Supplementary information

Photoisomerization Pathways of trans-Resveratrol

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S1. MRCI/ODM2 calculations

Table S1. Distribution of classified hopping structures.

Hopping type	Window A	Window B
cys-pyramidalized	4	1
Cyclic	5	24
Twisted-pyramidalized	43	28
HOOP	27	28
H dissociated	9	10
No hopping	12	9
Total of trajectories	100	100

S2. CASSCF/CASPT2 calculations

Analyzing the natural orbitals and their occupation considered in the 14,14 active space (Figure S2), we concluded that the orbitals π_6, π_7, π_6*, and π_7* could be excluded without compromising the system's description. Therefore, the (10,10) active space (Figure S1) was chosen to proceed with the calculations.

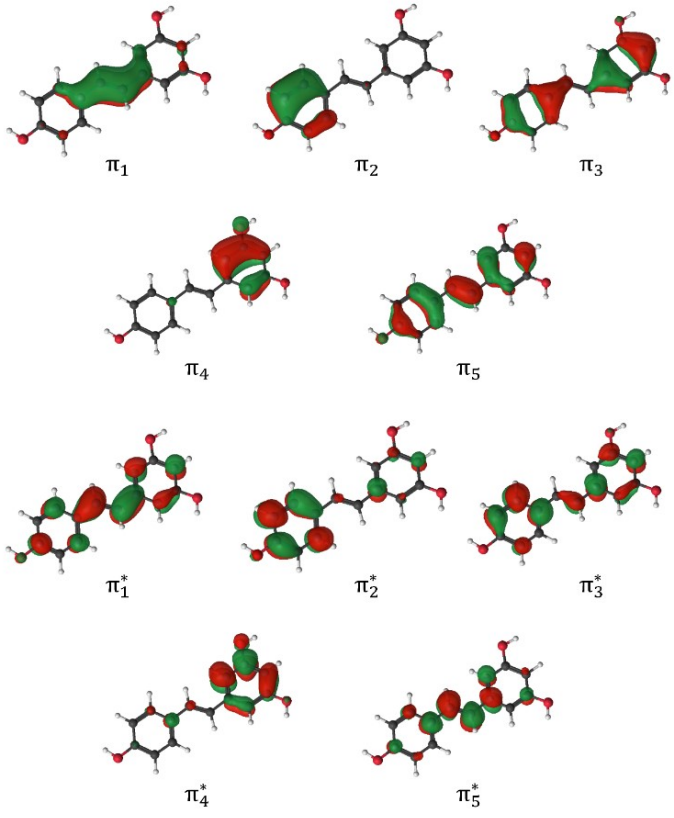

Figure S1. Orbitals used in the active space for CASSCF(10,10) calculations.

