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Supplementary Material

Salicylaldehyde Hydrazones: Buttressing of Outer Sphere Hydrogen Bonding and Copper Extraction Properties

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Contents

1. X-ray crystal structures

Details are available from CCDC as follows;

L6: deposition number 1517105

L10: deposition number 1517104

[Cu(**L1**-H)$_2$]: YUPBAO, deposition number: 1410136.

[Cu(**L5**-H)$_2$]: YUNZUE, deposition number: 1410135.

2. NMR Studies

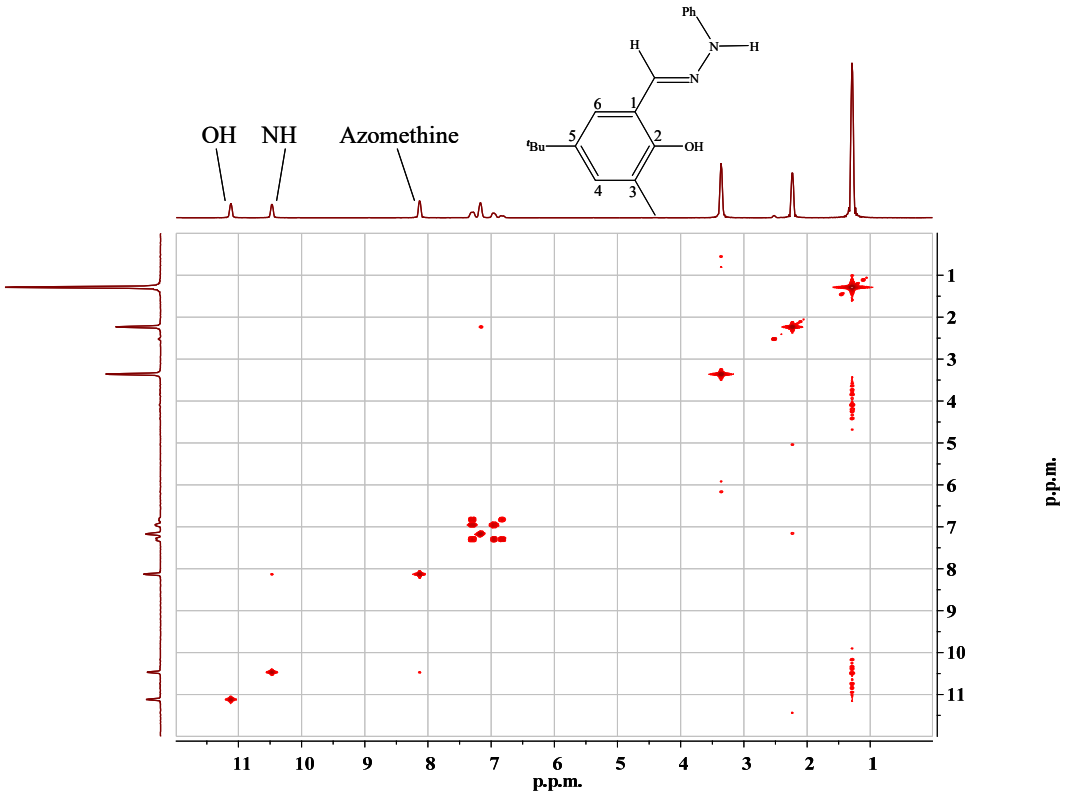


Figure S1 The COSY spectrum of the methyl-substituted phenylhydrazone **L7** in DMSO-d_6

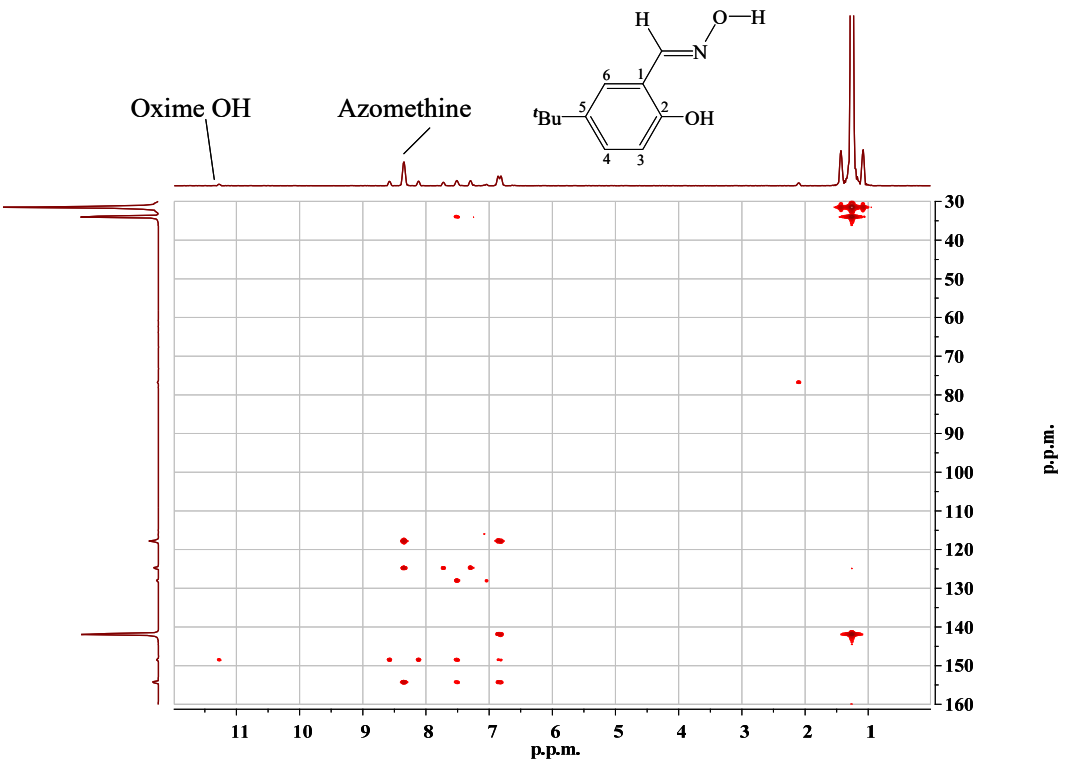
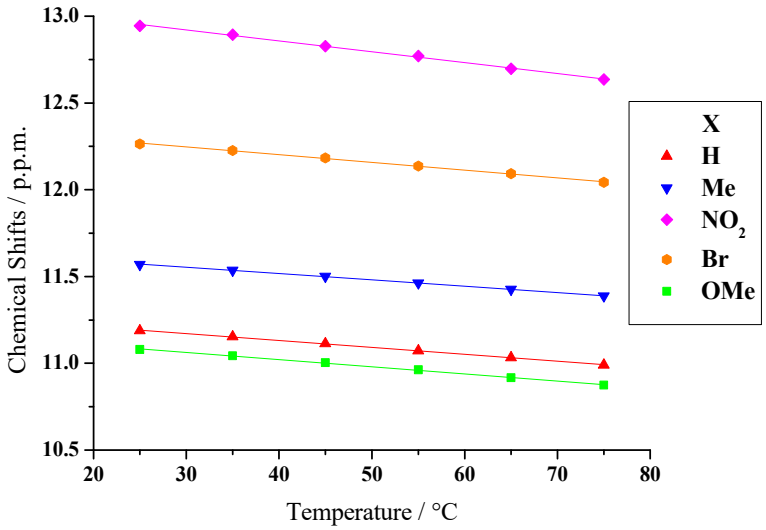
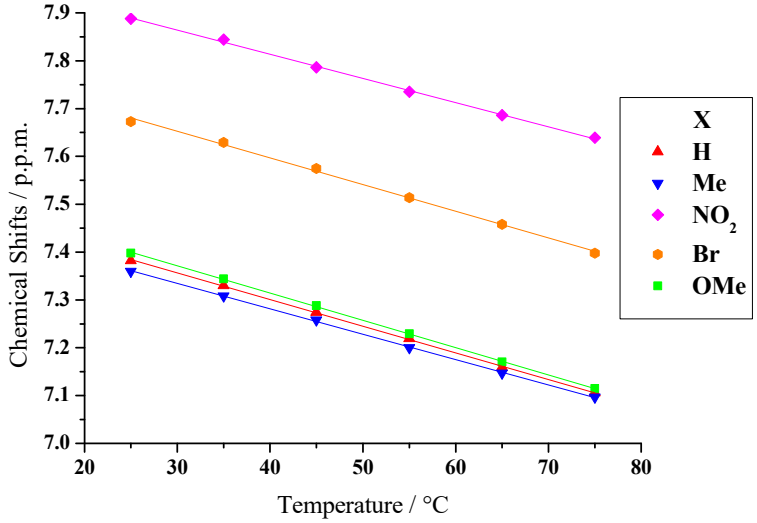


Figure S2 The HMBC spectrum of the unsubstituted oxime **O1** in DMSO-d_6.



(a) Phenol protons



(b) Hydrazone protons

Figure S3 The temperature dependence of chemical shifts of the OH and NH protons in **L1-L5**

3. Solvent extraction

Conditions used in the stripping of copper from [Cu(**L1**-H)$_2$] etc. and in the analysis of copper concentrations.

Cu Complex	Organic Phase		Aqueous Phase		ICP-OES	
	Conc. / M	Volume / ml	Conc. / M	Volume / ml	Solvent	Dilution Factor
[Cu(L1-H)$_2$]	0.005	5.00	0.010	5.00	butan-1-ol	10
[Cu(L2-H)$_2$]	0.005	5.00	0.010	5.00	butan-1-ol	**20**
[Cu(L3-H)$_2$]	**0.0005**	**10.00**	0.010	**10.00**	**nitrobenzene**	**2**
[Cu(L4-H)$_2$]	0.005	5.00	0.010	5.00	**nitrobenzene**	10
[Cu(L5-H)$_2$]	0.005	5.00	0.010	5.00	butan-1-ol	10

4. Computational work

4.1 DFT Optimised Structures used in the calculations of energies of formation in Table 3 of main text

Optimised Cartesian coordinates (Angstroms) and total energies (Hartrees) for the ligands and copper complexes studied at the B3LYP/6-31+G(d,p) level of theory using Gaussian 09 Revision E.01.

20 sets of coordinates in total: atomic number, x, y and z coordinates for each. All geometries are at an energy minimum as confirmed by harmonic vibrational frequency calculations.

Ligands: **L1** (X=H, Y=N), **L3** (X=NO$_2$, Y=N), **L4** (X=Br, Y=N), **L5** (X=OMe, Y=N), **O1** (X=H, Y=O).

The energy of Cu^{II} atom is −1639.2524799 Hartrees.

Superscript “1” in captions to Tables indicates that the system is a spin singlet and “2” a doublet

Ligands

L1. ^{1}A. Energy = –652.8730971. 33 atoms.

1	-2.657862	1.813227	-0.020329
8	-1.875400	2.413683	0.017558
6	-0.761950	1.643718	0.011615
6	-0.817416	0.230342	-0.027905
6	0.392887	-0.494778	-0.031188
1	0.318106	-1.577192	-0.062241
6	1.645660	0.117719	0.003418
6	1.657893	1.527609	0.041451
1	2.604334	2.059774	0.067728
6	0.486590	2.276215	0.045324
1	0.514670	3.360925	0.073947
6	-2.079810	-0.501411	-0.067597
1	-2.010753	-1.590335	-0.118925
7	-3.219444	0.113395	-0.058848
7	-4.396828	-0.573194	-0.168119
1	-5.145995	-0.014276	0.216103
6	-4.469737	-1.992133	0.146139
1	-5.524217	-2.275139	0.169286
1	-3.980406	-2.586781	-0.632600
1	-4.008243	-2.238208	1.116316
6	2.970139	-0.668795	-0.001263
6	3.778734	-0.332592	1.275598
1	4.010532	0.734988	1.340839
1	3.219409	-0.608363	2.176180
1	4.728513	-0.880584	1.281890
6	3.801109	-0.277295	-1.247711
1	4.030331	0.792707	-1.263119
1	4.752501	-0.822414	-1.259942
1	3.258974	-0.515750	-2.169198
6	2.745853	-2.193103	-0.036465
1	3.713221	-2.706739	-0.036929
1	2.187280	-2.543768	0.838414
1	2.207001	-2.505919	-0.937606

L3. ^{1}A. Energy = −857.3742433. 35 atoms.

