SUPPORTING INFORMATION

Lewis Acid Catalyzed Heavy Atom Tunneling – the Case of 1H-Bicyclo[3.1.0]-hexa-3,5-dien-2-one

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Contents

Experimental details

Synthesis. 4-Diazo-2,5-cyclohexadien-1-one **10** was synthesized as reported earlier[1].

Matrix Isolation. Experiments were performed by standard techniques[2] using Sumitomo Heavy Industries two-staged closed-cycle helium refrigerator systems (3 K). Matrices were generated by co-deposition of precursor **10** along with an excess of host gas onto a cesium iodide window (IR) or an oxygen-free high-conductivity copper rod (EPR). Gas mixtures were prepared with Ar (99.999%), and 0.5–1% of H_2O, ICF_3 or BF_3. Photolysis was performed using a LED light source (λ = 505 nm, 5 W) and a mercury high pressure arc lamp (Ushio, 500 W) equipped with dichroic mirrors (Oriel), a KG1 short-pass filter (Schott) and a cut-off filter (λ > 515 nm).

Low-Temperature Spectroscopy. IR spectra were recorded with a Bruker Vertex V70 FTIR spectrometer with a resolution of 0.5 cm^{-1}. The IR beam of the spectrometer was passed through an IR long-pass interference filter (blocking > 2000 cm^{-1}). Matrix-isolation EPR spectra were recorded on a Bruker Elexsys 500 X-band spectrometer. The kinetic data was fitted to a pseudo-first order by using the equation of Wildman and Siebrand.[3] This model assumes a distribution of reaction rates by introducing a dispersion coefficient β into the first order expression.

Calculations. Geometry optimizations, vibrational frequencies, and IRC profiles were calculated using the M06-2X hybrid functional[4] with D3 empirical dispersion correction.[5] coupled to the def2-TZVP basis set[6]. Tight convergence criteria for gradients and a full (99 590) integration grid were used throughout. DFT energy values reported are corrected for zero-point energy. Open-shell singlet structures were optimized with CASSCF(8,8)/6-31G* and NEVPT2(8,8)/6-31G* following the methodology reported.[1] DFT and multiconfigurational calculations were performed with the programs Gaussian 09[7] and Molpro 2012,[8] respectively. Experimental EPR spectra were analyzed using the Easyspin program package.[9]

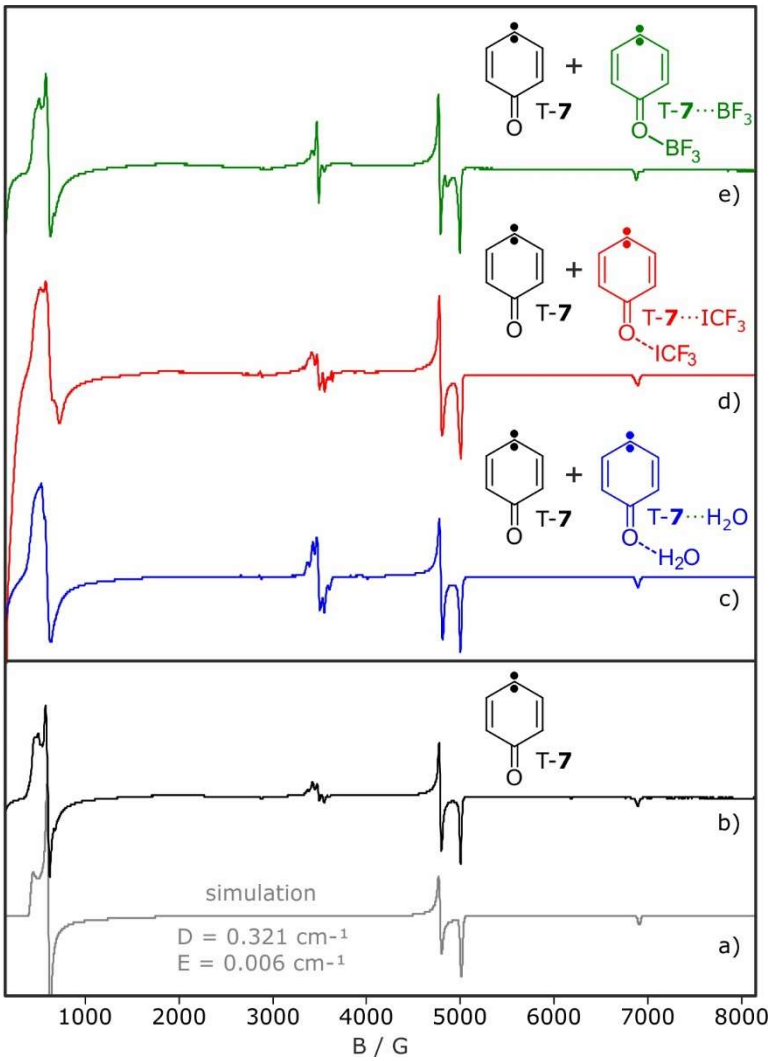


Figure S1. EPR spectra of T-**7**, T-**7**···H_2O, T-**7**···ICF_3 and T-**7**···BF_3 in argon at 4 K. a) Simulated spectrum with D = 0.321 cm^{-1}, E = 0.006 cm^{-1} and μ = 9.733 MHz. b) Spectrum obtained after 505 nm photolysis of diazo precursor **9**. c) Spectrum obtained after annealing a matrix containing T-**7** and 1% of H_2O to 20 K for 10 min. d) Spectrum obtained after annealing a matrix containing T-**7** and 1% of CF_3I to 20 K for 10 min. e) Spectrum obtained after annealing a matrix containing T-**7** and 1% of BF_3 to 20 K for 10 min.

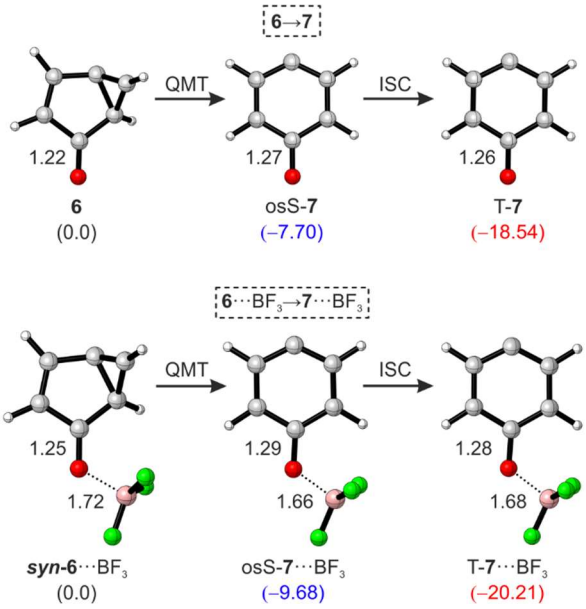


Figure S2. Influence of the Lewis acid BF_3 on the thermochemistry of the reaction. Selected bond distances in Å and relative energies in kcal mol^{-1} at the NEVPT2(8,8)/6-31G* level of theory.

