

## The dual behaviour of $\beta$ -vinylporphyrins in the presence of $\alpha,\alpha'$ - dioxothiones

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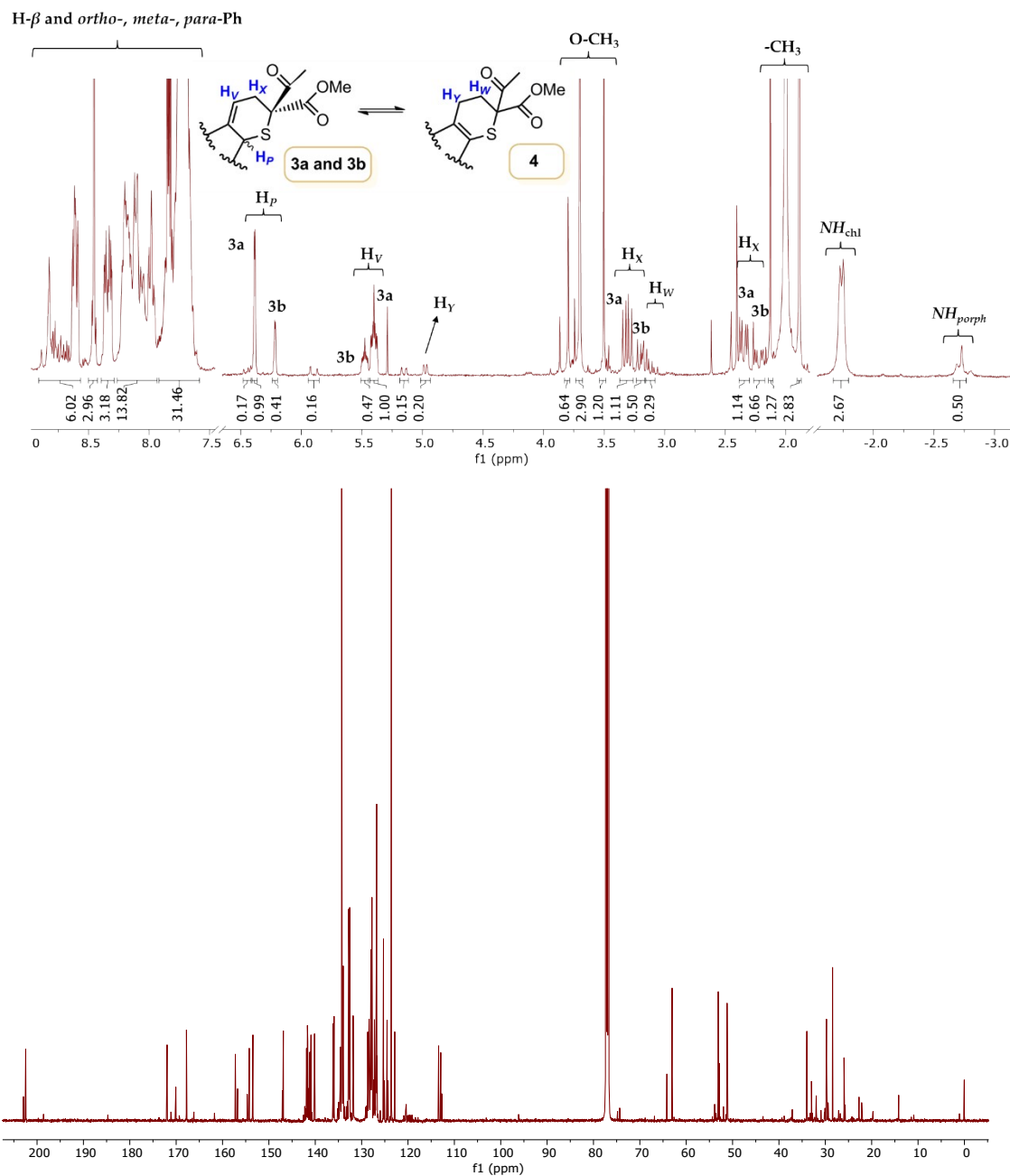
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## NMR Data



**Figure S1.**  $^1\text{H}$  NMR (above) and  $^{13}\text{C}$  NMR (below) spectra of the reactional mixture of chlorins **3a** and **3b** in tautomeric equilibrium with porphyrin **4**, in  $\text{CDCl}_3$ .

