Supporting Information

Two-Step, One-Flask Synthesis of a Meso-Substituted Phlorin

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HPLC Method Development

The HPLC method for monitoring the yields of the phlorin 1, 5-isocorrole 2, porphodimethene 3, porphyrin 4, and corrole 5 from crude, oxidized reaction mixtures was adapted from an HPLC method reported for the quantitation of phlorin\textsuperscript{1} or 5-isocorrole, porphyrin, and porphodimethene.\textsuperscript{2} Modifications to the mobile phase composition (ratio of hexanes and acetone) and flow rate were made to resolve the more complex mixture of five porphyrinoid components. Detection wavelengths were selected for each porphyrinoid by recording the UV-vis spectrum for each peak (via a diode array UV-vis detector), and determining the $\lambda_{\text{max}}$ of the Soret band. The wavelengths selected were as follows: 434 nm (phlorin), 418 nm (5-isocorrole), 420 nm (porphodimethene), 410 nm (porphyrin), and 406 nm (corrole).

To facilitate peak assignment, a standard mixture of the five porphyrinoids was analyzed each day prior to examining experimental samples. Typically, the standard mixture was analyzed at the start of the day, after every ~10 injections, and at the end of each day. Porphyrinoid retention times were generally consistent throughout a day. However, some variability in retention time was observed from day-to-day. To minimize retention time reproducibility issues, 50% water saturated hexanes was utilized to diminish the effect of variable adventitious water on the normal phase silica column. Figure S1 shows representative chromatograms recorded at various points during the study. Although the precise retention times show some variation, resolution of the five porphyrinoids was generally good, and assignment of the peaks by comparison to chromatograms recorded from the standard mixture was not difficult. In a small number of experiments, porphodimethene and porphyrin were observed to elute closely. Using fresh mobile phase solvents, or a slight change of the percentage of acetone in the mobile phase (e.g., from 4.5% to 3.5%) restored the separation.

Figure S1. Representative chromatograms of the standard mixture of five porphyrinoids, recorded on different days throughout the study. Differences in peak heights stem from minor differences in porphyrinoid quantities due to the gradual degradation of the phlorin that required periodic addition of fresh phlorin to the mixture.
Control and Reproducibility Experiments, and Detector Response Calibration.

Control and reproducibility experiments were performed to assess the accuracy and reproducibility of the pre-HPLC sample work-up steps and the HPLC analysis. Accuracy and precision of the adjustable pipet used to remove reaction aliquots from the condensation reaction mixtures and oxidized mixtures were examined gravimetrically and found to be satisfactory. Accuracy and precision of the solvent pump used to dispense 1-mL portions of CH$_2$Cl$_2$ to elute the products from the pre-HPLC silica pad were examined gravimetrically and found to be satisfactory. Residual CH$_2$Cl$_2$ solvent on the silica pad after elution of the porphyrinoids was assessed by comparing the mass of solvent passed through a silica pad to the mass of an equivalent volume of solvent not passed through a silica pad (a volume of 3.7 mL was used in keeping with volumes used during actual analyses). The ratio of the two masses was found to be 0.78. A low coefficient of variance of 1.7% was obtained from replicate measurements of this ratio. Solvent evaporation from reaction vials, microcentrifuge tubes, and autosampler vials was examined gravimetrically and found to be negligible. Reproducibility of HPLC injection was found to be satisfactory by performing replicate 1-μL injections of the standard porphyrinoid mix sample and comparing peak areas. The HPLC detector response (diode array UV-vis detector) was calibrated using CH$_2$Cl$_2$ solutions of each porphyrinoid. A detector response factor for each porphyrinoid was determined from the slope of the plot of peak area as a function of porphyrinoid quantity. The response factors were checked periodically to confirm consistent detector sensitivity.

Calculation of the Yields of Phlorin, 5-Isocorrole, Porphodimethene, Porphyrin, and Corrole from HPLC Peak Areas.

