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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 that is attractive 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.

Keywords

Porphyrin; Dipyrromethane; Hydroxymethyl; Formyl

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}

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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 alkoxy carbonyl 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 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**,^{44,45} **1f**)⁴⁴ 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 condensations⁴⁴ 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*-butyldimethylsilyloxymethyl)dipyrromethane (**1a**) as a colorless oil in 52% yield (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 reacted⁴⁷ 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 condensed² with pyrrole in the presence of TFA in CH_2Cl_2 to yield *tert*-butyl ester dipyrromethane **1b** in 18% yield (from **3**).

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} Reaction⁵¹ of **4** with 2,2'-dipyridyl disulfide gave the corresponding pyridyl thioester **5a** in 43% yield.

2.2. Syntheses of hydroxymethylporphyrins

2.2.1. A₄-Porphyrins with four hydroxymethyl groups—Our initial approach to *meso*-tetrakis(*tert*-butyldimethylsiloxyethyl)porphyrin [**H₂P1-(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. Treatment⁵¹ 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 NaBH₄ and treated with the catalyst⁵² Yb(OTf)₃ followed by DDQ oxidation to afford TBDMS-protected tetrakis(hydroxymethyl)porphyrin **H₂P1-(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 procedure⁴⁸ to give 1-acyldipyrromethane **7** in 62% yield (Scheme 4). Acyldipyrromethane **7** was reduced by NaBH₄ to give the dipyrromethane-1-carbinol, which upon self-condensation and oxidation gave the desired A₄-porphyrin **H₂P1-(OTBDMS)₄** in 8% yield. 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 CH₂Cl₂, 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 (FAB-MS) were not successful.

2.2.2. *trans*-A₂- and *trans*-A₂B₂-Porphyrins with two hydroxymethyl groups—*Trans*-A₂-porphyrins or A₂B₂-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*-A₂- or A₂B₂-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 **H₂P1-(OTBDMS)₄**. 5-Mesityldipyrromethane (**1c**) or unsubstituted dipyrromethane (**1d**) reacted⁴⁸ 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 NaBH₄ and the resulting dipyrromethane-1-carbinol was self-condensed^{48,52,57} in the presence of InCl₃ followed by oxidation with DDQ to afford TBDMS-protected bis(hydroxymethyl)porphyrin **H₂P2-(OTBDMS)₂** in 13% yield (Scheme 5). Cleavage of the TBDMS group by TBAF⁵⁸ afforded porphyrin **H₂P2-(OH)₂** quantitatively.

A *trans*-A₂-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 InCl₃. The protected bis(hydroxymethyl)porphyrin **H₂P3-(OTBDMS)₂** was obtained in 7.5% yield. Deprotection with TBAF afforded the *trans*-A₂-porphyrin **H₂P3-(OH)₂** in 66% yield. Similar

to **ZnP1-(OH)₄**, **H₂P3-(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-mesityldipyrrromethane **8** was treated with TBAF to remove the TBDMS group prior to porphyrin formation. The resulting 1-(α -hydroxyacetyl)dipyrrromethane **8'** was subjected to reduction, and the resulting unprotected hydroxymethyl-substituted dipyrromethane-1-carbinol was treated to self-condensation and oxidation. The desired *trans*-A₂B₂-porphyrin **H₂P2-(OH)₂** was obtained along with scrambled porphyrin species (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)dipyrrromethane 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)dipyrrromethanes 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*-AB₂C-Porphyrins bearing one or two one-carbon substituents—

Three *trans*-AB₂C-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-SnBu₂**⁶² was reduced by NaBH₄. The resulting dipyrromethane-1,9-dicarbinol was condensed with TBDMS-protected hydroxymethyldipyrrromethane **1a** to afford free base porphyrin **H₂P7-OTBDMS** in 12% yield (Scheme 7). Treatment of **H₂P7-OTBDMS** with Zn(OAc)₂·2H₂O afforded **ZnP7-OTBDMS** in 95% yield. The TBDMS group of **H₂P7-OTBDMS** and **ZnP7-OTBDMS** was removed by treatment with TBAF to yield **H₂P7-OH** and **ZnP7-OH** in 60% and 81% yield, respectively. The synthesis of **H₂P7-OH** and **ZnP7-OH** was previously carried out with the unprotected 5-hydroxymethyldipyrrromethane.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.

The synthesis of **ZnP8-OH** entailed the acylation of dipyrromethane **1a** (Scheme 8). Treatment of **1a** with EtMgBr and benzoyl chloride followed by tin complexation⁶² with Bu₂SnCl₂ yielded tin complex **11-SnBu₂** in 63% yield. The latter was then reduced by NaBH₄. 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 **H₂P8-OTBDMS** in 27% yield. Metalation gave zinc porphyrin **ZnP7-OTBDMS** in 95% yield, and deprotection with TBAF yielded **ZnP7-OH** in 71% yield.

A porphyrin bearing a formyl and an ester group at *trans*-meso positions was synthesized from a 1,9-diacyl-5-acetaldipyrromethane 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 $\text{Bu}_2\text{B-OTf}$ gave the boron complex **12-BBu₂** in 34% yield. The boron complex **12-BBu₂** was treated with MesMgBr and *p*-toluoyl chloride to form the 1,9-diacyl-dipyrromethane **13-BBu₂** 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 **H₂P9-acetal**. A small amount (~1%) of aldehyde-porphyrin (from deprotection of **H₂P9-acetal**) was also observed in the reaction mixture by LD-MS. The purified acetal/ester-porphyrin **H₂P9-acetal** was obtained in 14% yield. Treatment of **H₂P9-acetal** in the biphasic mixture of CH_2Cl_2 and $\text{TFA}/\text{H}_2\text{O}$ ^{32,65} gave the aldehyde/ester-porphyrin **H₂P9-CHO** in 85% yield.

2.3. Characterization

The porphyrins were generally characterized by ^1H NMR and ^{13}C NMR spectroscopy, laser-desorption mass spectrometry (LD-MS), high-resolution fast atom bombardment mass spectrometry (FAB-MS), and absorption spectroscopy. In some cases solubility limitations precluded ^{13}C NMR spectroscopy or FAB-MS. The hydroxymethylporphyrins exhibited the expected resonances upon ^1H NMR spectroscopy, including the doublet (6.82 to 7.29 ppm) for the methylene protons and the triplet (5.14 to 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 coworkers 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 ^1H 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 FAB-MS 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. Room temperature was determined to be 21-22 °C using a calibrated thermometer.

