Supporting Information

Mechanistic Insights of Cu(II)-Mediated *ortho*-C–H Amination of Arenes by Capturing Fleeting Intermediates and Theoretical Calculations

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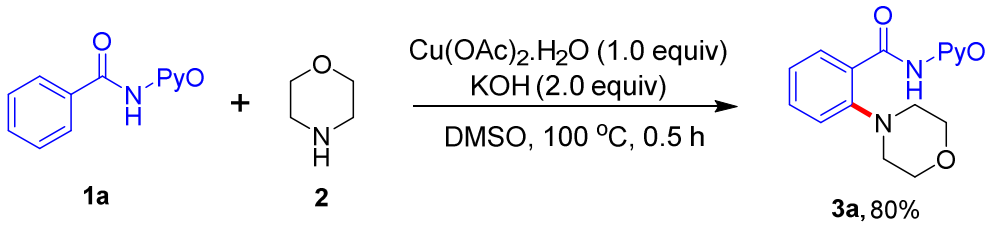
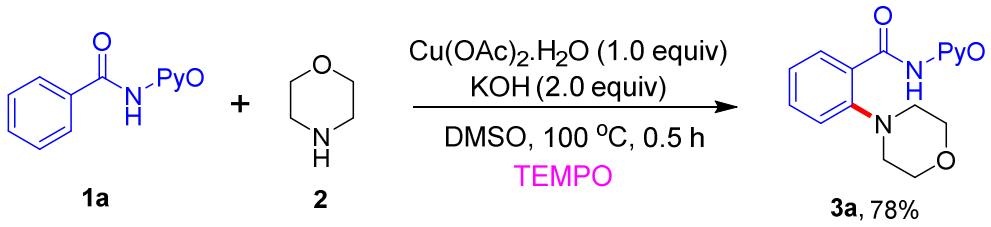
Supplementary Note 1

Initially, 2.0 equiv of 2,2,6,6- tetramethyl-1-piperidinyloxy (TEMPO), used as a radical scavenger, was added to the reaction of **1a** and **2**. Negligible effect on the yield of product **3a** (see below) rules out the possibility of the involvement of a free radical pathway in the reaction.



1a **2** **3a**, 80%



1a **2** **3a**, 78%

Table S1. List of species and their *m/z* values, representing the accuracy* in their mass measurements

Species	**Theoretical *m/z***	**Observed *m/z***	**Deviation**	**Accuracy (ppm)***
$[\mathbf{I_2}+K]^+ / [\mathbf{I_2}'+K]^+$	373.9725	373.9681	0.0044	11.8
$[\mathbf{I_4}+2K]^+$	438.9756	438.9726	0.0030	6.8
$[\mathbf{I_5}+H]^+$	362.0560	362.0528	0.0032	8.8
$[\mathbf{M}+K]^+$	459.0252	459.0201	0.0051	11.1
$[2\mathbf{M}+K]^+$	879.0873	879.0833	0.0040	4.5
$\mathbf{I_1}$	394.0226	394.0162	0.0064	16.2
$\mathbf{I_3}$	334.0020	333.9954	0.0066	19.8
$[\mathbf{3a}-H]^-$	298.1197	298.1137	0.0060	20.1
$[Cu^0(OAc)]^-$	121.9435	121.9414	0.0021	17.5
$[Cu^I(OAc)_2]^-$	180.9568	180.9522	0.0046	25.4
$[Cu^{II}(OAc)_3]^-$	239.9701	239.9648	0.0053	22.1
AcO^-	59.0139	59.0120	0.0019	32.2
$[K+2AcO]^-$	156.9909	156.9866	0.0043	27.4
$[DMSO+K]^+$	116.9771	116.9749	0.0022	18.8
K^+	38.9632	38.9624	0.0008	20.5

*verified further by the standards AcO^-, $[K+2AcO]^-$, $[DMSO+K]^+$, K^+ (see last four rows) and the product **3a**. Generally higher the *m/z* value, higher is the accuracy (low ppm).

