

Electronic Supplementary Information to the Dalton Trans paper:

A copper complex bearing a TEMPO moiety as catalyst for the aerobic oxidation of primary alcohols

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Table S1. Crystal data and structure refinement for **6a** and **6b**.

Compound	6a	6b
formula	C ₂₅ H ₂₀ ClN ₇ O	C ₂₅ H ₂₀ ClN ₇ O
Fw (g mol ⁻¹)	469.93	469.93
cryst size (mm ³)	0.52 × 0.45 × 0.20	0.20 × 0.10 × 0.07
cryst color	colorless	colorless
Temperature (K)	150(2)	193(2)
cryst syst, space group	monoclinic, <i>C2/c</i>	triclinic, <i>P</i> -1
<i>a</i> (Å)	26.644(5)	8.500(2)
<i>b</i> (Å)	8.943(2)	9.483(2)
<i>c</i> (Å)	19.223(4)	15.043(3)
<i>α</i> (deg)	90.00	99.31(3)
<i>β</i> (deg)	97.61(3)	93.73(3)
<i>γ</i> (deg)	90.00	102.40(3)
volume (Å ³)	4539.8(16)	1162.4(4)
<i>Z</i>	8	2
calcd density (g cm ⁻³)	1.375	1.343
F(000)	1952	488
abs coeff (mm ⁻¹)	0.202	0.197
<i>θ</i> for data collection (deg)	0.998–27.878	2.83–25.68
rflns collected (<i>R</i> _{int})	28018 (0.0718)	11933 (0.1386)
data/params	5398/307	4212/308
goodness of fit on F ²	1.021	0.904
R1 (wR2) [<i>I</i> > 2σ(<i>I</i>)]	0.0430 (0.0982)	0.0642 (0.1232)
R1 (wR2) (all data)	0.0650 (0.1104)	0.2916 (0.1931)
largest diff. peak and hole (<i>e</i> Å ³)	0.256 and -0.377	0.284 and -0.307

Figure S1. ORTEP view (thermal ellipsoids drawn at the 30% probability level) of compound **6a**.

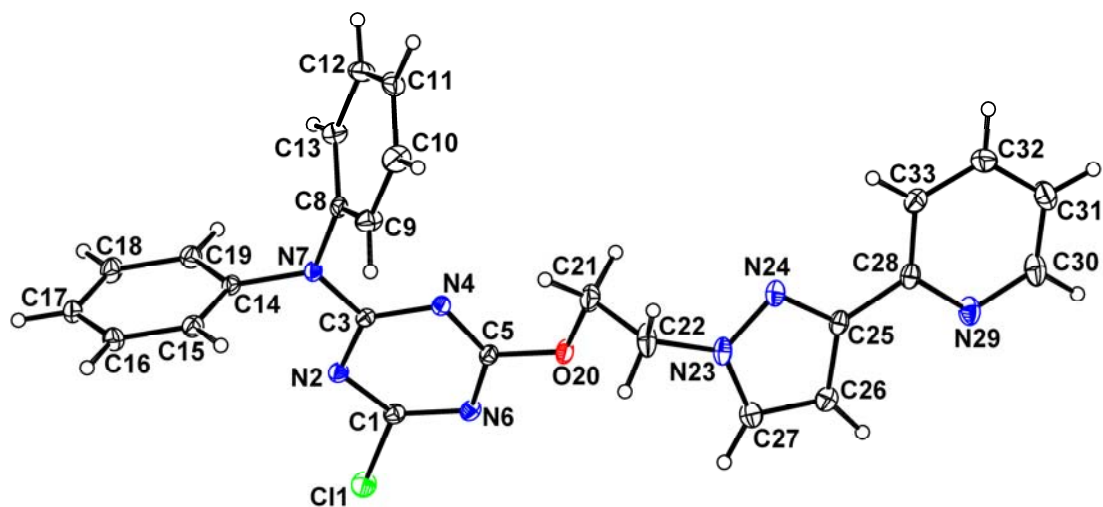


Figure S2. ORTEP view (thermal ellipsoids drawn at the 30% probability level) of compound **6b**.

