Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Mechanisms of acid generation from ionic photoacid generators for extreme ultraviolet and electron beam lithography

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Table S1. The VEA (eV) and BDE (eV) for different PAGs and ionic conformations calculated at the M062X-D3/6-311+G(d,p) level.

TPS-Tf							
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6	Average
VEA	1.84	1.61	1.68	1.64	1.64	1.78	1.70
BDE	0.23	0.22	0.23	0.18	0.15	0.23	0.21
M-TPS-Tf							
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6	Average
VEA	1.75	1.60	1.58	1.62	1.65	1.62	1.64
BDE	0.24	0.23	0.22	0.24	0.23	0.20	0.23
F-TPS-Tf							
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6	Average
VEA	1.83	1.66	1.66	1.67	1.85	1.85	1.75
BDE	0.28	0.26	0.25	0.23	0.28	0.27	0.26
TPS-Nf							
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6	Average
VEA	1.79	1.68	1.67	1.79	1.79	1.78	1.75
BDE	0.25	0.28	0.24	0.25	0.25	0.20	0.25
TPS-PF_6							
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6	Average
VEA	1.80	1.64	1.64	1.57	1.64	1.75	1.67
BDE	0.18	0.15	0.15	0.15	0.18	0.16	0.16
TPS-SbF_6							
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6	Average
VEA	1.64	1.63	1.63	1.63	1.64	1.62	1.63
BDE	0.16	0.19	0.19	0.20	0.23	0.20	0.20
TPS-TSM							
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6	Average
VEA	1.64	1.14	1.14	1.66	1.64	1.62	1.47
BDE	0.48	0.51	0.50	0.52	0.53	0.38	0.49
TPS-CPDI							
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6	Average
VEA	1.70	1.80	1.72	1.72	1.83	1.88	1.78
BDE	0.32	0.51	0.48	0.53	0.50	0.60	0.49
PAG-3							
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6	Average
VEA	1.73	1.82	1.82	1.80	1.80	1.80	1.80
BDE	0.38	0.45	0.45	0.45	0.45	0.52	0.45
PAG-4							
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6	Average
VEA	1.75	1.89	1.75	1.70	1.78	1.80	1.78
BDE	0.38	0.52	0.60	0.69	0.61	0.54	0.56
PAG-2-Nf							
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6	Average
VEA	1.63	1.46	1.68	1.47	1.54	1.52	1.55
BDE	0.23	0.22	0.39	0.26	0.26	0.37	0.29
PAG-1-Tf							
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6	Average
VEA	1.54	1.61	1.58	1.63	1.57	1.59	1.59
BDE	0.22	0.35	0.36	0.35	0.39	0.36	0.34
I-TPS-Tf							
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6	Average
VEA	1.95	1.71	1.95	1.74	1.86	1.97	1.86
BDE	0.25	0.19	0.24	0.20	0.29	0.31	0.25

PAG-5-Nf							
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6	Average
VEA	2.48	2.32	2.34	2.31	2.30	2.30	2.34
BDE	0.46	0.33	0.29	0.30	0.28	0.29	0.33
PAG-6-Tf							
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6	Average
VEA	2.49	2.52	2.51	2.54	2.54	2.54	2.52
BDE	0.24	0.22	0.22	0.22	0.22	0.22	0.22
PAG-7-Nf							
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6	Average
VEA	2.55	2.55	2.54	2.57	2.52	2.52	2.54
BDE	0.33	0.23	0.22	0.23	0.24	0.24	0.25
DPI-Tf							
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6	Average
VEA	2.03	2.12	2.12	2.12	2.12	2.11	2.10
BDE	0.12	0.12	0.12	0.12	0.11	0.14	0.12
DPI-Nf							
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6	Average
VEA	2.15	2.11	2.13	2.13	2.13	2.12	2.13
BDE	0.13	0.15	0.14	0.14	0.13	0.14	0.14
BBI-Tf							
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6	Average
VEA	1.92	2.02	2.01	1.92	2.01	2.00	1.98
BDE	0.11	0.11	0.11	0.11	0.11	0.19	0.12
BBI-Nf							
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6	Average
VEA	2.00	1.98	1.99	1.99	1.92	1.92	1.97
BDE	0.13	0.12	0.14	0.12	0.14	0.21	0.14
BBI-TSM							
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6	Average
VEA	2.20	2.31	2.32	2.33	2.23	2.24	2.27
BDE	0.21	0.26	0.25	0.25	0.35	0.32	0.27
PAG-8-Nf							
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6	Average
VEA	1.91	1.88	1.89	1.89	1.88	1.88	1.89
BDE	0.23	0.03	0.22	0.22	0.18	0.18	0.18
BBI-CPDI							
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6	Average
VEA	1.70	2.11	2.29	2.29	2.30	1.89	2.10
BDE	0.14	0.33	0.32	0.32	0.32	0.33	0.29
PAG-9-Tf							
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6	Average
VEA	1.55	1.60	1.46	1.42	1.46	1.53	1.50
BDE	—	—	0.14	—	0.14	0.16	0.15
PAG-10-Nf							
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6	Average
VEA	2.15	2.11	2.10	1.98	1.99	2.14	2.08
BDE	—	—	—	0.22	0.22	—	0.22

Table S2. The Laplacian bond order (LBO) of S-C/I-C bonds for different PAGs and ionic conformations calculated at the M062X-D3/6-311+G(d,p) level.

TPS-Tf						
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6
S_1-C_1	0.6662	0.6641	0.6690	0.6744	0.6744	0.6604
S_1-C_2	0.6468	0.6528	0.6738	0.6670	0.6669	0.6796
S_1-C_3	0.6889	0.6791	0.6636	0.6950	0.6948	0.6700
M-TPS-Tf						
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6
S_1-C_1	0.6799	0.6680	0.6736	0.6716	0.6690	0.6732
S_1-C_2	0.6523	0.6799	0.6784	0.6603	0.6752	0.6663
S_1-C_3	0.6808	0.6646	0.6680	0.6788	0.6636	0.6579
F-TPS-Tf						
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6
S_1-C_1	0.6886	0.6729	0.6930	0.6941	0.6607	0.6607
S_1-C_2	0.6522	0.6483	0.6794	0.6513	0.6811	0.6811
S_1-C_3	0.6780	0.6795	0.6483	0.6680	0.6653	0.6653
TPS-Nf						
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6
S_1-C_1	0.6650	0.6653	0.6592	0.6650	0.6649	0.6836
S_1-C_2	0.6493	0.6572	0.6655	0.6493	0.6493	0.6726
S_1-C_3	0.6739	0.6738	0.6777	0.6739	0.6739	0.6515
TPS-PF_6						
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6
S_1-C_1	0.6735	0.6827	0.6626	0.6672	0.6591	0.6582
S_1-C_2	0.6546	0.6924	0.6790	0.6869	0.6790	0.6667
S_1-C_3	0.6758	0.6913	0.6733	0.6755	0.6649	0.6777
TPS-SbF_6						
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6
S_1-C_1	0.6645	0.6781	0.6773	0.6810	0.6646	0.6819
S_1-C_2	0.6690	0.6828	0.6795	0.6758	0.6690	0.6879
S_1-C_3	0.6611	0.6766	0.6799	0.6837	0.6611	0.6767
TPS-TSM						
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6
S_1-C_1	0.6689	0.6745	0.6676	0.6618	0.6478	0.6601
S_1-C_2	0.6674	0.6725	0.6719	0.6703	0.6655	0.6632
S_1-C_3	0.6736	0.6738	0.6688	0.6511	0.6630	0.6584
TPS-CPDI						
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6
S_1-C_1	0.6728	0.6602	0.6562	0.6562	0.6725	0.6662
S_1-C_2	0.6732	0.6751	0.6801	0.6601	0.6815	0.6428
S_1-C_3	0.6823	0.6664	0.6601	0.6802	0.6598	0.6702
PAG-3						
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6
S_1-C_1	0.6695	0.6652	0.6908	0.6624	0.6624	0.6595
S_1-C_2	0.6680	0.6418	0.6650	0.6519	0.6518	0.6523
S_1-C_3	0.6956	0.6909	0.6419	0.6847	0.6848	0.6861
PAG-4						
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6
S_1-C_1	0.6747	0.6583	0.6788	0.6533	0.6544	0.6439
S_1-C_2	0.6784	0.6658	0.6532	0.6736	0.6627	0.6678
S_1-C_3	0.6477	0.6845	0.6641	0.6736	0.6779	0.6872
PAG-2-Nf						
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6

S_1-C_1	0.6795	0.6712	0.6722	0.6658	0.6667	0.6521
S_1-C_2	0.6467	0.6769	0.6496	0.6868	0.6827	0.6790
S_1-C_3	0.7000	0.6942	0.6789	0.6755	0.6873	0.6616
PAG-1-Tf						
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6
S_1-C_1	0.6689	0.6726	0.6775	0.6746	0.6789	0.6730
S_1-C_2	0.5790	0.5587	0.5676	0.5542	0.5672	0.5507
S_1-C_3	0.6856	0.7077	0.7032	0.7131	0.7015	0.7153
I-TPS-Tf						
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6
S_1-C_1	0.6810	0.6737	0.6815	0.6748	0.6886	0.6881
S_1-C_2	0.6501	0.6591	0.6508	0.6703	0.6570	0.6681
S_1-C_3	0.6836	0.6816	0.6844	0.6671	0.6676	0.6537
PAG-5-Nf						
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6
S_1-C_1	0.6245	0.6284	0.6284	0.6284	0.6268	0.6213
S_1-C_2	0.6767	0.6782	0.6782	0.6782	0.6754	0.6667
S_1-C_3	0.7048	0.6961	0.6961	0.6961	0.7022	0.6979
PAG-6-Tf						
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6
I_1-C_1	0.3922	0.4044	0.4080	0.4101	0.4100	0.3914
I_1-C_2	0.4041	0.3949	0.4005	0.3914	0.3913	0.4101
PAG-7-Nf						
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6
I_1-C_1	0.3850	0.4067	0.4012	0.3833	0.4065	0.4065
I_1-C_2	0.4101	0.3835	0.3934	0.4167	0.3995	0.3996
DPI-Tf						
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6
I_1-C_1	0.3125	0.3669	0.3668	0.2996	0.3669	0.3089
I_1-C_2	0.3693	0.3008	0.2996	0.3666	0.3007	0.3692
DPI-Nf						
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6
I_1-C_1	0.2923	0.3029	0.3674	0.3060	0.3061	0.3034
I_1-C_2	0.3750	0.3725	0.3044	0.3639	0.3636	0.3713
BBI-Tf						
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6
I_1-C_1	0.3178	0.2998	0.3061	0.3164	0.3061	0.3054
I_1-C_2	0.3577	0.3695	0.3640	0.3563	0.3641	0.3628
BBI-Nf						
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6
I_1-C_1	0.3029	0.3061	0.3105	0.3105	0.3152	0.3152
I_1-C_2	0.3651	0.3606	0.3627	0.3627	0.3652	0.3652
BBI-TSM						
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6
I_1-C_1	0.2670	0.3132	0.3153	0.3144	0.2767	0.2693
I_1-C_2	0.3429	0.2785	0.2764	0.2757	0.3304	0.3329
PAG-8-Nf						
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6
I_1-C_1	0.3062	0.3827	0.3131	0.3817	0.3156	0.3853
I_1-C_2	0.3834	0.3124	0.3817	0.3131	0.3854	0.3155
BBI-CPDI						
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6
I_1-C_1	0.3460	0.2817	0.2990	0.2801	0.2810	0.2921
I_1-C_2	0.2952	0.2834	0.2801	0.2989	0.2992	0.2871
PAG-9-Tf						

	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6
S_1-C_1	0.6712	0.6923	0.6902	0.6646	0.6907	0.6696
S_1-C_2	0.6225	0.6117	0.5940	0.6307	0.6309	0.6367
S_1-C_3	0.7042	0.7017	0.6881	0.6895	0.6692	0.7041
PAG-10-Nf						
	Conformation 1	Conformation 2	Conformation 3	Conformation 4	Conformation 5	Conformation 6
S_1-C_1	0.6249	0.6369	0.6380	0.6356	0.6199	0.6416
S_1-C_2	0.6582	0.6675	0.6617	0.6600	0.6543	0.6955
S_1-C_3	0.6866	0.6935	0.7042	0.6814	0.6833	0.6663

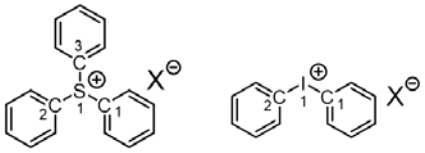
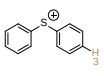
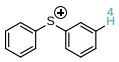


Table S3. Calculated energy barriers (eV) for the PAG anion (Tf^-) capturing a proton from DPS^+.

