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# Monomeric Chiral and Achiral Basket-Handle Porphyrins: Synthesis, Structural Features, and Arrested Tautomerism

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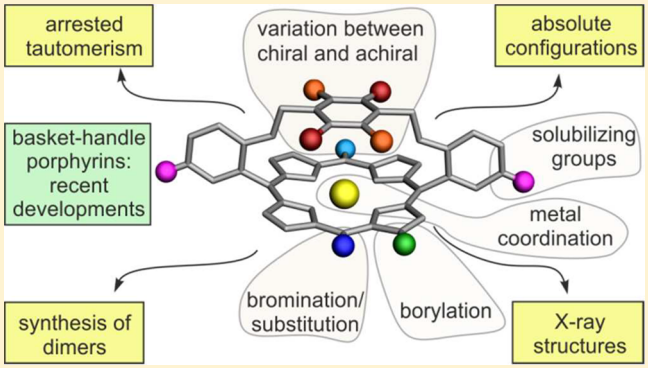
Supporting Information

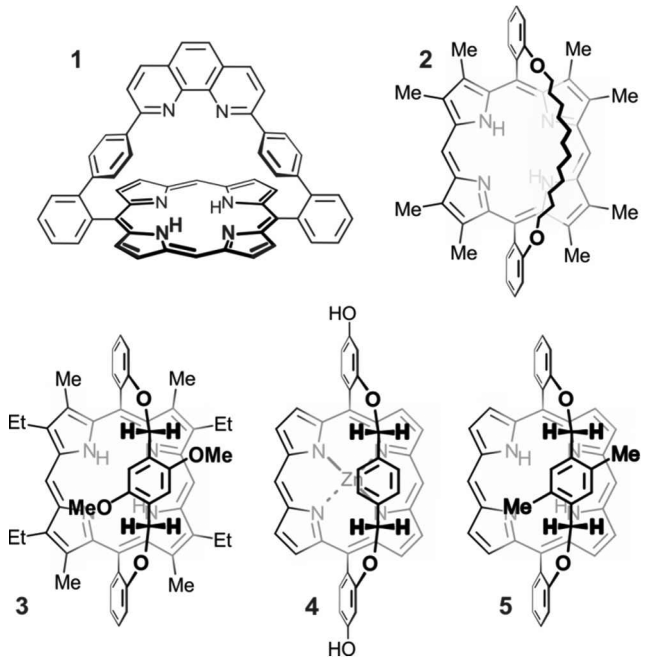
**ABSTRACT:** Chiral and achiral basket-handle porphyrins (BHPs) with different *p*-xylene straps and peripheral solubilizing groups were synthesized using a previously established synthetic approach. Subsequent modification, functionalization, and metalation of the tetrapyrrolic macrocycle yielded more than 80 BHPs. The chiral representatives were resolved into their enantiomers, whose absolute configurations were determined by comparison of their ECD spectra with other experimental or quantum chemically calculated spectra. NMR studies and coupled-cluster calculations proved that the free base BHPs, although highly symmetric, exhibited the phenomenon of "arrested tautomerism". Comparison of the solid-state structures of three metalated BHPs offered detailed insight into their three-dimensional shape. Finally, directly linked dimeric porphyrins with a BHP subunit were synthesized from functionalized BHPs to prove their value as synthetic building blocks.




## INTRODUCTION

Porphyrins are one of the most versatile chemical structures and therefore have been widely investigated since they not only combine interesting optical, photophysical, and catalytic properties but also allow these properties to be tailored to particular needs.[1] This facilitates their use in almost all fields of natural sciences, such as medicine,[2] biology,[3] physics,[4] and particularly in chemistry.[1]

Within the field of chemistry, the construction of defined three-dimensional geometries of either monomeric tetrapyrroles[5] or arrays of multiple systems[6,7] has been a central topic, especially during the past few decades. This required suitable strategies for the construction, modification, and combination of the building blocks. Porphyrins with steric shielding on one or both sides of the macrocyclic plane, known as capped or basket-handle porphyrins[8−12] (BHPs, examples **1**−**5**), although known for a long time, have however not attained a pronounced impact.[13,14] This was mainly due to the difficult syntheses of such systems, which often involved multiple steps[8] and/or low yields[15−19] and their unfavorable properties such as chemical instability, poor solubility,[16] or lack of possibilities for subsequent modification. Just recently we have described a synthetic approach that overcomes these difficulties and gives access to multigram quantities of BHPs. Both chiral (**5**) and achiral forms have thus become available, and these can also be further modified.[12]

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There is one example of a related system in the literature, compound **3**, for which we expect the same chirality as in our systems, but this was not discussed at the time.[10]

This work gives extensive insight into the versatility of the synthesis of the BHPs, their further modification, and their use as synthetic building blocks. Furthermore, we will present detailed structural investigations, especially regarding their planar chirality and arrested tautomerism.

## RESULTS AND DISCUSSION

In our previous report on 5,15-bridged BHPs[12] we introduced a short and efficient synthesis of the BHPs and gave the first examples of their modification. The various sites available for modification are summarized in a structural representation (Figure 1). The following sections will provide detailed insight regarding each of the modification sites.

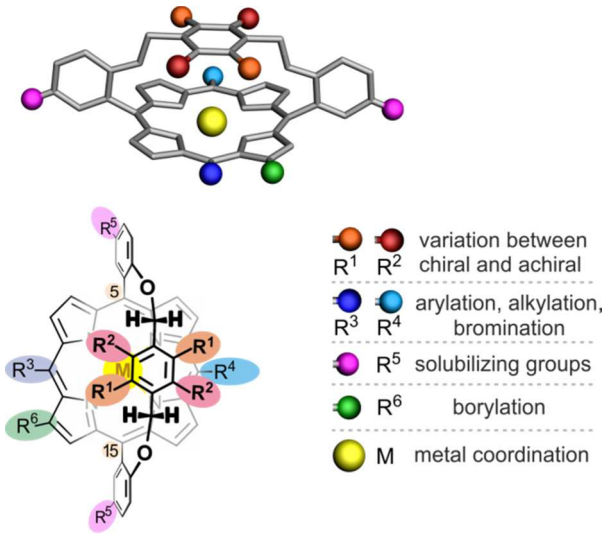


**Figure 1.** Possible sites for the modification of the 5,15-bridged BHPs (adapted from ref 12, copyright 2015, American Chemical Society).

**Variation between Chiral and Achiral Forms and Introduction of Solubilizing Groups.** The synthetic approach to the BHPs starts with the construction of a suitable *p*-xylene-linked[20] dialdehyde **9**, which reacts with dipyrrylmethane **8** to yield the BHPs **10** after a two-step, one-pot reaction consisting of a cyclocondensation and a subsequent oxidation of the initially formed porphyrinogen (Table 1). This strategy requires the careful selection of the appropriate dialdehyde **9**, since the decision between a later planar-chiral, $C_2$-symmetric BHP or an achiral, $C_{2v}$-symmetric BHP has to be made at the stage of the dialdehyde synthesis. By a choice of handle derivatives **6a,b** with four identical substituents ($R^1 = R^2$), the resulting BHPs have $C_{2v}$ symmetry and are therefore achiral. If the substituents along the diagonal of the xylene unit are not identical ($R^1 \neq R^2$), as in **6c,d**, the porphyrin formation yields a racemic mixture of two planar-chiral enantiomers. A total of four achiral BHPs (**10a,c,e,i**) with either four methyl groups or four hydrogens within the xylene ring were synthesized by this strategy. Likewise, five planar-chiral BHPs (**10b,d,f–h**) were prepared with either two bromine or two methyl substituents along the diagonal of the xylene ring and two hydrogens at the remaining positions.

The second site open to modification prior to the porphyrin formation is the position para to the hydroxy function in the salicylic aldehydes **7**, used for the preparation of the *p*-xylene-linked dialdehyde **9**. This position is the ideal site for solubilizing groups for two reasons. First, the position para to the hydroxy function is the most remote with regard to the porphyrin core and the basket handle in the final BHP and therefore has the least influence on the BHP properties. Second, the required substituted salicylic aldehydes **7** are easily prepared by literature procedures.[21,22] The parent compound salicylic aldehyde **7a** eventually gives a BHP with no solubilizing substituent yet is still sufficiently soluble for most applications. Introduction of a *tert*-butyl group slightly increases the solubility, while a *tert*-octyl substituent improves it significantly. These findings were expected and were in agreement with factors usually mentioned when discussing the solvation of porphyrins.[23] As will be shown later, in sterically controlled Ir-catalyzed C–H activation reactions,[24] these alkyl substituents are sterically necessary to prohibit C–H activation at the remaining phenyl positions. Interestingly, the phenyl-substituted dialdehydes **9j,k** did not yield any porphyrin when subjected to the otherwise successful condensation conditions. We currently have no hints as to whether this is due to solubility problems at the porphyrinogen or porphyrin stage or whether it is a problem caused by a different reactivities of the phenyl-substituted dialdehyde. However, in summary, the systematic choice of suitable salicylic aldehydes and *p*-xylene units permits the directed synthesis of BHPs.

**Synthesis of *meso*-Substituted BHPs by Mixed Condensation or by "Senge Reaction" with Lithium Organyls.** Although 5,15-disubstituted porphyrins with two remaining free *meso*-positions can easily be prepared[25] and have frequently been investigated, their closely related 5,10,15-tri- and 5,10,15,20-tetrasubstituted analogues might be of even greater interest.[5,26] Therefore, we adopted two of our protocols to the construction of such systems to our BHPs. First, altering the parameters at the porphyrin-forming step, we exchanged half of the amount of the unsubstituted dipyrrylmethane **8a** with substituted species (**8b,c**), which resulted in a setup usually called "mixed condensation" (Table 2).[26] As expected, we obtained a statistical mixture of the respective di-, tri-, and tetrasubstituted BHPs.

If only the trisubstituted BHP **11** was the desired product and there was no use for the di- and tetrasubstituted side products **10** and **12**, a more direct approach was favorable. As we previously reported, the method developed by Senge,[27] which uses lithium organyls for the selective *meso*-substitution of initially *meso*-unsubstituted porphyrins, can also be applied to our BHPs. So far only achiral phenyl- and *n*-butyl-substituted BHPs (entries 8 and 9, BHPs **11e,f**) without solubilizing groups have been synthesized by this strategy.[12] We have expanded this protocol to further alkyl and aryl substituents and applied it to several BHPs with solubilizing groups, but also to a chiral species (Table 2).

***meso*-Bromination and Debromination of the BHPs.** Our previous work on the bromination of BHPs only included the full *meso*-bromination of the simplest chiral and achiral BHPs **10a,b**.[12] Herein we report the full scope of this reaction. Regardless of the substitution pattern of the handle or the presence of solubilizing groups, all BHPs with two free *meso*-positions **10a–h** were fully *meso*-brominated using 2.1 equiv of NBS in chloroform. Furthermore, aryl- and alkyl-substituted BHPs **11b,e,h** with only one free *meso*-position were brominated with 1.05 equiv of NBS in almost quantitative yields. Finally, we synthesized the monobrominated BHPs


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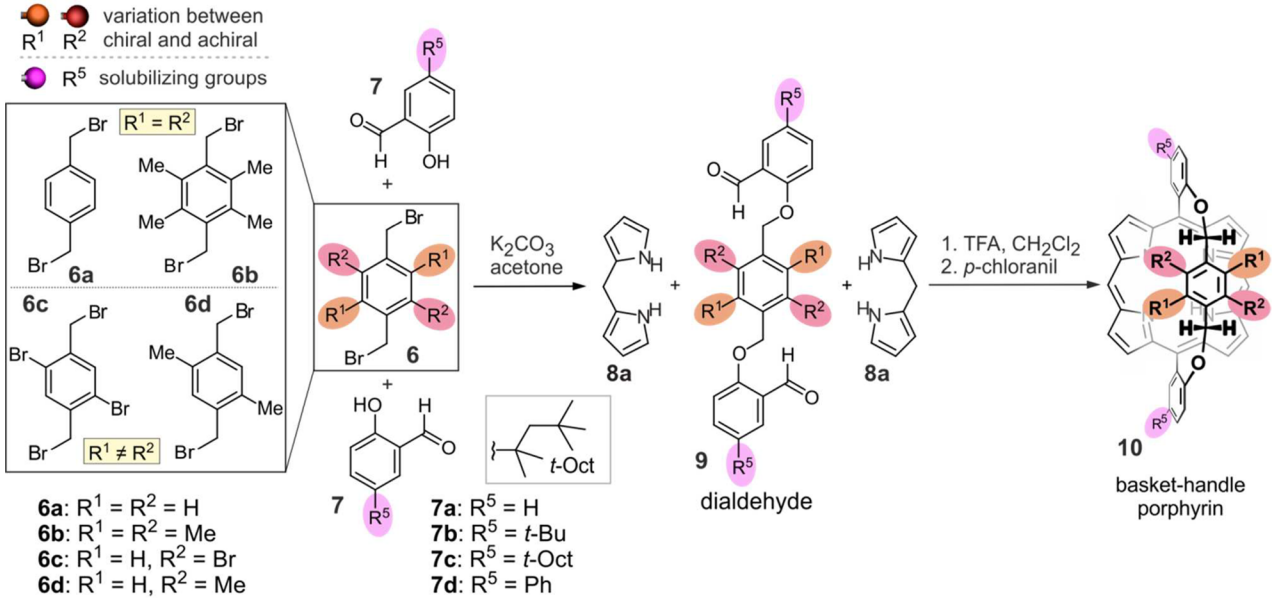
**Table 1. Variation of the *p*-Xylene Unit Leading to Chiral or Achiral BHPs (10) and Introduction of Solubilizing Groups**




| entry | xylene unit | salicylic aldehyde | substitution pattern | yield **9** (%) | yield **10** (%) |
|---|---|---|---|---|---|
| 1 | **6b** | **7a** | **9a/10a**: $R^1 = R^2$ = Me, $R^5$ = H | 99 | ~30 |
| 2 | **6d** | **7a** | **9b/10b**:[a] $R^1$ = H, $R^2$ = Me, $R^5$ = H | 98 | ~30 |
| 3 | **6b** | **7b** | **9c/10c**: $R^1 = R^2$ = Me, $R^5$ = *t*-Bu | 99 | ~30 |
| 4 | **6d** | **7b** | **9d/10d**:[a] $R^1$ = H, $R^2$ = Me, $R^5$ = *t*-Bu | 97 | 30 |
| 5 | **6b** | **7c** | **9e/10e**: $R^1 = R^2$ = Me, $R^5$ = *t*-Oct | 97 | 32 |
| 6 | **6d** | **7c** | **9f/10f**:[a] $R^1$ = H, $R^2$ = Me, $R^5$ = *t*-Oct | 98 | 30 |
| 7 | **6c** | **7a** | **9g/10g**:[a] $R^1$ = H, $R^2$ = Br, $R^5$ = H | 95 | 26 |
| 8 | **6c** | **7c** | **9h/10h**:[a] $R^1$ = H, $R^2$ = Br, $R^5$ = *t*-Oct | 98 | 32 |
| 9 | **6a** | **7c** | **9i/10i**: $R^1 = R^2$ = H, $R^5$ = *t*-Oct | 96 | 24 |
| 10 | **6b** | **7d** | **9j/10j**: $R^1 = R^2$ = Me, $R^5$ = Ph | 97 | |
| 11 | **6d** | **7d** | **9k/10k**: $R^1$ = H, $R^2$ = Me, $R^5$ = Ph | 95 | |

[a]Synthesized as a racemic mixture.

**14d,e** with one remaining free *meso*-position (Table 3). Since bromination of porphyrins with more than one free *meso*-position is not selective,[28] the bromination of **10a,c** yielded a mixture of mono- and dibrominated BHPs along with the unreacted BHP. The highest yields of monobrominated BHPs **14d,e** were obtained with 1.2 equiv of NBS, and the reaction mixture was easily resolved by column chromatography. As previously reported, it was essential to carry out all bromination reactions without pyridine, as this led to decomposition.[12] The reverse reaction, the hydrodebromination of brominated porphyrins via a method described by Osuka et al. using $Pd(PPh_3)_4$ as a catalyst and formic acid as a hydrogen source,[29] was successfully applied to the brominated BHP **13c**.

**Highly Regioselective Ir-Catalyzed *β*-Borylation of Porphyrins by C−H Bond Activation.** The previous report on the direct borylation of BHPs via Ir-catalyzed C−H activation was limited to the 5,15-bridged BHP **10c**, possessing two remaining free *meso*-positions.[12] However, the protocol was found not to be suitable for the *β*-borylation of *meso*-phenyl-substituted porphyrins, since C−H activation at the phenyl ring occurred as an undesired side reaction.[30] Instead, the direct borylation of BHP **11b** with 3,5-di-*tert*-butylphenyl substitution in one *meso*-position and *tert*-butyl groups at the basket-handle aryls seemed more promising (Table 4). The *tert*-butyl groups at the *meso*-phenyl substituent and the *meso*-bridge phenyls were essential for the regioselectivity of the reaction, since without them borylation of any sterically unhindered phenyl group was possible. Therefore, the *tert*-butyl groups at the *meso*-bridge phenyls not only increased solubility but also acted as directing groups in the sterically controlled C−H activation reactions. Depending on the amount of the pinacolborane source—either HBpin or $(BPin)_2$—the yield was optimized to give favorably diborylated BHP **15g** in 77% yield with an excess of the borylation reagent or monoborylated BHP **15f** in 55% yield using 2 equiv of the borylating agent. Unreacted starting material and the two products were easily resolved by recycling gel-permeation chromatography.

**Suzuki Coupling with BHP Building Blocks.** To demonstrate the applicability of functionalized BHPs as synthetic building blocks, we synthesized two directly linked dimeric porphyrins, each containing a BHP unit (Scheme 1). Both dimers were synthesized by Suzuki coupling under conditions reported previously.[31] Dimer **18** was formed from the *β*-brominated tetraarylporphyrin **16a** and the *β*-borylated BHP **15a** in a yield of 83%. Miyaura borylation[32] of **16b** yielded the *β*-borylated tetraarylporphyrin **17**, which was coupled with *meso*-brominated BHP **14e** to give the dimer **19** (78% yield). Both dimers were found to adopt a conformation with the *meso*-aryl substituent of the tetraarylporphyrin unit located on the sterically unhindered side of the BHP. Investigations regarding the stereostructures and chirality of these dimers are in progress and will be reported later.



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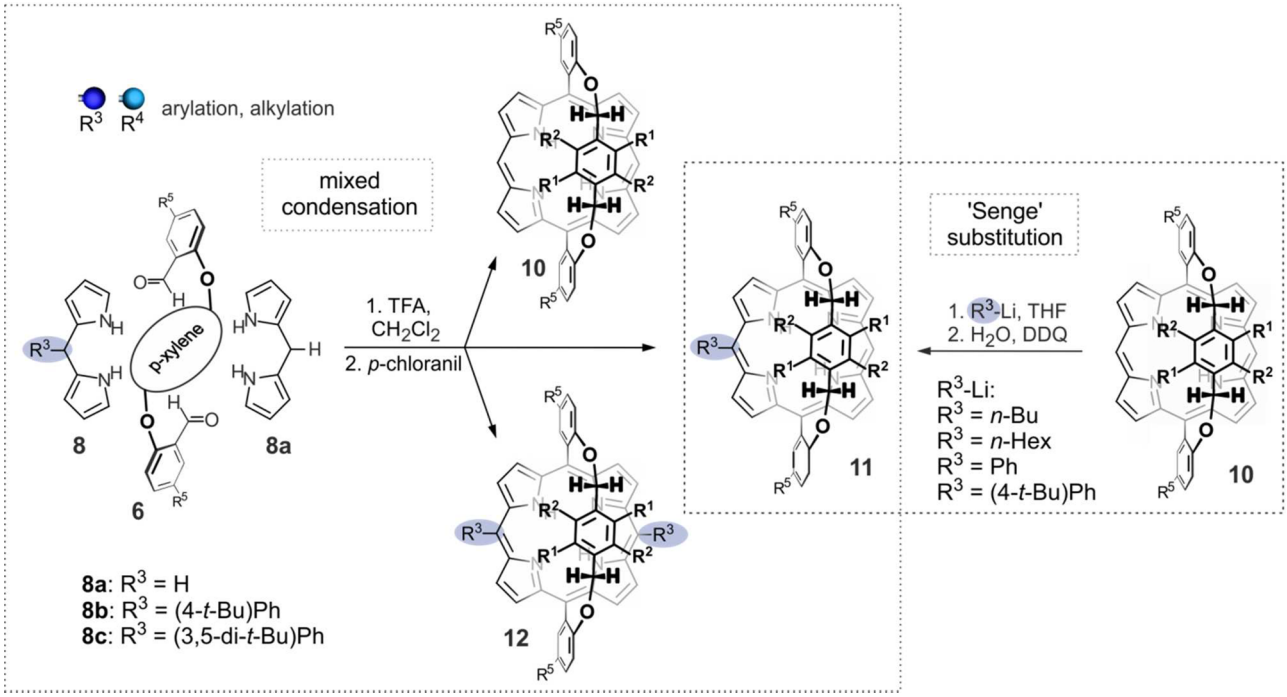
**Table 2. *meso*-Substituted BHPs by Mixed Condensation (Entries 1−7) with 5-Substituted Dipyrrylmethanes (8b,c) or by Senge-Type Nucleophilic Substitution (Entries 8−16)**




| entry | 8 | $R^3$-Li | BHP | substitution pattern | yield (%) |
|---|---|---|---|---|---|
| 1 | **8b** | | **11a** | $R^1 = R^2$ = Me, $R^5$ = H, $R^3$ = (4-*t*-Bu)Ph | 14 |
| 2 | **8b** | | **11b** | $R^1 = R^2$ = Me, $R^5$ = *t*-Bu, $R^3$ = (4-*t*-Bu)Ph | 15 |
| 3 | **8c** | | **11c** | $R^1 = R^2$ = Me, $R^5$ = *t*-Bu, $R^3$ = (3,5-di-*t*-Bu)Ph | 14 |
| 4 | **8c** | | **11d** | $R^1 = R^2$ = Me, $R^5$ = *t*-Oct, $R^3$ = (3,5-di-*t*-Bu)Ph | 15 |
| 5 | **8b** | | **12a** | $R^1 = R^2$ = Me, $R^5$ = H, $R^3$ = (4-*t*-Bu)Ph | 6 |
| 6 | **8c** | | **12b** | $R^1 = R^2$ = Me, $R^5$ = *t*-Bu, $R^3$ = (3,5-di-*t*-Bu)Ph | 6 |
| 7 | **8b** | | **12c** | $R^1 = R^2$ = Me, $R^5$ = *t*-Bu, $R^3$ = (4-*t*-Bu)Ph | 7 |
| 8 | | *n*-Bu | **11e** | $R^1 = R^2$ = Me, $R^5$ = H, $R^3$ = *n*-Bu | 82 |
| 9 | | Ph | **11f** | $R^1 = R^2$ = Me, $R^5$ = H, $R^3$ = Ph | 72 |
| 10 | | *n*-Hex | **11g** | $R^1 = R^2$ = Me, $R^5$ = H, $R^3$ = *n*-Hex | 75 |
| 11 | | (4-*t*-Bu)Ph | **11a** | $R^1 = R^2$ = Me, $R^5$ = H, $R^3$ = (4-*t*-Bu)Ph | 65 |
| 12 | | (4-*t*-Bu)Ph | **11b** | $R^1 = R^2$ = Me, $R^5$ = *t*-Bu, $R^3$ = (4-*t*-Bu)Ph | 68 |
| 13 | | *n*-Bu | **11h**[a] | $R^1$ = H, $R^2$ = Me, $R^5$ = H, $R^3$ = *n*-Bu | 72 |
| 14 | | *n*-Bu | **11i** | $R^1 = R^2$ = Me, $R^5$ = *t*-Bu, $R^3$ = *n*-Bu | 76 |
| 15 | | Ph | **11j** | $R^1 = R^2$ = Me, $R^5$ = *t*-Oct, $R^3$ = Ph | 65 |
| 16 | | Ph | **11k** | $R^1 = R^2$ = Me, $R^5$ = *t*-Bu, $R^3$ = Ph | 64 |

[a]Synthesized as a racemic mixture.

