Quantum chemical study of the thiiranium ion intermediates and regioselectivity features of the halogenide addition

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Supplementary Information

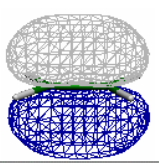
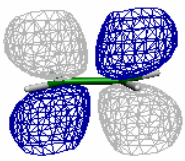
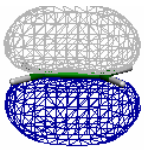
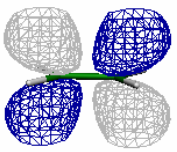
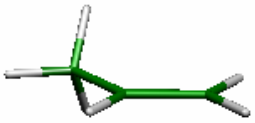
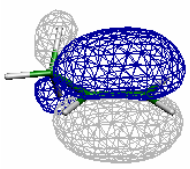
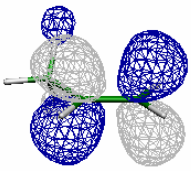
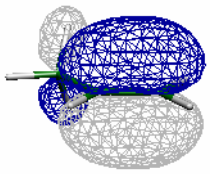
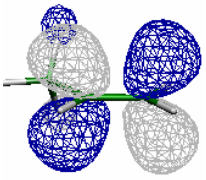
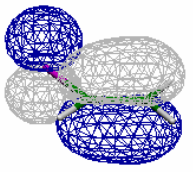
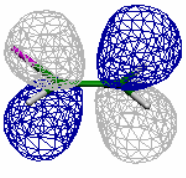
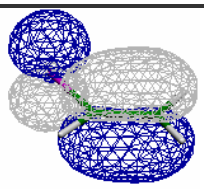
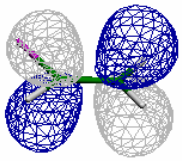
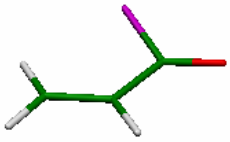
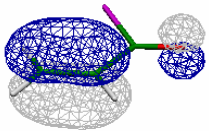
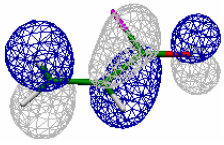
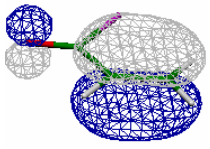
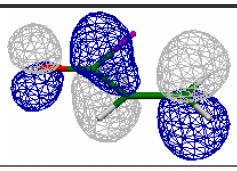
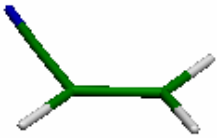
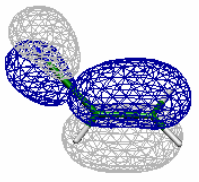
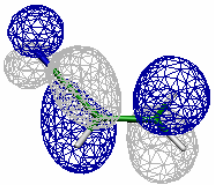
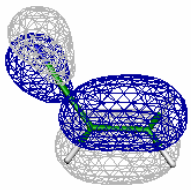
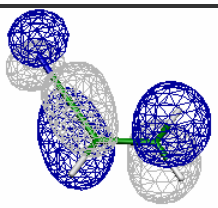
Table S1. Lowdin charge densities and total energies (E) in Hartrees of starting ethane **2** and substituted ethenes **2a-e** calculated in vacuum and solvent model using Ab initio Hartree-Fock method with 6-311+G basis

No	In vacuum			In solvated media		
	C(α)	C(β)	E	C(α)	C(β)	E
2	-0.18	-0.18	-78.01932	-0.26	-0.26	-78.02088
2a	-0.13	-0.24	-117.04680	-0.15	-0.37	-117.04826
2b	-0.19	-0.15	-536.92457	-0.29	-0.25	-536.92904
2c	-0.11	-0.15	-649.63344	-0.23	-0.23	-649.64228
2d	-0.03	-0.17	-169.72828	-0.08	-0.26	-169.73694
2e	-0.08	-0.22	-154.88605	-0.19	-0.34	-154.88836

Table S2. Lowdin charge densities and total energies (E) in Hartrees of episulfonium intermediates **3**, **3a-e** calculated in vacuum and solvent model using Ab initio Hartree-Fock method with 6-311+G basis