Position of proton					
Proton transfer energy (eV)	1.39	1.42	1.32	1.47	1.60

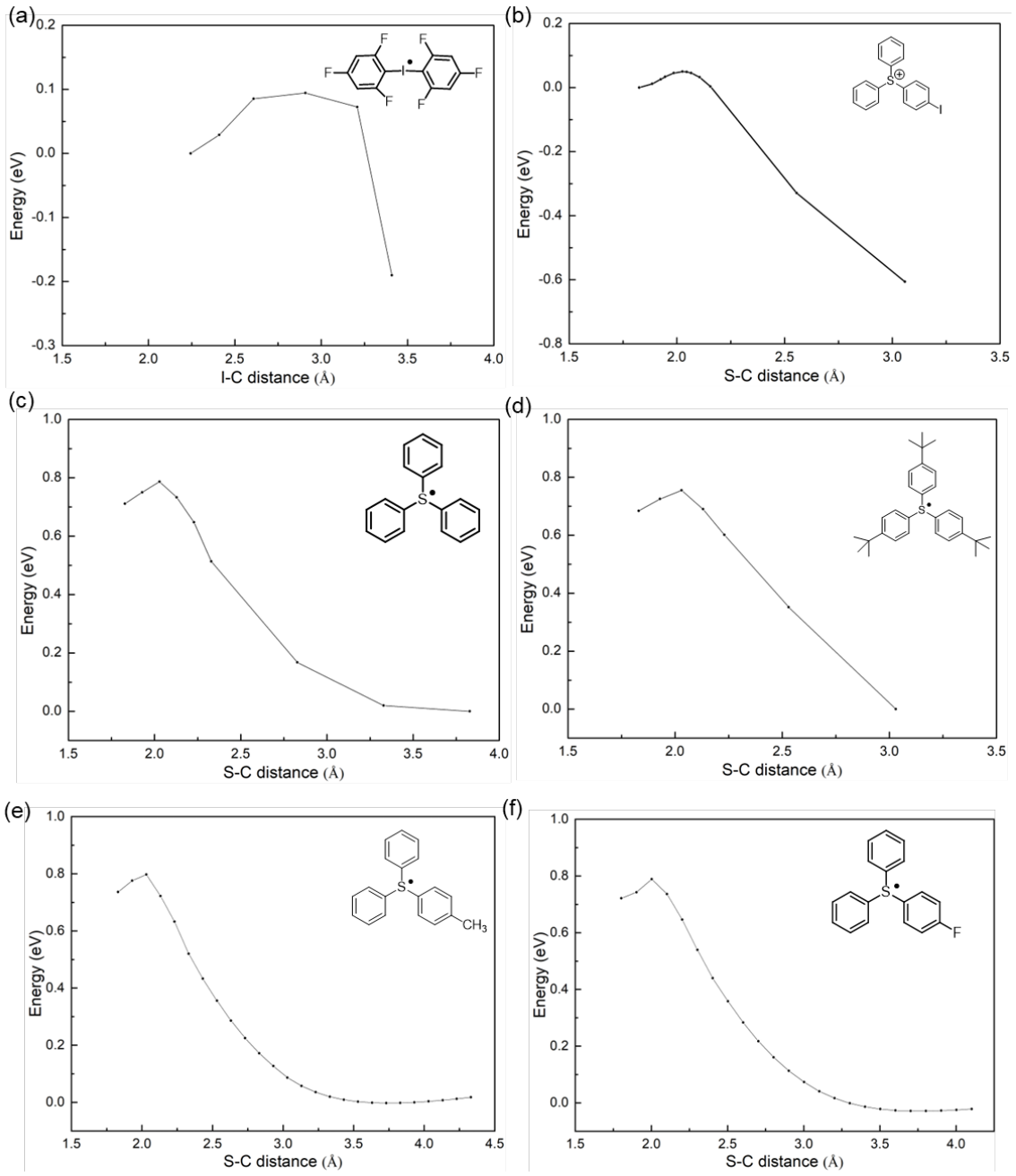


Figure S1. The potential energy as a function of the S-C/I-C bond length: (a) the radical dissociated from PAG-6-Tf and PAG-7-Nf, (b) the radical dissociated from I-TPS-Tf, (c) the radical dissociated from TPS-Tf, TPS-Nf, TPS-PF_6, TPS-SbF_6, TPS-TSM, TPS-CPDI, PAG-3, and PAG-4, (d) the radical dissociated from PAG-2-Nf, (e) the radical dissociated from M-TPS-Tf, and (f) the radical dissociated from F-TPS-Tf.

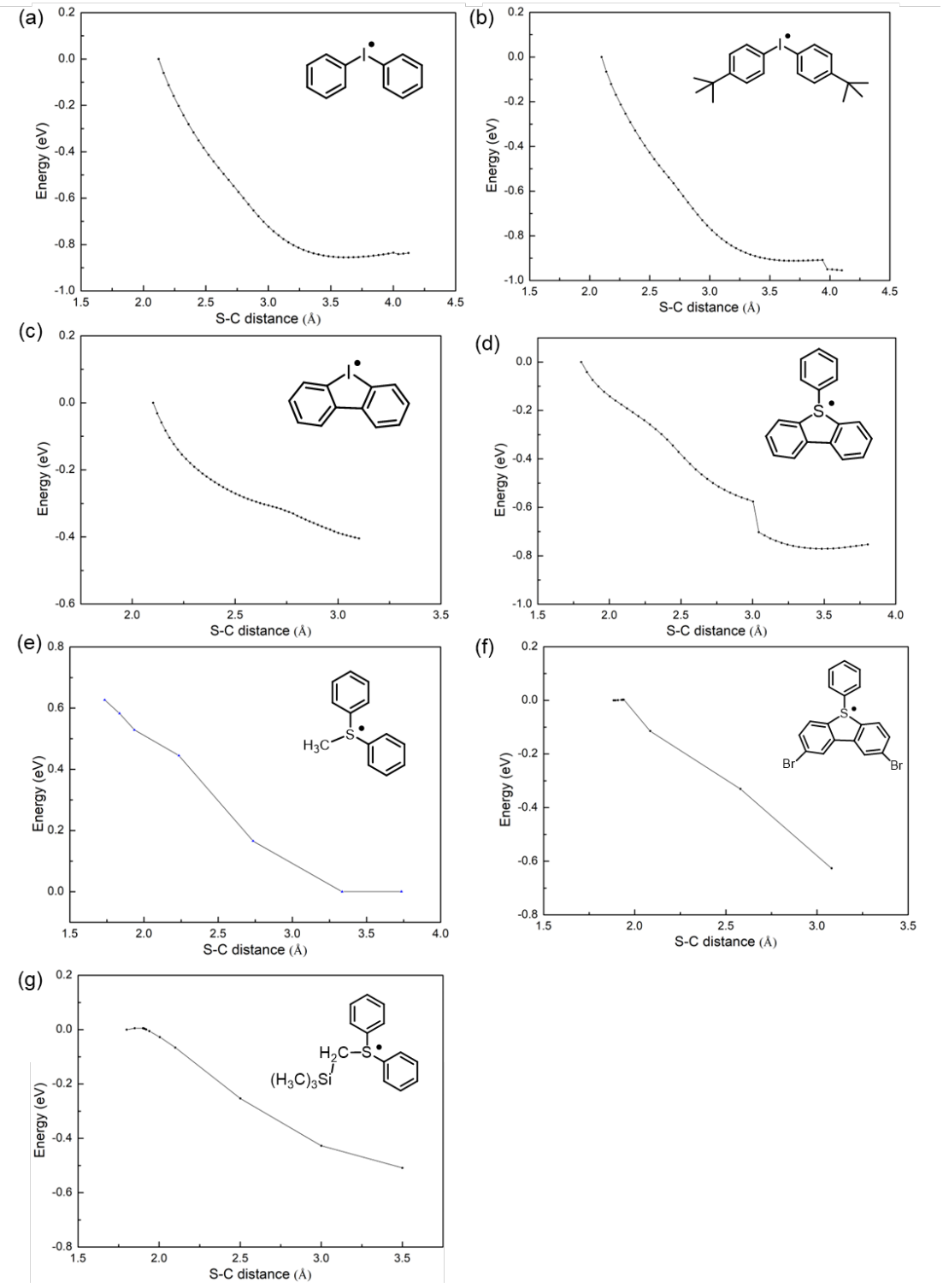


Figure S2. The potential energy as a function of the S-C/I-C bond length: (a) the radical dissociated from DPI-Tf and DPI-Nf, (b) the radical dissociated from BBI-Tf, BBI-Nf, BBI-TSM and BBI-CPDI, (c) the radical dissociated from PAG-8-Nf, (d) the radical dissociated from PAG-10-Nf (e) the radical dissociated from PAG-9-Tf, (f) the radical dissociated from PAG-5-Nf, and (g) the radical dissociated from PAG-1-Tf.

