophenyl boronic pinacol ester (117 mg, 0.47 mmol), Pd(PPh₃)₄ (5.4 mg, 0.005 mmol), K₃PO₄ (200 mg, 0.942 mmol) in THF (60 mL) gave 20 mg (0.027 mmol, 59 %) of the title compound. *R*_f = 0.6 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (600 MHz, CDCl₃, 25 °C, TMS): δ = -2.66 (s, 2H, NH), 0.98 (t, 6H, ³J = 7.3 Hz, CH₂CH₂CH₂CH₂CH₂CH₃), 1.44 (m, 4H, CH₂CH₂CH₂CH₂CH₂CH₃), 1.56 (m, 4H, CH₂CH₂CH₂CH₂CH₂CH₃), 1.85 (m, 4H, CH₂CH₂CH₂CH₂CH₂CH₃), 2.58 (m, 4H, CH₂CH₂CH₂CH₂CH₂CH₃), 5.02 (t, 4H, ³J = 8.1 Hz, CH₂CH₂CH₂CH₂CH₂CH₃), 8.36 (d, 4H, ³J = 8.1 Hz, Ar-H), 8.65 (d, 4H, ³J = 8.1 Hz, Ar-H), 8.69 (s, 2H, H_β), 8.78 (d, 2H, ³J = 4.7 Hz, H_β), 9.52 (d, 2H, ³J = 4.7 Hz, H_β), 9.62 ppm (s, 2H, H_β); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): δ = 22.63, 30.22, 31.81, 35.73, 38.95, 115.72, 121.70, 122.07, 134.88, 135.02, 147.77, 149.37 ppm; UV/VIS (DMF): λ_{max} (lg ε) = 421 (5.02), 519 (3.89), 554 (3.76), 595 (3.47), 652 nm (3.55); HRMS (MS ES⁺): *m/z* calcd for [C₄₄H₄₅N₆O₄] [M+H]⁺: 721.3502, found 721.3520.

[5,10-Bis(4-ethynylphenyl)-15,20-bis(4-methylphenyl)porphyrinato]zinc (II) 63: Following the general procedure D, 5,10-bis(4-ethynylphenyl)-15,20-bis(4-methylphenyl)porphyrin **27** (15 mg, 0.022 mmol) was treated with 300 mg of zinc oxide to give 13 mg (0.017 mmol, 81 %) of the desired product after recrystallization from CH₂Cl₂/MeOH. *R*_f = 0.4 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (600 MHz, CDCl₃, 25 °C, TMS): δ = 2.77 (s, 6H, CH₃), 3.34 (s, 2H, C≡CH), 7.59 (d, 4H, ³J = 7.7 Hz, Ar-H), 7.92 (d, 4H, ³J = 7.7 Hz, Ar-H), 8.13 (d, 4H, ³J = 7.7 Hz, Ar-H), 8.22 (d,

4H, $^3J = 7.7$ Hz, Ar-*H*), 8.95 (m, 4H, H_β), 9.02 ppm (m, 4H, H_β); ^{13}C NMR (150 MHz, CDCl_3 , 25 °C, TMS): $\delta = 14.02, 21.38, 29.52, 77.97, 83.62, 119.79, 121.26, 127.19, 130.26, 131.43, 132.03, 134.19, 134.32, 137.09, 139.56, 143.37, 149.62, 150.27$ ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 427 (4.94), 560 (3.64), 601 nm (3.40); HRMS: m/z calcd for $[\text{C}_{50}\text{H}_{32}\text{N}_4\text{Zn}] [\text{M}]^+$: 752.1918, found 752.1916.

[5,10-Bis(4-methoxycarbonylphenyl)-15,20-bis(4-

methylphenyl)porphyrinato]zinc(II) 64: Following the general procedure D, 5,10-bis(4-methoxycarbonylphenyl)-15,20-bis(4-methylphenyl)porphyrin **43** (15 mg, 0.019 mmol) was treated with 300 mg of zinc oxide to give 13 mg (0.015 mmol, 81 %) of the title compound after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. $R_f = 0.1$ ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 1:1$, v/v); m.p. >300 °C; ^1H NMR (600 MHz, CDCl_3 , 25 °C, TMS): $\delta = 2.75$ (s, 6H, CH_3), 4.13 (s, 6H, OCH_3), 7.59 (d, 4H, $^3J = 7.2$ Hz, Ar-*H*), 8.13 (d, 4H, $^3J = 7.5$ Hz, Ar-*H*), 8.33 (d, 4H, $^3J = 7.9$ Hz, Ar-*H*), 8.46 (d, 4H, $^3J = 7.5$ Hz, Ar-*H*), 8.91 (m, 4H, H_β), 8.97 ppm (m, 4H, H_β); ^{13}C NMR (150 MHz, CDCl_3 , 25 °C, TMS): $\delta = 13.95, 29.21, 52.22, 119.46, 121.76, 127.09, 129.26, 130.05, 131.32, 132.12, 137.13, 139.50, 147.56, 149.39, 150.29, 150.48, 166.64, 167.23$ ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 428 (5.02), 560 (3.72), 601 nm (3.35); HRMS (MS ES+): m/z calcd for $[\text{C}_{50}\text{H}_{37}\text{N}_4\text{O}_4\text{Zn}] [\text{M}+\text{H}]^+$: 821.2106, found 821.2146.

[5,10-Bis(4-cyanophenyl)-15,20-bis(4-methylphenyl)porphyrinato]zinc(II) 65:

Following the general procedure D, 5,10-bis(4-cyanophenyl)-15,20-bis(4-methylphenyl)porphyrin **44** (10 mg, 0.014 mmol) was treated with 300 mg of zinc oxide to yield 8 mg (0.010 mmol, 72 %) of the desired product after recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. $R_f = 0.27$ ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 1:1$, v/v); m.p. >300 °C; ^1H NMR (600 MHz, CDCl_3 , 25 °C, TMS): $\delta = 2.76$ (s, 6H, CH_3), 7.61 (d, 4H, $^3J = 7.2$ Hz, Ar-*H*), 8.11 (m, 8H, Ar-*H*), 8.37 (d, 4H, $^3J = 7.7$ Hz, Ar-*H*), 8.86 (d, 2H, $^3J = 4.4$ Hz, H_β), 8.89 (s, 2H, H_β), 9.03 (s, 2H, H_β), 9.06 ppm (d, 2H, $^3J = 4.4$ Hz, H_β); ^{13}C NMR (150 MHz, CDCl_3 , 25 °C, TMS): $\delta = 13.95, 21.38, 29.55, 111.63, 127.27, 130.28, 131.01, 132.42, 132.84, 134.22, 134.71, 137.31, 150.40$ ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 421 (4.94), 548 (3.74), 628 nm (3.52); HRMS: m/z calcd for $[\text{C}_{48}\text{H}_{30}\text{N}_6\text{Zn}] [\text{M}]^+$: 754.1823, found 754.1875.

[5,10-Dibromo-15,20-bis(3-methoxyphenyl)porphyrinato]zinc(II) 66:

5,10-Dibromo-15,20-bis(3-methoxyphenyl)porphyrin **37** (50 mg, 0.07 mmol) was reacted following procedure D. Column chromatography on silica gel (CH_2Cl_2) gave a single product. Recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{H}_2\text{O}$ gave purple crystals (49 mg, 0.07 mmol, 90 %). $R_f = 0.27$ ($\text{CH}_2\text{Cl}_2/n\text{-hexane} = 3:1$, v/v); m.p. 187 °C; ^1H NMR (500 MHz, CDCl_3 , 25 °C, TMS): $\delta = 3.91$ (s, 6H, Ar- OCH_3), 7.29 (m, 2H, Ar- H_p), 7.68 (m, 4H, Ar- H_o , Ar- H_m), 7.79 (m, 2H, Ar- H_o), 8.43 (s, 2H, $H_{\beta 7,8}$), 8.76 (AB, 2H, $^3J = ^3J = 4.6$ Hz, $H_{\beta 2,13}$), 8.89 (s, 2H, $H_{\beta 17,18}$), 9.21 ppm (AB, 2H, $^3J = ^3J = 4.6$ Hz, $H_{\beta 3,12}$); ^{13}C NMR (126 MHz, CDCl_3 , 25 °C, TMS): $\delta = 55.55, 103.95, 113.35, 120.70, 121.90, 127.50, 127.63, 132.30, 132.67, 132.70, 133.18, 143.57, 148.41, 149.13, 150.79, 150.94, 158.03$ ppm; UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 424 (5.26), 556 (4.26), 595 nm (3.83); MS (TOF, MS, ES+, 70 eV): m/z (%): 740 (39 %, $[\text{M}]^+$); HRMS: m/z calcd for $[\text{C}_{34}\text{H}_{22}\text{N}_4\text{Br}_2\text{O}_2\text{Zn}] [\text{M}]^+$: 739.9401, found: 739.9391.

[5,10-Bis(4-cyanophenyl)-15,20-bis(3-methoxyphenyl)porphyrinato]zinc(II) 67:

Following the general procedure D, 5,10-bis(4-cyanophenyl)-15,20-bis(3-methoxyphenyl)porphyrin **52** (0.013 mmol) was treated with 300 mg of zinc oxide to give 8 mg (0.009 mmol, 72 %) of the title compound after recrystallization from CH₂Cl₂/MeOH. R_f = 0.3 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 3.99 (s, 6H, OCH₃), 7.36 (d, 2H, ³*J* = 8.2 Hz, Ar-*H*), 7.67 (t, 2H, ³*J* = 8.2, 7.6 Hz, Ar-*H*), 7.78 (s, 2H, Ar-*H*), 7.82 (d, 2H, ³*J* = 7.6 Hz, Ar-*H*), 8.09 (d, 4H, ³*J* = 8.2 Hz, Ar-*H*), 8.36 (d, 4H, ³*J* = 8.2 Hz, Ar-*H*), 8.85 (d, 2H, ³*J* = 4.7 Hz, *H*_β), 8.88 (s, 2H, *H*_β), 9.03 (s, 2H, *H*_β), 9.06 ppm (d, 2H, ³*J* = 4.7 Hz, *H*_β); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): δ = 29.54, 55.35, 111.66, 113.34, 118.89, 120.38, 121.76, 127.31, 130.28, 131.17, 132.41, 134.70, 143.52, 147.54, 149.07, 149.38, 150.18, 150.50, 157.78 ppm; UV/VIS (DMF): $\lambda_{\max}$ (lg ϵ) = 428 (5.06), 560 (3.69), 599 nm (3.45); HRMS: m/z calcd for [C₄₈H₃₀N₆O₂Zn] [M]⁺: 786.1722, found 786.1625.

[5,10-Bis(3-methoxyphenyl)-15,20-bis(4-nitrophenyl)porphyrinato]zinc(II) 68:

Following the general procedure D, 5,10-bis(3-methoxyphenyl)-15,20-bis(4-nitrophenyl)porphyrin **53** (10 mg, 0.013 mmol) was treated with 300 mg of zinc oxide to give 8 mg (0.009 mmol, 81 %) of the desired product after recrystallization from CH₂Cl₂/MeOH. R_f = (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (600 MHz, CDCl₃, 25 °C, TMS): δ = 3.98 (s, 6H, OCH₃), 7.35 (d, 2H, ³*J* = 8.2 Hz, Ar-*H*), 7.67 (t, 2H, ³*J* = 7.7, 8.07 Hz, Ar-*H*), 7.77 (s, 2H, Ar-*H*), 7.82 (d, 2H, ³*J* = 7.0 Hz, Ar-*H*), 8.42 (d, 4H, ³*J* = 7.7 Hz, Ar-*H*), 8.65 (d, 4H, ³*J* = 7.7 Hz, Ar-*H*), 8.86 (d, 2H, ³*J* = 4 Hz, *H*_β), 8.89 (s, 2H, *H*_β), 9.03 (s, 2H, *H*_β), 9.07 ppm (d, 2H, ³*J* = 4 Hz, *H*_β); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): δ = 13.89, 22.54, 29.55, 55.35, 113.32, 118.05, 120.43, 121.90, 127.43, 131.11, 132.47, 134.83, 143.51, 147.55, 148.99, 149.57, 150.21, 150.56, 157.77 ppm; UV/VIS (DMF): $\lambda_{\max}$ (lg ϵ) = 421 (5.13), 550 (3.97), 592 nm (3.29); HRMS: m/z calcd for [C₄₆H₃₀N₆O₆Zn]: 826.1518, found 826.1584.

(5,10-Diformyl-15,20-diphenylporphyrinato)copper(II) 70: A 100 ml three-necked flask equipped with a reflux condenser containing anhydrous DMF (75 eq.) was charged drop wise and slowly with POCl₃ (74 eq.) at 0-2 °C under an argon atmosphere. After 20 min the POCl₃-DMF complex solidified. After removal of the ice-bath, 1,2-dichloroethane (5 mL) was added and the solution was heated gently to 50 °C. (5,10-Diphenylporphyrinato)copper(II) **69** was added slowly at 50 °C as a solution in 1,2-dichloroethane (25 mL). After complete addition the mixture was heated to 90 °C for 12 h. After cooling with an ice-bath a saturated aqueous sodium acetate solution was added very carefully and then the mixture was heated to 80 °C for 3 h for completion of the hydrolysis. After cooling to RT the porphyrin was extracted into CH₂Cl₂ (3 ×), followed by washing once with water, twice with aqueous NaHCO₃, and then finally twice with brine. Finally, the organic phase was dried with anhydrous Na₂SO₄ and the solvent was evaporated under reduced pressure. After column chromatography on silica gel (h = 46 cm, ϕ = 3 cm) with CH₂Cl₂ the first fraction containing pure product was obtained as dark green crystals after recrystallization from CH₂Cl₂/MeOH (45.1 mg, 0.077 mmol, 77 %). R_f = 0.4 (CH₂Cl₂/*n*-hexane = 3:1, v/v); m.p. 220 °C; UV/VIS (CH₂Cl₂): $\lambda_{\max}$ (lg ϵ) = 432 (4.45), 562 (3.50), 602 nm (3.43); MS (EI, 70 eV): m/z (%): 581 (4 %, [M]⁺), 552 (1 %, [M - CHO]⁺), 523 (2 %, [M - C₂H₂O₂]⁺), 445 (2 %, [M - C₂H₂O₂ - C₆H₆]⁺); HRMS: m/z calcd for [C₃₄H₂₂N₄O₂Cu] [M+2H]²⁺: 581.1039, found 581.1042.

5,10,15-Tris(3,4,5-trifluorophenyl)porphyrin 71: Obtained from the synthesis of **42** (5 mg, 7 μ mol, < 1 %). R_f = 0.6 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. 290 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = -3.21 (br s, 1H, NH), 7.85 (m, 6H, Ar-*H_o*), 8.91, 8.87 (AB, 4H, ³*J* = ³*J* = ³*J* = ³*J* = 4.9 Hz, *H*_{β7,8,12,13}), 8.99 (AB, 2H, ³*J* = ³*J* = 4.6 Hz, *H*_{β3,17}), 9.40 (AB, 2H, ³*J* = ³*J* = 4.6 Hz, *H*_{β2,18}), 10.30 ppm (s, 1H, *H*_{meso}); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 106.70, 119.19, ~131, 132.86, 137.62, 148.50, 151.83 , , ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ϵ) = 410 (4.98), 506 (4.02), 538 (3.46), 581 (3.58), 634 nm (3.20); MS (70 eV, EI) *m/z* (%): 700 (16 %, [M]^{•+}), 570 (14 %, [M – C₆H₂F₃ + H]^{•+}), 350 (100 %, [M]²⁺), 285 (20 %, [M – C₆H₂F₃ + H]²⁺); HRMS: *m/z* calcd for [C₃₈H₁₇F₉N₄] [M]⁺: 700.1310, found: 700.1280.

5,10,15-Tris(4-bromophenyl)porphyrin 72: Obtained from the synthesis of **41** (12 mg, 0.02 mmol, < 1 %). R_f = 0.48 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS): δ = -3.09 (br s, 1H, NH), 7.88 (AB, 6H, ³*J* = ³*J* = ³*J* = ³*J* = ³*J* = 8.1 Hz, Ar-*H_m*), 8.06 (AB, 6H, ³*J* = ³*J* = ³*J* = ³*J* = ³*J* = 8.1 Hz, Ar-*H_o*), 8.85 (m, 4H, *H*_{β7,8,12,13}), 8.97 (AB, 2H, ³*J* = ³*J* = 4.7 Hz, *H*_{β3,17}), 9.32 (AB, 2H, ³*J* = ³*J* = 4.7 Hz, *H*_{β2,18}), 10.20 ppm (s, 1H, *H*_{meso}); ¹³C NMR (63 MHz, CDCl₃, 25 °C, TMS): δ = 105.33, 118.30, 118.99, 122.62, 129.98, 130.08, ~131, 135.81, 135.95, 140.54 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ϵ) = 413 (5.09), 508 (4.32), 542 (3.95), 583 (3.90), 637 nm (3.68); MS (TOF, MS, ES+, 70 eV) *m/z* (%): 772 (32 %, [M]⁺); HRMS: *m/z* calcd for [C₃₈H₂₃N₄Br₃] [M]⁺: 771.9473, found: 771.9454.

X-ray single crystal structure determination of 29: Growth and handling of crystals followed the concept developed by Hope.^[36] Intensity data were collected at 118 K with a Rigaku CCD system utilizing Mo-K α radiation (λ = 0.71073 Å). The intensities were corrected for Lorentz, polarization and extinction effects. The structure was solved with Direct Methods using the SHELXTL PLUS program system and refined against |F²| with the program XL from SHELX-97 using all data.^[37] Nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed into geometrically calculated positions and refined using a riding model. The N-H hydrogen atoms were refined as disordered over all four positions with occupancies of 50 % each. CCDC-829928 contains 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. *Crystal data:* C₃₄H₂₄Br₂N₄. *FW* = 648.39, red parallelepiped from CH₂Cl₂/CH₃OH, crystal size 0.5 x 0.3 x 0.2 mm, monoclinic, *C2/c*, *a* = 30.27(2) Å, *b* = 12.148(7) Å, *c* = 15.884(10) Å, β = 111.123(14)°, *V* = 5448(6) Å³, *Z* = 8, *d_{calcd}* = 1.581 Mg.m⁻³, μ (Mo K α) = 3.008 mm⁻¹, *T_{min}* = 0.315, *T_{max}* = 0.585, θ_{max} = 31.24°, 21370 reflections collected, 4765 independent reflections, *R_{int}* = 0.1081, 3368 reflections with *I* > 2.0σ(*I*), 364 parameters, *R* (*I* > 2.0σ(*I*)) = 0.0757, *R* (all data) = 0.1092, *wR2* (all data) = 0.2168, *S* = 1.042, ρ_{max} = 1.744 e.Å⁻³ (near Br atoms).

