Electronic supplementary information (ESI) available for

Mechanisms of the Knoevenagel Hetero Diels-Alder Sequence in Multicomponent Reactions to Dihydropyrans: Experimental and Theoretical Investigations into the Role of Water

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1) Computational data

Table S1 Calculated total electronic energies (E_e)[a], ZPE corrected total electronic energies (E_e+ZPVE)[a] and Gibbs free energies (G_{298})[a] for gas phase compounds at the B3LYP/6-311++G(d,p) level and solution SCF energies (E_{sol})[a] and solution Gibbs free energies (G_{sol})[a,d] for solution compounds at the SMD-CPCM-B3LYP/6-311++G(d,p)// B3LYP/6-311++G(d,p) level for Knoevenagel reaction.

Compounds	E_e	E_e + ZPE	G_{298}	E_{sol} water	G_{sol} water[d]	E_{sol} acetone	G_{sol} acetone[d]
	water-unassisted Knoevenagel reaction						
H_2O	-76.45853	-76.43724	-76.45489	-76.46963	-76.46599	-76.46727	-76.46363
H_2CO	-114.54185	-114.51534	-114.53700	-114.54403	-114.53918	-114.54929	-114.54444
2,4 pentanedione	-345.90266	-345.78136	-345.81526	-345.91501	-345.82761	-345.92428	-345.83688
diketo/keto-enol TS[b]	-345.80887	-345.69340	-345.72302	-345.82160	-345.73575	-345.83166	-345.74581
***cis* keto-enol**	-345.91120	-345.78882	-345.82155	-345.91872	-345.82907	-345.92850	-345.83885
W0-1[c]	-460.45535	-460.30570	-460.35096	-460.46018	-460.35579	-460.47364	-460.36925
W0-TS1[b]	-460.41162	-460.26277	-460.29897	-460.42962	-460.31697	-460.44445	-460.33180
W0-2	-460.46548	-460.31069	-460.34738	-460.48558	-460.36748	-460.49408	-460.37598
W0-TS2-A[b]	-460.38849	-460.23856	-460.27381	-460.40778	-460.29310	-460.41228	-460.29760
W0-TS2-B1[b]	-460.37246	-460.22368	-460.26028	-460.39373	-460.28155	-460.40002	-460.28784
W0-B	-460.45687	-460.30086	-460.33670	-460.47247	-460.35230	-460.47819	-460.35802
W0-TS2-B2[b]	-460.42278	-460.27201	-460.30707	-460.44184	-460.32613	-460.44691	-460.33120
W0-3•H_2O	-460.46030	-460.30977	-460.34978	-460.47526	-460.36474	-460.48483	-460.37431
W0-3	-383.99161	-383.8653	-383.90008	-384.00156	-383.91003	-384.01270	-383.92117
	water-assisted Knoevenagel reaction						
2,4 pentanedione •H_2O	-422.37272	-422.22673	-422.26451	-422.38730	-422.27909	-422.39443	-422.28622
diketo/keto-enol•H2O TS[b]	-422.31633	-422.17604	-422.21109	-422.33452	-422.22928	-422.33745	-422.23221
***cis* keto-enol•H_2O**	-422.37988	-422.23337	-422.27193	-422.39287	-422.28492	-422.40113	-422.29318
W1-1[c]	-536.92476	-536.74979	-536.79574	-536.94353	-536.81451	-536.95151	-536.82249
W1-TS1[b]	-536.88364	-536.71118	-536.75046	-536.90469	-536.77151	-536.91395	-536.78077
W1-2	-536.93701	-536.75741	-536.79779	-536.95564	-536.81642	-536.96564	-536.82642
W1-2'	-536.93622	-536.75683	-536.79866	-536.95879	-536.82123	-536.96405	-536.82649
W1-2"	-536.93325	-536.75446	-536.79711	-536.95959	-536.82345	-536.96522	-536.82908
W1-TS2-A[b]	-536.88193	-536.70751	-536.74444	-536.91000	-536.77251	-536.90891	-536.77142
W01w-TS2-A[b]	-536.85816	-536.68407	-536.72521	-536.88297	-536.75001	-536.88589	-536.75297
W1-TS2-B1[b]	-536.86969	-536.69665	-536.73466	-536.89820	-536.76317	-536.89816	-536.76313
W1-B	-536.92979	-536.74881	-536.78799	-536.95113	-536.80933	-536.95243	-536.81063
W1-TS2-B2[b]	-536.90108	-536.72546	-536.76314	-536.92945	-536.79151	-536.92724	-536.78930
W1-3•H_2O	-536.93381	-536.75832	-536.80188	-536.94867	-536.81674	-536.95663	-536.82470
W2-2	-613.41048	-613.20613	-613.25264	-613.43572	-613.27788	-613.43910	-613.28127
W2-TS2-A [b]	-613.36130	-613.16169	-613.20223	-613.39111	-613.23203	-613.38747	-613.22840

[a] in atomic unit (a.u.) ; 1 a.u. = 627.5 kcal mol^{-1}. [b]One imaginary frequency, transition state. [c]Other **W0-1** and **W1-1** conformers have been located and differ only very little in energy (~0.1 kcal mol^{-1}).
[d]$G_{sol} = G_{298} + (E_{sol} - E_e)$.

Table S2 Calculated relative electronic energies (ΔE_e)[a], relative ZPE corrected electronic energies ($\Delta(E_e+ZPVE)$)[a] and relative Gibbs free energies (ΔG_{298})[a] for gas phase compounds at the B3LYP/6-311++G(d,p) level and relative solution SCF energies ($\Delta E_{e\ solv}$)[a] and relative solution Gibbs free energies (ΔG_{sol})[a] for solution compounds at the SMD-CPCM-B3LYP/6-311++G(d,p)// B3LYP/6-311++G(d,p) level for Knoevenagel reaction (with respect to the separated reactants).

Compounds	ΔE_e	$\Delta(E_e + ZPE)$	ΔG_{298}	ΔE_{sol} water	ΔG_{sol} water	ΔE_{sol} acetone	ΔG_{sol} acetone
2,4 pentanedione	0.0	0.0	0.0	0.0	0.0	0.0	0.0
diketo/keto-enol TS[b]	58.9	55.2	57.9	58.6	57.6	58.1	57.1
cis **keto-enol**	-5.4	-4.7	-3.9	-2.3	-0.9	-2.6	-1.2
	water-unassisted Knoevenagel reaction (energies relatives to the separated reactants)						
cis **keto-enol +H_2CO +x H_2O**	0.0	0.0	0.0	0.0	0.0	0.0	0.0
W0-1	-1.4	-1.0	4.8	1.6	7.8	2.6	8.8
W0-TS1	26.0	26.0	37.4	20.8	32.2	20.9	32.3
W0-2	-7.8	-4.1	7.0	-14.3	0.5	-10.2	4.6
W0-TS2-A	40.5	41.2	53.2	34.5	47.2	41.1	53.8
W0-TS2-B1	50.6	50.5	61.7	43.3	54.4	48.8	59.9
W0-B	-2.4	2.1	13.7	-6.1	10.0	-0.3	15.9
W0-TS2-B2	19.0	20.2	32.3	13.1	26.4	19.4	32.7
W0-3•H_2O	-4.5	-3.5	5.5	-7.8	2.2	-4.4	5.6
W0-3	1.8	1.0	2.2	-5.3	-4.9	-1.4	-0.9
	water-assisted Knoevenagel reaction (energies relatives to the separated reactants)						
2,4 pentanedione •H_2O	-7.2	-5.1	3.5	-1.7	9.1	-1.8	9.0
diketo/keto-enol•H_2O TS	28.2	26.7	37.1	31.4	40.4	33.9	42.9
cis **keto-enol•H_2O**	-11.7	-9.3	-1.1	-5.2	5.4	-6.0	4.6
W1-1	-8.3	-5.3	11.1	-7.0	12.4	-4.0	15.3
W1-TS1	17.5	19.0	39.5	17.4	39.4	19.5	41.5
W1-2	-16.0	-10.0	9.8	-14.6	11.2	-12.9	12.9
W1-2'	-15.5	-9.7	9.3	-16.6	8.2	-11.9	12.8
W1-2''	-13,6	-8,2	10,2	-17,1	6,8	-12,7	11,2
W1-TS2-A	18.6	21.3	43.3	14.0	38.7	22.7	47.4
W01w-TS2-A	33,6	36,0	55,4	31,1	52,9	37,2	59,0
W1-TS2-B1	26.3	28.1	49.4	21.4	44.6	29.4	52.6
W1-B	-11.4	-4.6	16.0	-11.8	15.6	-4.6	22.8
W1-TS2-B2	6.6	10.0	31.6	1.8	26.8	11.2	36.2
W1-3•H_2O	-13.9	-10.6	7.3	-10.2	11.0	-7.3	13.9
W2-2	-25.3	-17.3	9.8	-21.2	14.0	-16.8	18.4
W2-TS2-A	5.5	10.6	41.5	6.8	42.8	15.6	51.6

[a] in kcal mol^{-1}.

Table S3 Calculated total electronic energies (E_e)[a], ZPE corrected total electronic energies (E_e+ZPVE)[a] and Gibbs free energies (G_{298})[a] for gas phase compounds at the B3LYP/6-311++G(d,p) level and solution SCF energies (E_{sol})[a] and solution Gibbs free energies (G_{sol})[a,c] for solution compounds at the SMD-CPCM-B3LYP/6-311++G(d,p)// B3LYP/6-311++G(d,p) level for Diels-Alder reaction.

Compounds	E_e	E_e + ZPE	G_{298}	E_{sol} water	G_{sol} water[c]	E_{solv} acetone	G_{sol} acetone[c]
	water-unassisted Diels-Alder reaction						
styrene	-309.73085	-309.59806	-309.62946	-309.73317	-309.63178	-309.74179	-309.64040
W0-3	-383.99161	-383.86530	-383.90008	-384.00156	-383.91003	-384.01270	-383.92117
W0-TS3-α[b] *exo*	-693.69466	-693.43277	-693.47757	-693.71075	-693.49366	-693.72870	-693.51161
W0-TS3-β[b] *exo*	-693.68150	-693.41954	-693.46334	-693.69802	-693.47986	-693.71351	-693.49535
W0-TS3-α[b] *endo*	-693.69549	-693.43351	-693.47744	-693.71178	-693.49373	-693.72900	-693.51095
W0-TS3-β[b] *endo*	-693.68287	-693.42060	-693.46350	-693.69757	-693.47820	-693.71324	-693.49387
W0-4-α	-693.75255	-693.48516	-693.52848	-693.76451	-693.54044	-693.78028	-693.55621
W0-4-β	-693.75294	-693.48541	-693.52847	-693.76740	-693.54293	-693.78276	-693.55829
	water-assisted Diels-Alder reaction						
W1-3	-460.45930	-460.30910	-460.35019	-460.47526	-460.36615	-460.48483	-460.37572
W1- TS3-α[b] *endo*	-770.16818	-769.88187	-769.93086	-770.18501	-769.94769	-770.20131	-769.96399
W1-4-α	-770.21648	-769.92542	-769.97585	-770.23980	-769.99917	-770.25192	-770.01129

[a] in atomic unit (a.u.) ; 1 a.u. = 627.5 kcal mol^{-1}. [b]One imaginary frequency, transition state.
[c]$G_{sol} = G_{298} + (E_{sol} - E_e)$.