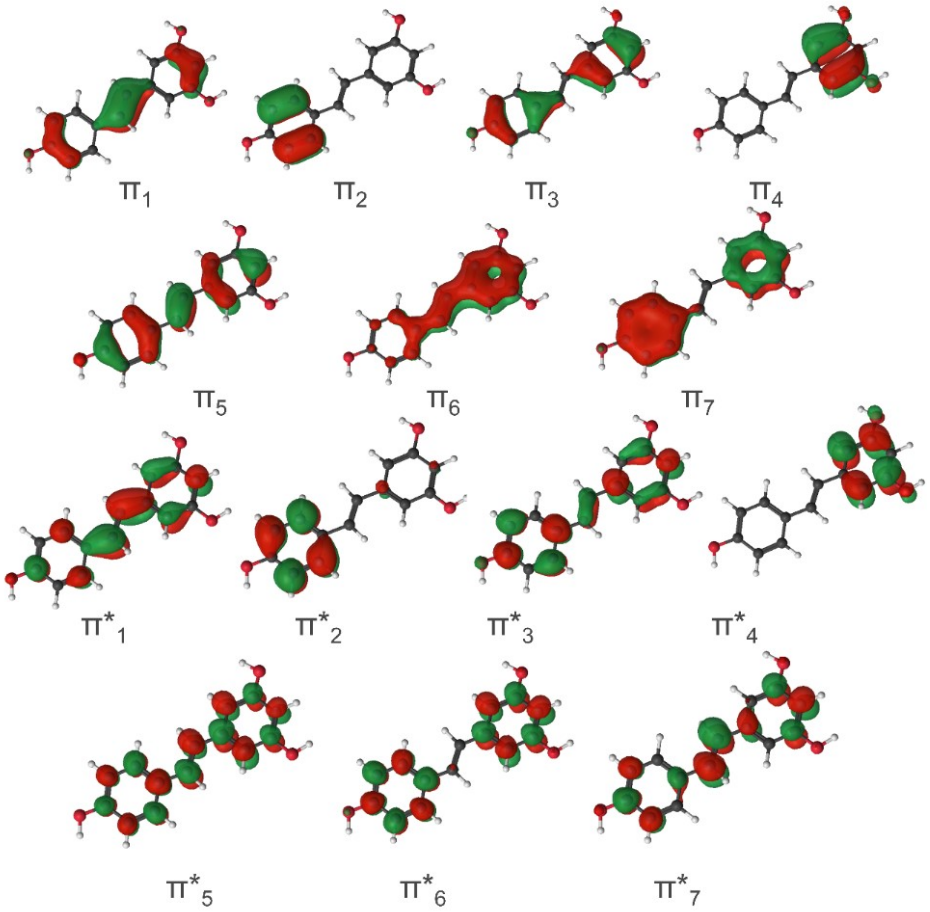

Figure S2. Orbitals used in the active space for CASSCF(14,14) calculations.

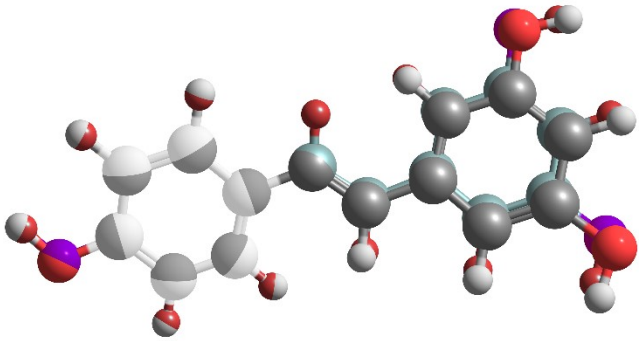

Figure S3. Overlay of the ground state structures of trans-resveratrol optimized at the CASSCF(10,10) and MRCI/ODM3 levels.

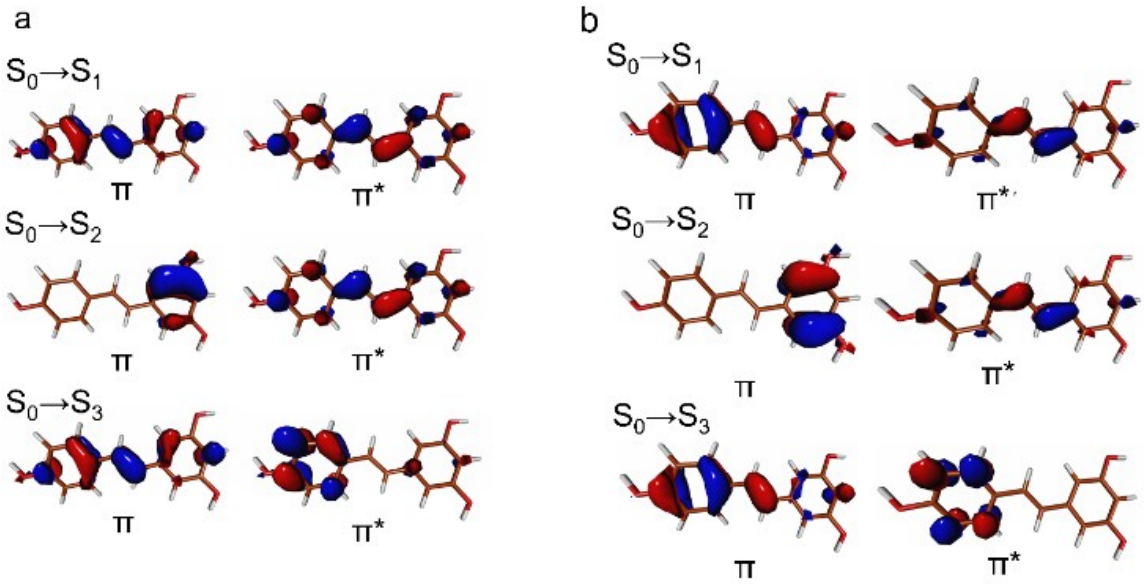

Figure S4. Natural orbitals involved in the main transitions $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, and $S_0 \rightarrow S_3$ of *trans*-resveratrol computed with (a) SA-CASSCF and (b) MRCI/ODM3.

Table S2. Vertical excitation energies and oscillator strength (*f*) for *trans*-resveratrol at XMS-CASPT2//CASSCF level.