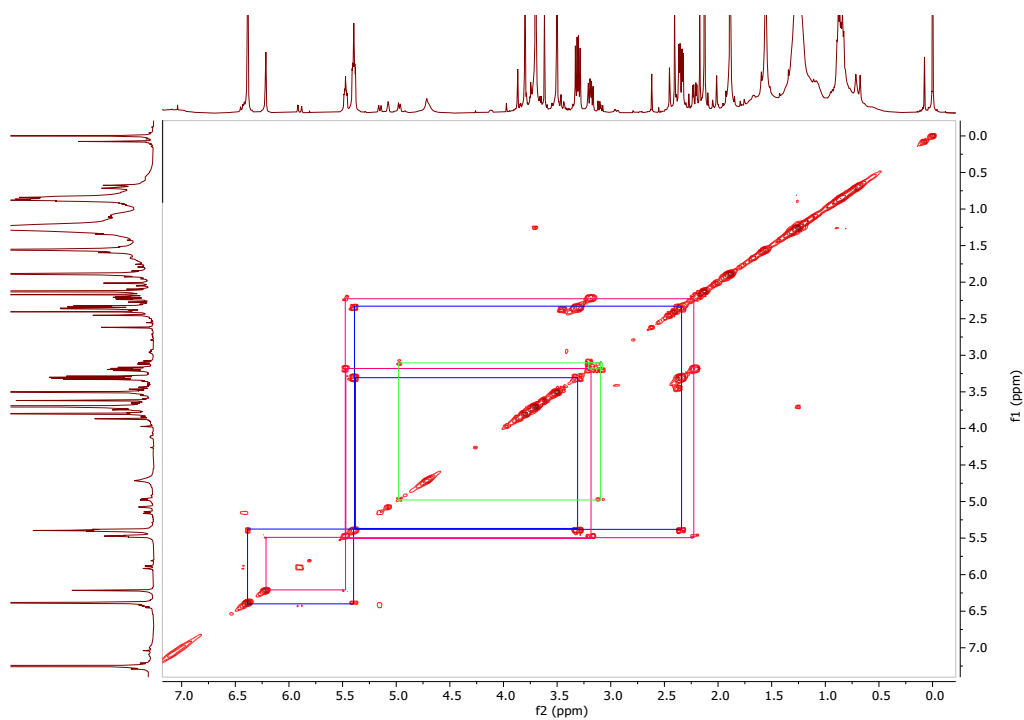


Figure S2.  $^1\text{H}/^1\text{H}$  COSY of chlorins **3a** and **3b** in tautomeric equilibrium with porphyrin **4**, in  $\text{CDCl}_3$ .