1	-2.624266	1.417669	0.007687
8	-1.782705	1.943386	0.015439
6	-0.763981	1.078994	-0.021616
6	-0.974970	-0.327511	-0.047701
6	0.128007	-1.197439	-0.058341
1	-0.083681	-2.261123	-0.090743
6	1.453714	-0.753009	-0.020327
6	1.646370	0.632295	0.028535
1	2.639536	1.061469	0.076562
6	0.573911	1.522692	0.009821
7	0.899495	2.954075	0.026408
6	-2.319473	-0.900828	-0.058449
1	-2.385476	-1.989258	-0.106582
7	-3.372686	-0.148084	-0.024788
7	-4.625811	-0.669481	-0.098224
1	-5.296161	-0.011152	0.272983
6	-4.883412	-2.069528	0.198950
1	-5.965264	-2.207723	0.245414
1	-4.496197	-2.712346	-0.598868
1	-4.437351	-2.387324	1.154796
6	2.668642	-1.699109	-0.028704
6	3.502455	-1.477953	1.256724
1	3.867453	-0.449288	1.333990
1	2.907158	-1.689247	2.151581
1	4.374880	-2.141480	1.263067
6	3.547065	-1.398220	-1.267453
1	3.917731	-0.368579	-1.263027
1	4.417360	-2.064266	-1.287630
1	2.982626	-1.546966	-2.194364
6	2.250580	-3.181402	-0.083327
1	3.144425	-3.813661	-0.086393
1	1.648835	-3.469759	0.785806
1	1.682021	-3.413525	-0.990787
8	1.940203	3.288288	0.606060
8	0.145744	3.732964	-0.552241

L4. ^{1}A. Energy = −3223.9998974. 33 atoms.

1	-2.524485	1.449728	-0.058444
8	-1.625202	1.860843	-0.031539
6	-0.721337	0.863688	-0.025085
6	-1.095025	-0.502320	-0.040647
6	-0.093199	-1.491725	-0.034045
1	-0.420596	-2.525888	-0.048417
6	1.267963	-1.188815	-0.009008
6	1.616800	0.174133	0.008630
1	2.657650	0.476769	0.029132
6	0.647468	1.168852	0.000066
35	1.175939	2.996050	0.022929
6	-2.495401	-0.917543	-0.064560
1	-2.683531	-1.992612	-0.095330
7	-3.457298	-0.050669	-0.065886
7	-4.762070	-0.436007	-0.156796
1	-5.357565	0.295433	0.205621
6	-5.172930	-1.791661	0.173455
1	-6.264164	-1.811790	0.204712
1	-4.846479	-2.494560	-0.600439
1	-4.777596	-2.130477	1.144647
6	2.371051	-2.262735	0.001426
6	3.224455	-2.115519	1.284839
1	3.699603	-1.131663	1.346780
1	2.608573	-2.246143	2.181286
1	4.018710	-2.871005	1.303326
6	3.281152	-2.084774	-1.238341
1	3.760207	-1.101001	-1.254113
1	4.074464	-2.841412	-1.240001
1	2.706364	-2.191208	-2.164729
6	1.793761	-3.691396	-0.029203
1	2.613412	-4.417538	-0.023156
1	1.165869	-3.897065	0.844634
1	1.200339	-3.872440	-0.932098

L5. ^{1}A. Energy = −767.3955437. 37 atoms.

1	-2.587522	1.685901	-0.057024
8	-1.728637	2.171358	-0.026343
8	0.748669	3.056984	0.028645
7	-3.389222	0.094280	-0.070158
7	-4.653746	-0.419190	-0.162949
1	-5.311853	0.249271	0.213218
6	-0.744014	1.247281	-0.021406
6	-0.992225	-0.138609	-0.043257

6	0.094482	-1.044142	-0.037781
1	-0.139116	-2.102973	-0.056877
6	1.415074	-0.613320	-0.008809
6	1.642960	0.781839	0.014456
1	2.660787	1.150890	0.037875
6	0.596597	1.699918	0.007863
6	-2.349576	-0.677364	-0.070928
1	-2.438441	-1.765397	-0.104580
6	-4.925642	-1.805226	0.187703
1	-4.535225	-2.482863	-0.579047
1	-6.009450	-1.933645	0.226550
1	-4.492472	-2.090680	1.160145
6	2.617316	-1.576549	-0.000699
6	2.180951	-3.054384	-0.035261
1	1.572283	-3.319992	0.835952
1	3.066005	-3.699676	-0.027871
1	1.609053	-3.289084	-0.939617
6	3.453652	-1.354914	1.283360
1	3.838396	-0.332207	1.347110
1	4.313469	-2.035292	1.303408
1	2.850387	-1.540352	2.178656
6	3.506656	-1.312153	-1.240329
1	4.365276	-1.994258	-1.248491
1	3.896022	-0.289261	-1.252188
1	2.940979	-1.464035	-2.165950
6	2.063186	3.589841	0.056708
1	2.635909	3.298364	-0.833680
1	2.606896	3.275558	0.957477
1	1.942653	4.674049	0.068552

O1. ^{1}A. Energy = –633.4104371. 29 atoms.

1	3.230508	1.233878	-0.000325
8	2.527207	1.920971	-0.000103
6	1.319317	1.312272	-0.000010
6	1.169565	-0.094569	-0.000103
6	-0.131074	-0.644422	-0.000123
1	-0.209157	-1.726557	-0.000187
6	-1.282068	0.141014	-0.000057
6	-1.090985	1.539495	0.000055
1	-1.951979	2.201255	0.000132
6	0.172910	2.116184	0.000076

1	0.297721	3.194203	0.000136
6	2.310833	-0.998474	-0.000139
1	2.126009	-2.075454	-0.000262
7	3.522121	-0.562275	0.000046
8	4.455231	-1.611745	0.000160
6	-2.705565	-0.445643	0.000010
6	-3.463776	0.033026	-1.262328
1	-3.542460	1.123927	-1.301225
1	-2.955011	-0.298195	-2.174067
1	-4.481594	-0.374223	-1.272464
6	-3.463771	0.033459	1.262194
1	-3.542302	1.124383	1.300771
1	-4.481640	-0.373660	1.272409
1	-2.955075	-0.297572	2.174040
6	-2.703094	-1.987059	0.000257
1	-3.734613	-2.354769	0.000124
1	-2.208459	-2.395234	-0.887948
1	-2.208809	-2.394963	0.888782
1	5.308747	-1.156614	0.000315

Deprotonated ligands

[**L1**-H]$^{-}$. ^{1}A. Energy = –652.2922529. 32 atoms.

8	-1.764423	2.654307	0.065102
6	-0.779305	1.866767	0.036402
6	-0.874927	0.407055	-0.052463
6	0.299522	-0.380784	-0.057314
1	0.154411	-1.458757	-0.116332
6	1.597341	0.127902	0.005395
6	1.698244	1.542681	0.081352
1	2.682537	2.010310	0.130469
6	0.587130	2.360454	0.097493
1	0.698124	3.441446	0.159540
6	-2.126901	-0.331530	-0.121173
1	-1.983360	-1.422187	-0.122974
7	-3.321111	0.159659	-0.193333
7	-4.393233	-0.745045	-0.300690
1	-5.205836	-0.240001	0.029847
6	-4.309980	-2.061387	0.327717
1	-5.323224	-2.475011	0.378105
1	-3.703309	-2.750992	-0.269464

1	-3.880472	-2.029319	1.345716
6	2.864893	-0.742027	-0.010378
6	3.699252	-0.497252	1.273109
1	3.982672	0.555694	1.369883
1	3.119356	-0.765384	2.163419
1	4.621790	-1.096215	1.266867
6	3.738518	-0.390871	-1.242256
1	4.025400	0.665687	-1.238380
1	4.659579	-0.991911	-1.260474
1	3.185027	-0.578525	-2.169153
6	2.548449	-2.249814	-0.078415
1	3.481892	-2.827539	-0.082298
1	1.955244	-2.576114	0.783153
1	1.992534	-2.505101	-0.987403

[**L3**-H]$^{-}$. ^{1}A. Energy = –856.8207380. 34 atoms.

8	-1.553373	2.238822	0.115217
6	-0.701771	1.339656	0.020289
6	-1.062777	-0.096370	-0.041632

6	-0.085183	-1.088828	-0.045764
1	-0.436216	-2.118409	-0.080092
6	1.303222	-0.837257	-0.015039
6	1.683445	0.501399	0.015415
1	2.729627	0.785027	0.035057
6	0.757348	1.552646	0.007966
7	1.312139	2.877980	0.028095
6	-2.445082	-0.568695	-0.077770
1	-2.528048	-1.661878	-0.006484
7	-3.503529	0.157743	-0.208532
7	-4.737116	-0.481224	-0.278672
1	-5.431529	0.198808	0.001637
6	-4.950363	-1.779263	0.351785
1	-6.029572	-1.954663	0.402973
1	-4.511987	-2.587496	-0.244339
1	-4.525315	-1.838951	1.369487
6	2.370622	-1.947960	-0.027929
6	3.254331	-1.846340	1.240298
1	3.748023	-0.872069	1.305966
1	2.647238	-1.970872	2.144082
1	4.032637	-2.622160	1.237892
6	3.273531	-1.802523	-1.278324
1	3.772002	-0.828596	-1.298972
1	4.049244	-2.580796	-1.293634
1	2.680013	-1.890259	-2.195346
6	1.750311	-3.359442	-0.057247
1	2.546491	-4.114131	-0.060447
1	1.120048	-3.543825	0.819999
1	1.139573	-3.516023	-0.953420
8	2.518605	3.018672	0.364705
8	0.611208	3.846590	-0.295283

[**L4**-H]$^{-}$. ^{1}A. Energy = –3223.4306717. 32 atoms.

8	-1.171721	2.283906	-0.044756
6	-0.568088	1.186331	-0.043854
6	-1.213465	-0.129550	-0.077732
6	-0.450545	-1.315173	-0.060321
1	-1.010020	-2.248432	-0.082987
6	0.943584	-1.357093	-0.018475
6	1.598820	-0.103436	0.011341
1	2.683400	-0.049712	0.044347

6	0.884856	1.074928	0.001056
35	1.867548	2.732577	0.049758
6	-2.659253	-0.313029	-0.112010
1	-2.958207	-1.369752	-0.064322
7	-3.558291	0.609873	-0.206442
7	-4.899818	0.212857	-0.271504
1	-5.440481	1.009425	0.040239
6	-5.342728	-1.017737	0.377082
1	-6.435244	-0.987119	0.446476
1	-5.075249	-1.899171	-0.216279
1	-4.919101	-1.150053	1.389101
6	1.765942	-2.655700	-0.005881
6	2.634380	-2.726113	1.275991
1	3.311899	-1.869249	1.346399
1	2.000931	-2.720268	2.170073
1	3.244368	-3.640676	1.289616
6	2.701838	-2.706673	-1.240418
1	3.385669	-1.852127	-1.257955
1	3.307947	-3.623955	-1.238942
1	2.117046	-2.680418	-2.166635
6	0.876491	-3.914530	-0.039251
1	1.504165	-4.814547	-0.026618
1	0.208831	-3.959247	0.828344
1	0.259395	-3.948603	-0.943900

[**L5**-H]$^{-}$. ^{1}A. Energy = −766.8141297. 36 atoms.

8	-1.508240	2.459235	-0.021490
8	1.088583	3.073418	0.061523
7	-3.507654	0.312581	-0.208479
7	-4.731930	-0.380309	-0.283716
1	-5.432207	0.279697	0.030549
6	-0.697397	1.499523	-0.030043
6	-1.055311	0.089361	-0.078798
6	-0.054742	-0.917223	-0.066234
1	-0.405224	-1.947129	-0.097183
6	1.307441	-0.658230	-0.020737
6	1.689477	0.716013	0.019895
1	2.746402	0.964465	0.056024
6	0.754825	1.731335	0.017488
6	-2.426941	-0.393360	-0.123083
1	-2.493915	-1.490624	-0.091211

6	-4.890371	-1.663360	0.397301
1	-4.432047	-2.478191	-0.173933
1	-5.962676	-1.876444	0.469644
1	-4.449388	-1.672384	1.410801
6	2.391023	-1.748716	-0.010792
6	1.795725	-3.169749	-0.067974
1	1.148569	-3.369909	0.793008
1	2.602763	-3.913791	-0.062906
1	1.204159	-3.320874	-0.977527
6	3.241930	-1.649985	1.281796
1	3.719370	-0.668841	1.372087
1	4.033438	-2.413444	1.294339
1	2.610799	-1.791999	2.166269
6	3.330010	-1.586899	-1.234126
1	4.121070	-2.350820	-1.229094
1	3.812097	-0.603926	-1.241484
1	2.763076	-1.682627	-2.166928
6	2.449274	3.413581	0.113451
1	3.001718	3.057888	-0.771750
1	2.944959	3.011528	1.012384
1	2.491732	4.506565	0.143147

[**O1**-H]$^{-}$. ^{1}A. Energy = −632.8424356. 28 atoms.

