

Support Information

A Radical Rebound Mechanism to Methane Oxidation Reaction Promoted by the Dicopper Center of pMMO Enzyme: A Computational Perspective.

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1. Dinuclear copper complex model built from pMMO dicopper site.

The coordinates of the atoms highlighted by a star were kept frozen during geometry optimization.

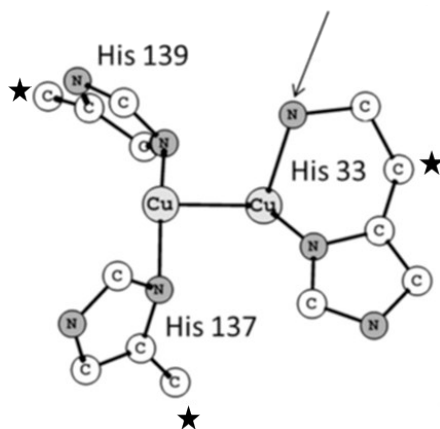


Figure S1: The dinuclear copper model built from the crystal structure of pMMO enzyme. The coordinates of the atoms highlighted by a star were kept frozen during geometry optimization.

2. Detailed Computational Results

B3LYP-D2/BS1 Calculated energies (in hartree) and structures (cartesian coordinates in Å) for all species.

3(a) – Peroxo – ³A**Etotal (u.a.) = -4530.31002752**

29	2.115041000	-0.186847000	-0.386977000
29	-1.280564000	-0.751787000	-0.365042000
8	0.308759000	0.122411000	-0.781003000
8	0.556239000	-1.328100000	-0.506770000
6	4.188312000	-2.271291000	0.398795000
6	5.507960000	-2.508897000	0.120881000
7	3.820308000	-1.085160000	-0.227293000
6	4.899754000	-0.623348000	-0.860205000
7	5.933362000	-1.460491000	-0.670479000
1	3.615912000	-4.064344000	1.414029000
1	2.258894000	-3.116538000	0.759984000
1	6.165132000	-3.312776000	0.415415000
1	4.950023000	0.287409000	-1.437430000
1	6.863078000	-1.344705000	-1.053800000
6	3.540301000	3.470048000	0.824052000
6	3.548659000	2.100846000	0.799378000
7	2.711784000	3.836131000	-0.224253000
6	2.244126000	2.724487000	-0.829775000
7	2.737636000	1.647912000	-0.229298000
1	4.804199000	3.933014000	2.469324000
1	3.445419000	5.054165000	2.269969000
1	2.500052000	4.787994000	-0.497585000
1	4.073834000	1.415986000	1.448279000
1	1.567164000	2.726352000	-1.671024000
1	3.099736000	-2.576189000	2.226062000
1	4.841945000	5.145958000	1.177009000
7	-2.516103000	-2.117679000	0.164401000
6	-3.801881000	-1.827113000	0.610002000
6	-2.408503000	-3.441390000	0.104716000
6	-4.461237000	-3.009342000	0.814587000
7	-3.565728000	-4.008948000	0.492521000
1	-1.535369000	-3.993030000	-0.211505000
1	-5.460524000	-3.222548000	1.162795000
6	-4.067701000	0.496870000	-0.401230000
1	-3.749273000	0.040293000	1.673536000
1	-5.335525000	-0.432471000	1.080666000
1	-3.746469000	-5.004388000	0.538630000
6	-4.667320000	1.889492000	-0.083019000
1	-4.520233000	0.046048000	-1.289741000
7	-2.612449000	0.706582000	-0.655374000
8	-3.919234000	2.750433000	0.380462000

7	-5.988638000	2.024751000	-0.286446000
1	-2.508874000	1.055785000	-1.612250000
1	-2.391581000	1.534294000	-0.073736000
6	-6.729191000	3.251009000	0.021424000
1	-6.492388000	1.266765000	-0.728238000
1	-7.584710000	3.018041000	0.663279000
1	-6.053525000	3.930779000	0.542977000
1	-7.083066000	3.724500000	-0.900790000
6	3.240441000	-3.050998000	1.245668000
6	4.191355000	4.456870000	1.730365000
6	-4.272171000	-0.419023000	0.822350000