S_0 Geom	ANO-S-VDZ				ANO-RCC-VDZP			
	IPEA 0.00		IPEA 0.25		IPEA 0.00		IPEA 0.25	
	Energy (eV)	*f*	Energy (eV)	*f*	Energy (eV)	*f*	Energy (eV)	*f*
S_1	3.94	0.948	4.46	1.074	4.10 4.24[a]	0.986 0.445[a]	4.60	1.11
S_2	4.59	0.010	5.10	0.017	4.73 4.52[a]	0.009 0.196[a]	5.25	0.01
S_3	4.72	0.012	5.36	0.007	4.90 5.79[a]	0.008 0.002[a]	5.53	0.004

[a]Computational results obtained using active space XMS-CASPT2(12,10)//CASSCF (12,10).

Table S3. Intersystem crossing rates involving the $S_1 \rightarrow T_1$ transition for *trans* and *cis*-resveratrol, computed at the CAM-B3LYP/def2-TZVP level in the gas phase

	trans-resveratrol	cis-resveratrol
ISC rate constant (s^{-1})	95.7	$5.55 \cdot 10^5$
Time (s)	0.01	$1.80 \cdot 10^{-6}$

Values were obtained using the path integral formalism as implemented in Orca program [70] of the main text.

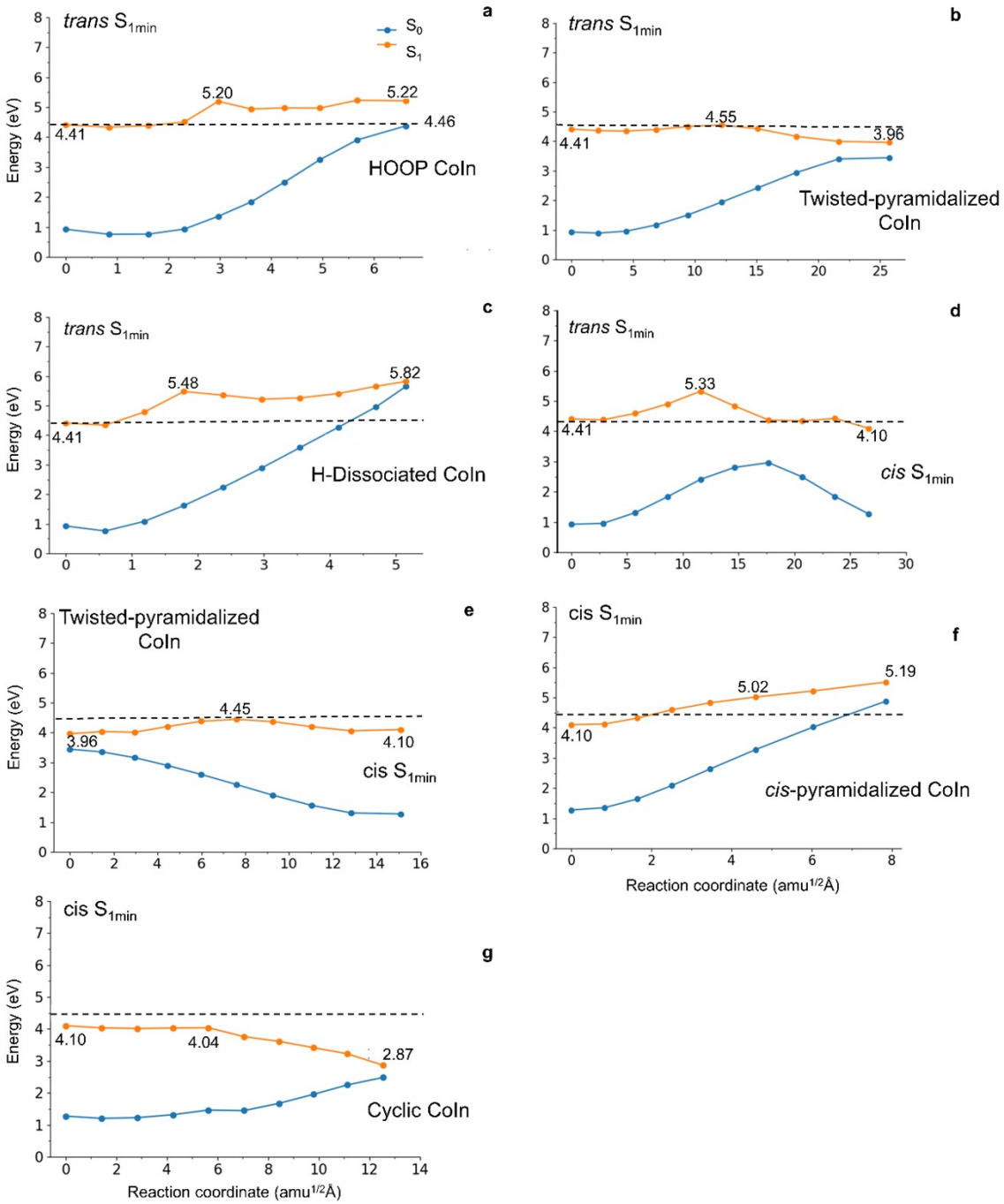

Figure S5. Energy profiles between the *trans*-S_1 minimum and the (a) HOOP conical intersection, (b) twisted-pyramidalized conical intersection, (c) H-dissociated conical intersection, (d) *cis*-S_1 minimum. Energy profiles between (e) twisted-pyramidalized conical intersection and *cis*-S_1 minimum, (f) *cis*-S_1 minimum and *cis*-pyramidalized conical intersection, (g) *cis*-S_1 minimum and cyclic conical intersection. All energy profiles were done with XMS-CASPT2 on CASSCF energies using ANO-S-VDZP basis set, which explains the non-null energy gaps at the conical intersections.

