Supporting Information for

Perturbing the O-H···O hydrogen bond in 1-oxo-3-hydroxy-2-propene

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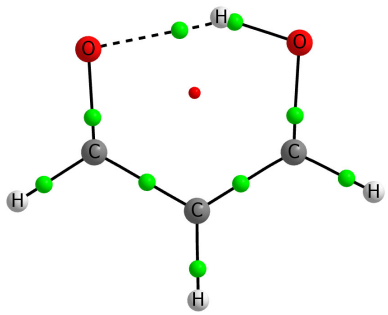
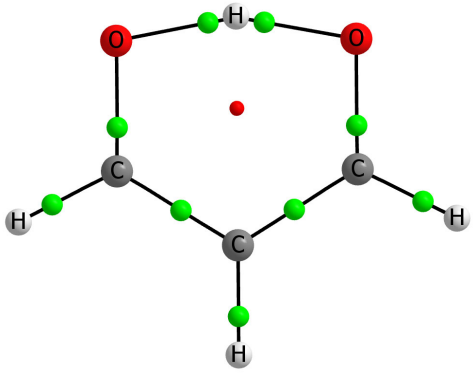
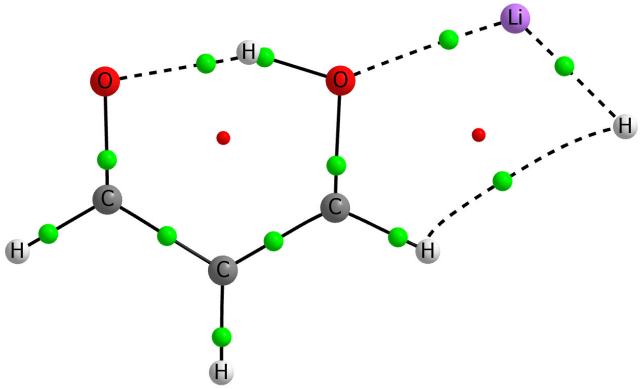
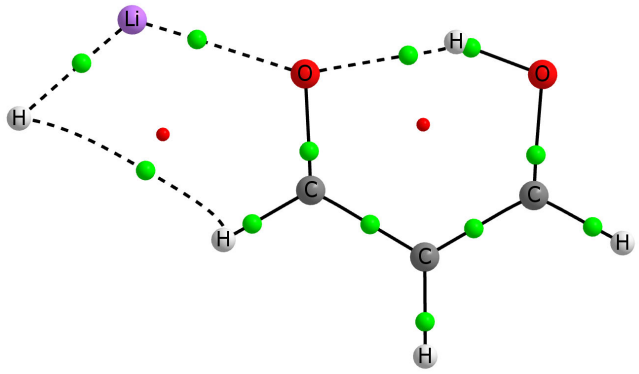
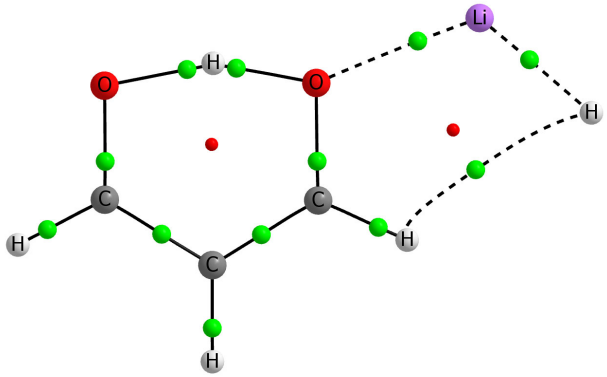
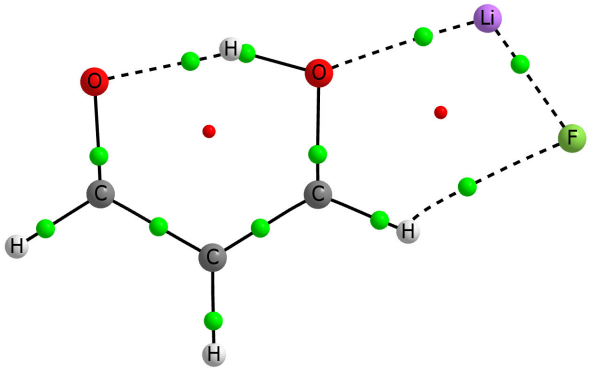
