Electronic Supplementary Information for Dalton Transactions


# Supplementary Information

# Structural and Functional Mimic of Galactose Oxidase by a Copper Complex of a Sterically Demanding [$N_2O_2$] Ligand

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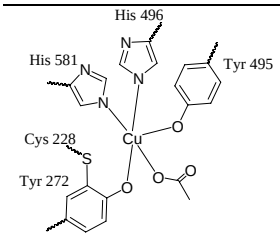
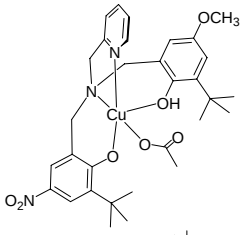
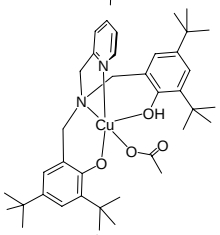
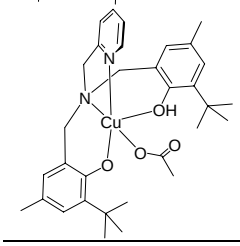
**Table S1.** Comparison of the metrical data of the galactose oxidase models with the enzyme active-site.

| Structure | Axial[a] Cu-OH (Å) | Equatorial[b] Cu-O (phenolate) (Å) | equatorial Cu-N (amine) (Å) | equatorial Cu-N (pyridine) (Å) | equatorial Cu-O (acetate) (Å) | Refs. |
|---|---|---|---|---|---|---|
|  GOase active site | 2.7 | 1.9 | 2.2 | 2.1 | 2.3 | 3a |
|  | 2.399(2) | 1.912(2) | 2.024(3) | 1.990(3) | 1.955(2) | 11 |
|  | 2.418(5) | 1.883(4) | 2.043(5) | 2.001(6) | 1.957(5) | 12 |
|  | Weak interaction (~2.47)<br>2.3465(16) | 1.8871(14)<br>1.8737(14) | 2.0340(18)<br>2.0447(17) | 1.9967(18)<br>1.9850(18) | 1.9582(15)<br>1.9759(15) | This work[c] |

[a] phenolic-*OH* in the synthetic model complexes.

[b] phenolate *O* in the synthetic model complexes.

[c] two molecules in the asymmetric unit.

The density functional theory calculations were performed for the copper **1b** complex namely, {[(3-*t*-butyl-5-methyl-2-hydoxybenzyl)(3'-*t*-butyl-5'-methyl-2'-oxobenzyl)(2-pyridylmethyl)]amine}Cu(OAc) and its *1-electron* and *2-electron* oxidized forms as well as Intermediates **1**, **2** and **3** by using the GAUSSIAN 03[1] suite of quantum chemical programs.

**Table S2**.

Optimized coordinates of [2]**1b** at the B3LYP/LANL2DZ, 6-31G(d) level of theory.

E = -1851.329001 Hartree/particle

| | | | |
|---|---|---|---|
| Cu | 0.319163 | 0.366675 | -1.28435 |
| O | 2.221525 | 0.397841 | -1.03563 |
| O | -0.64112 | 0.464699 | 0.90563 |
| O | 0.238475 | 2.327732 | -1.63746 |
| O | -0.26136 | 2.972142 | 0.469145 |
| N | 0.184594 | -1.75146 | -1.06669 |
| N | -1.53784 | 0.069197 | -2.2009 |
| C | 2.941638 | -0.5031 | -0.38841 |
| C | 4.056008 | -0.11499 | 0.430555 |
| C | 4.42397 | 1.370459 | 0.615827 |
| C | 4.680375 | 2.037198 | -0.75847 |
| H | 4.952726 | 3.091385 | -0.61728 |
| H | 3.793791 | 1.983211 | -1.39206 |
| H | 5.511204 | 1.544191 | -1.27893 |
| C | 3.27049 | 2.097833 | 1.347571 |
| H | 3.126882 | 1.681391 | 2.352241 |
| H | 2.329347 | 2.007655 | 0.804545 |
| H | 3.505231 | 3.164691 | 1.458538 |
| C | 5.701215 | 1.556504 | 1.460933 |
| H | 5.588827 | 1.161286 | 2.477446 |
| H | 5.920845 | 2.626847 | 1.54984 |
| H | 6.574001 | 1.078139 | 1.000495 |
| C | 4.79186 | -1.12847 | 1.046195 |
| H | 5.640929 | -0.85715 | 1.665223 |
| C | 4.498246 | -2.49751 | 0.925471 |
| C | 5.33992 | -3.53339 | 1.634167 |
| H | 4.948023 | -4.54349 | 1.472184 |
| 1 | 5.370663 | -3.36054 | 2.717967 |

| | | | |
|---|---|---|---|
| H | 6.379987 | -3.52348 | 1.281432 |
| C | 3.412438 | -2.85483 | 0.130982 |
| H | 3.156349 | -3.90691 | 0.009022 |
| C | 2.648876 | -1.88731 | -0.52702 |
| C | 1.534156 | -2.30242 | -1.44346 |
| H | 1.471209 | -3.40125 | -1.47562 |
| H | 1.72293 | -1.9438 | -2.4636 |
| C | -0.14939 | -2.13021 | 0.346803 |
| H | 0.646447 | -1.70966 | 0.964373 |
| H | -0.08362 | -3.22654 | 0.422603 |
| C | -1.49982 | -1.68458 | 0.854537 |
| C | -2.499 | -2.6304 | 1.087429 |
| H | -2.30715 | -3.67362 | 0.839981 |
| C | -3.72072 | -2.26515 | 1.649826 |
| C | -4.82543 | -3.27388 | 1.868519 |
| H | -5.54466 | -3.27774 | 1.037444 |
| H | -5.39246 | -3.05801 | 2.781072 |
| H | -4.42697 | -4.29076 | 1.956204 |
| C | -3.88745 | -0.92432 | 2.00916 |
| C | -4.8271 | -0.65428 | 2.476552 |
| C | -2.91785 | 0.075544 | 1.824925 |
| C | -3.19679 | 1.518687 | 2.309634 |
| C | -3.39787 | 2.455587 | 1.09288 |
| H | -3.63989 | 3.469379 | 1.435764 |
| H | -4.23026 | 2.099154 | 0.473557 |
| H | -2.50545 | 2.534397 | 0.47106 |
| C | -4.4885 | 1.605161 | 3.153642 |
| H | -4.60449 | 2.631975 | 3.517334 |
| H | -4.45532 | 0.945538 | 4.028315 |
| H | -5.3865 | 1.365211 | 2.572964 |
| C | -2.05139 | 2.027662 | 3.221301 |
| H | -1.08274 | 2.074804 | 2.724751 |
| H | -1.9518 | 1.380011 | 4.100366 |
| H | -2.28367 | 3.039962 | 3.572515 |
| C | -1.71092 | -0.32869 | 1.196795 |
| C | -0.83964 | -2.23827 | -2.01801 |
| H | -1.27884 | -3.18669 | -1.68078 |
| H | -0.33476 | -2.44115 | -2.97133 |
| C | -1.92033 | -1.21548 | -2.28936 |
| C | -3.20657 | -1.56535 | -2.70273 |
| H | -3.49605 | -2.61055 | -2.75051 |
| C | -4.10132 | -0.55389 | -3.04558 |
| H | -5.10864 | -0.80127 | -3.36843 |
| C | -3.6887 | 0.777446 | -2.96744 |
| H | -4.35475 | 1.592569 | -3.2297 |
| C | -2.39511 | 1.047117 | -2.53203 |

| | | | |
|---|---|---|---|
| H | -2.00289 | 2.053633 | -2.43705 |
| C | 0.140338 | 3.196551 | -0.69866 |
| C | 0.566634 | 4.610304 | -1.06591 |
| H | 0.191949 | 5.329526 | -0.33476 |
| H | 0.221048 | 4.868683 | -2.07119 |
| H | 1.662197 | 4.651189 | -1.07611 |
| H | -0.71593 | 1.472018 | 0.868675 |

**Table S3**

Optimized coordinates of $^{3}$**1b**$^{+}$ at the B3LYP/LANL2DZ, 6-31G(d) level of theory.