5,10-A₂B₂-type meso Substituted Porphyrins – A Unique Class of Porphyrins with Realigned Dipole Moment

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Abstract: Current applications in porphyrin chemistry require the use of unsymmetrically substituted porphyrins. Many current industrial interests in optics and biomedicine require systems with either push-pull (electron donating and withdrawing groups) or amphiphilic systems (hydrophobic and hydrophilic groups). In this context we present the class of 5,10-A₂B₂-type porphyrins where two different substituents are positioned in diagonally opposite meso positions.

Thus, the intramolecular dipole moment in these tetrapyrroles is positioned along a β–β vector passing through two pyrrole rings. This is opposite to the situation of the frequently used 5,15-A₂BC porphyrins where the dipole moment is oriented along a meso-meso axis. We have elaborated syntheses of the 5,10-A₂B₂ porphyrins using transition metal catalyzed transformations of 5,10-A₂ porphyrins or direct substitutions reactions thereof which give the target

molecules in 22–77 % overall yield. The compounds exhibit interesting structural, spectroscopic and optical features and can serve as building blocks for new porphyrin arrays and applications.

Keywords: porphyrinoids • nonlinear optics • tetrapyrroles • macrocycles • nitrogen heterocycles

Introduction

Porphyrins are important natural products and industrially relevant dyes. Although their basic structure and chemistry has been known now for almost a century, research into their chemistry and technical and biomedical uses continues apace. Indeed, the last quarter of a century has seen an almost explosive growth of new porphyrinoid, pyrrole-based chromophores. After the landmark discovery of porphycene as a C-skeleton isomer of porphyrin by Vogel^[1] and the calixphyrins^[2] related to Baeyer's "Azetonpyrrol"^[2b] a whole cornucopia of expanded, contracted and isomeric porphyrins, and cyclopyrroles have been - and continue to be - discovered.^[2c,2d] In light of this quest for ever more elaborate porphyrinoid systems it might come as a surprise to the nonspecialist that many important classes of the chemically simpler, "true" porphyrins, i.e., 18π-aromatic tetrapyrrolic systems have remained elusive until recently.

Figure 1. Selected A_x- and ABCD-type porphyrins.

Especially the group of the so-called A_x- and ABCD-type porphyrins contained several missing links. This terminology relates to the various regioisomers of meso substituted porphyrins with different residues at the methine bridges.^[3] Figure 1 illustrates the constitution of selected members of the porphyrin "alphabet soup".^[4] Going back only about a decade, most of the less symmetrical compounds in this series were either unknown or had been prepared merely through mixed condensations in minuscule yields. In practical terms only the symmetric 5,15-A₂- 4 and

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5,10,15,20- A_4 -type **6** systems could be prepared with ease. Especially the A_2 -**2** and 5,10- A_2 -type **3** porphyrins remained almost unexplored white specks on the porphyrin landscape. The underlying problem is the propensity of pyrrole compounds to undergo acid-catalyzed scrambling reactions.^[5] This negated many total synthesis approaches and even made it problematic to use preformed building blocks such as dipyrromethanes for [2+2] or [3+1] condensation reactions. The only alternative at that time was the use of mixed (aldehyde + pyrrole) condensation reactions. Nevertheless, the required chromatographic work-up and acid instability of certain groups made this prohibitive for, e. g., the ABCD-type systems **10**.

In the meantime flexible total synthesis routes have been developed for many of these systems by Lindsey's group and judicious choice of the ABCD residues, their kinetic stability, steric hindrance, and the sequence of use of the individual building blocks allows the large scale preparation of many but not all desired compounds.^[6] In parallel we developed porphyrin syntheses based on the step-wise introduction of functional groups into preformed macrocycles, i.e. through functionalization reactions. This goes back to our initial observation that porphyrins can be substituted in high yield at the meso positions with organolithium reagents,^[7] and by now has evolved to a strategy which utilized various organometallic reactions for the step-wise transformation of unsubstituted porphyrin (**2**, $A = H$) $\rightarrow A$ - $\rightarrow AB$ - $\rightarrow ABC$ - $\rightarrow ABCD$ -type porphyrins.^[4,8]

Next to access to porphine,^[9] this strategy required access to the monosubstituted porphyrins **2** and appropriate synthetic routes were developed by us based on condensation and substitution reactions.^[10] Logical construction of the ABCD-type systems **10** via step-wise functionalization also required a means to introduce a second meso substituent in a neighboring meso position, i.e. a way to generate the 5,10-regioisomers. Of the two possibilities, use of an appropriate precursor, e. g., reaction of tripyrrane^[11a] with pyrrole and aldehyde, or exploitation of the regioselectivity of S_NAr reactions in porphyrins,^[11b] both could be used to develop an entry into the 5,10- A_2 -type systems **3**.^[10b,12] Thus, only the 5,10- A_2B_2 porphyrins remained an unexplored entity in the world of meso substituted porphyrins. Here, we present general synthetic routes for the preparation of these A_2B_2 -type porphyrins and discuss some of their properties.^[13]

Results and Discussion

Synthetic rational and brief review of the literature: Current application developments indicate a considerable demand for unsymmetrically substituted porphyrins. Examples for this are amphiphilic porphyrins in photodynamic cancer therapy (PDT),^[14a] synthons for crystal engineering and supramolecular chemistry,^[14b] push-pull systems for biomimetic studies on electron transfer,^[14c] and uses in optics, esp. in nonlinear optics (NLO).^[14d] Unsymmetrical substitution is used to either position donor/acceptor residues in a manner suitable for the desired interaction or to yield systems with a strong intermolecular dipole moment to enhance optical effects. Thus, contemporary studies habitually employ 5,15- A_2BC porphyrins **8**, where B and C are used for macrocycle diversification.

Porphyrins of type **8** require a step-wise functionalization or a total synthesis.^[8] While the precursor 5,15- A_2 porphyrins **4** are easily obtained in high yield^[15] introduction of the two different

meso substituents B and C requires first an appropriate monofunctionalization for the introduction of B (e. g., monobromination and then C–C coupling) and then introduction of C; alternatively for a one-pot reaction with R^1Li/R^2I is possible.^[7b,7f] In a fundamental sense this yields porphyrins with an intramolecular dipole moment aligned along a 5,15 meso-meso axis (Fig. 2, **8**). The 5,10- A_2B_2 type systems are accessible more easily. They require no selective monofunctionalization, rather a double substitution of the "free" 15,20-positions (e. g., unspecific dibromination and then C–C coupling; see Scheme 2). Here, only two different substituents (A and B) are required to construct unsymmetrical systems. Thus, in the case of electron withdrawing/donating groups porphyrins will be obtained where the dipole moment passes through the middle of two opposing β – β units ($N\cdots N$) (Fig. 2, **9**).

Figure 2. Orientation of the intramolecular dipole moment in 5,15- A_2BC - and 5,10- A_2B_2 -type porphyrins.

5,10-Disubstituted porphyrins were first reported by Longo but not characterized.^[16a] In the early 21st century examples for condensation reactions,^[16b] total syntheses^[16c] and N-confused derivatives^[16d] were reported. This was then followed by the more general methods described above for porphyrins^[10b,12] and calixphyrins.^[16e] This opened the possibility to use the 5,10- A_2 porphyrins as simple starting materials for the synthesis of 5,10- A_2B_2 systems as outlined above. A few 5,10- A_2B_2 compounds have been reported before; however, all were prepared in low yields through statistical condensation methods using pyrroles, dipyrromethanes or tripyrranes with the usual attendant problems of tedious chromatographic separation, scrambling and other limitations.^[17] The only exception is Lindsey's elegant study on the development of total syntheses using diacyldipyrromethanes. This method was successfully used to prepare three compounds with aryl substituents.^[6a]

Based on the current state of the art in porphyrin functionalization reactions there are several methods for the introduction of the B residue into an A_2 porphyrin. The majorities of them employ organometallic reagents and are discussed in subsequent sections.

Synthesis via RLi reactions: Based on our earlier experience with the use of organolithium reagents for the meso functionalization of porphyrins,^[7] it was logical to apply these for the current problem as well. For initial experiments we used the nickel(II)porphyrin **11**, which typically shows good reactivity with RLi. In order to achieve "full" substitution of both 15,20 meso positions we used 6 equivalents of hexyllithium. Indeed, the target compound **17** was obtained in 58 %. The different reactivity of free base and metallo porphyrins became evident when a similar experiment was performed with **12**. Here, a low yield of the monosubstituted porphyrin **18**, i.e. an 5,10- A_2B system, was obtained. Full, disubstitution to **19** was only achieved when the number of hexyllithium equivalents was raised to 10. A similar reactivity was found for **13** which could be transformed into **20** in 26 %. Use of n -

BuLi and reaction with **12** to give **21** did not improve the yield significantly, while the use of 20 equiv. of *n*-BuLi with **14** in the presence of TMEDA only gave the A₂B porphyrin **22**.

Scheme 1. Synthesis of 5,10-A₂B₂-porphyrins using organolithium reagents. i) 1. R₂Li, THF, 2. H₂O, 3. DDQ.

Next we tried to introduce residues with functional groups using the same methodology *via in situ* generation of organolithium reagents. For example, reaction of **12** with 4-(*N,N*-dimethylamino)phenyllithium gave **23** in 71 % yield. However, the reaction is somewhat inefficient as it required 100 equivalents of RLi. Likewise the *p*-hydroxyphenyl derivative **24** could be prepared in good yield. Reaction of the methoxyphenylporphyrin **15** gave **25**, accompanied by a small amount of **26**. Likewise, the *p*-phenylethynyl group could be introduced into the tolylporphyrin **12** to yield **27**. Finally, the free base porphyrin **16** was prepared through a condensation approach in 5 % yield and reacted with *p*-phenylethynyllithium to **28**. We also attempted the introduction of stronger electron withdrawing groups through similar reactions. However, a reaction of **12** using *n*-BuLi/*p*-bromobenzonitrile (−100 °C) only gave only the butylated product **21**. No reaction was observed with 1-bromo-4-nitrobenzene/*n*-BuLi and only starting material was recovered.

Synthesis via Heck reactions: In order to expand the scope of these compounds we next turned our attention to the use of Pd-catalyzed reactions. Many of these have now been applied to porphyrin chemistry.^[4] The Heck reaction^[18a] was initially applied for the β-substitution of porphyrins^[18b] and we were interested in preparing meso vinyl acceptor substituted porphyrins.

The Heck reaction requires a bromo-substituted coupling partner and thus preparation of bromoporphyrins was the first step. DiMagno *et al.*^[19] had shown that 5,15-A₂ porphyrins can easily be

brominated with NBS in both meso positions and the same conditions could be applied straightforwardly to the 5,10-A₂-type systems. Using the ditolylporphyrin for exploration of this reaction it was brominated to **29**. In order to prevent the incorporation of Pd from the catalysts we transformed it into the respective zinc(II) **30** and nickel(II)porphyrin **31**. First we reacted the zinc(II) porphyrin **30** with butyl acrylate. Heating at 120 °C for 24 h gave the desired {(*all-E*)-5,10-bis(4-(2-butoxycarbonyl)ethenyl)-15,20-di(*p*-tolylporphyrinato)}zinc(II) **32** the sole product in 64 %. Similarly, reaction with a methyl vinylketone gave **33**. The *E*-configuration is clearly evidenced by the respective NMR coupling constant of 16 Hz. Reaction of the zinc(II) complex **30** with nitrostyrene gave the analogous porphyrin **34** in good yield. The nickel(II) complex **31** is less reactive and reaction with nitrostyrene gave **35** in much lower yield (Scheme 2).

Scheme 2. Synthesis of 5,10-A₂B₂-porphyrins using Heck reactions. i) NBS, pyridine, CHCl₃; ii) ZnO, CH₂Cl₂, TFA or Ni(acac)₂, toluene, Δ; iii) Pd(OAc)₂, NaOAc, PPh₃, DMF, Δ.

Synthesis via Suzuki reactions: Next we focused on applications of the Suzuki reaction for the task at hand. Suzuki reactions have been very fruitfully applied to porphyrins and offer the advantage that no prior metallation is necessary.^[20] Again, bromoporphyrins are required as coupling partners and, in addition to the ones mentioned above, a few more (**36-40**) were synthesized to gain access to a broader range of A/B substituent systems. Likewise, two new 5,10-A₂ porphyrins (**41,42**) were prepared using condensations reactions.

By now optimized catalyst/base systems have been established for Suzuki reactions with 5,15-A₂ systems.^[20d] These could be easily applied for the modification of 5,10-A₂ porphyrins. As shown in Scheme 3 a large set of compounds could be prepared using Pd(PPh₃)₄ as palladium catalyst and K₃PO₄ as a base. Yields varied from 22 to 59 %, both aryl- and alkylhalogenoporphyrins could be used, and reaction times from 7 to 13 h. For example, the bromotolylporphyrin **29** was reacted with 4-methoxycarbonylphenyl boronic acid for 7 h and gave **43** in 52 % yield. The best yield for this reagent was obtained for the pentylporphyrin derivative **57**. The reactivity of 4-cyanophenyl boronic acid towards aryl and alkyl haloporphyrins was investigated as well. The best results of 47 % each were obtained for **44** and the (3-methoxyphenyl)porphyrin **52**. Alkyl haloporphyrins, e.g., 5,10-dibromo-15,20-dipentylporphyrin or 5,10-dibromo-15,20-dihexylporphyrin gave the corresponding products **58** and **61** in 40 % yield, respectively. Even lower yields were obtained for porphyrins **48** and **49**, materials synthesized from 5,10-dibromo-15,20-diphenylporphyrin **70**.

Introduction of the nitrophenyl residue proceed well with good yields, e.g. for compounds **45**, **50**, **53** and the alkylporphyrins **59** and **62**. The 3-nitrophenyl boronic acid required longer reaction times than the 4-nitrophenyl boronic acid and gave lower yield. This was not the case for the 3-cyanophenyl versus 4-cyanophenyl reagent. Reactions with the electron poor 2,3-difluorophenylporphyrins proceeded poorly with yield ranging from 22 to 30 %. Clearly, the Suzuki reaction provides convenient access to various 5,10-A₂B₂-type porphyrins. Still, some scope for optimization exists. A number of the free base porphyrins prepared from the reactions described above, were converted into the respective zinc(II) porphyrins for comparative photophysical analyses. The metalloporphyrins **63-68** were obtained through standard reactions in good yield.

Scheme 3. Synthesis of 5,10-A₂B₂-porphyrins using Suzuki reactions. i) boronic acid or ester, K₃PO₄, Pd(PPh₃)₄, THF, Δ.

	R ¹	R ²	
63			(81 %)
64			(81 %)
65			(72 %)
66			(90 %)
67			(72 %)
68			(81 %)

Functionalization reactions: The target systems can also be prepared through simple functionalization reactions. Examples for this are the partial reduction of nitro groups in, e.g., a tetra-nitrophenylporphyrin.^[21a] Perhaps not elegant in synthetic chemistry terms such strategies offer a quick entry into various systems and have recently been used to generate 5,10-type precursors for Huisgen Cu(I) coupling chemistry.^[21b]

Other, "simple" reactions may be performed as well. For example, the Vilsmeier formylation^[22a] has been used often for the modification of porphyrins.^[22b-d] Using "excess" conditions it can be used to diformylate metallo octaethylporphyrins^[22c] and 5,15-A₂-type porphyrins,^[22d] but mostly gives mixtures of the mono- and diformyl product. In the case of the 5,10-A₂ porphyrin **69** standard Vilsmeier-Haack formylation gave the respective 5,10-A₂(CHO)₂-porphyrin **70** in very good yield (77 %) and as the sole product (Scheme 4). Other possibilities for selective functionalizations are the use of (e.g., **41**) organotin reactions.^[23]

Scheme 4. Synthesis of the diformylporphyrin **64**. i) DMF, POCl₃, dichloroethane, 50–90 °C.

Structural studies: In order to establish some basic structural features of the 5,10-A₂B₂-type porphyrins a X-ray crystallographic analysis of compound **29** was performed. The molecular structure in the crystal is shown in Figure 3. Overall, the structural properties are similar to those of 5,15-A₂B₂- and A₄-type porphyrins. There is no evidence for core elongation or other changes to the core structure. For example, the core size (average N···N distance) is 2.064 Å and similar to that of 5,10,15,20-tetraphenylporphyrin (TPP).^[24] Similarly, the bond lengths and angles of the tetrapyrrole framework

are in line with "normal" porphyrin systems.^[25] The packing of the molecules (not shown) is characterized by the formation of weak π - π aggregates in a head-to-tail fashion.^[25]

Figure 3. View of the molecular structure of **29** in the crystal. Hydrogen atoms have been removed for clarity and thermal ellipsoids show 50 % occupancy.

The conformation of the molecule is nonplanar.^[25a,b] The average deviation of the 24 macrocycle atoms from their least-squares-plane (Δ_{24}) is 0.159 Å, slightly less than the tetragonal form of TPP.^[26] The macrocycle exhibits a ruffled distortion mode, with alternate C_m displacements of 0.15–0.34 Å from the 24-macrocycle atom plane. A detailed normal structural decomposition analysis (NSD)^[27] reveals a more complex situation. The conformation is characterized by almost similarly strong out-of-plane contributions from *sad* and *ruf* distortions (B_{1u} and B_{2u}), a moderate contribution from *doming* (A_{2u}), and a minor one from *wave* (E_{gx}). With regard to in-plane distortion modes, the most significant contributor is *macrocycle-breathing* (A_{1g}). In a first approximation this is similar to the structure of 5,10-diphenylporphyrin,^[28] which exhibits less *sad* distortion and more *wave* contribution.