**Metalation of BHPs.** Previously we described a series of achiral BHPs which contained different metals in the oxidation state +2, namely Pd, Ni, Zn, Cu, and Mg.[12] We were able to expand the scope of metallo-BHPs to oxidation states higher than +2 by synthesizing BHPs with In(III) and V(IV) as complexed metals in quantitative yield (Table 5). The remaining free axial coordination site is occupied by chloride for all reported In(III) BHPs and by an oxo ion for the V(IV) BHP. As already described earlier for most of the $M^{II}$-BHPs, demetalation by acidic, basic, or reductive conditions was not possible for the ions in higher oxidation states, which is due to the steric shielding of the handle that prevents the metal ion from being expelled from the porphyrin.[12]

**Solid-State Structures and Conformations in Solution.** Previous results of NMR investigations and computational structure optimizations gave first insight into the stereostructures of BHPs. Additional information about the three-dimensional shape of a metalated *p*-xylene-strapped BHP was obtained by the crystal structure of **Ni-10a**.[12] By slow diffusion of methanol (containing 5% water) into a dilute solution of the respective BHP in chloroform, we succeeded in growing crystals of **V-10d** and **In-10d** suitable for X-ray diffraction investigations. These results (Figure 2) in combination with DFT-optimized structures were used to get a more detailed insight into the conformational differences of the BHPs.

The solid-state structures of **Ni-10a**, **In-10d**, and **V-10d** showed most of the possible conformations that the BHPs can adopt. **Ni-10a** and **V-10d** possessed a large gap between the porphyrin macrocycle (defined by the four nitrogen atoms) and the bridge (using a centroid of the carbons of the xylene ring) with a distance above 4.70 Å, while this gap was significantly smaller in **In-10d** (3.50 Å). Another difference was found when comparing the angles between the planes of the xylene unit and tetrapyrrole. While these planes were nearly coplanar for **In-**


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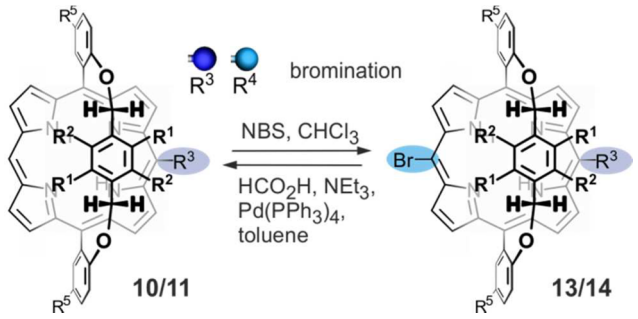
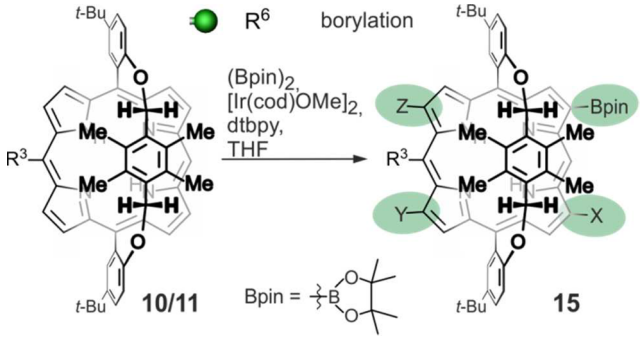
**Table 3. Bromination (Entries 1−14) and Debromination (Entry 15) of BHPs**




| entry | reactant | reagent | product | yield (%) |
|---|---|---|---|---|
| 1 | **10a**: $R^1$ = Me, $R^2$ = Me, $R^3$ = H, $R^5$ = H | NBS (2.1 equiv) | **13a**: $R^1$ = Me, $R^2$ = Me, $R^3$ = Br, $R^5$ = H | 98 |
| 2 | **10b**: $R^1$ = H, $R^2$ = Me, $R^3$ = H, $R^5$ = H | NBS (2.1 equiv) | **13b**:[a] $R^1$ = H, $R^2$ = Me, $R^3$ = Br, $R^5$ = H | 98 |
| 3 | **10c**: $R^1$ = Me, $R^2$ = Me, $R^3$ = H, $R^5$ = *t*-Bu | NBS (2.1 equiv) | **13c**: $R^1$ = Me, $R^2$ = Me, $R^3$ = Br, $R^5$ = *t*-Bu | 97 |
| 4 | **10d**: $R^1$ = H, $R^2$ = Me, $R^3$ = H, $R^5$ = *t*-Bu | NBS (2.1 equiv) | **13d**:[a] $R^1$ = H, $R^2$ = Me, $R^3$ = Br, $R^5$ = *t*-Bu | 99 |
| 5 | **10e**: $R^1$ = Me, $R^2$ = Me, $R^3$ = H, $R^5$ = *t*-Oct | NBS (2.1 equiv) | **13e**: $R^1$ = Me, $R^2$ = Me, $R^3$ = Br, $R^5$ = *t*-Oct | 97 |
| 6 | **10f**: $R^1$ = H, $R^2$ = Me, $R^3$ = H, $R^5$ = *t*-Oct | NBS (2.1 equiv) | **13f**:[a] $R^1$ = H, $R^2$ = Me, $R^3$ = Br, $R^5$ = *t*-Oct | 96 |
| 7 | **10g**: $R^1$ = H, $R^2$ = Br, $R^3$ = H, $R^5$ = H | NBS (2.1 equiv) | **13g**:[a] $R^1$ = H, $R^2$ = Br, $R^3$ = Br, $R^5$ = H | 97 |
| 8 | **10h**: $R^1$ = H, $R^2$ = Br, $R^3$ = H, $R^5$ = *t*-Oct | NBS (2.1 equiv) | **13h**:[a] $R^1$ = H, $R^2$ = Br, $R^3$ = Br, $R^5$ = *t*-Oct | 99 |
| 9 | **10i**: $R^1$ = H, $R^2$ = H, $R^3$ = H, $R^5$ = *t*-Oct | NBS (2.1 equiv) | **13h**: $R^1$ = H, $R^2$ = H, $R^3$ = Br, $R^5$ = *t*-Oct | 99 |
| 10 | **11h**: $R^1$ = H, $R^2$ = Me, $R^3$ = *n*-Bu, $R^5$ = H | NBS (1.05 equiv) | **14a**:[a] $R^1$ = H, $R^2$ = Me, $R^3$ = *n*-Bu, $R^5$ = H | 96 |
| 11 | **11e**: $R^1$ = Me, $R^2$ = Me, $R^3$ = *n*-Bu, $R^5$ = H | NBS (1.05 equiv) | **14b**: $R^1$ = Me, $R^2$ = Me, $R^3$ = *n*-Bu, $R^5$ = H | 94 |
| 12 | **11b**: $R^1$ = Me, $R^2$ = Me, $R^3$ = (4-*t*-Bu)Ph, $R^5$ = *t*-Bu | NBS (1.05 equiv) | **14c**: $R^1$ = Me, $R^2$ = Me, $R^3$ = (4-*t*-Bu)Ph, $R^5$ = *t*-Bu | 99 |
| 13 | **10c**: $R^1$ = Me, $R^2$ = Me, $R^3$ = H, $R^5$ = *t*-Bu | NBS (1.2 equiv) | **14d**: $R^1$ = Me, $R^2$ = Me, $R^3$ = H, $R^5$ = *t*-Bu | 62 |
| 14 | **10a**: $R^1$ = Me, $R^2$ = Me, $R^3$ = H, $R^5$ = H | NBS (1.2 equiv) | **14e**: $R^1$ = Me, $R^2$ = Me, $R^3$ = H, $R^5$ = H | 59 |
| 15 | **13c**: $R^1$ = Me, $R^2$ = Me, $R^3$ = Br, $R^5$ = *t*-Bu | $HCO_2H$, $NEt_3$, $Pd(PPh_3)_4$ | **10c**: $R^1$ = Me, $R^2$ = Me, $R^3$ = H, $R^5$ = *t*-Bu | 91 |

[a]Synthesized as a racemic mixture.

**Table 4. Direct Borylation by Ir-Catalyzed C−H Activation**




| reactant | X | Y | Z | product (yield (%)) |
|---|---|---|---|---|
| **10c** ($R^3$ = H) | H | H | H | **15a**[a] (22)[b] |
| **10c** ($R^3$ = H) | H | H | Bpin | **15b**[a] (16)[b,e] |
| **10c** ($R^3$ = H) | H | Bpin | H | **15c**[a] (16)[b,e] |
| **10c** ($R^3$ = H) | H | Bpin | Bpin | **15d**[a] (20)[b] |
| **10c** ($R^3$ = H) | Bpin | Bpin | Bpin | **15e** (13)[b] |
| **11b** ($R^3$ = Ar[d]) | H | H | H | **15f**[a] (55)[c] |
| **11b** ($R^3$ = Ar[d]) | Bpin | H | H | **15g** (77)[c] |

[a]Synthesized as a racemic mixture. [b]Statistical product distribution, not optimized for a specific product. [c]Optimized yield. [d]Ar = 3,5-*t*-$Bu_2$Ph. [e]Inseparable mixture of the two regioisomers.

**10d**, they were strongly tilted for the metalated BHPs with large gaps (44° for **Ni-10a** and 33° for **V-10d**).

For a more systematic investigation of the conformational behavior of the BHPs, we performed conformational analyses of **Ni-10**, **Zn-10**, and **2H-10**,with either two or four methyls in the strap, using B97-D3/def2-TZVP. Surprisingly, these analyses all yielded only one possible conformation according to a Boltzmann statistical weighting. All achiral BHPs with a four-methyl strap (**M-10a** and **M-10c**) showed a large gap between the bridge and the porphyrin, while the chiral BHPs with only two methyls (**M-10d**) in the strap had a short distance. This was easily observed by comparing the dihedral angles C-1′−C-2′−O-3′−C-4′, which were nearly 0° in cases containing the tetramethylated bridge and nearly 90° for the dimethylated species. In addition, the methylene protons at the 4′-position of **M-10d** were always oriented toward the methyl group of the xylene unit, while the conformation with the methylene protons directed toward the hydrogen of the xylene unit was in all cases significantly higher in energy and should not be observable in solution. The reason for the different gaps is the interplay of steric hindrance (especially of the methyl groups) with the stabilizing dispersion effects (e.g., $\pi-\pi$ stacking) between the bridge and the porphyrin plane. The steric hindrance with four methyl groups was obviously higher than the stabilizing effect of the $\pi-\pi$ stacking in **2H-10c**, **Zn-10a**, and **Ni-10a**, and thus a maximum distance between the bridge and the porphyrin was reached. For the chiral BHPs with only two methyls the stabilization of the molecule by the $\pi-\pi$ stacking became stronger than the steric hindrance and the distance between strap and porphyrin plane became smaller.

NMR investigations clearly confirmed the findings discussed above for the solid-state structures and the calculated conformations. The chiral BHPs (with two methyl or two bromine substituents in the xylene unit) show distinct differences in their chemical shifts and symmetry in comparison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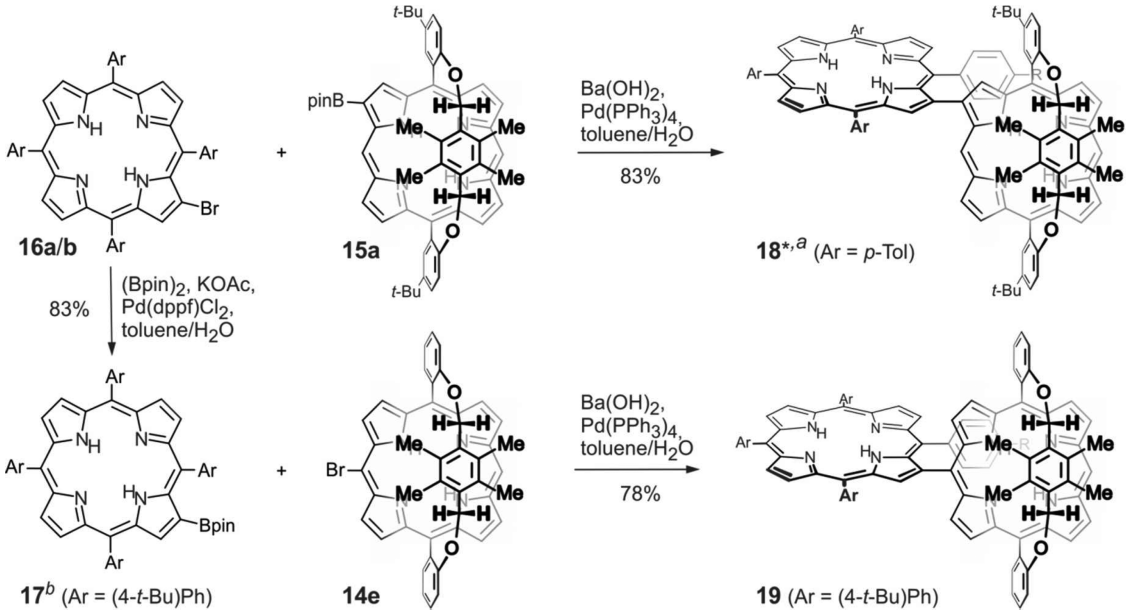
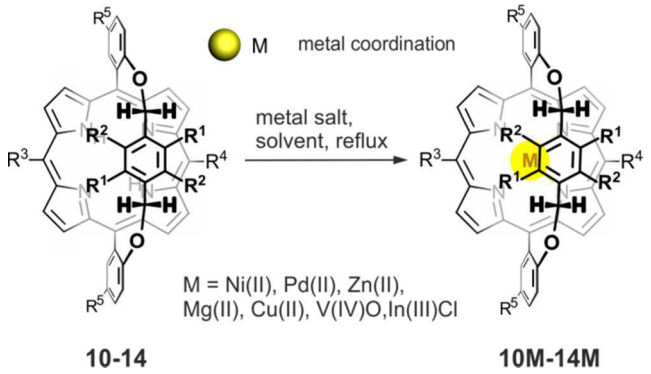
**Scheme 1. Synthesis of Directly Linked Dimeric Porphyrins from BHP Building Blocks**




[a]Synthesized as a racemic mixture; **18** was synthesized from **16a** (Ar = *p*-Tol). [b]**17** was prepared from **16b**.

**Table 5. Metalation of BHPs**




| reactant | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | product | M |
|---|---|---|---|---|---|---|---|
| **10a** | Me | Me | H | H | H | **M-10a** | Ni,[b] Pd,[c] Zn,[d] Mg,[e] Cu[f] |
| **10b** | Me | H | H | H | H | **M-10b**[a] | Ni, Zn, In[g] |
| **10c** | Me | Me | H | H | *t*-Bu | **M-10c** | Pd, In, Zn, Ni |
| **10d** | Me | H | H | H | *t*-Bu | **M-10d**[a] | Ni, Pd, Zn, Mg, Cu, In, V[h] |
| **10e** | Me | Me | H | H | *t*-Oct | **M-10e** | Zn |
| **10f** | Me | H | H | H | *t*-Oct | **M-10f**[a] | In |
| **10h** | Br | H | H | H | *t*-Oct | **M-10h**[a] | In |
| **10i** | H | H | H | H | *t*-Oct | **M-10i** | Ni |
| **11a** | Me | Me | H | (4-*t*-Bu)Ph | H | **M-11a** | Zn, Cu, Ni |
| **11b** | Me | Me | H | (4-*t*-Bu)Ph | *t*-Bu | **M-11b** | Pd, Ni, Cu, Zn |
| **11e** | Me | Me | H | *n*-Bu | H | **M-11e** | Zn, Ni |
| **11i** | Me | Me | H | *n*-Bu | *t*-Bu | **M-11i** | Zn |
| **11h** | Me | H | H | *n*-Bu | H | **M-11h**[a] | Zn |
| **11g** | Me | Me | H | *n*-Hex | H | **M-11g** | Zn, Ni |
| **12a** | Me | Me | (4-*t*-Bu)Ph | (4-*t*-Bu)Ph | H | **M-12a** | Zn, Ni |
| **13h** | Br | H | Br | Br | *t*-Oct | **M-13h**[a] | In |
| **13f** | Me | H | Br | Br | *t*-Oct | **M-13f**[a] | In |
| **13c** | Me | Me | Br | Br | *t*-Bu | **M-13c** | Ni |
| **14d** | Me | Me | Br | H | *t*-Bu | **M-14d** | Ni |

[a]Synthesized as a racemic mixture. [b]$Ni(acac)_2$, $(CH_2Cl)_2$, $\Delta T$. [c]$Pd(OAc)_2$, $(CH_2Cl)_2$, $\Delta T$. [d]$Zn(OAc)_2$, $CHCl_3$, $\Delta T$. [e]$MgBr_2{\cdot}OEt_2$, $NEt_3$, $CHCl_3$, $\Delta T$. [f]$Cu(OAc)_2$, $CHCl_3$, $\Delta T$. [g]$InCl_3$, glacial acetic acid, $\Delta T$. [h]$VO(acac)_2$, quinoline, $\Delta T$.



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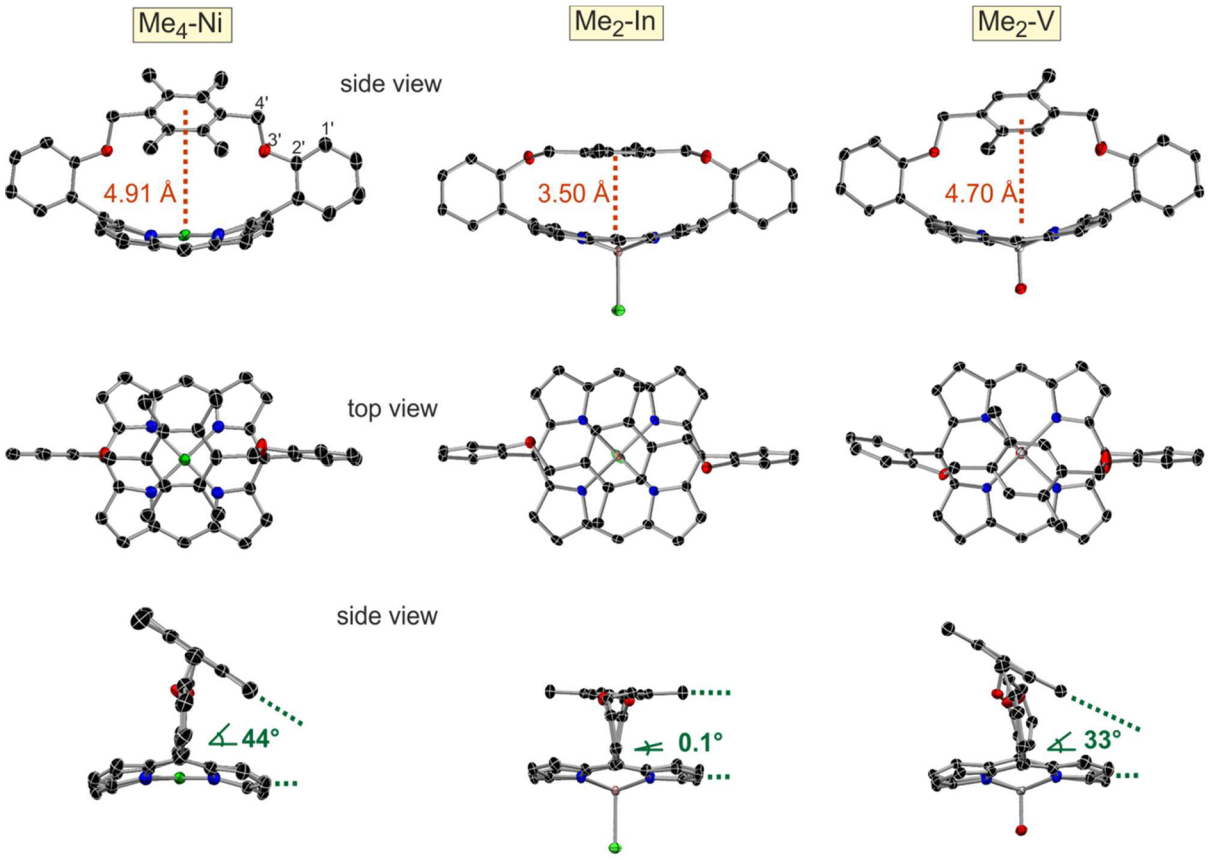


**Figure 2.** ORTEP representations of the X-ray single crystal structures of **Ni-10a**, **In-10d**, and **V-10d**: (top, red) distance between the centroid of the pyrrole nitrogens and the centroid of the aromatic xylene carbons; (bottom, green) angle between the xylene plane and the tetrapyrrolic plane. All disorder, hydrogens bonded to carbon, and peripheral *tert*-butyl groups removed for clarity.

to the achiral BHPs (with four methyl substituents in the xylene unit). The two protons of the methylene unit as well as the methyl groups and the hydrogens of the xylene ring represent ideal diagnostic groups. For the achiral BHPs the two methylene protons appeared as a sharp singlet, thus being magnetically identical, and showed no interaction with the pyrrolic protons in $^1$H NOE experiments. This proved a $C_{2v}$-symmetric conformation in solution on the NMR time scale. The sharp shape of the signal of the methylene protons (as well as for all protons within the strap) indicated a rigid conformation, as changes in the location of the strap unit relative to the porphyrin macrocycle would induce peak broadening due to an altering position of the protons within the porphyrin ring current. In contrast, each of the two methylene protons of the chiral BHPs appeared as a sharp doublet with largely different chemical shifts (Figure 3), proving a $C_2$-symmetric conformation in solution. Both protons showed a strong interaction with the methyl group of the strap, while only one of these protons showed a $^1$H NOE interaction with only one pyrrole unit (see the Supporting Information for NOE spectra), and none of the methylene protons interacted with a proton of the xylene ring. This proved that in solution the solely present conformation has the methylene protons directed at the methyl group, which confirmed the assumptions from the calculations. Furthermore, we compared the $^1$H chemical shifts of the methylene protons and the methyl groups between various BHPs (Figure 3) which differ only in the number of methyl groups in the strap and the coordinated metal ion. The results showed that the chemical shift of these

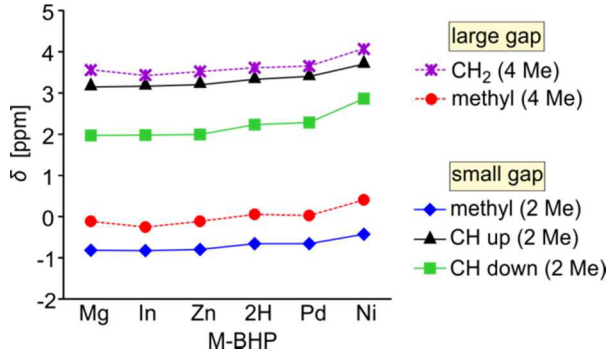


**Figure 3.** $^1$H NMR shifts of the benzylic xylene protons and the xylene methyl groups of chiral (**M-10d**) and achiral (**M-10c**) BHPs.

groups varied largely between the chiral and the achiral BHPs and this difference correlated with the distance between the xylene unit and the porphyrin and was caused by the ring current of the porphyrin, which is inversely proportional to the distance to the porphyrin. These results not only substantiated the discussed differences between the chiral and achiral BHPs but also proved that the conformations among only chiral or only achiral porphyrins are very similar.

Due to the open-shell nature of the coordinated V(IV) ion, it was not possible to acquire NMR data for **V-10d** that would provide information about its conformation in solution. To find the reason **V-10d** showed significant deviations in the crystal structure in comparison to the other BHPs with dimethylated bridges, we performed a conformational analysis of **V-10d** using


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B97D3/def2-TZVP. In contrast with the results described above, where solid-state structures and conformations derived from the calculations and from NMR investigations were in accordance, the solid-state structure and the computed minmum of **V-10d** differed clearly, as the DFT analysis predicted the same conformation for the vanadium BHP as for all other chiral BHPs: i.e., with a small gap between the strap and the porphyrin. To exclude that this is an artifact from the method used, single-point energy calculations were done using B3LYP-D3, PW6B95-D3, and SCS-CC2 (all with the def2-TZVP basis set), and all methods confirmed the previous results (the large-gap structure is about 11 kcal/mol higher in energy). Another hint at the conformation in solution was obtained by ECD investigations. The calculated ECD spectra of small-gap **V-10d** (see the Supporting Information) showed a much better fit with the experimental curves than the conformation with the large gap. Thus, most probably, the deviations in the X-ray structure are due to only packing effects.