E = -1851.1153803 Hartree/particle

| | | | |
|---|---|---|---|
| Cu | -0.15196 | 0.275692 | 1.24423 |
| O | -2.08593 | 0.395566 | 0.683615 |
| O | 0.649122 | 0.518382 | -0.86332 |
| O | -0.20325 | 2.118852 | 1.820882 |
| O | 0.118627 | 2.974283 | -0.24199 |
| N | -0.13618 | -1.79936 | 0.915731 |
| N | 1.595253 | -0.11497 | 2.229383 |
| C | -2.90533 | -0.47175 | 0.244806 |
| C | -4.1278 | -0.04335 | -0.44949 |
| C | -4.43741 | 1.446024 | -0.64185 |
| C | -4.50962 | 2.158278 | 0.735464 |
| H | -4.76569 | 3.212193 | 0.579867 |
| H | -3.55991 | 2.109781 | 1.270307 |
| H | -5.29068 | 1.716688 | 1.365603 |
| C | -3.33583 | 2.095618 | -1.5229 |
| H | -3.28457 | 1.609229 | -2.50416 |
| H | -2.34923 | 2.05055 | -1.05927 |
| H | -3.58537 | 3.149615 | -1.6887 |
| C | -5.79159 | 1.657385 | -1.34991 |
| H | -5.80364 | 1.231261 | -2.35949 |
| H | -5.97505 | 2.731495 | -1.4503 |
| H | -6.62818 | 1.23512 | -0.78121 |
| C | -4.95413 | -1.04106 | -0.93487 |
| H | -5.86 | -0.76948 | -1.46386 |
| C | -4.68239 | -2.42067 | -0.78619 |
| C | -5.63298 | -3.43922 | -1.34507 |
| H | -5.27619 | -4.46121 | -1.19416 |
| H | -5.78559 | -3.28215 | -2.42036 |
| H | -6.62013 | -3.34859 | -0.87284 |
| C | -3.51267 | -2.81844 | -0.09608 |

| | | | |
|---|---|---|---|
| H | -3.31768 | -3.88005 | 0.035211 |
| C | -2.63699 | -1.8923 | 0.422602 |
| C | -1.48168 | -2.34647 | 1.281419 |
| H | -1.44112 | -3.44464 | 1.257958 |
| H | -1.66756 | -2.05052 | 2.321819 |
| C | 0.16722 | -2.10033 | -0.53431 |
| H | -0.63574 | -1.63574 | -1.11161 |
| H | 0.091945 | -3.189 | -0.66599 |
| C | 1.50588 | -1.62636 | -1.03535 |
| C | 2.495142 | -2.55268 | -1.37671 |
| H | 2.308464 | -3.61376 | -1.22084 |
| C | 3.698665 | -2.13611 | -1.9391 |
| C | 4.780744 | -3.11867 | -2.32293 |
| H | 5.739344 | -2.86512 | -1.85453 |
| H | 4.946743 | -3.12739 | -3.40717 |
| H | 4.521014 | -4.13831 | -2.02126 |
| C | 3.865403 | -0.76387 | -2.16827 |
| H | 4.796134 | -0.45163 | -2.62634 |
| C | 2.910319 | 0.218257 | -1.86222 |
| C | 3.186378 | 1.705686 | -2.18655 |
| C | 3.355511 | 2.508363 | -0.87292 |
| H | 3.577591 | 3.556891 | -1.10207 |
| H | 4.189906 | 2.106238 | -0.2861 |
| H | 2.458769 | 2.501398 | -0.25029 |
| C | 4.493536 | 1.885319 | -2.99053 |
| H | 4.622489 | 2.947082 | -3.2246 |
| H | 4.4723 | 1.339564 | -3.94029 |
| H | 5.378748 | 1.569273 | -2.42768 |
| C | 2.052755 | 2.298813 | -3.06257 |
| H | 1.075488 | 2.314376 | -2.5774 |
| H | 1.957951 | 1.733151 | -3.99634 |
| H | 2.294518 | 3.335644 | -3.32098 |
| C | 1.717635 | -0.25096 | -1.26106 |
| C | 0.892568 | -2.39582 | 1.817159 |
| H | 1.34031 | -3.28204 | 1.353066 |
| H | 0.386111 | -2.73483 | 2.72912 |
| C | 1.960867 | -1.40889 | 2.229275 |
| C | 3.217225 | -1.80655 | 2.683976 |
| H | 3.49695 | -2.85512 | 2.66562 |
| C | 4.096877 | -0.83596 | 3.161543 |
| H | 5.080879 | -1.12143 | 3.52113 |
| C | 3.6992 | 0.502362 | 3.174059 |
| H | 4.354057 | 1.283253 | 3.544822 |
| C | 2.436768 | 0.82619 | 2.690231 |
| H | 2.060025 | 1.842086 | 2.661025 |
| C | -0.18762 | 3.091623 | 0.960275 |

| | | | |
|---|---|---|---|
| C | -0.59092 | 4.442669 | 1.519118 |
| H | -0.28505 | 5.23932 | 0.83899 |
| H | -0.15841 | 4.597573 | 2.511402 |
| H | -1.68129 | 4.468473 | 1.630642 |
| H | 0.711537 | 1.516482 | -0.83706 |

**Table S4**

Optimized coordinates of $^{4}$**1b**$^{2+}$ at the B3LYP/LANL2DZ, 6-31G(d) level of theory.

E = -1850.8016879 Hartree/particle

| | | | |
|---|---|---|---|
| Cu | -0.05045 | 0.721476 | -0.82166 |
| O | -1.78597 | -0.2517 | -0.47224 |
| O | 1.357578 | -0.84573 | -0.16938 |
| O | -0.11791 | 0.092791 | -2.72125 |
| O | 0.5574 | -2.04483 | -2.52158 |
| N | -0.05322 | 1.523592 | 1.067363 |
| N | 0.640776 | 2.571409 | -1.35099 |
| C | -2.67915 | -0.08652 | 0.425087 |
| C | -3.84007 | -0.98482 | 0.480528 |
| C | -4.03333 | -2.09001 | -0.56411 |
| C | -4.1296 | -1.4585 | -1.97971 |
| H | -4.29031 | -2.25368 | -2.71553 |
| H | -3.22165 | -0.91504 | -2.24974 |
| H | -4.97981 | -0.77063 | -2.04606 |
| C | -2.84728 | -3.09052 | -0.50218 |
| H | -2.76756 | -3.54487 | 0.491984 |
| H | -1.89552 | -2.61584 | -0.74851 |
| H | -3.02309 | -3.8987 | -1.22009 |
| C | -5.33078 | -2.88792 | -0.31892 |
| H | -5.32446 | -3.40697 | 0.645961 |
| H | -5.42912 | -3.65255 | -1.09521 |
| H | -6.22399 | -2.25583 | -0.37275 |
| C | -4.73924 | -0.78601 | 1.517659 |
| H | -5.60499 | -1.43139 | 1.599659 |
| C | -4.59348 | 0.222473 | 2.491543 |
| C | -5.59946 | 0.396696 | 3.587697 |
| H | -5.11422 | 0.389315 | 4.572269 |
| H | -6.36285 | -0.38399 | 3.570938 |
| H | -6.10347 | 1.36915 | 3.497412 |
| C | -3.47281 | 1.097152 | 2.41117 |
| H | -3.37614 | 1.885989 | 3.153826 |
| C | -2.5395 | 0.977288 | 1.411488 |
| C | -1.45335 | 2.024217 | 1.289041 |