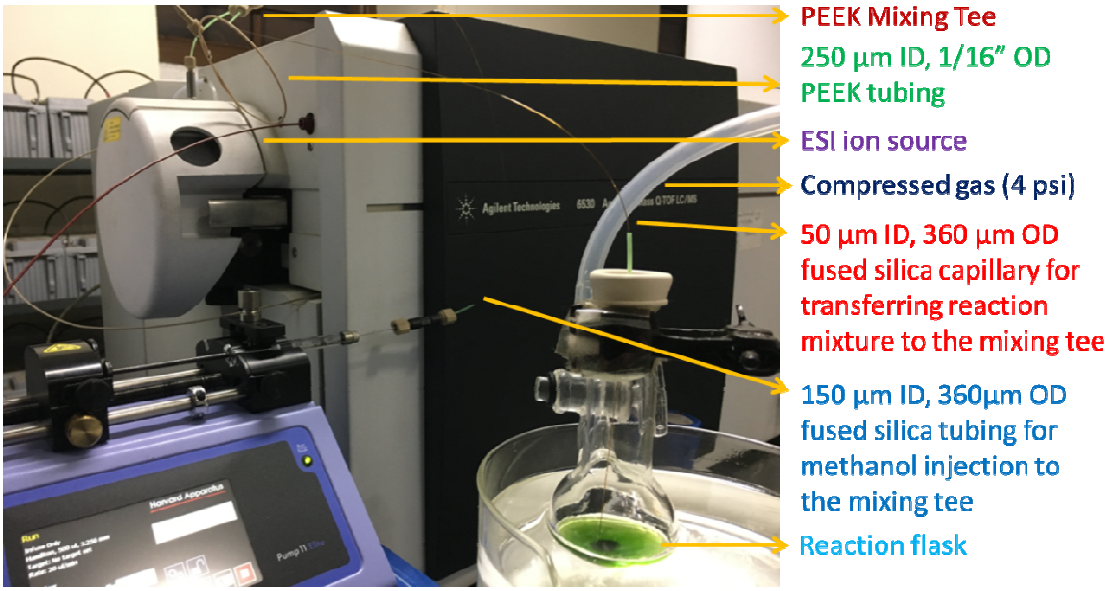


Figure S1. Online ESI-MS with pressurized sample infusion setup used for real-time reaction monitoring to track different species formed during the progress of the reaction.

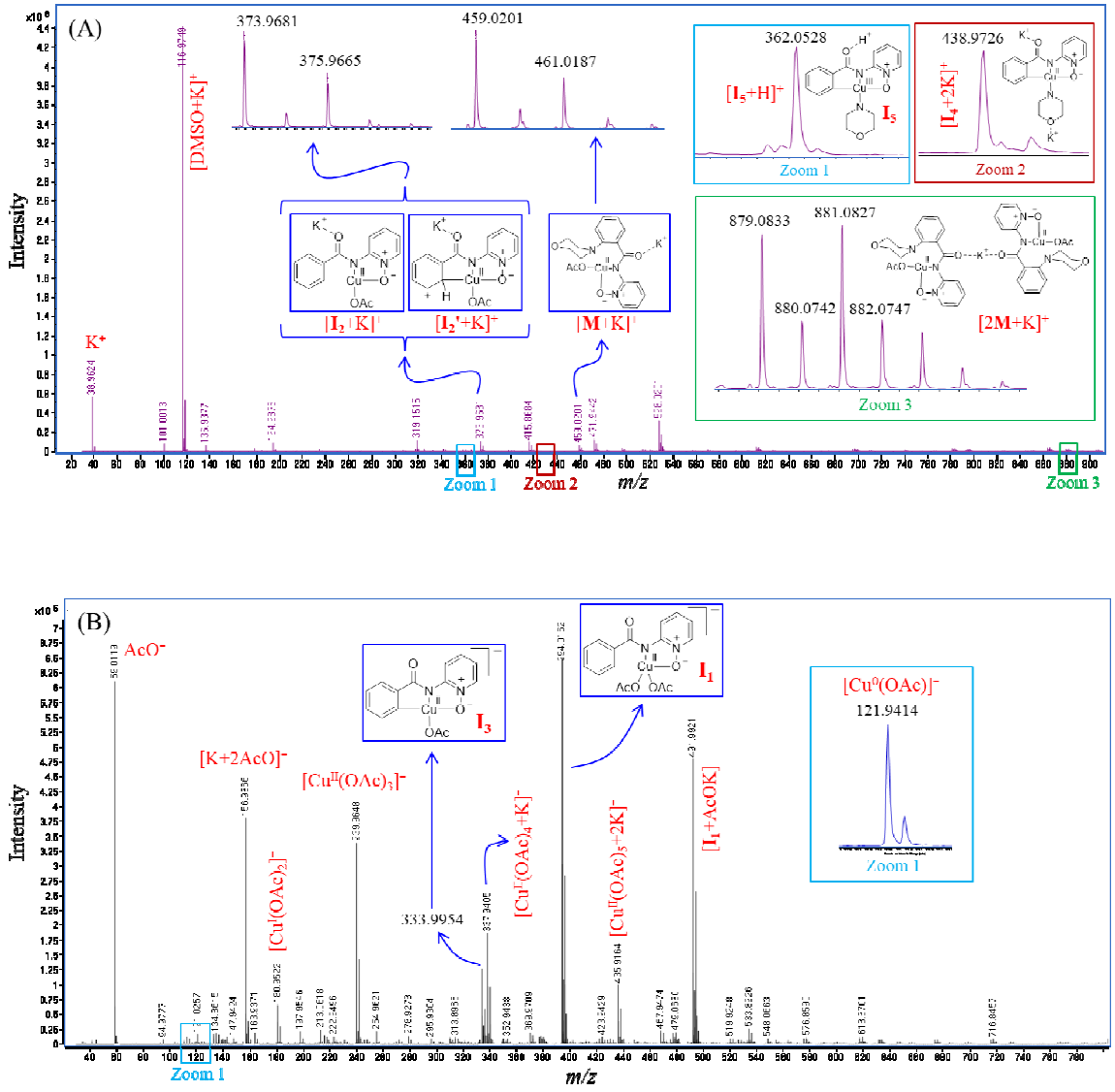


Figure S2. Average ESI mass spectra of the reaction mixture at (A) positive ion mode, and (B) negative ion mode, recorded during the progress of the reaction (0-16 min). Insets show different species formed during the reaction. The mass accuracy list is given in Table S1.