Table S4 Calculated relative electronic energies (ΔE_e)[a], relative ZPE corrected electronic energies ($\Delta(E_e+ZPVE)$)[a] and relative Gibbs free energies (ΔG_{298})[a] for gas phase compounds at the B3LYP/6-311++G(d,p) level and relative solution SCF energies (ΔE_{sol})[a] and relative solution Gibbs free energies (ΔG_{sol})[a] for solution compounds at the SMD-CPCM-B3LYP/6-311++G(d,p)// B3LYP/6-311++G(d,p) level for Diels-Alder reaction (with respect to the separated reactants).

Compounds	ΔE_e	$\Delta(E_e+ZPE)$	ΔG_{298}	ΔE_{sol} water	ΔG_{sol} water	ΔE_{solv} acetone	ΔG_{sol} acetone
	water-unassisted Diels-Alder reaction (energies relatives to the separated reactants)						
W0-3	1.8	1.0	2.2	-5.3	-4.9	-1.4	-0.9
W0-TS3-α *exo*	19.3	20.2	34.9	9.8	25.3	14.8	30.4
W0-TS3-β *exo*	27.5	28.5	43.8	17.7	34.0	24.4	40.6
W0-TS3-α *endo*	18.7	19.7	34.9	9.1	25.3	14.6	30.8
W0-TS3-β[b] *endo*	26.7	27.8	43.7	18.0	35.0	24.5	41.5
W0-4-α	-17.1	-12.7	2.9	-24.0	-4.0	-17.6	2.4
W0-4-β	-17.3	-12.8	2.9	-25.8	-5.6	-19.1	1.1
	water-assisted Diels-Alder reaction (energies relatives to the separated reactants)						
W1-3	-3.9	-3.1	5.2	-7.8	1.3	-4.4	4.7
W1- TS3-α *endo*	9.9	12.8	35.9	6.8	32.8	11.5	37.5
W1-4-α	-20.4	-14.6	7.6	-27.5	0.5	-20.3	7.8

[a] in kcal mol^{-1}.

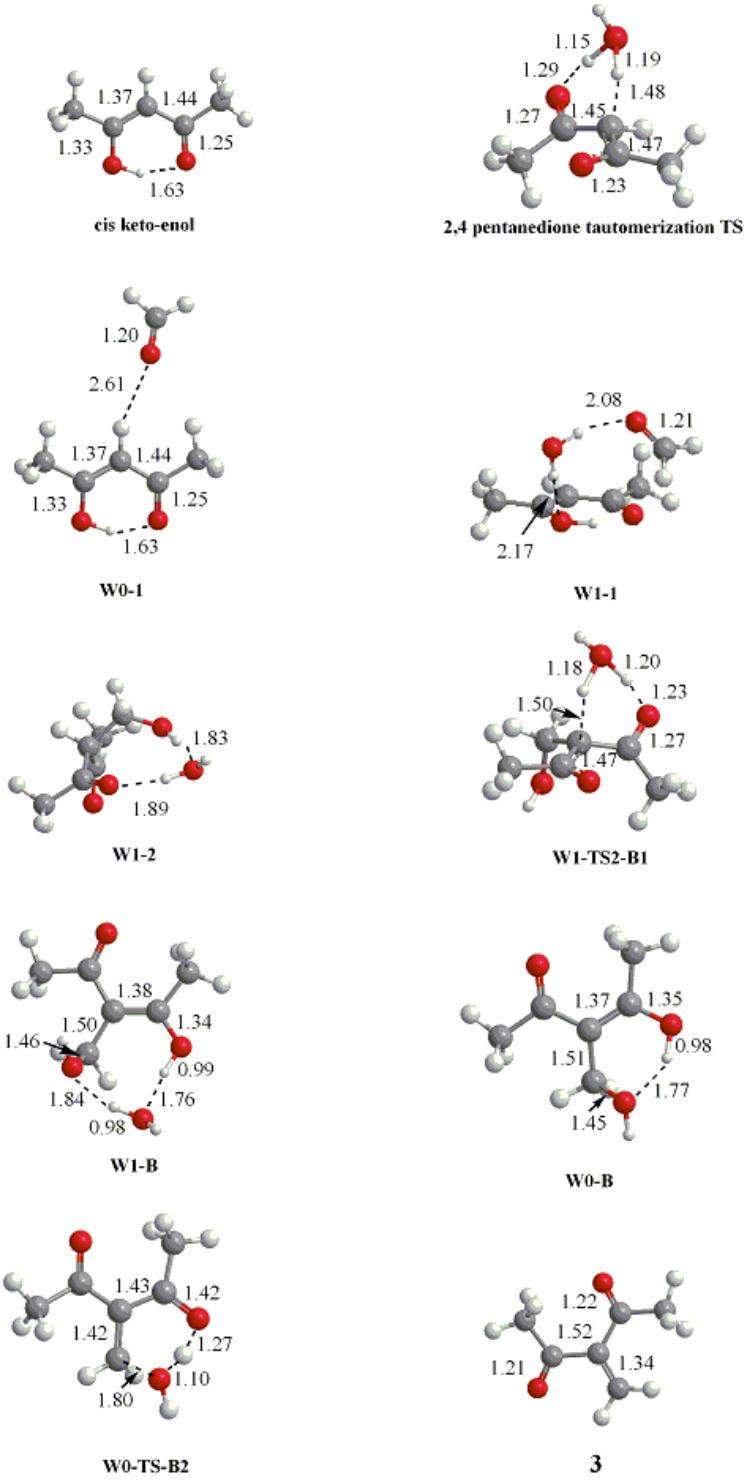


Fig. S1 Selected B3LYP/6-311++G** structural parameters for stationary structures found in the water-unassisted pathway (**W0**) and in water-assisted pathway (**W1**). Bond lengths are given in angströms.

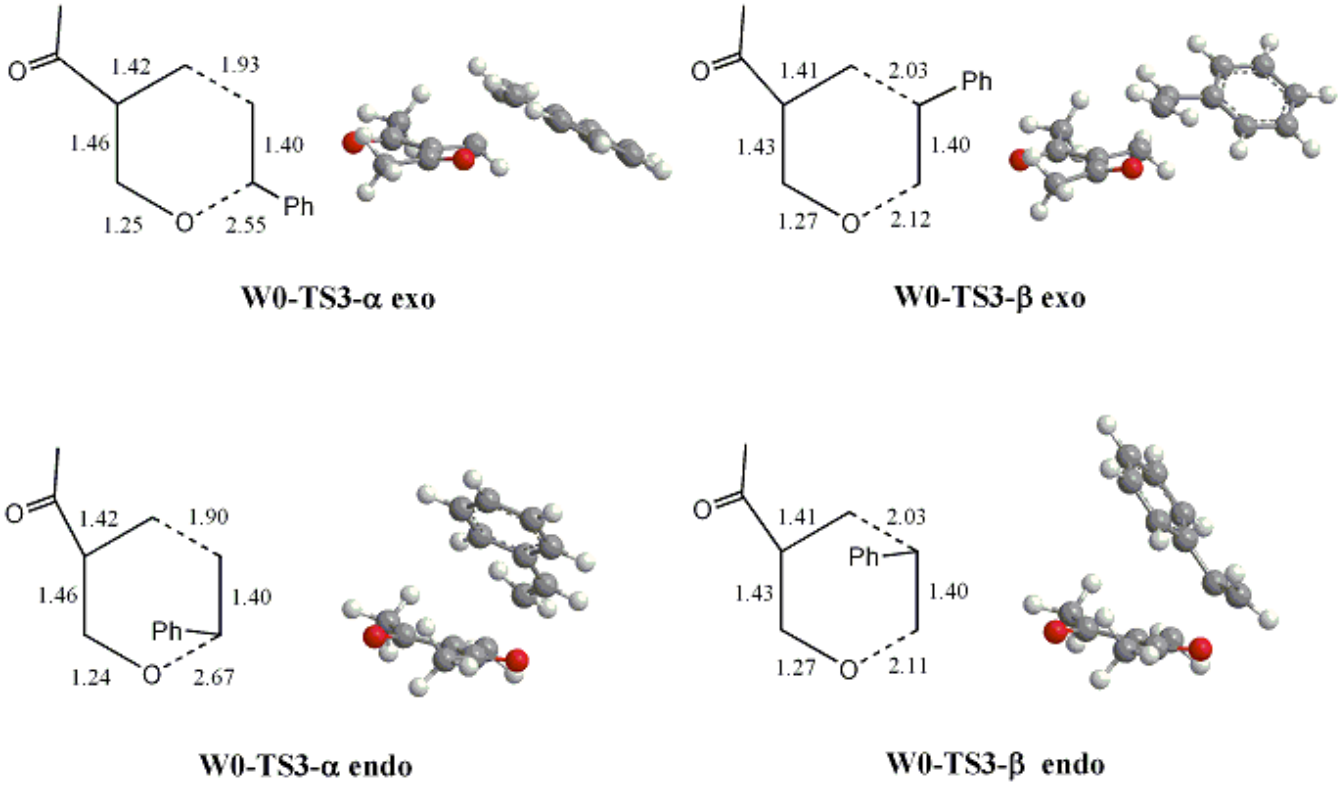


Fig. S2 Selected B3LYP/6-311++G** structural parameters for stationary transition states hetero Diels-Alder structures found in water-unassisted pathway (**W0**). Bond lengths are given in angströms.

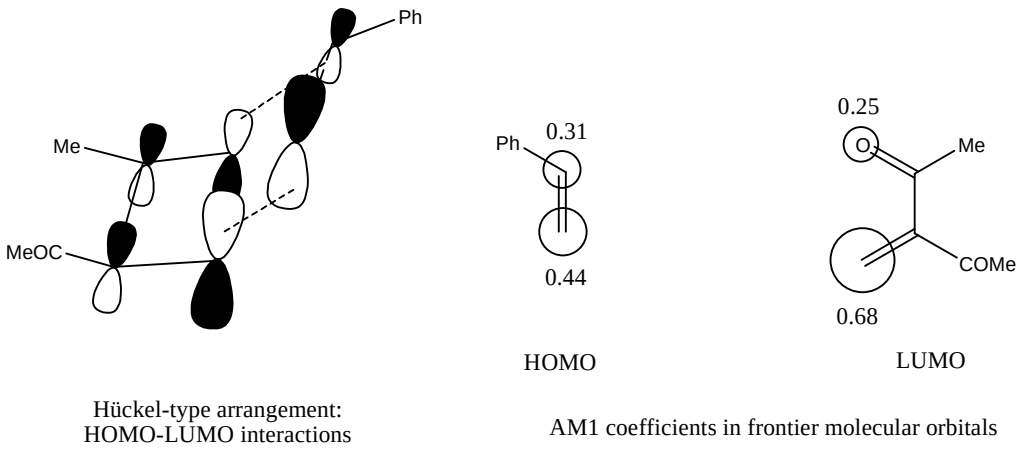
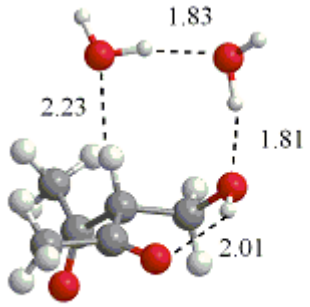
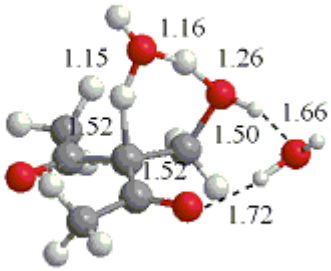


Fig. S3 Hückel-type arrangement and AM1 coefficients in HOMO styrene and LUMO hetero-diene.



