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Synthesis of porphyrins bearing 1–4 hydroxymethyl groups and other one-carbon oxygenic substituents in distinct patterns

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Abstract—Porphyrins that bear one-carbon oxygenic substituents (hydroxymethyl, formyl, ester) directly attached to the macrocycle afford a compact architecture of utility for diverse applications. Routes to 9 porphyrins bearing such groups in distinct architectures (A_4-, *trans*-A_2-, *trans*-A_2B_2-, *trans*-AB-, and *trans*-AB_2C-porphyrins) have been explored (A=hydroxymethyl), including porphyrins bearing two one-carbon units in different oxidation states (hydroxymethyl/ester, formyl/ester). The hydroxymethyl group was introduced via TBDMS-protected dipyrromethane precursors.

1. Introduction

Porphyrins and hydroporphyrins equipped with compact substituents are attractive for diverse applications. The core macrocycle lacking any peripheral substituents other than hydrogen is of modest molecular weight (porphine, $C_{20}H_{14}N_4$, 310.4 u) whereas common substituted porphyrins are substantially larger (β-octaethylporphyrin, $C_{36}H_{46}N_4$, 534.8 u) if not nearly twice that (*meso*-tetraphenylporphyrin, $C_{44}H_{30}N_4$, 614.7 u). Tailoring porphyrins by modifying the *meso*-aryl groups typically further increases the size and molecular weight, which is undesirable for a number of applications including the following:

- For medical applications wherein molecules passively cross the blood–brain barrier, a molecular weight of less than ~800 u is considered essential.[1]
- For the development of manganese porphyrins that function as catalytic superoxide dismutase mimics in therapeutic applications, potent electron-withdrawing substituents attached to the porphyrin nucleus are required (to shift the electrochemical potential) while maintaining low molecular weight and tailored hydrophilic or amphipathic character.[2,3]
- For molecular information storage applications wherein redox-active molecules are assembled on an electroactive surface, small size permits a high charge density.[4,5]
- For the self-assembly of porphyrins in a manner analogous to that of bacteriochlorophyll *c*,[6,7] attachment of coordinative groups directly to the porphyrin *meso* positions provided a viable architecture[8–10] whereas the same groups at the *p*-positions of *meso*-aryl groups failed.[11]

To create porphyrinic architectures suitable for these and many other types of fundamental studies, we have begun developing motifs and synthetic routes to access substituted macrocycles that generally contain no β-substituents and few if any *meso*-aryl substituents. As one example, a symmetrically branched alkyl moiety ('swallowtail') bearing phosphonate or phosphate groups at the termini has been introduced and found to impart high water solubility to porphyrins.[12] As a second example, a new route to the fully unsubstituted porphine[13] enables this core macrocycle to be used in substitution chemistry. In chlorin chemistry, we have developed routes to sparsely substituted chlorins[14] so that the effects of auxochromic groups (formyl, acetyl, vinyl, ethynyl, aryl)[15,16] can be clearly delineated. Senge et al. has developed novel routes to porphyrins that are sparsely substituted and where the substituents are one-carbon entities.[17,18]

Porphyrins bearing diverse one-carbon substituents and derivatives (e.g., formyl,[17–32] carboxy,[2,20,33] alkoxycarbonyl,[2,29,34,35] amide,[2] hydroxymethyl,[4,20,23,24,27,29,30] alkoxymethyl,[28] *N*-alkylaminomethyl,[28,36] imino,[20,21,28,37]

Keywords: Porphyrin; Dipyrromethane; Hydroxymethyl; Formyl.
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trifluoromethyl,[2,3,38] cyano,[20,31,37,39–41] nitrile-oxide,[42] amidino[31]) have been examined and serve a broad range of applications. A common procedure to access porphyrins bearing many types of one-carbon oxygenic substituents is to selectively formylate one *meso* position followed by conversion of the formyl group to other one-carbon units such as hydroxymethyl,[8,23,24] carboxy,[33] oxime,[20] etc. Although selective Vilsmeier formylation at one porphyrin *meso* position proceeds in high yield,[17,21,22,25,27,29] the method is ineffective when the starting porphyrin is unsymmetrical and has multiple reactive positions.

Statistical approaches have often been employed to prepare *meso*-substituted porphyrins that bear two different one-carbon oxygenic substituents. Examples are provided by the intriguing model porphyrins **I** and **II** prepared to mimic the self-assembling features of bacteriochlorophyll *c*; the porphyrins contain α-hydroxyalkyl and acyl groups disposed at two trans *meso* positions and solubilizing 3,5-di-*tert*-butylphenyl groups at the other two *meso* positions (Chart 1). The choice of *meso*-substituents in the model compound (versus β-substituents in the biological target) stems from the ostensibly more facile synthetic methodology for introducing *meso* versus β-substituents in the porphyrin macrocycle. However, the synthesis of **I** entailed preparation of 5,15-bis(3,5-di-*tert*-butylphenyl)porphyrin followed by copper metalation, diformylation, copper demetalation, and statistical reduction to achieve the hydroxymethyl and formyl substituent pattern.[8] The synthesis of **II** entailed treatment of 5,15-bis(3,5-di-*tert*-butylphenyl)porphyrin to *meso*-bromination, palladium-mediated ethynylation, hydration to form the diacetylporphyrin, and statistical reduction to obtain the α-hydroxyethyl and acetyl substituent pattern.[8] These unavoidably difficult syntheses point up the limitations of existing methodology for the placement of small oxygenic functional groups close to the porphyrin perimeter, particularly in the presence of otherwise identical groups in distinct oxidation states.

All of the aforementioned studies and applications would benefit from efficient synthetic access to porphyrinic analogues bearing a broad range of one-carbon substituents. One-carbon oxygenic substituents (hydroxymethyl, aldehyde, ketone, and ester) offer low molecular weight, small size, limited hydrophobicity, and the capacity for further synthetic elaboration. More recent approaches to such porphyrins have employed 5-substituted dipyrromethanes bearing one-carbon substituents (or protected variants) such as ethoxycarbonyl,[2] 1,3-dithian-2-yl,[19] 1,3-dithiolan-2-yl,[32] 5,5-dimethyl-1,3-dioxan-2-yl,[32] hydroxymethyl,[4] *S*-acetylthiomethyl,[4] and *Se*-acetylselenomethyl.[4] We have extended these approaches to the more general problem of introducing multiple one-carbon substituents at the porphyrin *meso* positions.

In this paper, we describe our studies concerning the synthesis of A_4-, *trans*-A_2-, *trans*-A_2B_2-, *trans*-AB-, and *trans*-AB_2C-porphyrins bearing primarily hydroxymethyl groups, but also alkoxycarbonyl and formyl groups at *meso* positions. The general synthetic approach relies on dipyrromethane building blocks that bear various one-carbon units. Key building blocks in this regard include the *tert*-butyldimethylsilyl (TBDMS)-protected 5-hydroxymethyldipyrromethane and *S*-2-pyridyl hydroxythioacetate, which allow introduction of protected hydroxymethyl groups at designated *meso* positions. TBDMS protection was employed to avoid possible side reactions by the hydroxymethyl group during the synthesis. A long-term goal is to extend these approaches established with porphyrins to hydroporphyrins such as chlorins and bacteriochlorins.

2. Results and discussion

2.1. Synthesis of precursors for porphyrins

2.1.1. Dipyrromethanes bearing one-carbon substituents. Seven dipyrromethanes (**1a–g**) were employed in the porphyrin syntheses described herein (Chart 2). Four

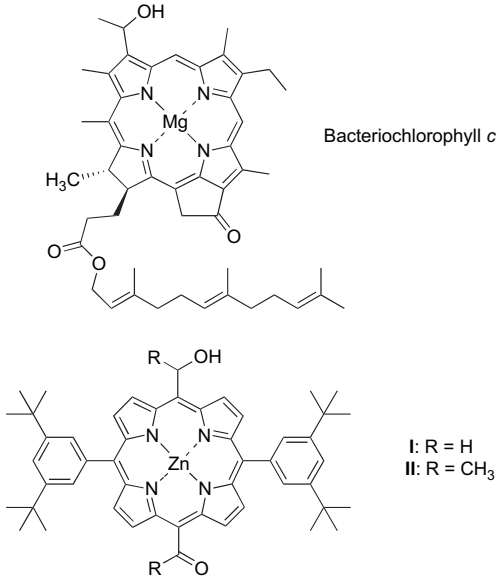


Chart 1.

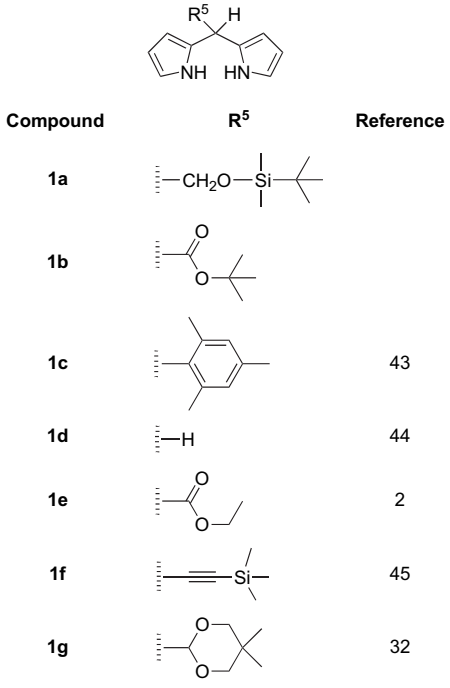
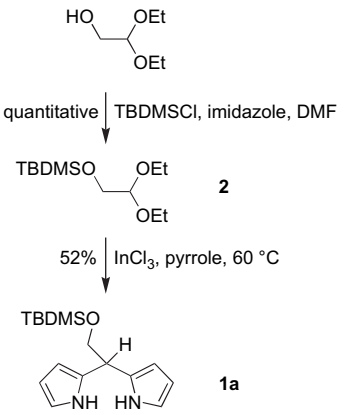


Chart 2.

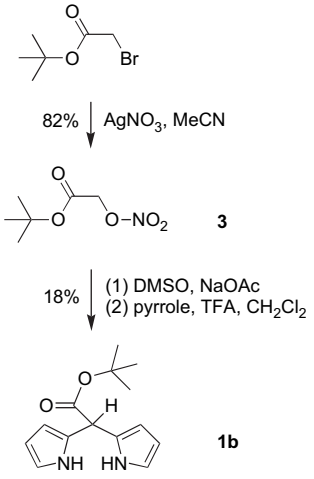
5-substituted dipyrromethanes (**1a**, **1b**, **1e**, and **1g**) bear various one-carbon groups in protected form. Dipyrromethanes **1a** and **1b** are new compounds. The new dipyrromethanes bear a *tert*-butyldimethylsilyl (TBDMS)-protected hydroxymethyl group (**1a**) or a *tert*-butoxycarbonyl group (**1b**). The 5-ethoxycarbonyldipyrromethane (**1e**)[2] and acetal-dipyrromethane (**1g**)[32] have been reported previously. The remaining dipyrromethanes (**1c**,[43,44] **1d**,[44] **1f**[45]) also are known compounds.

The synthesis of **1a** started with the protection of glycolaldehyde diethyl acetal with *tert*-butyldimethylsilyl chloride (TBDMSCl). The TBDPS-protected analogue is known.[46] The protection reaction yielded diethyl acetal **2** quantitatively. The reaction of acetal **2** and pyrrole was carried out under the same conditions employed for aldehyde and pyrrole condensations[44] except that higher temperature was required. Thus, a sample of **2** was treated with pyrrole and $InCl_3$ at 60 °C to afford 5-(*tert*-butyldimethylsiloxymethyl)dipyrromethane (**1a**) as a colorless oil in 52% yield (Scheme 1).



