Supporting Information

DFT Study of the Mechanism of Copper-catalyzed Synthesis of 2*H*-indazoles from Aryl Azide

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M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, Jr., J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision C.01*, Gaussian, Inc., Wallingford, CT, 2010.

Cartesian coordinates and electronic energies

Aryl azide

E= -720.2549315au

H	1.334767	-3.084842	-0.325995
C	1.973568	-2.201228	-0.229162
C	3.362331	-2.346451	-0.232588
C	1.345034	-0.939851	-0.107305
C	4.169441	-1.203837	-0.108910
H	3.813013	-3.336954	-0.330480
C	2.181638	0.209424	0.020962
C	-0.121369	-0.924583	-0.121150
C	3.584067	0.059367	0.016793
H	5.259210	-1.292834	-0.108436
N	1.561782	1.468327	0.153255
H	-0.579531	-1.933586	-0.188458
N	-0.852600	0.140146	-0.085342
H	4.215962	0.946455	0.116006
N	2.256063	2.492722	0.262832
N	2.724887	3.545472	0.372344
C	-2.251644	0.022703	-0.032150
C	-3.018929	0.964405	-0.756337
C	-2.921517	-0.946140	0.753111
C	-4.415854	0.904896	-0.736369
H	-2.491884	1.723582	-1.339522
C	-4.321267	-0.983141	0.786322
H	-2.337705	-1.637724	1.367227
C	-5.074700	-0.067843	0.034925
H	-4.995812	1.629909	-1.314841
H	-4.826458	-1.727127	1.409581
H	-6.167286	-0.099878	0.064425

N_2

E= -109.5142887au

N	0.000000	0.000000	0.558112
N	0.000000	0.000000	-0.558112

2T

E= -610.8124577au

N	-0.260379	0.097524	0.002019
C	0.519244	1.209936	-0.188869
C	1.849020	0.774603	-0.122031
H	0.086802	2.183944	-0.395581
C	1.740694	-0.649103	0.114014
C	3.126973	1.387548	-0.236513
N	0.447889	-1.052238	0.186863
C	2.907377	-1.450921	0.244858
H	3.222111	2.461656	-0.418428
C	4.247997	0.582967	-0.108561
H	2.819705	-2.524392	0.428183
C	4.137705	-0.824065	0.131500
H	5.243965	1.027212	-0.190707
H	5.053718	-1.414203	0.226526
C	-1.685891	0.041950	0.006168
C	-2.323034	-1.178894	-0.278906
C	-2.444166	1.190592	0.295430
C	-3.721183	-1.239483	-0.285531
H	-1.709297	-2.055854	-0.486688
C	-3.843103	1.116742	0.274946
H	-1.950577	2.127537	0.562232
C	-4.487724	-0.094703	-0.015824
H	-4.213875	-2.189704	-0.509021
H	-4.428998	2.011336	0.502754
H	-5.579578	-0.147553	-0.025548

Pre2

E= -555.4338223au

I	2.418615	-0.022669	0.000005
Cu	-0.042419	-0.041384	-0.000891
N	-1.700306	-1.440086	-0.004123
N	-1.604698	1.495501	0.004270
C	-2.890475	-0.620517	-0.340669

C	-2.846557	0.759538	0.336534
H	-3.832945	-1.137574	-0.061151
H	-2.906912	-0.498363	-1.435577
H	-2.875735	0.638315	1.431256
H	-3.753631	1.334995	0.053477
C	-1.666907	2.107476	-1.340391
H	-0.691477	2.558358	-1.572771
H	-1.873776	1.340972	-2.101034
H	-2.454222	2.889294	-1.398430
C	-1.306374	2.537724	1.009921
H	-0.342011	3.004560	0.763204
H	-2.092338	3.321851	1.042667
H	-1.216807	2.075909	2.004226
C	-1.483614	-2.507209	-1.006246
H	-0.563453	-3.053108	-0.753512
H	-2.332611	-3.222079	-1.040209
H	-1.351114	-2.056506	-2.000857
C	-1.812572	-2.042793	1.343226
H	-1.960915	-1.260233	2.100963
H	-2.658590	-2.760312	1.399162
H	-0.875871	-2.567701	1.578878

$\mathbf{1I_{CuI}}$

E= -1275.6918758au

I	3.721851	0.334157	-0.957970
Cu	1.470365	-0.453940	-0.023092
N	1.248517	-0.727488	2.171148
N	1.007772	-2.647209	-0.128295
C	1.439116	-2.193587	2.298805
C	0.627759	-2.985043	1.264413
H	1.167224	-2.542756	3.318913
H	2.513386	-2.397129	2.164620
H	-0.444574	-2.759987	1.381141
H	0.749962	-4.071898	1.461895
N	-3.053718	0.407064	-0.080222
C	-2.987846	1.684836	0.124340
C	-1.751677	2.470404	0.200934
H	-3.907035	2.274396	0.317261
C	-0.443338	2.028642	-0.159380
C	-1.873465	3.779445	0.731581
N	-0.159169	0.743661	-0.734534
C	0.675118	2.846651	0.074018
H	-2.874247	4.136817	0.994705
C	-0.764745	4.599456	0.949349
N	-0.823241	0.394042	-1.739377
H	1.661544	2.467938	-0.213750
C	0.516717	4.122901	0.628483
H	-0.897247	5.600853	1.366713
N	-1.299181	-0.089899	-2.674828
H	1.397681	4.750664	0.786910
C	-4.322297	-0.201081	-0.163370
C	-4.495451	-1.472122	0.429694
C	-5.408920	0.381133	-0.857996
C	-5.733395	-2.120417	0.370156
H	-3.649237	-1.925289	0.952543
C	-6.638989	-0.284502	-0.932088
H	-5.267398	1.333626	-1.376320
C	-6.811482	-1.531205	-0.311430
H	-5.855830	-3.096176	0.849169
H	-7.464903	0.170511	-1.486647
H	-7.772839	-2.048259	-0.372578
C	2.259538	-3.328742	-0.528612
H	2.540947	-2.997025	-1.537559
H	3.081775	-3.044091	0.141801
H	2.138680	-4.433559	-0.518730
C	-0.071656	-3.017522	-1.066389
H	0.218769	-2.722628	-2.085333
H	-0.271319	-4.110486	-1.060665
H	-0.997424	-2.487249	-0.799204
C	2.336116	-0.009843	2.872744
H	2.176691	1.072926	2.768863
H	2.369347	-0.266190	3.953112
H	3.297787	-0.254638	2.398656
C	-0.060155	-0.304340	2.709761
H	-0.880197	-0.758672	2.136679
H	-0.170835	-0.575536	3.781831
H	-0.151954	0.786176	2.610700

$TS12I_{CuI}$

E= -1275.6545358au

I	-2.448738	0.903209	-1.702405
Cu	-1.169159	-0.425532	0.122051
N	-1.077530	-2.467405	-0.569793
N	-2.604429	-1.376201	1.729195
C	-2.298194	-3.122813	-0.032992
C	-2.521236	-2.828105	1.455225
H	-2.246920	-4.222704	-0.181071
H	-3.147922	-2.750154	-0.626571
H	-1.688279	-3.238563	2.047723
H	-3.438571	-3.358303	1.790332
N	2.772657	0.298054	0.028513
C	2.769512	1.594715	0.106543
C	1.632063	2.456378	0.413562
H	3.695148	2.156630	-0.137779
C	0.328133	2.035486	0.865200
C	1.857639	3.841037	0.211075
N	-0.072270	0.739244	1.139946
C	-0.676306	3.031861	1.028327
H	2.859939	4.159090	-0.095377
C	0.846975	4.792457	0.345336
N	1.122609	0.007740	2.149164
H	-1.660048	2.700995	1.365898
C	-0.439060	4.372426	0.733007
H	1.054980	5.848450	0.155670
N	1.241614	-0.977012	2.708472
H	-1.248127	5.099962	0.843332
C	3.987578	-0.349547	-0.250576
C	5.188833	-0.036404	0.431241
C	4.002059	-1.394325	-1.204661
C	6.366605	-0.742732	0.154892
H	5.175772	0.735645	1.205794
C	5.187420	-2.079115	-1.490211
H	3.076662	-1.629159	-1.737076
C	6.375754	-1.761351	-0.810087
H	7.282226	-0.497385	0.701429
H	5.184571	-2.870345	-2.245825
H	7.296865	-2.310285	-1.023780
C	-2.283005	-1.072626	3.137090
H	-3.041370	-1.487047	3.834827
H	-1.298356	-1.487549	3.393531
H	-2.238009	0.018234	3.265974
C	-3.945458	-0.846451	1.405700
H	-3.958741	0.238280	1.582804
H	-4.173756	-1.000032	0.342136
H	-4.729076	-1.327555	2.030203
C	0.158097	-3.053923	-0.001490
H	0.218655	-4.143610	-0.201519
H	1.029049	-2.556382	-0.449285
H	0.206299	-2.889518	1.084810
C	-1.050744	-2.584659	-2.046505
H	-1.024340	-3.647634	-2.362180
H	-1.936178	-2.086650	-2.465888
H	-0.160290	-2.068865	-2.432662