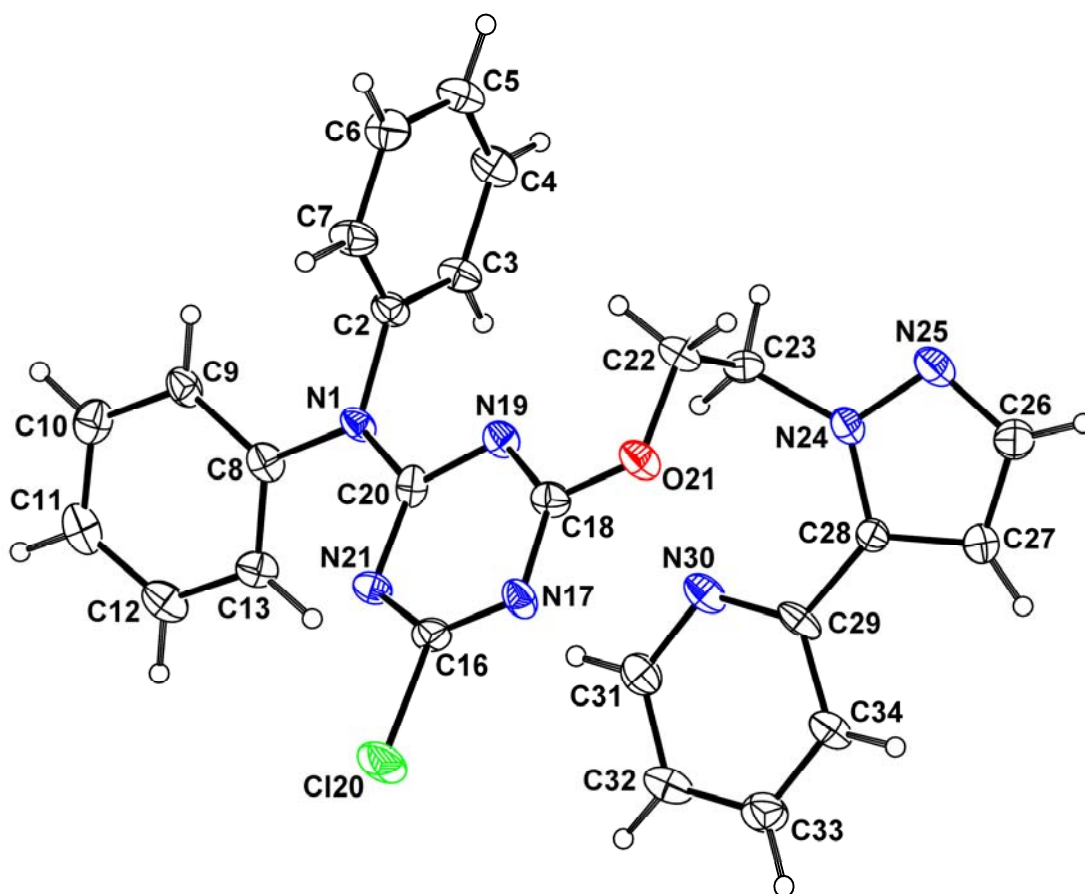


Table S2. Crystal data and structure refinement for **7a** and **7b**

Compound	7a	7b
formula	C ₆₈ H ₇₈ N ₁₈ O ₅	C ₃₆ H ₃₈ N ₉ O ₃
Fw (g mol ⁻¹)	1227.48	648.79
cryst size (mm ³)	0.45 × 0.23 × 0.12	0.35 × 0.25 × 0.05
cryst color	pink	pink
Temperature (K)	150(2)	150(2)
cryst syst, space group	monoclinic, <i>P</i> 2 ₁ / <i>c</i>	triclinic, <i>P</i> -1
<i>a</i> (Å)	7.7743(16)	9.4680(19)
<i>b</i> (Å)	29.216(6)	12.639(3)
<i>c</i> (Å)	14.248(3)	15.721(3)
<i>α</i> (deg)	90.00	106.96(3)
<i>β</i> (deg)	90.85(3)	95.71(3)
<i>γ</i> (deg)	90.00	107.34(3)
volume (Å ³)	3236.0(11)	1681.4(8)
<i>Z</i>	2	2
calcd density (g cm ⁻³)	1.260	1.281
F(000)	1304	690
abs coeff (mm ⁻¹)	0.083	0.085
<i>θ</i> for data collection (deg)	2.71–27.54	0.998–27.485
rflns collected (<i>R</i> _{int})	13021 (0.0246)	14725 (0.0583)
data/params	7332/415	7687/460
goodness of fit on F ²	1.053	1.017
R1 (wR2) [<i>I</i> > 2σ(<i>I</i>)]	0.0531 (0.1379)	0.0598 (0.1358)
R1 (wR2) (all data)	0.0835 (0.1549)	0.1285 (0.1714)
largest diff. peak and hole (<i>e</i> Å ³)	0.294 and -0.290	0.433 and -0.275