W2-2



W2-TS2-A

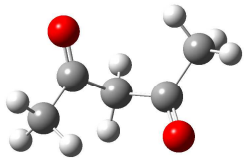
Fig. S4 Selected B3LYP/6-311++G** structural parameters for selected stationary structures found in water-assisted pathway (**W2**). Bond lengths are given in angströms.

Note on the keto-enol tautomerism of 2,4-pentanedione

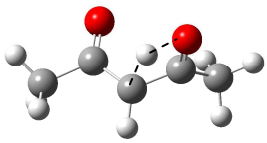
The keto-enol tautomerism of 2,4-pentanedione (acetylacetone) has been studied by Alagona and Ghio in both THF and aqueous solutions (ref. 37). They showed that the inclusion of an explicit water molecule in the transition state structure was lowering the activation barrier (~31-35 kcal mol^{-1} with respect to the intermediate, IEF-PCM-B3LYP/6-31G*). Our results are in very agreement (see below). Thus, based on our NMR experimental findings and both the already published and our theoretical results, we did not discussed on the keto-enol tautomerism of acetylacetone in the main text. Nevertheless, we described here our computed simulations for the acetylacetone tautomerism reaction (SMD-CPCM-B3LYP/6-311++G** // B3LYP/6-311++G**, water solution, see Tables S1 and S2).

In the unassisted water mechanism, the computed TS barrier was exceedingly high (57.6 kcal mol^{-1}) due to the presence of a strained four-membered ring but this barrier was lowering by 17.2 kcal mol^{-1} with respect to the separated reactants when an explicit water molecule was employed to complete the ring of a six-membered transition state ($\Delta G_{water}^{\ddagger}{}_{enol}$ = 40.4 kcal mol^{-1} with respect to the separated reactants and 31.3 kcal mol^{-1} with respect to the 2,4-pentanedione•H_2O intermediate).

a) Water-unassisted mechanism

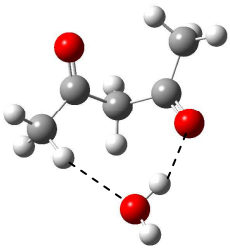


2,4-pentanedione

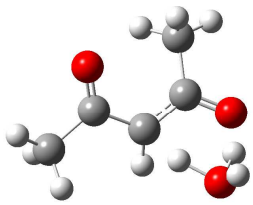


water-unassisted TS

b) Water-assisted mechanism



2,4-pentanedione – H_2O



water-assisted TS

B3LYP/6-311++G(d,p) Cartesian coordinates

Symbol, 0, x, y, z

H_2O
O,0,0.0055622165,0.,0.0043655691
H,0,-0.0054004087,0.,0.9663544931
H,0,0.9373935718,0.,-0.2348690323

H_2CO
C,0,-0.0000007046,0.0003584931,-0.0022475933
O,0,0.0000015417,-0.0001098526,1.199750953
H,0,0.9393505384,-0.0001276007,-0.589852194
H,0,-0.9393489465,0.0031213251,-0.5898508684

2,4 pentanedione
C,0,-0.0054419475,0.0061230728,-0.0070212866
C,0,-0.0034517697,0.0003912954,1.5024165096
C,0,1.3746818475,-0.0113261106,2.1804434395
C,0,1.8094210521,-1.4722405362,2.3697655153
O,0,2.4319644472,-2.0470534898,1.5051606463
O,0,-1.0164714056,-0.0247438535,2.1647395917
C,0,1.3840007422,-2.1343901372,3.657793092
H,0,0.3809832321,0.9658945313,-0.3665923298
H,0,-1.0165071527,-0.1429552734,-0.3834092998
H,0,0.6664274971,-0.7688803312,-0.3878776042
H,0,1.2806127009,0.4927584937,3.1430583086
H,0,2.1186481401,0.4829270405,1.5545009695
H,0,1.6039264243,-3.2005321159,3.6243358681
H,0,0.3174685791,-1.9655892328,3.8341550235
H,0,1.9206427862,-1.6762642219,4.4955964391

diketo – ketoenol TS
C,0,-0.6109863706,0.2398600688,0.148890264
C,0,0.1996081134,0.1338441905,1.381947304
C,0,1.6087363808,-0.2036683346,1.5603996025
C,0,1.8989935664,-1.6358985831,1.7497107666
O,0,1.0359738686,-2.498553384,1.8604181843
O,0,-0.3071061925,0.2794742911,2.5343615115
C,0,3.3743089116,-2.0039326973,1.8168263006
H,0,-0.0634435892,0.7982546285,-0.6142268133
H,0,-1.5856410372,0.6895688836,0.3335691333
H,0,-0.7413970163,-0.779400483,-0.2353545026
H,0,0.8671629581,0.1169582446,2.8741276094
H,0,2.3556753401,0.3601015129,1.0059038391
H,0,3.504190377,-2.8312161548,2.5157093314
H,0,4.0037467353,-1.1619415934,2.1103758231
H,0,3.6948650669,-2.3477815246,0.8277950767

***cis*-keto-enol**
C,0,-0.001082042,-0.0022571514,-0.0008791851
C,0,-0.004427031,-0.0546035133,1.5094741536

O,0,1.072517283,-0.1500503859,2.1281575139
C,0,-1.2691533269,0.0205472629,2.2027912864
C,0,-1.3210915703,-0.0081497281,3.5719417705
C,0,-2.5843108306,0.0649493263,4.3667162873
O,0,-0.2269393411,-0.1068465576,4.3143684981
H,0,-0.7122747363,-0.7207005667,-0.4176458298
H,0,1.0002325047,-0.2110185857,-0.374962222
H,0,-0.3092252166,0.9933647941,-0.3365879589
H,0,-2.1884592217,0.1009898038,1.639182911
H,0,-2.6788471122,-0.8276361057,4.9918895387
H,0,-3.4584487095,0.1469867949,3.721765422
H,0,-2.548146664,0.92759648,5.0382578402
H,0,0.543996013,-0.1481547359,3.6738321926

W0-1: *cis*-keto-enol●H_2CO
C,0,0.,0.,0.
C,0,0.,0.,1.511081
C,0,1.2585676472,0.,2.2144995107
C,0,1.2883766648,-0.0295065789,3.5852389576
O,0,0.1792296684,-0.0550314911,4.3115069215
O,0,-1.0898501726,-0.017988886,2.1203610028
C,0,2.5433087672,-0.0346925197,4.3967573459
O,0,3.7692453325,0.3911237727,-0.388240721
C,0,4.6767848401,0.6143268244,-1.145785785
H,0,0.9722958503,0.2679724407,-0.4148287228
H,0,-0.7710588359,0.6830002792,-0.3618722713
H,0,-0.2639440477,-1.0040690083,-0.3485396994
H,0,2.1846277513,0.0263436208,1.6583690703
H,0,2.5529176993,0.8291200981,5.0679138796
H,0,3.4277063379,-0.0082357195,3.7612581276
H,0,2.5738994666,-0.9310170895,5.0232627638
H,0,-0.5819996976,-0.0469277048,3.6534923939
H,0,5.7336576264,0.5905994356,-0.8163900307
H,0,4.503159115,0.8551814781,-2.2124489999

W0-TS1 CC coupling H_2CO●2,4-pentanedione transition state
C,0,0.0005909547,0.014407836,0.003527307
C,0,0.0126047239,-0.0021812041,1.501867951
O,0,1.1589296283,-0.008597876,2.0714268669
C,0,-1.1697439507,-0.0834897981,2.2837682801
C,0,-1.342379534,0.8015885592,3.4804171184
C,0,-2.7871148234,1.0886722968,3.8586896864
O,0,-0.4132963306,1.2705146994,4.1008802745
C,0,-0.66539441,-1.7752236196,3.2856678933
O,0,0.5031780929,-1.5775941487,3.7536892932
H,0,-0.9935940867,-0.1776191327,-0.3992734169
H,0,0.7170988907,-0.7115815938,-0.3878167445
H,0,0.3251840913,1.0039660782,-0.3363629055
H,0,-2.083008369,-0.2518707532,1.7198232458
H,0,-2.8165698339,1.5685341668,4.8358155935
H,0,-3.387188968,0.1743740723,3.8726063386
H,0,-3.2341102332,1.7596244699,3.1176961385

H,0,1.0552221285,-0.610175824,2.9847145837
H,0,-0.8072251053,-2.4705843134,2.4434560306
H,0,-1.5215079355,-1.7496265361,3.9745677778

W0-2
C,0,-0.1075401366,0.0648327053,0.0877103742
C,0,-0.1994274656,-0.3722091844,1.5295377403
O,0,0.7389940455,-0.8931890177,2.0972120122
C,0,-1.5391828326,-0.1748468335,2.2562362412
C,0,-2.0959273513,1.2439614914,2.1013555253
C,0,-3.6001519356,1.3852911389,2.0267795876
C,0,-1.4127247553,-0.5089844727,3.7647082112
O,0,-1.120211469,-1.8733358611,3.9888861675
O,0,-1.3549689057,2.2029253108,2.07644618
H,0,-1.0101930966,-0.2059175901,-0.4678010498
H,0,0.7696872309,-0.3830315912,-0.3772864075
H,0,-0.0168747659,1.1543262053,0.0564986228
H,0,-2.2482563302,-0.8898683388,1.8185812851
H,0,-3.8836448337,2.4324683991,2.1233261106
H,0,-4.0931125433,0.7874316058,2.7985733342
H,0,-3.9485789906,1.0040417068,1.0602741781
H,0,-0.2238392988,-2.0163280142,3.6571842061
H,0,-2.3615297589,-0.3105080728,4.267735733
H,0,-0.6503585079,0.1428780941,4.2056831701

W0-TS2-A: **transition state H_2O elimination**
C,0,-0.2777382781,-0.3376377505,0.2394492403
C,0,0.1789534397,0.287557297,1.5296793097
C,0,1.4798789595,-0.0432778102,2.1492768721
C,0,1.5295768983,0.4175943791,3.5780903178
O,0,1.6807672021,1.916940712,3.2909517302
O,0,-0.5358389805,1.1417781035,2.0833710313
C,0,2.4041251184,-1.0595709051,1.6156642767
O,0,2.3263384461,-1.4800567527,0.4698054162
C,0,3.5194636321,-1.5699882857,2.5238605732
H,0,0.3933791333,-0.0518760858,-0.5736603078
H,0,-1.2918218604,0.0019079478,0.0303246363
H,0,-0.2300148665,-1.4270757501,0.2895882272
H,0,1.9465884736,1.3963437824,2.2228564736
H,0,4.1265383103,-2.2733995254,1.9563117888
H,0,3.114142353,-2.07797101,3.404829022
H,0,4.1576808982,-0.7534900983,2.8760825234
H,0,0.7437427058,2.1550858782,3.0803179956
H,0,2.4134474599,0.1356684998,4.1385018286
H,0,0.6212704843,0.2998996444,4.1663582217