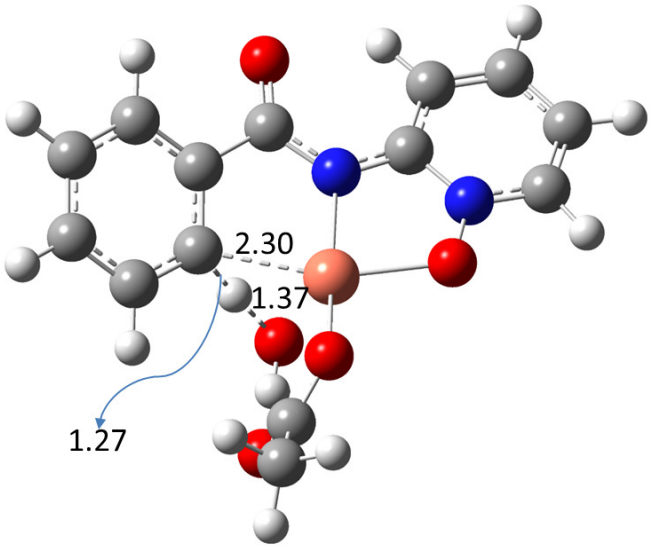


Figure S3a. TS for the metallacycle ($\mathbf{I_3}$) formation. The geometry for the TS in the metallacycle formation step (free-energy of activation is 22.9 kcal/mol). Single point energies computed at: UM06L/LANL2TZ (f) (Cu): 6-311++G(3df,2p) (SMD). Geometries, frequency, and thermochemical data from UM06L/LANL2DZ (Cu): 6-31+G(d,p) (SMD) level of theory. All distances are in Angstroms.

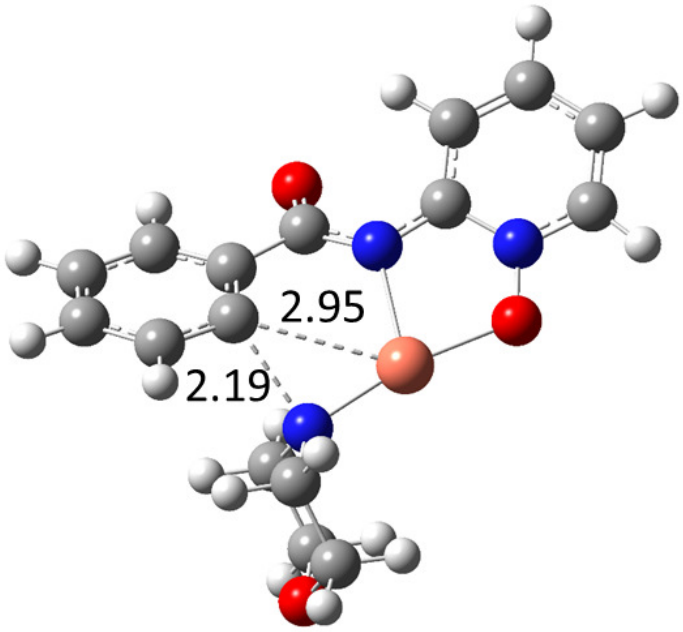


Figure S3b. TS for the reductive elimination (Cu(II) to Cu(0) pathway). The geometry for the TS in the reductive elimination step in the Cu(II) to Cu(0) pathway (free-energy of activation is 38.6 kcal/mol). Single point energies computed at: UM06L/LANL2TZ (f) (Cu): 6-311++G(3df,2p) (SMD). Geometries, frequency, and thermochemical data from UM06L/LANL2DZ (Cu): 6-31+G(d,p) (SMD) level of theory. All distances are in Angstroms.