8	-2.471796	2.119655	-0.000129
6	-1.371042	1.505027	-0.000093
6	-1.237823	0.048161	0.000019
6	0.042879	-0.554680	0.000048
1	0.063521	-1.642964	0.000132
6	1.242834	0.153332	-0.000009
6	1.122797	1.570585	-0.000126
1	2.024345	2.184542	-0.000203
6	-0.099118	2.209448	-0.000166
1	-0.155277	3.296197	-0.000259
6	-2.364706	-0.861556	0.000106
1	-2.110200	-1.929676	0.000189
7	-3.621359	-0.561411	0.000104
8	-4.380900	-1.808331	0.000219
6	2.631190	-0.507770	-0.000008
6	3.427708	-0.079164	1.259063
1	3.544062	1.008362	1.306591
1	2.905673	-0.395283	2.169158

1	4.432034	-0.526923	1.262645
6	3.427970	-0.078576	-1.258713
1	3.544243	1.008983	-1.305747
1	4.432332	-0.526255	-1.262256
1	2.906167	-0.394344	-2.169063
6	2.551799	-2.047368	-0.000367
1	3.562919	-2.474484	-0.000174
1	2.028536	-2.423865	0.885478
1	2.029046	-2.423483	-0.886674
1	-5.283242	-1.466151	0.000209

Ligand dimers

[**L1**]$_2$. ^{1}A. Energy = −1305.7596759. 66 atoms.

1	-1.333313	-0.229104	-0.263571
1	1.374221	0.068342	0.828286
8	-1.834745	-1.090350	-0.228038
6	-3.158489	-0.775957	-0.179672
6	-3.597609	0.568641	-0.163947
6	-4.983636	0.821435	-0.121429
1	-5.294722	1.861147	-0.111973
6	-5.941277	-0.194455	-0.090759
6	-5.460773	-1.518756	-0.103850
1	-6.160381	-2.348978	-0.080033
6	-4.100046	-1.807705	-0.148038
1	-3.749167	-2.835116	-0.160829
6	-2.662291	1.691538	-0.183714
1	-3.090117	2.695857	-0.172519
7	-1.382347	1.485836	-0.221283
7	-0.483287	2.496613	-0.285649
1	0.424352	2.174556	0.039738
6	-0.856554	3.853930	0.065871
1	0.056737	4.450594	0.109123
1	-1.511695	4.292484	-0.696046
1	-1.369239	3.911903	1.040273
6	-7.456986	0.076322	-0.045408
6	-8.057905	-0.551797	1.236021
1	-7.896012	-1.633531	1.273039
1	-7.606273	-0.115912	2.133766
1	-9.139208	-0.374913	1.277197
6	-8.133401	-0.554812	-1.287171

1	-7.975308	-1.636898	-1.330332
1	-9.215101	-0.376632	-1.265323
1	-7.734810	-0.122261	-2.211251
6	-7.784795	1.582408	-0.037483
1	-8.870626	1.721619	-0.003072
1	-7.360613	2.088441	0.836733
1	-7.416894	2.085369	-0.938551
8	1.846095	0.945827	0.841905
6	3.155248	0.697028	0.558445
6	3.615023	-0.609438	0.273382
6	4.983612	-0.791822	-0.010119
1	5.310912	-1.803634	-0.226221
6	5.904170	0.258167	-0.024001
6	5.404175	1.542886	0.266380
1	6.074709	2.397027	0.272327
6	4.059839	1.761717	0.553025
1	3.694130	2.758315	0.780947
6	2.719466	-1.764244	0.258309
1	3.166403	-2.734699	0.034165
7	1.454638	-1.627616	0.509419
7	0.604339	-2.683026	0.549175
1	-0.346925	-2.365168	0.386781
6	0.964628	-3.953474	-0.053524
1	0.074154	-4.585151	-0.056795
1	1.738545	-4.461757	0.533297
1	1.328827	-3.842028	-1.088187
6	7.399970	0.062856	-0.336166
6	7.780957	0.894797	-1.585407
1	7.590665	1.962202	-1.436197
1	7.205694	0.572128	-2.459984
1	8.846609	0.774913	-1.814116
6	8.248295	0.537090	0.869170
1	8.080399	1.594997	1.093526
1	9.316508	0.406494	0.659011
1	8.004587	-0.037768	1.769187
6	7.753030	-1.410669	-0.617978
1	8.823521	-1.497544	-0.832670
1	7.210628	-1.801677	-1.485794
1	7.536694	-2.054205	0.241871

[**L3**]$_2$. ^{1}A. Energy = −1714.7757087. 70 atoms.

1	-1.280229	-0.166957	0.379792
1	1.280045	0.166716	-0.377607
8	-1.796976	0.697335	0.326147
6	-3.089031	0.367834	0.194818
6	-3.482388	-1.000676	0.144475
6	-4.842104	-1.322528	0.031360
1	-5.094836	-2.376766	-0.010502
6	-5.859159	-0.359027	-0.024910
6	-5.461743	0.976883	0.041604
1	-6.184027	1.782420	0.014275
6	-4.112749	1.338238	0.139310
7	-3.819953	2.769251	0.190096
6	-2.496879	-2.079281	0.211119
1	-2.870697	-3.102907	0.174555
7	-1.230883	-1.805032	0.323800
7	-0.285173	-2.740607	0.436536
1	0.648174	-2.377959	0.264964
6	-0.541519	-4.141381	0.176742
1	0.417223	-4.659820	0.204699
1	-1.197852	-4.572085	0.943622
1	-1.007367	-4.299777	-0.809135
6	-7.353352	-0.712203	-0.151045
6	-7.929202	-0.067494	-1.435303
1	-7.836261	1.022710	-1.421183
1	-7.410430	-0.436788	-2.326560
1	-8.993494	-0.308698	-1.536093
6	-8.116096	-0.168619	1.081505
1	-8.023743	0.918072	1.170415
1	-9.183045	-0.407426	1.003626
1	-7.734291	-0.613818	2.006631
6	-7.587037	-2.233525	-0.230563
1	-8.659211	-2.433576	-0.325543
1	-7.091872	-2.679124	-1.100354
1	-7.236439	-2.749963	0.669792
8	1.796884	-0.697514	-0.323682
6	3.089015	-0.367909	-0.193564
6	3.482358	1.000649	-0.144297
6	4.842130	1.322637	-0.032297
1	5.094834	2.376912	0.008797
6	5.859267	0.359198	0.023815
6	5.461856	-0.976753	-0.041722

1	6.184199	-1.782243	-0.014502
6	4.112803	-1.338236	-0.138288
7	3.820034	-2.769254	-0.188257
6	2.496722	2.079141	-0.210929
1	2.870459	3.102825	-0.175117
7	1.230690	1.804696	-0.322737
7	0.284787	2.740063	-0.435395
1	-0.648447	2.377324	-0.263348
6	0.541069	4.141016	-0.176499
1	-0.417780	4.659272	-0.204019
1	1.196797	4.571446	-0.944053
1	1.007587	4.299958	0.808970
6	7.353535	0.712487	0.148735
6	7.930243	0.068627	1.433030
1	7.837231	-1.021582	1.419729
1	7.412111	0.438563	2.324395
1	8.994618	0.309839	1.532918
6	8.115479	0.168120	-1.083968
1	8.023085	-0.918631	-1.172109
1	9.182476	0.406995	-1.006948
1	7.733056	0.612709	-2.009131
6	7.587220	2.233869	0.227116
1	8.659449	2.434028	0.321253
1	7.092609	2.680006	1.096947
1	7.236006	2.749713	-0.673340
8	-2.675999	3.159715	-0.073609
8	-4.743119	3.536202	0.480733
8	4.743005	-3.536269	-0.479326
8	2.676318	-3.159670	0.076537

[**L4**]$_2$. ^{1}A. Energy = –6448.0188853. 66 atoms.

1	-1.252415	-0.208004	0.183171
1	1.252257	0.207358	-0.181400
8	-1.821557	0.614038	0.144780
6	-3.105141	0.194708	0.090498
6	-3.438311	-1.182387	0.086225
6	-4.794683	-1.553454	0.041370
1	-5.015633	-2.615315	0.038545
6	-5.835023	-0.622108	0.003171
6	-5.479426	0.737900	0.000482
1	-6.240187	1.508948	-0.034143

6	-4.146224	1.126588	0.043543
35	-3.708805	2.985912	0.021011
6	-2.405860	-2.217414	0.106909
1	-2.738069	-3.256038	0.070340
7	-1.150215	-1.890608	0.170482
7	-0.161785	-2.793479	0.214799
1	0.745909	-2.372366	0.047012
6	-0.372618	-4.191377	-0.087515
1	0.602519	-4.680126	-0.106897
1	-0.984456	-4.676887	0.683662
1	-0.865404	-4.336188	-1.062665
6	-7.321892	-1.021376	-0.043413
6	-7.964496	-0.472649	-1.340829
1	-7.897863	0.618210	-1.398365
1	-7.469647	-0.884772	-2.226911
1	-9.025705	-0.744187	-1.384940
6	-8.057919	-0.424765	1.180992
1	-7.996411	0.667666	1.200969
1	-9.119470	-0.697670	1.157311
1	-7.629809	-0.800477	2.116594
6	-7.517109	-2.549696	-0.021189
1	-8.586628	-2.782763	-0.053143
1	-7.049639	-3.034251	-0.885290
1	-7.109385	-2.999988	0.890431
8	1.821613	-0.614506	-0.143565
6	3.105154	-0.194934	-0.089899
6	3.438081	1.182232	-0.085756
6	4.794425	1.553505	-0.041662
1	5.015202	2.615402	-0.038937
6	5.834932	0.622323	-0.004109
6	5.479564	-0.737740	-0.001230
1	6.240476	-1.508657	0.032977
6	4.146401	-1.126653	-0.043539
35	3.709303	-2.986019	-0.020692
6	2.405501	2.217136	-0.105852
1	2.737640	3.255793	-0.069590
7	1.149812	1.890230	-0.168547
7	0.161383	2.792991	-0.212118
1	-0.746447	2.371993	-0.044876
6	0.372289	4.191165	0.088619
1	-0.602937	4.679688	0.109020
1	0.982955	4.676218	-0.683806
1	0.866412	4.336900	1.062948

6	7.321763	1.021840	0.041663
6	7.965137	0.473258	1.338754
1	7.898618	-0.617604	1.396392
1	7.470747	0.885399	2.225084
1	9.026350	0.744885	1.382258
6	8.057259	0.425315	-1.183103
1	7.996075	-0.667136	-1.202923
1	9.118741	0.698541	-1.160067
1	7.628499	0.800794	-2.118502
6	7.516727	2.550192	0.019278
1	8.586225	2.783433	0.050623
1	7.049664	3.034708	0.883622
1	7.108406	3.000376	-0.892127

[**L5**]$_2$. ^{1}A. Energy = −1534.8084963. 74 atoms.