4.2. Noncommercial compounds

Dipyromethanes **1c**,⁴³ **1d**,⁴⁵ **1f**,⁴⁴ 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 Dipyromethane **1e**,² Mukaiyama reagent **5b**,⁴⁸ and the diacyldipyromethane-tin complex **10-SnBu**⁶² were prepared as described in the literature.

4.3. Synthesis of precursors

4.3.1. 5-(*tert*-Butyldimethylsiloxymethyl)dipyromethane (1a**)**—Following a literature procedure⁴⁴ 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%): ^1H 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 = $\text{C}_{16}\text{H}_{26}\text{N}_2\text{OSi}$]; Anal. Calcd for $\text{C}_{16}\text{H}_{25}\text{N}_2\text{OSi}$: C 66.16, H 9.02, N 9.64. Found: C 66.12, H 9.16, N 9.61.

4.3.2. 5-*tert*-Butoxycarbonyldipyromethane (1b**)**—Following a literature procedure⁴⁷ 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 \times 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 CH₂Cl₂ (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 CH₂Cl₂ (100 mL). The mixture was washed with water and brine, dried (Na₂SO₄) and concentrated. Chromatography [silica, hexanes/CH₂Cl₂ (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; ¹H 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); ¹³C NMR δ 28.2, 44.8, 82.5, 107.0, 108.6, 118.0, 127.5, 170.9; Anal. Calcd for C₁₄H₁₈N₂O₂: 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 procedure⁴⁶ 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 (Na₂SO₄) and concentrated to yield a light yellow liquid (12.4 g, quantitative): ¹H 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); ¹³C 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 = C₁₂H₂₈NO₃Si].

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 AgNO₃ (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 Et₂O (3 × 50 mL). The Et₂O extracts were combined, washed with water and brine, dried (Na₂SO₄) and concentrated to yield a colorless oil (3.4 g, 82%): ¹H NMR δ 1.49 (s, 9H), 4.77 (s, 2H); ¹³C NMR δ 28.1, 67.8, 84.1, 165.0; Anal. Calcd for C₆H₁₁NO₅: 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 (Na₂SO₄) and concentrated *in vacuo* to yield a viscous liquid. The resulting ester was dissolved in 30 mL 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 (Na₂SO₄) and concentrated to yield a white solid (5.2 g, 55%): mp 48–49 °C; ¹H NMR (300 MHz) δ 0.15 (s, 6H), 0.94 (s, 9H), 4.22 (s, 2H), the carboxylic acid proton was not observed; ¹³C NMR δ -5.3, 18.5, 25.9, 61.6, 175.3; Anal. calcd. for C₈H₁₈O₃Si: 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; $^1\text{H NMR}$ 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); $^{13}\text{C NMR}$ δ -5.6, 18.2, 25.7, 68.9, 123.4, 130.6, 137.1, 150.5, 151.6, 200.3; FAB-MS obsd 284.1126, calcd 284.1141 [(M + H)⁺, M = C₁₃H₂₁NO₂SSi].

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 NH₄Cl. The mixture was extracted with CH₂Cl₂. The organic layer was separated, washed with water, dried (Na₂SO₄) and concentrated. Chromatography [silica, hexanes/CH₂Cl₂(1:4)] yielded a dark purple oil (0.77 g, 38%): $^1\text{H NMR}$ 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); $^{13}\text{C NMR}$ δ -5.2, 18.6, 26.0, 67.0, 110.7, 117.0, 125.5, 129.6, 188.6; FAB-MS obsd. 240.1425, calcd 240.1420 [(M + H)⁺, M = C₁₂H₂₁NO₂Si]; Anal. calcd. for C₁₂H₂₁NO₂Si: 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*-butyldimethylsilyloxymethyl)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 NH₄Cl solution was added. The mixture was extracted with ethyl acetate. The organic layer was separated, dried (Na₂SO₄) and concentrated. Chromatography [silica, CH₂Cl₂/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); $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ (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 C₂₄H₄₂N₄O₃Si₂: 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, CH₂Cl₂ then CH₂Cl₂/ethyl acetate (9:1)] yielded a brown solid (0.77 g, 74%): mp 40-42 °C; $^1\text{H NMR}$ 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); $^{13}\text{C NMR}$ 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 C₂₆H₃₆N₂O₂Si: 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, CH₂Cl₂ then CH₂Cl₂/ethyl acetate (10:1)] yielded a brown solid (0.54 g, 85%): mp 64-66 °C; $^1\text{H NMR}$ 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); $^{13}\text{C NMR}$ 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) dipyrinato]tin(IV) (11-SnBu₂)—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 NH₄Cl solution and ethyl acetate. The organic layer was separated, washed with brine, dried (Na₂SO₄) and concentrated. The resulting yellow oil was dissolved in ethyl acetate (20 mL) and treated with TEA (1 mL) and Bu₂SnCl₂ (733 mg, 2.41 mmol) at room temperature for 30 min. The reaction mixture was washed with water and brine, dried (Na₂SO₄) and concentrated. Chromatography [silica, hexanes/CH₂Cl₂ (1:2 with 0.5% TEA)] yielded a yellow viscous oil (1.1 g, 63%): ¹H 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); ¹³C 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; FAB-MS obsd 731.2721, calcd 730.2613 (C₃₈H₅₀N₂O₃SiSn); Anal. Calcd for C₃₈H₅₀N₂O₃SiSn: 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-BBu₂)—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 NH₄Cl solution was added, and the reaction mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried (Na₂SO₄) and concentrated. The resulting solid was dissolved in CH₂Cl₂ (2 mL) and treated with TEA (335 μL, 2.40 mmol) and Bu₂B-OTf (2.00 mL, 2.00 mmol) at room temperature for 30 min. The solvent was removed under reduced pressure. Chromatography [silica, hexanes/CH₂Cl₂ (1:4)] yielded a yellow-greenish oil (0.17 g, 34%): ¹H 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); ¹³C 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; FAB-MS 503.3426, calcd 503.3445 [(M + H)⁺, M = C₃₁H₄₃BN₂O₃].

