

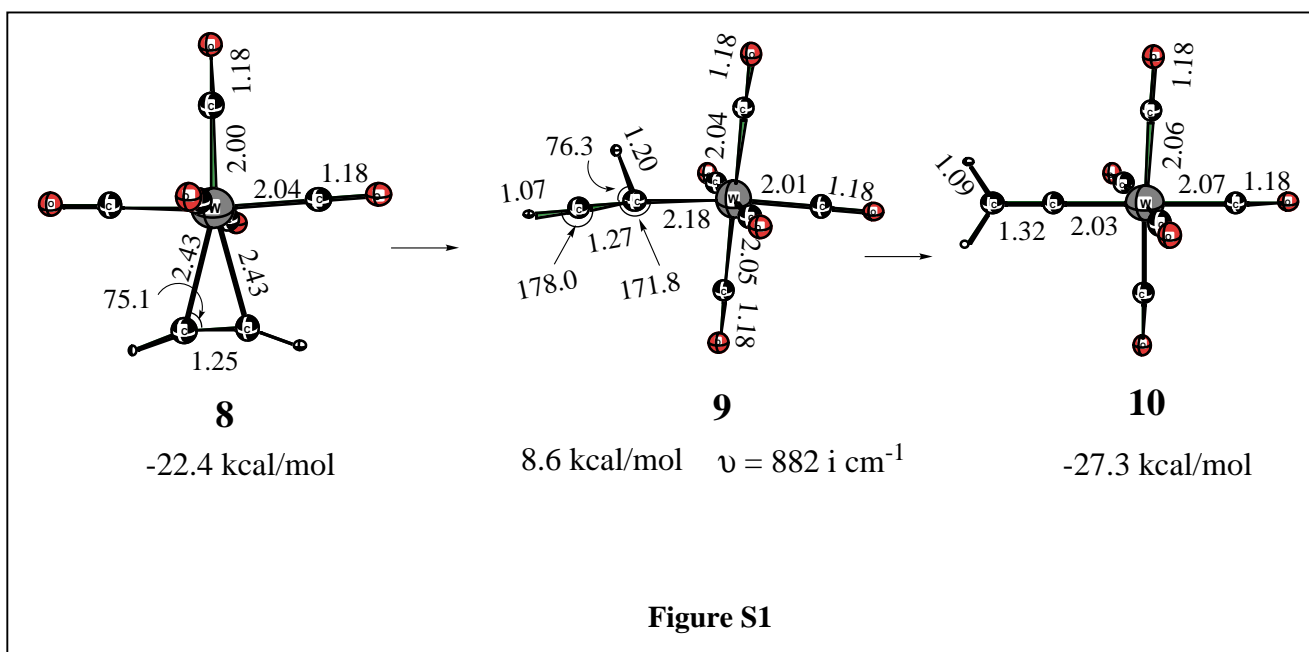
Supporting Information  
for  
Computational studies of tungsten-catalyzed  
*endo*-selective cycloisomerization of 4-pentyn-1-ol

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**Figure S1:** the optimized stationary point structures (in Å and deg) and relative energies (relative to  $W(CO)_5 + \text{acetylene}$ ) for the adduct formation between acetylene and  $W(CO)_5$ .