1	-1.276104	0.025401	-0.482788
1	1.276216	-0.025799	0.483569
8	-1.820254	-0.809461	-0.434699
8	-3.648235	-2.706357	-0.264820
7	-1.227727	1.729442	-0.399894
7	-0.274923	2.683542	-0.494218
1	0.631002	2.295913	-0.241276
6	-3.112001	-0.421244	-0.285988
6	-3.484545	0.934266	-0.216288
6	-4.849813	1.267670	-0.073334
1	-5.101693	2.321279	-0.024317
6	-5.845299	0.298788	0.005687
6	-5.445681	-1.054609	-0.059615
1	-6.196126	-1.832966	0.001765
6	-4.107906	-1.416310	-0.200538
6	-2.489076	2.004722	-0.274578
1	-2.858092	3.030119	-0.210842
6	-0.540558	4.049485	-0.086209
1	-1.212237	4.550123	-0.793985
1	0.410417	4.585230	-0.082637
1	-0.989497	4.108730	0.919274
6	-7.340291	0.638463	0.160966

6	-7.590088	2.158095	0.227119
1	-7.080315	2.617957	1.080573
1	-8.662583	2.349000	0.341213
1	-7.259842	2.665671	-0.685600
6	-7.886508	0.008667	1.465773
1	-7.787560	-1.081345	1.465866
1	-8.950099	0.245470	1.588164
1	-7.348337	0.392473	2.339155
6	-8.130635	0.076805	-1.046167
1	-9.197252	0.312072	-0.948443
1	-8.035943	-1.010774	-1.124233
1	-7.769763	0.511047	-1.984774
6	-4.598390	-3.759509	-0.202540
1	-5.312112	-3.706473	-1.034779
1	-5.146851	-3.751872	0.748361
1	-4.024675	-4.684413	-0.279585
8	1.820213	0.809165	0.435188
8	3.647965	2.706288	0.264931
7	1.227900	-1.729709	0.400466
7	0.275177	-2.683929	0.494679
1	-0.630807	-2.296293	0.241975
6	3.111937	0.421122	0.286273
6	3.484634	-0.934353	0.216462
6	4.849915	-1.267623	0.073315
1	5.101869	-2.321213	0.024239
6	5.845292	-0.298651	-0.005838
6	5.445538	1.054711	0.059516
1	6.195897	1.833147	-0.001988
6	4.107757	1.416277	0.200639
6	2.489247	-2.004878	0.274773
1	2.858263	-3.030255	0.210608
6	0.540837	-4.049696	0.086128
1	1.212788	-4.550496	0.793529
1	-0.410082	-4.585544	0.082687
1	0.989455	-4.108587	-0.919522
6	7.340285	-0.638184	-0.161361
6	7.590220	-2.157804	-0.227274
1	7.080360	-2.617882	-1.080559
1	8.662716	-2.348621	-0.341515
1	7.260161	-2.665239	0.685592
6	7.886152	-0.008566	-1.466404
1	7.787060	1.081434	-1.466664
1	8.949747	-0.245265	-1.588982

1	7.347837	-0.392593	-2.339599
6	8.130837	-0.076226	1.045493
1	9.197450	-0.311430	0.947582
1	8.036096	1.011363	1.123371
1	7.770209	-0.510306	1.984268
6	4.598043	3.759519	0.202646
1	5.311838	3.706457	1.034819
1	5.146419	3.751989	-0.748299
1	4.024266	4.684374	0.279810

[**O1**]$_2$. ^{1}A. Energy = −1266.8378187. 58 atoms.

1	-1.232963	0.204354	-0.000133
1	1.232971	-0.204842	0.000440
8	-1.745490	1.056137	0.000215
6	-3.071220	0.745522	0.000154
6	-3.512135	-0.597619	-0.000121
6	-4.898391	-0.854809	-0.000164
1	-5.208035	-1.894477	-0.000386
6	-5.854287	0.161691	0.000087
6	-5.370820	1.485877	0.000339
1	-6.071191	2.315595	0.000506
6	-4.010807	1.778593	0.000375
1	-3.660928	2.806101	0.000572
6	-2.577982	-1.719388	-0.000360
1	-2.970694	-2.738585	-0.000468
7	-1.306293	-1.518810	-0.000439
8	-0.554042	-2.682122	-0.000648
6	-7.370761	-0.106459	0.000046
6	-8.007300	0.525139	-1.262361
1	-7.846286	1.606934	-1.302317
1	-7.583456	0.090205	-2.173934
1	-9.089260	0.349356	-1.271592
6	-8.007230	0.524299	1.262909
1	-7.846195	1.606063	1.303597
1	-9.089192	0.348531	1.272072
1	-7.583353	0.088734	2.174165
6	-7.699377	-1.612271	-0.000440
1	-8.785678	-1.750283	-0.000558
1	-7.304325	-2.117138	-0.888836
1	-7.304449	-2.117686	0.887699
8	1.745652	-1.056513	0.000538
6	3.071329	-0.745679	0.000326
6	3.512093	0.597513	-0.000090

6	4.898323	0.854865	-0.000229
1	5.207842	1.894570	-0.000521
6	5.854343	-0.161513	0.000012
6	5.371031	-1.485761	0.000420
1	6.071504	-2.315392	0.000642
6	4.011056	-1.778634	0.000573
1	3.661286	-2.806179	0.000907
6	2.577810	1.719172	-0.000333
1	2.970388	2.738424	-0.000660
7	1.306168	1.518364	-0.000157
8	0.553587	2.681447	-0.000350
6	7.370795	0.106822	-0.000027
6	8.007290	-0.523705	1.262937
1	7.846452	-1.605495	1.303692
1	7.583242	-0.088150	2.174120
1	9.089219	-0.347723	1.272191
6	8.007496	-0.524823	-1.262327
1	7.846780	-1.606668	-1.302111
1	9.089410	-0.348757	-1.271588
1	7.583538	-0.090155	-2.173974
6	7.699242	1.612669	-0.000681
1	8.785529	1.750802	-0.000711
1	7.304172	2.118156	0.887351
1	7.304219	2.117363	-0.889187
1	0.367614	-2.353814	-0.000488
1	-0.367926	2.352675	-0.000628

Copper complexes

[Cu(**L1**-H)$_2$]. ^{2}A. Energy = −2944.9570708. 65 atoms.

29	-0.000005	0.000018	-0.000009
8	1.543683	-1.112957	0.132690
6	2.825319	-0.798529	0.095565
6	3.307182	0.538695	0.078053
6	4.703085	0.776611	0.033651
1	5.024541	1.813565	0.022907
6	5.649317	-0.241402	0.008539
6	5.146086	-1.562525	0.033216
1	5.835819	-2.402068	0.017198
6	3.788300	-1.834657	0.076166
1	3.431529	-2.860330	0.093253

6	2.439518	1.692705	0.131196
1	2.946308	2.656733	0.167150
7	1.139861	1.676788	0.180320
7	0.437746	2.853611	0.329348
1	-0.530770	2.656926	0.080778
6	0.995187	4.093622	-0.179699
1	0.187196	4.828291	-0.201358
1	1.780325	4.485335	0.477122
1	1.410636	3.987801	-1.195802
6	7.167487	0.008448	-0.037667
6	7.763442	-0.643590	-1.309524
1	7.587066	-1.723504	-1.333459
1	7.319690	-0.213037	-2.213761
1	8.847297	-0.482247	-1.350316
6	7.834433	-0.615033	1.213160
1	7.659594	-1.693930	1.271489
1	8.918903	-0.454089	1.189869
1	7.441744	-0.163386	2.130625
6	7.513705	1.510078	-0.064695
1	8.601087	1.636381	-0.101639
1	7.094184	2.009757	-0.944906
1	7.152336	2.028510	0.830294
8	-1.543703	1.112977	-0.132743
6	-2.825337	0.798538	-0.095599
6	-3.307185	-0.538690	-0.078052
6	-4.703085	-0.776620	-0.033634
1	-5.024530	-1.813578	-0.022864
6	-5.649328	0.241383	-0.008539
6	-5.146112	1.562511	-0.033251
1	-5.835853	2.402046	-0.017249
6	-3.788328	1.834656	-0.076216
1	-3.431570	2.860332	-0.093331
6	-2.439509	-1.692692	-0.131177
1	-2.946289	-2.656726	-0.167108
7	-1.139852	-1.676760	-0.180309
7	-0.437711	-2.853570	-0.329320
1	0.530803	-2.656857	-0.080762
6	-0.995111	-4.093589	0.179752
1	-0.187098	-4.828234	0.201419
1	-1.780240	-4.485336	-0.477059
1	-1.410559	-3.987763	1.195855
6	-7.167495	-0.008484	0.037677
6	-7.763457	0.643580	1.309518

1	-7.587103	1.723498	1.333420
1	-7.319692	0.213063	2.213766
1	-8.847308	0.482217	1.350320
6	-7.834451	0.614954	-1.213166
1	-7.659624	1.693851	-1.271525
1	-8.918920	0.453998	-1.189868
1	-7.441758	0.163286	-2.130619
6	-7.513694	-1.510118	0.064748
1	-8.601074	-1.636434	0.101702
1	-7.094161	-2.009768	0.944969
1	-7.152325	-2.028569	-0.830231

[Cu(**L3**-H)$_2$]. ^{2}A. Energy = −3353.9796734. 69 atoms.

29	-0.000002	0.000121	0.176770
8	-1.643776	-0.920320	-0.071788
6	-2.876013	-0.507721	-0.041699
6	-3.225626	0.869562	0.136975
6	-4.574467	1.265398	0.119956
1	-4.777916	2.320813	0.268648
6	-5.638990	0.380256	-0.079442
6	-5.300339	-0.962279	-0.265114
1	-6.060791	-1.714310	-0.434316
6	-3.975050	-1.401477	-0.230838
7	-3.766000	-2.832984	-0.419835
6	-2.240448	1.915029	0.344940
1	-2.651244	2.913557	0.481165
7	-0.948590	1.765496	0.410351
7	-0.134479	2.825261	0.674644
1	0.825818	2.610224	0.407017
6	-0.582818	4.184507	0.450559
1	0.300117	4.822529	0.507702
1	-1.053473	4.313624	-0.537901
1	-1.293021	4.508852	1.220897
6	-7.116193	0.815889	-0.095510
6	-7.880192	0.089832	1.038492
1	-7.837176	-0.997895	0.925659
1	-7.460451	0.342113	2.018352
1	-8.936306	0.383063	1.034181
6	-7.750327	0.444786	-1.458108

1	-7.707801	-0.632041	-1.647940
1	-8.804323	0.744905	-1.480349
1	-7.234538	0.950247	-2.281659
6	-7.275943	2.334518	0.111605
1	-8.338554	2.597216	0.086711
1	-6.880673	2.659842	1.080304
1	-6.777879	2.909989	-0.676651
8	1.643968	0.920712	-0.070151
6	2.876126	0.507875	-0.040825
6	3.225579	-0.869432	0.137753
6	4.574383	-1.265456	0.120374
1	4.777707	-2.320889	0.269118
6	5.638945	-0.380502	-0.079442
6	5.300420	0.962086	-0.265167
1	6.060934	1.713961	-0.434761
6	3.975234	1.401474	-0.230490
7	3.766340	2.833024	-0.419620
6	2.240311	-1.914778	0.345858
1	2.650999	-2.913342	0.482222
7	0.948430	-1.765177	0.411007
7	0.134172	-2.824877	0.674885
1	-0.826068	-2.609809	0.407124
6	0.582453	-4.184155	0.450931
1	-0.300671	-4.822031	0.506826
1	1.291694	-4.508807	1.222051
1	1.054241	-4.313049	-0.536990
6	7.116091	-0.816307	-0.095837
6	7.750014	-0.445316	-1.458563
1	7.707609	0.631509	-1.648427
1	7.234005	-0.950734	-2.282003
1	8.803965	-0.745573	-1.480991
6	7.880404	-0.090327	1.038008
1	7.837512	0.997403	0.925142
1	8.936475	-0.383714	1.033525
1	7.460792	-0.342513	2.017948
6	7.275690	-2.334955	0.111261
1	8.338260	-2.597793	0.086158
1	6.777382	-2.910362	-0.676888
1	6.880573	-2.660221	1.080042
8	-2.725862	-3.358769	0.000803
8	-4.660854	-3.477546	-0.978881
8	4.661379	3.477377	-0.978577
8	2.726182	3.358979	0.000803

[Cu(**L4**-H)$_2$]. ^{2}A. Energy = −8087.2186529. 65 atoms.