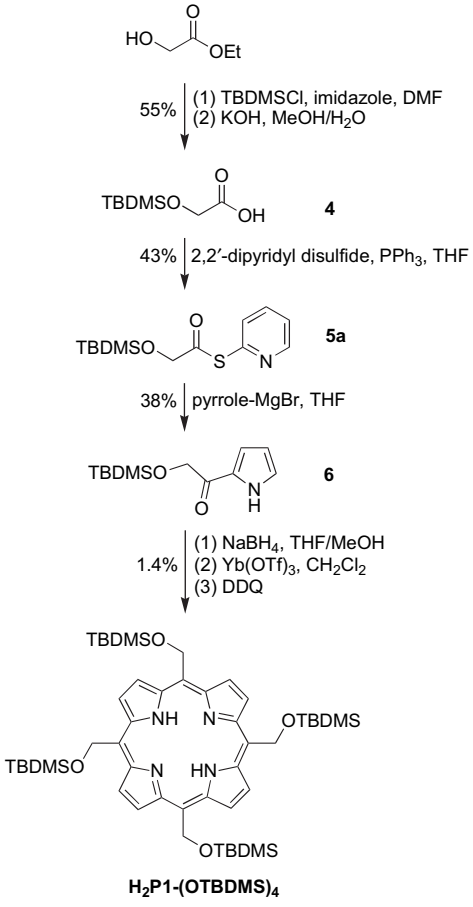
Scheme 1.

Compared to 5-ethoxycarbonyldipyrromethane (**1e**), 5-*tert*-butoxycarbonyldipyrromethane (**1b**) possesses a more base-resistant ester moiety due to the bulkiness of the *tert*-butyl group. *tert*-Butyl bromoacetate reacted[47] with excess silver nitrate in acetonitrile to afford nitrate ester **3** in 82% yield (Scheme 2). Treatment of **3** with sodium acetate in DMSO gave *tert*-butyl glyoxalate, which in crude form was condensed[2] with pyrrole in the presence of TFA in CH_2Cl_2 to yield *tert*-butyl ester dipyrromethane **1b** in 18% yield (from **3**).



Scheme 2.

2.1.2. A Mukaiyama reagent bearing a hydroxymethyl moiety. Mukaiyama reagents (*S*-2-pyridyl thioacyl compounds) are valuable species in porphyrin synthesis. The acylation of a dipyrromethane with a Mukaiyama reagent selectively introduces the desired acyl group at the 1-position of the dipyrromethane.[48] An attempt to synthesize *S*-2-pyridyl hydroxythioacetate without TBDMS protection was not successful. The synthesis of TBDMS-protected glycolic acid **4** from glycolic acid and TBDMSCl has been reported but with limited data.[49] However, in our hands the yield of the reaction varied and sometimes was lower than 10%. Alternatively, ethyl glycolate was treated with TBDMSCl to afford the TBDMS-protected glycolate (Scheme 3). Without purification, the ester was hydrolyzed to afford TBDMS-protected glycolic acid **4** in 55% yield, a known compound with limited characterization data.[49,50] Reaction[51] of **4** with 2,2′-dipyridyl disulfide gave the corresponding pyridyl thioester **5a** in 43% yield.



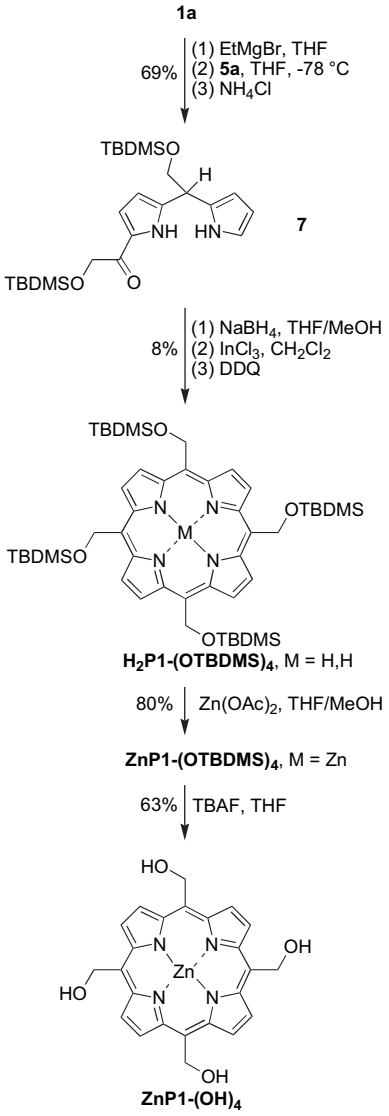
Scheme 3.

2.2. Syntheses of hydroxymethylporphyrins

2.2.1. A_4-Porphyrins with four hydroxymethyl groups. Our initial approach to *meso*-tetrakis(*tert*-butyldimethyl-

siloxymethyl)porphyrin [**H_2P1-(OTBDMS)$_4$**] relied on condensation of acetal **2** and pyrrole. This approach failed to give a workable yield of porphyrin. An alternative approach relied on a more advanced intermediate, namely the self-condensation of a pyrrole-carbinol bearing a protected hydroxymethyl group. Treatment[51] of pyrrole at −78 °C with EtMgBr followed by Mukaiyama reagent **5a** gave TBDMS-protected α-hydroxyacetylpyrrole **6** in 38% yield. Compound **6** was then reduced by $NaBH_4$ and treated with the catalyst[52] $Yb(OTf)_3$ followed by DDQ oxidation to afford TBDMS-protected tetrakis(hydroxymethyl)porphyrin **H_2P1-(OH)$_4$** in 1.4% yield.

The low yield prompted examination of an even more advanced intermediate, the dipyrromethane-1-carbinol bearing two protected hydroxymethyl groups. Thus, dipyrromethane **1a** was treated with EtMgBr followed by Mukaiyama reagent **5a** with a known procedure[48] to give 1-acyldipyrromethane **7** in 62% yield (Scheme 4). Acyldipyrromethane **7** was reduced by $NaBH_4$ to give the dipyrromethane-1-carbinol, which upon self-condensation and oxidation gave the desired A_4-porphyrin **H_2P1-(OTBDMS)$_4$** in 8% yield.



Scheme 4.

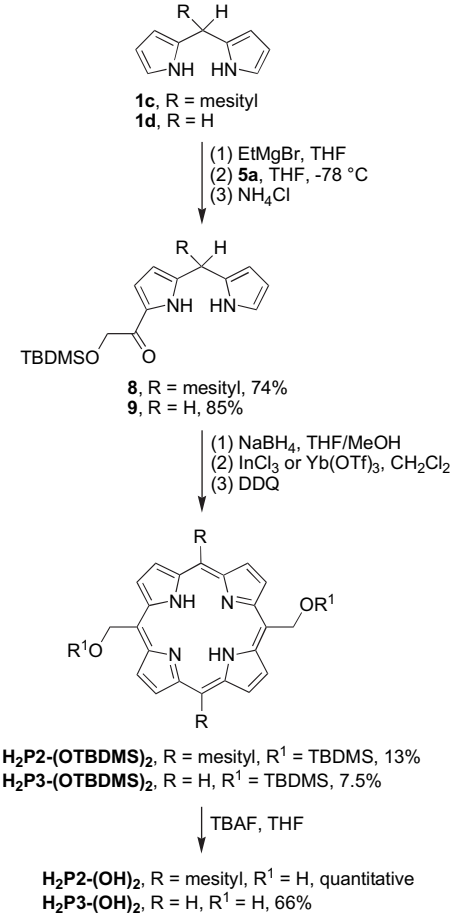
Treatment of the latter with $Zn(OAc)_2$ gave the zinc chelate **ZnP1-(OTBDMS)$_4$**. The TBDMS protecting groups were removed by treatment with TBAF to give 5,10,15,20-tetrakis(hydroxymethyl)porphyrin [**ZnP1-(OH)$_4$**] in 63% yield.

Porphyrin **ZnP1-(OH)$_4$** was difficult to purify by chromatography due to its poor solubility in organic solvents such as CH_2Cl_2, ethyl ether, MeOH, and THF. The reaction mixture from the deprotection reaction was washed with water, acetone, and THF. The structure of the resulting purple solid was confirmed by mass spectrometry and NMR spectroscopy (in DMSO-d_6). The molecule ion of **ZnP1-(OH)$_4$** was observed by laser-desorption mass spectrometry (LD-MS) with 1,4-bis(5-phenyloxazol-2-yl)benzene (POPOP) as the matrix. Measurement without a matrix, which typically affords excellent results with porphyrins,[53] or with other matrixes (dithranol, α-cyano-4-hydroxycinnamic acid, 3,5-dihydroxybenzoic acid) failed to display the expected mass signal. High-resolution experiments by electrospray ionization mass spectrometry (ESI-MS) and fast atom bombardment mass spectrometry (FABMS) were not successful.

2.2.2. *trans*-A_2- and *trans*-A_2B_2-Porphyrins with two hydroxymethyl groups. *trans*-A_2-Porphyrins or A_2B_2-porphyrins can be synthesized by the condensation of a dipyrromethane and an aldehyde.[54] However, alkyl-substituted dipyrromethanes are somewhat susceptible to scrambling.[54–56] An alternative synthetic route to a *trans*-A_2- or A_2B_2-porphyrin is via a 1-acyldipyrromethane.[48] Two 1-acyldipyrromethanes bearing one hydroxymethyl moiety were obtained from the corresponding dipyrromethanes in a manner similar to that of the synthesis for **H_2P1-(OTBDMS)$_4$**. 5-Mesityldipyrromethane (**1c**) or unsubstituted dipyrromethane (**1d**) reacted[48] with EtMgBr and pyridyl thioester **5a** to afford TBDMS-protected 1-acyldipyrromethane **8** or **9** in 74 or 85% yield, respectively (Scheme 5). 1-Acyl-5-mesityldipyrromethane **8** was reduced by $NaBH_4$ and the resulting dipyrromethane-1-carbinol was self-condensed[48,52,57] in the presence of $InCl_3$ followed by oxidation with DDQ to afford TBDMS-protected bis(hydroxymethyl)porphyrin **H_2P2-(OTBDMS)$_2$** in 13% yield (Scheme 5). Cleavage of the TBDMS group by TBAF[58] afforded porphyrin **H_2P2-(OH)$_2$** quantitatively.

A *trans*-A_2-porphyrin was synthesized in a similar manner. The self-condensation of the carbinol derived from 1-acyldipyrromethane **9** was catalyzed by $Yb(OTf)_3$ instead of $InCl_3$. The protected bis(hydroxymethyl)porphyrin **H_2P3-(OTBDMS)$_2$** was obtained in 7.5% yield. Deprotection with TBAF afforded the *trans*-A_2-porphyrin **H_2P3-(OH)$_2$** in 66% yield. Similar to **ZnP1-(OH)$_4$**, **H_2P3-(OH)$_2$** also showed poor solubility and was purified by washing with water, acetone, and THF.

We also explored a route in which 1-acyl-5-mesityldipyrromethane **8** was treated with TBAF to remove the TBDMS group prior to porphyrin formation. The resulting 1-(α-hydroxyacetyl)dipyrromethane **8′** was subjected to reduction, and the resulting unprotected hydroxymethyl-substituted dipyrromethane-1-carbinol was treated to self-condensation and oxidation. The desired *trans*-A_2B_2-porphyrin **H_2P2-(OH)$_2$** was obtained along with scrambled porphyrin species



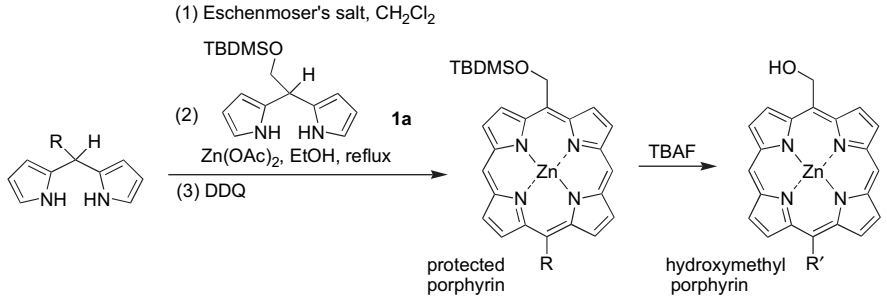
Scheme 5.

