Supporting Information

Photoactive diazo-oxochlorins as potential *in-situ* alkylating reagents

Tillmann Köpke, Maren Pink and Jeffrey M. Zaleski*
Department of Chemistry, Indiana University, Bloomington, IN, USA.

X-ray structure analysis

Data collection, structure solution, and refinement. Data collections were carried out at IUMSC using a Bruker platform diffractometer equipped with a SMART6000 CCD detector and Mo Kα radiation (λ = 0.71073 Å, graphite monochromator) or at the APS, ChemMatCARS, using synchrotron radiation (λ = 0.49595, diamond 111 monochromator, two mirrors to exclude higher harmonics). The intensity data were corrected for absorption (SADABS).[1] Final cell constants were calculated from the xyz centroids of strong reflections in the actual data after integration (SAINT).[2] Space groups were determined based on intensity statistics and systematic absences. Structures were solved with direct methods using SIR-92[3] or SHELXL-97[4] and refined with full-matrix least squares / difference Fourier cycles using SHELXL-97. All non-hydrogen atoms were refined with anisotropic displacement parameters unless noted otherwise. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative or individual isotropic displacement parameters.

Cu2a. Dark brown crystal (approximate dimensions 0.18 × 0.12 × 0.05 mm^3). The final full matrix least squares refinement converged to R1 = 0.0496 and wR2 = 0.1349 (F^2, all data). The remaining electron density is located near the alkyl rest.

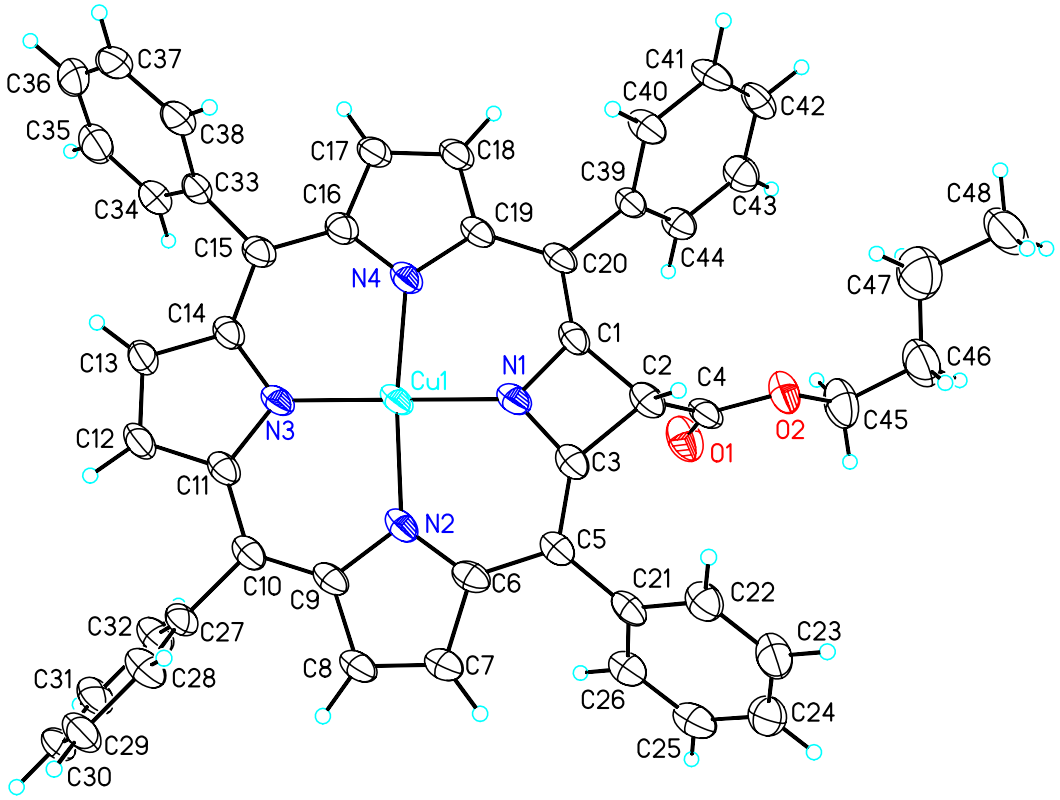

Figure 1S. ORTEP plot of **Cu2a** at 50% probability.