$2I_{CuI}$

E= -1166.2528559au

I	2.129805	-0.645740	-1.925363
Cu	0.659315	0.005026	0.151380
N	1.616177	1.760264	1.139636
N	1.483813	-1.105193	2.089614
C	2.666503	1.098251	1.952107
C	2.110070	-0.005128	2.857313
H	3.204766	1.844005	2.579303
H	3.395405	0.671612	1.244316
H	1.350319	0.414841	3.536170
H	2.928987	-0.384842	3.506097
N	-2.432073	0.364291	-0.052373
C	-3.611860	-0.325270	0.021005
C	-3.286593	-1.688499	0.003661
H	-4.564445	0.196257	0.002781
C	-1.848157	-1.715093	-0.099580
C	-4.022807	-2.905108	0.030556
N	-1.331948	-0.451344	-0.105999
C	-1.145517	-2.941606	-0.216558
H	-5.113077	-2.899180	0.109894
C	-3.316817	-4.093938	-0.059904

H	-0.064283	-2.935148	-0.374352
C	-1.892685	-4.110171	-0.194543
H	-3.856789	-5.044684	-0.048017
H	-1.385189	-5.072667	-0.303108
C	-2.299221	1.772323	-0.243047
C	-1.385708	2.250008	-1.200562
C	-3.114281	2.653586	0.486950
C	-1.302632	3.631549	-1.424943
H	-0.766883	1.543614	-1.760942
C	-3.022521	4.031754	0.245282
H	-3.798767	2.264239	1.244798
C	-2.118033	4.523438	-0.708752
H	-0.606109	4.007607	-2.178957
H	-3.654406	4.720583	0.812186
H	-2.050319	5.598533	-0.895246
C	0.454486	-1.782936	2.897140
H	0.870181	-2.231073	3.826307
H	-0.332848	-1.063825	3.170813
H	-0.007256	-2.583581	2.301427
C	2.502168	-2.080610	1.652227
H	2.022696	-2.864383	1.049498
H	3.242140	-1.591090	1.004461
H	3.014586	-2.551759	2.520146
C	0.722555	2.583673	1.979819
H	1.285327	3.364977	2.536451
H	-0.019328	3.074910	1.335907
H	0.181922	1.957310	2.703607
C	2.263965	2.626439	0.128704
H	2.858737	2.001123	-0.553442
H	1.486932	3.134067	-0.460280
H	2.908634	3.394936	0.607026

$\mathbf{1T_{CuI}}$

E= -1275.699273au

I	-3.134088	1.919482	0.094749
Cu	-2.348289	-0.512863	-0.000203
N	-3.312893	-1.900371	-1.470100
N	-3.180947	-1.915341	1.522083
C	-4.254168	-2.664173	-0.615769
C	-3.625808	-3.082381	0.721957
H	-4.629822	-3.569242	-1.140237
H	-5.125586	-2.016587	-0.430263
H	-2.742908	-3.715958	0.538524
H	-4.353885	-3.703678	1.286455
N	-0.370534	-0.671918	-0.145138
N	0.637124	-0.080936	-0.120804
N	1.816166	0.299904	-0.092800
C	2.124210	1.677994	-0.127736
C	1.120221	2.668406	-0.162565
C	3.501321	2.051683	-0.118352
C	1.464291	4.023154	-0.186305
H	0.064547	2.376368	-0.162775
C	3.807037	3.433153	-0.139404
C	4.633536	1.122243	-0.086733
H	0.668346	4.772024	-0.210500
C	2.813869	4.413772	-0.174573
H	4.861793	3.726405	-0.130534
H	5.623012	1.622738	-0.034150
N	4.542101	-0.166393	-0.138943
H	3.085713	5.472112	-0.191537
C	5.702288	-0.950295	-0.026829
C	5.795602	-2.109650	-0.831428
C	6.744260	-0.670358	0.889894
C	6.921111	-2.936055	-0.756627
H	4.975753	-2.329589	-1.519896
C	7.857442	-1.516536	0.974750
H	6.653349	0.189421	1.559868
C	7.957679	-2.645366	0.146886
H	6.986293	-3.819892	-1.398099
H	8.648580	-1.295503	1.697651
H	8.828326	-3.303244	0.216822
C	-2.172302	-2.315329	2.524968
H	-2.577417	-3.045947	3.256874
H	-1.302238	-2.759636	2.018836
H	-1.836192	-1.421504	3.071029
C	-4.318820	-1.257581	2.201984
H	-3.956910	-0.355900	2.715084
H	-5.065313	-0.930322	1.465696

H	−4.798905	−1.939310	2.936001
C	−4.047388	−1.122761	−2.491679
H	−4.703954	−0.395037	−1.993385
H	−3.325911	−0.558446	−3.099951
H	−4.646022	−1.778071	−3.159362
C	−2.331024	−2.787262	−2.125847
H	−2.822513	−3.511601	−2.809954
H	−1.623941	−2.174705	−2.703627
H	−1.754444	−3.344982	−1.374013

$\mathbf{TS12T_{CuI}}$

E= -1275.6635625au

I	2.272327	1.115722	−1.851660
Cu	1.741032	−0.650296	−0.072304
N	1.718542	−0.006137	2.052526
N	3.530387	−1.867153	0.562484
C	3.061032	−0.409869	2.540888
C	3.474894	−1.801706	2.042371
H	3.103903	−0.388902	3.650931
H	3.779423	0.341931	2.177968
H	2.745729	−2.554587	2.383876
H	4.451835	−2.074907	2.496075
H	−6.809728	−0.986338	−0.209748
C	−5.897024	−1.583637	−0.297717
C	−5.961573	−2.956107	−0.499050
C	−4.645507	−0.931673	−0.203191
C	−4.752078	−3.684112	−0.614391
H	−6.924399	−3.466980	−0.571088
C	−3.400246	−1.660832	−0.313330
C	−4.460180	0.469468	−0.020617
C	−3.508627	−3.068774	−0.530190
H	−4.789371	−4.765734	−0.776841
N	−2.240377	−0.919830	−0.201656
H	−5.305455	1.172873	0.047097
N	−3.220473	0.865983	0.015581
H	−2.595204	−3.657814	−0.626347
N	−0.992942	−1.919562	−0.344670
N	0.153513	−1.752815	−0.325943
C	−2.717079	2.139817	0.267255
C	−1.551109	2.555849	−0.415306
C	−3.324192	3.006508	1.209722
C	−1.025398	3.831263	−0.180674
H	−1.071996	1.875777	−1.122713
C	−2.789656	4.280934	1.429324
H	−4.198923	2.665489	1.770526
C	−1.642791	4.700494	0.734672
H	−0.123573	4.138212	−0.716648
H	−3.266274	4.946273	2.155377
H	−1.226947	5.695706	0.914453
C	4.769646	−1.255321	0.035542
H	5.669305	−1.818872	0.363199
H	4.721667	−1.237338	−1.062181
H	4.852556	−0.212030	0.368629
C	3.430688	−3.262510	0.088145
H	3.434307	−3.268045	−1.011873
H	4.275088	−3.887534	0.448645
H	2.484026	−3.704722	0.432998
C	1.565526	1.465265	2.125071
H	0.567998	1.743354	1.759336
H	1.687616	1.835985	3.164414
H	2.308209	1.939525	1.467234
C	0.640256	−0.656694	2.827785
H	−0.332031	−0.381568	2.395238
H	0.737025	−1.750738	2.776037
H	0.661892	−0.347257	3.894061

Pre3

E= -763.1929444au

I	−2.336280	−1.159809	0.017685
Cu	0.043029	−1.919757	0.000242
Cu	−0.004527	0.523071	−0.004422
I	2.386507	−1.052534	−0.022349
N	−0.009431	2.095644	1.502550
C	−0.421571	3.277937	0.703697
H	−0.188840	4.223584	1.238624
H	−1.516564	3.233394	0.592255
C	−0.982207	1.830757	2.585711
H	−1.057118	2.686421	3.289347

H	-1.970579	1.624664	2.150523
H	-0.664227	0.938443	3.143570
C	1.339903	2.275210	2.082629
H	1.636571	1.349037	2.594226
H	2.076277	2.462968	1.289237
H	1.360824	3.118797	2.804812
C	0.242121	3.307828	-0.681962
H	1.337585	3.337157	-0.570643
H	-0.054732	4.240649	-1.207322
N	-0.088977	2.108407	-1.493834
C	-1.442834	2.209541	-2.082697
H	-1.510805	3.057192	-2.797161
H	-1.678205	1.271892	-2.605128
H	-2.194797	2.343826	-1.293078
C	0.906399	1.913735	-2.571511
H	0.645890	1.010599	-3.141560
H	0.936327	2.780021	-3.265364
H	1.901774	1.761023	-2.130134