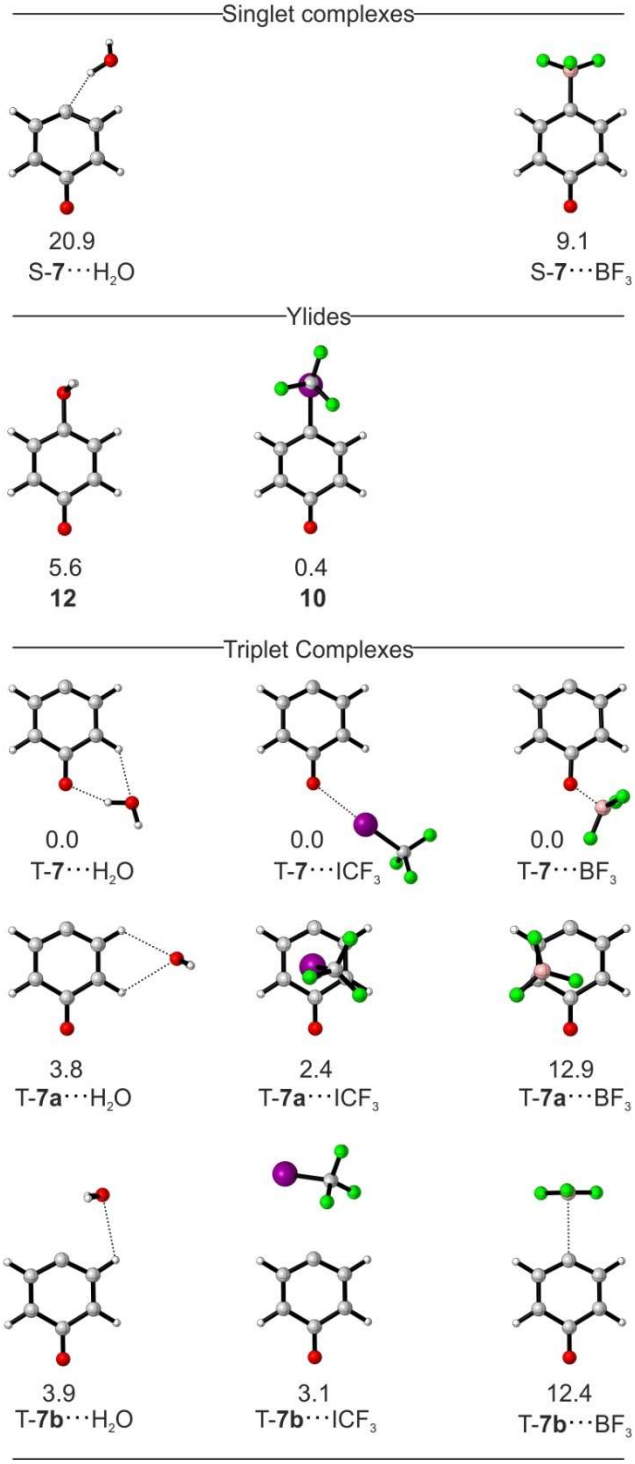


Figure S3. Lowest-energy complexes between singlet and triplet **7** and H_2O, CF_3I and BF_3 selected from a starting ensemble of 100 geometries and the (manually generated) singlet ylidic structures. Energies relative to the carbonyl complexes are given in kcal mol^{-1} at the M06-2X/def2-TZVP level of theory.

Spectroscopic changes upon complex formation (Figure 2 and Table S1). Annealing of a matrix containing T-**7** doped with 1% of H_2O results in a blue shift of the band at 819 cm^{-1} by 5 cm^{-1}, while the carbonyl stretch at 1497 cm^{-1} is split into two bands at 1487 and 1503 cm^{-1} attributed to a Fermi resonance. At the same time, the OH stretching vibration of H_2O undergoes a large red shift from 3638 cm^{-1} to 3476 cm^{-1}, indicating the formation of a strong hydrogen-bonded complex. When carbene T-**7** interacts with CF_3I, similar shifts of the characteristic IR bands are found. The IR bands of BF_3 show pronounced shifts upon interaction with carbene T-**7**. Strong bands of the BF_3 complex are found at 1239, 1188, and 612 cm^{-1}. The band of T-**7** at 819 cm^{-1} undergoes a blue shift of 7 cm^{-1}, while the carbonyl group is obscured by the BF_3 signals.

Table S1. Experimental and calculated vibrational frequencies of 4-oxocyclohexa-2,5-dienylidene T-**7** and the corresponding Lewis acid complexes T-**7**···H_2O, T-**7**···ICF_3 and T-**7**···BF_3 in argon at 3 K. All calculations were carried out at the M06-2X/def2-TZVP level of theory.

Ar, 3 K		T-7				Ar/1%H_2O		T-7···H_2O				Ar/1%CF_3I		T-7···ICF_3				Ar/0.5%BF_3		T-7···BF_3			
$\tilde{\nu}$ / cm^{-1}	rel. Int.	#	$\tilde{\nu}$ / cm^{-1}	rel. Int.	Sym.	$\tilde{\nu}$ / cm^{-1}	rel. Int.	#	$\tilde{\nu}$ / cm^{-1}	rel. Int.	Sym.	$\tilde{\nu}$ / cm^{-1}	rel. Int.	#	$\tilde{\nu}$ / cm^{-1}	rel. Int.	Sym.	$\tilde{\nu}$ / cm^{-1}	rel. Int.	#	$\tilde{\nu}$ / cm^{-1}	rel. Int.	Sym.
447	5	3	451	6	B2	not assigned		8	475	2	A	453	11	12	464	9	A	not assigned		9	467	2	A'
472	5	4	491	9	B1	478	3	9	493	8	A	474	5	13	494	6	A	overlapped		10	488	7	A''
521	2	5	530	1	A1	523	2	10	535	3	A	523	7	14	537	3	A	534	<1	12	555	<1	A'
-	-	-	-	-	-	not observed		11	549	57	A	-	-	-	-	-	-	-	-	-	-	-	-
567	2	6	581	3	B2	568	3	12	585	2	A	568	4	17	584	3	A	564	1	13	571	2	A'
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	612	28	14	624	35	A'
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	641	9	15	665	172	A'
699, 702	14	7	726	12	B1	704	6	13	724	7	A	700	4	18	726	8	A	overlapped		16	722	5	A''
-	-	-	-	-	-	-	-	-	-	-	-	overlapped		19	763	25	A	-	-	-	-	-	-
774, 776	2	9	799	3	A1	781	1	15	802	3	A	783	9	21	804	5	A	not assigned		17	783	1	A''
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	802	24	18	831	58	A'
819	91	10	851	71	B1	824	121	16	852	42	A	821	68	22	854	45	A	826	88	19	855	26	A''
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	847	52	20	872	102	A'
938	10	11	953	4	A1	940	6	17	956	4	A	939	6	23	956	4	A	945	8	21	966	3	A'
1077	7	15	1102	7	B2	1082	9	21	1114	3	A	overlapped		27	1112	5	A	1098	4	25	1125	3	A'
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1188	100	27	1234	158	A''
-	-	-	-	-	-	-	-	-	-	-	-	overlapped		28	1130	512	A	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	overlapped		30	1226	178	A	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	overlapped		31	1228	174	A	-	-	-	-	-	-
1247, 1248	9	17	1273	2	B2	1254	3	23	1289	2	A	overlapped		32	1281	1	A	1271	15	28	1288	63	A'
1260	12	18	1288	11	B2	1267	36	24	1300	6	A	overlapped		33	1298	7	A	1289	13	29	1310	74	A'
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1308	21	30	1338	64	A'
1363	4	19	1416	8	A1	1365	6	25	1418	4	A	1366	8	34	1419	6	A	overlapped		31	1421	2	A'
1376	12	20	1416	4	B2	1378	6	26	1424	5	A	1389	5	35	1426	4	A	overlapped		32	1438	3	A'
1465	3	22	1529	6	A1	1467	6	28	1552	7	A	1488	74	37	1551	22	A	overlapped		34	1571	100	A'
1497	100	23	1576	100	A1	1487	100	29	1575	100	A	1503, 1508	100	38	1579	100	A	overlapped		35	1614	19	A'
-	-	-	-	-	-	1503	118	30	1635	51	A	-	-	-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	3476	303	35	3721	261	A	-	-	-	-	-	-	-	-	-	-	-	-