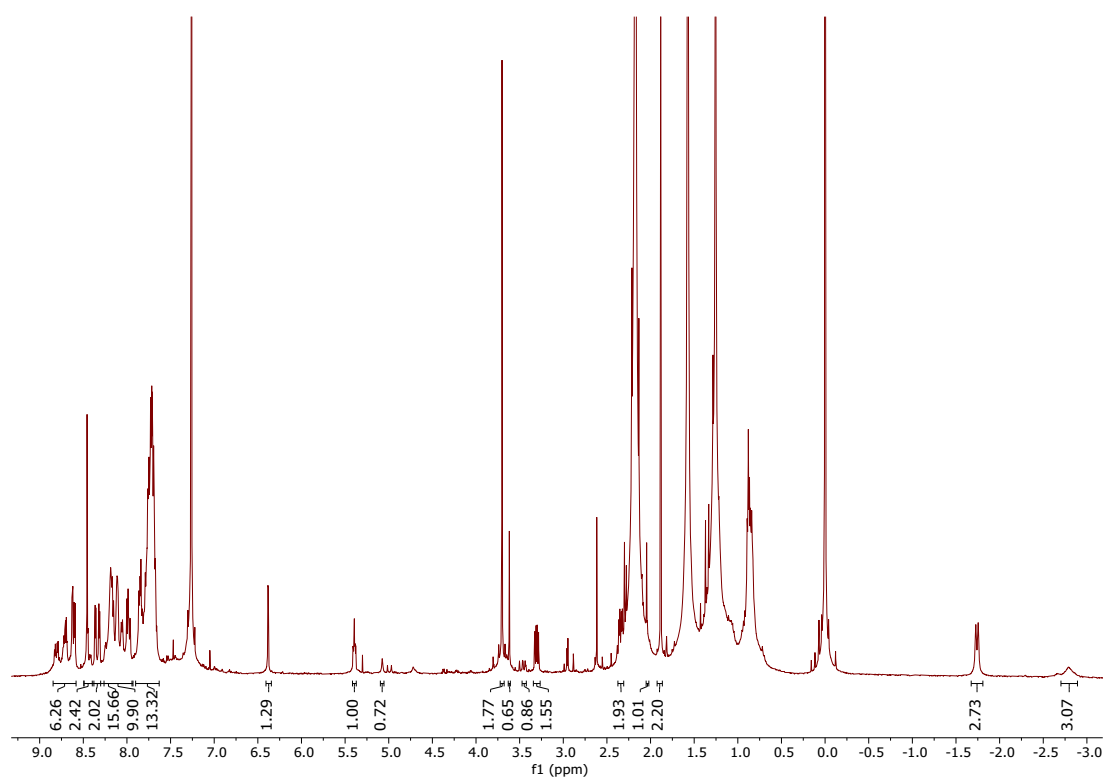


Figure S3.  $^1\text{H}$  NMR spectrum of chlorin **3a**/porphyrin **4** in tautomeric equilibrium, in  $\text{CDCl}_3$ .

