Supplementary Information

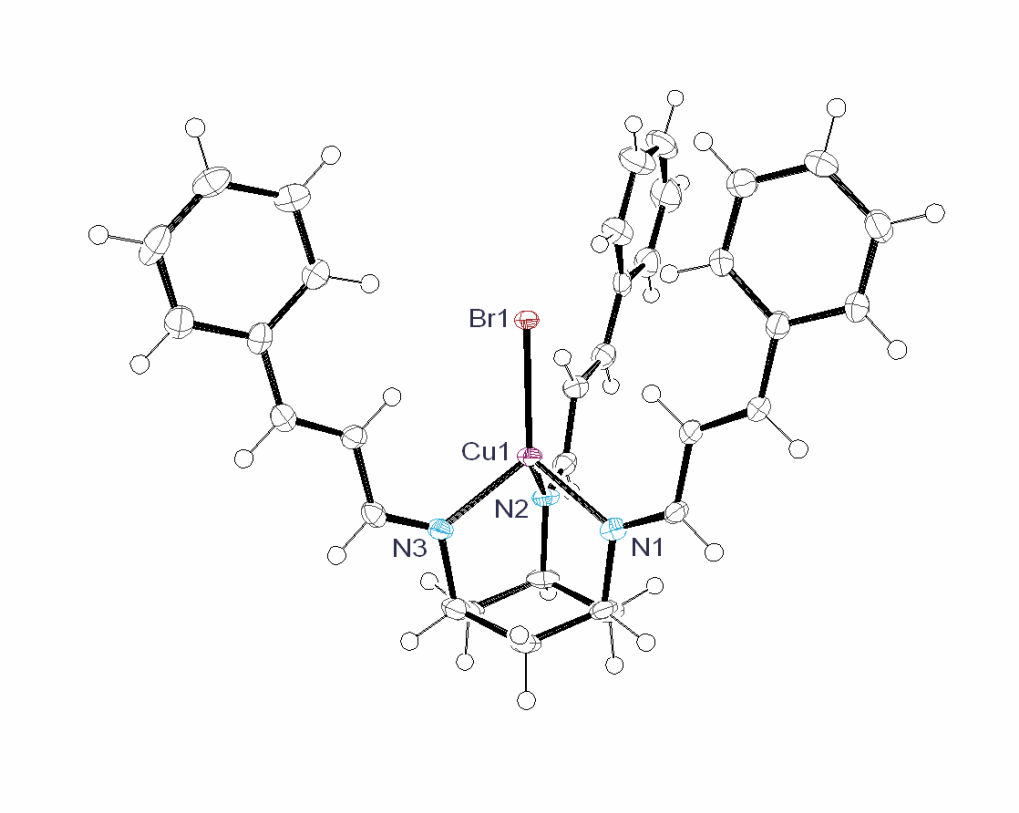


Figure S1: ORTEP (50% probability ellipsoids) depiction of **2a**. Selected bond distances /Å and angles /°: Br(1)-Cu(1) 2.4068(7), Cu(1)-N(1) 2.075(3), Cu(1)-N(2) 2.059(3), Cu(1)-N(3) 2.051(3); N(1)-Cu(1)-Br(1) 122.87(8), N(2)-Cu(1)-Br(1) 120.91(8), N(3)-Cu(1)-Br(1) 123.16(9), N(2)-Cu(1)-N(1) 92.44(12), N(3)-Cu(1)-N(1) 93.91(11), N(3)-Cu(1)-N(2) 95.85(12).

Figure S2: NMR spectrum of **2a** with imine proton signal of **2** inset.