(18% total spectroscopic yield). This result establishes the importance of protecting the hydroxymethyl group during the porphyrin-forming process.

2.2.3. *trans*-AB-Porphyrins bearing one or two one-carbon substituents. *trans*-AB-Porphyrins present a compact architecture for use in various applications or further synthetic elaboration. Two *meso* positions without substituents can be derivatized for a wide variety of applications. We recently described the synthesis of *trans*-AB-porphyrins via condensation of a 1,9-bis(*N*,*N*-dimethylaminomethyl)dipyrromethane and a dipyrromethane.[59] By following such a method, three *trans*-AB-porphyrins with distinct substitution patterns were synthesized (Scheme 6). The substituents include hydroxymethyl, ethoxycarbonyl, *tert*-butoxycarbonyl, and ethynyl groups.

Thus, 1,9-bis(*N*,*N*-dimethylaminomethyl)dipyrromethanes were synthesized from the corresponding dipyrromethanes (**1b**, **1e**, and **1f**) by treatment with Eschenmoser's reagent.[60] The resulting crude products were used in the porphyrin syntheses without further purification. The condensation reaction was performed in refluxing ethanol containing $Zn(OAc)_2$ followed by oxidation with DDQ. Zinc porphyrins **ZnP4-OTBDMS**, **ZnP5-OTBDMS**, and **ZnP6-OTBDMS** were purified by chromatography and obtained in pure form but in low yield. The zinc porphyrins were then treated with TBAF to remove the TBDMS group, affording hydroxymethylporphyrins **ZnP4-OH**, **ZnP5-OH**, and **ZnP6-OH**. Porphyrin **ZnP6-OH** contains a free hydroxymethyl group and an ethynyl group owing to removal of both the TBDMS and TMS groups, respectively. The molecule ion of **ZnP6-OH** was observed by LD-MS with POPOP as the matrix. Similar to **ZnP1-(OH)$_4$**, high-resolution mass measurements for **ZnP6-OH** were not successful.

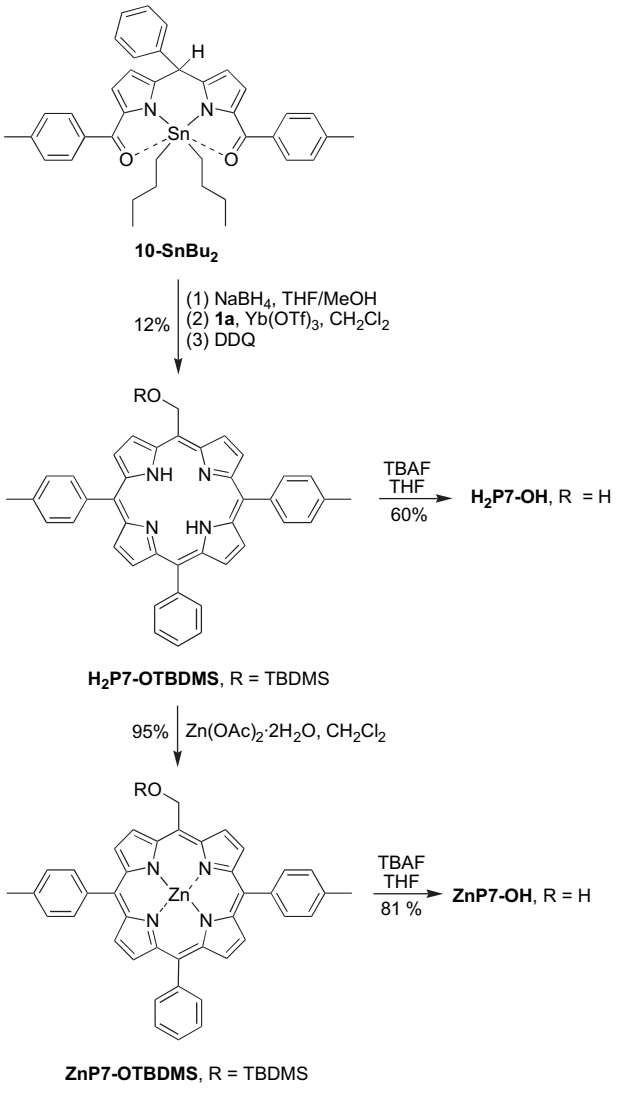
2.2.4. *trans*-AB$_2$C-Porphyrins bearing one or two one-carbon substituents. Three *trans*-AB$_2$C-porphyrins with different patterns of one-carbon substitution were synthesized following literature procedures for the condensation of a dipyrromethane-1,9-dicarbinol and a dipyrromethane.[52,61] A porphyrin with one hydroxymethyl and three aryl groups was first synthesized. Tin complex **10-SnBu$_2$**[62] was reduced by $NaBH_4$. The resulting dipyrromethane-1,9-dicarbinol was condensed with TBDMS-protected hydroxymethyldipyrromethane **1a** to afford free base porphyrin **H$_2$P7-OTBDMS** in 12% yield (Scheme 7).



dipyrromethane	R	protected porphyrin	yield	hydroxymethyl porphyrin	R′	yield
1b	*t*-BuO$_2$C—	**ZnP4-OTBDMS**	4.0%	**ZnP4-OH**	*t*-BuO$_2$C—	51%
1e	EtO$_2$C—	**ZnP5-OTBDMS**	7.5%	**ZnP5-OH**	EtO$_2$C—	66%
1f	TMS—	**ZnP6-OTBDMS**	2.4%	**ZnP6-OH**	H—	49%

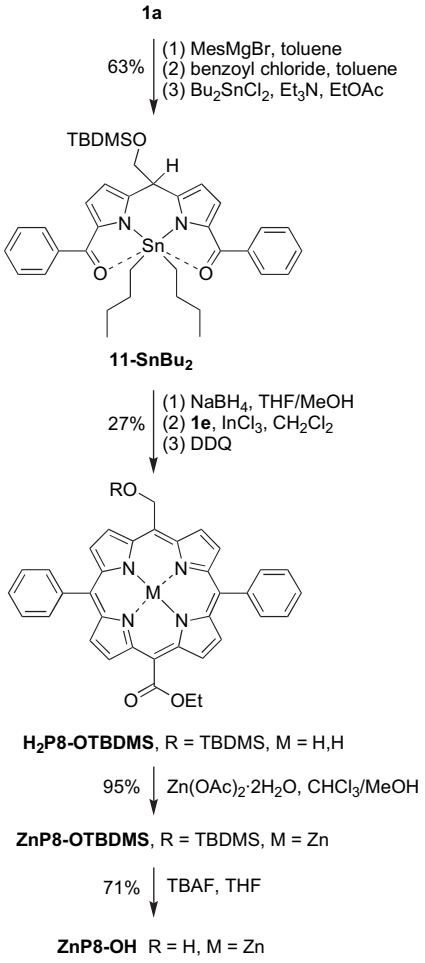
Scheme 6.

Treatment of **H_2P7-OTBDMS** with $Zn(OAc)_2 \cdot 2H_2O$ afforded **ZnP7-OTBDMS** in 95% yield. The TBDMS group of **H_2P7-OTBDMS** and **ZnP7-OTBDMS** was removed by treatment with TBAF to yield **H_2P7-OH** and **ZnP7-OH** in 60 and 81% yields, respectively. The synthesis of **H_2P7-OH** and **ZnP7-OH** was previously carried out with the unprotected 5-hydroxymethyldipyrromethane.[4] Although the yields are comparable in the two routes, the presence of a protecting group opens access to synthetic routes that are not possible with the free hydroxy group. An example is provided for porphyrins bearing two different one-carbon groups, such as **ZnP8-OH**, which bears one hydroxymethyl group and one ester group at opposite *meso* positions.



Scheme 7.

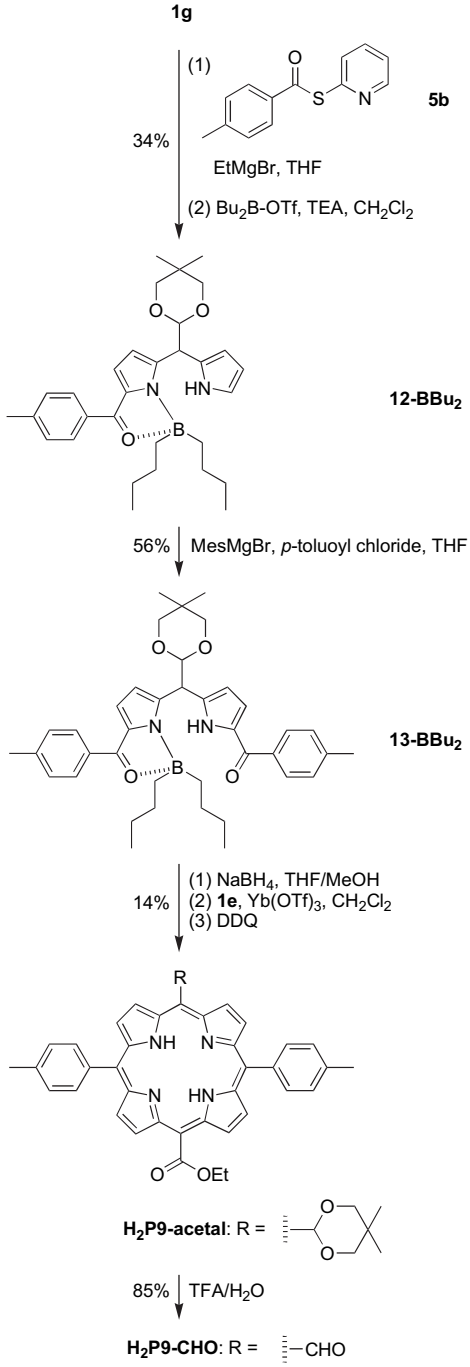
The synthesis of **ZnP8-OH** entailed the acylation of dipyrromethane **1a** (Scheme 8). Treatment of **1a** with EtMgBr and benzoyl chloride followed by tin complexation[62] with Bu_2SnCl_2 yielded tin complex **11-SnBu$_2$** in 63% yield. The latter was then reduced by $NaBH_4$. The resulting dipyrromethane-1,9-dicarbinol was condensed with ester-dipyrromethane **1e** in the presence of $InCl_3$ followed by oxidation with DDQ to afford the free base porphyrin **H_2P8-OTBDMS** in 27% yield. Metalation gave zinc porphyrin **ZnP8-OTBDMS** in 95% yield, and deprotection with TBAF yielded **ZnP8-OH** in 71% yield.



Scheme 8.

A porphyrin bearing a formyl and an ester group at trans *meso* positions was synthesized from a 1,9-diacyl-5-acetal-dipyrromethane and an ester-dipyrromethane (Scheme 9). The direct diacylation of the acetal-dipyrromethane **1g**[32] with EtMgBr and *p*-toluoyl chloride was not successful. We then tried to introduce the two 4-methylbenzoyl substituents in separate steps. Following known procedures,[32,63,64] reaction of dipyrromethane **1g** with EtMgBr followed by Mukaiyama reagent **5b**[48] gave the crude 1-*p*-toluoyl-5-(5,5-dimethyl-1,3-dioxan-2-yl)dipyrromethane, which upon dialkylboron complexation with Bu_2B–OTf gave the boron complex **12-BBu$_2$** in 34% yield. The boron complex **12-BBu$_2$** was treated with MesMgBr and *p*-toluoyl chloride to form the 1,9-diacyldipyrromethane **13-BBu$_2$** in 56% yield. The latter was reduced by $NaBH_4$ and the resulting dipyrromethane-1,9-dicarbinol was condensed with ester-dipyrromethane **1e** to afford acetal/ester-porphyrin **H_2P9-acetal**. A small amount of aldehyde-porphyrin (from deprotection of **H_2P9-acetal**) was also observed in the reaction mixture by LD-MS. The purified acetal/ester-porphyrin **H_2P9-acetal** was obtained in 14% yield. Treatment of **H_2P9-acetal** in the biphasic mixture of CH_2Cl_2 and TFA/

H_2O[32,65] gave the aldehyde/ester-porphyrin **H_2P9-CHO** in 85% yield.



