Assessing counterion effects in gold-catalyzed Domino Spirocyclization: An Industrial Perspective on Hydrogen Bonding

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Table S1. Key optimized bond lengths[Å], stretching vibrational frequencies[cm $^{-}$], and Gibbs free energy and Gibbs energy barrier[kcal/mol] in Fig.1.

X^-	Species	R_{N-H}	R_{X-H}	θ_{N-H-X}	R_{X-N}	υ_{N-H}	Yield %	ΔG (kcal/mol)	$\Delta\Delta G^{\ddagger}$ (kcal/mol)
—	A-int1	1.013	—	—	—	3629.46	0	-6.2	26.1
	A-ts3	1.029	—	—	—	3508.67			
	A-int3	1.031	—	—	—	3340.47			
SbF_6^-	**B-int1**	**1.031**	**1.742**	**154.0**	**2.707**	**3354.16**	**75**	**-8.3**	**21.0**
	B-ts3	**1.029**	**1.787**	**143.1**	**2.682**	**3390.98**			
	B-int3	**1.047**	**1.606**	**168.7**	**2.641**	**3108.08**			
OTf^-	C-int1	1.055	1.646	161.9	2.669	2957.52	61	-7.2	25.5
	C-ts3	1.049	1.715	170.7	2.752	3100.59			
	C-int3	1.073	1.578	172.6	2.646	2663.62			
BF_4^-	D-int1	1.046	1.603	173.1	2.645	3107.45	0	-6.1	25.9
	D-ts3	1.039	1.674	175.9	2.712	3224.60			
	D-int3	1.043	1.689	154.4	2.668	3161.11			