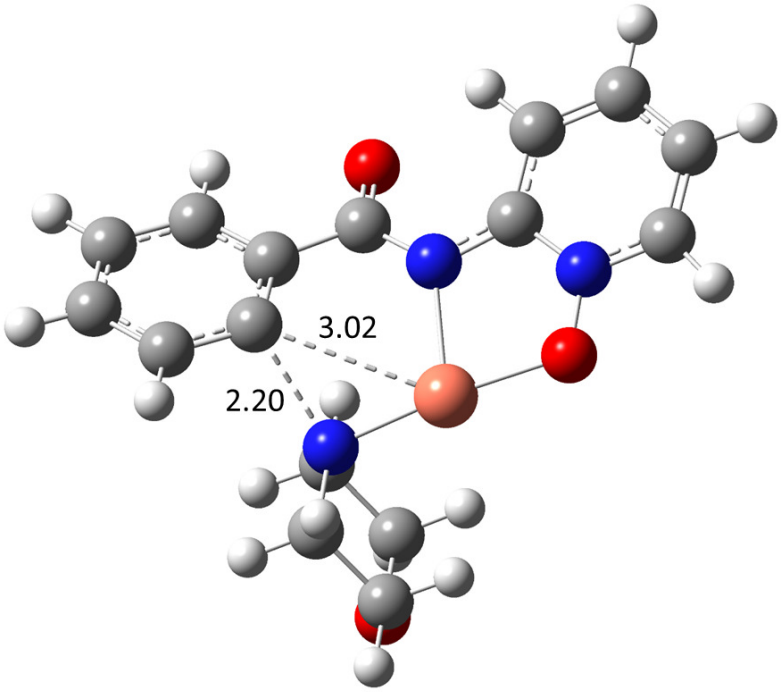


Figure S3c. TS for the reductive elimination (Cu(III) to Cu(I) pathway). The geometry for the TS (triplet) in the reductive elimination step in the Cu(III) to Cu(I) pathway (free-energy of activation is 39.9 kcal/mol). Single point energies computed at: UM06L/LANL2TZ (f) (Cu): 6-311++G(3df,2p) (SMD). Geometries, frequency, and thermochemical data from UM06L/LANL2DZ (Cu): 6-31+G(d,p) (SMD) level of theory. Despite several attempts, only the triplet TS could be located, and both the closed-shell and open-shell singlets (if at all they exist) could not be found. All distances are in Angstroms.

Materials and Methods

Reagents were obtained from commercial sources. LC-MS grade solvents were obtained from Thermo Fisher Scientific.

Online ESI–MS Study. The online ESI–MS experiment for real-time monitoring of different species, formed during the progress of the reaction, was performed using a pressurized sample infusion method originally described by McIndoe and coworkers.[1] Figure S1 shows a photograph of the setup used in this study. The reaction in a Schlenk flask was conducted at 0.25 mmol scale (containing **1a** and **2a**) with 1.0 equiv $Cu(OAc)_2.H_2O$ and 2.0 of equiv KOH in 2 mL DMSO at 100 ^oC. The nitrogen gas pressure in the Schlenk flask was kept at 4 psi, and the syringe (500 µL Hamilton 1750 series) flow rate (methanol) was maintained at 30 µL/min. The MS (Agilent 6530 Q-TOF LC/MS) instrumental parameters were: drying gas temperature 300 ^oC, drying gas flow 5 L/min, nebulizer pressure 25 psi, capillary voltage ± 4 kV (positive and negative ion mode), fragmentor voltage 110 V, collision energy 0 eV, scan rate 1 spectra/s. The capillary voltage was applied at time zero. The dead time is approximately 25 second and does not account for the onset of the reaction seen in Figure 1. Data analysis was performed using Mass Hunter software (Agilent Technologies).

Computational Details. All the geometries were optimized using the contemporarily widely used M06L density functional[2] (different Kohn–Sham orbitals were used for different spins – unrestricted version). This functional was chosen because of its excellent performance to describe the geometry and energetics of systems containing transition metals.[3] Copper was treated with the Los Alamos pseudopotential (LANL), and the associated double-zeta quality D95 basis–sets (LANL2DZ mixed basis). Rest of the atoms were optimized using the 6–31+g(d,p) basis–sets. Harmonic frequencies, zero-point energies, and thermal corrections are also computed at the same level of theory. Minimum energy structures on the potential energy surface were computed to have no imaginary frequencies, and transition structures, exactly one. Intrinsic Reaction Coordinate (IRC) calculations were performed to confirm that the transition states connect to the right minima on both sides. Subsequently, single point energies were computed using the LANL2TZ (f) mixed basis–sets (for Cu), and 6–311++g(3df,2p) for the other atoms. Based on the $\langle S \rangle^2$ values (< 0.77 for a doublet electronic state and < 2.01 for a triplet electronic state), spin contamination was noted to be insignificant throughout all the calculations. Unless otherwise stated, the ground electronic states of all the Cu(II) and Cu(0) systems have doublet ground electronic states, and that of Cu(III) and Cu(I) species correspond to closed shell singlets. This was determined after carefully

optimizing the higher spin states as well (at the same level of theory) and calculating their relative energies and free energies. The TS for the Cu(III) to Cu(I) reductive elimination process alone corresponds to a triplet electronic state. The SMD implicit solvation model was used in all the calculations to model solvation effects (solvent – dimethylsulfoxide). All the computations were performed using the *Gaussian 09* suite of electronic structure programs.

List of Cartesian coordinates of optimized structures

Legend:

The coordinates of all the Cu containing structures are provided here. Followed by the description of the structure, the charge and multiplicities are provided. Then, the atomic number or atomic symbol of the atoms involved, and the X, Y and Z coordinates of all the atoms are provided. For the computational methods used in the optimization, kindly refer to the main text. For the TSs – exactly one imaginary frequency was found. For the minima, no imaginary frequency was found.