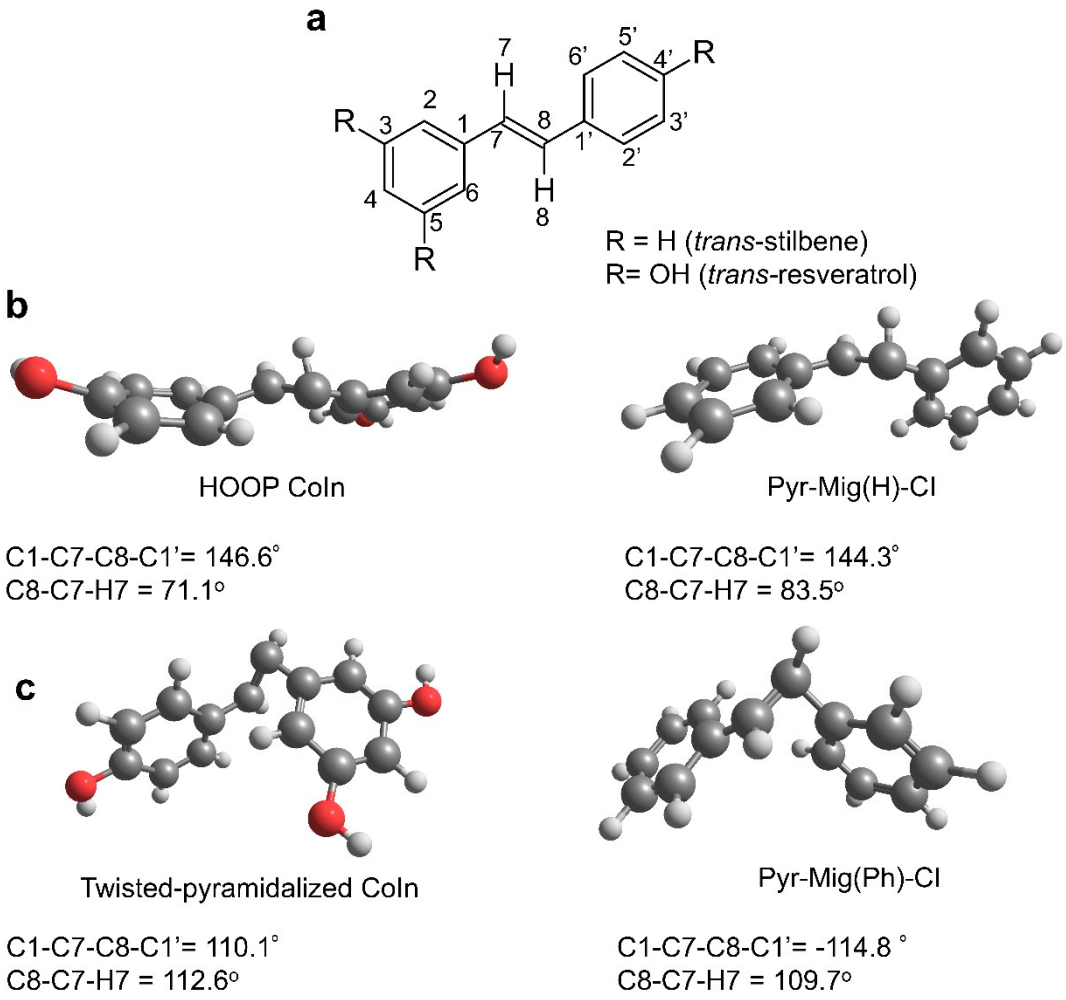

Figure S6. a) *trans*-stilbene/resveratrol structures. Comparison between the avoided regions observed in the present work (left) and in studies conducted by Wier *et al*. [27] (right) b) HOOP CoIn structure and the Pyr-Mig(H)-CI analog; c) Twisted-pyramidalized CoIn and the Pyr-Mig(Ph)CI analog.

S3. Cartesian coordinates

Cartesian coordinates in angstroms of the geometries optimized in the gas phase at the CASSCF (10,10) level.

trans-S_{0min}
Energy (SA-CASSCF): -761.95686037
Energy (XMS-CASPT2):-764.23355123

O	-2.649287440	5.053426780	-3.126987040
H	-3.430451960	5.481289160	-2.810608530
C	0.069679000	-0.010540590	0.035369210
H	0.625134870	0.040280280	-0.888916310
C	-0.927444440	0.873981880	0.251973500
H	-1.501458460	0.793675440	1.163032490
C	-1.355197470	1.962281430	-0.642918040
C	-0.676651660	2.317502580	-1.824635460
H	0.217791270	1.788214680	-2.112859050
H	-0.585510190	3.601207220	-3.533831090
C	-1.118537260	3.338309850	-2.630882180
C	-2.266585220	4.059783270	-2.291501230
C	-2.958852420	3.740175320	-1.127304770
C	-2.499291500	2.699150810	-0.313650860
H	-3.045543270	2.460690640	0.588098130
C	1.787632850	-3.115787420	1.239249040
C	1.368984580	-2.071159540	0.440937840
C	1.352777430	-3.223075630	2.554222130
H	1.716318980	-2.003108930	-0.580431480
H	1.695737970	-4.046949040	3.163630710
C	0.486581020	-1.096511860	0.943274790
C	0.487241600	-2.257012900	3.057595770
O	0.033862950	-2.300451180	4.334304440