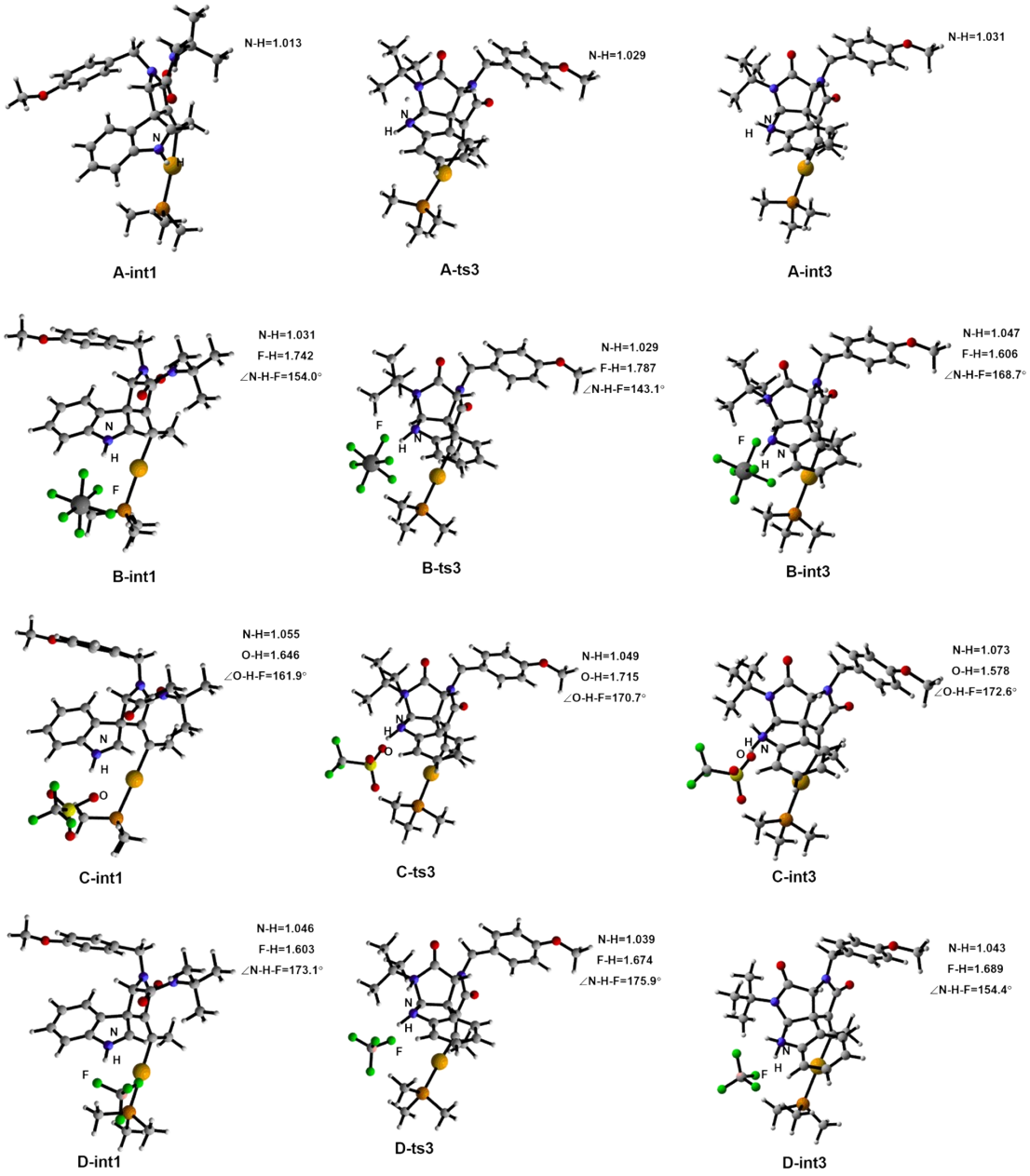

Fig. S1. Optimized TSs and intermediate structures in Fig. 1.

Table S2. Key optimized bond lengths[Å], stretching vibrational frequencies[cm $^{-}$], and Gibbs free energy and Gibbs energy barrier[kcal/mol] in Fig.2 .

X^-	Species	R_{O-H}	R_{X-H}	Θ_{O-H-X}	R_{X-O}	υ_{O-H}	character	Yield %	ΔG (kcal/mol)	$\Delta\Delta G^{\ddagger}$ (kcal/mol)
—	A-int1	0.968	—	—	—	3827.01	—	trace	-12.5	30.5
	A-ts3	0.967	—	—	—	3843.74	—			
	A-int3	0.971	—	—	—	3794.99	—			
OTf^-	**B-int1**	**1.192**	**1.200**	**178.4**	**2.391**	**1762.27**		95	-13.7	33.3
	B-ts3	**1.002**	**1.642**	**170.5**	**2.636**	**3202.42**				
	B-int3	**1.535**	**1.026**	**167.9**	**2.547**	**2763.17**				
$BF4^-$	C-int1	1.016	1.501	164.8	2.496	2988.38		12	-11.7	32.4
	C-ts3	1.002	1.562	173.2	2.560	3226.12				
	C-int3	1.060	1.347	174.9	2.404	2226.52				