W0-3●H_2O: α,β-unsaturated ketone (I)●H_2O complexe
C,0,-1.4369568582,-2.1565529904,0.0155643595
C,0,-1.5907614909,-0.6552743154,0.0134208612
C,0,-0.3665984612,0.2406302697,0.0476584879
C,0,-0.5244158726,1.5009353778,0.4927342154
O,0,-2.71210358,-0.1610915192,0.0237456678

C,0,0.9727700464,-0.261491847,-0.4121654651
O,0,1.0930965865,-1.3548770126,-0.94443717
C,0,2.1915266877,0.6303928802,-0.2306101824
H,0,-0.714691916,-2.481473305,0.7704915526
H,0,-2.4148391609,-2.6031387748,0.2001057119
H,0,-1.0364443634,-2.4902429727,-0.9447874461
H,0,0.3135502027,2.1860252293,0.562027443
H,0,-1.4990600792,1.8855843922,0.785106496
H,0,3.0676113665,0.079670184,-0.5732367333
H,0,2.3257507565,0.9188475499,0.8167388656
H,0,2.0970622495,1.5501506686,-0.8175449958
O,0,-3.6660069239,2.4539182911,0.7334313717
H,0,-3.5042061085,1.5990125964,0.298376743
H,0,-4.0773290808,2.2029712977,1.5701292173

W0-TS2-B1: **tautomerization transition state (pathway B)**
C,0,0.502170332,0.49643766,0.4279324875
C,0,-0.327290338,-0.4280633387,1.221144553
O,0,-0.0728052104,-1.6691692323,1.3048791864
C,0,-1.5338027696,-0.171284229,2.0367122396
C,0,-2.6590524932,0.4405933713,1.3228928222
C,0,-3.8912026341,0.8393401718,2.1165982676
C,0,-1.2391594149,0.2100006824,3.4653247746
O,0,-0.7623716561,1.5755777143,3.5162062164
O,0,-2.6363807947,0.5846682501,0.1009674926
H,0,-0.1599247828,0.9473844527,-0.3189648618
H,0,1.3398581537,-0.0080164175,-0.0515959189
H,0,0.8404294213,1.3102495739,1.0767536153
H,0,-1.1163403533,-1.6828206977,1.9196579544
H,0,-4.7039186144,1.0460794928,1.4213183626
H,0,-3.6795229972,1.7420830774,2.6980572809
H,0,-4.1960810576,0.0552922729,2.8149157907
H,0,-0.5905936142,1.8129166999,4.4345500728
H,0,-0.4821523101,-0.4540829605,3.9008826512
H,0,-2.1528691318,0.1084727916,4.0594999542

W0-B: ceto-enol intermediate (pathway B).
C,0,0.4604897591,0.4563680251,0.0896724388
C,0,1.4846201865,-0.4578040326,0.1035864822
C,0,0.7906686856,1.9268417674,0.2137648669
C,0,-0.9445944827,0.0163684516,0.0219840093
C,0,1.3659719924,-1.9480269715,0.1372463737
O,0,2.7716374877,-0.0642667688,0.0929121319
C,0,-2.0455716609,1.0722864766,0.0842214057
O,0,-1.2702724149,-1.1606691203,-0.0815692506
O,0,1.8614715516,2.2730921041,-0.7073251085
H,0,1.1253637627,2.1640948917,1.2339446114
H,0,-0.0786715646,2.5440216154,-0.0075329857
H,0,2.3530836078,-2.3718922804,0.324985824
H,0,0.9883792025,-2.3187364526,-0.8192729691
H,0,0.6499896187,-2.2770752867,0.8890661688
H,0,2.8144004898,0.8755654084,-0.1783379761

H,0,-3.0044547616,0.5566376416,0.0855461354
H,0,-2.0044852499,1.7389328669,-0.7831133763
H,0,-1.9691012395,1.691725659,0.983154388
H,0,2.1092140297,3.1933810048,-0.56697217

W0-TS2-B2: H_2O elimination transition structure (pathway B).
C,0,0.1231602966,-0.1507891275,0.2700909732
C,0,-0.8380365411,0.9045585697,0.139713971
C,0,-0.4415188816,-1.4145605959,0.6053670587
C,0,1.5424322907,0.0135117376,-0.0534966645
C,0,-0.4918795363,2.3604754702,0.1107762423
O,0,-2.0608226493,0.5796431568,-0.0117615698
C,0,2.4196040122,-1.2338971644,-0.1374776193
O,0,2.0520796309,1.1121526835,-0.2465693471
O,0,-1.687222518,-1.7339766152,-0.655640645
H,0,-1.1583995314,-1.4345247675,1.4224782195
H,0,0.1846466612,-2.2960468196,0.5536645013
H,0,-1.4115566186,2.9453616037,0.1112731684
H,0,0.0927084292,2.5758457309,-0.787886676
H,0,0.1504003342,2.6324463562,0.94975404
H,0,-2.0586783815,-0.7160080453,-0.4460521498
H,0,3.4078246424,-0.9277513205,-0.4768940654
H,0,2.0134258587,-1.9719380618,-0.8354152601
H,0,2.5185581997,-1.7136509596,0.8413661982
H,0,-2.3387576981,-2.3710908314,-0.3307543757

2,4-pentanedione●H_2O
C,0,-0.0302226999,-0.02596919,0.005671564
C,0,0.0687149924,0.04867732,1.5044012559
C,0,1.4689331063,0.0267689512,2.1116635638
C,0,2.0041873268,-1.4223594411,2.1857065394
O,0,2.1582346173,-2.0714178624,1.1753033926
O,0,-0.9169799514,0.1027674328,2.2177186761
C,0,2.3105253274,-1.9450991617,3.5631934113
O,0,-0.3612363413,-0.3969780345,4.952936578
H,0,0.4065878821,0.877843989,-0.4327206151
H,0,-1.0705258081,-0.1188277909,-0.3025664492
H,0,0.5633183145,-0.8717045075,-0.3541718983
H,0,1.4347539738,0.478138136,3.1025507176
H,0,2.1577475489,0.584170682,1.4705213793
H,0,2.6187888286,-2.988409545,3.5098006283
H,0,1.4385676823,-1.818188426,4.2135401783
H,0,3.1133030561,-1.3440231911,4.0055561548
H,0,-1.0958216432,-0.4132270005,5.572445582
H,0,-0.7439999681,-0.1615169171,4.0892146664

2,4-pentanedione tautomerization TS
C,0,-0.0645689297,0.2537906414,0.2477125406
C,0,0.3296476068,-0.6029224861,1.3732325263
C,0,1.7021967452,-0.736615682,1.809046084
O,0,0.6211873189,1.1820207277,-0.1622789549
C,0,-1.4141016098,-0.0482644996,-0.3867995447

C,0,2.8803696356,-0.2172588853,1.0437628329
O,0,1.9338679511,-1.2730659973,2.9381270454
H,0,-0.1999708949,-0.3202866562,2.7250743887
H,0,-2.1776634265,-0.2591131573,0.3671032245
H,0,-1.7240405351,0.7922791904,-1.0066903892
H,0,-1.3260001558,-0.9392334732,-1.0183808476
H,0,2.9292610872,0.8688655965,1.1645528186
H,0,3.7905862109,-0.6675845629,1.439751492
H,0,2.7774111597,-0.3960392159,-0.0266953037
H,0,0.8601756025,-1.0862167039,3.6361965617
O,0,-0.1768926311,-0.6477028808,3.8725244685
H,0,-0.1026484434,0.1063567227,4.4709356489
H,0,-0.2338886689,-1.5333211389,1.4699108

cis-keto-enol●H_2O

C,0,-0.1034686145,-0.0144421517,-0.0431372954
C,0,-0.059086558,-0.0349967967,1.4632364232
O,0,1.0504249332,-0.0615520073,2.0489817164
C,0,-1.2872656629,0.0056049298,2.2093577892
C,0,-1.2845174572,0.0249170505,3.5823962646
C,0,-2.5189854611,0.0696669,4.4218190962
O,0,-0.1618313826,0.0028026648,4.2835110823
O,0,3.2711145088,-0.3594135418,0.2883407494
H,0,-1.0418126748,-0.416464894,-0.4281403203
H,0,0.7452618893,-0.5627677157,-0.4534354638
H,0,-0.0156944166,1.0246343072,-0.3797513894
H,0,-2.2315111153,0.0236660391,1.6840294438
H,0,-2.5480194232,-0.8035608827,5.0798581328
H,0,-3.419587434,0.0898892683,3.8095543617
H,0,-2.4963783765,0.9561671652,5.0620864326
H,0,0.58647548,-0.0259550452,3.6190750622
H,0,2.6202837898,-0.2455696056,1.0029765889
H,0,4.0661826986,-0.6929235252,0.7126697214

W1-1: H_2CO●H_2O●_cis_-keto-enol

C,0,0.0344408568,-0.0545517972,0.0691710396
C,0,0.0738654151,-0.0740068917,1.5775433117
C,0,1.3386369176,0.0941590392,2.2444653897
C,0,1.429254798,0.0262311395,3.6107679697
O,0,0.3495065417,-0.1555253698,4.3668038118
O,0,-0.9830077425,-0.2662454183,2.2196609555
C,0,2.7009411583,0.1256174816,4.3833226012
C,0,-1.7508511213,-3.0800897496,2.6906840912
O,0,-0.6965742107,-3.632218706,2.887547823
O,0,0.6792141729,-2.9923502626,5.4955680863
H,0,0.7019835907,0.7075301317,-0.3390862643
H,0,-0.9854371997,0.1177661394,-0.2733150688
H,0,0.3725086034,-1.02514936,-0.3103508346
H,0,2.2364327895,0.2498412329,1.6630883959
H,0,2.6268906145,0.9321375587,5.118264763
H,0,3.5520807316,0.3076328895,3.7284961879
H,0,2.8616213874,-0.806245173,4.9344450339

H,0,-0.4264774536,-0.2107913737,3.728881573
H,0,0.4764626049,-2.0524829332,5.4193905303
H,0,0.3229631478,-3.3756446701,4.6809491695
H,0,-2.2247586912,-3.072418918,1.6929703709
H,0,-2.3019090478,-2.5618578543,3.4954676535

W1-TS1: CC coupling transition state
C,0,-0.0113071407,0.0144511025,-0.01324081
C,0,0.0024326074,-0.0109387914,1.5076795935
O,0,1.0530867692,-0.0324621109,2.1270521415
C,0,-1.3164346161,0.0204565,2.1627436115
C,0,-1.5165046253,-0.519896912,3.4701286001
C,0,-2.8429012731,-1.1741198692,3.7877784106
O,0,-0.672845092,-0.4965865174,4.4097547683
C,0,-1.3404005609,2.1800983836,2.5921733765
O,0,-0.1604899138,2.5820221148,2.7853760451
O,0,0.895315031,1.3415635888,4.5963884942
H,0,-0.4878650045,-0.8884466858,-0.4078445957
H,0,1.011371982,0.0762745872,-0.3825662577
H,0,-0.584117776,0.8722961483,-0.3799522744
H,0,-2.1636497321,-0.1036528157,1.4943872348
H,0,-3.1280387985,-0.9643749052,4.8201532334
H,0,-2.7243070758,-2.2591030752,3.6931139256
H,0,-3.6354153577,-0.8629633872,3.1057505466
H,0,0.2950530298,0.4146283704,4.45924362
H,0,0.729276135,1.7034247544,5.4748267625
H,0,0.4841079967,2.0022913537,3.821855363
H,0,-2.0254605782,2.0346935922,3.4358291733
H,0,-1.8220772824,2.4087353803,1.6367564266

