Supporting Information

Mechanistic Insight into Cu/Ag-Cocatalyzed C–H Activation of Arenes with Oxygen as the Terminal Oxidant

Gui-Yu Ruan,† Zheng-Hang Qi,† Ye Zhang, Wei Liu, and Yong Wang**

College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China.

E-mail: yowang@suda.edu.cn; weiliu@suda.edu.cn

CONTENTS

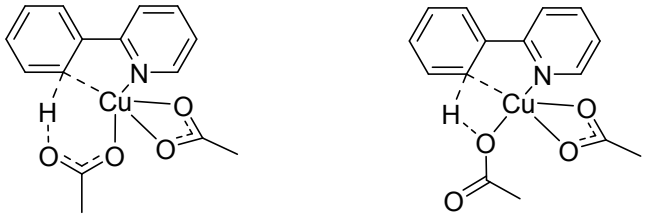
1. Computational Details.

The geometry optimizations and energy estimations were carried out by the density functional theory with the three-parameter hybrid functional (B3LYP)[S1] using Gaussian09 suite of programs.[S2] The B3LYP calculations were carried out by 6-311+G(d,p) basis set for the C, H, O, N, Cu atoms and lanl2dz basis set for Ag. For all reactions, intermediates and transition states of the copper-catalyzed intramolecular C–H functionalization/C–N cyclization are fully optimized at the B3LYP/6-311+G(d,p)+lanl2dz level. Frequency calculations of transition states were also performed to ensure one and only one imaginary frequency. For the solvent effect, the single-point calculations on the gas-phase optimized geometry with SMD solvation model (solvent = 1-butanol) were applied. The single-point calculations were carried out using M06 with lanl2dz for Ag and 6-311+G(d,p) for other atoms. The reported Gibbs free energy in this study was calculated by adding the gas-phase Gibbs free energy correction with the solution-phase single-point energy.

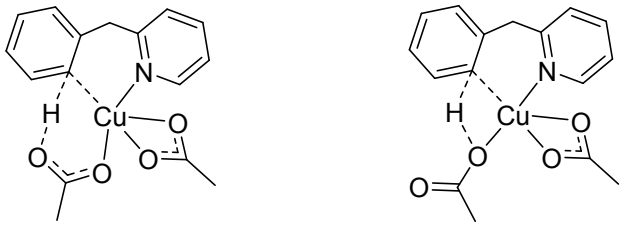
S1 (a) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, 58, 1200. (b) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, 98, 11623. (c) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648. (d) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B.* **1988**, 37, 785.

S2 Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, G. H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T. Jr.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski J.; and Fox D. J., Gaussian, 09, Revision C.01, Gaussian, Inc., Wallingford CT, 2010.

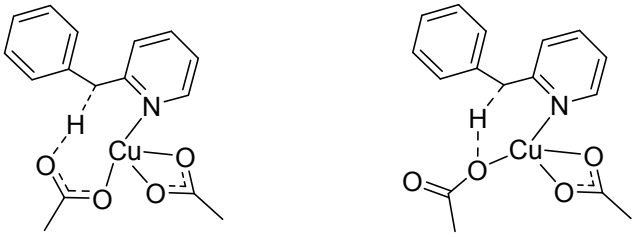
2. Skeletal formula of the reported structures



TS$_{6\text{-m}}$ **TS$_{4\text{-m}}$**

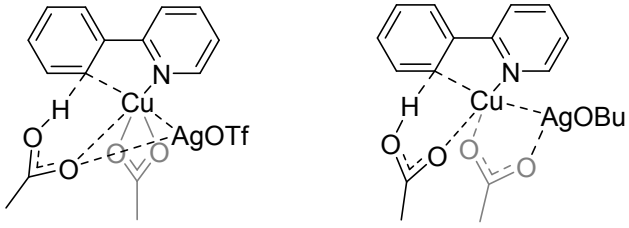


TS'$_{6\text{-m}}$ **TS'$_{4\text{-m}}$**

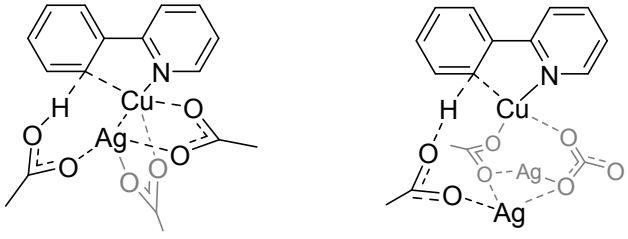


TS''$_{6\text{-m}}$ **TS''$_{4\text{-m}}$**

Figure S1. Skeletal formula of the six- and four-membered aromatic (**TS** and **TS′**) and benzylic (**TS′′**) C–H activation transition states of 2-phenylpyridine 1 and 2-benzylpyridine 2 with one $Cu(OAc)_2$



TS1 **TS2**



TS3 **TS4**

Figure S2. Skeletal formula of the transition states for the aromatic C–H activation of 2-phenylpyridine 1 with Ag(I) additives.