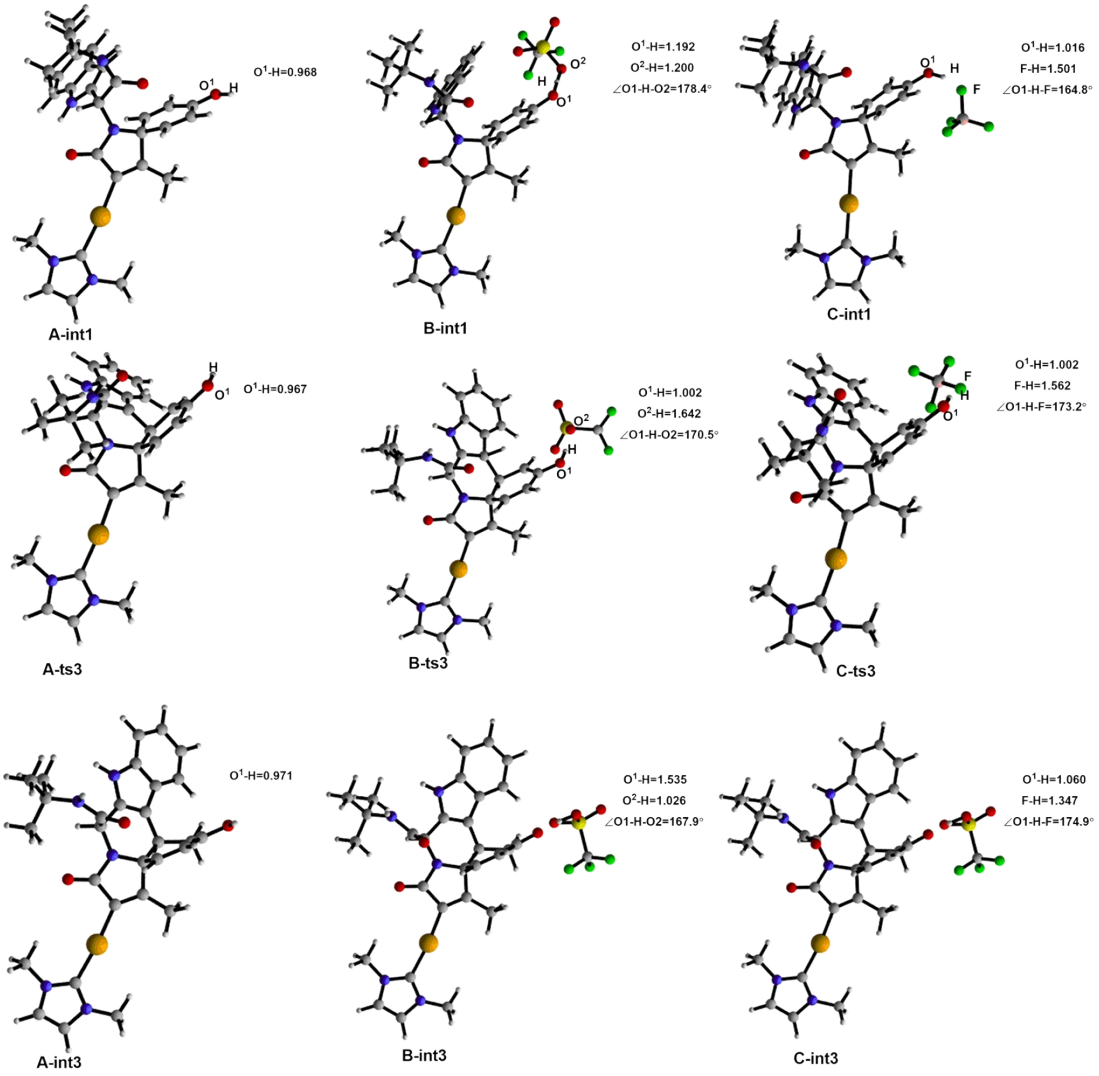

Fig. S2. Optimized TSs and intermediate structures in Fig. 2.

Table S3. Key optimized bond lengths[Å], stretching vibrational frequencies[cm $^{-}$], and Gibbs free energy and Gibbs energy barrier[kcal/mol] in Fig.3 .

	Species	R_{O-H}	R_{X-H}	θ_{O-H-X}	R_{X-O}	υ_{O-H}	Yield %	ΔG (kcal/mol)	$\Delta\Delta G^{\ddagger}$ (kcal/mol)
OMs^{-}	**A-1**	**0.984**	**1.738**	**157.4**	**2.673**	**3498.38**	**⩾95**	**4.5**	**20.5**
	A-ts1	**1.020**	**1.531**	**165.3**	**2.531**	**2794.72**			
	A-int1	**1.564**	**1.016**	**162.6**	**2.551**	**2869.99**			
OTf^{-}	**B-1**	0.978	1.818	152.5	2.570	3632.44	⩽5	11.4	20.9
	B-ts1	0.987	1.709	159.0	2.654	3414.94			
	B-int1	1.325	1.103	172.2	2.422	1867.00			
NTf_2^{-}	**C-1**	0.975	1.792	155.3	2.709	3693.41	⩽5	11.4	21.7
	C-ts1	0.980	1.792	162.0	2.740	3580.96			
	C-int1	1.036	1.472	172.7	2.503	2553.60			
—	**D-1**	0.965	—	—	—	3884.21	⩽5	11.5	21.0
	D-ts1	0.965	—	—	—	3879.87			
	D-int1	0.969	—	—	—	3832.58			