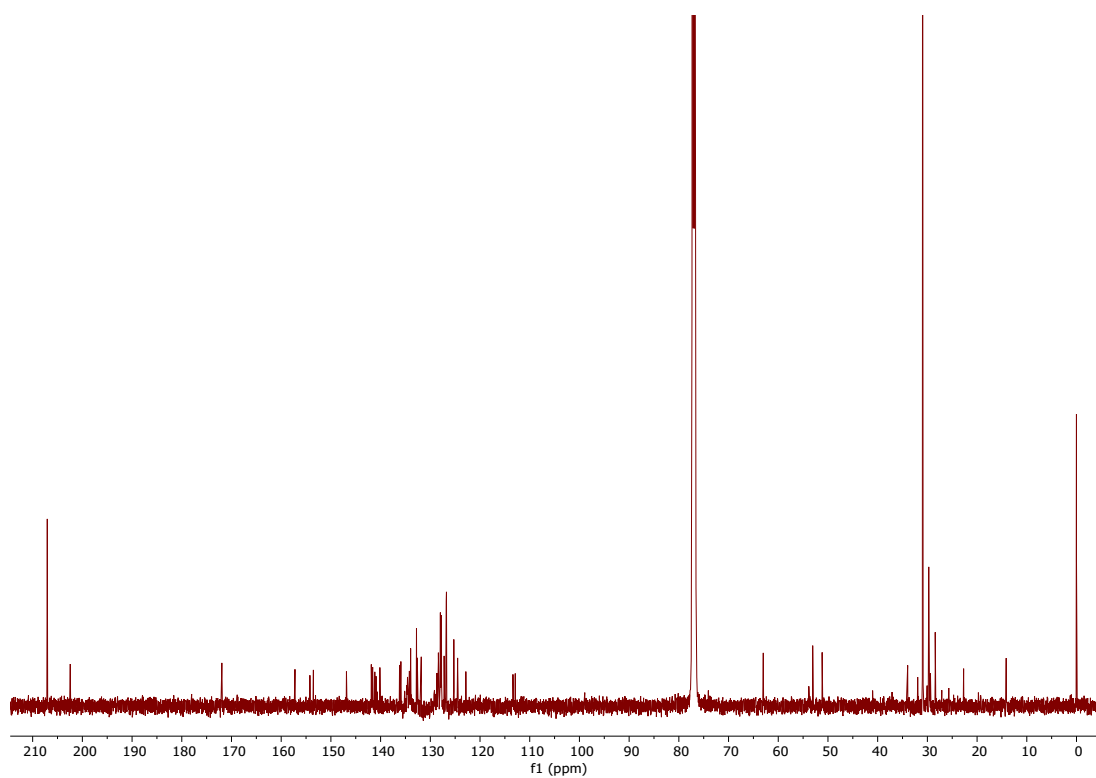


Figure S4.  $^{13}\text{C}$  NMR spectrum of chlorin 3a/porphyrin 4 in tautomeric equilibrium, in  $\text{CDCl}_3$ .

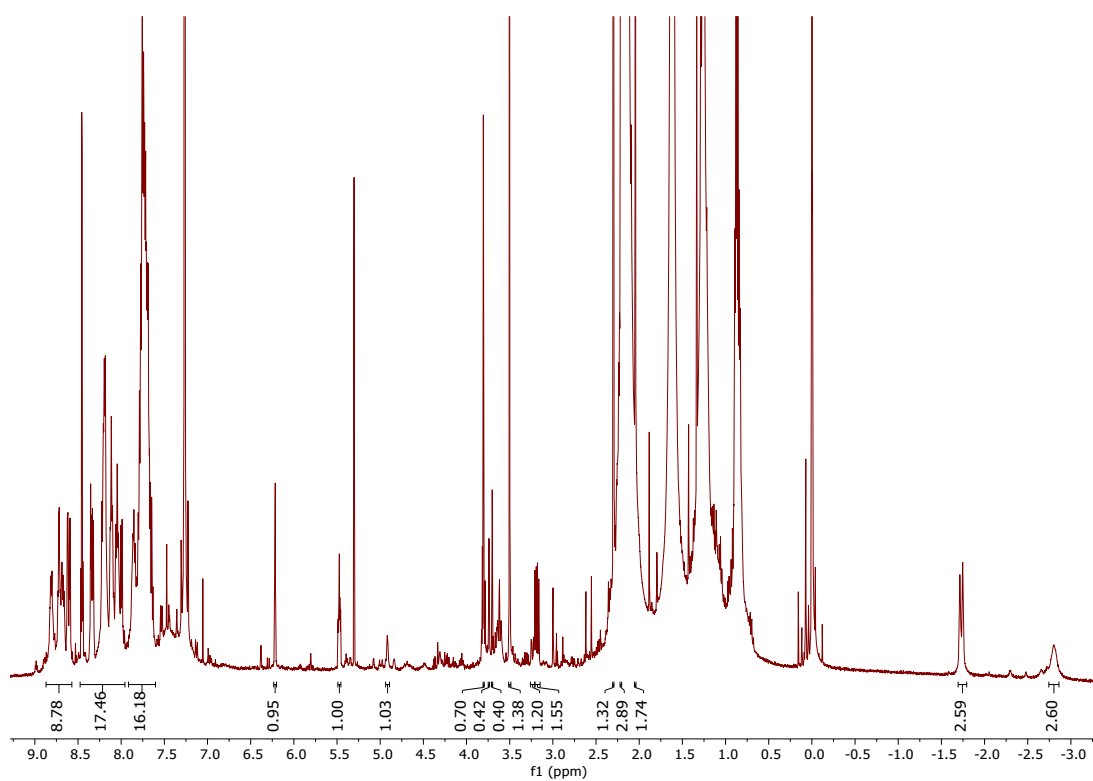


Figure S5.  $^1\text{H}$  NMR spectrum of chlorin 3b/porphyrin 4 in tautomeric equilibrium, in  $\text{CDCl}_3$ .