| | | | |
|---|---|---|---|
| H | -1.45576 | 2.63389 | 2.20225 |
| H | -1.67516 | 2.700149 | 0.453806 |
| C | 0.320175 | 0.501234 | 2.101283 |
| H | -0.39978 | -0.31513 | 2.000747 |
| H | 0.172699 | 0.946984 | 3.0939 |
| C | 1.725556 | -0.04803 | 2.014718 |
| C | 2.563934 | 0.056692 | 3.096408 |
| H | 2.247349 | 0.608274 | 3.978907 |
| C | 3.843187 | -0.56832 | 3.106868 |
| C | 4.729387 | -0.44148 | 4.307114 |
| H | 4.848712 | 0.608707 | 4.60214 |
| H | 5.718728 | -0.87036 | 4.134226 |
| H | 4.282073 | -0.9566 | 5.169345 |
| C | 4.234996 | -1.32196 | 1.982369 |
| H | 5.20856 | -1.79358 | 2.021398 |
| C | 3.449422 | -1.48941 | 0.850757 |
| C | 3.923195 | -2.34966 | -0.32735 |
| C | 3.98776 | -1.49937 | -1.62439 |
| H | 4.330408 | -2.12946 | -2.45142 |
| H | 4.706112 | -0.67941 | -1.51272 |
| H | 3.023625 | -1.07172 | -1.90128 |
| C | 5.338729 | -2.92168 | -0.09697 |
| H | 5.618911 | -3.52852 | -0.96314 |
| H | 5.387779 | -3.57455 | 0.781048 |
| H | 6.093748 | -2.13437 | 0.005306 |
| C | 2.964161 | -3.5616 | -0.48701 |
| H | 1.917988 | -3.27378 | -0.60583 |
| H | 3.028844 | -4.21961 | 0.386104 |
| H | 3.256103 | -4.14521 | -1.36623 |
| C | 2.145313 | -0.80803 | 0.839222 |
| C | 0.896737 | 2.677249 | 1.049461 |
| H | 1.897364 | 2.279643 | 1.248805 |
| H | 0.659439 | 3.379719 | 1.858417 |
| C | 0.90753 | 3.36767 | -0.2945 |
| C | 1.236914 | 4.709429 | -0.46164 |
| H | 1.440073 | 5.33566 | 0.401346 |
| C | 1.304463 | 5.228691 | -1.75682 |
| H | 1.561189 | 6.271946 | -1.91305 |
| C | 1.032918 | 4.395931 | -2.84323 |
| H | 1.071898 | 4.765894 | -3.86191 |
| C | 0.695627 | 3.067998 | -2.60003 |
| H | 0.457052 | 2.37452 | -3.39847 |
| C | 0.023514 | -1.05286 | -3.19489 |
| C | -0.38416 | -1.39307 | -4.59311 |
| H | 0.515397 | -1.55912 | -5.19778 |
| H | -0.97376 | -0.58601 | -5.02735 |

| | | | |
|---|---|---|---|
| H | -0.95097 | -2.32889 | -4.59682 |
| H | 0.90209 | -1.74383 | -1.64204 |

**Table S5**

Optimized coordinates of Intermediate **1** at the B3LYP/LANL2DZ, 6-31G(d) level of theory.

E = -1968.7829201 Hartree/particle

| | | | |
|---|---|---|---|
| Cu | 0.128677 | 0.612123 | -0.27462 |
| O | 2.133531 | 0.300339 | -0.00992 |
| O | -0.62244 | -1.11134 | 1.107475 |
| O | -0.13589 | 1.563349 | 1.341633 |
| N | 0.073672 | -0.78965 | -1.88732 |
| N | -1.63418 | 1.233631 | -1.13252 |
| C | 2.863024 | -0.66393 | -0.40635 |
| C | 4.035905 | -1.08312 | 0.374238 |
| C | 4.407518 | -0.36678 | 1.678122 |
| C | 4.731627 | 1.120654 | 1.378692 |
| H | 5.014299 | 1.624712 | 2.309502 |
| H | 3.876693 | 1.647242 | 0.952174 |
| H | 5.576341 | 1.204473 | 0.685013 |
| C | 3.235844 | -0.47131 | 2.691302 |
| H | 3.018263 | -1.52002 | 2.926115 |
| H | 2.324702 | -0.00217 | 2.317109 |
| H | 3.522868 | 0.025348 | 3.624923 |
| C | 5.653092 | -0.99099 | 2.339583 |
| H | 5.495343 | -2.04026 | 2.614203 |
| H | 5.877359 | -0.44444 | 3.260896 |
| H | 6.54052 | -0.92597 | 1.699695 |
| C | 4.76482 | -2.15454 | -0.11144 |
| H | 5.628158 | -2.50463 | 0.442175 |
| C | 4.44579 | -2.83822 | -1.30677 |
| C | 5.305908 | -3.97333 | -1.78156 |
| H | 4.814551 | -4.56138 | -2.56157 |
| H | 5.57422 | -4.64132 | -0.95547 |
| H | 6.24898 | -3.59101 | -2.19746 |
| C | 3.321824 | -2.41713 | -2.05629 |
| H | 3.086299 | -2.93344 | -2.98391 |
| C | 2.537283 | -1.3653 | -1.6424 |
| C | 1.424677 | -0.85436 | -2.52521 |
| H | 1.374782 | -1.48374 | -3.42593 |
| H | 1.66584 | 0.164668 | -2.85115 |

| | | | |
|---|---|---|---|
| C | -0.31844 | -2.15574 | -1.38281 |
| H | 0.487075 | -2.47345 | -0.71636 |
| H | -0.32923 | -2.8416 | -2.24281 |
| C | -1.6428 | -2.24041 | -0.66365 |
| C | -2.72633 | -2.90408 | -1.24582 |
| H | -2.61949 | -3.32205 | -2.24507 |
| C | -3.93135 | -3.05158 | -0.56044 |
| C | -5.10488 | -3.78184 | -1.17173 |
| H | -6.04276 | -3.23709 | -1.01547 |
| H | -5.23226 | -4.77618 | -0.72512 |
| H | -4.97296 | -3.92194 | -2.24932 |
| C | -4.01313 | -2.52937 | 0.737235 |
| H | -4.94882 | -2.66173 | 1.267705 |
| C | -2.95764 | -1.87254 | 1.388322 |
| C | -3.10198 | -1.36834 | 2.844132 |
| C | -3.03495 | 0.180499 | 2.897581 |
| H | -3.17099 | 0.519161 | 3.931172 |
| H | -3.83897 | 0.61673 | 2.29339 |
| H | -2.09354 | 0.615749 | 2.542997 |
| C | -4.46045 | -1.77171 | 3.45689 |
| H | -4.50285 | -1.42283 | 4.493929 |
| H | -4.59899 | -2.85815 | 3.469385 |
| H | -5.30586 | -1.31957 | 2.92683 |
| C | -2.00688 | -1.99778 | 3.744385 |
| H | -0.98819 | -1.76488 | 3.423145 |
| H | -2.10359 | -3.08899 | 3.757926 |
| H | -2.12063 | -1.63728 | 4.772916 |
| C | -1.77048 | -1.72783 | 0.639157 |
| C | -0.90843 | -0.2773 | -2.88287 |
| H | -1.36284 | -1.10611 | -3.44046 |
| H | -0.3595 | 0.331194 | -3.61189 |
| C | -1.9758 | 0.600521 | -2.26668 |
| C | -3.21059 | 0.818361 | -2.87558 |
| H | -3.47071 | 0.29036 | -3.78775 |
| C | -4.09597 | 1.724255 | -2.29217 |
| H | -5.06271 | 1.913178 | -2.74941 |
| C | -3.72793 | 2.379162 | -1.11593 |
| H | -4.39072 | 3.089963 | -0.63445 |
| C | -2.48474 | 2.099198 | -0.55772 |
| H | -2.12855 | 2.548629 | 0.361784 |
| H | -0.79281 | -0.45095 | 1.804985 |
| C | 0.698921 | 2.632546 | 1.72134 |
| H | 0.3908 | 2.937641 | 2.734384 |
| H | 1.749408 | 2.310912 | 1.791545 |
| C | 0.592186 | 3.822051 | 0.7835 |
| C | 1.411654 | 3.906465 | -0.35125 |

| | | | |
|---|---|---|---|
| C | -0.35716 | 4.829887 | 1.000343 |
| H | 2.174014 | 3.146892 | -0.51655 |
| H | -0.98379 | 4.790386 | 1.889426 |
| C | 1.278346 | 4.963485 | -1.25478 |
| C | -0.4932 | 5.890104 | 0.101775 |
| H | 1.930772 | 5.022637 | -2.12228 |
| H | -1.22567 | 6.670397 | 0.290882 |
| C | 0.321781 | 5.956529 | -1.03116 |
| H | 0.222836 | 6.785528 | -1.72637 |

**Table S6**

Optimized coordinates of Intermediate **2** at the B3LYP/LANL2DZ, 6-31G(d) level of theory.