NLO properties: Understanding the nonlinear absorption (NLA) properties of macrocyclic dyes is important for the development of related applications. Besides instantaneous two-photon absorption (TPA) arising at nonresonant frequencies, which has potential for 3D-microfabrication and multiphoton microscopy, porphyrins exhibit sequential TPA, i.e. reverse saturable absorption (RSA) and saturable absorption (SA) at resonant or close to resonant wavelengths. The latter two processes occur when the absorption arising from higher excited state is higher and lower respectively to that of the ground state. RSA has potential for use in pulse sensors and in optical limiting devices that protect sensitive optical components or the human eye from laser-induced damage. SA finds application for mode locking, laser pulse compression and laser amplification.

Our open aperture Z-scan studies at close to resonant wavelength revealed that 5,10-A₂B₂ compounds exhibit an interesting NLO effect, which has not been observed for porphyrins in the ns regime before. The compounds exhibit pure RSA response when low laser energies inputs were used, which is a standard response commonly observed for macrocyclic dyes under such experimental conditions. However, when the input energy was increased with the onfocus intensity I_{00} reaching approximately 0.4 GW cm⁻², the RSA response was observed to switch to SA in the tight focal regime. When the input energy was increased further on,

with I_{00} being on the order of $\sim 0.5 \text{ GW cm}^{-2}$, a similar RSA/SA signal was detected, though with a much more pronounced SA peak. The SA response within an RSA remained highly symmetrical for all of the measurements (not shown ^[29]).

Interestingly, compounds with similar substituents but in a 5,15- A_2B_2 substitution pattern, exhibit a pure RSA response both at lower and higher inputs.^[30] This clearly demonstrates that the RSA/SA switch is intrinsic to 5,10- A_2B_2 compounds. The origin of the behavior is not understood at this stage. Most likely the RSA/SA switch is the result of absorption arising from higher excited states. Further studies are necessary in order to understand the observed switch.

Conclusion

We here present a conceptionally new class of *push-pull* porphyrins i.e., 5,10- A_2B_2 porphyrins with the intramolecular dipole moment positioned along the β - β vector passing through two pyrrole rings. Starting from 5,10- A_2 precursors, numerous 5,10- A_2B_2 compounds with varied push-pull character can be obtained using organolithium, palladium catalyzed cross coupling or other functionalization reactions. These approaches allow the synthesis in moderate to good yields and open an avenue for further studies on these yet poorly explored compounds.

In the past push-pull molecules with a similar orientation of the intramolecular dipole moment, i.e. along the β - β vector passing through two pyrrole rings were obtained through the functionalization of the β position of the porphyrin ring, e.g., in TTP derivatives.^[31] In the well studied 5,15- A_2BC compounds the push-pull character is tuned through the B and C substituents. Here, the dipole moment is aligned along the 5,15 meso-meso axis. Nevertheless, access to these 5,15- A_2BC compounds is more complex in comparison to 5,10- A_2B_2 as it involves firstly an appropriate monofunctionalization of the 5,15- A_2 precursor and secondly further additional steps for the incorporation of the third functional group C. In case of 5,10- A_2B_2 compounds only two substituent are needed to introduce dipole moment, which consequently involves less steps and omits the troublesome monofunctionalization.

The 5,10- A_2B_2 compounds are candidates for many potential applications. Inequivalent substituents can be used to bring in about an amphiphilic character of the molecule which turns those compounds into drug candidates for PDT applications. The push-pull character can be tuned via A and B substituents and makes 5,10- A_2B_2 porphyrins an interesting group of compounds for ET studies and optics, especially NLO. Our preliminary NLO studies indeed revealed that those compounds exhibit interesting properties in this area. 5,10- A_2B_2 type systems can also be used as crystal engineering synthons to access new supramolecular structures. For example, Maeda *et al.* reported recently on L-shaped porphyrin trimers which assemblies exhibited efficient ET. Those compounds were prepared via functionalisation of 5,10- A_2B_2 dibrominated precursor with appropriate 5,15- A_2BC porphyrins.^[32] 5,10- A_2B_2 porphyrins may also serve as new ligand systems, as was shown recently for the related calixphyrins.^[33]

Experimental Section

General methods: Instrumentation and standard techniques used were as described elsewhere.^[8] NLO studies were carried out with open aperture Z-scan technique.^[34] Experimental set-up and sample preparation details can be found elsewhere.^[13]

Starting materials: Tripyrrane,^[35] and various 5,10-di(alkyl/aryl)porphyrins^[10b] were prepared according to published procedures.

General procedure A – Condensation method for 5,10- A_2 porphyrins: A three-necked flask was charged with a solution of tripyrrane (1 equiv.), pyrrole (1 equiv.), and the corresponding aldehyde (2.1 equiv.) in dry CH_2Cl_2 (1 L). The mixture was shielded from light and stirred under argon for 30 min. TFA (100 %) was added and stirring was continued at RT for 16 h. This was followed by oxidation with DDQ (4 eq.), stirring for 60 min, and addition of triethylamine (1 mL). Typically, the reaction mixture was filtered through a short silica-gel column, eluting with CH_2Cl_2 , then the solution was concentrated *in vacuo* and the residue purified by column chromatography on silica gel.

General procedure B – Reactions with organolithium compounds: A 250 mL Schlenk flask was charged with the porphyrin (1 equiv.) in 50 mL THF under argon. The solution was cooled to -70°C for alkyl lithium reagents or 0°C for aryl lithium reagents. The respective LiR compound was added drop wise over 15 min and the color changed from red to brown-green. The cold bath was removed and the solution was stirred for 30 min at RT. A mixture of 1 mL in 5 mL THF was added and the color changed to green. The mixture was stirred for 15 min and, unless noted otherwise, oxidized with DDQ (5.5 equiv.) followed by stirring for 30 min. This was accompanied by a color change to red. The solution was filtered through silica gel (CH_2Cl_2) and the solvent removed under reduced pressure. For *in situ* preparation of RLi reagents *n*-butyllithium (2 equiv.) was slowly added (ca. 1 h) under an argon atmosphere to a 100 mL Schlenk flask charged with a solution of the bromine (1 equiv.) in 10 mL dry diethyl ether at -78°C . The reaction mixture was then warmed up to -40°C and THF was added drop wise until the aryllithium was formed as a bright pink suspension. To this vigorously stirred mixture was added rapidly a solution of the porphyrin (0.9 equiv.) in 80 mL dry THF under an argon atmosphere. The color of the reaction mixture changed from purple to brown within 30 min, subsequently 5 mL water in 5 mL dry THF was added for hydrolysis. After stirring the mixture for 10 min, a solution of 10-15 equiv. of DDQ in CH_2Cl_2 was added and the reaction mixture was stirred for another 60 min at RT.

General procedure C – Bromination of 5,10- A_2 porphyrins: A 100 mL round bottom flask was charged with the porphyrin (1 equiv.) dissolved in chloroform (50 mL) and pyridine (0.2 mL) and was cooled to 0°C . Next *N*-bromosuccinimide (NBS) (2.5 equiv.) was added and the solution stirred for 10 min. The color changed from red to brown-red. The reaction was then quenched via addition of 4 mL acetone. The solvent was removed under reduced pressure, the residue dissolved in CH_2Cl_2 and filtered through silica gel (CH_2Cl_2). The solvent was removed under reduced pressure and the residue was washed with MeOH and dried.

General procedure D – Insertion of zinc(II): The free base porphyrin (1 equiv.) and zinc oxide (2–3 equiv.) were dissolved in CH_2Cl_2 (50 mL) and treated with three to five drops of TFA. After stirring for 10 min the color changed from green to purple-red. The reaction was followed by TLC control and the solution filtered through silica gel (CH_2Cl_2) and the solvent removed under reduced pressure.

General procedure E – Heck reactions: A 50 mL three-necked flask equipped with condenser was charged with the zinc(II)porphyrin (10 equiv.), sodium acetate (56 equiv.), arylboronic acid or arylboronic ester (10 equiv.) and triphenylphosphine (4 equiv.) in 15 mL dry DMF under argon. Next, the respective olefin was added and the solution heated at 120°C for 24 h. The reaction was followed by TLC control. After completion of the reaction the solution was cooled to RT and extracted with CH_2Cl_2 , washed with water (50 mL) and dried over Na_2SO_4 . The solvent was removed under reduced pressure and the residue was dissolved in CH_2Cl_2 . The solution was filtered through alumina (Brockmann grade III) (eluent: CH_2Cl_2 , 1 % triethylamine) and the solvent was removed under reduced pressure. Final purification involved recrystallization from CH_2Cl_2 /*n*-hexane.

General procedure F – Suzuki reactions: A Schlenk flask was charged with K_3PO_4 (20 equiv.) and anhydrous THF (60 mL) under an argon atmosphere, then porphyrin (1 equiv.), arylboronic acid or arylboronic ester (10 equiv.) and $Pd(PPh_3)_4$ (0.1 equiv.) were added. The reaction was heated at reflux for 7–10 h (TLC control) and protected from light. After completion, the solvent was evaporated and the residue was dissolved in CH_2Cl_2 . The mixture was washed with saturated $NaHCO_3$, water, and brine and then dried over Na_2SO_4 . The organic solvent was evaporated and the crude product was purified by flash chromatography followed by recrystallization.

General procedure G – Insertion of nickel(II): Porphyrin (1 equiv.) and $Ni(acac)_2$ (1.1 equiv.) were dissolved in toluene (20 mL) and heated to reflux. The progress of the reaction was monitored by TLC. Upon completion, the solvent was removed *in vacuo* and the product was isolated after passage through a plug of silica gel using CH_2Cl_2 as the eluent.

5,10-Bis(2,6-difluorophenyl)porphyrin 16: Following the general procedure A, tripyrrane (0.500 g, 2.22 mmol), pyrrole (0.154 mL, 2.22 mmol) and 2,6-difluorobenzaldehyde (0.788 g, 5.55 mmol) were added to a dry CH_2Cl_2 solution (1 L). After 30 min, TFA (0.15 mL) was added and stirring was continued for 16 h. DDQ (2.015 g, 8.88 mmol) was added and the crude product was purified by column chromatography (CH_2Cl_2 /*n*-hexane = 1:2, v/v) to give 50 mg (0.093 mmol, 5 %) of a

purple powder after recrystallization from CH₂Cl₂/MeOH. *R*_f = 0.3 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -3.42 (s, 2H, NH), 7.49 (t, 4H, ³*J* = 8.2 Hz, Ar-*H*), 7.91 (m, 2H, Ar-*H*), 9.08 (d, 4H, ³*J* = 4.7 Hz, *H*_β), 9.53 (d, 4H, ³*J* = 4.7 Hz, *H*_β), 10.41 ppm (s, 2H, *H*_{meso}); compound too insoluble for ¹³C NMR; UV/VIS (CH₂Cl₂): λ_{max} (lg ε) = 418 (5.07), 516 (3.68), 550 (3.29), 593 (3.14), 649 nm (2.99); HRMS: *m/z* calcd for [C₃₂H₁₉N₄F₄] [M+H]⁺: 535.1546, found: 535.1536.

[5,10-Di(*n*-hexyl)-15,20-diphenylporphyrinato]nickel(II) 17: (5,10-Diphenylporphyrinato)nickel(II) **11** (37 mg, 0.07 mmol) was reacted with a 2.5 M solution of *n*-hexyllithium in *n*-hexane (0.17 mL, 0.43 mmol, 6 equiv.) following procedure B. Purification on silica gel (CH₂Cl₂/*n*-hexane = 1:1, v/v) and recrystallization from CH₂Cl₂/MeOH gave purple crystals (28 mg, 0.04 mmol, 58 %). *R*_f = 0.69 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. 167 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 0.90 (t, 6H, ³*J* = ³*J* = 7.3 Hz, C₅H₁₀CH₃), 1.35 (m, 8H, C₃H₆(CH₂)₃CH₃), 1.59 (m, 4H, C₂H₄CH₂C₃H₇), 2.29 (m, 4H, CH₂CH₂C₄H₉), 4.54 (t, 4H, ³*J* = ³*J* = 7.8 Hz, CH₂C₃H₇), 7.66 (m, 6H, Ar-*H*_{meso}, Ar-*H*_β), 7.97 (m, 4H, Ar-*H*_α), 8.63 (br s, 2H, *H*_{β7,8}), 8.73 (AB, 2H, ³*J*_{H12,H13} = ³*J*_{H13,H17} = ³*J*_{H12,H13} = ³*J*_{H18,H17} = 5.1 Hz, *H*_{β2,13}), 9.24 (AB, 2H, ³*J*_{H3,H2} = ³*J*_{H12,H13} = 5.1 Hz, *H*_{β3,12}), 9.34 ppm (br s, 2H, *H*_{β17,18}); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 14.10, 22.65, 30.05, 31.77, 34.20, 37.41, 117.58, 118.20, 126.83, 127.57, 129.51, 129.81, 131.94, 132.22, 133.62, 140.92, 141.66, 141.74, 141.97, 142.03, ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ε) = 416 (5.21), 532 nm (4.06); MS (70 eV, EI, 350 °C): *m/z* (%) = 686 (100 % [M]⁺), 615 (89 % [M - C₃H₇]⁺), 544 (50 % [M - 2 C₃H₇]⁺); HRMS: *m/z* calcd for [C₄₄H₄₈N₄] [M+H]⁺: 687.2998, found: 687.2936.

5-(*n*-Hexyl)-10,15-bis(4-methylphenyl)porphyrin 18: 5,10-Bis(4-methylphenyl)porphyrin **12** (32 mg, 0.07 mmol) was reacted with a 2.5 M solution of *n*-hexyllithium in *n*-hexane (0.22 mL, 0.39 mmol, 6 equiv.) following procedure B. Purification on silica gel (CH₂Cl₂/*n*-hexane = 1:1, v/v) and recrystallization from CH₂Cl₂/MeOH gave purple crystals (12 mg, 0.02 mmol, 18 %). *R*_f = 0.49 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. 168 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = -2.93 (br s, 2H, NH), 0.92 (t, 3H, ³*J* = 7.2 Hz, C₅H₁₀CH₃), 1.52 (m, 4H, C₃H₆(CH₂)₃CH₃), 1.81 (m, 2H, C₂H₄CH₂C₃H₇), 2.55 (m, 2H, CH₂CH₂C₄H₉), 2.70 (s, 6H, Ar-CH₃), 5.01 (t, 2H, ³*J* = 8.2 Hz, CH₂C₃H₇), 7.54 (m, 4H, Ar-*H*_{meso}), 8.07 (m, 4H, Ar-*H*_α), 8.81, 8.85 (AB, 2H, ³*J*_{H12,H13} = ³*J*_{H13,H17} = 4.7 Hz, *H*_{β12,13}), 8.93 (AB, 1H, ³*J*_{H8,H7} = 4.9 Hz, *H*_{β8}), 8.97 (AB, 1H, ³*J*_{H17,H18} = 4.7 Hz, *H*_{β17}), 9.27 (AB, 1H, ³*J*_{H18,H17} = 4.7 Hz, *H*_{β18}), 9.37 (AB, 1H, ³*J*_{H2,H3} = 4.7 Hz, *H*_{β2}), 9.47 (AB, 1H, ³*J*_{H7,H8} = 4.9 Hz, *H*_{β7}), 9.58 (AB, 1H, ³*J*_{H3,H2} = 4.7 Hz, *H*_{β3}), 10.10 ppm (s, 1H, 20-*H*_{meso}); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 14.12, 21.53, 22.73, 29.70, 30.28, 31.93, 38.78, 104.11, 118.95, 120.02, 120.11, 127.19, 127.58, ~131, 134.38, 134.60, 137.26, 138.81 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ε) = 413 (4.99), 510 (4.19), 545 (3.79), 585 (3.71), 641 nm (3.56); MS (70 eV, EI): *m/z* (%): 574 (100 % [M]⁺), 503 (63 % [M - C₃H₇]⁺), 413 (89 % [M - C₃H₇ - C₃H₇ + H]⁺), 287 (4 % [M]⁺), 252 (2 % [M - C₃H₇]⁺); HRMS: *m/z* calcd for [C₂₈H₃₈N₄] [M]⁺: 574.3096, found: 574.3094.

5,10-(*n*-Diethyl)-15,20-bis(4-methylphenyl)porphyrin 19: 5,10-Bis(4-methylphenyl)porphyrin **12** (79 mg, 0.16 mmol) was reacted with a 2.5 M solution of *n*-hexyllithium in *n*-hexane (0.65 mL, 1.61 mmol, 10 equiv.) following procedure B. Purification on silica gel (CH₂Cl₂/*n*-hexane = 1:1, v/v) and recrystallization from CH₂Cl₂/MeOH gave purple crystals (23 mg, 0.03 mmol, 22 %). *R*_f = 0.55 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. 172 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = -2.64 (br s, 2H, NH), 0.99 (t, 6H, ³*J* = ³*J* = 7.2 Hz, C₅H₁₀CH₃), 1.44 (m, 4H, C₃H₆(CH₂)₃CH₃), 1.54 (m, 4H, C₂H₄CH₂C₃H₇), 1.83 (m, 4H, C₂H₄CH₂C₃H₇), 2.56 (m, 4H, CH₂CH₂C₄H₉), 2.73 (s, 6H, Ar-CH₃), 4.97 (t, 4H, ³*J* = ³*J* = 7.9 Hz, CH₂C₃H₇), 7.56 (AB, 4H, ³*J* = ³*J* = ³*J* = 7.9 Hz, Ar-*H*_{meso}), 8.10 (AB, 4H, ³*J* = ³*J* = ³*J* = 7.9 Hz, Ar-*H*_α), 8.81 (s, 2H, *H*_{β17,18}), 8.92 (AB, 2H, ³*J* = 4.9 Hz, *H*_{β2,13}), 9.44 (AB, 2H, ³*J*_{H3,H2} = ³*J*_{H12,H13} = 4.9 Hz, *H*_{β3,12}), 9.53 ppm (s, 2H, *H*_{β7,8}); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 14.16, 21.50, 22.75, 30.28, 31.93, 35.65, 38.81, 118.81, 119.81, 127.38, ~128, ~131, 134.42, 139.47 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ε) = 419 (4.92), 517 (3.82), 554 (3.61), 595 (3.34), 651 nm (3.45); MS (70 eV, EI): *m/z* (%): 658 (16 % [M]⁺), 587 (67 % [M - C₃H₇]⁺), 516 (27 % [M - 2 C₃H₇]⁺), 425 (4 % [M - 2 C₃H₇ - C₃H₇]⁺), 334 (4 % [M - 2 C₃H₇ - 2 C₃H₇]⁺), 329 (37 % [M]⁺), 294 (18 % [M - C₃H₇]⁺), 259 (43 % [M - 2 C₃H₇]⁺); HRMS: *m/z* calcd for [C₃₀H₃₀N₄] [M]⁺: 658.4035, found: 658.4014.