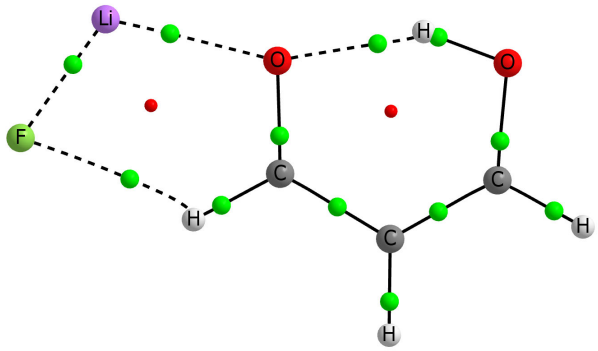
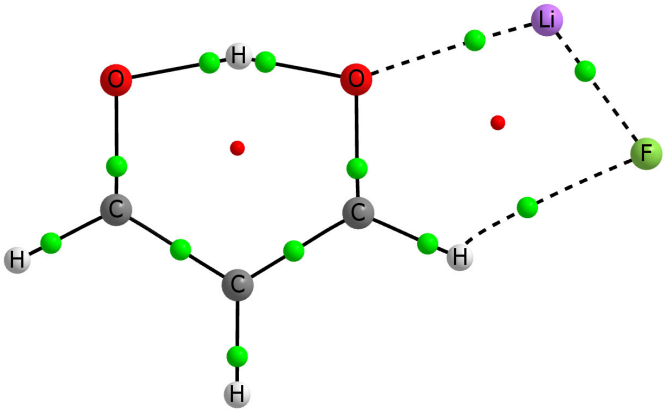
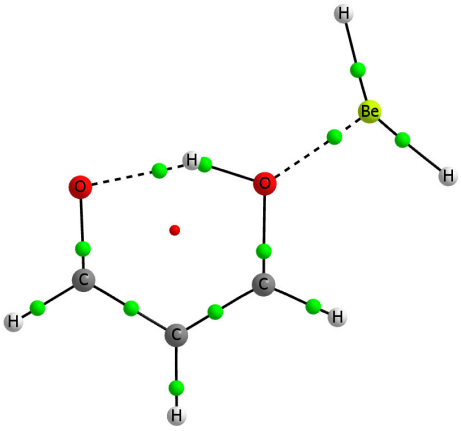
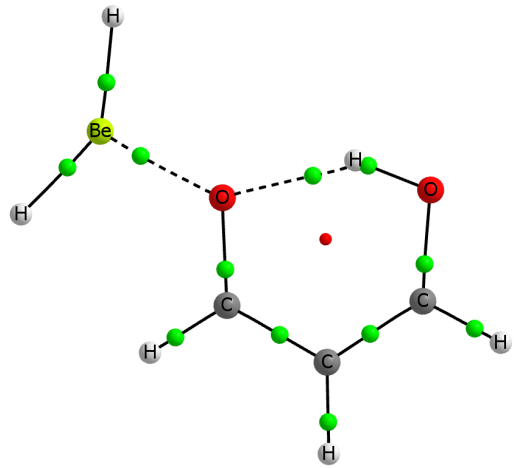
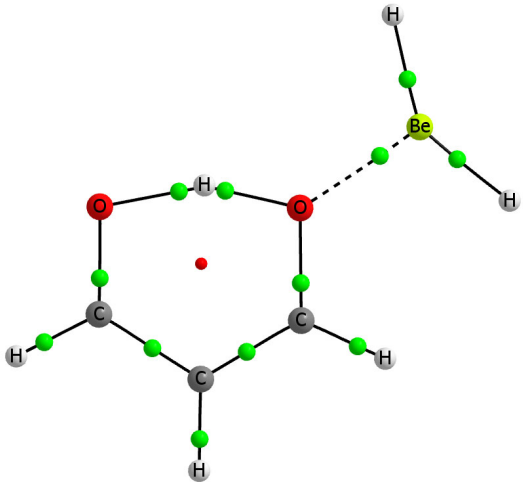
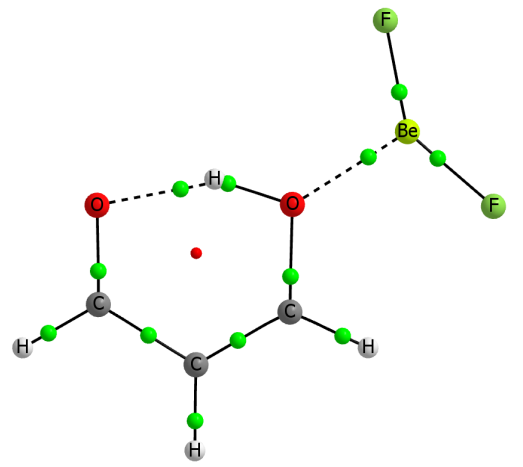
Table S1. Structures (Å), total energies (au), and molecular graphs of 1-oxo-3-hydroxy-2-propene:Acid complexes