Cu(II) reactant in the first step (ligand dissociation)

-1 2

29	-0.202701	0.993394	0.336157
8	0.053231	2.972610	0.559412
6	0.470080	3.325558	-0.605113
8	0.634733	2.522686	-1.549367
8	1.545590	0.579325	1.188931
6	1.282522	0.031608	2.325266
8	0.136876	-0.062404	2.808772
7	-0.747380	-0.891488	-0.263694
6	0.095349	-1.979016	-0.231990
8	-0.216799	-3.120060	0.139295
6	1.481104	-1.709451	-0.715737
6	1.776785	-0.630785	-1.557705
6	2.508521	-2.582057	-0.339123
6	3.076708	-0.428019	-2.010544
1	0.993867	0.067552	-1.842470
6	3.812406	-2.368688	-0.775954
1	2.271733	-3.418721	0.313296
6	4.099683	-1.290372	-1.615471
1	3.294974	0.412962	-2.664576
1	4.606772	-3.041675	-0.462929
1	5.117170	-1.125359	-1.961140
6	-2.095088	-1.052879	-0.255749
6	-2.864452	-2.224822	-0.415632
6	-4.243543	-2.170797	-0.502602
1	-2.336397	-3.166299	-0.470330
6	-4.149100	0.198771	-0.253834
6	-4.902276	-0.940741	-0.419731
1	-4.807967	-3.089305	-0.632676
1	-4.552599	1.200374	-0.175649
1	-5.981056	-0.856597	-0.477194
8	-2.136991	1.281905	-0.008193
7	-2.798373	0.136747	-0.168542
6	2.469300	-0.533453	3.070231
1	2.513029	-0.116983	4.080839
1	2.343471	-1.615935	3.177383
1	3.413703	-0.339520	2.557309
6	0.735857	4.797462	-0.805190
1	1.613466	4.946279	-1.438888
1	-0.117858	5.245945	-1.324309
1	0.870023	5.325642	0.140904

Cu(II) product in the ligand dissociation step (step 1)

0 2

```
29   -0.081350    0.929293   -0.411051
 8   -0.798846    2.628930   -0.942402
 6   -1.065953    3.280946    0.150993
 8   -0.898472    2.783779    1.277416
 7    0.615042   -0.850723    0.000466
 6   -0.129846   -2.005321   -0.122627
 8    0.342766   -3.123838   -0.349627
 6   -1.605382   -1.832952    0.022005
 6   -2.170438   -0.873130    0.873443
 6   -2.450529   -2.716843   -0.661560
 6   -3.552908   -0.779452    1.016455
 1   -1.521775   -0.210319    1.445662
 6   -3.830764   -2.617641   -0.525337
 1   -2.010078   -3.473572   -1.304788
 6   -4.385449   -1.647770    0.313029
 1   -3.975994   -0.035700    1.686087
 1   -4.478226   -3.297676   -1.072237
 1   -5.464069   -1.575589    0.422161
 6    1.978172   -0.884020    0.091860
 6    2.816206   -1.961839    0.427640
 6    4.184724   -1.789823    0.525155
 1    2.357407   -2.923545    0.603985
 6    3.923666    0.515573   -0.033536
 6    4.751800   -0.535568    0.284190
 1    4.812002   -2.634689    0.790459
 1    4.251965    1.528303   -0.229217
 1    5.819806   -0.363282    0.344423
 8    1.835246    1.403050   -0.425443
 7    2.584175    0.333308   -0.121218
 6   -1.568105    4.681246   -0.043201
 1   -1.974016    5.084397    0.885087
 1   -0.740797    5.319421   -0.369332
 1   -2.328317    4.718858   -0.827145
```

Cu(II) TS in the metallacycle formation step (step 2)

```
-1 2
 Cu         0.246198   -0.741371   -0.064675
 O          1.568165   -1.983081   -0.758544
 C          2.603594   -2.406037   -0.113194
 O          2.804906   -2.291564    1.108261
 N         -1.111452    0.695152   -0.018011
 C         -0.720409    2.007753    0.026483
 O         -1.470344    2.994655    0.028542
 C          0.767180    2.142061    0.009600
 C          1.577888    1.070677    0.436486
 C          1.338979    3.321087   -0.478814
 C          2.966181    1.195321    0.298873
 C          2.722394    3.427149   -0.598850
 H          0.687956    4.136949   -0.786030
 C          3.537942    2.357590   -0.219663
 H          3.609653    0.378624    0.625225
 H          3.165378    4.336455   -0.997239
 H          4.618067    2.437766   -0.320183
 C         -2.402883    0.282129   -0.042609
 C         -3.584780    1.022692    0.140722
 C         -4.824941    0.409419    0.091282
 H         -3.481441    2.083984    0.319576
```

C	−3.749153	−1.682553	−0.327145
C	−4.911002	−0.963620	−0.147378
H	−5.723666	0.999702	0.241701
H	−3.707567	−2.747878	−0.515693
H	−5.861160	−1.483116	−0.193987
O	−1.455659	−1.828673	−0.465726
N	−2.536710	−1.079548	−0.275599
C	3.645264	−3.068075	−0.988353
H	4.286775	−3.731968	−0.405563
H	3.191954	−3.618840	−1.815855
H	4.278899	−2.288544	−1.427055
O	0.673884	−0.640066	2.233945
H	1.169478	0.268143	1.338659
H	1.397936	−1.284474	2.170826