4.3.13. 10-(Dibutylboryl)-1,9-di-*p*-toluoyl-5-(5,5-dimethyl-1,3-dioxan-2-yl) dipyrromethane (13-BBu₂)—Following a general procedure,⁶⁴ a solution of **12-BBu₂** (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 NH₄Cl solution was added and the reaction mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried (Na₂SO₄) and concentrated. Chromatography (silica, CH₂Cl₂) yielded an orange solid (0.12 g, 56%): ¹H 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); ¹³C 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; FAB-MS obsd 621.3864, calcd 621.3864 [(M + H)⁺, M = C₃₉H₄₉BN₂O₄].

4.4. Synthesis of porphyrins

4.4.1. Synthesis of A₄-, *trans*-A₂ or *trans*-A₂B₂-porphyrins from 1-acyldipyrromethanes, exemplified for 5,10,15,20-tetrakis(*tert*-butyldimethylsiloxymethyl)porphyrin [H₂P1-(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 NaBH₄ (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 NH₄Cl solution. The mixture was extracted with ethyl acetate. The organic layer was separated, washed with water, and dried (Na₂SO₄). The solvents were removed to yield the dipyrromethane-1-carbinol as a brownish oil. The dipyrromethane-1-carbinol was dissolved in CH₂Cl₂ (90 mL). The solution was treated with InCl₃ (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 CH₂Cl₂ as eluant. The filtrate was concentrated. Chromatography [silica, hexanes/CH₂Cl₂ (1:4)] yielded a red solid (15.0 mg, 8%): ¹H 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); ¹³C 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; FAB-MS obsd 886.5059, calcd 886.5100 (C₄₉H₇₈N₄O₄Si₄); 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 procedure⁴ with modification, a solution of H₂P1-(OTBDMS)₄ (14.0 mg, 15.8 μmol) in CH₂Cl₂/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, CH₂Cl₂) yielded a red solid (12.0 mg, 80%): ¹H NMR (300 MHz) δ 0.16 (s, 24H), 0.96 (s, 36H), 6.89 (s, 8H), 9.61 (s, 8H); ¹³C NMR (75 MHz) δ -4.5, 18.7, 26.3, 64.9, 116.1, 129.6, 150.1; LD-MS obsd 948.3; FAB-MS obsd 948.4158, calcd 948.4235 (C₄₉H₇₆N₄O₄Si₄Zn); 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 procedure⁵⁸ 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%): ¹H 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); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 62.6, 116.8, 129.5, 149.6; LD-MS (POPOP) obsd 492.5, calcd 492.1 (C₂₄H₂₀N₄O₄Zn). 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 [H₂P2-(OTBDMS)₂]

—Following the procedure for H₂P1-(OTBDMS)₄, the self-condensation of the carbinol derived from 1-acyldipyrromethane **8** (88 mg, 0.20 mmol) followed by chromatography (silica, CH₂Cl₂) yielded a purple solid (11 mg, 13%): ¹H 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; FAB-MS obsd 834.4772, calcd 834.4724 ($\text{C}_{52}\text{H}_{66}\text{N}_4\text{O}_2\text{Si}_2$); 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-dimesitylporphyrin [$\text{H}_2\text{P2}(\text{OH})_2$]—Following a literature procedure⁵⁸ with modification, a solution of $\text{H}_2\text{P2}(\text{OTBDMS})_2$ (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): ^1H 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; FAB-MS obsd 606.3017, calcd 606.2995 ($\text{C}_{40}\text{H}_{38}\text{N}_4\text{O}_2$); λ_{abs} 415, 513, 544, 589 nm; λ_{em} 645, 720 nm.

4.4.6. 5,15-Bis(*tert*-butyldimethylsilyloxymethyl)porphyrin [$\text{H}_2\text{P3}(\text{OTBDMS})_2$]—Following the procedure for $\text{H}_2\text{P1}(\text{OTBDMS})_4$, 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%): ^1H 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; FAB-MS obsd 598.3158, calcd 598.3159 ($\text{C}_{34}\text{H}_{46}\text{N}_4\text{O}_2\text{Si}_2$); λ_{abs} 402, 500, 532, 573 nm.

4.4.7. 5,15-Bis(hydroxymethyl)porphyrin [$\text{H}_2\text{P3}(\text{OH})_2$]—Following the procedure for $\text{H}_2\text{P1}(\text{OH})_4$, the reaction of $\text{H}_2\text{P2}(\text{OTBDMS})_2$ (12.3 mg, 20.5 μmol) yielded a purple solid (5.0 mg, 66%): ^1H 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 = $\text{C}_{22}\text{H}_{18}\text{N}_4\text{O}_2$]. 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)dipyrrromethanes and dipyrromethanes, exemplified for Zn(II)-5-(*tert*-butoxycarbonyl)-15-(*tert*-butyldimethylsilyloxymethyl)porphyrin [$\text{ZnP4}(\text{OTBDMS})$]—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). Dipyrrromethane **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%): ^1H 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; FAB-MS 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 **H₂P2-(OH)₂**, the reaction of **ZnP4-OTBDMS** (38 mg, 62 μ mol) followed by chromatography [silica, CH_2Cl_2 /ethyl acetate (9:1)] yielded a purple solid (16 mg, 51%): ¹H 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); ¹³C 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; FAB-MS 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*-Butyldimethylsilyloxymethyl)-15-ethoxycarbonylporphyrin (ZnP5-OTBDMS)—

Following the procedure for **ZnP4-OTBDMS**, the reaction of **1e** (109 mg, 500 μ mol) and **1a** (145 mg, 500 μ mol) followed by chromatography [silica, CH_2Cl_2 /THF (99:1)] yielded a purple solid (22 mg, 7.5%): ¹H 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); ¹³C 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; FAB-MS 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 **H₂P2-(OH)₂**, the reaction of **ZnP5-OTBDMS** (21.0 mg, 35.0 μ mol) followed by chromatography [silica, CH_2Cl_2 /MeOH (10:1)] yielded a purple solid (11 mg, 66%): ¹H 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; FAB-MS 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*-Butyldimethylsilyloxymethyl)-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%): ¹H 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); ¹³C 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; FAB-MS 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-hydroxymethylporphyrin (H₂P6-OH)—Following the procedure for **H₂P2-(OH)₂**, the reaction of **ZnP6-OTBDMS** (12.1 mg, 19.7 μ mol) followed by chromatography [silica, CH_2Cl_2 /ethyl acetate (4:1)] yielded a purple solid (4.1 mg, 49%): ¹H 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*-AB₂C-porphyrins from 1,9-diacylidipyrromethane and dipyrromethane, exemplified for 5-(*tert*-butyldimethylsilyloxymethyl)-15-phenyl-10,20-di-*p*-tolylporphyrin (H₂P7-OTBDMS)—Following a literature procedure^{52,62} with modifications, a solution of **10-SnBu₂** (588 mg, 852 μ mol) in dry THF/MeOH (10:1, 33 mL) was treated with NaBH₄ (642 mg, 17.0 mmol) for 2 h. A second batch