The percent yield of each porphyrinoid was determined by comparing the peak area (monitored at the appropriate wavelength for each porphyrinoid) to the theoretical peak area calculated from the following general equation:

$$Peak \ Area_{theo} = \left[ \text{detector response} \times \frac{\text{area units}}{\mu\text{mol}} \right] \times \left[ 1.00 \ \mu\text{L} \times \frac{\mu\text{mol}}{\text{L}} \right] \times \left[ 1.20 \ \text{mL} \times \frac{\mu\text{L}}{1.20 \ \text{mL} + \text{TEA mL}} \right] \times \left[ 0.70 \ \text{mL} \times \frac{1}{0.70 \ \text{mL} + 3.00 \ \text{mL}} \right]$$

The detector response is the HPLC response factor determined by calibration for each porphyrinoid (phlorin, 1.42 x 10$^6$ area units/μmol at 434 nm; 5-isocorrole, 1.09 x 10$^6$ area units/μmol at 418 nm; porphodimethene, 2.08 x 10$^6$ area units/μmol at 420 nm; porphyrin, 8.34 x 10$^6$ area units/μmol at 410 nm; and corrole, 4.17 x 10$^6$ area units/μmol at 406 nm). The sample injection volume is 1.00 μL. The theoretical concentration is the maximum concentration of a porphyrinoid that could be obtained from the concentration of reactants. The term (1.20 mL / 1.20 mL + TEA mL) accounts for the slight dilution of the 1.2 mL reaction aliquot upon addition of a volume of triethylamine (assuming additivity of volumes, note that the volume of triethylamine differs for different reactions based on the concentration of acid catalyst). The term (0.70 mL / 0.70 mL + 3.00 mL) accounts for dilution upon passing a 0.70 mL aliquot through the silica pad and eluting with CH$_2$Cl$_2$ (3.0 mL). The final term (1 / 0.78) is an empirically derived correction factor for the volume of the CH$_2$Cl$_2$ that is retained on the silica
A specific example is considered below, based on the illustrative chromatogram and peak area data shown in Figure S2.

Figure S2. Illustrative chromatogram and peak area data from a crude, oxidized mixture from the reaction of pyrrole (10 mM), pentafluorobenzaldehyde (5.0 mM), and acetone (40 mM) mediated by TFA (215 mM) at a condensation reaction time of 1 h.

The percent yield of phlorin 1 was determined by comparing the observed peak area to the theoretical peak area, calculated from the following equation:

\[
\text{Peak Area}_{\text{theoretical}} = \left(1.42 \times 10^6 \frac{\text{area units}}{\mu\text{mol}}\right) \times 1.00 \mu\text{L} \left(\frac{0.00167 \mu\text{mol}}{\mu\text{L}}\right) \left(\frac{1.20 \text{ mL}}{1.20 \text{ mL} + 0.072 \text{ mL}}\right) \left(\frac{0.70 \text{ mL}}{0.70 \text{ mL} + 3.00 \text{ mL}}\right) \left(\frac{1}{0.78}\right)
\]

The theoretical concentration of phlorin is 0.00167 M as the limiting reagent is the aldehyde, and three equivalents of aldehyde are needed for each molecule of phlorin. The aliquot (1.2 mL) of the reaction mixture was basified with 0.072 mL of triethylamine. Thus, the theoretical peak area is 541.5 area units. The actual peak area for phlorin was 143.0 area units, corresponding to a yield of 26.4%.

The percent yield of porphodimethene 3 was determined by comparing the observed peak area to the theoretical peak area, calculated from the following equation:

\[
\text{Peak Area}_{\text{theoretical}} = \left(2.08 \times 10^6 \frac{\text{area units}}{\mu\text{mol}}\right) \times 1.00 \mu\text{L} \left(\frac{0.00250 \mu\text{mol}}{\mu\text{L}}\right) \left(\frac{1.20 \text{ mL}}{1.20 \text{ mL} + 0.072 \text{ mL}}\right) \left(\frac{0.70 \text{ mL}}{0.70 \text{ mL} + 3.00 \text{ mL}}\right) \left(\frac{1}{0.78}\right)
\]

The theoretical concentration of porphodimethene is 0.00250 M as the limiting reagent is both the pyrrole and aldehyde (four equivalents of pyrrole and two equivalents of aldehyde are needed for each molecule of porphodimethene). The aliquot (1.2 mL) of the reaction mixture was basified with 0.072 mL of triethylamine. Thus, the theoretical peak area is 1189.9 area units. The actual peak area for porphodimethene was 22.8 area units, corresponding to a yield of 1.9%.