Cu(II) metallacycle formed in step 2

−1 2

29	−0.380457	0.680907	−0.303838
8	−1.535258	2.254557	−0.724233
6	−1.986673	2.738460	0.380389
8	−1.661668	2.338777	1.515953
7	0.941910	−0.790811	−0.006871
6	0.436857	−2.058471	0.130668
8	1.096178	−3.091814	0.320329
6	−1.053983	−2.054244	0.018990
6	−1.708409	−0.826926	−0.209042
6	−1.769614	−3.251291	0.141260
6	−3.101845	−0.841440	−0.304680
6	−3.158919	−3.241257	0.037187
1	−1.228735	−4.179930	0.317759
6	−3.825783	−2.033850	−0.185706
1	−3.646385	0.089492	−0.473370
1	−3.721753	−4.167061	0.130294
1	−4.911787	−2.023733	−0.264663
6	2.247207	−0.455642	0.032309
6	3.384495	−1.255949	0.251754
6	4.655852	−0.706730	0.244701
1	3.217650	−2.311305	0.422275
6	3.702076	1.441541	−0.190665
6	4.819743	0.661717	0.017413
1	5.518728	−1.343263	0.416274
1	3.723246	2.508905	−0.371609
1	5.797217	1.130198	0.000932
8	1.422133	1.708477	−0.382820
7	2.458219	0.904795	−0.179958
6	−3.010859	3.842499	0.227563
1	−3.066913	4.461793	1.125274
1	−2.804033	4.470447	−0.642475
1	−3.996824	3.389792	0.071739

Cu(II) Product in the ligand dissociation step (Step 3)

0 2

29	0.311539	−1.474548	0.000069
7	−0.388283	0.358095	−0.001468
6	0.554471	1.354930	−0.000295

```
  8    0.317599    2.568463    0.000422
  6    1.932296    0.774111   -0.000074
  6    2.079045   -0.628731    0.000136
  6    3.048938    1.615508   -0.000043
  6    3.368646   -1.159808    0.000363
  6    4.329660    1.067806    0.000181
  1    2.900377    2.693899   -0.000195
  6    4.488527   -0.318561    0.000382
  1    3.525225   -2.237714    0.000553
  1    5.201383    1.716936    0.000186
  1    5.488257   -0.748662    0.000566
  6   -1.730027    0.486162   -0.000657
  6   -2.527297    1.643953   -0.000389
  6   -3.907921    1.549916    0.000387
  1   -2.015798    2.597599   -0.000770
  6   -3.730695   -0.835468    0.000548
  6   -4.520642    0.293588    0.000869
  1   -4.509327    2.453438    0.000582
  1   -4.105357   -1.851134    0.000875
  1   -5.598117    0.178916    0.001492
  8   -1.673475   -1.872636   -0.000643
  7   -2.380897   -0.739299   -0.000243
```

Cu(II) product formed in the ligand association step (step 4)

```
-1 2
29    0.288586   -0.292630   -0.000100
 7   -1.645154    0.424752   -0.000095
 6   -1.779410    1.786451    0.000486
 8   -2.845477    2.427474    0.001294
 6   -0.447968    2.471052    0.000055
 6    0.727315    1.688271   -0.000366
 6   -0.400373    3.871097    0.000101
 6    1.944881    2.378528   -0.000737
 6    0.828313    4.527539   -0.000287
 1   -1.333943    4.431772    0.000434
 6    2.006297    3.776919   -0.000704
 1    2.885397    1.820687   -0.001070
 1    0.870825    5.614320   -0.000265
 1    2.970685    4.283394   -0.001006
 6   -2.678927   -0.439517   -0.000051
 6   -4.066770   -0.195940   -0.000215
 6   -4.981339   -1.236396   -0.000239
 1   -4.379428    0.839548   -0.000284
 6   -3.166687   -2.792217   -0.000048
 6   -4.526231   -2.556202   -0.000129
 1   -6.045651   -1.019897   -0.000354
 1   -2.717958   -3.778140   -0.000008
 1   -5.204811   -3.401842   -0.000113
 8   -0.981769   -2.061149   -0.000047
 7   -2.269120   -1.775359   -0.000037
 6    2.820531   -1.075729   -1.168485
 6    2.820763   -1.074778    1.168627
 6    4.006225   -2.027115   -1.169153
 1    3.229298   -0.040593   -1.221203
 1    2.234894   -1.235367   -2.084387
 6    4.006452   -2.026177    1.169794
 1    3.229528   -0.039603    1.220419
```

```
 1    2.235315   -1.233686    2.084777
 1    4.671963   -1.849737   -2.021065
 1    3.645290   -3.070234   -1.217941
 1    4.672355   -1.848141    2.021440
 1    3.645492   -3.069246    1.219480
 7    1.989410   -1.283103    0.000237
 8    4.804417   -1.858291    0.000180
```