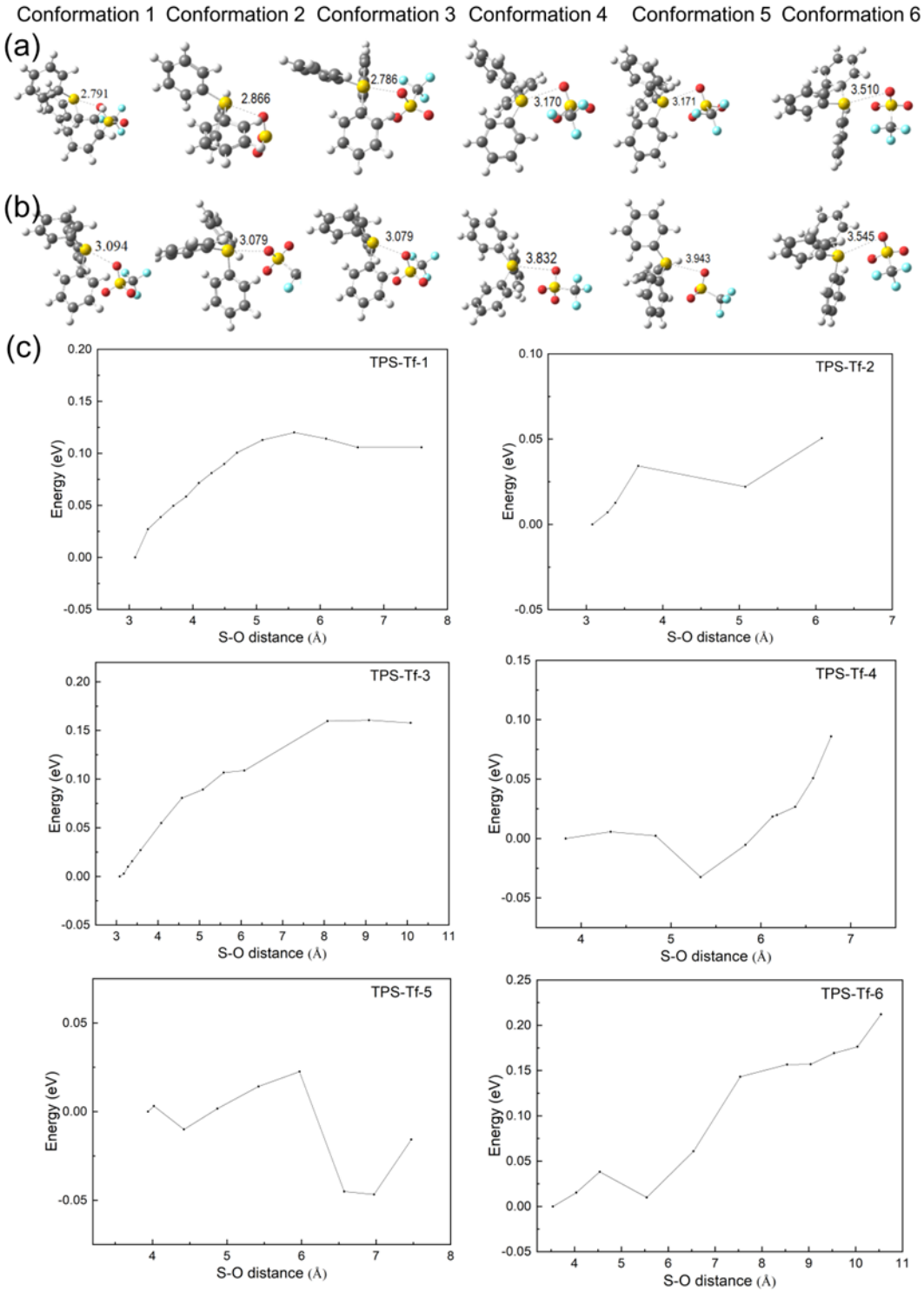


Figure S3. (a) The six different conformations of TPS-Tf before secondary electron attachment. (b) The six different conformations of TPS-Tf after secondary electron attachment. (c) The potential energy as a function of the S-O bond length for the six different conformations of TPS-Tf after secondary electron attachment.

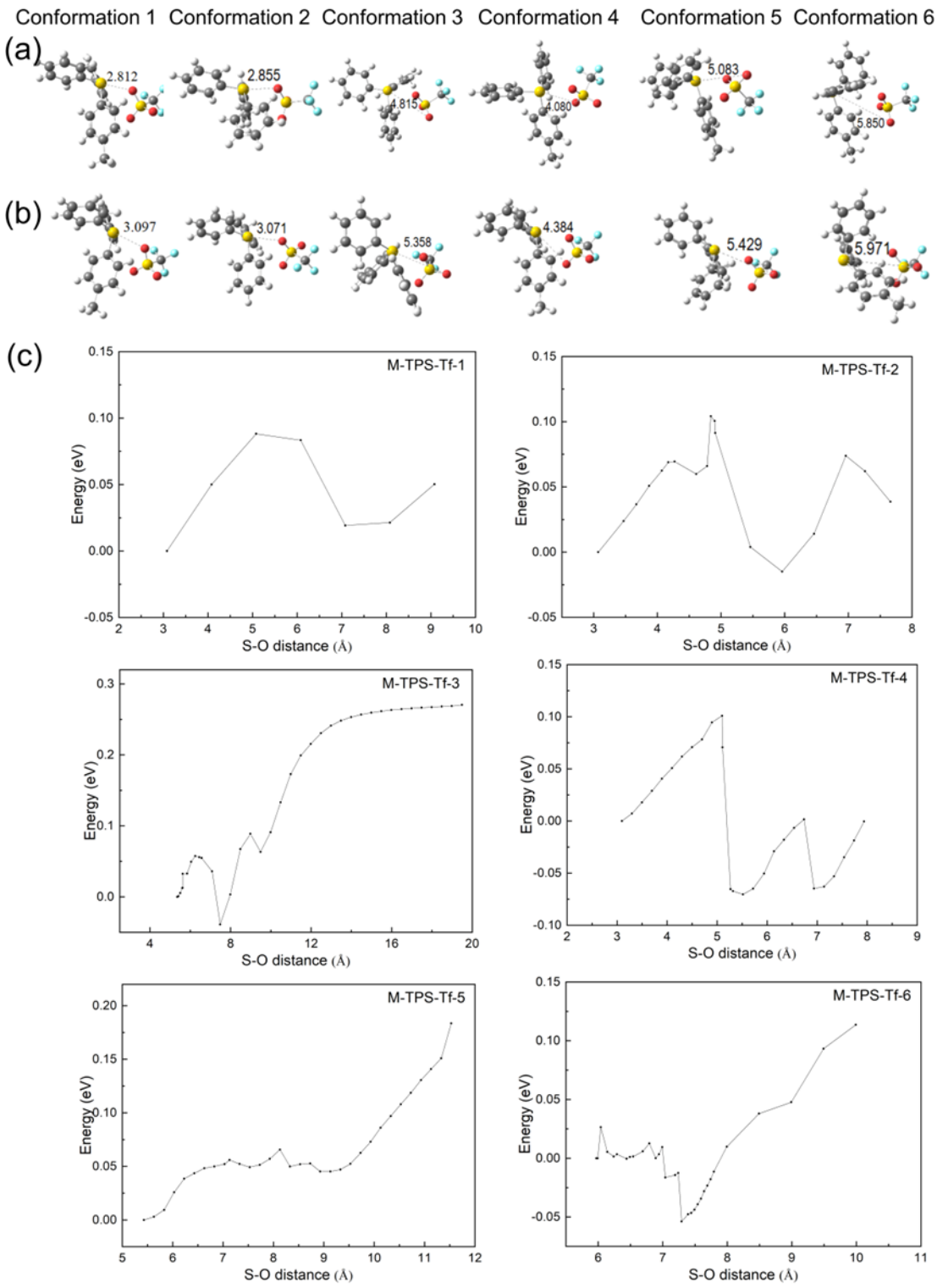


Figure S4. (a) The six different conformations of M-TPS-Tf before secondary electron attachment. (b) The six different conformations of M-TPS-Tf after secondary electron attachment. (c) The potential energy as a function of the S-O bond length for the six different conformations of M-TPS-Tf after secondary electron attachment.

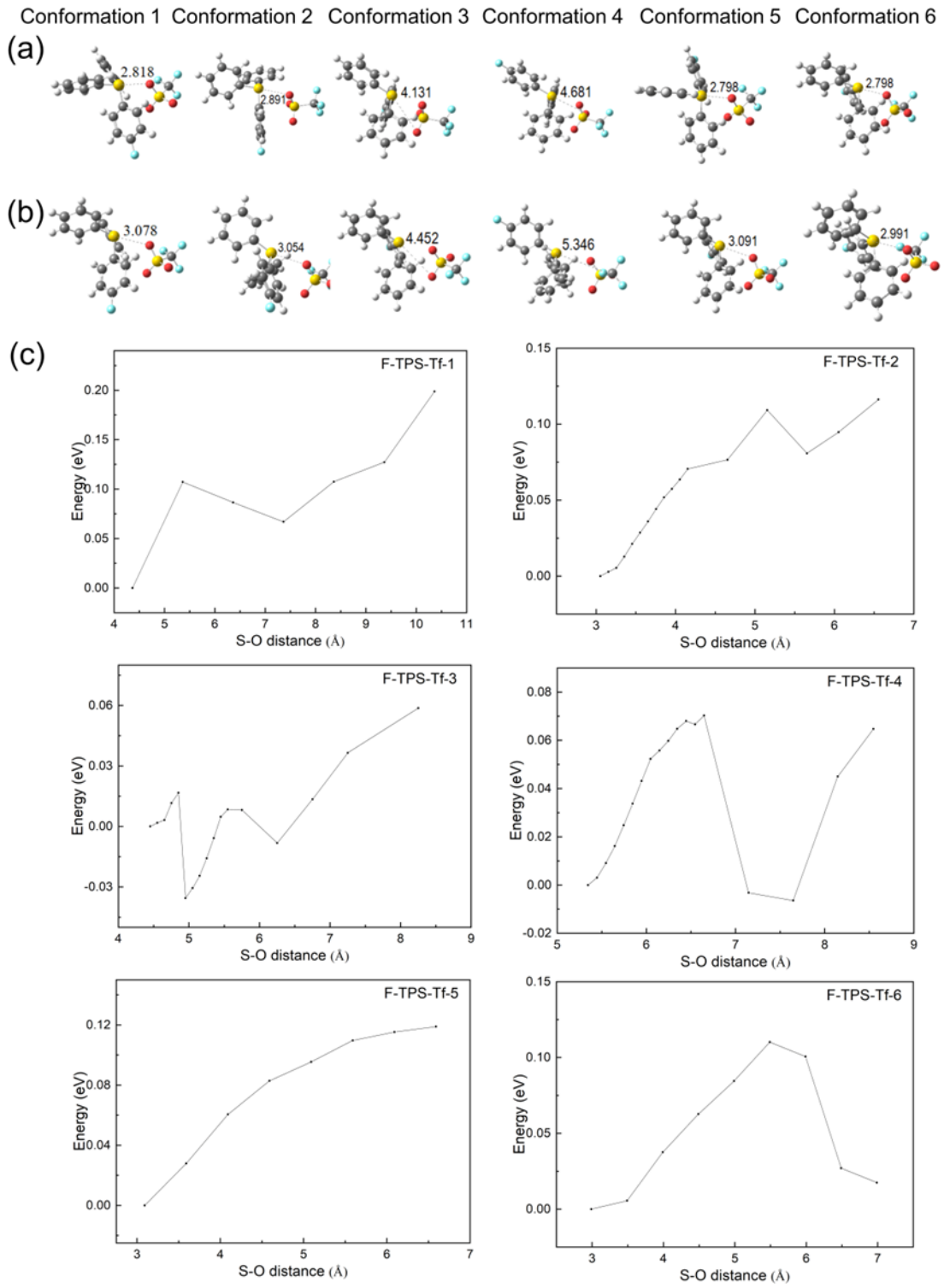


Figure S5. (a) The six different conformations of F-TPS-Tf before secondary electron attachment. (b) The six different conformations of F-TPS-Tf after secondary electron attachment. (c) The potential energy as a function of the S-O bond length for the six different conformations of F-TPS-Tf after secondary electron attachment.