29	0.000000	-0.000005	-0.000011
8	1.721689	-0.828994	-0.131018
6	2.915210	-0.309320	-0.073722
6	3.173038	1.089422	0.039198
6	4.503611	1.570623	0.108864
1	4.635270	2.643734	0.198034
6	5.609720	0.734850	0.064349
6	5.351335	-0.649646	-0.060929
1	6.173764	-1.354963	-0.105600
6	4.063651	-1.144945	-0.128123
35	3.788878	-3.025481	-0.300940
6	2.113203	2.061640	0.080330
1	2.415690	3.108548	0.156882
7	0.837410	1.828382	0.033393
7	0.019163	2.990292	0.023585
1	-0.911088	2.650796	0.267169
6	-0.059458	3.602338	-1.313198
1	-0.804326	4.400335	-1.262766
1	0.901212	4.047448	-1.586147
1	-0.356462	2.886382	-2.094223
6	7.061829	1.236978	0.142078
6	7.828466	0.815106	-1.135157
1	7.848088	-0.272093	-1.259930
1	7.366316	1.246281	-2.029755
1	8.867327	1.161682	-1.086956
6	7.757071	0.618617	1.379769
1	7.775047	-0.474835	1.333219
1	8.794932	0.965074	1.446942
1	7.241164	0.905596	2.302399
6	7.140047	2.771073	0.263350
1	8.189055	3.081265	0.312457
1	6.689295	3.272096	-0.600392
1	6.646521	3.135398	1.170984
8	-1.721686	0.828987	0.131000
6	-2.915208	0.309316	0.073705
6	-3.173040	-1.089426	-0.039208
6	-4.503616	-1.570622	-0.108869

1	-4.635278	-2.643734	-0.198035
6	-5.609721	-0.734844	-0.064364
6	-5.351331	0.649650	0.060927
1	-6.173759	1.354967	0.105616
6	-4.063646	1.144943	0.128125
35	-3.788866	3.025479	0.300937
6	-2.113208	-2.061646	-0.080342
1	-2.415698	-3.108553	-0.156891
7	-0.837414	-1.828392	-0.033410
7	-0.019171	-2.990304	-0.023601
1	0.911081	-2.650812	-0.267187
6	0.059449	-3.602349	1.313183
1	0.804313	-4.400349	1.262751
1	-0.901223	-4.047454	1.586133
1	0.356457	-2.886393	2.094206
6	-7.061835	-1.236966	-0.142053
6	-7.828526	-0.814742	1.135033
1	-7.848069	0.272489	1.259549
1	-7.366467	-1.245743	2.029762
1	-8.867410	-1.161250	1.086844
6	-7.757002	-0.618911	-1.379939
1	-7.775009	0.474551	-1.333653
1	-8.794851	-0.965407	-1.447101
1	-7.241025	-0.906100	-2.302465
6	-7.140080	-2.771091	-0.262935
1	-8.189088	-3.081261	-0.312176
1	-6.689528	-3.271904	0.601033
1	-6.646374	-3.135670	-1.170370

[Cu(**L5**-H)$_2$]. ^{2}A. Energy = −3174.00869999. 73 atoms.

29	0.000018	0.000098	-0.000051
8	-1.634919	-0.945220	-0.118840
8	-3.514140	-2.768751	-0.080752
7	-0.960103	1.784040	-0.189265
7	-0.142753	2.878749	-0.344148
1	0.809911	2.599484	-0.107122
6	-2.872780	-0.504545	-0.088301

6	-3.232361	0.862869	-0.080387
6	-4.600896	1.239294	-0.036475
1	-4.822823	2.301105	-0.031322
6	-5.627289	0.309335	-0.003892
6	-5.259818	-1.060386	-0.020393
1	-6.037634	-1.814284	0.002087
6	-3.933320	-1.461490	-0.062789
6	-2.252788	1.926791	-0.139534
1	-2.664137	2.934842	-0.180602
6	-0.578038	4.179236	0.125461
1	-1.313711	4.631533	-0.550474
1	0.300436	4.827630	0.141742
1	-1.013734	4.141646	1.138237
6	-7.118186	0.691960	0.047471
6	-7.327795	2.218650	0.057754
1	-6.860543	2.687799	0.930377
1	-8.399133	2.443536	0.096559
1	-6.924363	2.690867	-0.844586
6	-7.761799	0.113246	1.331657
1	-7.685543	-0.978066	1.369620
1	-8.825999	0.373654	1.378083
1	-7.272575	0.512613	2.226667
6	-7.849451	0.118073	-1.190932
1	-8.914202	0.379306	-1.162786
1	-7.776885	-0.973129	-1.237457
1	-7.423132	0.520079	-2.116393
6	-4.500843	-3.787414	-0.042062
1	-5.166277	-3.737612	-0.914019
1	-5.100836	-3.732387	0.875800
1	-3.956829	-4.733332	-0.059196
8	1.635009	0.945333	0.118787
8	3.514338	2.768755	0.080786
7	0.960027	-1.783868	0.189169
7	0.142535	-2.878484	0.343992
1	-0.810073	-2.599075	0.106913
6	2.872848	0.504588	0.088284
6	3.232347	-0.862846	0.080366
6	4.600860	-1.239353	0.036494
1	4.822724	-2.301177	0.031336
6	5.627310	-0.309455	0.003957
6	5.259921	1.060288	0.020460
1	6.037783	1.814139	-0.001987
6	3.933445	1.461469	0.062817

6	2.252705	-1.926707	0.139473
1	2.663993	-2.934781	0.180538
6	0.577635	-4.179027	-0.125632
1	1.313199	-4.631459	0.550330
1	-0.300940	-4.827284	-0.141975
1	1.013388	-4.141476	-1.138385
6	7.118187	-0.692164	-0.047365
6	7.327712	-2.218867	-0.057693
1	6.860470	-2.687960	-0.930350
1	8.399038	-2.443810	-0.096462
1	6.924217	-2.691092	0.844615
6	7.761875	-0.113441	-1.331510
1	7.685670	0.977875	-1.369442
1	8.826065	-0.373897	-1.377903
1	7.272667	-0.512758	-2.226550
6	7.849440	-0.118358	1.191082
1	8.914177	-0.379650	1.162964
1	7.776935	0.972846	1.237640
1	7.423066	-0.520371	2.116515
6	4.501098	3.787365	0.042139
1	5.166502	3.737515	0.914117
1	5.101116	3.732316	-0.875705
1	3.957136	4.733313	0.059268

[**Cu**(O1-H)$_2$]. ^{2}A. Energy = −2906.0465832. 57 atoms.

29	0.000019	0.000021	0.000049
8	-1.550617	-1.128152	0.000142
6	-2.827978	-0.783507	0.000138
6	-3.282019	0.567894	0.000106
6	-4.673917	0.839185	0.000049
1	-4.970823	1.882979	0.000020
6	-5.640319	-0.157726	0.000045
6	-5.164177	-1.490273	0.000106
1	-5.873338	-2.313364	0.000102
6	-3.813755	-1.796467	0.000160
1	-3.481015	-2.830004	0.000214
6	-2.390779	1.702835	0.000198
1	-2.825588	2.703127	0.000311
7	-1.100890	1.626304	0.000187
8	-0.443600	2.848541	0.000366
6	-7.153437	0.123103	-0.000119

6	-7.796274	-0.501992	1.262400
1	-7.642015	-1.584772	1.304657
1	-7.370610	-0.068109	2.173660
1	-8.877281	-0.319816	1.270208
6	-7.796061	-0.502749	-1.262375
1	-7.641649	-1.585534	-1.303998
1	-8.877090	-0.320703	-1.270418
1	-7.370332	-0.069321	-2.173820
6	-7.468096	1.631776	-0.000579
1	-8.553007	1.780762	-0.000551
1	-7.067828	2.133136	0.887533
1	-7.067973	2.132580	-0.889070
8	1.550632	1.128194	-0.000221
6	2.827997	0.783525	-0.000196
6	3.282002	-0.567883	-0.000066
6	4.673899	-0.839200	-0.000012
1	4.970789	-1.882998	0.000090
6	5.640316	0.157697	-0.000103
6	5.164198	1.490253	-0.000267
1	5.873377	2.313327	-0.000348
6	3.813780	1.796472	-0.000314
1	3.481057	2.830013	-0.000446
6	2.390751	-1.702813	-0.000051
1	2.825565	-2.703104	-0.000090
7	1.100860	-1.626287	-0.000005
8	0.443552	-2.848502	-0.000031
6	7.153433	-0.123145	0.000026
6	7.796177	0.501682	-1.262673
1	7.641903	1.584452	-1.305147
1	7.370449	0.067600	-2.173808
1	8.877186	0.319511	-1.270522
6	7.796154	0.502976	1.262096
1	7.641731	1.585768	1.303514
1	8.877186	0.320951	1.270080
1	7.370512	0.069728	2.173668
6	7.468095	-1.631818	0.000792
1	8.553006	-1.780804	0.000644
1	7.067705	-2.133390	-0.887146
1	7.068101	-2.132414	0.889458
1	-0.504077	-2.568613	0.000093
1	0.504011	2.568692	0.000199

4.2 DFT Optimised Structures used in structure analysis in Table 3 of main text

[Cu(L1-H)$_2$]

6	-2.86413	0.83508	-0.01024
6	-3.32178	-0.51033	0.089974
6	-3.8446	1.843719	-0.11882
6	-4.70893	-0.77256	0.065274
6	-5.20225	1.546257	-0.14003
6	-5.67849	0.222706	-0.05097
6	-2.4332	-1.6403	0.245677
8	-1.58682	1.172292	-0.00049
7	-1.13423	-1.59605	0.281881
7	-0.4068	-2.73682	0.53754
6	2.808862	-0.67957	-0.13313
6	3.267422	0.662533	-0.22852
6	3.789711	-1.69403	-0.0355
6	4.659019	0.926999	-0.20964
6	5.142793	-1.39636	-0.02072
6	5.623022	-0.06926	-0.10499
6	2.379443	1.793041	-0.37639
8	1.532487	-1.01815	-0.13686
7	1.080019	1.749765	-0.41165
7	0.353368	2.89293	-0.66257
29	-0.02756	0.077175	-0.06763
6	7.13662	0.209973	-0.08141
6	7.456632	1.713604	-0.19151
6	7.818247	-0.51302	-1.26902
6	7.74021	-0.31292	1.245323
6	-7.1758	-0.14171	-0.0734
6	-7.46821	-1.07801	-1.27125
6	-8.07475	1.102955	-0.21272
6	-7.55868	-0.86401	1.24131
6	0.89698	4.188015	-0.298
6	-0.94914	-4.03482	0.181195
1	-3.50815	2.87391	-0.18998
1	0.554032	-2.55027	0.253165
1	-5.0173	-1.81278	0.145057
1	-5.90006	2.371451	-0.2301
1	-2.92291	-2.60491	0.376434
1	3.450723	-2.7237	0.031078
1	-0.6077	2.705579	-0.37953

1	4.962413	1.966725	-0.28463
1	5.8465	-2.2203	0.059912
1	2.868996	2.75822	-0.50355
1	7.083934	2.142423	-1.12833
1	8.541754	1.861301	-0.17094
1	7.03099	2.283381	0.641879
1	7.420779	-0.15433	-2.22472
1	7.663396	-1.5958	-1.22892
1	8.899565	-0.33098	-1.25827
1	7.287491	0.191492	2.105905
1	8.82131	-0.13142	1.272481
1	7.580617	-1.38883	1.367776
1	-8.53152	-1.34506	-1.29932
1	-6.89385	-2.00779	-1.20942
1	-7.21344	-0.59102	-2.21876
1	-9.1264	0.796972	-0.22766
1	-7.87662	1.647604	-1.14237
1	-7.94525	1.796471	0.625352
1	-8.62178	-1.13327	1.235628
1	-7.37413	-0.22062	2.108384
1	-6.98304	-1.7847	1.380748
1	1.331773	4.197646	0.715502
1	0.07624	4.907518	-0.33853
1	1.663656	4.520257	-1.00753
1	-1.71494	-4.36343	0.893251
1	-0.12769	-4.75325	0.22584
1	-1.3845	-4.05087	-0.83192

[Cu(L3-H)$_2$]

6	-2.8751	0.821861	0.015607
6	-3.3425	-0.53659	0.052587
6	-3.89586	1.822962	-0.00241
6	-4.7145	-0.81135	0.042853
6	-5.262	1.496744	-0.01379
6	-5.70765	0.180262	0.004286
6	-2.44813	-1.67721	0.125163
8	-1.60828	1.10804	-0.00424
7	-1.14597	-1.65103	0.157383
7	-0.43616	-2.79349	0.324659
6	2.799727	-0.75073	-0.1084
6	3.267042	0.603992	-0.13044