1I'$_{CuI}$

E= -1483.4632619au

I	1.403287	2.072603	1.098358
Cu	0.149380	0.558617	-0.567789
N	-4.147383	-0.370617	0.056650
C	-4.597157	0.832180	0.209832
C	-3.861159	2.051598	-0.139184
H	-5.597212	1.019615	0.651093
C	-2.561304	2.114542	-0.721873
C	-4.477751	3.280206	0.204208
N	-1.799822	0.966452	-1.134890
C	-1.908510	3.348587	-0.870632
H	-5.481006	3.246620	0.640861
C	-3.839516	4.509604	0.028915
N	-2.335799	0.147227	-1.927225
H	-0.896995	3.354295	-1.282422
C	-2.539647	4.541350	-0.498511
H	-4.346124	5.435261	0.313276
N	-2.608693	-0.694329	-2.663218
H	-2.015522	5.491519	-0.628795
C	-4.890928	-1.462361	0.543490
C	-4.868184	-2.660672	-0.206385
C	-5.603106	-1.431453	1.766185
C	-5.581423	-3.781236	0.231384
H	-4.296851	-2.681922	-1.137294
C	-6.297188	-2.565238	2.206749
H	-5.570531	-0.531816	2.387282
C	-6.299242	-3.740103	1.438480
H	-5.567355	-4.696759	-0.366916
H	-6.831056	-2.533646	3.161225
H	-6.841555	-4.623395	1.786929
Cu	2.405844	-0.301016	0.169953
I	1.058501	-1.511358	-1.862851
N	2.907698	-1.709509	1.806881
C	4.371350	-1.518204	1.948845
H	4.833498	-2.356758	2.513769
H	4.528268	-0.605325	2.545051
C	2.210853	-1.367465	3.064357
H	2.535429	-2.015504	3.906435
H	2.400885	-0.314057	3.315879
H	1.127988	-1.489846	2.918282
C	2.578095	-3.097762	1.420868
H	1.493747	-3.179062	1.261956
H	3.066206	-3.357851	0.471607
H	2.891228	-3.822361	2.203246
C	5.076311	-1.378962	0.591651
H	4.893503	-2.278706	-0.016872
H	6.174088	-1.316455	0.756105
N	4.584629	-0.213091	-0.183347
C	5.153447	1.052763	0.325545
H	6.259716	1.072309	0.221621
H	4.720459	1.892657	-0.235659
H	4.887730	1.195143	1.382135
C	4.915961	-0.362903	-1.616272
H	4.516889	0.499848	-2.168854
H	6.012871	-0.420631	-1.782397
H	4.435603	-1.269337	-2.012013

TS12I'$_{CuI}$

E= -1483.4253485au

I	1.460971	1.930337	1.267983
Cu	0.071666	0.574629	-0.418711
N	-4.341673	-0.330126	-0.045881
C	-4.704944	0.913192	0.038043
C	-3.900089	2.073568	-0.323906
H	-5.706807	1.176532	0.437824
C	-2.506908	2.046346	-0.737403
C	-4.532485	3.329856	-0.181275
N	-1.742603	0.926278	-0.846636
C	-1.854107	3.303812	-0.955120
H	-5.588042	3.346707	0.110558
C	-3.852106	4.537377	-0.359326
N	-2.457220	-0.222070	-2.033917
H	-0.812849	3.270499	-1.285327
C	-2.490555	4.519065	-0.722018
H	-4.376632	5.486794	-0.223323
N	-2.065839	-1.199346	-2.463353
H	-1.946236	5.456125	-0.870254
C	-5.175116	-1.323817	0.491358
C	-5.256257	-2.559943	-0.193121
C	-5.883119	-1.170922	1.709288
C	-6.062273	-3.590899	0.299264
H	-4.688435	-2.679261	-1.118714
C	-6.669025	-2.217397	2.206895
H	-5.774339	-0.245189	2.281400
C	-6.772458	-3.426460	1.500947
H	-6.127555	-4.534462	-0.250412
H	-7.197224	-2.091179	3.156895
H	-7.387288	-4.241377	1.893138
Cu	2.477799	-0.298643	0.162830
I	0.942623	-1.645944	-1.548283
N	3.419442	-1.644447	1.652831
C	4.857465	-1.299305	1.535660
H	5.496638	-2.077726	2.005060
H	5.019902	-0.367654	2.100657
C	2.924595	-1.368157	3.019162
H	3.457100	-1.976374	3.780446
H	3.051050	-0.300112	3.247655
H	1.850725	-1.599803	3.065952
C	3.174847	-3.064626	1.319908
H	2.094104	-3.260651	1.354169
H	3.516342	-3.283559	0.298759
H	3.694498	-3.741629	2.030774
C	5.292851	-1.105244	0.075939
H	5.109643	-2.030018	-0.494033
H	6.387734	-0.918517	0.043931
N	4.545346	-0.013081	-0.596159
C	5.067366	1.315104	-0.208424
H	6.123715	1.443678	-0.527233
H	4.449428	2.094830	-0.675462
H	5.000151	1.450411	0.879807
C	4.618229	-0.160120	-2.066109
H	4.035925	0.644814	-2.537254
H	5.664929	-0.108520	-2.433152
H	4.170920	-1.119823	-2.362205

2I'$_{CuI}$

E= -1374.0314737au

I	-0.544736	0.827949	-2.143836
Cu	0.586977	-0.127128	0.026077
Cu	-1.953904	-0.109484	-0.045134
I	-0.725477	-0.928958	2.200134
N	-3.483944	-1.598691	-0.723791
C	-4.687126	-0.747332	-0.878304
H	-5.609192	-1.364917	-0.956028
H	-4.584559	-0.203289	-1.830895
C	-3.115700	-2.214341	-2.014657
H	-3.929506	-2.857541	-2.413928
H	-2.875294	-1.426468	-2.743090
H	-2.215110	-2.829728	-1.874597
C	-3.693338	-2.656665	0.284921
H	-2.759746	-3.222958	0.410596
H	-3.937339	-2.215583	1.260953
H	-4.507413	-3.351512	-0.015905
C	-4.851327	0.250960	0.275933
H	-4.915770	-0.293022	1.231719

H	-5.812461	0.795851	0.150812
N	-3.712151	1.194750	0.376798
C	-3.815006	2.274258	-0.626200
H	-4.721948	2.896057	-0.462740
H	-2.919788	2.909047	-0.564135
H	-3.841869	1.852997	-1.640567
C	-3.639339	1.780501	1.730423
H	-2.780222	2.465135	1.777907
H	-4.561495	2.344210	1.989363
H	-3.474285	0.981507	2.467770
H	1.134876	3.779755	2.293996
C	1.911070	3.542939	1.561960
C	2.226415	2.200366	1.312561
C	2.590506	4.571808	0.892190
C	3.226487	1.900020	0.371628
H	1.716199	1.395687	1.849761
C	3.588319	4.257225	-0.042995
H	2.340108	5.616554	1.094303
N	3.567831	0.536778	0.114009
C	3.906502	2.920221	-0.314185
H	4.110785	5.053085	-0.580147
C	4.824207	0.037534	-0.075525
N	2.599515	-0.426303	0.065235
H	4.651244	2.667433	-1.072551
C	4.690843	-1.346227	-0.264567
H	5.694835	0.683176	-0.009145
C	3.273607	-1.588358	-0.162470
C	5.583852	-2.426967	-0.498290
C	2.740980	-2.895184	-0.297327
H	6.661097	-2.258237	-0.574815
C	5.045553	-3.697332	-0.627313
C	3.637556	-3.927537	-0.527001
H	1.665630	-3.065401	-0.209504
H	5.707536	-4.548344	-0.808959
H	3.262721	-4.949342	-0.631772

1T'$_{CuI}$

E= -1483.4636448au

I	1.775468	2.093132	-0.338384
Cu	0.726052	-0.288014	-0.634898
Cu	3.168845	-0.216350	0.091433
I	1.928582	-2.574002	-0.377169
N	4.209510	-0.201454	2.051469
C	5.574063	0.239958	1.673516
H	6.304198	0.027856	2.484554
H	5.542822	1.333903	1.547664
C	3.592321	0.753854	2.994749
H	4.174743	0.840648	3.936860
H	3.512515	1.741487	2.517950
H	2.575482	0.412090	3.236602
C	4.222692	-1.551560	2.652286
H	3.188352	-1.868412	2.846119
H	4.659651	-2.277839	1.953233
H	4.797999	-1.568268	3.602819
C	6.061881	-0.418441	0.374729
H	6.061777	-1.514020	0.489763
H	7.114133	-0.114083	0.185871
N	5.195253	-0.093689	-0.785157
C	5.475095	1.261602	-1.304267
H	6.515568	1.343012	-1.685580
H	4.770638	1.488004	-2.116701
H	5.318561	2.013189	-0.518161
C	5.379265	-1.085052	-1.866548
H	4.709508	-0.834518	-2.701779
H	6.425944	-1.102036	-2.238053
H	5.102121	-2.083779	-1.499632
N	-1.203549	-0.139067	-1.046288
N	-2.227332	0.293159	-0.692909
N	-3.391170	0.515668	-0.344948
C	-3.822249	1.835676	-0.080595
C	-2.933924	2.929990	-0.114977
C	-5.198531	2.037920	0.233060
C	-3.391653	4.224547	0.148034
H	-1.877559	2.760411	-0.342826
C	-5.623355	3.362168	0.490797
C	-6.216118	0.984446	0.308043
H	-2.685258	5.058177	0.116199
C	-4.744743	4.447049	0.451871

H	−6.678996	3.525584	0.729566
H	−7.236415	1.360195	0.531026
N	−5.984836	−0.277905	0.159794
H	−5.108012	5.456721	0.658255
C	−7.052329	−1.191246	0.185348
C	−6.829480	−2.446011	0.798025
C	−8.306999	−0.937421	−0.419159
C	−7.851300	−3.399236	0.850105
H	−5.848902	−2.641052	1.239217
C	−9.316605	−1.907358	−0.383056
H	−8.467228	0.004137	−0.952157
C	−9.099252	−3.135988	0.259946
H	−7.669587	−4.359377	1.341622
H	−10.276513	−1.704997	−0.867590
H	−9.890028	−3.890763	0.284779