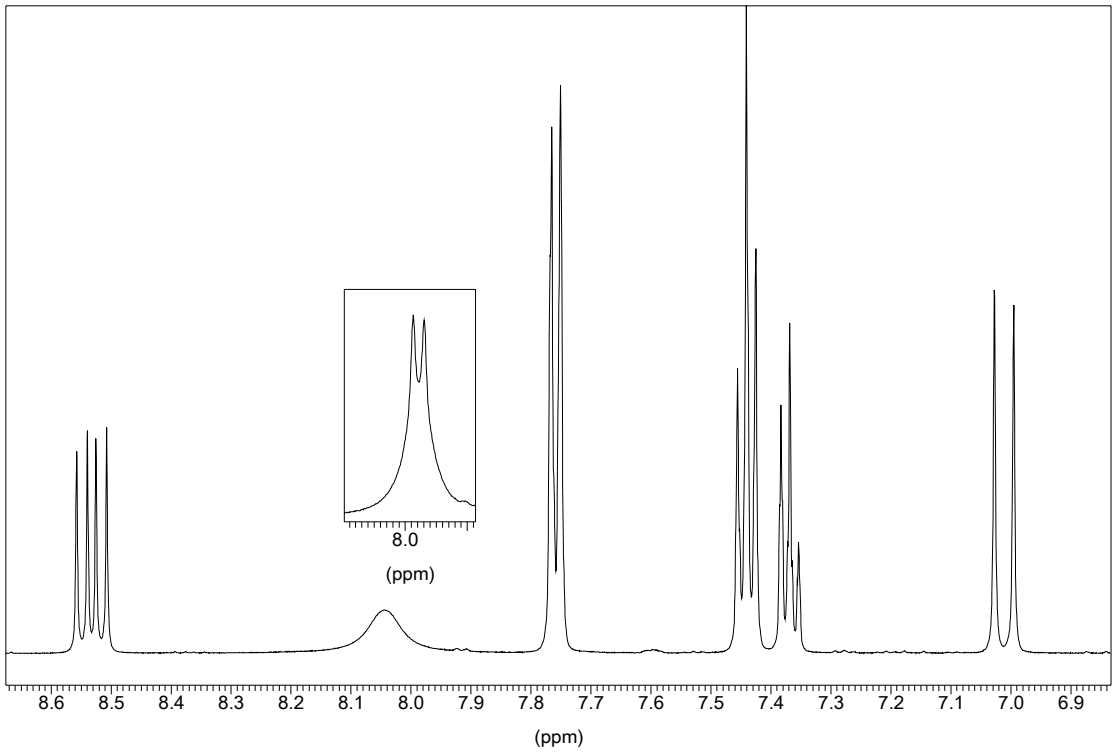


Figure S3: NMR of aliphatic region of **3** showing the inequivalence of the tach backbone protons