3(b) – Peroxo – ³A

Etotal (u.a.) = -4530.30206957

29	2.036189000	-0.181411000	-0.389274000
29	-1.198824000	-0.788554000	-0.351561000
8	0.324065000	-0.095472000	-1.236266000
8	0.597832000	-1.469721000	-0.774545000
6	4.193271000	-2.150201000	0.538578000
6	5.543815000	-2.283645000	0.357296000
7	3.789984000	-0.955333000	-0.046820000
6	4.880326000	-0.389258000	-0.567235000
7	5.953549000	-1.164732000	-0.339682000
1	3.706196000	-4.018396000	1.453588000
1	2.347438000	-3.220403000	0.630306000
1	6.230559000	-3.059558000	0.659288000
1	4.911109000	0.553946000	-1.090852000
1	6.898918000	-0.966345000	-0.642466000
6	3.446860000	3.488154000	0.876087000
6	3.361757000	2.122062000	0.904783000
7	2.639849000	3.867628000	-0.184751000
6	2.101602000	2.766081000	-0.750351000
7	2.523005000	1.682590000	-0.108187000
1	4.764690000	3.915948000	2.488452000
1	3.508099000	5.142825000	2.246923000
1	2.485580000	4.820368000	-0.492032000
1	3.844328000	1.429519000	1.577578000
1	1.438099000	2.780375000	-1.602549000
1	2.917959000	-2.619013000	2.202807000
1	4.892065000	5.059113000	1.138244000
7	-2.368463000	-2.065184000	0.479761000

6	-3.686344000	-1.800356000	0.842316000
6	-2.172967000	-3.371857000	0.633648000
6	-4.270359000	-2.979593000	1.220836000
7	-3.300143000	-3.951376000	1.084816000
1	-1.257678000	-3.903776000	0.419080000
1	-5.264778000	-3.205069000	1.575294000
6	-4.017242000	0.362757000	-0.482227000
1	-3.872370000	0.183020000	1.651195000
1	-5.352518000	-0.489084000	0.982782000
1	-3.416250000	-4.937380000	1.284984000
6	-4.726625000	1.734392000	-0.369375000
1	-4.360649000	-0.214248000	-1.346534000
7	-2.560336000	0.646328000	-0.648717000
8	-4.087297000	2.677135000	0.097239000
7	-6.018594000	1.766427000	-0.738046000
1	-2.423982000	0.999037000	-1.600880000
1	-2.418171000	1.487838000	-0.065472000
6	-6.856199000	2.963810000	-0.630117000
1	-6.423695000	0.942298000	-1.162512000
1	-7.771907000	2.728583000	-0.078564000
1	-6.288576000	3.724605000	-0.091868000
1	-7.116018000	3.338864000	-1.625992000
6	3.240441000	-3.050999000	1.245668000
6	4.191353000	4.456870000	1.730365000
6	-4.272169000	-0.419022000	0.822350000

3(c) – Bis-oxo-¹A

Etotal (u.a.) = -4530.30667145

29	1.740247000	-0.071535000	-0.127203000
29	-1.010299000	-0.419898000	0.072516000
8	0.215722000	0.841200000	-0.076645000
8	0.514209000	-1.384218000	-0.003921000
6	3.839419000	-2.306453000	0.098590000
6	4.973402000	-2.618024000	-0.604071000
7	3.343815000	-1.105407000	-0.409549000
6	4.170128000	-0.716296000	-1.384724000
7	5.159873000	-1.609887000	-1.526694000
1	3.606074000	-4.081556000	1.259682000
1	2.146763000	-3.056822000	1.167366000
1	5.649843000	-3.454586000	-0.517191000
1	4.074823000	0.185804000	-1.968470000
1	5.914799000	-1.549656000	-2.198584000
6	3.533393000	3.439807000	0.862777000