TS12T'$_{CuI}$

E= -1483.4285645au

I	1.463486	−0.340330	2.373332
Cu	0.206361	−0.827123	0.133585
Cu	2.657586	−0.114688	−0.026791
I	1.052824	0.010054	−2.201230
N	4.340948	−1.554530	−0.296798
C	5.524221	−0.707222	−0.010076
H	6.455645	−1.176064	−0.395173
H	5.628138	−0.643306	1.084674
C	4.260853	−2.678266	0.659924
H	5.158431	−3.331034	0.609090
H	4.147628	−2.285255	1.680759
H	3.371108	−3.282255	0.430455
C	4.377704	−2.080596	−1.677245
H	3.461246	−2.656239	−1.868100
H	4.401047	−1.255416	−2.402289
H	5.261672	−2.734233	−1.839843
C	5.391164	0.702487	−0.602647
H	5.249867	0.636020	−1.693154
H	6.337299	1.260412	−0.430791
N	4.227642	1.439818	−0.051979
C	4.497451	1.940641	1.312258
H	5.336464	2.669116	1.318508
H	3.590763	2.424991	1.700860
H	4.736595	1.107115	1.986657
C	3.867641	2.572643	−0.930064
H	2.987565	3.082862	−0.512832
H	4.698103	3.304825	−1.020735
H	3.599441	2.194258	−1.926928
H	−8.353583	−0.425537	−0.247797
C	−7.501998	−1.109246	−0.181069
C	−7.692274	−2.484790	−0.157317
C	−6.195918	−0.570408	−0.116989
C	−6.559579	−3.331131	−0.072108
H	−8.697228	−2.910334	−0.203704
C	−5.032540	−1.421839	−0.028735
C	−5.862467	0.815068	−0.145824
C	−5.264488	−2.828535	−0.012718
H	−6.700194	−4.416030	−0.051369
N	−3.812867	−0.774440	0.028294
H	−6.620651	1.609827	−0.223697
N	−4.585775	1.071900	−0.106257
H	−4.410747	−3.504755	0.054407
N	−2.664039	−1.833083	0.131548
C	−3.924511	2.292179	0.001294
N	−1.508325	−1.749866	0.159839
C	−2.669459	2.442939	−0.630165
C	−4.463929	3.363932	0.753405
C	−1.984051	3.657795	−0.534750
H	−2.250846	1.602996	−1.188639
C	−3.768530	4.575004	0.835930
H	−5.411107	3.230017	1.282748
C	−2.530185	4.729273	0.191730
H	−1.015232	3.763139	−1.029798
H	−4.190501	5.398458	1.419277
H	−1.987587	5.675415	0.267431

1D'$_{CuI}$

E= -1483.4789899au

I	0.123743	−0.539884	−2.196413
Cu	−0.697430	0.106285	0.300418

N	-2.436880	1.162415	0.192412
C	-3.628088	0.675314	-0.018356
C	-4.041921	-0.723441	-0.035973
H	-4.449842	1.384704	-0.216381
C	-3.268002	-1.858369	0.354025
C	-5.369294	-0.957415	-0.479082
N	-1.957208	-1.655281	0.845442
C	-3.827188	-3.149463	0.266781
H	-5.971922	-0.091100	-0.768496
C	-5.917199	-2.236366	-0.564688
N	-1.355316	-2.634923	1.346891
H	-3.223550	-4.012046	0.560994
C	-5.133489	-3.339860	-0.190032
H	-6.941498	-2.374668	-0.918121
N	-0.614251	-3.371027	1.842419
H	-5.538049	-4.353659	-0.250308
C	-2.275292	2.576688	0.088029
C	-1.499958	3.237063	1.063234
C	-2.842061	3.313690	-0.973920
C	-1.333115	4.625343	0.996276
H	-1.043511	2.648972	1.863620
C	-2.653700	4.700523	-1.039564
H	-3.386218	2.791893	-1.765517
C	-1.908621	5.362574	-0.051788
H	-0.743864	5.132049	1.765675
H	-3.081744	5.262794	-1.874377
H	-1.764508	6.445115	-0.106665
Cu	1.847617	-0.222856	-0.188598
I	1.024949	0.220555	2.333160
H	3.368592	-2.045834	1.862428
C	3.395781	-2.661208	0.951355
N	3.450742	-1.781555	-0.234348
H	4.263617	-3.354238	0.992798
H	2.470568	-3.253923	0.917580
C	4.687618	-0.965912	-0.218163
C	3.357171	-2.598096	-1.461332
H	5.571071	-1.571736	-0.517881
H	4.857164	-0.646309	0.822502
C	4.592264	0.265524	-1.129811
H	2.402891	-3.143179	-1.457213
H	3.357620	-1.954539	-2.351681
H	4.196310	-3.323902	-1.532916
H	4.381063	-0.051035	-2.163621
H	5.577185	0.782027	-1.146035
N	3.509633	1.190548	-0.718697
C	3.911008	2.007421	0.443779
C	3.126552	2.076161	-1.836826
H	4.769019	2.670714	0.198599
H	3.056648	2.619693	0.764716
H	4.183958	1.362336	1.290189
H	2.313342	2.739050	-1.507662
H	3.979400	2.699598	-2.182461
H	2.748272	1.469966	-2.672648

TS12D'$_{CuI}$

E= -1483.4495708au

I	-0.116497	-0.269724	2.287132
Cu	0.918395	-0.218132	-0.336042
N	2.029839	1.460775	-0.342310
C	3.282825	1.450717	0.053873
C	4.114450	0.309971	0.276172
H	3.773944	2.426692	0.195220
C	3.720115	-1.058272	-0.061359
C	5.425093	0.553716	0.780236
N	2.486994	-1.309533	-0.543798
C	4.721333	-2.071776	0.131834
H	5.686452	1.588762	1.023095
C	6.353185	-0.454856	0.969880
N	2.366569	-2.952527	-1.184077
H	4.450046	-3.098615	-0.113604
C	5.978081	-1.777326	0.630674
H	7.346863	-0.237800	1.366756
N	1.496477	-3.382118	-1.785851
H	6.690379	-2.596851	0.767881
C	1.375270	2.705352	-0.545095
C	0.664456	2.910776	-1.746855
C	1.415384	3.730221	0.424694
C	0.040635	4.141457	-1.988931

H	0.631113	2.105416	-2.485265
C	0.778836	4.954175	0.176078
H	1.919952	3.547608	1.376837
C	0.096600	5.168894	-1.031723
H	-0.485608	4.300782	-2.934569
H	0.811373	5.740765	0.935447
H	-0.394106	6.126963	-1.223535
Cu	-1.766111	-0.349121	0.255967
I	-0.818477	-1.260639	-2.061667
H	-3.752338	0.802716	-1.907610
C	-3.413674	1.689679	-1.353970
N	-3.179230	1.351883	0.065838
H	-4.171385	2.495687	-1.459955
H	-2.468090	2.023318	-1.802787
C	-4.415804	0.842271	0.707765
C	-2.674393	2.542651	0.783979
C	-4.699407	-0.622621	0.349235
H	-4.288999	0.941608	1.797566
H	-5.294040	1.463055	0.427835
H	-1.746165	2.885226	0.307197
H	-3.412955	3.372309	0.773273
H	-2.441571	2.270055	1.823221
N	-3.606164	-1.526457	0.778922
H	-5.670679	-0.924923	0.797341
H	-4.803984	-0.726239	-0.742774
C	-3.676069	-2.813605	0.056772
C	-3.653851	-1.780147	2.234740
H	-4.616691	-3.360719	0.279379
H	-3.605316	-2.634852	-1.025599
H	-2.820842	-3.438175	0.352625
H	-2.796710	-2.406511	2.518416
H	-3.565967	-0.837883	2.792447
H	-4.597097	-2.290651	2.524618

2D'$_{CuI}$

E= -1373.9652962au

I	-0.551617	-1.639665	-1.613603
Cu	0.782698	0.138061	-0.118890
N	2.673029	-0.415196	0.188309
C	3.692825	0.425782	0.084049
C	3.630977	1.829825	-0.077897
H	4.701160	-0.009858	0.140458
C	2.339816	2.526823	-0.247036
C	4.837673	2.585194	-0.053986
N	1.169414	1.953223	-0.302343
C	2.408494	3.980803	-0.391347
H	5.777164	2.050267	0.121092
C	4.849600	3.955522	-0.246653
H	1.462039	4.510710	-0.513238
C	3.614019	4.643610	-0.435988
H	5.790174	4.510508	-0.227354
H	3.619282	5.729183	-0.576326
C	2.923012	-1.813356	0.176242
C	2.211053	-2.626479	1.084672
C	3.851509	-2.401026	-0.711554
C	2.452439	-4.003634	1.122669
H	1.480626	-2.159450	1.750886
C	4.083870	-3.780342	-0.665791
H	4.361947	-1.776774	-1.450017
C	3.389370	-4.585044	0.252550
H	1.903400	-4.626358	1.834092
H	4.799626	-4.231060	-1.359162
H	3.570169	-5.663098	0.281348
Cu	-1.839877	0.116944	-0.002688
I	-0.751471	0.171853	2.381683
H	-2.507961	0.921377	-2.963007
C	-2.115940	1.833173	-2.490709
N	-2.534145	1.894643	-1.073626
H	-2.473963	2.721588	-3.052242
H	-1.018992	1.789411	-2.536715
C	-4.013211	1.855134	-0.939636
C	-1.956293	3.094343	-0.429411
C	-4.550871	0.418129	-0.945275
H	-4.279711	2.352041	0.005933
H	-4.501561	2.432900	-1.751162
H	-0.856364	3.002310	-0.439938
H	-2.263423	4.025743	-0.949434
H	-2.279531	3.136206	0.620936