No	In vacuum				In solvated media			
	C(α)	C(β)	S	E	C(α)	C(β)	S	E
3	-0.14	-0.14	+0.55	-514.86094	-0.17	-0.17	+0.44	-514.94084
3a	+0.02	-0.09	+0.52	-553.89706	+0.01	-0.11	+0.60	-553.98091
3b	-0.12	-0.08	+0.52	-973.74231	-0.14	-0.11	+0.49	-973.82417
3c	-0.11	-0.05	+0.55	-1086.44031	-0.14	-0.07	+0.54	-1086.52807
3d	-0.24	-0.34	+0.06	-606.53547	-0.28	-0.40	+0.53	-606.62616
3e	-0.12	-0.55	+0.38	-591.74142	-0.14	-0.56	+0.21	-591.81818

Table S3. The HOMO and LUMO spatial distribution and energies (in Hartrees) presented for starting derivatives **2**, **2a-e** optimized at Ab initio Hartree-Fock 6-311+G level in vacuum and in solvated media using the polarizable continuum model (PCM) approach

Compound No 1	In vacuum 2		In solvated media 3	
				
2	**HOMO** -0.3791	**LUMO** +0.1613	**HOMO** -0.3828	**LUMO** -0.1568
				
2a	**HOMO** -0.3836	**LUMO** +0.1376	**HOMO** -0.3632	**LUMO** +0.1568
				
2b	**HOMO** -0.3863	**LUMO** +0.1376	**HOMO** -0.3878	**LUMO** +0.1415
				
2c	**HOMO** -0.4297	**LUMO** +0.0514	**HOMO** -0.4187	**LUMO** +0.0544
				