Scheme 9.

2.3. Characterization

The porphyrins were generally characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, laser-desorption mass spectrometry (LD-MS), high-resolution fast atom bombardment mass spectrometry (FABMS), and absorption spectroscopy. In some cases solubility limitations precluded ^{13}C NMR spectroscopy or FABMS. The hydroxymethylporphyrins exhibited the expected resonances upon ^{1}H NMR spectroscopy, including the doublet (6.82–7.29 ppm) for the methylene protons and the triplet (5.14–6.31 ppm) for the hydroxyl proton. One outlier was the resonance of the methylene at 6.18 ppm for *trans*-hydroxymethyl/ethynyl-porphyrin **ZnP6-OTBDMS**. Such multiplets were clearly observed when deuterated THF or DMSO was used as solvent, but were less distinguishable with $CDCl_3$. The carbon of the hydroxymethyl group (TBDMS-protected or free) gave a characteristic resonance in the region 61–66 ppm upon ^{13}C NMR spectroscopy. The porphyrins that contained an ethyl ester moiety also gave a resonance in the same region.

2.4. Solubility

Most of the TBDMS-protected hydroxymethylporphyrins are soluble in CH_2Cl_2. Two exceptions were **ZnP4-OTBDMS** and **ZnP5-OTBDMS**, which are zinc *trans*-AB-porphyrins bearing a protected hydroxymethyl group and an ester group. Such porphyrins were soluble in THF. In general, the presence of the ester group tends to decrease the solubility of the porphyrins in solvents such as CH_2Cl_2. The unprotected hydroxymethylporphyrins generally required a more polar solvent such as DMF or THF for dissolution. Indeed, **ZnP8-OH**, which bears a hydroxymethyl group, an ester group, and an apical zinc site in a linear alignment, is soluble in THF but not in CH_2Cl_2. It has been reported that in bacteriochlorophyll *c*, the hydroxymethyl group, the carbonyl group, the central zinc ion and the linear alignment of the three elements are essential for self-assembly.[6,7] The low solubility of porphyrins such as **ZnP8-OH** in less polar solvents likely stems from analogous self-assembly, as reported by Balaban and co-workers for compounds **I** and **II**.

3. Conclusions

A set of rational synthetic methods has been explored to gain access to *meso*-substituted porphyrins bearing distinct patterns of hydroxymethyl and related one-carbon oxygenic substituents. The patterns include A_4-, *trans*-A_2-, *trans*-A_2B_2-, *trans*-AB-, and *trans*-AB_2C-porphyrins where A is hydroxymethyl. For porphyrins bearing exclusively one-carbon units such as A_4-, *trans*-AB-, and *trans*-A_2-porphyrins, the current rational methods afforded low yields (<10%). On the other hand, *trans*-AB_2C-porphyrins bearing two different one-carbon groups (hydroxymethyl/ester, formyl/ester) were obtained in somewhat better yields (14–27%). While much remains to be done in porphyrin chemistry to increase yields in a global manner, the existing routes provide access in a rational manner to porphyrins bearing substituent patterns of interest across a range of fields encompassing light-harvesting, life sciences, and materials chemistry. The work presented herein also may provide the foundation for extension to the synthesis of chlorins and bacteriochlorins that bear similar substituents.

4. Experimental section

4.1. General methods

All ^{1}H NMR spectra (400 MHz) and ^{13}C NMR spectra (100 MHz) were recorded in $CDCl_3$ unless noted otherwise.

Mass spectra of porphyrins were obtained by high-resolution FABMS or by LD-MS, the latter without or with a matrix.[53] Absorption spectra were collected in CH_2Cl_2 at room temperature unless noted otherwise. Melting points are uncorrected. Silica gel (40 μm average particle size) and alumina (80–200 mesh) were used for column chromatography. All reagents were used as received. Dry THF was obtained by distillation over Na/benzophenone.

4.2. Noncommercial compounds

Dipyrromethanes **1c**,[43] **1d**,[44] **1f**,[45] and **1g**[32] were prepared using a literature method that entails reaction of an aldehyde in 100 equiv of pyrrole containing a Lewis acid (e.g., $InCl_3$).[44] Dipyrromethane **1e**,[2] Mukaiyama reagent **5b**,[48] and the diacyldipyrromethane–tin complex **10-SnBu$_2$**[62] were prepared as described in the literature.

4.3. Synthesis of precursors

4.3.1. 5-(*tert*-Butyldimethylsiloxymethyl)dipyrromethane (1a). Following a literature procedure[44] with modification, a mixture of **2** (12.4 g, 50.0 mmol) and pyrrole (347 mL, 5.00 mol) was treated with $InCl_3$ (1.11 g, 5.00 mmol) at 60 °C under argon for 2 h. The reaction was quenched with TEA (5 mL) and stirred for 15 min at room temperature. The reaction mixture was then concentrated. Chromatography [silica, hexanes/ethyl acetate (4:1)] yielded a light yellow oil (7.5 g, 52%). ^{1}H NMR δ 0.04 (s, 6H), 0.91 (s, 9H), 4.06 (d, J=5.2 Hz, 2H), 4.24 (t, J=5.2 Hz, 1H), 5.99 (m, 2H), 6.12–6.17 (m, 2H), 6.69 (m, 2H), 8.40–8.60 (br, 2H); ^{13}C NMR δ −5.3, 18.4, 26.2, 40.1, 67.7, 106.1, 108.3, 117.0, 131.8; ESI-TOF obsd 313.17076, calcd 313.17066 [(M+Na)$^+$, M=$C_{16}H_{26}N_2OSi$]. Anal. Calcd for $C_{16}H_{25}N_2OSi$: C, 66.16; H, 9.02; N 9.64. Found: C, 66.12; H, 9.16; N, 9.61.

4.3.2. 5-*tert*-Butoxycarbonyldipyrromethane (1b). Following a literature procedure[47] with modification, a solution of **3** (2.50 g, 14.1 mmol) in anhydrous DMSO (30 mL) was treated with anhydrous sodium acetate (1.00 g, 12.2 mmol) at room temperature for 20 min. The reaction mixture was poured into a mixture of brine and ice (150 mL). The mixture was extracted with ether (10×30 mL). The organic layers were combined, washed with saturated aqueous Na_2CO_3, and concentrated. The resulting oil was dissolved in CH_2Cl_2 and washed with brine. The organic layer was separated, dried (Na_2SO_4), and concentrated to yield crude *tert*-butyl glyoxalate as a thick colorless oil (1.36 g). The latter was dissolved in CH_2Cl_2 (50 mL). Pyrrole (17.4 mL, 250 mmol) was added to the solution. The mixture was degassed with argon for 10 min. TFA (77 μL, 1.0 mmol) was added. The mixture was stirred at room temperature under argon for 15 h. TEA (1 mL) was added to the mixture. Stirring was continued for 30 min. The reaction mixture was poured into CH_2Cl_2 (100 mL). The mixture was washed with water and brine, dried (Na_2SO_4), and concentrated. Chromatography [silica, hexanes/CH_2Cl_2 (1:1)] yielded a light yellow oil, which was contaminated with residual pyrrole. The crude sample was concentrated and entrained with hexanes (3×20 mL). Volatile materials were removed to yield an off-white powder (0.64 g, 18%): mp 75–77 °C. ^{1}H NMR δ 1.49 (s, 9H), 4.99 (s, 1H), 6.06–6.09 (m, 2H), 6.13–6.16 (m, 2H), 6.70–6.72 (m, 2H), 8.44 (br, 2H); ^{13}C NMR δ 28.2, 44.8, 82.5, 107.0, 108.6, 118.0, 127.5, 170.9. Anal. Calcd for $C_{14}H_{18}N_2O_2$: C, 68.27; H, 7.37; N 11.37. Found: C, 68.30; H, 7.40, N 11.31.

4.3.3. 1-(*tert*-Butyldimethylsiloxy)-2,2-diethoxyethane (2). Following a literature procedure[46] with modification, a solution of glycolaldehyde diethyl acetal (6.70 g, 50.0 mmol) in DMF (150 mL) was treated with *tert*-butyldimethylsilyl chloride (18.8 g, 125 mmol) and imidazole (17.0 g, 250 mmol) at room temperature under argon for 14 h. The reaction mixture was poured into water (5 mL). The mixture was extracted with ethyl acetate. The organic layer was washed with water and brine, dried (Na_2SO_4), and concentrated to yield a light yellow liquid (12.4 g, quantitative). ^{1}H NMR δ 0.07 (s, 6H), 0.90 (s, 9H), 1.22 (t, J=7.2 Hz, 6H), 3.56–3.76 (m, 4H), 3.63 (d, J=5.2 Hz, 2H), 4.49 (t, J=5.2 Hz, 1H); ^{13}C NMR δ −5.1, 15.6, 18.6, 26.1, 63.0, 64.8, 103.2; ESI-MS obsd 271.16894, calcd 271.16999 [(M+Na)$^+$, M=$C_{12}H_{28}NO_3Si$].

4.3.4. *tert*-Butoxycarbonylmethyl nitrate (3). Following a literature procedure,[47] a solution of *tert*-butyl bromoacetate (4.60 g, 23.6 mmol) in anhydrous acetonitrile (20 mL) was treated with $AgNO_3$ (7.31 g, 47.2 mmol) at room temperature in the dark for 48 h. The solvent was removed. The resulting residue was extracted with Et_2O (3×50 mL). The Et_2O extracts were combined, washed with water and brine, dried (Na_2SO_4), and concentrated to yield a colorless oil (3.4 g, 82%). ^{1}H NMR δ 1.49 (s, 9H), 4.77 (s, 2H); ^{13}C NMR δ 28.1, 67.8, 84.1, 165.0. Anal. Calcd for $C_6H_{11}NO_5$: C 40.69, H 6.26, N 7.91. Found: C 40.95, H 6.41, N 7.80.

4.3.5. (*tert*-Butyldimethylsiloxy)acetic acid (4). Following literature procedures,[49,50] a solution of ethyl glycolate (5.21 g, 50.0 mmol) and imidazole (4.08 g, 60.0 mmol) in DMF (50 mL) was treated with *tert*-butyldimethylsilyl chloride (9.04 g, 60.0 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. Water (50 mL) was added to the reaction mixture. The mixture was extracted with ether (2×100 mL). The combined organic layer was washed with water (2×100 mL), dried (Na_2SO_4), and concentrated in vacuo to yield a viscous liquid. The resulting ester was dissolved in 30 mL of THF. A solution of KOH (2.95 g, 52.5 mmol) in MeOH/water (1:2, 18 mL) was slowly added to the solution at −10 °C. The reaction mixture was allowed to warm up to 5 °C over 30 min and diluted with 175 mL of water and ether (125 mL). The mixture was acidified with aqueous HCl (5.5 mL, 55 mmol) at 0 °C and extracted with ether (3×125 mL). The combined organic layer was washed with water, dried (Na_2SO_4), and concentrated to yield a white solid (5.2 g, 55%): mp 48–49 °C. ^{1}H NMR (300 MHz) δ 0.15 (s, 6H), 0.94 (s, 9H), 4.22 (s, 2H), the carboxylic acid proton was not observed; ^{13}C NMR δ −5.3, 18.5, 25.9, 61.6, 175.3. Anal. Calcd for $C_8H_{18}O_3Si$: C, 50.49; H, 9.53. Found: C, 50.40; H, 9.56.