E = -1968.8297627 Hartree/particle

| | | | |
|---|---|---|---|
| Cu | 0.075183 | 0.578416 | -0.37898 |
| O | 2.243635 | -0.23399 | -0.44944 |
| O | -0.98747 | -0.7544 | 1.205936 |
| O | 0.882716 | 1.791205 | 1.167992 |
| N | -0.38766 | -1.06043 | -1.81748 |
| N | -1.4319 | 1.568222 | -1.40569 |
| C | 2.521731 | -1.59674 | -0.5139 |
| C | 3.457321 | -2.23018 | 0.333404 |
| C | 4.261251 | -1.4712 | 1.418419 |
| C | 5.131811 | -0.35663 | 0.778021 |
| H | 5.701978 | 0.165898 | 1.5545 |
| H | 4.563044 | 0.40045 | 0.227478 |
| H | 5.845145 | -0.79223 | 0.070491 |
| C | 3.308875 | -0.8853 | 2.495748 |
| H | 2.741302 | -1.68931 | 2.976641 |
| H | 2.574642 | -0.16393 | 2.116809 |
| H | 3.890483 | -0.37129 | 3.269487 |
| C | 5.23794 | -2.40304 | 2.168133 |
| H | 4.716764 | -3.20713 | 2.698163 |
| H | 5.788115 | -1.82104 | 2.914981 |
| H | 5.974343 | -2.85201 | 1.493577 |
| C | 3.632975 | -3.60743 | 0.135999 |
| H | 4.338676 | -4.1394 | 0.762981 |
| C | 2.950164 | -4.3467 | -0.83727 |
| C | 3.206024 | -5.82709 | -1.00066 |
| H | 2.533097 | -6.26899 | -1.74182 |
| H | 3.063417 | -6.36585 | -0.05643 |

| | | | |
|---|---|---|---|
| H | 4.234356 | -6.02109 | -1.32994 |
| C | 2.044207 | -3.66749 | -1.64927 |
| H | 1.502521 | -4.20951 | -2.42125 |
| C | 1.813831 | -2.29597 | -1.50197 |
| C | 0.866785 | -1.58747 | -2.44333 |
| H | 0.606346 | -2.28167 | -3.25827 |
| H | 1.369572 | -0.72598 | -2.89571 |
| C | -1.13654 | -2.16715 | -1.15213 |
| H | -0.43318 | -2.64224 | -0.46478 |
| H | -1.41624 | -2.91766 | -1.90968 |
| C | -2.3801 | -1.75345 | -0.39791 |
| C | -3.64516 | -2.12055 | -0.86543 |
| H | -3.71989 | -2.66836 | -1.80257 |
| C | -4.80265 | -1.82273 | -0.14761 |
| C | -6.17147 | -2.21686 | -0.65367 |
| H | -6.77307 | -1.33701 | -0.91513 |
| H | -6.73331 | -2.77583 | 0.103638 |
| H | -6.10084 | -2.84632 | -1.54615 |
| C | -4.65925 | -1.14962 | 1.071799 |
| H | -5.56197 | -0.93167 | 1.630278 |
| C | -3.42167 | -0.75725 | 1.603351 |
| C | -3.32902 | -0.04066 | 2.973353 |
| C | -2.69231 | 1.367096 | 2.820798 |
| H | -2.66937 | 1.872096 | 3.793322 |
| H | -3.28844 | 1.980072 | 2.135411 |
| C | -1.66616 | 1.36173 | 2.4361 |
| C | -4.7218 | 0.181595 | 3.601578 |
| H | -4.60592 | 0.689688 | 4.564624 |
| H | -5.24312 | -0.76246 | 3.790584 |
| H | -5.36049 | 0.810342 | 2.97214 |
| C | -2.52758 | -0.90232 | 3.986002 |
| H | -1.49529 | -1.11754 | 3.684462 |
| H | -3.01784 | -1.87005 | 4.133931 |
| H | -2.47821 | -0.39449 | 4.955752 |
| C | -2.28581 | -1.07717 | 0.828498 |
| C | -1.20295 | -0.39299 | -2.85396 |
| H | -1.88096 | -1.10315 | -3.35009 |
| H | -0.51757 | -0.02758 | -3.62942 |
| C | -1.99177 | 0.811664 | -2.36919 |
| C | -3.19679 | 1.175118 | -2.9742 |
| H | -3.62732 | 0.54035 | -3.74264 |
| C | -3.83045 | 2.351928 | -2.58223 |
| H | -4.76739 | 2.650979 | -3.04268 |
| C | -3.24298 | 3.136732 | -1.5887 |
| H | -3.69877 | 4.062429 | -1.25352 |
| C | -2.04812 | 2.701247 | -1.02613 |

| | | | |
|---|---|---|---|
| H | -1.55485 | 3.272673 | -0.24502 |
| H | -0.97966 | -0.35615 | 2.087491 |
| C | 1.176304 | 2.97412 | 1.393589 |
| H | 0.81054 | 3.434369 | 2.329276 |
| C | 1.979628 | 3.839609 | 0.538511 |
| C | 2.221085 | 5.159689 | 0.963705 |
| C | 2.517598 | 3.388755 | -0.68436 |
| H | 1.80702 | 5.503064 | 1.908937 |
| H | 2.33499 | 2.369143 | -1.00959 |
| C | 2.987874 | 6.018539 | 0.181589 |
| C | 3.282812 | 4.250566 | -1.46055 |
| H | 3.174829 | 7.035847 | 0.511072 |
| H | 3.701529 | 3.907231 | -2.40183 |
| C | 3.517612 | 5.563307 | -1.02933 |
| H | 4.117135 | 6.231697 | -1.64066 |
| H | 2.668991 | 0.156854 | 0.327345 |

**Table S7**

Optimized coordinates of Intermediate **3** at the B3LYP/LANL2DZ, 6-31G(d) level of theory.

E = -1773.5602817 Hartree/particle

| | | | |
|---|---|---|---|
| Cu | -0.14556 | 0.307986 | 1.197255 |
| O | -2.20242 | 0.364112 | 1.006692 |
| O | 0.588925 | 0.773338 | -0.94641 |
| O | -0.05857 | 2.197004 | 1.454725 |
| N | -0.08375 | -1.77476 | 0.651984 |
| N | 1.59016 | -0.15937 | 2.182517 |
| C | -2.93157 | -0.38256 | 0.27951 |
| C | -4.13461 | 0.149815 | -0.37071 |
| C | -4.54887 | 1.612944 | -0.16575 |
| C | -4.82127 | 1.87393 | 1.339628 |
| H | -5.12186 | 2.918196 | 1.47954 |
| H | -3.94058 | 1.682277 | 1.956365 |
| H | -5.63727 | 1.240934 | 1.70645 |
| C | -3.43164 | 2.55993 | -0.6808 |
| H | -3.25098 | 2.402514 | -1.75063 |
| H | -2.48857 | 2.418023 | -0.14919 |
| H | -3.7505 | 3.599907 | -0.54813 |
| C | -5.84024 | 1.955997 | -0.93658 |
| H | -5.72001 | 1.838402 | -2.01948 |
| H | -6.09904 | 3.003076 | -0.75054 |

| | | | |
|---|---|---|---|
| H | -6.69155 | 1.347602 | -0.61107 |
| C | -4.8523 | -0.71924 | -1.17509 |
| H | -5.73808 | -0.36278 | -1.68775 |
| C | -4.49311 | -2.0712 | -1.37329 |
| C | -5.33866 | -2.96799 | -2.23056 |
| H | -4.74343 | -3.75531 | -2.70376 |
| H | -5.86213 | -2.40573 | -3.00952 |
| H | -6.1059 | -3.46621 | -1.61992 |
| C | -3.34388 | -2.57982 | -0.71879 |
| H | -3.08398 | -3.62718 | -0.85505 |
| C | -2.56869 | -1.78338 | 0.091201 |
| C | -1.43209 | -2.37718 | 0.89177 |
| H | -1.39245 | -3.45912 | 0.695217 |
| H | -1.64801 | -2.24389 | 1.958098 |
| C | 0.297435 | -1.93935 | -0.79266 |
| H | -0.51582 | -1.49741 | -1.37461 |
| H | 0.322982 | -3.01524 | -1.02265 |
| C | 1.612468 | -1.31761 | -1.19562 |
| C | 2.704501 | -2.12126 | -1.53648 |
| H | 2.607956 | -3.20296 | -1.46695 |
| C | 3.901405 | -1.56255 | -1.98211 |
| C | 5.081 | -2.42423 | -2.36958 |
| H | 6.005785 | -2.07649 | -1.89501 |
| H | 5.24929 | -2.40541 | -3.45361 |
| H | 4.926979 | -3.46822 | -2.07948 |
| C | 3.971845 | -0.16718 | -2.08977 |
| H | 4.902206 | 0.257813 | -2.44754 |
| C | 2.912128 | 0.696613 | -1.77575 |
| C | 3.041778 | 2.22967 | -1.95047 |
| C | 2.9086 | 2.95579 | -0.58529 |
| H | 3.039439 | 4.034464 | -0.72575 |
| H | 3.686003 | 2.610583 | 0.105492 |
| H | 1.947964 | 2.821274 | -0.07379 |
| C | 4.420995 | 2.624547 | -2.5215 |
| H | 4.461168 | 3.711952 | -2.64277 |
| H | 4.601844 | 2.177944 | -3.50495 |
| H | 5.241421 | 2.33981 | -1.85403 |
| C | 1.985905 | 2.751463 | -2.96181 |
| H | 0.947356 | 2.566229 | -2.66645 |
| H | 2.127519 | 2.279289 | -3.93977 |
| H | 2.096219 | 3.833855 | -3.08911 |
| C | 1.732194 | 0.075718 | -1.31509 |
| C | 0.913808 | -2.41262 | 1.55515 |
| H | 1.401904 | -3.26189 | 1.060049 |
| H | 0.371757 | -2.82177 | 2.416316 |
| C | 1.9546 | -1.44934 | 2.095637 |

