## **ELECTRONIC SUPPLEMENTARY INFORMATION**

## Rethinking the $X^-$ + CH<sub>3</sub>Y [X = OH, SH, CN, NH<sub>2</sub>, PH<sub>2</sub>; Y = F, Cl, Br, I] S<sub>N</sub>2 reactions

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## Content

Energies, structures, and frequencies for the stationary points of the potential energy surface of the  $OH^- + CH_3Y$  [Y = F, Cl, Br, I] S<sub>N</sub>2 reactions obtained at different levels of theory (data are taken from D. A. Tasi, Z. Fábián and G. Czakó, *J. Phys. Chem. A*, 2018, **122**, 5773)

**Table S1.** Energies, structures, and frequencies for the PreMIN [Y = F, Cl, Br] ion-dipole complexes ( $C_s$  symmetry) obtained at different levels of theory



Level <sup>a</sup>		MP2/aug-cc-pVDZ		CCS	D(T)-F12b/aug-cc-p	VDZ	CCS	CCSD(T)-F12b/aug-cc-pVTZ			
System	FCH <sub>3</sub> …OH	CICH <sub>3</sub> ···OH	BrCH <sub>3</sub> …OH	FCH <sub>3</sub> …OH	CICH <sub>3</sub> ···OH	BrCH <sub>3</sub> …OH	FCH <sub>3</sub> …OH	CICH <sub>3</sub> …OH	BrCH <sub>3</sub> …OH		
Energy [E <sub>h</sub> ]	-215.076647	575.087560	-531.052094	-215.329005	-575.310262	-531.271684	-215.366077	-575.357305	-531.321117		
$r_1[Å]$	2.664	2.614	2.578	2.656	2.611	2.545	2.649	2.600	2.532		
$r_2$ [Å]	1.453	1.849	2.011	1.423	1.826	2.016	1.424	1.834	2.022		
r <sub>3</sub> [Å]	0.971	0.971	0.971	0.963	0.963	0.963	0.963	0.963	0.963		
r4[Å]	1.094	1.092	1.091	1.086	1.083	1.080	1.085	1.081	1.079		
r <sub>5</sub> [Å]	1.092	1.091	1.090	1.085	1.082	1.080	1.083	1.080	1.078		
a <sub>1</sub> [deg]	171.9	169.1	168.9	170.1	168.2	170.3	170.6	168.6	170.3		
$a_2[deg]$	161.8	158.7	148.6	156.6	154.5	134.8	158.2	154.6	134.9		
a <sub>3</sub> [deg]	107.7	107.1	106.1	108.3	107.6	105.9	108.3	107.3	105.6		
$a_4[deg]$	108.6	108.3	107.6	109.4	109.0	107.2	109.3	108.7	106.9		
$d_1[deg]$	120.1	120.2	120.1	120.1	120.2	120.0	120.1	120.2	120.0		
ZPE [cm <sup>-1</sup> ]	10791	10450	10290	10711	10387	10242	10753	10413	10231		
$\omega_1 [\text{cm}^{-1}]$	44 <i>i</i>	24	38	97 <i>i</i>	30 <i>i</i>	59	56i	20	58		
$\omega_2 [\mathrm{cm}^{-1}]$	93	82	86	85	80	94	94	84	74		
$\omega_3 [\text{cm}^{-1}]$	165	159	137	124	158	111	157	150	113		
$\omega_4 [\text{cm}^{-1}]$	174	175	165	158	162	174	169	176	170		
$\omega_5 [\text{cm}^{-1}]$	188	192	185	184	188	196	188	190	196		
$\omega_6 [\text{cm}^{-1}]$	904	622	502	948	615	457	941	617	450		
$\omega_7 [\mathrm{cm}^{-1}]$	1114	960	898	1119	959	892	1122	953	888		
$\omega_8 [\text{cm}^{-1}]$	1131	990	928	1145	997	920	1146	987	917		
$\omega_9 [\mathrm{cm}^{-1}]$	1392	1283	1226	1404	1295	1211	1409	1298	1211		
$\omega_{10} [{\rm cm}^{-1}]$	1470	1439	1428	1479	1459	1444	1485	1465	1447		
$\omega_{11} [\rm cm^{-1}]$	1470	1442	1430	1483	1459	1447	1489	1467	1452		
$\omega_{12} [\mathrm{cm}^{-1}]$	3144	3157	3161	3096	3127	3144	3101	3132	3146		
$\omega_{13} [\mathrm{cm}^{-1}]$	3270	3292	3304	3199	3240	3273	3204	3248	3277		
$\omega_{14}$ [cm <sup>-1</sup> ]	3280	3298	3309	3215	3248	3282	3218	3256	3286		
$\omega_{15} [\rm cm^{-1}]$	3788	3785	3783	3783	3785	3781	3783	3783	3778		

**Table S2.** Energies, structures, and frequencies for the WaldenTS [Y = F, Cl, Br] transition states (C<sub>s</sub> symmetry) obtained at different levels of theory