6	3.492608000	2.070331000	0.902171000
7	2.720726000	3.789709000	-0.204951000
6	2.203515000	2.678052000	-0.756830000
7	2.660646000	1.611234000	-0.107280000
1	4.790472000	3.960812000	2.499079000
1	3.444927000	5.084663000	2.233326000
1	2.549240000	4.736606000	-0.521104000
1	3.989837000	1.394788000	1.581859000
1	1.490017000	2.663558000	-1.565464000
1	3.506499000	-2.584209000	2.203338000
1	4.855590000	5.112087000	1.152817000
7	-2.245071000	-1.840912000	0.265710000
6	-3.604586000	-1.734776000	0.541095000
6	-1.957628000	-3.128954000	0.107340000
6	-4.127891000	-2.999954000	0.540191000
7	-3.076905000	-3.854992000	0.269627000
1	-0.976912000	-3.519842000	-0.120873000
1	-5.130651000	-3.358403000	0.717641000
6	-3.844542000	0.700646000	-0.140599000
1	-4.047260000	-0.082701000	1.844797000
1	-5.357630000	-0.544017000	0.764848000
1	-3.137573000	-4.863744000	0.201086000
6	-4.579350000	2.003669000	0.266614000
1	-4.038422000	0.414439000	-1.178817000
7	-2.389670000	0.972736000	0.014161000
8	-4.032560000	2.741541000	1.084063000
7	-5.797035000	2.185274000	-0.272233000
1	-2.085754000	1.601206000	-0.735272000
1	-2.325142000	1.569731000	0.856273000
6	-6.661491000	3.320597000	0.063226000
1	-6.123706000	1.532288000	-0.972529000
1	-7.643152000	2.958092000	0.384120000
1	-6.190388000	3.873755000	0.877330000
1	-6.780487000	3.977994000	-0.804742000
6	3.240442000	-3.050995000	1.245668000
6	4.191343000	4.456860000	1.730364000
6	-4.272160000	-0.419016000	0.822351000

3(d) – Bis-oxo-³A

Etotal (u.a.) = -4530.28101771

29	1.779903000	-0.121770000	-0.281722000
29	-1.103121000	-0.614000000	-0.220495000

8	0.099911000	0.452163000	-0.957769000
8	0.440032000	-1.539130000	-0.230969000
6	4.032752000	-2.165413000	0.345381000
6	5.327712000	-2.318563000	-0.073613000
7	3.539910000	-0.978153000	-0.188946000
6	4.525901000	-0.439178000	-0.909479000
7	5.615949000	-1.222200000	-0.860177000
1	3.733289000	-4.020900000	1.357586000
1	2.234574000	-3.210562000	0.836207000
1	6.050776000	-3.095418000	0.122731000
1	4.470774000	0.492634000	-1.450897000
1	6.493765000	-1.040833000	-1.330305000
6	3.417653000	3.493489000	0.896898000
6	3.379776000	2.124378000	0.868491000
7	2.503683000	3.891045000	-0.066077000
6	1.946291000	2.798349000	-0.628188000
7	2.461468000	1.703251000	-0.080446000
1	4.847418000	3.911513000	2.414679000
1	3.524759000	5.088998000	2.330656000
1	2.295103000	4.850585000	-0.313653000
1	3.944748000	1.419873000	1.460085000
1	1.186302000	2.817841000	-1.394280000
1	3.130927000	-2.608793000	2.245033000
1	4.815959000	5.114114000	1.112099000
7	-2.255098000	-1.921570000	0.507186000
6	-3.591979000	-1.755994000	0.855107000
6	-1.946360000	-3.206847000	0.662638000
6	-4.077956000	-2.980134000	1.227829000
7	-3.028536000	-3.869700000	1.102046000
1	-0.980512000	-3.641435000	0.452397000
1	-5.053759000	-3.285611000	1.574337000
6	-3.966828000	0.387805000	-0.452879000
1	-3.968978000	0.192201000	1.684601000
1	-5.354215000	-0.559897000	0.901642000
1	-3.067391000	-4.862583000	1.300166000
6	-4.686669000	1.757477000	-0.343879000
1	-4.253526000	-0.173775000	-1.346765000
7	-2.510699000	0.700766000	-0.533430000
8	-4.078587000	2.679620000	0.198989000
7	-5.947190000	1.801167000	-0.801873000
1	-2.297297000	1.069120000	-1.465667000
1	-2.402920000	1.528581000	0.079614000
6	-6.794997000	2.994191000	-0.709726000
1	-6.322877000	0.989631000	-1.275278000
1	-7.735266000	2.743381000	-0.208841000
1	-6.258255000	3.745802000	-0.128743000
1	-7.006371000	3.386608000	-1.710058000

6	3.240441000	-3.050999000	1.245668000
6	4.191353000	4.456870000	1.730365000
6	-4.272169000	-0.419022000	0.822350000