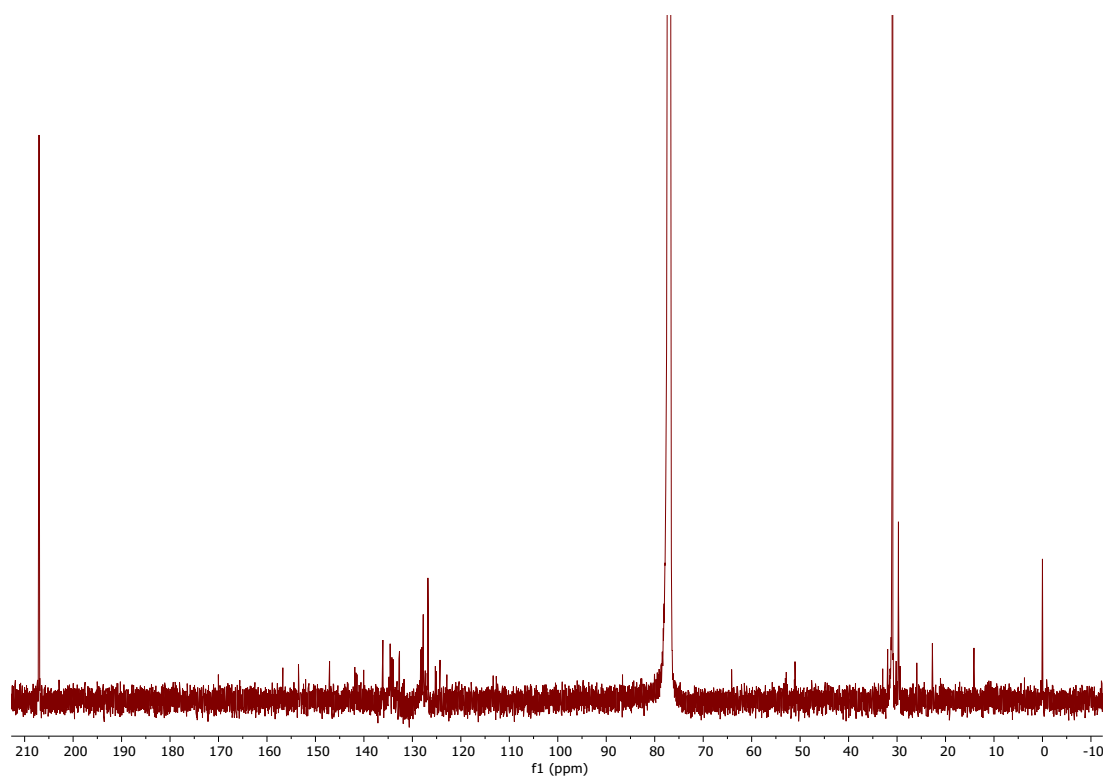


Figure S6.  $^{13}\text{C}$  NMR spectrum of chlorin 3b/porphyrin 4 in tautomeric equilibrium, in  $\text{CDCl}_3$ .

### Mass Spectrometry Data

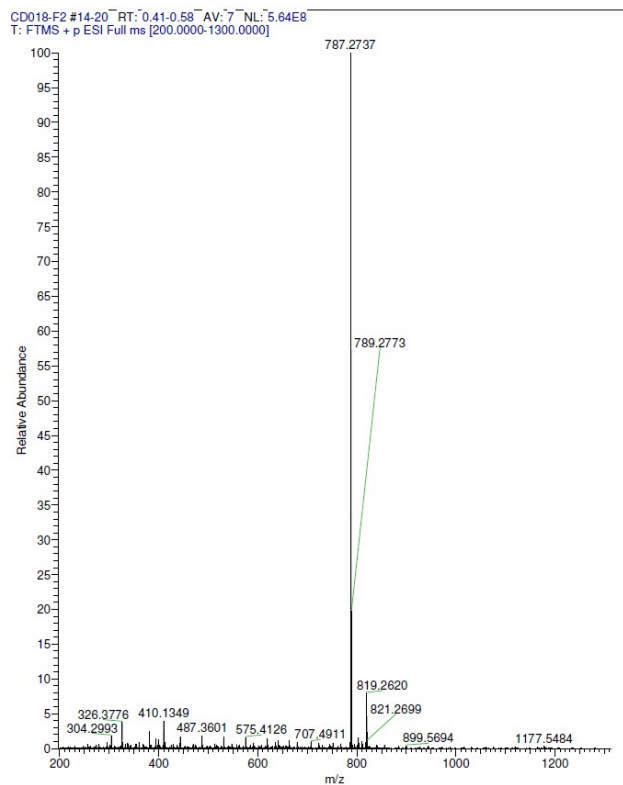


Figure S7. HRMS of chlorin 3a/porphyrin 4 in tautomeric equilibrium.