TS for the reduction elimination step in the Cu(II) to Cu(0) pathway

```
-1 2
29    0.116432   -1.190261    0.242672
 7    1.295406    0.573024    0.072679
 6    0.780965    1.723887   -0.460883
 8    1.376594    2.459979   -1.277114
 6   -0.609755    2.054568   -0.020460
 6   -1.380478    1.272517    0.872697
 6   -1.145475    3.272622   -0.487853
 6   -2.617291    1.761534    1.312489
 6   -2.378851    3.742964   -0.053993
 1   -0.544530    3.856300   -1.183399
 6   -3.111791    2.988314    0.874529
 1   -3.220485    1.175122    2.008168
 1   -2.764648    4.691812   -0.418872
 1   -4.064728    3.359860    1.250444
 6    2.600673    0.274904    0.007749
 6    3.707346    1.144995   -0.117837
 6    5.008096    0.686111   -0.040087
 1    3.487036    2.193062   -0.276710
 6    4.175358   -1.531803    0.268897
 6    5.250580   -0.678775    0.158694
 1    5.835036    1.384543   -0.132779
 1    4.256021   -2.601353    0.418731
 1    6.253785   -1.083795    0.226212
 8    1.920665   -1.983464    0.266488
 7    2.899248   -1.080770    0.179808
 6   -2.715581   -1.414267    1.040556
 6   -2.348273   -0.569524   -1.124449
 6   -3.148190   -2.744432    0.444970
 1   -3.620263   -0.785308    1.154029
 1   -2.288688   -1.571252    2.039216
 6   -2.785876   -1.897599   -1.717332
 1   -3.237129    0.088633   -1.044077
 1   -1.631162   -0.078884   -1.796690
 1   -3.927359   -3.226853    1.044984
 1   -2.276493   -3.421222    0.386737
 1   -3.305067   -1.769094   -2.673298
 1   -1.898617   -2.535469   -1.880578
 7   -1.746826   -0.771394    0.179310
 8   -3.703854   -2.566600   -0.855412
```

Cu(0) product in the reductive elimination step (Cu(II) to Cu(0) path)

```
-1 2
 29      0.147017    1.055194   -0.750151
  7      0.983551   -0.679684    0.071726
  6      0.281104   -1.778624    0.518543
  8      0.814710   -2.775362    1.099445
```

```
  6     -1.145934   -1.815740    0.162389
  6     -2.043981   -0.743108   -0.222891
  6     -1.716331   -3.125060    0.128190
  6     -3.303458   -1.045008   -0.737472
  6     -2.971656   -3.403819   -0.378463
  1     -1.075845   -3.929534    0.479427
  6     -3.774894   -2.360970   -0.864343
  1     -3.970190   -0.241235   -1.029983
  1     -3.324664   -4.433163   -0.409984
  1     -4.760041   -2.547136   -1.283447
  6      2.313219   -0.571827    0.095062
  6      3.300470   -1.423296    0.658787
  6      4.653351   -1.158493    0.578532
  1      2.917357   -2.301840    1.163131
  6      4.160069    0.834230   -0.651175
  6      5.101391    0.000097   -0.093604
  1      5.365939   -1.841069    1.034487
  1      4.402091    1.743990   -1.188903
  1      6.152176    0.252573   -0.182883
  8      2.009912    1.470216   -1.173534
  7      2.831008    0.580560   -0.577820
  6     -2.685903    1.644896   -0.442381
  6     -1.542555    0.872864    1.506752
  6     -2.188405    3.037887   -0.134655
  1     -3.661350    1.492938    0.046075
  1     -2.816300    1.525700   -1.521887
  6     -1.112450    2.293396    1.786352
  1     -2.502204    0.655200    2.001291
  1     -0.788667    0.175284    1.882071
  1     -2.903786    3.785497   -0.487169
  1     -1.054619    2.468971    2.863850
  1     -0.112450    2.464070    1.344410
  7     -1.701193    0.652844    0.038281
  8     -2.031002    3.244360    1.262539
  1     -1.217657    3.194855   -0.646724
```

Cu(III) reactant in the reductive elimination step
(formed by the oxidation of the Cu(II) product in step 4)

```
0 1
29     0.191171   -0.394025    0.427947
 7    -1.307376    0.771827    0.001730
 6    -0.990276    2.041319   -0.413674
 8    -1.774908    2.871478   -0.881013
 6     0.453975    2.299086   -0.187849
 6     1.272102    1.258648    0.282544
 6     0.965320    3.589798   -0.348104
 6     2.577550    1.547497    0.658849
 6     2.285485    3.864519   -0.010178
 1     0.296541    4.366685   -0.714007
 6     3.081539    2.847045    0.511641
 1     3.237018    0.796078    1.078275
 1     2.686737    4.867091   -0.129415
 1     4.107508    3.052223    0.807927
 6    -2.554853    0.233920   -0.023293
 6    -3.790209    0.835962   -0.315265
 6    -4.957692    0.091549   -0.275373
```