6	3.821229	-1.7541	-0.06257
6	4.642522	0.883401	-0.0923
6	5.181201	-1.42624	-0.02168
6	5.630196	-0.10601	-0.03413
6	2.373939	1.743406	-0.22056
8	1.53319	-1.0412	-0.12587
7	1.071844	1.717187	-0.26718
7	0.363838	2.858243	-0.45696
29	-0.03707	0.033059	-0.05479
6	7.139428	0.197643	0.009448
6	7.4291	1.711203	-0.0154
6	7.831621	-0.44778	-1.21577
6	7.745541	-0.38998	1.307209
6	-7.19804	-0.20529	-0.011
6	-7.49631	-1.06254	-1.26539
6	-8.11446	1.032842	-0.04463
6	-7.535	-1.02366	1.259389
6	0.943632	4.162501	-0.22932
6	-1.01763	-4.09599	0.091429
7	-3.58633	3.246765	-0.01064
8	-2.40525	3.623975	0.035889
8	-4.52923	4.0471	-0.05797
7	3.510755	-3.18003	-0.05295
8	2.335703	-3.55727	-0.17218
8	4.448367	-3.97827	0.066655
1	0.548331	-2.6587	0.097462
1	-5.01071	-1.85717	0.069955
1	-5.95406	2.325706	-0.03583
1	-2.94361	-2.64321	0.196012
1	-0.62212	2.727509	-0.23487
1	4.933262	1.928771	-0.11277
1	5.878955	-2.25225	0.018282
1	2.869758	2.709248	-0.2912
1	7.056331	2.185146	-0.93033
1	8.510632	1.877238	0.021302
1	6.989711	2.227171	0.845608
1	7.428929	-0.04488	-2.15143
1	7.697092	-1.53365	-1.23368
1	8.908778	-0.24642	-1.19353
1	7.283733	0.058023	2.193779
1	8.82277	-0.19197	1.347149
1	7.604118	-1.47344	1.367629
1	-8.55438	-1.34776	-1.28826

1	-6.90538	-1.98409	-1.28119
1	-7.27396	-0.50607	-2.18217
1	-9.16145	0.712958	-0.06075
1	-7.94214	1.643801	-0.93703
1	-7.97658	1.667047	0.837508
1	-8.59232	-1.31243	1.255983
1	-7.34525	-0.43724	2.164755
1	-6.94201	-1.94169	1.323913
1	1.445246	4.234718	0.74983
1	0.123464	4.880891	-0.26048
1	1.666406	4.428797	-1.01109
1	-1.72809	-4.37254	0.881051
1	-0.19665	-4.81406	0.101372
1	-1.53474	-4.15697	-0.88039

[Cu(L4-H)$_2$]

6	-2.87299	0.767801	-0.02118
6	-3.33598	-0.57797	0.051628
6	-3.87378	1.762004	-0.08497
6	-4.71918	-0.84521	0.051126
6	-5.2326	1.477015	-0.08255
6	-5.69381	0.151585	-0.01367
6	-2.43906	-1.71251	0.136382
8	-1.60398	1.101594	-0.02997
7	-1.13881	-1.66922	0.171247
7	-0.41397	-2.81406	0.337717
6	2.795052	-0.69343	-0.06261
6	3.259035	0.650197	-0.11476
6	3.795294	-1.69386	0.000308
6	4.64642	0.919708	-0.09625
6	5.149049	-1.40752	0.016181
6	5.613835	-0.07781	-0.03324
6	2.363615	1.785124	-0.19857
8	1.527014	-1.02921	-0.07942
7	1.063121	1.742561	-0.24384
7	0.339944	2.889029	-0.408
29	-0.03861	0.036518	-0.04482
6	7.126838	0.203708	-0.0136
6	7.441088	1.710939	-0.07966
6	7.798871	-0.48122	-1.22879

6	7.741915	-0.35952	1.290979
6	-7.19094	-0.21226	-0.00874
6	-7.5092	-1.11679	-1.22412
6	-8.09286	1.034811	-0.09191
6	-7.53602	-0.97064	1.295936
6	0.890736	4.17761	-0.04927
6	-0.96645	-4.10452	-0.01275
35	3.23396	-3.51943	0.084107
35	-3.31471	3.586143	-0.19573
1	0.563818	-2.63453	0.117865
1	-5.02377	-1.88729	0.107378
1	-5.92823	2.304267	-0.13776
1	-2.92683	-2.68324	0.20955
1	-0.64034	2.708888	-0.20085
1	4.947096	1.961395	-0.13704
1	5.850076	-2.23295	0.069209
1	2.85197	2.756337	-0.26007
1	7.061333	2.167059	-1.00055
1	8.525842	1.860048	-0.06193
1	7.020703	2.253809	0.774035
1	7.391428	-0.09609	-2.16983
1	7.649746	-1.56543	-1.21966
1	8.879152	-0.29451	-1.22235
1	7.295552	0.116306	2.170902
1	8.822388	-0.1753	1.314264
1	7.58708	-1.43926	1.380894
1	-8.57262	-1.38372	-1.234
1	-6.93357	-2.04744	-1.19996
1	-7.2772	-0.60475	-2.16415
1	-9.14413	0.728061	-0.08858
1	-7.91897	1.603924	-1.01158
1	-7.94307	1.705253	0.761315
1	-8.59759	-1.24461	1.309626
1	-7.33246	-0.34929	2.174669
1	-6.95313	-1.89176	1.39574
1	1.356528	4.174874	0.950357
1	0.066359	4.892826	-0.05387
1	1.636119	4.519726	-0.7779
1	-1.70345	-4.44618	0.72452
1	-0.14094	-4.81843	-0.01554
1	-1.44259	-4.10428	-1.00741

[Cu(L5-H)$_2$]

6	-2.84008	0.760959	-0.08829
6	-3.29993	-0.5761	-0.00035
6	-3.8255	1.789249	-0.12171
6	-4.68864	-0.8436	0.060994
6	-5.18263	1.49196	-0.06082
6	-5.64801	0.160695	0.034414
6	-2.40153	-1.71207	0.006036
8	-1.57154	1.104559	-0.14194
7	-1.10251	-1.66827	-0.05321
7	-0.36832	-2.82604	-0.14142
6	2.816992	-0.66114	0.15729
6	3.276265	0.674012	0.081973
6	3.804279	-1.69329	0.190407
6	4.669066	0.946366	0.032001
6	5.156898	-1.39295	0.1405
6	5.624207	-0.05661	0.057812
6	2.377695	1.808703	0.075966
8	1.549825	-1.00776	0.199214
7	1.078057	1.764821	0.128008
7	0.343558	2.923843	0.215874
29	-0.0115	0.049342	0.033008
6	7.139623	0.212797	0.007463
6	7.461767	1.716653	-0.09446
6	7.756499	-0.49115	-1.22622
6	7.809865	-0.33331	1.292113
6	-7.14899	-0.18834	0.105766
6	-7.53039	-1.09966	-1.08651
6	-8.04798	1.063039	0.051599
6	-7.44755	-0.93325	1.429959
6	0.870828	4.157205	-0.33443
6	-0.89494	-4.06219	0.402312
8	3.289953	-2.96385	0.270849
8	-3.31393	3.061039	-0.21463
6	4.199731	-4.05242	0.291696
6	-4.22424	4.148908	-0.23544
1	0.6042	-2.60352	0.0745
1	-4.99526	-1.88431	0.128392
1	-5.89542	2.304394	-0.08641
1	-2.88679	-2.68733	0.026762
1	-0.62756	2.7003	-0.00573

1	4.969713	1.987097	-0.02489
1	5.877293	-2.20181	0.163896
1	2.862302	2.784427	0.061936
1	7.03783	2.163077	-1.00054
1	8.547211	1.858396	-0.13328
1	7.08715	2.27327	0.771423
1	7.309271	-0.1169	-2.15347
1	7.603543	-1.5746	-1.19653
1	8.837085	-0.30967	-1.26984
1	7.402466	0.157267	2.182739
1	8.891407	-0.15363	1.267059
1	7.654907	-1.411	1.405312
1	-8.59631	-1.35533	-1.04874
1	-6.96298	-2.03534	-1.0789
1	-7.33293	-0.59814	-2.04014
1	-9.09988	0.76197	0.102844
1	-7.91135	1.62377	-0.87965
1	-7.85853	1.738912	0.892776
1	-8.51094	-1.19448	1.49293
1	-7.19739	-0.30821	2.294094
1	-6.87052	-1.85961	1.510743
1	1.640401	4.595972	0.311953
1	0.042054	4.865851	-0.39193
1	1.298348	4.023746	-1.34256
1	-1.32208	-3.93422	1.411287
1	-0.06603	-4.77093	0.455817
1	-1.66478	-4.49747	-0.24618
1	3.587976	-4.95434	0.349075
1	4.861216	-4.00834	1.166971
1	4.808357	-4.08605	-0.6215
1	-3.61312	5.050647	-0.30288
1	-4.82643	4.188418	0.681833
1	-4.89233	4.099899	-1.10548

5. Syntheses of ligands and copper complexes

5-*tert*-Butyl-2-hydroxybenzaldehyde (1) was prepared by the Levin method (R. Aldred, R. Johnston, D. Levin, J. Neilan, *J. Chem. Soc., Perkin Trans. 1*, **1994**, 1823-1831) and used as a precursor for **3** and **4**.

5-*tert*-Butyl-2-hydroxy-3-nitrobenzaldehyde (3). Nitric acid (4.17 ml, 95.2 mmol) was added dropwise to a solution of **1** (15.0 g, 84.2 mmol) in glacial acetic acid (15 ml) at 0 °C. The mixture was stirred at 55 °C for 20 h and then allowed to cool to room temperature. The orange solution was extracted with DCM (150 ml) and washed with water (2 x 100 ml) and tried over $MgSO_4$. The solvent was removed *in vacuo*. Purification by silica-60 wet flash column chromatography (2 % ethyl acetate in hexane eluent) yielded an orange solid (7.66 g, 41 %). (Anal. Calc. for $C_{11}H_{13}N_1O_4$: C, 59.19; H, 5.87; N, 6.27. Found: C, 59.0; H, 5.9; N, 6.3%); ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.36 (s, 9H, C(C*H*$_3$)$_3$), 8.15 (d, 1H, Ar-H), 8.34 (d, 1H, Ar-*H*), 10.43 (s, 1H, C*H*O), 11.25 (s, 1H, O*H*); ^{13}C NMR ($CDCl_3$, 250 MHz): δ 31.3 (3C, C(*C*H$_3$)$_3$), 35.0 (1C, *C*(CH$_3$)$_3$), 125.4 (1C, Ar-*C*), 128.3 (1C, Ar-*C*), 134.7 (1C, Ar-*C*), 135.2 (1C, Ar-*C*), 143.9 (1C, Ar-*C*), 154.9 (1C, Ar-*C*), 189.8 (1C, *C*HO). ESIMS *m/z* 224 (MH^+). Melting Point 86-87 °C.

3-Bromo-5-*tert*-butyl-2-hydroxybenzaldehyde (4). Bromine (29.1 g, 0.180 mol) in glacial acetic acid (300 ml) was added to a solution of **1** (31.27 g, 0.177 mol) and sodium acetate (26.83 g, 0.326 mol) in glacial acetic acid (500 ml) via a dropping funnel over 50 min. The yellow solution was stirred at 50 °C for 12 h. The solvent was removed *in vacuo* and water (400 ml) and DCM (250 ml) were added to the precipitate. After separation the aqueous phase was extracted again with DCM (2 x 100 ml). The combined organic phases were washed with $Na_2S_2O_5$ solution (300 ml, 10 % w/w), saturated $NaHCO_3$ solution (400 ml) and dried over $MgSO_4$. After removing the solvent *in vacuo* the solid was recrystallized from light petroleum spirits (bp 40-60 °C) to give yellow crystals (33.9 g, 75 %). (Anal. Calc. for $C_{11}H_{13}BrO_2$: C, 51.38; H, 5.10. Found: C, 51.3; H, 5.2%); ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.33 (s, 9H, C(C*H*$_3$)$_3$), 7.52 (d, 1H, Ar-*H*), 7.82 (d, 1H, Ar-*H*), 9.86 (s, 1H, C*H*O), 11.42 (s, 1H, O*H*). ^{13}C NMR ($CDCl_3$, 250 MHz): δ 31.6 (3C, C(*C*H$_3$)$_3$), 34.7 (1C, *C*(CH$_3$)$_3$), 111.2 (1C, Ar-*C*), 121.1 (1C, Ar-*C*), 129.8 (1C, Ar-*C*), 138.0 (1C, Ar-*C*), 144.6 (1C, Ar-*C*), 156.2 (1C, Ar-*C*), 196.6 (1C, *C*HO). ESIMS *m/z* 257 (MH^+).