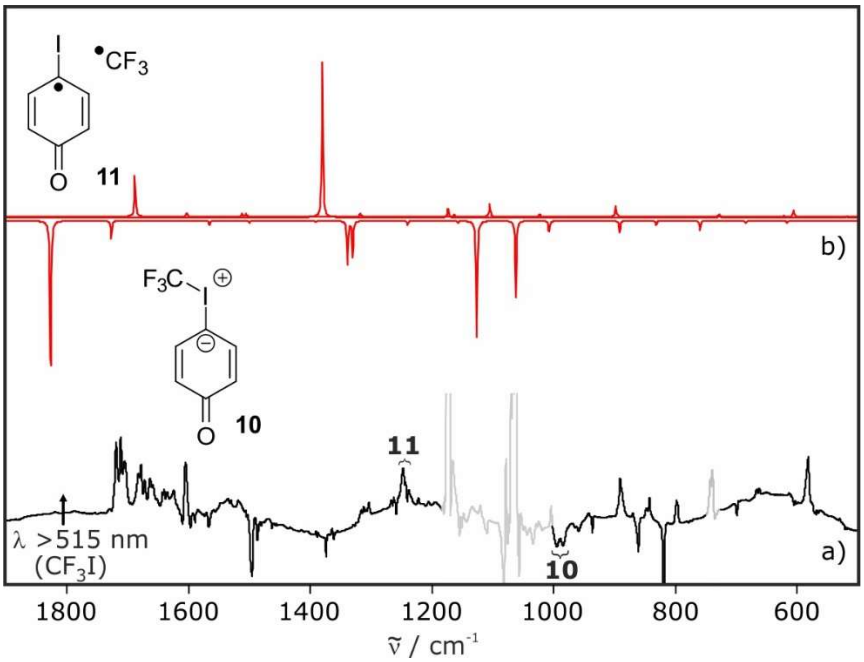


Figure S4. a) IR difference spectrum showing the photolysis of a matrix containing **10** (as well as T-**7** and T-**7**···ICF_3) with >515 nm. The low intensity of the bands suggests that **10** is formed as minor product. CF_3I approaching the carbene centre gives **10**, while interactions at the carbonyl group lead to the triplet complex T-**7**···ICF_3. b) Calculated spectra of **10** (pointing down) and **11** (both radical fragments calculated separately, pointing up) at the M06-2X/def2-TZVP level of theory.

Table S2. Experimental (Ar, 3 K) and calculated (M06-2X/def2-TZVP) vibrational frequencies of **10**. Only calculated vibrations with relative intensities >10 are shown.

Ar, 3K		**10**			
$\tilde{\nu}$ / cm^{-1}	rel. Int.	#	$\tilde{\nu}$ / cm^{-1}	rel. Int.	Sym.
862	15	22	866	16	A'
966, 960	20	24	972	16	A'
986, 995	100	26	1023	100	A'
overlapped		27	1083	179	A'
overlapped		31	1272	49	A'
overlapped		32	1281	65	A"
1568	20	37	1640	25	A'
overlapped		38	1732	233	A'

Table S3. Experimental (Ar, 3 K) and calculated (M06-2X/def2-TZVP) vibrational frequencies of **11**. Only calculated vibrations with relative intensities >5 are shown. Both radical fragments were calculated separately.

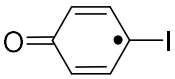
Ar, 3K		**11**							
						•CF_3			
$\tilde{\nu}$ / cm^{-1}	rel. Int.	#	$\tilde{\nu}$ / cm^{-1}	rel. Int.	Sym.	#	$\tilde{\nu}$ / cm^{-1}	rel. Int.	Sym.
870	5	13	871	7	B1	-	-	-	-
overlapped		17	1063	8	A1	-	-	-	-
1122	7	-	-	-	-	4	1126	6	A1
1244, 1249	100	-	-	-	-	5	1318	50	E
		-	-	-	-	6	1318	50	E
overlapped		26	1604	27	A1	-	-	-	-

Table S4. Experimental and calculated vibrational frequencies of **6** and the corresponding Lewis acid complexes **6**···H_2O and **6**···ICF_3 in argon at 3 K. All calculations were carried out at the M06-2X/def2-TZVP level of theory. The symmetry of all vibrations is A. *Overlapped with non-complex **6**.

Ar, 3K		**6**			Ar/1%H_2O		*syn* **6**···H_2O			*anti* **6**···H_2O			Ar/1%CF_3I		*syn* **6**···ICF_3			*anti* **6**···ICF_3		
$\tilde{\nu}$ / cm^{-1}	rel. Int.	#	$\tilde{\nu}$ / cm^{-1}	rel. Int.	$\tilde{\nu}$ / cm^{-1}	rel. Int	#	$\tilde{\nu}$ / cm^{-1}	rel. Int.	#	$\tilde{\nu}$ / cm^{-1}	rel. Int.	$\tilde{\nu}$ / cm^{-1}	rel. Int.	#	$\tilde{\nu}$ / cm^{-1}	rel. Int.	#	$\tilde{\nu}$ / cm^{-1}	rel. Int.
-	-	-	-	-	not observed		10	554	47	10	548	30	-	-	-	-	-	-	-	-
583	37	6	652	16	583	*	12	651	17	12	655	13	583	*	17	655	11	17	647	21
611	3	7	694	3	*		13	696	2	13	699	2	*		18	698	2	18	692	2
669	1	8	721	2	*		14	728	1	14	733	1	*		19	729	2	19	728	1
-	-	-	-	-	-	-	-	-	-	-	-	-	overlapped		20	763	9	20	763	13
744	25	9	790	13	745	*	15	796	11	15	806	11	744	*	21	799	9	21	793	13
799	17	10	847	9	800	*	16	849	7	16	847	6	798	*	22	849	6	22	847	9
844	19	11	874	12	845	*	17	877	12	17	886	10	844	*	23	880	11	23	879	12
889	7	12	948	3	*		18	949	4	18	953	3	895	*	24	956	3	24	949	5
1006	15	15	1049	9	1006	*	21	1038	7	21	1052	7	1005	*	27	1046	6	27	1048	12
1051	2	16	1086	3	1050	*	22	1089	3	22	1102	2	overlapped		28	1090	5	28	1094	3
-	-	-	-	-	-	-	-	-	-	-	-	-	overlapped		29	1129	179	29	1126	252
1122	12	17	1144	8	1123	*	23	1152	3	23	1150	3	1122	*	30	1150	5	30	1148	3
1129	1	18	1154	3	*		24	1165	7	24	1178	5	*		31	1162	2	31	1162	4
-	-	-	-	-	-	-	-	-	-	-	-	-	overlapped		32	1225	65	32	1226	86
-	-	-	-	-	-	-	-	-	-	-	-	-	overlapped		33	1230	63	33	1232	88
1237	1	19	1272	1	1237	*	25	1290	1	25	1276	1	*		34	1290	1	34	1277	1
1306, 1312	15	20	1333	8	1304, 1312	*	26	1341	8	26	1347	7	1305, 1311	*	35	1340	6	35	1341	11
1520	5	21	1613	4	1521	*	27	1608	3	27	1613	7	1521	*	36	1609	3	36	1609	7
-	-	-	-	-	overlapped		28	1642	30	28	1634	34	-	-	-	-	-	-	-	-
1713	100	22	1816	27	1707, 1713	*	29	1805	85	29	1811	78	1705	100	37	1811	100	37	1812	100
1721	76	23	1855	100	1721	*	30	1826	47	30	1832	30	1717	*	38	1832	29	38	1833	91
-	-	-	-	-	3480	100	35	3737	100	35	3714	100	-	-	-	-	-	-	-	-
-	-	-	-	-	overlapped		36	3944	33	36	3952	28	-	-	-	-	-	-	-	-