The percent yield of porphyrin 4 was determined by comparing the observed peak area to the theoretical peak area, calculated from the following equation:

\[
\text{Peak Area}_{\text{theoretical}} = \left(8.34 \times 10^6 \frac{\text{area units}}{\mu\text{mol}}\right) \times 1.00 \mu\text{L} \left(\frac{0.00125 \mu\text{mol}}{\mu\text{L}}\right) \left(\frac{1.20 \text{ mL}}{1.20 \text{ mL} + 0.072 \text{ mL}}\right) \left(\frac{0.70 \text{ mL}}{0.70 \text{ mL} + 3.00 \text{ mL}}\right) \left(\frac{1}{0.78}\right)
\]
The theoretical concentration of porphyrin is 0.00125 M as the limiting reagent is the aldehyde, and four equivalents of aldehyde are needed for each molecule of porphyrin. The aliquot (1.2 mL) of the reaction mixture was basified with 0.072 mL of triethylamine. Thus, the theoretical peak area is 2385.5 area units. The actual peak area for phlorin was 135.8 area units, corresponding to a yield of 5.7%.

The percent yield of corrole 5 was determined by comparing the observed peak area to the theoretical peak area, calculated from the following equation:

\[
\text{Peak Area}_{\text{theoretical}} = \left( 4.17 \times 10^6 \frac{\text{area units}}{\mu\text{mol}} \right) \times 1.00 \mu\text{L} \times \frac{0.00167 \ \mu\text{mol}}{\mu\text{L}} \times \left( \frac{1.20 \ \text{mL}}{1.20 \ \text{mL} + 0.072 \ \text{mL}} \right) \times \left( \frac{0.70 \ \text{mL}}{0.70 \ \text{mL} + 3.00 \ \text{mL}} \right) \times 1
\]

The theoretical concentration of corrole is 0.00167 M as the limiting reagent is the aldehyde, and three equivalents of aldehyde are needed for each molecule of corrole. The aliquot (1.2 mL) of the reaction mixture was basified with 0.072 mL of triethylamine. Thus, the theoretical peak area is 1590.3 area units. The actual peak area for corrole was 19.2 area units, corresponding to a yield of 1.2%.

Plots of Porphyrinoid Yields from Analytical-Scale Reactions.

Figures S3-S8 provide plots of the yield of phlorin 1, porphyrin 4, and corrole 5 as a function of the various reaction parameters that were investigated (pentafluorobenzaldehyde concentration, acetone concentration, acid catalyst, acid catalyst concentration, DDQ quantity, and condensation reaction time). Figures S3 and S4 provide a summary of experiments performed with 2.5 mM pentafluorobenzaldehyde, under TFA or BF\(_3\)OEt\(_2\) catalysis respectively. Figures S5 and S6 provide a summary of experiments performed with 5.0 mM pentafluorobenzaldehyde, under TFA or BF\(_3\)OEt\(_2\) catalysis respectively. Figures S7 and S8 provide a summary of experiments performed with 7.5 mM pentafluorobenzaldehyde, under TFA or BF\(_3\)OEt\(_2\) catalysis respectively.