| | | | |
|---|---|---|---|
| C | 3.190558 | -1.88548 | 2.572737 |
| H | 3.471601 | -2.93055 | 2.485618 |
| C | 4.048225 | -0.95889 | 3.164759 |
| H | 5.013772 | -1.27647 | 3.547113 |
| C | 3.653751 | 0.377294 | 3.258478 |
| H | 4.293448 | 1.124583 | 3.715416 |
| C | 2.413728 | 0.741723 | 2.744462 |
| H | 2.043179 | 1.761461 | 2.761108 |
| H | 0.742802 | 1.730871 | -0.9551 |
| O | -0.86783 | 2.510543 | 2.569096 |
| H | -1.76496 | 2.509444 | 2.181207 |

**Table S8**. Comparison of the structural parameters of **1b** in different oxidation states

| **Parameter** | **1b** (X-ray data) (Å) | $^{2}$**1b** (Å) | $^{3}$**1b**$^{+}$ (Å) | $^{4}$**1b**$^{2+}$ (Å) |
|---|---|---|---|---|
| Cu1-O1 | 1.8871 | 1.9188 | 2.0171 | 2.0201 |
| Cu1-O2 | 2.3465 | 2.3933 | 2.2676 | 2.2054 |
| Cu1-O3 | 1.9582 | 1.9942 | 1.9319 | 2.0020 |
| Cu1-N1 | 2.0340 | 2.1335 | 2.1009 | 2.0522 |
| Cu1-N2 | 1.9967 | 2.0921 | 2.0435 | 2.0445 |
| O4···H (H-bond) | 1.990 | 1.6176 | 1.6825 | 0.9914 |
| O1-C1 | 1.341 | 1.3225 | 1.2713 | 1.2768 |
| O2-C24 | 1.381 | 1.3633 | 1.3754 | 1.2803 |
| O2-H | 0.75 | 1.0108 | 1.0003 | 1.7840 |
| Cu1-O3-C31 | 124.31 | 122.65 | 121.09 | 130.14 |
| O1-Cu1-N2 | 166.86 | 159.90 | 164.81 | 140.45 |
| O3-Cu1-N1 | 174.01 | 172.65 | 171.55 | 174.89 |
| O1-Cu1-O2 | 104.92 | 106.17 | 94.24 | 98.91 |

**Table S9**: Mulliken spin density analysis for **1b** complex in different oxidation states.

| **Moiety** | **Center** | **Spin Density** | | |
|---|---|---|---|---|
| | | $^{2}$**1b** | $^{3}$**1b**$^{+}$ | $^{4}$**1b**$^{2+}$ |
| Metal | Cu | 0.485 | 0.569 | 0.574 |
| | O2 | 0.172 | 0.342 | 0.332 |
| | C8 | -0.016 | 0.062 | 0.099 |
| | C9 | 0.041 | 0.241 | 0.249 |
| Equatorial | C23 | -0.012 | -0.139 | -0.138 |
| Phenolate | C25 | 0.042 | 0.372 | 0.366 |
| | C30 | -0.009 | -0.081 | -0.031 |
| | C32 | 0.044 | 0.217 | 0.154 |
| | **Total** | **0.262** | **1.014** | **1.031** |
| | O3 | -0.000 | 0.007 | 0.275 |
| | C63 | 0.001 | 0.001 | 0.111 |
| | C39 | -0.000 | 0.006 | 0.151 |
| | C40 | 0.001 | -0.001 | -0.031 |
| Axial Phenol | C42 | -0.001 | 0.002 | 0.370 |
| | C47 | 0.001 | 0.004 | -0.136 |
| | C49 | -0.001 | 0.001 | 0.241 |
| | **Total** | **0.001** | **0.020** | **0.981** |
| Acetate | O4 | 0.084 | 0.152 | 0.066 |
| | O5 | 0.003 | 0.002 | 0.001 |
| Amine N | N6 | 0.103 | 0.113 | 0.182 |
| Pyridine N | N7 | 0.052 | 0.091 | 0.090 |

**Table S10**. Electronic spectra for **1a**, **1b** and $^{1}$**1b**$^{+}$ in $CH_2Cl_2/CH_3CN$ (1:1)

| **Compound** | **Ligand based**[a] **transition** nm (L mol$^{-1}$ cm$^{-1}$) | **Charge Transfer transition**[b] (equatorial phenolate to metal) nm (L mol$^{-1}$ cm$^{-1}$) | ***d-d***[b] **transition** nm (L mol$^{-1}$ cm$^{-1}$) |
|---|---|---|---|
| **1a** | 219 (33132)<br>267 (6631)<br>284 (7489) | | |
| **1b** | 223 (35807)<br>266 (11214)<br>283 (10933) | 465 (823) | 673 (285) |
| $^{1}$**1b**$^{+}$ [c] | 221 (113376)<br>266 (27891)<br>307 (13314)<br>363 (5940) | 500 (891) | 670 (510) |

[a] = 1 x 10$^{-5}$ mol dm$^{-3}$; [b] = 1 x 10$^{-3}$ mol dm$^{-3}$; [c] = Generated electrochemically by exhaustive electrolysis at + 0.9 V. TEAP (0.1 M) was used as a supporting electrolyte.

**Table S11**. Coordination environment around Cu(II) center in the optimized structures of the mechanistic intermediates, $^{3}$**1b**$^{+}$, intermediate **1**, intermediate **2** and intermediate **3**.

| **Parameter** | $^{3}$**1b**$^{+}$ | Intermediate **1** | Intermediate **2** | Intermeiate **3** |
|---|---|---|---|---|
| Cu1-O1 | 2.0171 | 2.0461 | 2.3167 | 2.0664 |
| Cu1-O2 | 2.2676 | 2.3333 | 2.3275 | 2.3133 |
| Cu1-O3 | 1.9319 | 1.8939 | 2.1251 | 1.9084 |
| Cu1-N1 | 2.1009 | 2.1374 | 2.2292 | 2.1538 |
| Cu1-N2 | 2.0435 | 2.0566 | 2.0748 | 2.0498 |