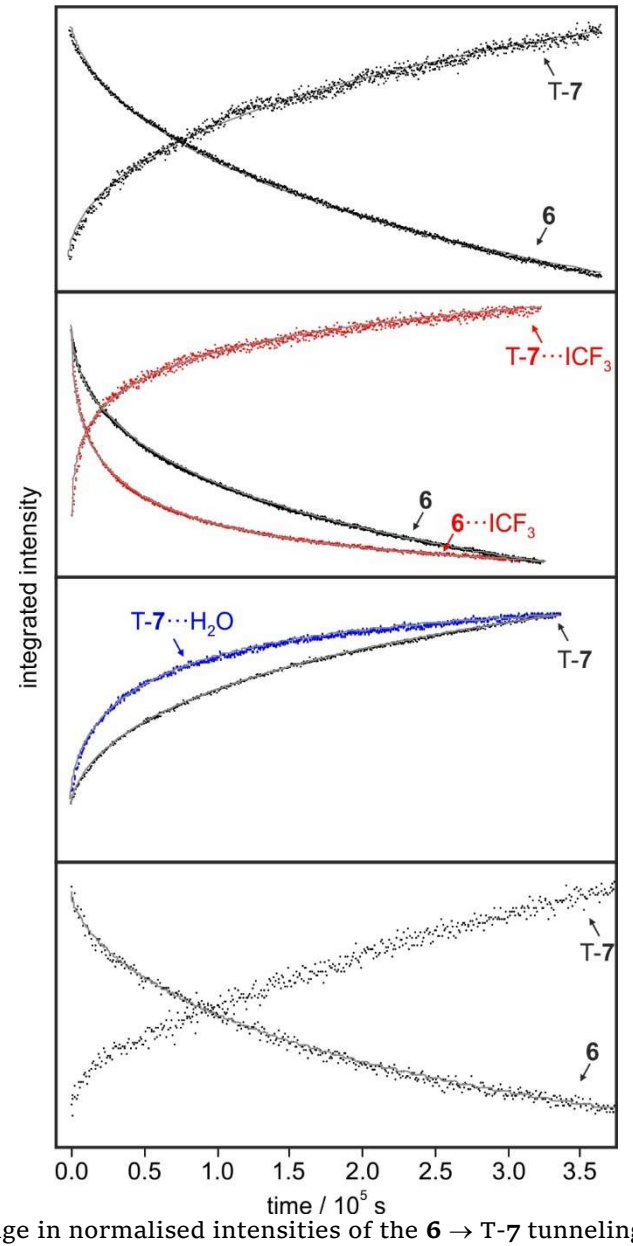
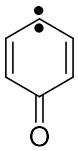


Figure S5. Plots of the change in normalised intensities of the **6** → T-**7** tunneling rearrangement over time. The rearrangement is significantly enhanced by photolysis and irradiation caused by the glowbar of the IR spectrometer, which is sufficient to accelerate the reaction. Therefore, a cut-off filter was introduced to measure the kinetics of the **6** → T-**7** reaction, removing light above 2000 cm^{-1}. a) Reaction in pure argon. Increase of T-**7** (819 cm^{-1}) and decrease of **6** (1721 cm^{-1}). b) Reaction in the presence of H_2O. Increase of T-**7** (819 cm^{-1}) and T-**7**···H_2O (824 cm^{-1}). c) Reaction in the presence of CF_3I. Increase of T-**7**···ICF_3 (1488 cm^{-1}) and decrease of **6** (1721 cm^{-1}) and **6**···ICF_3 (1707 cm^{-1}). d) Reaction in the presence of BF_3. Increase of T-**7** (819 cm^{-1}) and decrease of **6** (1721 cm^{-1}).



T-7

C_{2v}

M06-2X/def2-TZVP

E = -306.125795

ZPVE = 0.0794303

C	0.000000	1.239719	-1.146406
C	0.000000	1.244574	0.222764
C	0.000000	-1.244574	0.222764
C	0.000000	-1.239719	-1.146406
C	0.000000	0.000000	-1.773810
H	0.000000	2.159239	-1.717514
H	0.000000	2.162699	0.796178
H	0.000000	-2.162699	0.796178
H	0.000000	-2.159239	-1.717514
C	0.000000	0.000000	0.976089
O	0.000000	0.000000	2.214089

T-7

C_{2v}

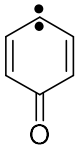
CASSCF(8,8)/6-31G*

E = −304.38945825

NEVPT2(8,8)/6-31G*

E = −305.18339979

C	0.000000	0.000000	0.980648
O	0.000000	0.000000	2.236306
C	0.000000	1.248900	0.228956
C	0.000000	-1.248900	0.228956
C	0.000000	1.245288	-1.153448
C	0.000000	-1.245288	-1.153448
C	0.000000	0.000000	-1.786934
H	0.000000	2.170441	0.803842
H	0.000000	-2.170441	0.803842
H	0.000000	2.169262	-1.724117
H	0.000000	-2.169262	-1.724117



osS-7

C2v

CASSCF(8,8)/6-31G*

E = −304.36701092

NEVPT2(8,8)/6-31G*

E = −305.16612021

C	0.000000	0.000000	0.975193
O	0.000000	0.000000	2.244047
C	0.000000	1.241084	0.233997
C	0.000000	-1.241084	0.233997
C	0.000000	1.240470	-1.160957
C	0.000000	-1.240470	-1.160957
C	0.000000	0.000000	-1.776473
H	0.000000	2.163742	0.807444
H	0.000000	-2.163742	0.807444
H	0.000000	2.164273	-1.731624
H	0.000000	-2.164273	-1.731624

csS-7

C_{2v}

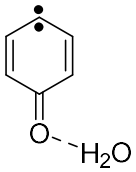
M06-2X/def2-TZVP

E = -306.0703155

ZPVE = 0.075118

C	0.000000	1.270396	-1.200049
C	0.000000	1.228328	0.202632
C	0.000000	-1.228328	0.202632
C	0.000000	-1.270396	-1.200049
C	0.000000	0.000000	-1.592695
H	0.000000	2.175517	-1.784887
H	0.000000	2.179056	0.720717
H	0.000000	-2.179056	0.720717
H	0.000000	-2.175517	-1.784887
C	0.000000	0.000000	0.985464
O	0.000000	0.000000	2.217592

H_2O C_{2v} M06-2X/def2-TZVP E = -76.4260828 ZPVE = 0.0215142	O	0.000000	0.000000	0.116199
	H	0.000000	0.764341	-0.464800
	H	0.000000	-0.764341	-0.464800

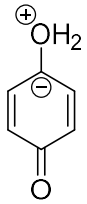
 T-**7**···H_2O C1 M06-2X/def2-TZVP E = -382.564789 ZPVE = 0.104094	C	0.107844	-0.619378	0.000557
	C	0.195656	0.832811	0.001494
	C	-0.942303	1.595177	0.001637
	C	-2.158605	0.925095	0.000789
	C	-2.340690	-0.453130	0.000008
	C	-1.212564	-1.226937	-0.000125
	H	1.186916	1.272072	0.003159
	H	-0.895558	2.676560	0.002368
	H	-3.330654	-0.890989	-0.000689
	H	-1.253352	-2.308665	-0.001001
	O	1.126945	-1.331492	-0.000097
	O	3.304446	0.467476	-0.016759
	H	2.740977	-0.322858	-0.009857
	H	4.204525	0.164179	0.114715

csS-**7**···H_2O C1 M06-2X/def2-TZVP E = -382.5339413 ZPVE = 0.103150	C	-0.107027	-0.627744	-0.006080
	C	1.234232	-1.220803	-0.048878
	C	2.335830	-0.423639	-0.077244
	C	2.073155	0.896900	0.296816
	C	0.938109	1.599702	-0.107768
	C	-0.192306	0.839715	-0.075412
	H	1.300923	-2.300939	-0.014260
	H	3.341946	-0.818553	-0.146762
	H	0.905692	2.680416	-0.168335
	H	-1.182169	1.281774	-0.030373
	O	-1.108925	-1.332202	0.038558
	O	-3.288228	0.449772	-0.015043
	H	-4.159760	0.170110	0.270999
	H	-2.721360	-0.338151	0.012001