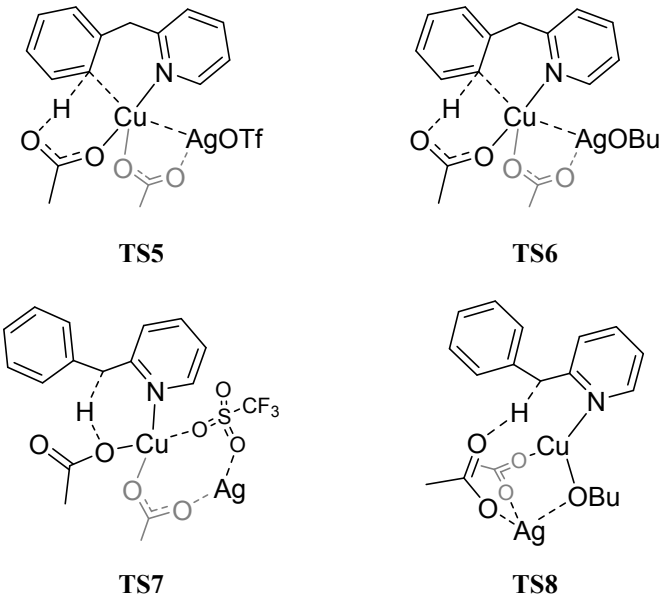


Figure S3. Skeletal formula of the transition states for the benzylic vs aromatic C–H activation of 2-benzylpyridine 2 with AgOTf and AgOAc additives.

3. Cartesian coordinates of all transition states

$TS_{6\text{-}m}$

C	0.00000000	0.00000000	0.00000000
C	1.39568230	0.00000000	0.00000000
C	2.09625378	1.20361003	0.00000000
C	1.39655774	2.41461577	-0.00942956
C	-0.01956985	2.43555780	-0.03987892
C	-0.69472300	1.20803122	-0.01801775
H	-0.54069581	-0.94015523	0.01048233
H	1.93883685	-0.93824196	0.01820841
H	3.18000850	1.19138533	0.04550159
H	-1.77952827	1.20146770	-0.04093814
C	3.90729802	5.26153994	-0.16770800
C	3.12414162	6.25476623	0.41865147
C	3.38470226	3.98555913	-0.33533173
C	1.83427794	5.92865994	0.81511711
H	3.49888207	7.25946195	0.56502777
C	2.08077730	3.71803320	0.09323223
H	3.96733449	3.20638232	-0.80904117
N	1.33742076	4.69672298	0.65786499
H	1.17212228	6.65108950	1.27781252
Cu	-0.54891138	4.15987691	1.13436114
H	-2.35855493	5.20423676	5.01618896
C	-2.89031716	4.77243883	4.16829473
C	-1.94079022	4.50384736	3.03576715
H	-3.63768750	5.49515980	3.82775716
H	-3.40578438	3.85731581	4.45934096
O	-2.16683092	3.56737042	2.20709340
O	-0.90799455	5.22233716	2.86510782
O	-1.53547435	5.52584689	-0.27333081
C	-1.65749568	5.08889071	-1.43785284
O	-1.19819712	3.95725322	-1.83016834
C	-2.40338786	5.90287058	-2.47541230
H	-2.52275804	6.93193888	-2.13895321
H	-1.88203228	5.86738985	-3.43322117
H	-3.39278164	5.46001015	-2.62196906
H	-0.64070890	3.31959860	-0.83084914
H	4.91533211	5.48339489	-0.49920066

$TS_{4\text{-}m}$

C	0.00000000	0.00000000	0.00000000
C	1.39604540	0.00000000	0.00000000
C	2.10185169	1.20122429	0.00000000
C	1.40470996	2.41337119	0.00181194
C	-0.01027653	2.42492162	-0.01421586
C	-0.69823699	1.20667407	-0.00851344

H	-0.54015622	-0.94027448	-0.00576769
H	1.93784577	-0.93918685	0.00911770
H	3.18585558	1.18498146	0.03204684
H	-1.78068517	1.22189634	-0.06948811
C	3.90175369	5.26542563	-0.23483485
C	3.11676631	6.27288345	0.32415124
C	3.38556219	3.98232124	-0.36158899
C	1.83122131	5.95282461	0.73720180
H	3.48647866	7.28367226	0.43639111
C	2.08445422	3.71985269	0.07720169
H	3.97094899	3.19292022	-0.81408593
N	1.34010771	4.71363507	0.61654796
H	1.16667914	6.68334456	1.18372840
Cu	-0.52131680	4.19176926	1.11174134
H	-3.28447869	6.61175551	3.47030293
C	-3.13884031	5.54146393	3.61960090
C	-2.11797387	5.01951787	2.65267699
H	-4.07936221	5.00400962	3.50727046
H	-2.76598367	5.39089207	4.63699761
O	-2.23179758	3.86787304	2.13348318
O	-1.09599690	5.71472030	2.33953168
O	-1.27481965	4.41887125	-1.22627344
C	-2.44373327	4.09224968	-1.72963917
O	-2.94350939	2.97682618	-1.65949232
C	-3.14458199	5.24188381	-2.44058412
H	-4.13012500	4.92862609	-2.78292859
H	-3.23641993	6.09843108	-1.76809929
H	-2.54283206	5.56354129	-3.29486471
H	-0.65488191	3.36124897	-0.63047814
H	4.90710752	5.48194477	-0.57762502