Figure S3. ORTEP view (thermal ellipsoids drawn at the 30% probability level) of compound **7a** (ligand pypzt-1). A half-occupied lattice water molecule is omitted for clarity. Hydrogen atoms are omitted for clarity.

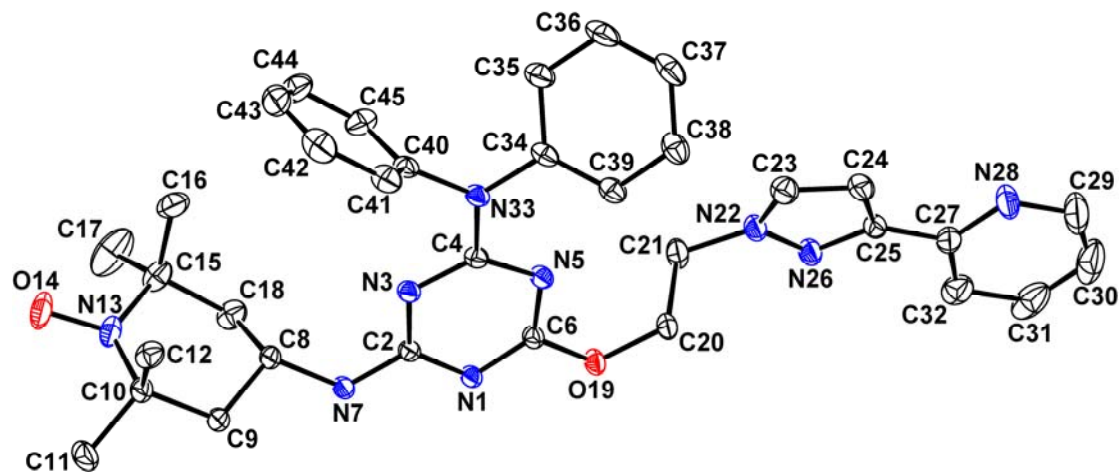
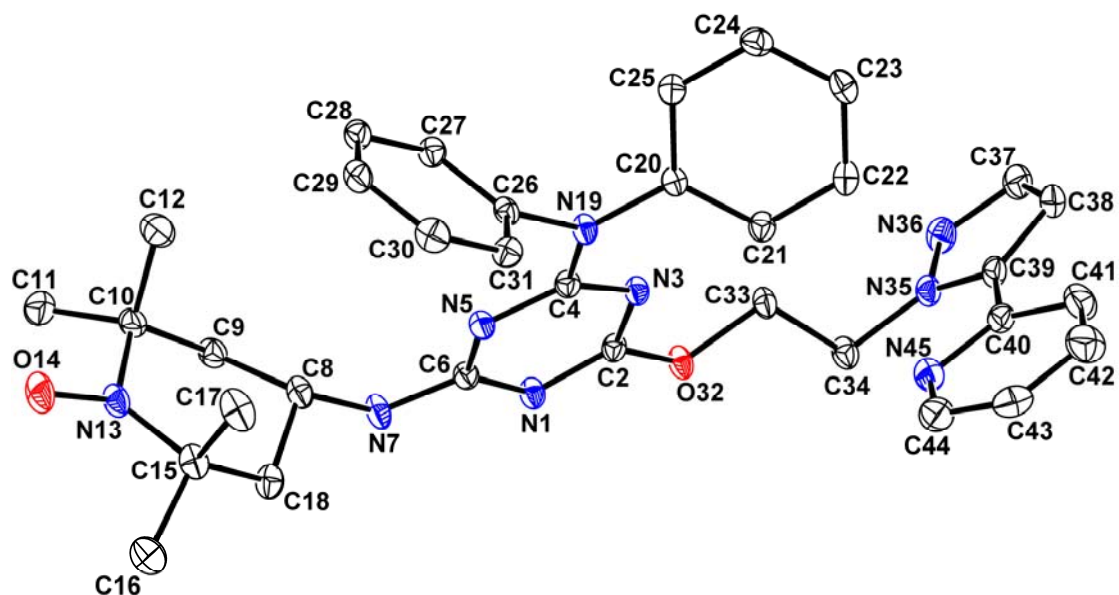