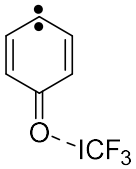
T-**7a**···H_2O Cs M06-2X/def2-TZVP E = -382.5574326 ZPVE = 0.103008	C	0.913584	0.947141	0.000000
	C	2.041621	0.027431	0.000000
	C	1.844324	-1.327459	0.000000
	C	0.528227	-1.775851	0.000000
	C	-0.612115	-0.982853	0.000000
	C	-0.422913	0.374097	0.000000
	H	3.031623	0.465931	0.000000
	H	2.675325	-2.021429	0.000000
	H	-1.611961	-1.397826	0.000000
	H	-1.264241	1.054255	0.000000
	O	1.088666	2.173923	0.000000
	O	-3.633851	0.027964	0.000000
	H	-4.112831	0.354475	-0.765964
	H	-4.112831	0.354475	0.765964

T-**7b**···H_2O C1 M06-2X/def2-TZVP E = -382.5574167 ZPVE = 0.102727	C	-1.726710	-0.245670	0.001055
	C	-0.643760	-1.217590	-0.002110
	C	0.665319	-0.817040	-0.005070
	C	0.901391	0.552985	-0.005780
	C	-0.057830	1.558660	-0.002680
	C	-1.369230	1.164958	0.000855
	H	-0.926080	-2.262850	-0.001630
	H	1.490388	-1.517830	-0.006600
	H	0.219744	2.605204	-0.002960
	H	-2.185270	1.876338	0.003643
	O	-2.911500	-0.604100	0.003860
	O	3.857430	-0.290560	0.013390
	H	3.561813	0.270861	0.736222
	H	3.656834	0.207712	-0.784360

S-**7**···H_2O C1 M06-2X/def2-TZVP E = -382.5303782 ZPVE = 0.103037	C	1.660921	-0.310886	0.093537
	C	1.408232	1.143867	0.033701
	C	0.161571	1.612009	-0.208837
	C	-0.867659	0.659473	-0.045463
	C	-0.704706	-0.673313	-0.480711
	C	0.523221	-1.192155	-0.238979
	H	2.248859	1.794704	0.241187
	H	-0.054585	2.671731	-0.274174
	H	-1.565806	-1.284775	-0.727214
	H	0.712699	-2.258521	-0.223956
	O	2.760124	-0.756122	0.354840
	O	-3.643392	-0.318947	0.248726
	H	-2.924334	0.255622	0.549666
	H	-4.440162	-0.012176	0.686468

 **12** Cs M06-2X/def2-TZVP E = -382.559337 ZPVE = 0.107523	C	1.581501	-0.011072	0.000000
	C	0.814532	1.225986	0.000000
	C	-0.555710	1.246480	0.000000
	C	-1.215550	0.028714	0.000000
	C	-0.588160	-1.207938	0.000000
	C	0.781602	-1.228964	0.000000
	H	1.375125	2.151138	0.000000
	H	-1.111870	2.176470	0.000000
	H	-1.161000	-2.131134	0.000000
	H	1.316692	-2.169074	0.000000
	O	2.816103	-0.030948	0.000000
	O	-2.707920	0.068644	0.000000
	H	-3.096860	-0.324105	-0.798580
	H	-3.096860	-0.324105	0.798580

ICF_3 C_{3v} M06-2X/def2-TZVP E = -635.2963403 ZPVE = 0.014368	C	0.000000	0.000000	-1.173840
	I	0.000000	0.000000	0.967124
	F	0.000000	1.239297	-1.637580
	F	1.073263	-0.619650	-1.637580
	F	-1.073263	-0.619650	-1.637580



T-**7**···ICF_3

C1
M06-2X/def2-TZVP
E = -941.4311387
ZPVE = 0.094655

C	-2.748970	-0.481022	-0.095210
C	-2.685014	0.965202	-0.225370
C	-3.813634	1.729470	-0.102540
C	-5.005199	1.060921	0.150108
C	-5.166739	-0.312142	0.290837
C	-4.044312	-1.085386	0.167719
H	-1.713685	1.402893	-0.420540
H	-3.781678	2.807193	-0.198220
H	-6.137764	-0.748118	0.488110
H	-4.071121	-2.163386	0.262816
O	-1.731957	-1.185433	-0.203970
I	1.059909	-0.334861	-0.079380
C	3.088443	0.323882	0.105119
F	3.908338	-0.703306	0.302030
F	3.229317	1.158345	1.130160
F	3.488708	0.959069	-0.991890

csS-**7**···ICF_3

C1
M06-2X/def2-TZVP
E = -941.4001055
ZPVE = 0.093497

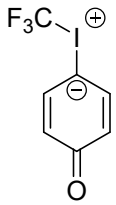
C	-2.733924	-0.477525	-0.063733
C	-2.671926	0.989886	-0.109157
C	-3.803186	1.736317	0.016148
C	-4.968834	0.993782	-0.179909
C	-5.155181	-0.295212	0.324269
C	-4.047549	-1.077157	0.205597
H	-1.706074	1.441908	-0.301019
H	-3.791087	2.819108	0.009354
H	-6.135016	-0.700373	0.545208
H	-4.096675	-2.158037	0.249103
O	-1.735437	-1.171863	-0.199332
I	1.053466	-0.334817	-0.079342
C	3.084499	0.319329	0.093268
F	3.904083	-0.709979	0.281138
F	3.234206	1.150013	1.120450
F	3.478964	0.957865	-1.004003

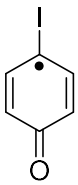
T-**7a**···ICF_3

C1
M06-2X/def2-TZVP
E = -941.4266825
ZPVE = 0.094026

C	-2.909196	0.991806	0.007044
C	-2.749231	0.108995	-1.141037
C	-2.632331	-1.246503	-0.975922
C	-2.667687	-1.731551	0.327183
C	-2.810292	-0.973958	1.482635
C	-2.929946	0.381625	1.328440
H	-2.732706	0.574777	-2.118680
H	-2.516697	-1.914378	-1.820490
H	-2.822328	-1.437050	2.461060
H	-3.041938	1.050571	2.172213
O	-3.020825	2.214915	-0.137243
I	0.650845	-0.136147	-0.329596
C	2.695643	0.135497	0.251113
F	2.822897	1.200324	1.027188
F	3.465463	0.301549	-0.814008
F	3.134276	-0.921086	0.919674

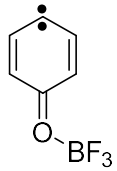
T-**7b**···ICF_3 C1 M06-2X/def2-TZVP E = -941.4279641 ZPVE = 0.094474	C	4.261176	-0.110438	0.032442
	C	3.421453	-1.231078	0.428498
	C	2.057735	-1.153779	0.342889
	C	1.519573	0.034347	-0.137287
	C	2.233511	1.157877	-0.537885
	C	3.597961	1.089769	-0.455524
	H	3.927790	-2.117058	0.790299
	H	1.420215	-1.978372	0.635412
	H	1.727699	2.045041	-0.896861
	H	4.234483	1.916339	-0.744672
	O	5.494784	-0.175731	0.108871
	I	-1.973654	-0.910239	-0.153082
	C	-1.666483	1.176846	0.221492
	F	-2.825073	1.789566	0.392994
	F	-1.042949	1.743861	-0.802197
	F	-0.933573	1.355607	1.308142