W1-2

C,0,-0.0233616962,0.0298533129,-0.0073015701
C,0,-0.0148874628,-0.0130567195,1.5028212943
C,0,1.3758913187,0.0169082636,2.1832634206
C,0,1.262263447,-0.0877004729,3.7084791338
O,0,1.6690039559,-1.0613915627,4.3152432661
O,0,-1.036979037,-0.065497012,2.1479942826
C,0,2.335370023,-1.0152432406,1.539957672
O,0,1.7166872439,-2.2470804009,1.2348311104
C,0,0.6512978602,1.0800782062,4.4398523965
O,0,2.0362697339,-3.7331045627,3.5769110693
H,0,0.6799347946,0.7728335435,-0.3937420156
H,0,-1.0322353609,0.2489473338,-0.3549751013
H,0,0.2859561164,-0.9503110477,-0.3809546842
H,0,1.7781677031,1.0188725996,1.9695474273
H,0,0.7699948049,0.9479237706,5.5144440692
H,0,-0.411200572,1.1272936511,4.1860735053
H,0,1.1066902973,2.0228907345,4.1226681357
H,0,1.9778796031,-2.9110401277,4.0924785166
H,0,2.7918317113,-4.2224463283,3.9139350589
H,0,1.8253504869,-2.867140494,1.979561006
H,0,3.1990248156,-1.1507465691,2.1990350864
H,0,2.7050576773,-0.5998586813,0.5982139535

W1-2'

C,0,-0.0216251975,-0.0122122727,0.0192408251
C,0,-0.0384300272,-0.0067265882,1.5302918841
C,0,1.3244711162,0.012057299,2.2324745311
C,0,1.7689007992,-1.4476266303,2.4890841207
O,0,3.1173244859,-1.5268920159,2.9437682049
O,0,-1.0675496344,-0.0487317511,2.1697897592
C,0,1.3293686211,0.8254743967,3.5330459909
O,0,1.85045533,0.3767012266,4.5364573871
C,0,0.7185065939,2.2036677902,3.5104370547
O,0,4.2639723587,-0.1773531978,0.7650837881
H,0,0.7188065636,-0.7187077563,-0.3655324422
H,0,-1.0124158229,-0.246628598,-0.3676685765
H,0,0.2822983364,0.9789340664,-0.3360297655
H,0,2.0646211748,0.4712641872,1.5640312567
H,0,1.0272451236,2.7579441951,4.3956468069
H,0,-0.3708019919,2.1064211018,3.5030463906
H,0,1.0061610433,2.7457628929,2.6048379302
H,0,1.0932996064,-1.9103721077,3.2148035984
H,0,1.7259680628,-2.0216407696,1.5623238219
H,0,3.1296561422,-1.0945316128,3.810768568
H,0,5.1352872444,-0.3885329989,0.4191204058
H,0,4.1418628314,-0.731419103,1.5565818206

W1-2'' (H_2O linked to a carbonyl group)

C,0,0.,0.,0.
C,0,0.,0.,1.50936533
O,0,1.0323569262,0.,2.1473201832

C,0,-1.3602217721,-0.044388218,2.2265115366
C,0,-2.3365258518,1.0115979048,1.7143405247
C,0,-3.7930190456,0.6311372947,1.6289206456
C,0,-1.1907971453,0.1278576138,3.7596498522
O,0,-0.4845876209,-0.9473445389,4.341986774
O,0,-1.9320846187,2.1246161197,1.4273055266
H,0,-0.725960321,-0.7165688434,-0.3953262426
H,0,0.9979527732,-0.2339284656,-0.3681401542
H,0,-0.2917406798,0.9925463448,-0.3549891211
H,0,-1.7831665301,-1.0418352057,2.0516885942
H,0,-4.4140155101,1.5071384975,1.4461359658
H,0,-4.1121228061,0.1163086835,2.5398180758
H,0,-3.9215422349,-0.0808115181,0.8052345257
H,0,0.4246406917,-0.8827586348,4.0211858131
H,0,-2.1720581987,0.14891018,4.2385167922
H,0,-0.6960392159,1.0863523088,3.9514752821
H,0,-3.2255716657,3.4483253468,0.8335601398
O,0,-4.073987009,3.8285836797,0.5532684529
H,0,-3.956984907,4.7821841738,0.5794659409

W1-TS2-A: H_2O elimination transition structure (pathway A).
C,0,-0.0073389279,0.0164758299,-0.0045745674
C,0,-0.0027429373,-0.0210923737,1.5248267022
O,0,1.0759721167,-0.0709900733,2.1051525264
C,0,-1.2981157146,-0.0314639414,2.2229267611
C,0,-1.4276659518,0.3109314789,3.641725598
C,0,-0.2460472993,0.3812057976,4.5724654311
C,0,-2.5747261716,0.2966678414,1.4595250618
O,0,-3.7110763681,-0.4743617592,2.0310669253
O,0,-2.5690316908,0.5188854862,4.108435139
O,0,-2.3637653483,-2.4097276029,2.350689316
H,0,-0.4332916266,0.9540654297,-0.3761285458
H,0,1.0225253734,-0.0648127907,-0.3488767749
H,0,-0.5929932037,-0.8019292623,-0.4360871387
H,0,-1.6043424606,-1.5627972546,2.3255075257
H,0,-0.6054810133,0.6476994216,5.5661444243
H,0,0.4867271365,1.1066832733,4.2134579714
H,0,0.2809101554,-0.5750258577,4.6013557096
H,0,-2.8696431178,1.3445461272,1.5475905735
H,0,-2.5383220855,0.0275545392,0.4069254092
H,0,-3.7009256569,-0.1155117046,2.9642562045
H,0,-2.2181955286,-3.049796845,1.6425764319
H,0,-3.2097820262,-1.6355912165,2.1542128629

W01w-TS2-A: H_2O elimination transition structure (pathway A, H_2O on carbonyl group).
C,0,0.994487756,0.7162407906,1.1748881177
C,0,0.1296090526,-0.2846162548,1.8922538669
O,0,0.5435234535,-1.4422335071,2.0632932555
C,0,-1.2327500639,0.0462798725,2.3739609975
C,0,-1.8379476306,1.3779411071,2.2645617223
C,0,-3.0588598432,1.6992769135,3.1142337353
C,0,-1.7193165961,-0.9762685152,3.3621772572

O,0,-2.0192561577,-2.0894630387,2.3512638081
O,0,-1.4009960153,2.2231113063,1.4836780938
H,0,0.5330000702,0.9980735278,0.2257709894
H,0,1.9712681205,0.266038213,1.0005580082
H,0,1.0855071594,1.6419664708,1.7462167809
H,0,-1.9040281941,-1.0940169898,1.6530088319
H,0,-3.4131075255,2.7001666864,2.8730798435
H,0,-2.8126087864,1.6557225158,4.1799077639
H,0,-3.8672188003,0.9843168276,2.9326515049
H,0,-1.1172343564,-2.4618953878,2.2033734039
H,0,-2.663972724,-0.7583352969,3.8466556703
H,0,-0.9844679665,-1.3710632692,4.0607931277
H,0,-2.2012925971,3.9150687695,1.3729980837
O,0,-2.7470802219,4.71436085,1.4882113484
H,0,-2.5917856672,5.2512122014,0.7066440777

W1-TS2-B1: tautomerization transition structure (pathway B).

C,0,0.0878026649,-0.3471225441,0.0968727418
C,0,0.3278015433,-0.0282372477,1.5167585607
C,0,1.7169013216,-0.0347038856,1.9933459799
O,0,0.9394662,-0.8692677137,-0.613587229
C,0,-1.3059020565,-0.1013959596,-0.4759061149
C,0,2.918010931,0.2257603431,1.1440040829
O,0,1.9362599177,-0.3010018028,3.2152651831
H,0,-0.0926172472,-1.1383582421,2.4292759048
H,0,-1.343013322,-0.5221069986,-1.4795847195
H,0,-2.0809448534,-0.5662184813,0.1404402046
H,0,-1.5379160368,0.9674391511,-0.5350092073
H,0,3.7357294759,0.5642329992,1.7815374065
H,0,3.2073678793,-0.7109653695,0.658694727
H,0,2.706910558,0.9388615564,0.3483325985
H,0,0.9871862801,-0.9904547223,3.5984821295
O,0,0.0356682259,-1.7031114704,3.4558453013
H,0,-0.6967958654,-1.5020168405,4.0491846559
C,0,-0.5392439563,1.0412452108,2.1868545934
H,0,-1.5985111491,0.8475796551,1.987069218
H,0,-0.400893716,1.0283870833,3.2684293446
O,0,-0.2083606097,2.3872811307,1.8151585493
H,0,-0.3615309842,2.4985703386,0.8711500174

W1-B: dienol ●H_2O (pathway B).

C,0,0.1524754232,0.9255909149,-0.0860147506
C,0,0.1561241818,0.0363827888,1.0946545462
C,0,1.3433720568,-0.3175762616,1.7012225701
O,0,1.1484884233,1.5149820895,-0.4887156211
C,0,-1.1597745168,1.1231389704,-0.8444670014
C,0,2.7179720039,0.0169132756,1.2056016678
O,0,1.4205518996,-1.0491847572,2.8159528975
H,0,-0.4889042663,-1.0802954692,5.4832888291
H,0,-0.9847495464,1.8579206433,-1.6284867351
H,0,-1.4939342172,0.1869385387,-1.3026390321
H,0,-1.9695242727,1.4754712736,-0.1984900461

H,0,3.4328868242,-0.6425096683,1.6987344637
H,0,2.7913621712,-0.0617593921,0.1229822505
H,0,2.9623134803,1.0542030138,1.4508775891
H,0,0.5898203165,-1.1567322531,3.3356860739
O,0,-0.6685464969,-1.2748772772,4.5590379683
H,0,-1.2597091759,-0.5762959335,4.2172848285
C,0,-1.1490473077,-0.5045277702,1.6094441839
H,0,-1.8769567396,-0.598315594,0.8035897426
H,0,-1.0313937538,-1.4978503467,2.0442116648
O,0,-1.75894203,0.2888204674,2.6746584377
H,0,-1.6238300658,1.221536455,2.4759396408