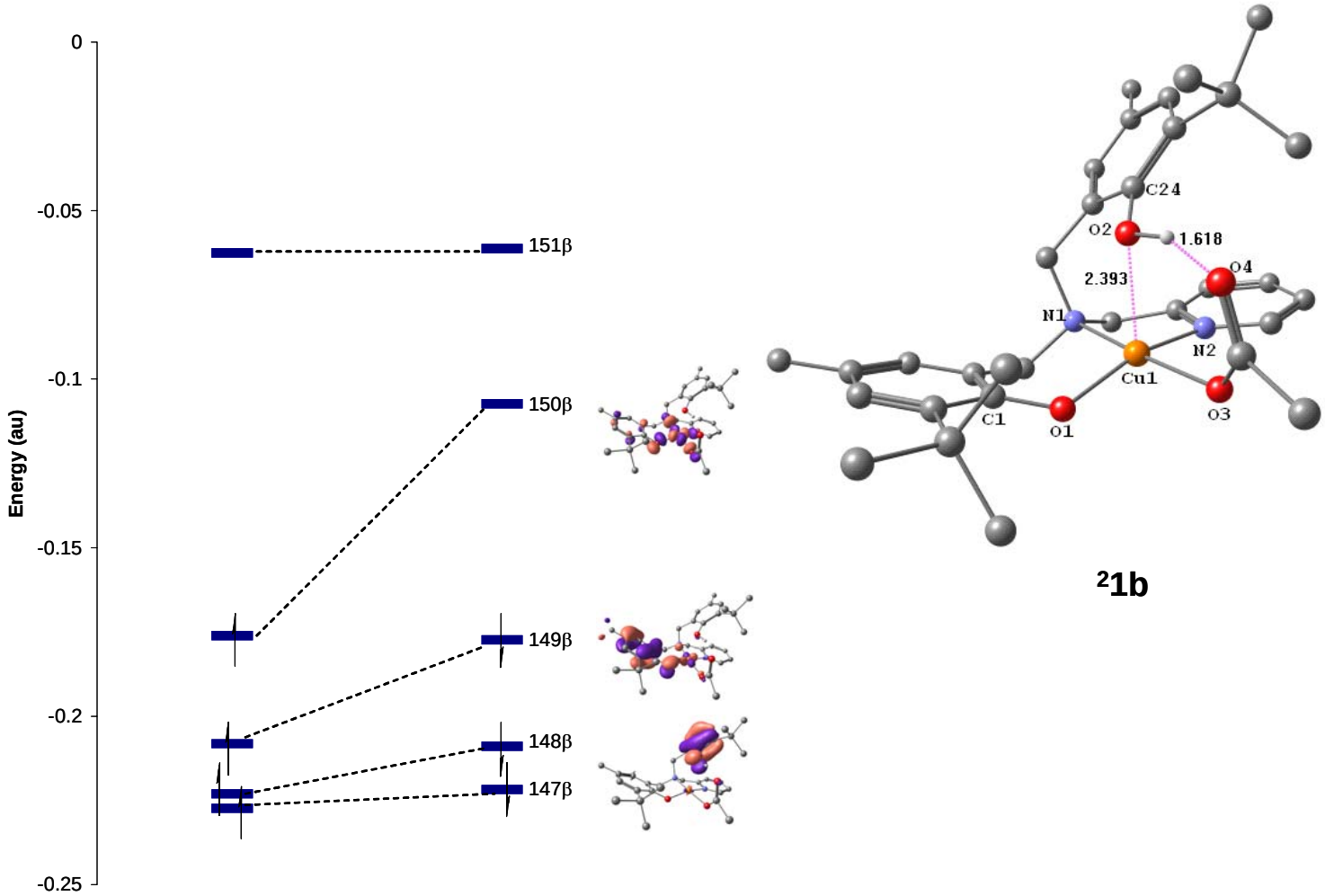



**Figure S1**. Optimized geometry of $^{2}$**1b** and its frontier molecular orbitals are shown. (Energy in Hartree). .

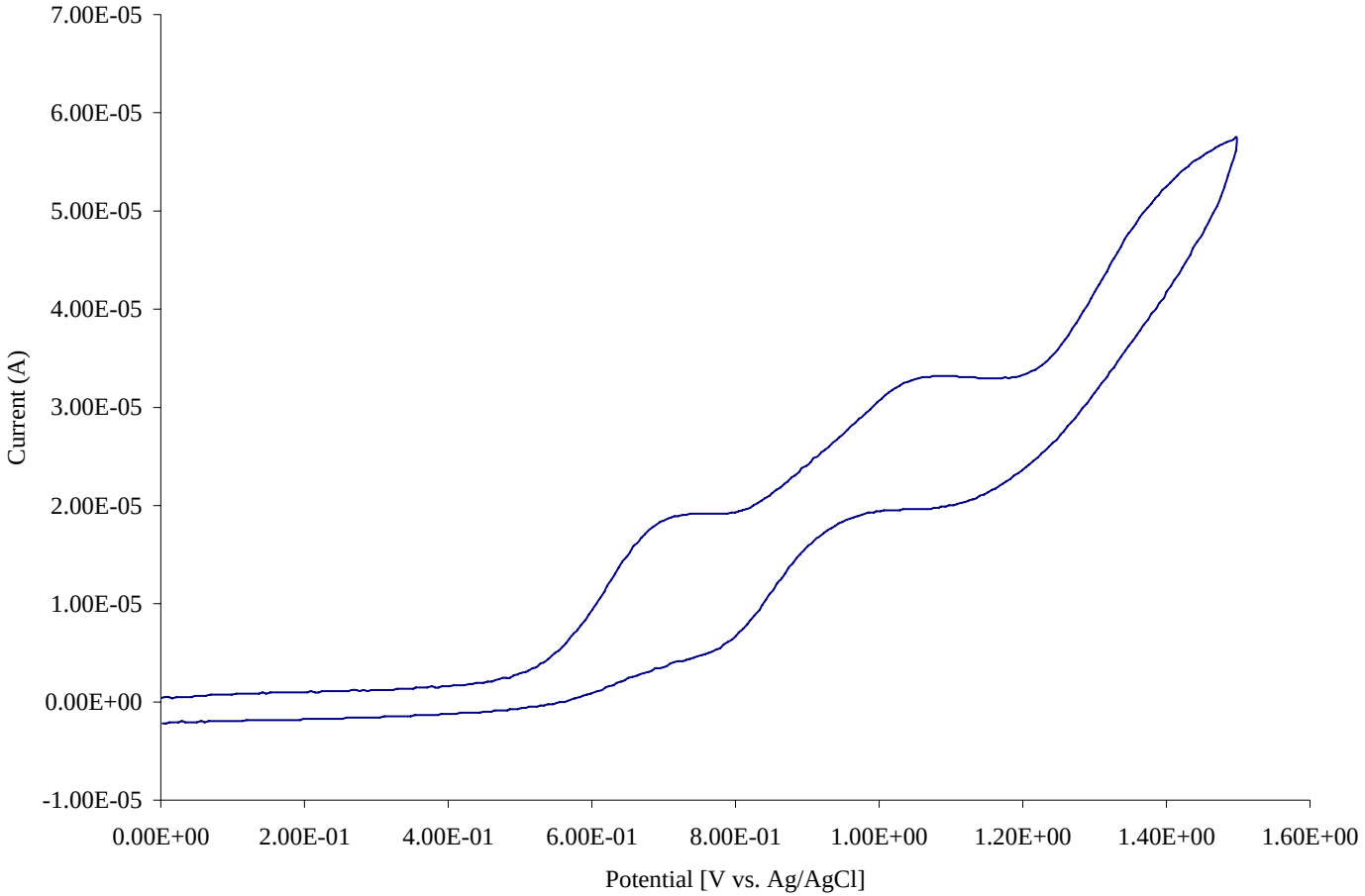



**Figure S2**. Cyclic voltammogram (298 K) of the copper complex **1b** ($5 \times 10^{-3}$ mol $dm^{-3}$) in $CH_3CN/CH_2Cl_2$ (1:1) solution {$1 \times 10^{-1}$ mol $dm^{-3}$ $[NEt_4](BF_4)$} recorded at 50 mV $s^{-1}$.