 **10** Cs M06-2X/def2-TZVP E = -941.432042 ZPVE = 0.096238	C	0.681348	3.595726	0.000000
	C	0.680893	2.814776	1.238637
	C	0.680893	1.462071	1.238669
	C	0.704862	0.763450	0.000000
	C	0.680893	1.462071	-1.238669
	C	0.680893	2.814776	-1.238637
	H	0.682636	3.372162	2.166072
	H	0.675022	0.908354	2.169691
	H	0.675022	0.908354	-2.169691
	H	0.682636	3.372162	-2.166072
	O	0.683286	4.819749	0.000000
	I	0.602519	-1.230099	0.000000
	C	-1.615601	-1.719695	0.000000
	F	-1.758734	-3.035136	0.000000
	F	-2.180645	-1.209256	-1.074567
	F	-2.180645	-1.209256	1.074567

 **11** (without CF_3) C2v M06-2X/def2-TZVP E = -603.8389325 ZPVE = 0.0817291	C	0.000000	0.000000	-3.031918
	C	0.000000	-1.234177	-2.272413
	C	0.000000	-1.226496	-0.906745
	C	0.000000	0.000000	-0.219638
	C	0.000000	1.226496	-0.906745
	C	0.000000	1.234177	-2.272413
	H	0.000000	-2.158539	-2.835078
	H	0.000000	-2.152525	-0.348245
	H	0.000000	2.152525	-0.348245
	H	0.000000	2.158539	-2.835078
	O	0.000000	0.000000	-4.271492
	I	0.000000	0.000000	1.852788

$^{\bullet}CF_3$ C3v M06-2X/def2-TZVP E = -337.5999 ZPVE = 0.0125585	C	0.000000	0.000000	0.324571
	F	0.000000	1.250120	-0.072127
	F	-1.082635	-0.625060	-0.072127
	F	1.082635	-0.625060	-0.072127

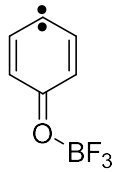
BF_3 D3h M06-2X/def2-TZVP E = -324.6075519 ZPVE = 0.012653	B	0.000000	0.000000	0.000000
	F	0.000000	1.309722	0.000000
	F	1.134252	-0.654861	0.000000
	F	-1.134252	-0.654861	0.000000



T-**7**···BF_3

C1
M06-2X/def2-TZVP
E = -630.7616739
ZPVE = 0.094921

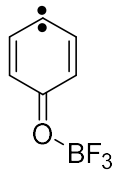
C	0.420172	0.552794	0.000000
C	-1.001036	0.824848	0.000000
C	-1.434021	2.122195	0.000000
C	-0.467505	3.121207	0.000000
C	0.912498	2.940791	0.000000
C	1.359299	1.651037	0.000000
H	-1.687376	-0.009246	0.000000
H	-2.489402	2.360105	0.000000
H	1.594459	3.780490	0.000000
H	2.410930	1.396530	0.000000
O	0.899633	-0.613159	0.000000
B	-0.013872	-1.961599	0.000000
F	-0.763435	-1.859701	1.141179
F	-0.763435	-1.859701	-1.141179
F	0.894343	-2.957470	0.000000



T-**7**···BF_3

Cs
CASSCF(8,8)/6-31G*
E = –627.58605374
NEVPT2(8,8)/6-31G*
E = –628.97977234

C	-0.547775	-0.423126	0.000001
C	-0.846190	0.992762	0.000001
C	-2.166388	1.400988	0.000001
C	-3.150744	0.410877	0.000000
C	-2.937707	-0.969725	-0.000001
C	-1.623349	-1.389610	0.000000
H	-0.030914	1.703781	0.000002
H	-2.426251	2.454865	0.000002
H	-3.762546	-1.675039	-0.000002
H	-1.345306	-2.439170	0.000000
O	0.644044	-0.895489	0.000001
B	2.005565	0.085413	-0.000001
F	1.863908	0.826205	-1.152536
F	1.863907	0.826212	1.152529
F	3.013294	-0.826251	0.000002



osS-**7**···BF_3

Cs
CASSCF(8,8)/6-31G*
E = –627.56066122
NEVPT2(8,8)/6-31G*
E = –628.96300266

C	-0.562263	-0.422216	0.000000
C	-3.812102	-1.592920	0.000000
C	-3.134360	0.468058	0.000000
C	-2.969393	-0.909248	0.000000
C	-2.385314	2.498329	0.000000
C	-2.146998	1.439509	0.000000
H	-1.657179	-1.360565	0.000000
H	-1.404753	-2.417023	0.000000
H	-0.828624	0.996794	0.000000
H	0.002370	1.690170	0.000000
O	0.623855	-0.925488	0.000000
B	1.864146	0.772012	-1.152395
F	1.864146	0.772012	1.152395
F	1.989513	0.023595	0.000000
F	2.988804	-0.898862	0.000000

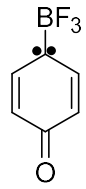
csS-**7**···BF_3

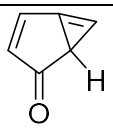
C1
M06-2X/def2-TZVP
E = -630.7359767
ZPVE = 0.092500

C	-0.546007	-0.466797	-0.025930
C	-1.638292	-1.382604	-0.014275
C	-2.923516	-0.881383	0.061526
C	-2.929625	0.456483	-0.167105
C	-2.112137	1.483539	0.110650
C	-0.826878	0.946575	-0.002872
H	-1.443970	-2.446307	-0.032518
H	-3.806120	-1.486630	0.215883
H	-2.310121	2.544326	0.090570
H	-0.016239	1.633122	-0.218058
O	0.635882	-0.933039	-0.057623
B	1.896169	-0.004902	0.007876
F	2.957550	-0.844029	0.062545
F	1.851065	0.771962	-1.135447
F	1.732192	0.773115	1.138875

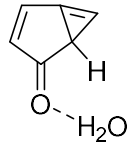
T-**7a**···BF_3 C1 M06-2X/def2-TZVP E = -630.7390733 ZPVE = 0.092838	C	1.613674	0.779782	0.094007
	C	2.000261	-0.301778	-0.798861
	C	1.559812	-1.582095	-0.590751
	C	0.733675	-1.796256	0.504041
	C	0.308228	-0.834151	1.415060
	C	0.740767	0.450876	1.213721
	H	2.642580	-0.041158	-1.630317
	H	1.838378	-2.392525	-1.251979
	H	-0.336248	-1.094349	2.245778
	H	0.458560	1.264194	1.870502
	O	2.011573	1.936518	-0.087193
	B	-1.937301	0.200903	-0.352916
	F	-1.188014	0.180853	-1.428070
	F	-2.158424	1.329099	0.276662
	F	-2.514435	-0.902296	0.063056

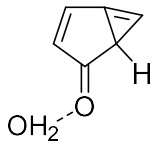
T-**7b**···BF_3 C1 M06-2X/def2-TZVP E = -630.7400437 ZPVE = 0.092974	C	2.798536	-0.002014	0.014812
	C	2.049543	1.246164	-0.003721
	C	0.680406	1.246555	-0.035840
	C	0.061018	0.004920	-0.049743
	C	0.674267	-1.239864	-0.036199
	C	2.043265	-1.246442	-0.003971
	H	2.625674	2.162483	0.008127
	H	0.105749	2.163642	-0.051946
	H	0.095287	-2.154317	-0.052790
	H	2.614806	-2.165629	0.007673
	O	4.035538	-0.005179	0.045225
	B	-2.719020	-0.000568	0.013104
	F	-2.750849	-0.110349	1.319132
	F	-2.732755	-1.078759	-0.734912
	F	-2.735611	1.187128	-0.545377