Cu2b. Red needle (approximate dimensions 0.15 × 0.015 × 0.01 mm^3). The final full matrix least squares refinement converged to R1 = 0.0512 and wR2 = 0.1569 (F^2, all data). The remaining electron density is located on bonds.

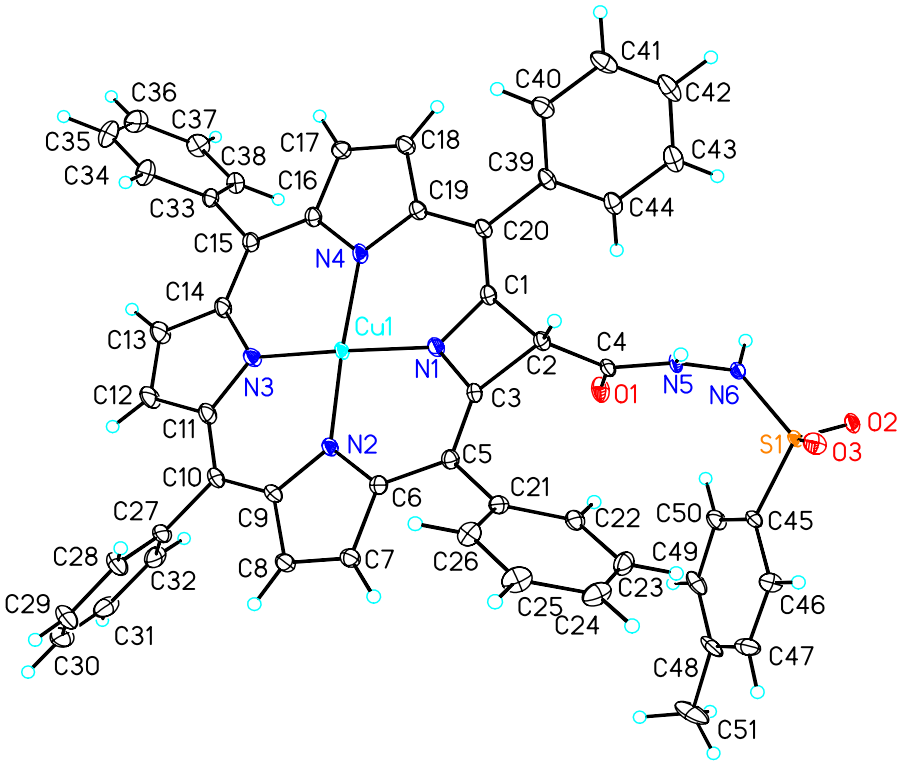

Figure 2S. ORTEP plot of **Cu2b** at 50% probability.

Cu2c. Red needle (approximate dimensions 0.018 × 0.008 × 0.002 mm^3). The final full matrix least squares refinement converged to R1 = 0.0759 and wR2 = 0.1906 (F^2, all data). The remaining electron density is located on bonds.