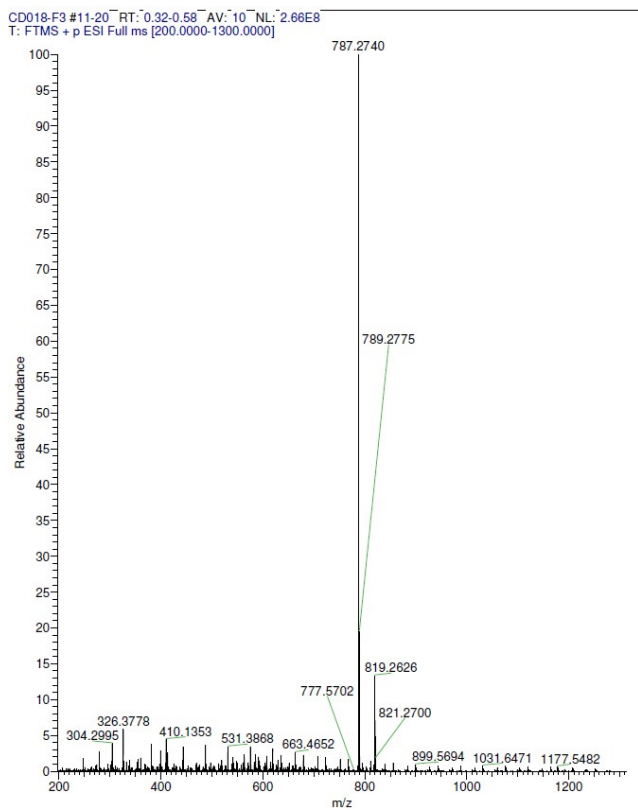


Figure S8. HRMS of chlorin 3b/porphyrin 4 in tautomeric equilibrium.

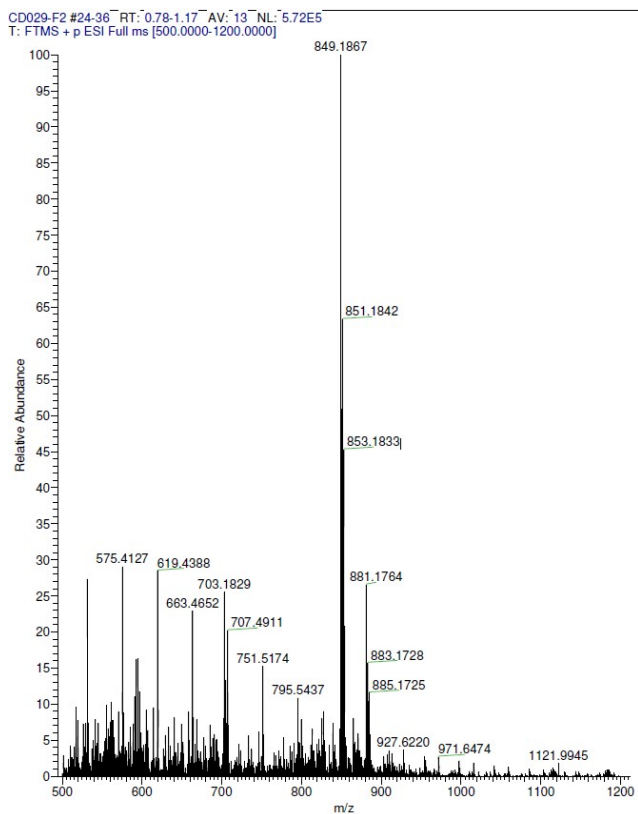
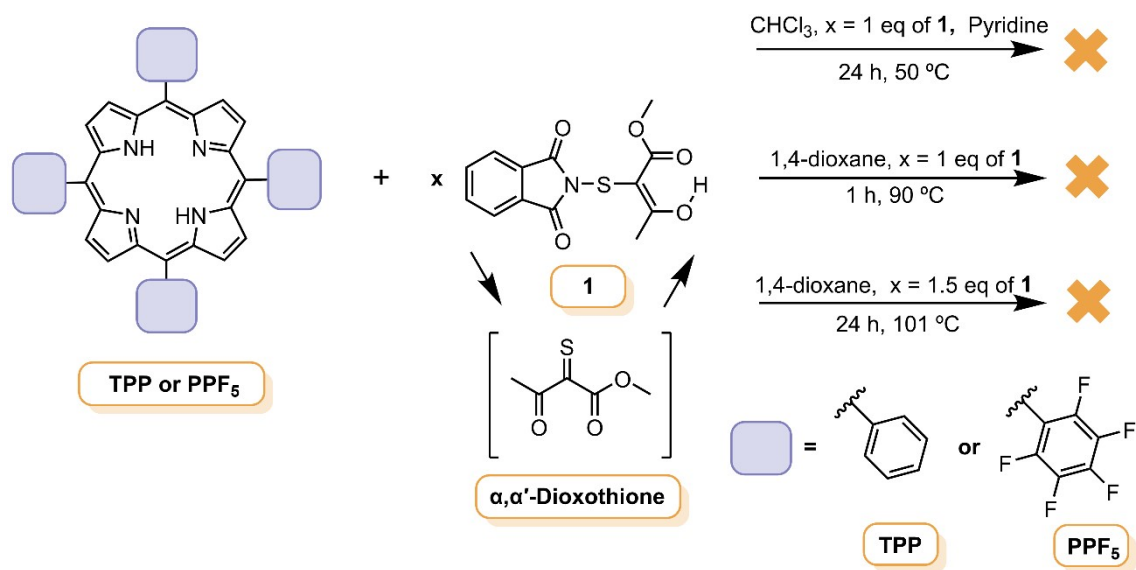