**Assignment of the Absolute Configuration of Metalated BHPs.** We previously reported the absolute stereostructure of **Ni-10b**, which we obtained by comparing online ECD spectra with calculated spectra.[12] Measurements were done after resolution of the enantiomers by HPLC on a chiral phase. Using the same approach, we succeeded in resolving the enantiomers of all metallo-BHPs **M-10d** on a Chiralpak IA column using isocratic solvent mixtures (for chromatographic details, see the Supporting Information) and measured the online ECD spectra of the enantiomers. The faster-eluting enantiomers always displayed a negative couplet within the Soret band region while, vice versa, the slower-eluting enantiomers showed a positive, mirror-image couplet (Figure 4). All ECD spectra were very similar, regardless of the central metal, even for open-shell ions such as Cu(II) and V(IV). As

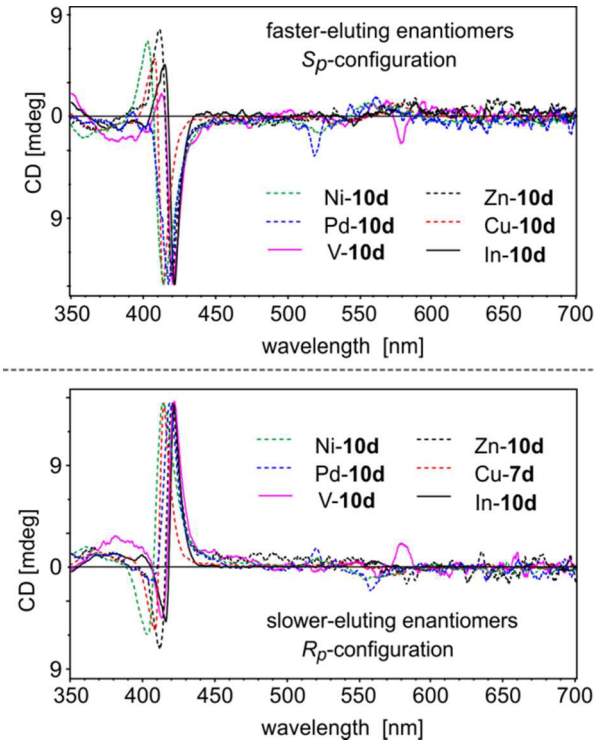


**Figure 4.** Experimental ECD spectra of (top) $S_p$-**M-10d** and (bottom) $R_p$-**M-10d**: online measurements, scaled to the most intense signal.

previous investigations of the absolute configurations of porphyrins with different kinds of chirality (stereocenters,[33] helical chirality,[34,35] axial chirality[36,37]) had shown that the metal centers do not influence the ECD spectra significantly (e.g., sign inversion had never been observed), the absolute configurations of the metalated BHPs were determined by simple comparison of the experimental ECD spectra. Thus, as all faster-eluting enantiomers show a negative ECD signal at ~420 nm, they do have the $S_p$ configuration, while all slower-eluting species are $R_p$-configured.

To verify the previous determination of the absolute configurations of the enantiomers of **Ni-10b**,[12] we compared the results of TD B3LYP, TD BHLYP, and TD CAM-B3LYP calculations of **Ni-10b** and **Zn-10b** with those of SCS-CC2. Using a UV shift of 38 nm, the SCS-CC2-predicted ECD spectra for **Zn-10b** showed a nice fit with the experimental results and confirmed the previously published results for **Ni-10b**.[12] CAM-B3LYP and BHLYP gave nearly identical results (except for different UV shifts), and thus BHLYP could be neglected in the following. Both functionals, B3LYP and CAM-B3LYP, permitted a correct determination of the absolute configuration (see Figure S1 in the Supporting Information) of the investigated BHPs with $\Delta_{ESI}$ values[38] above 85% for CAM-B3LYP (0.08 eV, 48 nm shift) and above 70% for B3LYP (0.08 eV, 30 nm shift). However, the CAM-B3LYP ECD curves showed a much better fit with the experimental spectra and the SCS-CC2 results than the B3LYP curves. The reasons for this were several wrongly predicted CT states (ghost states[39]) in the B3LYP spectra, which falsified the results. All of these states had an electron−hole distance $D$[40] above 2.7 Å and an overlap $S$[41] of less than 10%, clearly confirming that B3LYP cannot correctly handle these excitations. The SCS-CC2-predicted ECD curves (shift of 58 nm) of **Ni-10b** fit very well to the measured spectra, and again CAM-B3LYP and BHLYP showed comparable spectra while the match of the B3LYP results was significantly worse. In the B3LYP calculations a high number of excitations from the $d_{z^2}$ to the $d_{x^2-y^2}$ orbital of the nickel atom occurred. These were only partially observed in the SCS-CC2 computations. In addition, several ghost states below the Soret band region showed wrong ECD signs in comparison to the results of the experiment or the other calculations (selected electron hole distances $D$ and overlaps $S$ for the TDDFT results can be found in Table S3 in the Supporting Information). In general, TDB3LYP was found to seriously suffer from ghost states when the excited states of BHPs were calculated and thus CAMB3LYP or BHLYP should be preferred for these investigations.

**Assignment of the Absolute Configuration and Investigation of the Tautomerism of the Chiral Free-Base BHPs.** The enantiomers of the chiral free-base BHPs were—like those of the metaled chiral BHPs—resolvable by HPLC on a chiral phase. However, to our surprise the online CD measurements gave ECD spectra that were not comparable with those of the metalated BHPs. Initially we attributed this effect to be related to the NH tautomerism, a characteristic of porphyrins, which has been known for over half a century and has been studied extensively.[42−44] Our chiral free base BHPs, which are $C_2$ symmetric, were synthesized as racemic mixtures, with each enantiomer potentially existing as a mixture of two tautomers. These tautomers are, at the same time, diastereomers (Figure 5).

We expected a strong influence of the tautomerism on the ECD spectra. Indeed, a comparison of the calculated curves of


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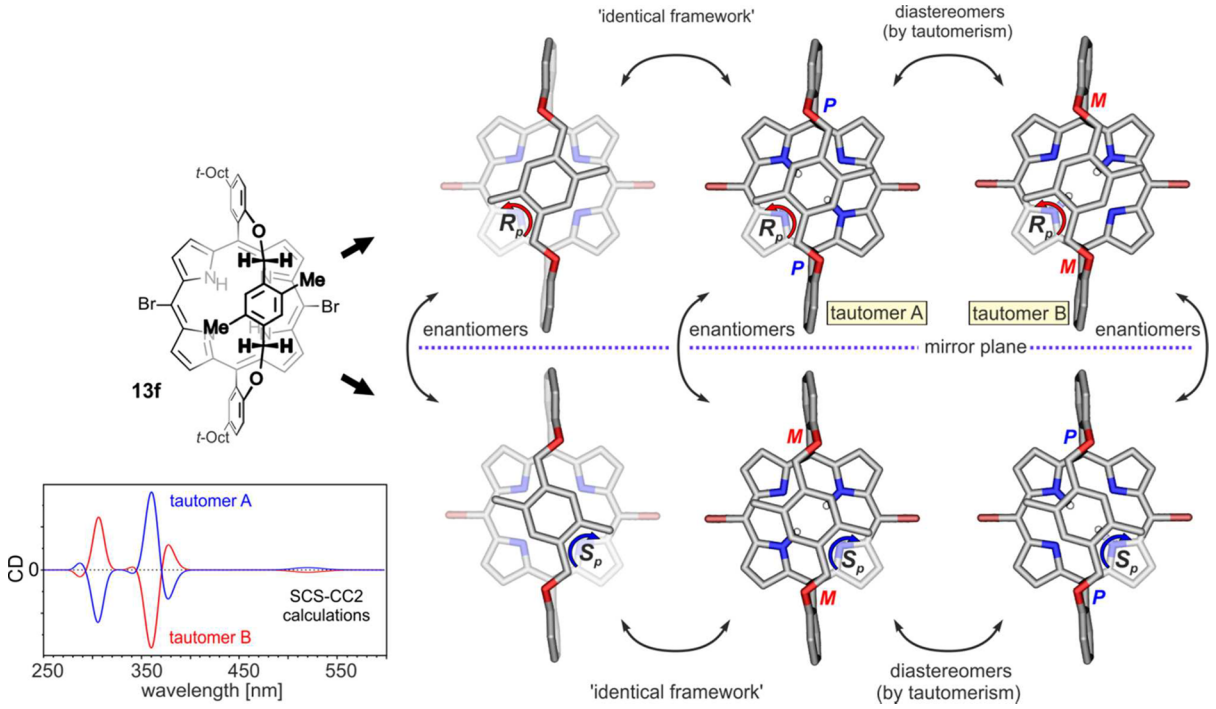


**Figure 5.** Tautomerism in chiral BHPs. *tert*-Octyl substituents and selected protons are omitted for clarity.

the tautomers showed that they are nearly mirror images (Figure 5). Thus, the Boltzmann statistical weighting of the single curves had to be as precise as possible to get reliable ECD spectra, and several methods were evaluated to obtain the relative energies of the tautomers of **13f**. The initially used optimization method B97D3/def2-TZVP preferred the tautomer with the hydrogens orthogonal to the bridge methyl groups (tautomer A, Figure 5) only by 0.88 kcal/mol ($\Delta E$). In the following, tautomer A is always the reference compound, so that positive relative energies refer to a preference of the NH protons parallel to the CH protons of the *p*-xylene bridge. A further optimization with B3LYP-D3/def2-TZVP gave a $\Delta E$ value of 1.04 kcal/mol; however, the $\Delta G$ value was only 0.26 kcal/mol. A single-point calculation of these conformations using B2GP-PLYP-D3/def2-TZVPP only slightly changed the $\Delta E$ value to 1.08 kcal/mol. Keeping in mind that the typical error range of the used methods is higher than the relative energies found with the DFT methods, no unambiguous preference for one of the tautomers could be given. It thus seemed advisible to change the strategy and perform DLPNO-CCSD(T)/def2-TZVP single-point energy calculations, and in parallel, we started NMR investigations to get a more reliable ratio of the tautomers of **13f**.

In the case of both tautomers being equally present for each enantiomer in the racemic mixture, one would expect two NH signals in a 1:1 ratio, since the protons are identical within the molecule but diastereotopic between the two tautomers. In the case, however, that one of the two diasteromeric tautomers should prevail, the two signals should reflect the diastereomeric ratio. Our NMR investigations showed a single signal for the NH protons, which we expected to result from a rapid interconversion of the two tautomers, which is well-known for porphyrins.[45] NMR investigations at lower temperatures to slow down the interconversion of the tautomers and to detect them side by side[46] surprisingly did not show any hints at diastereomers appearing, even at temperatures of 225 K. Finally 2D NMR experiments unequivocally proved that already at room temperature only one tautomer was present for each enantiomer (Figure 6). This was also corroborated by high-

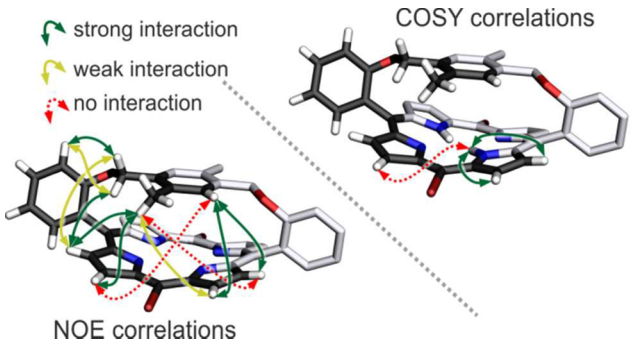


**Figure 6.** Selected NOE and COSY correlations of the chiral free base BHPs, here shown for $S_p$-**13f** as an example. Selected protons and solubilizing groups are omitted for clarity. Copies of the NOE and COSY spectra of **13f** and **10f,h** are included in the Supporting Information.

level quantum chemical calculations with DLPNO-CCSD(T)/def2-TZVP, which no longer predicted an equilibrium of the two tautomers but correctly provided an energy difference of $\Delta E$ = 3.24 kcal/mol: i.e., large enough to result in only one prevailing tautomer. NOE interactions of the methyl group of the xylene unit to the $\beta$-hydrogens of only one pyrrole and of the aromatic hydrogen of the strap to only the other pyrrolic $\beta$-hydrogens allowed unambiguous differentiation of these pyrrole units. COSY interactions positioned the NH-containing pyrrole unit in proximity to the aromatic hydrogen of the xylene strap, while the other pyrrole clearly was located close to the methyl group of the strap. As expected from the calculations, this combination of NOE and COSY correlations thus established tautomer A as the only existing one, the NH protons being


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assigned to the nitrogen atoms orthogonal to the methyl groups of the bridge (Figure 6). This arrested tautomerism is remarkable, since the BHPs are highly symmetric; the tetrapyrrolic framework without the strap is even $C_{2v}$ symmetric, which means all pyrrole units would be identical. The loss of the mirror planes resulting in $C_2$ symmetry is caused only by the unsymmetric substitution of the strap unit, meaning that the energy difference of the two possible tautomers is not due to the presence of an electronically or sterically modified porphyrin macrocycle but is induced solely from the periphery. Furthermore, it is surprising that this phenomenon occurs even at room temperature. Usually temperatures around 200 K or below are necessary to observe arrested tautomerism in porphyrins, even in systems that are electronically unsymmetric: e.g., by $\beta$-substitution.[45] Dispersive interactions, e.g. $\pi-\pi$ stacking, are an explanation of the energy difference of the two tautomers. This can be deduced from the quantum-chemical calculations, which show a distance of 3.40 Å between the planes of the xylene unit and the porphyrin macrocycle for tautomer A, while this distance is 3.50 Å for tautomer B, clearly indicating a stronger interaction between the bridge and the porphyrin for tautomer A.

With the correct ratio of the tautomers in hand, we were quite surprised about the bad matching of the TDDFT calculated spectra with the experimental ECD curves. Even SCS-CC2/def2-SVP results did not fit with the initially measured curves. As mentioned above, we originally tried to acquire ECD spectra of the free base BHPs by online measurements on an HPLC-ECD system, but it seems now that these results were not reliable.[38] Therefore, we resolved the enantiomers of **13f** by HPLC on a chiral phase on a semipreparative column (Chiralpak IA, *n*-hexane/dichloromethane 20/80) and measured offline UV/vis (see the Supporting Information) and ECD spectra (Figure 7). The results showed that only within a small window of high dilution ($c = 1 \times 10^{-5}$ M) was the absorption of the Soret band still within the limits of the Beer–Lambert law, while at the same time it was high enough to permit an ECD signal to be detectable. However, the ECD signals were still not comparable with those of the metalated BHPs, because the free base BHP did not show a couplet in the Soret band region but more or less a single maximum/minimum. The concentration effect described here has been found for all investigated chiral free base BHPs, and thus HPLC-ECD measurements of these have to be done very cautiously or, better, verified with offline ECD spectra.

Finally, only the combination of high-quality experimental measurements (NMR, offline ECD) with high-level calculations (DLPNO-CCSD(T), SCS-CC2) permitted an unambiguous determination of the absolute configurations of the enantiomers of the free base BHP **13f** (exemplarily shown for the slower-eluting enantiomer in Figure 7b). These results showed that the enantiomer with a positive peak at ~430 nm did have the $R_P$,*P*,*P* configuration, while that with the negative signal was $S_P$,*M*,*M*-configured. The arrested tautomerism occurred in all chiral free base BHPs we have synthesized so far, and thus the absolute configurations of these compounds were determined by simple comparison of their experimental ECD spectra with those of **13f** (in the case of **10f** we again confirmed this determination with SCS-CC2 calculations; see Figure S3 in the Supporting Information).

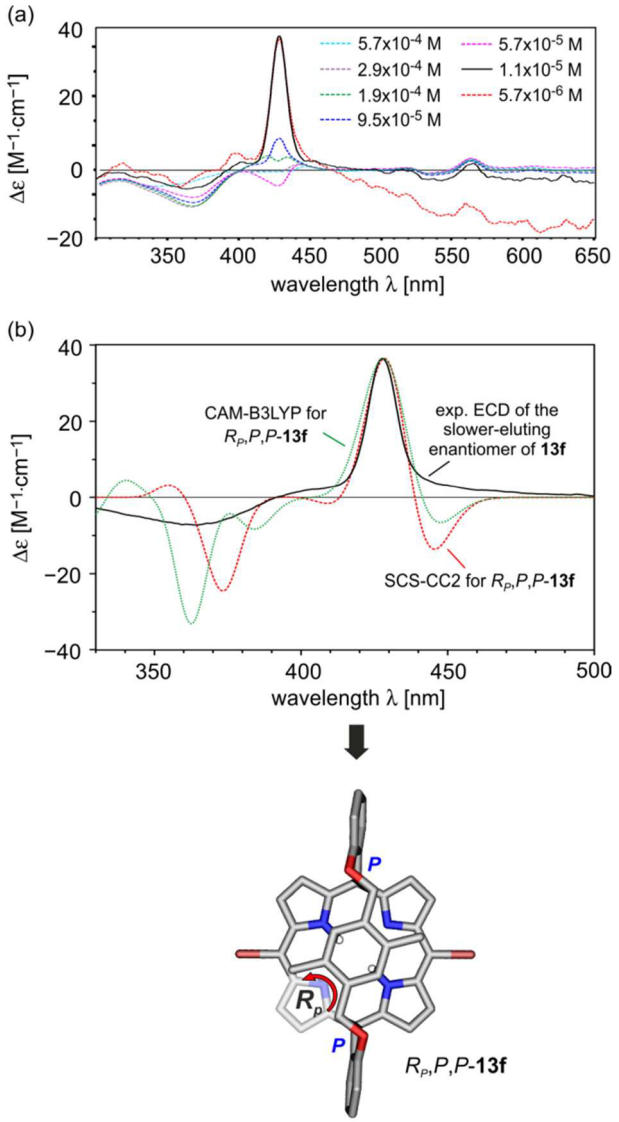


**Figure 7.** (a) ECD spectra of the slower-eluting enantiomer of **13f** measured at different concentrations. (b) Determination of the absolute configuration of the slower-eluting enantiomer of **13f** by comparison of its experimental ECD spectrum with those calculated for $R_P$,*P*,*P*-**13f** (the intensities of the calculated spectra are scaled to fit the signal at 430 nm of the experimental curve).

## CONCLUSIONS

In summary, we have shown that the BHPs can be modified and functionalized in various positions, which permits the design of a plethora of different structures that can be tuned to their desired purpose. A total of more than 80 different examples are presented in this paper (for a summarizing table see the Supporting Information). It is possible to introduce a broad variety of metals into the porphyrin center, including In(III) or V(IV). The crystal structures of the BHPs shown here gave further insight into this interesting class of compounds and helped to further evaluate the reliability of the ECD calculations. The arrested tautomerism of the chiral free base BHPs induced by the strap is so far unique for porphyrins, and further investigations to utilize this property are under way and will be published in an upcoming paper. In addition, we have successfully resolved several racemates of chiral BHPs to give the pure enantiomers and have elucidated


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their absolute configurations by a combination of experimental and computational ECD investigations. We have shown that TD B3LYP suffers from ghost states and that TD CAM-B3LYP should in general be preferred to calculate excited states of BHPs.

## COMPUTATIONAL DETAILS

The optimizations and single-point calculations were performed with ORCA.[47,48] All functionals were used with dispersion corrections (D3).[49,50] The chain of spheres[51] approximation was applied for the hybrid and double-hybrid functionals (B3LYP-D3,[52,53] PW6B95-D3,[54] B2GP-PLYP-D3[55]) and RI for B97-D3.[56] If not stated otherwise, the def2-TZVP[57] basis set was used. For the tautomers of **13f** additionally DLPNO-CCSD(T)[58,59] computations have been performed. In all cases, except for **V-10d**, the *tert*-butyl or *tert*-octyl groups have been replaced by hydrogens to save computational time. All TD DFT calculations have been done with Gaussian09[60] using the functionals B3LYP, CAM-B3LYP, and BHLYP in combination with the def2-SVP[57] basis set (def2-TZVP for bromine and metal atoms). The SCS-CC2[61] calculations were performed with Turbomole in combination with the def2-SVP basis set (def2-TZVP for metal atoms) and using the RI approximation. Evaluation of the computed and experimental ECD spectra were done with SpecDis[38,62] applying $\sigma$ values of 0.08 eV (**Ni-10b**, **Zn-10b**, **10f**), 0.04 eV (**V-10d**), or 0.1 eV (**13f**) and the following UV shifts:[63] **Ni-10b**, 52 nm (SCS-CC2), 48 nm (CAM-B3LYP), 56 nm (BHLYP), 30 nm (B3LYP); **Zn-10b**, 38 nm (SCS-CC2), 45 nm (CAM-B3LYP), 55 nm (BHLYP), 40 nm (B3LYP); **13f**, 68 nm (SCS-CC2), 58 nm (CAM-B3LYP); **10f**, 60 nm (SCS-CC2), 53 nm (CAM-B3LYP); **V-10d**, 55 nm (small gap between strap and porphyrin), 62 nm (large gap) (BHLYP).

## EXPERIMENTAL SECTION

**General Considerations.** All reagents were obtained from commercial sources and used as received. THF was purified and dried by distillation from potassium. All other solvents were used as technical grade. Unless otherwise stated, all reactions were carried out under an atmosphere of dry nitrogen or argon using oven-dried (120 °C) glassware. Analytical TLCs were performed on ready-made plates coated with silica gel on aluminum. Flash chromatography was performed using silica gel 60 (230−400 mesh). $^1$H and $^{13}$C NMR spectra were recorded in $CDCl_3$ at ambient temperature on spectrometers operating at 400 MHz for $^1$H. The $^{13}$C nucleus was observed with $^1$H decoupling. Solvent residual signals were used as an internal standard. Chemical shifts ($\delta$) and coupling constants ($J$) are given in ppm and Hz, respectively. The peak patterns are indicated as the following format multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublets; dt, doublet of triplets; etc.). HRMS (ESI-TOF) spectra were measured in the positive mode. Analytical enantiomeric resolution was performed on a standard HPLC system equipped with Diacel Chiralpak IA (4.6 × 250 mm; 3 $\mu$m) as a chiral phase. Online CD spectra were recorded at room temperature (scanning rate 500 nm/min, bandwidth 5 or 10 nm, response time 0.5 s) by HPLC-CD coupling in the stopped-flow mode. Recycling gel permeation chromatography (recycling GPC) was performed on an HPLC system with two columns in line (SDV material, particle size 10 $\mu$m, pore size 50 Å, dimension 20 × 600 mm; SDV material, particle size 10 $\mu$m, pore size 100 Å, dimension 20 × 600 mm) at a flow rate of 4.5 mL/min in amylene-stabilized chloroform. Salicylic aldehydes **7c**[64] and **7d**[65] were prepared by reported procedures. Chromatographic details for the enantiomeric resolution of the chiral representatives are included in the Supporting Information. Crystal data collection and processing parameters are given in the Supporting Information. The BHPs in the Experimental Section are denoted by their compound number, and brief information regarding their substitution is added ("strap: 2Me/4Me/2Br/4H" describes the substitution $R^1/R^2$ of the xylene unit, "H-/*t*-Bu-/*t*-Oct-aryl" describes the presence of substituents $R^5$ (solubilizing groups) at the *meso*-aryls, "*meso*:" denotes the substituents at the *meso*-positions $R^3/R^4$ not occupied by the basket-handle strap).

**General Procedure A: Preparation of the Strap-Dialdehydes 9.** The dibromoxylene-strap **6** (20 mmol, 1.0 equiv), salicylaldehyde **7** (42 mmol, 2.1 equiv), powdered anhydrous $K_2CO_3$ (14.0 g, 0,10 mol, 5.0 equiv), and 600 mL of acetone were heated to reflux for 10 h. The solvent was removed, and the remaining solid was suspended in 400 mL of chloroform. Dilute HCl was added until all material was dissolved. The organic phase was separated, washed with $NaHCO_3$ solution, and dried over $NaSO_4$. Evaporation of the solvent yielded **9** in sufficient purity for the condensation step. An analytical sample was recrystallized from ethyl acetate to afford white flakes. Strap-dialdehydes **9a−c** were reported before.[12]

*6,6′-((2,5-Dimethyl-1,4-phenylene)dimethylenedioxy)bis(3-(tert-butyl))dibenzaldehyde (**9d**).* Prepared from dibromoxylene-strap **6d** (5.84 g) and salicylaldehyde **7b** (7.48 g). White solid, 9.43 g, 97% yield; mp 146−150 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.32 (s, 18H), 2.37 (s, 6H), 5.13 (s, 4H), 7.04 (d, $^3J$ = 8.8 Hz, 2H), 7.29 (s, 2H), 7.61 (dd, $^3J$ = 8.7 Hz, $^4J$ = 2.7 Hz, 2H), 7.89 (d, $^4J$ = 2.6 Hz, 2H), 10.52 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 190.3, 159.6, 144.3, 134.6, 134.5, 133.5, 131.0, 125.3, 124.8, 113.0, 77.7, 77.6, 77.4, 77.0, 69.2, 34.6, 31.6, 18.9 ppm. MS (EI): $m/z$ 309.1 (60) [M − salicylic aldehyde group]$^{\bullet+}$, 132.18 (100) [M − 2 × salicylic aldehyde group]$^{\bullet+}$, 102.0 (70). HRMS (ESI): calcd for $C_{32}H_{38}NaO_4$ [M + Na]$^+$ 509.26623, found 509.26611.