W1-TS2-B2: H_2O elimination transition structure (pathway B).
C,0,-0.0107734245,0.0104965713,0.0296853403
C,0,-0.0098526704,-0.0607063772,1.4920793952
C,0,1.1952845806,-0.032035154,2.2658349443
O,0,1.0024185839,0.1793509488,-0.644244826
C,0,-1.3448135683,-0.1364418264,-0.7132340385
C,0,2.559513923,-0.1439639884,1.635180981
O,0,1.1852862701,0.0691014399,3.532910094
H,0,-0.2843766792,1.9730917684,5.2517112338
H,0,-1.1524327656,0.0263995517,-1.7723514493
H,0,-1.7610093852,-1.1406972604,-0.5833489769
H,0,-2.1013783606,0.5795992894,-0.3775210957
H,0,3.2876438522,-0.3157655852,2.4279765997
H,0,2.5990440062,-0.9321725053,0.883369897
H,0,2.8012802189,0.7803495363,1.1039907603
H,0,0.2110334368,0.6781487366,4.3276286938
O,0,-0.6011811787,1.1855166879,4.7992060888
H,0,-1.355966768,1.3252126466,3.7684224693
C,0,-1.2601683547,-0.2339492628,2.2093564769
H,0,-2.0968124154,-0.5963139922,1.6257791716
H,0,-1.1800093404,-0.7718395153,3.1502149645
O,0,-1.8927247511,1.1669105019,2.7791350116
H,0,-1.6181388537,1.8533229572,2.1542574238

W1-3●H_2O: α,β-unsaturated ketone (I)●2H_2O complexe
C,0,0.0314613133,0.2884725545,0.1302221081
C,0,0.1407875342,-0.2293451451,1.5372594722
C,0,1.46579833,-0.1515964881,2.2572948235
O,0,1.0234446719,0.67700426,-0.460931619
C,0,-1.3407660221,0.3646605592,-0.4993493975
C,0,2.7004073639,-0.6914083476,1.5916414824
O,0,1.5063468352,0.3207331444,3.3843908915
H,0,-0.1499892793,2.8365186075,4.5752933934
H,0,-1.24124039,0.805067025,-1.4901435086
H,0,-1.7852278818,-0.6309500166,-0.5906625971
H,0,-2.0042485936,0.9735935607,0.1222647009
H,0,3.5199826168,-0.7209491939,2.3086447332
H,0,2.5110708184,-1.6883036027,1.1830321986
H,0,2.950999954,-0.0489401332,0.7440554134
H,0,0.148621732,1.4192839831,4.0358405979

O,0,-0.576913693,2.0326720139,4.2651836286
H,0,-1.9484225731,2.0169669212,3.0041002779
C,0,-0.9079437767,-0.723923444,2.2071533244
H,0,-1.8938462948,-0.7902062287,1.7686660208
H,0,-0.803373968,-1.0664784471,3.2306097041
O,0,-2.6293644769,1.8986410322,2.3139450898
H,0,-3.4158266257,2.3355916542,2.6520364199

W1-3

C,0,-0.024601227,-0.0994718925,-0.030164575
C,0,-0.029907006,0.0289244262,1.4815286395
C,0,1.2733450703,-0.031550429,2.2221259202
C,0,2.4564957984,-0.0550130438,1.5906558513
O,0,-1.0739184029,0.2088271211,2.0821234589
C,0,1.2620138329,-0.0565384499,3.7346009645
O,0,2.0887011824,0.578168974,4.3683654315
C,0,0.2510427374,-0.9204698917,4.4438326687
O,0,4.4303484857,2.1670661773,4.2631844788
O,0,5.5832847092,0.623391787,2.2514355591
H,0,0.4463940735,-1.0332928309,-0.3479834945
H,0,-1.0552341936,-0.0717208283,-0.3797847542
H,0,0.5295569304,0.7237960641,-0.4895132208
H,0,3.5773882267,1.7014537186,4.3342540491
H,0,0.5643095493,-1.0604095619,5.4777583821
H,0,0.134168176,-1.8851365142,3.9431739442
H,0,-0.7231595172,-0.4276119312,4.4085307825
H,0,3.4052007678,-0.0602256006,2.1169225245
H,0,2.5187747478,-0.0710568738,0.5090457367
H,0,6.4330074442,0.2637174003,2.5200416333
H,0,4.2245114519,3.1058544757,4.2481945869
H,0,5.3286299672,1.2494827435,2.9563413703

Styrene $H_2CCH(C_6H_5)$

C,0,0.1613216392,-0.0071512892,-0.0038332826
C,0,0.101103535,-0.042598552,1.3873505115
C,0,1.2747017044,-0.0237870158,2.1365886848
C,0,2.5069228105,0.0306987591,1.4812250775
C,0,2.5646829529,0.066021804,0.0934859415
C,0,1.3906246276,0.047866256,-0.6781898151
H,0,-0.7574059488,-0.0221157577,-0.5815128802
H,0,-0.8617417029,-0.0848981298,1.8842820778
H,0,1.2332284938,-0.0512694973,3.2195312917
H,0,3.4257603995,0.0455462998,2.0570631532
H,0,3.5314420552,0.1079581156,-0.394432539
C,0,1.3937058536,0.0837246592,-2.1497197357
C,0,2.4532722292,0.1392249891,-2.9627331423
H,0,0.4048284446,0.0615638608,-2.6027458356
H,0,2.3259893193,0.1610997665,-4.0382878435
H,0,3.4740816715,0.1648425311,-2.5980716639

W0-3 α,β-unsaturated ketone (I)

C,0,0.0425510264,0.0465005445,0.054704448

C,0,-0.0342194891,0.1616069863,1.3874670313
C,0,1.2791950617,0.2484264639,2.1549425849
O,0,2.2617565275,0.6916868131,1.5964774496
H,0,1.0107527348,0.0507742698,-0.432642144
H,0,-0.8341475929,-0.04184799,-0.5743355228
C,0,-1.352387076,0.2378338888,2.1010697516
O,0,-1.4064573446,0.5721697811,3.2697120366
C,0,-2.6239168494,-0.072981538,1.3316246429
C,0,1.3484348133,-0.2755342054,3.5686795325
H,0,-2.5742394072,-1.0564413438,0.8573742787
H,0,-3.4620432664,-0.0412617493,2.025797716
H,0,-2.7900759397,0.6678906124,0.5441628738
H,0,2.3952685459,-0.3983867728,3.8444879626
H,0,0.8621257487,0.4315704789,4.2439747842
H,0,0.8111538949,-1.2220062395,3.6715025738

W0-TS3-α-exo

C,0,0.229664478,0.504616979,0.3803647917
C,0,-0.026782377,0.0669036643,1.7031978627
C,0,1.1347078413,0.0591017192,2.5817323762
O,0,2.2057990034,0.5086959061,2.1323615099
C,0,0.5377793664,2.4022044653,0.287513247
C,0,1.8171728239,2.6467593828,0.7952133966
H,0,1.1911603993,0.22126405,-0.0338459467
H,0,-0.5888158362,0.4433119072,-0.3278244337
C,0,-1.3956245665,-0.1774989452,2.1788947263
O,0,-1.6429314876,-0.5842501261,3.3102664115
C,0,-2.560300249,0.0604989828,1.2189206927
C,0,1.0769274992,-0.4079222221,4.0169262814
H,0,-0.297365602,2.7802407232,0.8653511009
H,0,0.3973591147,2.4968651057,-0.7846662245
H,0,1.9139966165,2.925597923,1.8369021834
C,0,3.0548514165,2.5690483685,0.0548837447
C,0,3.1081461073,2.3177432088,-1.3317316247
C,0,4.3264376139,2.2440122518,-1.9934180063
C,0,5.5198404308,2.4242157936,-1.2912734246
C,0,5.4874201712,2.6741169832,0.0815721289
C,0,4.2714271912,2.7416301762,0.7463800854
H,0,4.2454918022,2.9074997849,1.8171159068
H,0,6.4120161216,2.8066654861,0.6314378281
H,0,6.4691129198,2.3692288269,-1.811946583
H,0,4.3494595856,2.0512561464,-3.0599350021
H,0,2.1931085927,2.1915747413,-1.8979136647
H,0,-2.5424280906,1.0666383737,0.7895119949
H,0,-2.5387098861,-0.6536663281,0.3900031887
H,0,-3.4872855719,-0.0757096034,1.7739568989
H,0,2.0767103783,-0.3276120568,4.4445386475
H,0,0.7187642952,-1.4377514872,4.0760943445
H,0,0.3639985378,0.1847198189,4.5944155618

W0-TS3-β-exo

C,0,0.0608266522,0.384212387,0.3748164068
C,0,-0.0125245787,0.025454541,1.7375117406
C,0,1.2127071485,0.196430447,2.4620051044
O,0,2.1728280754,0.7557872803,1.8559741614
C,0,1.5612703495,2.5643197156,0.9420175631
C,0,0.4582188082,2.3519771178,0.1086880432
H,0,0.9760292561,0.1289939275,-0.142605103
H,0,-0.8298775406,0.3223416601,-0.2382060574
C,0,-1.2907899727,-0.3172415136,2.3932242691
O,0,-1.3525548706,-0.6717083553,3.563485331
C,0,-2.5727476541,-0.2504731391,1.5705047985
C,0,1.3998392643,-0.1612616312,3.9135757562
H,0,2.5593463234,2.6636629886,0.5396535383
H,0,1.4251797059,2.9357888471,1.9468982552
H,0,-0.4930333986,2.7095546218,0.4917106451
C,0,0.5894208423,2.4364276433,-1.3735009475
C,0,1.7373571391,1.9948312121,-2.0470073577
C,0,1.8270555059,2.082149254,-3.4336911916
C,0,0.7703034002,2.6065163001,-4.177332744
C,0,-0.3797558388,3.0397472684,-3.5203867383
C,0,-0.4693575756,2.951335667,-2.1330635222
H,0,-1.3678763397,3.2956798959,-1.6304803635
H,0,-1.2086236514,3.4491394869,-4.0871707403
H,0,0.8421104255,2.6741129171,-5.2567242994
H,0,2.7243357235,1.7364357919,-3.9349236125
H,0,2.5668901443,1.5748617635,-1.4877522686
H,0,-2.705991035,0.7283546911,1.1003953929
H,0,-2.5648107496,-1.000370064,0.7738667707
H,0,-3.4131861955,-0.4489022305,2.2338280268
H,0,2.4331626402,0.0455681376,4.1927629803
H,0,1.160175959,-1.2113913785,4.0897112111
H,0,0.7144222648,0.4076647496,4.5472149515

W0-TS3-α-endo

C,0,0.1309428035,0.4502942808,0.2025876771
C,0,-0.0275297905,-0.141571991,1.4827280476
C,0,1.2323632007,-0.4875679234,2.1400121032
O,0,2.2866265213,-0.1390004763,1.5829563224
C,0,0.6651817827,2.2730756361,0.2435655328
C,0,1.7901044538,2.4328351813,1.0623780225
H,0,0.9960371101,0.100013733,-0.3483294755
H,0,-0.7595847862,0.5739167906,-0.4038421599
C,0,-1.3450790721,-0.3016738044,2.1088126917
O,0,-1.509976815,-0.8769791848,3.180802048
C,0,-2.5723575629,0.242382952,1.3771558181
C,0,1.2908516605,-1.2048785279,3.4671693635
H,0,-0.2617385544,2.7262027017,0.5791896881
H,0,0.8381732913,2.3954282327,-0.8209725381
H,0,2.772863804,2.3283674103,0.6171551425
C,0,1.7550299912,2.7071429241,2.4712120875
C,0,0.5478075892,2.7563902523,3.2012056586
C,0,0.5588042921,2.9725489041,4.5754402828