3 180.0

2 180.0

Level <sup>a</sup>		MP2/aug-cc-pVDZ		CCS	D(T)-F12b/aug-cc-p	VDZ	CCS	CCSD(T)-F12b/aug-cc-pVTZ			
System	[F·CH <sub>3</sub> ·OH] <sup>-</sup>	[Cl·CH <sub>3</sub> ·OH] <sup>-</sup>	[Br·CH <sub>3</sub> ·OH] <sup>-</sup>	[F·CH <sub>3</sub> ·OH] <sup>-</sup>	[Cl·CH <sub>3</sub> ·OH] <sup>-</sup>	[Br·CH <sub>3</sub> ·OH] <sup>-</sup>	[F·CH <sub>3</sub> ·OH] <sup>-</sup>	[Br·CH <sub>3</sub> ·OH] <sup>-</sup>			
Energy [E <sub>h</sub> ]	-215.061411	-575.083708	-531.051006	-215.310794	-575.306035	-531.271222	-215.348288	-575.353404	-531.320799		
$r_1$ [Å]	2.010	2.237	2.325	1.988	2.223	2.345	1.991	2.227	2.364		
<i>r</i> <sub>2</sub> [Å]	0.971	0.972	0.972	0.963	0.964	0.964	0.963	0.964	0.964		
r <sub>3</sub> [Å]	1.083	1.084	1.086	1.073	1.074	1.076	1.072	1.072	1.075		
<i>r</i> <sub>4</sub> [Å]	1.083	1.083	1.085	1.074	1.074	1.076	1.072	1.072	1.074		
r <sub>5</sub> [Å]	1.755	2.056	2.147	1.754	2.057	2.129	1.754	2.053	2.117		
$a_1[deg]$	106.0	110.0	112.6	105.0	107.5	110.7	104.8	107.8	112.4		
$a_2$ [deg]	83.3	76.6	73.8	84.2	77.5	73.8	84.2	77.1	72.9		
$a_3[\text{deg}]$	119.3	117.1	115.8	119.4	117.1	115.3	119.3	117.0	115.0		
$a_4$ [deg]	93.9	99.7	101.9	93.6	99.7	102.6	93.7	99.8	103.1		
$d_1[\text{deg}]$	84.2	74.4	71.1	84.8	74.5	70.0	84.7	74.3	69.3		
ZPE [cm <sup>-1</sup> ]	10916	10501	10303	10850	10423	10216	10825	10415	10176		
$\omega_1 [\text{cm}^{-1}]$	565i	424 <i>i</i>	299 <i>i</i>	602 <i>i</i>	434 <i>i</i>	254 <i>i</i>	600 <i>i</i>	426 <i>i</i>	216 <i>i</i>		
$\omega_2 [\text{cm}^{-1}]$	167	114	88	168	103	67	143	83	36		
$\omega_3 [\text{cm}^{-1}]$	305	205	169	305	206	161	304	203	157		
$\omega_4 [\text{cm}^{-1}]$	328	219	181	328	217	172	328	217	166		
$\omega_5 [\text{cm}^{-1}]$	373	291	252	367	287	248	365	287	249		
$\omega_6 [\text{cm}^{-1}]$	672	481	414	683	490	399	674	477	376		
$\omega_7 [\text{cm}^{-1}]$	1098	980	924	1088	958	905	1083	960	905		
$\omega_8 [\text{cm}^{-1}]$	1122	990	931	1113	967	911	1109	971	910		
$\omega_9 [\text{cm}^{-1}]$	1231	1139	1112	1221	1122	1117	1214	1127	1127		
$\omega_{10} [\rm cm^{-1}]$	1401	1406	1406	1401	1413	1422	1399	1417	1428		
$\omega_{11} [cm^{-1}]$	1402	1410	1410	1402	1416	1425	1400	1421	1432		
$\omega_{12} [\rm cm^{-1}]$	3178	3200	3191	3154	3180	3169	3155	3180	3170		
$\omega_{13} [\rm cm^{-1}]$	3386	3391	3372	3340	3354	3330	3343	3354	3328		
$\omega_{14} [\rm{cm}^{-1}]$	3386	3397	3377	3342	3358	3333	3346	3357	3331		
$\omega_{15} [\mathrm{cm}^{-1}]$	3784	3780	3779	3788	3776	3772	3787	3774	3771		

**Table S3.** Energies, structures, and frequencies for the PostHMIN [Y = F, Cl, Br, I] H-bonded complexes (C<sub>s</sub> symmetry) obtained at different levels of theory



1	С						
2	0	1	$r_1$				
3	Η	1	$r_2$	2	$a_1$		
4	Η	2	$r_3$	1	$a_2$	3	180.0
5	Y	4	$r_4$	2	$a_3$	1	0.0
6	Η	1	$r_5$	2	$a_4$	3	$d_1$
7	Η	1	$r_5$	2	$a_4$	3	$-d_1$