Melting Point 82-83 °C.

5-*tert*-Butyl-2-hydroxy-3-methoxybenzaldehyde (5). Sodium (3.20 g, 139 mmol) was added to anhydrous methanol (42 ml) to prepare a 4 M $NaOCH_3$/MeOH solution. **4** (5.40 g, 20.0 mmol) was dissolved in the minimum anhydrous methanol and poured into a refluxing mixture of the 4 M $NaOCH_3$/MeOH solution (35 ml), ethyl acetate (2.5 ml) and Cu(I)Br (1.0 g, 7 mmol) under nitrogen. The resulting solution was refluxed overnight. After the solvent was removed *in vacuo*, the solid was dissolved in 3 M HCl (100 ml) and extracted with ethyl acetate (3 x 100 ml). The combined organic phases were dried with $MgSO_4$, evaporated *in vacuo* and purified by silica-60 wet flash column chromatography (9% diethyl-ether in petrolether eluent) to yield a yellow solid (2.23 g, 54%). (Anal. Calc. for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.3; H, 7.7%); ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.34 (s, 9H, C(C*H*$_3$)$_3$), 3.94 (s, 3H, OC*H*$_3$), 7.15 (d, 1H, Ar-*H*), 7.18 (d, 1H, Ar-*H*), 9.92 (s, 1H, C*H*O), 10.96 (s, 1H, O*H*); ^{13}C NMR ($CDCl_3$, 250 MHz): δ 31.7 (3C, C(*C*H$_3$)$_3$), 34.8 (1C, *C*(CH$_3$)$_3$), 56.8 (1C, O*C*H$_3$), 116.9 (1C, Ar-*C*), 120.5 (1C, Ar-*C*), 121.0 (1C, Ar-*C*), 143.2 (1C, Ar-*C*), 148.2 (1C, Ar-*C*), 150.0 (1C, Ar-*C*), 197.2 (1C, Ar*C*HO). ESIMS *m/z* 209 (MH^+). Melting Point 56-57 °C.

5-*tert*-Butyl-2-hydroxy-3-methylbenzaldehyde (2). Hexamethylenetetramine (30.9 g, 220 mmol) and 4-*tert*-butyl-2-methylphenol (7.45 g, 45 mmol) were mixed and heated in trifluoroacetic acid (110 ml) to 90 °C for 16 h under reflux. The hot mixture was poured into 1 M HCl (200 ml), stirred for 6 h and extracted with DCM (3 × 150 ml). The combined organic phases were washed with water, dried over $MgSO_4$ and the solvent removed *in vacuo*. Chromatography (5% ethyl acetate in hexane eluent) was carried out to yield a pale yellow solid (6.07 g, 70%). (Anal. Calc. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.7; H, 8.8%); ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.33 (s, 9H, C(C*H*$_3$)$_3$), 2.28 (s, 3H, C*H*$_3$), 7.36 (m, 1H, Ar-*H*), 7.45 (m, 1H, Ar-*H*), 9.88 (s, 1H, C*H*O), 11.12 (s, 1H, O*H*); ^{13}C NMR ($CDCl_3$, 250 MHz): δ 15.7 (1C, *C*H$_3$) 31.7 (3C, C(*C*H$_3$)$_3$), 34.4, (1C, *C*(CH$_3$)$_3$), 119.8 (1C, Ar-*C*), 126.6 (1C,

Ar-*C*), 127.7 (1C, Ar-*C*), 136.1 (1C, Ar-*C*), 142.6 (1C, Ar-*C*), 158.3 (1C, Ar-*C*), 197.3 (1C, *C*HO). ESIMS *m/z* 193 (MH^+). Melting Point 37-38 °C.

General procedure for the preparation of the methylhydrazones. A solution of the appropriate precursor aldehyde in ethanol was slowly added to one equivalent of methylhydrazine in ethanol. The resulting mixture was stirred for 30 min and the solvent was removed *in vacuo* to yield the product which was washed with a small volume of ethanol and needed no further purification.

5-*tert*-Butyl-2-hydroxy-benzaldehyde methylhydrazone (L1) Combining ethanolic solutions of methylhydrazine (0.49 g, 10.6 mmol) and **1** (1.83 g, 10.3 mmol) gave a yellow solid (2.08 g, 98%). (Anal. Calc. for $C_{12}H_{18}N_2O$: C, 69.87; H, 8.80; N, 13.58. Found: C, 70.5; H, 8.3; N, 13.9%); ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.34 (s, 9H, C(C*H*$_3$)$_3$), 2.97 (s, 3H, NHC*H*$_3$), 6.89 (d, 1H, Ar-*H*), 7.13 (d, 1H, Ar-*H*), 7.23 (dd, 1H, Ar-*H*), 7.69 (s, 1H, C*H*N); ^{13}C NMR ($CDCl_3$, 250 MHz): δ 31.9 (3C, C(*C*H$_3$)$_3$), 34.4 (1C, *C*(CH$_3$)$_3$), 35.0 (1C, NH*C*H$_3$), 116.3 (1C, Ar-*C*), 118.9 (1C, Ar-*C*), 126.1 (1C, Ar-*C*), 126.7 (1C, Ar-*C*), 140.5 (1C, *C*HN), 142.1 (1C, Ar-*C*), 155.3 (1C, Ar-*C*). ESIMS *m/z* 207 (MH^+). Melting Point 42-43 °C.

5-*tert*-Butyl-2-hydroxy-3-methylbenzaldehyde methylhydrazone (L2). Similarly, ethanolic solutions of methylhydrazine (0.50 g, 10.8 mmol) and **2** (1.92 g, 10.0 mmol) gave a yellow solid (2.19 g, 99%). (Anal. Calc. for $C_{13}H_{20}N_2O$: C, 70.87; H, 9.15; N, 12.72. Found: C, 70.7; H, 9.6; N, 12.9%); ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.30 (s, 9H, C(C*H*$_3$)$_3$), 2.28 (s, 3H, C*H*$_3$), 2.98 (s, 3H, NHC*H*$_3$), 6.98 (d, 1H, Ar-*H*), 7.10 (d, 1H, Ar-*H*), 7.70 (s, 1H, C*H*N); ^{13}C NMR ($CDCl_3$, 250 MHz): δ 16.4 (1C, *C*H$_3$), 31.9 (3C, C(*C*H$_3$)$_3$), 34.3 (1C, *C*(CH$_3$)$_3$), 35.3 (1C, NH*C*H$_3$), 118.1 (1C, Ar-*C*), 123.9 (1C, Ar-*C*), 125.0 (1C, Ar-*C*), 128.3 (1C, Ar-*C*), 141.1 (1C, *C*HN), 141.6 (1C, Ar-*C*), 153.5 (1C, Ar-*C*). ESIMS *m/z* 221 (MH^+). Melting Point 95-96 °C.

5-*tert*-Butyl-2-hydroxy-3-nitrobenzaldehyde methylhydrazone (L3). Similarly, ethanolic solutions of methylhydrazine (0.62 g, 13.4 mmol) and **3** (3.01 g, 13.4 mmol)

yielded an orange solid (3.26 g, 97%). (Anal. Calc. for $C_{12}H_{17}N_3O_3$: C, 57.36; H, 6.82; N, 16.72. Found: C, 57.4; H, 6.7; N, 16.3%); ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.33 (s, 9H, C(C*H*$_3$)$_3$), 3.03 (s, 3H, NHC*H*$_3$), 7.64 (d, 1H, Ar-*H*), 7.72 (s, 1H, C*H*N), 7.90 (d, 1H, Ar-*H*); ^{13}C NMR ($CDCl_3$, 250 MHz): δ 31.5 (3C, C(*C*H$_3$)$_3$), 34.2 (1C, *C*(CH$_3$)$_3$), 34.7 (1C, NH*C*H$_3$), 121.4 (1C, Ar-*C*), 123.6 (1C, Ar-*C*), 131.1 (1C, Ar-*C*), 134.1 (1C, *C*HN), 136.5 (1C, Ar-*C*), 142.4 (1C, Ar-*C*), 150.4 (1C, Ar-*C*). ESIMS *m/z* 252 (MH^+). Melting Point 116-117 °C.

3-Bromo-5-tert-butyl-2-hydroxybenzaldehyde methylhydrazone (L4). Similarly, ethanolic solutions of methylhydrazine (0.75 g, 16.3 mmol) and **4** (4.12 g, 16.0 mmol) gave a yellow solid (4.20 g, 92%). (Anal. Calc. for $C_{12}H_{17}BrN_2O$: C, 50.54; H, 6.01; N, 9.82. Found: C, 50.9; H, 5.9; N, 9.6%); ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.29 (s, 9H, C(C*H*$_3$)$_3$), 2.98 (s, 3H, NHC*H*$_3$), 7.07 (d, 1H, Ar-*H*), 7.43 (d, 1H, Ar-*H*), 7.60 (s, 1H, C*H*N); ^{13}C NMR ($CDCl_3$, 250 MHz): δ 31.8 (3C, C(*C*H$_3$)$_3$), 34.5 (1C, *C*(CH$_3$)$_3$), 34.8 (1C, NH*C*H$_3$), 110.3 (1C, Ar-*C*), 120.1 (1C, Ar-*C*), 125.4 (1C, Ar-*C*), 129.9 (1C, Ar-*C*), 138.7 (1C, *C*HN), 143.4 (1C, Ar-*C*), 151.8 (1C, Ar-*C*). ESIMS *m/z* 285 (MH^+). Melting Point 104-105 °C.

5-*tert*-Butyl-2-hydroxy-3-methoxybenzldehyde methylhydrazone (L5). Similarly, ethanolic solutions of methylhydrazine (0.28 g, 6.1 mmol) and **(5)** (1.25 g, 6.0 mmol) yielded a yellow solid (1.34 g, 94%). (Anal. Calc. for $C_{12}H_{17}BrN_2O$: C, 66.07; H, 8.53; N, 11.85. Found: C, 65.7; H, 9.1; N, 11.6%); ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.31 (s, 9H, C(C*H*$_3$)$_3$), 2.97 (s, 3H, NHC*H*$_3$), 3.92 (s, 3H, OC*H*$_3$), 6.76 (d, 1H, Ar-*H*), 6.88 (d, 1H, Ar-*H*), 7.67 (s, 1H, C*H*N); ^{13}C NMR ($CDCl_3$, 250 MHz): δ 31.9 (1C, *C*(CH$_3$)$_3$), 34.7 (3C, C(*C*H$_3$)$_3$), 34.9 (1C, NH*C*H$_3$), 56.7 (1C, OC*H*$_3$), 110.3 (1C, Ar-*C*), 118.1 (1C, Ar-*C*), 118.9 (1C, Ar-*C*), 140.3 (1C, *C*HN), 142.1 (1C, Ar-*C*), 144.9 (1C, Ar-*C*), 147.7 (1C, Ar-*C*). ESIMS *m/z* 237 (MH^+). Melting Point 79-80 °C.

General procedure for preparation of the phenylhydrazones. A solution of the appropriate precursor aldehyde in ethanol was slowly added to one equivalent of

phenylhydrazine hydrochloride and three equivalents of sodium acetate in water. The resulting mixture was stirred and heated at 90 °C for 30 min. After cooling the solvent was removed *in vacuo*. The solid was dissolved in DCM, washed with water twice, and dried over $MgSO_4$. The solvent was evaporated *in vacuo* to give the product product which was washed with a small volume of ethanol and needed no further purification.