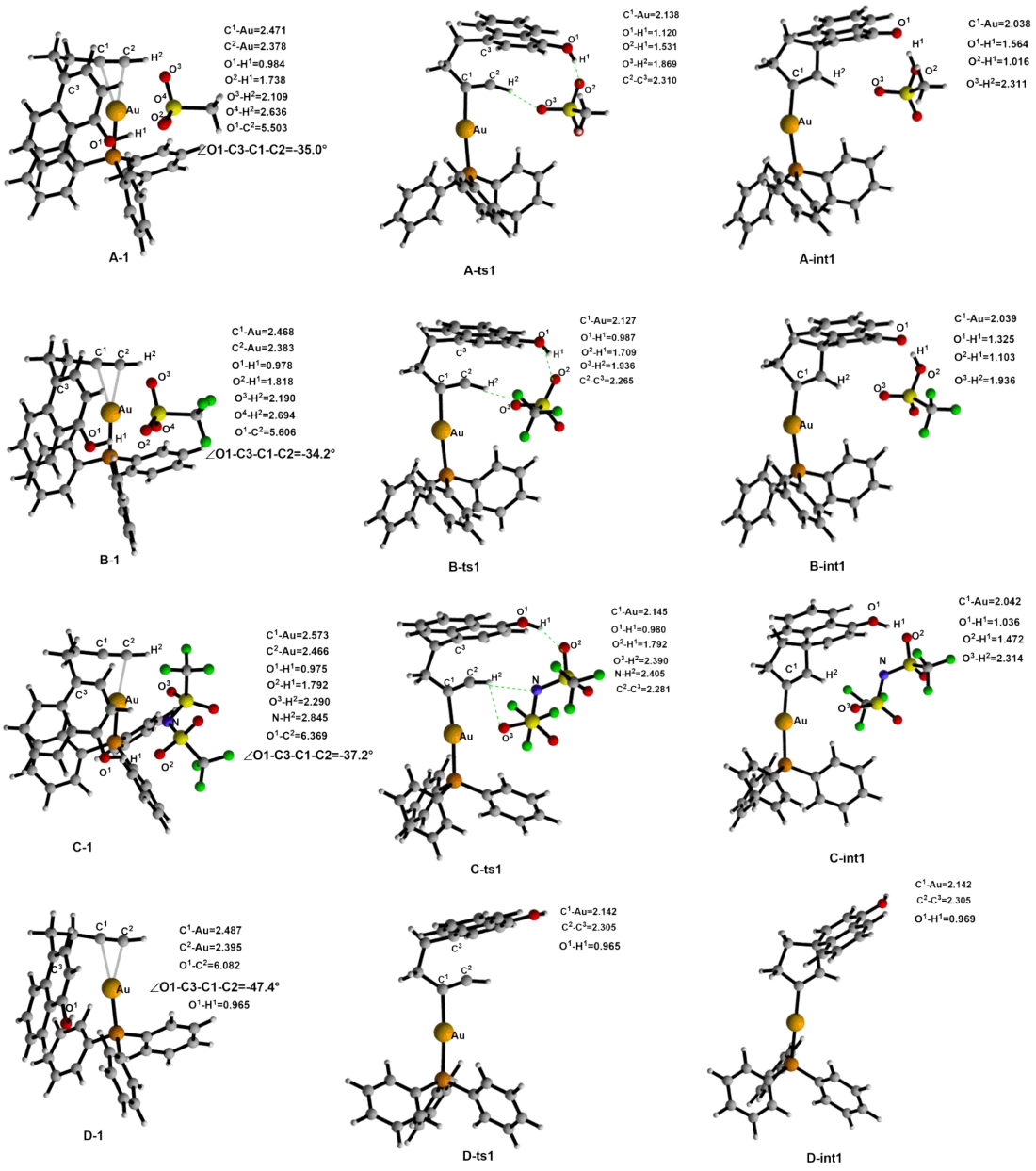

Fig. S3. Optimized TSs and intermediate structures in Fig. 3.

Table S4. Key optimized bond lengths[Å], stretching vibrational frequencies[cm $^{-}$], and Gibbs free energy and Gibbs energy barrier[kcal/mol] in Fig.4 .

	Species	$R_{X\text{-}Au}$	Yield %	ΔG (kcal/mol)	$\Delta\Delta G^{\ddagger}$ (kcal/mol)
OTf^{-}	**A-1**	**2.672**	**92**	**-24.6**	**28.0**
	A-ts1	**2.554**			
	A-int1	**2.144**			
NTf_2^{-}	**B-1**	2.162	0	-15.2	35.1
	B-ts1	2.788			
	B-int1	2.853			
Phenolic *Ugi* adduct as substrate	**C-1**	2.676	0	-21.2	29. 8
	C-ts1	2.548			
	C-int1	2.160			