4.3.6. *S*-2-Pyridyl (*tert*-butyldimethylsiloxy)thioacetate (5a). Following a literature procedure,[51] a solution of **4** (3.81 g, 20.0 mmol) in anhydrous THF (40 mL) was treated with 2,2′-dipyridyl disulfide (8.80 g, 39.9 mmol) and

triphenylphosphine (10.5 g, 40.0 mmol) at room temperature under argon for 24 h. The reaction mixture was concentrated. Chromatography [silica, hexanes/ethyl acetate (9:1) then hexanes/ethyl acetate (3:2)] yielded a yellow solid (2.4 g, 43%): mp 50–52 °C. ^{1}H NMR δ 0.18 (s, 6H), 0.99 (s, 9H), 4.38 (s, 2H), 7.28–7.34 (m, 1H), 7.58–7.62 (m, 1H), 7.72–7.78 (m, 1H), 8.64–8.68 (m, 1H); ^{13}C NMR δ −5.6, 18.2, 25.7, 68.9, 123.4, 130.6, 137.1, 150.5, 151.6, 200.3; FABMS obsd 284.1126, calcd 284.1141 [(M+H)$^+$, M=$C_{13}H_{21}NO_2SSi$].

4.3.7. 2-(*tert*-Butyldimethylsiloxyacetyl)pyrrole (6). Following a general procedure,[51] a solution of EtMgBr (1.0 M solution in THF, 17 mL, 17 mmol) was slowly added to a stirred solution of pyrrole (1.17 mL) in dry THF (17.2 mL) under Ar. The mixture was stirred at room temperature for 10 min and then cooled to −78 °C. A solution of **5a** (2.41 g, 8.49 mmol) in THF (8.5 mL) was quickly added to the mixture. The reaction mixture was stirred at −78 °C for 20 min and quenched with saturated aqueous NH_4Cl. The mixture was extracted with CH_2Cl_2. The organic layer was separated, washed with water, dried (Na_2SO_4), and concentrated. Chromatography [silica, hexanes/CH_2Cl_2 (1:4)] yielded a dark purple oil (0.77 g, 38%). ^{1}H NMR δ 0.14 (s, 6H), 0.96 (s, 9H), 4.72 (s, 2H), 6.27–6.29 (m, 1H), 7.06–7.08 (m, 2H), 10.20–10.60 (br s, 1H); ^{13}C NMR δ −5.2, 18.6, 26.0, 67.0, 110.7, 117.0, 125.5, 129.6 188.6; FABMS obsd 240.1425, calcd 240.1420 [(M+H)$^+$, M=$C_{12}H_{21}NO_2Si$]. Anal. Calcd for $C_{12}H_{21}NO_2Si$: C, 60.21; H, 8.84; N, 5.85. Found: C, 60.26; H, 8.81; N, 5.84.

4.3.8. 1-[(*tert*-Butyldimethylsiloxy)acetyl]-5-(*tert*-butyldimethylsiloxymethyl)dipyrromethane (7). Following a literature procedure,[48] a solution of **1a** (265 mg, 0.914 mmol) in dry THF (1 mL) was treated with EtMgBr (1.0 M in THF, 2.28 mL, 2.28 mmol) at room temperature under argon for 15 min. The reaction mixture was cooled to −78 °C. A solution of **5a** (285 mg, 1.01 mmol) in dry THF (1 mL) was slowly added. The reaction mixture was stirred at −78 °C for 10 min, and then allowed to warm to room temperature. Stirring was continued for 45 min. Saturated aqueous NH_4Cl solution was added. The mixture was extracted with ethyl acetate. The organic layer was separated, dried (Na_2SO_4), and concentrated. Chromatography [silica, CH_2Cl_2/ethyl acetate (49:1)] yielded a viscous yellow oil. The oil turned to a yellow solid upon standing (290 mg, 69%): mp 121–122 °C (blackened at 118 °C). ^{1}H NMR (300 MHz) δ 0.03 (s, 6H), 0.11 (s, 6H), 0.90 (s, 9H), 0.93 (s, 9H), 4.05–4.10 (m, 2H), 4.41–4.47 (m, 1H), 4.61 (s, 2H), 5.96–6.02 (m, 1H), 6.02–6.08 (m, 1H), 6.11–6.18 (m, 1H), 6.67–6.74 (m, 1H), 6.95–7.02 (m, 1H), 8.65 (br, 1H), 9.63 (br, 1H); ^{13}C NMR (75 MHz) δ −5.4, −5.1, 18.4, 18.7, 26.1, 26.2, 40.5, 67.1, 67.6, 106.7, 108.6, 109.3, 117.3, 117.5, 129.4, 130.2, 139.6, 187.6. Anal. Calcd for $C_{24}H_{42}N_4O_3Si_2$: C, 62.29; H, 9.15; N, 6.05. Found: C, 62.33; H, 9.28, N, 6.01.

4.3.9. 1-[(*tert*-Butyldimethylsiloxy)acetyl]-5-mesityldipyrromethane (8). Following the procedure for **7**, the reaction of **1c** (630 mg, 2.38 mmol) and Mukaiyama reagent **5a** (754 mg, 2.66 mmol) followed by chromatography [silica, CH_2Cl_2 then CH_2Cl_2/ethyl acetate (9:1)] yielded a brown solid (0.77 g, 74%): mp 40–42 °C. ^{1}H NMR δ 0.10 (s, 6H), 0.91 (s, 9H), 2.05 (s, 6H), 2.28 (s, 3H), 4.60 (s, 2H), 5.90 (s, 1H), 6.06–6.10 (m, 2H), 6.18–6.21 (m, 1H), 6.65–6.68 (m, 1H) 6.88 (s, 2H), 7.02–7.05 (m, 1H), 7.74–7.84 (br, 1H), 9.06–9.22 (br, 1H); ^{13}C NMR δ −5.4, 18.4, 20.6, 20.8, 25.6, 25.8, 38.5, 67.3, 107.1, 108.9, 109.6, 116.8, 117.7, 128.9, 130.5, 133.0, 137.2, 137.4, 140.0, 187.8. Anal. Calcd for $C_{26}H_{36}N_2O_2Si$: C, 71.51; H, 8.31; N, 6.42. Found: C, 71.59; H, 8.09; N, 6.25.

4.3.10. 1-(*tert*-Butyldimethylsiloxy)acetyldipyrromethane (9). Following the procedure for **7**, the reaction of **1d** (0.29 g, 2.0 mmol) and Mukaiyama reagent **5a** (0.62 g, 2.2 mmol) followed by chromatography [silica, CH_2Cl_2 then CH_2Cl_2/ethyl acetate (10:1)] yielded a brown solid (0.54 g, 85%): mp 64–66 °C. ^{1}H NMR δ 0.1 (s, 6H), 0.94 (s, 9H), 4.10 (s, 2H), 4.75 (s, 2H), 5.99–6.02 (m, 1H), 6.10–6.13 (m, 2H), 6.61–6.64 (m, 1H), 6.96–6.99 (m, 1H), 9.15–9.25 (br s, 1H), 10.50–10.60 (br s, 1H); ^{13}C NMR δ −5.0, 19.0, 26.3, 66.2, 106.2, 106.3, 108.4, 109.8, 109.9, 117.4, 119.2, 128.4, 141.6, 188.0. Anal. Calcd for $C_{17}H_{26}N_2O_2Si$; C, 64.11; H, 8.23; N, 8.80. Found: C, 64.10; H, 8.18; N, 8.69.

4.3.11. Dibutyl[5,10-dihydro-1,9-dibenzoyl-5-(*tert*-butyldimethylsiloxymethyl)dipyrrinato]tin(IV) (11-SnBu$_2$). Following a literature procedure,[62] EtMgBr (1.0 M in THF, 10 mL, 10 mmol) was added dropwise to a solution of **1a** (700 mg, 2.41 mmol) in toluene (5 mL) in an ice bath. The reaction was stirred at 0 °C for 30 min. Benzoyl chloride (590 μL, 5.06 mmol) was added dropwise, and the mixture was stirred at 0 °C for 1 h. The reaction mixture was poured into a mixture of saturated aqueous NH_4Cl solution and ethyl acetate. The organic layer was separated, washed with brine, dried (Na_2SO_4), and concentrated. The resulting yellow oil was dissolved in ethyl acetate (20 mL) and treated with TEA (1 mL) and Bu_2SnCl_2 (733 mg, 2.41 mmol) at room temperature for 30 min. The reaction mixture was washed with water and brine, dried (Na_2SO_4), and concentrated. Chromatography [silica, hexanes/CH_2Cl_2 (1:2 with 0.5% TEA)] yielded a yellow viscous oil (1.1 g, 63%). ^{1}H NMR δ −0.12 (s, 6H), 0.62 (t, J=7.2 Hz, 3H), 0.85 (s, 9H), 0.94–1.40 (m, 3H), 1.12–1.20 (m, 2H), 1.30–1.38 (m, 4H), 1.56–1.64 (m, 4H), 1.76–1.82 (m, 2H), 3.79 (d, J=7.2 Hz, 2H), 4.46 (d, J=7.2 Hz, 1H), 6.45 (d, J=4.0 Hz, 2H), 7.12 (d, J=4.0 Hz, 2H), 7.48–7.60 (m, 6H), 7.88–7.94 (m, 4H); ^{13}C NMR δ −5.6, 13.71, 13.86, 18.6, 23.2, 25.6, 25.9, 26.1, 26.8, 27.2, 27.8, 43.7, 71.3, 116.1, 123.9, 128.6, 129.2, 131.7, 136.3, 137.9, 150.1, 184.6; FABMS obsd 731.2721, calcd 730.2613 ($C_{38}H_{50}N_2O_3SiSn$). Anal. Calcd for $C_{38}H_{50}N_2O_3SiSn$: C, 62.69; H, 7.06; N, 3.83. Found: C, 62.55; H, 6.91; N, 3.84.

4.3.12. 10-(Dibutylboryl)-1-*p*-toluoyl-5-(5,5-dimethyl-1,3-dioxan-2-yl)dipyrromethane (12-BBu$_2$). Following a general procedure,[63] a solution of **1g** (260 mg, 1.00 mmol) in THF (1 mL) was treated with EtMgBr (1.0 M in THF, 2.5 mL, 2.5 mmol) at −78 °C for 10 min. A solution of **5b** (230 mg, 1.00 mmol) in THF (1 mL) was added dropwise to the reaction mixture. The mixture was stirred at room temperature for 10 min. Saturated aqueous NH_4Cl solution was added, and the reaction mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried (Na_2SO_4), and concentrated. The resulting

solid was dissolved in CH_2Cl_2 (2 mL) and treated with TEA (335 μL, 2.40 mmol) and Bu_2B–OTf (2.00 mL, 2.00 mmol) at room temperature for 30 min. The solvent was removed under reduced pressure. Chromatography [silica, hexanes/CH_2Cl_2 (1:4)] yielded a yellow-greenish oil (0.17 g, 34%). ^{1}H NMR δ 0.50–1.30 (m, 24H), 2.43 (s, 3H), 3.40–3.48 (m, 2H), 3.63–3.69 (m, 2H), 4.54 (d, J=3.6 Hz, 1H), 4.79 (d, J=3.6 Hz, 1H), 5.88–5.93 (m, 1H), 6.07–6.12 (m, 1H), 6.64 (d, J=4.4 Hz, 1H), 6.70–6.74 (m, 1H), 7.22 (d, J=4.4 Hz, 1H), 7.32 (d, J=8.0 Hz, 2H), 8.09 (d, J=8.0 Hz, 2H), 8.95 (br, 1H); ^{13}C NMR δ 14.3, 14.5, 21.9, 22.0, 22.8 (br), 23.2 (br), 23.28, 26.2, 26.4, 27.0, 27.2, 30.4, 42.9, 77.51, 77.56, 103.1, 108.03, 108.07, 117.3, 117.6, 119.8, 128.1, 128.4, 129.86, 129.90, 133.8, 145.1, 147.1, 175.4; LD-MS obsd 500.3; FABMS 503.3426, calcd 503.3445 [(M+H)$^+$, M=$C_{31}H_{43}BN_2O_3$].