**Table S1.** Calculated total energies (in a.u.) of the all structures reported in the paper.

Structure	B3LYP/lanl2dz	B3LYP/SDD
<b>1</b>	-270.453191712	-270.496553948
<b>N1'</b>	-270.365269744	-270.423434533
<b>N1</b>	-270.369220088	-270.427458752
<b>N2</b>	-270.379184615	-270.424707903
<b>N3</b>	-270.374549307	-270.421253871
<b>N4</b>	-270.384550018	-270.426336623
<b>N5</b>	-270.369216445	-270.413266811
<b>N6</b>	-270.504921046	-270.553554055
<b>X1</b>	-270.370310272	-270.413232569
<b>X2</b>	-270.505835085	-270.552751279
<b>WN1</b>	-904.951668492	-904.382873203
<b>WN2</b>	-791.625480846	-791.040285203
<b>WN3</b>	-904.909714703	-904.346702238
<b>WN4</b>	-904.944583400	-904.374557470
<b>WN5</b>	-904.942452995	-904.369684631
<b>WN6</b>	-904.944759119	-904.367564949
<b>WN7</b>	-904.876882719	-904.306378838
<b>WN8</b>	-904.944239088	-904.366670353
<b>WN9</b>	-904.944242817	-904.366713250
<b>WN10</b>	-904.912370886	-904.340316019
<b>WN11</b>	-904.917860719	-904.353952937
<b>WN12</b>	-904.929314165	-904.366226235
<b>WN13</b>	-904.929225385	-904.366090038
<b>WN14</b>	-904.999265704	-904.434355803
<b>WX1</b>	-904.877550021	-904.309278691
<b>WX2</b>	-905.003782613	-904.436999200
<b>5</b>	-747.816711128	-747.227106930
<b>6</b>	-634.459833665	-633.849223491
<b>7</b>	-521.058889736	-520.429171344
<b>8</b>	-711.813012057	-711.218308325
<b>9</b>	-711.760827474	-711.170066020
<b>10</b>	-711.820843725	-711.221520962



O 2.502480 .185892 2.760842  
 C -2.206758 -1.170920 -3.49715  
 C -3.587308 -.596072 -.756169  
 H -2.271636 -1.624232 .650707  
 H -1.946406 -1.994414 -1.029757  
 H -4.247329 -1.443879 -.992929  
 H -3.492262 .004776 -1.669869  
 C -4.290473 -.243323 .314470  
 H -5.331960 .427120 .005781  
 H -4.300845 -.298155 1.275025  
 O -3.578364 1.518431 .454790  
 H -4.004348 2.079259 1.136354

**Structure WN3**

C -1.191410 .531656 -.294251  
 C -2.374485 .991241 -.393087  
 C -3.768929 1.431503 -.561513  
 C -4.778172 .754619 .411698  
 C -4.502299 -.742896 .612632  
 O -4.137368 -1.302470 -.699850  
 W .904029 -.007189 .006631  
 C .363698 -1.503498 1.277964  
 O .048442 -2.375165 2.015216  
 C 2.849836 -.412180 .321422  
 O 3.997305 -.646542 .509493  
 C .931976 1.311101 1.564803  
 O .950840 2.072799 2.468576  
 C .877213 -1.322673 -1.550478  
 O .877345 -2.091839 -2.450035  
 C 1.419961 1.496512 -1.277850  
 O 1.721198 2.364475 -2.020488  
 H -4.067049 1.233864 -1.597636  
 H -3.784613 2.522671 -.428137  
 H -5.781956 .899311 -.005312  
 H -4.748905 1.245830 1.392517  
 H -5.395939 -1.239870 1.013806  
 H -3.670739 -.890505 1.316805  
 H -4.145620 -2.281494 -.687083  
 H -1.929745 -.340231 -.747015

**Structure WN4**

W -0.759612 0.012026 -0.017107  
 C -0.174141 -1.227733 1.515751  
 O 0.148357 -1.926159 2.404836  
 C 0.165311 -1.210606 -1.368387  
 O 0.733958 -1.910274 -2.131156  
 C -2.517642 -1.035423 -0.277029  
 O -3.523967 -1.635165 -0.424836  
 C -1.243919 1.298869 -1.524669  
 O -1.509964 2.046963 -2.398308  
 C -1.719120 1.199845 1.358874  
 O -2.259451 1.882569 2.152066  
 C 0.975172 1.054144 0.265266  
 C 2.020153 1.831067 0.500717  
 H 1.737220 2.769596 1.001143  
 C 3.512066 1.727015 0.194305  
 H 3.768796 2.623564 -0.390907  
 H 4.055477 1.826076 1.147493  
 C 4.045663 0.487116 -0.555769  
 H 3.477620 0.320832 -1.482363  
 H 5.076503 0.727498 -0.858297  
 C 4.095713 -0.822138 0.258584  
 H 4.887553 -1.476329 -0.137058  
 H 4.318375 -0.614646 1.310329  
 O 2.821251 -1.547327 0.277619  
 H 2.706609 -2.049787 -0.555946