Level <sup>a</sup>		MP2/aug	-cc-pVDZ			CCSD(T)-F12	o/aug-cc-pVDZ		CCSD(T)-F12b/aug-cc-pVTZ			
System	CH <sub>3</sub> OH…F <sup>-</sup>	CH <sub>3</sub> OH…Cl <sup>−</sup>	CH <sub>3</sub> OH…Br <sup>-</sup>	СН <sub>3</sub> ОН…Г	CH <sub>3</sub> OH…F <sup>-</sup>	CH <sub>3</sub> OH···F <sup>-</sup> CH <sub>3</sub> OH···Cl <sup>-</sup> CH <sub>3</sub> OH···Br <sup>-</sup> CH <sub>3</sub> OH···F <sup>-</sup> CH <sub>3</sub> OH···F <sup>-</sup>					CH <sub>3</sub> OH…Br <sup>-</sup>	CH <sub>3</sub> OH…I <sup>−</sup>
Energy [E <sub>h</sub> ]	-215.134521	-575.170641	-531.141221	-410.292504	-215.387088	-575.395174	-531.364831	-410.511585	-215.423961	-575.442094	-531.413905	-410.551631
$r_1[\text{Å}]$	1.404	1.420	1.422	1.425	1.387	1.404	1.407	1.409	1.388	1.405	1.408	1.410
$r_2[\text{\AA}]$	1.108	1.103	1.103	1.102	1.101	1.096	1.095	1.094	1.099	1.094	1.093	1.092
r <sub>3</sub> [Å]	1.065	0.994	0.988	0.983	1.062	0.985	0.980	0.975	1.061	0.985	0.980	0.975
r <sub>4</sub> [Å]	1.372	2.104	2.307	2.578	1.344	2.101	2.304	2.578	1.345	2.097	2.303	2.584
r5[Å]	1.112	1.106	1.105	1.105	1.105	1.098	1.097	1.097	1.103	1.096	1.096	1.095
$a_1$ [deg]	109.6	107.7	107.4	107.2	110.0	108.1	107.8	107.6	109.9	108.1	107.8	107.5
$a_2$ [deg]	105.7	104.9	105.1	105.4	106.3	105.5	105.7	106.0	106.3	105.4	105.6	106.0
$a_3[deg]$	175.7	166.9	165.2	163.8	175.7	166.2	164.6	163.2	175.8	166.8	164.7	163.4
$a_4$ [deg]	112.7	112.0	111.9	111.9	112.8	112.1	112.0	111.9	112.8	112.0	112.0	111.9
$d_1$ [deg]	119.6	119.5	119.5	119.4	119.7	119.6	119.5	119.5	119.7	119.6	119.5	119.5
ZPE [cm <sup>-1</sup> ]	11202	11491	11486	11478	11120	11482	11462	11480	11153	11485	11497	11487
$\omega_1 [\text{cm}^{-1}]$	83	77	81	80	49	53	33	79	58	30	72	78
$\omega_2 [\text{cm}^{-1}]$	163	108	92	82	162	110	94	83	164	110	95	85
$\omega_3 [\text{cm}^{-1}]$	406	206	174	151	406	217	177	156	407	217	180	155
$\omega_4 [\text{cm}^{-1}]$	1110	787	718	650	1137	775	707	640	1131	783	712	639
$\omega_5 [\text{cm}^{-1}]$	1143	1080	1075	1068	1154	1106	1100	1094	1156	1102	1096	1089
$\omega_6 [\text{cm}^{-1}]$	1160	1118	1113	1106	1170	1130	1124	1120	1173	1133	1126	1120
$\omega_7 [\text{cm}^{-1}]$	1192	1170	1171	1170	1205	1184	1184	1185	1214	1183	1184	1183
$\omega_8 [\text{cm}^{-1}]$	1434	1447	1447	1434	1450	1466	1466	1451	1455	1470	1470	1451
$\omega_9 [\text{cm}^{-1}]$	1471	1473	1456	1452	1481	1484	1468	1470	1486	1489	1472	1474
$\omega_{10} [\rm cm^{-1}]$	1492	1474	1475	1476	1505	1485	1485	1488	1510	1490	1491	1493
$\omega_{11} [cm^{-1}]$	1620	1510	1506	1505	1635	1521	1518	1518	1639	1525	1523	1522
$\omega_{12} [cm^{-1}]$	2123	3015	3023	3030	2070	2976	2986	2992	2080	2979	2988	2994
$\omega_{13} [cm^{-1}]$	2961	3084	3094	3103	2914	3024	3036	3045	2919	3028	3040	3049
$\omega_{14} [cm^{-1}]$	2999	3114	3123	3132	2928	3053	3064	3074	2936	3058	3068	3078
$\omega_{15} [\mathrm{cm}^{-1}]$	3043	3319	3427	3516	2973	3378	3480	3566	2979	3373	3476	3564

**Table S4.** Energies, structures, and frequencies for the [F<sup>-</sup>…HCH<sub>2</sub>OH] H-bonded complexes (C<sub>s</sub> symmetry) obtained at different levels of theory



1	С						
2	0	1	$r_1$				
3	Η	1	$r_2$	2	$a_1$		
4	Η	2	$r_3$	1	$a_2$	3	180.0
5	F	3	$r_4$	1	$a_3$	2	0.0
6	Η	1	$r_5$	2	$a_4$	3	$d_1$
7	Η	1	$r_5$	2	$a_4$	3	$-d_1$

Level	MP2/aug-cc-pVDZ	CCSD(T)-F12b/aug-cc-pVDZ	CCSD(T)-F12b/aug-cc-pVTZ
Energy [E <sub>h</sub> ]	-215.102006	-215.353465	-215.390333
$r_1$ [Å]	1.461	1.443	1.445
$r_2$ [Å]	1.114	1.107	1.105
r <sub>3</sub> [Å]	0.965	0.958	0.958
<i>r</i> <sub>4</sub> [Å]	1.833	1.814	1.817
r5[Å]	1.106	1.098	1.096
$a_1[deg]$	110.5	111.0	111.1
$a_2[deg]$	106.9	107.3	107.2
a <sub>3</sub> [deg]	160.3	159.8	159.2
$a_4$ [deg]	110.0	110.1	110.1
$d_1[\text{deg}]$	120.2	120.2	120.2
ZPE [cm <sup>-1</sup> ]	11379	11375	11373
$\omega_1 [\text{cm}^{-1}]$	100	106	100
$\omega_2 [\mathrm{cm}^{-1}]$	194	191	183
$\omega_3 [\text{cm}^{-1}]$	201	212	210
$\omega_4 [\text{cm}^{-1}]$	371	358	354
$\omega_5 [\text{cm}^{-1}]$	962	990	985
$\omega_6 [\text{cm}^{-1}]$	1055	1069	1067
$\omega_7 [\mathrm{cm}^{-1}]$	1178	1190	1190
$\omega_8 [\text{cm}^{-1}]$	1320	1339	1339
$\omega_9 [\text{cm}^{-1}]$	1476	1492	1496
$\omega_{10} [{\rm cm}^{-1}]$	1496	1512	1511
$\omega_{11} [cm^{-1}]$	1530	1545	1547
$\omega_{12} [cm^{-1}]$	2896	2861	2866
$\omega_{13} [cm^{-1}]$	3060	3008	3013
$\omega_{14}$ [cm <sup>-1</sup> ]	3089	3026	3033
$\omega_{15}$ [cm <sup>-1</sup> ]	3833	3851	3852