TS′$_{6\text{-}m}$

C	-0.40065400	3.54746300	1.62426800
C	-1.78157700	3.54413400	1.43089900
C	-2.36756100	2.61056800	0.57561500
C	-1.57443500	1.67766100	-0.09349800
C	-0.17623900	1.66979300	0.08421700
C	0.39091100	2.61488300	0.95769200
H	0.05377900	4.27474700	2.28839700
H	-2.40465500	4.26813500	1.94500100
H	-3.44348900	2.61731500	0.42736900
H	1.46511700	2.61468300	1.10685300
C	-2.20289900	0.65572300	-1.01763000
H	-3.21365900	0.96120800	-1.29492400
H	-1.61731100	0.60742600	-1.94349000
C	-3.46767100	-2.78197900	0.01490400
C	-2.31231900	-3.30018800	0.59022300
C	-3.44042400	-1.49163600	-0.49955100
C	-1.17826900	-2.50175700	0.63000100
H	-2.28082700	-4.30017000	1.00334300
C	-2.26591800	-0.73932000	-0.43233800
H	-4.32160700	-1.05853600	-0.95667200
N	-1.15648400	-1.25141700	0.13499100
H	-0.24925400	-2.84827200	1.06487100
Cu	0.64842800	-0.26445400	0.26999100
H	4.53151000	-1.84427200	1.40748500
C	3.87946700	-1.39945400	2.16496100
C	2.61222000	-0.94767200	1.49459100
H	4.39786300	-0.55373200	2.61574100
H	3.66168400	-2.16248500	2.91293800
O	2.47326400	0.24889400	1.10398300
O	1.66411500	-1.76810200	1.28281200
O	1.40640300	-0.70226000	-1.75332300
C	1.50509900	0.28381700	-2.51224200
O	1.03901400	1.44925100	-2.23766900
C	2.22484300	0.15139700	-3.83856500
H	1.69308300	0.69877800	-4.61823200
H	3.21828900	0.59872000	-3.74055300
H	2.33467000	-0.89802700	-4.10879900
H	0.51212800	1.44245000	-1.05907000
H	-4.37614400	-3.37174200	-0.03263900

TS′$_{4\text{-}m}$

C	0.08623600	3.63896600	-1.59988100
C	1.47528900	3.59534000	-1.72071600
C	2.20350200	2.57471900	-1.11045700
C	1.55351000	1.58274500	-0.37255600
C	0.15014500	1.62024400	-0.23844000
C	-0.56880600	2.65273500	-0.86894800
H	-0.47793000	4.43605900	-2.07136600
H	1.99481800	4.35783700	-2.29118100
H	3.28503600	2.55667100	-1.20329200
H	-1.64848300	2.67681600	-0.77304100
C	2.34966900	0.51521400	0.33781900
H	3.41560400	0.74297600	0.27982400
H	2.06387400	0.53764000	1.40527000
C	3.05913700	-3.09844000	-0.56654900

C	1.77113300	-3.54984900	-0.84338100
C	3.24151700	-1.77135200	-0.21033400
C	0.72558900	-2.64760900	-0.75469600
H	1.57334600	-4.57650500	-1.12292600
C	2.14661600	-0.90278700	-0.13091900
H	4.22884200	-1.39030300	0.01823800
N	0.90512800	-1.35435600	-0.41102000
H	-0.29664100	-2.94072300	-0.95562200
Cu	-0.78487500	-0.23250000	-0.41670900
H	-4.99237500	-0.47188000	-1.71141200
C	-4.46664300	-1.26080300	-1.17448800
C	-3.03985000	-0.86775200	-0.92693300
H	-4.51300500	-2.20157200	-1.72315200
H	-4.95666100	-1.40532000	-0.20706900
O	-2.69943300	0.34946800	-0.85006400
O	-2.13671400	-1.75139100	-0.76288400
O	-0.97605500	0.76797200	2.00375000
C	-0.26579200	0.52007400	3.06822200
O	0.96412300	0.53485100	3.12256600
C	-1.10100100	0.20715900	4.30192900
H	-1.83448600	-0.56909600	4.07315800
H	-0.45977000	-0.10852700	5.12387500
H	-1.65648900	1.10232900	4.59435900
H	-0.34427300	1.18884800	0.90828200
H	3.90720700	-3.77108000	-0.62724200