4.3.13. 10-(Dibutylboryl)-1,9-di-*p*-toluoyl-5-(5,5-dimethyl-1,3-dioxan-2-yl)dipyrromethane (13-BBu$_2$). Following a general precedure,[64] a solution of **12-BBu$_2$** (172 mg, 343 μmol) in THF (343 μL) was treated with MesMgBr (1.0 M in THF, 0.69 mL, 0.69 mmol) at room temperature for 5 min. A solution of *p*-toluoyl chloride (99.7 μL, 754 μmol) in THF was added dropwise to the mixture. The reaction was stirred at room temperature for 10 min. Saturated aqueous NH_4Cl solution was added and the reaction mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried (Na_2SO_4), and concentrated. Chromatography (silica, CH_2Cl_2) yielded an orange solid (0.12 g, 56%). ^{1}H NMR δ 0.50–1.30 (m, 24H), 2.41 (s, 3H), 2.47 (s, 3H), 3.40–3.52 (m, 2H), 3.68–3.78 (m, 2H), 4.59 (d, J=4.0 Hz, 1H), 4.83 (d, J=4.0 Hz, 1H), 6.00–6.06 (m, 1H), 6.70 (d, J=4.0 Hz, 1H), 6.73–6.78 (m, 1H), 7.22–7.28 (m, 3H), 7.35 (d, J=8.0 Hz, 2H), 7.80 (d, J=8.0 Hz, 2H), 8.12 (d, J=8.0 Hz, 2H), 10.1 (br, 1H); ^{13}C NMR δ 14.3, 14.5, 21.8, 21.9, 22.1, 22.7 (br), 23.1 (br), 23.3, 26.2, 26.4, 27.14, 27.21, 30.4, 43.0, 77.67, 77.76, 102.4, 111.4, 117.7, 119.3, 119.8, 128.0, 129.11, 129.24, 130.02, 130.04, 131.1, 134.1, 126.1, 136.4, 142.3, 145.1, 145.5, 176.4, 184.3; FABMS obsd 621.3864, calcd 621.3864 [(M+H)$^+$, M=$C_{39}H_{49}BN_2O_4$].

4.4. Synthesis of porphyrins

4.4.1. Synthesis of A$_4$-, *trans*-A$_2$ or *trans*-A$_2$B$_2$-porphyrins from 1-acyldipyrromethanes, exemplified for 5,10,15,20-tetrakis(*tert*-butyldimethylsiloxymethyl)porphyrin [H$_2$P1-(OTBDMS)$_4$]. Following a literature procedure,[48,57] a solution of **7** (206 mg, 0.446 mmol) in dry THF (9 mL) was treated with $NaBH_4$ (421 mg, 11.2 mmol) at room temperature. A sample of MeOH (3 mL) was added dropwise. The reaction mixture was stirred for 1 h at room temperature. The reaction mixture was poured into saturated aqueous NH_4Cl solution. The mixture was extracted with ethyl acetate. The organic layer was separated, washed with water, and dried (Na_2SO_4). The solvents were removed to yield the dipyrromethane-1-carbinol as a brownish oil. The dipyrromethane-1-carbinol was dissolved in CH_2Cl_2 (90 mL). The solution was treated with $InCl_3$ (49.3 mg, 0.223 mmol) at room temperature under argon for 1 h. A sample of DDQ (75.9 mg, 0.335 mmol) was added. The reaction mixture was stirred for 15 min. A sample of TEA (5 mL) was added. The mixture was stirred for 5 min. The reaction mixture was concentrated. The resulting black solid was passed through a silica pad with CH_2Cl_2 as eluant. The filtrate was concentrated. Chromatography [silica, hexanes/CH_2Cl_2 (1:4)] yielded a red solid (15.0 mg, 8%). ^{1}H NMR δ −3.07 to −3.03 (br, 2H), 0.19 (s, 24H), 0.96 (s, 36H), 6.97 (s, 8H), 9.65 (s, 8H); ^{13}C NMR δ −4.4, 18.6, 26.2, 64.8, 115.8 (the α and β carbons were not observed presumably due to tautomerization); LD-MS obsd 886.3; FABMS obsd 886.5059, calcd 886.5100 ($C_{49}H_{78}N_4O_4Si_4$); λ_{abs} 414, 512, 589, 644 nm.

4.4.2. Zinc metalation of a free base porphyrin, exemplified for Zn(II)-5,10,15,20-tetrakis(*tert*-butyldimethylsiloxymethyl)porphyrin [ZnP1-(OTBDMS)$_4$]. Following a literature procedure[4] with modification, a solution of **H$_2$P1-(OTBDMS)$_4$** (14.0 mg, 15.8 μmol) in CH_2Cl_2/MeOH (4:1, 5 mL) was treated with $Zn(OAc)_2$ (14.4 mg, 78.9 μmol) at room temperature for 30 min. The reaction mixture was concentrated. Chromatography (silica, CH_2Cl_2) yielded a red solid (12.0 mg, 80%). ^{1}H NMR (300 MHz) δ 0.16 (s, 24H), 0.96 (s, 36H), 6.89 (s, 8H), 9.61 (s, 8H); ^{13}C NMR (75 MHz) δ −4.5, 18.7, 26.3, 64.9, 116.1, 129.6, 150.1; LD-MS obsd 948.3; FABMS obsd 948.4158, calcd 948.4235 ($C_{49}H_{76}N_4O_4Si_4Zn$); λ_{abs} 416, 548 nm.

4.4.3. TBDMS removal with TBAF (method A), exemplified for Zn(II)-5,10,15,20-tetrakis(hydroxymethyl)porphyrin [ZnP1-(OH)$_4$]. Following a literature procedure[58] with modification, a solution of **ZnP1-(OTBDMS)$_4$** (14.9 mg, 15.7 μmol) in THF (3 mL) was treated with TBAF (1.0 M in THF, 157 μL, 157 μmol) at room temperature for 2 h. The reaction mixture was concentrated to dryness. The resulting dark solid was suspended in acetone and filtered through a Buchner filter. The filtered material was washed with water, THF, and acetone. The resulting purple solid was washed from the filter by DMF. Removal of DMF under reduced pressure yielded a purple solid (4.9 mg, 63%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.10 (t, J=5.2 Hz, 4H), 6.84 (d, J=5.2 Hz, 8H), 9.80 (s, 8H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 62.6, 116.8, 129.5, 149.6; LD-MS (POPOP) obsd 492.5, calcd 492.1 ($C_{24}H_{20}N_4O_4Zn$). A solution of the title compound in DMSO was diluted in THF. The diluted solution was subjected to absorption measurement; λ_{abs}=420, 556 nm.

4.4.4. 5,15-Bis(*tert*-butyldimethylsiloxymethyl)-10,20-dimesitylporphyrin [H$_2$P2-(OTBDMS)$_2$]. Following the procedure for **H$_2$P1-(OTBDMS)$_4$**, the self-condensation of the carbinol derived from 1-acyldipyrromethane **8** (88 mg, 0.20 mmol) followed by chromatography (silica, CH_2Cl_2) yielded a purple solid (11 mg, 13%). ^{1}H NMR δ −2.90 to −2.70 (br, 2H), 0.21 (s, 12H), 0.94 (s, 18H), 1.82 (s, 12H), 2.65 (s, 6H), 6.93 (s, 4H), 7.29 (s, 4H), 8.76 (d, J=4.7 Hz, 4H), 9.5 (d, J=4.7 Hz, 4H); ^{13}C NMR δ −4.5, 18.7, 21.8, 26.2, 29.9, 64.4, 115.6, 118.0, 127.9, 137.9, 138.9, 139.7 (the α and β carbons were not observed presumably due to tautomerization); LD-MS obsd 834.6; FABMS obsd 834.4772, calcd 834.4724 ($C_{52}H_{66}N_4O_2Si_2$); λ_{abs} (toluene) 418, 514 nm; λ_{em} (toluene) 650, 725 nm.

4.4.5. TBDMS removal with TBAF (method B), exemplified for 5,15-bis(hydroxymethyl)-10,20-dimesitylpor-

phyrin [H_2P2-(OH)$_2$]. Following a literature procedure[58] with modification, a solution of **H_2P2-(OTBDMS)$_2$** (7.0 mg, 8.3 μmol) in THF (2.0 mL) was treated with TBAF (1.0 M in THF, 80 μL, 80 μmol) at room temperature under argon for 9 h. The reaction was quenched with water. The mixture was extracted with CH_2Cl_2 and with ethyl acetate. The combined organic extract was dried (Na_2SO_4) and concentrated to yield the crude product as a solid. Chromatography [silica, CH_2Cl_2 then CH_2Cl_2/ethyl acetate (9:1)] yielded a purple solid (5.0 mg, quantitative). ^{1}H NMR (THF-d_8) δ −2.75 to −2.58 (br, 2H), 1.83 (s, 12H), 2.64 (s, 6H), 5.26 (t, J=5.6 Hz, 2H), 6.82 (d, J=5.6 Hz, 4H), 7.34 (s, 4H), 8.71 (d, J=4.4 Hz, 4H), 9.67 (d, J=4.4 Hz, 4H); LD-MS obsd 606.1; FABMS obsd 606.3017, calcd 606.2995 ($C_{40}H_{38}N_4O_2$); λ_{abs} 415, 513, 544, 589 nm; λ_{em} 645, 720 nm.

4.4.6. 5,15-Bis(*tert*-butyldimethylsiloxymethyl)porphyrin [H_2P3-(OTBDMS)$_2$]. Following the procedure for **H_2P1-(OTBDMS)$_4$**, the self-condensation of the carbinol derived from **9** (0.51 g, 1.6 mmol) followed by chromatography (silica, CH_2Cl_2) yielded a purple solid (36 mg, 7.5%). ^{1}H NMR (300 MHz) δ −3.35 to −2.85 (br, 2H), 0.19 (s, 12H), 0.97 (s, 18H), 7.00 (s, 4H), 9.41 (d, J=4.4 Hz, 4H), 9.69 (d, J=4.4 Hz, 4H), 10.21 (s, 2H); ^{13}C NMR (75 MHz) δ −4.4, 18.7, 26.2, 64.2, 105.1, 115.6, 128.7, 132.2, 145.1, 147.9; LD-MS obsd 598.3; FABMS obsd 598.3158, calcd 598.3159 ($C_{34}H_{46}N_4O_2Si_2$); λ_{abs} 402, 500, 532, 573 nm.

4.4.7. 5,15-Bis(hydroxymethyl)porphyrin [H_2P3-(OH)$_2$]. Following the procedure for **H_2P1-(OH)$_4$**, the reaction of **H_2P2-(OTBDMS)$_2$** (12.3 mg, 20.5 μmol) yielded a purple solid (5.0 mg, 66%). ^{1}H NMR (DMSO-d_6) δ −3.39 (br, 2H), 6.31 (t, J=5.8 Hz, 2H), 6.87 (d, J=5.8 Hz, 4H), 9.69 (d, J=4.7 Hz, 4H), 9.94 (d, J=4.7 Hz, 4H), 10.5 (s, 2H); LD-MS obsd 370.2; ^{13}C NMR (DMSO-d_6) δ 61.4, 104.6, 116.6, 129.1, 132.1, 144.2, 147.1; LD-MS 370.2; ESI-TOF obsd 371.15025, calcd 371.15020.1430 [(M+H)$^+$, M=$C_{22}H_{18}N_4O_2$]. A solution of the title compound in DMSO was diluted in THF. The diluted solution was subjected to absorption measurement; λ_{abs} 401, 499, 531, 574 nm.