*6,6′-((2,3,5,6-Tetramethyl-1,4-phenylene)dimethylenedioxy)bis-(3-(tert-octyl))dibenzaldehyde (**9e**).* Prepared from dibromoxylene-strap **6b** (6.40 g) and salicylaldehyde **7c** (9.83 g). White solid, 11.6 g, 97% yield; mp 208−210 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.75 (s, 18H), 1.39 (s, 12H), 1.76 (s, 4H), 2.36 (s, 12H), 5.22 (s, 4H), 7.16 (d, $^3J$ = 8.8 Hz, 2H), 7.64 (dd, $^3J$ = 8.8 Hz, $^4J$ = 2.7 Hz, 2H), 7.88 (d, $^4J$ = 2.7 Hz, 2H), 10.40 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 16.5, 31.7, 32.0, 32.5, 38.3, 56.8, 66.3, 112.5, 124.6, 125.6, 133.1, 134.0, 134.9, 143.2, 159.7, 190.2 ppm. MS (EI): $m/z$ 393.4 (100) [M − salicylic aldehyde group]$^{\bullet+}$, 160.2 (99) [M − 2 × salicylic aldehyde group]$^{\bullet+}$, 57.1 (22). HRMS (ESI): calcd for $C_{42}H_{58}NaO_4$ [M + Na]$^+$ 649.42273, found 649.42253.

*6,6′-((2,5-Dimethyl-1,4-phenylene)dimethylenedioxy)bis(3-(tert-octyl))dibenzaldehyde (**9f**).* Prepared from dibromoxylene-strap **6d** (5.84 g) and salicylaldehyde **7c** (9.83 g). White solid, 12.3 g, 98% yield; mp 155−159 °C. $^1$H NMR (400 MHz, $CCl_3$): $\delta$ 0.72 (s, 18H), 1.37 (s, 12H), 1.74 (s, 4H), 2.36 (s, 6H), 5.13 (s, 4H), 7.02 (d, $^3J$ = 8.7 Hz, 2H), 7.28 (s, 2H), 7.58 (dd, $^3J$ = 8.7 Hz, $^4J$ = 2.7 Hz, 2H), 7.87 (d, $^3J$ = 2.7 Hz, 2H), 10.52 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 18.7, 31.6, 32.0, 32.5, 38.3, 56.9, 69.0, 77.4, 112.6, 124.5, 125.8, 130.8, 134.1, 134.3, 134.4, 143.2, 159.3, 190.1 ppm. MS (EI): $m/z$ 365.4 (100) [M − salicylic aldehyde group]$^{\bullet+}$, 132.2 (91) [M − 2 × salicylic aldehyde group]$^{\bullet+}$, 57.1 (20). HRMS (ESI): calcd for $C_{40}H_{54}NaO_4$ [M + Na]$^+$ 621.39143, found 621.39253.

*6,6′-((2,5-Dibromo-1,4-phenylene)dimethylenedioxy)-dibenzaldehyde (**9g**).* Prepared from dibromoxylene-strap **6c** (8.44 g) and salicylaldehyde **7a** (5.12 g). White solid, 9.54 g, 95% yield; mp 203−207 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 5.23 (s, 4H), 7.05 (m, 2H), 7.12 (m, 2H), 7.59 (m, 2H), 7.83 (s, 2H), 7.90 (m, 2H), 10.59 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 189.7, 160.5, 137.4, 136.4, 132.9, 129.5, 125.6, 122.2, 122.1, 121.6, 113.3, 77.7, 77.6, 77.4, 77.0, 69.5 ppm. MS (EI): $m/z$ 381.8 (62) [M − salicylic aldehyde group]$^{\bullet+}$, 261.8 (100) [M − salicylic aldehyde group, −CHO]$^{\bullet+}$, 102.0 (70). HRMS (ESI): calcd for $C_{22}H_{16}Br_2NaO_4$ [M + Na]$^+$ 524.93076, found 524.93038.

*6,6′-((2,5-Dibromo-1,4-phenylene)dimethylenedioxy)bis(3-(tert-octyl))dibenzaldehyde (**9h**).* Prepared from dibromoxylene-strap **6c** (8.44 g) and salicylaldehyde **7c** (9.83 g). White solid, 13.8 g, 98% yield; mp 77−80 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.72 (s, 18H), 1.38 (s, 12H), 1.74 (s, 4H), 5.21 (s, 4H), 6.97 (d, $^3J$ = 8.8 Hz, 2H), 7.59 (dd, $^3J$ = 8.8 Hz, $^4J$ = 2.6 Hz, 2H), 7.82 (s, 2H), 7.90 (d, $^4J$ = 2.6 Hz, 2H), 10.59 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 209.8, 152.2, 143.8, 138.0, 132.8, 130.5, 126.2, 124.9, 121.5, 111.2, 69.1, 66.0, 57.3, 51.0, 38.6, 32.7, 32.2, 32.1, 32.1, 31.8, 31.2 ppm. MS (EI): $m/z$ 495.2 (82) [M − salicylic aldehyde group]$^{\bullet+}$, 423.1 (53), 262.0 (93)


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[M − 2 × salicylic aldehyde group]$^{\bullet+}$, 161.1 (100), 57.1 (92). HRMS (ESI): calcd for $C_{38}H_{48}Br_2O_4$ [M]$^+$ 726.19194, found 726.19209.

*6,6′-((1,4-Phenylene)dimethylenedioxy)bis(3-(tert-octyl))-dibenzaldehyde (**9i**).* Prepared from dibromoxylene-strap **6a** (5.28 g) and salicylaldehyde **7c** (9.83 g). White solid, 11.0 g, 96% yield; mp 111−115 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.71 (s, 18H), 1.36 (s, 12H), 1.73 (s, 4H), 5.19 (s, 4H), 6.98 (d, $^3J$ = 8.8 Hz, 2H), 7.48 (s, 4H), 7.56 (dd, $^3J$ = 8.8 Hz, $^4J$ = 2.7 Hz, 2H), 7.86 (d, $^3J$ = 2.6 Hz, 2H), 10.55 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 190.3, 159.2, 143.4, 136.7, 134.2, 128.0, 126.1, 124.6, 112.8, 77.7, 77.6, 77.4, 77.0, 70.5, 57.0, 38.5, 32.7, 32.2, 32.1, 31.8 ppm. MS (EI): *m*/*z* 337.3 (76) [M − salicylic aldehyde group]$^{\bullet+}$, 104.1 (100) [M − 2 × salicylic aldehyde group]$^{\bullet+}$, 57.1 (40). HRMS (ESI): calcd for $C_{38}H_{50}NaO_4$ [M + Na]$^+$ 593.36013, found 593.36065.

*6,6′-((2,3,5,6-Tetramethyl-1,4-phenylene)dimethylenedioxy)bis-(3-phenyl)dibenzaldehyde (**9j**).* Prepared from dibromoxylene-strap **6b** (6.40 g) and salicylaldehyde **7d** (8.14 g). White solid, 10.8 g, 97% yield; mp 211−216 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.39 (s, 12H), 5.30 (s, 4H), 7.33 (d, $^3J$ = 8.6 Hz, 2H), 7.37 (d, $^3J$ = 7.4 Hz, 2H), 7.44−7.47 (m, 4H), 7.61 (m, 4H), 7.87, (dd, $^3J$ = 8.6 Hz, $^4J$ = 2.5 Hz, 2H), 8.13 (d, $^4J$ = 2.5 Hz, 2H), 10.46 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 16.6, 66.4, 113.4, 125.5, 126.8, 126.9, 127.5, 133.0, 134.4, 134.5, 135.0, 139.7, 161.1, 189.9 ppm. MS (EI): *m*/*z* 357.3 (76) [M − salicylic aldehyde group]$^{\bullet+}$, 160.1 (100) [M − 2 × salicylic aldehyde group]$^{\bullet+}$. HRMS (ESI): calcd for $C_{38}H_{34}NaO_4$ [M + Na]$^+$ 577.23493, found 577.23386.

*6,6′-((2,5-Dibromo-1,4-phenylene)dimethylenedioxy)bis(3-phenyl)dibenzaldehyde (**9k**).* Prepared from dibromoxylene-strap **6d** (5.84 g) and salicylaldehyde **7d** (8.14 g). White solid, 10.2 g, 95% yield; mp 180−186 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.26 (s, 2H), 1.54 (s, 15H), 2.41 (s, 6H), 5.21 (s, 4H), 7.19 (d, $^3J$ = 8.7 Hz, 2H), 7.33−7.37 (m, 4H), 7.43−7.46 (m, 4H), 7.57−7.61 (m, 54H), 7.82 (dd, $^3J$ = 8.6 Hz, $^4J$ = 2.5 Hz, 2H), 8.12 (d, $^4J$ = 2.5 Hz, 2H), 10.58 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 18.6, 69.1, 113.4, 125.3, 126.7, 126.8, 127.4, 128.9, 130.8, 134.2, 134.3, 134.3, 139.5, 160.6, 189.6 ppm. MS (EI): *m*/*z* 329.2 (100) [M − salicylic aldehyde group]$^{\bullet+}$, 197 (45), 132.1 (94) [M − 2 × salicylic aldehyde group]$^{\bullet+}$. HRMS (ESI): calcd for $C_{36}H_{30}NaO_4$ [M + Na]$^+$ 549.20363, found 549.20486.

**General Procedure B: Condensation of Strapped Dialdehydes with Dipyrromethane.** Dipyrromethane **8a** (2.92 g, 0.02 mol, 2.0 equiv) and the strap-dialdehyde **9** (0.01 mol, 1 equiv) were dissolved in dichloromethane (900 mL), and the solution was degassed by an argon stream for 20 min. The reaction mixture was shielded from ambient light, TFA (1.5 mL) was added, and the mixture was stirred at room temperature until TLC indicated full consumption of the starting material (between 3 and 5 h). $NEt_3$ (5 mL) and *p*-chloranil (14.7 g, 0.06 mol, 6 equiv) were added, and the mixture was heated to reflux for 1 h. After evaporation of about 700 mL of dichloromethane, *n*-hexane (300 mL) was added and the black solution was filtered over a plug of silica (150 g) and washed with dichloromethane/*n*-hexane 2/1, which yielded a purple solution. After evaporation of the solvents, the porphyrin was recrystallized from chloroform/methanol to yield purple crystals of high purity. BHPs **10a−c** were reported before.[12]

**BHP 10d** (strap: 2Me, *t*-Bu-aryl, *meso*: 2H). Prepared from strap-dialdehyde **9d** (4.86 g). 2.45 g, 30% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −3.41 (s, 2H), −0.66 (s, 6H), 1.77 (s, 18H), 2.23 (d, $^3J$ = 13.2 Hz, 2H), 3.39 (app t, $^{app}J$ = 6.6 Hz 4H), 7.01 (d, $^3J$ = 8.4 Hz, 2H), 7.68 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.6 Hz, 2H), 8.83 (d, $^3J$ = 4.6 Hz, 2H), 9.06 (d, $^3J$ = 4.5 Hz, 2H), 9.09 (d, $^4J$ = 2.6 Hz, 2H), 9.21 (d, $^3J$ = 4.5 Hz, 2H), 9.23 (d, $^3J$ = 4.6 Hz, 2H), 9.97 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 14.5, 32.2, 35.0, 72.3, 104.3, 112.5, 120.6, 120.9, 126.2, 126.2, 126.7, 128.3, 129.9, 130.4, 130.5, 132.1, 133.7, 134.1, 145.9, 158.9 ppm. MS (MALDI): *m*/*z* 736.312 [M]$^{\bullet+}$. HRMS (ESI): calcd for $C_{50}H_{49}N_4O_2$ [M + H]$^+$ 737.38555, found 737.38500.

**BHP 10e** (strap: 4Me, *t*-Oct-aryl, *meso*: 2H). Prepared from strap-dialdehyde **9e** (6.26 g). 2.80 g, 32% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −2.91 (s, 2H), −0.05 (s, 12H), 1.17 (s, 18H), 1.81 (s, 12H), 2.17 (s, 4H), 3.61 (s, 4H), 6.56 (d, $^3J$ = 8.3 Hz, 2H), 7.58 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.5 Hz, 2H), 8.83 (d, $^3J$ = 4.6 Hz, 4H), 9.04 (d, $^4J$ = 2.4 Hz, 2H), 9.13 (d, $^3J$ = 4.6 Hz, 4H), 9.92 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 13.4, 29.9, 32.5, 32.5, 33.0, 38.7, 57.5, 63.6, 103.8, 110.0, 114.0, 126.4, 127.2, 130.5, 130.5, 130.9, 140.9, 156.3 ppm. MS (MALDI): *m*/*z* 876.492 [M]$^{\bullet+}$. HRMS (ESI): calcd for $C_{60}H_{69}N_4O_2$ [M + H]$^+$ 877.54150, found 877.54208.

**BHP 10f** (strap: 2Me, *t*-Oct-aryl, *meso*: 2H). Prepared from strap-dialdehyde **9f** (5.98 g). 2.54 g, 30% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −3.40 (s, 2H), −0.64 (s, 6H), 1.17 (s, 18H), 1.81 (s, 6H), 1.84 (s, 6H), 2.14 (d, $^3J$ = 14.6 Hz, 2H), 2.21 (d, $^3J$ = 14.6 Hz, 2H), 2.25 (d, $^3J$ = 13.5 Hz, 2H), 3.40 (s, 2H), 3.43 (s, 1H), 7.02 (d, $^3J$ = 8.4 Hz, 2H), 7.69 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.5 Hz, 2H), 8.81 (d, $^3J$ = 4.6 Hz, 2H), 9.05 (d, $^3J$ = 4.5 Hz, 2H), 9.09 (d, $^4J$ = 2.5 Hz, 2H), 9.21 (d, $^3J$ = 4.5 Hz, 2H), 9.24 (d, $^3J$ = 4.6 Hz, 2H), 9.97 (s, 2H) ppm. $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ 14.5, 32.0, 32.5, 32.9, 33.0, 38.9, 57.5, 72.3, 104.3, 112.6, 120.4, 120.9, 126.2, 127.7, 129.1, 130.4, 133.9, 144.7, 158.8 ppm. MS (MALDI): *m*/*z* 848.675 [M]$^{\bullet+}$. HRMS (ESI): calcd for $C_{58}H_{65}N_4O_2$ [M + H]$^+$ 849.51020, found 849.51107.

**BHP 10g** (strap: 2Br, H-aryl, *meso*: 2H). Prepared from strap-dialdehyde **9g** (5.02 g). 1.96 g, 26% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −3.38 (s, 2H), 2.16 (d, $^3J$ = 14.8 Hz, 2H), 3.33 (d, $^3J$ = 14.8 Hz, 2H), 3.78 (s, 2H), 7.11 (dd, $^3J$ = 7.9 Hz, $^4J$ = 1.2 Hz, 2H), 7.69 (td, $^3J$ = 7.9 Hz, $^4J$ = 1.8 Hz, 2H), 7.81 (td, $^3J$ = 7.9 Hz, $^4J$ = 1.3 Hz, 2H), 8.76 (d, $^3J$ = 4.6 Hz, 2H), 9.04 (dd, $^3J$ = 7.4 Hz, $^4J$ = 1.8 Hz, 2H), 9.07 (d, $^3J$ = 4.6 Hz, 2H), 9.25 (dd, $^3J$ = 4.6 Hz, $^4J$ = 1.2, 4H), 10.04 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 160.7, 135.1, 133.3, 131.6, 130.4, 125.1, 123.9, 122.2, 114.6, 111.1, 105.4, 77.7, 77.6, 77.4, 77.0, 73.5 ppm. MS (MALDI): *m*/*z* 751.957 [M]$^{\bullet+}$. HRMS (ESI): calcd for $C_{40}H_{27}Br_2N_4O_2$ [M + H]$^+$: 753.04953, found 753.05002.

**BHP 10h** (strap: 2Br, *t*-Oct-aryl, *meso*: 2H). Prepared from strap-dialdehyde **9h** (7.04 g). 3.12 g, 32% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −3.33 (s, 2H), 1.17 (s, 18H), 1.82 (d, $^3J$ = 13.1 Hz, 12H), 2.12−2.23 (m, 6H), 3.33 (d, $^3J$ = 14.6 Hz, 2H), 3.80 (s, 2H), 7.03 (d, $^3J$ = 8.4 Hz, 2H), 7.70 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.4 Hz, 2H), 8.76 (d, $^3J$ = 4.6 Hz, 2H), 9.05 (d, $^3J$ = 4.6 Hz, 2H), 9.10 (d, $^4J$ = 2.4 Hz, 2H), 9.24−9.26 (m, 4H), 10.04 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 31.9, 32.5, 32.9, 33.0, 38.9, 57.5, 73.3, 105.1, 111.6, 114.4, 121.0, 124.9, 127.7, 129.4, 133.2, 133.9, 145.4, 158.3 ppm. MS (MALDI): *m*/*z* 976.316 [M]$^{\bullet+}$. HRMS (ESI): calcd for $C_{56}H_{59}Br_2N_4O_2$ [M + H]$^+$ 977.29993, found 977.30022.

**BHP 10i** (strap: 4H, *t*-Oct-aryl, *meso*: 2H). Prepared from strap-dialdehyde **9i** (5.71 g). 1.97 g, 24% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −2.51 (s, 2H), 1.14 (s, 18H), 1.81 (s, 12H), 2.16 (s, 4H), 3.08 (s, 4H), 3.32 (s, 4H), 6.73 (d, $^3J$ = 8.4 Hz, 2H), 7.62 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.5 Hz, 2H), 8.85 (d, $^3J$ = 4.5 Hz, 4H), 9.10 (d, $^4J$ = 2.4 Hz, 2H), 9.20 (d, $^3J$ = 4.6 Hz, 4H), 9.98 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 157.3, 143.1, 133.9, 132.4, 132.2, 131.2, 128.0, 127.8, 123.1, 115.5, 113.6, 104.7, 71.3, 57.7, 38.9, 33.2, 32.7, 32.6, 30.1 ppm. MS (MALDI): *m*/*z* 820.445 [M]$^{\bullet+}$. HRMS (ESI): calcd for $C_{56}H_{61}N_4O_2$ [M + H]$^+$ 821.47890, found 821.48016.

**General Procedure C: *meso*-Substituted BHPs via Mixed Condensation of Strap-Dialdehydes with Dipyrromethanes.** *meso*-unsubstituted dipyrromethane **8a**[66] (1.46 g, 0.01 mol, 1.0 equiv), *meso*-substituted dipyrromethane **8**[66] (0.01 mol, 1.0 equiv), and the strap-dialdehyde **9** (0.01 mol, 1 equiv) were dissolved in dichloromethane (900 mL), and the solution was degassed by an argon stream for 20 min. The reaction mixture was shielded from ambient light, TFA (1.5 mL) was added, and the mixture was stirred at room temperature until TLC indicated full consumption of the starting material (between 3 and 5 h). $NEt_3$ (5 mL) and *p*-chloranil (14.7 g, 0.06 mol, 6 equiv) were added, and the mixture was heated to reflux for 1 h. After evaporation of about 700 mL of dichloromethane, *n*-hexane (300 mL) was added and the black solution was filtered over a plug of silica (150 g) and washed with dichloromethane/*n*-hexane 2/1, which yielded a purple solution. Column chromatography (silica, dichloromethane/*n*-hexane) yielded *meso*-substituted BHP **11** along with *meso*-unsubstituted BHP **10** and *meso*-disubstituted BHP **12**. Analytical samples were recrystallized from chloroform/methanol to afford purple crystals.



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**BHP 11a/12a** (strap: 4Me, H-aryl; *meso*: (4-*t*-Bu)Ph). Prepared from substituted dipyrromethane **8b** (2.78 g) and strap-dialdehyde **9a** (4.02 g), column chromatography with DCM/*n*-hexane 30/70. **10a** (strap: 4Me, H-aryl; *meso*: 2 × H): 0.45 g, 7%, characterization identical with that reported before. **11a** (strap: 4Me, H-aryl; *meso*: H/(4-*t*-Bu)Ph): 1.09 g, 14% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −2.57 (s, 2H), 0.05 (s, 6H), 0.13 (s, 6H), 1.60 (s, 9H), 3.71 (s, 4H), 6.68 (dd, $^3J$ = 7.9 Hz, $^4J$ = 1.4 Hz, 4H), 7.54−7.62 (m, 4H), 7.74 (d, $^3J$ = 8.4 Hz, 2H), 8.06 (s, 2H), 8.73−8.76 (m, 4H), 8.84 (d, $^3J$ = 4.6 Hz, 2H), 8.95 (dd, $^3J$ = 7.0 Hz, $^4J$ = 1.9 Hz, 2H), 9.08 (d, $^3J$ = 4.6 Hz, 2H), 9.79 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 13.5, 13.5, 29.9, 31.8, 35.5, 63.6, 102.9, 110.8, 113.7, 119.4, 120.1, 123.8, 128.1, 130.0, 130.5, 131.0, 131.1, 131.2, 131.6, 134.2, 139.1, 150.4, 158.7 ppm. MS (MALDI): *m*/*z* 784.319 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{54}H_{49}N_4O_2$ $[M + H]^+$ 785.38500, found 785.38671. **12a** (strap: 4Me, H-aryl; *meso*: 2 × (4-*t*-Bu)Ph): 0.55 g, 6% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −2.19 (s, 2H), 0.18 (s, 12H), 1.60 (s, 18H), 3.76 (s, 4H), 6.69 (dd, $^3J$ = 7.8 Hz, $^4J$ = 1.3 Hz, 2H), 7.49−7.61 (m, 4H), 7.74 (d, $^3J$ = 8.6 Hz, 4H), 8.06 (d, $^3J$ = 7.7 Hz, 4H), 8.72 (d, $^3J$ = 4.7 Hz, 4H), 8.75 (d, $^3J$ = 4.8 Hz, 4H), 8.92 (dd, $^3J$ = 7.1 Hz, $^4J$ = 1.9 Hz, 2H) ppm. $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ 13.6, 16.1, 31.6, 31.8, 35.0, 63.8, 77.4, 110.9, 114.0, 119.1, 119.4, 123.9, 125.8, 127.9, 128.2, 129.9, 130.7, 130.9, 131.0, 131.1, 131.9, 134.3, 138.9, 140.8, 146.0, 146.4, 150.4, 158.8 ppm. MS (MALDI): *m*/*z* 916.438 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{64}H_{61}N_4O_2$ $[M + H]^+$ 917.47890, found 917.48068.