N	-3.969911	-0.394027	0.152473
H	-5.660232	0.439133	-0.885772
H	-4.281225	-0.077317	-1.892132
C	-4.188622	-1.837663	-0.082868
C	-4.518386	-0.023151	1.474412
H	-5.269094	-2.092103	-0.074502
H	-3.749322	-2.124376	-1.048622
H	-3.678712	-2.408720	0.706464
H	-4.006969	-0.613421	2.247453
H	-4.322063	1.035332	1.691539
H	-5.611305	-0.211662	1.524602

TS23D'$_{CuI}$

E= -1373.950843au

N	-2.365518	1.208055	-0.255477
C	-3.426909	0.757668	-0.904840
C	-4.122335	-0.364099	-0.416361
H	-3.811727	1.334945	-1.755661
C	-3.631396	-0.800482	0.886989
C	-5.268288	-0.966352	-1.001103
N	-2.587849	-0.250548	1.478887
C	-4.391232	-1.830452	1.565510
H	-5.597114	-0.626669	-1.987930
C	-5.950462	-1.967257	-0.334287
H	-4.053109	-2.159392	2.549059
C	-5.500849	-2.380714	0.954338
H	-6.825952	-2.439640	-0.784786
H	-6.046298	-3.169589	1.481929
C	-1.739757	2.445632	-0.539285
C	-1.494582	3.350231	0.514635
C	-1.353134	2.774569	-1.858149
C	-0.897599	4.586463	0.242066
H	-1.781280	3.068045	1.529473
C	-0.768308	4.021133	-2.117182
H	-1.507401	2.046772	-2.658839
C	-0.538735	4.930539	-1.071604
H	-0.715989	5.286311	1.062160
H	-0.486712	4.279817	-3.142141
H	-0.078138	5.900154	-1.279219
Cu	1.654955	-0.510399	-0.003990
Cu	-0.916801	-0.071757	0.608686
I	-0.186122	-1.767429	-1.427446
I	1.066089	0.775802	2.237190
H	2.588071	2.564958	-0.446449
C	3.468307	1.929617	-0.615805
N	3.046931	0.694681	-1.308269
H	4.220261	2.492880	-1.209921
H	3.891769	1.690409	0.369327
C	4.185359	-0.234316	-1.502255
C	2.433724	1.038692	-2.606836
C	4.548281	-0.990483	-0.217643
H	3.896967	-0.950563	-2.288070
H	5.084339	0.305291	-1.872306
H	1.582182	1.712114	-2.433674
H	3.156463	1.541735	-3.284790
H	2.054654	0.124688	-3.087108
N	3.426721	-1.823275	0.281409
H	5.453098	-1.608995	-0.401541
H	4.806155	-0.273285	0.577607
C	3.620344	-2.159148	1.708426
C	3.291282	-3.070882	-0.500916
H	4.544608	-2.753971	1.867089
H	3.669118	-1.234533	2.300925
H	2.756033	-2.740518	2.060375
H	2.414914	-3.627774	-0.141186
H	3.118715	-2.842599	-1.561438
H	4.197402	-3.706411	-0.405521

CuI

E= -207.6927743au

I	0.000000	0.000000	0.848018
Cu	0.000000	0.000000	-1.549826

TMEDA

E= -347.6691909au

N	-1.999558	-0.199867	-0.337948
C	-0.588412	-0.385974	-0.686817
H	-0.424099	-1.473653	-0.786957

H	-0.419889	0.057378	-1.684680
C	-2.455833	1.183871	-0.376079
H	-2.072591	1.828244	0.449921
H	-2.156097	1.644914	-1.331987
H	-3.558189	1.204363	-0.320239
C	-2.422027	-0.894722	0.872440
H	-2.032380	-0.459548	1.821931
H	-3.524431	-0.882792	0.933560
H	-2.097703	-1.947935	0.824943
C	0.459742	0.222874	0.279413
H	0.398625	-0.271818	1.278963
H	0.210794	1.286415	0.438871
N	1.824210	0.176902	-0.265140
C	2.722223	1.048465	0.490623
H	2.842337	0.749066	1.559838
H	3.722099	1.041568	0.024889
H	2.343298	2.083642	0.468156
C	2.360310	-1.182825	-0.317375
H	3.374982	-1.158894	-0.747795
H	2.424264	-1.670697	0.685661
H	1.740394	-1.819636	-0.966695

Pre1

E= -1110.9021673au

I	-0.013316	-2.357304	-0.041894
Cu	-1.284371	0.011072	-0.006597
Cu	1.284347	-0.011438	-0.006826
I	0.013369	2.357112	-0.042134
N	2.991773	0.006901	-1.474037
C	4.158024	-0.321669	-0.621350
H	5.112962	-0.056298	-1.126246
H	4.165443	-1.414038	-0.479411
C	2.807676	-1.015400	-2.522804
H	3.690992	-1.085750	-3.194175
H	2.619113	-1.992402	-2.054524
H	1.925046	-0.755608	-3.125176
C	3.137968	1.336497	-2.098572
H	2.218503	1.577340	-2.650534
H	3.263818	2.110335	-1.328916
H	4.005931	1.366989	-2.793227
C	4.101763	0.378292	0.743742
H	4.049534	1.469419	0.600624
H	5.043669	0.169076	1.297853
N	2.915206	-0.020445	1.534910
C	3.084551	-1.360048	2.131114
H	3.922446	-1.378685	2.862087
H	2.151724	-1.648070	2.635934
H	3.271792	-2.107921	1.348521
C	2.647941	0.965770	2.600267
H	1.760541	0.649274	3.167568
H	3.504489	1.060751	3.302708
H	2.427369	1.943651	2.147771
N	-2.991428	-0.006927	-1.474272
C	-4.157630	0.322795	-0.621985
C	-3.138301	-1.336700	-2.098261
C	-2.806463	1.014779	-2.523463
C	-4.102339	-0.376967	0.743250
H	-4.164121	1.415197	-0.480245
H	-5.112666	0.058160	-1.127095
H	-4.006086	-1.366949	-2.793151
H	-2.218828	-1.578372	-2.649849
H	-3.264876	-2.110123	-1.328312
H	-1.923854	0.754173	-3.125516
H	-3.689585	1.085352	-3.195067
H	-2.617415	1.991876	-2.055579
N	-2.915637	0.020891	1.534654
H	-5.044196	-0.166839	1.297091
H	-4.051042	-1.468165	0.600360
C	-2.649100	-0.965664	2.599888
C	-3.084286	1.360503	2.131044
H	-3.505795	-1.060258	3.302200
H	-2.429047	-1.943601	2.147261
H	-1.761587	-0.649794	3.167356
H	-2.151348	1.647951	2.635985
H	-3.271052	2.108584	1.348536
H	-3.922237	1.379484	2.861942

$[(TMEDA)_2Cu]^+$

E= -891.4860804au

Cu	−0.000009	0.000068	0.000040
N	−1.635705	−1.081229	−1.038878
C	−2.826093	−0.241936	−0.725884
H	−3.765298	−0.797489	−0.926192
H	−2.815180	0.620424	−1.411211
C	−1.469456	−1.173913	−2.510100
H	−2.353225	−1.634591	−2.995962
H	−1.319201	−0.169685	−2.930880
H	−0.587753	−1.790132	−2.739991
C	−1.820064	−2.453468	−0.503800
H	−0.940444	−3.061699	−0.755300
H	−1.925204	−2.431943	0.589830
H	−2.718291	−2.938984	−0.936672
C	−2.826143	0.241978	0.725779
H	−2.815349	−0.620376	1.411113
H	−3.765327	0.797594	0.926002
N	−1.635727	1.081203	1.038867
C	−1.820044	2.453500	0.503916
H	−2.718210	2.939028	0.936899
H	−0.940368	3.061658	0.755393
H	−1.925278	2.432067	−0.589707
C	−1.469468	1.173744	2.510099
H	−0.587755	1.789929	2.740041
H	−2.353229	1.634387	2.996009
H	−1.319223	0.169472	2.930779
N	1.635716	−1.081126	1.038959
C	2.826135	−0.241929	0.725823
C	1.819918	−2.453396	0.503898
C	1.469622	−1.173761	2.510202
C	2.826123	0.241899	−0.725868
H	2.815330	0.620469	1.411103
H	3.765317	−0.797534	0.926096
H	2.718164	−2.938959	0.936678
H	0.940287	−3.061558	0.755526
H	1.924928	−2.431913	−0.589745
H	0.587900	−1.789910	2.740207
H	2.353414	−1.634490	2.995973
H	1.319487	−0.169512	2.930976
N	1.635710	1.081119	−1.038967
H	3.765309	0.797488	−0.926161
H	2.815290	−0.620495	−1.411152
C	1.469502	1.173688	−2.510201
C	1.819998	2.453410	−0.503988
H	2.353272	1.634359	−2.996067
H	1.319294	0.169423	−2.930911
H	0.587784	1.789859	−2.740163
H	0.940343	3.061574	−0.755526
H	1.925152	2.431971	0.589643
H	2.718197	2.938941	−0.936902

Pre4

E= -219.2846208au

I	0.000000	0.000000	2.492928
Cu	0.000000	0.000000	0.000000
I	0.000000	0.000000	−2.492928