C	0.052436950	-1.195264440	2.266576420
H	-0.603907730	-0.463348140	2.705923210
O	2.630350460	-4.076392270	0.795940550
H	2.868945420	-3.925584950	-0.106167560
H	0.389060880	-3.045201330	4.795035410
H	-3.846982210	4.292925890	-0.851314040

cis-S_{0min}
Energy (SA-CASSCF): -761.95133193
Energy (XMS-CASPT2): -764.23311640

O	-1.00994929	5.05615263	-1.04423036
H	-0.08491597	5.23837840	-1.11071720
C	-1.64933969	-1.51128525	-0.54507220
H	-2.05904698	-2.48670718	-0.77490642
C	-2.23486187	-0.45476208	-1.15261421
H	-3.10197237	-0.67768968	-1.76254486
C	-1.85749979	0.97781957	-1.11227348

C	-0.53134563	1.41696425	-1.18770141
H	0.26989380	0.69971500	-1.26101512
H	0.80777013	3.10123427	-1.22753616
C	-0.22353800	2.77992386	-1.16608062
C	-1.24573225	3.72298685	-1.07262085
C	-2.57248134	3.30010628	-1.01455114
C	-2.86601503	1.95367672	-1.04444337
H	-3.90106851	1.64119743	-1.00783597
C	1.52167668	-2.58223240	1.17783574
C	0.44854053	-2.53769945	0.28588183
C	1.64104408	-1.64178589	2.19339533
H	0.37503378	-3.28730865	-0.48794036
H	2.46352051	-1.66862214	2.89399331
C	-0.50701023	-1.52919334	0.40334642
C	0.66984735	-0.65280679	2.31648500
O	0.82663761	0.22756101	3.33096187
C	-0.39467427	-0.58827322	1.44200965
H	-1.13836513	0.18395052	1.55342049
O	2.42748358	-3.57535807	1.00755851
H	3.10321710	-3.53428936	1.66704330
H	0.13185147	0.86887673	3.32896498
H	-3.35784186	4.04029291	-0.95334206

ring-closed S_0min
Energy (SA-CASSCF): -761.89858320
Energy (XMS-CASPT2): -764.19057183