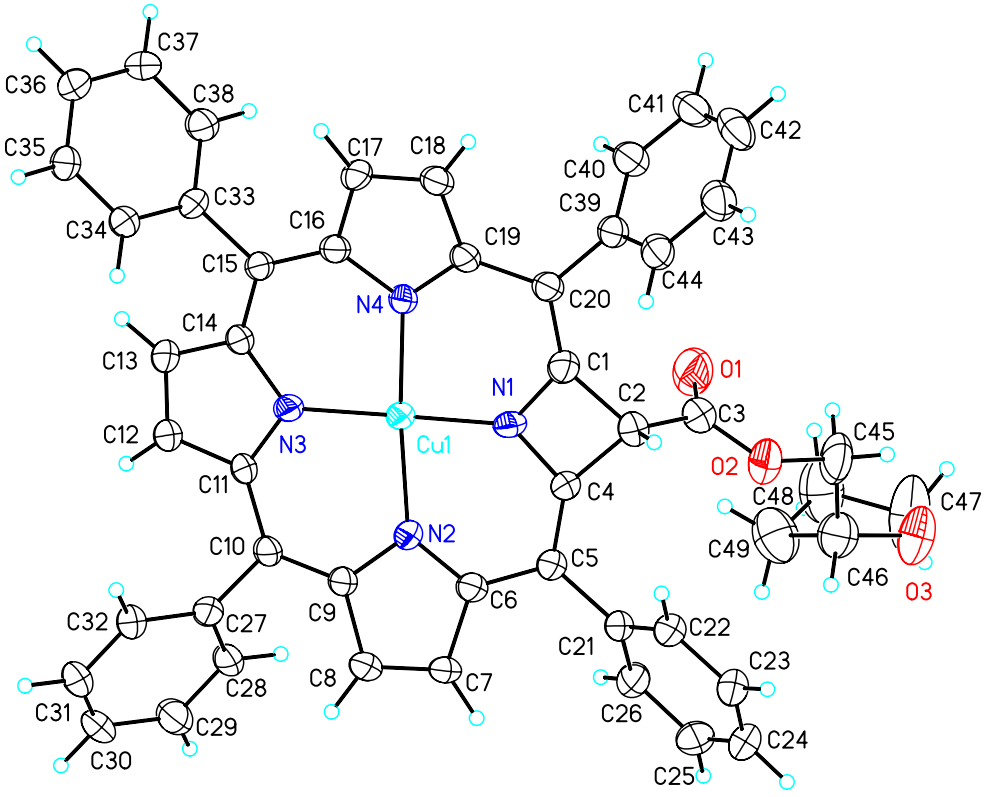

Figure 3S. ORTEP plot of **Cu2c** at 50% probability, disorder omitted for clarity.

H2a. Red-brown crystal (approximate dimensions 0.28 × 0.15 × 0.05 mm^3). H2n and H4n were refined for all parameters. The butyl group is disordered over two sites (88:12) and was refined with a set of restraints and constraints. The final full matrix least squares refinement converged to R1 = 0.0549 and wR2 = 0.1574 (F^2, all data). The remaining electron density is minuscule and located near the disordered butyl group.