1E'$_{CuI}$

E= -939.5413711au

Cu	−0.336781	−0.462032	0.183014
N	−0.118349	1.398014	−0.713444
C	1.006596	1.996853	−0.997890
C	2.347452	1.426312	−0.997513
H	0.980279	3.069022	−1.264276
C	2.692279	0.043579	−0.868803
C	3.407822	2.353523	−1.167050
N	1.662116	−0.907765	−0.753887
C	4.053143	−0.334549	−0.888461
H	3.145001	3.410878	−1.276000
C	4.748264	1.971236	−1.189754
N	1.968101	−2.124368	−0.884252
H	4.303499	−1.392643	−0.774884
C	5.069042	0.610582	−1.044431
H	5.534355	2.720558	−1.315603
N	1.888088	−3.279720	−0.950633
H	6.112508	0.281812	−1.051583
C	−1.299193	2.191511	−0.708861

C	−2.478574	1.635472	−1.247977
C	−1.331708	3.490537	−0.153819
C	−3.656717	2.390733	−1.271372
H	−2.449015	0.609106	−1.626585
C	−2.520657	4.231041	−0.170904
H	−0.439787	3.889219	0.336396
C	−3.684568	3.690785	−0.739621
H	−4.564357	1.950967	−1.695488
H	−2.541045	5.228019	0.280712
H	−4.613327	4.269644	−0.745948
I	−1.769222	−2.358848	−0.938197
I	0.191482	−0.102028	2.742350

TS12E'$_{CuI}$

E= -939.5207889au

Cu	0.013097	−0.357328	0.151727
N	−0.133541	1.571828	−0.479559
C	0.892057	2.393201	−0.478247
C	2.256724	2.096319	−0.168006
H	0.705515	3.439189	−0.773674
C	2.767999	0.751003	0.114031
C	3.163791	3.195168	−0.191553
N	1.953272	−0.316651	0.096481
C	4.186721	0.660431	0.370172
H	2.746399	4.183117	−0.416072
C	4.518511	3.063302	0.063738
N	2.837490	−1.806555	0.274028
H	4.588670	−0.325931	0.600115
C	5.015142	1.766776	0.350546
H	5.182728	3.930897	0.048280
N	2.413144	−2.827736	−0.042227
H	6.080455	1.626900	0.564555
C	−1.420995	2.074674	−0.798459
C	−2.293249	1.256188	−1.547074
C	−1.862629	3.350583	−0.381399
C	−3.562571	1.723080	−1.904356
H	−1.953961	0.257556	−1.838377
C	−3.137486	3.806625	−0.739642
H	−1.221830	3.961650	0.259960
C	−3.990887	3.001046	−1.509276
H	−4.225198	1.077301	−2.488187
H	−3.472421	4.790852	−0.396650
H	−4.989485	3.357560	−1.779605
I	−0.188898	−2.542465	−1.452630
I	−1.556612	−0.610614	2.278963

[(TMEDA)Cu]$^{+}$

E= -543.7441968au

Cu	0.000000	1.154665	0.000000
N	1.536866	−0.200324	−0.000465
C	0.690621	−1.398090	−0.345138
C	2.165464	−0.355210	1.343842
C	2.604432	−0.008656	−1.024250
C	−0.690621	−1.398090	0.345139
H	0.568656	−1.406596	−1.439554
H	1.221767	−2.329804	−0.071506
H	2.851554	−1.222742	1.355495
H	2.734489	0.553408	1.584658
H	1.395845	−0.499357	2.114997
H	3.198135	0.878693	−0.764009
H	3.274779	−0.887016	−1.066269
H	2.150003	0.144773	−2.013529
N	−1.536866	−0.200324	0.000465
H	−1.221767	−2.329803	0.071507
H	−0.568656	−1.406595	1.439555
C	−2.604431	−0.008655	1.024250
C	−2.165464	−0.355211	−1.343842
H	−3.274779	−0.887015	1.066270
H	−2.150002	0.144775	2.013528
H	−3.198135	0.878694	0.764008
H	−2.734489	0.553407	−1.584659
H	−1.395845	−0.499360	−2.114997
H	−2.851555	−1.222743	−1.355493

Pre5

E= -566.9581773au

I	2.476706	−1.119752	−0.009840
Cu	0.019998	−0.177711	0.005096

I	-2.429278	-1.172577	-0.030171
N	-0.015480	1.681908	-1.505537
C	0.187484	2.834749	-0.612679
H	-0.131912	3.787447	-1.099543
H	1.269404	2.926652	-0.426288
C	1.077745	1.562172	-2.478595
H	1.159039	2.457056	-3.140773
H	2.025699	1.400543	-1.943107
H	0.902245	0.673886	-3.103439
C	-1.310348	1.744921	-2.193337
H	-1.441643	0.833581	-2.793903
H	-2.131413	1.753794	-1.462746
H	-1.386952	2.640866	-2.855785
C	-0.553787	2.697515	0.727039
H	-1.621589	2.500967	0.537145
H	-0.490407	3.672655	1.269683
N	-0.050675	1.589894	1.555388
C	1.276297	1.865709	2.118438
H	1.269874	2.759560	2.787717
H	1.609777	0.985281	2.685921
H	2.013140	2.010995	1.316477
C	-1.001215	1.268373	2.628973
H	-0.610336	0.418078	3.207860
H	-1.164537	2.128490	3.321326
H	-1.958013	0.953951	2.184254

1F’

E= -1264.0716086au

N	-0.204771	1.383123	-0.158382
C	0.857560	2.147700	-0.125678
C	2.258597	1.753190	-0.116878
H	0.695182	3.236744	-0.140936
C	2.790223	0.454973	0.137048
C	3.183964	2.802484	-0.361223
N	1.889840	-0.616060	0.423678
C	4.181482	0.246755	0.123695
H	2.787920	3.805424	-0.544402
C	4.561768	2.592368	-0.381254
N	2.379228	-1.676405	0.882423
H	4.582041	-0.751446	0.319523
C	5.060633	1.303169	-0.136297
H	5.241836	3.423110	-0.579757
N	2.637841	-2.723463	1.301574
H	6.136816	1.114696	-0.142420
C	-1.473185	2.056101	-0.098163
C	-2.451526	1.775135	-1.071441
C	-1.752253	2.976959	0.932205
C	-3.689733	2.427982	-1.025566
H	-2.214124	1.082548	-1.882673
C	-3.002308	3.610970	0.980367
H	-1.003098	3.168685	1.705522
C	-3.971551	3.342837	0.002588
H	-4.435436	2.225631	-1.798861
H	-3.216734	4.315908	1.787727
H	-4.942556	3.842257	0.040915
Cu	-0.301335	-0.582732	-0.101183
H	0.144973	-2.391378	2.584848
C	-0.843475	-1.918807	2.672720
N	-1.457472	-1.770663	1.329314
H	-1.471608	-2.539977	3.341293
H	-0.722268	-0.925374	3.128310
C	-1.568672	-3.098918	0.663546
C	-2.796330	-1.144350	1.487121
H	-2.395946	-3.694668	1.099410
H	-0.637503	-3.651831	0.866299
C	-1.784382	-2.965518	-0.847932
H	-2.682348	-0.159989	1.961733
H	-3.270090	-0.992647	0.507472
H	-3.460085	-1.772315	2.114484
H	-2.729522	-2.437266	-1.049020
H	-1.877790	-3.974050	-1.297605
N	-0.689507	-2.191153	-1.504823
C	0.511977	-3.043845	-1.700576
C	-1.138518	-1.708979	-2.836452
H	0.298365	-3.881642	-2.393281
H	1.324265	-2.435660	-2.123827
H	0.849420	-3.464173	-0.743672
H	-0.337254	-1.113830	-3.297878

H	−1.387533	−2.552241	−3.510506
H	−2.029932	−1.076177	−2.721852

TS12F'

E= -1264.0412967au

N	−0.377991	1.342592	0.178725
C	0.599217	2.226630	0.174822
C	2.009305	1.984314	0.126073
H	0.307453	3.285015	0.243796
C	2.611227	0.704022	−0.197356
C	2.853459	3.094846	0.422791
N	1.826254	−0.392128	−0.433006
C	4.039025	0.648359	−0.232872
H	2.379932	4.045186	0.685617
C	4.234951	2.999932	0.383977
N	2.630290	−1.435620	−1.466789
H	4.509011	−0.299481	−0.503772
C	4.822423	1.760146	0.035565
H	4.859125	3.866759	0.608747
N	2.451267	−2.508787	−1.815314
H	5.910639	1.668848	−0.016852
C	−1.715149	1.850314	0.121436
C	−2.120259	2.711551	−0.919281
C	−2.631116	1.485649	1.129157
C	−3.432256	3.204139	−0.944547
H	−1.411246	2.973977	−1.709437
C	−3.935982	1.994529	1.103280
H	−2.296366	0.844142	1.948355
C	−4.341594	2.849044	0.064273
H	−3.743471	3.868092	−1.755029
H	−4.635689	1.731153	1.900735
H	−5.362034	3.239055	0.043715
Cu	−0.066805	−0.610649	−0.016981
H	−0.058138	−2.853422	−1.886265
C	−1.005564	−2.363538	−2.156231
N	−1.657107	−1.760234	−0.963283
H	−1.664925	−3.114039	−2.634209
H	−0.785665	−1.570777	−2.885550
C	−2.017993	−2.806565	0.035165
C	−2.879499	−1.040832	−1.402259
C	−0.788172	−3.373233	0.748050
H	−2.703780	−2.342393	0.761535
H	−2.573737	−3.634932	−0.448326
H	−2.600958	−0.249515	−2.111885
H	−3.590136	−1.730315	−1.897331
H	−3.369736	−0.575374	−0.537297
N	0.033063	−2.299435	1.377437
H	−1.112718	−4.114265	1.505272
H	−0.142842	−3.907784	0.034302
C	1.399614	−2.798926	1.675575
C	−0.589123	−1.826574	2.641437
H	1.367147	−3.617172	2.420441
H	1.867533	−3.169971	0.754954
H	2.009118	−1.976416	2.073159
H	0.011716	−1.005499	3.057973
H	−1.606225	−1.455528	2.453854
H	−0.642174	−2.644083	3.387232