Porphodimethene 3 was generally observed in low yields (<2%), and 5-isocorrole 2 was not detected. Thus, porphodimethene 3 and 5-isocorrole 2 are not included in the plots. A small number of reaction conditions afforded modest yields of porphodimethene. These conditions are summarized in Table S1 found after Figures S3-S8.
Figure S3. Yields of porphyrinoids from the reactions of pyrrole (10 mM), pentafluorobenzaldehyde (2.5 mM), and acetone with catalysis from TFA as a function of the following reaction parameters: (A) acetone concentration (panel A1 provides the yield of phlorin 1 at each of the three time points, and panel A2 provides the highest yield of phlorin 1, porphyrin 4, and corrole 5 observed at reaction times of 15 min, 1 h, or 4 h), (B) TFA concentration (panel B1 provides the yield of phlorin 1 at each of the three time points, and panel B2 provides the highest yield of phlorin 1, porphyrin 4, and corrole 5 observed at reaction times of 15 min, 1 h, or 4 h), (C) DDQ quantity used to oxidize reaction aliquots (1.2 mL), and (D) condensation reaction time. The reactions were performed in CH₂Cl₂ at room temperature, and were monitored by HPLC. Porphodimethene 3 was generally observed in low yields (<2%), and 5-isocorrole 2 was not detected.
Figure S4. Yields of porphyrinoids from the reactions of pyrrole (10 mM), pentafluorobenzaldehyde (2.5 mM), and acetone with catalysis from BF$_3$OEt$_2$ as a function of the following reaction parameters: (A) acetone concentration (panel A1 provides the yield of phlorin 1 at each of the three time points, and panel A2 provides the highest yield of phlorin 1, porphyrin 4, and corrole 5 observed at reaction times of 15 min, 1 h, or 4 h), (B) BF$_3$OEt$_2$ concentration (panel B1 provides the yield of phlorin 1 at each of the three time points, and panel B2 provides the highest yield of phlorin 1, porphyrin 4, and corrole 5 observed at reaction times of 15 min, 1 h, or 4 h), (C) DDQ quantity used to oxidize reaction aliquots (1.2 mL), and (D) condensation reaction time. The reactions were performed in CH$_2$Cl$_2$ at room temperature, and were monitored by HPLC. Porphodimethene 3 was generally observed in low yields (<2%), and 5-isocorrole 2 was not detected.
Figure S5. Yields of porphyrinoids from the reactions of pyrrole (10 mM), pentafluorobenzaldehyde (5.0 mM), and acetone with catalysis from TFA as a function of the following reaction parameters: (A) acetone concentration (panel A1 provides the yield of phlorin 1 at each of the three time points, and panel A2 provides the highest yield of phlorin 1, porphyrin 4, and corrole 5 observed at reaction times of 15 min, 1 h, or 4 h), (B) TFA concentration (panel B1 provides the yield of phlorin 1 at each of the three time points, and panel B2 provides the highest yield of phlorin 1, porphyrin 4, and corrole 5 observed at reaction times of 15 min, 1 h, or 4 h), (C) DDQ quantity used to oxidize reaction aliquots (1.2 mL), and (D) condensation reaction time. The reactions were performed in CH₂Cl₂ at room temperature, and were monitored by HPLC. Porphodimethene 3 was generally observed in low yields (<2%), and 5-isocorrole 2 was not detected.
Figure S6. Yields of porphyrinoids from the reactions of pyrrole (10 mM), pentafluorobenzaldehyde (5.0 mM), and acetone with catalysis from BF$_3$OEt$_2$ as a function of the following reaction parameters: (A) acetone concentration (panel A1 provides the yield of phlorin 1 at each of the three time points, and panel A2 provides the highest yield of phlorin 1, porphyrin 4, and corrole 5 observed at reaction times of 15 min, 1 h, or 4 h), (B) BF$_3$OEt$_2$ concentration (panel B1 provides the yield of phlorin 1 at each of the three time points, and panel B2 provides the highest yield of phlorin 1, porphyrin 4, and corrole 5 observed at reaction times of 15 min, 1 h, or 4 h), (C) DDQ quantity used to oxidize reaction aliquots (1.2 mL), and (D) condensation reaction time. The reactions were performed in CH$_2$Cl$_2$ at room temperature, and were monitored by HPLC. Porphodimethene 3 was generally observed in low yields (<2%), and 5-isocorrole 2 was not detected.
A1 Yield of Phlorin
10 mM pyrrole, 7.5 mM aldehyde, 215 mM TFA

A2 Yield of Porphyrinoids
10 mM pyrrole, 7.5 mM aldehyde, 215 mM TFA

B1 Yield of Phlorin
10 mM pyrrole, 7.5 mM aldehyde, 80 mM acetone

B2 Yield of Porphyrinoids
10 mM pyrrole, 7.5 mM aldehyde, 80 mM acetone

C Yield of Porphyrinoids
10 mM pyrrole, 7.5 mM aldehyde, 80 mM acetone, 215 mM TFA; 15 min

D Yield of Porphyrinoids
10 mM pyrrole, 7.5 mM aldehyde, 80 mM acetone, 215 mM TFA