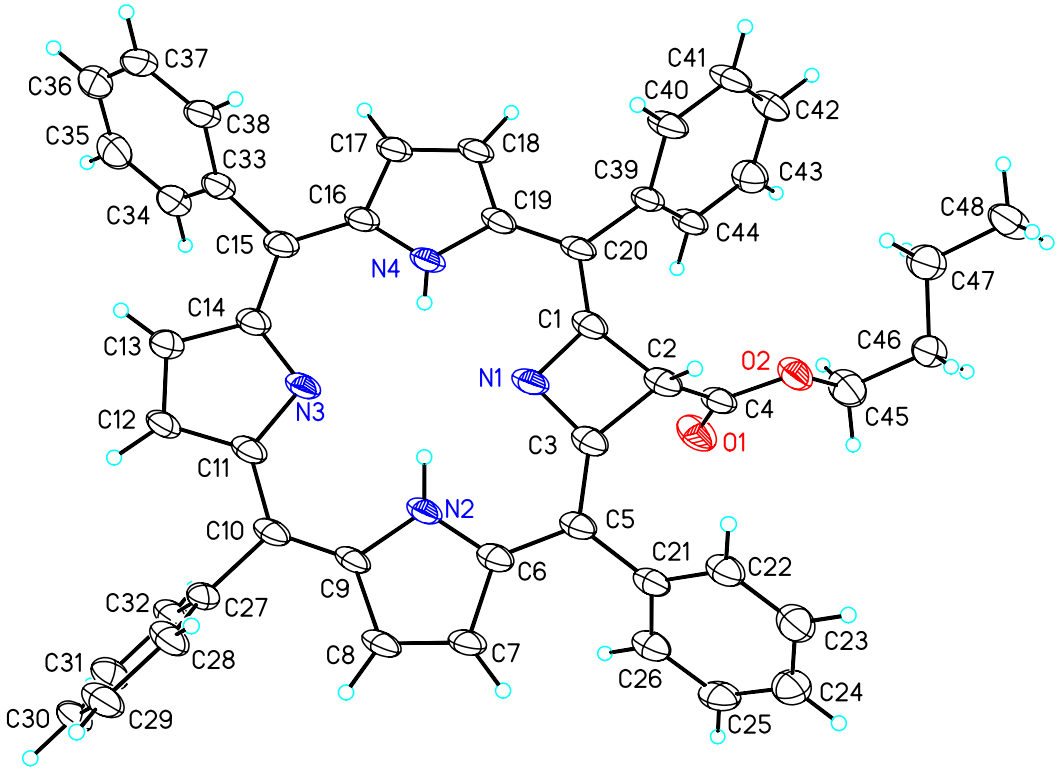

Figure 4S. ORTEP plot of **H2a** at 50% probability, disorder omitted for clarity.

Cu4. Dark crystal (approximate dimensions 0.15 × 0.13 × 0.10 mm^3). The final full matrix least squares refinement converged to R1 = 0.0595 and wR2 = 0.1660 (F^2, all data). The remaining electron density is located in the vicinity of the metal.

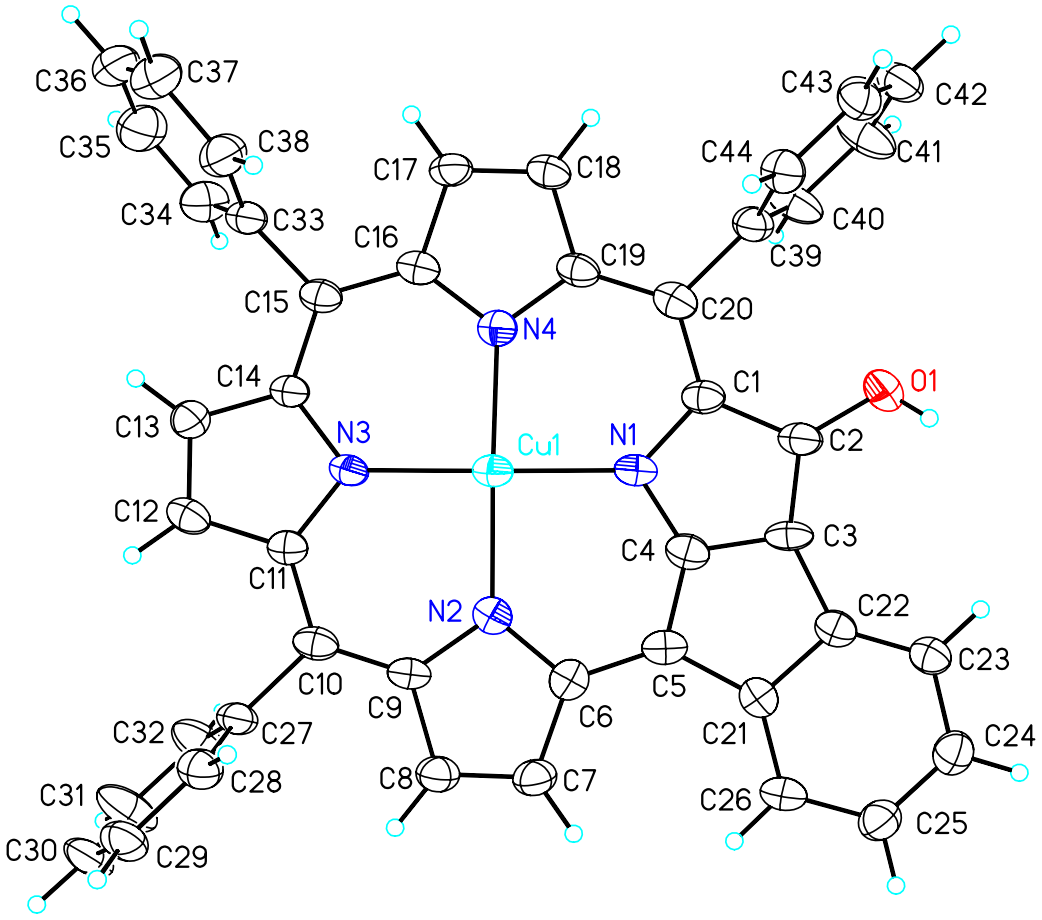

Figure 5S. ORTEP plot of **Cu4** at 50% probability, all disorder omitted for clarity.