	**1** MP2= -266.70194280 NIMAG= 0 C,-0.0985920137,0.,0.0464953349 O,-0.0387775045,0.,1.2894512904 H,0.836805299,0.,-0.5285506099 C,-1.3355459477,0.,-0.6807835651 H,-1.3401544589,0.,-1.7589277237 C,-2.5131732456,0.,0.0049034509 H,-3.4766886818,0.,-0.4906817834 O,-2.5964771066,0.,1.3233776836 H,-1.6483545336,0.,1.6447159223
	**1**(ts) MP2= -266.69753851 NIMAG= 1 C,1.1854240801,0.,-0.3727246333 O,1.1825128883,0.,0.9081519642 H,2.1590853689,0.,-0.8618542603 C,0.,0.,-1.1089202091 H,0.,0.,-2.1855588128 C,-1.1854240801,0.,-0.3727246333 H,-2.1590853689,0.,-0.8618542603 O,-1.1825128883,0.,0.9081519642 H,0.,0.,1.1401074708
	**1**:LiH(OH) MP2= -274.74064245 NIMAG= 0 C,-0.1625693391,0.,-0.0365729891 O,0.0603365221,0.,1.1897078029 H,0.6894810041,0.,-0.7256180356 C,-1.4895771608,0.,-0.5867000297 H,-1.6449084565,0.,-1.6531536029 C,-2.5577080754,0.,0.2508799595 H,-3.5991239563,0.,-0.0510538323 O,-2.4002201358,0.,1.5851991902 H,-1.3934330233,0.,1.7295174921 Li,-4.1218204159,0.,2.5180736493 H,-5.4553335727,0.,1.5711424971