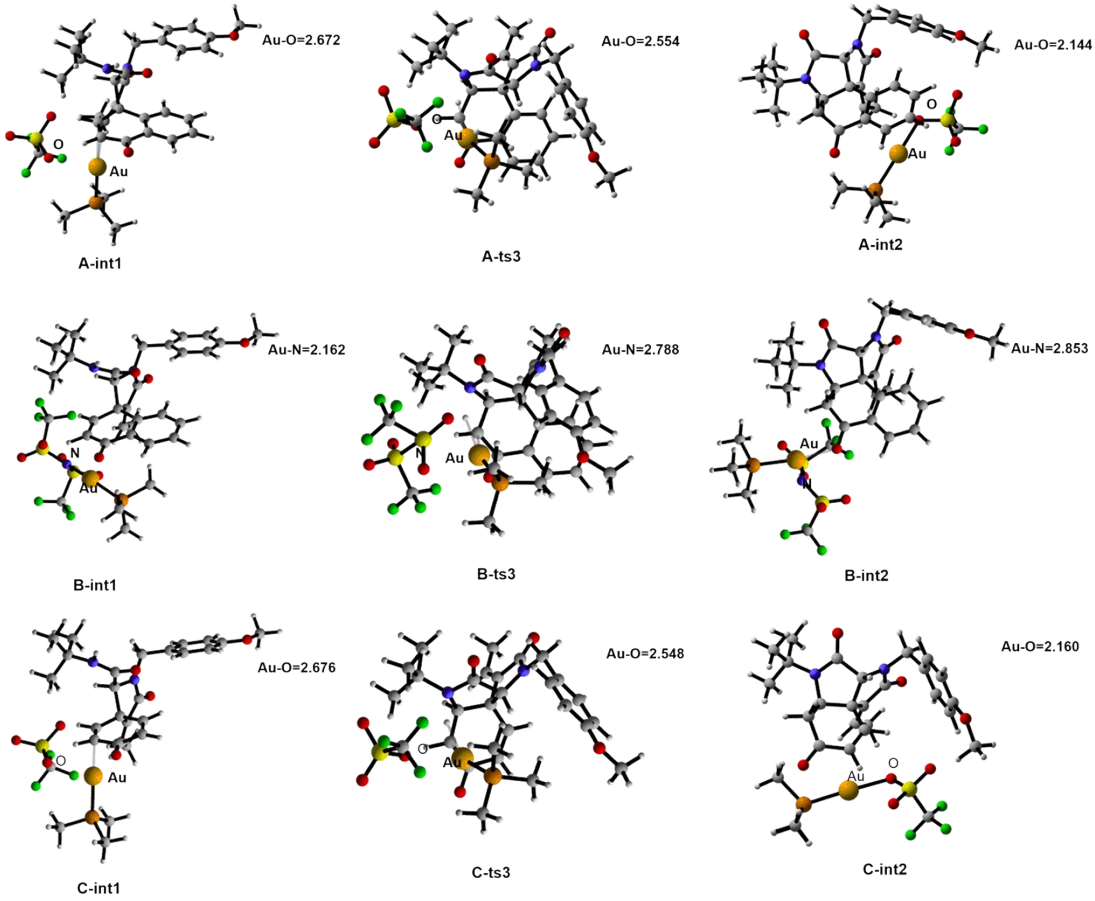

Fig. S4. Optimized TSs and intermediate structures in Fig.4.

Table S5. Key optimized bond lengths[Å], stretching vibrational frequencies[cm $^{-}$], and Gibbs free energy and Gibbs energy barrier[kcal/mol] in Fig.5 .

Substrate	Species	R_{O-H}	R_{X-H}	Θ_{O-H-X}	R_{X-O}	υ_{O-H}	Yield %	ΔG (kcal/mol)	$\Delta\Delta G^{\ddagger}$ (kcal/mol)
2	**2-int1**	**1.192**	**1.200**	**178.4**	**2.391**	**1762.27**	95	-13.7	33.3
	2-ts3	**1.002**	**1.642**	**170.5**	**2.636**	**3202.42**			
	2-int3	**1.535**	**1.026**	**167.9**	**2.547**	**2763.17**			
5	5-int1	1.205	1.185	177.1	2.389	1769.64	26	-11.3	41.2
	5-ts3	1.002	1.638	171.4	2.634	3201.12			
	5-int3	1.534	1.025	168.5	2.546	2773.98			
6	6-int1	1.250	1.152	177.3	2.401	1779.59	35	-22.7	49.2