C,0,1.7655565435,3.1614482688,5.2454014514
C,0,2.9727841,3.1248393382,4.5371756812
C,0,2.9685223673,2.8914266182,3.1735719858
H,0,3.9038634265,2.8308338239,2.6284221914
H,0,3.9118576428,3.2659923745,5.0597425866
H,0,1.7701297057,3.3366867849,6.3152347391
H,0,-0.3760556112,2.9965650365,5.1232049265
H,0,-0.4004204696,2.633408502,2.695126
H,0,-2.7817984993,-0.3495770094,0.4806033472
H,0,-3.4267690805,0.1690361002,2.0486183858
H,0,-2.4480097192,1.2826595146,1.0619179708
H,0,2.3380307886,-1.3544315286,3.7311201295
H,0,0.7703300244,-2.1634439058,3.4127310228
H,0,0.7785494998,-0.6323710093,4.2429032692

W0-TS3-β-endo

C,0,-0.943537,-0.521231,-1.615760
C,0,-1.563916,0.270442,-0.626364
C,0,-2.320227,-0.465347,0.344010
O,0,-2.295015,-1.728795,0.275395
C,0,-0.379800,-2.580034,0.011317
C,0, 0.432166, -1.736489,-0.752156
H,0, -1.511151, -1.360817,-1.996226
H,0,-0.310966,-0.036132,-2.349012
C,0,-1.295314, 1.719332, -0.498611
O,0,-1.878034,2.418594,0.320174
C,0,-0.289862,2.362677, -1.444975
C,0,-3.076123,0.162813,1.487271
H,0,-0.873502,-3.422017,-0.451791
H,0,-0.314830,-2.608343,1.089630
H,0,0.715984,-2.131425,-1.724366
C,0,1.459870 ,-0.867134,-0.124782
C,0,1.274888 ,-0.283564,1.136265
C,0,2.253351,0.537662,1.691998
C,0,3.435110,0.794596,0.998927
C,0,3.630140,0.223539,-0.258165
C,0,2.650455,-0.594842,-0.813847
H,0,2.812402,-1.036493,-1.792443
H,0,4.546254,0.414072,-0.806187
H,0,4.195344,1.433537,1.433228
H,0,2.088398,0.981966,2.667151
H,0,0.360593,-0.464214,1.690174
H,0,-0.641767,2.313392,-2.480083
H,0,-0.178132,3.407829,-1.160522
H,0,0.683369,1.867326,-1.397499
H,0,-3.554455,-0.629172,2.063930
H,0,-3.823909,0.865182,1.114343
H,0,-2.412446,0.752413,2.124352

W1-3: **α,β-unsaturated ketone (I)**

C,0,-0.0037813548,-0.0467956009,0.0725441116
C,0,-0.1178605516,0.1037760151,1.3991619115

C,0,1.1648816062,0.1114082852,2.2115571148
O,0,2.1903342817,0.502332243,1.6784639907
H,0,0.9767078988,-0.1222666142,-0.3829490967
H,0,-0.86400274,-0.0908784826,-0.5832749485
C,0,-1.4505767156,0.2881046085,2.0671753588
O,0,-1.5159749714,0.6688682324,3.2202837886
C,0,-2.7137098656,0.0287714622,1.2672656265
C,0,1.1588098108,-0.4173972971,3.6205344743
H,0,-2.7102846244,-0.972295764,0.8285433783
H,0,-3.5694512546,0.1368758175,1.9315144504
H,0,-2.8089172211,0.7497979815,0.4501019249
H,0,2.1827509444,-0.5917472651,3.9489643255
H,0,0.6722556813,0.3112815199,4.2731172442
H,0,0.5695548528,-1.3356203514,3.6914820279
H,0,3.8967644483,0.2288782282,2.5317380054
O,0,4.6229260553,-0.0788209874,3.0992375459
H,0,5.3523416095,0.5257279692,2.938005049

W1-TS3-α-endo

C,0,-1.7410884562,-1.4166460918,-1.0039917129
C,0,-1.7767930843,-0.6194392343,0.1701211509
C,0,-0.771675977,-0.9701481508,1.1662721772
O,0,0.0538132783,-1.8542504227,0.8630066981
C,0,-0.36619028,-0.9477134921,-2.2584425742
C,0,0.8655318193,-0.8508795842,-1.6034299455
H,0,-1.3968967262,-2.4321235341,-0.8504710858
H,0,-2.5738528708,-1.3309677419,-1.6930283567
C,0,-2.7154220124,0.4980063439,0.3261313084
O,0,-2.8204818051,1.1421674486,1.3658269956
C,0,-3.6276533574,0.8537312634,-0.8473926234
C,0,-0.6758431768,-0.2919297897,2.5093209707
H,0,-0.8022742677,-0.0329568265,-2.6457394044
H,0,-0.4841302974,-1.7966939514,-2.9239921343
H,0,1.4853216191,-1.7377480338,-1.5227029196
C,0,1.3692604797,0.3327046754,-0.9675855695
C,0,0.6265849434,1.5330555725,-0.9045572514
C,0,1.1344544653,2.6456328956,-0.2441117228
C,0,2.3944835745,2.5899917545,0.3500982191
C,0,3.1467234484,1.4110598907,0.2945155666
C,0,2.640194566,0.2925276075,-0.3448798116
H,0,3.1947307711,-0.6388962867,-0.3464759758
H,0,4.1214145882,1.3676686562,0.7666050483
H,0,2.7912717528,3.4619097529,0.8580999449
H,0,0.5502258233,3.5571016684,-0.1953987149
H,0,-0.3413973063,1.6011673926,-1.3828119323
H,0,-4.3815891944,0.0749501764,-0.9997885942
H,0,-4.1366366784,1.7867813874,-0.6095793433
H,0,-3.0804440129,0.969337778,-1.787585883
H,0,0.1602153443,-0.7247275062,3.0591687806
H,0,-1.6050682051,-0.4141674535,3.0699352593
H,0,-0.5410320916,0.7851180879,2.3925635003
H,0,1.75421479,-2.5696042368,0.8281141481

O,0,2.6337605926,-2.8568624268,0.5211479169
H,0,2.8251779437,-3.6678985885,0.9993658709

W0-4-α

C,0,-1.2581153838,0.1061409795,-1.6872735126
C,0,-1.1230953295,-1.2514847593,-1.6882742522
O,0,-0.2026561665,0.9625758894,-1.6595851955
C,0,-2.5369387492,0.8890291202,-1.7168676528
C,0,-2.3132794355,-2.1242304591,-1.6318084966
C,0,0.2627607914,-1.8672448328,-1.7382235621
C,0,1.149486719,0.4690662284,-1.5537027168
C,0,1.276901358,-0.8660219302,-2.2883568618
C,0,1.6129865539,0.4199260307,-0.1041500229
O,0,-3.4631692562,-1.702118354,-1.5833449246
C,0,-2.0812559177,-3.6308835575,-1.6213382369
C,0,0.7376455236,0.5606360055,0.9736685355
C,0,1.2134059401,0.5030433337,2.2843858496
C,0,2.5692383052,0.3106742066,2.5342377207
C,0,3.4528438903,0.1814481385,1.4627199763
C,0,2.976985734,0.2375022374,0.1560104791
H,0,-3.1103528283,0.7290624799,-0.800915884
H,0,-3.1816799797,0.5594313682,-2.5313333903
H,0,-2.3003039017,1.9482300076,-1.8223063116
H,0,0.5786568786,-2.2055239382,-0.743306832
H,0,0.2592001171,-2.7543334429,-2.3757074392
H,0,1.7367802586,1.2309025982,-2.0729264385
H,0,2.2973678911,-1.2425980333,-2.1905510609
H,0,1.0899852691,-0.6920747423,-3.3529193358
H,0,-1.3717436902,-3.9285245444,-0.8439621367
H,0,-1.6730551517,-3.9688813861,-2.5795122957
H,0,-3.0375481274,-4.1232812079,-1.4521748977
H,0,-0.3166716721,0.7258033064,0.7944633734
H,0,0.5192415218,0.612978796,3.1101167624
H,0,2.9371890738,0.2688666666,3.5530861037
H,0,4.5128916629,0.0432339681,1.6443104853
H,0,3.677114101,0.1476308273,-0.6690608286

W1-4-α

C,0,-0.9175336866,1.2171180808,-1.7155339635
C,0,-0.9020669152,-0.1445179557,-1.7387987366
O,0,0.2230957811,1.9726592996,-1.6936950433
C,0,-2.1221519947,2.1105230378,-1.7077744835
C,0,-2.1688101977,-0.9089377856,-1.6832278469
C,0,0.4186753689,-0.8873222832,-1.8051935982
C,0,1.5260553907,1.3476580735,-1.5748417101
C,0,1.5269825203,0.0214202004,-2.3328473701
C,0,1.9550363768,1.2310740771,-0.1185954223
O,0,-3.2753109385,-0.383907972,-1.667632522
C,0,-2.0697375161,-2.4282415982,-1.6349887147
C,0,1.0949387627,1.5007870218,0.9466753519
C,0,1.5402693051,1.3803384002,2.2637755613
C,0,2.8510215415,0.9964908531,2.5320974456

C,0,3.7207412215,0.7370840537,1.4728165222
C,0,3.2752993464,0.8544407482,0.1596241254
H,0,-2.7442321906,1.9114724641,-0.8331388272
H,0,-2.7582897151,1.9156890308,-2.5721803086
H,0,-1.8054711798,3.1536760896,-1.7024304229
H,0,0.6965928882,-1.2753095603,-0.8175096552
H,0,0.3304086996,-1.756154973,-2.4617101089
H,0,2.189847644,2.0591629306,-2.0727743425
H,0,2.5052763487,-0.4540267985,-2.2370481188
H,0,1.3663278128,0.2304488546,-3.3954481025
H,0,-1.3917132645,-2.76715272,-0.8465083354
H,0,-1.6888257493,-2.8233693158,-2.5822704302
H,0,-3.0660155877,-2.8313999006,-1.4606943504
H,0,0.0782153217,1.8168874374,0.754443949
H,0,0.858833726,1.5945268862,3.0794958804
H,0,3.1961883641,0.9082283391,3.5559260515
H,0,4.7478988102,0.4500241357,1.6684973541
H,0,3.9677061991,0.6622452973,-0.6542743426
O,0,0.4441357754,4.9032190539,-2.0415042571
H,0,0.2635039026,5.0614083756,-2.9728335778
H,0,0.3721128286,3.9447301214,-1.9283476497