5,10-Di(*n*-hexyl)-15,20-di(*iso*-butyl)porphyrin 20: 5,10-Di(*iso*-butyl)porphyrin **13** (30 mg, 0.07 mmol) was reacted with a 2.5 M solution of *n*-hexyllithium in *n*-hexane (0.29 mL, 0.71 mmol, 10 equiv.) following procedure B. Purification on silica gel (*n*-hexane/ethyl acetate = 5:1, v/v) and recrystallization from CH₂Cl₂/MeOH gave purple crystals (11 mg, 0.02 mmol, 26 %). *R*_f = 0.67 (CH₂Cl₂/*n*-hexane = 2:3, v/v); m.p. 97 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = -2.65 (br s, 2H, NH), 0.95 (t, 6H, ³*J* = ³*J* = 7.2 Hz, C₅H₁₀CH₃), 1.19 (d, 12H, ³*J* = ³*J* = ³*J* = 6.7 Hz, CH₂CH(CH₃)₂), 1.47 (m, 8H, C₃H₆(CH₂)₃CH₃), 1.82 (m, 4H, C₂H₄CH₂C₃H₇), 2.52 (m, 4H, CH₂CH₂C₄H₉), 2.75 (m, 2H, CH₂CH(CH₃)₂), 4.82 (d, 4H, ³*J* = ³*J* = 7.3 Hz, CH₂CH(CH₃)₂), 4.93 (t, 4H, ³*J* = ³*J* = 8.0 Hz, CH₂C₃H₇), 9.46 ppm (m, 8H, *H*_β); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 14.16, 22.77, 23.33, 30.29, 31.94, 35.58, 36.68, 38.66, 43.76, 117.17, 118.51, ~129 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ε) = 418 (4.97), 520 (4.12), 554 (3.99), 599 (3.74), 659 nm (3.83); MS (70 eV, EI): *m/z* (%): 590 (100 % [M]⁺), 547 (69 % [M - C₃H₇]⁺), 519 (11 % [M - C₃H₇]⁺), 295 (4 % [M]⁺); HRMS: *m/z* calcd for [C₄₀H₅₄N₄] [M]⁺: 590.4348, found: 590.4346.

5,10-Di(*n*-butyl)-15,20-bis(4-methylphenyl)porphyrin 21: Following procedure B and the details given for **27** reaction of *n*-butyllithium (4 mL of 2.5 M solution in *n*-hexane, 10 mmol), a solution of *p*-bromobenzenitrile (0.72 g, 4.0 mmol) in 15 mL of dry diethyl ether at -100 °C and 5,10-bis(4-methylphenyl)porphyrin **12** (50 mg, 0.110 mmol) gave 24 mg (0.034 mmol, 31 %) of the title compound. m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.67 (s, 2H, NH), 1.17 (t, 6H, ³*J* = 7., 7.6 Hz, CH₂CH₂CH₂CH₃), 2.34 (m, 4H, CH₂CH₂CH₂CH₃), 2.57 (m, 4H, CH₂CH₂CH₂CH₃), 2.76 (s, 6H, Ar-CH₃), 5.04 (t, 4H, ³*J* = 7.6, 8.2 Hz, CH₂CH₂CH₂CH₃), 7.57 (d, 4H, ³*J* =

7.6 Hz, Ar-*H*), 8.08 (d, 4H, ³*J* = 7.6 Hz, Ar-*H*), 8.78 (s, 2H, *H*_β), 8.91 (d, 2H, ³*J* = 4.7 Hz, *H*_β), 9.46 (d, 2H, ³*J* = 4.7 Hz, *H*_β), 9.6 ppm (s, 2H, *H*_β); ¹³C NMR (63 MHz, CDCl₃, 25 °C, TMS): δ = 14.06 21.36, 23.54, 29.55, 35.23, 40.77, 118.66, 119.63, 127.19, 127.27, 134.25 137.02, 139.28 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ε) = 418 (4.92), 518 (3.56), 555 (3.36), 603 (3.05), 647 nm (3.02); HRMS: *m/z* calcd for [C₄₂H₄₆N₄] [M+H]⁺: 603.3488, found: 604.3472.

5-(*n*-Butyl)-10,15-diphenylporphyrin 22: 5,10-Diphenylporphyrin **14** (1 eq.) was placed in a Schlenk flask and dissolved in dry THF under argon. The solution was cooled down -78 °C. Then *n*-butyllithium (20 eq., 2.5 M solution in *n*-hexane) and *N,N,N',N'*-tetramethylethylenediamine (3.3 eq.) were added drop wise. The mixture was allowed to warm up to RT and was stirred for 30 additional min. The reaction was quenched with 3 mL water and stirred for another 15 min. DDQ (5.5 eq.) was added. Stirring was continued for 15 min followed by filtration of the reaction mixture through 200 mL silica gel and washing with CH₂Cl₂. The eluted porphyrin fractions were evaporated to dryness. The residue was dissolved in CH₂Cl₂ and purified via column chromatography on silica gel with CH₂Cl₂/*n*-hexane (1:1, v/v, *h* = 44 cm, *φ* = 3 cm). The product was obtained as purple crystals after recrystallization from CH₂Cl₂/MeOH (31.7 mg, 0.06 mmol, 26 %). *R*_f = 0.6 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. 155 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = -2.90 (s, 2H, NH), 1.15 (t, 3H, ³*J* = 7.3 Hz, CH₂CH₃), 1.84 (m, 2H, CH₂CH₃), 2.56 (m, 2H, CH₂CH₂CH₃), 5.04 (t, 2H, ³*J* = 7.9 Hz, CH₂CH₂CH₃), 7.78 (m, 6H, Ar-*H*), 8.23 (m, 4H, Ar-*H*), 8.84 (dd, 2H, ³*J* = 4.8 Hz, *H*_β), 8.94 (d, 1H, ³*J* = 4.8 Hz, *H*_β), 8.98 (d, 1H, ³*J* = 4.6 Hz, *H*_β), 9.30 (d, 1H, ³*J* = 4.7 Hz, *H*_β), 9.40 (d, 1H, ³*J* = 4.7 Hz, *H*_β), 9.50 (d, 1H, ³*J* = 4.9 Hz, *H*_β), 9.60 (d, 1H, ³*J* = 4.7 Hz, *H*_β), 10.14 ppm (s, 1H, *H*_{meso}); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 14.2, 23.7, 34.9, 40.9, 104.3, 118.8, 119.9, 120.2, 126.5, 126.8, 127.6, 128.4, 130.4, 131.0, 131.3, 131.6, 131.8, 134.4, 134.7, 141.7, 142.8 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ε) = 412 (5.33), 509 (4.23), 543 (3.68), 585 (3.26), 641 nm (3.06); MS (EI, 70 eV): *m/z* (%): 518 (98 % [M]⁺), 475 (100 % [M - C₃H₇]⁺), 259 (4 % [M]⁺); HRMS (ES⁺): *m/z* calcd for [C₃₆H₃₁N₄] [M+H]⁺: 519.2549, found 519.2579.

5,10-Bis(4-(*N,N*-dimethylamino)phenyl)-15,20-bis(4-methylphenyl)porphyrin 23: 5,10-Bis(4-methylphenyl)porphyrin **12** (63 mg, 0.13 mmol) was reacted with 4-(*N,N*-dimethylamino)phenyllithium following procedure B. Purification on silica gel (CH₂Cl₂) and recrystallization from CH₂Cl₂/MeOH gave purple crystals (67 mg, 0.09 mmol, 71 %). *R*_f = 0.67 (CH₂Cl₂/MeOH = 95:5, v/v); m.p. >300 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = -2.68 (br s, 2H, NH), 2.69 (s, 6H, Ar-CH₃), 3.22 (s, 12H, N(CH₃)₂), 7.09 (AB, 4H, ³*J* = ³*J* = ³*J* = ³*J* = 8.8 Hz, 5,10-Ar-*H*_α), 7.53 (AB, 4H, ³*J* = ³*J* = ³*J* = ³*J* = 7.7 Hz, 15,20-Ar-*H*_α), 8.07 (AB, 4H, ³*J* = ³*J* = ³*J* = ³*J* = 8.8 Hz, 5,10-Ar-*H*_β), 8.09 (AB, 4H, ³*J* = ³*J* = ³*J* = ³*J* = 7.7 Hz, 15,20-Ar-*H*_β), 8.81 ppm (m, 8H, *H*_β); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 21.52, 40.74, 110.67, 119.46, 120.89, 127.35, 130.46, 134.51, 135.74, 137.15, 139.49, 149.90 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ε) = 425 (4.86), 522 (4.13), 565 (4.15), 598 (sh), 656 nm (3.90); MS (TOF, MS, ES⁺, 70 eV): *m/z* (%): 728 (100 % [M]⁺); HRMS: *m/z* calcd for [C₃₀H₃₄N₆] [M]⁺: 728.3627, found: 728.3624.

5,10-Bis(4-hydroxyphenyl)-15,20-bis(4-methylphenyl)porphyrin 24: 5,10-Bis(4-methylphenyl)porphyrin **12** (52 mg, 0.11 mmol) was reacted with 4-hydroxyphenyllithium following procedure B. Purification on silica gel (CH₂Cl₂) and recrystallization from CH₂Cl₂/MeOH gave purple crystals (41 mg, 0.06 mmol, 57 %). *R*_f = 0.36 (CH₂Cl₂); m.p. 102 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 2.67 (s, 6H, Ar-CH₃), 7.01 (AB, 4H, ³*J* = ³*J* = ³*J* = ³*J* = 8.2 Hz, 5,10-Ar-*H*_α), 7.52 (AB, 4H, ³*J* = ³*J* = ³*J* = ³*J* = 7.6 Hz, 15,20-Ar-*H*_α), 7.98 (AB, 4H, ³*J* = ³*J* = ³*J* = ³*J* = 8.2 Hz, 5,10-Ar-*H*_β), 8.07 (AB, 4H, ³*J* = ³*J* = ³*J* = ³*J* = 7.6 Hz, 15,20-Ar-*H*_β), 8.84 ppm (m, 8H, *H*_β); UV/VIS (CH₂Cl₂): λ_{max} (lg ε) = 420 (4.88), 517 (3.83), 553 (3.64), 592 (3.42), 648 nm (3.43); MS (TOF, MS, ES⁺, 70 eV): *m/z* (%): 674 (27 % [M]⁺), 337 (2 % [M]⁺); HRMS: *m/z* calcd for [C₂₈H₂₄N₄O₂] [M]⁺: 674.2682, found: 674.2645.

5,10-Bis(4-(*N,N*-dimethylamino)phenyl)-15,20-bis(3-methoxyphenyl)porphyrin 25: 5,10-Bis(3-methoxyphenyl)porphyrin **15** (79 mg, 0.16 mmol) was reacted with 4-(*N,N*-dimethylamino)phenyllithium following procedure B. Purification on silica gel (CH₂Cl₂/MeOH = 98 : 2, v/v) gave two fractions. The first contained the monarylated species **26** and the second the title compound. Recrystallization from CH₂Cl₂/*n*-hexane gave purple crystals (28 mg, 0.04 mmol, 32 %). *R*_f = 0.67 (CH₂Cl₂/MeOH = 95:5, v/v); m.p. 236 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = -2.62 (br s, 2H, NH), 3.22 (s, 12H, N(CH₃)₂), 3.99 (s, 6H, OCH₃), 7.10 (AB, 4H, ³*J* = ³*J* = ³*J* = ³*J* = 8.6 Hz, 5,10-Ar-*H*_α), 7.33 (m, 2H, 15,20-Ar-*H*_β), 7.64 (m, 2H, 15,20-Ar-*H*_α), 7.84 (m, 4H, 15,20-Ar-*H*_β), 8.11 (AB, 4H, ³*J* = ³*J* = ³*J* = ³*J* = 8.6 Hz, 5,10-Ar-*H*_α), 8.88 (m, 4H, *H*_{β2,7,8,13}), 8.97 ppm (m, 4H, *H*_{β3,12,17,18}); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 40.69, 55.47, 110.68, 113.48, 119.02, 120.45, 127.42, 127.69, 130.38, 135.73, 143.77, 149.95, 157.95 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ε) = 425 (5.00), 522 (4.17), 565 (4.16), 596 (sh), 656 nm (3.90); MS (EI, 70 eV): *m/z* (%): 760 (7 % [M]⁺), 380 (100 % [M]⁺); HRMS: *m/z* calcd for [C₃₀H₃₄N₆O₂] [M]⁺: 760.3526, found: 760.3500.

5-[4-(*N,N*-Dimethylamino)phenyl]-10,15-bis(3-methoxyphenyl)porphyrin 26: Obtained from the synthesis of **25** as purple crystals (5 mg, 0.01 mmol, 5 %). *R*_f = 0.4 (CH₂Cl₂/MeOH = 95:5, v/v); m.p. 98 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = -2.97 (br s, 2H, NH), 3.23 (s, 6H, N(CH₃)₂), 3.9

MS (EI, 70 eV): m/z (%): 641 (48 %, [M]⁺), 321 (100 %, [M]²⁺); HRMS: m/z calcd for [C₄₂H₃₈N₅O₂] [M]⁺: 641.2791, found: 641.2771.

5,10-Bis(4-ethynylphenyl)-15,20-bis(4-methylphenyl)porphyrin 27: Following procedure B, *n*-butyllithium (4 mL of 2.5M solution in *n*-hexane, 10 mmol) was slowly added (ca. 1h) under an argon atmosphere to a 100 mL Schlenk flask charged with a solution of *p*-bromophenylethyne (0.91 g, 5.0 mmol) in 15 mL of dry diethyl ether at -70 °C. The reaction mixture was then warmed to -40 °C and THF was added drop wise until the aryllithium was formed as a white/pink suspension. To this vigorously stirred mixture was added rapidly a solution of 5,10-bis(4-methylphenyl)porphyrin **12** (56 mg, 0.125 mmol) in 50 mL of dry THF. The color of the mixture changed from deep purple to brown within 30 min, subsequently a mixture of 5 mL water in 5 mL of THF was added for hydrolysis. After stirring of the mixture for 20 min, a solution of DDQ (283 mg, 1.25 mmol) in CH₂Cl₂ was added and the reaction mixture was stirred for another 60 min at RT. The crude product was subjected to column chromatography using CH₂Cl₂/*n*-hexane (1:1, v/v) to give 24 mg (0.034 mmol, 31 %), of a purple solid after recrystallization from CH₂Cl₂/MeOH. R_f = 0.73 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.78 (s, 2H, NH), 2.73 (s, 6H, Ar-CH₃), 3.34 (s, 2H, -C≡CH), 7.58 (d, 4H, ³J = 7.6 Hz, Ar-*H*), 7.92 (d, 4H, ³J = 8.2 Hz, Ar-*H*), 8.11 (d, 4H, ³J = 7.6 Hz, Ar-*H*), 8.20 (d, 4H, ³J = 7.6 Hz, Ar-*H*), 8.84 (m, 4H, H_β), 8.90 ppm (m, 4H, H_β); ¹³C NMR (63 MHz, CDCl₃, 25 °C, TMS): δ = 21.09, 77.84, 83.22, 118.42, 120.29, 121.14, 127.01, 130.17, 134.06, 134.19, 137.03, 138.61, 142.37; UV/VIS (DMF): λ_{max} (lg ϵ) = 420 (4.92), 516 (3.61), 551 (3.38), 592 (3.20), 655 nm (3.19); HRMS: m/z calcd for [C₅₀H₃₈N₄] [M+H]⁺: 691.2862, found: 691.2858.

5,10-Bis(4-ethynylphenyl)-15,20-bis(2,6-difluorophenyl)porphyrin 28: Following procedure B and the details given for **27** reaction of *p*-bromophenylethyne (0.55 g, 3.0 mmol) and 5,10-bis(2,6-difluorophenyl)porphyrin **16** (40 mg, 0.075 mmol) gave 14 mg (0.019 mmol, 25 %) of the title compound. R_f = 0.6 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.71 (s, 2H, NH), 3.51 (s, 2H, -C≡CH), 7.43 (t, 4H, ³J = 8.2 Hz, Ar-*H*), 7.81 (m, 2H, Ar-*H*), 7.96 (t, 4H, ³J = 8.2 Hz, Ar-*H*), 8.23 (t, 4H, ³J = 7.6 Hz, Ar-*H*), 8.92 (m, 4H, H_β), 9.02 ppm (m, 4H, H_β); UV/VIS (DMF): λ_{max} (lg ϵ) = 414 (5.09), 508 (3.83), 543 (3.18), 585 (3.30), 637 nm (2.89); HRMS: m/z calcd for [C₄₈H₂₇F₄N₄] [M+H]⁺: 735.2172, found: 735.2197.

5,10-Dibromo-15,20-bis(4-methylphenyl)porphyrin 29: 5,10-Bis(4-methylphenyl)porphyrin **12** (93 mg, 0.19 mmol) was reacted with NBS (84 mg, 0.47 mmol) following procedure C to yield purple crystals (102 mg, 0.16 mmol, 83 %). R_f = 0.59 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. 285 °C (dec.); ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = -2.91 (br s, 2H, NH), 2.69 (s, 6H, Ar-CH₃), 7.54 (AB, 4H, ³J = ³J = 7.9 Hz, Ar-*H*), 8.01 (AB, 4H, ³J = ³J = 7.9 Hz, Ar-*H*), 8.74 (s, 2H, H_{β1,18}), 8.82 (AB, 2H, ³J = 4.8 Hz, H_{β2,13}), 9.52 (AB, 2H, ³J = 4.8 Hz, H_{β3,12}), 9.54 ppm (s, 2H, H_{β7,8}); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 21.53, 103.15, 121.75, 127.55, ~131, 134.40, 137.73, 138.57 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ϵ) = 423 (5.03), 523 (4.21), 558 (4.07), 602 (3.77), 659 nm (3.81); MS (TOF, MS, ES⁺, 70 eV): m/z (%): 646 (49 %, [M]⁺); HRMS: m/z calcd for [C₃₄H₂₄N₄Br₂] [M]⁺: 646.0368, found: 646.0347.