5-*tert*-Butyl-2-hydroxy-benzaldehyde phenylhydrazone (L6) Phenylhydrazine hydrochloride (10.21 g, 70.6 mmol) and **(1)** (12.38 g, 69.5 mmol) were combined as in the general procedure to give a pale yellow solid (15.79 g, 85%). Yellow block crystals suitable for XRD analysis were grown by slow cooling and evaporation of an ethanol solution. (Anal. Calc. for $C_{17}H_{20}N_2O$: C, 76.09; H, 7.51; N, 10.44. Found: C, 75.7; H, 7.9; N, 10.7%); ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.30 (s, 9H, C(C*H*$_3$)$_3$), 6.93 (m, 4H, Ar-*H*), 7.12 (d, 1H, Ar-*H*), 7.28 (m, 3H, Ar-*H*), 7.84 (s, 1H, C*H*N); ^{13}C NMR ($CDCl_3$, 250 MHz): δ 31.9 (3C, C(*C*H$_3$)$_3$), 34.4 (1C, *C*(CH$_3$)$_3$), 113.0 (2C, Ar-*C*), 116.5 (1C, Ar-*C*), 118.2 (1C, Ar-*C*), 121.1 (1C, Ar-*C*), 126.4 (1C, Ar-*C*), 127.7 (1C, Ar-*C*), 129.9 (2C, Ar-*C*), 142.2 (1C, *C*HN), 142.6 (1C, Ar-*C*), 144.0 (1C, Ar-*C*), 155.1 (1C, Ar-*C*). ESIMS *m/z* 269 (MH^+). Melting Point 172-173 °C.

5-*tert*-Butyl-2-hydroxy-3-methylbenzaldehyde phenylhydrazone (L7) Phenylhydrazine hydrochloride (0.75 g, 5.20 mmol) and **(2)** (1.00 g, 5.20 mmol) were combined as in the general procedure to give a yellow solid (1.17 g, 80%). (Anal. Calc. for $C_{18}H_{22}N_2O$: C, 76.56; H, 7.85; N, 9.92. Found: C, 76.7; H, 8.0; N, 10.0%); ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.32 (s, 9H, C(C*H*$_3$)$_3$), 2.34 (s, 3H, C*H*$_3$), 6.96 (m, 3H, Ar-*H*), 7.17 (d, 1H, Ar-*H*), 7.30 (m, 2H, Ar-*H*), 7.44 (d, 1H, Ar-*H*), 7.88 (s, 1H, C*H*N); ^{13}C NMR ($CDCl_3$, 250 MHz): δ 16.4 (1C, *C*H$_3$), 31.9 (3C, C(*C*H$_3$)$_3$), 34.3 (1C, *C*(CH$_3$)$_3$), 113.0 (2C, Ar-*C*), 117.4 (1C, Ar-*C*), 121.1 (1C, Ar-*C*), 124.1 (1C, Ar-*C*), 125.3 (1C, Ar-*C*), 129.2 (1C, Ar-*C*), 129.9 (2C, Ar-*C*), 142.1 (1C, *C*HN), 142.5 (1C, Ar-*C*), 144.0 (1C, Ar-*C*), 153.4 (1C, Ar-*C*). ESIMS *m/z* 283 (MH^+). Melting Point 104-105 °C.

5-*tert*-Butyl-2-hydroxy-3-nitrobenzaldehyde phenylhydrazone (L8) Phenylhydrazine hydrochloride (0.65 g, 4.48 mmol) and **(3)** (1.00 g, 4.48 mmol) were combined as in the general procedure to give a yellow solid (1.31 g, 87%). (Anal. Calc. for $C_{17}H_{19}N_3O_3$: C, 65.16; H, 6.11; N, 13.41. Found: C, 65.1; H, 6.1; N, 13.1%); ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.37 (s, 9H, C(C*H*$_3$)$_3$), 6.94 (t, 1H, Ar-*H*), 7.09 (m, 2H, Ar-*H*), 7.32 (m, 2H, Ar-*H*), 8.01 (m, 1H, Ar-*H*), 8.04 (m, 1H, Ar-*H*), 8.05 (m, 1H, C*H*N); ^{13}C NMR ($CDCl_3$, 250 MHz): δ 31.5 (3C, C(*C*H$_3$)$_3$), 34.8 (1C, *C*(CH$_3$)$_3$), 113.2 (2C, Ar-*C*), 121.3 (1C, Ar-*C*), 121.9 (1C, Ar-*C*), 124.5 (1C, Ar-*C*), 129.9 (2C, Ar-*C*), 131.2 (1C, Ar-*C*), 134.0 (1C, *C*HN), 135.3 (1C, Ar-*C*), 143.3 (1C, Ar-*C*), 144.0 (1C, Ar-*C*), 150.5 (1C, Ar-*C*). ESIMS *m/z* 314 (MH^+). Melting Point 124-125 °C.

3-Bromo-5-*tert*-butyl-2-hydroxybenzaldehyde phenylhydrazone (L9) Phenylhydrazine hydrochloride (1.69 g, 11.67 mmol) and **(4)** (3.00 g, 11.67 mmol) were combined as in the general procedure to give a white solid (3.25 g, 80%). (Anal. Calc. for $C_{17}H_{19}BrN_2O$: C, 58.80; H, 5.52; N, 8.07. Found: C, 58.3; H, 5.0; N, 7.7%); ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.31 (s, 9H, C(C*H*$_3$)$_3$), 6.95 (t, 1H, Ar-*H*), 7.02 (m, 2H, Ar-*H*), 7.10 (d, 1H, Ar-*H*), 7.31 (m, 2H, Ar-*H*), 7.51 (d, 1H, Ar-*H*), 7.84 (s, 1H, C*H*N); ^{13}C NMR ($CDCl_3$, 250 MHz): δ 31.7 (3C, C(*C*H$_3$)$_3$), 34.5 (1C, *C*(CH$_3$)$_3$), 110.5 (1C, Ar-*C*), 113.1 (2C, Ar-*C*), 119.3 (1C, Ar-*C*), 121.6 (1C, Ar-*C*), 125.7 (1C, Ar-*C*), 130.0 (2C, Ar-*C*), 130.9 (1C, Ar-*C*), 140.6 (1C, *C*HN), 143.4 (1C, Ar-*C*), 143.9 (1C, Ar-*C*), 151.6 (1C, Ar-*C*). ESIMS *m/z* 347 (MH^+). Melting Point 144-145 °C.

5-*tert*-Butyl-2-hydroxy-3-methoxybenzaldehyde phenylhydrazone (L10) Phenylhydrazine hydrochloride (1.39 g, 9.60 mmol) and **(5)** (2.00 g, 9.60 mmol) were combined as in the general procedure to give a white solid (2.55 g, 90%). Colourless block crystals suitable for XRD analysis were grown by vapor diffusion of DCM/Petrolether. (Anal. Calc. for $C_{18}H_{22}N_2O_2$: C, 72.46; H, 7.43; N, 9.39. Found: C, 72.3; H, 7.8; N, 9.4%); ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.33 (s, 9H, C(C*H*$_3$)$_3$), 3.96

(s, 3H, OC*H*$_3$), 6.79 (d, 1H, Ar-*H*), 6.97 (m, 4H, Ar-*H*), 7.29 (m, 2H, Ar-*H*), 7.88 (s, 1H, C*H*N); ^{13}C NMR ($CDCl_3$, 250 MHz): δ 31.9 (3C, C(*C*H$_3$)$_3$), 34.7 (1C, *C*(CH$_3$)$_3$), 56.7 (1C, O*C*H$_3$), 110.9 (1C, Ar-*C*), 113.0 (2C, Ar-*C*), 118.1 (1C, Ar-*C*), 118.3 (1C, Ar-*C*), 121.1 (1C, Ar-*C*), 129.9 (2C, Ar-*C*), 141.7 (1C, ArCHN), 142.6 (1C, Ar-*C*), 143.9 (1C, Ar-*C*), 144.9 (1C, Ar-*C*), 148.0 (1C, Ar-*C*). ESIMS *m/z* 299 (MH^+). Melting Point 132-133 °C.

Cu(II) Complex Syntheses

General Procedure A solution of the ligand in ethanol was added to 0.5 equivalents of copper(II) acetate in ethanol. Colour changes due to complex formation occurred immediately, along with precipitation. The resulting mixture was stirred for 3 h. The precipitation was filtered, washed with ethanol and dried *in vacuo* to give the product which required no further purification.

[Cu(L1-H)$_2$]. $Cu(OAc)_2 \cdot H_2O$ (0.46 g, 2.29 mmol) and **L1** (0.94 g, 4.55 mmol) yielded a dark brown solid (1.04 g, 96%). (Anal. Calc. for $C_{24}H_{34}CuN_4O_2$: C, 60.80; H, 7.23; N, 11.82. Found: C, 61.0; H, 7.4; N, 11.3%). ESIMS *m/z* 474 (MH^+).

[Cu(L2-H)$_2$]. $Cu(OAc)_2 \cdot H_2O$ (0.68 g, 3.40 mmol) and **L2** (1.49 g, 6.76 mmol) gave a light brown solid (1.55 g, 91%). (Anal. Calc. for $C_{26}H_{38}CuN_4O_2$: C, 62.19; H, 7.63; N, 11.16. Found: C, 62.7; H, 7.8; N, 10.7%). ESIMS *m/z* 502 (MH^+).

[Cu(L3-H)$_2$]. $Cu(OAc)_2 \cdot H_2O$ (0.24 g, 1.20 mmol) and **L3** (0.60 g, 2.39 mmol) yielded a yellow solid (0.47 g, 70%). (Anal. Calc. for $C_{24}H_{32}CuN_6O_6$: C, 51.10; H, 5.72; N, 14.90. Found: C, 51.9; H, 5.5; N, 14.6%). ESIMS *m/z* 564 (MH^+).

[Cu(L4-H)$_2$]. $Cu(OAc)_2 \cdot H_2O$ (0.20 g, 1.00 mmol) and **L4** (0.57 g, 2.00 mmol) gave a light brown solid (0.55 g, 87%). (Anal. Calc. for $C_{24}H_{32}Br_2CuN_4O_2$: C, 45.62; H, 5.10; N, 8.87. Found: C, 45.7; H, 4.9; N, 9.0%). ESIMS *m/z* 632 (MH^+).

[Cu(L5-H)$_2$]. $Cu(OAc)_2 \cdot H_2O$ (0.20 g, 1.00 mmol) and **L5** (0.47 g, 2.00 mmol) yielded a dark brown solid (0.52 g, 97%). (Anal. Calc. for $C_{26}H_{38}CuN_4O_4$: C, 58.46; H, 7.17; N, 10.49. Found: C, 58.0; H, 6.7; N, 9.6%). ESIMS *m/z* 534 (MH^+).

[Cu(L6-H)$_2$]. $Cu(OAc)_2 \cdot H_2O$ (0.10 g, 0.50 mmol) and **L6** (0.27 g, 1.00 mmol) gave a light brown solid (0.27 g, 90%). (Anal. Calc. for $C_{34}H_{38}CuN_4O_2$: C, 68.26; H, 6.40; N, 9.37. Found: C, 65.3; H, 6.0; N, 8.8%). ESIMS *m/z* 598 (MH^+).

[Cu(L7-H)$_2$]. $Cu(OAc)_2 \cdot H_2O$ (0.10 g, 0.50 mmol) and **L7** (0.30 g, 1.00 mmol) yielded a light brown solid (0.27 g, 81%). (Anal. Calc. for $C_{36}H_{42}CuN_4O_2$: C, 69.04; H, 6.76; N, 8.95. Found: C, 69.1; H, 6.9; N, 9.0%). ESIMS *m/z* 626 (MH^+).

[Cu(L8-H)$_2$]. $Cu(OAc)_2 \cdot H_2O$ (0.10 g, 0.50 mmol) and **L8** (0.32 g, 1.00 mmol) gave a dark brown solid (0.28 g, 82%). (Anal. Calc. for $C_{34}H_{36}CuN_6O_6$: C, 59.34; H, 5.27; N, 12.21. Found: C, 58.4; H, 4.8; N, 11.7%). ESIMS *m/z* 688 (MH^+).

[Cu(L9-H)$_2$]. $Cu(OAc)_2 \cdot H_2O$ (0.20 g, 1.00 mmol) and **L9** (0.69 g, 2.00 mmol) yielded a brown solid (0.68 g, 90%). (Anal. Calc. for $C_{34}H_{36}BrCuN_4O_2$: C, 54.01; H, 4.80; N, 7.41. Found: C, 53.9; H, 4.8; N, 7.4%). ESIMS *m/z* 756 (MH^+).

[Cu(L10-H)$_2$]. $Cu(OAc)_2 \cdot H_2O$ (0.34 g, 1.70 mmol) and **L10** (1.00 g, 3.40 mmol) yielded a brown solid (1.04 g, 91%). (Anal. Calc. for $C_{36}H_{42}CuN_4O_4$: C, 65.68; H, 6.43; N, 8.51. Found: C, 65.3; H, 6.6; N, 8.2%). ESIMS *m/z* 658 (MH^+).