**BHP 11b/12b** (strap: 4Me, *t*-Bu-aryl; *meso*: (4-*t*-Bu)Ph). Prepared from substituted dipyrromethane **8b** (2.78 g) and strap-dialdehyde **9c** (5.14 g), column chromatography with DCM/*n*-hexane 30/70 → 50/50. **10c** (strap: 4Me, *t*-Bu-aryl; *meso*: 2 × H): 0.38 g, 5% yield; characterization identical with that reported before. **11b** (strap: 4Me, *t*-Bu-aryl; *meso*: H/(4-*t*-Bu)Ph): 1.34 g, 15% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −2.51 (s, 2H), 0.06 (s, 6H), 0.13 (s, 6H), 1.63 (s, 18H), 3.71 (s, 4H), 6.62 (d, $^3J$ = 8.5 Hz, 2H), 7.62 (dd, $^3J$ = 8.5 Hz, $^4J$ = 2.6 Hz, 2H), 7.76 (d, $^3J$ = 8.5 Hz, 2H), 8.09 (s, 2H), 8.76−8.79 (m, 4H), 8.86 (d, $^3J$ = 4.7 Hz, 2H), 9.05 (d, $^4J$ = 2.6 Hz, 2H), 9.07 (d, $^3J$ = 4.7 Hz, 2H), 9.78 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 13.5, 13.6, 31.8, 32.2, 34.8, 35.0, 63.9, 102.8, 110.3, 114.2, 120.1, 123.8, 125.7, 126.1, 130.7, 130.9, 131.1, 131.1, 131.3, 134.3, 139.1, 142.2, 150.4, 156.5 ppm. MS (MALDI): *m*/*z* 896.478 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{62}H_{65}N_4O_2$ $[M + H]^+$ 897.51020, found 897.50939. **12b** (strap: 4Me, *t*-Bu-aryl; *meso*: 2 × (4-*t*-Bu)Ph): 0.72 g, 7% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −2.13 (s, 2H), 0.19 (s, 12H), 1.63 (s, 18H), 1.77 (s, 18H), 3.77 (s, 4H), 6.64 (d, $^3J$ = 8.5 Hz, 2H), 7.61 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.5 Hz, 2H), 7.77 (d, $^3J$ = 8.5 Hz, 4H), 8.10 (d, $^3J$ = 7.5 Hz, 4H), 8.76 (d, $^3J$ = 4.7 Hz, 2H), 8.78 (d, $^3J$ = 4.7 Hz, 2H), 9.03 (d, $^4J$ = 2.4 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 13.6, 31.8, 32.2, 34.7, 35.0, 64.1, 110.5, 114.6, 119.0, 123.9, 125.8, 126.1, 130.8, 130.9, 131.0, 131.4, 134.4, 138.9, 142.2, 145.9, 146.3, 150.3, 156.6 ppm. MS (MALDI): *m*/*z* 1029.604 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{72}H_{77}N_4O_2$ $[M + H]^+$ 1029.6047, found 1029.6002.

**BHP 11c/12c** (strap: 4Me, *t*-Bu-aryl; *meso*: (3,5-di-*t*-Bu)Ph). Prepared from substituted dipyrromethane **8c** (3.34 g) and strap-dialdehyde **9c** (5.14 g), column chromatography with DCM/*n*-hexane 20/80 → 50/50. **10c** (strap: 4Me, *t*-Bu-aryl; *meso*: 2 × H): 0.38 g, 5% yield; characterization identical with that reported before. **11c** (strap: 4Me, *t*-Bu-aryl; *meso*: H/(3,5-di-*t*-Bu)Ph): 1.33 g, 14% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −2.47 (s, 2H), 0.04 (s, 6H), 0.26 (s, 6H), 1.59 (s, 18H), 1.82 (s, 18H), 3.73 (q, 4H), 6.64 (d, $^3J$ = 8.4 Hz, 2H), 7.65 (d, $^3J$ = 8.4 Hz, $^4J$ = 2.5 Hz, 2H), 7.85 (app t, $^{app}J$ = 1.8 Hz, 1H), 8.78 (d, $^3J$ = 4.7 Hz, 2H), 8.82 (d, $^3J$ = 4.7 Hz, 2H), 8.90 (d, $^3J$ = 4.6 Hz, 2H), 9.09 (s, 2H), 9.10 (d, $^4J$ = 1.9 Hz, 2H), 9.79 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 13.4, 13.5, 31.9, 32.3, 34.8, 35.1, 63.8, 102.8, 110.2, 114.2, 120.9, 121.3, 125.6, 126.1, 129.6, 130.7, 130.7, 130.9, 131.0, 131.2, 131.3, 141.2, 142.2, 148.8, 156.6 ppm. MS (MALDI): *m*/*z* 952.425 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{66}H_{73}N_4O_2$ $[M + H]^+$ 953.57280, found 953.57183. **12c** (strap: 4Me, *t*-Bu-aryl; *meso*: 2 × (3,5-di-*t*-Bu)Ph): 0.68 g, 6% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −2.19 (s, 2H), 0.20 (s, 12H), 1.53 (s, 36H), 1.74 (s, 18H), 3.75 (s, 4H), 6.62 (d, $^3J$ = 8.4 Hz, 2H), 7.59 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.5 Hz, 2H), 7.78 (app t, $^{app}J$ = 1.8 Hz, 2H), 8.71 (d, $^3J$ = 4.7 Hz, 4H), 8.76 (d, $^3J$ = 4.7 Hz, 4H), 9.00 (d, $^4J$ = 1.4 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 13.5, 31.9, 32.2, 34.7, 35.1, 64.0, 110.3, 114.5, 120.2, 121.0, 125.6, 126.1, 129.6, 130.8, 131.0, 131.0, 131.6, 141.0, 142.2, 146.3, 146.6, 149.0, 156.6 ppm. MS (MALDI): *m*/*z* 1140.964 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{80}H_{93}N_4O_2$ $[M + H]^+$ 1141.72930, found 1141.73052.

**BHP 11d/12d** (strap: 4Me, *t*-Oct-aryl; *meso*: (3,5-di-*t*-Bu)Ph). Prepared from substituted dipyrromethane **8c** (3.34 g) and strap-dialdehyde **9e** (5.98 g), column chromatography with DCM/*n*-hexane 20/70 → 40/60. **10e** (strap: 4Me, *t*-Oct-aryl; *meso*: 2 × H): 0.78 g, 9% yield; characterization identical with that reported above. **11d** (strap: 4Me, *t*-Oct-aryl; *meso*: H/(3,5-di-*t*-Bu)Ph): 1.59 g, 15% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −2.56 (s, 2H), −0.01 (s, 6H), 0.22 (s, 6H), 1.41 (s, 18H), 1.79 (d, $^3J$ = 7.9 Hz, 12H), 2.13 (d, $^3J$ = 14.7 Hz, 2H), 2.18 (d, $^3J$ = 14.7 Hz, 2H), 3.67 (d, $^3J$ = 10.0 Hz, 2H), 3.71 (d, $^3J$ = 10.0 Hz, 2H), 6.59 (d, $^3J$ = 8.4 Hz, 2H), 7.57 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.6 Hz, 2H), 7.76 (app t, $^{app}J$ = 1.8 Hz, 2H), 8.70 (d, $^3J$ = 4.7 Hz, 2H), 8.72 (d, $^3J$ = 4.7 Hz, 2H), 8.83 (d, $^3J$ = 4.6 Hz, 2H), 9.00 (d, $^4J$ = 2.6 Hz, 2H), 9.09 (d, $^3J$ = 4.6 Hz, 2H), 9.80 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 13.5, 13.5, 31.9, 32.3, 32.5, 32.7, 33.0, 35.1, 38.6, 53.6, 57.5, 63.8, 102.7, 110.0, 114.3, 121.0, 121.2, 126.5, 127.1, 129.3, 130.7, 130.9, 131.0, 131.0, 140.9, 141.2, 156.4 ppm. MS (MALDI): *m*/*z* 1064.650 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{74}H_{89}N_4O_2$ $[M + H]^+$ 1065.69800, found 1065.69961. **12d** (strap: 4Me, *t*-Oct-aryl; *meso*: 2 × (3,5-di-*t*-Bu)Ph): no tetraaryl-BHP fraction was observed.

**General Procedure D: *meso*-Substitution of BHPs with Organolithium Reagents.** The BHP (100 $\mu$mol, 1 equiv) was dissolved in absolute THF (25 mL) and cooled to −10 °C. R-Li (300 $\mu$mol, 3 equiv) was added dropwise over 5 min and the reaction mixture was stirred until no remaining BHP was detected by TLC. Water (2 mL) was added, and the solution was warmed to room temperature. DDQ (91 mg, 400 $\mu$mol, 4 equiv) was added and the mixture was stirred for 1 h. THF was completely removed, and dichloromethane (100 mL) was added. The organic solution was washed with dilute HCl, $NaHCO_3$, and water and dried over $NaSO_4$. After evaporation of the solvent the remaining solid was purified by column chromatography (silica, dichloromethane/*n*-hexane). The raw product was recrystallized from chloroform/methanol to yield purple crystals. BHPs **11e,f** were reported before.

**BHP 11g** (strap: 4Me, H-aryl; *meso*: H/*n*-Hex). Prepared from BHP **10a** (65 mg) and *n*-HexLi (0.12 mL, 2.5 M in *n*-hexane), column chromatography with DCM/*n*-hexane 20/70 → 50/50. 55 mg, 75% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −2.41 (s, 2H), 0.04 (s, 6H), 0.13 (s, 6H), 1.35−1.41 (m, 2H), 1.47−1.51 (m, 4H), 1.73−1.77 (m, 2H), 2.46−2.50 (m, 2H), 3.71 (d, $^3J$ = 9.9 Hz, 2H), 3.76 (d, $^3J$ = 9.9 Hz, 2H), 4.82 (app t, $^{app}J$ = 8.0 Hz, 2H), 6.69 (dd, $^3J$ = 7.9 Hz, $^4J$ = 1.5 Hz, 2H), 7.54−7.63 (m, 4H), 8.79 (d, $^3J$ = 4.6 Hz, 2H), 8.82 (d, $^3J$ = 4.6 Hz, 2H), 8.94 (dd, $^3J$ = 7.1 Hz, $^4J$ = 1.9 Hz, 2H), 9.02 (d, $^3J$ = 4.6 Hz, 2H), 9.27 (d, $^3J$ = 4.6 Hz, 2H), 9.68 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 13.5, 14.3, 22.9, 30.3, 32.1, 35.1, 39.0, 63.6, 102.2, 110.8, 113.2, 119.4, 120.7, 128.1, 128.3, 129.9, 130.6, 130.9, 131.0, 131.2, 131.3, 131.6, 158.7 ppm. MS (MALDI): *m*/*z* 736.298 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{50}H_{48}N_4O_2$ $[M]^+$ 736.37718, found 736.37766.

**BHP 11a** (strap: 4Me, H-aryl; *meso*: H/(4-*t*-Bu)Ph). Prepared from BHP **10a** (65 mg) and (4-*t*-Bu)PhLi (0.1 mL, ∼ 3 M in diethyl ether),[67] column chromatography with DCM/*n*-hexane 20/70 → 50/50. 51 mg, 65% yield; characterization identical with that reported above.

**BHP 11b** (strap: 4Me, *t*-Bu-aryl; *meso*: H/(4-*t*-Bu)Ph). Prepared from BHP **10c** (76 mg) and (4-*t*-Bu)PhLi (0.1 mL, ∼ 3 M in diethyl ether),[67] column chromatography with DCM/*n*-hexane 30/70 → 50/50. 61 mg, 68% yield; characterization identical with that reported above.

**BHP 11h** (strap: 2Me, H-aryl; *meso*: H/*n*-Bu). Prepared from BHP **10b** (63 mg) and *n*-BuLi (0.12 mL, 2.5 M in *n*-hexane), column chromatography with DCM/*n*-hexane 20/70 → 50/50. 49 mg, 72% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −2.95 (s, 2H), −0.61 (s, 3H), −0.53 (s, 3H), 2.44−2.56 (m, 4H), 3.50 (d, $^3J$ = 12.9


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Hz, 2H), 3.60 (d, $^3J$ = 15.9 Hz, 2H), 7.10 (d, $^3J$ = 7.9 Hz, 2H), 7.66−7.70 (m, 2H), 7.74−7.78 (m, 2H), 8.73 (dd, $^3J$ = 12.0 Hz, $^4J$ = 4.7 Hz, 2H), 8.98−9.00 (m, 4H), 9.03 (d, $^3J$ = 4.7 Hz, 1H), 9.09−9.11 (m, 2H), 9.35 (d, $^3J$ = 4.7 Hz, 2H), 9.74 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 14.3, 14.6, 14.8, 22.8, 23.7, 29.5, 29.9, 32.1, 34.8, 41.2, 53.6, 72.2, 72.3, 102.9, 111.8, 112.1, 121.0, 121.0, 121.4, 121.5, 122.9, 122.9, 126.6, 126.6, 127.3, 129.8, 130.0, 130.1, 130.2, 130.3, 130.4, 130.5, 130.8, 131.2, 131.3, 131.8, 132.2, 133.0, 135.1, 135.2, 161.1, 161.2 ppm. MS (MALDI): $m/z$ 680.330 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{46}H_{41}N_4O_2$ $[M + H]^+$ 681.32240, found 681.32395.

**BHP 11i** (strap: 4Me, *t*-Bu-aryl; *meso*: H/*n*-Bu). Prepared from BHP **10c** (76 mg) and *n*-BuLi (0.12 mL, 2.5 M in *n*-hexane), column chromatography with DCM/*n*-hexane 40/60 → 50/50. 62 mg, 76% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ −2.37 (s, 2H), 0.02 (s, 6H), 0.14 (s, 6H), 1.10 (t, $^3J$ = 7.4 Hz, 3H), 1.72 (m, 2H), 1.78 (s, 18H), 2.41−2.51 (m, 2H), 3.70 (d, $^3J$ = 9.8 Hz, 2H), 3.75 (d, $^3J$ = 9.8 Hz, 2H), 4.81−4.88 (m, 2H), 6.63 (d, $^3J$ = 8.4 Hz, 2H), 7.62 (dd, $^3J$ = 8.3 Hz, $^4J$ = 2.5 Hz, 2H), 8.80 (d, $^3J$ = 4.6 Hz, 2H), 8.83 (d, $^3J$ = 4.7 Hz, 2H), 9.01−9.04 (m, 4H), 9.29 (d, $^3J$ = 4.8 Hz, 2H), 9.68 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 13.5, 13.5, 14.3, 23.6, 31.8, 32.3, 34.7, 34.8, 40.9, 63.8, 102.2, 110.2, 113.7, 120.5, 125.8, 126.1, 128.0, 130.7, 130.8, 130.8, 131.0, 131.0, 131.1, 131.4, 142.1, 156.6 ppm. MS (MALDI): $m/z$ 821.500 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{56}H_{61}N_4O_2$ $[M + H]^+$ 821.47890, found 821.47958.

**BHP 11j** (strap: 4Me, *t*-Oct-aryl; *meso*: H/Ph). Prepared from BHP **10c** (76 mg) and PhLi (0.12 mL, 1.9 M in dibutyl ether), column chromatography with DCM/*n*-hexane 40/60 → 70/30. 54 mg, 64% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ −2.57 (s, 2H), 0.07 (s, 6H), 0.10 (s, 6H), 1.14 (s, 18H), 1.47 (s, 2H), 1.80 (d, $^3J$ = 8.3 Hz, 12H), 3.69 (s, 4H), 6.59 (d, $^3J$ = 8.4 Hz, 2H), 7.58 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.5 Hz, 2H), 7.68−7.77 (m, 3H), 8.70 (d, $^3J$ = 4.6 Hz, 2H), 8.75 (d, $^3J$ = 4.7 Hz, 2H), 8.84 (d, $^3J$ = 4.6 Hz, 2H), 9.01 (d, $^4J$ = 2.5 Hz, 2H), 9.09 (d, $^3J$ = 4.6 Hz, 2H), 9.80 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 156.6, 142.4, 141.1, 134.6, 131.5, 131.2, 131.2, 131.1, 131.1, 130.9, 130.9, 127.8, 127.3, 127.0, 126.7, 119.9, 114.6, 110.3, 103.2, 77.7, 77.6, 77.4, 77.0, 64.0, 57.7, 38.8, 33.2, 32.9, 32.7, 32.7, 32.6, 13.8, 13.7, 13.6 ppm. MS (MALDI): $m/z$ 952.700 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{66}H_{73}N_4O_2$ $[M + H]^+$ 953.57280, found 953.57257.

**BHP 11k** (strap: 4Me, *t*-Bu-aryl; *meso*: H/Ph). Prepared from BHP **10e** (88 mg) and PhLi (0.12 mL, 1.9 M in dibutyl ether), column chromatography with DCM/*n*-hexane 20/80 → 50/50. 57 mg, 65% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ −2.57 (s, 2H), 0.03 (s, 6H), 0.12 (s, 6H), 1.75 (s, 18H), 3.69 (d, $^3J$ = 1.1 Hz, 4H), 6.61 (d, $^3J$ = 8.4 Hz, 2H), 7.60 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.5 Hz, 2H), 7.72 (dd, $^3J$ = 5.3 Hz, $^4J$ = 2.1 Hz, 3H), 8.13 (s, 2H), 8.69 (d, $^3J$ = 4.6 Hz, 2H), 8.76 (d, $^3J$ = 4.7 Hz, 2H), 8.85 (d, $^3J$ = 4.6 Hz, 2H), 9.02 (d, $^4J$ = 2.5 Hz, 2H), 9.10 (d, $^3J$ = 4.6 Hz, 2H), 9.80 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 156.7, 142.4, 142.3, 134.6, 131.6, 131.2, 131.2, 131.1, 131.1, 131.0, 130.9, 127.8, 127.0, 126.4, 125.8, 119.9, 114.5, 110.4, 103.2, 64.1, 35.0, 32.4, 13.8, 13.7 ppm. MS (MALDI): $m/z$ 840.357 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{58}H_{57}N_4O_2$ $[M + H]^+$ 841.44760, found 841.44959.

**General Procedure E: *meso*-Bromination of BHPs.** The BHP (100 μmol, 1 equiv) was dissolved in chloroform (20 mL) and cooled to 5 °C. NBS was added in small portions over 2 min and the mixture stirred at 5 °C for 10 min. After filtration over a plug of silica the solvent was removed and the resulting solid recrystallized from chloroform/methanol to yield purple crystals. If a product mixture was obtained, the different brominated BHPs were resolved by column chromatography. BHPs **13a,b** were reported before.[12]

**BHP 13c** (strap: 4Me, *t*-Bu-aryl; *meso*: 2 × Br). Prepared from BHP **10c** (76 mg) and NBS (37 mg, 0.21 mmol, 2 equiv). 91 mg, 97% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ −2.04 (s, 2H), 0.23 (s, 12H), 1.75 (s, 18H), 3.80 (s, 4H), 6.63 (d, $^3J$ = 8.5 Hz, 2H), 7.62 (dd, $^3J$ = 8.5 Hz, $^4J$ = 2.5 Hz, 2H), 8.71 (d, $^3J$ = 4.8 Hz, 4H), 8.92 (d, $^4J$ = 2.5 Hz, 2H), 9.31 (d, $^3J$ = 4.8 Hz, 4H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 13.8, 32.2, 34.7, 53.6, 63.8, 110.2, 125.9, 136.6, 130.0, 130.9, 131.2, 132.1, 132.6, 142.2, 156.4 ppm. MS (MALDI): $m/z$ 922.272 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{52}H_{51}Br_2N_4O_2$ $[M + H]^+$ 921.23733, found 921.23844.

**BHP 13d** (strap: 2Me, *t*-Bu-aryl; *meso*: 2 × Br). Prepared from BHP **10d** (73 mg) and NBS (37 mg, 0.21 mmol, 2 equiv). 89 mg, 99% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ −2.96 (s, 2H), −0.47 (s, 6H), 1.76 (s, 18H), 2.46 (d, $^3J$ = 13.4 Hz, 2H), 3.49 (d, $^3J$ = 13.4 Hz, 2H), 3.66 (s, 2H), 7.01 (d, $^3J$ = 8.4 Hz, 2H), 7.68 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.6 Hz, 2H), 8.64 (d, $^3J$ = 4.8 Hz, 2H), 8.87 (d, $^3J$ = 4.7 Hz, 2H), 8.97 (d, $^4J$ = 2.5 Hz, 2H), 9.36 (d, $^3J$ = 4.8 Hz, 2H), 9.38 (d, $^3J$ = 4.7 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 158.9, 145.9, 134.1, 133.6, 132.1, 131.1, 130.8, 128.5, 127.1, 127.0, 121.8, 120.4, 115.0, 102.4, 72.4, 35.1, 32.3, 14.8 ppm. MS (MALDI): $m/z$ 892.177 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{50}H_{47}Br_2N_4O_2$ $[M + H]^+$ 893.20603, found 893.20622.

**BHP 13e** (strap: 4Me, *t*-Oct-aryl; *meso*: 2 × Br). Prepared from BHP **10e** (88 mg) and NBS (37 mg, 0.21 mmol, 2 equiv). 99 mg, 97% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ −2.12 (s, 2H), 0.22 (s, 12H), 1.14 (s, 18H), 1.52 (d, $^3J$ = 1.7 Hz, 4H), 1.79 (s, 12H), 2.15 (s, 4H), 3.78 (s, 4H), 6.61 (d, $^3J$ = 8.4 Hz, 2H), 7.59 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.5 Hz, 2H), 8.68 (d, $^3J$ = 4.8 Hz, 2H), 8.92 (d, $^4J$ = 2.5 Hz, 2H), 9.31 (d, $^3J$ = 4.8 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 156.5, 141.1, 132.7, 132.3, 131.4, 131.0, 129.9, 127.7, 126.9, 110.2, 77.7, 77.6, 77.4, 77.0, 63.9, 57.6, 38.8, 33.2, 32.8, 32.7, 32.7, 14.1, 1.4 ppm. MS (MALDI): $m/z$ 1032.278 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{60}H_{67}Br_2N_4O_2$ $[M + H]^+$ 1033.36253, found 1033.36225.

**BHP 13f** (strap: 2Me, *t*-Oct-aryl; *meso*: 2 × Br). Prepared from BHP **10f** (85 mg) and NBS (37 mg, 0.21 mmol, 2 equiv). 96 mg, 96% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ −3.53 (s, 2H), −0.57 (s, 6H), 1.17 (s, 18H), 1.84 (d, $^3J$ = 13.4 Hz, 12H), 2.20 (q, $^3J$ = 14.5 Hz, 4H), 2.34 (d, $^3J$ = 13.5 Hz, 2H), 3.42 (d, $^3J$ = 13.4 Hz, 2H), 3.52 (s, 2H), 6.96 (d, $^3J$ = 8.4 Hz, 2H), 7.66 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.5 Hz, 2H), 8.56 (d, $^3J$ = 4.8 Hz, 2H), 8.79 (d, $^3J$ = 4.8 Hz, 2H), 9.02 (d, $^4J$ = 2.5 Hz, 2H), 9.30−9.33 (m, 4H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 14.5, 32.0, 32.5, 32.9, 33.0, 38.9, 57.5, 72.2, 102.0, 114.5, 120.1, 121.4, 126.6, 127.8, 129.1, 130.6, 130.7, 131.5, 133.3, 133.4, 133.9, 144.6, 158.6 ppm. MS (MALDI): $m/z$ 1004.291 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{58}H_{63}Br_2N_4O_2$ $[M + H]^+$ 1005.33123, found 1005.33244.

**BHP 13g** (strap: 2Br, H-aryl; *meso*: 2 × Br). Prepared from BHP **10g** (75 mg) and NBS (37 mg, 0.21 mmol, 2 equiv). 88 mg, 97% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ −2.87 (s, 2H), 2.36 (d, $^3J$ = 14.4 Hz, 2H), 3.36 (d, $^3J$ = 14.4 Hz, 2H), 4.04 (s, 2H), 7.12 (dd, $^3J$ = 8.0 Hz, $^4J$ = 1.2 Hz, 2H), 7.69 (td, $^3J$ = 7.8 Hz, $^4J$ = 1.8 Hz, 2H), 7.78 (td, $^3J$ = 7.6 Hz, $^4J$ = 1.3 Hz, 2H), 8.58 (d, $^3J$ = 4.8 Hz, 2H), 8.91 (d, $^3J$ = 4.8 Hz, 2H), (dd, $^3J$ = 7.8 Hz, $^4J$ = 1.8 Hz, 2H), 9.39 (d, $^3J$ = 4.8 Hz, 2H), 9.42 (d, $^3J$ = 4.8 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 160.7, 134.7, 134.6, 133.6, 132.9, 132.3, 132.1, 131.6, 130.7, 125.6, 123.9, 122.3, 115.0, 113.5, 103.6, 77.4, 73.6 ppm. MS (MALDI): $m/z$ 907.838 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{40}H_{25}Br_4N_4O_2$ $[M + H]^+$ 908.87055, found 908.87262.