 $a_1$ 



Level <sup>a</sup>	MP2/aug-	-cc-pVDZ	CCSD(T)-F12t	o/aug-cc-pVDZ	CCSD(T)-F12	CCSD(T)-F12b/aug-cc-pVTZ		
System	[OHHCH2Br]	[OHHCH2I]	[OH…HCH2…Br] <sup>−</sup>	[OH···HCH <sub>2</sub> ···I] <sup>-</sup>	[OHHCH2Br]	[OH···HCH <sub>2</sub> ···I] <sup>-</sup>		
Energy [E <sub>h</sub> ]	-531.051907	-410.197092	-531.271324	-410.411903	-531.320719	-410.452219		
$r_1[Å]$	1.093	1.092	1.083	1.083	1.081	1.081		
$r_2[\text{\AA}]$	1.094	1.094	1.085	1.085	1.084	1.084		
r <sub>3</sub> [Å]	1.093	1.093	1.084	1.083	1.082	1.082		
r <sub>4</sub> [Å]	1.993	2.203	1.986	2.196	1.988	2.196		
r <sub>5</sub> [Å]	2.063	2.069	2.042	2.045	2.025	2.034		
r <sub>6</sub> [Å]	0.971	0.972	0.963	0.963	0.963	0.963		
$a_1[deg]$	110.6	110.4	110.2	110.5	110.5	110.7		
$a_2$ [deg]	111.9	112.3	111.9	112.2	112.0	112.4		
a <sub>3</sub> [deg]	106.4	105.7	106.2	105.5	106.0	105.3		
$a_4$ [deg]	111.3	108.6	112.3	110.2	113.7	110.9		
<i>a</i> <sub>5</sub> [deg]	169.6	157.3	159.4	142.2	160.5	146.1		
$d_1[\text{deg}]$	124.4	125.4	124.2	125.3	124.7	125.8		
$d_2[\text{deg}]$	-116.1	-115.8	-116.1	-115.4	-115.7	-115.1		
d <sub>3</sub> [deg]	59.1	51.9	53.5	51.52	54.8	52.45		
$d_4$ [deg]	117.2	80.6	86.6	69.9	88.7	80.0		
ZPE [cm <sup>-1</sup> ]	10276	10139	10225	10066	10258	10091		
$\omega_1 [\text{cm}^{-1}]$	72 <i>i</i>	82 <i>i</i>	97 <i>i</i>	104 <i>i</i>	78 <i>i</i>	98 <i>i</i>		
$\omega_2 [\text{cm}^{-1}]$	39	82	67	75	81	92		
$\omega_3 [\text{cm}^{-1}]$	167	143	124	144	135	139		
$\omega_4 [\text{cm}^{-1}]$	179	178	186	177	188	184		
$\omega_5 [\text{cm}^{-1}]$	205	194	190	183	201	185		
$\omega_6 [\text{cm}^{-1}]$	547	477	537	451	536	453		
$\omega_7 [\text{cm}^{-1}]$	886	812	876	783	883	792		
$\omega_8 [\text{cm}^{-1}]$	953	891	949	884	953	885		
$\omega_9 [\text{cm}^{-1}]$	1258	1202	1265	1195	1272	1202		
$\omega_{10} [\text{cm}^{-1}]$	1436	1424	1451	1439	1458	1444		
$\omega_{11} [cm^{-1}]$	1437	1427	1460	1453	1466	1456		
$\omega_{12} [\mathrm{cm}^{-1}]$	3128	3127	3103	3102	3102	3102		
$\omega_{13} [cm^{-1}]$	3264	3265	3224	3226	3223	3226		
$\omega_{14} [cm^{-1}]$	3275	3280	3233	3241	3235	3243		
$\omega_{15} [cm^{-1}]$	3779	3778	3785	3781	3783	3780		

Table S6. Energies, structures, and frequencies for the HTS [Y = Cl] H-bonded transition states (C<sub>s</sub> symmetry) obtained at different levels of theory



Level	MP2/aug-cc-pVDZ	CCSD(T)-F12b/aug-cc-pVDZ	CCSD(T)-F12b/aug-cc-pVTZ
Energy [E <sub>h</sub> ]	-575.087425	-575.310238	-575.357197
$r_1$ [Å]	1.094	1.084	1.084
<i>r</i> <sub>2</sub> [Å]	1.840	1.819	1.824
r <sub>3</sub> [Å]	1.093	1.084	1.082
<i>r</i> <sub>4</sub> [Å]	2.075	2.111	2.059
r <sub>5</sub> [Å]	0.971	0.963	0.963
$a_1[deg]$	110.5	110.6	110.9
<i>a</i> <sub>2</sub> [deg]	107.0	107.8	107.3
a <sub>3</sub> [deg]	112.4	108.4	112.8
$a_4$ [deg]	168.9	172.1	169.7
$d_1[\text{deg}]$	120.2	120.0	120.2
ZPE [cm <sup>-1</sup> ]	10448	10357	10403
$\omega_1 [\text{cm}^{-1}]$	68 <i>i</i>	93 <i>i</i>	66 <i>i</i>
$\omega_2 [\text{cm}^{-1}]$	63	37i	43
$\omega_3 [\text{cm}^{-1}]$	185	130	152
$\omega_4 [\text{cm}^{-1}]$	189	191	193
$\omega_5 [\text{cm}^{-1}]$	218	199	208
$\omega_6 [\text{cm}^{-1}]$	649	641	649
$\omega_7 [\text{cm}^{-1}]$	947	962	954
$\omega_8 [\text{cm}^{-1}]$	1014	1013	1012
$\omega_9 [\text{cm}^{-1}]$	1304	1314	1326
$\omega_{10} [{\rm cm}^{-1}]$	1447	1461	1469
$\omega_{11} [cm^{-1}]$	1447	1464	1474
$\omega_{12} [\mathrm{cm}^{-1}]$	3127	3108	3103
$\omega_{13} [cm^{-1}]$	3259	3221	3219
$\omega_{14} [cm^{-1}]$	3266	3225	3221
$\omega_{15} [\mathrm{cm}^{-1}]$	3781	3785	3784