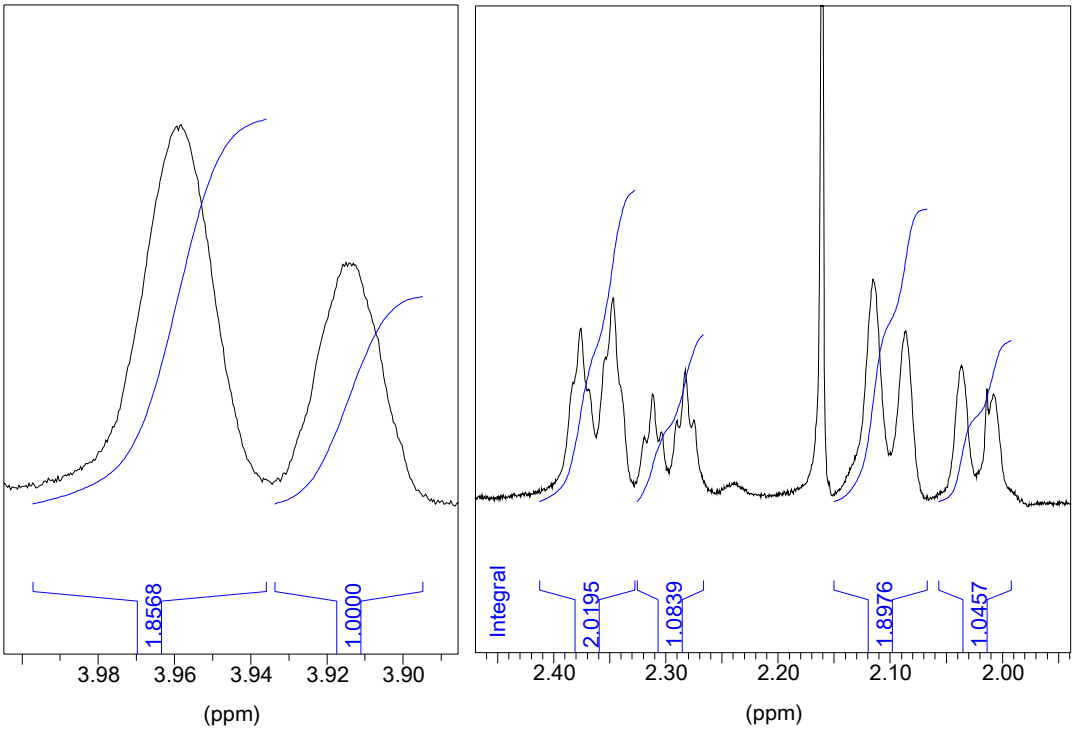
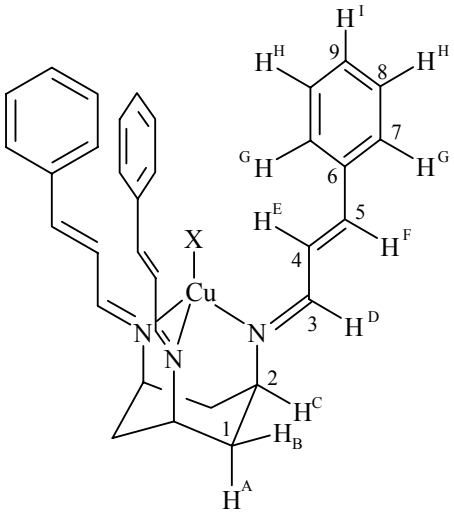
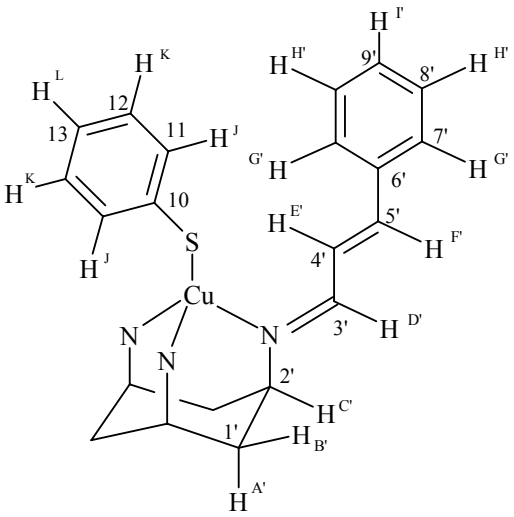


Figure S4: Labelling of protons and carbons for assignment of NMR spectra of complexes for a) C3 symmetric complexes **1**, **2**, **2a** and **4** and b) C5 symmetric complex **3**.



a) labelling of protons and carbons for complexes **2**, **2a** and **4**



b) Other 2 cinnamyl groups are labelled A to I and 1 to 9 as for a) and are equivalent. Thiophenolate group sits between the two equivalent cinnamyl rings.

Electronic Supplementary Information for Dalton Transactions

Microanalyses

Some CHN micro-analyses contain solvent in the empirical formulae. The analyses were found to be repeatable over different preparations and different batches. Solvent inclusion is not an unusual feature of this type of complex, since the 'cavity' formed by the cinnamyl groups of the ligand traps solvent easily (see P. H. Walton and C. J. Boxwell, *Chem. Commun.,* 1999, 1647). We can, therefore, support a claim that solvent inclusion is realistic feature of the products. In the case of **1** and **3** it is not possible to confirm CH_2Cl_2 content by NMR since CD_2Cl_2 is the only suitable solvent in which we can obtain spectra. (We have tried other solvents, including CD_3CN and have been unsuccessful in acquiring spectra. This is possibly due to product decomposition in these other solvents.) For **4** we observe a water peak in the ^1H NMR spectrum.