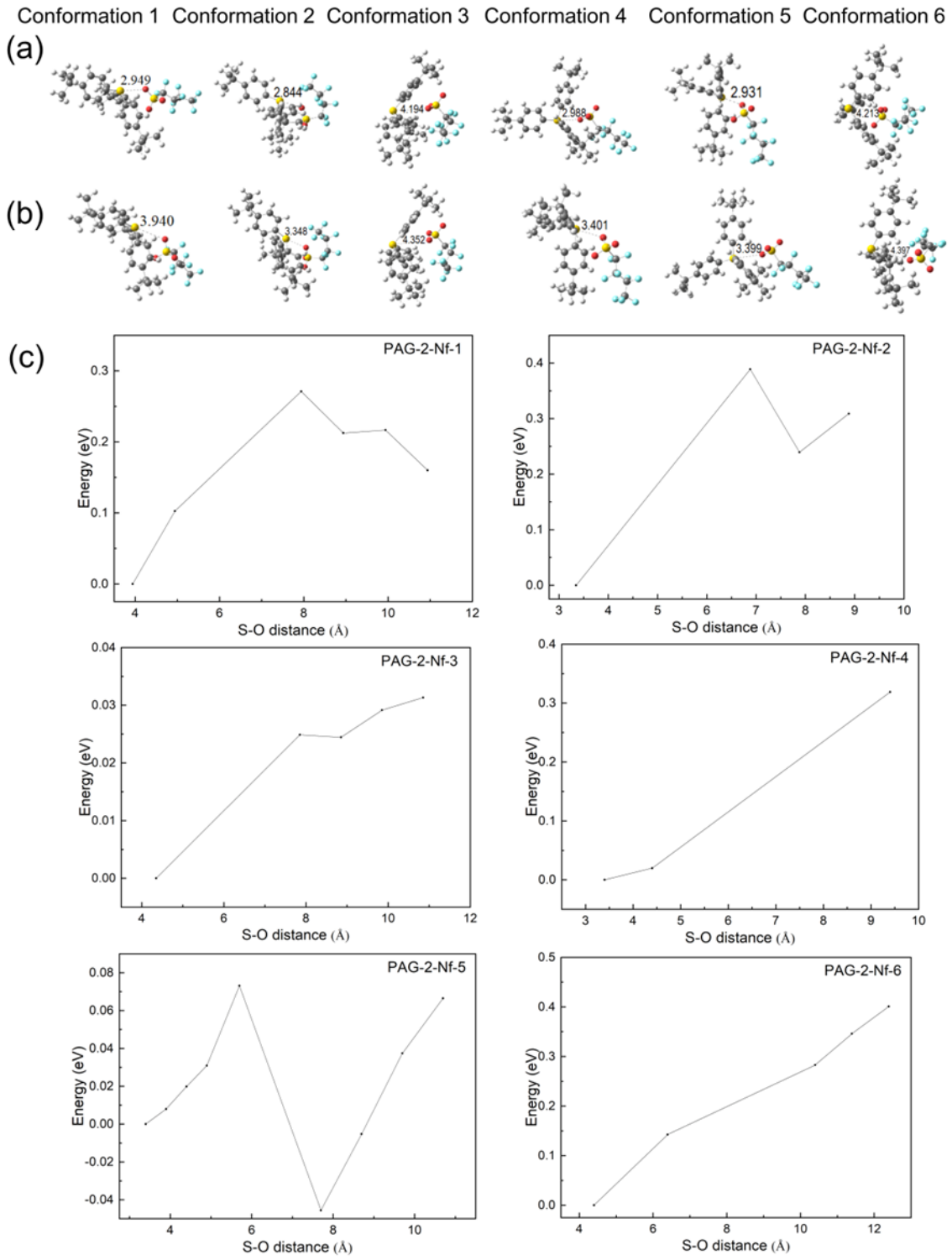


Figure S6. (a) The six different conformations of PAG-2-Nf before secondary electron attachment. (b) The six different conformations of PAG-2-Nf after secondary electron attachment. (c) The potential energy as a function of the S-O bond length for the six different conformations of PAG-2-Nf after secondary electron attachment.

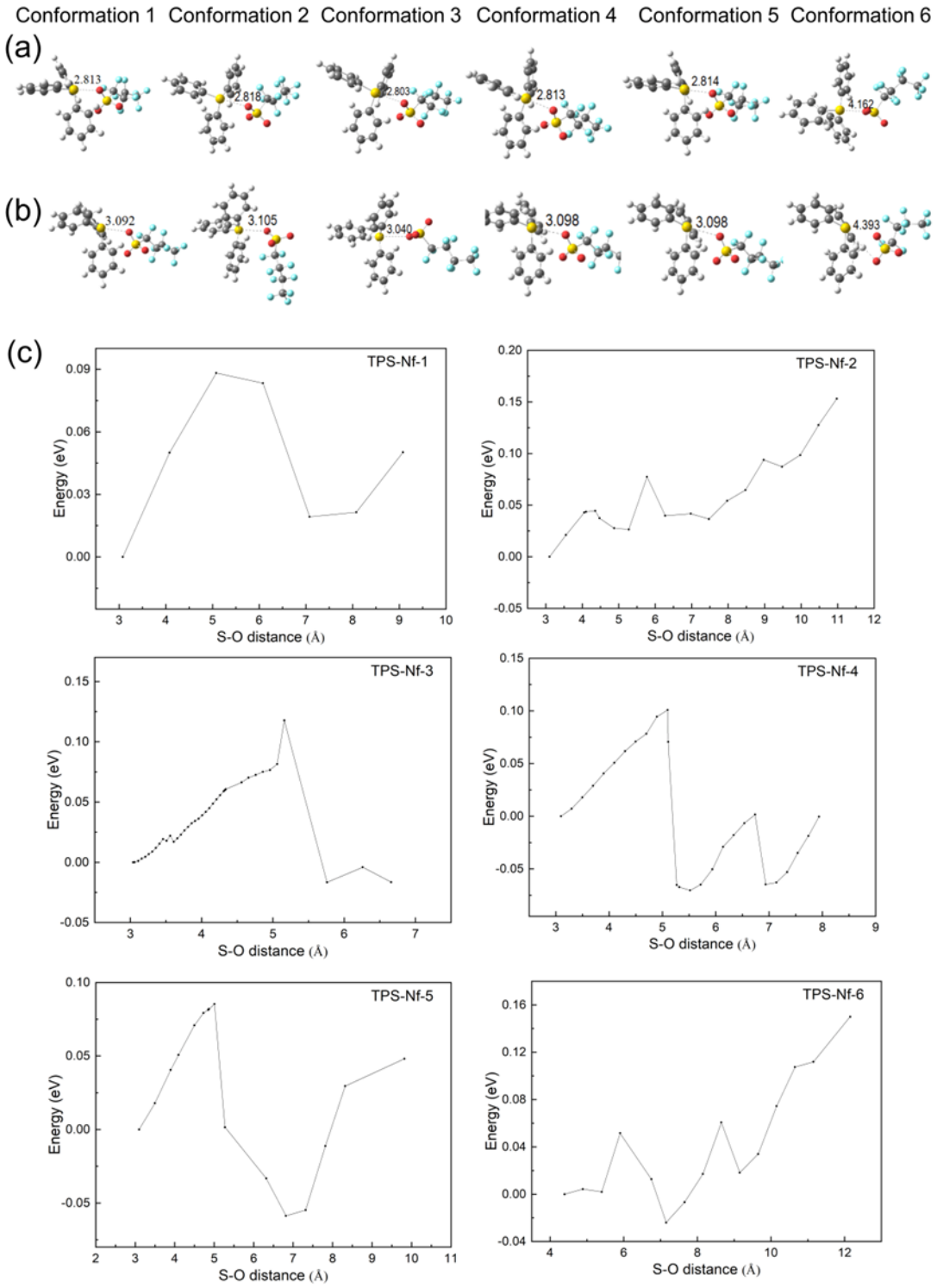


Figure S7. (a) The six different conformations of TPS-Nf before secondary electron attachment. (b) The six different conformations of TPS-Nf after secondary electron attachment. (c) The potential energy as a function of the S-O bond length for the six different conformations of TPS-Nf after secondary electron attachment.

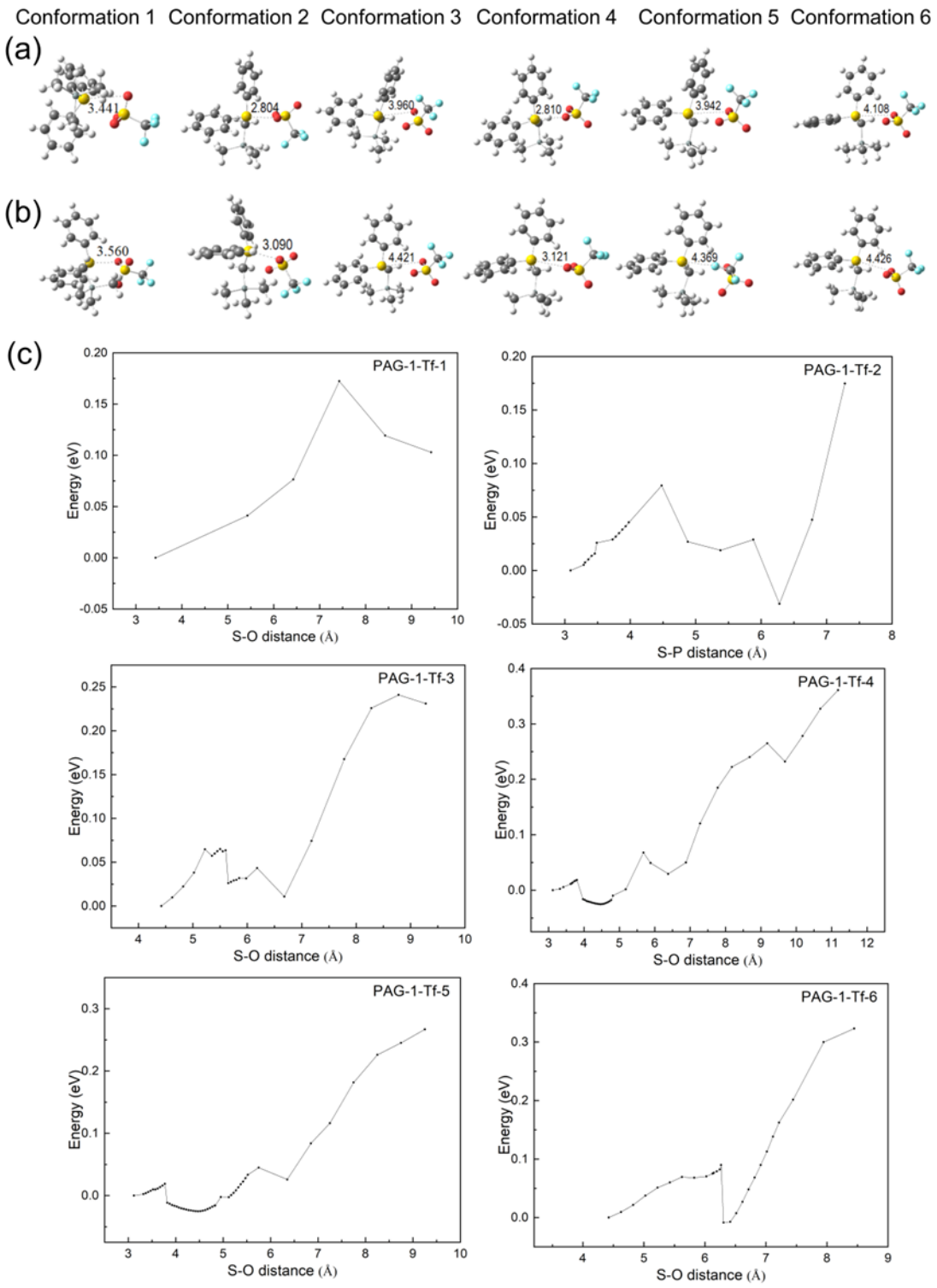


Figure S8. (a) The six different conformations of PAG-1-Tf before secondary electron attachment. (b) The six different conformations of PAG-1-Tf after secondary electron attachment. (c) The potential energy as a function of the S-O bond length for the six different conformations of PAG-1-Tf after secondary electron attachment.