**BHP 13h** (strap: 2Br, *t*-Oct-aryl; *meso*: 2 × Br). Prepared from BHP **10h** (98 mg) and NBS (37 mg, 0.21 mmol, 2 equiv). 113 mg, 99% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ −3.94 (s, 2H), 1.18 (s, 18H), 1.83 (s, 6H), 1.87 (s, 6H), 2.08 (d, $^3J$ = 14.6 Hz, 2H), 2.14−2.29 (m, 4H), 3.27 (d, $^3J$ = 14.6 Hz, 2H), 3.75 (s, 2H), 6.96 (d, $^3J$ = 8.4 Hz, 2H), 7.66 (dd, $^3J$ = 8.5 Hz, $^4J$ = 2.5 Hz, 2H), 8.46 (d, $^3J$ = 4.8 Hz, 2H), 8.75 (d, $^3J$ = 4.8 Hz, 2H), 9.06 (d, $^4J$ = 2.5 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 32.0, 32.5, 33.0, 33.1, 39.0, 57.6, 73.2, 102.8, 113.1, 114.4, 121.0, 124.9, 127.8, 129.5, 131.1, 131.4, 132.6, 133.2, 133.6, 134.1, 145.3, 158.1 ppm. MS (MALDI): $m/z$ 1136.179 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{56}H_{57}Br_4N_4O_2$ $[M + H]^+$ 1133.12095, found 1133.11982.

**BHP 13i** (strap: 4H, *t*-Oct-aryl; *meso*: 2 × Br). Prepared from BHP **10i** (82 mg) and NBS (37 mg, 0.21 mmol, 2 equiv). 97 mg, 99% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ −2.04 (s, 2H), 1.14 (s, 18H), 1.80 (s, 12H), 2.16 (s, 4H), 3.41 (s, 4H), 3.45 (s, 4H), 6.69 (d, $^3J$ = 8.4 Hz, 2H), 7.61 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.5 Hz, 2H), 8.67 (d, $^3J$ = 4.8 Hz, 4H), 8.99 (d, $^4J$ = 2.5 Hz, 2H), 9.34 (d, $^3J$ = 4.8 Hz, 4H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 156.9, 142.7, 134.1, 132.9, 132.4, 131.2, 127.9, 127.8, 123.8, 115.8, 114.7, 102.4, 77.2, 71.0, 57.5, 53.6, 38.7, 33.0, 32.4 ppm. MS (MALDI): $m/z$ 976.226 $[M]^{\bullet+}$. HRMS


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(ESI): calcd for $C_{56}H_{59}Br_2N_4O_2$ $[M + H]^+$ 977.29993, found 977.30318.

**BHP 14a** (strap: 2Me, H-aryl; *meso*: *n*-Bu/Br). Prepared from BHP **11h** (68 mg) and NBS (19 mg, 105 μmol, 1 equiv). 71 mg, 96% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ −2.58 (s, 2H), −0.52 (s, 3H), −0.37 (s, 3H), 1.11 (t, $^3J$ = 7.4 Hz, 3H), 1.75 (q, $^3J$ = 7.4 Hz, 2H), 2.38−2.51 (m, 2H), 2.63 (d, $^3J$ = 12.4 Hz, 2H), 3.56 (app t, $^{app}J$ = 11.3 Hz, 2H), 3.73 (s, 1H), 3.79 (s, 1H), 4.67−4.75 (m, 2H), 7.09 (app t, $^{app}J$ = 1.4 Hz, 1H), 7.11 (app t, $^{app}J$ = 1.4 Hz, 1H), 7.68 (app tt, $^3J$ = 1.6 Hz, $^{app}J$ = 7.7 Hz, 2H), 7.74 (app tt, $^3J$ = 1.6 Hz, $^{app}J$ = 7.5 Hz, 2H), 8.65−8.68 (m, 2H), 8.90−8.93 (m, 3H), 8.95 (d, $^3J$ = 4.7 Hz, 1H), 9.24 (dd, $^3J$ = 4.7 Hz, $^4J$ = 1.4 Hz, 2H), 9.38 (d, $^3J$ = 4.8 Hz, 1H), 9.40 (d, $^3J$ = 4.8 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 14.3, 14.7, 14.9, 23.7, 29.9, 34.5, 41.0, 72.1, 72.2, 100.5, 113.2, 113.4, 120.7, 120.8, 121.3, 121.9, 122.0, 122.8, 122.8, 126.9, 127.1, 127.6, 130.2, 130.2, 130.2, 130.7, 130.7, 130.8, 131.1, 131.1, 131.2, 131.7, 132.3, 133.0, 133.3, 134.7, 134.8, 143.4, 143.7, 144.0, 147.4, 161.0, 161.0 ppm. MS (MALDI): *m*/*z* 758.249 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{46}H_{40}BrN_4O_2$ $[M + H]^+$ 759.23292, found 759.23368.

**BHP 14b** (strap: 4Me, H-aryl; *meso*: *n*-Bu/Br). Prepared from BHP **11e** (71 mg) and NBS (19 mg, 105 μmol, 1 equiv). 73 mg, 94% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ −1.94 (s, 2H), 0.11 (s, 6H), 0.32 (s, 6H), 1.08 (t, $^3J$ = 7.4 Hz, 2H), 1.62−1.79 (m, 2H), 2.30−2.48 (m, 2H), 3.80 (d, $^3J$ = 9.9 Hz, 2H), 3.84 (d, $^3J$ = 9.8 Hz, 2H), 4.73 (d, $^3J$ = 7.2 Hz, 2H), 6.71 (dd, $^3J$ = 7.9 Hz, $^4J$ = 1.2 Hz, 2H), 7.51−7.64 (m, 4H), 8.74 (d, $^4J$ = 2.4 Hz, 2H), 8.76 (d, $^4J$ = 2.4 Hz, 1H), 8.88 (dd, $^3J$ = 7.2 Hz, $^4J$ = 1.2 Hz, 2H), 9.19 (d, $^3J$ = 4.7 Hz, 2H), 9.32 (d, $^3J$ = 4.8 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 158.7, 145.9, 145.5, 132.3, 131.6, 131.6, 131.4, 131.2, 131.0, 130.7, 130.1, 128.5, 128.4, 121.0, 119.3, 114.3, 110.7, 99.6, 63.6, 40.6, 34.4, 23.6, 14.3, 14.0, 13.6 ppm. MS (MALDI): *m*/*z* 786.417 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{48}H_{44}BrN_4O_2$ $[M + H]^+$ 787.26422, found 787.26544.

**BHP 14c** (strap: 4Me, *t*-Bu-aryl; *meso*: (4-*t*-Bu)Ph/Br). Prepared from BHP **11b** (90 mg) and NBS (19 mg, 105 μmol, 1 equiv). 97 mg, 99% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ −2.05 (s, 2H), 0.08 (s, 6H), 0.36 (s, 6H), 1.59 (s, 18H), 1.75 (s, 9H), 3.74 (d, $^3J$ = 9.9 Hz, 2H), 3.83 (d, $^3J$ = 9.9 Hz, 2H), 6.64 (d, $^3J$ = 8.4 Hz, 2H), 7.61 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.5 Hz, 2H), 7.71−7.79 (m, 2H), 8.04 (d, $^3J$ = 7.7 Hz, 2H), 8.68 (d, $^3J$ = 4.7 Hz, 2H), 8.70 (d, $^3J$ = 4.7 Hz, 2H), 8.79 (d, $^3J$ = 4.7 Hz, 2H), 8.97 (d, $^4J$ = 2.5 Hz, 2H), 9.38 (d, $^3J$ = 4.8 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 156.7, 150.8, 146.9, 146.6, 146.3, 145.5, 142.3, 138.6, 134.4, 132.5, 131.9, 131.6, 131.5, 131.2, 131.0, 130.8, 126.5, 126.1, 124.2, 120.6, 115.5, 110.4, 100.5, 64.1, 35.2, 34.9, 32.4, 32.0, 14.3, 13.7 ppm. MS (MALDI): *m*/*z* 976.369 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{62}H_{64}BrN_4O_2$ $[M + H]^+$ 975.42072, found 975.42239.

**BHP 14d** (strap: 4Me, *t*-Bu-aryl; *meso*: H/Br). Prepared from BHP **10c** (75 mg) and NBS (22 mg, 125 μmol, 1.2 equiv). column chromatography with chloroform/*n*-hexane 40/60 → 70/30. 52 mg, 62% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ −2.49 (s, 2H), 0.04 (s, 6H), 0.23 (s, 6H), 1.77 (s, 18H), 3.67 (d, $^3J$ = 10.0 Hz, 2H), 3.74 (d, $^3J$ = 10.0 Hz, 2H), 6.61 (d, $^3J$ = 8.4 Hz, 2H), 7.62 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.5 Hz, 2H), 8.78 (d, $^3J$ = 3.2 Hz, 2H), 8.80 (d, $^3J$ = 3.4 Hz, 2H), 8.99 (d, $^4J$ = 2.5 Hz, 2H), 9.04 (d, $^3J$ = 4.6 Hz, 2H), 9.44 (d, $^3J$ = 4.6 Hz, 2H), 9.77 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 13.4, 13.7, 32.2, 34.8, 63.8, 101.7 103.9, 110.2, 114.9, 125.7, 126.4, 130.4, 130.7, 131.0, 131.1, 131.4, 131.7, 131.9, 142.2, 156.4 ppm. MS (MALDI): *m*/*z* 844.321 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{52}H_{52}BrN_4O_2$ $[M + H]^+$ 843.32697, found 843.32682. BHPs **10c** (11%) and **13c** (25%) were isolated as side products.

**BHP 14e** (strap: 4Me, H-aryl; *meso*: H/Br). Prepared from BHP **10a** (64 mg) and NBS (22 mg, 125 μmol, 1.2 equiv). column chromatography with chloroform/*n*-hexane 40/60 → 70/30. 45 mg, 59% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ −2.52 (s, 2H), −0.02 (s, 6H), 0.23 (s, 6H), 3.70 (d, $^3J$ = 9.7 Hz, 2H), 3.76 (d, $^3J$ = 9.7 Hz, 2H), 6.69 (d, $^3J$ = 7.9 Hz, 2H),), 7.50−7.65 (m, 4H) 8.73−8.86 (m, 4H), 8.87−8.97 (m, 2H), 9.06 (d, $^3J$ = 4.8 Hz, 2H), 9.39−9.50 (m, 2H), 9.79 (s, 1H) ppm. $^1$3C NMR (100 MHz, $CDCl_3$): δ 158.6, 132.0, 131.6, 131.1, 130.8, 130.5, 130.2, 128.2, 119.4, 114.4, 110.8, 104.0, 63.6, 13.8, 13.5 ppm. MS (MALDI): *m*/*z* 730.225 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{44}H_{36}BrN_4O_2$ $[M + H]^+$ 731.20162, found 731.20411. BHPs **10a** (12%) and **13a** (26%) were isolated as side products.

**General Procedure F: β-Borylation of BHPs.** The BHP (0.2 mmol), dtbpy (11 mg, 0.03 mmol), $[Ir(cod)OMe]_2$ (11 mg, 0.02 mmol), and $(Bpin)_2$ were dissolved in absolute THF under an inert atmosphere and heated to reflux. After filtration over a plug of silica, the solvent was evaporated and the crude product was purified by preparative recycling GPC to yield the borylated BHPs. The product ratio can be influenced by variation of the amount of $(Bpin)_2$ and the reaction time. BHPs **15a−e** were reported before.[12]

**BHP 15f** (strap: 4Me, *t*-Bu-aryl; *meso*: (4-*t*-Bu)Ph/H; *β*: Bpin). Prepared from BHP **11b** (180 mg) and $(Bpin)_2$ (100 mg, 0.4 mol, 2 equiv) by heating for 24 h. 119 mg, 55% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ −2.30 (s, 2H), 0.06 (d, $^3J$ = 16.7 Hz, 6H), 0.24 (d, $^3J$ = 19.8 Hz, 6H), 1.21 (s, 12H), 1.22 (s, 18), 1.66 (s, 6H), 1.70 (s, 6H), 1.75 (d, $^3J$ = 2.7 Hz, 18H), 3.64 (d, $^3J$ = 9.9 Hz, 1H), 3.70 (d, $^3J$ = 9.9 Hz, 1H), 3.77 (app t, $^{app}J$ = 9.7 Hz, 2H), 6.58 (d, $^3J$ = 8.4 Hz, 1H), 6.62 (d, $^3J$ = 8.4 Hz, 1H), 7.56−7.63 (m, 2H), 7.76 (app t, $^{app}J$ = 1.8 Hz, 1H), 8.68 (q, $^3J$ = 4.7 Hz, 2H), 8.72 (q, $^3J$ = 4.7 Hz, 2H), 8.83 (d, $^3J$ = 4.6 Hz, 1H), 9.00 (d, $^4J$ = 2.5 Hz, 1H), 9.02 (d, $^4J$ = 2.5 Hz, 1H), 9.15 (d, $^3J$ = 4.6 Hz, 1H), 9.42 (s, 1H), 10.39 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 13.3, 13.3, 13.9, 14.0, 24.7, 24.8, 24.9, 24.9, 24.9, 25.0, 25.4, 25.5, 26.1, 26.4, 26.6, 26.8, 27.0, 27.2, 27.3, 27.7, 29.0, 29.8, 29.9, 31.6, 31.8, 32.2, 32.3, 34.8, 35.1, 63.7, 63.8, 77.4, 82.9, 82.9, 83.1, 84.2, 104.3, 110.0, 110.1, 113.4, 114.8, 120.9, 125.7, 125.9, 126.1, 126.2, 129.5, 130.8, 130.8, 130.8, 130.9, 130.9, 131.1, 131.1, 131.2, 131.3, 141.1, 142.0, 142.1, 146.2, 148.8, 156.6 ppm. MS (MALDI): *m*/*z* 1078.623 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{72}H_{84}BN_4O_4$ $[M + H]^+$ 1079.65801, found 1079.65867. BHPs **11b** (26%) and **15g** (14%) were isolated as side products.

**BHP 15g** (strap: 4Me, *t*-Bu-aryl; *meso*: (4-*t*-Bu)Ph/H; *β*: 2 × Bpin). Prepared from BHP **11b** (180 mg) and $(Bpin)_2$ (400 mg, 1.6 mol, 8 equiv) by heating for 4 d. 184 mg, 77% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ −1.99 (s, 2H), −0.15 (s, 6H), 0.09 (s, 2H), 0.59 (s, 6H), 1.21 (s, 9H), 1.68 (s, 12H), 1.71 (s, 12H), 1.76 (s, 18H), 3.66 (d, $^3J$ = 9.9 Hz, 2H), 3.91 (d, $^3J$ = 9.9 Hz, 2H), 6.61 (d, $^3J$ = 8.5 Hz, 2H), 7.59 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.5 Hz, 2H), 7.75 (app t, $^{app}J$ = 1.8 Hz, 1H), 8.67 (s, 4H), 9.01 (d, $^4J$ = 2.5 Hz, 2H), 9.42 (s, 2H), 10.85 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 1.2, 13.1, 14.6, 24.7, 25.1, 25.5, 25.5, 29.9, 31.6, 31.8, 32.3, 34.7, 35.1, 63.7, 77.4, 82.9, 84.1, 105.7, 109.9, 113.9, 120.6, 120.9, 126.0, 126.2, 129.4, 130.6, 130.9, 130.9, 131.3, 131.6, 140.9, 141.9, 142.5, 148.9, 156.8 ppm. MS (MALDI): *m*/*z* 1204.738 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{78}H_{95}B_2N_4O_6$ $[M + H]^+$ 1205.74322, found 1205.74606. BHPs **11b** (4%) and **15f** (12%) were isolated as side products.

**2-Bromo-5,10,15,20-tetrakis(4-*tert*-butylphenyl)porphyrin (16b).** 5,10,15,20-Tetrakis(4-*tert*-butylphenyl)porphyrin (1.00 g, 1.19 mmol) was dissolved in 1,2-dichlorobenzene (200 mL) and heated to 160 °C. NBS (212 mg, 1.19 mmol) was added and the solution stirred at 160 °C for 45 min. A 150 mL amount of the solvent was removed, and MeOH (300 mL) was added. The precipitate was isolated and purified by column chromatography (silica, *n*-hexane/dichloromethane 1/1). The obtained solid was recrystallized from chloroform/methanol to yield purple crystals of **16b**. 764 mg, 70% yield; mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ −2.82 (s, 2H), 1.59 (s, 9H), 1.60 (s, 9H), 1.61 (s, 9H), 1.62 (s, 9H), 7.71−7.80 (m, 8H), 7.97−8.03 (m, 2H),), 8.08−8.17 (m, 6H), 8.79 (s, 1H), 8.80−8.96 (m, 6H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 150.6, 150.5, 150.3, 140.7, 139.6, 139.5, 139.2, 136.6, 135.0, 134.8, 134.7, 123.9, 123.8, 123.7, 123.7, 121.8, 120.4, 120.1, 119.9, 83.8, 35.1, 35.0, 35.0, 31.9, 31.9, 25.4 ppm. MS (MALDI): *m*/*z* 916.347 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{60}H_{62}BrN_4$ $[M + H]^+$ 917.41524, found 917.41752.

**2-(4,4,5,5-Tetramethyl[1,3,2]dioxaborolan-2-yl)-5,10,15,20-tetrakis(4-tolyl)porphyrin (17).** Porphyrin **16b** (350 mg, 0.38 mmol), $(Bpin)_2$ (260 mg, 0.95 mmol) and KOAc (370 mg, 3.79 mmol) were dissolved in toluene (100 mL) and water (20 mL) and degassed with an argon stream in an ultrasonic bath for 15 min. $Pd(dppf)Cl_2$ (31 mg, 0.038 mmol) was added and the mixture was degassed for a further 20 min. Then the reaction mixture was heated to



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110 °C for 6 h. After it was cooled to room temperature, the organic phase was filtered over a plug of silica and fully eluted with ethyl acetate. After evaporation of all solvents, the residue was purified by column chromatography (silica, *n*-hexane/dichloromethane 2/1 → 0/1). The product was recrystallized from chloroform/methanol to yield a purple solid. 304 mg, 83% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ −2.57 (s, 2H), 1.59 (s, 9H), 1.62 (s, 9H), 1.62 (s, 9H), 1.64 (s, 9H), 7.75−7.83 (m, 8H), 8.12−8.27 (m, 8H), 8.64 (d, $^3J$ = 4.9 Hz, 1H), 8.77 (d, $^3J$ = 4.8 Hz, 1H), 8.85 (d, $^3J$ = 5.3 Hz, 4H), 9.14 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 150.6, 150.5, 150.3, 140.7, 139.6, 139.5, 139.2, 136.6, 135.0, 134.8, 134.7, 123.9, 123.8, 123.7, 123.7, 121.8, 120.4, 120.1, 119.9, 83.8, 35.1, 35.0, 35.0, 31.9, 31.9, 25.4 ppm. MS (MALDI): *m*/*z* 964.566 $[M]^+$. HRMS (ESI): calcd for $C_{66}H_{74}BN_4O_2$ $[M + H]^+$ 965.58993, found 965.59112.

***β,β*-Dimer 18.** Porphyrin **16a**[32] (94 mg, 0.125 mmol), porphyrin **15a** (89 mg, 0.100 mmol), and $Ba(OH)_2$ (315 mg, 1.0 mmol) were dissolved in toluene (100 mL) and water (20 mL) and degassed with an argon stream in an ultrasonic bath for 15 min. $Pd(PPh_3)_4$ (10 mg, 0.01 mmol) was added and the mixture degassed for further 20 min. Then the reaction mixture was heated to 110 °C for 6 h. After it was cooled to room temperature, the organic phase was filtered over a plug of silica and fully eluted with ethyl acetate. After evaporation of all solvents, the residue was purified by column chromatography (silica, *n*-hexane/dichloromethane 2/1 → 0/1). 125 mg, 83% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ −2.75 (s, 2H), −2.42 (s, 3H), −0.08 (s, 6H), 0.11 (s, 3H), 0.15 (s, 3H), 1.74 (s, 9H), 1.77 (s, 9H), 2.47 (s, 3H), 2.69 (s, 6H), 2.74 (s, 3H), 3.60 (s, 2H), 3.63 (d, $^3J$ = 10.1 Hz, 2H), 3.69 (d, $^3J$ = 10.1 Hz, 2H), 4.78 (d, $^3J$ = 7.7 Hz, 2H), 6.51 (d, $^3J$ = 8.5, 2H), 6.60 (d, $^3J$ = 8.5 Hz, 2H), 7.04 (d, $^3J$ = 7.5 Hz, 2H), 7.38−7.58 (m, 18H), 7.58−7.66 (m, 4H), 8.11 (d, $^3J$ = 7.7 Hz, 2H), 8.18 (d, $^3J$ = 7.8 Hz, 4H), 8.37 (s, 1H), 8.50 (d, $^3J$ = 5.3 Hz, 2H), 8.77 (d, $^3J$ = 4.8 Hz, 1H), 8.85 (d, $^3J$ = 4.5 Hz, 2H), 8.88 (d, $^3J$ = 4.8 Hz, 1H), 8.91 (d, $^3J$ = 4.6 Hz, 2H), 8.97 (d, $^3J$ = 4.8 Hz, 2H), 8.99−9.03 (m, 2H), 9.10 (d, $^3J$ = 2.5 Hz, 1H), 9.16 (d, $^3J$ = 4.6 Hz, 1H), 9.20−9.23 (m, 2H), 9.64 (s, 1H), 9.95 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 156.4, 156.3, 142.1, 141.9, 139.9, 139.5, 139.3, 138.1, 137.5, 137.5, 137.3, 136.9, 135.3, 134.8, 134.8, 134.7, 133.9, 131.1, 131.0, 130.9, 130.9, 130.8, 130.6, 130.5, 127.7, 127.5, 127.3, 127.2, 126.8, 126.2, 126.1, 126.0, 125.6, 125.0, 122.0, 120.5, 120.2, 120.1, 113.9, 112.7, 110.0, 109.8, 103.5, 102.7, 68.1, 63.6, 63.4, 34.8, 34.8, 32.3, 32.2, 32.2, 31.9, 29.9, 21.7, 21.7, 21.5, 20.2, 14.3, 13.6, 13.4, 13.3, 13.3 ppm. MS (MALDI): *m*/*z* 1332.815 $[M]^+$. HRMS (ESI): calcd for $C_{100}H_{89}N_8O_2$ $[M + H]^+$ 1433.71030, found 1433.71399.

***β,meso*-Dimer 19.** Porphyrin **16b** (96 mg, 0.100 mmol), porphyrin **14e** (105 mg, 0.125 mmol), and $Ba(OH)_2$ (315 mg, 1.0 mmol) were dissolved in toluene (100 mL) and water (20 mL) and degassed with an argon stream in an ultrasonic bath for 15 min. $Pd(PPh_3)_4$ (10 mg, 0.01 mmol) was added and the mixture degassed for further 20 min. Then the reaction mixture was heated to 110 °C for 6 h. After it was cooled to room temperature, the organic phase was filtered over a plug of silica and fully eluted with ethyl acetate. After evaporation of all solvents, the residue was purified by column chromatography (silica, *n*-hexane/dichloromethane 2/1 → 0/1). 125 mg, 78% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ −2.66 (s, 2H), −2.30 (s, 2H), −1.14 (s, 9H), −0.10 (s, 6H), 0.24 (s, 6H), 1.37 (s, 9H), 1.58 (s, 9H), 1.67 (s, 9H), 3.63 (d, $^3J$ = 10.1 Hz, 2H), 3.70 (d, $^3J$ = 10.1 Hz, 2H), 5.19 (d, $^3J$ = 8.2 Hz, 1H), 6.63 (dd, $^3J$ = 8.3 Hz, $^4J$ = 2.2 Hz, 2H), 6.96 (d, $^3J$ = 8.2 Hz, 2H), 7.47−7.57 (m, 4H), 7.68 (d, $^3J$ = 8.4 Hz, 2H), 7.73 (d, $^3J$ = 8.4 Hz, 2H), 7.84 (d, $^3J$ = 7.8 Hz 2H), 8.15 (d, $^3J$ = 8.4 Hz, 2H), 8.26 (d, $^3J$ = 8.2 Hz, 2H), 8.37 (d, $^3J$ = 4.9 Hz, 1H), 8.39 (d, $^3J$ = 8.4 Hz, 2H), 8.47 (d, $^3J$ = 4.7 Hz, 2H), 8.48 (d, $^3J$ = 4.7 Hz, 2H), 8.69 (d, $^3J$ = 4.8 Hz, 1H), 8.84 (d, $^3J$ = 4.6 Hz, 2H), 8.90−8.97 (m, 4H), 9.02 (d, $^3J$ = 4.8 Hz, 1H), 9.06 (d, $^3J$ = 4.8 Hz, 1H), 9.09 (d, $^3J$ = 4.6 Hz, 2H), 9.60 (s, 1H), 9.80 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 158.7, 150.7, 150.6, 150.4, 147.4, 139.8, 139.4, 139.3, 136.4, 134.8, 134.8, 134.6, 133.0, 132.0, 131.0, 131.0, 130.5, 129.8, 129.2, 128.4, 127.8, 123.9, 123.7, 123.6, 122.5, 120.6, 120.5, 120.3, 119.4, 113.9, 110.7, 102.9, 63.6, 53.6, 35.1, 35.0, 34.9, 32.1, 31.9, 31.9, 31.8, 31.7, 29.9, 28.8, 13.7, 13.3. MS (MALDI): *m*/*z* 1204.738 $[M]^{\bullet+}$. MS (MALDI): *m*/*z* 1488.759 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{104}H_{97}N_8O_2$ $[M + H]^+$ 1489.77290, found 1489.77454.