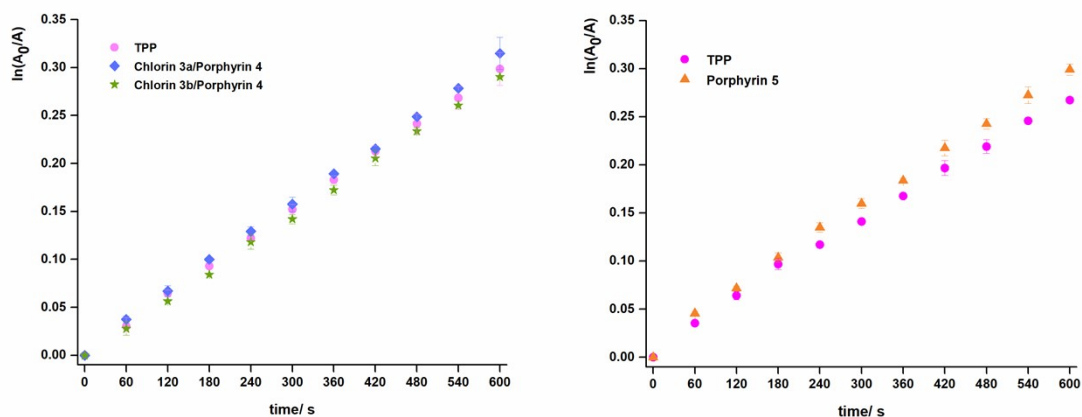
Figure S9. HRMS of porphyrin 5.

## Synthesis



**Scheme S1.** Representation of the different attempts of cycloaddition reaction between **TPP** or **PPF<sub>5</sub>** and the  $\alpha,\alpha'$ -dioxothione.

## Photophysical Characterization Data



**Figure S10.** Photo-oxidation of DMA, in DMF, photosensitized by cycloadducts **chlorin 3a/porphyrin 4** and **chlorin 3b/porphyrin 4** (left) and **porphyrin 5** (right), and the reference **TPP** during 600 s at  $420 \text{ nm} \pm 5 \text{ nm}$ . The symbols may be overlapped, and the error bars corresponds to the standard deviation of two independent assays.