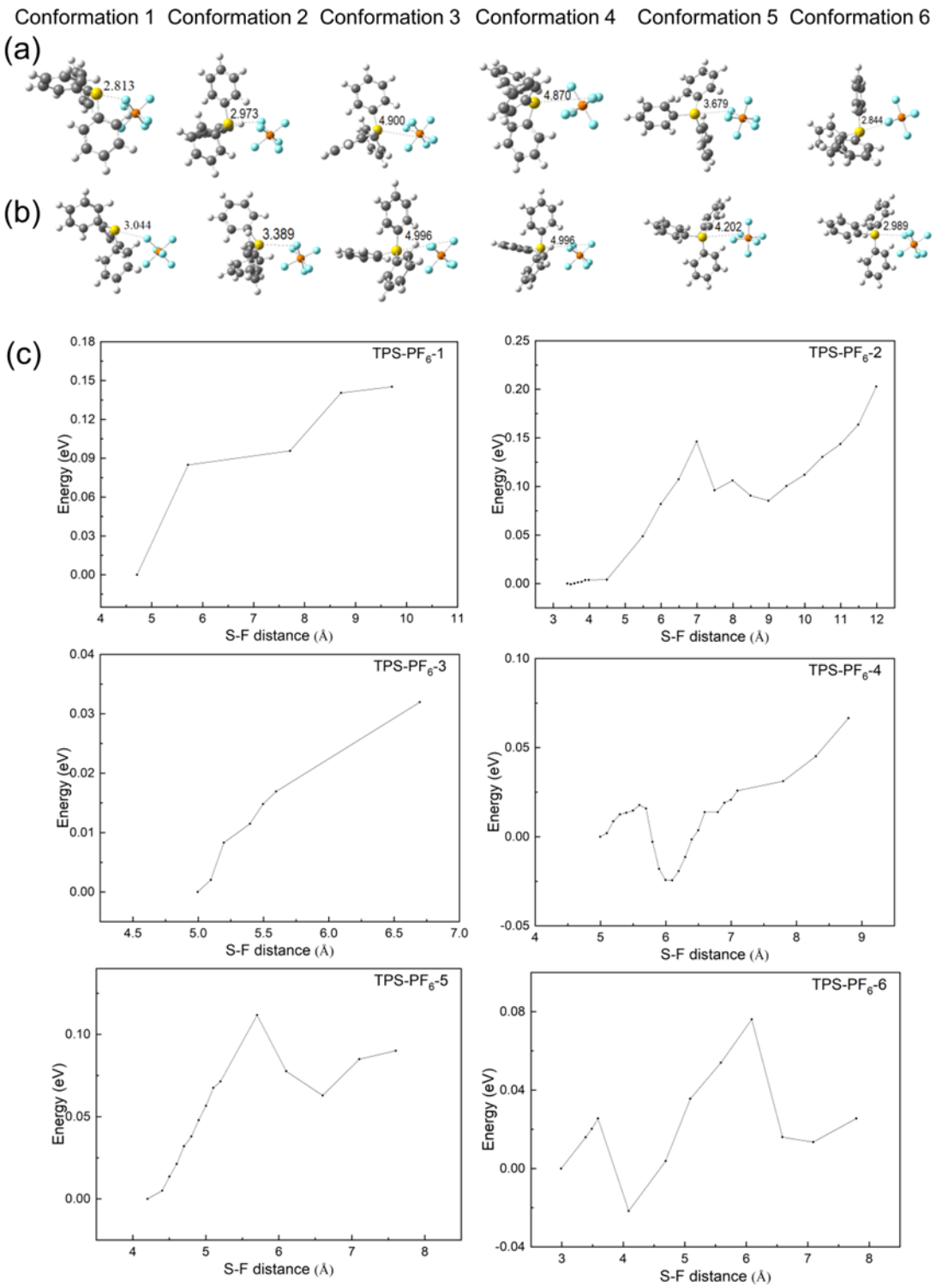


Figure S9. (a) The six different conformations of TPS-PF_6 before secondary electron attachment. (b) The six different conformations of TPS-PF_6 after secondary electron attachment. (c) The potential energy as a function of the S-F bond length for the six different conformations of TPS-PF_6 after secondary electron attachment.

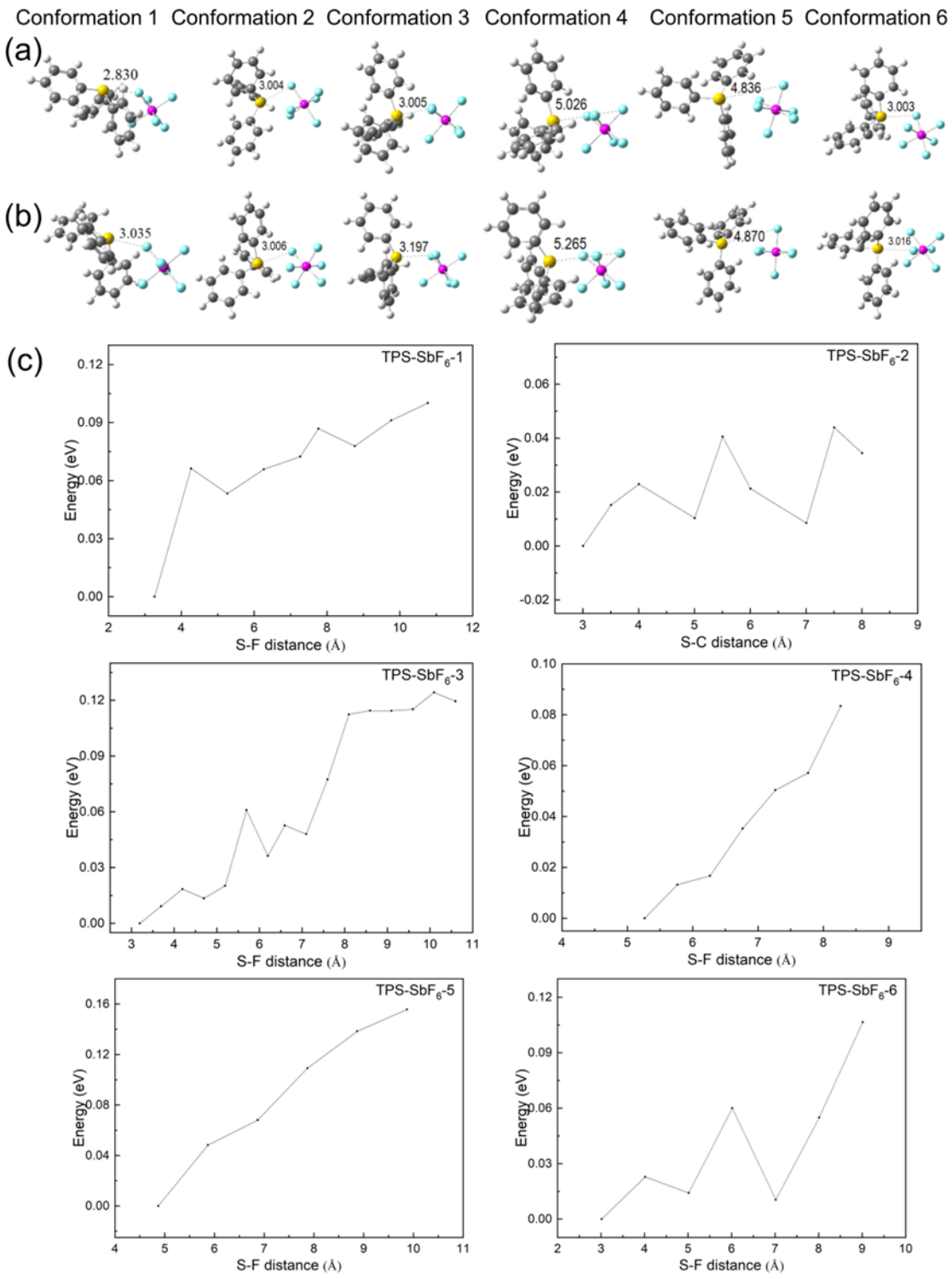


Figure S10. (a) The six different conformations of TPS-SbF_6 before secondary electron attachment. (b) The six different conformations of TPS-SbF_6 after secondary electron attachment. (c) The potential energy as a function of the S-F bond length for the six different conformations of TPS-SbF_6 after secondary electron attachment.