E Yield of Porphyrinoids
10 mM pyrrole, 7.5 mM aldehyde, 160 mM acetone, 215 mM TFA
Figure S7. Yields of porphyrinoids from the reactions of pyrrole (10 mM), pentafluorobenzaldehyde (7.5 mM), and acetone with catalysis from TFA as a function of the following reaction parameters: (A) acetone concentration (panel A1 provides the yield of phlorin 1 at each of the three time points, and panel A2 provides the highest yield of phlorin 1, porphyrin 4, and corrole 5 observed at reaction times of 15 min, 1 h, or 4 h), (B) TFA concentration (panel B1 provides the yield of phlorin 1 at each of the three time points, and panel B2 provides the highest yield of phlorin 1, porphyrin 4, and corrole 5 observed at reaction times of 15 min, 1 h, or 4 h), (C) DDQ quantity used to oxidize reaction aliquots (1.2 mL), (D) condensation reaction time with 80 mM acetone, and (E) condensation reaction time with 160 mM acetone. The reactions were performed in CH$_2$Cl$_2$ at room temperature, and were monitored by HPLC. Porphodimethene 3 was generally observed in low yields (<2%), and 5-isocorrole 2 was not detected.
Figure S8. Yields of porphyrinoids from the reactions of pyrrole (10 mM), pentafluorobenzaldehyde (7.5 mM), and acetone with catalysis from BF$_3$OEt$_2$ as a function of the following reaction parameters: (A) acetone concentration (panel A1 provides the yield of phlorin 1 at each of the three time points, and panel A2 provides the highest yield of phlorin 1, porphyrin 4, and corrole 5 observed at reaction times of 15 min, 1 h, or 4 h), (B) BF$_3$OEt$_2$ concentration (panel B1 provides the yield of phlorin 1 at each of the three time points, and panel B2 provides the highest yield of phlorin 1, porphyrin 4, and corrole 5 observed at reaction times of 15 min, 1 h, or 4 h), (C) DDQ quantity used to oxidize reaction aliquots (1.2 mL), and (D) condensation reaction time. The reactions were performed in CH$_2$Cl$_2$ at room temperature, and were monitored by HPLC. Porphodimethene 3 was generally observed in low yields (<2%), and 5-isocorrole 2 was not detected.
Table S1. Summary of Reaction Conditions that Afforded Porphodimethene 3 in Yields Exceeding 2%.\(^a\)

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<th>[aldehyde], mM</th>
<th>[acetone], mM</th>
<th>acid</th>
<th>[acid], mM</th>
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<th>% yield of porphodimethene(^b)</th>
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\(^a\)The reactions were performed in CH\(_2\)Cl\(_2\) with the indicated reactants on a 10 mL scale at room temperature. The reactions were monitored at 15 min, 1 h, and 4 h. \(^b\)The yield was determined by HPLC.

Characterization of Phlorin Isolated from the Reaction of Pyrrole (10 mM), Pentafluorobenzaldehyde (5.0 mM), and Acetone (80 mM) Mediated by TFA (215 mM).

Figures S9-S13 provide characterization data for phlorin 1 isolated from a preparative-scale reaction performed under the best condition identified from analytical-scale reactions utilizing 5.0 mM pentafluorobenzaldehyde. Figure S9 contains HPLC data, Figure S10 provides UV-vis spectra, and Figures S11-S13 report \(^1\)H NMR spectra.
Figure S9. HPLC chromatograms recorded at different stages of phlorin I purification: (A) crude reaction mixture, (B) after silica gel chromatography, (C) after neutral alumina chromatography, (D) after crystallization from CH$_2$Cl$_2$/hexanes. Note that the other porphyrinoid byproducts are no longer detected after silica gel chromatography.
Figure S10. UV-vis spectra (in CH$_2$Cl$_2$) recorded at different stages of phlorin 1 purification: (A) after neutral alumina chromatography, (B) after crystallization from CH$_2$Cl$_2$/hexanes.
Figure S11. $^1$H NMR spectrum of phlorin 1 in CDCl$_3$, recorded after purification by neutral alumina chromatography.
Figure S12. $^1$H NMR spectrum of phlorin 1 in CDCl$_3$, recorded after purification by crystallization from CH$_2$Cl$_2$/hexanes.
Figure S13. $^1$H NMR spectrum of phlorin 1 in DMSO-$d_6$, recorded after purification by crystallization from CH$_2$Cl$_2$/hexanes.
Characterization of Phlorin Isolated from the Reaction of Pyrrole (10 mM), Pentafluorobenzaldehyde (7.5 mM), and Acetone (160 mM) Mediated by TFA (215 mM).