**Structure WN5**

C -4.392116 .154763 .427091  
 C -3.790571 1.432916 -.189158

C -3.900254 -1.119169 -.256139  
 C -2.271092 1.524728 -.198172  
 O -2.452233 -1.174977 .016428  
 C -1.273135 .644470 -.110925  
 W .740733 .001271 .002864  
 C 1.166521 1.358687 -1.461239  
 C .302998 -1.350949 1.479660  
 C 2.718311 -.476599 .131056  
 C .485791 -1.407342 -1.443696  
 C 1.008329 1.430027 1.444817  
 O 1.403123 2.144359 -2.310717  
 O .070554 -2.126276 2.337990  
 O 3.868522 -.745448 .205594  
 O .340649 -2.227076 -2.288100  
 O 1.158697 2.255280 2.274499  
 H -5.487067 .197830 .348760  
 H -4.139463 .095681 1.493268  
 H -4.151692 1.547255 -1.224564  
 H -4.172368 2.303759 .360589  
 H -4.377020 -2.012080 .168216  
 H -4.078049 -1.086738 -1.341081  
 H -1.874367 2.542245 -3.15886  
 H -1.977440 -1.838102 -.526527

**Structure WN6**

C -1.115756 .380956 -.041024  
 C -2.034202 1.362048 -.148618  
 O -1.936063 -1.067711 .127460  
 W 1.061109 .009098 .006397  
 C -3.553261 1.289898 -.140965  
 C -3.368197 -1.230919 -.289474  
 C .872911 -1.078829 1.718841  
 C 3.070257 -.204810 .074251  
 C .979455 -1.668343 -1.131717  
 C 1.231267 1.715443 1.123730  
 C 1.192113 1.118071 -1.702181  
 C -4.110912 -.062729 .352560  
 O .777378 -1.709652 2.716837  
 O 4.249568 -.324021 .116131  
 O .976164 -2.648193 -1.807290  
 O 1.334138 2.700731 1.766236  
 O 1.252574 1.759429 -2.693091  
 H -1.601494 2.354988 -.271240  
 H -1.310741 -1.782547 -.123105  
 H -3.927364 1.501315 -1.155479  
 H -3.943751 2.093177 .498003  
 H -3.691754 -2.204930 .089906  
 H -3.405563 -1.206901 -1.385197  
 H -5.178555 -.149872 .113229  
 H -4.008411 -.141974 1.441652

**Structure WN7**

O -1.633807 1.454794 -2.081796  
 H -1.776442 1.836907 -.883845  
 C -1.089777 2.384319 -3.078140  
 H -1.863037 3.113811 -3.357665  
 H -.865805 1.755533 -3.950357  
 C .197174 3.120557 -2.625813  
 H -.051978 4.009139 -2.030578  
 H .717661 3.470574 -3.526956  
 C 1.146634 2.210001 -1.804461  
 H 1.313981 1.272915 -2.348338  
 H 2.120918 2.694305 -1.676219  
 C .557432 1.932164 -.416376  
 H 1.103688 2.320890 .443918  
 C -.767277 1.615233 -.212957  
 W .059937 -.430906 .475928  
 C .196111 .336513 2.360317  
 O .285208 .768257 3.455405  
 C -.055587 -1.176778 -1.431886

O -.096949 -1.628535 -2.517692  
 C .211640 -2.281616 1.233738  
 O .299184 -3.372196 1.683183  
 C -1.979237 -.662738 .667394  
 O -3.140369 -.798395 .778583  
 C 2.087684 -.351136 .300886  
 O 3.266341 -.342195 .201706

**Structure WN8**

C -4.456436 -.107797 .356541  
 C -3.901341 1.269529 -.067890  
 C -2.382205 1.349905 -.068913  
 C -1.462940 .364952 -.002782  
 O -2.272629 -1.080556 .098116  
 C -3.700274 -1.241319 -.331049  
 W .724156 .009431 .000633  
 C .627078 -.319885 -2.006003  
 O .553557 -.516157 -3.171771  
 C .675682 .337378 2.016963  
 O .627444 .522735 3.182571  
 C 2.739547 -.139836 -.008374  
 O 3.923149 -.214304 -.014950  
 C .698262 -1.989705 .351120  
 O .760660 -3.160062 .560493  
 C .946746 2.014561 -.327769  
 O 1.096151 3.171190 -.517509  
 H -1.957870 2.349970 -.148904  
 H -1.636882 -1.794400 -.126617  
 H -4.273384 1.529647 -1.071781  
 H -4.297144 2.038722 .608735  
 H -4.015006 -2.233576 .006016  
 H -3.732995 -1.171937 -1.424923  
 H -5.521075 -1.88710 .102146  
 H -4.364582 -.237058 1.441761