H5-Dimer. Dark brown crystal (approximate dimensions 0.25 × 0.22 × 0.10 mm^3). Solvent (ether and dichloromethane) are included in the structure. Two ether molecules are disordered over a special position, one of which is in addition disordered with dichloromethane. The solvent molecules were refined with an appropriate set of restraints and constraints. The final full matrix least squares refinement converged to R1 = 0.0579 and wR2 = 0.1795 (F^2, all data). The remaining electron density is located near the disordered solvent.

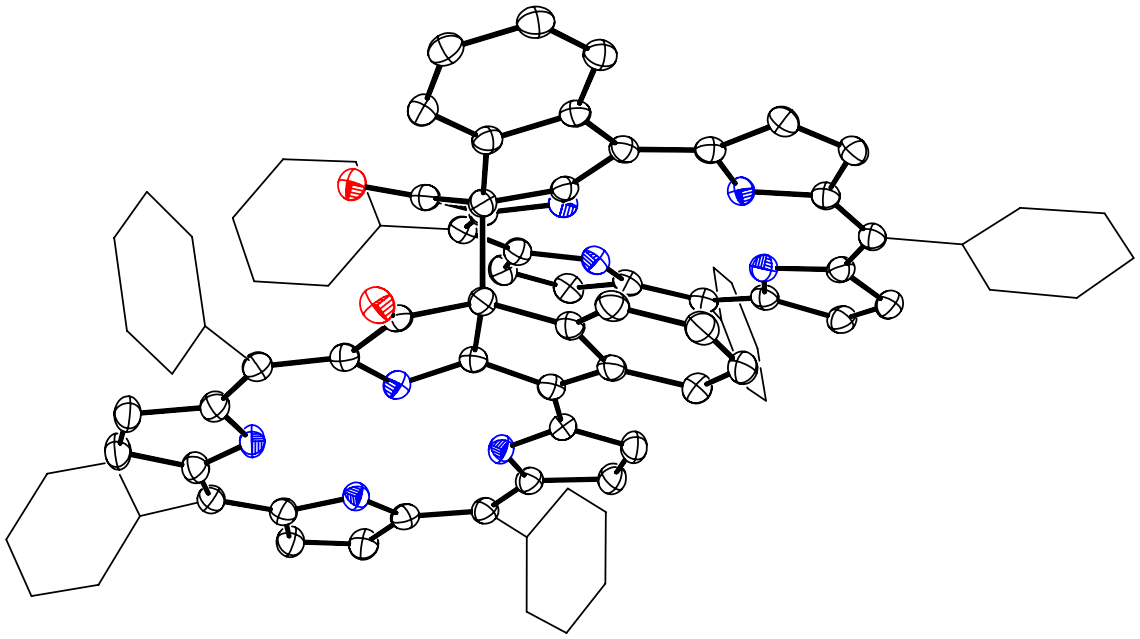

Figure 6S. ORTEP plot of **H5-Dimer** at 50% probability, hydrogen atoms omitted and spectator phenyl rings simplified for clarity.

References

[1] SAINT, Bruker Analytical X-Ray Systems, Madison, WI, current version.

[2] An empirical correction for absorption anisotropy, R. Blessing, Acta Cryst. A51, 33 - 38 (1995).

[3] SIR-92, A. Altomare; G. Cascarno; C. Giacovazzo; A. Gualardi; J. Appl. Cryst. 26, 343-350 (1993).

[4] SHELXTL-Plus, Bruker Analytical X-Ray Systems, Madison, WI, current version.