

Table S1. Optimized Coordinates of [Cu(ttz)(CO)]

| | | | |
|----|-----------|-----------|-----------|
| C | -0.058176 | -4.684176 | -0.363459 |
| O | -0.082520 | -5.832225 | -0.438827 |
| C | -0.842015 | -1.466849 | -3.076043 |
| C | -0.716594 | 0.550926 | -2.514451 |
| C | -1.863567 | 0.217822 | 1.884372 |
| C | -2.174514 | -1.852903 | 2.018929 |
| C | 2.564940 | 0.264549 | 0.678477 |
| C | 2.942609 | -1.798475 | 0.622522 |
| H | 2.646964 | 1.342079 | 0.780120 |
| H | -0.991924 | -2.372604 | -3.654548 |
| H | -0.731678 | 1.636349 | -2.495546 |
| H | -2.555262 | -2.825190 | 2.314347 |
| H | -1.906846 | 1.294597 | 2.015549 |
| H | 0.015930 | 1.429061 | 0.104038 |
| B | 0.004725 | 0.231929 | 0.010828 |
| Cu | -0.027593 | -2.873920 | -0.233973 |
| N | -1.006231 | -0.214978 | -3.569104 |
| N | -2.603238 | -0.678225 | 2.542198 |
| N | 3.552511 | -0.613511 | 0.869461 |
| H | 3.439308 | -2.761536 | 0.680037 |
| N | -0.472351 | -1.505984 | -1.793276 |
| N | -0.390539 | -0.183474 | -1.429499 |
| N | -1.023740 | -0.367237 | 1.003795 |
| N | -1.225070 | -1.723685 | 1.088711 |
| N | 1.408609 | -0.340959 | 0.332811 |
| N | 1.652273 | -1.692509 | 0.295275 |

Table S2. Optimized Coordinates of [Cu(tp)(CO)]

| | | | |
|----|-----------|-----------|-----------|
| C | -0.001653 | -4.679791 | 0.006850 |
| O | -0.000919 | -5.833172 | 0.014842 |
| C | -1.530551 | -1.778434 | -2.650431 |
| C | -1.845283 | -0.515958 | -3.183628 |
| C | -1.317262 | 0.389890 | -2.269812 |
| C | -1.314396 | 0.389283 | 2.271918 |
| C | -1.843720 | -0.516596 | 3.185015 |
| C | -1.535102 | -1.778966 | 2.648265 |
| C | 2.623835 | 0.390226 | 0.007439 |
| C | 3.679661 | -0.515161 | 0.012692 |
| C | 3.061145 | -1.777792 | 0.010122 |
| H | 3.510206 | -2.765669 | 0.013600 |
| H | 4.740869 | -0.291646 | 0.018557 |
| H | 2.617138 | 1.474920 | 0.008208 |
| H | -1.753893 | -2.766498 | -3.039748 |
| H | -2.379704 | -0.293028 | -4.100613 |
| H | -1.317404 | 1.474635 | -2.261766 |
| H | -1.761334 | -2.766933 | 3.035927 |
| H | -2.375254 | -0.293750 | 4.103676 |
| H | -1.310112 | 1.473971 | 2.265989 |
| H | 0.000817 | 1.413939 | 0.001214 |
| B | -0.000933 | 0.212584 | 0.000118 |
| Cu | 0.000190 | -2.870256 | 0.000887 |
| N | 1.724903 | -1.648876 | 0.003597 |
| N | -0.859419 | -1.649036 | -1.495012 |
| N | -0.730490 | -0.308559 | -1.265440 |
| N | -0.731922 | -0.309460 | 1.264917 |
| N | -0.865326 | -1.649694 | 1.492040 |
| N | 1.460767 | -0.308649 | 0.001725 |

Table S3. Optimized Coordinates of [Cu(tpm)(CO)]+

| | | | |
|---|-----------|-----------|-----------|
| C | -0.003804 | -4.785840 | 0.008277 |
| O | -0.007082 | -5.931333 | 0.019663 |
| C | -1.515126 | -1.701345 | -2.625848 |
| C | -1.802456 | -0.407973 | -3.109770 |
| C | -1.264340 | 0.456882 | -2.177346 |
| C | -0.000943 | 0.113692 | 0.000482 |