**Structure WN9**

C -4.121619 -.108674 .358699  
 C -3.568009 1.270347 -.061548  
 C -2.048978 1.352508 -.061974  
 C -1.128158 .369102 .002292  
 O -1.936944 -1.078796 .098091  
 C -3.364330 -1.239253 -.332239  
 W 1.058867 .015007 .000674  
 C .949214 -.377001 -1.993709  
 O .868947 -.609895 -3.152405  
 C 1.026034 .406798 2.060054  
 O .986899 .629213 3.165506  
 C 3.074016 -.136072 -.019344  
 O 4.257479 -.212050 -.033149  
 C 1.031635 -1.971362 .418598  
 O 1.091841 -3.133594 .668645  
 C 1.277448 2.009013 -.391427  
 O 1.423641 3.159490 -.617611  
 H -1.625852 2.353183 -.138778  
 H -1.300737 -1.790672 -.131490  
 H -3.940107 1.532926 -1.064640  
 H -3.964838 2.037039 .617099  
 H -3.678561 -2.232640 .001457  
 H -3.396701 -1.166343 -1.425712  
 H -5.186199 -.189872 .104233  
 H -4.029562 -.241084 1.443354

**Structure WN10**

O 2.019022 -1.030438 -.033620  
 C 1.515127 .373595 .033188  
 C 2.424519 1.370701 .110303  
 C 3.934831 1.175746 .090574  
 C 4.323797 -.244861 -.381144  
 C 3.440965 -1.295687 .302921  
 W -.668294 .018768 -.003007

C	-1.048411	2.032681	-.301468
O	-1.253710	3.176703	-.456137
C	-.742572	-1.953904	.386095
O	-.952759	-3.107344	.631014
C	-2.704898	-.182204	-.156963
O	-3.873754	-.309504	-.252455
C	-.636480	.374574	2.005412
O	-.582258	.586355	3.163389
C	-.423977	-.302322	-2.008517
O	-.256688	-.480236	-3.160121
H	.609436	-1.490689	.190436
H	3.637699	-2.310198	-.055022
H	3.545740	-1.259101	1.396257
H	5.378492	-.455081	-.158057
H	4.191573	-.328750	-1.467484
H	4.349189	1.366590	1.093623
H	4.390946	1.922474	-.574305
H	2.054468	2.391739	.178142

**Structure WN11**

C	1.562021	.103164	.058435
C	2.405371	1.168449	.137209
C	3.922837	1.068919	.052433
C	4.356185	-.320350	-.464919
C	3.528669	-1.402573	.238680
O	2.084555	-1.228954	-.036058
H	-.088943	-1.759964	-.274662
H	3.758636	-2.409978	-.119942
H	3.677529	-1.360515	1.328072
H	5.425866	-.493414	-.285667
H	4.184656	-.389601	-1.547249
H	4.373532	1.261402	1.039610
H	4.303950	1.854464	-.615880
H	1.990715	2.168410	.233283
W	-.675490	-.022591	-.007474
C	-1.434263	-1.872729	-.127045
O	-1.992765	-2.931077	-.163996
C	-2.664247	.423671	-.221783
O	-3.807003	.666030	-.371487
C	-.537041	-.282252	2.015600
O	-.400983	-.431768	3.173859
C	-.357863	.183273	-2.019232
O	-.115574	.296440	-3.163085
C	-.617290	2.019840	.376141
O	-.596479	3.162389	.626070

**Structure WN12**

C	1.239785	.142512	-.126517
C	2.018945	1.254036	-.050695
C	3.533564	1.233811	-.208428
C	4.025389	-.143542	-.707452
C	3.256074	-1.255217	.017557
O	1.804662	-1.145191	-.256582
H	-.258881	-.134755	-1.671736
H	3.526591	-2.255313	-.330743
H	3.406379	-1.191802	1.105725
H	5.103158	-.263226	-.534569
H	3.849415	-.239555	-1.786694
H	4.011170	1.482559	.753135
H	3.838367	2.020610	-.913138
H	1.548372	2.221573	.096606
W	-1.018234	.018999	-.089007
C	-2.197640	-.255591	-1.736056
O	-2.867535	-.409422	-2.691491
C	-2.822131	-.049624	.895232
O	-3.861954	-.093690	1.444448
C	-.746460	-2.014546	.055652
O	-.618483	-3.179810	-.116315
C	-1.089088	2.022910	-.424323
O	-1.117383	3.181572	-.642352