	**1**:LiH(CO) MP2= -274.74482785 NIMAG= 0 C,-2.4687496639,0.,-0.0769525076 O,-2.7758111196,0.,1.2036433539 H,-3.3345132803,0.,-0.7279551233 C,-1.1907052801,0.,-0.5601314554 H,-1.0213938657,0.,-1.6242316934 C,-0.0867566574,0.,0.335157743 H,0.9351987577,0.,-0.055904677 O,-0.2332587632,0.,1.5888012568 H,-1.907140805,0.,1.6886934289 Li,1.5251202794,0.,2.4441707718 H,2.9125538613,0.,1.5706287515
	**1**:LiH(ts) MP2= -274.73873745 NIMAG= 1 C,1.1942333168,0.,-0.3666021708 O,1.1946046057,0.,0.9051655943 H,2.1642978563,0.,-0.8636968214 C,-0.002479598,0.,-1.1066491276 H,-0.0004511476,0.,-2.183177878 C,-1.1830736394,0.,-0.3946669917 H,-2.1733544434,0.,-0.8444681028 O,-1.165329557,0.,0.9162931086 H,-0.0168727554,0.,1.14501648 Li,-2.9864156072,0.,1.6254573952 H,-4.2296604755,0.,0.5580904478
	**1**:LiF(OH) MP2= -373.99985235 NIMAG= 0 C,-0.1868943779,0.,-0.0443748221 O,0.0735448291,0.,1.1752030266 H,0.6450667905,0.,-0.7580829713 C,-1.5271970425,0.,-0.5570094623 H,-1.7096038424,0.,-1.6192282101 C,-2.5761047335,0.,0.3058879433 H,-3.6311973507,0.,0.0463485098 O,-2.3791346535,0.,1.6369974003 H,-1.3711972258,0.,1.755829412 Li,-4.1386920595,0.,2.5125169386 F,-5.2734669435,0.,1.3373343365

	**1**:LiF(CO) MP2= -374.00336718 NIMAG= 0 C,-2.4379447193,0.,-0.086421344 O,-2.7860854215,0.,1.1849898015 H,-3.2823567667,0.,-0.7650682102 C,-1.145141116,0.,-0.5262131884 H,-0.9406618196,0.,-1.5841905405 C,-0.0692081605,0.,0.4052123676 H,0.9724835329,0.,0.065899115 O,-0.2657602799,0.,1.654359579 H,-1.9294231164,0.,1.6940141589 Li,1.5343674033,0.,2.4438535605 F,2.7042739268,0.,1.2994845497
	**1**:LiF(ts) MP2= -373.99770572 NIMAG= 1 C,1.1691722505,0.,-0.3807726581 O,1.2111784187,0.,0.8924608257 H,2.1235751959,0.,-0.9073479227 C,-0.0479021539,0.,-1.0815615111 H,-0.0781994611,0.,-2.1576965625 C,-1.2096366516,0.,-0.3348113787 H,-2.221386231,0.,-0.7399798962 O,-1.1462181279,0.,0.9753300966 H,0.0136257026,0.,1.1678853427 Li,-3.0003431412,0.,1.6192118686 F,-4.0183672456,0.,0.3380437295
	**1**:$BeH_2(OH)$ MP2= -282.56000229 NIMAG= 0 C,-0.2368352925,0.,0.0823796046 O,-0.1306596403,0.,1.3205502055 H,0.6736816788,0.,-0.5262822212 C,-1.5152264324,0.,-0.5888868476 H,-1.5744655131,0.,-1.6651563818 C,-2.6493249233,0.,0.1466683717 H,-3.6598308445,0.,-0.2376810847 O,-2.5979753075,0.,1.494093531 H,-1.6084479128,0.,1.7531549136 Be,-3.9523946612,0.,2.5277783459 H,-5.0481486291,0.,1.7181318166 H,-3.5382421421,0.,3.8154830065