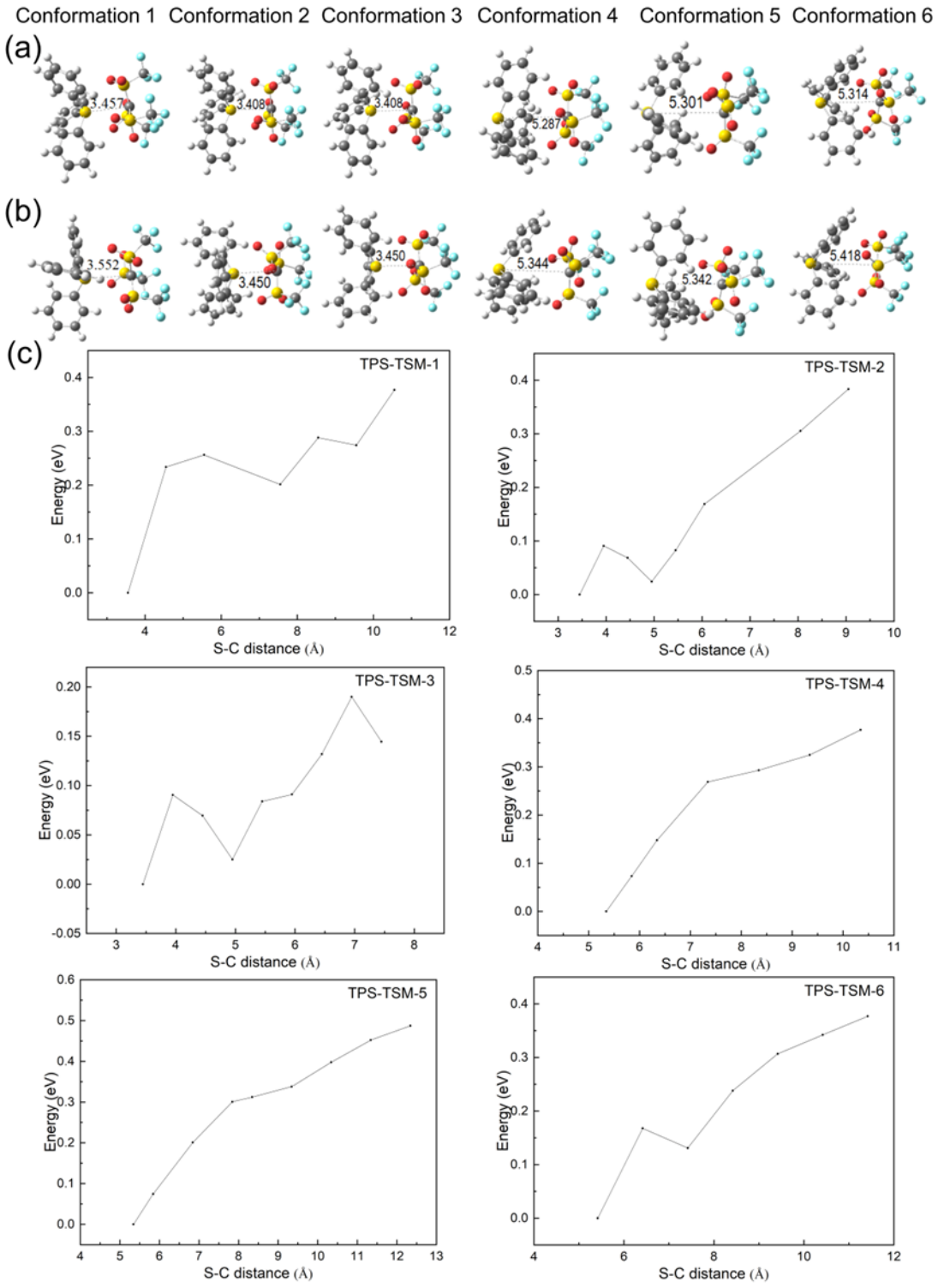


Figure S11. (a) The six different conformations of TPS-TSM before secondary electron attachment. (b) The six different conformations of TPS-TSM after secondary electron attachment. (c) The potential energy as a function of the S-C bond length for the six different conformations of TPS-TSM after secondary electron attachment.

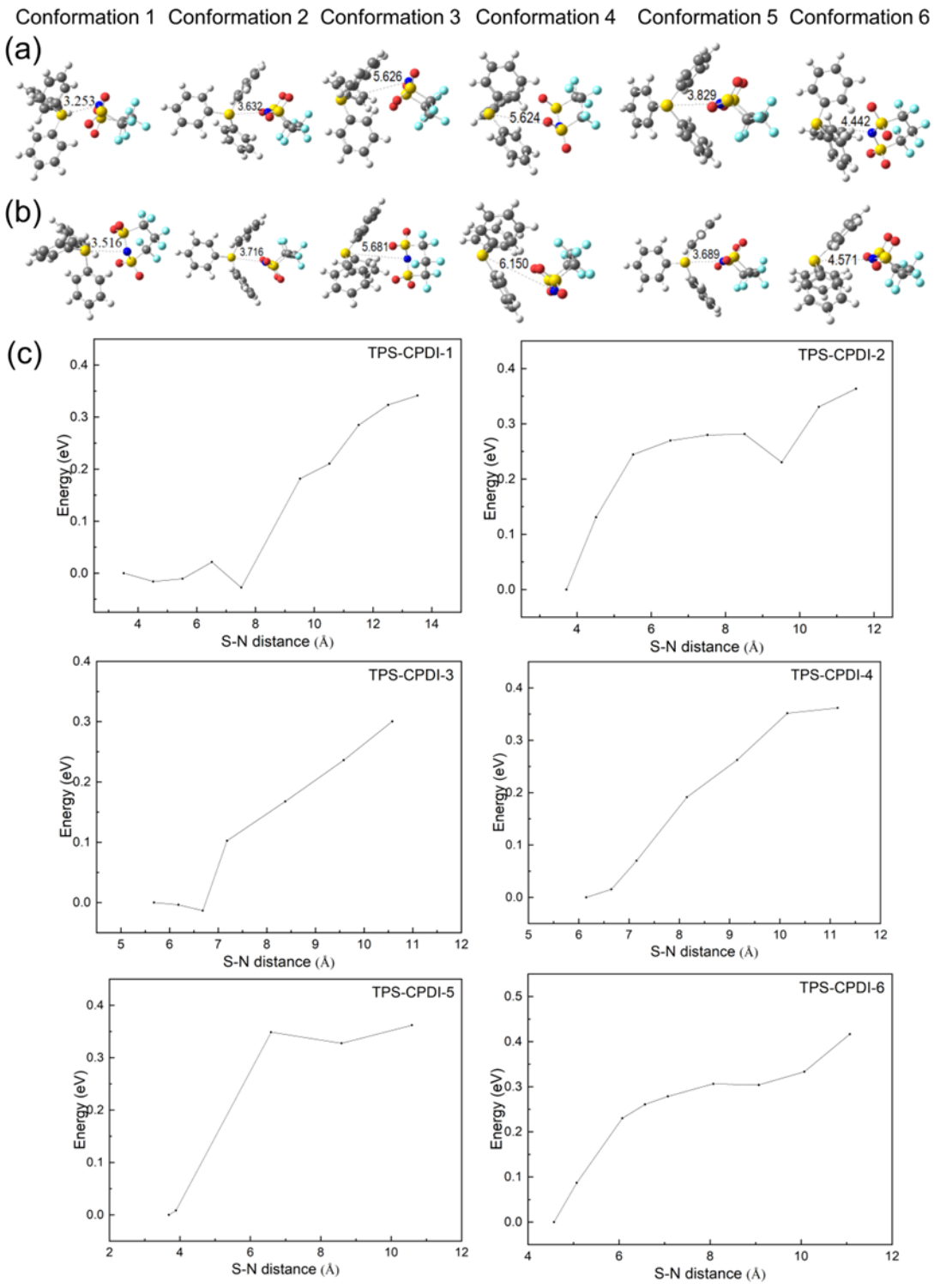


Figure S12. (a) The six different conformations of TPS-CPDI before secondary electron attachment. (b) The six different conformations of TPS-CPDI after secondary electron attachment. (c) The potential energy as a function of the S-N bond length for the six different conformations of TPS-CPDI after secondary electron attachment.

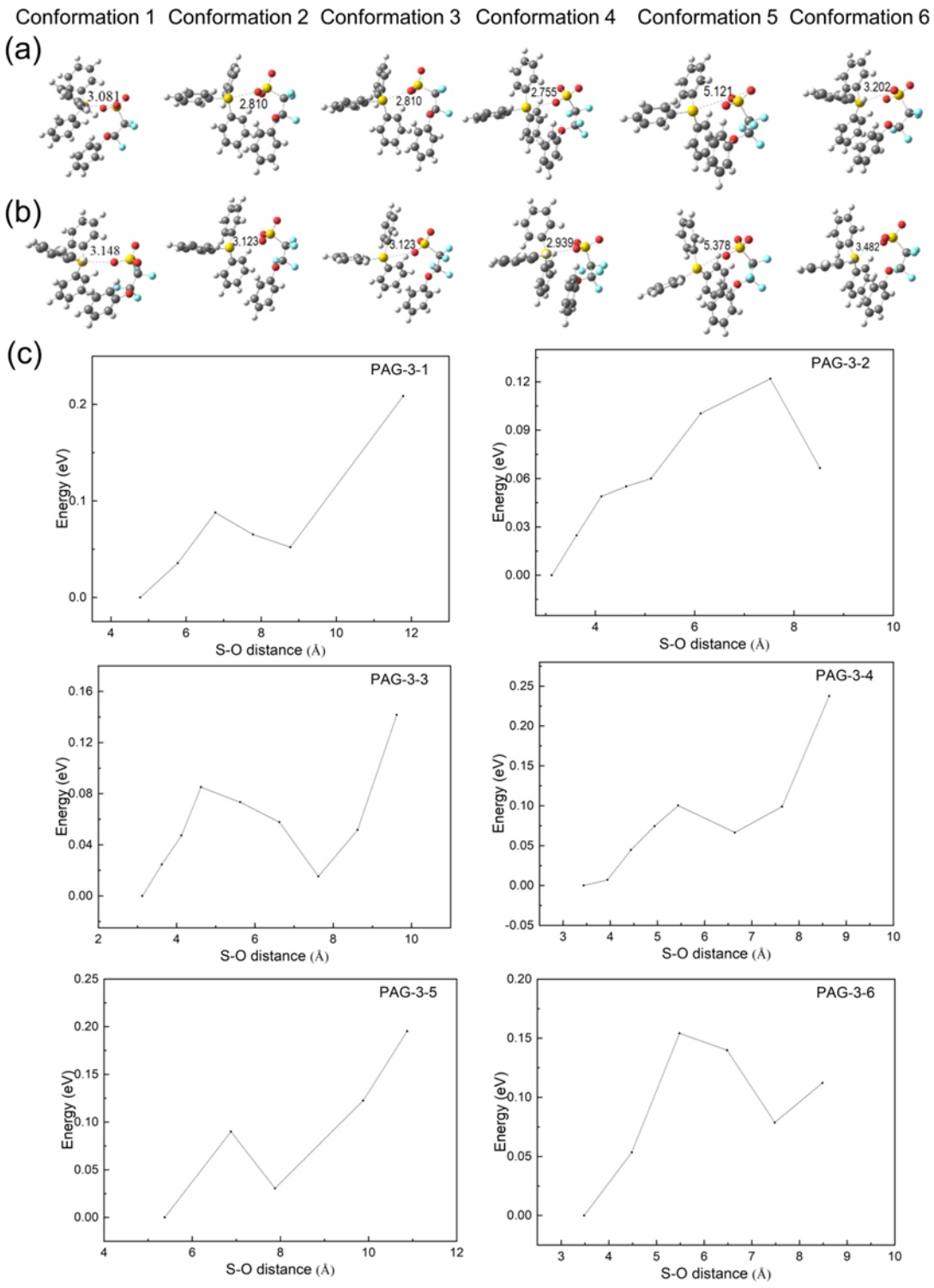


Figure S13. (a) The six different conformations of PAG-3 before secondary electron attachment. (b) The six different conformations of PAG-3 after secondary electron attachment. (c) The potential energy as a function of the S-O bond length for the six different conformations of PAG-3 after secondary electron attachment.