W0-4-β

C,0,-2.3820748575,1.1179103903,-0.0362627895
C,0,-2.3276319837,-0.2435276086,0.0448729959
O,0,-1.2721919799,1.89820131,-0.0395727276
C,0,-3.604996776,1.9761265705,-0.1508857265
C,0,-3.5709012144,-1.0382836159,0.1396973208
C,0,-0.9897343954,-0.9659439087,0.0230646897
C,0,-0.0077920009,1.295925964,0.275824625
C,0,0.1540565384,-0.0469675945,-0.4348205266
C,0,1.5365572943,-0.6326210363,-0.2228942468
O,0,-4.6854332624,-0.5405966799,0.2483592638
C,0,-3.4424817891,-2.5567497046,0.1129401419
C,0,2.4114712242,-0.7859092391,-1.3040251556
C,0,3.690624747,-1.3105834279,-1.1258205575
C,0,4.1201692482,-1.6886049784,0.1442882169
C,0,3.2611398179,-1.5384399978,1.2318342573
C,0,1.9822967967,-1.0166183561,1.0487650405
H,0,-4.1128802882,2.0461837531,0.8148737832
H,0,-4.3291925327,1.5532109582,-0.8444686279
H,0,-3.3020950342,2.9754996334,-0.466500855
H,0,-0.7557075934,-1.3768868928,1.0126606405
H,0,-1.0365849253,-1.8242348805,-0.652508881
H,0,0.7417199721,2.0215451841,-0.0393282107
H,0,0.0552091762,1.1743036493,1.36322845
H,0,0.028809663,0.1465856059,-1.5058220841
H,0,-2.7472803115,-2.91903789,0.8757747076
H,0,-3.066608985,-2.9011117105,-0.8559368129
H,0,-4.4278730994,-2.9868018191,0.28481162
H,0,2.0859794547,-0.4935238464,-2.29738904
H,0,4.3497218859,-1.4239203284,-1.9793849783

H,0,5.1141703403,-2.0972767053,0.2861312626
H,0,3.586081979,-1.8289642283,2.2247697903
H,0,1.3284118911,-0.9125375697,1.9082114139

W2-2
C,0,-0.2599039216,0.2792977989,0.0331626749
C,0,-0.053663481,-0.0315932128,1.4965664362
O,0,0.9710390652,-0.5223671072,1.9200608455
C,0,-1.20055183,0.3407979602,2.4461920833
C,0,-1.3738648872,-0.656702466,3.5962572035
C,0,-1.4344217236,-2.1228723236,3.2538682306
C,0,-0.9545525035,1.7713882589,2.9773862273
O,0,-2.0379591041,2.2491855433,3.7750124502
O,0,-1.5073383428,-0.2645849698,4.7418032666
O,0,-4.0566789972,0.5126429569,0.7611135248
H,0,-0.6057002672,1.3081311537,-0.1025128194
H,0,0.6630679992,0.1131662476,-0.5207104718
H,0,-1.0542924705,-0.3633336189,-0.3606394499
H,0,-2.1399570813,0.3328093886,1.876682871
H,0,-1.8064227029,-2.6858721758,4.1087543408
H,0,-0.4298145544,-2.4705830213,2.997379409
H,0,-2.0750751643,-2.2886126639,2.3828452666
H,0,-0.0274521066,1.7905309905,3.5586947787
H,0,-0.8539224078,2.4723298635,2.1471973614
H,0,-2.0856606173,1.6456341148,4.5335762359
H,0,-4.5193470898,0.5434495989,-0.0806448715
H,0,-4.3135604814,1.3276685883,1.2365479556
H,0,-3.565639602,2.6941542744,2.9126435769
O,0,-4.3266423069,2.8096169754,2.3063896955
H,0,-5.0541159592,3.1388636858,2.8412936565

W2-TS2-A: H_2O elimination transition state (pathway A, 2 water molecules)
C,0,0.0012088872,0.0029904716,-0.0005562236
C,0,0.0005066469,0.0009361209,1.5308031378
O,0,1.0836876294,0.0016677057,2.1034531864
C,0,-1.2986403029,-0.0510460061,2.2386583721
C,0,-1.3976634516,0.2367810005,3.6782744568
C,0,-0.1843427979,0.2306774176,4.5765670216
C,0,-2.5649754687,0.2641471218,1.4617715377
O,0,-3.5494836958,-0.8653590312,1.4314922026
O,0,-2.5043501497,0.4557718657,4.2018063095
O,0,-2.0491919505,-2.5398897084,2.1910797538
O,0,-5.0206704795,-0.0344142916,3.4403935482
H,0,-0.2846076718,0.9885179258,-0.3827225283
H,0,1.0154597175,-0.2126421197,-0.3334966221
H,0,-0.6882394137,-0.7270787531,-0.4341513275
H,0,-1.4456295546,-1.5624301735,2.3023707713
H,0,0.3650715338,-0.7089756951,4.4929171495
H,0,-0.517868538,0.3906627362,5.6016514855
H,0,0.5208600079,1.0071777173,4.273458509
H,0,-3.10315,1.1023996944,1.9011825619
H,0,-2.3707385824,0.479351893,0.4164936194

H,0,-4.2528012517,-0.6717630572,2.111397341
H,0,-1.63738183,-3.1364772341,1.5533274441
H,0,-2.9115265916,-1.9023284045,1.7529857661
H,0,-5.558227267,-0.5115331258,4.0786550888
H,0,-4.177439001,0.216367281,3.888748211

2)

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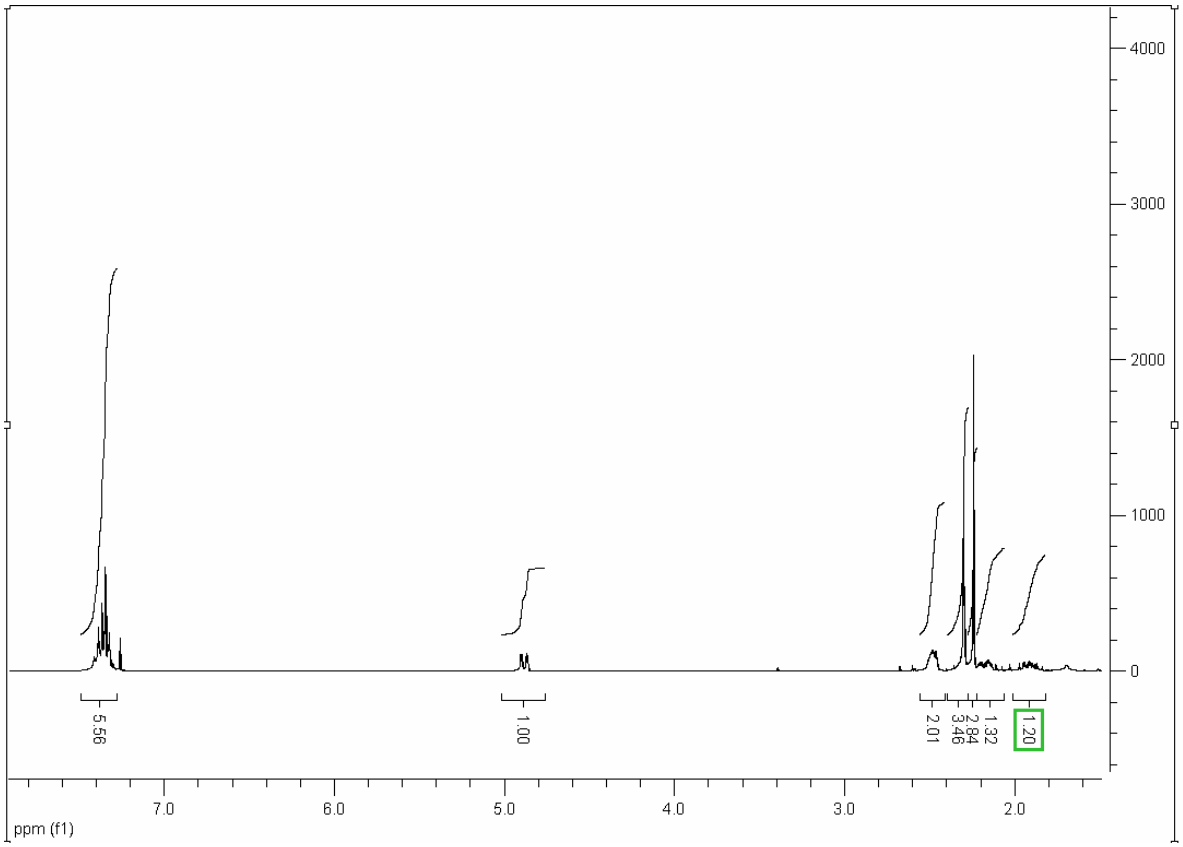
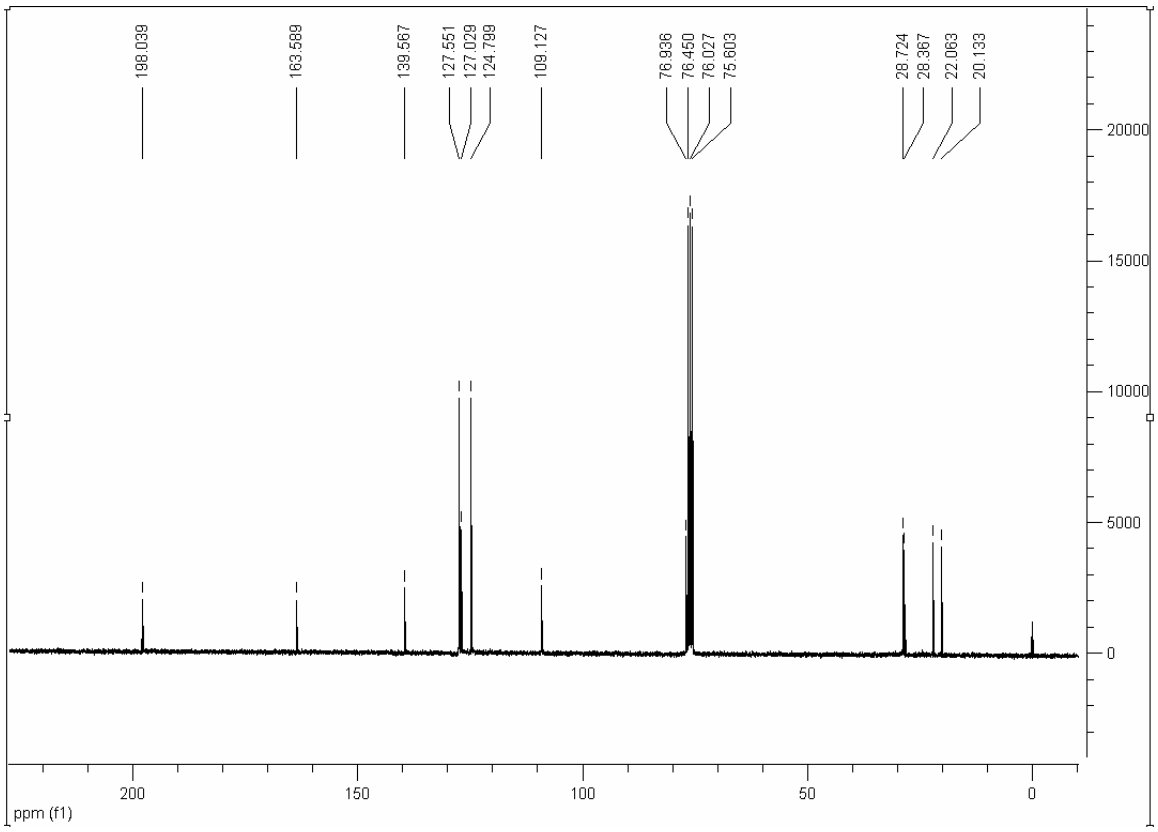
3) Copy of the ^{1}H and ^{13}NMR spectra of the dihydropyran derivative (*3-Acyl-2-methyl-6-phenyl-5,6-dihydropyran*)

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163.589
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127.551
127.029
124.799
109.127
76.936
76.450
76.027
75.603
28.724
28.367
22.063
20.133
20000
15000
10000
5000
0
200
150
100
50
0
ppm (f1)