	**1**:$BeH_2(CO)$ MP2= -282.56577741 NIMAG= 0 C,-2.3862360611,0.,0.0253836566 O,-2.6079514417,0.,1.3152815268 H,-3.294595433,0.,-0.5652880518 C,-1.1437939643,0.,-0.5583038271 H,-1.0616581413,0.,-1.6325364343 C,0.0173824554,0.,0.2398408147 H,1.0125491335,0.,-0.2075297547 O,-0.0489762854,0.,1.5060851274 H,-1.7201452793,0.,1.7630386993 Be,1.3725906976,0.,2.448169067 H,2.4362859663,0.,1.5847137772 H,1.0864536634,0.,3.7737768489
	**1**:$BeH_2(ts)$ MP2= -282.55876893 NIMAG= 1 C,-0.2688561338,0.,0.0753740415 O,-0.1990294664,0.,1.3362231034 H,0.6699451274,0.,-0.479102932 C,-1.513032767,0.,-0.6075646092 H,-1.5631449233,0.,-1.6830154845 C,-2.6485886249,0.,0.1544205962 H,-3.662372181,0.,-0.2292612647 O,-2.5507902196,0.,1.4723844292 H,-1.411030119,0.,1.665510547 Be,-3.8955090707,0.,2.5121533429 H,-5.0055009498,0.,1.7158425002 H,-3.493976852,0.,3.80551603
	**1**:$BeF_2(OH)$ MP2= -481.07105491 NIMAG= 0 C,-0.2344786146,0.,0.0725982921 O,-0.1231335874,0.,1.3111971166 H,0.6736428066,0.,-0.5387917611 C,-1.5161507187,0.,-0.5906946681 H,-1.5832708191,0.,-1.6662353524 C,-2.643863915,0.,0.1549271674 H,-3.6579435217,0.,-0.2195012247 O,-2.5729928551,0.,1.501720719 H,-1.5736055458,0.,1.7462827031 Be,-3.9456611441,0.,2.5183135245 F,-5.09574575,0.,1.6637306432 F,-3.5646659553,0.,3.8866861005