4(b) – TS1-1A

Ettotal (u.a.) = -4570.77877840

29	1.695349000	-0.134312000	-0.182205000
29	-1.213385000	-0.639385000	-0.238623000
8	0.063330000	0.596349000	-0.191263000
8	0.477961000	-1.681029000	-0.431397000
1	0.616097000	-2.152878000	-1.314879000
6	1.008600000	-3.771214000	-1.084868000
1	2.084097000	-3.657353000	-1.178214000
1	0.460867000	-4.044420000	-1.987777000
1	0.645642000	-4.169000000	-0.145715000
6	3.926045000	-2.244896000	0.186424000
6	5.159809000	-2.453813000	-0.375252000
7	3.404560000	-1.066331000	-0.346816000
6	4.316093000	-0.583297000	-1.191393000
7	5.383975000	-1.398698000	-1.234438000
1	3.585990000	-2.760145000	2.245964000
1	3.444824000	-4.118823000	1.119633000
1	5.885549000	-3.238793000	-0.225013000
1	4.225434000	0.331507000	-1.757418000
1	6.211265000	-1.258112000	-1.800809000
6	3.392121000	3.453825000	0.966917000
6	3.429069000	2.084792000	0.888273000
7	2.345199000	3.827296000	0.138190000
6	1.781594000	2.727163000	-0.393197000
7	2.423520000	1.646467000	0.038154000
1	4.951317000	3.950793000	2.332439000
1	3.551592000	5.035418000	2.408700000
1	2.049326000	4.780181000	-0.033550000
1	4.098386000	1.394784000	1.379632000
1	0.911966000	2.717049000	-1.029084000
1	2.159464000	-2.885694000	1.199864000
1	4.701338000	5.159675000	1.059331000
7	-2.550908000	-2.021744000	-0.132522000
6	-3.842435000	-1.765903000	0.322099000
6	-2.501588000	-3.309967000	-0.456383000
6	-4.562024000	-2.928608000	0.253203000
7	-3.699149000	-3.885801000	-0.237773000
1	-1.639510000	-3.833621000	-0.837199000

1	-5.583796000	-3.155148000	0.517673000
6	-3.951567000	0.729341000	-0.151100000
1	-3.785266000	-0.187958000	1.780643000
1	-5.349338000	-0.436528000	1.014425000
1	-3.925045000	-4.859045000	-0.402255000
6	-4.503505000	2.052201000	0.440370000
1	-4.368797000	0.514712000	-1.139923000
7	-2.482298000	0.890011000	-0.270964000
8	-3.755607000	2.739827000	1.132307000
7	-5.800001000	2.308992000	0.188857000
1	-2.264264000	1.431581000	-1.109777000
1	-2.213783000	1.522655000	0.499581000
6	-6.506864000	3.474580000	0.725197000
1	-6.303951000	1.698263000	-0.440575000
1	-5.837374000	3.982989000	1.420937000
1	-6.781856000	4.160315000	-0.083643000
1	-7.410314000	3.152899000	1.253113000
6	3.240442000	-3.050995000	1.245668000
6	4.191343000	4.456860000	1.730364000
6	-4.272160000	-0.419016000	0.822351000

4(b) – TS1 – ³A

Etotal (u.a.) = -4570.79899200

29	1.768650000	-0.117227000	-0.243320000
29	-1.078663000	-0.642719000	-0.118956000
8	0.081545000	0.610557000	-0.577858000
8	0.471064000	-1.679683000	-0.044093000
1	0.570738000	-2.105102000	-1.195115000
6	0.664196000	-2.047645000	-2.499424000
1	1.691277000	-2.358269000	-2.701751000
1	0.462719000	-0.993714000	-2.702614000
1	-0.092014000	-2.738316000	-2.879091000
6	3.999832000	-2.215757000	0.269027000
6	5.271646000	-2.406778000	-0.203334000
7	3.502405000	-1.037874000	-0.283466000
6	4.465138000	-0.538636000	-1.060703000
7	5.543006000	-1.340807000	-1.036945000
1	3.728379000	-4.021236000	1.376245000
1	2.210790000	-3.210592000	0.904680000
1	5.990808000	-3.188910000	-0.013346000
1	4.403787000	0.382734000	-1.619590000