TS″$_{6\text{-m}}$

C	-2.62604600	2.48109500	-1.67641900
C	-1.73414200	3.41325200	-1.13427500
C	-0.41561600	3.06721800	-0.87989200
C	0.08040400	1.77413600	-1.16525600
C	-0.82949400	0.85664600	-1.73948100
C	-2.16118400	1.20856800	-1.98232700
H	-3.65824300	2.75216700	-1.86442800
H	-2.07695900	4.41612800	-0.90201800
H	0.25782200	3.80187000	-0.45004100
H	-2.82655100	0.48040000	-2.43373800
C	1.48936500	1.46723700	-0.87846800
C	3.95993500	-1.31939100	-1.24979600
C	3.41312700	-0.05992400	-1.27311100
C	3.17122500	-2.41794000	-0.85779500
C	2.05593500	0.15947400	-0.89531500
H	3.99303100	0.79063200	-1.60982800
C	1.87215600	-2.16598500	-0.47803600
H	3.55856200	-3.42763800	-0.84520500
N	1.33431100	-0.92638600	-0.46100400
H	1.20990800	-2.96565000	-0.16567200
Cu	-0.46095400	-0.75611000	0.34429700
H	-4.52991600	-2.37356400	0.45527900
C	-3.64742000	-2.98768300	0.27787600
C	-2.40990800	-2.13783900	0.27346300
H	-3.73657400	-3.53383400	-0.66118200
H	-3.56657200	-3.71653000	1.08981500
O	-2.36325200	-1.04962700	0.92606700
O	-1.37070500	-2.49460400	-0.36600100
O	0.04172100	0.25853100	2.03788000
C	0.75603200	1.16850200	2.48705900
O	1.55295500	1.91064300	1.78783700
C	0.71995100	1.49634800	3.95736400
H	0.20406400	0.71215400	4.50735200
H	1.73303800	1.63609600	4.33702000
H	0.18447100	2.44071500	4.08922000
H	-0.47411800	-0.10375000	-2.09621600
H	1.53206800	1.69660200	0.72038400
H	2.18158900	2.25267900	-1.17349200
H	4.99021500	-1.46842600	-1.55461900

TS″$_{4\text{-m}}$

C	3.08415300	2.21555300	-2.17755700
C	3.72529400	1.97721800	-0.96068100
C	3.32534900	0.92350900	-0.14900100
C	2.27317600	0.06236400	-0.52523600
C	1.63639600	0.31912700	-1.75573400
C	2.04137700	1.37643700	-2.56702200
H	3.39279700	3.03976900	-2.81016300
H	4.53893900	2.61900900	-0.64043300
H	3.82567400	0.75722100	0.79923200
H	1.53985900	1.53967300	-3.51511600
C	1.91641500	-1.04000500	0.39137400
C	0.19687700	-4.36508200	0.17726000
C	1.15719800	-3.41418600	0.43624900
C	-1.03342900	-3.97317800	-0.37796600
C	0.92425000	-2.04886400	0.12981400
H	2.11995100	-3.69185600	0.84764400
C	-1.24545900	-2.62915100	-0.59757400
H	-1.80183400	-4.69330500	-0.62639000
N	-0.31390700	-1.68071400	-0.34007300

H	-2.18298300	-2.26095200	-0.99892700
Cu	-1.10831700	0.11933600	0.06754700
H	-4.77569700	1.50011400	-2.00653300
C	-4.07946200	2.13242400	-1.45770800
C	-2.96391600	1.31341100	-0.87611400
H	-4.59542600	2.67872600	-0.66704200
H	-3.65060500	2.86821100	-2.14403200
O	-2.21757400	1.80003700	0.03679300
O	-2.72254200	0.13943700	-1.28400200
O	0.12338600	0.35149400	1.65574500
C	0.30859400	1.20162400	2.70383500
O	1.35740500	1.23287000	3.29523600
C	-0.90373500	2.03020000	3.03920700
H	-1.68833100	1.37767100	3.43372200
H	-0.63455800	2.76449400	3.79608300
H	-1.30396600	2.51830000	2.14972600
H	0.83693300	-0.32664000	-2.09633000
H	1.05361900	-0.24100300	1.32676200
H	2.76506000	-1.41356300	0.95901400
H	0.39524300	-5.41071800	0.38536500