[5,10-Dibromo-15,20-bis(4-methylphenyl)porphyrinato]zinc(II) 30: 5,10-Dibromo-15,20-bis(4-methylphenyl)porphyrin **29** (83 mg, 0.13 mmol) was reacted following procedure D. Column chromatography on silica gel (CH₂Cl₂) gave a single product. Recrystallization from CH₂Cl₂/MeOH/H₂O gave purple crystals (66 mg, 0.09 mmol, 72 %). R_f = 0.42 (CH₂Cl₂/*n*-hexane = 2:1, v/v); m.p. >310 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 2.75 (s, 6H, Ar-CH₃), 7.61 (AB, 4H, ³J = ³J = 7.7 Hz, Ar-*H*), 8.06 (AB, 4H, ³J = ³J = 7.7 Hz, Ar-*H*), 8.76 (s, 2H, H_{β7,8}), 8.77 (AB, 2H, ³J = 4.7 Hz, H_{β2,13}), 8.86 (s, 2H, H_{β1,18}), 9.29 ppm (AB, 2H, ³J = 4.7 Hz, H_{β3,12}); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 21.32, 103.73, 122.44, 127.44, 132.29, 132.50, 132.65, 133.20, 134.52, 137.60, 139.29, 148.43, 149.07, 150.92, 151.08 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ϵ) = 424 (5.09), 557 (4.21), 597 nm (3.83); MS (TOF, MS, ES⁺, 70 eV): m/z (%): 708 (39 %, [M]⁺); HRMS: m/z calcd for [C₃₄H₂₂N₄Br₂Zn] [M]⁺: 707.9503, found: 707.9469.

[5,10-Dibromo-15,20-bis(4-methylphenyl)porphyrinato]nickel(II) 31: Following the general procedure G, 5,10-dibromo-15,20-bis(4-methylphenyl)porphyrin **29** (100 mg, 0.154 mmol) and Ni(acac)₃ (43.5 mg, 0.169 mmol) were dissolved in toluene (20 mL) and heated to reflux for 6 h to give 80 mg (0.113 mmol, 80 %) after recrystallization from CH₂Cl₂/MeOH. R_f = 0.7 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, 25 °C, CDCl₃): δ = 2.66 ppm (s, 6H, CH₃), 7.49 (d, 4H, ³J = 7.6 Hz, Ar-*H*), 7.82 (d, 4H, ³J = 8.2 Hz, Ar-*H*), 8.66 (s, 2H, H_β), 8.74 (d, 2H, ³J = 5.3 Hz, H_β), 9.39 (d, 2H, ³J = 5.3 Hz, H_β), 9.46 ppm (s, 2H, H_β); UV/VIS (CH₂Cl₂): λ_{max} (lg ϵ) = 421 (5.08), 538 (3.92), 589 nm (3.38); HRMS: m/z calcd for [C₃₄H₂₂N₄Br₂Ni] [M]⁺: 701.9565, found 701.9681; elemental analysis calcd (%) for C₃₄H₂₂N₄Br₂Ni (705.07): C 57.91, H 3.15, N 7.95, found: C 57.65, H 3.40, N 8.01.

{(all-*E*)-5,10-Bis[4-(2-butoxycarbonyl)ethenyl]-15,20-bis(4-methylphenyl)porphyrinato]zinc(II) 32: [5,10-Dibromo-15,20-bis(4-methylphenyl)porphyrinato]zinc(II) **30** (77.7 mg, 0.11 mmol) was reacted with butyl acrylate (1.00 mL, 7.01 mmol) following procedure E to yield purple crystals (60 mg, 0.07 mmol, 64 %). R_f = 0.34 (CH₂Cl₂, 1 % triethylamine, v/v, alumina); m.p. 176 °C; ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS): δ = 1.08 (t, 6H, ³J = 7.4 Hz, C₃H₇CH₂), 1.60 (m, 4H, C₃H₇CH₂CH₂), 1.88 (m, 4H, CH₂CH₂C₃H₇), 2.70 (s, 6H, Ar-CH₃), 4.43 (t, 4H, ³J = 6.8 Hz, CH₂C₃H₇), 6.73 (d, 2H, ³J = 15.7 Hz, CH=CH-CO), 7.54 (d, 4H, ³J = 7.5 Hz, Ar-*H*), 7.99 (d, 4H, ³J = 7.5 Hz, Ar-*H*), 8.70 (s, 2H, H_{β1,18}), 8.84 (AB, 2H, ³J = 4.7 Hz, H_{β2,13}), 9.39 (AB, 2H, ³J = 4.7 Hz, H_{β3,12}), 9.52 (s, 2H, H_{β7,8}), 10.23 ppm (d, 2H, ³J = 15.7 Hz, CH=CH-CO); ¹³C

NMR (126 MHz, CDCl₃, 25 °C, TMS): δ = 13.74, 19.46, 21.26, 31.06, 64.66, 112.98, 123.51, 127.19, 128.77, 129.80, 130.09, 131.80, 132.78, 134.44, 137.21, 140.03, 146.86, 148.97, 149.41, 149.67, 150.31, 166.38 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ϵ) = 438 (5.14), 572 (4.00), 616 nm (3.92); MS (TOF, MS, ES⁺, 70 eV): m/z (%): 805 (100 %, [M+H]⁺); HRMS: m/z calcd for [C₄₈H₃₈N₄O₄Zn] [M+H]⁺: 805.2732, found: 805.2706.

{(all-*E*)-5,10-Bis(4-methylphenyl)-15,20-bis[4-(3-oxobut-1-enyl)porphyrinato]zinc(II) 33: [5,10-Dibromo-15,20-bis(4-methylphenyl)porphyrinato]zinc(II) **30** (77.7 mg, 0.11 mmol) was reacted with methyl vinyl ketone (0.57 mL, 7.02 mmol) following procedure E to yield purple crystals (35 mg, 0.05 mmol, 50 %). R_f = 0.5 (CH₂Cl₂, 5 % MeOH, v/v); m.p. 215 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 2.50 (s, 6H, CO-CH₃), 2.71 (s, 6H, Ar-CH₃), 6.58 (d, 2H, ³J = 15.7 Hz, CH=CH-CO), 7.55 (AB, 4H, ³J = ³J = 7.5 Hz, Ar-*H*), 8.00 (d, 4H, ³J = 7.5 Hz, Ar-*H*), 8.80 (s, 2H, H_{β1,18}), 8.89 (AB, 2H, ³J = 4.7 Hz, H_{β2,13}), 9.22 (s, 2H, H_{β7,8}), 9.28 (AB, 2H, ³J = 4.7 Hz, H_{β3,12}), 9.80 ppm (d, 2H, ³J = 15.7 Hz, CH=CH-CO); ¹³C NMR (63 MHz, CDCl₃, 25 °C, TMS): δ = 20.78, 27.29, 112.81, 123.21, 126.81, 128.53, 129.33, 131.04, 131.61, 132.49, 133.88, 136.96, 139.20, 144.93, 148.25, 148.83, 149.32, 149.98, 196.33 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ϵ) = 443 (4.44), 577 (4.18), 621 nm (4.14); MS (TOF, MS, ES⁺, 70 eV): m/z (%): 689 (100 %, [M+H]⁺); HRMS: m/z calcd for [C₄₂H₃₈N₄O₂Zn] [M]⁺: 689.1895, found: 689.1889.

{(all-*E*)-5,10-Bis(4-methylphenyl)-15,20-bis[2-(3-nitrophenyl)vinyl]porphyrinato}zinc(II) 34: Following the general procedure E, [5,10-Dibromo-15,20-bis(4-methylphenyl)porphyrinato]zinc(II) **30** (100 mg, 0.140 mmol), was dissolved in DMF (50 mL) under a nitrogen atmosphere. The 3-nitrostyrene (1.36 mL, 9.8 mmol), sodium acetate (65 mg, 0.784 mmol), palladium acetate (3.1 mg, 0.014 mmol) and triphenylphosphine (14.7 mg, 0.056 mmol) were added and the temperature was raised to 120 °C for 16 h (TLC control). The crude product was extracted with CH₂Cl₂ and washed with water. The product was purified by silica gel column chromatography using CH₂Cl₂/*n*-hexane (1:1, v/v) and gave 70 mg (0.082 mmol, 60 %) of the desired compound after recrystallization from CH₂Cl₂/MeOH. R_f = 0.12 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. > 300 °C; ¹H NMR (600 MHz, CD₂Cl₂, 25 °C, TMS): δ = 2.76 (s, 6H, CH₃), 6.58 (d, 2H, ³J = 16 Hz, vinyl), 7.49 (d, 4H, ³J = 7.7 Hz, Ar-*H*), 7.69 (t, 4H, ³J = 7.7 Hz, Ar-*H*), 7.91 (d, 4H, ³J = 7.7 Hz, Ar-*H*), 7.93 (d, 2H, ³J = 7.7 Hz, Ar-*H*), 8.29 (d, 2H, ³J = 8.2 Hz, Ar-*H*), 8.65 (s, 2H, H_β), 8.71 (d, 2H, ³J = 16 Hz, vinyl), 8.88 (s, 2H, H_β), 8.93 (d, 2H, ³J = 4.4 Hz, H_β), 9.23 ppm (d, 2H, ³J = 4.4 Hz, H_β); ¹³C NMR (125 MHz, CD₂Cl₂, 25 °C, TMS): δ = 138.67, 139.29, 146.90, 148.53, 148.92, 149.72, 150.38 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 445 (5.12), 584 (3.98), 630 nm (3.80).

{(all-*E*)-5,10-Bis(4-methylphenyl)-15,20-[2-(3-nitrophenyl)vinyl]porphyrinato}nickel(II) 35: Following the general procedure E, [5,10-dibromo-15,20-bis(4-methylphenyl)porphyrinato]nickel(II) **31** (25 mg, 0.140 mmol), 3-nitrostyrene (0.35 mL, 2.48 mmol), sodium acetate (16 mg, 0.196 mmol), palladium acetate (0.16 mg, 0.003 mmol) and triphenylphosphine (3.7 mg, 0.014 mmol) in DMF (50 mL) gave 5 mg (0.006 mmol, 34 %) of a purple compound after recrystallization from CH₂Cl₂/MeOH. R_f = 0.47 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 2.66 (s, 6H, CH₃), 6.71 (d, 2H, ³J = 15.8 Hz, alkene-*H*), 7.49 (d, 4H, ³J = 7.6 Hz, Ar-*H*), 7.64 (t, 2H, ³J = 7.6 Hz, Ar-*H*), 7.82 (d, 4H, ³J = 7.6 Hz, Ar-*H*), 7.93 (d, 2H, ³J = 7.7 Hz, Ar-*H*), 8.22 (d, 2H, ³J = 7.6 Hz, Ar-*H*), 8.59 (s, 2H, Ar-*H*), 8.61 (s, 2H, H_β), 8.73 (d, 2H, ³J = 4.7 Hz, H_β), 9.14 (d, 2H, ³J = 16 Hz, H_β), 9.18 (d, 2H, ³J = 15.8 Hz, alkene-*H*), 9.23 ppm (s, 2H, H_β); ¹³C NMR (150 MHz, CD₂Cl₂, 25 °C, TMS): δ = 21.44, 29.34, 112.65, 120.79, 122.47, 127.78, 129.56, 129.84, 130.91, 132.22, 133.38, 137.61, 138.51, 139.87, 141.39, 142.31, 148.63 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 444 (4.87), 563 (3.83), 614 nm (3.75).

5,10-Dibromo-15,20-diphenylporphyrin 36: Following the general procedure C, 5,10-diphenylporphyrin **14** (90 mg, 0.19 mmol) and NBS (87 mg, 0.48 mmol) gave 84 mg (0.14 mmol, 70 %) of a purple solid after recrystallization from CH₂Cl₂/MeOH. R_f = 0.59 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. > 300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.88 (s, 2H, NH), 7.78 (m, 4H, Ar-*H*), 8.17 (m, 4H, Ar-*H*), 8.78 (m, 4H, H_β), 9.57 (m, 4H, H_β); UV/VIS (CH₂Cl₂): λ_{max} (lg ϵ) = 421 (4.98), 522 (3.57), 557 (3.33), 600 (2.89), 663 nm (2.86).

5,10-Dibromo-15,20-bis(3-methoxyphenyl)porphyrin 37: 5,10-Bis(3-methoxyphenyl)porphyrin **15** (77 mg, 0.15 mmol) was reacted with NBS (66 mg, 0.37 mmol) following procedure C to yield red crystals (74 mg, 0.11 mmol, 74 %). R_f = 0.43 (CH₂Cl₂/*n*-hexane = 2:1, v/v); m.p. 198 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = -2.82 (br s, 2H, NH), 3.97 (s, 6H, Ar-OCH₃), 7.33 (m, 2H, Ar-*H*), 7.63 (m, 2H, Ar-*H*), 7.72 (m, 4H, Ar-*H*), 8.77 (s, 2H, H_{β1,18}), 8.87 (AB, 2H, ³J = 4.8 Hz, H_{β2,13}), 9.56 (AB, 2H, ³J = 4.8 Hz, H_{β3,12}), 9.63 ppm (s, 2H, s, H_{β7,8}); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 55.51, 103.44, 113.71, 120.50, 121.19, 127.52, 127.65, ~131, 142.76, 158.03 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ϵ) = 423 (5.01), 521 (3.44), 556 (3.82), 600 (3.56), 658 nm (3.55); MS (TOF, MS, ES⁺, 70 eV): m/z (%): 678 (52 %, [M]⁺); HRMS: m/z calcd for [C₃₄H₂₄N₄Br₂O₂] [M]⁺: 678.0266, found: 678.0243.

5,10-Dibromo-15,20-bis(2,6-difluorophenyl)porphyrin 38: Following the general procedure C, 5,10-bis(2,6-difluorophenyl)porphyrin **16** (200 mg, 0.374 mmol) and NBS (166 mg, 0.94 mmol) gave 150 mg (0.21 mmol, 58 %) of a purple solid after recrystallization from CH₂Cl₂/MeOH; R_f = 0.48 (CH₂Cl₂/*n*-hexane = 1:1, v/v). m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.92 (s, 2H, NH), 7.43 (t, 4H, ³J = 7.8 Hz, Ar-*H*), 7.83 (m, 2H, Ar-*H*), 8.83 (s, 4H, H_β), 9.36 (d, 2H, ³J = 4.7 Hz, H_β), 9.59 ppm (d, 2H, ³J = 4.7 Hz, H_β); UV/VIS (CH₂Cl₂): λ_{max} (lg ϵ) = 419 (4.94), 516

(3.73), 555 (3.18), 596 (3.11), 649 nm (2.49); HRMS (MS ES+): m/z calcd for $[C_{32}H_{16}N_4Br_2F_4] [M]^+$: calcd 689.9678 found 689.9372.

5,10-Dibromo-15,20-di(*n*-pentylporphyrin 39: Following the general procedure C 5,10-di(*n*-pentylporphyrin (90 mg, 0.2 mmol) and NBS (89 mg, 0.5 mmol) gave 73 mg (0.12 mmol, 60 %) of a purple solid after recrystallization from $CH_2Cl_2/MeOH$. $R_f = 0.62$ (CH_2Cl_2/n -hexane = 1:1, v/v); m.p. >198 °C; 1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = -3.15$ (s, 2H, *NH*), 1.00 (t, 6H, $^3J = 7.3$, 7.0 Hz, $CH_2CH_2CH_2CH_2CH_3$), 1.56 (m, 4H, $CH_2CH_2CH_2CH_2CH_3$), 1.77 (m, 4H, $CH_2CH_2CH_2CH_2CH_3$), 2.44 (m, 4H, $CH_2CH_2CH_2CH_2CH_3$), 4.77 (t, 4H, $^3J = 7.7$, 8 Hz, $CH_2CH_2CH_2CH_2CH_3$), 9.20 (m, 4H, H_β), 9.49 ppm (m, 4H, H_α); ^{13}C NMR (150 MHz, 25 °C, $CDCl_3$): $\delta = 13.86$, 22.71, 29.40, 32.40, 35.24, 38.25, 101.90, 121.45 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 422 (4.48), 524 (3.48), 559 (3.25), 605 (2.78), 664 nm (3.14); HRMS (MS ES+): m/z calcd for $[C_{30}H_{33}N_4Br_2] [M+H]^+$: 607.1072, found: 607.1097.

5,10-Dibromo-15,20-di(*n*-hexylporphyrin 40: Following the general procedure C 5,10-di(*n*-hexylporphyrin (70 mg, 0.14 mmol) and NBS (65 mg, 0.36 mmol) gave 47 mg (0.07 mmol, 50 %) of a purple solid after recrystallization from $CH_2Cl_2/MeOH$. m.p. >300 °C; $R_f = 0.6$ (CH_2Cl_2/n -hexane = 1:1, v/v); 1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = -2.81$ (s, 2H, *NH*), 0.97 (t, 6H, $^3J = 7.6$, 7.01 Hz, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.42 (m, 4H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.45 (m, 4H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.82 (m, 4H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.49 (m, 4H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 4.87 (t, 4H, $^3J = 8.2$, 7.6 Hz, $CH_2CH_2CH_2CH_2CH_2CH_3$), 9.52 (m, 4H, H_β), 9.62 ppm (m, 4H, H_α); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 14.15$, 22.73, 30.25, 31.86, 35.66, 38.83, 102.06, 121.72 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 420 (4.88), 522 (3.63), 558 (3.51), 603 (3.26), 663 nm (3.18); HRMS (MS ES+): m/z calcd for $[C_{32}H_{37}N_4Br_2] [M+H]^+$ calcd: 637.1364, found 637.1379.