2d	**HOMO** -0.4002	**LUMO** +0.0885	**HOMO** -0.3954	**LUMO** +0.0931

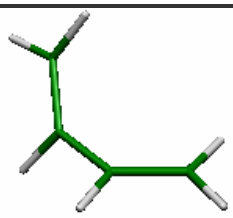
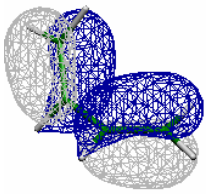
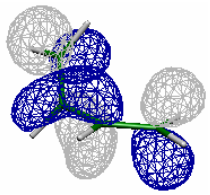
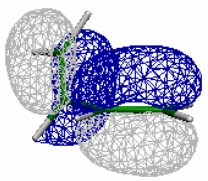
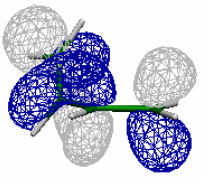
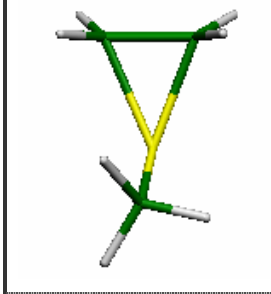
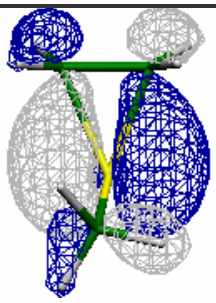
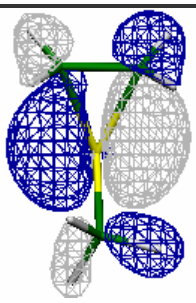
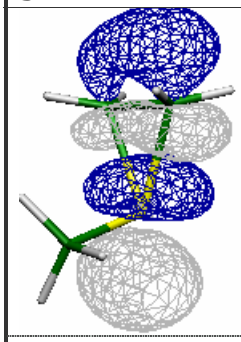
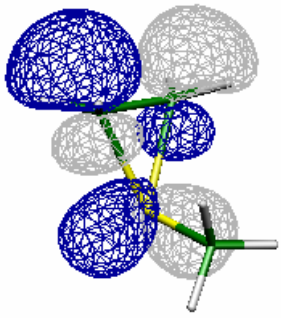
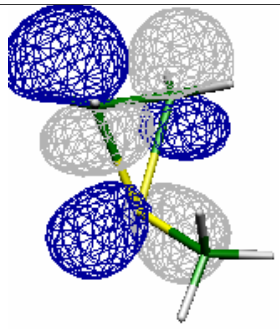
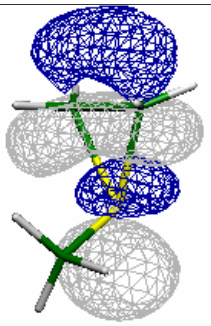
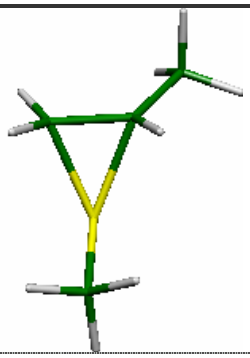
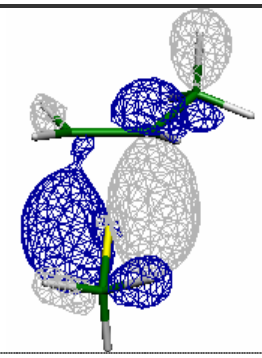
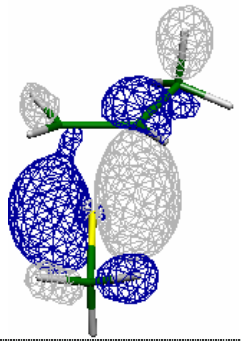
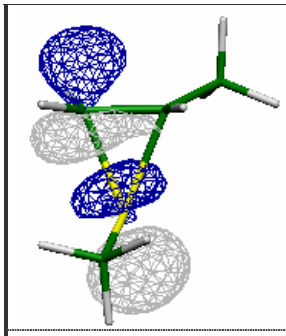
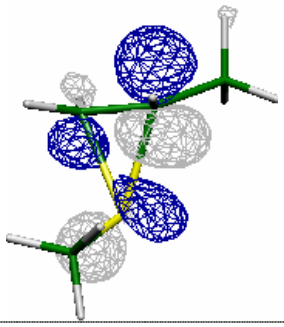
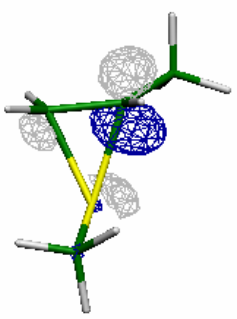
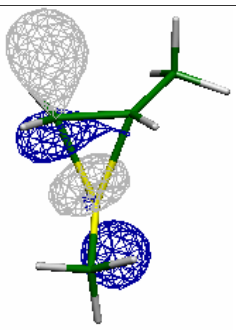
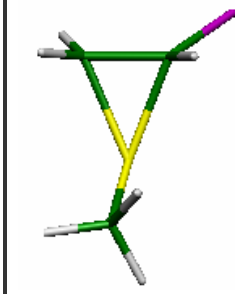
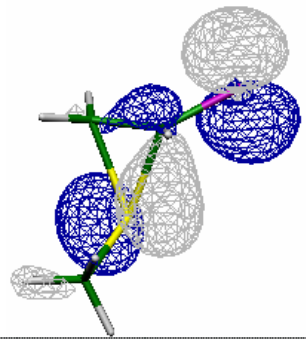
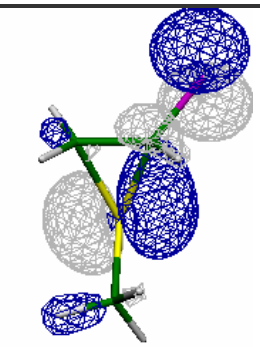