O	-0.930037340	4.618759960	-0.100688920
H	-0.044557540	4.745446520	0.207121830
C	-1.578363360	-1.756857820	-0.664632920
H	-1.772242080	-2.725598970	-1.104709160
C	-2.490317700	-0.645985300	-0.953363860
H	-3.488713430	-0.851903870	-1.313322630
C	-2.064223960	0.639096890	-0.798443360
C	-0.615538370	0.859195620	-0.350140770
H	0.025613960	0.594864180	-1.202061650
H	0.677587650	2.557212490	0.301611280
C	-0.322027340	2.309313440	-0.016900330
C	-1.194034820	3.300320130	-0.287603330
C	-2.527371610	3.049028390	-0.833341010
C	-2.923702230	1.773926360	-1.079232340
H	-3.913418770	1.575881760	-1.466678070
C	1.587073340	-2.390429620	1.047403180
C	0.443759770	-2.639519250	0.371549420
C	1.867629020	-1.081155480	1.630288740
H	0.245292630	-3.614018360	-0.051436490
H	2.752879310	-0.961614820	2.236380620
C	-0.519308010	-1.571698090	0.118654680
C	0.997856350	-0.065039940	1.485619680
O	1.255227480	1.099407720	2.139807780

C	-0.322781460	-0.184023760	0.750147040
H	-1.102199120	-0.068125820	1.518170030
O	2.557149550	-3.305042390	1.281585030
H	2.332822220	-4.140151450	0.898354900
H	0.455863820	1.571601280	2.313214360
H	-3.166791840	3.897174090	-1.026358060

trans-S_{1min}
Energy (SA-CASSCF): -761.79192724
Energy (XMS-CASPT2): -764.071498

O	-2.662513000	5.018527000	-3.130112000
H	-3.336989000	5.561351000	-2.750245000
C	0.071281000	-0.073704000	-0.017443000
H	0.566248000	-0.039258000	-0.972928000
C	-0.947775000	0.928169000	0.261172000
H	-1.430854000	0.887252000	1.223553000
C	-1.368259000	1.942065000	-0.588056000
C	-0.816215000	2.149239000	-1.948144000
H	-0.049022000	1.486476000	-2.310830000
H	-0.845606000	3.286655000	-3.725020000
C	-1.249703000	3.137276000	-2.733024000
C	-2.279427000	4.044131000	-2.275320000
C	-2.839511000	3.880660000	-0.971748000
C	-2.399032000	2.870543000	-0.164033000
H	-2.824731000	2.750463000	0.822064000
C	1.925075000	-3.007803000	1.233632000
C	1.517843000	-2.028311000	0.432110000
C	1.354696000	-3.197184000	2.568844000
H	1.952909000	-1.906889000	-0.549986000
H	1.715043000	-4.004331000	3.185810000
C	0.467073000	-1.084041000	0.854378000
C	0.343023000	-2.302461000	2.997339000
O	-0.219577000	-2.434098000	4.226359000
C	-0.100474000	-1.277566000	2.190059000
H	-0.870462000	-0.627863000	2.565070000
O	2.876001000	-3.916187000	0.936249000
H	3.223328000	-3.767023000	0.068523000
H	0.153313000	-3.164375000	4.695290000
H	-3.608845000	4.560795000	-0.630407000

cis-S_1min
Energy (SA-CASSCF): -761.78254296
Energy (XMS-CASPT2): -764.08283114

O	-1.247525000	5.152129000	-1.254782000
H	-0.330654000	5.381480000	-1.284025000
C	-1.367106000	-1.439352000	-0.666085000
H	-1.559156000	-2.325362000	-1.258001000
C	-2.278578000	-0.325606000	-0.881449000

H	-3.317845000	-0.590564000	-1.038448000
C	-1.963803000	1.031639000	-0.994729000
C	-0.604765000	1.535857000	-1.048837000
H	0.215379000	0.840487000	-1.047759000
H	0.668727000	3.253831000	-1.181980000
C	-0.352119000	2.897670000	-1.135988000
C	-1.413430000	3.811749000	-1.182839000
C	-2.778229000	3.335649000	-1.168297000
C	-3.033877000	2.023100000	-1.088877000
H	-4.056382000	1.672170000	-1.079371000
C	1.501737000	-2.830215000	1.247054000
C	0.497067000	-2.716108000	0.322671000
C	1.727498000	-1.809378000	2.228387000
H	0.357403000	-3.495390000	-0.410616000
H	2.527378000	-1.869393000	2.948443000
C	-0.358590000	-1.542029000	0.297041000
C	0.836578000	-0.664743000	2.240928000
O	1.099499000	0.207957000	3.235820000
C	-0.143613000	-0.524626000	1.347433000
H	-0.807209000	0.320641000	1.398852000
O	2.298432000	-3.928167000	1.216892000
H	2.908058000	-3.927155000	1.938264000
H	0.500300000	0.939986000	3.204050000
H	-3.574318000	4.064564000	-1.228281000

cis-pyramidalized CoIn
Energy (SA-CASSCF): -761.60600233
Energy (XMS-CASPT2):-764.0428195

