Supporting Information

for

Effects of Thioether Substituents on the O_2 Reactivity of β-Diketiminate-Cu(I) Complexes: Probing the Role of the Methionine Ligand in Copper Monooxygenases

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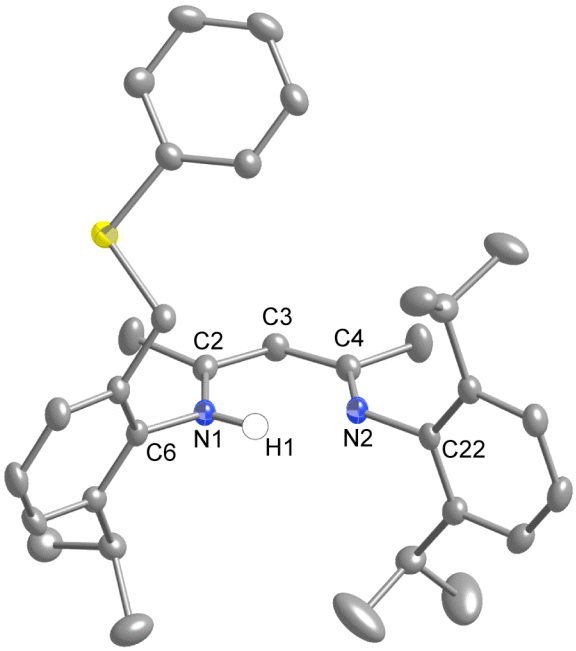

Figure S1. X-ray structure of the ligand precursor $Me_2L^{iPr,SPh}H$, with all atoms shown as 50% ellipsoids and hydrogen atoms (except for H1) omitted for clarity. Selected bond distances (Å): C2-N1, 1.310(3); C4-N2, 1.331(3); C2-C3, 1.417(3); N1-C6, 1.422(3); N2-C22, 1.432(3); C4-C3, 1.384(3).

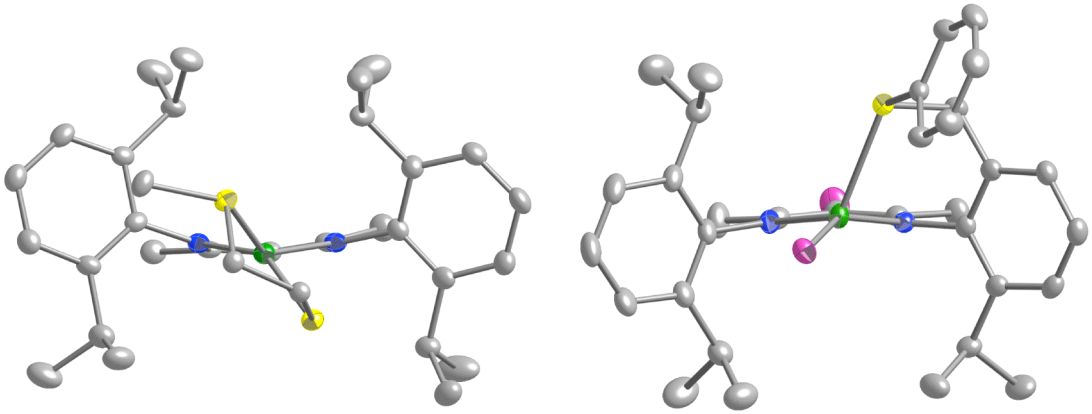

Figure S2. Comparison of the X-ray structures of $Me_2L^{iPr,SPh}CuCl$ (right) with $Me_2L^{iPr2}Cu(SCPh_2CH_2SMe)$ (left, from Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc.* **2000**, *122*, 6331) viewed approximately along the Cu-C(backbone) vector reveals gross similarities between their distorted tetrahedral geometries, but also specific differences, particularly the disposition of their respective thiolate, chloride, and thioether donors with respect to the N-Cu-N plane. Atom colors: C, gray; N, blue; S, yellow; Cu, green; Cl, pink.

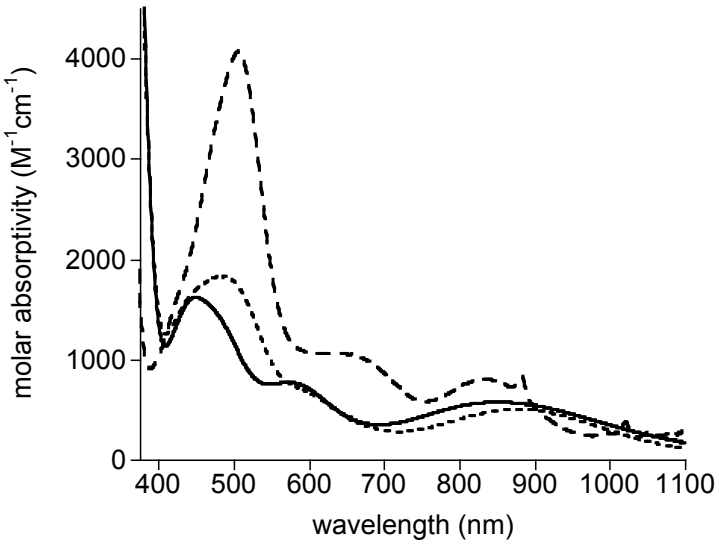

Figure S3. UV-vis absorption spectra of solutions of $Me_2L^{iPr,SX}CuCl$ (X = Me, solid line; X = Ph, dotted line) and $Me_2L^{iPr2}CuCl$ (dashed line, from Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc.* **1999**, *121*, 7270) in CH_2Cl_2.

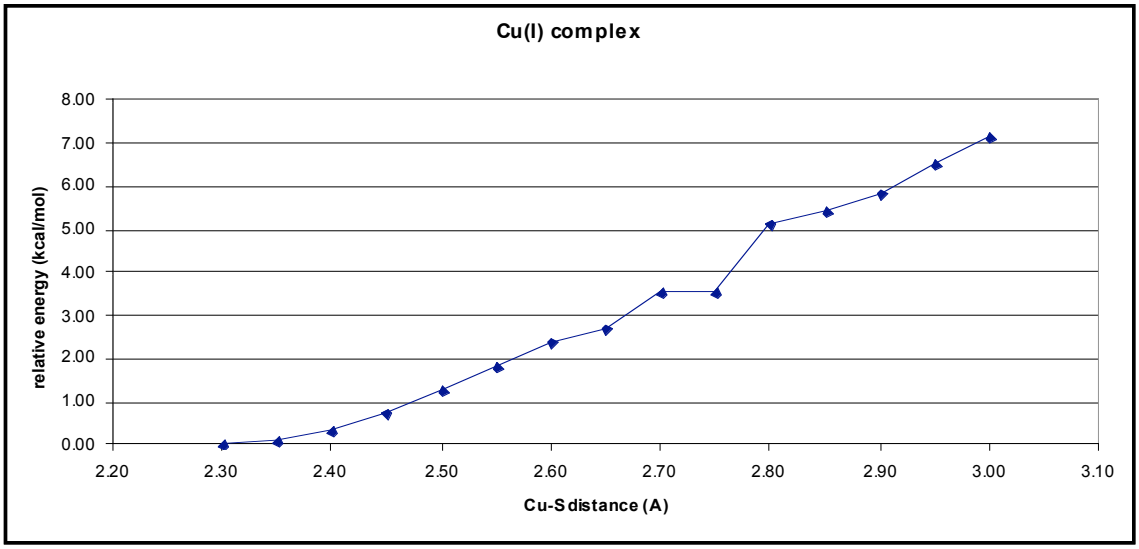

Figure S4. Plot of the calculated electronic energy (kcal/mol) versus the Cu–S distance (Å) in $Me_2L^{iPr,SMe}Cu$. Energies are relative to the minimum energy structure, where the Cu–S bond length is 2.301 Å.

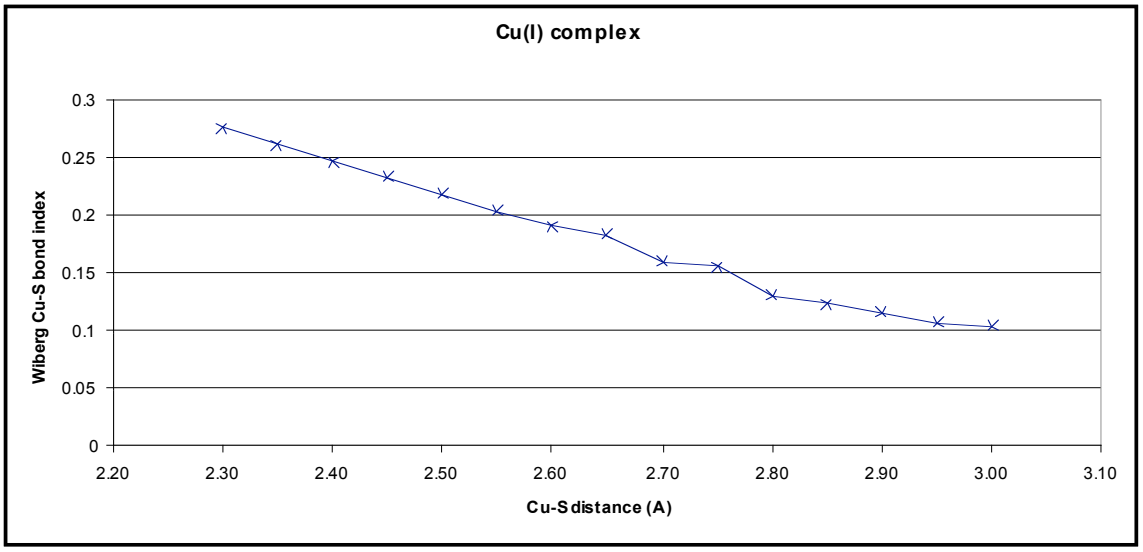

Figure S5. Plot of the Cu–S Wiberg bond index versus the Cu–S distance (Å) in $Me_2L^{iPr,SMe}Cu$. The calculated minimum energy structure for $Me_2L^{iPr,SMe}Cu$ corresponds to a Cu–S bond length of 2.301 Å.