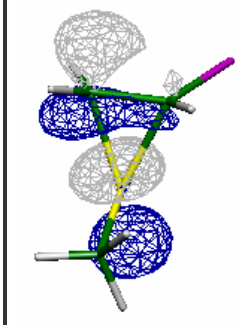
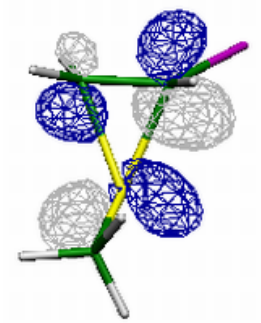
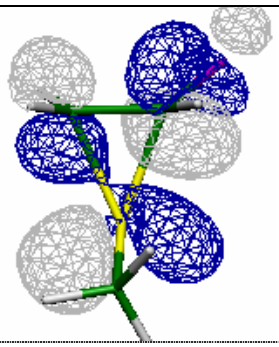
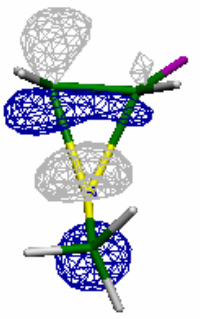
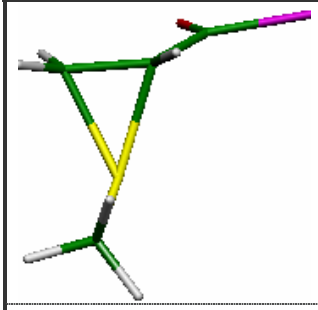
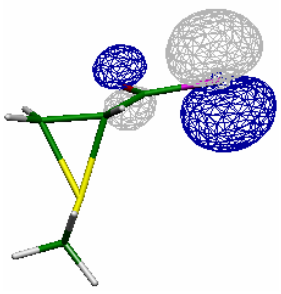
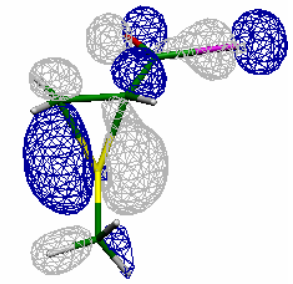
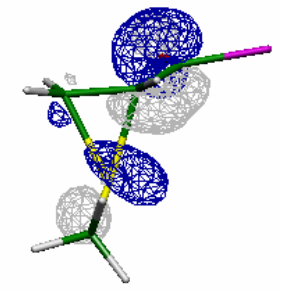
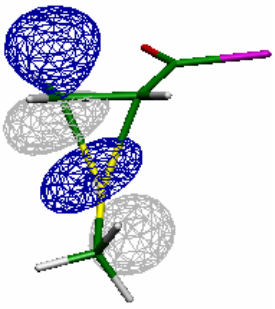
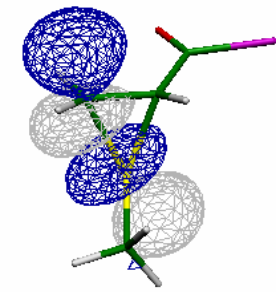
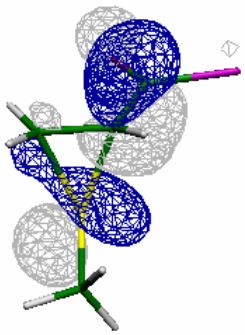
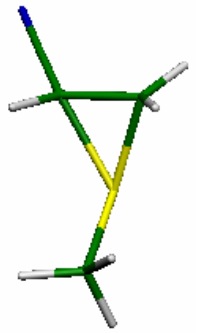
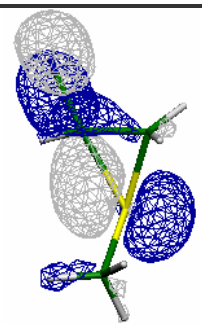
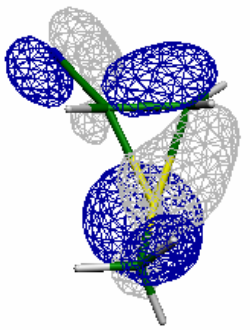
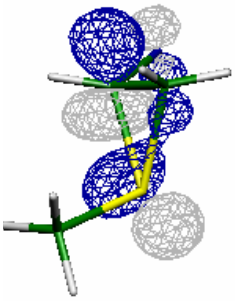
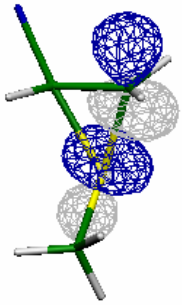
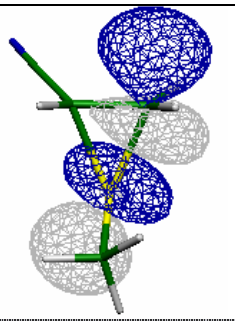
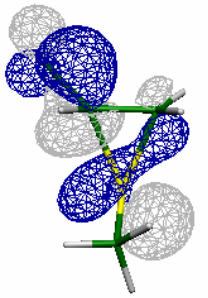
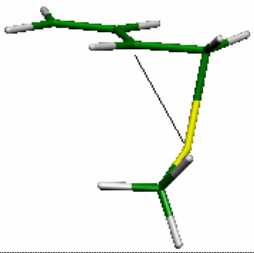
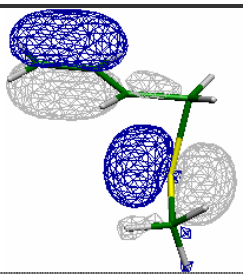
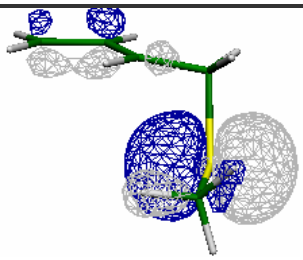
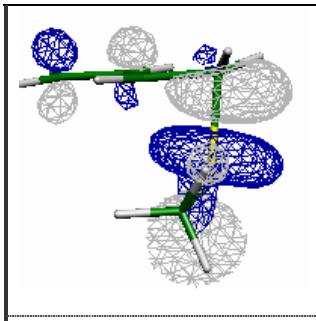
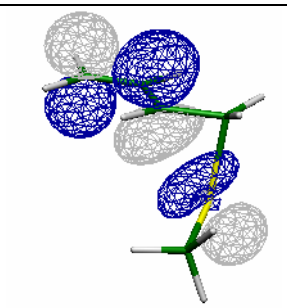
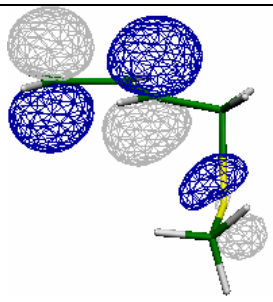
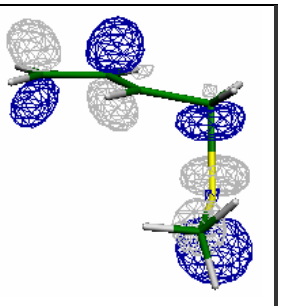
				