of NaBH₄ (642 mg, 17.0 mmol) was added, and the reaction mixture was stirred for another 2 h. Saturated aqueous NH₄Cl was added, and the mixture was extracted with CH₂Cl₂. The organic layer was separated, dried (K₂CO₃) and concentrated. The resulting dicarbinol was dissolved in CH₂Cl₂ (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/CH₂Cl₂ (1:3)] yielded a purple solid (77 mg, 12%): ¹H 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, ¹*J* = 7.6 Hz, ²*J* = 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); ¹³C 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; FAB-MS obsd 710.3429, calcd 710.3441 (C₄₇H₄₆N₄OSi); 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 H₂P7-OTBDMS (70.0 mg, 98.5 μmol) followed by chromatography (silica, CH₂Cl₂) yielded a purple solid (72 mg, 95%): ¹H 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); ¹³C 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; FAB-MS obsd 772.2573, calcd 772.2576 (C₄₇H₄₄N₄OSiZn); λ_{abs} 419, 548 nm.

4.4.16. 5-Hydroxymethyl-15-phenyl-10,20-di-*p*-tolylporphyrin (H₂P7-OH)—Following the procedure for H₂P2-(OH)₂, the reaction of H₂P7-OTBDMS (50.2 mg, 70.7 μmol) followed by chromatography [silica, CH₂Cl₂/ethyl acetate (4:1)] yielded a purple solid (25 mg, 60%): ¹H 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); ¹³C 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; FAB-MS obsd 596.2570, calcd 596.2576 (C₄₁H₃₂N₄O); 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 H₂P2-(OH)₂, the reaction of ZnP7-OTBDMS (10.8 mg, 14.0 μmol) followed by chromatography [silica, CH₂Cl₂/ethyl acetate (4:1)] yielded a red purple solid (7.5 mg, 81%): ¹H 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); ¹³C 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; FAB-MS obsd 658.1736, calcd 658.1711 (C₄₁H₃₀N₄OZn); λ_{abs} 419, 548 nm.

4.4.18. 5-(*tert*-Butyldimethylsiloxymethyl)-15-ethoxycarbonyl-10,20-diphenylporphyrin (H₂P8-OTBDMS)—Following the procedure for H₂P7-OTBDMS, a sample of NaBH₄ (151 mg, 4.00 mmol) was added in portions to a stirred solution of **11-SnBu₂** (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 CH₂Cl₂ (30 mL). The organic phase was separated, washed with water, dried (Na₂SO₄), and concentrated to give the dipyrromethane-1,9-dicarbonyl as a yellow oil. The latter was immediately subjected to condensation with dipyrromethane **1e** (44.0 mg, 200 μmol) in the presence of InCl₃ (5.70 mg, 25.0 μmol) in CH₂Cl₂ (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/CH₂Cl₂ (1:3)] to obtain a purple solid (37 mg, 27%): ¹H 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); ¹³C 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; FAB-MS obsd 678.3051, calcd 678.3026 (C₄₂H₄₂N₄O₃Si); λ_{abs} 415, 512, 546, 586 nm.

4.4.19. Zn(II)-5,15-Diphenyl-10-ethoxycarbonyl-20-(tert-butyl)dimethylsiloxymethylporphyrin (ZnP8-OTBDMS)—Following the procedure for **ZnP1-(OTBDMS)**₄, the reaction of **H₂P8-OTBDMS** (37.0 mg, 54.0 μmol) followed by chromatography [silica, hexanes/CH₂Cl₂ (3:4)] yielded a purple solid (38 mg, 95%): ¹H 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); ¹³C 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; FAB-MS obsd 740.2169, calcd 740.2161 (C₄₂H₄₀N₄O₃SiZn); λ_{abs} 416, 547, 580 nm.

4.4.20. Zn(II)-5-Ethoxycarbonyl-15-hydroxymethyl-10,20-diphenylporphyrin (ZnP8-OH)—Following the procedure for **H₂P2-(OH)**₂, the reaction of **ZnP8-OTBDMS** (50.0 mg, 67.0 μmol) followed by chromatography [silica, CH₂Cl₂/ethyl acetate (10:1)] yielded a purple solid (30 mg, 71%): ¹H 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); ¹³C 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; FAB-MS obsd 626.1306, calcd 626.1296 (C₃₆H₂₆N₄O₃Zn); 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 (H₂P9-acetal)—The general procedure for **H₂P7-(OTBDMS)** was followed for the reaction of **13-BBu₂** (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, CH₂Cl₂) yielded the title compound as a purple solid (18 mg, 14%): ¹H 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); ¹³C 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; FAB-MS obsd 676.3049, calcd 676.3050 (C₄₃H₄₀N₄O₄); λ_{abs} 415, 512, 546, 588, 642 nm.

4.4.22. 5-Ethoxycarbonyl-15-formyl-10,20-di-*p*-tolylporphyrin (H₂P9-CHO)—Following a general procedure,^{32,65} solution of **H₂P9-acetal** (7.2 mg, 11 μmol) in CH₂Cl₂ (1

mL) was treated with a mixture of TFA/H₂O (8:1, 900 μ L) at room temperature for 28 h. The reaction mixture was diluted in CH₂Cl₂, washed with saturated aqueous NaHCO₃ and water, dried (Na₂SO₄) and concentrated. Chromatography (silica, CH₂Cl₂) yielded a purple solid (5.5 mg, 85%): ¹H 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); ¹³C 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; FAB-MS obsd 590.2321, calcd 590.2318 (C₃₈H₃₀N₄O₃); λ_{abs} 422, 525, 567, 604, 661 nm.