5,10-Bis(4-bromophenyl)porphyrin 41: 4-Bromobenzaldehyde (0.74 g, 4 mmol) was reacted according to a procedure given before.^[12] Column chromatography on silica gel (CH_2Cl_2/n -hexane = 1:4, v/v) gave the 5,10,15-tris(4-bromophenyl)porphyrin **71** as the first fraction, followed by the title compound and then traces of (4-bromophenyl)porphyrin. Recrystallization from $CH_2Cl_2/MeOH$ gave 46 mg (0.07 mmol, 4 %) of purple crystals. $R_f = 0.38$ (CH_2Cl_2/n -hexane = 1:1, v/v); m.p. >300 °C; 1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = -3.45$ (br s, 2H, *NH*), 7.89 (AB, 4H, $^3J = ^2J = ^3J = 8.1$ Hz, *Ar-H*), 8.05 (AB, 4H, $^3J = ^2J = ^3J = 8.1$ Hz, *Ar-H*), 8.89 (s, 2H, $H_{\beta(7,8)}$), 8.96 (AB, 2H, $^3J = ^2J = 4.7$ Hz, $H_{\beta(12,13)}$), 9.30 (AB, 2H, $^3J = ^2J = 4.7$ Hz, $H_{\beta(12,13)}$), 9.38 (s, 2H, $H_{\beta(17,18)}$), 10.17 ppm (s, 2H, H_{meso}); ^{13}C NMR (63 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 104.53$, 118.41, 122.52, 129.90, ~131, 135.89, 140.98, ppm; UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 407 (5.36), 502 (4.33), 534 (3.67), 575 (3.87), 629 nm (3.38); MS (70 eV, EI): m/z (%): 620 (9 %), $[M]^+$, 540 (4 %), $[M - Br]^+$, 464 (3 %), $[M - C_6H_4Br + Br]^+$, 310 (14 %, $[M]^+$); HRMS: m/z calcd for $[C_{32}H_{20}N_4Br_2] [M]^+$: 618.0055, found: 618.0061.

5,10-Bis(3,4,5-trifluorophenyl)porphyrin 42: 3,4,5-Trifluorobenzaldehyde (0.64 g, 4 mmol) was reacted according to a procedure given before.^[12] Column chromatography on silica gel (CH_2Cl_2/n -hexane = 1:1, v/v) gave the 5,10,15-tris(3,4,5-trifluorophenyl)porphyrin **72** as the first fraction, followed by the title compound and then traces of (3,4,5-trifluorophenyl)porphyrin. Recrystallization from $CH_2Cl_2/MeOH$ gave 10 mg (0.02 mmol, 1 %) of purple crystals. $R_f = 0.47$ (CH_2Cl_2/n -hexane = 1:1, v/v); m.p. 285 °C; 1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = -3.52$ (br s, 2H, *NH*), 7.85 (m, 4H, *Ar-H*), 8.92 (s, 2H, $H_{\beta(12,13)}$), 8.98 (AB, 2H, $^3J = ^2J = 4.4$ Hz, $H_{\beta(12,13)}$), 9.39 (AB, 2H, $^3J = ^2J = 4.6$ Hz, $H_{\beta(7,8)}$), 9.45 (AB, 2H, $^3J = ^2J = 4.6$ Hz, $H_{\beta(17,18)}$), 10.27 ppm (s, 2H, H_{meso}); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 105$, 27, 119.16, 130.96, 131.41, 132.32, 138.26, 148.31, 151.67 ppm; UV/VIS (CH_2Cl_2): λ_{max} (lg ϵ) = 405 (5.03), 500 (4.09), 532 (3.47), 573 (3.73), 627 nm (3.06); MS (70 eV, EI, 350 °C): m/z (%): 570 (100 %, $[M]^+$), 439 (1 %, $[M - C_6H_2F_3]^+$), 285 (50 %, $[M]^+$), 251 (6 %, $[M - C_6H_2F_3]^+$); HRMS: m/z calcd for $[C_{32}H_{10}F_6N_4] [M]^+$: 570.1279, found: 570.1259.

5,10-Bis(4-methoxycarbonylphenyl)-15,20-bis(4-methylphenyl)porphyrin 43: Following the general procedure F 5,10-dibromo-15,20-bis(4-methylphenyl)porphyrin **29** (33 mg, 0.05 mmol), 4-methoxycarbonylphenylboronic acid (90 mg, 0.5 mmol), $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol) and K_3PO_4 (212 mg, 1 mmol) in THF (60 mL) gave 20 mg (0.02 mmol, 52 %) of a purple solid after recrystallization from $CH_2Cl_2/MeOH$. $R_f = 0.28$ (CH_2Cl_2/n -hexane = 1:1, v/v); m.p. >300 °C; 1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = -2.76$ (s, 2H, *NH*), 2.70 (s, 6H, CH_3), 4.13 (s, 6H, OCH_3), 7.59 (d, 4H, $^3J = 7.6$ Hz, *Ar-H*), 8.12 (d, 4H, $^3J = 7.6$ Hz, *Ar-H*), 8.32 (d, 4H, $^3J = 8.2$ Hz, *Ar-H*), 8.46 (d, 4H, $^3J = 8.2$ Hz, *Ar-H*), 8.80 (d, 2H, $^3J = 4.7$ Hz, H_β), 8.82 (s, 2H, H_β), 8.90 (s, 2H, H_β), 8.92 ppm (d, 2H, $^3J = 4.7$ Hz, H_β); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 21.46$, 52.37, 118.09, 120.85, 126.80, 127.03, 127.48, 129.12, 129.76, 134.10, 137.09, 138.54, 146.66, 166.89 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 420 (4.92), 516 (4.27), 551 (4.08), 581 (3.87), 655 nm (3.97); HRMS (MS ES+): m/z calcd for $[C_{50}H_{39}N_4O_4] [M+H]^+$: 759.2971, found 759.2941.

5,10-Bis(4-cyanophenyl)-15,20-bis(4-methylphenyl)porphyrin 44: Following the general procedure F 5,10-dibromo-15,20-bis(4-methylphenyl)porphyrin **29** (30 mg, 0.046 mmol), 4-cyanophenylboronic acid (68 mg, 0.46 mmol), $Pd(PPh_3)_4$ (5.3 mg, 0.0046 mmol) and K_3PO_4 (196 mg, 0.925 mmol) in THF (50 mL) gave 15 mg (0.021 mmol, 47 %) of a purple solid after recrystallization from $CH_2Cl_2/MeOH$. $R_f = 0.34$ (CH_2Cl_2/n -hexane = 1:1, v/v); m.p. >300 °C; 1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = -2.79$ (s, 2H, *NH*), 2.74 (s, 6H, CH_3), 7.60 (d, 4H, $^3J = 8.2$ Hz, *Ar-H*), 8.10 (m, 8H, *Ar-H*), 8.36 (d, 4H, $^3J = 8.2$ Hz, *Ar-H*), 8.75 (d, 2H, $^3J = 4.7$ Hz, H_β), 8.78 (s, 2H, H_β), 8.92 (s, 2H, H_β), 8.95 ppm (d, 2H, $^3J = 4.7$ Hz, H_β); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 21.10$, 111.51, 118.57, 121.13, 130.13, 134.29, 137.11, 137.28, 138.30, 146.55, ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 420 (4.94), 515 (3.79), 551 (3.62), 584 (3.44), 655 nm (3.68); HRMS (MS ES+): m/z calcd for $[C_{48}H_{33}N_6] [M+H]^+$: 693.2767, found 693.2734.

5,10-Bis(4-methylphenyl)-15,20-bis(4-nitrophenyl)porphyrin 45: Following the general procedure F 5,10-dibromo-15,20-bis(4-methylphenyl)porphyrin **29** (30 mg, 0.0462 mmol), 4-nitrophenylboronic acid pinacol ester (116 mg, 0.462 mmol), $Pd(PPh_3)_4$ (5.3 mg, 0.0046 mmol) and K_3PO_4 (196 mg, 0.925 mmol) in THF (50 mL) gave 16 mg (0.021 mmol, 47 %) of a purple solid after recrystallization from $CH_2Cl_2/MeOH$. $R_f = 0.5$ (CH_2Cl_2/n -hexane = 1:1, v/v); m.p. > 300 °C; 1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = -2.76$ (s, 2H, *NH*), 2.74 (s, 6H, CH_3), 7.60 (d, 4H, $^3J = 7.6$ Hz, *Ar-H*), 8.11 (d, 4H, $^3J = 7.6$ Hz, *Ar-H*), 8.42 (d, 4H, $^3J = 8.2$ Hz, *Ar-H*), 8.67 (d, 4H, $^3J = 8.2$ Hz, *Ar-H*), 8.76 (d, 2H, $^3J = 4.7$ Hz, H_β), 8.80 (s, 2H, H_β), 8.92 (s, 2H, H_β), 8.96 ppm (d, 2H, $^3J = 4.7$ Hz, H_β); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 21.09$, 116.47, 121.48, 127.12, 134.66, 137.33, 138.25, 147.31, 148.53 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 421 (4.90), 516 (3.64), 552 (3.46), 584 (3.34), 655 nm (3.60); HRMS (MS ES+): m/z calcd for $[C_{46}H_{32}N_6O_4] [M+H]^+$: 733.2563, found 733.2573.

5,10-Bis(4-methylphenyl)-15,20-bis(3-nitrophenyl)porphyrin 46: Following the general procedure F 5,10-dibromo-15,20-bis(4-methylphenyl)porphyrin **29** (33 mg, 0.05 mmol), 4-methoxycarbonylphenylboronic acid (90 mg, 0.5 mmol), $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol), K_3PO_4 (212 mg, 1 mmol) in THF (60 mL) gave 10 mg (0.013 mmol, 30 %) of a purple solid after recrystallization from $CH_2Cl_2/MeOH$. $R_f = 0.3$ (CH_2Cl_2/n -hexane = 1:1, v/v); m.p. >300 °C; 1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = -2.77$ (s, 2H, *NH*), 2.74 (s, 6H, CH_3), 7.60 (d, 4H, $^3J = 7.6$ Hz, *Ar-H*), 7.99 (t, 2H, $^3J = 7.6$ Hz, *Ar-H*), 8.13 (d, 2H, $^3J = 7$ Hz, *Ar-H*), 8.57 (m, 2H, *Ar-H*), 8.72 (d, 4H, $^3J = 8.2$ Hz, *Ar-H*), 8.79 (d, 2H, $^3J = 4.7$ Hz, H_β), 8.93 (s, 2H, H_β), 8.96 (d, 2H, $^3J = 4.7$ Hz, H_β), 9.11 ppm (s, 2H, H_β); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 29.59$, 116.46, 121.52, 122.88, 127.44, 127.66, 128.20, 134.38, 137.61, 138.62, 139.69, 143.64, 146.84 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 421 (4.90), 516 (3.64), 551 (3.46), 589 (3.34), 646 nm (3.16); HRMS (MS ES+): m/z calcd for $[C_{44}H_{32}N_4O_4] [M+H]^+$: 733.2563, found 733.2540.

5,10-Bis(3-Cyanophenyl)-15,20-bis(4-methylphenyl)porphyrin (47): Following the general procedure F 5,10-dibromo-15,20-bis(4-methylphenyl)porphyrin **29** (20 mg, 0.0308 mmol), 4-cyanophenylboronic acid (46 mg, 0.308 mmol), and $Pd(PPh_3)_4$ (3.6 mg, 0.003 mmol), K_3PO_4 (131 mg, 0.617 mmol) in THF (60 mL) gave 10 mg (0.014 mmol, 47 %) m.p. >300 °C; 1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = -2.79$ (s, 2H, *NH*), 2.74 (s, 6H, CH_3), 7.61 (d, 4H, $^3J = 7.5$ Hz, *Ar-H*), 7.92 (m, 2H, *Ar-H*), 8.14 (m, 6H, *Ar-H*), 8.49 (t, 2H, $^3J = 7$, 6.4 Hz, *Ar-H*), 8.75 (s, 2H, *Ar-H*), 8.74 (d, 2H, $^3J = 4.7$ Hz, H_β), 8.78 (s, 2H, H_β), 8.93 (s, 2H, H_β), 8.96 ppm (d, 2H, $^3J = 4.7$ Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 21.10$, 110.92, 116.32, 118.48, 121.10, 127.25, 131.16, 134.10, 136.62, 137.26, 137.84, 138.32, 142.99 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 419 (4.88), 514 (3.61), 548 (3.44), 589 (3.31), 646 nm (3.38); HRMS (MS ES+): m/z calcd for $[C_{48}H_{32}N_6] [M+H]^+$: 693.2767, found 693.2743.

5,10-Bis(4-methoxycarbonylphenyl)-15,20-diphenylporphyrin 48: Following the general procedure F 5,10-dibromo-15,20-diphenylporphyrin **36** (30 mg, 0.048 mmol), 4-methoxycarbonylphenylboronic acid (86 mg, 0.48 mmol), $Pd(PPh_3)_4$ (5.5 mg, 0.005 mmol) and K_3PO_4 (205 mg, 0.967 mmol) in THF (50 mL) gave 10 mg (0.013 mmol, 30 %) of a purple solid after recrystallization from $CH_2Cl_2/MeOH$. $R_f = 0.5$ (CH_2Cl_2/n -hexane = 1:1, v/v); m.p. > 300 °C; 1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = -2.76$ (s, 2H, *NH*), 4.14 (s, 6H, CH_3), 7.79 (d, 4H, $^3J = 7.6$ Hz, *Ar-H*), 8.24 (d, 4H, $^3J = 8.2$ Hz, *Ar-H*), 8.33 (d, 4H, $^3J = 8.2$ Hz, *Ar-H*), 8.47 (d, 4H, $^3J = 8.2$ Hz, *Ar-H*), 8.82 (m, 4H, H_β), 8.90 ppm (m, 4H, H_β); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 45.57$, 51.99, 118.30, 126.29, 127.44, 129.19, 134.07, 141.47, 146.45, 166.85 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 418 (4.94), 514 (3.80), 548 (3.61), 588 (3.34), 646 nm (3.32); HRMS (MS ES+): m/z calcd for $[C_{48}H_{32}N_4O_4] [M+H]^+$: 731.2658, found 731.2625.

5,10-Bis(4-cyanophenyl)-15,20-diphenylporphyrin 49: Following the general procedure F 5,10-dibromo-15,20-diphenylporphyrin **36** (20 mg, 0.032 mmol), 4-cyanophenylboronic acid (47 mg, 0.32 mol), $Pd(PPh_3)_4$ (3.7 mg, 0.003 mmol), K_3PO_4 (136 mg, 0.644 mmol) in THF (50 mL) gave 6 mg (0.009 mmol, 29 %) of a purple solid after recrystallization from $CH_2Cl_2/MeOH$. $R_f = 0.3$ (CH_2Cl_2/n -hexane = 1:1, v/v); m.p. >300 °C; 1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = -2.80$ (s, 2H, *NH*), 7.80 (m, 4H, *Ar-H*), 8.11 (d, 4H, $^3J = 7.6$ Hz, *Ar-H*), 8.23 (d, 4H, $^3J = 7.6$ Hz, *Ar-H*), 8.37 (d, 4H, $^3J = 8.2$ Hz, *Ar-H*), 8.76 (d, 2H, $^3J = 4.7$ Hz, H_β), 8.80 (s, 2H, H_β), 8.90 (s, 2H, H_β), 8.93 ppm (d, 2H, $^3J = 4.7$ Hz, H_β); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 29.26$, 111.58, 117.12, 118.54, 120.94, 126.37, 127.56, 130.14, 130.23, 134.08, 134.52, 141.22, 146.48 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 418 (4.98), 514 (3.64), 548 (3.26), 588 (2.87), 645 nm (2.56); HRMS (MS ES+): m/z calcd for $[C_{46}H_{29}N_4] [M+H]^+$: 665.2454, found 665.2468.

5,10-Bis(4-nitrophenyl)-15,20-diphenylporphyrin 50: Following the general procedure F 5,10-dibromo-15,20-diphenylporphyrin **36** (20 mg, 0.032 mmol), 4-nitrophenylboronic pinacol ester (80 mg, 0.32 mmol), $Pd(PPh_3)_4$ (3.7 mg, 0.003 mmol),

K₃PO₄ (135 mg, 0.64 mmol) in THF (60 mL) gave 10 mg (0.014 mmol, 43 %) of the title compound. *R*_f = 0.3 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.77 (s, 2H, *NH*), 7.82 (m, 4H, *Ar-H*), 8.23 (d, 4H, ³*J* = 6.4 Hz, *Ar-H*), 8.42 (d, 4H, ³*J* = 8.8 Hz, *Ar-H*), 8.67 (d, 4H, ³*J* = 8.8 Hz, *Ar-H*), 8.78 (d, 2H, ³*J* = 4.7 Hz, *H_β*), 8.82 (s, 2H, *H_β*), 8.90 (s, 2H, *H_β*), 8.94 ppm (d, 2H, ³*J* = 4.7 Hz, *H_β*); UV/VIS (DMF): λ_{max} (lg ε) = 421 (4.95), 516 (3.69), 552 (3.58), 592 (3.29), 646 nm (3.45); HRMS (MS ES+) *m/z* calcd for [C₄₄H₂₉N₆O₄] [M+H]⁺: 705.2250, found 705.2278.

5,10-Bis(4-methoxycarbonylphenyl)-15,20-bis(3-methoxyphenyl)porphyrin 51: Following the general procedure F 5,10-dibromo-15,20-bis(3-methoxyphenyl)porphyrin **37** (20 mg, 0.029 mmol), 4-methoxycarbonylphenylboronic acid (52 mg, 0.293 mmol), Pd(PPh₃)₄ (94 mg, 0.0029 mmol), K₃PO₄ (124 mg, 0.587 mmol) in THF (50 mL) gave 9 mg (0.011 mmol, 32 %) of a purple solid after recrystallization from CH₂Cl₂/MeOH. *R*_f = 0.3 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. > 300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.78 (s, 2H, *NH*), 4.01 (s, 6H, OCH₃), 4.14 (s, 6H, OCH₃), 7.37 (d, 2H, ³*J* = 8.2 Hz, *Ar-H*), 7.67 (t, 2H, ³*J* = 8.2 Hz, *Ar-H*), 7.82 (d, 4H, ³*J* = 7.6 Hz, *Ar-H*), 8.33 (d, 4H, ³*J* = 7.6 Hz, *Ar-H*), 8.47 (d, 4H, ³*J* = 7.6 Hz, *Ar-H*), 8.82 ppm (m, 4H, *H_β*), 8.93 (m, 4H, *H_β*); ¹³C NMR (125 MHz, CDCl₃, 25 °C, TMS): δ = 52.33, 55.37, 113.46, 118.79, 120.35, 127.81, 129.48, 134.40, 143.06, 146.74, 157.80, 167.18 ppm; UV/VIS (DMF): λ_{max} (lg ε) = 419 (4.96), 514 (3.74), 549 (3.47), 588 (3.34), 646 nm (3.36); HRMS (MS ES+) *m/z* calcd for [C₅₀H₃₉N₆O₆] [M+H]⁺: 791.2870, found 791.2865.