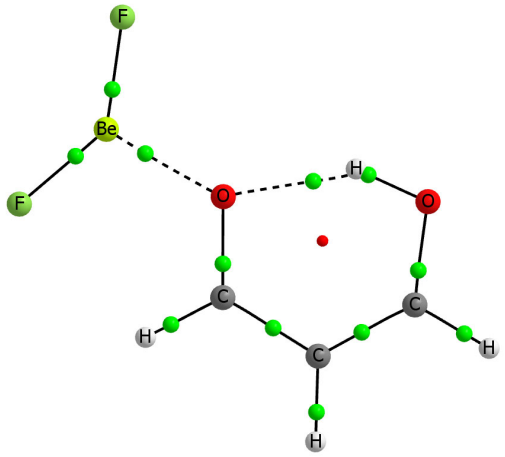
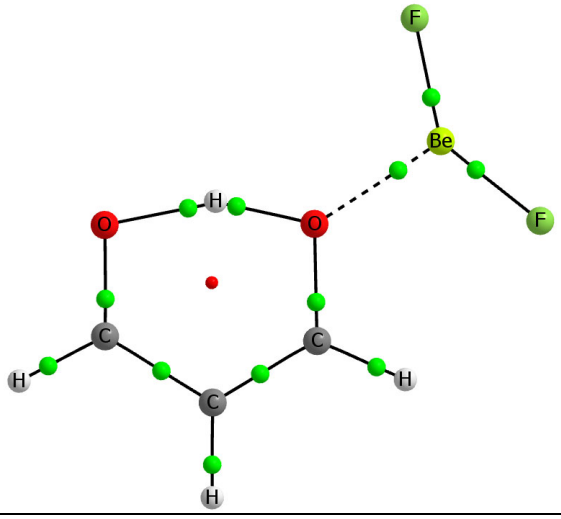
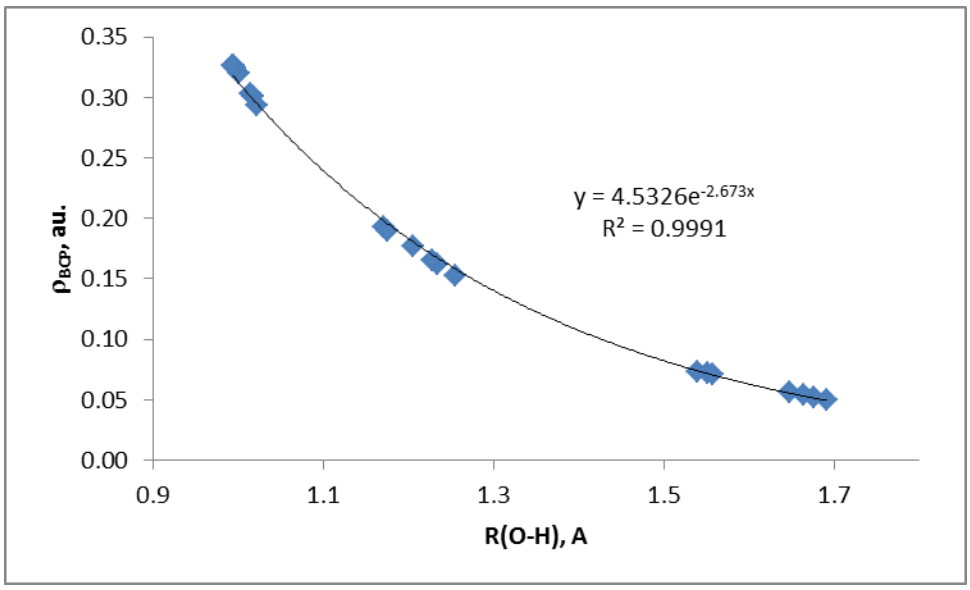
	**1**:$BeF_2(CO)$ MP2= -481.07825942 NIMAG= 0 C,-2.3917206387,0.,0.0197017568 O,-2.6230795281,0.,1.3074790105 H,-3.2962101613,0.,-0.5766491269 C,-1.146282032,0.,-0.5579458078 H,-1.0599004972,0.,-1.6316454851 C,0.0121907262,0.,0.2423663568 H,1.0065345374,0.,-0.2049221056 O,-0.058444529,0.,1.5091477413 H,-1.7427937868,0.,1.7655145367 Be,1.3660563565,0.,2.4340353569 F,2.5046530408,0.,1.5541971788 F,1.0909018225,0.,3.8313520377
	**1**:BeF_2(ts) MP2= -481.07030865 NIMAG= 1 C,-0.2593215076,0.,0.0687207484 O,-0.1800476272,0.,1.3266141514 H,0.6739579374,0.,-0.4956536942 C,-1.5115684478,0.,-0.6058663031 H,-1.5702595409,0.,-1.6808934405 C,-2.6406988778,0.,0.1608476475 H,-3.6569712897,0.,-0.2142067287 O,-2.5324203971,0.,1.4827776396 H,-1.4078406287,0.,1.6708382822 Be,-3.8923955935,0.,2.5040665587 F,-5.0621495977,0.,1.6715643802 F,-3.5170543292,0.,3.8755479187