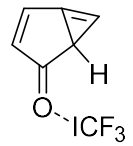
 S-**7**···BF_3 Cs M06-2X/def2-TZVP E = -630.7472493 ZPVE = 0.094980	C	0.043450	-2.505250	0.000000
	C	-0.017480	-1.739250	1.275430
	C	-0.088260	-0.400640	1.252530
	C	0.009350	0.304400	0.000000
	C	-0.088260	-0.400640	-1.252530
	C	-0.017480	-1.739250	-1.275430
	H	0.009840	-2.325900	2.185800
	H	-0.122330	0.195740	2.155780
	H	-0.122330	0.195740	-2.155780
	H	0.009840	-2.325900	-2.185800
	O	0.118760	-3.708410	0.000000
	B	0.062670	1.961800	0.000000
	F	0.658130	2.418840	1.151080
	F	0.658130	2.418840	-1.151080
	F	-1.325850	2.162580	0.000000

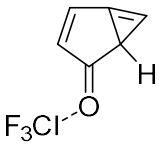
 **6** C1 M06-2X/def2-TZVP E = -306.1028493 ZPVE = 0.078912	C	0.280949	-0.969476	0.384047
	C	-0.972546	-0.196671	-0.019602
	C	-0.554114	1.259663	-0.094509
	C	0.761199	1.422085	0.092973
	C	1.337236	0.083538	0.238573
	H	-1.249043	2.030930	-0.394811
	H	1.322606	2.340215	-0.000812
	O	-2.099092	-0.594522	-0.120835
	C	1.557958	-1.022456	-0.395744
	H	0.168842	-1.533473	1.305644
	H	2.086239	-1.541598	-1.177773

6 C1 CASSCF(8,8)/6-31G* E = –304.34945689 NEVPT2(8,8)/6-31G* E = –305.15385661	C	0.225663	-0.991571	-0.374081
	C	-0.986626	-0.141722	0.005979
	C	-0.500686	1.285925	0.091277
	C	0.838325	1.387241	-0.088330
	C	1.362392	0.021713	-0.234887
	C	1.464343	-1.089395	0.465410
	H	0.113892	-1.581733	-1.282772
	O	-2.155187	-0.488985	0.089631
	H	-1.167383	2.097054	0.362510
	H	1.440958	2.285367	-0.018049
	H	1.923958	-1.602903	1.298208

 *syn* **6**···H_2O C1 M06-2X/def2-TZVP E = -382.5397523 ZPVE = 0.103571	C	-0.000420	0.748182	-0.177050
	C	-0.070893	-0.732616	0.156710
	C	1.322611	-1.279876	-0.030105
	C	2.205799	-0.318222	-0.330540
	C	1.480364v	0.952806	-0.299162
	H	1.558934v	-2.312310	0.184196
	H	3.277038	-0.427619	-0.418775
	O	-1.049301	-1.406283	0.368674
	C	0.869531	1.754206	0.512165
	H	-0.703018	1.058039	-0.944975
	H	0.916914v	2.453056	1.330143
	O	-3.118266	0.484801	-0.220112
	H	-2.581263	-0.250034	0.111727
	H	-3.970016	0.103842	-0.442916

 *anti* **6**···H_2O C1 M06-2X/def2-TZVP E = -382.5414452 ZPVE = 0.103916	C	-1.338914	-0.865919	-0.309029
	C	0.138584	-0.576754	-0.094764
	C	0.286873	0.927525	-0.090115
	C	-0.899297	1.544583	-0.171342
	C	-1.929310	0.503875	-0.156520
	H	1.246739	1.397317	0.080115
	H	-1.081685	2.606389	-0.095149
	O	1.051200	-1.365504	-0.087931
	C	-2.459330	-0.418135	0.578893
	H	-1.537569	-1.474698	-1.186660
	H	-3.056142	-0.685907	1.434468
	O	3.293048	0.350275	0.183739
	H	2.718285	-0.421720	0.065650
	H	4.164754	0.009413	0.392381

 *syn* **6**···ICF_3 C1 M06-2X/def2-TZVP E = -941.4080075 ZPVE = 0.094269	C	-2.544664	0.776562	0.486753
	C	-2.666754	-0.671490	0.034077
	C	-4.137146	-0.918060	-0.203530
	C	-4.864599	0.198491	-0.065130
	C	-3.928087	1.287354	0.214796
	H	-4.499367	-1.868150	-0.569190
	H	-5.917167	0.316682	-0.277110
	O	-1.813473	-1.521490	0.005342
	C	-2.964208	1.979360	-0.299610
	H	-2.080450	0.887617	1.463046
	H	-2.629488	2.714299	-1.012170
	C	2.888011	0.398849	-0.028130
	I	0.926872	-0.455860	0.009634
	F	3.055152	1.164349	-1.102410
	F	3.100886	1.154749	1.044716
	F	3.823376	-0.544000	-0.052680



anti **6**···ICF_3

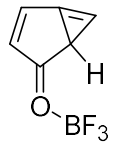
C1

M06-2X/def2-TZVP

E = -941.4076227

ZPVE = 0.093981

C	-4.173377	-0.733996	-0.199940
C	-2.685604	-0.429338	-0.110010
C	-2.554895	1.074174	-0.193110
C	-3.747626	1.683192	-0.218820
C	-4.763454	0.638913v	-0.079520
H	-1.596445	1.567660	-0.113050
H	-3.932540	2.746764	-0.183750
O	-1.767304	-1.208705	-0.130320
C	-5.225882	-0.242846	0.745959
H	-4.431614	-1.393344	-1.023460
H	-5.752675	-0.464816	1.658656
C	3.055617	0.354207	0.087269
I	1.054614	-0.396075	-0.050980
F	3.901960	-0.401637	-0.602140
F	3.133698	1.592630	-0.390790
F	3.467507	0.380066	1.350137



syn **6**···BF_3

C1

M06-2X/def2-TZVP

E = -630.7355996

ZPVE = 0.093458

C	-1.010011	0.777508	0.342608
C	-0.534877	-0.584000	-0.042540
C	-1.707388	-1.482140	-0.132000
C	-2.852130	-0.809330	0.079772
C	-2.501470	0.592161	0.281826
H	-1.620975	-2.508990	-0.454870
H	-3.854036	-1.189670	-0.055080
O	0.624298	-0.997760	-0.089520
C	-2.036700	1.604322	-0.372820
H	-0.484991	1.186335	1.200566
H	-2.145858	2.401043	-1.089170
B	1.893639	0.056017	-0.012160
F	1.846086	0.508298	1.275732
F	1.588327	1.011993	-0.936710
F	2.954335	-0.717830	-0.312970

syn **6**···BF_3

C1

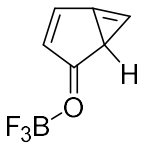
CASSCF(8,8)/6-31G*

E = –627.54772255

NEVPT2(8,8)/6-31G*

E = –628.94757104

C	1.009724	-0.772495	0.339917
C	0.527229	0.596794	-0.039729
C	1.691270	1.506325	-0.133975
C	2.855928	0.835621	0.069295
C	2.529080	-0.580174	0.266633
H	1.592796	2.544097	-0.430322
H	3.857124	1.238083	-0.032220
O	-0.649328	1.015333	-0.094159
C	2.014768	-1.555671	-0.452674
H	0.516475	-1.207701	1.204881
H	2.117030	-2.300689	-1.228410
B	-1.944745	-0.106716	0.021764
F	-1.832504	-0.540223	1.320132
F	-1.620518	-1.043874	-0.923873
F	-3.012824	0.683136	-0.255657



anti **6**···BF_3

C1

M06-2X/def2-TZVP

E = -630.7360261

ZPVE = 0.093789

C	-1.824016	-1.017612	-0.322486
C	-0.531995	-0.339028	-0.003291
C	-0.769949	1.124563	0.070584
C	-2.071489	1.406598	-0.109483
C	-2.783260	0.140058	-0.244852
H	0.005095	1.822322	0.348152
H	-2.538235	2.373279	0.009225
O	0.563149	-0.900507	-0.009851
C	-3.123526	-0.909396	0.423461
H	-1.753414	-1.658440	-1.196559
H	-3.735299	-1.405298	1.157734
B	1.970442	-0.039139	0.020592
F	1.874984	0.772177	-1.073370
F	2.919333	-0.990629	-0.043460
F	1.904557	0.644762	1.202795