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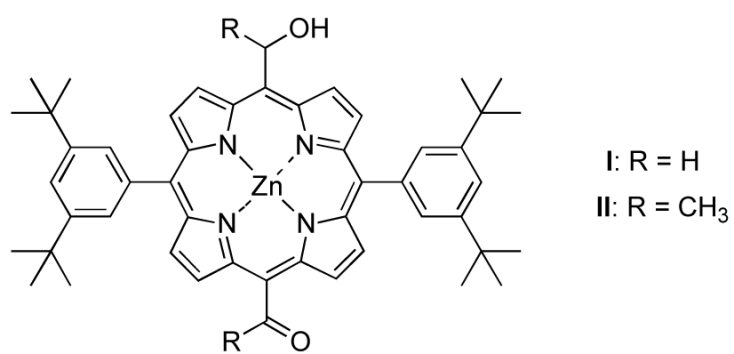
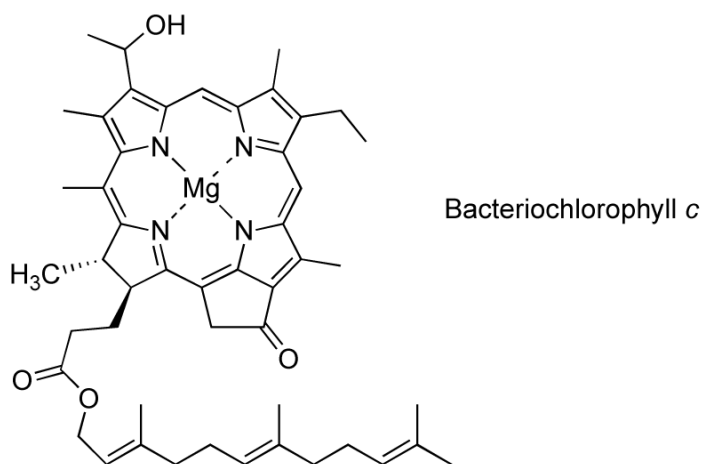
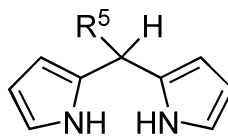
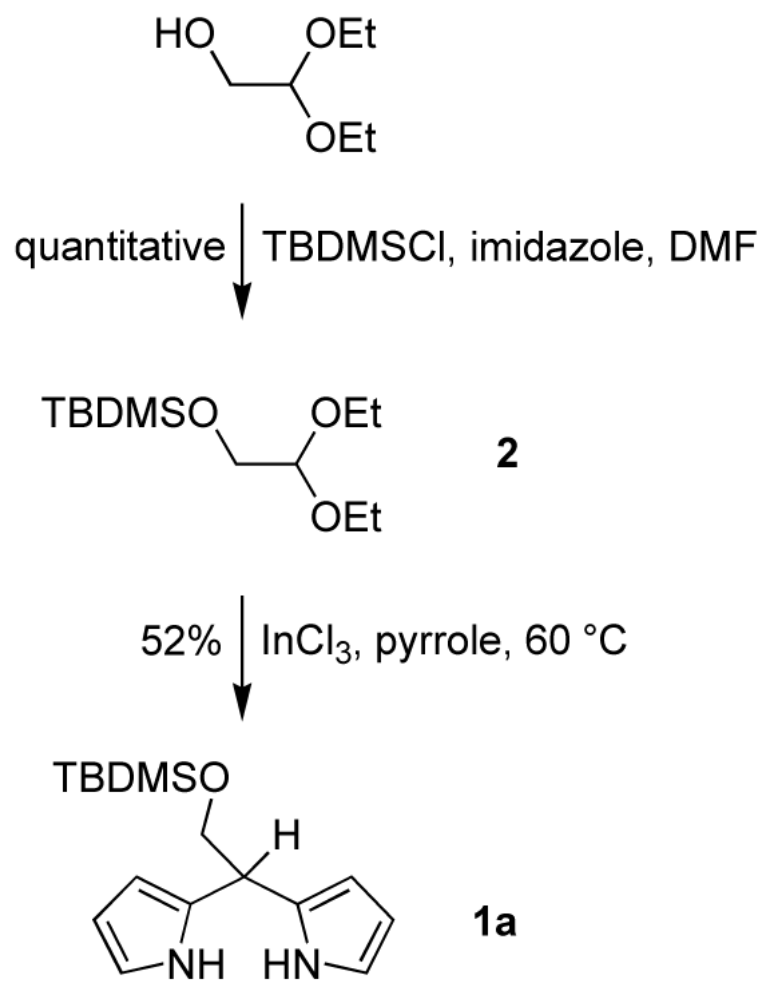


Chart 1.