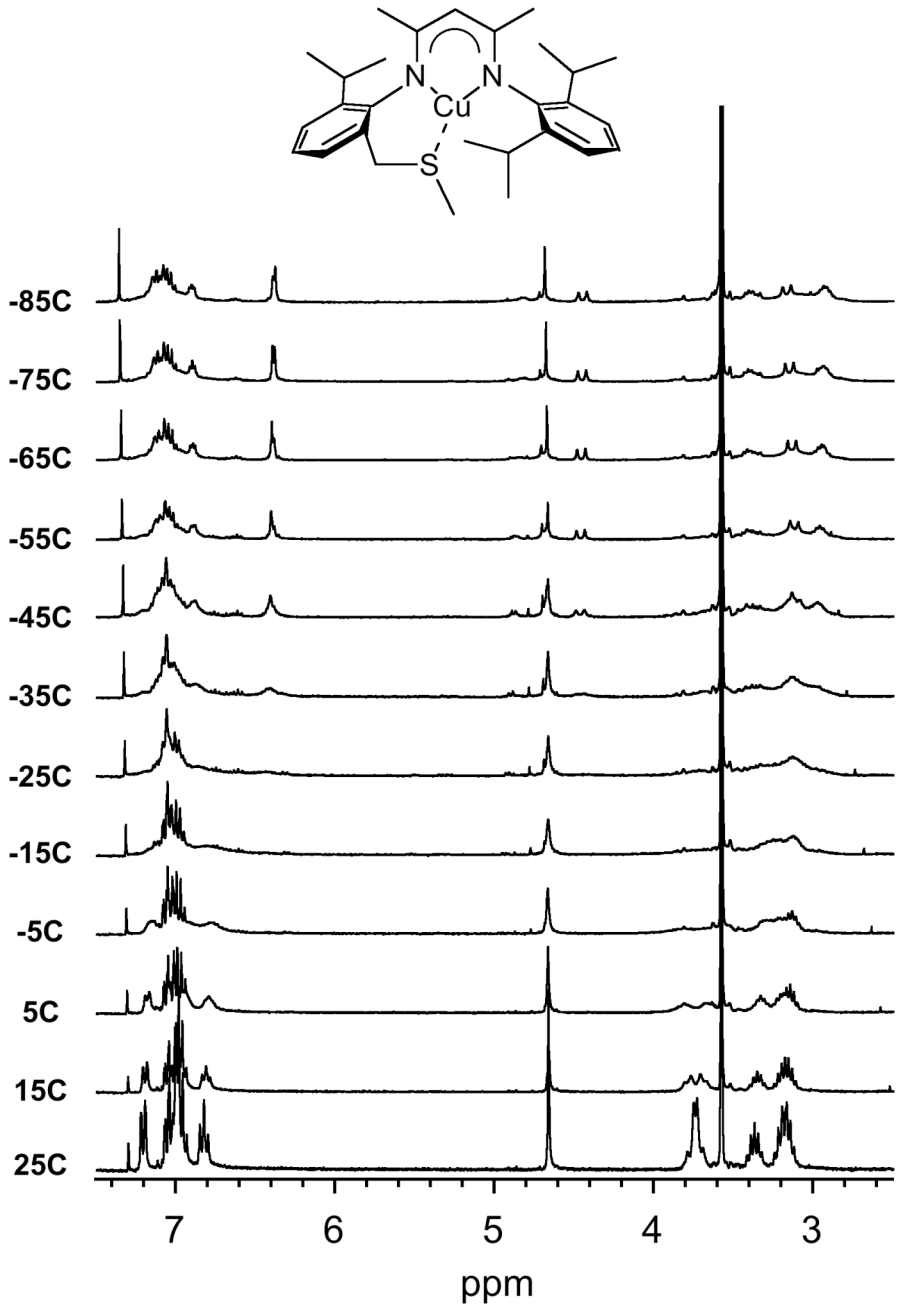

Figure S6. VT-^{1}H NMR data for $Me_2L^{iPr,SMe}Cu$ in THF-d_8. The methyl region (1-2 ppm) is omitted for clarity.

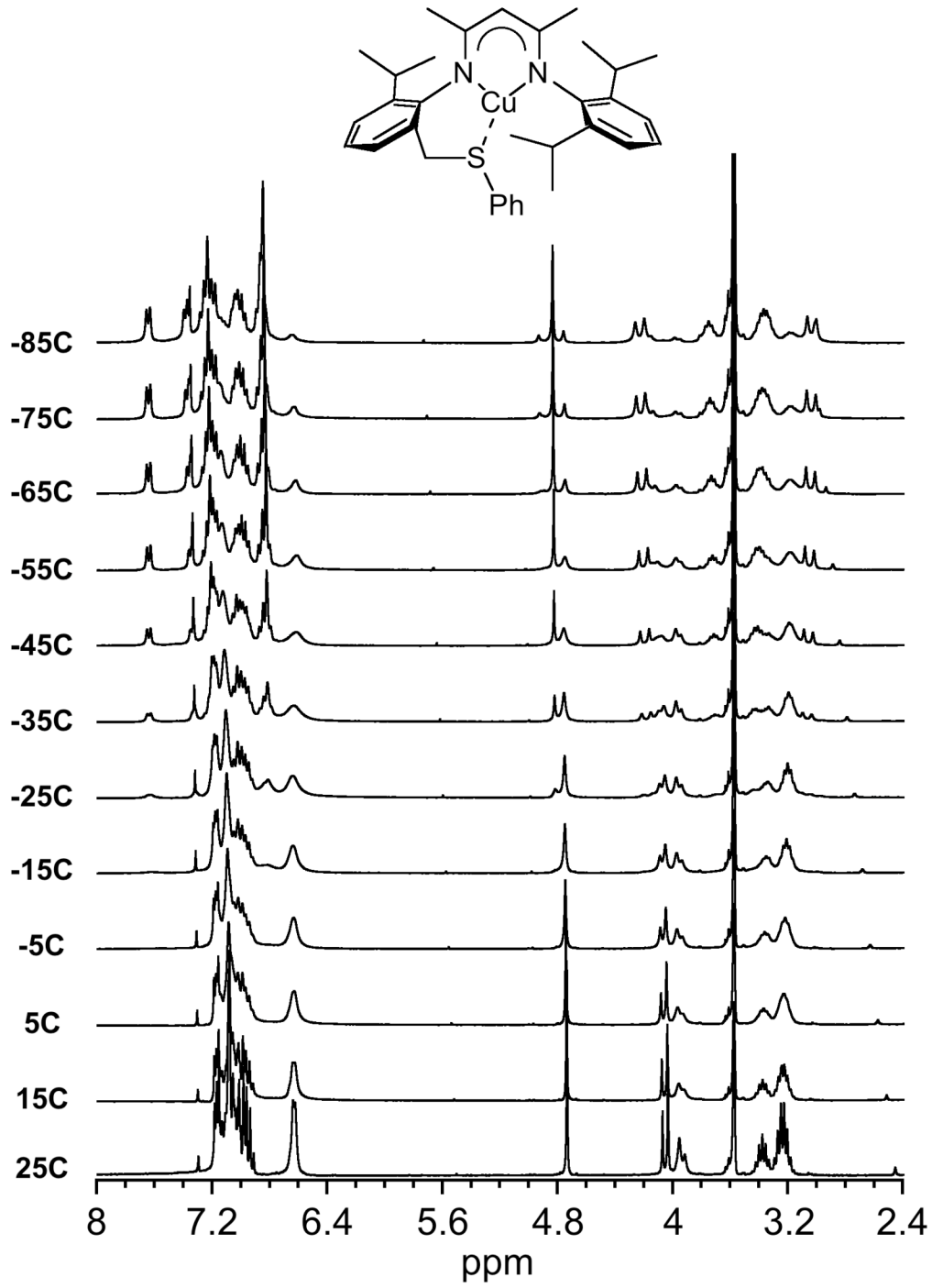

Figure S7. VT-^{1}H NMR data for $Me_2L^{iPr,SPh}Cu$ in THF-d_8.

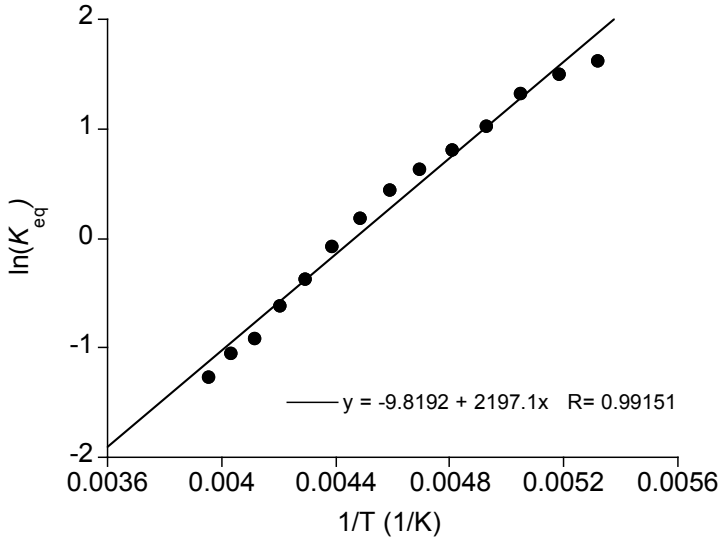

Figure S8. Van't Hoff plot for the equilibrium between species *A* and *B* (see text), determined by integration of the VT-^{1}H NMR spectra of $Me_2L^{iPr,SPh}Cu$ in THF-d_8.

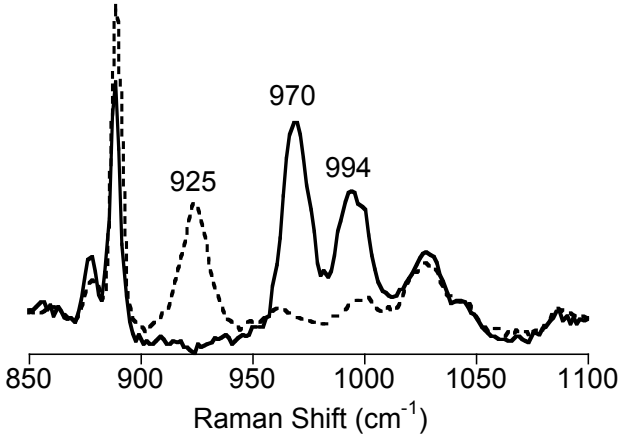

Figure S9. Resonance Raman spectra with O-isotope sensitive peaks labeled of frozen solutions (77K) of the product of the reaction of $Me_2L^{iPr,SPh}Cu$ in CH_2Cl_2 with $^{16}O_2$ (solid line) or $^{18}O_2$ (dashed line), using λ_{ex} = 406.7 nm.

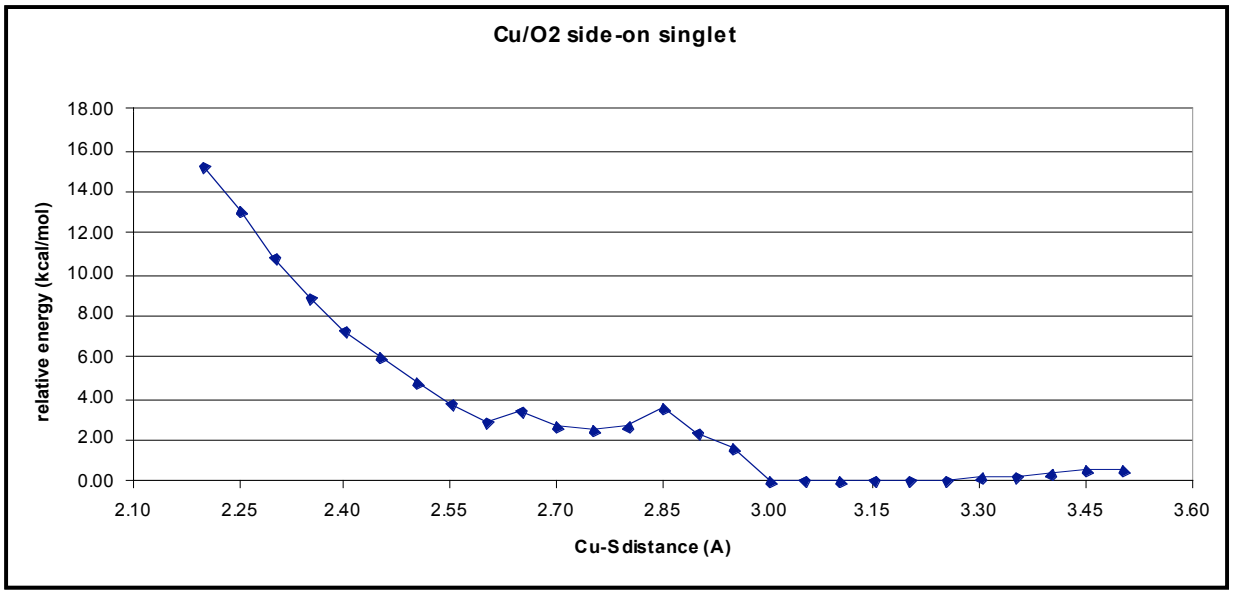

Figure S10. Plot of DFT electronic energy (kcal/mol) versus the Cu–S distance (Å) in the singlet side-on $Me_2L^{iPr,SMe}CuO_2$. Energies are relative to the minimum energy structure, where the Cu–S bond length is 3.033 Å.