**Table S7.** Energies, structures, and frequencies for the HMIN [Y = Cl, Br, I] H-bonded complexes (C<sub>s</sub> symmetry) obtained at different levels of theory



1	С						
2	Η	1	$r_1$				
3	Y	1	$r_2$	2	$a_1$		
4	0	2	$r_3$	1	$a_2$	3	180.0
5	Η	4	$r_4$	2	$a_3$	1	180.0
6	Η	1	$r_5$	3	$a_4$	2	$d_1$
7	Η	1	$r_5$	3	$a_4$	2	$-d_1$

Level <sup>a</sup>		MP2/aug-cc-pVDZ		CO	CSD(T)-F12b/aug-cc-pV	DZ	C	CCSD(T)-F12b/aug-cc-pVTZ			
System	HO <sup>-</sup> ···HCH <sub>2</sub> Cl	HO <sup>-</sup> ···HCH <sub>2</sub> Br	HO <sup>-</sup> ···HCH <sub>2</sub> I	HO <sup>-</sup> ···HCH <sub>2</sub> Cl	HO <sup>-</sup> ···HCH <sub>2</sub> Br	HO <sup>-</sup> ···HCH <sub>2</sub> I	HO <sup>-</sup> ···HCH <sub>2</sub> Cl	HO <sup>-</sup> ···HCH <sub>2</sub> Br	HO <sup>-</sup> ···HCH <sub>2</sub> I		
Energy [E <sub>h</sub> ]	-575.088461	-531.053604	-410.200277	-575.311695	-531.273305	-410.415318	-575.358296	-531.322392	-410.455315		
$r_1[\text{\AA}]$	1.124	1.138	1.153	1.121	1.130	1.144	1.116	1.126	1.141		
$r_2[\text{\AA}]$	1.830	1.981	2.183	1.805	1.972	2.168	1.814	1.974	2.169		
r <sub>3</sub> [Å]	1.769	1.714	1.652	1.756	1.709	1.649	1.764	1.717	1.654		
r4[Å]	0.970	0.971	0.971	0.963	0.963	0.963	0.962	0.962	0.963		
r5[Å]	1.098	1.099	1.100	1.090	1.089	1.089	1.087	1.087	1.088		
$a_1[deg]$	110.5	109.8	108.8	110.8	109.8	108.6	110.7	109.6	108.4		
$a_2$ [deg]	158.7	164.4	168.5	163.7	165.6	169.7	160.8	164.4	169.2		
a3[deg]	136.5	123.4	116.1	125.3	120.2	114.9	130.6	122.7	115.9		
a4[deg]	105.9	105.3	104.9	106.4	105.2	104.8	106.1	105.1	104.7		
$d_1[\text{deg}]$	121.4	121.7	121.9	121.4	121.6	121.8	121.3	121.6	121.7		
ZPE [cm <sup>-1</sup> ]	10409	10231	10078	10356	10188	10072	10391	10223	10063		
$\omega_1 [\mathrm{cm}^{-1}]$	63	65	70	33	23	56	55	65	61		
$\omega_2 [\mathrm{cm}^{-1}]$	64	69	89	69	69	104	67	67	98		
$\omega_3 [\text{cm}^{-1}]$	192	219	272	207	239	272	200	227	272		
$\omega_4 [\text{cm}^{-1}]$	245	261	282	260	272	301	256	265	284		
$\omega_5 [\mathrm{cm}^{-1}]$	260	288	309	267	277	312	259	275	300		
$\omega_6 [\mathrm{cm}^{-1}]$	677	575	517	676	569	509	676	566	506		
$\omega_7 [\mathrm{cm}^{-1}]$	1038	995	939	1057	995	940	1051	996	937		
$\omega_8 [\text{cm}^{-1}]$	1051	1002	963	1064	1007	968	1056	1008	967		
$\omega_9 [\mathrm{cm}^{-1}]$	1402	1381	1360	1427	1395	1373	1427	1396	1371		
$\omega_{10} [{\rm cm}^{-1}]$	1467	1463	1461	1486	1479	1474	1490	1480	1473		
$\omega_{11} [cm^{-1}]$	1492	1490	1481	1517	1508	1503	1519	1513	1505		
$\omega_{12} [cm^{-1}]$	2743	2543	2319	2635	2505	2295	2685	2536	2309		
$\omega_{13} [cm^{-1}]$	3132	3123	3113	3083	3092	3089	3095	3099	3092		
$\omega_{14} [\mathrm{cm}^{-1}]$	3197	3194	3189	3139	3156	3155	3153	3164	3161		
$\omega_{15} [\text{cm}^{-1}]$	3793	3793	3793	3793	3793	3794	3791	3791	3792		

Table S8. Energies, structures, and frequencies for the FSMIN [Y = Cl, Br, I] front-side complexes (C<sub>s</sub> symmetry) obtained at different levels of theory



1	С						
2	Y	1	$r_1$				
3	Η	1	$r_2$	2	$a_1$		
4	Η	1	$r_3$	2	$a_2$	3	$d_1$
5	Η	1	$r_3$	2	$a_2$	3	$-d_1$
6	0	2	$r_4$	1	$a_3$	3	0.0
7	Η	6	$r_5$	2	$a_4$	3	180.0