TS(**6**→ T-**7**) C1 M06-2X/def2-TZVP E = -306.0850946 ZPVE = 0.077435	C	-0.162150	-1.091020	0.109139
	C	0.981657	-0.144740	-0.042780
	C	0.546831	1.261426	-0.067780
	C	-0.782240	1.392182	0.058763
	C	-1.523270	0.185213	0.241080
	C	-1.529390	-1.022230	-0.279250
	H	0.085146	-1.888290	0.807700
	O	2.132340	-0.522400	-0.020760
	H	1.246172	2.066437	-0.247600
	H	-1.324290	2.321726	-0.060670
	H	-2.254370	-1.805660	-0.448410

TS(*syn* **6**···H_2O → T-**7**···H_2O) C1 M06-2X/def2-TZVP E = -382.5253532 ZPVE = 0.102207	C	-0.059807	0.747062	0.094776
	C	-0.072062	-0.732156	0.176265
	C	1.253047	-1.320117	-0.043430
	C	2.191728	-0.385281	-0.273040
	C	1.717761	0.954503	-0.312890
	H	1.429156	-2.382080	0.060129
	H	3.257476	-0.570967	-0.310010
	O	-1.108095	-1.372467	0.277183
	C	0.931657	1.738833	0.378221
	H	-0.930595	1.117585	-0.448210
	H	0.832440	2.787566	0.617623
	O	-3.122427	0.512778	-0.209310
	H	-2.612534	-0.267859	0.066775
	H	-3.905720	0.176198	-0.648750

TS(*anti* **6**···H_2O → T-**7**···H_2O) C1 M06-2X/def2-TZVP E = -382.5252107 ZPVE = 0.102281	C	1.248154	-1.004730	0.090272
	C	-0.155259	-0.547300	-0.032630
	C	-0.289700	0.915562	-0.046660
	C	0.899053	1.531808	0.068964
	C	2.028203	0.680923	0.228410
	H	-1.248980	1.394340	-0.198160
	H	1.056998	2.596203	-0.049710
	O	-1.084542	-1.339310	0.009403
	C	2.498070	-0.425990	-0.290770
	H	1.323507	-1.844880	0.778243
	H	3.460449	-0.886340	-0.460850
	O	-3.300053	0.367390	-0.026990
	H	-2.697131	-0.394730	0.009302
	H	-4.189209	0.009089	-0.043660

TS(*syn* **6**···ICF_3 → T-**7**···ICF_3) C1 M06-2X/def2-TZVP E = -941.3920381 ZPVE = 0.092379	C	2.480618	0.767172v	-0.443700
	C	2.647683	-0.660546	-0.074730
	C	4.003590	-0.974128	0.385216
	C	4.805548	0.105487	0.390524
	C	4.231340	1.303864	-0.110590
	H	4.264599	-1.956507	0.754229
	H	5.791871	0.141767	0.835463
	O	1.766769v	-1.483990	-0.260800
	C	3.109062	1.971319	-0.002160
	H	1.906204	0.868839	-1.363490
	H	2.775497	2.997014	-0.064880
	I	-0.939447	-0.462616	-0.080110
	C	-2.879227	0.419823	0.123247
	F	-3.264065	0.444929	1.395548
	F	-2.884499	1.673314	-0.324760
	F	-3.792918	-0.258077	-0.563660

TS(*anti* **6**···ICF_3 → T-**7**···ICF_3) C1 M06-2X/def2-TZVP E = -941.39155 ZPVE = 0.092637	C	-3.967440	-0.809585	-0.318544
	C	-2.633958	-0.432576	0.209413
	C	-2.498544	1.009811	0.441630
	C	-3.615238	1.685560	0.119709
	C	-4.669909	0.906896	-0.429250
	H	-1.613737	1.434331	0.896545
	H	-3.794479	2.729267	0.344374
	O	-1.732933	-1.249709	0.302921
	C	-5.268611	-0.233471	-0.190480
	H	-3.873897	-1.556207	-1.105075
	H	-6.246789	-0.671354	-0.327118
	I	1.023196	-0.412841	0.081614
	C	3.003443	0.374239	-0.129664
	F	3.073731	1.620466	0.332504
	F	3.887813	-0.355920	0.541697
	F	3.378955	0.395117	-1.404702

TS(*syn* **6**···BF_3 → T-**7**···BF_3) C1 M06-2X/def2-TZVP E = -630.7291475 ZPVE = 0.092407	B	1.867816	0.031190	-0.008940
	F	1.635033	0.881573	-1.065260
	F	1.796103	0.696653	1.200224
	F	2.964163	-0.748510	-0.146600
	C	-0.932330	0.803997	0.100050
	C	-0.541960	-0.575380	-0.060150
	C	-1.652680	-1.501450	-0.074770
	C	-2.830670	-0.851780	0.070348
	C	-2.647080	0.536579	0.237840
	H	-1.523260	-2.556810	-0.268780
	H	-3.813040	-1.268290	-0.103800
	O	0.648485	-0.978830	0.009368
	C	-2.105020	1.596436	-0.257780
	H	-0.267770	1.327954	0.788091
	H	-2.222080	2.653913	-0.434230

TS(*anti* **6**···BF_3 → T-**7**···BF_3) C1 M06-2X/def2-TZVP E = -630.7283305 ZPVE = 0.092444	B	-1.925145	-0.056120	0.018174
	F	-1.745990	0.692562	1.160895
	F	-1.982853	0.740192	-1.104550
	F	-2.909712	-0.979050	0.101866
	C	1.726183	-1.107120	0.042931
	C	0.529878	-0.321230	-0.142510
	C	0.739080	1.115238	-0.121140
	C	2.041668	1.407136	0.092197
	C	2.837145	0.256957	0.269980
	H	-0.050691	1.822322	-0.327430
	H	2.497913	2.380703	-0.022920
	O	-0.586752	-0.899350	-0.133800
	C	3.146909	-0.895370	-0.218400
	H	1.543108	-1.943200	0.715332
	H	3.951239	-1.601440	-0.347720

References

1. Ertelt, M.; Hrovat, D. A.; Borden, W. T.; Sander, W., *Chem. Eur. J.* **2014,** *20*, 4713.
2. Dunkin, I. R., *Matrix-Isolation Techniques: A Practical Approach*. Oxford University Press: New York, 1998.
3. Siebrand, W.; Wildman, T. A., *Acc. Chem. Res.* **1986,** *19* (8), 238-243.
4. Zhao, Y.; Schultz, N. E.; Truhlar, D. G., *J. Chem. Theory Comput.* **2006,** *2* (2), 364-382.
5. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H., *J. Chem. Phys.* **2010,** *132* (15).
6. Weigend, F.; Ahlrichs, R., *Phys. Chem. Chem. Phys.* **2005,** *7* (18), 3297-3305.
7. Frisch, M. J. T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision D.1; Gaussian, Inc.: Wallingford CT, 2009.
8. Werner, H. J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schutz, M., *WIREs Comput. Mol. Sci.* **2012,** *2* (2), 242-253.
9. Stoll, S.; Schweiger, A., *J. Magn. Reson.* **2006,** *178* (1), 42-55.