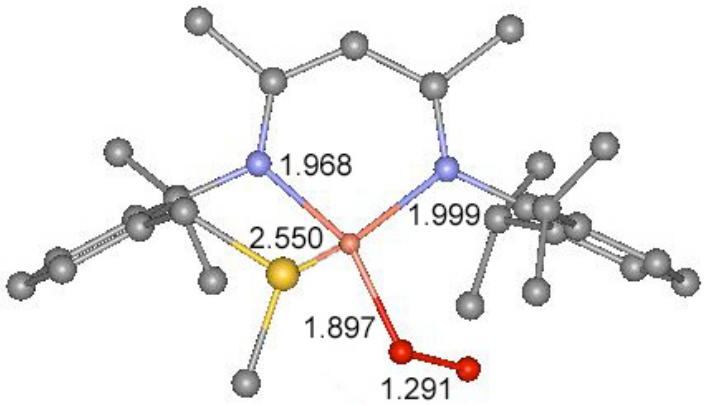

Figure S11. Minimum energy structure calculated using DFT of the singlet end-on $Me_2L^{iPr,SMe}CuO_2$ adduct. Hydrogen atoms are omitted for clarity. Pink is Cu; gray, C; blue, N; yellow, S. Distances have units of Å.

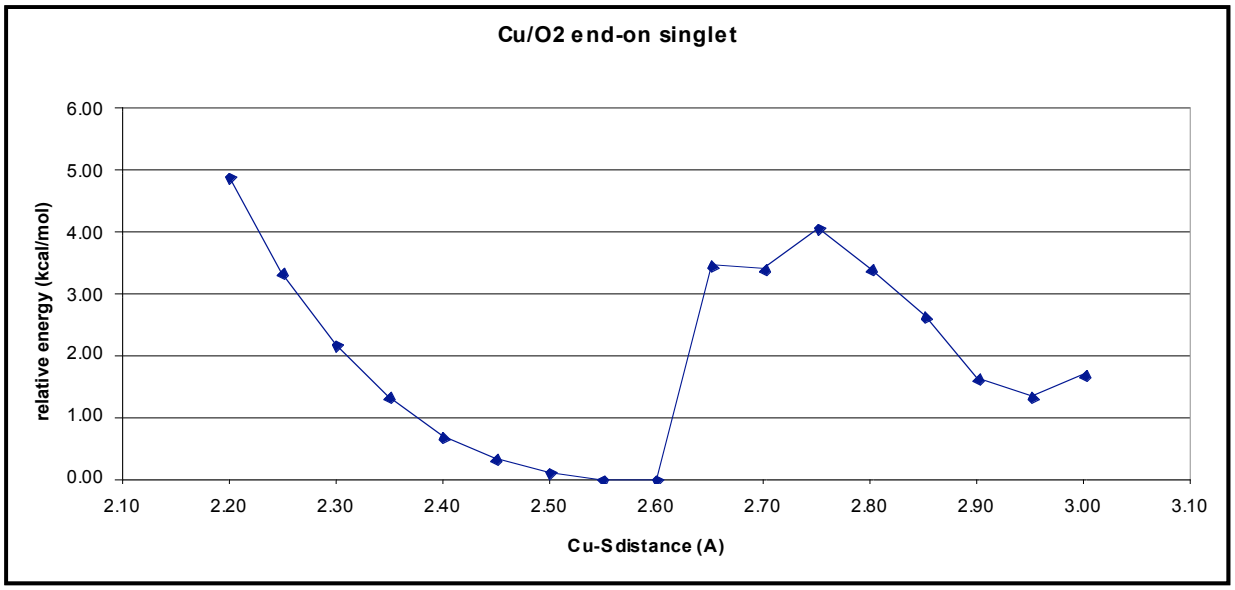

Figure S12. Plot of the DFT electronic energy (kcal/mol) versus the Cu–S distance (Å) in the singlet end-on $Me_2L^{iPr,SMe}CuO_2$. Energies are relative to the minimum energy structure, where the Cu–S bond length is 2.550 Å.

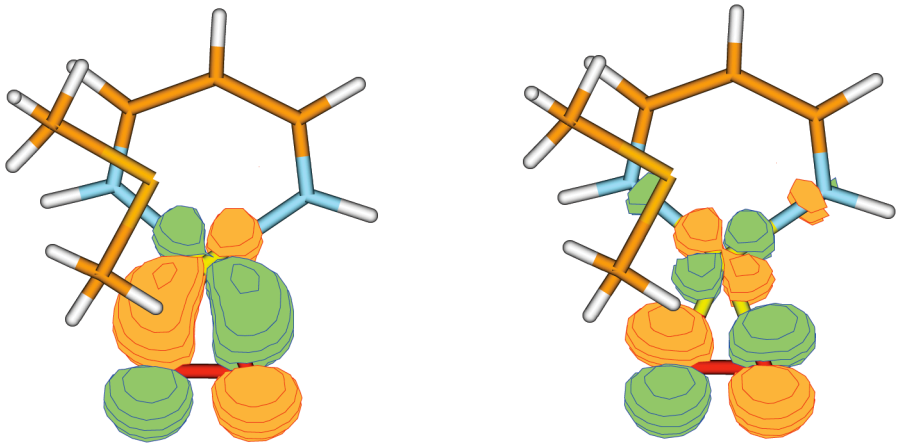

Figure S13. Principle partially occupied orbitals in the CASSCF wave function for the side-on singlet $Me_2L^{iPr,SMe}CuO_2$. Occupation numbers are shown in parentheses. Orange represents C, blue N, red O, orange S, white H, and yellow Cu.

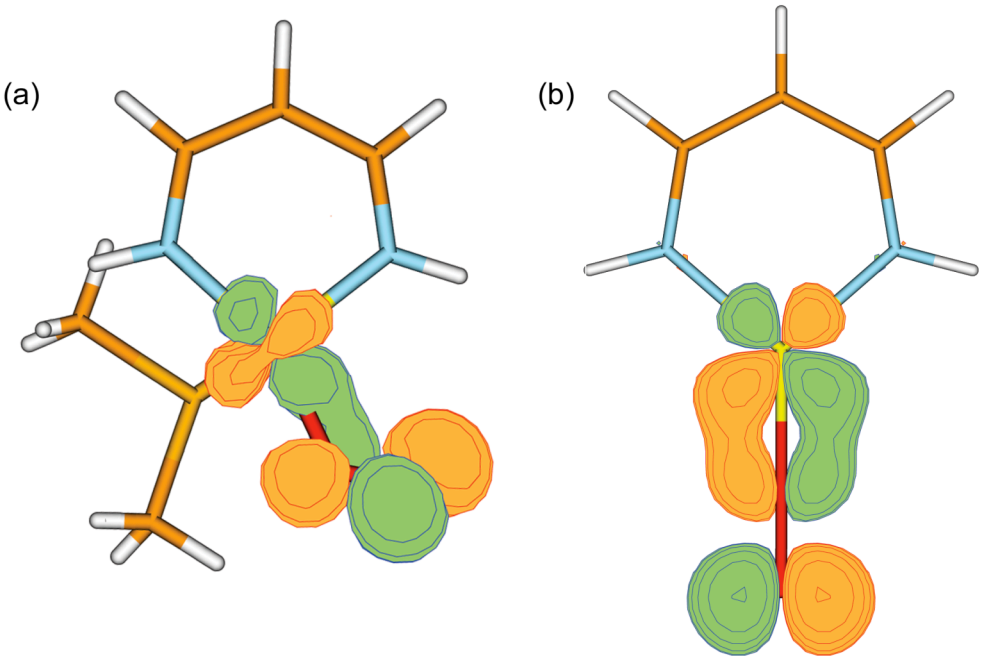

Figure S14. Cu/O_2 bonding molecular orbital in the η^1 isomers of the Cu-O_2 adducts supported by (a) $(Me_2L^{iPr,SMe})^-$ and (b) $(Me_2L^{iPr2})^-$. Orange represents C, blue N, red O, orange S, white H, and yellow Cu.

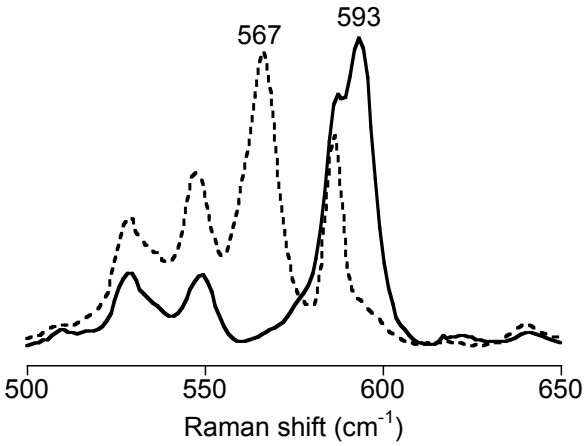

Figure S15. Resonance Raman spectra with O-isotope sensitive peaks labeled of frozen solutions (77K) of the species resulting from vigorous argon purging of the oxygenation product $Me_2L^{iPr,SPh}CuO_2$ obtained using $^{16}O_2$ (solid line) or $^{18}O_2$ (dashed line), with λ_{ex} = 457.9 nm.

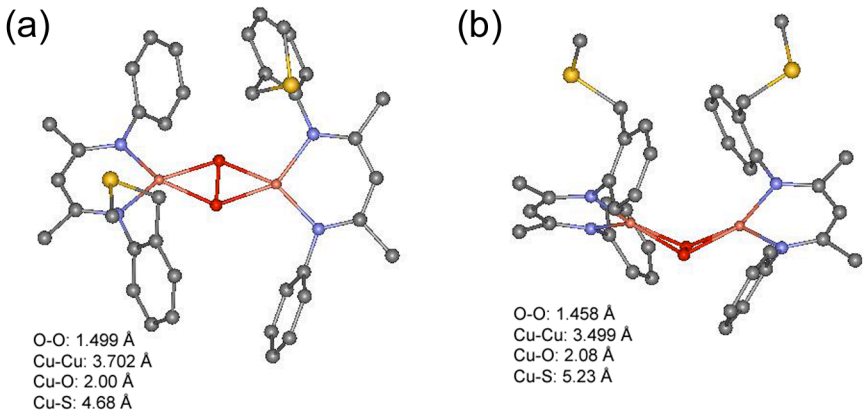

Figure S16. Minimum energy structures calculated using DFT of the (a) singlet and (b) triplet $[(Me_2L^{H,SMe}Cu)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)]$. Hydrogen atoms are omitted for clarity. Pink is Cu; gray, C; blue, N; yellow, S. Distances have units of Å.