Figures S14-S18 provide characterization data for phlorin 1 isolated from a preparative-scale reaction performed under the best condition identified from analytical-scale reactions utilizing 7.5 mM pentafluorobenzaldehyde. Figure S14 contains HPLC data, Figure S15 provides UV-vis spectra, and Figures S16-S18 report $^1$H NMR spectra.
**Figure S14.** HPLC chromatograms recorded at different stages of phlorin 1 purification: (A) crude reaction mixture, (B) after silica gel chromatography, (C) after neutral alumina chromatography, (D) after crystallization from CH$_2$Cl$_2$/hexanes. Note that the other porphyrinoid byproducts are no longer detected after silica gel chromatography.
Figure S15. UV-vis spectra (in CH$_2$Cl$_2$) recorded at different stages of phlorin 1 purification: (A) after neutral alumina chromatography, (B) after crystallization from CH$_2$Cl$_2$/hexanes.
Figure S16. $^1$H NMR spectrum of phlorin 1 in CDCl$_3$, recorded after purification by neutral alumina chromatography.
Figure S17. $^1$H NMR spectrum of phlorin 1 in CDCl$_3$, recorded after purification by crystallization from CH$_2$Cl$_2$/hexanes.
Figure S18. $^1$H NMR spectrum of phlorin 1 in DMSO-$d_6$, recorded after purification by crystallization from CH$_2$Cl$_2$/hexanes.
Characterization of Phlorin Isolated from the Reaction of Pyrrole (10 mM), Pentafluorobenzaldehyde (2.5 mM), and Acetone (80 mM) Mediated by TFA (215 mM).

Figures S19-S23 provide characterization data for phlorin 1 isolated from a preparative-scale reaction performed under the best condition identified from analytical-scale reactions utilizing 2.5 mM pentafluorobenzaldehyde. Figure S19 contains HPLC data, Figure S20 provides UV-vis spectra, and Figures S21-S23 report $^1$H NMR spectra.
Figure S19. HPLC chromatograms recorded at different stages of phlorin 1 purification: (A) crude reaction mixture, (B) after silica gel chromatography, (C) after neutral alumina chromatography, (D) after crystallization from CH$_2$Cl$_2$/hexanes. Note that the other porphyrinoid byproducts were largely removed by silica gel chromatography, and a low level of residual porphyrin was no longer detected after neutral alumina chromatography.
Figure S20. UV-vis spectra (in CH$_2$Cl$_2$) recorded at different stages of phlorin 1 purification: (A) after neutral alumina chromatography, (B) after crystallization from CH$_2$Cl$_2$/hexanes.
Figure S21. $^1$H NMR spectrum of phlorin 1 in CDCl$_3$, recorded after purification by neutral alumina chromatography.
Figure S22. $^1$H NMR spectrum of phlorin 1 in CDCl$_3$, recorded after purification by crystallization from CH$_2$Cl$_2$/hexanes.
Figure S23. $^1$H NMR spectrum of phlorin 1 in DMSO-$d_6$, recorded after purification by crystallization from CH$_2$Cl$_2$/hexanes.
Estimation of the Yield of Porphodimethene 3, Porphyrin 4, and Corrole 5 from Preparative-Scale Reactions.

Similar chromatographic retention of porphodimethene 3, porphyrin 4, and corrole 5 rendered it difficult to cleanly separate these three porphyrinoids while isolating phlorin 1 from the preparative-scale reactions. Rather, a fraction containing a mixture of porphodimethene 3 and porphyrin 4, and a fraction containing largely corrole 5 with a low level of porphodimethene 3 and porphyrin 4 were generally obtained from silica gel chromatography. The quantity of each porphyrinoid was estimated by determining the dry mass of the two fractions, and assessing the ratio of porphyrinoids in each fraction by $^1$H NMR spectroscopy.

To illustrate the analysis, the estimation of the yield of porphodimethene 3, porphyrin 4, and corrole 5 from the reaction of pyrrole (10 mM), pentafluorobenzaldehyde (5.0 mM), and acetone (80 mM) mediated by TFA (215 mM) is presented. The reaction was performed on a 4.50 mmol scale of aldehyde. Silica gel chromatography afforded a fraction containing porphodimethene 3 and porphyrin 4 (fraction 1) and a fraction containing largely corrole 5 with a low level of porphodimethene 3 and porphyrin 4 (fraction 2). The mass of fraction 1 was 68.6 mg, and the mass of fraction 2 was 7.6 mg.