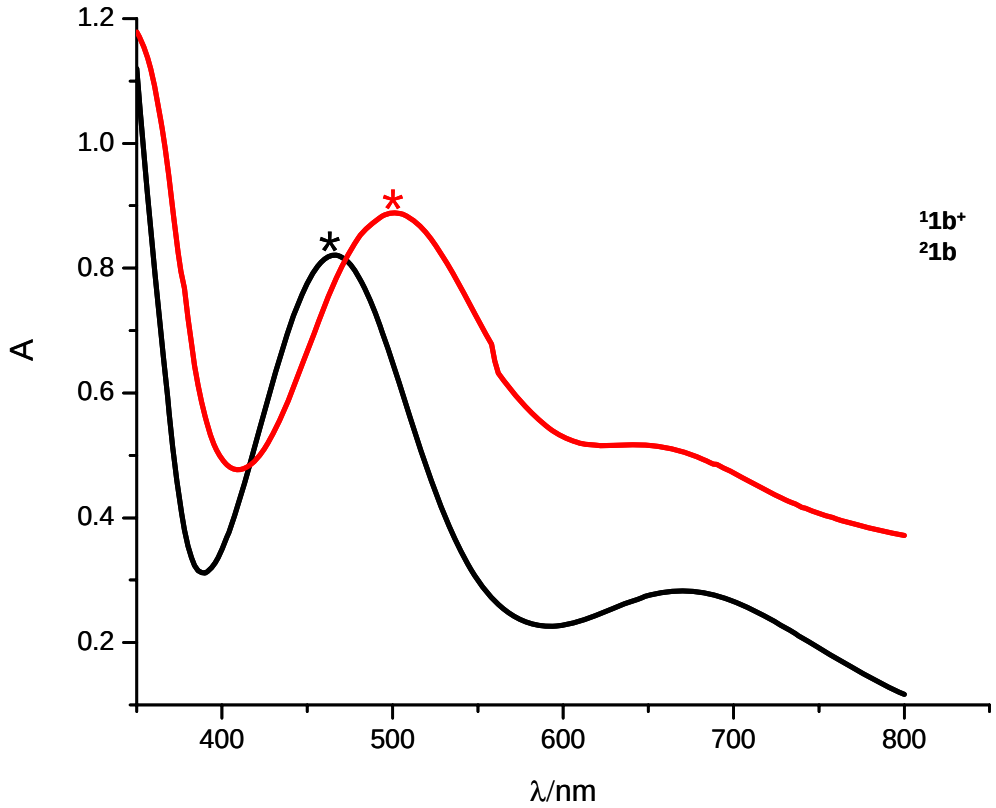



**Figure S3**. UV-VIS absorption spectra of **1b** and electrochemically generated $^{1}$**1b**$^{+}$ in $CH_2Cl_2/CH_3CN$ (1:1) + tetraethylammonium perchlorate (TEAP, 0.1 M). The peak due to ligand to metal charge transfer (LMCT) is marked by * in the plot.

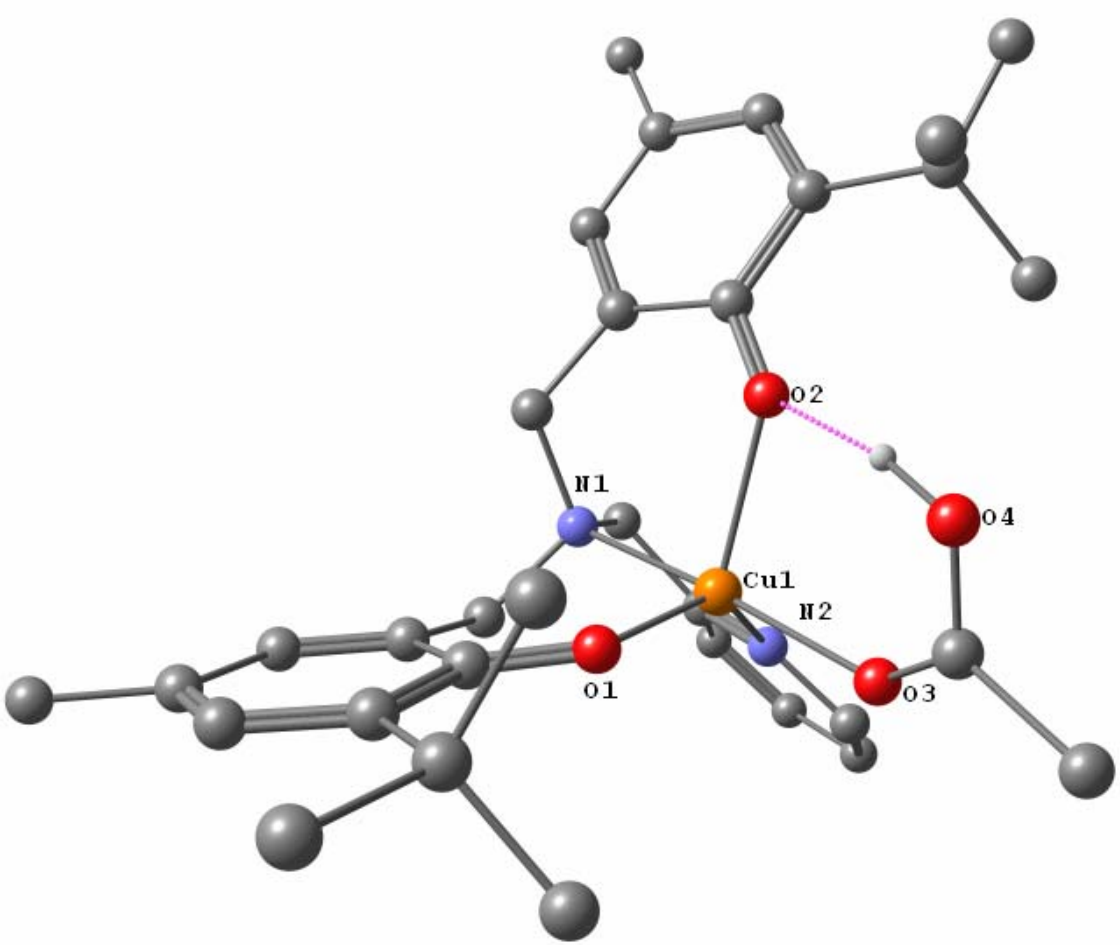



**Figure S4**. Geometry optimized structure of $^{4}$**1b**$^{2+}$ showing the proton transfer occurring between the axial phenol and metal bound acetate.