C	-.281648	.314239	1.836742
O	.111938	.471541	2.931816

**Structure WN13**

C	1.242663	.146280	-.151363
C	2.015541	1.261503	-.083018
C	3.533851	1.239638	-.206971
C	4.035442	-.143416	-.679768
C	3.254906	-1.247443	.045056
O	1.808003	-1.142950	-.254863
H	-.140466	-1.107599	-1.586048
H	3.531930	-2.251327	-.286722
H	3.386536	-1.171061	1.134714
H	5.109971	-.259957	-.485919
H	3.879170	-.252890	-1.760769
H	3.991746	1.499474	.761055
H	3.853284	2.017778	-.914805
H	1.539597	2.230451	.032956
W	-1.025814	.018173	-.073808
C	-2.121220	-.279696	-1.773537
O	-2.747794	-.448072	-2.755520
C	-2.857865	-.049618	.855519
O	-3.916091	-.092744	1.369408
C	-.752841	-2.013257	.095652
O	-.624111	-3.177611	-1.751555
C	-1.114189	2.020927	-.409466
O	-1.153572	3.180164	-.625133
C	-.306413	.324620	1.855092
O	.087362	.491648	2.947911

**Structure WN14**

C	3.878004	.659111	-.039525
C	2.618822	1.503567	-.357692
C	1.612588	.671932	-1.159501
C	1.738035	-.709456	-1.219949
O	2.629829	-1.451572	-.482501
C	3.481912	-.723898	.494128
H	1.106244	1.148202	-1.993586
H	2.181417	1.886184	.571419
H	4.501901	1.163761	.708357
H	1.274375	-1.315575	-1.990528
H	4.341751	-1.381826	.636543
H	2.924172	-.650744	1.434637
H	4.484202	.533324	-.946171
H	2.899853	2.383269	-.950100
W	-.618068	.006939	.014348
C	-.550446	-2.032492	.101635
O	-.545392	-3.210442	.176094
C	-1.510471	-.094808	-1.816951
O	-2.049830	-.157460	-2.867018
C	-2.396510	-.059491	.881643
O	-3.463854	-.092552	1.398575
C	-.754850	2.041420	-.007873
O	-.845701	3.219526	-.004793
C	.260240	.093179	1.844019
O	.744845	.145696	2.923150

**Structure WX1**

O	2.458649	-1.161625	-.037787
C	1.655525	.333472	-.524990
C	2.698179	1.323679	-.055758
C	4.066526	.635557	-.329238
C	3.898159	-.838109	-.128962
C	1.184469	-.182921	-1.705132
W	-.626447	.010901	.011019
C	.119133	.636119	1.801626
O	.559806	1.002392	2.834196
C	-.933346	1.937708	-.564238
O	-1.125454	3.058285	-.890569
C	-2.430987	-.037591	.881083

O	-3.495096	-.053715	1.400397
C	-1.504430	-.664127	-1.712593
O	-2.025683	-1.057480	-2.693768
C	-.298267	-1.938732	.562429
O	-.154799	-3.059890	.891946
H	2.014546	-1.363775	-1.088571
H	2.594183	1.560020	1.008343
H	2.599931	2.255707	-.624707
H	4.882805	1.125956	.212012
H	4.291798	.679967	-1.401311
H	4.492970	-1.542712	-.460131
H	4.118082	-.969066	1.191801
H	.893634	.393180	-2.581062