1	6.405065000	-1.186150000	-1.544277000
6	3.438931000	3.487114000	0.885236000
6	3.457395000	2.118942000	0.808778000
7	2.477241000	3.878283000	-0.032983000
6	1.946630000	2.782655000	-0.613568000
7	2.525512000	1.692642000	-0.123734000
1	4.882359000	3.919707000	2.386252000
1	3.511935000	5.043969000	2.361222000
1	2.219675000	4.835842000	-0.237469000
1	4.068919000	1.419240000	1.358685000
1	1.146461000	2.792462000	-1.337255000
1	3.191322000	-2.562703000	2.228202000
1	4.777012000	5.156160000	1.120103000
7	-2.310167000	-1.982825000	0.483049000
6	-3.643427000	-1.780563000	0.820897000
6	-2.045328000	-3.276310000	0.645489000
6	-4.176266000	-2.989526000	1.179989000
7	-3.154218000	-3.910879000	1.064226000
1	-1.085820000	-3.740671000	0.475604000
1	-5.165205000	-3.264927000	1.514136000
6	-3.922840000	0.420433000	-0.418483000
1	-3.955117000	0.150949000	1.707644000
1	-5.359671000	-0.520844000	0.888243000
1	-3.224589000	-4.901240000	1.264826000
6	-4.615698000	1.801485000	-0.283098000
1	-4.206453000	-0.105173000	-1.335339000
7	-2.461396000	0.690397000	-0.454294000
8	-4.009379000	2.694709000	0.305073000
7	-5.862742000	1.883865000	-0.776973000
1	-2.200049000	1.088755000	-1.360334000
1	-2.316585000	1.480919000	0.195465000
6	-6.691405000	3.087986000	-0.667680000
1	-6.240996000	1.093393000	-1.282433000
1	-6.153845000	3.812389000	-0.053726000
1	-6.874855000	3.513996000	-1.659870000
1	-7.646735000	2.841016000	-0.193803000
6	3.240468000	-3.050945000	1.245673000
6	4.191316000	4.456792000	1.730358000
6	-4.272158000	-0.418999000	0.822352000

5(a) – Intermediate – ³A

Ettotal (u.a.) = -4570.81251744

29	1.786460000	-0.124338000	-0.207114000
29	-1.058319000	-0.600223000	-0.051603000

8	0.110759000	0.692772000	-0.344767000
8	0.472738000	-1.674925000	-0.059780000
1	0.503428000	-2.127526000	-0.929401000
6	0.706081000	-1.262272000	-3.030317000
1	0.098814000	-1.707189000	-3.811781000
1	1.747599000	-1.559450000	-2.942019000
1	0.361601000	-0.376028000	-2.505013000
6	3.969554000	-2.276188000	0.197419000
6	5.204115000	-2.523192000	-0.343380000
7	3.479599000	-1.097982000	-0.360693000
6	4.409783000	-0.651660000	-1.206524000
7	5.459963000	-1.490058000	-1.222189000
1	3.653029000	-4.060578000	1.330822000
1	2.172736000	-3.116585000	1.006698000
1	5.907834000	-3.323870000	-0.173839000
1	4.345230000	0.256485000	-1.786475000
1	6.295231000	-1.379083000	-1.783036000
6	3.470574000	3.474025000	0.873624000
6	3.497988000	2.104865000	0.809914000
7	2.530320000	3.852304000	-0.071666000
6	2.018435000	2.749398000	-0.653793000
7	2.590960000	1.666039000	-0.140202000
1	4.873475000	3.932040000	2.405199000
1	3.489696000	5.038543000	2.341728000
1	2.275415000	4.807003000	-0.292124000
1	4.100614000	1.413470000	1.380064000
1	1.233203000	2.749383000	-1.393190000
1	3.330453000	-2.567059000	2.227565000
1	4.782638000	5.160315000	1.130245000
7	-2.319471000	-1.974272000	0.396210000
6	-3.658345000	-1.782912000	0.717117000
6	-2.071061000	-3.279103000	0.472942000
6	-4.211754000	-3.008760000	0.972994000
7	-3.195943000	-3.930245000	0.815607000
1	-1.111353000	-3.742685000	0.304387000
1	-5.211113000	-3.296281000	1.263047000
6	-3.861792000	0.533792000	-0.311276000
1	-3.989496000	0.056654000	1.772649000
1	-5.362526000	-0.511652000	0.831656000
1	-3.280075000	-4.931790000	0.942027000
6	-4.548731000	1.903640000	-0.070119000
1	-4.104959000	0.106480000	-1.288822000
7	-2.398780000	0.787904000	-0.251409000
8	-3.966954000	2.722526000	0.638033000
7	-5.765586000	2.053782000	-0.620403000
1	-2.093501000	1.297141000	-1.085156000
1	-2.271494000	1.484040000	0.501460000