TS1

C	0.00000000	0.00000000	0.00000000
C	1.41852695	0.00000000	0.00000000
C	2.13058139	1.20253308	0.00000000
C	1.44387533	2.41481025	-0.02085855
C	0.04933511	2.43528391	-0.05727012
C	-0.66044260	1.23586816	-0.05306548
O	-2.24447869	-1.24527957	-2.08676980
C	-2.20994540	-2.38464272	-2.64175249
C	-3.22597034	-2.78176763	-3.67063124
Ag	-1.76227930	-5.03590874	-0.29696445
O	-1.26447858	-3.17923282	-2.31474883
O	-1.61106381	-3.01508810	0.61744590
C	-1.62432195	-2.48420985	1.76315519
C	-2.20089370	-3.22249051	2.94382082
O	-1.14888029	-1.32166572	1.96637305
H	-0.64422629	-0.81572061	0.93548516
H	-1.74547170	1.25795099	-0.06383471
H	-0.47835880	3.38204491	-0.08738266
H	1.99997203	3.34548925	-0.02948415
H	3.21473567	1.20412387	-0.02209275
H	-3.16074951	-3.66579891	2.67283117
H	-1.52301228	-4.03679926	3.21594246
H	-2.31843774	-2.55771887	3.79717104
H	-3.37227257	-3.86181817	-3.66794889
H	-4.16660220	-2.25877286	-3.50057373
H	-2.84664561	-2.49589473	-4.65632570
Cu	-0.56225752	-1.72055536	-1.03911800
C	1.80487073	-3.53692689	-0.77637840
C	2.08618655	-1.31484283	-0.08815742
C	3.10310995	-3.86426971	-0.40343627
H	1.14901854	-4.28411362	-1.20707857
C	3.39582951	-1.58593849	0.30987447
C	3.90565409	-2.87057678	0.14908689
H	3.45354481	-4.87801223	-0.54501544
H	3.99858599	-0.80418164	0.75307062
H	4.92007267	-3.09384163	0.45941614
N	1.31740568	-2.29868323	-0.61680477
O	0.67320577	-6.50013711	-1.01390520
S	-0.31573341	-7.49290933	-1.49106449
O	-0.20451222	-7.96204930	-2.86443060
O	-1.71893825	-7.10480331	-1.06801564
C	0.00090488	-9.01008292	-0.42094536
F	-0.11858271	-8.70341132	0.88109152
F	-0.86786792	-9.98401867	-0.70654738
F	1.24085474	-9.46863456	-0.63167893

TS2

C	0.00000000	0.00000000	0.00000000
C	1.41328538	0.00000000	0.00000000
C	2.12425915	1.20521552	0.00000000
C	1.43489041	2.41454954	-0.02115536
C	0.03874377	2.42987403	-0.05731898
C	-0.66782522	1.22973950	-0.06114081
O	-2.01221103	-0.95069673	-2.01687009
C	-2.87520634	-1.47247517	-2.79369297
C	-4.05662187	-0.60020105	-3.15950659
Ag	-1.27501377	-4.04377316	-2.84976987
O	-2.83115893	-2.63368425	-3.26865919
O	-1.60046799	-3.10474542	0.20639286
C	-1.73175822	-2.64670184	1.36412733
C	-2.51145541	-3.42882884	2.39621239
O	-1.25533924	-1.51789608	1.74843336
H	-0.66147618	-0.87963952	0.80444012
H	-1.75202078	1.24262187	-0.08683480
H	-0.49148515	3.37559154	-0.08522838

H	1.98764364	3.34728223	-0.03103775
H	3.20855807	1.20768520	-0.02049630
H	-3.50861829	-2.98823939	2.48794279
H	-2.61213543	-4.46848118	2.08789708
H	-2.02808110	-3.35867446	3.37145533
H	-4.74571339	-0.57454800	-2.31044651
H	-3.72526768	0.42141259	-3.34900020
H	-4.57757416	-1.00320179	-4.02612301
Cu	-0.52277619	-1.78254017	-1.10927325
C	1.83244706	-3.54802282	-0.73976641
C	2.07905862	-1.31307391	-0.06578355
C	3.12120378	-3.85262481	-0.31127891
H	1.20653653	-4.30559791	-1.22214005
C	3.37164583	-1.57153849	0.38896648
C	3.89633316	-2.85358607	0.26549197
H	3.49272829	-4.86144690	-0.43664990
H	3.94702688	-0.77927741	0.84928778
H	4.89832292	-3.06716750	0.62052233
N	1.33305836	-2.30768780	-0.61548635
O	0.29380214	-5.34769171	-2.48923996
C	0.11455277	-6.70778033	-2.78692600
C	1.38369632	-7.49807665	-2.44061919
H	-0.10678803	-6.86422483	-3.85797082
H	-0.73074479	-7.14356910	-2.22457509
C	1.27477834	-8.99407324	-2.75583297
H	2.22322619	-7.05915695	-2.99306108
H	1.59773841	-7.35849576	-1.37347444
C	2.54429484	-9.77878136	-2.40946610
H	0.42449877	-9.41999152	-2.20936675
H	1.04762341	-9.12451276	-3.82093605
H	2.43695812	-10.84124472	-2.64728167
H	3.40699925	-9.39919950	-2.96634558
H	2.77922089	-9.69976802	-1.34301355