1	-3.790279	1.885491	-0.574543
6	-3.693222	-1.839755	0.346720
6	-4.911420	-1.263999	0.058045
1	-5.905396	0.568646	-0.505089
1	-3.547380	-2.877533	0.618573
1	-5.803802	-1.877285	0.096844
8	-1.400961	-1.695860	0.602613
7	-2.557258	-1.105002	0.306691
6	2.812817	-1.738256	1.012602
6	1.231549	-2.732902	-0.443926
6	3.709034	-1.470446	-0.192375
1	3.119062	-2.708585	1.440158
1	2.970407	-0.997220	1.801999
6	2.146109	-2.426312	-1.614631
1	1.457855	-3.753762	-0.090726
1	0.183487	-2.729306	-0.758615
1	4.765648	-1.515801	0.087514
1	3.500476	-0.474054	-0.612321
1	2.040884	-3.174881	-2.405142
1	1.894404	-1.435273	-2.033970
7	1.400967	-1.845179	0.707899
8	3.508580	-2.443540	-1.209922

TS for the reduction elimination step in the Cu(III) to Cu(I) pathway

0 3

29	-0.111985	-1.163962	-0.461920
7	-1.051585	0.628189	-0.028011
6	-0.443961	1.735617	0.534916
8	-0.975216	2.465823	1.386394
6	0.926310	2.037628	0.039306
6	1.608076	1.277851	-0.918557
6	1.555926	3.198583	0.530836
6	2.857101	1.662804	-1.400737
6	2.799416	3.596125	0.057390
1	1.029352	3.788911	1.277754
6	3.447290	2.832435	-0.924293
1	3.381078	1.056204	-2.139400
1	3.265361	4.500361	0.439969
1	4.414408	3.149350	-1.311143
6	-2.395388	0.466898	0.038040
6	-3.392418	1.412585	0.367479
6	-4.735494	1.109341	0.263718
1	-3.063420	2.385413	0.703172
6	-4.166382	-1.082065	-0.479820
6	-5.136406	-0.160811	-0.163719
1	-5.475148	1.863212	0.516081
1	-4.360344	-2.091699	-0.819228
1	-6.179704	-0.440433	-0.249962
8	-1.978230	-1.737430	-0.696076
7	-2.849759	-0.776592	-0.374297
6	2.582116	-1.759082	-0.831007
6	2.040696	-0.792301	1.270079
6	2.354928	-3.141546	-0.233560
1	3.644052	-1.486133	-0.715815
1	2.348212	-1.766097	-1.902332
6	1.819022	-2.186732	1.836195
1	3.088223	-0.489167	1.435395

```
  1     1.394066   -0.068909    1.784241
  1     3.010682   -3.892376   -0.683691
  1     1.303016   -3.441768   -0.408603
  1     2.080805   -2.244904    2.896610
  1     0.750546   -2.451136    1.718660
  7     1.748045   -0.782523   -0.152530
  8     2.624007   -3.146323    1.162209
```

Cu(I) product in the reductive elimination step (Cu(II) to Cu(0) path)

```
0 1
 29    -0.095450   -1.054747   -0.757085
  7    -1.020797    0.701036   -0.044846
  6    -0.325367    1.604441    0.686160
  8    -0.731334    2.286842    1.643155
  6     1.086499    1.815139    0.181665
  6     2.033166    0.820233   -0.172782
  6     1.443078    3.158594    0.018469
  6     3.262186    1.217665   -0.712108
  6     2.662640    3.544967   -0.528669
  1     0.716369    3.910132    0.316048
  6     3.569187    2.562723   -0.908210
  1     4.006516    0.476651   -0.979058
  1     2.895806    4.598159   -0.657603
  1     4.530104    2.831444   -1.338882
  6    -2.355070    0.531193    0.044291
  6    -3.323586    1.379271    0.617660
  6    -4.675687    1.099942    0.535980
  1    -2.957526    2.261072    1.127973
  6    -4.156505   -0.890929   -0.679592
  6    -5.100995   -0.055501   -0.125615
  1    -5.397021    1.776248    0.984803
  1    -4.386891   -1.808575   -1.206302
  1    -6.149041   -0.318369   -0.212855
  8    -1.995835   -1.498626   -1.147667
  7    -2.829590   -0.621117   -0.593879
  6     2.777053   -1.519243   -0.469386
  6     1.630504   -0.860555    1.528372
  6     2.322157   -2.936726   -0.211858
  1     3.752025   -1.350441    0.011805
  1     2.882463   -1.351239   -1.544679
  6     1.242574   -2.303937    1.747656
  1     2.587980   -0.634222    2.020774
  1     0.861407   -0.209944    1.952421
  1     3.054108   -3.648928   -0.600394
  1     1.352680   -3.101523   -0.724685
  1     1.198560   -2.526399    2.816575
  1     0.242958   -2.480846    1.305870
  7     1.762949   -0.583421    0.067278
  8     2.181996   -3.202554    1.175960
```

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