Figure S4. ORTEP view (thermal ellipsoids drawn at the 30% probability level) of compound **7b** (ligand pypzt-2). A lattice ethylacetate molecule disordered over two positions is not shown for clarity. Hydrogen atoms are omitted for clarity.



Structural determination

The molecular structure of compounds **6a**, **6b**, **7a** and **7b** were determined by single-crystal X-ray diffraction methods. Crystallographic data and refinement details are given in Tables S2 and S3.

X-ray crystallographic data for **6a**, **7a** and **7b** were collected on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Suitable crystals were affixed to the end of a glass fiber using silicone grease and transferred to the goniostat. DENZO-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1996**, 276, 307) was used for data integration and SCALEPACK^{Error! Bookmark not defined.} corrected data for Lorentz-polarisation effects. The structures were solved by direct methods and refined by a full-matrix least-squares method on F^2 using the SHELXTL crystallographic software package ((a) G. M. Sheldrick, *SHELXL97*, Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, **1997**; (b) G. M. Sheldrick, *SHELXS97*, Program for Crystal Structure Solution; University of Göttingen: Göttingen, Germany, **1997**).

X-ray crystallographic data for **6b** were collected on Nonius KappaCCD diffractometer and the crystal was mounted to the glass fiber using the oil drop method (T. Kottke and D. Stalke, *J. Appl. Crystallogr.*, 1993, **26**, 615-619) and data were collected at 193 K. The intensity data were corrected for Lorentz and polarization effects and for absorption. The nonhydrogen atoms were refined anisotropically. The H atoms were situated in calculated positions and refined using riding model.

Crystallographic data **6a**, **6b**, **7a** and **7b** have been deposited in the Cambridge Structural Database. CCDC 676753–676756 contain the supplementary crystallographic data for **6a**, **6b**, **7a** and **7b**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Table S3. Distances characterising the interaction between $\text{Br}_4(\text{Cu}^{\text{I}}\text{Br}_2^-)$ and the atoms of the triazine ring Cg10, and the interaction between $\text{Br}_4(\text{Cu}^{\text{I}}\text{Br}_2^-)$ and the atoms of the pyridine ring Cg11 (see Figures 2A and 2B)

Atoms in contact	Distance (Å)
<i>Cg10</i>	
Br4...N51	3.785
Br4...C52	3.933
Br4...N53	4.088
Br4...C54	4.058
Br4...N55	3.922
Br4...C56	3.756
<i>Cg11</i>	
Br4...C65	4.076
Br4...N66	3.989
Br4...C67	3.912
Br4...C68	3.961
Br4...C69	4.067
Br4...C70	4.119

Table S4. Distances characterising the interaction between N1S(acetonitrile) and the atoms of the triazine ring Cg7 (see Figures 2C and 2D)

Atoms in contact	Distance (Å)
N1S...N1	3.398(10)
N1S...C2	3.550(11)
N1S...N3	3.772(11)
N1S...C4	3.822(12)
N1S...N5	3.673(11)
N1S...C6	3.375(11)

Visible spectroscopic studies

For these investigations, 0.01mmol of the ligand was dissolved in 3 mL of acetonitrile 0.01mmol of CuBr₂ was subsequently added and the visible spectrum of the resulting complex solution was recorded on a Perkin-Elmer Lambda 900 spectrophotometer, using the diffuse reflectance technique, with MgO as a reference. Next, 0.01 mmol of base was added to the previous mixture and the ensuing solution was measured.