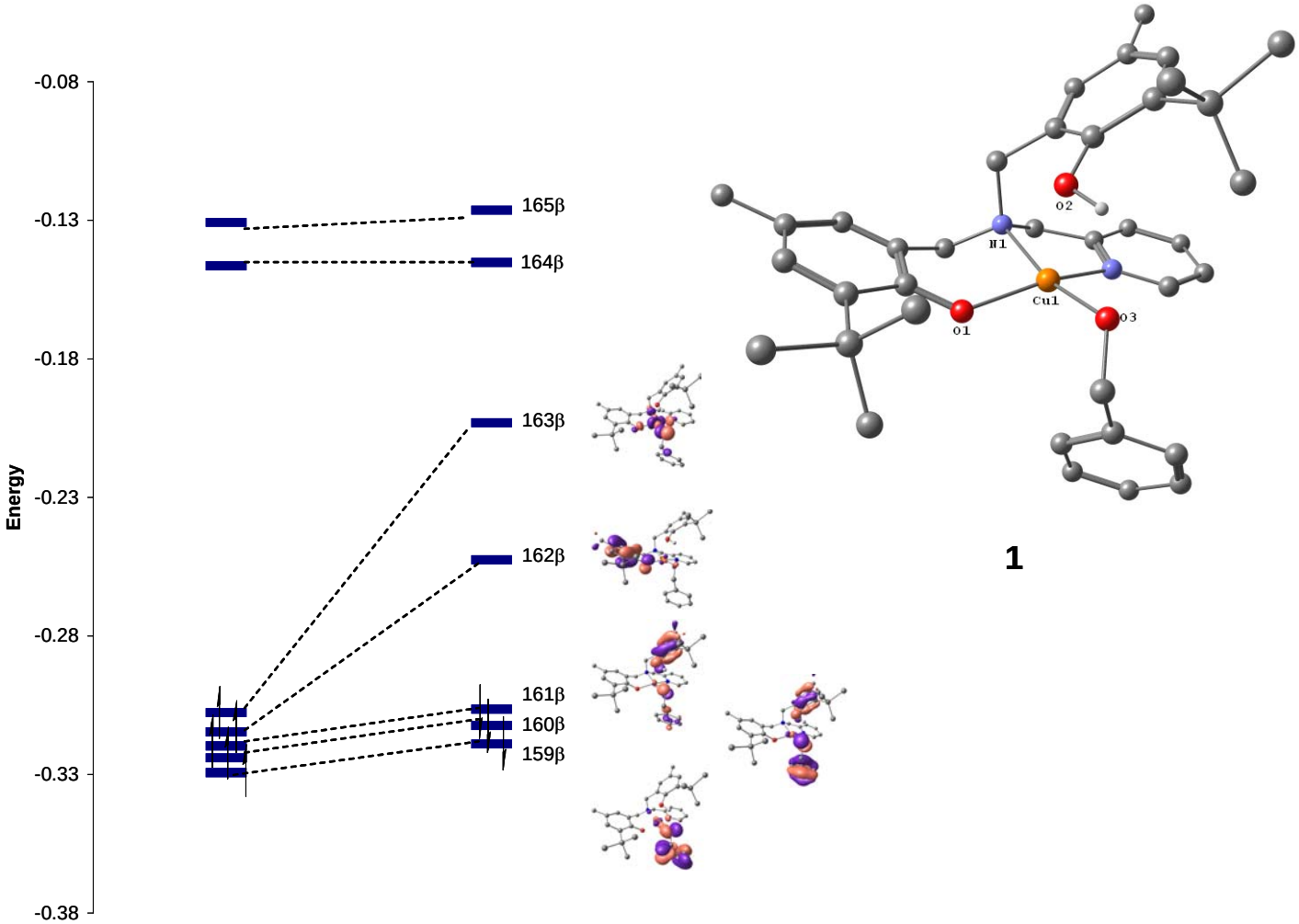



**Figure S5**. Frontier molecular orbitals of intermediate **1** are shown (Energy units are Hartree).

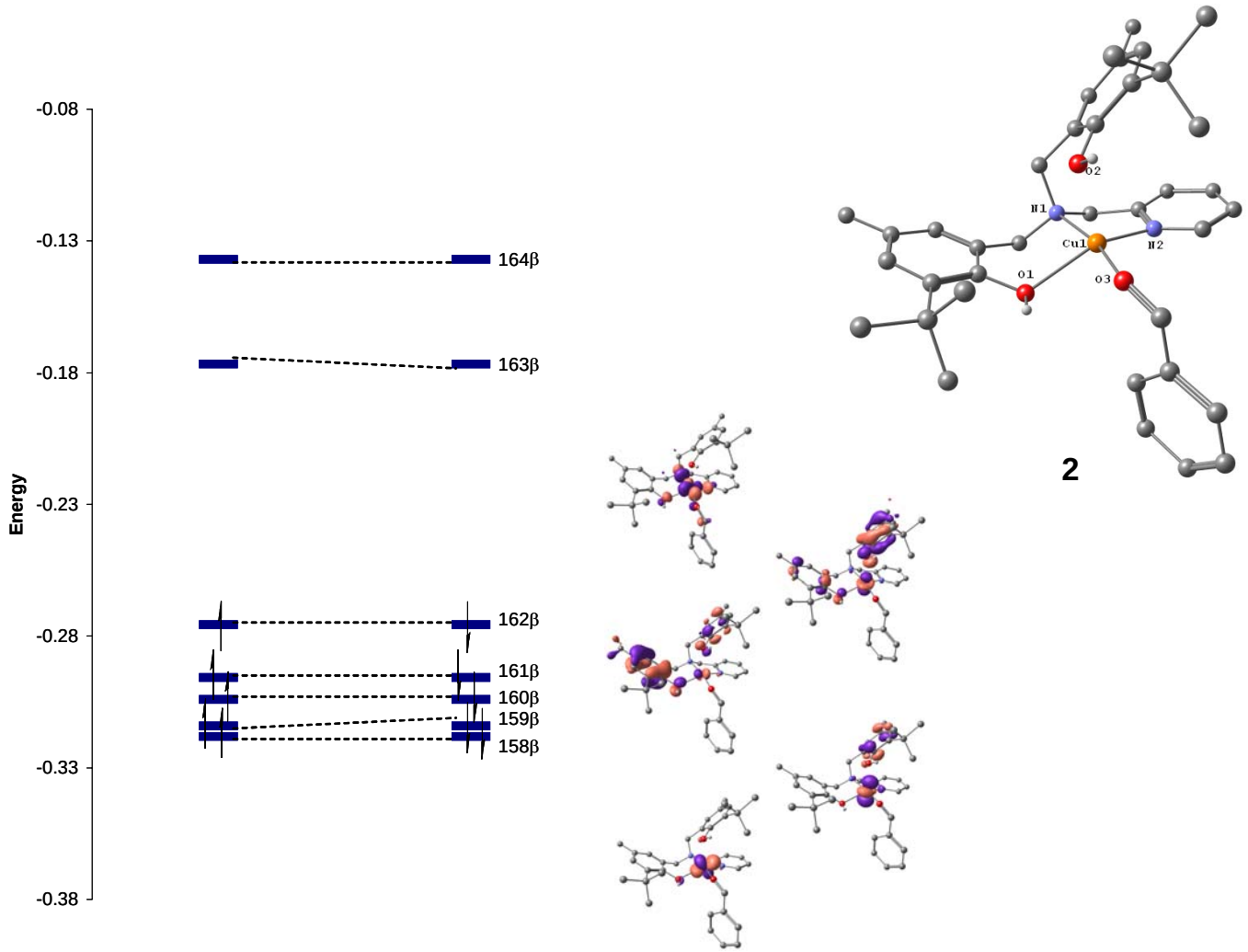



**Figure S6**. Frontier molecular orbitals of Intermediate **2** are shown (Energy units are Hartree).

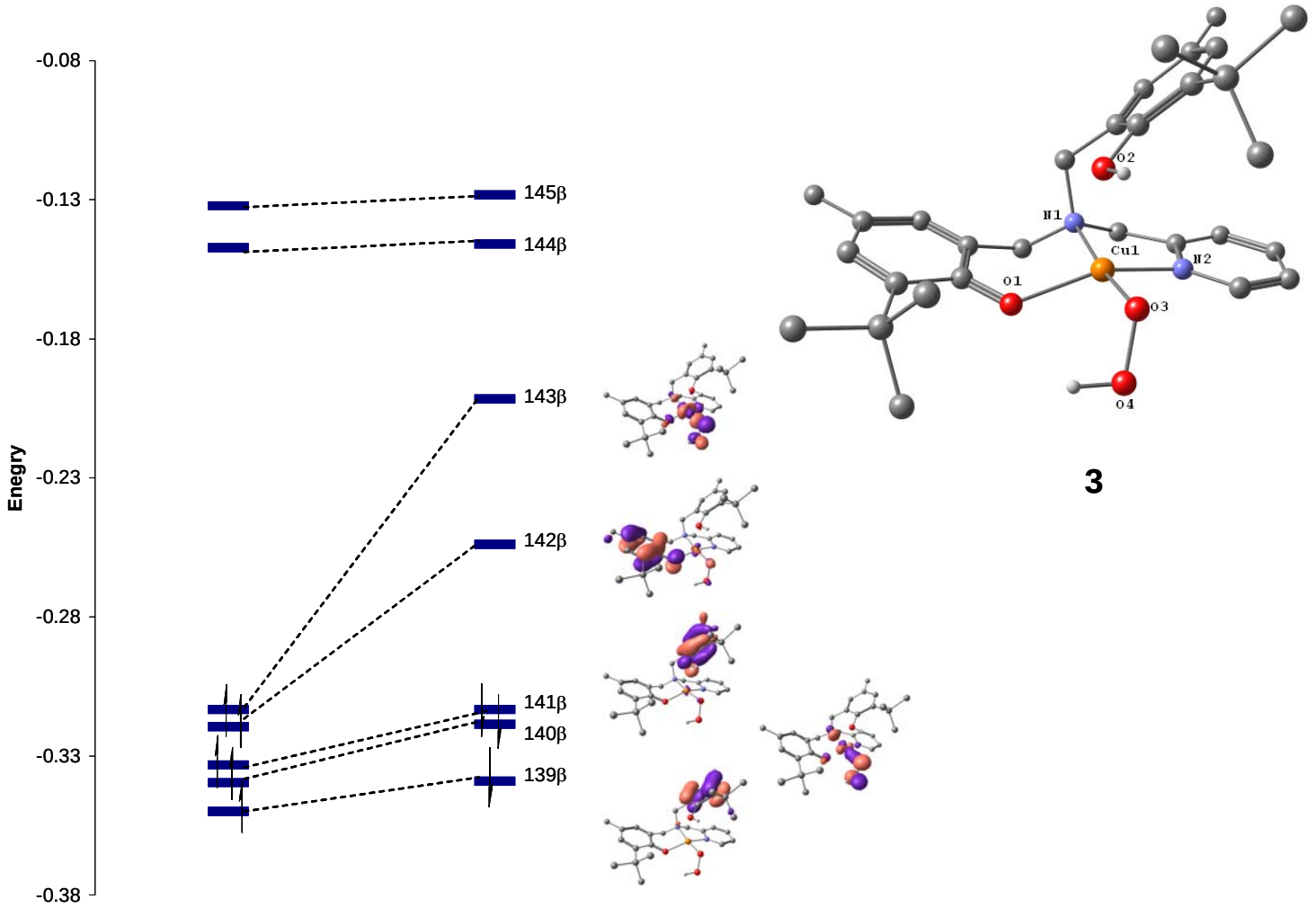



**Figure S7**. Frontier molecular orbital of Intermediate **3** are shown (Energy units are Hartree).

## References

[1]. GAUSSIAN 03: Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.