Level <sup>a</sup>		MP2/aug-cc-pVDZ		CCS	D(T)-F12b/aug-cc-pVL	DΖ	CCSD(T)-F12b/aug-cc-pVTZ			
System	[CH <sub>3</sub> ···Cl···OH] <sup>-</sup>	[CH <sub>3</sub> ···Br···OH] <sup>-</sup>	[CH <sub>3</sub> …I…OH] <sup>−</sup>	[CH <sub>3</sub> ···Cl···OH] <sup>-</sup>	[CH <sub>3</sub> ···Br···OH] <sup>-</sup>	[CH <sub>3</sub> …I…OH] <sup>-</sup>	[CH <sub>3</sub> ···Cl···OH] <sup>−</sup>	[CH <sub>3</sub> ···Br···OH] <sup>-</sup>	[CH <sub>3</sub> …I…OH] <sup>-</sup>	
Energy [E <sub>h</sub> ]	-575.064112	-531.042704	-410.207449	-575.289955	-531.263473	-410.423612	-575.336075	-531.312826	-410.464027	
$r_1[\text{Å}]$	1.806	2.024	2.274	1.782	2.015	2.257	1.797	2.016	2.256	
$r_2[\text{\AA}]$	1.100	1.101	1.102	1.092	1.092	1.093	1.090	1.090	1.091	
r <sub>3</sub> [Å]	1.100	1.101	1.102	1.092	1.092	1.093	1.090	1.090	1.091	
$r_4$ [Å]	2.691	2.422	2.402	2.661	2.398	2.365	2.593	2.399	2.366	
r5[Å]	0.973	0.972	0.972	0.965	0.964	0.963	0.964	0.964	0.963	
$a_1[deg]$	109.5	109.3	109.4	109.8	109.2	109.4	109.6	109.0	109.2	
$a_2$ [deg]	109.7	109.5	109.6	110.1	109.4	109.6	109.8	109.3	109.4	
a <sub>3</sub> [deg]	175.9	178.3	178.6	176.1	178.8	178.9	177.8	178.7	178.9	
$a_4[deg]$	116.5	103.2	103.9	108.5	101.7	103.7	106.3	101.6	103.5	
$d_1$ [deg]	120.0	119.9	119.4	119.9	119.9	119.9	120.0	119.9	119.9	
ZPE [cm <sup>-1</sup> ]	10356	10248	10166	10353	10281	10149	10349	10249	10153	
$\omega_1 [\text{cm}^{-1}]$	8	10	28 <i>i</i>	25	83	77 <i>i</i>	41 <i>i</i>	8	33 <i>i</i>	
$\omega_2 [\text{cm}^{-1}]$	100	141	142	50	141	150	117	146	146	
$\omega_3 [\text{cm}^{-1}]$	122	148	147	99	144	156	134	150	150	
$\omega_4 [\text{cm}^{-1}]$	136	205	281	153	217	280	146	218	280	
$\omega_5 [\text{cm}^{-1}]$	223	476	433	297	485	437	277	483	436	
$\omega_6 [\text{cm}^{-1}]$	709	523	625	707	533	628	689	524	625	
$\omega_7 [\text{cm}^{-1}]$	995	860	761	1023	864	758	994	863	758	
$\omega_8 [\text{cm}^{-1}]$	996	863	769	1027	869	765	994	865	767	
$\omega_9 [\text{cm}^{-1}]$	1332	1229	1164	1356	1244	1178	1349	1244	1174	
$\omega_{10}  [{\rm cm}^{-1}]$	1469	1453	1444	1484	1472	1461	1492	1477	1467	
$\omega_{11} [cm^{-1}]$	1469	1453	1445	1487	1473	1461	1492	1477	1467	
$\omega_{12} [\mathrm{cm}^{-1}]$	3059	3047	3040	3025	3023	3013	3029	3026	3016	
$\omega_{13}$ [cm <sup>-1</sup> ]	3160	3155	3151	3104	3116	3106	3112	3120	3111	
$\omega_{14}$ [cm <sup>-1</sup> ]	3161	3156	3152	3107	3116	3107	3114	3121	3111	
$\omega_{15}$ [cm <sup>-1</sup> ]	3772	3777	3777	3761	3780	3799	3760	3778	3797	

 Table S9. Energies, structures, and frequencies for the DITS [Y = F, Cl, Br, I] double-inversion transition states (C<sub>s</sub> symmetry) obtained at different levels of theory