Atomic Coordinates for Computed Structures.

1) $Me_2L^{iPr,SMe}Cu$ (B3LYP/DZP level)

Cu	.1027460774	.7618268588	-.9459867221
N	.0309504609	2.0865616172	.5993614070
N	-1.5530380467	-.2121041323	-.6377902849
S	1.6440653921	1.7926477454	-2.3083351647
C	-1.3803907867	3.5645975761	1.9902574129
C	2.9869734810	3.1400208981	2.6225188062
C	1.7541819791	2.5506404728	2.3217400418
C	1.0908604891	1.6517506917	3.3631683838
C	.9891101973	2.3039440896	4.7530153524
C	1.8391381923	.3060697971	3.4504624475
C	1.5619883444	3.4401426511	-1.3986573160
C	3.3348845571	1.2225492060	-1.9045563874
C	-1.7763412946	-1.4701419536	-1.2802656778
C	-2.3251843544	-1.5191329958	-2.5821928190
C	-2.4599998656	-2.7645900060	-3.2064996926
C	-1.1736845443	2.3403017116	1.1113900306
C	-2.0691164927	-3.9402367857	-2.5733463984
C	-1.5136632204	-3.8786550650	-1.2976423336
C	-1.3517529429	-2.6579569106	-.6353899578
C	-2.7162313989	-.2489528545	-3.3304774163
C	-1.6796633560	.0749231452	-4.4247155394
C	-4.1330329058	-.3184105909	-3.9254656573
C	-.6394058358	-2.5947785839	.7117992458
C	.8836006680	-2.4996742286	.4868242599
C	-.9780385945	-3.7598844197	1.6539519687
C	-2.3119454380	1.5391363950	.8817821219
C	-2.4696652660	.3264519127	.1651801381
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C	2.0043421365	3.3765741060	.0297075994
C	3.2380970540	3.9386204693	.3755602695
C	3.7252144638	3.8461670581	1.6747382178
H	3.3915958998	3.0260593356	3.6241491334
H	-1.1948946106	-4.7960217659	-.8122045701
H	-2.1885192785	-4.8975886486	-3.0723942215
H	-2.8775062039	-2.8139132734	-4.2082393900
H	.5086795248	3.7073439247	-1.5082035258
H	2.1684991068	4.1453598690	-1.9715305710
H	4.6764206270	4.2961561917	1.9410294316
H	-1.0982106406	3.3696418016	3.0293899377
H	-.7670992396	4.3995861423	1.6401019986
H	.0770389325	1.4242976232	3.0280443001
H	-2.4285829238	3.8695463097	1.9831027089
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H	3.8152091926	4.4546753553	-.3879789557
H	-.9477415711	-1.6707357816	1.2084919618
H	1.4164528165	-2.3918666485	1.4383144933
H	1.1313495586	-1.6377338250	-.1435168939
H	1.2579382555	-3.3990410627	-.0149354550
H	-.5275138448	-3.5903085585	2.6375910109
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H	-2.0591882533	-3.8646106912	1.7897124683
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H	-4.8797949358	-.5473146385	-3.1584154812
H	-4.2110168391	-1.0851541708	-4.7035981467
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H	.4899339386	3.2769513599	4.7093401737
H	1.9755047075	2.4597002849	5.2026348174
H	1.3416684682	-.3675241551	4.1573065426
H	2.8711929178	.4489090448	3.7893051648
H	1.8700561843	-.1873667310	2.4746851043
H	4.0711880445	1.8594018788	-2.3990210087
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H	-3.6533302518	-1.3652098832	.8039321745

2) $Me_2L^{iPr,SMe}CuO_2$ side-on singlet (B3LYP/DZP level)

Cu	.4022244665	.5147144384	-.5736879136
O	2.2417723527	.1377891049	-.7457788501
O	1.4783591920	-.7869333486	-1.3754719669
N	.1505491712	2.0589907868	.5602020212
N	-1.4299691904	-.0309710786	-.7469178692
S	.7436716637	2.7128017461	-2.6361492454
C	2.8875714865	.4144130046	2.7946890818
C	.7573256140	4.0848994851	-1.3946068153
C	2.5219212988	2.5619003135	-3.0174367736
C	-1.6571377606	-1.2669202815	-1.4406254778
C	-1.9172065310	-1.2532071128	-2.8287790181
C	-2.1188587041	-2.4766200272	-3.4773480680
C	-1.0612855565	2.4611677546	.9427813646
C	-2.0431561439	-3.6819629030	-2.7873792801
C	-1.7457297802	-3.6800778657	-1.4272362744
C	-1.5414520315	-2.4847856148	-.7301009679
C	-1.9256362430	.0389960886	-3.6376147935
C	-.7417919356	.0587922517	-4.6237929671
C	-3.2579557067	.2687188106	-4.3733080420
C	-1.1637331316	-2.5279384857	.7479705755
C	.2409851116	-3.1365946373	.9339515655
C	-2.2045314821	-3.2734419845	1.6015911747
C	-2.2497546202	1.7798087051	.6357167540
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C	-3.8313564815	.0783010090	-.2632634412
C	1.3078314824	2.8698388355	.7771790963
C	1.6247566215	3.8586839074	-.1837184708
C	2.7741567818	4.6325842280	-.0098931484
C	3.6051528097	4.4352628366	1.0908375676
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C	2.1507178260	2.6466995926	1.8852667106
C	1.8595642480	1.5565510916	2.9092398061
C	1.7975242705	2.1065323084	4.3452551691

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H	-.2980578155	4.1921981520	-1.1286962671
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H	-.7872405772	4.5889325257	1.2620020385
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H	1.0566870795	2.9074240700	4.4404356552
H	2.7637850757	2.5098708780	4.6664734815
H	2.6443499184	-.3903813331	3.4972242980
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H	2.9285774777	3.5145436776	-3.3664232111
H	2.5988635843	1.8249619838	-3.8190957908
H	3.0680858218	2.1938844325	-2.1486052093
H	-4.5335605064	.6962129414	.2972790263
H	-3.8926607863	-.9491806931	.1058153577

3) $Me_2L^{iPr,SMe}CuO_2$ side-on triplet (B3LYP/DZP level)

Cu	.3412540095	.7822815929	-.9110819842
O	2.3591278879	-.3146366257	-1.2323841281
O	1.2945007285	-.6717663833	-1.8745087366
N	.1435528494	2.1626448946	.4754812756
N	-1.4839757972	-.0169542652	-.7507884525
S	1.0090661565	2.7188862702	-2.6338341170
C	2.5896811336	.3066351614	2.7180716571
C	.9975597443	4.1211144764	-1.4131382952
C	2.8034078759	2.5379111847	-2.9324831976
C	-1.7111113995	-1.2763833575	-1.3898438285
C	-1.9697282752	-1.3048014320	-2.7815169503
C	-2.1309081519	-2.5452588559	-3.4073035670
C	-1.0538247344	2.4782307145	.9769883034

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C	.2690051718	-2.9050148192	1.0096306907
C	-2.1282999292	-3.3578965780	1.6866268151
C	-2.2359781842	1.7669017145	.7127346664
C	-2.4279087429	.5817391186	-.0358606795
C	-3.8187170153	-.0250104985	.0138389733
C	1.3136091296	2.9111759830	.7915501928
C	1.7673031042	3.8698260104	-.1448433604
C	2.9486386634	4.5739438293	.1048501152
C	3.6827636109	4.3362246609	1.2652208577
C	-1.1739497543	3.6772870727	1.9013115680
C	3.2442557879	3.3718578249	2.1684106237
C	2.0705014536	2.6389401044	1.9529468038
C	1.6748719733	1.5310804628	2.9182114889
C	1.6822257693	1.9846819743	4.3874987536
H	3.8333791184	3.1734456386	3.0593876311
H	-1.6557015831	-4.6240580435	-.7738326741
H	-2.1588379847	-4.6873207271	-3.1921483980
H	-2.3324451020	-2.5789837059	-4.4744157991
H	-.0686446931	4.2694540084	-1.2228666150
H	1.3766266024	5.0105652956	-1.9239709035
H	4.5944351168	4.8931970320	1.4588390216
H	-.6795686118	3.4819675277	2.8583391516
H	-.6884628698	4.5585276972	1.4716510546
H	.6574590366	1.2196228739	2.6666837775
H	-2.2200646795	3.9133746887	2.1000198395
H	-4.1448676691	-.3483246375	-.9781795983
H	-1.9165239251	.8176750042	-2.9225137771
H	-3.1246394987	2.1555829406	1.1930685454
H	3.2883508774	5.3158637377	-.6134250182
H	-1.2862725840	-1.4561446968	1.2007235664
H	.5617381621	-2.8474358948	2.0646081635
H	.9398834462	-2.2649510953	.4312927804
H	.4216041441	-3.9358858408	.6712257689
H	-1.8674360276	-3.2601726263	2.7458621924
H	-2.0419054796	-4.4181833948	1.4266284660
H	-3.1789820325	-3.0728903964	1.5678679038
H	-.9312468683	1.0077744159	-5.1659546522
H	-.9995956907	-.7485556057	-5.3888352458
H	.0602049099	-.0619186784	-4.1466924521
H	-3.4624209580	1.0921068180	-4.8363826494
H	-4.2306851871	.1469096597	-3.5499900989
H	-3.6179798388	-.6625951333	-4.9973638304
H	1.3171492017	1.1788451979	5.0325890900
H	1.0423517830	2.8592131581	4.5443116085
H	2.6894927933	2.2453448988	4.7305458842
H	2.2774484652	-.5163236567	3.3700566176
H	3.6307558838	.5513869431	2.9574441341
H	2.5569573241	-.0455912296	1.6827468447
H	3.2088693722	3.4435827025	-3.3903633704
H	2.9141689147	1.7026852510	-3.6250693644

H	3.3325239106	2.3085132380	-2.0071186723
H	-4.5406440140	.6896263583	.4121455645
H	-3.8281119016	-.9124244957	.6556001904

4) $Me_2L^{iPr,SMe}CuO_2$ end-on singlet (B3LYP/DZP level)