	6-ts3	0.989	1.787	144.0	2.652	3470.66
	6-int3	1.554	1.019	172.2	2.568	2899.74

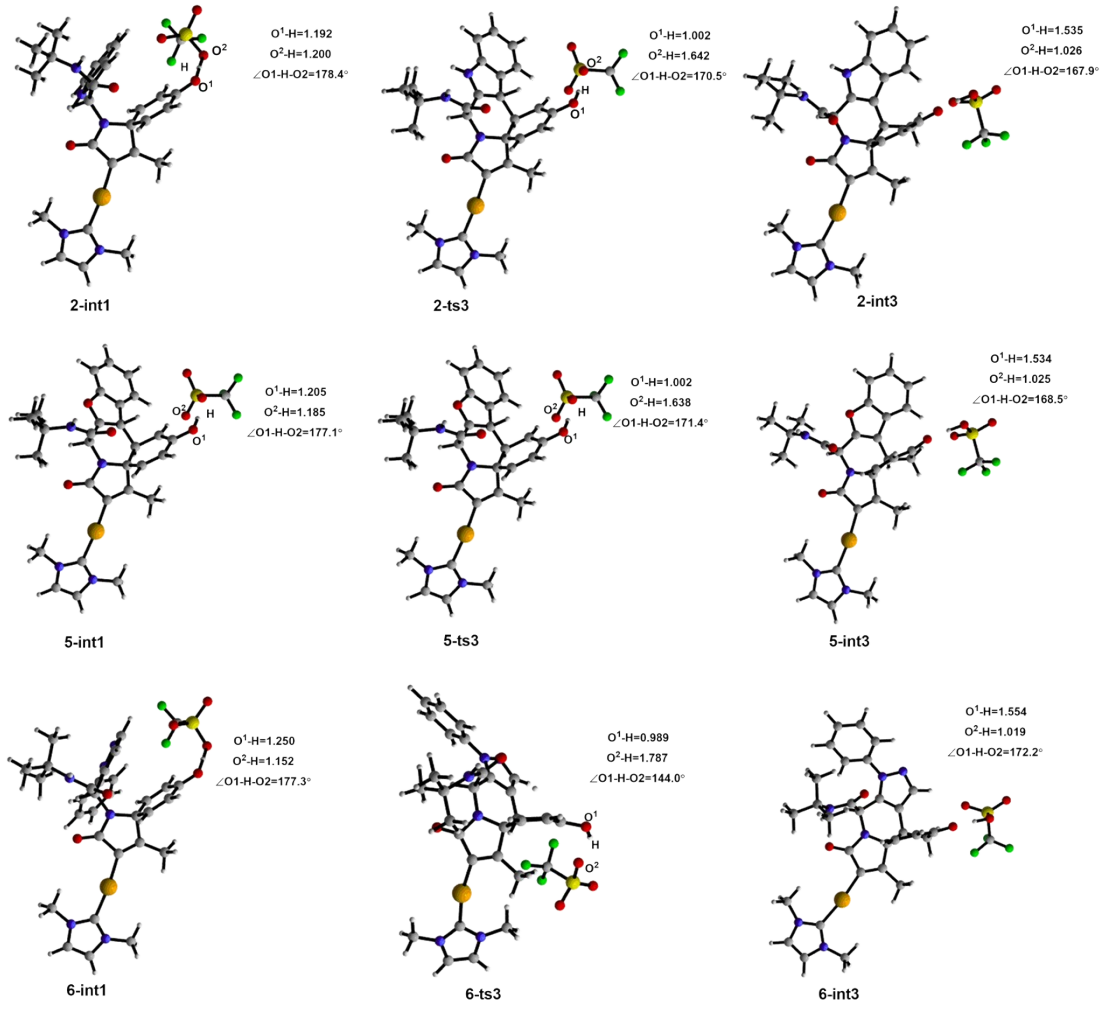

Fig. S5. Optimized TSs and intermediate structures in Fig. 5.

Table S6. Key optimized bond lengths[Å], stretching vibrational frequencies[cm $^{-}$], and Gibbs free energy and Gibbs energy barrier[kcal/mol] in Fig.6 .

X^-	Species	R_{O-H}	R_{X-H}	Θ_{O-H-X}	R_{X-O}	υ_{O-H}	ΔG^{gas} (kcal/mol)	$\Delta\Delta G^{\ddagger gas}$ (kcal/mol)
–	**A-int1**	0.968	–	–	–	3835.86	-6.3	23.0
	A-ts3	0.968	–	–	–	3830.12		
	A-int3	0.972	–	–	–	3761.68		

OTf^-	**B-int1**	**1.178**	**1.214**	**175.5**	**2.391**	**1731.44**	-11.6	33.0
	B-ts3	**1.015**	**1.551**	**155.9**	**2.512**	**2944.27**		
	B-int3	**1.484**	**1.035**	**161.2**	**2.487**	**2530.17**		
$BF4^-$	C-int1	1.016	1.494	170.4	2.501	2976.85	-21.0	23.2
	C-ts3	1.001	1.589	167.4	2.575	3264.00		
	C-int3	1.022	1.454	166.2	2.459	2867.15		
$NTf2^-$	D-int1	1.035	1.578	176.6	2.611	2473.82	-23.8	20.9
	D-ts3	1.014	1.652	168.4	2.653	2899.23		
	D-int3	1.646	1.057	172.5	2.698	2918.73		
OMs^-	E-int1	1.541	1.024	178.6	2.564	2773.04	-19.3	34.7
	E-ts3	1.188	1.205	173.3	2.389	1707.33		
	E-int3	1.628	1.005	173.5	2.628	3153.98		
$SbF6^-$	F-int1	0.999	1.577	173.6	2.573	3286.17	-9.5	22.1
	F-ts3	0.995	1.575	160.0	2.552	3351.81		
	F-int3	1.013	1.511	163.0	2.498	3045.72		