4.4.8. Synthesis of *trans*-AB-porphyrins from 1,9-(*N*,*N*-dimethylaminomethyl)dipyrromethanes and dipyrromethanes, exemplified for Zn(II)-5-(*tert*-butoxycarbonyl)-15-(*tert*-butyldimethylsiloxymethyl)porphyrin [ZnP4-OTBDMS]. Following a literature procedure,[59] a solution of **1b** (460 mg, 1.87 mmol) in anhydrous CH_2Cl_2 (25 mL) was treated with Eschenmoser's salt (692 mg, 3.74 mmol) at room temperature for 3 h. Saturated aqueous $NaHCO_3$ (20 mL) was added to the reaction mixture. The organic layer was separated, washed with brine, dried (Na_2SO_4), and concentrated to give a thick orange oil. The crude product was dissolved in EtOH (178 mL). Dipyrromethane **1a** (543 mg, 1.87 mmol) was added to the solution. The solution was treated with anhydrous $Zn(OAc)_2$ (3.43 g, 18.7 mmol) and refluxed exposed to air for 5 h. The mixture was cooled to room temperature. DDQ (1.28 g, 5.61 mmol) was added to the reaction mixture. The reaction mixture was stirred for 20 min. TEA (1 mL) was then added. The reaction mixture was concentrated. The crude product was filtered through a silica pad with CH_2Cl_2 as the eluant. After a fast-moving orange fraction was discarded, the eluate was collected and concentrated. Chromatography [silica, hexanes/CH_2Cl_2 (4:1)] yielded a purple solid (46 mg, 4.0%). ^{1}H NMR (THF-d_8) δ 0.22 (s, 6H), 0.91 (s, 9H), 2.10 (s, 9H), 7.21 (s, 2H), 9.47–9.49 (m, 4H), 9.64 (d, J=4.4 Hz, 2H), 9.88 (d, J=4.4 Hz, 2H), 10.28 (s, 2H); LD-MS obsd 617.0; FABMS obsd 616.1873, calcd 616.1848 ($C_{32}H_{36}N_4SiO_3Zn$); λ_{abs} (toluene) 409, 538, 575.

4.4.9. Zn(II)-5-(*tert*-butoxycarbonyl)-15-hydroxymethylporphyrin (ZnP4-OH). Following the procedure for **H_2P2-(OH)$_2$**, the reaction of **ZnP4-OTBDMS** (38 mg, 62 μmol) followed by chromatography [silica, CH_2Cl_2/ethyl acetate (9:1)] yielded a purple solid (16 mg, 51%). ^{1}H NMR (THF-d_8) δ 2.11 (s, 9H), 5.23 (t, J=5.6 Hz, 1H), 7.00 (d, J=5.6 Hz, 2H), 9.48 (d, J=4.4 Hz, 4H), 9.65 (d, J=4.4 Hz, 2H), 9.93 (d, J=4.4 Hz, 2H), 10.27 (s, 2H); ^{13}C NMR (THF-d_8) δ 29.1, 64.5, 83.4, 106.8, 111.8, 119.8, 131.2, 131.7, 132.6, 133.1, 149.2, 150.5, 150.9, 151.6, 172.1; LD-MS obsd 503.4; FABMS obsd 502.0960, calcd 502.0983 ($C_{26}H_{22}N_4O_3Zn$); λ_{abs} (toluene) 409, 538, 573.

4.4.10. Zn(II)-5-(*tert*-butyldimethylsiloxymethyl)-15-ethoxycarbonylporphyrin (ZnP5-OTBDMS). Following the procedure for **ZnP4-OTBDMS**, the reaction of **1e** (109 mg, 500 μmol) and **1a** (145 mg, 500 μmol) followed by chromatography [silica, CH_2Cl_2/THF (99:1)] yielded a purple solid (22 mg, 7.5%). ^{1}H NMR (300 MHz, THF-d_8) δ 0.22 (s, 6H), 0.91 (s, 9H), 1.82 (t, J=7.2 Hz, 3H), 5.07 (q, J=7.2 Hz, 2H), 7.21 (s, 2H), 9.44–9.51 (m, 4H), 9.65 (t, J=4.7 Hz, 2H), 9.88 (d, J=4.4 Hz, 2H), 10.3 (s, 2H); ^{13}C NMR (75 MHz, THF-d_8) δ −4.3, 15.4, 19.1, 26.5, 63.1, 65.7, 106.9, 109.8, 118.5, 131.0, 132.1, 133.2, 149.8, 150.7, 150.9, 151.3; LD-MS obsd 588.2; FABMS obsd 588.1539, calcd 588.1535 ($C_{30}H_{32}N_4O_3Zn$); λ_{abs} 404, 536, 574 nm.

4.4.11. Zn(II)-5-ethoxycarbonyl-15-hydroxymethylporphyrin (ZnP5-OH). Following the procedure for **H_2P2-(OH)$_2$**, the reaction of **ZnP5-OTBDMS** (21.0 mg, 35.0 μmol) followed by chromatography [silica, CH_2Cl_2/MeOH (10:1)] yielded a purple solid (11 mg, 66%). ^{1}H NMR (THF-d_8) δ 1.82 (t, J=6.5 Hz, 3H), 5.08 (q, J=6.5 Hz, 2H), 5.28 (t, J=4.0 Hz, 1H), 7.00 (d, J=4.0 Hz, 2H), 9.45–9.49 (m, 4H), 9.65 (d, J=5.0 Hz, 2H), 9.93 (d, J=5.0 Hz, 2H), 10.28 (s, 2H); LD-MS obsd 474.3; FABMS obsd 474.0695, calcd 474.0670 ($C_{24}H_{18}N_4O_3Zn$); λ_{abs} 404, 536 nm.

4.4.12. Zn(II)-5-(*tert*-butyldimethylsiloxymethyl)-15-[2-(trimethylsilyl)ethynyl]porphyrin (ZnP6-OTBDMS). Following the procedure for **ZnP4-OTBDMS**, the reaction of **1f** (1.38 g, 5.70 mmol) and **1a** (1.65 g, 5.70 mmol) followed by chromatography [silica, hexanes/CH_2Cl_2 (1:3)] yielded a purple solid (85 mg, 2.4%). ^{1}H NMR (300 MHz) δ 0.21 (s, 6H), 0.78 (s, 9H), 0.97 (s, 9H), 6.18 (s, 2H), 8.69 (d, J=4.4 Hz, 2H), 8.88–8.96 (m, 4H), 9.31 (s, 2H), 9.44 (d, J=4.4 Hz, 2H); ^{13}C NMR (75 MHz, THF-d_8) δ −4.3, 0.7, 19.1, 26.5, 65.6, 99.0, 100.4, 107.3, 109.8, 118.2, 130.9, 131.9, 132.7, 132.9, 150.5, 150.8, 151.6, 153.2; LD-MS obsd 612.5; FABMS obsd 612.1760, calcd 612.1719 ($C_{32}H_{36}N_4OSi_2Zn$); λ_{abs} 417, 551, 588 nm.

4.4.13. Zn(II)-5-ethynyl-15-hydoxymethylporphyrin (H_2P6-OH). Following the procedure for **H_2P2-(OH)$_2$**, the reaction of **ZnP6-OTBDMS** (12.1 mg, 19.7 μmol) followed by chromatography [silica, CH_2Cl_2/ethyl acetate (4:1)] yielded a purple solid (4.1 mg, 49%). ^{1}H NMR (THF-d_8) δ 4.62 (s, 1H), 5.24 (t, J=6.0 Hz, 1H), 6.96 (d, J=6.0 Hz, 2H), 9.42–9.45 (m, 4H), 9.81 (d, J=4.4 Hz, 2H), 9.88 (d, J=4.4 Hz, 2H), 10.2 (s, 2H); LD-MS (POPOP) obsd 426.0, calcd 426.0 ($C_{23}H_{14}N_4OZn$); λ_{abs} 413, 549, 586 nm.

4.4.14. Synthesis of *trans*-AB$_2$C-porphyrins from 1,9-diacyldipyrromethane and dipyrromethane, exemplified for 5-(*tert*-butyldimethylsiloxymethyl)-15-phenyl-10,20-di-*p*-tolylporphyrin (H_2P7-OTBDMS). Following a literature procedure[52,62] with modifications, a solution of **10-SnBu$_2$** (588 mg, 852 μmol) in dry THF/MeOH (10:1, 33 mL) was treated with $NaBH_4$ (642 mg, 17.0 mmol) for 2 h. A second batch of $NaBH_4$ (642 mg, 17.0 mmol) was added, and the reaction mixture was stirred for another 2 h. Saturated aqueous NH_4Cl was added, and the mixture was extracted with CH_2Cl_2. The organic layer was separated, dried (K_2CO_3) and concentrated. The resulting dicarbinol was dissolved in CH_2Cl_2 (340 mL) and treated with **1a** (247 mg, 852 μmol) and Yb(OTf)$_3$ (675 mg, 1.09 mmol) under argon for 30 min. DDQ (579 mg, 2.55 mmol) was added. The mixture was stirred for 1 h. TEA (2 mL) was added. The reaction mixture was concentrated. Chromatography [silica, hexanes/CH_2Cl_2 (1:3)] yielded a purple solid (77 mg, 12%). ^{1}H NMR δ −2.87 to −2.80 (br, 2H), 0.20 (s, 6H), 0.95 (s, 9H), 2.72 (s, 6H), 7.01 (s, 2H), 7.56 (d, J=8.0 Hz, 4H), 7.71–7.78 (m, 3H), 8.10 (d, J=8.0 Hz, 4H), 8.19 (dd, ^1J=7.6 Hz, ^2J=1.6 Hz, 2H), 8.80 (d, J=4.8 Hz, 2H), 8.83 (d, J=4.8 Hz, 2H), 8.98 (d, J=4.8 Hz, 2H), 9.59 (d, J=4.8 Hz, 2H); ^{13}C NMR (75 MHz) δ −4.4, 18.7, 21.7, 26.2, 64.8, 115.8, 120.2, 120.7, 126.9, 127.6, 127.9, 134.8, 137.6, 139.7, 142.5 (one carbon resonance apparently was overlapped; the α and β carbons were not observed presumably due to tautomerization); LD-MS obsd 710.7; FABMS obsd 710.3429, calcd 710.3441 ($C_{47}H_{46}N_4OSi$); λ_{abs} 417, 515, 549, 590, 646 nm.

4.4.15. Zn(II)-5-(*tert*-butyldimethylsiloxymethyl)-15-phenyl-10,20-di-*p*-tolylporphyrin (ZnP7-OTBDMS). Following the procedure for **ZnP1-(OTBDMS)$_4$**, the reaction of **H_2P7-OTBDMS** (70.0 mg, 98.5 μmol) followed by chromatography (silica, CH_2Cl_2) yielded a purple solid (72 mg, 95%). ^{1}H NMR δ 0.18 (s, 6H), 0.96 (s, 9H), 2.71 (s, 6H), 6.87 (s, 2H), 7.54 (d, J=8.0 Hz, 4H), 7.69–7.78 (m, 3H), 8.07 (d, J=8.0 Hz, 4H), 8.16–8.22 (m, 2H), 8.90 (d, J=4.0 Hz, 2H), 8.93 (d, J=4.0 Hz, 2H), 8.99 (d, J=4.8 Hz, 2H), 9.55 (d, J=4.8 Hz, 2H); ^{13}C NMR (75 MHz) δ −4.4, 18.7, 21.7, 26.3, 65.1, 116.6, 121.2, 121.8, 126.7, 127.5, 127.7, 129.5, 132.0, 132.1, 132.9, 134.6, 134.7, 137.4, 140.2, 143.2, 150.2, 150.5, 150.7, 151.3; LD-MS obsd 772.8; FABMS obsd 772.2573, calcd 772.2576 ($C_{47}H_{44}N_4OSiZn$); λ_{abs} 419, 548 nm.