6	-6.591112000	3.249938000	-0.428976000
1	-6.125164000	1.321369000	-1.218486000
1	-6.057970000	3.922878000	0.244515000
1	-6.759787000	3.749612000	-1.388666000
1	-7.553697000	2.974031000	0.013662000
6	3.240390000	-3.050998000	1.245664000
6	4.191359000	4.456889000	1.730367000
6	-4.272124000	-0.419042000	0.822352000

5(b) – TS2 – ³A

Etotal (u.a.) = -4570.80044538

29	1.672435000	-0.134404000	-0.205229000
29	-1.134922000	-0.756861000	-0.160209000
8	0.006205000	0.478313000	-0.746146000
8	0.447869000	-1.772880000	0.071997000
1	0.564995000	-2.287021000	0.893101000
6	1.044744000	-2.390357000	-2.159275000
1	0.425618000	-3.269539000	-2.292919000
1	2.103737000	-2.508220000	-1.964566000
1	0.634216000	-1.405350000	-2.354857000
6	4.010950000	-2.120870000	0.368746000
6	5.314911000	-2.225426000	-0.037873000
7	3.473381000	-0.955083000	-0.169016000
6	4.443186000	-0.379892000	-0.880431000
7	5.564740000	-1.119829000	-0.824346000
1	3.885783000	-3.855096000	1.610223000
1	2.406006000	-3.507350000	0.696232000
1	6.067475000	-2.971745000	0.166672000
1	4.358049000	0.555469000	-1.412443000
1	6.441337000	-0.898862000	-1.279863000
6	3.339867000	3.492135000	0.977848000
6	3.371501000	2.127087000	0.868350000
7	2.257537000	3.881840000	0.204536000
6	1.674942000	2.787362000	-0.328100000
7	2.334085000	1.700695000	0.053782000
1	4.971593000	3.916946000	2.274396000
1	3.601065000	5.025143000	2.460488000
1	1.952548000	4.836750000	0.063132000
1	4.060137000	1.429876000	1.320941000
1	0.788595000	2.786486000	-0.943259000
1	2.832962000	-2.525107000	2.119729000
1	4.679701000	5.174066000	1.058286000

7	-2.395425000	-2.073224000	0.468824000
6	-3.716100000	-1.810721000	0.814505000
6	-2.215699000	-3.387777000	0.555513000
6	-4.322725000	-3.001447000	1.114358000
7	-3.360420000	-3.976837000	0.947291000
1	-1.299661000	-3.911638000	0.328011000
1	-5.327688000	-3.233187000	1.433499000
6	-3.995207000	0.342035000	-0.490107000
1	-3.842144000	0.168522000	1.645914000
1	-5.352158000	-0.458951000	0.992128000
1	-3.494052000	-4.970799000	1.089116000
6	-4.609499000	1.761410000	-0.369258000
1	-4.395350000	-0.214579000	-1.342890000
7	-2.534456000	0.528864000	-0.676050000
8	-3.906063000	2.661596000	0.085431000
7	-5.902703000	1.871818000	-0.718904000
1	-2.322053000	0.751983000	-1.651604000
1	-2.305382000	1.403899000	-0.176915000
6	-6.660540000	3.120951000	-0.606131000
1	-6.363909000	1.074924000	-1.137892000
1	-6.884542000	3.523853000	-1.599935000
1	-7.595271000	2.939431000	-0.066593000
1	-6.050193000	3.836899000	-0.053301000
6	3.240435000	-3.050972000	1.245669000
6	4.191289000	4.456811000	1.730357000
6	-4.272098000	-0.418990000	0.822357000