$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$0.0 \\ 0.0 \\ d_1 \\ -d_1$	$egin{array}{cccc} a_1 & & & & & & & & & & & & & & & & & & &$	1 2 3 5 5	r <sub>1</sub> r <sub>2</sub> r <sub>3</sub> r <sub>4</sub> r <sub>5</sub> r <sub>5</sub>	1 2 3 4 4 4	H O H C Y H H	1 2 3 4 5 6 7
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Level <sup>a</sup>	MP2/aug-cc-pVDZ					CCSD(T)-F12b/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVTZ			
System	[FCH2···HOH]	[ClCH <sub>2</sub> …HOH] <sup>-</sup>	[BrCH2···HOH]	[ICH2···HOH]	[FCH2···HOH]	[ClCH <sub>2</sub> …HOH] <sup>-</sup>	[BrCH <sub>2</sub> …HOH] <sup>-</sup>	[ICH2···HOH]	[FCH2···HOH]	[ClCH <sub>2</sub> …HOH] <sup>-</sup>	[BrCH <sub>2</sub> …HOH] <sup>-</sup>	[ICH2···HOH]	
Energy [E <sub>h</sub> ]	-215.022786	-575.051718	-531.020094	-410.171834	-215.279804	-575.280312	-531.244345	-410.391913	-215.316518	-575.326688	-531.293366	-410.432194	
$r_1$ [Å]	0.967	0.967	0.967	0.966	0.961	0.960	0.960	0.960	0.960	0.960	0.960	0.960	
$r_2[\text{\AA}]$	1.009	1.009	1.009	1.007	0.996	0.996	0.996	0.994	0.996	0.996	0.996	0.993	
r <sub>3</sub> [Å]	2.020	2.012	2.017	2.033	2.066	2.049	2.051	2.068	2.059	2.047	2.053	2.074	
r4[Å]	1.457	1.806	1.941	2.118	1.434	1.779	1.933	2.101	1.435	1.786	1.935	2.102	
r <sub>5</sub> [Å]	1.086	1.086	1.087	1.088	1.077	1.077	1.077	1.078	1.075	1.075	1.075	1.076	
$a_1[deg]$	98.9	100.0	100.4	100.8	99.1	100.1	100.6	101.1	99.1	100.2	100.5	101.0	
$a_2[deg]$	155.3	167.0	170.1	173.8	150.7	162.8	167.1	171.0	151.6	163.7	166.8	170.6	
a <sub>3</sub> [deg]	82.4	89.0	90.6	93.1	81.6	88.0	90.0	92.5	81.9	88.4	89.9	92.3	
$a_4[deg]$	114.0	115.2	115.2	115.7	114.4	115.7	115.2	115.8	114.4	115.5	115.1	115.8	
$d_1[\text{deg}]$	84.8	83.4	83.5	83.2	85.6	83.9	84.3	84.0	85.5	84.2	84.5	84.1	
ZPE [cm <sup>-1</sup> ]	10300	10144	10050	9974	10363	10178	10064	9991	10349	10155	10059	9980	
$\omega_1 [\text{cm}^{-1}]$	968 <i>i</i>	859i	858i	828 <i>i</i>	978i	851 <i>i</i>	877 <i>i</i>	838 <i>i</i>	983i	864 <i>i</i>	889i	846 <i>i</i>	
$\omega_2 [\text{cm}^{-1}]$	108	96	82	73	110	102	87	74	109	97	83	77	
$\omega_3 [\text{cm}^{-1}]$	196	210	205	191	201	193	206	203	195	206	208	193	
$\omega_4 [\text{cm}^{-1}]$	213	216	214	208	217	218	214	208	217	217	215	207	
$\omega_5 [\text{cm}^{-1}]$	274	259	254	250	292	272	255	242	286	266	257	243	
$\omega_6 [\text{cm}^{-1}]$	450	485	479	469	424	459	451	445	426	443	445	442	
$\omega_7 [\text{cm}^{-1}]$	851	708	621	581	827	703	602	566	827	698	599	563	
$\omega_8 [\text{cm}^{-1}]$	908	874	869	841	929	840	839	817	923	843	839	813	
$\omega_9 [\text{cm}^{-1}]$	1069	962	917	880	1082	968	907	857	1081	960	903	853	
$\omega_{10}  [{\rm cm}^{-1}]$	1390	1354	1332	1313	1394	1363	1314	1299	1393	1344	1309	1290	
$\omega_{11} [cm^{-1}]$	1663	1674	1672	1670	1686	1694	1694	1694	1689	1696	1696	1694	
$\omega_{12} [{\rm cm}^{-1}]$	3016	3001	3010	3048	3172	3168	3164	3170	3160	3158	3167	3171	
$\omega_{13} [\text{cm}^{-1}]$	3212	3211	3207	3198	3174	3174	3177	3203	3176	3177	3179	3210	
$\omega_{14}$ [cm <sup>-1</sup> ]	3397	3381	3381	3368	3345	3331	3345	3333	3347	3336	3348	3334	
$\omega_{15} [{\rm cm}^{-1}]$	3854	3858	3858	3859	3872	3873	3873	3873	3869	3870	3870	3870	

**Table S10.** Energies, structures, and frequencies for the FSTS [Y = Cl, Br, I] front-side attack transition states (C<sub>s</sub> symmetry) obtained at different levels of theory



1 2 3 4 5 6	C Y O H H H	1 1 3 1 1	$r_1$ $r_2$ $r_3$ $r_4$ $r_5$	2 1 2 3	$egin{array}{c} a_1\ a_2\ a_3\ a_4 \end{array}$	2 3 2	180.0 180.0 $d_1$
6	Η	1	$r_5$	3	$a_4$	2	$d_1$
7	Η	1	$r_5$	3	$a_4$	2	$-d_1$