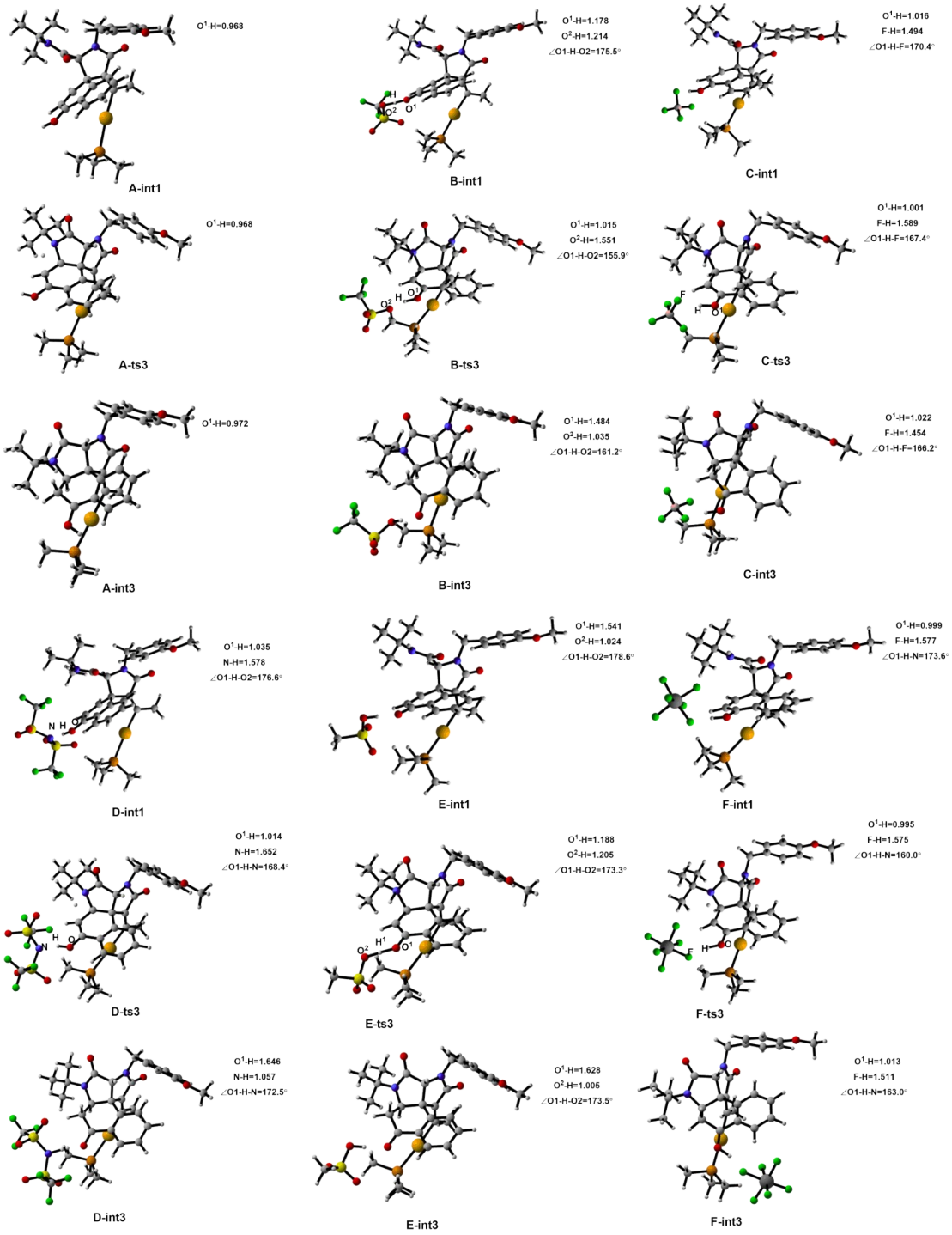

Fig. S6. Optimized TSs and intermediate structures in Fig. 6.