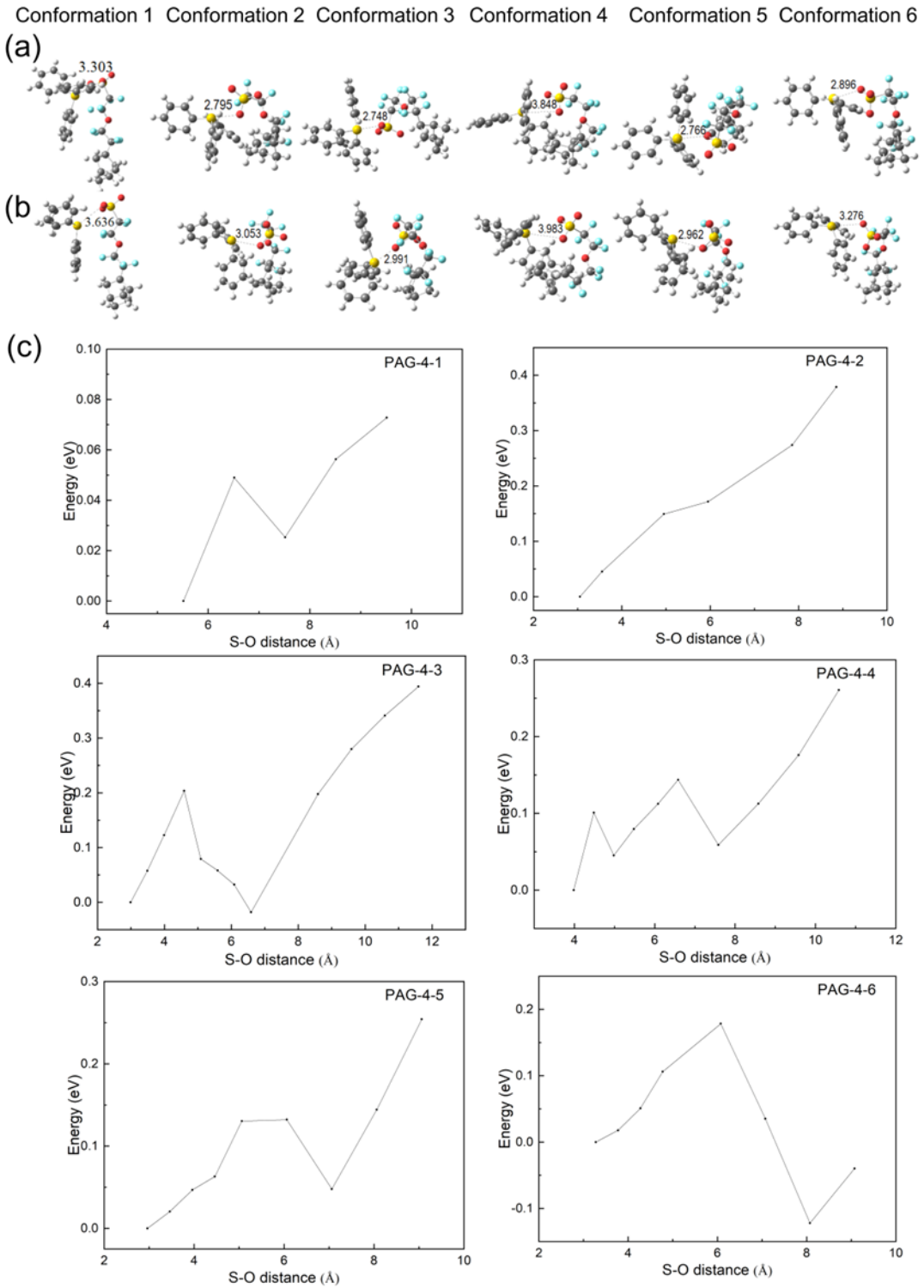


Figure S14. (a) The six different conformations of PAG-4 before secondary electron attachment. (b) The six different conformations of PAG-4 after secondary electron attachment. (c) The potential energy as a function of the S-O bond length for the six different conformations of PAG-4 after secondary electron attachment.

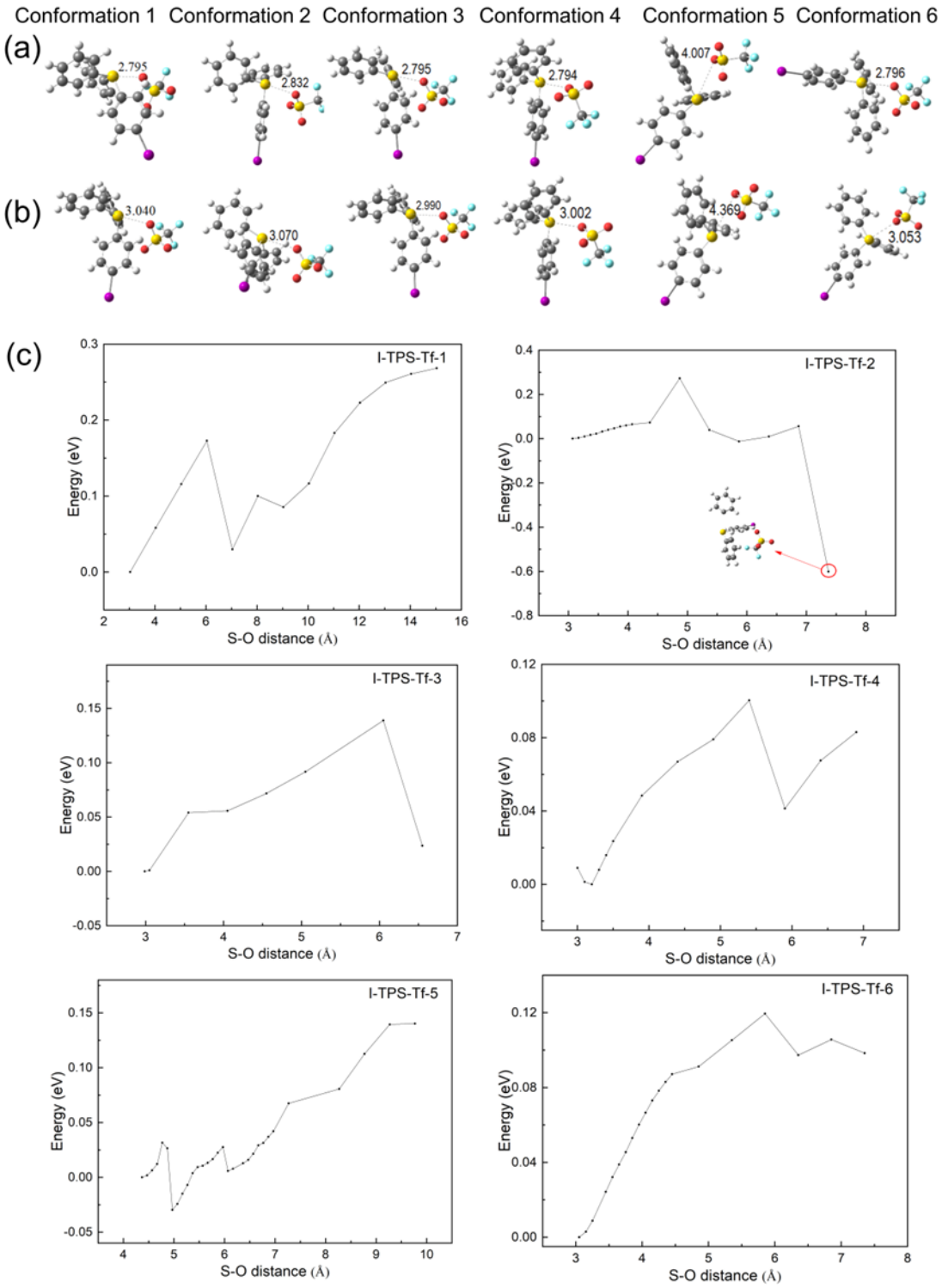


Figure S15. (a) The six different conformations of I-TPS-Tf before secondary electron attachment. (b) The six different conformations of I-TPS-Tf after secondary electron attachment. (c) The potential energy as a function of the S-O bond length for the six different conformations of I-TPS-Tf after secondary electron attachment.

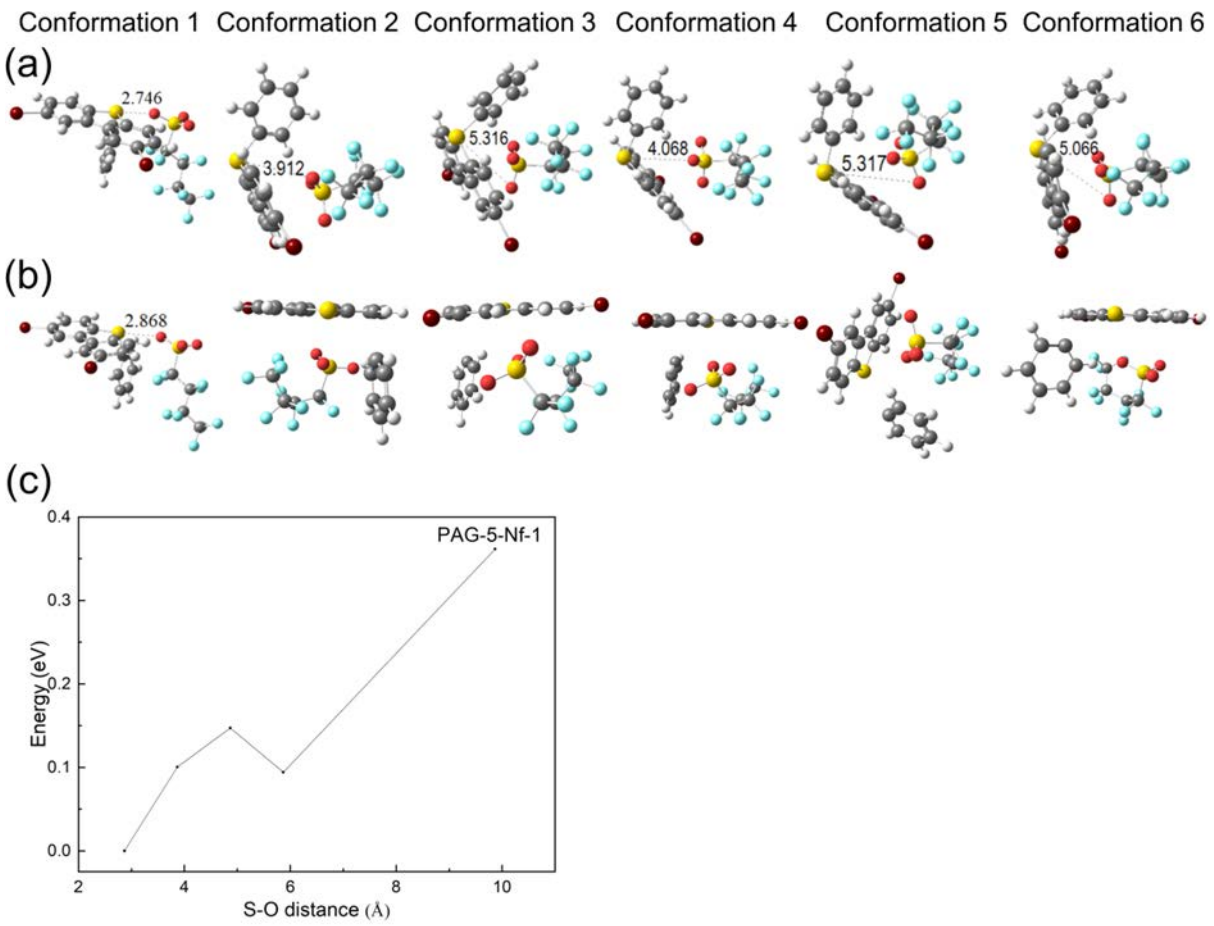


Figure S16. (a) The six different conformations of PAG-5-Nf before secondary electron attachment. (b) The six different conformations of PAG-5-Nf after secondary electron attachment. (c) The potential energy as a function of the S-O bond length for Configuration 1 of PAG-5-Nf after secondary electron attachment.