Level <sup>a</sup>		MP2/aug-cc-pVDZ		0	CSD(T)-F12b/aug-cc-pVI	DZ	CCSD(T)-F12b/aug-cc-pVTZ		
System	[Cl···CH <sub>3</sub> ···OH] <sup>-</sup>	[Br…CH <sub>3</sub> …OH] <sup>-</sup>	[I…CH <sub>3</sub> …OH] <sup>-</sup>	[Cl···CH <sub>3</sub> ···OH] <sup>-</sup>	[Br…CH <sub>3</sub> …OH] <sup>-</sup>	[I…CH <sub>3</sub> …OH] <sup>-</sup>	[Cl···CH <sub>3</sub> ···OH] <sup>-</sup>	[Br…CH <sub>3</sub> …OH] <sup>-</sup>	[I…CH <sub>3</sub> …OH] <sup>-</sup>
Energy [E <sub>h</sub> ]	-575.016551	-530.988546	-410.141617	-575.239499	-531.209470	-410.357819	-575.286634	-531.259233	-410.398481
$r_1$ [Å]	2.215	2.346	2.536	2.268	2.403	2.600	2.263	2.402	2.597
$r_2$ [Å]	2.048	2.076	2.102	2.077	2.115	2.140	2.080	2.118	2.144
r <sub>3</sub> [Å]	0.976	0.976	0.977	0.969	0.969	0.970	0.968	0.968	0.969
<i>r</i> <sub>4</sub> [Å]	1.103	1.102	1.102	1.087	1.086	1.086	1.086	1.085	1.084
r <sub>5</sub> [Å]	1.097	1.096	1.096	1.084	1.083	1.083	1.082	1.081	1.081
$a_1[deg]$	80.7	80.4	79.1	80.5	80.3	78.9	80.7	80.4	78.9
$a_2[deg]$	92.9	93.6	96.6	92.6	93.3	96.5	92.4	92.9	96.2
$a_3[deg]$	78.6	79.0	79.8	76.5	76.8	77.4	76.4	76.7	77.4
$a_4[deg]$	81.5	81.1	81.2	79.9	79.1	79.1	79.8	79.0	79.0
$d_1[\text{deg}]$	121.7	121.5	121.6	121.0	120.6	120.5	121.0	120.6	120.5
ZPE [cm <sup>-1</sup> ]	10439	10347	10244	10314	10238	10078	10335	10210	10119
$\omega_1 [\text{cm}^{-1}]$	632 <i>i</i>	584 <i>i</i>	549 <i>i</i>	639 <i>i</i>	579 <i>i</i>	549 <i>i</i>	627 <i>i</i>	578 <i>i</i>	545 <i>i</i>
$\omega_2 [\text{cm}^{-1}]$	174	192	187	150	176	124	149	139	147
$\omega_3 [\text{cm}^{-1}]$	224	207	192	185	179	153	186	169	159
$\omega_4 [\text{cm}^{-1}]$	244	208	193	219	193	157	212	177	172
$\omega_5 [\text{cm}^{-1}]$	450	420	386	418	386	347	420	388	350
$\omega_6 [\text{cm}^{-1}]$	770	733	692	743	696	645	740	691	642
$\omega_7 [\text{cm}^{-1}]$	837	810	782	798	764	730	800	761	738
$\omega_8 [\text{cm}^{-1}]$	939	897	860	889	849	803	899	845	809
$\omega_9 [\text{cm}^{-1}]$	1228	1201	1175	1174	1148	1115	1192	1156	1122
$\omega_{10} [{\rm cm}^{-1}]$	1434	1429	1426	1444	1441	1434	1450	1444	1441
$\omega_{11} [cm^{-1}]$	1508	1500	1493	1499	1488	1478	1502	1490	1484
$\omega_{12}$ [cm <sup>-1</sup> ]	3032	3040	3046	3058	3071	3076	3060	3070	3077
$\omega_{13} [\rm{cm}^{-1}]$	3106	3119	3130	3137	3158	3169	3140	3159	3170
$\omega_{14}$ [cm <sup>-1</sup> ]	3204	3213	3218	3208	3224	3232	3212	3227	3233
$\omega_{15} [\rm{cm}^{-1}]$	3727	3724	3709	3706	3705	3693	3708	3705	3696

**Table S11.** Energies, structures, and frequencies for the FSTS [Y = F] front-side attack transition states (C<sub>1</sub> symmetry) obtained at different levels of theory



1	С						
2	Y	1	$r_1$				
3	0	1	$r_2$	2	$a_1$		
4	Η	3	$r_3$	1	$a_2$	2	$d_1$
5	Η	1	$r_4$	2	$a_3$	3	$d_2$
6	Η	1	$r_5$	3	$a_4$	2	$d_3$
7	Η	1	$r_6$	3	$a_5$	2	$d_4$

Level	MP2/aug-cc-pVDZ	CCSD(T)-F12b/aug-cc-pVDZ	CCSD(T)-F12b/aug-cc-pVTZ
Energy [E <sub>h</sub> ]	-214.990402	-215.239070	-215.276335
$r_1$ [Å]	1.749	1.748	1.753
$r_2[\text{\AA}]$	1.916	1.911	1.917
r <sub>3</sub> [Å]	0.974	0.966	0.966
r4[Å]	1.116	1.104	1.101
r5[Å]	1.117	1.106	1.103
r6[Å]	1.096	1.085	1.083
$a_1[deg]$	79.7	79.7	79.7
a2 [deg]	94.6	95.8	95.6
a3[deg]	80.3	79.9	79.7
a4[deg]	80.9	80.4	80.1
a5 [deg]	94.7	95.0	94.8
$d_1[\text{deg}]$	-175.1	-174.7	-174.8
$d_2$ [deg]	-160.4	-159.0	-159.1
$d_3[\text{deg}]$	146.8	148.2	148.0
d <sub>4</sub> [deg]	-103.2	-101.9	-101.8
ZPE [cm <sup>-1</sup> ]	10715	10680	10667
$\omega_1 [\text{cm}^{-1}]$	673 <i>i</i>	731 <i>i</i>	729 <i>i</i>
$\omega_2 [\text{cm}^{-1}]$	255	245	227
$\omega_3 [\text{cm}^{-1}]$	276	262	247
$\omega_4 [\text{cm}^{-1}]$	356	343	335
$\omega_5 [\text{cm}^{-1}]$	561	540	538
$\omega_6 [\text{cm}^{-1}]$	912	920	916
$\omega_7 [\text{cm}^{-1}]$	958	967	957
$\omega_8 [\text{cm}^{-1}]$	1128	1133	1126
$\omega_9 [\text{cm}^{-1}]$	1312	1318	1317
$\omega_{10}  [{\rm cm}^{-1}]$	1418	1427	1431
$\omega_{11} [cm^{-1}]$	1566	1571	1570
$\omega_{12} [cm^{-1}]$	2864	2850	2869
$\omega_{13} [\rm cm^{-1}]$	2903	2891	2901
$\omega_{14}$ [cm <sup>-1</sup> ]	3179	3160	3167
$\omega_{15} [\text{cm}^{-1}]$	3741	3735	3734