Fig. S1. Relationship between electron densities at the O-H hydrogen bonds and interatomic distances.



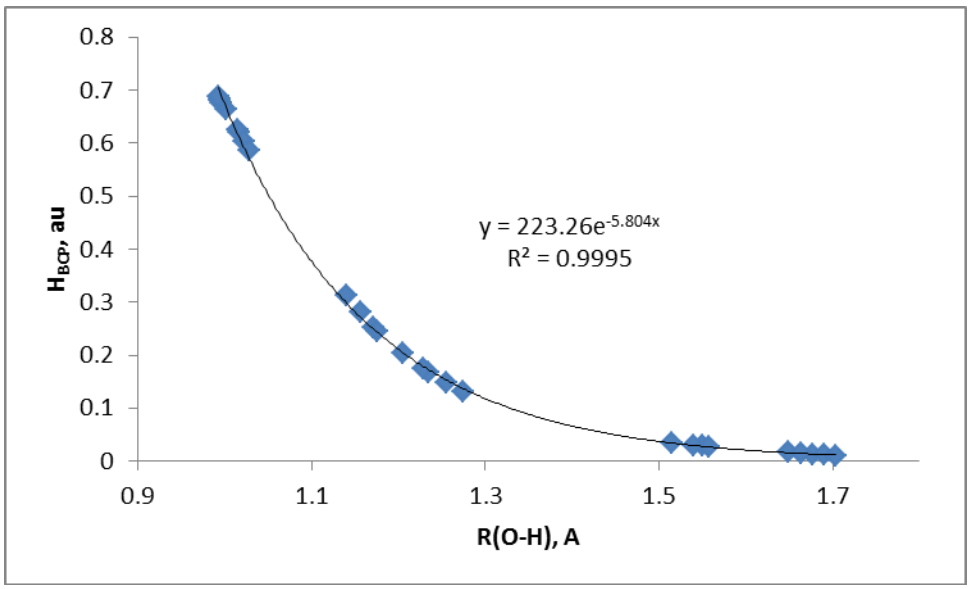


Table S2. Components of spin-spin coupling constants ^{2h}J(O-O), ^{1h}J(H-O), and ^{1}J(O-H) (Hz)

Monomer/Complex	PSO	DSO	FC	SD	^{2h}J(O-O)
1	5.0	0.0	4.3	2.2	11.5
ts	8.2	0.0	13.2	3.3	24.7
1:LiH at C=O	4.1	0.0	4.2	1.9	10.2
O-H	4.5	0.0	7.3	1.9	13.7
ts	6.6	0.0	14.6	2.7	24.0
1:LiF at C=O	4.1	0.0	4.5	1.8	10.5
O-H	4.4	0.0	7.2	1.9	13.5
ts	6.6	0.0	14.8	2.6	24.1
1:BeH_2 at C=O	3.8	0.0	4.4	1.7	10.0
O-H	4.1	0.0	8.5	1.7	14.3
ts	5.8	0.0	15.6	2.3	23.8
1:BeF_2 - at C=O	3.6	0.0	4.2	1.7	9.6
O-H	4.1	0.0	9.5	1.7	15.4
ts	5.6	0.0	15.8	2.3	23.6

Monomer/Complex	PSO	DSO	FC	SD	^{1}J(O-H)
1	-4.8	-0.5	-72.4	-0.1	-77.7
ts	1.3	-0.7	-20.0	-0.2	-19.6
1:LiH at C=O	-5.0	-0.4	-73.6	-0.1	-79.2
O-H	-3.6	-0.5	-77.0	0.0	-81.3
ts	0.8	-0.7	-31.1	-0.1	-31.2
1:LiF at C=O	-4.9	-0.5	-73.1	-0.1	-78.6
O-H	-3.7	-0.5	-77.9	0.0	-82.2
ts	0.9	-0.7	-30.0	-0.1	-30.0
1:BeH_2 at C=O	-4.8	-0.4	-75.9	-0.2	-81.4
O-H	-3.0	-0.6	-86.1	0.0	-89.7
ts	0.5	-0.8	-41.1	-0.1	-41.4
1:BeF_2 at C=O	-4.9	-0.5	-76.5	-0.2	-82.1
O-H	-2.7	-0.7	-85.3	0.0	-88.7
ts	0.3	-0.8	-46.5	0.0	-47.1

Monomer/Complex	PSO	DSO	FC	SD	^{1h}J(H-O)
1	2.2	-0.7	6.6	-0.2	7.9
ts	1.3	-0.7	-20.0	-0.2	-19.7
1 at O	2.0	-0.7	6.8	-0.2	7.9
at OH	2.3	-0.7	6.2	-0.4	7.4
ts	1.6	-0.7	-15.0	-0.3	-14.5
1 at O	2.0	-0.7	6.9	-0.2	8.1
at OH	2.3	-0.7	6.2	-0.4	7.4
ts	1.5	-0.7	-16.0	-0.3	-15.5
1 at O	1.8	-0.7	6.8	-0.2	7.8
at OH	2.2	-0.7	5.3	-0.4	6.4
ts	1.7	-0.7	-13.3	-0.4	-12.8
1 at O	1.8	-0.8	6.8	-0.1	7.7
at OH	2.3	-0.8	4.7	-0.5	5.8
ts	1.9	-0.8	-10.9	-0.4	-10.3