**General Procedure G: Metalation of BHPs.** The BHP (0.1 mmol, 1 equiv) was dissolved in an appropriate solvent (30 mL), the metal salt (0.3 mmol, 3 equiv) was added, and the mixture was heated to reflux until no remaining starting material was detected by TLC or UV/vis. The solvent was removed and the remaining solid redissolved in chloroform. After filtration through a plug of silica and evaporation of the solvent, the porphyrin was recrystallized from chloroform/methanol. All metalation reactions proceeded with yields >97%.

All metallo-BHPs **M-X** were prepared from the corresponding free-base BHP **X**: for Ni-BHPs, $(CH_2Cl)_2$ (100 mL), $Ni(acac)_2$ (78 mg); for Zn-BHPs, $CHCl_3$ (100 mL), $Zn(OAc)_2$ (66 mg, dissolved in 2 mL of MeOH); for Pd-BHPs, $(CH_2Cl)_2$ (100 mL), $Pd(OAc)_2$ (67 mg); for Mg-BHPs, $CHCl_3$ (100 mL), $NEt_3$ (0.5 mL), $MgBr_2{\cdot}OEt_2$ (78 mg); for Cu-BHPs, $CHCl_3$ (100 mL), $Cu(OAc)_2$ (60 mg, dissolved in 1 mL of MeOH); for In-BHPs, glacial acetic acid (100 mL), NaOAc (136 mg, 1 mmol), $InCl_3$ (66 mg); for V-BHPs, quinoline (100 mL), $VO(acac)_2$ (79 mg).

The metal complexes of the BHPs **10a** (Ni, Pd, Zn, Mg, Cu) and **10b** (Ni) were reported before.[12]

**BHP Zn-10b** (strap: 2Me, H-aryl; *meso*: 2 × H) prepared from **10b** (66 mg). 68 mg, 98% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ −0.78 (s, 6H), 2.05 (d, $^3J$ = 13.6 Hz, 2H), 3.24 (s, 2H), 3.29 (d, $^3J$ = 13.6 Hz, 3H), 7.09 (dd, $^3J$ = 8.0 Hz, $^4J$ = 1.2 Hz, 2H), 7.68 (dd, $^3J$ = 7.8 Hz, $^4J$ = 1.7 Hz, 2H), 7.80 (dd, $^3J$ = 7.5 Hz, $^4J$ = 1.2 Hz, 2H), 8.89 (d, $^3J$ = 4.4 Hz, 2H), 9.06 (dd, $^3J$ = 7.4 Hz, $^4J$ = 1.8 Hz, 2H), 9.20 (d, $^3J$ = 4.5 Hz, 2H), 9.30 (d, $^3J$ = 4.4 Hz, 2H), 9.32 (d, $^3J$ = 4.5 Hz, 2H), 10.06 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 1.2, 14.3, 14.4, 22.9, 29.5, 29.9, 32.1, 71.9, 77.4, 105.8, 113.0, 120.6, 121.7, 123.3, 126.3, 130.0, 130.3, 130.6, 131.6, 132.5, 132.7, 132.9, 135.9, 148.9, 149.0, 149.5, 151.0, 161.2 ppm. MS (MALDI): *m*/*z* 686.158 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{42}H_{30}N_4O_2Zn$ $[M + H]^{\bullet+}$ 686.16547, found 686.16668.

BHP **In-10b** (strap: 2Me, H-aryl; *meso*: 2 × H) prepared from **10b** (66 mg). 76 mg, 99% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ −0.80 (s, 6H), 2.11 (d, $^3J$ = 12.7 Hz, 2H), 3.14 (s, 2H), 3.22 (d, $^3J$ = 12.7 Hz, 2H), 7.04 (dd, $^3J$ = 7.9 Hz, $^4J$ = 1.1 Hz, 2H), 7.71 (app dt, $^4J$ = 1.8 Hz, $^{app}J$ = 7.8 Hz, 2H), 7.81 (app dt, $^4J$ = 1.3 Hz, $^{app}J$ = 7.7 Hz, 2H), 8.91 (d, $^3J$ = 4.5 Hz, 2H), 9.12 (dd, $^3J$ = 7.4 Hz, $^4J$ = 1.8 Hz, 2H), 9.16 (d, $^3J$ = 4.5 Hz, 2H), 9.45 (d, $^3J$ = 4.6 Hz, 2H), 9.49 (d, $^3J$ = 4.6 Hz, 2H), 10.31 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 14.4, 71.3, 105.8, 115.3, 120.6, 121.2, 123.1, 126.5, 130.2, 130.5, 130.9, 132.3, 132.9, 133.1, 133.7, 134.9, 148.4, 148.5, 150.0, 151.1, 160.4 ppm. MS (MALDI): *m*/*z* 772.100 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{42}H_{30}InN_4O_2$ $[M - Cl]^+$ 737.14021, found 737.14033.

**BHP Pd-10c** (strap: 4Me, *t*-Bu-aryl; *meso*: 2 × H) prepared from **10c** (77 mg). 86 mg, 99% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ −0.02 (s, 12H), 1.76 (s, 18H), 3.65 (s, 4H), 6.62 (d, $^3J$ = 8.4 Hz, 2H), 7.61 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.5 Hz, 2H), 8.92 (d, $^3J$ = 4.7 Hz, 4H), 9.00 (d, $^4J$ = 2.5 Hz, 2H), 9.09 (d, $^3J$ = 4.7 Hz, 4H), 9.95 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 13.4, 32.2, 34.8, 64.1, 77.4, 105.8, 110.6, 125.3, 126.3, 130.6, 130.7, 131.0, 131.0, 131.3, 140.0, 142.2, 142.4, 156.5 ppm. MS (MALDI): *m*/*z* 866.227 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{52}H_{50}N_4NaO_2Pd$ $[M + Na]^+$ 891.28608, found 891.28868.

**BHP In-10c** (strap: 4Me, *t*-Bu-aryl; *meso*: 2 × H) prepared from **10c** (77 mg). 90 mg, 97% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ −0.26 (s, 12H), 1.79 (s, 18H), 3.43 (s, 4H), 6.53 (d, $^4J$ = 8.2 Hz, 2H), 7.63 (dd, $^3J$ = 8.2 Hz, $^4J$ = 2.5 Hz, 2H), 8.94 (d, $^3J$ = 4.5 Hz, 4H), 9.13 (d, $^4J$ = 2.5 Hz, 2H), 9.89 (d, $^3J$ = 4.5 Hz, 4H), 10.24 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ 13.1, 14.3, 22.8, 29.9, 31.7, 32.2, 34.8, 63.1, 105.1, 109.7, 117.5, 125.6, 126.5, 130.2, 130.5, 131.1, 132.5, 132.6, 142.3, 148.3, 152.0, 156.0 ppm. MS (MALDI): *m*/*z* 912.311 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{52}H_{50}InN_4O_2$ $[M - Cl]^+$ 877.29671, found 877.29659.

**BHP Zn-10c** (strap: 4Me, *t*-Bu-aryl; *meso*: 2 × H) prepared from **10c** (77 mg). 81 mg, 97% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ −0.12 (s, 12H), 1.77 (s, 18H), 3.52 (s, 4H), 6.57 (d, $^3J$ = 8.4 Hz, 2H), 7.60 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.5 Hz, 2H), 8.99 (d, $^3J$ = 4.5


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Hz, 4H), 9.08 (d, $^3J$ = 2.5 Hz, 2H), 9.25 (d, $^3J$ = 4.5 Hz, 4H), 10.04 (s, 2H) ppm. Due to limited solubility in common deuterated solvents, $^{13}$C NMR data are not available. MS (MALDI): $m/z$ 826.379 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{52}H_{51}N_4O_2Zn$ $[M + H]^+$ 827.32980, found 827.32918.

**BHP Ni-10c** (strap: 4Me, *t*-Bu-aryl; *meso*: 2 × H) prepared from **10c** (77 mg). 79 mg, 98% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.40 (s, 12H), 1.69 (s, 18H), 4.06 (s, 4H), 6.71 (d, $^3J$ = 8.4 Hz, 2H), 7.59 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.5 Hz, 2H), 8.79 (d, $^3J$ = 4.7 Hz, 4H), 8.87 (d, $^4J$ = 2.5 Hz, 2H), 8.94 (d, $^3J$ = 4.7 Hz, 4H), 9.51 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 156.7, 142.3, 142.2, 140.8, 132.6, 132.4, 132.1, 131.6, 128.6, 127.6, 126.4, 112.1, 110.3, 103.8, 64.2, 51.0, 34.8, 32.3, 32.3, 14.6 ppm. MS (MALDI): $m/z$ 820.307 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{52}H_{50}N_4NaNiO_2$ $[M + Na]^+$ 843.31795, found 843.31916.

**BHP Ni-10d** (strap: 2Me, *t*-Bu-aryl; *meso*: 2 × H) prepared from **10d** (73 mg). 79 mg, 99% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −0.43 (s, 6H), 1.70 (s, 18H), 2.86 (d, $^3J$ = 13.1 Hz, 2H), 3.76 (d, $^3J$ = 13.1 Hz, 2H), 4.23 (s, 2H), 7.06 (d, $^3J$ = 8.4 Hz, 2H), 7.66 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.6 Hz, 2H), 8.71 (d, $^3J$ = 4.7 Hz, 2H), 8.88 (d, $^4J$ = 2.6 Hz, 2H), 8.99 (d, $^3J$ = 4.7 Hz, 2H), 9.02 (d, $^3J$ = 4.7 Hz, 2H), 9.05 (d, $^3J$ = 4.7 Hz, 2H), 9.59 (s, 2H) ppm. $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ 14.9, 32.1, 34.9, 72.9, 104.1, 111.7, 119.8, 122.8, 126.6, 127.8, 129.7, 131.1, 131.3, 132.3, 132.9, 141.4, 141.6, 142.9, 145.6, 158.6 ppm. MS (MALDI): $m/z$ 792.216 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{50}H_{46}N_4Ni_1O_2$ $[M]^+$ 792.29742, found 792.29688.

**BHP Pd-10d** (strap: 2Me, *t*-Bu-aryl; *meso*: 2 × H) prepared from **10d** (73 mg). 83 mg, 98% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −0.66 (s, 6H), 1.75 (s, 18H), 2.28 (d, $^3J$ = 13.6 Hz, 2H), 3.46 (d, $^3J$ = 13.6 Hz, 2H), 3.58 (s, 2H), 7.04 (d, $^3J$ = 8.2 Hz, 2H), 7.68 (dd, $^3J$ = 8.2 Hz, $^4J$ = 2.0 Hz, 2H), 8.79 (d, $^3J$ = 4.8 Hz, 2H), 9.02 (d, $^4J$ = 2.0 Hz, 2H), 9.09 (d, $^3J$ = 4.5 Hz, 2H), 9.12 (d, $^3J$ = 4.5 Hz, 2H), 9.17 (d, $^3J$ = 4.8 Hz, 2H), 9.97 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 14.5, 29.9, 32.1, 35.0, 72.5, 106.2, 114.1, 120.9, 121.4, 126.7, 128.2, 130.5, 130.6, 131.5, 131.9, 132.1, 133.8, 140.2, 140.4, 140.6, 142.1, 146.1, 185.9 ppm. MS (MALDI): $m/z$ 838.205 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{50}H_{46}N_4O_2Pd$ $[M]^+$ 840.26556, found 840.26501.

**BHP Zn-10d** (strap: 2Me, *t*-Bu-aryl; *meso*: 2 × H) prepared from **10d** (73 mg). 79 mg, 98% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −0.80 (s, 6H), 1.78 (s, 18H), 1.99 (d, $^3J$ = 13.4 Hz, 2H), 3.22 (s, 2H), 3.27 (d, $^3J$ = 13.4 Hz, 2H), 7.01 (d, $^3J$ = 8.4 Hz, 2H), 7.68 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.6 Hz, 2H), 8.91 (d, $^3J$ = 4.5 Hz, 2H), 9.12 (d, $^4J$ = 2.6 Hz, 2H), 9.19 (d, $^3J$ = 4.5 Hz, 2H), 9.29 (d, $^3J$ = 4.5 Hz, 2H), 9.33 (d, $^3J$ = 4.5 Hz, 2H), 10.06 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 1.2, 14.3, 29.9, 32.2, 35.0, 72.0, 105.7, 113.6, 120.5, 120.9, 126.2, 126.4, 127.9, 130.4, 131.7, 132.3, 132.9, 132.9, 135.1, 146.1, 148.9, 149.0, 149.5, 151.1, 159.0 ppm. MS (MALDI, positiv): $m/z$ 798.315 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{50}H_{46}N_4O_2Zn$ $[M]^+$ 798.29122, found 798.29111.

**BHP Mg-10d** (strap: 2Me, *t*-Bu-aryl; *meso*: 2 × H) prepared from **10d** (73 mg). 76 mg, 97% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −0.82 (s, 6H), 1.77 (s, 18H), 1.97 (d, $^3J$ = 14.7 Hz, 2H), 3.13 (s, 2H), 3.21 (d, $^3J$ = 13.6 Hz, 2H), 6.97 (d, $^3J$ = 8.4 Hz, 2H), 7.65 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.6 Hz, 2H), 8.76 (d, $^3J$ = 4.3 Hz, 2H), 9.03 (d, $^3J$ = 4.5 Hz, 2H), 9.12 (d, $^4J$ = 2.6 Hz, 2H), 9.22 (d, $^3J$ = 4.4 Hz, 2H), 9.27 (d, $^3J$ = 4.3 Hz, 2H), 9.99 (s, 2H). $^{13}$C NMR data are not available due to decomposition during the measurement. MS (MALDI): $m/z$ 758.207 $[M]^{\bullet+}$. HRMS (ESI, positive) calcd for $C_{50}H_{46}MgN_4O_2$ $[M]^+$ 758.34712, found 758.34657.

**BHP Cu-10d** (strap: 2Me, *t*-Bu-aryl; *meso*: 2 × H) prepared from **10d** (73 mg). 76 mg, 98% yield. mp >300 °C. MS (MALDI): $m/z$ 797.254 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{50}H_{46}CuN_4O_2$ $[M + H]^+$ 797.29168, found 797.29113.

**BHP In-10d** (strap: 2Me, *t*-Bu-aryl; *meso*: 2 × H) prepared from **10d** (73 mg). 88 mg, 99% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −0.83 (s, 6H), 1.81 (s, 18H), 1.98 (d, $^3J$ = 13.0 Hz, 2H), 3.10 (s, 2H), 3.23 (d, $^3J$ = 13.0 Hz, 2H), 7.01 (d, $^3J$ = 8.3 Hz, 2H), 7.74 (dd, $^3J$ = 8.3 Hz, $^4J$ = 2.5 Hz, 2H), 8.95 (d, $^3J$ = 4.6 Hz, 2H), 9.18 (d, $^3J$ = 4.6 Hz, 2H), 9.22 (d, $^4J$ = 2.5 Hz, 2H), 9.45 (d, $^3J$ = 4.6 Hz, 2H), 9.51 (d, $^3J$ = 4.6 Hz, 2H), 10.31 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 14.1, 32.1, 35.0, 71.6, 105.7, 115.8, 120.4, 120.7, 126.1, 127.0, 128.5, 130.1, 132.4, 133.0, 133.2, 133.7, 134.3, 146.1, 148.4, 148.5, 149.9, 151.1, 158.4 ppm. MS (MALDI): $m/z$ 884.254 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{50}H_{46}ClInN_4O_2$ $[M + H]^+$ 884.23427, found 884.23358.

**BHP V-10d** (strap: 2Me, *t*-Bu-aryl; *meso*: 2 × H) prepared from **10d** (73 mg). 80 mg, 99% yield. mp >300 °C. MS (MALDI): $m/z$ 801.323 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{50}H_{46}N_4O_3V$ $[M]^+$ 801.30096, found 801.30041.

**BHP Zn-10e** (strap: 4Me, *t*-Oct-aryl; *meso*: 2 × H) prepared from **10e** (75 mg). 79 mg, 98% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −0.80 (s, 6H), 1.78 (s, 18H), 1.99 (d, $^3J$ = 13.4 Hz, 2H), 3.22 (s, 2H), 3.27 (d, $^3J$ = 13.4 Hz, 2H), 7.01 (d, $^3J$ = 8.4 Hz, 2H), 7.68 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.6 Hz, 2H), 8.91 (d, $^3J$ = 4.5 Hz, 2H), 9.12 (d, $^4J$ = 2.6 Hz, 2H), 9.19 (d, $^3J$ = 4.5 Hz, 2H), 9.29 (d, $^3J$ = 4.5 Hz, 2H), 9.33 (d, $^3J$ = 4.5 Hz, 2H), 10.06 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 1.2, 14.3, 29.9, 32.2, 35.0, 72.0, 105.7, 113.6, 120.5, 120.9, 126.2, 126.4, 127.9, 130.4, 131.7, 132.3, 132.9, 132.9, 135.1, 146.1, 148.9, 149.0, 149.5, 151.1, 159.0 ppm. MS (MALDI): $m/z$ 798.315 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{50}H_{46}N_4O_2Zn$ $[M]^+$ 798.29122, found 798.29111.

BHP **In-10f** (strap: 2Me, *t*-Oct-aryl; *meso*: 2 × Br) prepared from **10f** (89 mg). 79 mg, 98% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −0.80 (s, 6H), 1.22 (s, 18H), 1.88 (d, $^3J$ = 11.2 Hz, 12H), 2.02 (d, $^3J$ = 13.4 Hz, 2H), 2.19 (d, $^3J$ = 14.5 Hz, 2H), 2.28 (d, $^3J$ = 14.5 Hz, 2H), 3.12 (s, 2H), 3.26 (d, $^3J$ = 13.4 Hz, 2H), 7.03 (d, $^3J$ = 8.3 Hz, 2H), 7.75 (dd, $^3J$ = 8.3 Hz, $^4J$ = 2.5 Hz, 2H), 8.94 (d, $^3J$ = 4.5 Hz, 2H), 9.20 (d, $^3J$ = 4.5 Hz, 2H), 9.25 (d, $^4J$ = 2.5 Hz, 2H), 9.47 (d, $^3J$ = 4.6 Hz, 2H), 9.52 (d, $^3J$ = 4.5 Hz, 2H), 10.33 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 14.4, 31.9, 32.5, 33.0, 38.9, 57.5, 71.6, 105.7, 115.8, 120.3, 120.7, 126.1, 127.9, 129.3, 130.1, 132.3, 132.9, 133.1, 133.7, 134.1, 144.9, 148.3, 148.4, 149.9, 151.1, 158.3 ppm. MS (MALDI): $m/z$ 996.339 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{58}H_{62}InN_4O_2$ $[M - Cl]^+$ 961.39061, found 961.39169.

**BHP In-10h** (strap: 2Br, *t*-Oct-aryl; *meso*: 2 × H) prepared from **10h** (98 mg). 112 mg, 99% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.19 (s, 18H), 1.85 (d, $^3J$ = 11.3 Hz, 12H), 2.12 (s, 6H), 2.16 (d, $^3J$ = 14.6 Hz, 2H), 2.26 (d, $^3J$ = 14.6 Hz, 2H), 3.18 (d, $^3J$ = 14.4 Hz, 2H), 3.50 (s, 2H), 7.02 (d, $^3J$ = 8.4 Hz, 2H), 7.74 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.5 Hz, 2H), 8.87 (d, $^3J$ = 4.5 Hz, 2H), 9.17 (d, $^3J$ = 4.5 Hz, 2H), 9.24 (d, $^4J$ = 2.5 Hz, 2H), 9.49 (d, $^3J$ = 4.5 Hz, 2H), 9.54 (d, $^3J$ = 4.5 Hz, 2H), 10.40 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 20.9, 31.8, 32.5, 33.0, 33.0, 38.9, 57.5, 72.6, 106.8, 114.2, 121.0, 124.7, 128.0, 129.7, 132.0, 132.7, 133.0, 133.4, 134.1, 134.8, 145.7, 148.7, 149.0, 149.7, 150.5, 157.8, 177.3 ppm. MS (MALDI): $m/z$ 1124.111 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{56}H_{56}Br_2ClInN_4NaO_2$ $[M + Na]^+$ 1147.13895, found 1147.13764.

**BHP Ni-10i** (strap: 4H, *t*-Oct-aryl; *meso*: 2 × H) prepared from **10i** (83 mg). 87 mg, 99% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.10 (s, 18H), 1.76 (s, 12H), 2.11 (s, 4H), 3.75 (s, 4H), 4.11 (s, 4H), 6.76 (d, $^3J$ = 8.4 Hz, 2H), 7.60 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.5 Hz, 2H), 8.83 (d, $^3J$ = 4.7 Hz, 4H), 8.91 (d, $^4J$ = 2.5 Hz, 2H), 9.02 (d, $^3J$ = 4.7 Hz, 4H), 9.60 (s, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 156.8, 142.6, 142.3, 141.0, 134.8, 132.9, 132.0, 130.0, 129.0, 127.5, 125.2, 114.4, 112.2, 104.2, 71.2, 57.5, 38.7, 32.9, 32.4 ppm. MS (MALDI): $m/z$ 876.402 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{56}H_{58}N_4NiO_2$ $[M]^+$ 876.39078, found 876.39185.

**BHP Zn-11a** (strap: 4Me, H-aryl; *meso*: H/(4-*t*-Bu)Ph) prepared from **11a** (80 mg). 84 mg, 98% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −0.15 (s, 6H), −0.02 (s, 6H), 1.62 (s, 9H), 3.52 (d, $^3J$ = 1.2 Hz, 4H), 6.59−6.67 (m, 2H), 7.54−7.62 (m, 4H), 7.74 (d, $^3J$ = 8.0, 2H), 7.99−8.18 (m, 2H), 8.82−8.87 (m, 4H), 8.93−8.98 (m, 4H), 9.19 (d, $^3J$ = 4.4, 2H), 9.92 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 158.8, 151.4, 151.3, 150.3, 149.5, 148.9, 140.2, 134.4, 132.7, 132.5, 132.2, 132.2, 131.4, 131.3, 131.1, 130.7, 130.0, 127.6, 123.8, 121.4, 119.8, 115.2, 111.1, 104.6, 63.8, 35.2, 32.1, 13.5 ppm. MS (MALDI): $m/z$ 846.343 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{54}H_{46}N_4O_2Zn$ $[M]^+$ 846.29067, found 846.29060.

BHP **Cu-11a** (strap: 4Me, H-aryl; *meso*: H/(4-*t*-Bu)Ph) prepared from **11a** (80 mg). 84 mg, 97% yield. mp >300 °C. MS (MALDI): *m/*


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*z* 845.315 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{54}H_{46}N_4O_2Cu$ $[M]^+$ 845.29168, found 845.29225.

BHP **Ni-11a** (strap: 4Me, H-aryl; *meso*: H/(4-*t*-Bu)Ph) prepared from **11a** (80 mg). 83 mg, 98% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.41 (s, 6H), 0.69 (s, 6H), 1.52 (s, 9H), 4.11 (d, $^3J$ = 9.8 Hz, 2H), 4.21 (d, $^3J$ = 9.8 Hz, 2H), 6.81 (dd, $^3J$ = 8.1 Hz, $^4J$ = 1.1 Hz, 2H), 7.44−7.50 (m, 2H), 7.53−7.60 (m, 2H), 7.63−7.67 (m, 2H), 7.87 (d, $^3J$ = 7.8 Hz, 2H), 8.66 (d, $^3J$ = 4.9 Hz, 2H), 8.68 (d, $^3J$ = 4.9 Hz, 2H), 8.78 (dd, $^3J$ = 7.2 Hz, $^4J$ = 1.8 Hz, 2H), 8.80 (d, $^3J$ = 4.7 Hz, 2H), 8.88 (dd, $^3J$ = 4.7 Hz, $^4J$ = 1.0 Hz, 2H), 9.40 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 14.3, 14.9, 29.9, 31.8, 35.0, 63.9, 77.4, 103.0, 110.7, 119.1, 119.4, 124.0, 129.0, 129.9, 130.2, 131.5, 131.8, 131.8, 132.4, 132.4, 132.6, 133.5, 140.4, 141.1, 141.6, 142.0, 158.8 ppm. MS (MALDI): *m*/*z* 840.284 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{54}H_{46}N_4NiO_2$ $[M + H]^+$ 840.29742, found 840.29714.