TS3

C	0.00000000	0.00000000	0.00000000
C	1.41787195	0.00000000	0.00000000
C	2.13995286	1.19706483	0.00000000
C	1.45913140	2.41159239	-0.00540064
C	0.06269671	2.43573911	-0.01671400
C	-0.65448158	1.24199749	-0.02176461
O	-1.50893250	-0.73624533	-2.57337320
C	-2.60333590	-0.07549185	-2.60706661
C	-2.83368201	0.72148644	-3.87905576
O	-3.45463965	-0.02586700	-1.69671880
O	-2.84417127	-1.47601471	2.15571359
C	-1.70657169	-1.62230821	2.64158515
C	-1.56826623	-1.90420585	4.12459389
O	-0.59745694	-1.54591879	1.99445320
H	-0.50995743	-0.90657384	0.90174912
H	-1.73892269	1.27233971	-0.02330069
H	-0.46106126	3.38548561	-0.02057871
H	2.01777307	3.34090280	-0.01242378
H	3.22431184	1.19126314	-0.02485910
H	-1.20614711	-0.99991189	4.62202683
H	-2.52866804	-2.18865629	4.55105425
H	-0.82742605	-2.68819739	4.28987547
H	-3.87022519	1.04882664	-3.94098774
H	-2.17995891	1.59839655	-3.86683863
H	-2.56655203	0.12410916	-4.75188018
Cu	-0.52723666	-1.68694838	-1.19469373
C	1.76460321	-3.56447602	-0.61733333
C	2.06968228	-1.32272454	-0.03039524
C	3.03834917	-3.90207716	-0.17846222
H	1.08008395	-4.28377827	-1.04993133
C	3.35892367	-1.59918840	0.43209229
C	3.84446095	-2.89840377	0.35494017
H	3.38316801	-4.92527109	-0.25351652
H	3.95877345	-0.80924779	0.86433493
H	4.84043238	-3.12851890	0.71601062
N	1.30286160	-2.31129468	-0.54448378
H	-1.37967767	-5.97389082	-2.44834020
C	-2.22922091	-5.32206065	-2.65986901
C	-2.13054508	-4.03939855	-1.85088633
H	-3.16514826	-5.83659592	-2.44886898
H	-2.19080753	-5.06753626	-3.72288131
O	-3.15134407	-3.60326408	-1.28905523
O	-0.96518455	-3.50123098	-1.82446826
Ag	-3.33474683	-1.64091019	-0.04784602

TS4

C	0.00000000	0.00000000	0.00000000
C	1.41641782	0.00000000	0.00000000
C	2.14074548	1.19637592	0.00000000
C	1.46207843	2.41167254	-0.01052412
C	0.06560673	2.43679936	-0.03287546
C	-0.65017231	1.24275384	-0.03719828

O	-1.92210784	-0.62495898	-2.11971917
C	-3.12170121	-0.67430721	-2.54546890
C	-3.42271310	0.24626959	-3.71841061
Ag	-3.01953517	-2.69703192	0.19676020
O	-4.03358464	-1.39756375	-2.07623204
O	-2.90341600	-1.61902558	2.09739413
C	-1.83928456	-1.35400816	2.69733933
C	-1.88160210	-1.12390231	4.19203685
O	-0.68045059	-1.24373321	2.15512529
H	-0.53759929	-0.84439324	0.99590245
H	-1.73438695	1.27199299	-0.05223296
H	-0.45711265	3.38711787	-0.04948627
H	2.02185258	3.34032157	-0.01908916
H	3.22506379	1.18773021	-0.02609334
H	-2.81982423	-1.48337953	4.61075154
H	-1.03242862	-1.61537432	4.66911633
H	-1.78874225	-0.05081244	4.38290871
H	-2.91989116	1.20506308	-3.58668958
H	-3.02319584	-0.21049820	-4.62883322
H	-4.49658428	0.39183175	-3.83201033
Cu	-0.56550931	-1.68415852	-1.16587511
C	1.75302408	-3.54228035	-0.73121728
C	2.06673046	-1.32199465	-0.06253837
C	3.03379127	-3.89234376	-0.32139381
H	1.06046995	-4.23838612	-1.18936842
C	3.36062110	-1.61397127	0.37517647
C	3.84478039	-2.90996972	0.24273251
H	3.37997243	-4.91042056	-0.44434417
H	3.96651651	-0.83933152	0.82662418
H	4.84534953	-3.15303190	0.58217178
N	1.29352528	-2.29266719	-0.59998410
O	-2.30119335	-4.05476585	-3.58886695
O	-0.83405239	-3.41203517	-2.02061427
O	-2.90872729	-4.09932721	-1.45049944
C	-2.00490783	-3.85985090	-2.37825477
Ag	-4.56272097	-3.51660428	-3.11193801