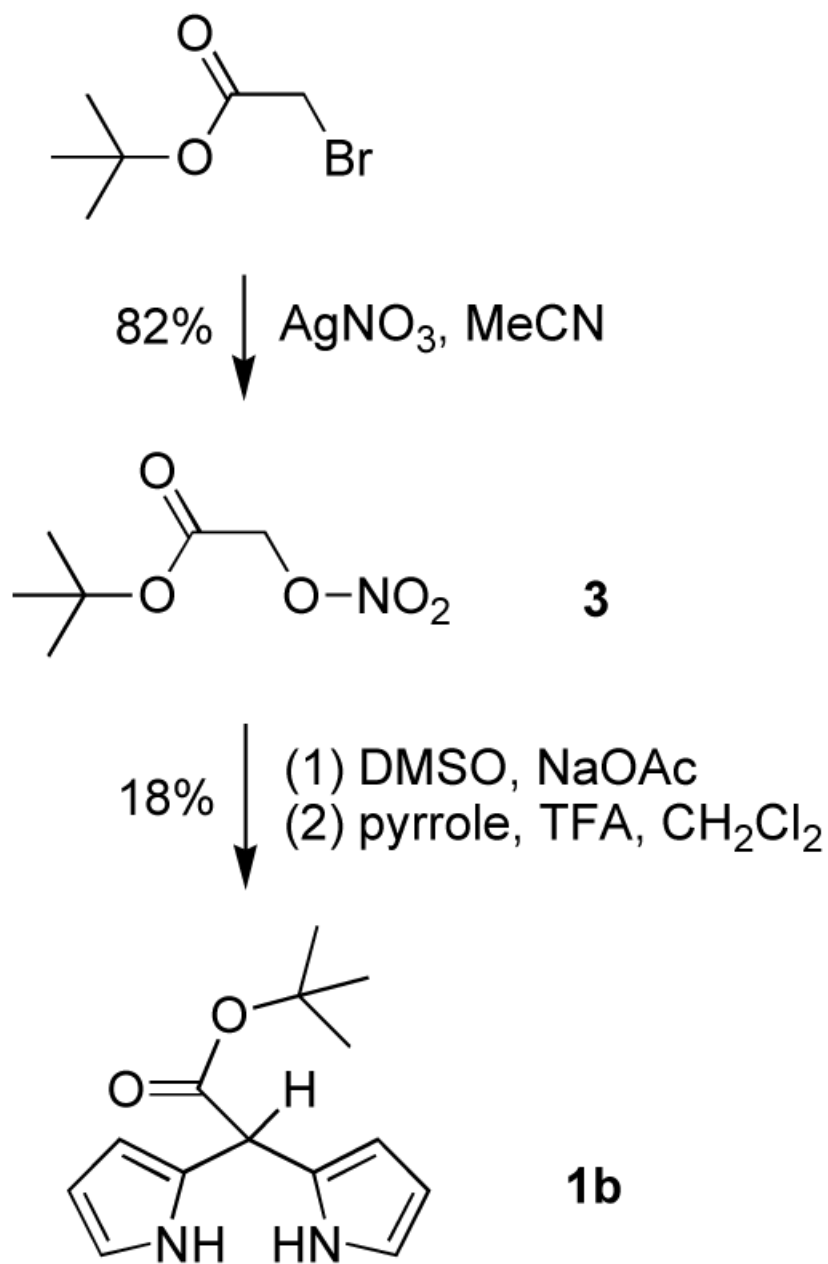


Compound	R ⁵	Reference
1a		
1b		
1c		43
1d		45
1e		2
1f		44
1g		32

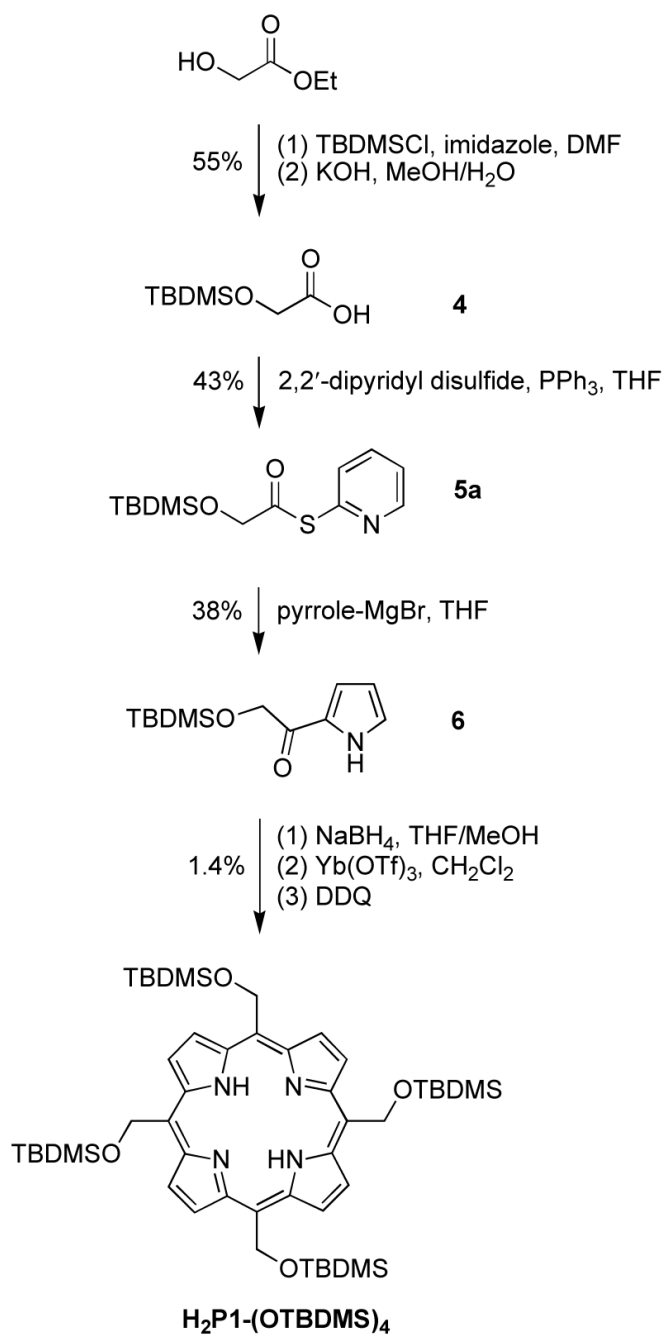
Chart 2.



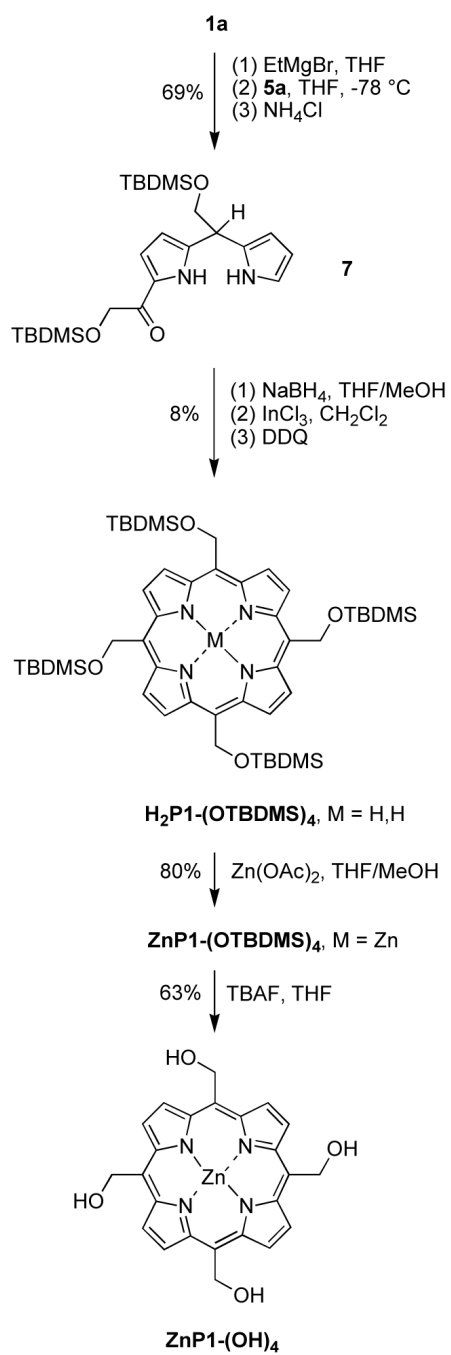
Scheme 1.