Cu	.3540714209	.9228562421	-.9885675864
O	1.3346510299	-.2840227922	-2.0744028616
O	1.0716915507	-1.5480225589	-2.0512580035
N	.1212296406	2.2318255412	.4625877565
N	-1.3991144238	-.0124172586	-.7729496418
S	1.0763981008	2.7661550587	-2.5961549008
C	2.4142539100	.2199521271	2.7584680670
C	1.1116462580	4.1673024412	-1.3716325246
C	2.8473674886	2.4073346526	-2.8503347823
C	-1.5598176215	-1.2761927021	-1.3881147188
C	-1.8514343940	-1.3507164378	-2.7757894477
C	-2.0198760280	-2.6101060565	-3.3565042090
C	-1.0681684814	2.4841849242	1.0002066934
C	-1.8686435242	-3.7753475788	-2.6108702840
C	-1.5190332993	-3.6955947975	-1.2654646438
C	-1.3428387596	-2.4629338052	-.6333687843
C	-1.9807273733	-.0981965910	-3.6342608301
C	-.8881592016	-.0546413829	-4.7208917194
C	-3.3806389712	.0344009420	-4.2604537322
C	-.8794675993	-2.4198346554	.8194782882
C	.5642336467	-2.9462333079	.9409431466
C	-1.8199312128	-3.1860938948	1.7659311950
C	-2.2263954053	1.7403649739	.7055274874
C	-2.3653833656	.5597582697	-.0569085271
C	-3.7377506519	-.0920656949	-.0309427802
C	1.3091298335	2.9173763165	.8240049289
C	1.8375905227	3.8616517428	-.0923875311
C	3.0565129809	4.4878445243	.1814342952
C	3.7590803591	4.1905330145	1.3475240784
C	-1.2132197153	3.6211922768	1.9955299687
C	3.2474521478	3.2442858557	2.2307265620
C	2.0326192388	2.5873642811	1.9927804226
C	1.5617909267	1.4912831390	2.9424279380
C	1.5535459367	1.9378218156	4.4145536694
H	3.8127193041	2.9990670462	3.1251851037
H	-1.3626384199	-4.6094612724	-.6999128945
H	-2.0000979003	-4.7445628522	-3.0832909038
H	-2.2601000056	-2.6790421658	-4.4134901393
H	.0489012219	4.3592860513	-1.2053147198
H	1.5455509941	5.0370524042	-1.8706268152
H	4.7034095012	4.6825339850	1.5594019888
H	-.8667079505	3.3117165326	2.9878768893
H	-.6130576091	4.4864633309	1.7015374503
H	.5358411452	1.2308280528	2.6691018670
H	-2.2570373981	3.9267121616	2.0862597387
H	-4.0834616477	-.3102723322	-1.0450719738
H	-1.8291531708	.7665689364	-2.9820220462
H	-3.1310083729	2.0842106311	1.1906201858
H	3.4499292930	5.2167166975	-.5227316881

H	-.8700264781	-1.3728274735	1.1340466083
H	.9350317267	-2.8107230754	1.9635102213
H	1.2218723718	-2.4213711967	.2442586887
H	.6143636343	-4.0152326090	.7062181014
H	-1.4783950015	-3.0854924746	2.8018464828
H	-1.8446768813	-4.2554314193	1.5306681438
H	-2.8472760212	-2.8113602684	1.7131411399
H	-.9642229840	.8748809888	-5.2964517404
H	-.9910002580	-.8909443852	-5.4212516197
H	.1069602602	-.1079870015	-4.2737696531
H	-3.4546930118	.9663355320	-4.8314242075
H	-4.1656643548	.0426892783	-3.4972984208
H	-3.5927984624	-.7921457933	-4.9471332386
H	1.1278094021	1.1511356469	5.0460318657
H	.9602529936	2.8468282515	4.5571410236
H	2.5643003075	2.1403562975	4.7842530683
H	2.0506834046	-.5844869968	3.4071700359
H	3.4634261711	.4087940139	3.0116589679
H	2.3758900906	-.1350326351	1.7243820167
H	3.2816163239	3.0959072377	-3.5778846896
H	2.8888325061	1.3838885218	-3.2270958863
H	3.3859293449	2.4650553934	-1.9023687553
H	-4.4683409640	.5493406642	.4638415838
H	-3.7005791402	-1.0473725834	.5016084657

5) $Me_2L^{iPr,SMe}CuO_2$ end-on triplet (B3LYP/DZP level)

Cu	.3356287362	.9164299778	-1.0192163587
O	1.6567122214	-.4778218256	-1.6844147326
O	1.3990293103	-1.4883075369	-2.3898302146
N	.1184164990	2.2557652935	.4531112118
N	-1.4120031782	-.0257907342	-.7651150641
S	1.2263686664	2.6398591224	-2.6049234934
C	2.3593012096	.3309749618	2.8239560569
C	1.1513400071	4.0943790537	-1.4392817665
C	3.0259210159	2.3654010185	-2.7483595235
C	-1.6107837268	-1.2892858089	-1.4002714414
C	-1.9339966406	-1.3328798798	-2.7776470468
C	-2.0773242540	-2.5798274698	-3.3955611865
C	-1.0711999037	2.4830185232	1.0083909519
C	-1.8902637581	-3.7633975058	-2.6891439268
C	-1.5449840094	-3.7089042154	-1.3415302249
C	-1.3942978314	-2.4889868127	-.6753696860
C	-2.1160675191	-.0616665749	-3.6009420672
C	-1.0562459204	.0361275971	-4.7147931865
C	-3.5351108313	.0542659367	-4.1866629509
C	-.9629200168	-2.4831326226	.7891940394
C	.5053324288	-2.9276620295	.9356353246
C	-1.8747248995	-3.3485629541	1.6786081221
C	-2.2180577250	1.7123100235	.7430300594
C	-2.3638843561	.5268579785	-.0164303013
C	-3.7275410825	-.1402727352	.0566826098
C	1.2906085760	2.9596291767	.8169303318
C	1.8407794227	3.8649375039	-.1261550080
C	3.0480612522	4.5131466389	.1495111824

C	3.7211746844	4.2757070051	1.3458537881
C	-1.2323099041	3.6354438821	1.9855028059
C	3.1936171723	3.3626469856	2.2554851089
C	1.9908398869	2.6854865816	2.0162974383
C	1.5156715363	1.6111625555	2.9895231497
C	1.5170187428	2.0795285443	4.4547052537
H	3.7384314341	3.1590326462	3.1728509630
H	-1.3798094144	-4.6342982602	-.7969437478
H	-2.0009156165	-4.7222256280	-3.1872334005
H	-2.3308837315	-2.6222686601	-4.4512135276
H	.0764970288	4.2486626496	-1.3219544831
H	1.5730656210	4.9547048048	-1.9647281057
H	4.6553953118	4.7850716869	1.5609300443
H	-.8304940976	3.3737583946	2.9702318651
H	-.6884765912	4.5208991520	1.6441549569
H	.4875769540	1.3496172221	2.7273281195
H	-2.2851258054	3.8937830468	2.1115854833
H	-4.0976936976	-.3877263233	-.9421050959
H	-1.9676290858	.7894665492	-2.9304515764
H	-3.1172741189	2.0436357778	1.2470684006
H	3.4550307029	5.2113550063	-.5777243166
H	-1.0262102134	-1.4544289667	1.1534838774
H	.8179975416	-2.8803365012	1.9849248589
H	1.1722473189	-2.2916406601	.3488030781
H	.6401229850	-3.9588023281	.5906778584
H	-1.5864900047	-3.2467781373	2.7305728259
H	-1.8018434968	-4.4104827206	1.4207743894
H	-2.9263107963	-3.0586143780	1.5870866460
H	-1.1467622504	.9871792082	-5.2513238892
H	-1.1712623135	-.7730571344	-5.4444308738
H	-.0462954845	-.0326420735	-4.3016287700
H	-3.6494572737	.9985618704	-4.7304115914
H	-4.2969552219	.0223630700	-3.4010749102
H	-3.7478763377	-.7595671707	-4.8883289360
H	1.0792697345	1.3088553605	5.0976613636
H	.9388353512	2.9999249916	4.5855597252
H	2.5313056931	2.2701684856	4.8213321481
H	1.9927648973	-.4607567057	3.4866779159
H	3.4103891797	.5179010089	3.0704398215
H	2.3151413138	-.0411169086	1.7961644889
H	3.4818073374	3.1486625063	-3.3575201390
H	3.1526084622	1.3979311457	-3.2356955705
H	3.4890933992	2.3353309286	-1.7608171635
H	-4.4531402110	.5047601368	.5543277154
H	-3.6685949387	-1.0813359202	.6118480289

6) $Me_2L^{iPr,SMe}CuO_2$ side-on singlet (B3LYP/TZP level)

Cu	.4663883693	.4654466196	-.4470928915
O	2.3208950698	.1136408912	-.5504308309
O	1.5935713102	-.8302827455	-1.2031387456
N	.1716424270	2.0116488135	.6301281228
N	-1.3571152821	-.0847348207	-.6949000536
S	.6917872094	2.4530687885	-2.5742201977
C	2.9732570493	.5877356401	2.9094659429

C	.6711741701	3.9125230509	-1.4378868666
C	2.4645683048	2.3469535637	-2.9790298203
C	-1.6267081712	-1.2823176800	-1.4469365667
C	-1.9028993923	-1.1981988593	-2.8299977053
C	-2.1747875624	-2.3786879314	-3.5237416995
C	-1.0436948689	2.4081461110	.9905115876
C	-2.1521203733	-3.6128444976	-2.8895705931
C	-1.8474446302	-3.6812424485	-1.5376191910
C	-1.5746802367	-2.5312655574	-.7957141104
C	-1.8819525801	.1177008930	-3.6003581308
C	-.7309443087	.1231236656	-4.6218684845
C	-3.2203766427	.4279203133	-4.2973819866
C	-1.2160627687	-2.6608000949	.6785895144
C	.1563879840	-3.3392520210	.8403757921
C	-2.3006179752	-3.4002725866	1.4804494231
C	-2.2182523271	1.7128949036	.6795691413
C	-2.3590120349	.5519089999	-.1004384690
C	-3.7721121870	.0339795256	-.2775970754
C	1.3021536179	2.8676206785	.7924187390
C	1.5667323890	3.8031276050	-.2316386456
C	2.6869020874	4.6250622052	-.1236407068
C	3.5375006675	4.5218997469	.9738344744
C	-1.1932532760	3.6826919643	1.7947344425
C	3.2704015053	3.5866075600	1.9641639621
C	2.1574680302	2.7419568701	1.8950070089
C	1.9090324116	1.6980395905	2.9731653740
C	1.8260370250	2.3167087076	4.3788844147
H	3.9428296248	3.5071649036	2.8103782851
H	-1.8095053007	-4.6490751579	-1.0514851879
H	-2.3604821557	-4.5174262403	-3.4501998961
H	-2.3946742871	-2.3302408120	-4.5842327715
H	-.3807433667	3.9940823456	-1.1614081403
H	.9288954276	4.7974769423	-2.0214821023
H	4.4056181636	5.1664319945	1.0514965511
H	-.6226182114	3.6212038422	2.7236132545
H	-.8068068056	4.5439025803	1.2447351657
H	.9440038280	1.2355855797	2.7579079582
H	-2.2388290404	3.8655120860	2.0363326772
H	-4.0542893396	.0366191390	-1.3317757242
H	-1.6930098266	.9210085454	-2.8892038286
H	-3.1325454310	2.1279809959	1.0761300339
H	2.8949707743	5.3472432072	-.9061199133
H	-1.1312141979	-1.6557943913	1.0928304303
H	.4510266188	-3.3617140277	1.8936215218
H	.9207019399	-2.8024279701	.2759443964
H	.1286207807	-4.3713171417	.4791587288
H	-2.0384690427	-3.4248318955	2.5415814932
H	-2.4130737401	-4.4350681474	1.1467807967
H	-3.2752126409	-2.9144096449	1.3850025694
H	-.6515679194	1.1017013046	-5.1021199433
H	-.8929622630	-.6239773152	-5.4038743787
H	.2199371911	-.1031530808	-4.1359631384
H	-3.1693640398	1.3997544557	-4.7963668321
H	-4.0517707965	.4595274671	-3.5885697810
H	-3.4645787854	-.3180178779	-5.0586566309
H	1.5714239954	1.5503491650	5.1156884073
H	1.0658014476	3.1008579860	4.4294534578