TS5

C	-5.78399700	-0.01706900	-0.83108100
C	-5.85891300	1.37435500	-0.87915500
C	-4.78510300	2.15350500	-0.44624800
C	-3.62592700	1.54801800	0.03843500
C	-3.54521600	0.14150700	0.11157500
C	-4.62826700	-0.62654400	-0.35165200
H	-6.61911500	-0.62013700	-1.16941900
H	-6.75302200	1.85696900	-1.25833200
H	-4.85629800	3.23602900	-0.48365800
H	-4.55840700	-1.70729900	-0.32753400
C	-2.46659000	2.39331000	0.52184200
H	-2.77091000	3.43765000	0.60556200
H	-2.18745200	2.06459000	1.53088200
C	0.63503400	3.38643300	-1.44744200
C	1.11357200	2.13129100	-1.80102200
C	-0.54226000	3.47876900	-0.71158900
C	0.38107700	1.01861200	-1.41794500
H	2.03928800	1.99200400	-2.34231500
C	-1.22829400	2.32328600	-0.34408900
H	-0.93033500	4.44275900	-0.40710500
N	-0.76593400	1.11122300	-0.71822200
H	0.74637900	0.02657200	-1.65203700
Cu	-1.63073800	-0.63637900	-0.33588000
H	-2.99454400	-4.42340500	-2.23290800
C	-2.52428000	-4.68949900	-1.28537400
C	-1.65585800	-3.54855200	-0.79288700
H	-1.93697400	-5.59981700	-1.39008800
H	-3.32184700	-4.86228300	-0.55664100
O	-2.17157200	-2.37978500	-0.92242500
O	-0.54106900	-3.81948800	-0.30637000
O	-0.63601700	-1.09389900	1.52713200
C	-1.37870500	-0.98253300	2.53566800
O	-2.58393100	-0.55078100	2.47579400
C	-0.86260600	-1.38841900	3.89316700
H	0.21332800	-1.22487700	3.95201900
H	-1.38248800	-0.84725600	4.68277500
H	-1.05410000	-2.45742200	4.02905000
H	-2.96842700	-0.28568900	1.28206200
H	1.17564300	4.28298000	-1.72807800
Ag	1.17261300	-2.68901800	0.51050500
F	2.72252700	1.00124800	1.43718400
C	3.93601900	0.61950600	0.99421300
S	3.81015000	-0.97943600	0.00325400
F	4.74023100	0.47564300	2.05039500
F	4.41931000	1.60708800	0.22340300
O	3.18522700	-1.91162100	1.01308900
O	2.86941100	-0.64281200	-1.08655500
O	5.18124500	-1.30556900	-0.35991200

TS6

C	-4.64448500	0.70863900	-2.18306600
C	-4.78550300	2.07823200	-1.96168900
C	-4.03663600	2.70999400	-0.96823700
C	-3.14460500	1.97324400	-0.18919400
C	-3.00892700	0.58599300	-0.38542200
C	-3.75310900	-0.02803400	-1.40691700
H	-5.22540000	0.22026800	-2.95784600
H	-5.47534400	2.65804200	-2.56532900
H	-4.15283100	3.77644900	-0.80047700
H	-3.63071000	-1.09037800	-1.57735400
C	-2.30722100	2.64300900	0.87667300
H	-2.70533600	3.63123700	1.11219700
H	-2.35640100	2.04856500	1.79612400
C	1.11743800	4.15614800	0.23167300
C	1.80833900	3.02478500	-0.17620000
C	-0.22626800	4.03108500	0.56821700
C	1.13311000	1.81242600	-0.24760200
H	2.85865500	3.05086700	-0.43464100
C	-0.85518100	2.79137300	0.48190400
H	-0.79656000	4.88842200	0.90340300
N	-0.17458000	1.69899300	0.06229600
H	1.69362100	0.92123100	-0.53502100
Cu	-0.99441000	-0.13332600	-0.10337100
H	-2.47143800	-4.12244700	-1.79752200
C	-2.04588700	-4.17747200	-0.79295300
C	-1.05338500	-3.04940400	-0.60420600
H	-1.56600200	-5.14285100	-0.64513300
H	-2.86758000	-4.05650200	-0.08289400
O	-1.49869800	-1.87261700	-0.81611800
O	0.11844000	-3.34127600	-0.27174000
O	-0.83103200	-0.74155100	1.96321500
C	-1.94144900	-0.90430200	2.51538600
O	-3.06663000	-0.60495500	1.96912600
C	-2.01164300	-1.50424900	3.90132600
H	-2.25883100	-2.56591100	3.80805200
H	-1.04844100	-1.41345500	4.40169800
H	-2.80073500	-1.02988000	4.48578100
H	-2.93208500	-0.09535900	0.79530800
H	1.61161100	5.11909600	0.29571600
H	7.44271600	2.10546600	0.00079100
C	6.47203400	2.31550500	0.46221800
C	5.57797400	1.07164500	0.47060600
H	6.66008100	2.68297500	1.47563000
H	6.01286700	3.13220800	-0.10596800
C	5.28946400	0.52408900	-0.93031300
H	4.62828300	1.29316400	0.96653900
H	6.05487100	0.28498300	1.06868600
C	4.37172800	-0.70569600	-0.93973800
H	6.23427800	0.25532900	-1.42345000
H	4.82702200	1.30587100	-1.54798300
H	4.32023800	-1.08709700	-1.97476400
H	4.85460400	-1.49777400	-0.33858300
O	3.09956800	-0.38089100	-0.44019100
Ag	1.67746500	-1.87469700	-0.28362600