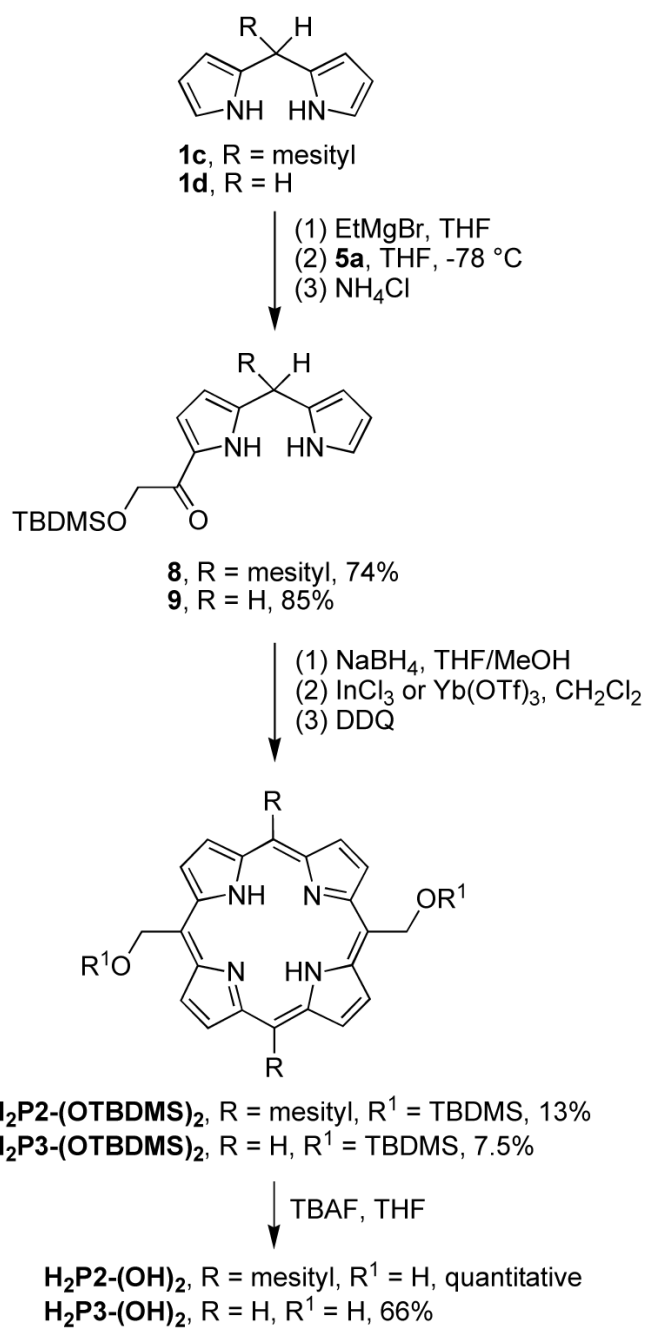
Scheme 2.



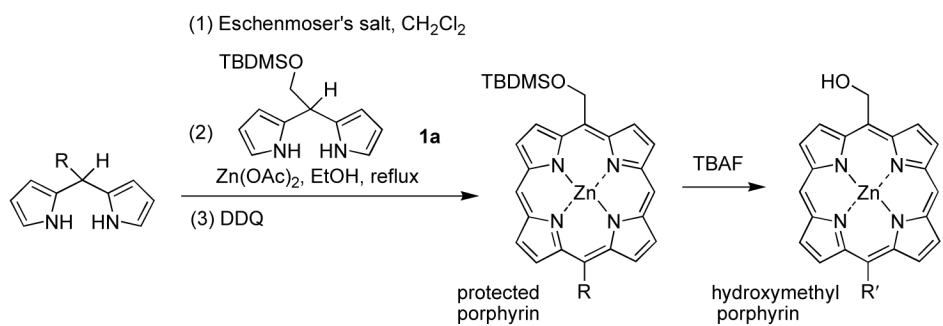
Scheme 3.



Scheme 4.