O	-0.451242000	4.491294000	-0.614882000
H	-1.084320000	5.196024000	-0.748985000
C	-1.888780000	-2.072241000	-0.376228000
H	-1.425306000	-2.253065000	-1.536010000
C	-2.246249000	-0.712333000	-0.641936000
H	-3.262709000	-0.347114000	-0.192088000
C	-1.792831000	0.663506000	-1.057051000
C	-0.394931000	0.978857000	-1.140634000
H	0.221220000	0.094243000	-1.244197000
H	0.971369000	2.382563000	-0.341924000
C	0.065663000	2.236116000	-0.851333000
C	-0.891924000	3.274400000	-0.895324000
C	-2.243097000	3.016328000	-0.882481000
C	-2.733597000	1.691680000	-1.017629000
H	-3.760477000	1.415574000	-0.946256000
C	1.582486000	-2.032991000	0.901868000
C	0.577467000	-1.985495000	-0.076773000
C	1.536638000	-1.092824000	1.888693000
H	0.645290000	-2.630492000	-0.926443000
H	2.506209000	-0.953326000	2.311080000
C	-0.741416000	-1.485059000	0.334239000
C	0.316067000	-0.534558000	2.334362000

O	0.165234000	0.299377000	3.371176000
C	-0.775397000	-0.605575000	1.447009000
H	-1.605316000	0.024416000	1.655300000
O	2.782544000	-2.627358000	0.608826000
H	2.691453000	-3.201321000	-0.153065000
H	0.869649000	0.137728000	3.988055000
H	-2.901333000	3.897552000	-1.015955000

Cyclic CoIn
Energy (SA-CASSCF): -761.78898581
Energy (XMS-CASPT2):-764.1281293

O	-0.650999757	4.564541560	-0.323038424
H	0.286546468	4.645018625	-0.220169518
C	-1.538727843	-1.670924654	-0.804941430
H	-1.793805381	-2.669401194	-1.122281804
C	-2.358986536	-0.578076444	-1.172278434
H	-3.370681005	-0.773354686	-1.522039398
C	-1.952694716	0.726081856	-1.085514664
C	-0.559328703	0.908519598	-0.736102637
H	0.133798687	0.262069205	-1.264366289
H	0.942090594	2.474780160	-0.361585426
C	-0.111927469	2.271486204	-0.478138479
C	-1.018578641	3.284988797	-0.480016390
C	-2.441660719	3.095284148	-0.681890776
C	-2.863447460	1.853308723	-0.999386390
H	-3.913199442	1.667057611	-1.184943129
C	1.543900466	-2.100595034	1.190788854
C	0.325096417	-2.503908223	0.615682883
C	1.874475661	-0.812089660	1.613324485
H	0.244816558	-3.514161251	0.241875221
H	2.810061772	-0.592554620	2.095748562
C	-0.562454905	-1.506124757	0.183056528
C	0.781696194	0.035980974	1.629156800
O	0.864634832	1.144410191	2.331770208
C	-0.401731512	-0.227215625	0.898564977
H	-1.305387567	0.155299700	1.346593341
O	2.493145944	-2.998884191	1.340853823
H	2.203894796	-3.856689234	1.060932236
H	0.097867586	1.687169709	2.204241690
H	-3.088370426	3.956898453	-0.643045435

HOOP CoIn
Energy (SA-CASSCF): -761.70668035
Energy (XMS-CASPT2):-764.0418625

O	-3.106045927	4.958108318	-3.350598866
H	-3.723674927	5.559900318	-2.955849866
C	-0.772494927	-0.230095682	-0.744007866
H	-1.916348927	-0.530668682	-0.851164866