H	2.7783981082	2.7588357286	4.6833402472
H	2.7609799159	-.1882524635	3.6504068685
H	3.9700754374	.9864348472	3.1195350773
H	2.9929030502	.1271323359	1.9202136755
H	2.8206436724	3.2869736599	-3.4036250501
H	2.5521807199	1.5600195780	-3.7271918062
H	3.0404814785	2.0638118857	-2.1006065933
H	-4.4803043326	.6487065307	.2754312781
H	-3.8559313022	-.9981642196	.0656365104

7) $Me_2L^{iPr,SMe}CuO_2$ end-on singlet (B3LYP/TZP level)

Cu	.4021818601	.8980849169	-.9634201870
O	1.3844125104	-.2810563882	-2.0693155956
O	1.1637934022	-1.5478874737	-2.0953479017
N	.1462351717	2.2074913324	.4545642860
N	-1.3460808507	-.0216382548	-.7951742384
S	1.0993012513	2.7230111274	-2.5749066201
C	2.3290967170	.2755094974	2.8509998968
C	1.1554769018	4.1315148098	-1.3698563695
C	2.8647862584	2.3723597932	-2.8499308343
C	-1.5266423455	-1.2821584757	-1.4187007869
C	-1.9199487570	-1.3416348822	-2.7760959834
C	-2.1474129521	-2.5913228378	-3.3470986561
C	-1.0521813669	2.4805085335	.9520313506
C	-1.9575499648	-3.7600324972	-2.6206034023
C	-1.5132324240	-3.6925424950	-1.3076921342
C	-1.2793609446	-2.4667922378	-.6860004705
C	-2.0815558814	-.0823547299	-3.6182007504
C	-1.0393466895	-.0532527876	-4.7509863975
C	-3.5067801474	.0819389646	-4.1762538626
C	-.7689942731	-2.4366608768	.7489349106
C	.6342124262	-3.0617446290	.8487138891
C	-1.7383819697	-3.1211148819	1.7293712504
C	-2.2021414761	1.7359295814	.6489516829
C	-2.3222087946	.5474966720	-.1017933676
C	-3.6909513538	-.1062857348	-.0872110799
C	1.3153531430	2.9096277057	.8373519375
C	1.8627187308	3.8328587542	-.0802377683
C	3.0652446108	4.4703449091	.2175460656
C	3.7213051118	4.2140411456	1.4153957801
C	-1.2195425030	3.6524725828	1.8972787320
C	3.1782584120	3.3049557571	2.3133905297
C	1.9850732505	2.6284858695	2.0456729206
C	1.4848246287	1.5546747534	3.0032061323
C	1.4502818573	2.0208074310	4.4677680220
H	3.7031314751	3.1045786737	3.2403599173
H	-1.3376734737	-4.6104352272	-.7581692974
H	-2.1391933936	-4.7235383675	-3.0844141150
H	-2.4669318560	-2.6539037047	-4.3812548000
H	.0995212239	4.3513725013	-1.2103748447
H	1.6080710915	4.9854537268	-1.8751118085
H	4.6526520837	4.7182402658	1.6464113193
H	-.8626086912	3.3984160581	2.8989840212
H	-.6433469777	4.5170001959	1.5610899211

H	.4658881872	1.2978158361	2.7126634836
H	-2.2690502558	3.9341890792	1.9765635793
H	-4.0104163848	-.3703764226	-1.0961854839
H	-1.8841657398	.7730509659	-2.9706625686
H	-3.1161427880	2.0883424690	1.1046870370
H	3.4802075524	5.1817057090	-.4890003147
H	-.6800824673	-1.3902903535	1.0448954800
H	1.0277002396	-2.9516496980	1.8637263822
H	1.3152158321	-2.5824688893	.1446156200
H	.6082096576	-4.1306643971	.6170707816
H	-1.3680923725	-3.0300390318	2.7546693272
H	-1.8419996094	-4.1875651712	1.5106625390
H	-2.7368032105	-2.6783079440	1.6938171024
H	-1.0929550299	.8953032471	-5.2938599901
H	-1.2117516016	-.8604142412	-5.4686981059
H	-.0309889067	-.1685079232	-4.3506318139
H	-3.5905109248	1.0215431233	-4.7299363677
H	-4.2540637480	.0956989123	-3.3785274770
H	-3.7677223645	-.7291106562	-4.8617815207
H	.9838208326	1.2564241144	5.0950970568
H	.8799351239	2.9461387072	4.5834296848
H	2.4535519695	2.1975104145	4.8648538283
H	1.9507637176	-.5154330189	3.5050201676
H	3.3746201961	.4599880487	3.1145844071
H	2.2995590184	-.0927671835	1.8231027216
H	3.3067216254	3.1230568087	-3.5050074691
H	2.8962239433	1.3928203403	-3.3243314411
H	3.3959477846	2.3282520337	-1.8997353476
H	-4.4319740243	.5545249865	.3607551341
H	-3.6652155813	-1.0344116757	.4881659620

8) [($Me_2L^{H,SMe}CuO_2)_2(\mu\text{-}O)_2$] (BLYP/DZP level)

Cu	-.0947874629	1.4797216015	1.4710327033
Cu	.1070035581	-1.4389514765	1.4122982186
O	1.1566857926	.0986043981	1.4964865836
O	-1.1385038306	-.0599798162	1.4908709289
N	1.1444649036	2.8688161257	.8334906767
N	-1.5192933713	2.7447470235	1.9935432306
N	1.4932747619	-2.7533442279	1.9209470214
N	-1.1484551892	-2.7987376670	.7407451090
C	1.8722382939	3.6820663217	-4.1199203064
C	-1.6399357005	-3.6515657130	-4.2118113475
H	3.1123275400	4.8590033520	1.1102146788
H	1.7038570608	2.8536449223	-4.8254842941
H	-1.9630563903	5.8904565538	3.1211357061
H	1.7748801177	4.6349155249	-4.6593319708
H	2.8831338891	3.6110436980	-3.6939350383
H	.0494231309	1.9015690367	-1.3157430640
H	-1.3899268121	-2.8653652050	-4.9404253773
H	-2.8708434452	4.4319644419	3.6215481268
H	2.1992618417	5.1556586090	-.3808451044
H	-1.5805797274	-4.6307077964	-4.7076343783
H	-2.3114431363	-5.0282897095	-.4333859984
H	-3.2070429474	-4.7313886123	1.0694334686

H	2.7822434232	-4.4466641514	3.5919025252
H	3.0365655565	-5.2562526675	2.0383024599
H	-2.6616495652	-3.5047743209	-3.8356903902
H	-2.0190611243	-6.0625642740	.9937540081
H	1.7965709883	-5.8752267736	3.1561388962
H	-.5958635271	-1.2496746259	-2.8552838820
H	.1282721876	-1.8919748968	-1.3579257754
H	-3.1860946516	5.1722364214	2.0451194299
H	.8792799187	1.2692127899	-2.7624563121
H	1.8933021393	6.1658118934	1.0609121124
S	.5886107640	3.6962416115	-2.7922536467
S	-.4207660629	-3.6896169544	-2.8263766567
C	-.0352203545	-4.6525653634	1.8283539220
C	-1.2973015439	4.0633755051	2.1563064519
C	1.0332481099	4.1710280306	1.1480654552
C	-.0885649701	4.7105678224	1.8172564246
C	-2.8303629682	2.2026535703	2.1765279026
C	2.2998338206	2.3517775403	.1637823352
C	2.8408609794	-2.2867623604	2.0257803476
C	-2.2373081146	-2.2469661089	-.0060914829
C	-3.0698089846	1.3070163378	3.2442826811
C	1.2064935601	-4.0526550295	2.1350578444
C	-4.3625664216	.8129821431	3.4737225959
C	-5.4245011306	1.1805488218	2.6276371107
C	-5.1829179852	2.0408247283	1.5408971045
C	-3.8938217137	2.5441447616	1.3097746311
C	3.5122382234	2.1896639592	.8684941921
C	4.6550635439	1.6851023318	.2310828679
C	4.5861483673	1.3046585961	-1.1192190412
C	3.3713327963	1.4225121477	-1.8145220877
C	2.2137380220	1.9422502128	-1.1987184992
C	-3.4904680147	-2.0484199775	.6119897474
C	-1.1110719885	-4.0917105861	1.1027999524
C	-4.5661903802	-1.4984034682	-.0998944545
C	-4.3908778093	-1.1077731051	-1.4369482723
C	-3.1352466481	-1.2669815918	-2.0466142025
C	-2.0431636654	-1.8351064359	-1.3575242997
C	3.8332709212	-2.7141619637	1.1136877344
C	5.1610334494	-2.2870454392	1.2627285673
C	5.5125780949	-1.4201353773	2.3132653740
C	4.5220690514	-.9663688363	3.2024812727
C	3.1899950696	-1.3822873822	3.0541678880
H	-.1339738052	-5.7048628047	2.0923242042
C	2.2656121310	-4.9610393955	2.7672232683
C	-2.2300867657	-5.0358174159	.6656317097
C	-2.3913621784	4.9410734628	2.7717115287
C	2.1261315730	5.1484768439	.7191303675
H	-.0429234844	5.7765071647	2.0371829124
H	-2.2356747460	1.0198624034	3.8861197492
H	-4.5397589676	.1368892734	4.3149649578
H	-6.4319241569	.7967885723	2.8113570805
H	-6.0007207921	2.3201157073	.8702085451
H	-3.6995670900	3.2061034738	.4619584143
H	3.5379287044	2.4550294453	1.9279071367
H	5.5845189258	1.5665682703	.7929540810
H	5.4655917256	.8962672597	-1.6241880346
H	3.3093236412	1.0889673624	-2.8551270598

C	.9189821237	2.0368588416	-1.9737793469
H	-3.5995449969	-2.3104776541	1.6665119520
H	-5.5278483617	-1.3527000726	.3979545651
H	-5.2186334098	-.6650802512	-1.9978750867
H	-2.9901213997	-.9327202147	-3.0785996571
C	-.7121505685	-1.9995983804	-2.0580587145
H	3.5533530915	-3.3852035266	.2974149176
H	5.9225234173	-2.6315930736	.5572857883
H	6.5501529694	-1.0966319643	2.4340747044
H	4.7859421909	-.2839572009	4.0153529445
H	2.4095625010	-1.0260989857	3.7276461521