5(c) – Methanol-Complex -³A

Etotal (u.a.) = -4570.88740421

29	1.724797000	-0.270891000	-0.014986000
29	-1.455799000	-1.523670000	-0.332554000
8	0.134942000	-0.689714000	-0.583616000
8	-0.488017000	-3.299371000	-0.028718000
1	-0.977398000	-4.093152000	0.238684000
6	0.613314000	-3.654763000	-0.906155000
1	0.238860000	-4.026197000	-1.867076000
1	1.239083000	-4.407934000	-0.420837000
1	1.160812000	-2.723504000	-1.042770000
6	4.021383000	-2.211245000	0.282691000
6	5.279836000	-2.404596000	-0.225989000
7	3.526717000	-1.011565000	-0.217931000
6	4.469833000	-0.500779000	-1.006642000
7	5.541363000	-1.316517000	-1.032229000

1	3.352542000	-4.118362000	1.028323000
1	2.177602000	-2.786688000	1.183158000
1	5.996935000	-3.198455000	-0.082022000
1	4.400677000	0.424843000	-1.558998000
1	6.389839000	-1.160170000	-1.561510000
6	3.221588000	3.367245000	1.384414000
6	3.389408000	2.070528000	0.969695000
7	1.846690000	3.539209000	1.426775000
6	1.239136000	2.393407000	1.047034000
7	2.154594000	1.473968000	0.758287000
1	5.215150000	4.084200000	1.634974000
1	4.051454000	4.804662000	2.761592000
1	1.370422000	4.388561000	1.701939000
1	4.309553000	1.526676000	0.821535000
1	0.165386000	2.268382000	1.003695000
1	3.566314000	-2.883231000	2.279914000
1	4.077594000	5.318611000	1.060574000
7	-3.217374000	-2.409802000	-0.287024000
6	-4.362815000	-1.745317000	0.136493000
6	-3.616204000	-3.552565000	-0.835084000
6	-5.452993000	-2.518368000	-0.163573000
7	-4.959225000	-3.652131000	-0.774274000
1	-2.979680000	-4.297331000	-1.290265000
1	-6.508507000	-2.372100000	0.009570000
6	-3.648685000	0.695402000	-0.063617000
1	-3.654626000	-0.519383000	1.725980000
1	-5.266290000	-0.104048000	1.152157000
1	-5.510754000	-4.428947000	-1.117965000
6	-3.358155000	1.951660000	0.799878000
1	-4.354724000	0.944921000	-0.862758000
7	-2.357488000	0.275237000	-0.662345000
8	-2.191159000	2.274621000	1.039497000
7	-4.439992000	2.590884000	1.273735000
1	-2.380230000	0.402400000	-1.674272000
1	-1.643161000	0.928671000	-0.314469000
6	-4.365174000	3.783147000	2.120416000
1	-5.354003000	2.295784000	0.956811000
1	-4.525449000	4.691930000	1.528969000
1	-5.125811000	3.719317000	2.903526000
1	-3.373091000	3.817326000	2.573504000
6	3.240443000	-3.050992000	1.245668000
6	4.191340000	4.456855000	1.730364000
6	-4.272158000	-0.419015000	0.822351000

3. Basis set definitions (BSII) used in CCSD(T)-F12 calculations

BSII:

Cu: cc-pwCVTZ, O: cc-pVTZ, N, cc-pVTZ, H: cc-pVTZ

Density-fitting set:

Cu: aug-cc-pVTZ/mp2fit

O: aug-cc-pVTZ/mp2fit

N: aug-cc-pVTZ/mp2fit

H: aug-cc-pVTZ/mp2fit

Coulomb/exchange fitting set:

Cu: def2-tzvpp/jkfit

O: aug-cc-pVTZ/jkfit

N: aug-cc-pVTZ/jkfit

H: aug-cc-pVTZ/jkfit

Resolution of the identity basis for F12:

Cu: def2-tzvpp/jkfit

O: aug-cc-pVTZ/optri

N: aug-cc-pVTZ/optri

H: aug-cc-pVTZ/optri

4. B3LYP/BS1 optimized structures for models used in CCSD(T)-F12 calculations.**(1)-D3h**

29	0.000000000	0.000000000	0.000000000
1	0.000000000	0.941614000	2.310524000
1	-0.815462000	-0.470807000	2.310524000
1	0.815462000	-0.470807000	2.310524000
1	-0.815462000	-0.470807000	-2.310524000
1	0.000000000	0.941614000	-2.310524000
1	0.815462000	-0.470807000	-2.310524000
7	0.000000000	0.000000000	1.904068000
7	0.000000000	0.000000000	-1.904068000