5,10-Bis(4-cyanophenyl)-15,20-bis(3-methoxyphenyl)porphyrin 52: Following the general procedure F 5,10-dibromo-15,20-bis(3-methoxyphenyl)porphyrin **37** (30 mg, 0.044 mmol), 4-cyanophenyl boronic acid (64 mg, 0.44 mmol), Pd(PPh₃)₄ (5 mg, 0.004 mmol) and K₃PO₄ (186 mg, 0.88 mmol) in THF (60 mL) gave 15 mg (0.020 mmol, 47 %) of a purple solid after recrystallization from CH₂Cl₂/MeOH. *R*_f = 0.3 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. > 300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.82 (s, 2H, *NH*), 4.02 (s, 6H, OCH₃), 7.38 (m, 2H, *Ar-H*), 7.69 (t, 4H, ³*J* = 8.2 Hz, *Ar-H*), 7.81 (m, 4H, *Ar-H*), 8.10 (d, 4H, ³*J* = 8.2 Hz, *Ar-H*), 8.36 (d, 4H, ³*J* = 7.6 Hz, *Ar-H*), 8.77 (d, 2H, ³*J* = 4.7 Hz, *H_β*), 8.79 (s, 2H, *H_β*), 8.94 (s, 2H, *H_β*), 8.97 ppm (d, 2H, ³*J* = 4.68 Hz, *H_β*); ¹³C NMR (125 MHz, CDCl₃, 25 °C, TMS): δ = 55.07, 111.58, 113.19, 115.85, 117.18, 118.53, 120.56, 127.19, 130.14, 134.51, 142.51, 146.47, 157.55 ppm; UV/VIS (DMF): λ_{max} (lg ε) = 419 (4.90), 513 (3.56), 547 (3.25), 592 (3.16), 643 nm (3.18); HRMS (MS ES+) *m/z* calcd for [C₄₈H₃₃N₆O₂] [M+H]⁺: 725.2655, found 725.2641.

5,10-Bis(3-methoxyphenyl)-15,20-bis(4-nitrophenyl)porphyrin 53: Following the general procedure F, 5,10-dibromo-15,20-bis(3-methoxyphenyl)porphyrin **37** (20 mg, 0.03 mmol), 4-nitrophenylboronic acid pinacol ester (74 mg, 0.3 mmol), Pd(PPh₃)₄ (3.4 mg, 0.003 mmol), K₃PO₄ (125 mg, 0.59 mmol) in THF gave 13 mg (0.017 mmol, 56 %) of the title compound. *R*_f = 0.3 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.78 (s, 2H, *NH*), 4.02 (s, 6H, OCH₃), 7.69 (t, 2H, ³*J* = 8.2 Hz, *Ar-H*), 7.82 (t, 4H, ³*J* = 7.6 Hz, *Ar-H*), 8.42 (d, 4H, ³*J* = 8.8 Hz, *Ar-H*), 8.67 (d, 4H, ³*J* = 8.2 Hz, *Ar-H*), 8.77 (d, 2H, ³*J* = 4.7 Hz, *H_β*), 8.81 (s, 2H, *H_β*), 8.94 (s, 2H, *H_β*), 8.98 ppm (d, 2H, ³*J* = 4.7 Hz, *H_β*); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): δ = 55.08, 113.20, 116.74, 120.75, 121.73, 126.97, 127.47, 134.64, 142.46, 147.34, 148.43, 157.56 ppm; UV/VIS (DMF): λ_{max} (lg ε) = 421 (4.89), 516 (3.58), 551 (3.36), 592 (3.28), 655 nm (3.48); HRMS (MS ES+) *m/z* calcd for [C₄₆H₃₃N₆O₆] [M+H]⁺: 765.2462, found 765.2495.

5,10-Bis(2,6-difluorophenyl)-15,20-bis(4-methoxycarbonylphenyl)porphyrin 54: Following the general procedure F, 5,10-dibromo-15,20-bis(2,6-difluorophenyl)porphyrin **38** (20 mg, 0.028 mmol), 4-methoxycarbonylphenylboronic acid (63 mg, 0.35 mmol), Pd(PPh₃)₄ (3.2 mg, 0.003 mmol) and K₃PO₄ (154 mg, 0.722 mmol) in THF (30 mL) gave 7 mg (0.008 mmol, 30 %) of purple solid after recrystallization from CH₂Cl₂/MeOH. *R*_f = 0.5 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.72 (s, 2H, *NH*), 4.15 (s, 6H, CH₃), 7.42 (t, 4H, ³*J* = 6.4 Hz, *Ar-H*), 7.83 (m, 2H, *Ar-H*), 8.34 (d, 4H, ³*J* = 8.2 Hz, *Ar-H*), 8.38 (d, 4H, ³*J* = 8.2 Hz, *Ar-H*), 8.93 ppm (m, 8H, *H_β*); UV/VIS (CH₂Cl₂): λ_{max} (lg ε) = 416 (4.98), 511 (3.77), 547 (3.30), 590 (3.27), 647 nm (2.95); HRMS (MS ES+) *m/z* calcd for [C₄₈H₃₁N₄O₄F₄] [M+H]⁺: 803.2281, found 803.2261.

5,10-Bis(4-cyanophenyl)-15,20-bis(2,6-difluorophenyl)porphyrin 55: Following the general procedure F, 5,10-dibromo-15,20-bis(2,6-difluorophenyl)porphyrin **38** (20 mg, 0.028 mmol), 4-cyanophenylboronic acid (52 mg, 0.35 mol), Pd(PPh₃)₄ (3.2 mg, 0.003 mmol), K₃PO₄ (154 mg, 0.722 mmol) in THF (30 mL) gave 6 mg (0.008 mmol, 28 %) of purple solid after recrystallization from CH₂Cl₂/MeOH. *R*_f = 0.5 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. > 300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.78 (s, 2H, *NH*), 7.42 (t, 4H, ³*J* = 7.6 Hz, *Ar-H*), 7.85 (m, 2H, *Ar-H*), 8.10 (d, 4H, ³*J* = 8.2 Hz, *Ar-H*), 8.35 (d, 4H, ³*J* = 8.2 Hz, *Ar-H*), 8.78 (s, 2H, *H_β*), 8.81 (d, 2H, ³*J* = 4.7 Hz, *H_β*), 8.91 (d, 2H, ³*J* = 4.7 Hz, *H_β*), 8.93 ppm (s, 2H, *H_β*); UV/VIS (CH₂Cl₂): λ_{max} (lg ε) = 417 (5.06), 511 (3.81), 548 (3.26), 585 (3.31), 645 nm (2.96); HRMS (MS ES+) *m/z* calcd for [C₄₆H₂₅N₆F₄] [M+H]⁺: 737.2077, found 737.2088.

5,10-Bis(2,6-difluorophenyl)-15,20-bis(4-nitrophenyl)porphyrin 56: Following the general procedure F, 5,10-dibromo-15,20-bis(2,6-difluorophenyl)porphyrin **38** (20 mg, 0.028 mmol), 4-nitrophenyl boronic pinacol ester (91 mg, 0.364 mmol), Pd(PPh₃)₄ (3.2 mg, 0.003 mmol), K₃PO₄ (154 mg, 0.722 mmol) in THF (30 mL) gave 5 mg (0.006 mmol, 22 %) of the title compound. *R*_f = 0.5 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.75 (s, 2H, *NH*), 7.44 (t, 4H, ³*J* = 8.2 Hz, *Ar-H*), 7.85 (m, 2H, *Ar-H*), 8.42 (d, 4H, ³*J* = 8.7 Hz, *Ar-H*), 8.68 (d, 4H, ³*J* = 8.2 Hz, *Ar-H*), 8.81 (s, 2H, *H_β*), 8.83 (d, 2H, ³*J* = 4.7 Hz, *H_β*), 8.92 (d, 2H, ³*J* = 4.7 Hz, *H_β*), 8.94 ppm (s, 2H, *H_β*); UV/VIS (CH₂Cl₂): λ_{max} (lg ε) = 418 (5.11), 512 (3.96), 550

(3.32), 591 (3.39), 646 nm (2.43); HRMS (MS ES+): *m/z* calcd for [C₄₄H₂₅N₆O₄F₄] [M+H]⁺: 777.1873, found 777.1884.

5,10-Bis(4-methoxycarbonylphenyl)-15,20-di(*n*-pentyl)porphyrin 57: Following the general procedure F 5,10-dibromo-15,20-di(*n*-pentyl)porphyrin **39** (30 mg, 0.049 mmol), 4-methoxycarbonylphenylboronic acid (88 mg, 0.49 mmol), Pd(PPh₃)₄ (5.7 mg, 0.0055 mmol), K₃PO₄ (209 mg, 0.986 mmol) in THF (50 mL) gave 20 mg (0.026 mmol, 57 %) of the title compound. *R*_f = 0.35 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.68 (s, 2H, *NH*), 1.02 (t, 6H, ³*J* = 7.6, 7.0 Hz, CH₂CH₂CH₂CH₂CH₃), 1.68 (m, 4H, CH₂CH₂CH₂CH₂CH₃), 1.85 (m, 4H, CH₂CH₂CH₂CH₂CH₃), 2.58 (m, 4H, CH₂CH₂CH₂CH₂CH₃), 4.14 (s, 6H, OCH₃), 5.03 (t, 4H, ³*J* = 8.2 Hz, CH₂CH₂CH₂CH₂CH₃), 8.28 (d, 4H, ³*J* = 8.2 Hz, *Ar-H*), 8.45 (d, 4H, ³*J* = 8.2 Hz, *Ar-H*), 8.71 (s, 2H, *H_β*), 8.83 (d, 2H, ³*J* = 4.7 Hz, *H_β*), 9.49 (d, 2H, ³*J* = 4.7 Hz, *H_β*), 9.61 ppm (s, 2H, *H_β*); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): δ = 13.35, 29.63, 32.33, 35.25, 38.21, 51.80, 126.90, 120.40, 126.79, 127.69, 129.01, 129.75, 134.04, 146.67, 166.92 ppm; UV/VIS (DMF): λ_{max} (lg ε) = 418 (4.93), 518 (4.03), 550 (3.95), 592 (3.85), 651 nm (3.88); HRMS (MS ES+): *m/z* calcd for [C₄₆H₄₇N₄O₄] [M+H]⁺: 719.3597, found 719.3620.

5,10-Bis(4-cyanophenyl)-15,20-di(*n*-pentyl)porphyrin 58: Following the general procedure F, 5,10-dibromo-15,20-di(*n*-pentyl)porphyrin **39** (40 mg, 0.065 mmol), 4-cyanophenyl boronic acid (95.5 mg, 0.65 mmol), Pd(PPh₃)₄ (7.5 mg, 0.007 mmol), K₃PO₄ (279 mg, 1.31 mmol) in THF (60 mL) gave 17 mg (0.026 mmol, 40 %) of the title compound. *R*_f = 0.4 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.70 (s, 2H, *NH*), 1.01 (t, 6H, ³*J* = 7 Hz, CH₂CH₂CH₂CH₂CH₃), 1.28 (m, 4H, CH₂CH₂CH₂CH₂CH₃), 1.83 (m, 4H, CH₂CH₂CH₂CH₂CH₃), 2.58 (m, 4H, CH₂CH₂CH₂CH₂CH₃), 5.03 (t, 4H, ³*J* = 8.2 Hz, CH₂CH₂CH₂CH₂CH₃), 8.08 (d, 4H, ³*J* = 8.2 Hz, *Ar-H*), 8.31 (d, 4H, ³*J* = 8.2 Hz, *Ar-H*), 8.67 (s, 2H, *H_β*), 8.77 (d, 2H, ³*J* = 4.7 Hz, *H_β*), 9.52 (d, 2H, ³*J* = 4.7 Hz, *H_β*), 9.62 ppm (s, 2H, *H_β*); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): δ = 13.71, 22.33, 29.27, 32.30, 35.29, 38.28, 111.37, 115.77, 118.62, 121.10, 130.09, 134.46, 146.69 ppm; UV/VIS (DMF): λ_{max} (lg ε) = 419 (4.97), 517 (3.75), 552 (3.58), 592 (3.27), 650 nm (3.41); HRMS (MS ES+): *m/z* calcd for [C₄₄H₄₁N₄] [M+H]⁺: 653.3393, found 653.3382.

5,10-Bis(4-nitrophenyl)-15,20-di(*n*-pentyl)porphyrin 59: Following the general procedure F, 5,10-dibromo-15,20-di(*n*-pentyl)porphyrin **39** (40 mg, 0.065 mmol), 4-nitrophenyl boronic pinacol ester (161 mg, 0.65 mmol), Pd(PPh₃)₄ (7.5 mg, 0.007 mmol), K₃PO₄ (279 mg, 1.31 mmol) in THF (60 mL) gave 22 mg (0.031 mmol, 47 %). *R*_f = 0.59 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.67(s, 2H, *NH*), 1.02 (t, 6H, ³*J* = 7.6, 7 Hz, CH₂CH₂CH₂CH₂CH₃), 1.30 (m, 4H, CH₂CH₂CH₂CH₂CH₃), 1.83 (m, 4H, CH₂CH₂CH₂CH₂CH₃), 2.58 (m, 4H, CH₂CH₂CH₂CH₂CH₃), 5.03 (t, 4H, ³*J* = 8.2 Hz, CH₂CH₂CH₂CH₂CH₃), 8.36 (d, 4H, ³*J* = 8.7 Hz, *Ar-H*), 8.65 (d, 4H, ³*J* = 8.2 Hz, *Ar-H*), 8.69 (s, 2H, *H_β*), 8.78 (d, 2H, ³*J* = 4.7 Hz, *H_β*), 9.53 (d, 2H, ³*J* = 4.7 Hz, *H_β*), 9.62 ppm (s, 2H, *H_β*); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): δ = 13.71, 29.1, 32.31, 35.31, 38.30, 115.33, 121.44, 134.59, 147.23, 148.66 ppm; UV/VIS (DMF): λ_{max} (lg ε) = 420 (4.90), 517 (3.73), 554 (3.45), 594 (3.15), 651 nm (3.33); HRMS (MS ES+): *m/z* calcd for [C₄₂H₄₁N₄O₄] [M+H]⁺: 693.3189, found 693.3160.

5,10-Di(*n*-hexyl)-15,20-bis(4-methoxycarbonylphenyl)porphyrin 60: Following the general procedure F, 5,10-dibromo-15,20-di(*n*-hexyl)porphyrin **40** (25 mg, 0.04 mmol), 4-methoxyphenylboronic acid (72 mg, 0.4 mmol), Pd(PPh₃)₄ (4.6 mg, 0.004 mmol), K₃PO₄ (169 mg, 0.8 mmol) in THF gave 10 mg (0.013 mmol, 34 %) of the title compound. *R*_f = 0.54 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS) δ = -2.68 (s, 2H, *NH*), 0.96 (t, 6H, ³*J* = 7.6 Hz, CH₂CH₂CH₂CH₂CH₂CH₃), 1.42 (m, 4H, CH₂CH₂CH₂CH₂CH₂CH₃), 1.54 (m, 4H, CH₂CH₂CH₂CH₂CH₂CH₃), 1.85 (m, 4H, CH₂CH₂CH₂CH₂CH₂CH₃), 2.56 (m, 4H, CH₂CH₂CH₂CH₂CH₂CH₃), 4.14 (s, 6H, OCH₃), 5.03 (t, 4H, ³*J* = 8.9, 7.6 Hz, CH₂CH₂CH₂CH₂CH₂CH₃), 8.28 (d, 4H, ³*J* = 8.2 Hz, *Ar-H*), 8.45 (d, 4H, ³*J* = 8.2 Hz, *Ar-H*), 8.71 (s, 2H, *H_β*), 8.83 (d, 2H, ³*J* = 4.7 Hz, *H_β*), 9.49 (d, 2H, ³*J* = 4.7 Hz, *H_β*), 9.61 ppm (s, 2H, *H_β*); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): δ = 13.68, 22.27, 24.91, 28.90, 29.62, 31.46, 35.41, 38.46, 51.93, 119.47, 127.49, 134 ppm; UV/VIS (DMF): λ_{max} (lg ε) = 416 (4.96), 518 (3.86), 552 (3.66), 598 (3.47), 655 nm (3.56); HRMS (MS ES+) *m/z* calcd for [C₄₈H₅₁N₄O₄] [M+H]⁺: 747.3910, found 747.3907.

5,10-Bis(4-cyanophenyl)-15,20-di(*n*-hexyl)porphyrin 61: Following the general procedure F 5,10-dibromo-15,20-di(*n*-hexyl)porphyrin **40** (30 mg, 0.047 mmol), 4-cyanophenylboronic acid (69 mg, 0.47 mmol), Pd(PPh₃)₄ (5.4 mg, 0.005 mmol), K₃PO₄ (200 mg, 0.942 mmol) in THF gave 13 mg (0.019 mmol, 40 %) of the title compound. *R*_f = 0.2 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = -2.66 (s, 2H, *NH*), 0.96 (t, 6H, ³*J* = 7.6, 7 Hz, CH₂CH₂CH₂CH₂CH₂CH₃), 1.43 (m, 4H, CH₂CH₂CH₂CH₂CH₂CH₃), 1.54 (m, 4H, CH₂CH₂CH₂CH₂CH₂CH₃), 1.85 (m, 4H, CH₂CH₂CH₂CH₂CH₂CH₃), 2.55 (m, 4H, CH₂CH₂CH₂CH₂CH₂CH₃), 5.04 (t, 4H, ³*J* = 8.2, 7.6 Hz, CH₂CH₂CH₂CH₂CH₂CH₃), 8.09 (d, 4H, ³*J* = 8.2 Hz, *Ar-H*), 8.32 (d, 4H, ³*J* = 8.2 Hz, *Ar-H*), 8.67 (s, 2H, *H_β*), 8.77 (d, 2H, ³*J* = 4.7 Hz, *H_β*), 9.52 (d, 2H, ³*J* = 4.7 Hz, *H_β*), 9.63 ppm (s, 2H, *H_β*); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): δ = 14.06, 22.66, 31.91, 35.70, 39.09, 121.11, 115.83, 119.11, 121.64, 130.59, 134.89, 147.13, 148.08 ppm; UV/VIS (DMF): λ_{max} (lg ε) = 418 (4.87), 517 (4.53), 551 (3.43), 592 (3.13), 650 nm (3.31); HRMS (MS ES+): *m/z* calcd for [C₄₆H₅₃N₄] [M+H]⁺: 681.3706, found 681.3710.