9) [($Me_2L^{H,SMe}CuO_2)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)$] singlet (BLYP/DZP level)

Cu	-.1257947699	1.8334843881	.9995108168
Cu	.2163302373	-1.8496485275	1.1377376791
O	.8038632463	.0706698546	1.1319959017
O	-.6866383636	-.0812766775	1.1031584514
N	1.1876656138	3.1642467370	.4430863786
N	-1.6039633563	3.0234936921	1.5040055535
N	1.6393571132	-3.1063415228	1.5972436213
N	-1.1625084439	-3.1245864798	.5315950199
C	3.1099004185	3.0993765751	-4.1516193877
C	-2.9635051552	-2.5620183621	-4.0955016359
H	2.8918682479	5.4333028778	.7103378449
H	3.2032472447	2.1811693193	-4.7518411091
H	-2.2478779848	6.2936328579	2.0635098926
H	3.1234729021	3.9674871031	-4.8238750173
H	3.9542470694	3.1725522601	-3.4506494505
H	.7152244790	1.5953666439	-1.6293274649
H	-3.0590576955	-1.5929474481	-4.6120484016
H	-3.0196651771	4.8968975481	2.8652403744
H	2.3126303603	5.2536096006	-.9576386683
H	-2.9165635951	-3.3605805663	-4.8524233149
H	-2.3111467313	-5.0184326816	-1.0717936586
H	-2.8393870808	-5.4845034420	.5563753936
H	3.0407572001	-5.1031607143	2.7844642933
H	3.4366636112	-5.3762015800	1.0830626299
H	-3.8366959747	-2.7246852344	-3.4497813932
H	-1.5372663413	-6.3999769667	-.2453013895
H	2.2351608652	-6.4168905209	1.8785990842
H	-2.0192258730	-.4345756309	-2.3153820174
H	-.7564287409	-1.2071445807	-1.3268531112
H	-3.4445054647	5.3019949342	1.1978969622
H	1.9327953517	.8151253277	-2.6689620853
H	1.6051965575	6.5097433702	.1029454184
S	1.4996770092	3.1582462224	-3.2503483790
S	-1.3965446809	-2.6622693437	-3.1204730122
C	.3193718126	-5.0303463622	.8763724080
C	-1.4718238946	4.3633751265	1.4256846842
C	.9272550545	4.4838892472	.5158102804
C	-.3066912854	5.0182567139	.9574679564
C	-2.8389893497	2.4265063618	1.9168823392
C	2.5004917340	2.6596910232	.1832635369
C	2.8868617339	-2.5619735925	2.0435431808

C	-2.4845178665	-2.6216846832	.3147116787
C	-2.8731145747	1.6767851305	3.1129055974
C	1.4857990242	-4.4329431445	1.4115006245
C	-4.0689460555	1.0848573527	3.5449138570
C	-5.2446852593	1.2197046260	2.7857073541
C	-5.2105874089	1.9412044115	1.5813635022
C	-4.0172233886	2.5354185076	1.1432335534
C	3.5119298424	2.8040572492	1.1583483593
C	4.7883537850	2.2620685918	.9608848553
C	5.0657671604	1.5405926534	-.2114115131
C	4.0563114857	1.3668812753	-1.1713825646
C	2.7683253064	1.9155018855	-1.0026709862
C	-3.5045009818	-2.9363968916	1.2413271925
C	-.9048980781	-4.4467013532	.4735041567
C	-4.8115612264	-2.4593644625	1.0746146875
C	-5.1155046845	-1.6267707387	-.0145983687
C	-4.1002052553	-1.2767626515	-.9176959331
C	-2.7791823819	-1.7564041990	-.7803914952
C	4.0432998099	-2.5968324075	1.2319030530
C	5.2457444641	-2.0367307861	1.6895882907
C	5.3111262513	-1.4258029004	2.9543611578
C	4.1564319006	-1.3685087915	3.7566509121
C	2.9519755795	-1.9267369356	3.3047543569
H	.3669415331	-6.1140079698	.7679038481
C	2.6128186752	-5.3878916037	1.8123568011
C	-1.9601581905	-5.3966783423	-.0990218886
C	-2.6093663344	5.2672863601	1.9141942084
C	1.9962390199	5.4829080601	.0728301976
H	-.3612083344	6.1063973883	.9582297181
H	-1.9537548711	1.5725674507	3.6942699644
H	-4.0814087546	.5158886569	4.4776695748
H	-6.1753759925	.7581499234	3.1258181107
H	-6.1162733753	2.0386225755	.9763286621
H	-3.9867047664	3.0823658871	.1989295754
H	3.2713144258	3.3298980845	2.0859092278
H	5.5555309280	2.3868568160	1.7293012311
H	6.0534986249	1.1022508133	-.3707169540
H	4.2615532535	.7814413551	-2.0726853398
C	1.7150410029	1.7114901417	-2.0682947493
H	-3.2497788963	-3.5586670631	2.1033414078
H	-5.5839574147	-2.7259139917	1.8009302524
H	-6.1282653290	-1.2394503787	-.1515747036
H	-4.3276364236	-.6056454887	-1.7516234209
C	-1.7337313419	-1.3676925189	-1.8005640815
H	3.9861368048	-3.0538114593	.2404640158
H	6.1337564463	-2.0731831810	1.0522680039
H	6.2491634119	-.9884033677	3.3065969556
H	4.1927645588	-.8878289864	4.7387955277
H	2.0508715007	-1.8847682233	3.9212850182

10) [($Me_2L^{H,SMe}CuO_2)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)$] triplet (BLYP/DZP level)

Cu	-.1675080478	1.7339956935	1.6758601291
Cu	.2048244875	-1.7439857721	1.5767111497
O	.6992363829	-.0203555390	2.4925089446
O	-.7577033097	-.0435108949	2.4553895397
N	.9651529141	2.8938720558	.5690095288
N	-1.5543675218	3.0934028823	2.1440067245
N	1.6553433743	-3.0527776062	2.0139707747
N	-.8877728468	-2.9290424760	.4697301651
C	1.5802280916	3.1906687285	-4.5418083206
C	-1.5101378679	-3.1038688495	-4.6812824392
H	2.9593182711	4.8197712636	.3032816009
H	1.2923086996	2.3041087610	-5.1273013257
H	-1.8419807856	6.4058566431	2.6143649147
H	1.5662049589	4.0744418800	-5.1963230465
H	2.5953301610	3.0600821999	-4.1388561157
H	-.3254059421	2.0296642106	-1.4788239741
H	-1.2344682520	-2.1935122212	-5.2384341369
H	-2.8005457147	5.1133116210	3.3949408062
H	1.9074190920	4.9494063460	-1.1195551272
H	-1.4806893872	-3.9621641296	-5.3656786980
H	-1.7670414558	-4.9688230551	-1.2678105011
H	-2.7927290014	-4.9362190267	.1810895132
H	3.0123516998	-5.0534115772	3.1865332250
H	3.3795899457	-5.4448180837	1.4997069717
H	-2.5292329557	-3.0029393463	-4.2753583877
H	-1.5621404157	-6.2167381623	-.0080593889
H	2.1235112347	-6.3623384676	2.3543587407
H	-.2873413609	-1.0630116473	-2.9390469041
H	.3776276788	-2.0087783876	-1.5784099725
H	-3.1560190456	5.6021391558	1.7280919319
H	.3112826842	1.1101869838	-2.8685556249
H	1.7868811791	6.1618877097	.1847092135
S	.3630907159	3.5234453075	-3.1998497691
S	-.2876230811	-3.4626531298	-3.3439500257
C	.3460221782	-4.9183204624	1.1438374340
C	-1.3266055145	4.4058266739	1.9433774569
C	.8837053832	4.2382014925	.6508255674
C	-.1649340035	4.9190343823	1.3165387514
C	-2.8253746084	2.6088268981	2.5735831156
C	2.0304021586	2.2431379594	-.1374364021
C	2.9005172307	-2.5240920734	2.4692076165
C	-1.9712246924	-2.3027323586	-.2303408104
C	-2.9140887002	1.8477052129	3.7636627609
C	1.4901015761	-4.3673746812	1.7746048371
C	-4.1475817216	1.3257155635	4.1794670634
C	-5.3085543072	1.5404132733	3.4141736746
C	-5.2239405989	2.2793939752	2.2202077638
C	-3.9944485065	2.8053294075	1.7978683960
C	3.2611688331	2.0003071771	.5110957652
C	4.2885719030	1.2917616415	-.1282818745
C	4.0968646737	.8008543921	-1.4301213470
C	2.8687564385	1.0213189987	-2.0733055258
C	1.8221753881	1.7432198158	-1.4566845854
C	-3.2070466043	-2.1072470062	.4263524284
C	-.7410138553	-4.2691495303	.5094752513

C	-4.2546330127	-1.4126238707	-.1963986994
C	-4.0759762075	-.8877999306	-1.4887929965
C	-2.8461878331	-1.0655941809	-2.1428232846
C	-1.7804946275	-1.7730947348	-1.5427675472
C	4.0782770640	-2.6234614216	1.6895302317
C	5.2802301976	-2.0620645690	2.1441869222
C	5.3273058692	-1.3823039321	3.3745763619
C	4.1561730007	-1.2626022699	4.1444878494
C	2.9505450500	-1.8217490771	3.6973292348
H	.3240219423	-6.0068720112	1.0959259425
C	2.5616667216	-5.3630671811	2.2329731770
C	-1.7764612878	-5.1539959957	-.1813097583
C	-2.3389233745	5.4396855652	2.4508481357
C	1.9474400912	5.0971231538	-.0288675033
H	-.0918912580	6.0066588246	1.3003906912
H	-2.0066291825	1.6702763606	4.3446243701
H	-4.2010758066	.7457969921	5.1053748325
H	-6.2680135080	1.1305167172	3.7403853648
H	-6.1181423733	2.4420010285	1.6112567920
H	-3.9234462832	3.3586176490	.8576497627
H	3.3880525834	2.3573026478	1.5352383445
H	5.2288154824	1.1094428181	.3976372964
H	4.8863252919	.2363673666	-1.9330522993
H	2.7057820110	.6121903459	-3.0747483408
C	.5113896601	1.9490262418	-2.1847287003
H	-3.3203635121	-2.4891025139	1.4449592430
H	-5.1999404932	-1.2671013739	.3337751270
H	-4.8801521519	-.3310316762	-1.9778211754
H	-2.6967671230	-.6306477060	-3.1369704692
C	-.4661552486	-1.9261053150	-2.2788335137
H	4.0364295388	-3.1309529198	.7225638354
H	6.1821678630	-2.1514704379	1.5318533405
H	6.2649796041	-.9448398874	3.7262355806
H	4.1795404166	-.7294535506	5.0993428545
H	2.0350657935	-1.7183437649	4.2829813865

Vibrational Frequencies. Vibrational frequencies were computed for truncated models only, owing to the prohibitive cost of computing frequencies for the entire ~80 atom model. Isopropyl groups on the phenyl rings were replaced with hydrogen atoms. Before frequencies were computed, the positions of these hydrogen atoms were optimized, while freezing the rest of the structure. Imaginary frequencies attributable to numerical noise from the computation are indicated by "()". Imaginary frequencies which are artifacts of the truncated model are indicated by "<>".