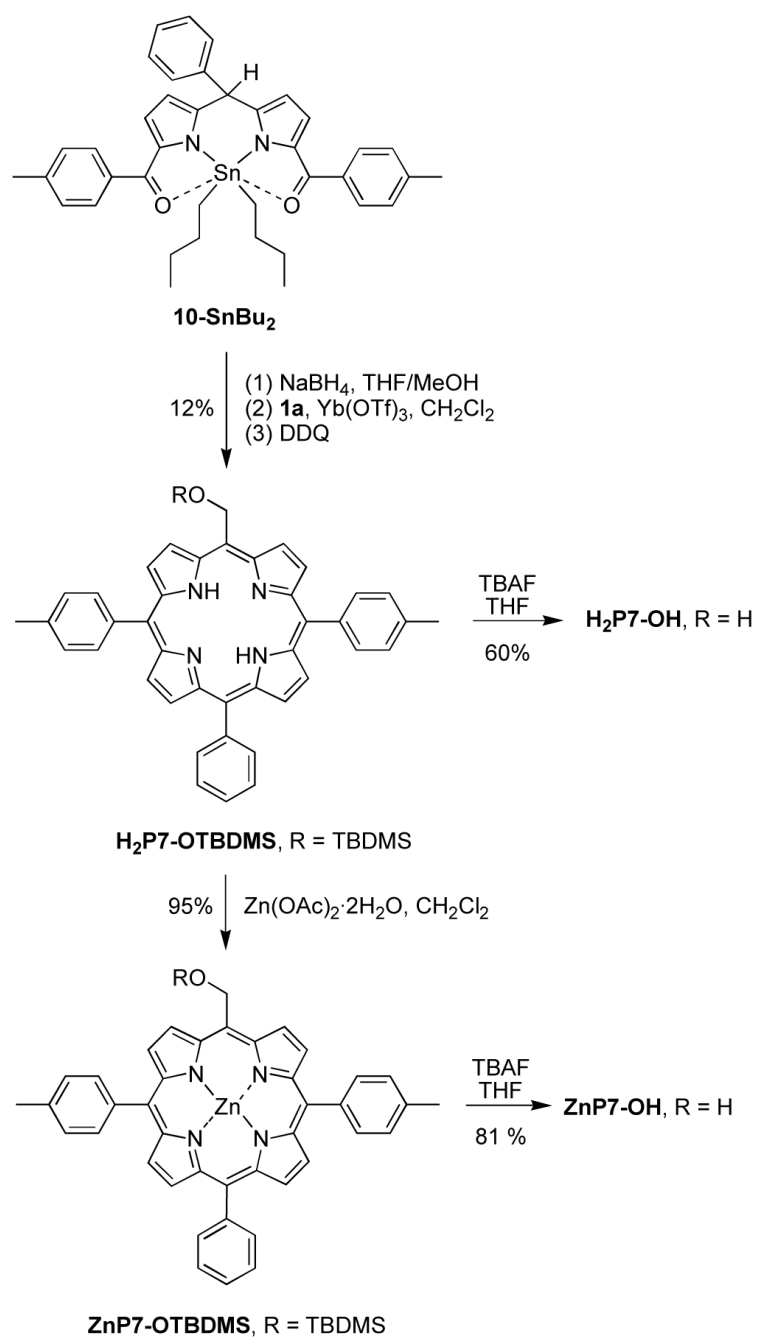


Scheme 5.

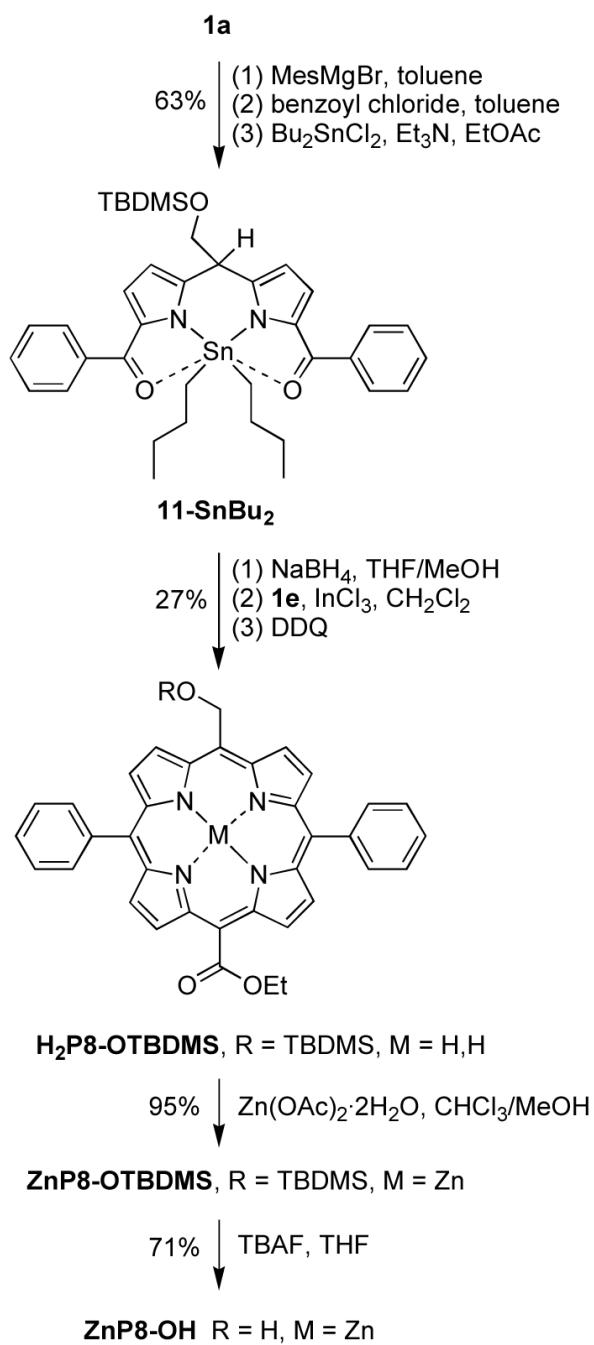


dipyromethane	R	protected porphyrin	yield	hydroxymethyl porphyrin	R'	yield
1b	$t\text{-BuO}_2\text{C}$ —	ZnP4-OTBDMS	4.0%	ZnP4-OH	$t\text{-BuO}_2\text{C}$ —	51%
1e	EtO_2C —	ZnP5-OTBDMS	7.5%	ZnP5-OH	EtO_2C —	66%
1f	TMS—	ZnP6-OTBDMS	2.4%	ZnP6-OH	H—	49%

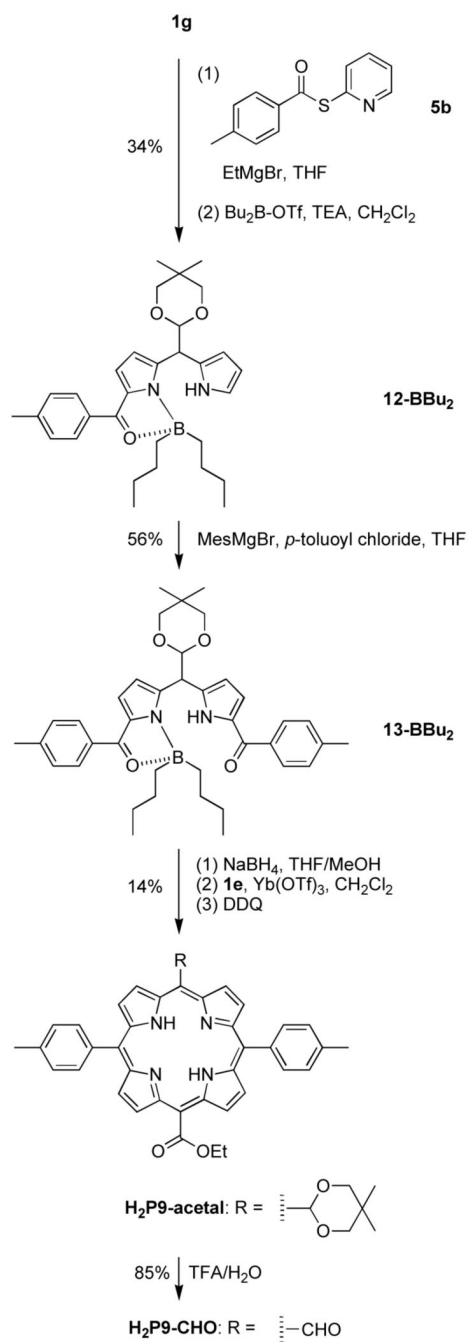
Scheme 6.



Scheme 7.



Scheme 8.



Scheme 9.