Pre6

E= -555.4199293au

I	−3.122414	−0.501939	−0.066065
Cu	−0.866149	0.372636	0.017214
N	1.002980	1.111126	0.109742
C	1.939789	−0.058920	−0.016006
H	1.641328	−0.773066	0.767228
H	1.738572	−0.534992	−0.988794
C	1.169786	2.085535	−1.004736
H	2.146908	2.601994	−0.961579
H	1.079025	1.558463	−1.965195
H	0.372347	2.839876	−0.940146
C	1.158093	1.808655	1.417744
H	2.142626	2.305072	1.503022
H	0.368969	2.568418	1.514424
H	1.046599	1.080634	2.234239
C	3.451876	0.247814	0.071423
H	3.727117	0.583690	1.099638
H	3.695371	1.078395	−0.611904
N	4.247249	−0.907458	−0.358738

C	5.634014	-0.519828	-0.623516
H	6.171098	-0.139037	0.277023
H	6.189526	-1.391863	-1.004778
H	5.661541	0.264761	-1.397360
C	4.198477	-2.013441	0.600624
H	4.801761	-2.851226	0.216758
H	4.591725	-1.738680	1.608237
H	3.167954	-2.380686	0.721209

1G'$_{CuI}$

E= -1275.6951515au

Cu	-0.340398	-0.328801	0.277061
N	-0.922117	1.596526	0.460889
C	-2.065877	2.068784	0.033332
C	-3.163380	1.350197	-0.594081
H	-2.256293	3.147553	0.163415
C	-3.315287	-0.075209	-0.690783
C	-4.206961	2.167841	-1.108008
N	-2.312906	-0.899252	-0.167011
C	-4.485940	-0.596582	-1.292185
H	-4.096104	3.253319	-1.020829
C	-5.346447	1.639895	-1.707435
N	-2.616340	-2.156027	0.009758
H	-4.596350	-1.681855	-1.356126
C	-5.480502	0.241416	-1.794568
H	-6.124532	2.300825	-2.095905
N	-2.226170	-3.163799	0.471134
H	-6.368500	-0.199290	-2.256302
C	0.024028	2.511088	1.010896
C	0.776907	2.096273	2.130046
C	0.256354	3.786883	0.451086
C	1.720437	2.959837	2.698371
H	0.598460	1.099311	2.544121
C	1.212886	4.638453	1.020284
H	-0.284749	4.094252	-0.448215
C	1.942549	4.233325	2.148247
H	2.287681	2.632546	3.573966
H	1.395400	5.618979	0.571281
H	2.688777	4.900257	2.588267
I	0.297283	-2.359904	1.713647
N	0.984326	-0.438323	-1.571699
C	2.380945	-0.307732	-1.066344
H	2.419890	0.646241	-0.515889
H	2.535297	-1.113475	-0.330814
C	0.726454	-1.756723	-2.188300
H	1.297565	-1.913841	-3.125614
H	0.979323	-2.546366	-1.465310
H	-0.346180	-1.834444	-2.424085
C	0.617008	0.647032	-2.503185
H	1.155125	0.586192	-3.470604
H	-0.463855	0.596265	-2.707667
H	0.839401	1.619134	-2.037381
C	3.511742	-0.368977	-2.117777
H	3.426543	0.477180	-2.842168
H	3.409233	-1.298743	-2.702207
N	4.837743	-0.404530	-1.486532
C	5.861420	-0.826824	-2.441489
H	5.984762	-0.127266	-3.303180
H	6.833930	-0.903106	-1.927648
H	5.610154	-1.822413	-2.842612
C	5.206243	0.873568	-0.877330
H	6.198249	0.778464	-0.406788
H	5.253427	1.713597	-1.612597
H	4.491633	1.149398	-0.087597

TS12G'$_{CuI}$

E= -1275.6718367au

Cu	0.477985	-0.314494	-0.140833
N	0.853803	1.604107	-0.465991
C	2.033013	2.149148	-0.235410
C	3.216541	1.515182	0.244338
H	2.138277	3.221336	-0.460789
C	3.339948	0.074659	0.490090
C	4.353625	2.355042	0.449188
N	2.299172	-0.747697	0.272900
C	4.629282	-0.383616	0.941135
H	4.231530	3.424070	0.247295
C	5.571465	1.872867	0.889662

N	2.779634	-2.464526	0.386603
H	4.741151	-1.449283	1.139086
C	5.689929	0.481408	1.134232
H	6.419205	2.543174	1.044378
N	2.169044	-3.328485	-0.051432
H	6.641560	0.070612	1.485500
C	-0.221899	2.425281	-0.903708
C	-1.101932	1.924173	-1.887241
C	-0.448435	3.711890	-0.363574
C	-2.171403	2.707789	-2.337321
H	-0.924249	0.925099	-2.296891
C	-1.522293	4.486986	-0.820687
H	0.202330	4.089135	0.430206
C	-2.385882	3.991925	-1.809989
H	-2.837764	2.312424	-3.108860
H	-1.690086	5.478897	-0.391379
H	-3.224630	4.598567	-2.161441
I	-0.287591	-2.419700	-1.457049
N	-4.913148	-0.216349	1.641809
C	-3.548968	-0.341199	2.166150
H	-3.421853	0.452785	2.923976
H	-3.495864	-1.305275	2.702136
C	-5.329347	-1.305805	0.764157
H	-4.855826	-1.302533	-0.243985
H	-5.101654	-2.272848	1.242577
H	-6.421703	-1.251452	0.614735
C	-5.238214	1.096879	1.097099
H	-4.749912	1.338031	0.124861
H	-6.329026	1.162211	0.940711
H	-4.954482	1.878184	1.822316
C	-2.405848	-0.262050	1.116641
H	-2.487937	0.677739	0.546508
H	-2.499537	-1.086779	0.391069
N	-1.006169	-0.322010	1.633320
C	-0.670873	0.834225	2.489903
H	-1.219799	0.830813	3.452796
H	0.407901	0.815794	2.711044
H	-0.902513	1.766292	1.953264
C	-0.728036	-1.584056	2.355451
H	0.348400	-1.634276	2.582131
H	-1.288320	-1.662915	3.307946
H	-0.984867	-2.435034	1.707393

1I$_{\textbf{Thermo}}$

E= -720.2530105au

N	0.653780	0.132725	0.109840
C	-0.190453	-0.746716	-0.321234
C	-1.647378	-0.624019	-0.215816
H	0.152130	-1.697474	-0.778791
C	-2.367866	0.515847	0.260242
C	-2.396423	-1.783402	-0.537672
N	-1.823720	1.776930	0.603167
C	-3.757034	0.418200	0.479699
H	-1.852734	-2.652262	-0.922534
C	-3.777238	-1.860521	-0.350597
N	-0.929480	2.333890	-0.052936
H	-4.273788	1.298290	0.868940
C	-4.458219	-0.753401	0.180929
H	-4.315974	-2.777077	-0.603285
N	-0.151845	3.031614	-0.542187
H	-5.537621	-0.794589	0.349532
C	2.031752	-0.150957	0.082692
C	2.918438	0.908563	-0.218149
C	2.565988	-1.422289	0.401500
C	4.299124	0.687552	-0.246178
H	2.496333	1.890799	-0.442401
C	3.951224	-1.628458	0.391650
H	1.892037	-2.230544	0.699657
C	4.823076	-0.580223	0.058265
H	4.972369	1.512661	-0.496137
H	4.352135	-2.611720	0.655415
H	5.904017	-0.745261	0.052426

TS12I$_{\textbf{Thermo}}$

E= -720.1878787au

N	-0.630162	0.081856	-0.043191
C	0.234687	-0.886002	-0.132098
C	1.672139	-0.719980	-0.106046

H	-0.102115	-1.931809	-0.288798
C	2.385903	0.559537	0.048084
C	2.455365	-1.880007	-0.234597
N	2.106569	1.810186	-0.231068
C	3.830102	0.501922	0.265094
H	1.935455	-2.838012	-0.343097
C	3.860681	-1.862678	-0.253533
N	0.405798	2.489141	0.462749
H	4.322767	1.432351	0.547820
C	4.548660	-0.658670	-0.017819
H	4.411734	-2.796247	-0.391200
N	-0.209729	3.421437	0.336006
H	5.640371	-0.651733	0.054711
C	-1.998747	-0.212598	-0.025606
C	-2.548502	-1.332937	0.647837
C	-2.875790	0.693802	-0.670379
C	-3.931344	-1.548323	0.647634
H	-1.888151	-2.002600	1.205911
C	-4.253100	0.457438	-0.684181
H	-2.447258	1.565122	-1.170719
C	-4.788713	-0.663072	-0.025526
H	-4.343721	-2.407948	1.184206
H	-4.915963	1.156854	-1.201563
H	-5.868500	-0.834901	-0.021921