C	-1.542820927	0.798390318	-0.291882866
H	-2.310351927	0.719475318	0.513705134
C	-1.573064927	2.178936318	-0.803270866
C	-0.930190927	2.432659318	-2.020238866
H	-0.300375927	1.631110318	-2.379875866
H	-0.969067927	3.602865318	-3.849274866
C	-1.404373927	3.426752318	-2.876928866
C	-2.451637927	4.209512318	-2.442224866
C	-2.919583927	4.161193318	-1.103962866
C	-2.520535927	3.114833318	-0.291541866
H	-2.752848927	3.033706318	0.755427134
C	0.371445073	-3.519470682	0.584044134
C	0.199629073	-2.440190682	-0.290002866
C	0.414476073	-3.360769682	1.946957134
H	0.185467073	-2.590723682	-1.351160866
H	0.799874073	-4.091484682	2.638339134
C	-0.299743927	-1.233210682	0.237474134
C	0.097971073	-2.098128682	2.472172134
O	0.076507073	-1.882599682	3.809938134
C	-0.249963927	-1.046770682	1.625807134
H	-0.539610927	-0.147408682	2.147377134
O	0.775000073	-4.735138682	0.093931134
H	0.364494073	-4.874757682	-0.745586866
H	0.583369073	-2.577807682	4.205780134
H	-3.697985927	4.873952318	-0.864159866

twisted-pyramidalized CoIn
Energy (SA-CASSCF): -761.7715369
Energy (XMS-CASPT2): -764.0880137

O	-2.664231000	5.014006000	-3.103265000
H	-3.327987000	5.553266000	-2.700449000
C	0.107602000	-0.110416000	-0.068457000
H	-0.162739000	-1.123608000	0.211542000
C	-0.943329000	0.852414000	0.228566000
H	-1.632961000	0.633405000	1.043329000
C	-1.370605000	1.965632000	-0.612134000
C	-0.837263000	2.139800000	-1.897690000
H	-0.075128000	1.456218000	-2.233293000
H	-0.876727000	3.301949000	-3.713192000
C	-1.284437000	3.167501000	-2.721541000
C	-2.263140000	4.030441000	-2.276142000
C	-2.821358000	3.873638000	-0.995791000
C	-2.375344000	2.846903000	-0.177026000
H	-2.799042000	2.729605000	0.810448000
C	1.882884000	0.381838000	3.173480000
C	1.328125000	-0.251574000	2.134248000
C	2.011849000	1.836989000	3.240728000
H	1.216291000	-1.326239000	2.139152000
H	2.452774000	2.280735000	4.119253000

C	0.871750000	0.490137000	0.954930000
C	1.595072000	2.563660000	2.158386000
O	1.697149000	3.913717000	2.094368000
C	1.066555000	1.937543000	0.997901000
H	0.964317000	2.532627000	0.114713000
O	2.348282000	-0.232674000	4.270643000
H	2.256945000	-1.172091000	4.194139000
H	2.128963000	4.255745000	2.862567000
H	-3.594153000	4.550183000	-0.657091000

H-dissociated CoIn
Energy (SA-CASSCF): -761.7302159
Energy (XMS-CASPT2):-764.0196151

O	-2.841838000	4.913198000	-3.101240000
H	-4.354405000	5.453427000	-2.031236000
C	-0.109455000	-0.113974000	0.008106000
H	0.111277000	-0.216794000	-1.067037000
C	-0.916346000	0.884271000	0.426623000
H	-1.519635000	0.906946000	1.323556000
C	-1.358833000	1.984642000	-0.587679000
C	-0.914891000	2.139353000	-1.914234000
H	-0.492649000	1.212303000	-2.349217000
H	-0.735053000	3.184880000	-3.697707000
C	-1.240013000	3.203351000	-2.729976000
C	-2.254877000	4.025865000	-2.300183000
C	-2.812449000	3.837162000	-1.014601000
C	-2.371084000	2.833543000	-0.133653000
H	-2.725804000	2.855930000	0.859715000
C	1.763938000	-3.194103000	1.185668000
C	1.072874000	-2.257452000	0.430081000
C	1.854083000	-2.944034000	2.577838000
H	1.256677000	-2.398976000	-0.700151000
H	2.498162000	-3.466056000	3.260372000
C	0.414558000	-1.157042000	0.941652000
C	0.958812000	-1.978497000	3.122028000
O	1.097727000	-1.578245000	4.432040000
C	0.228887000	-1.094390000	2.307956000
H	-0.252911000	-0.221872000	2.770236000
O	2.593513000	-4.064037000	0.621160000
H	3.376589000	-3.574396000	0.264150000
H	1.854522000	-2.041447000	4.708488000
H	-3.668647000	4.373030000	-0.723299000