2e	**HOMO** -0.3483	**LUMO** +0.1387	**HOMO** -0.3517	**LUMO** +0.1342

Table S4. The HOMO, LUMO and LUMO+1 energies (in Hartrees) and shapes presented for reaction intermediates episulfonium derivatives **3**, **3a-e** optimized at Ab initio Hartree-Fock 6-311+G level in vacuum and in solvated media using the PCM approach

In vacuum		In solvated media	
1	2	3	4
			
3	**HOMO -0.6303**	**HOMO -0.4783**	
			
LUMO+1 -0.0721	**LUMO -0.0780**	**LUMO +0.0478**	**LUMO+1 +0.0528**
			
3a	**HOMO -0.6016**	**HOMO -0.4604**	

			
LUMO+1 -0.0562	**LUMO -0.0638**	**LUMO +0.0499**	**LUMO+1 +0.0513**
			
3b	**HOMO -0.6091**	**HOMO -0.4721**	
			
LUMO+1 -0.07550	**LUMO -0.0865**	**LUMO +0.0479**	**LUMO+1 +0.0513**
			
3c	**HOMO -0.6181**	**HOMO -0.4944**	

			
LUMO+1 -0.0923	**LUMO -0.1193**	**LUMO -0.0009**	**LUMO+1 +0.0078**
			
3d	**HOMO -0.6239**	**HOMO -0.4868**	
			
LUMO+1 -0.0979	**LUMO -0.1053**	**LUMO +0.0649**	**LUMO+1 +0.0629**
			
3e	**HOMO -0.5282**	**HOMO -0.3934**	

			
LUMO+1 -0.0308	**LUMO -0.1373**	**LUMO -0.0439**	**LUMO+1 +0.0048**