$^1$H NMR peak integration of the spectrum recorded from fraction 1 (Figure S24) was used to determine the mole ratio of porphodimethene 3, porphyrin 4, and residual CH$_2$Cl$_2$ present in the sample. This was done by totaling the peak area(s) for each compound, and dividing by the total number of protons represented by the peaks. The mole ratio of porphodimethene 3, porphyrin 4, and residual CH$_2$Cl$_2$ was found to be 0.569 : 0.999 : 0.405. The mole ratio determined from the integrated $^1$H NMR spectrum was converted to a mass percent of porphodimethene 3, porphyrin 4, and residual CH$_2$Cl$_2$ through knowledge of each compound’s molecular weight. The mass percentages were determined to be 28.3%, 69.3%, and 2.4% respectively for porphodimethene 3, porphyrin 4, and residual CH$_2$Cl$_2$. Using the mass percentages along with the measured mass of the sample mixture, an estimated mass of porphodimethene 3 and porphyrin 4 in fraction 1 was determined to be 19.4 mg and 47.5 mg, respectively.

An analogous analysis was carried out with fraction 2. $^1$H NMR analysis (Figure S25) revealed a mole ratio of corrole 5, porphyrin 4, porphodimethene 3, and residual CH$_2$Cl$_2$ of 1.02 : 0.123 : 0.0632 : 0 respectively. The corresponding mass percent of corrole 5, porphyrin 4, and porphodimethene 3 in fraction 2 was calculated to be 83.2%, 12.3%, and 4.5% respectively. Thus, the estimated mass of corrole 5, porphyrin 4, and porphodimethene 3 in fraction 2 was determined to be 6.3 mg, 0.9 mg, and 0.3 mg, respectively.

The combined estimated mass of porphodimethene 3, porphyrin 4, and corrole 5 in fractions 1 and 2 are 19.7 mg, 48.4 mg, and 6.3 mg respectively. The theoretical yields of porphodimethene 3, porphyrin 4, and corrole 5 for this reaction condition are 1576.3 mg, 1096.4 mg, and 1194.7 mg. Thus, the percent yield of porphodimethene 3, porphyrin 4, and corrole 5 afforded by the reaction are estimated to be 1.2%, 4.4%, and 0.5%, respectively.

The validity of this analysis depends on the absence of significant levels of other impurities in fractions 1 and 2. $^1$H NMR, TLC, and HPLC analyses are consistent with the absence of complicating impurities. The low level of impurity detected in the $^1$H NMR spectrum of fraction 2 has minimal effect given the low mass of fraction 2 compared to fraction 1.
Figure S24. $^1$H NMR analysis in CDCl$_3$ of fraction 1 containing a mixture of porphodimethene 3 and porphyrin 4.
Figure S25. $^1$H NMR analysis in CDCl$_3$ of fraction 2 containing a mixture of porphodimethene 3, porphyrin 4, and corrole 5.
Characterization of 5-Methyl-5-Phenylphlorin 6 and Corrole 5 Isolated from the Reaction of Pyrrole, Pentafluorobenzaldehyde, and Acetophenone Mediated by TFA.

Figures S26-S27 provide characterization data for 5-methyl-5-phenylphlorin 6 isolated from a preparative-scale reaction of pyrrole (10 mM), pentafluorobenzaldehyde (5.0 mM), and acetophenone (80 mM) mediated by TFA (215 mM). Figure S26 contains a UV-vis spectrum, and Figure S27 shows the $^1$H NMR spectrum.

Figures S28-S29 provide characterization data of corrole 5 isolated from the same preparative-scale reaction. Figure S28 contains a UV-vis spectrum, and Figure S29 shows the $^1$H NMR spectrum.

**Figure S26.** UV-vis spectrum (in CH$_2$Cl$_2$) of 5-methyl-5-phenylphlorin 6.
Figure S27. $^1$H NMR spectrum of 5-methyl-5-phenylphlorin 6 in CDCl$_3$. Peaks assigned to phlorin 6 are indicated on the spectrum.
Figure S28. UV-vis spectrum (in CH$_2$Cl$_2$) of corrole 5.
**Figure S29.** $^1$H NMR spectrum of corrole 5 in CDCl$_3$. 