**BHP Pd-11b** (strap: 4Me, *t*-Bu-aryl; *meso*: H/(4-*t*-Bu)Ph) prepared from **11b** (90 mg). 100 mg, 99% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.07 (s, 6H), 0.08 (s, 6H), 1.59 (s, 9H), 1.74 (s, 18H), 3.68 (d, $^3J$ = 10.2 Hz, 2H), 3.71 (d, $^3J$ = 10.2 Hz, 2H), 6.63 (d, $^3J$ = 8.4 Hz, 2H), 7.60 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.5 Hz, 2H), 7.2 (s, 2H), 8.71 (d, $^3J$ = 4.8 Hz, 2H), 8.77 (d, $^3J$ = 4.8 Hz, 2H), 8.90 (d, $^3J$ = 4.8 Hz, 2H), 8.96 (d, $^4J$ = 2.5 Hz, 2H), 9.04 (d, $^3J$ = 4.8 Hz, 2H), 9.84 (s, 1H) ppm. $^{13}$C NMR (150 MHz, CDCl3): $\delta$ 13.5, 13.6, 31.8, 32.2, 34.8, 64.3, 105.2, 110.8, 115.9, 121.5, 123.7, 125.4, 126.2, 130.6, 130.8, 131.0, 131.0, 131.1, 131.3, 133.9, 138.9, 139.9, 140.4, 141.9, 142.3, 142.4, 150.4, 156.6 ppm. MS (MALDI): *m*/*z* 1000.310 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{62}H_{62}N_4NaO_2Pd$ $[M + Na]^+$ 1023.37998, found 1023.38267.

**BHP Ni-11b** (strap: 4Me, *t*-Bu-aryl; *meso*: H/(4-*t*-Bu)Ph) prepared from **11b** (90 mg). 96 mg, 98% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.40 (s, 6H), 0.70 (s, 6H), 1.54 (s, 9H), 1.70 (s, 18H), 4.09 (d, $^3J$ = 9.8 Hz, 2H), 4.20 (d, $^3J$ = 9.8 Hz, 2H), 6.75 (d, $^3J$ = 8.5 Hz, 2H), 7.60 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.5 Hz, 2H), 7.63−7.68 (m, 2H), 7.88 (d, $^3J$ = 7.7 Hz, 2H), 8.66 (d, $^3J$ = 4.9 Hz, 2H), 8.68 (d, $^3J$ = 4.9 Hz, 2H), 8.79 (d, $^3J$ = 4.7 Hz, 2H), 8.86 (d, $^4J$ = 2.5 Hz, 2H), 8.88 (d, $^3J$ = 4.7 Hz, 2H), 9.38 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 156.7, 150.6, 142.2, 142.2, 141.8, 141.3, 140.6, 137.9, 133.7, 132.7, 132.7, 132.5, 132.5, 132.1, 132.0, 131.8, 128.6, 127.9, 126.3, 124.2, 119.2, 112.7, 110.2, 103.2, 64.2, 35.1, 34.9, 32.4, 32.1, 32.0, 15.0, 14.5 ppm. MS (MALDI): *m*/*z* 952.392 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{62}H_{62}N_4NaNiO_2$ $[M + Na]^+$ 975.41185, found 975.41241.

**BHP Cu-11b** (strap: 4Me, *t*-Bu-aryl; *meso*: H/(4-*t*-Bu)Ph) prepared from **11b** (90 mg). 95 mg, 98% yield. mp >300 °C. MS (MALDI): *m*/*z* 957.399 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{62}H_{62}CuN_4O_2$ $[M + H]^+$ 957.41633, found 957.41400.

**BHP Zn-11b** (strap: 4Me, *t*-Bu-aryl; *meso*: H/(4-*t*-Bu)Ph) prepared from **11b** (90 mg). 95 mg, 99% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −0.15 (s, 6H), −0.04 (s, 6H), 1.61 (s, 9H), 1.76 (s, 18H), 3.51 (s, 4H), 6.56 (d, $^3J$ = 8.4 Hz, 2H), 7.59 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.5 Hz, 2H), 8.08 (s, 2H), 8.84 (d, $^3J$ = 4.6 Hz, 2H), 8.86 (d, $^3J$ = 4.6 Hz, 2H), 8.96 (d, $^3J$ = 4.5 Hz, 2H), 9.03 (d, $^4J$ = 2.5 Hz, 2H), 9.20 (d, $^3J$ = 4.5 Hz, 2H), 9.92 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 1.2, 13.2, 13.3, 31.9, 32.3, 34.8, 35.0, 64.1, 104.5, 110.7, 115.7, 123.6, 125.0, 130.6, 130.7, 130.8, 131.3, 131.9, 132.1, 132.2, 132.3, 134.3, 140.0, 142.4, 148.8, 149.2, 150.2, 151.3, 151.3, 156.6 ppm. MS (MALDI): *m*/*z* 958.419 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{62}H_{63}N_4O_2Zn$ $[M + H]^+$ 959.42370, found 959.42494.

**BHP Zn-11e** (strap: 4Me, H-aryl; *meso*: H/*n*-Bu) prepared from **11e** (72 mg). 76 mg, 98% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −0.14 (s, 6H), −0.04 (s, 6H), 1.15 (t, $^3J$ = 7.4 Hz, 3H), 1.83 (q, $^3J$ = 7.4 Hz, 2H), 2.55 (p, $^3J$ = 7.9 Hz, 2H), 3.53 (d, $^3J$ = 10.0 Hz, 2H), 3.58 (d, $^3J$ = 10.0 Hz, 2H), 4.89 (t, $^3J$ = 7.3 Hz, 2H), 6.60−6.67 (m, 2H), 7.55−7.62 (m, 4H), 8.90 (dd, $^3J$ = 4.5 Hz, $^4J$ = 2.2 Hz, 4H), 8.93−8.98 (m, 2H), 9.14 (d, $^3J$ = 4.5 Hz, 2H), 9.39 (d, $^3J$ = 4.6 Hz, 2H), 9.83 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 158.9, 150.9, 150.7, 149.6, 148.5, 132.7, 132.1, 132.1, 131.5, 131.3, 131.1, 130.7, 129.9, 129.3, 127.7, 121.9, 119.8, 114.7, 111.1, 104.1, 77.0, 63.8, 41.8, 35.6, 30.1, 24.1, 14.6, 13.5, 13.5 ppm. MS (MALDI): *m*/*z* 770.241 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{48}H_{43}N_4O_2Zn$ $[M + H]^+$ 771.26720, found 771.26606.

**BHP Ni-11e** (strap: 4Me, H-aryl; *meso*: H/*n*-Bu) prepared from **11e** (72 mg). 78 mg, 97% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.49 (s, 6H), 0.52 (s, 6H), 0.89−0.93 (m, 4H), 1.40 (m, 2H), 2.04−2.12 (m, 2H), 4.17 (s, 4H), 4.53 (app t, $^{app}J$ = 7.9 Hz, 2H), 6.82 (dd, $^3J$ = 0.7 Hz, $^4J$ = 8.1 Hz, 2H), 7.48 (app dt, $^4J$ = 1.0 Hz, $^{app}J$ = 7.6 Hz, 2H), 7.58 (app dt, $^4J$ = 1.7 Hz, $^{app}J$ = 7.9 Hz, 2H), 8.73 (d, $^3J$ = 5.0 Hz, 2H), 8.75 (d, $^3J$ = 4.8 Hz, 2H), 8.78 (dd, $^3J$ = 7.3 Hz, $^4J$ = 1.8 Hz, 2H), 8.82 (d, $^3J$ = 4.8 Hz, 2H), 9.14 (d, $^3J$ = 5.0 Hz, 2H), 9.32 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 14.0, 14.3, 14.5, 14.6, 23.2, 29.9, 31.7, 31.8, 32.1, 33.3, 38.9, 64.0, 102.6, 110.8, 111.7, 118.9, 119.4, 129.0, 129.9, 130.1, 130.3, 131.4, 132.0, 132.2, 132.4, 140.1, 141.3, 141.3, 158.8 ppm. MS (MALDI): *m*/*z* 764.142 $[M]^{\bullet+}$. HRMS (ESI, positive) calcd for $C_{48}H_{42}N_4NaNiO_2$ $[M + Na]^+$ 787.25535, found 787.25509.

**BHP Zn-11i** (strap: 4Me, *t*-Bu-aryl; *meso*: H/*n*-Bu) prepared from **11i** (82 mg). 88 mg, 98% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −0.19 (s, 6H), −0.10 (s, 6H), 1.14 (t, $^3J$ = 7.4 Hz, 3H), 1.79 (s, 18H), 1.83 (m, 2H), 2.51 (h, $^3J$ = 8.0 Hz, 7.3, 2H), 3.47 (d, $^3J$ = 10.4 Hz, 2H), 3.51 (d, $^3J$ = 10.2 Hz, 2H), 4.82 (t, $^3J$ = 8.1 Hz, 2H), 6.55 (d, $^3J$ = 8.3 Hz, 2H), 7.58 (dd, $^3J$ = 8.3 Hz, $^4J$ = 2.5 Hz, 2H), 8.84 (d, $^3J$ = 4.5 Hz, 2H), 8.86 (d, $^3J$ = 4.5 Hz, 2H), 9.01 (d, $^4J$ = 2.4 Hz, 2H), 9.11 (d, $^3J$ = 4.4, 2H), 9.32 (d, $^3J$ = 4.6 Hz, 2H), 9.78 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 156.7, 150.8, 150.6, 149.5, 148.4, 142.5, 132.2, 131.9, 131.6, 131.1, 131.0, 130.7, 129.1, 126.0, 125.2, 121.7, 115.1, 110.6, 104.0, 64.1, 41.7, 35.5, 35.0, 32.5, 30.1, 24.0, 14.6, 13.4 ppm. MS (MALDI): *m*/*z* 882.413 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{56}H_{59}N_4O_2Zn$ $[M + H]^+$ 883.39240, found 883.39227.

**BHP Zn-11h** (strap: 2Me, H-aryl; *meso*: H/*n*-Bu) prepared from **11h** (70 mg). 749 mg, 97% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −0.78 (s, 6H), 1.16 (t, $^3J$ = 7.4 Hz, 3H), 1.84 (d, $^3J$ = 7.4 Hz, 2H), 2.06 (d, $^3J$ = 14.1 Hz, 1H), 2.11 (d, $^3J$ = 14.1 Hz, 1H), 2.48−2.59 (m, 2H), 3.27−3.34 (m, 4H), 4.64−4.80 (m, 2H), 7.07 (dd, $^3J$ = 8.0 Hz, $^4J$ = 1.0, 1H), 7.08 (dd, $^3J$ = 8.0 Hz, $^4J$ = 1.0 Hz, 1H), 7.66 (app dt, $^4J$ = 1.8 Hz, $^{app}J$ = 7.8 Hz, 2H), 7.79 (app tt, $^3J$ = 1.3 Hz, $^{app}J$ = 7.8 Hz, 2H), 8.72 (d, $^3J$ = 4.6 Hz, 1H), 8.74 (d, $^3J$ = 4.6 Hz, 1H), 8.98 (app dt, $^4J$ = 1.8 Hz, $^{app}J$ = 7.6 Hz, 2H), 9.02 (d, $^3J$ = 4.6 Hz, 1H), 9.04 (d, $^3J$ = 4.6 Hz, 1H), 9.13 (d, $^3J$ = 3.2 Hz, 1H), 9.14 (d, $^3J$ = 3.2 Hz, 1H), 9.31 (d, $^3J$ = 4.6 Hz, 1H), 9.34 (d, $^3J$ = 4.6 Hz, 1H), 9.76 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 14.3, 14.7, 24.0, 35.3, 41.7, 53.6, 71.9, 72.1, 104.5, 112.8, 120.6, 120.7, 121.6, 121.7, 122.0, 123.2, 123.2, 126.3, 126.3, 129.6, 129.8, 129.8, 129.8, 130.2, 130.4, 130.6, 130.8, 130.8, 131.5, 132.0, 132.1, 132.6, 132.6, 135.9, 136.0, 148.3, 148.4, 148.6, 148.9, 149.4, 149.4, 149.9, 150.4, 161.1, 161.3 ppm. MS (MALDI, positiv): *m*/*z* 742.253 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{46}H_{38}N_4O_2Zn$ $[M]^+$ 742.22807, found 742.22823.

**BHP Zn-11g** (strap: 4Me, H-aryl; *meso*: H/*n*-Hex) prepared from **11g** (74 mg). 79 mg, 98% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −0.04 (s, 6H), −0.00 (s, 6H), 0.95 (t, J = 7.3 Hz, 3H), 1.41 (m, 2H), 1.48−1.58 (m, 2H), 1.78−1.88 (m, 2H), 2.52−2.62 (m, 2H), 3.60 (dd, J = 10.1 Hz, 4H), 4.85−4.92 (m, 2H), 6.62−6.69 (m, 2H), 7.54−7.63 (m, 4H), 8.89 (d, J = 4.5 Hz, 4H), 8.93−8.97 (m, 2H), 9.14 (d, J = 4.5 Hz, 2H), 9.39 (d, J = 4.6 Hz, 2H), 9.82 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 13.2, 13.3, 14.4, 22.9, 29.9, 30.5, 32.1, 35.8, 39.6, 63.7, 111.0, 114.7, 119.6, 121.8, 127.5, 129.1, 129.7, 130.5, 130.9, 131.0, 131.4, 131.8, 132.0, 132.6, 148.5, 149.5, 150.6, 150.8, 158.7 ppm. MS (MALDI): *m*/*z* 798.215 $[M]^{\bullet+}$. HRMS (ESI, positive) calcd for $C_{50}H_{47}N_4O_2Zn$ $[M + H]^+$ 799.29850, found 799.29746.

**BHP Ni-11g** (strap: 4Me, H-aryl; *meso*: H/*n*-Hex) prepared from **11g** (74 mg). 79 mg, 98% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.50 (s, 6H), 0.53 (s, 6H), 1.26 (m, 6H), 1.43 (m, 2H), 2.05−2.12 (m, 2H), 4.16 (s, 4H), 4.52 (app t, $^{app}J$ = 8.0 Hz, 2H), 6.82 (dd, $^3J$ = 8.1 Hz, $^4J$ = 0.8 Hz, 2H), 7.49 (app dt, $^4J$ = 1.1 Hz, $^{app}J$ = 7.6 Hz, 2H), 7.59 (app dt, $^4J$ = 1.8 Hz, $^{app}J$ = 7.9 Hz, 2H), 8.74 (dd, $^3J$ = 4.9 Hz, $^4J$ = 0.8 Hz, 4H), 8.77 (dd, $^3J$ = 7.3 Hz, $^4J$ = 1.8 Hz, 2H), 8.86 (d, $^3J$ = 4.8 Hz, 2H), 9.13 (d, $^3J$ = 4.9 Hz, 2H), 9.35 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 14.6, 14.6, 29.9, 33.7, 36.9, 64.0, 102.6, 11.8, 111.7, 119.0, 119.3, 129.0, 129.9, 130.1, 130.3, 131.4, 132.0, 132.2, 132.4, 140.1, 141.3, 141.3, 158.8 ppm. MS (MALDI): *m*/*z* 792.223 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{50}H_{46}N_4NiNaO_2$ $[M + Na]^+$ 815.28665, found 815.28512.



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**BHP Zn-12a** (strap: 4Me, H-aryl; *meso*: 2 × (4-*t*-Bu)Ph) prepared from **12a** (92 mg). 97 mg, 99% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.02 (s, 12H), 1.61 (s, 18H), 3.60 (s, 4H), 6.61−6.68 (m, 2H), 7.53−7.63 (m, 4H), 7.74 (d, $^3J$ = 7.9 Hz, 4H), 8.08 (br. s, 4H), 8.82 (d, $^3J$ = 4.6 Hz, 4H), 8.85 (d, $^3J$ = 4.6 Hz, 4H), 8.89−8.96 (m, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 159.0, 151.3, 150.4, 149.6, 140.2, 134.4, 133.1, 132.5, 131.4, 131.2, 130.8, 129.9, 127.5, 123.8, 119.9, 111.4, 77.7, 77.6, 77.4, 77.1, 77.0, 64.1, 35.2, 32.1, 30.1, 13.5, −2.8, −2.9 ppm. MS (MALDI): *m*/*z* 978.355 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{64}H_{59}N_4O_2Zn$ $[M + H]^+$ 979.39240, found 979.39141.

**BHP Ni-12a** (strap: 4Me, H-aryl; *meso*: 2 × (4-*t*-Bu)Ph) prepared from **12a** (90 mg). 97 mg, 98% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.66 (s, 12H), 1.54 (s, 18H), 4.22 (s, 4H), 6.69−6.77 (m, 2H), 7.35−7.41 (m, 4H), 7.66 (d, $^3J$ = 8.6 Hz, 4H), 7.87 (d, $^3J$ = 7.7 Hz, 4H), 8.65 (d, $^3J$ = 4.9 Hz, 4H), 8.69 (d, $^3J$ = 4.9 Hz, 4H), 8.72−8.75 (m, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 14.7, 31.8, 35.0, 64.0, 110.7, 119.3, 124.1, 128.9, 129.9, 130.3, 131.6, 131.9, 132.2, 132.6, 133.4, 137.6, 140.8, 141.5, 150.4, 158.7 ppm. MS (MALDI): *m*/*z* 972.399 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{64}H_{59}N_4NiO_2$ $[M + H]^+$ 973.39860, found 973.39745.

**BHP In-13h** (strap: 2Br, *t*-Oct-aryl; *meso*: 2 × Br) prepared from **13h** (113 mg). 126 mg, 98% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.15 (s, 18H), 1.81 (d, $^3J$ = 7.3 Hz, 12H), 2.05 (d, $^3J$ = 14.5 Hz, 2H), 2.12 (d, $^3J$ = 14.7 Hz, 2H), 2.21 (d, $^3J$ = 14.7 Hz, 2H), 3.31 (d, $^3J$ = 14.5 Hz, 2H), 3.77 (s, 2H), 7.04 (d, $^3J$ = 8.4 Hz, 2H), 7.73 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.5 Hz, 2H), 8.71 (d, $^3J$ = 4.7 Hz, 2H), 9.03 (d, $^3J$ = 4.8 Hz, 2H), 9.07 (d, $^4J$ = 2.5 Hz, 2H), 9.73 (d, $^3J$ = 4.8 Hz, 2H), 9.81 (d, $^3J$ = 4.8 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 31.8, 32.5, 33.0, 33.0, 38.9, 57.4, 72.9, 105.8, 114.6, 117.0, 121.2, 125.1, 128.3, 129.6, 133.1, 133.4, 133.5, 133.9, 135.0, 136.4, 145.8, 149.4, 149.6, 150.0, 150.8, 157.7 ppm. MS (MALDI): *m*/*z* 1282.052 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{56}H_{54}Br_4ClInN_4NaO_2$ $[M + Na]^+$ 1302.95998, found 1302.96124.

**BHP In-13f** (strap: 2Me, *t*-Oct-aryl; *meso*: 2 × Br) prepared from **13f** (101 mg). 114 mg, 98% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −0.58 (s, 6H), 1.16 (s, 18H), 1.82 (d, $^3J$ = 7.1 Hz, 12H), 2.11−2.23 (m, 6H), 3.28−3.43 (m, 4H), 7.02 (d, $^3J$ = 8.4 Hz, 2H), 7.73 (dd, $^3J$ = 8.4 Hz, $^4J$ = 2.5 Hz, 2H), 8.76 (d, $^3J$ = 4.8 Hz, 2H), 9.05 (d, $^3J$ = 4.8 Hz, 2H), 9.07 (d, $^4J$ = 2.5 Hz, 2H), 9.72 (d, $^3J$ = 4.8 Hz, 2H), 9.79 (d, $^3J$ = 4.8 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 14.5, 31.9, 32.5, 33.0, 33.0, 38.9, 57.5, 71.8, 104.6, 118.1, 120.4, 121.1, 126.6, 128.3, 129.2, 130.5, 133.4, 133.5, 134.1, 134.6, 135.3, 145.0, 148.8, 149.1, 150.2, 151.3, 158.2 ppm. MS (MALDI): *m*/*z* 1152.152 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{58}H_{60}Br_2ClInN_4NaO_2$ $[M + Na]^+$ 1175.17025, found 1175.16983.

**BHP Ni-13c** (strap: 4Me, *t*-Bu-aryl; *meso*: 2 × Br) prepared from **13c** (93 mg). 97 mg, 98% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.60 (s, 12H), 1.52(s, 2H), 1.69 (s, 18H), 4.18 (s, 4H), 6.76 (d, $^3J$ = 8.5 Hz, 2H), 7.61 (dd, $^3J$ = 8.5 Hz, $^4J$ = 2.5 Hz, 2H), 8.64 (d, $^3J$ = 4.9 Hz, 4H), 8.77 (d, $^4J$ = 2.5 Hz, 2H), 9.17 (d, $^3J$ = 4.9 Hz, 4H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 14.3, 14.8, 31.8, 32.2, 34.7, 64.1, 77.4, 110.2, 114.5, 126.6, 127.5, 127.8, 131.6, 132.1, 133.5, 133.6, 140.9, 142.2, 142.3, 156.4 ppm. MS (MALDI,): *m*/*z* 975.931 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{52}H_{48}Br_2N_4NaNiO_2$ $[M + Na]^+$ 999.13897, found 999.14153.

**BHP Ni-14d** (strap: 4Me, *t*-Bu-aryl; *meso*: H/Br) prepared from **14d** (85 mg). 89 mg, 98% yield. mp >300 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.33 (s, 6H), 0.70 (s, 6H), 1.72 (s, 18H), 4.09 (d, $^3J$ = 9.8 Hz, 2H), 4.19 (d, $^3J$ = 9.8 Hz, 2H), 6.75 (d, $^3J$ = 8.5 Hz, 2H), 7.62 (dd, $^3J$ = 8.5 Hz, $^4J$ = 2.5 Hz, 2H), 8.71 (d, $^3J$ = 4.7 Hz, 2H), 8.74 (d, $^3J$ = 4.9 Hz, 2H), 8.81 (d, $^3J$ = 4.7 Hz, 2H), 8.83 (d, $^4J$ = 2.5 Hz, 2H), 9.27 (d, $^3J$ = 4.9 Hz, 2H), 9.34 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 14.4, 14.8, 32.2, 34.7, 64.0, 77.4, 101.1, 103.9, 110.1, 113.2, 126.4, 127.6, 128.0, 131.5, 131.9, 132.2, 132.6, 132.9, 133.1, 133.3, 140.2, 141.4, 142.1, 142.2, 142.2, 156.5 ppm. MS (MALDI): *m*/*z* 898.172 $[M]^{\bullet+}$. HRMS (ESI): calcd for $C_{52}H_{49}BrN_4NaNiO_2$ $[M + Na]^+$ 921.22846, found 921.22673.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02259.

Crystallographic data for **In-10d** (CIF)
Crystallographic data for **V-10d** (CIF)
$^1$H and $^{13}$C NMR, NOESY, and COSY for **10f,h**, chromatographic details for the enantiomeric resolution of **10d,f,h**, **11h**, **13b,d,f**, **14a**, **Zn-10b**, **Zn-10d**, **Ni-10d**, **Pd-10d**, **Cu-10d**, **Pd-10d**, **Mg-10d**, **V-10d**, **In-10d**, and **In-13f**, UV/vis spectra, additional information on the crystallographic measurements, and Cartesian coordinates and energies of the computationally investigated compounds (PDF)

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### Notes

The authors declare no competing financial interest.

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(20) Note that instead of the formally correct expression "*p*-xylylene", the commonly found term "*p*-xylene" is used throughout the paper.




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