4.4.16. 5-Hydroxymethyl-15-phenyl-10,20-di-*p*-tolylporphyrin (H_2P7-OH). Following the procedure for **H_2P2-(OH)$_2$**, the reaction of **H_2P7-OTBDMS** (50.2 mg, 70.7 μmol) followed by chromatography [silica, CH_2Cl_2/ethyl acetate (4:1)] yielded a purple solid (25 mg, 60%). ^{1}H NMR (THF-d_8) δ −2.80 to −2.72 (br, 2H), 2.68 (s, 6H), 5.34 (t, J=5.6 Hz, 1H), 6.86 (d, J=5.6 Hz, 2H), 7.57 (d, J=7.6 Hz, 4H), 7.68–7.78 (m, 3H), 8.07 (d, J=7.6 Hz, 4H), 8.14–8.22 (m, 2H), 8.74–8.84 (m, 4H), 8.92 (d, J=4.0 Hz, 2H), 9.73 (d, J=4.0 Hz, 2H); ^{13}C NMR (75 MHz, THF-d_8) δ 21.7, 64.3, 118.4, 120.8, 121.3, 127.7, 128.4, 128.7, 129.1, 135.4, 138.4, 140.8, 143.5 (the α and β carbons were not observed due to tautomerization); LD-MS obsd 596.8; FABMS obsd 596.2570, calcd 596.2576 ($C_{41}H_{32}N_4O$); λ_{abs} 417, 515, 549, 590, 646 nm.

4.4.17. Zn(II)-5-hydroxymethyl-15-phenyl-10,20-di-*p*-tolylporphyrin (ZnP7-OH). Following the procedure for **H_2P2-(OH)$_2$**, the reaction of **ZnP7-OTBDMS** (10.8 mg, 14.0 μmol) followed by chromatography [silica, CH_2Cl_2/ethyl acetate (4:1)] yielded a red purple solid (7.5 mg, 81%). ^{1}H NMR (THF-d_8) δ 2.70 (s, 6H), 5.14 (t, J=6.0 Hz, 1H), 6.94 (d, J=6.0 Hz, 2H), 7.57 (d, J=8.0 Hz, 4H), 7.69–7.75 (m, 3H), 8.08 (d, J=8.0 Hz, 4H), 8.14–8.19 (m, 2H), 8.79 (d, J=4.8 Hz, 2H), 8.83 (d, J=4.8 Hz, 2H), 8.95 (d, J=4.8 Hz, 2H), 9.76 (d, J=4.8 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 21.1, 62.7, 117.7, 119.8, 120.3, 126.5, 127.2, 127.4, 129.9, 131.2, 131.7, 134.0, 134.1, 136.5, 140.0, 142.9, 148.8, 149.29, 149.33, 150.5; LD-MS obsd 658.4; FABMS obsd 658.1736, calcd 658.1711 ($C_{41}H_{30}N_4OZn$); λ_{abs} 419, 548 nm.

4.4.18. 5-(*tert*-Butyldimethylsiloxymethyl)-15-ethoxycarbonyl-10,20-diphenylporphyrin (H_2P8-OTBDMS). Following the procedure for **H_2P7-OTBDMS**, a sample of $NaBH_4$ (151 mg, 4.00 mmol) was added in portions to a stirred solution of **11-SnBu$_2$** (100 mg, 200 μmol) in THF/methanol (10:1, 8 mL). The progress of the reaction was followed by TLC. The reaction was complete in 40 min, at which point the reaction mixture was quenched with water (8 mL) and then poured into CH_2Cl_2 (30 mL). The organic phase was separated, washed with water, dried (Na_2SO_4), and concentrated to give the dipyrromethane-1,9-dicarbinol as a yellow oil. The latter was immediately subjected to condensation with dipyrromethane **1e** (44.0 mg, 200 μmol) in the presence of $InCl_3$ (5.70 mg, 25.0 μmol) in CH_2Cl_2 (80 mL) for 45 min. DDQ (136 mg, 0.60 mmol) was added to the reaction mixture. The reaction mixture was stirred for 20 min. TEA (1 mL) was added. The crude mixture was purified by chromatography [silica, hexanes/CH_2Cl_2 (1:3)] to obtain a purple solid (37 mg, 27%). ^{1}H NMR δ −2.94 to −2.85 (br, 2H), 0.23 (s, 6H), 0.96 (s, 9H), 1.79 (t, J=7.0 Hz, 3H), 5.08 (q, J=7.0 Hz, 2H), 6.94 (s, 2H), 7.26–7.82 (m, 6H), 8.18–8.22 (m, 4H), 8.93 (t, J=4,8 Hz, 4H), 9.43 (d, J=4.8 Hz, 2H), 9.58 (d, J=4.8 Hz, 2H); ^{13}C NMR δ −4.5, 15.0, 18.6, 26.2, 63.2, 64.6, 109.3, 118.4, 120.9, 127.0, 128.1, 134.7, 142.2, 171.5 (the α and β carbons were not observed presumably due to tautomerization); LD-MS obsd 679.1; FABMS obsd 678.3051, calcd 678.3026 ($C_{42}H_{42}N_4O_3Si$); λ_{abs} 415, 512, 546, 586 nm.

4.4.19. Zn(II)-5,15-diphenyl-10-ethoxycarbonyl-20-(*tert*-butyldimethylsiloxymethyl)porphyrin (ZnP8-OTBDMS). Following the procedure for **ZnP1-(OTBDMS)$_4$**, the reaction of **H_2P8-OTBDMS** (37.0 mg, 54.0 μmol) followed by chromatography [silica, hexanes/CH_2Cl_2 (3:4)] yielded a purple solid (38 mg, 95%). ^{1}H NMR (THF-d_8) δ 0.22 (s, 6H),

0.89 (s, 9H), 1.79 (t, J=7.0 Hz, 3H), 5.01 (q, J=7.0 Hz, 2H), 7.14 (s, 2H), 7.76–7.80 (m, 6H), 8.19–8.22 (m, 4H), 8.90 (d, J=4.8 Hz, 2H), 8.93 (d, J=4.8 Hz, 2H), 9.43 (d, J=4.8 Hz, 2H), 9.73 (d, J=4.8 Hz, 2H); ^{13}C NMR (75 MHz, THF-d_8) δ −4.9, 14.4, 17.8, 25.7, 62.3, 64.1, 109.7, 118.1, 120.4, 126.4, 127.4, 129.9, 130.0, 131.6, 132.2, 134.0, 142.2, 147.0, 149.1, 149.5, 149.7, 171.3; LD-MS obsd 740.5; FABMS obsd 740.2169, calcd 740.2161 ($C_{42}H_{40}N_4O_3SiZn$); λ_{abs} 416, 547, 580 nm.

4.4.20. Zn(II)-5-ethoxycarbonyl-15-hydroxymethyl-10,20-diphenylporphyrin (ZnP8-OH). Following the procedure for **H_2P2-(OH)$_2$**, the reaction of **ZnP8-OTBDMS** (50.0 mg, 67.0 μmol) followed by chromatography [silica, CH_2Cl_2/ethyl acetate (10:1)] yielded a purple solid (30 mg, 71%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.69 (t, J=7.0 Hz, 3H), 5.01 (q, J=7.3 Hz, 2H), 6.20 (t, J=5.8 Hz, 1H), 6.95 (d, J=5.9 Hz, 2H), 7.60–7.80 (m, 6H), 8.15–8.25 (m, 4H), 8.84 (d, J=2.2 Hz, 2H), 8.86 (d, J=2.3 Hz, 2H), 9.38 (d, J=4.8 Hz, 2H), 9.82 (d, J=4.8 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 14.4, 62.3, 62.4, 109.4, 120.2, 120.3, 125.5, 127.4, 130.0, 130.3, 131.4, 132.2, 134.0, 142.3, 147.0, 148.9, 149.6, 149.9, 171.3; LD-MS obsd 626.4; FABMS obsd 626.1306, calcd 626.1296 ($C_{36}H_{26}N_4O_3Zn$); λ_{abs} 416, 547, 582 nm.

4.4.21. 5-Ethoxycarbonyl-15-(5,5-dimethyl-1,3-dioxan-2-yl)-10,20-di-*p*-tolylporphyrin (H_2P9-acetal). The general procedure for **H_2P7-(OTBDMS)** was followed for the reaction of **13-BBu$_2$** (119 mg, 192 μmol) and **1e** (41.9 mg, 192 μmol). LD-MS analysis showed the presence of a small amount (~1%) of an aldehyde-porphyrin. Chromatography (silica, CH_2Cl_2) yielded the title compound as a purple solid (18 mg, 14%). ^{1}H NMR δ −3.00 to −2.94 (br, 2H), 1.11 (s, 3H), 1.77 (t, J=7.2 Hz, 3H), 1.91 (s, 3H), 2.72 (s, 6H), 4.27–4.36 (m, 4H), 5.05 (q, J=7.2 Hz, 2H), 7.57 (d, J=8.0 Hz, 4H), 7.94 (s, 1H), 8.06 (d, J=8.0 Hz, 4H), 8.91–8.99 (m, 4H), 9.42 (d, J=4.8 Hz, 2H), 9.93 (d, J=4.8 Hz, 2H); ^{13}C NMR δ 15.0, 21.8, 22.8, 25.2, 31.1, 63.2, 80.4, 106.3, 109.6, 114.3, 121.2, 127.6, 129.5, 129.9, 132.3, 132.7, 134.7, 137.8, 139.4, 171.4 (the α carbons were not observed presumably due to tautomerization); LD-MS obsd 676.4; FABMS obsd 676.3049, calcd 676.3050 ($C_{43}H_{40}N_4O_4$); λ_{abs} 415, 512, 546, 588, 642 nm.

4.4.22. 5-Ethoxycarbonyl-15-formyl-10,20-di-*p*-tolylporphyrin (H_2P9-CHO). Following a general procedure,[32,65] solution of **H_2P9-acetal** (7.2 mg, 11 μmol) in CH_2Cl_2 (1 mL) was treated with a mixture of TFA/H_2O (8:1, 900 μL) at room temperature for 28 h. The reaction mixture was diluted in CH_2Cl_2, and washed with saturated aqueous $NaHCO_3$ and water. The organic phase was dried (Na_2SO_4) and concentrated. Chromatography (silica, CH_2Cl_2) yielded a purple solid (5.5 mg, 85%). ^{1}H NMR δ −2.56 to −2.51 (br, 2H), 1.77 (t, J=7.2 Hz, 3H), 2.73 (s, 6H), 5.07 (q, J=7.2 Hz, 2H), 7.58 (d, J=7.6 Hz, 4H), 8.04 (d, J=7.6 Hz, 4H), 8.88 (d, J=4.8 Hz, 2H), 9.01(d, J=4.8 Hz, 2H), 9.35 (d, J=4.8 Hz, 2H), 10.00 (d, J=4.8 Hz, 2H), 12.51 (s, 1H); ^{13}C NMR δ 15.0, 21.8, 63.5, 109.3, 113.7, 123.2, 127.9, 129.1 (br) 130.5 (br), 132.5 (br), 134.6 (br), 170.8, 195.2 (the α carbons were not observed presumably due to tautomerization); LD-MS obsd 590.4; FABMS obsd 590.2321, calcd 590.2318 ($C_{38}H_{30}N_4O_3$); λ_{abs} 422, 525, 567, 604, 661 nm.

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