5,10-Di(*n*-hexyl)-15,20-bis(4-nitrophenyl)porphyrin 62: Following the general procedure F, 5,10-dibromo-15,20-di(*n*-hexyl)porphyrin **40** (33 mg, 0.047 mmol), 4-nitrophenyl boronic pinacol ester (117 mg, 0.47 mmol), Pd(PPh₃)₄ (5.4 mg, 0.005 mmol), K₃PO₄ (200 mg, 0.942 mmol) in THF (60 mL) gave 20 mg (0.027 mmol, 59 %) of

(600 MHz, CDCl₃, 25 °C, TMS): δ = -2.66 (s, 2H, *NH*), 0.98 (t, 6H, 3J = 7.3 Hz, CH₂CH₂CH₂CH₂CH₂CH₃), 1.44 (m, 4H, CH₂CH₂CH₂CH₂CH₂CH₃), 1.56 (m, 4H, CH₂CH₂CH₂CH₂CH₂CH₃), 1.85 (m, 4H, CH₂CH₂CH₂CH₂CH₂CH₃), 2.58 (m, 4H, CH₂CH₂CH₂CH₂CH₂CH₃), 5.02 (t, 4H, 3J = 8.1 Hz, CH₂CH₂CH₂CH₂CH₂CH₃), 8.36 (d, 4H, 3J = 8.1 Hz, *Ar-H*), 8.65 (d, 4H, 3J = 8.1 Hz, *Ar-H*), 8.69 (s, 2H, *H_β*), 8.78 (d, 2H, 3J = 4.7 Hz, *H_β*), 9.52 (d, 2H, 3J = 4.7 Hz, *H_β*), 9.62 ppm (s, 2H, *H_β*); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): δ = 22.63, 30.22, 31.81, 35.73, 38.95, 115.72, 121.70, 122.07, 134.88, 135.02, 147.77, 149.37 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 421 (5.02), 519 (3.89), 554 (3.76), 595 (3.47) ppm; HRMS (MS ES⁺): *m/z* calcd for [C₄₄H₄₅N₆O₄] [M+H]⁺: 721.3502, found 721.3520.

[5,10-Bis(4-ethynylphenyl)-15,20-bis(4-methylphenyl)porphyrinato]zinc (II) 63: Following the general procedure D, 5,10-bis(4-ethynylphenyl)-15,20-bis(4-methylphenyl)porphyrin **27** (15 mg, 0.022 mmol) was treated with 300 mg of zinc oxide to give 13 mg (0.017 mmol, 81 %) of the desired product after recrystallization from CH₂Cl₂/MeOH. *R_f* = 0.4 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (600 MHz, CDCl₃, 25 °C, TMS): δ = 2.77 (s, 6H, CH₃), 3.34 (s, 2H, C≡CH), 7.59 (d, 4H, 3J = 7.7 Hz, *Ar-H*), 7.92 (d, 4H, 3J = 7.7 Hz, *Ar-H*), 8.13 (d, 4H, 3J = 7.7 Hz, *Ar-H*), 8.22 (d, 4H, 3J = 7.7 Hz, *Ar-H*), 8.95 (m, 4H, *H_β*), 9.02 ppm (m, 4H, *H_β*); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): δ = 14.02, 21.38, 29.52, 77.97, 83.62, 119.79, 121.26, 127.19, 130.26, 131.43, 132.03, 134.19, 134.32, 137.09, 139.56, 143.37, 149.62, 150.27 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 427 (4.94), 560 (3.64), 601 nm (3.40); HRMS: *m/z* calcd for [C₅₀H₃₂N₄Zn] [M]⁺: 752.1918, found 752.1916.

[5,10-Bis(4-methoxycarbonylphenyl)-15,20-bis(4-methylphenyl)porphyrinato]zinc(II) 64: Following the general procedure D, 5,10-bis(4-methoxycarbonylphenyl)-15,20-bis(4-methylphenyl)porphyrin **43** (15 mg, 0.019 mmol) was treated with 300 mg of zinc oxide to give 13 mg (0.015 mmol, 81 %) of the title compound after recrystallization from CH₂Cl₂/MeOH. *R_f* = 0.1 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (600 MHz, CDCl₃, 25 °C, TMS): δ = 2.75 (s, 6H, CH₃), 4.13 (s, 6H, OCH₃), 7.59 (d, 4H, 3J = 7.2 Hz, *Ar-H*), 8.13 (d, 4H, 3J = 7.5 Hz, *Ar-H*), 8.33 (d, 4H, 3J = 7.9 Hz, *Ar-H*), 8.46 (d, 4H, 3J = 7.5 Hz, *Ar-H*), 8.91 (m, 4H, *H_β*), 8.97 ppm (m, 4H, *H_β*); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): δ = 13.95, 29.21, 52.22, 119.46, 121.76, 127.09, 129.26, 130.05, 131.32, 132.12, 137.13, 139.50, 147.56, 149.39, 150.29, 150.48, 166.64, 167.23 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 428 (5.02), 560 (3.72), 601 nm (3.35); HRMS (MS ES⁺): *m/z* calcd for [C₅₀H₃₇N₄O₄Zn] [M+H]⁺: 821.2106, found 821.2146.

[5,10-Bis(4-cyanophenyl)-15,20-bis(4-methylphenyl)porphyrinato]zinc(II) 65: Following the general procedure D, 5,10-bis(4-cyanophenyl)-15,20-bis(4-methylphenyl)porphyrin **44** (10 mg, 0.014 mmol) was treated with 300 mg of zinc oxide to yield 8 mg (0.010 mmol, 72 %) of the desired product after recrystallization from CH₂Cl₂/MeOH. *R_f* = 0.27 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (600 MHz, CDCl₃, 25 °C, TMS): δ = 2.76 (s, 6H, CH₃), 7.61 (d, 4H, 3J = 7.2 Hz, *Ar-H*), 8.11 (m, 8H, *Ar-H*), 8.37 (d, 4H, 3J = 7.7 Hz, *Ar-H*), 8.86 (d, 2H, 3J = 4.4 Hz, *H_β*), 8.89 (s, 2H, *H_β*), 9.03 (s, 2H, *H_β*), 9.06 ppm (d, 2H, 3J = 4.4 Hz, *H_β*); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): δ = 13.95, 21.38, 29.55, 111.63, 127.27, 130.28, 131.01, 132.42, 132.84, 134.22, 134.71, 137.31, 150.40 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 421 (4.94), 548 (3.74), 628 nm (3.52); HRMS: *m/z* calcd for [C₄₈H₃₀N₆Zn] [M]⁺: 754.1823, found 754.1875.

[5,10-Dibromo-15,20-bis(3-methoxyphenyl)porphyrinato]zinc(II) 66: 5,10-Dibromo-15,20-bis(3-methoxyphenyl)porphyrin **37** (50 mg, 0.07 mmol) was reacted following procedure D. Column chromatography on silica gel (CH₂Cl₂) gave a single product. Recrystallization from CH₂Cl₂/MeOH/H₂O gave purple crystals (49 mg, 0.07 mmol, 90 %). *R_f* = 0.27 (CH₂Cl₂/*n*-hexane = 3:1, v/v); m.p. 187 °C; ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS): δ = 3.91 (s, 6H, Ar-OCH₃), 7.29 (m, 2H, Ar-*H_β*), 7.68 (m, 4H, Ar-*H_α*, Ar-*H_γ*), 7.79 (m, 2H, Ar-*H_α*), 8.43 (s, 2H, *H_β*), 8.76 (AB, 2H, 3J = 3J = 4.6 Hz, *H_β*), 8.89 (s, 2H, *H_β*), 9.21 ppm (AB, 2H, 3J = 3J = 4.6 Hz, *H_β*); ¹³C NMR (126 MHz, CDCl₃, 25 °C, TMS): δ = 55.55, 103.95, 113.35, 120.70, 121.90, 127.50, 127.63, 132.30, 132.67, 132.70, 133.18, 143.57, 148.41, 149.13, 150.79, 150.94, 158.03 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ϵ) = 424 (5.26), 556 (4.26), 595 nm (3.83); MS (TOF, MS, ES⁺, 70 eV): *m/z* (%) = 740 (39 %, [M]⁺); HRMS: *m/z* calcd for [C₃₄H₂₂N₄Br₂O₂Zn] [M]⁺: 739.9401, found: 739.9391.

[5,10-Bis(4-cyanophenyl)-15,20-bis(3-methoxyphenyl)porphyrinato]zinc(II) 67: Following the general procedure D, 5,10-bis(4-cyanophenyl)-15,20-bis(3-methoxyphenyl)porphyrin **52** (0.013 mmol) was treated with 300 mg of zinc oxide to give 8 mg (0.009 mmol, 72 %) of the title compound after recrystallization from CH₂Cl₂/MeOH. *R_f* = 0.3 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 3.99 (s, 6H, OCH₃), 7.36 (d, 2H, 3J = 8.2 Hz, *Ar-H*), 7.67 (t, 2H, 3J = 8.2, 7.6 Hz, *Ar-H*), 7.78 (s, 2H, *Ar-H*), 7.82 (d, 2H, 3J = 7.6 Hz, *Ar-H*), 8.09 (d, 4H, 3J = 8.2 Hz, *Ar-H*), 8.36 (d, 4H, 3J = 8.2 Hz, *Ar-H*), 8.85 (d, 2H, 3J = 4.7 Hz, *H_β*), 8.88 (s, 2H, *H_β*), 9.03 (s, 2H, *H_β*), 9.06 ppm (d, 2H, 3J = 4.7 Hz, *H_β*); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): δ = 29.54, 55.35, 111.66, 113.34, 118.89, 120.38, 121.76, 127.31, 130.28, 131.17, 132.41, 134.70, 143.52, 147.54, 149.07, 149.38, 150.18, 150.50, 157.78 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 428 (5.06), 560 (3.69), 599 nm (3.45); HRMS: *m/z* calcd for [C₄₈H₃₀N₆O₂Zn] [M]⁺: 786.1722, found 786.1625.

[5,10-Bis(3-methoxyphenyl)-15,20-bis(4-nitrophenyl)porphyrinato]zinc(II) 68: Following the general procedure D, 5,10-bis(3-methoxyphenyl)-15,20-bis(4-nitrophenyl)porphyrin **53** (10 mg, 0.013 mmol) was treated with 300 mg of zinc oxide to give 8 mg (0.009 mmol, 81 %) of the desired product after recrystallization from CH₂Cl₂/MeOH. *R_f* = (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (600 MHz, CDCl₃, 25 °C, TMS): δ = 3.98 (s, 6H, OCH₃), 7.35 (d, 2H, 3J = 8.2 Hz, *Ar-H*), 7.67 (t, 2H, 3J = 7.7, 8.07 Hz, *Ar-H*), 7.77 (s, 2H, *Ar-H*), 7.82 (d, 2H, 3J = 7.0 Hz, *Ar-H*), 8.42

(d, 4H, 3J = 7.7 Hz, *Ar-H*), 8.65 (d, 4H, 3J = 7.7 Hz, *Ar-H*), 8.86 (d, 2H, 3J = 4 Hz, *H_β*), 8.89 (s, 2H, *H_β*), 9.03 (s, 2H, *H_β*), 9.07 ppm (d, 2H, 3J = 4 Hz, *H_β*); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): δ = 13.89, 22.54, 29.55, 55.35, 113.32, 118.05, 120.43, 121.90, 127.43, 131.11, 132.47, 134.83, 143.51, 147.55, 148.99, 149.57, 150.21, 150.56, 157.77 ppm; UV/VIS (DMF): λ_{max} (lg ϵ) = 421 (5.13), 550 (3.97), 592 nm (3.29); HRMS: *m/z* calcd for [C₄₆H₃₀N₆O₆Zn]: 826.1518, found 826.1584.

(5,10-Diformyl-15,20-diphenylporphyrinato)copper(II) 70: A 100 ml three-necked flask equipped with a reflux condenser containing anhydrous DMF (75 eq.) was charged drop wise and slowly with POCl₃ (74 eq.) at 0-2 °C under an argon atmosphere. After 20 min the POCl₃-DMF complex solidified. After removal of the ice-bath, 1,2-dichloroethane (5 mL) was added and the solution was heated gently to 50 °C. (5,10-Diphenylporphyrinato)copper(II) **69** was added slowly at 50 °C as a solution in 1,2-dichloroethane (25 mL). After complete addition the mixture was heated to 90 °C for 12 h. After cooling with an ice-bath a saturated aqueous sodium acetate solution was added very carefully and then the mixture was heated to 80 °C for 3 h for completion of the hydrolysis. After cooling to RT the porphyrin was extracted into CH₂Cl₂ (3 ×), followed by washing once with water, twice with aqueous NaHCO₃, and then finally twice with brine. Finally, the organic phase was dried with anhydrous Na₂SO₄ and the solvent was evaporated under reduced pressure. After column chromatography on silica gel (*h* = 46 cm, ϕ = 3 cm) with CH₂Cl₂ the first fraction containing pure product was obtained as dark green crystals after recrystallization from CH₂Cl₂/MeOH (45.1 mg, 0.077 mmol, 77 %). *R_f* = 0.4 (CH₂Cl₂/*n*-hexane = 3:1, v/v); m.p. 220 °C; UV/VIS (CH₂Cl₂): λ_{max} (lg ϵ) = 432 (4.45), 562 (3.50), 602 nm (3.43); MS (EI, 70 eV): *m/z* (%): 581 (4 %, [M]⁺), 552 (1 %, [M - CHO]⁺), 523 (2 %, [M - C₂H₂O₂]⁺), 445 (2 %, [M - C₂H₂O₂ - C₆H₆]⁺); HRMS: *m/z* calcd for [C₃₄H₂₂N₄O₂Cu] [M+2H]²⁺: 581.1039, found 581.1042.

5,10,15-Tris(3,4,5-trifluorophenyl)porphyrin 71: Obtained from the synthesis of **42** (5 mg, 7 μmol, < 1 %). *R_f* = 0.6 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. 290 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = -3.21 (br s, 1H, *NH*), 7.85 (m, 6H, *Ar-H_α*), 8.91, 8.87 (AB, 4H, 3J = 3J = 3J = 4.9 Hz, *H_β*), 8.99 (AB, 2H, 3J = 3J = 4.6 Hz, *H_β*), 9.40 (AB, 2H, 3J = 3J = 4.6 Hz, *H_β*), 10.30 ppm (s, 1H, *H_{meso}*); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 106.70, 119.19, ~131, 132.86, 137.62, 148.50, 151.83 , , ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ϵ) = 410 (4.98), 506 (4.02), 538 (3.46), 581 (3.58), 634 nm (3.20); MS (70 eV, EI) *m/z* (%): 700 (16 %, [M]⁺), 570 (14 %, [M - C₆H₅ + H]⁺), 350 (100 %, [M]²⁺), 285 (20 %, [M - C₆H₅ + H]²⁺); HRMS: *m/z* calcd for [C₃₈H₇F₉N₄] [M]⁺: 700.1310, found: 700.1280.

5,10,15-Tris(4-bromophenyl)porphyrin 72: Obtained from the synthesis of **41** (12 mg, 0.02 mmol, < 1 %). *R_f* = 0.48 (CH₂Cl₂/*n*-hexane = 1:1, v/v); m.p. >300 °C; ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS): δ = -3.09 (br s, 1H, *NH*), 7.88 (AB, 6H, 3J = 3J = 3J = 8.1 Hz, *Ar-H_α*), 8.85 (m, 4H, *H_β*), 8.97 (AB, 2H, 3J = 3J = 4.7 Hz, *H_β*), 9.32 (AB, 2H, 3J = 3J = 4.7 Hz, *H_β*), 10.20 ppm (s, 1H, *H_{meso}*); ¹³C NMR (63 MHz, CDCl₃, 25 °C, TMS): δ = 105.33, 118.30, 118.99, 122.62, 129.98, 130.08, ~131, 135.81, 135.95, 140.54 ppm; UV/VIS (CH₂Cl₂): λ_{max} (lg ϵ) = 413 (5.09), 508 (4.32), 542 (3.95), 583 (3.90), 637 nm (3.68); MS (TOF, MS, ES⁺, 70 eV) *m/z* (%): 772 (32 %, [M]⁺); HRMS: *m/z* calcd for [C₃₈H₂₃N₄Br₃] [M]⁺: 771.9473, found: 771.9454.

X-ray single crystal structure determination of 29: Growth and handling of crystals followed the concept developed by Hope.^[36] Intensity data were collected at 118 K with a Rigaku CCD system utilizing Mo-K α radiation (λ = 0.71073 Å). The intensities were corrected for Lorentz, polarization and extinction effects. The structure was solved with Direct Methods using the SHELXTL PLUS program system and refined against |F²| with the program XL from SHELX-97 using all data.^[37] Nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed into geometrically calculated positions and refined using a riding model. The N-H hydrogen atoms were refined as disordered over all four positions with occupancies of 50 % each. CCDC-829928 contains 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. Crystal data: C₃₄H₂₄Br₂N₄, *FW* = 648.39, red parallelepiped from CH₂Cl₂/CH₃OH, crystal size 0.5 x 0.3 x 0.2 mm, monoclinic, *C*2/*c*, *a* = 30.27(2) Å, *b* = 12.148(7) Å, *c* = 15.884(10) Å, β = 111.123(14)°, *V* = 5448(6) Å³, *Z* = 8, *d_{calcd}* = 1.581 Mg.m⁻³, μ (Mo K α) = 3.008 mm⁻¹, *T_{min}* = 0.315, *T_{max}* = 0.585, θ_{max} = 31.24°, 21370 reflections collected, 4765 independent reflections, *R_{int}* = 0.1081, 3368 reflections with *I* > 2.0 σ (*I*), 364 parameters, *R*1 (*I* > 2.0 σ (*I*)) = 0.0757, *R*1 (all data) = 0.1092, *wR*2 (all data) = 0.2168, *S* = 1.042, ρ_{max} = 1.744 e.Å⁻³ (near Br atoms).

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Entry for the Table of Contents (Please choose one layout only)

Layout 1:

Porphyrin Synthesis

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**5,10-A₂B₂-type meso Substituted
Porphyrins – A Unique Class of
Porphyrins with Realigned Dipole
Moment**

Transition metal catalyzed transformation or direct substitution of 5,10-A₂ porphyrins is an efficient way of generating push-pull 5,10-A₂B₂ porphyrins. Those compounds exhibit interesting structural, spectroscopic and optical features and offer potential for various applications.