1T$_{\textbf{Thermo}}$

E= -720.2549315au

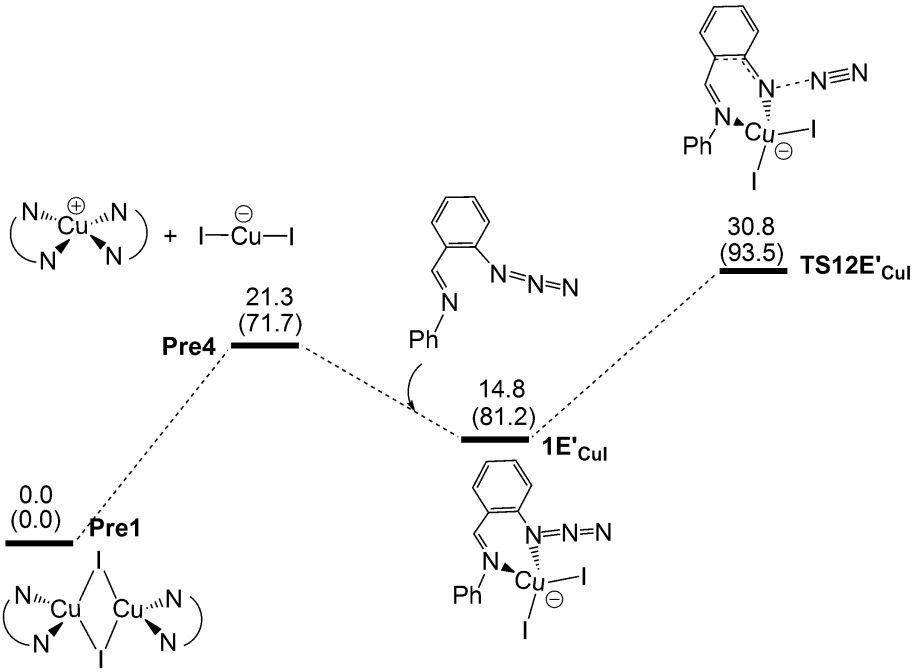
H	1.334767	-3.084842	-0.325995
C	1.973568	-2.201228	-0.229162
C	3.362331	-2.346451	-0.232588
C	1.345034	-0.939851	-0.107305
C	4.169441	-1.203837	-0.108910
H	3.813013	-3.336954	-0.330480
C	2.181638	0.209424	0.020962
C	-0.121369	-0.924583	-0.121150
C	3.584067	0.059367	0.016793
H	5.259210	-1.292834	-0.108436
N	1.561782	1.468327	0.153255
H	-0.579531	-1.933586	-0.188458
N	-0.852600	0.140146	-0.085342
H	4.215962	0.946455	0.116006
N	2.256063	2.492722	0.262832
N	2.724887	3.545472	0.372344
C	-2.251644	0.022703	-0.032150
C	-3.018929	0.964405	-0.756337
C	-2.921517	-0.946140	0.753111
C	-4.415854	0.904896	-0.736369
H	-2.491884	1.723582	-1.339522
C	-4.321267	-0.983141	0.786322
H	-2.337705	-1.637724	1.367227
C	-5.074700	-0.067843	0.034925
H	-4.995812	1.629909	-1.314841
H	-4.826458	-1.727127	1.409581
H	-6.167286	-0.099878	0.064425

TS12T$_{\textbf{Thermo}}$

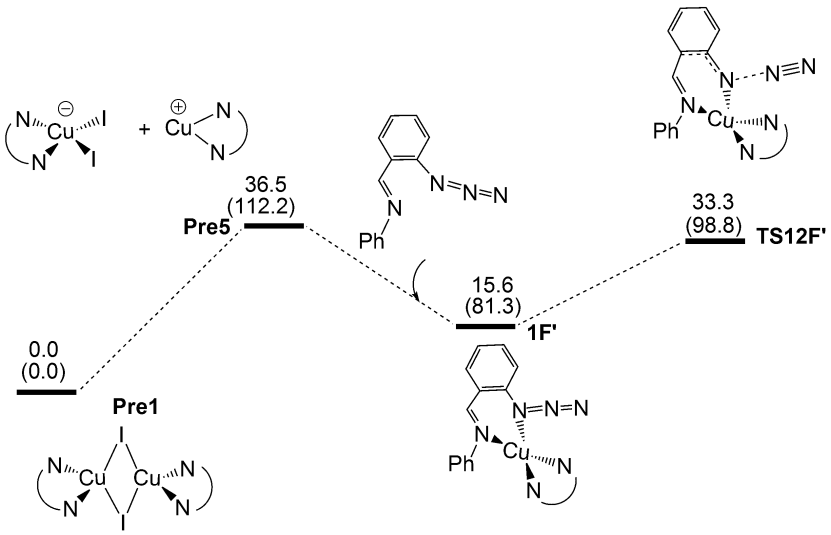
E= -720.2161391au

H	2.377832	-3.122568	-0.301413
C	2.646787	-2.067526	-0.191981
C	3.977941	-1.676814	-0.122656
C	1.611454	-1.106599	-0.121545
C	4.275554	-0.300016	0.016804
H	4.781621	-2.414700	-0.174659
C	1.899515	0.303437	0.022746
C	0.216819	-1.399613	-0.193326
C	3.277786	0.666177	0.085216
H	5.319663	0.022402	0.073707
N	0.807949	1.152963	0.084713
H	-0.161158	-2.428650	-0.307366
N	-0.570826	-0.364435	-0.145417
H	3.540231	1.720202	0.194848
N	1.340862	2.634883	0.279427
N	0.895635	3.684859	0.369398
C	-1.961241	-0.331165	-0.078561
C	-2.640646	0.739545	-0.703446
C	-2.704280	-1.309168	0.626303
C	-4.036162	0.808742	-0.651395
H	-2.053093	1.496511	-1.227227

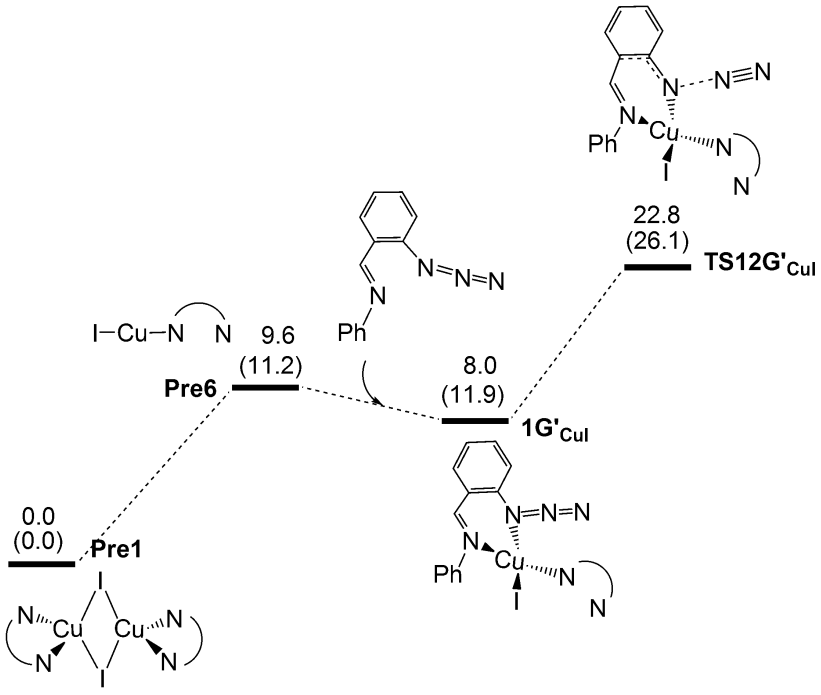
C	−4.100535	−1.228553	0.669626
H	−2.178169	−2.110421	1.152211
C	−4.772870	−0.174597	0.029950
H	−4.553007	1.637572	−1.143181
H	−4.666437	−1.988076	1.216827
H	−5.863563	−0.113261	0.072986



(a)



(b)



(c)

Figure S1. Energy profiles calculated for the bidentate coordination mechanism for (a) $[CuI_2]^-$ (b) $[Cu(TMEDA)]^+$ and (c) CuI(TMEDA). The solvent-corrected and gas phase (in parentheses) free energies are given in kcal/mol.

Calculated imaginary frequencies of all transition states species

TS12I$_{CuI}$	-503.69	For the Cu-internal pathway
TS12T$_{CuI}$	-624.83	For the Cu-terminal pathway
TS12I'$_{CuI}$	-446.37	For the diCu-internal pathway
TS12T'$_{CuI}$	-654.84	For the diCu-terminal pathway
TS12D'$_{CuI}$	-386.68	For the diCu-bidentate pathway
TS23D'$_{CuI}$	-127.05	For the diCu-bidentate pathway
TS12I$_{Thermo}$	-285.07	For the uncatalyzed-internal pathway
TS12T$_{Thermo}$	-669.21	For the uncatalyzed-terminal pathway
TS12E'$_{CuI}$	-377.34	For the $[CuI_2]^-$-bidentate pathway
TS12F'	-533.33	For the $[Cu(TMEDA)]^+$-bidentate pathway
TS12G'$_{CuI}$	-344.20	For the (TMEDA)CuI-bidentate pathway