**Structure WX2**

C	.706182	.125260	-1.838476
W	-1.020712	.006867	.031388
C	-1.020848	2.034884	.150643
O	-1.012611	3.216693	.229544
C	1.770494	.095723	-.957467
C	2.552005	1.264689	-.357047
C	3.901763	.615215	.057959
C	3.519451	-.858125	.302771
O	2.381254	-1.097009	-.638222
C	-2.598905	-.098799	1.218467
O	-3.550707	-.159965	1.926639
C	-2.298782	.085584	-1.565729
O	-3.055561	.129403	-2.470789
C	-.945595	-2.029990	-.115484
O	-.910333	-3.207819	-.184967
C	.175435	-.092364	1.661168
O	.860818	-.148428	2.629240
H	.466571	-.775229	-2.395087
H	2.033068	1.677661	.512831
H	2.669011	2.071688	-1.085844
H	4.331552	1.079943	.949632
H	4.629362	.687747	-.757560
H	4.290572	-1.582613	.036599
H	3.158276	-1.045045	1.318830
H	.441476	1.074263	-2.291217

**Structure 5**

C	0.000000	-0.000013	2.050933
O	0.000001	-0.000021	3.227495
W	0.000000	0.000003	0.000003
C	-2.050931	-0.000005	0.000002
O	-3.227492	-0.000011	0.000000
C	-0.000004	2.050934	0.000013
O	-0.000007	3.227495	0.000020
C	2.050931	0.000004	0.000000
O	3.227492	0.000003	-0.000004
C	0.000004	-2.050928	-0.000014
O	0.000006	-3.227490	-0.000030
C	-0.000001	0.000010	-2.050928
O	-0.000001	0.000011	-3.227490

**Structure 6**

W	-0.361017	0.000418	0.210502
C	0.642532	-0.000005	1.988985
O	1.238007	-0.000364	3.006827
C	-0.388594	-2.041425	0.225828
O	-0.389065	-3.220659	0.225426
C	-1.414067	0.001105	-1.539130
O	-2.006341	0.001671	-2.558837
C	-0.384342	2.042315	0.224605
O	-0.382676	3.221549	0.224089
C	1.317100	-0.001733	-0.767686
O	2.343127	-0.003080	-1.365758

**Structure 7**

C	0.000000	0.000000	2.024551
O	0.000000	0.000000	3.208814
W	0.000000	0.000000	0.000000
C	0.000000	2.024551	0.000000
O	0.000000	3.208814	0.000000
C	0.000000	-2.024551	0.000000
O	0.000000	-3.208814	0.000000
C	0.000000	0.000000	-2.024551
O	0.000000	0.000000	-3.208814

**Structure 8**

C	.626202	-.000804	-2.391559
H	1.630401	-.002237	-2.769260
C	-.627166	.001179	-2.391311
H	-1.631428	.002788	-2.768834
W	.000015	.000018	-.041004
C	2.042615	-.003287	.056336
O	3.219524	-.005155	.123435
C	-.003445	-2.044932	-.079374
O	-.005600	-3.224087	-.082604

C	.000739	.000077	1.957126
O	.001405	.000265	3.141114
C	-2.042555	.002967	.057396
O	-3.219401	.004475	.125263
C	.002956	2.044977	-.079347
O	.004550	3.224138	-.082612

**Structure 9**

C	-3.165816	.000027	1.272531
C	-1.944244	-.000072	.913815
W	.039195	.000031	.020665
C	.731603	-1.442840	1.286954
O	1.148635	-2.277730	2.012345
C	-.646548	-1.450436	-1.246890
O	-1.039225	-2.288485	-1.978828
C	1.799428	-.000066	-.959664
O	2.828964	-.000200	-1.544177
C	-.647029	1.449385	-1.247894
O	-1.040011	2.286779	-1.980426
C	.731137	1.444037	1.285917
O	1.147900	2.279562	2.010736

H	-4.184310	-.000188	1.611671
H	-1.885710	.000137	2.113201

**Structure 10**

C	-.016641	-3.336512	.000000
C	-.008843	-2.013833	.000000
H	.909293	-3.913622	.000000
W	.000000	.015442	.000000
C	.000909	-.048631	2.045129
O	.002710	-.100660	3.222302
C	.006651	2.087280	.000000
O	.011234	3.265747	.000000
C	2.057453	.063344	.000000
O	3.233278	.084678	.000000
C	.000909	-.048631	-2.045129
O	.002710	-.100660	-3.222302
C	-2.056793	.074945	.000000
O	-3.232661	.101611	.000000
H	-.949329	-3.902620	.000000