TS7

Cu	-0.35324800	-0.07505900	-0.48482800
H	-1.72597500	-4.09134200	-2.52861400
C	-1.73437800	-4.03872900	-1.43599500
C	-0.64636800	-3.08083300	-0.99478700
H	-1.55944500	-5.03532000	-1.03469000
H	-2.71052500	-3.66178100	-1.12931900
O	-0.87937500	-1.84664000	-1.13728600
O	0.41961200	-3.58585700	-0.53826900
O	-0.92454500	0.15149000	1.49248400
C	-0.86416200	-0.36174200	2.73045800
O	-1.62265900	-0.01788800	3.60913300
C	0.23286000	-1.38948700	2.90682700
H	1.20328500	-0.93773900	2.68754000
H	0.22063500	-1.75304400	3.93289800
H	0.08099300	-2.22492000	2.21860600
Ag	2.11174400	-2.28283700	-0.24611800
S	3.13395300	0.68994400	-0.55731000
O	3.95461200	1.25449300	-1.61468300
O	3.57170700	-0.65713400	-0.04553700
C	3.39171100	1.78951500	0.94993100
F	2.96550900	3.02815200	0.68373600
F	4.68199400	1.83663700	1.27939800
F	2.69648200	1.31516100	1.99374400
O	1.65983100	0.73975800	-0.77400600
H	-5.11352400	-1.09328900	-2.24456800
C	-5.02593300	-0.71558200	-1.23208400
C	-5.92151200	-1.14097100	-0.24907600
C	-4.01910300	0.19080200	-0.92422600
C	-5.80175700	-0.64893600	1.05321900

H	-6.70407600	-1.84982200	-0.49438200
C	-3.89577700	0.71008400	0.37932700
H	-3.32885200	0.50283100	-1.69698800
C	-4.80208000	0.26057700	1.36448500
H	-6.48944300	-0.97750800	1.82411300
C	-2.86255300	1.68390800	0.77966100
H	-4.70260900	0.63116000	2.37886800
H	-3.18853800	2.30871500	1.61096500
H	-1.93767600	0.92856300	1.31912600
C	-2.07571300	2.44943600	-0.21471800
C	-2.22180400	3.84246000	-0.30142100
N	-1.18159100	1.79405800	-1.00199900
C	-1.50130700	4.55781200	-1.24400400
H	-2.91965600	4.34041700	0.36026800
C	-0.48341000	2.50336500	-1.91116500
C	-0.62005100	3.87165000	-2.07812000
H	-1.62393100	5.63143400	-1.33021600
H	0.23047700	1.94503900	-2.50258400
H	-0.03232600	4.38382700	-2.82901200

TS8

C	4.11820800	2.81410100	-0.81119800
C	5.06671700	1.78563400	-0.88122800
C	4.72861500	0.48834800	-0.51835200
C	3.42801200	0.16629000	-0.06754800
C	2.51006600	1.22888000	0.05032100
C	2.84827900	2.53100900	-0.34008500
H	4.38361200	3.82548000	-1.10639300
H	6.07023000	1.99580400	-1.24275100
H	5.46246400	-0.30184100	-0.60242800
H	2.10700200	3.31928800	-0.25310900
C	3.09916700	-1.22358200	0.27850100
H	3.99704200	-1.81557000	0.45665700
H	2.54874300	-1.19217200	1.68672300
C	1.53777400	-4.20977200	-1.30462900
C	0.58593500	-3.60851700	-2.14926200
C	2.30055000	-3.41515700	-0.49084000
C	0.41519400	-2.25048900	-2.05042100
H	-0.01559800	-4.18498500	-2.83320700
C	2.15962000	-1.99605900	-0.49071600
H	3.05981300	-3.84448000	0.15399600
N	1.14721000	-1.44318100	-1.23561900
H	-0.34450500	-1.75332600	-2.63382400
Cu	0.27933900	0.33315400	-0.97856900
H	-2.32013300	4.65083400	-0.76768400
C	-1.32089500	4.28495900	-0.99223800
C	-1.15414800	2.86210300	-0.48882800
H	-0.59267200	4.92105600	-0.48297300
H	-1.11483200	4.33943800	-2.06463100
O	-0.20137200	2.19536000	-1.03639500
O	-1.90167900	2.45409100	0.41682400
O	0.23281700	-0.44303200	2.07319000
C	0.95694300	-0.82203500	3.00953800
O	2.19079000	-1.17251700	2.84287700
C	0.47258500	-0.87939200	4.44342400
H	0.80000300	-1.81078300	4.91590400
H	0.91446800	-0.05205900	5.00275000
H	-0.61298200	-0.79748600	4.48458600
H	1.68096800	-5.28481500	-1.31110800
H	-6.54526800	-0.98126800	-1.07302400
C	-5.84913700	-1.28602900	-0.28116500
C	-4.51256400	-0.54498200	-0.40972600
H	-6.32978800	-1.08528400	0.67713400
H	-5.70835200	-2.36736600	-0.36722700
C	-3.80001500	-0.81041300	-1.73541100
H	-3.86414300	-0.85415100	0.42627100
H	-4.67883600	0.53706800	-0.29553700
C	-2.48934500	-0.03539500	-1.92959100
H	-4.47165800	-0.54337600	-2.56406600
H	-3.58962000	-1.88607900	-1.83069400
H	-2.12959300	-0.21725300	-2.95836800
H	-2.69628200	1.04079100	-1.85542200
O	-1.51583500	-0.44941600	-0.99678000
Ag	-1.80368600	0.26769700	1.26448100
H	1.58471700	1.04868700	0.59468200