1) $Me_2L^{iPr,SMe}Cu$ (B3LYP/DZP level)

34.34	39.62	49.09	52.81	56.81	69.85
89.02	97.30	104.93	116.51	128.12	145.73
150.42	161.95	173.00	205.52	211.77	223.63
258.69	272.24	287.40	312.76	334.22	340.24
367.61	426.44	446.60	458.57	477.91	512.47
532.75	546.23	548.57	555.88	594.03	629.29
633.27	644.19	661.24	690.87	705.86	718.12
745.09	755.24	767.10	768.59	823.21	836.98
842.22	849.11	873.19	888.59	913.87	939.87
951.55	960.62	962.72	978.62	987.15	989.46
1000.68	1004.87	1034.56	1044.41	1050.64	1051.56
1060.56	1063.13	1091.38	1123.87	1181.70	1182.73
1184.47	1188.36	1204.09	1214.46	1256.68	1266.48
1289.65	1292.80	1298.26	1324.62	1339.53	1339.80
1366.85	1413.74	1418.67	1458.54	1468.42	1478.94
1480.47	1486.00	1491.12	1492.20	1493.13	1497.12
1499.61	1512.36	1520.24	1564.62	1600.18	1614.43
1625.48	1635.19	1638.97	3055.54	3057.22	3068.46
3082.54	3113.01	3119.72	3142.05	3144.06	3151.38
3161.49	3169.73	3174.45	3176.44	3180.50	3184.31
3195.87	3201.97	3202.15	3204.68	3209.22	3210.37

2) $Me_2L^{iPr,SMe}CuO_2$ side-on singlet (B3LYP/DZP level)

29.74	46.72	52.56	56.26	67.71	73.31
84.98	91.03	98.41	105.52	115.17	123.53
128.11	134.75	149.84	160.24	170.99	189.46
196.35	214.44	224.68	241.87	276.42	298.07
321.70	338.66	347.51	366.91	424.30	441.19
456.01	460.64	486.75	488.76	508.15	538.72
548.28	558.34	567.56	598.36	628.87	662.59
670.44	674.04	692.91	716.88	719.73	757.16
761.48	774.46	775.48	826.47	842.74	856.65
860.96	869.55	898.03	921.56	946.50	964.17
964.91	976.43	986.79	990.59	993.88	1007.16
1013.13	1048.30	1049.63	1052.45	1059.67	1062.13
1062.70	1093.76	1110.14	1125.05	1184.79	1185.63
1191.50	1195.36	1206.38	1220.70	1254.56	1275.92
1295.05	1297.60	1305.51	1310.92	1338.69	1340.54
1373.42	1419.27	1421.01	1458.76	1474.71	1479.08
1481.70	1488.18	1488.53	1491.29	1491.62	1494.68
1504.99	1513.22	1521.78	1570.69	1608.76	1628.76
1629.31	1635.77	1640.01	3059.63	3059.93	3064.30

3069.61	3118.07	3120.77	3126.18	3152.71	3156.92
3157.60	3173.63	3176.96	3177.74	3186.84	3186.88
3200.59	3203.67	3211.81	3214.67	3216.15	3225.36

3) $Me_2L^{iPr,SMe}CuO_2$ side-on triplet (B3LYP/DZP level)

23.10	32.92	51.51	61.18	67.78	73.87
77.14	87.69	91.04	98.19	113.55	114.38
123.78	124.02	129.52	132.01	146.22	164.20
167.87	193.22	210.13	228.99	233.66	273.14
292.63	304.44	336.64	345.81	363.16	378.88
425.60	443.51	459.86	485.34	509.42	533.70
545.63	556.82	561.31	596.64	628.66	651.44
660.40	666.30	692.05	712.15	717.11	753.42
755.41	770.04	773.09	829.88	841.71	844.65
850.55	870.14	895.69	915.49	945.70	959.29
960.82	969.61	986.13	986.32	989.84	1004.50
1007.97	1041.95	1047.78	1050.13	1055.41	1061.28
1062.98	1093.48	1124.80	1182.60	1185.35	1189.54
1192.42	1203.76	1217.09	1236.31	1262.21	1275.77
1287.71	1297.26	1302.68	1312.67	1339.41	1339.85
1371.96	1418.10	1419.50	1460.49	1470.41	1477.89
1481.28	1486.65	1488.30	1490.64	1493.84	1497.66
1502.81	1512.04	1521.32	1566.68	1609.05	1623.60
1625.27	1635.14	1639.62	3057.62	3057.86	3065.59
3074.22	3115.89	3120.28	3129.13	3151.34	3153.48
3158.43	3174.05	3175.59	3177.40	3182.57	3184.25
3198.75	3202.44	3207.30	3210.86	3212.89	3216.03

4) $Me_2L^{iPr,SMe}CuO_2$ end-on singlet (B3LYP/DZP level)

(-33.09)	39.09	44.97	54.68	70.13	75.45
78.95	91.24	104.36	110.38	115.72	124.45
130.40	142.58	146.76	154.32	168.13	176.74
203.00	206.45	215.76	228.47	266.46	283.40
294.85	316.80	334.38	344.61	366.23	416.29
435.10	444.32	461.95	482.18	509.47	537.61
544.94	550.86	559.39	596.33	625.14	649.54
657.55	661.62	690.46	709.46	713.73	752.67
753.99	769.39	771.54	829.82	837.65	840.11
848.34	873.84	894.83	920.19	944.85	957.46
960.79	969.67	985.27	989.58	991.41	1003.66
1009.45	1040.76	1046.64	1049.84	1053.51	1060.85
1062.37	1094.66	1124.11	1180.78	1185.18	1189.61
1191.28	1203.66	1217.19	1251.17	1258.73	1271.76
1288.34	1296.19	1303.20	1319.40	1339.22	1339.88
1366.65	1416.71	1417.11	1455.29	1470.38	1478.69
1484.99	1486.55	1489.61	1490.97	1493.62	1496.85
1498.71	1507.78	1520.17	1567.50	1610.50	1617.75
1623.09	1633.12	1638.94	3053.25	3060.57	3063.28
3080.57	3115.46	3122.27	3137.22	3148.58	3152.79
3158.07	3169.52	3173.63	3176.68	3183.94	3186.33
3199.59	3202.79	3211.52	3213.48	3213.99	3214.87

5) $Me_2L^{iPr,SMe}CuO_2$ end-on triplet (B3LYP/DZP level)

28.67	41.22	43.98	56.67	57.77	67.18
73.30	81.59	96.02	98.41	107.40	113.67
114.70	129.00	131.95	133.37	140.52	164.14
176.35	201.25	210.25	217.12	237.86	271.93
285.71	300.37	312.05	335.92	344.95	365.24
424.17	445.51	459.99	482.37	511.12	534.38
546.71	552.94	558.04	595.29	628.57	648.13
652.40	661.90	690.71	712.61	716.64	750.59
756.71	769.43	771.20	829.50	839.71	841.70
844.88	873.38	891.25	914.51	943.23	955.04
960.42	966.99	983.20	988.36	990.25	1004.27
1006.57	1038.48	1046.54	1051.50	1052.74	1060.72
1062.27	1092.77	1124.14	1182.40	1184.66	1188.59
1189.64	1203.70	1215.95	1250.83	1271.33	1288.34
1294.87	1299.24	1319.24	1337.37	1340.21	1341.41
1372.07	1417.32	1417.90	1456.78	1468.76	1477.81
1480.55	1486.60	1491.21	1493.27	1494.69	1496.53
1500.23	1510.49	1520.61	1568.05	1603.61	1620.93
1624.40	1635.45	1639.08	3054.42	3061.09	3067.88
3082.67	3114.86	3122.12	3141.71	3147.21	3151.09
3160.92	3173.31	3173.84	3176.44	3181.93	3183.24
3197.14	3203.43	3205.08	3208.95	3210.67	3212.74

6) $Me_2L^{iPr,SMe}CuO_2$ side-on singlet (B3LYP/TZP level)

<-136.83><-104.42>		(-20.52)	54.05	66.95	70.26
78.63	84.44	96.58	109.23	126.48	137.17
151.32	152.49	163.48	170.70	184.57	188.51
200.73	221.95	225.25	239.37	274.51	293.79
320.23	339.10	350.51	369.35	427.91	446.05
462.19	475.62	490.80	501.74	511.45	542.13
553.15	570.71	571.07	598.71	629.66	663.11
676.07	678.80	694.74	705.87	720.81	761.75
775.12	776.09	777.51	825.94	845.30	858.11
861.44	871.50	900.70	926.21	959.21	959.56
973.73	979.34	990.57	1001.15	1003.63	1006.55
1011.02	1040.96	1046.29	1052.91	1053.08	1058.26
1062.90	1086.16	1088.14	1120.64	1179.78	1181.07
1186.50	1191.93	1201.85	1212.55	1245.31	1267.09
1276.35	1282.72	1295.99	1299.62	1321.13	1333.35
1368.10	1412.38	1414.39	1432.52	1468.03	1469.77
1470.92	1479.42	1480.51	1482.51	1482.97	1485.75
1491.72	1499.84	1508.02	1553.64	1579.77	1605.87
1606.80	1613.68	1618.04	3025.93	3028.66	3033.21
3036.06	3078.78	3081.28	3086.66	3111.37	3117.04
3117.72	3129.98	3141.07	3141.53	3150.86	3151.45
3165.62	3167.84	3189.10	3194.40	3195.86	3198.60

7) $Me_2L^{iPr,SMe}CuO_2$ end-on singlet (B3LYP/TZP level)

<-98.37>	<-93.87>	(-36.35)	38.10	50.90	64.59
66.97	82.27	85.72	101.47	109.58	114.86
121.24	131.40	139.82	147.80	155.84	170.75
193.21	204.33	215.36	224.51	268.72	273.89
301.95	323.42	328.73	344.81	366.68	416.44
442.69	450.57	463.14	479.23	512.44	540.47
548.96	556.80	563.06	598.94	627.60	656.53
658.21	666.92	693.18	704.70	712.05	755.54
756.51	769.50	773.14	832.38	838.70	845.64
854.00	870.13	895.74	923.46	955.73	958.32
971.70	971.88	985.71	995.59	998.22	1004.66
1006.91	1039.67	1045.57	1046.45	1051.51	1057.35
1059.06	1091.64	1123.99	1178.71	1183.26	1188.36
1188.61	1203.33	1214.93	1231.30	1256.81	1270.53
1282.43	1291.14	1296.73	1312.96	1331.70	1337.28
1358.76	1407.69	1409.24	1441.92	1463.06	1471.23
1473.48	1477.04	1478.23	1482.39	1485.51	1487.26
1492.31	1501.42	1511.51	1558.83	1596.74	1611.01
1615.16	1624.35	1630.03	3038.79	3046.91	3047.57
3065.83	3092.62	3104.09	3116.49	3124.26	3129.35
3134.54	3150.34	3155.38	3155.46	3166.29	3167.12
3178.63	3182.31	3194.72	3195.29	3197.40	3197.98