(2)-D2h-Singlet

8	0.000000000	0.732750000	0.000000000
8	0.000000000	-0.732750000	0.000000000
29	-1.727519000	0.000000000	0.000000000
29	1.727519000	0.000000000	0.000000000
1	3.584333000	1.610597000	0.814355000
1	3.584333000	1.610597000	-0.814355000
1	2.456168000	2.454937000	0.000000000
1	2.456168000	-2.454937000	0.000000000
1	3.584333000	-1.610597000	-0.814355000
1	3.584333000	-1.610597000	0.814355000
1	-3.584333000	-1.610597000	0.814355000
1	-3.584333000	-1.610597000	-0.814355000
1	-2.456168000	-2.454937000	0.000000000
1	-3.584333000	1.610597000	-0.814355000
1	-3.584333000	1.610597000	0.814355000
1	-2.456168000	2.454937000	0.000000000
7	2.963086000	1.564279000	0.000000000
7	2.963086000	-1.564279000	0.000000000
7	-2.963086000	-1.564279000	0.000000000
7	-2.963086000	1.564279000	0.000000000

(2)-D2h-Triplet

8	0.000000000	0.768059000	0.000000000
8	0.000000000	-0.768059000	0.000000000
29	-1.752990000	0.000000000	0.000000000
29	1.752990000	0.000000000	0.000000000
1	3.651454000	1.575221000	0.815633000
1	3.651454000	1.575221000	-0.815633000
1	2.517578000	2.416864000	0.000000000
1	2.517578000	-2.416864000	0.000000000
1	3.651454000	-1.575221000	-0.815633000
1	3.651454000	-1.575221000	0.815633000
1	-3.651454000	-1.575221000	0.815633000
1	-3.651454000	-1.575221000	-0.815633000
1	-2.517578000	-2.416864000	0.000000000
1	-3.651454000	1.575221000	-0.815633000
1	-3.651454000	1.575221000	0.815633000
1	-2.517578000	2.416864000	0.000000000
7	3.031635000	1.529370000	0.000000000
7	3.031635000	-1.529370000	0.000000000
7	-3.031635000	-1.529370000	0.000000000
7	-3.031635000	1.529370000	0.000000000

(3)-D2h-Singlet

8	0.000000000	1.112860000	0.000000000
8	0.000000000	-1.112860000	0.000000000
29	-1.389652000	0.000000000	0.000000000
29	1.389652000	0.000000000	0.000000000
1	3.302069000	1.518199000	0.819746000
1	3.302069000	1.518199000	-0.819746000
1	2.150279000	2.350176000	0.000000000
1	2.150279000	-2.350176000	0.000000000
1	3.302069000	-1.518199000	-0.819746000
1	3.302069000	-1.518199000	0.819746000
1	-3.302069000	-1.518199000	0.819746000
1	-3.302069000	-1.518199000	-0.819746000
1	-2.150279000	-2.350176000	0.000000000
1	-3.302069000	1.518199000	-0.819746000
1	-3.302069000	1.518199000	0.819746000
1	-2.150279000	2.350176000	0.000000000
7	2.686611000	1.474688000	0.000000000
7	2.686611000	-1.474688000	0.000000000
7	-2.686611000	-1.474688000	0.000000000
7	-2.686611000	1.474688000	0.000000000

(3)-D2h-Triplet

8	0.000000000	1.126844000	0.000000000
8	0.000000000	-1.126844000	0.000000000
29	-1.438140000	0.000000000	0.000000000
29	1.438140000	0.000000000	0.000000000
1	3.347726000	1.544957000	0.818241000
1	3.347726000	1.544957000	-0.818241000
1	2.202991000	2.382679000	0.000000000
1	2.202991000	-2.382679000	0.000000000
1	3.347726000	-1.544957000	-0.818241000
1	3.347726000	-1.544957000	0.818241000
1	-3.347726000	-1.544957000	0.818241000
1	-3.347726000	-1.544957000	-0.818241000
1	-2.202991000	-2.382679000	0.000000000
1	-3.347726000	1.544957000	-0.818241000
1	-3.347726000	1.544957000	0.818241000
1	-2.202991000	2.382679000	0.000000000
7	2.731007000	1.503466000	0.000000000
7	2.731007000	-1.503466000	0.000000000
7	-2.731007000	-1.503466000	0.000000000
7	-2.731007000	1.503466000	0.000000000