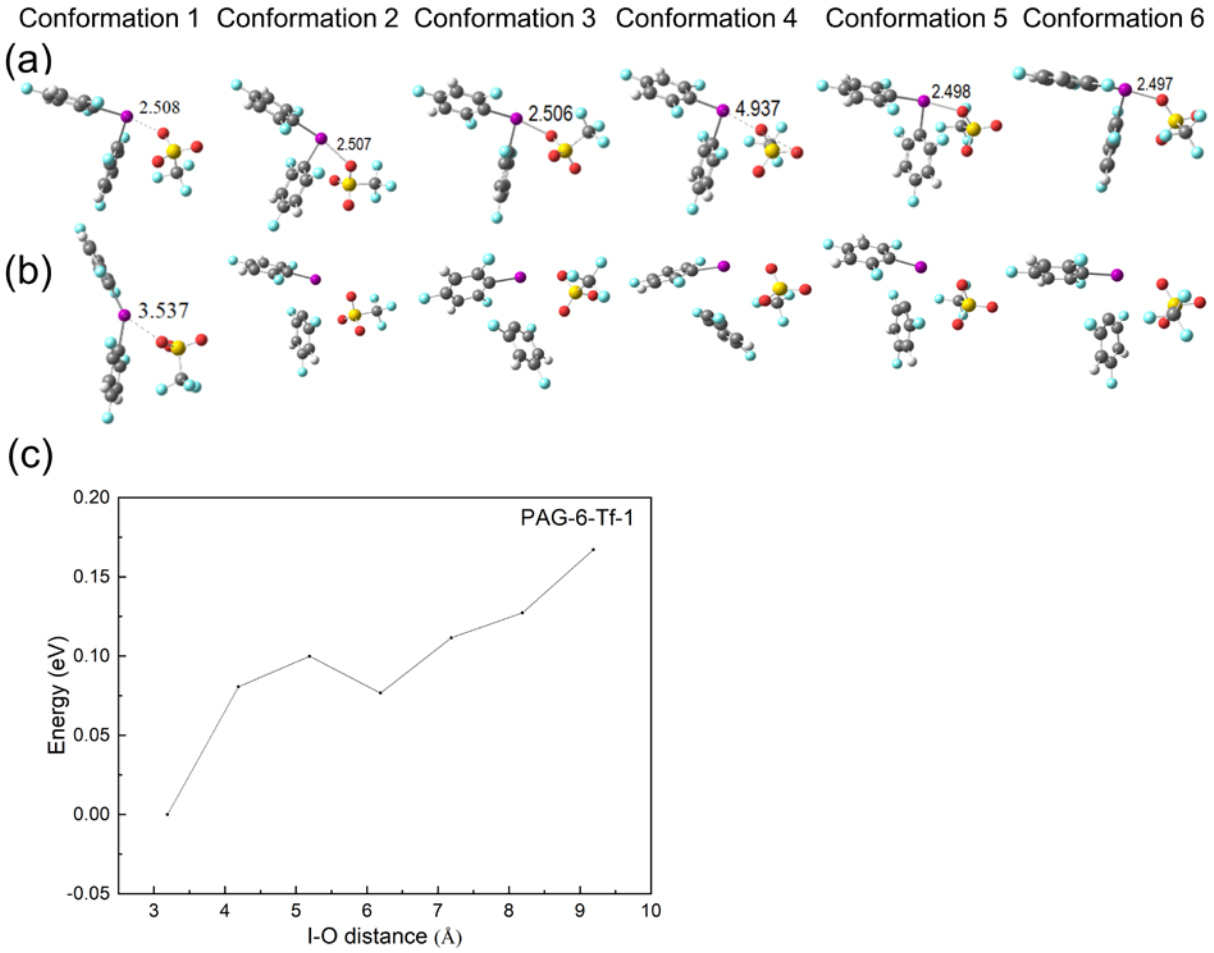


Figure S17. (a) The six different conformations of PAG-6-Tf before secondary electron attachment. (b) The six different conformations of PAG-6-Tf after secondary electron attachment. (c) The potential energy as a function of the I-O bond length for the Conformation 1 of PAG-6-Tf after secondary electron attachment.

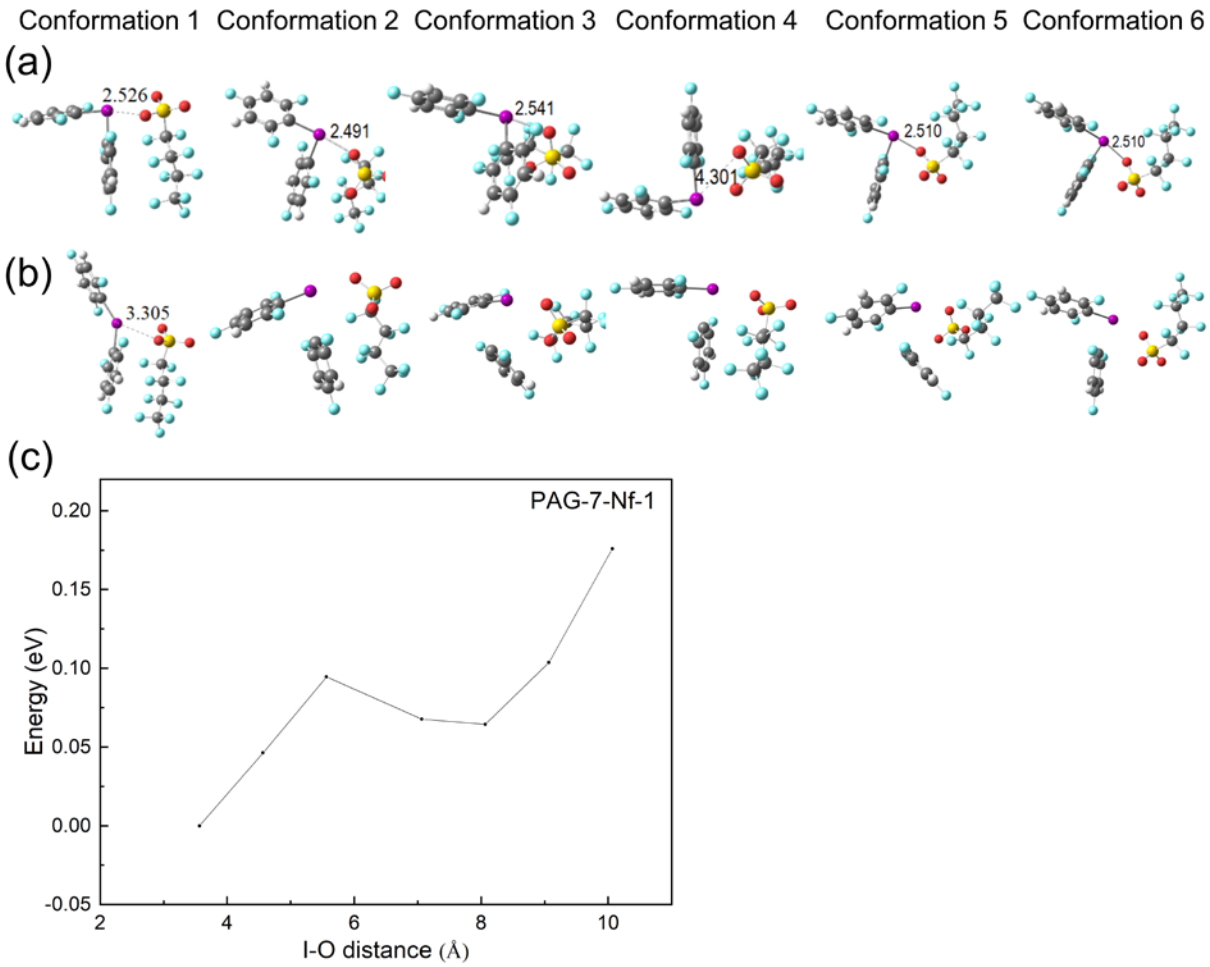


Figure S18. (a) The six different conformations of PAG-7-nf before secondary electron attachment. (b) The six different conformations of PAG-7-nf after secondary electron attachment. (c) The potential energy as a function of the I-O bond length for the Conformation 1 of PAG-7-Nf after secondary electron attachment.

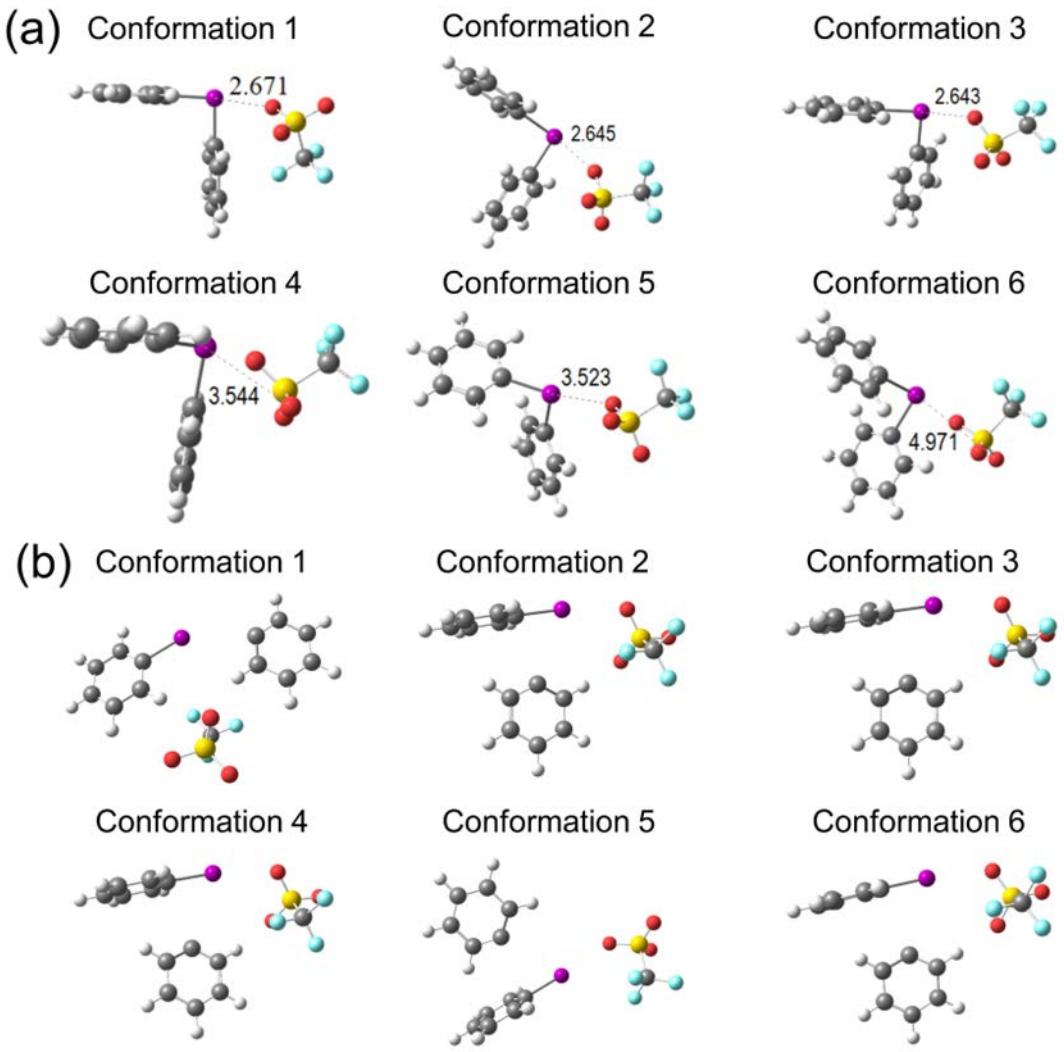


Figure S19. (a) The six different conformations of DPI-Tf before secondary electron attachment. (b) The six different conformations of DPI-Tf after secondary electron attachment.

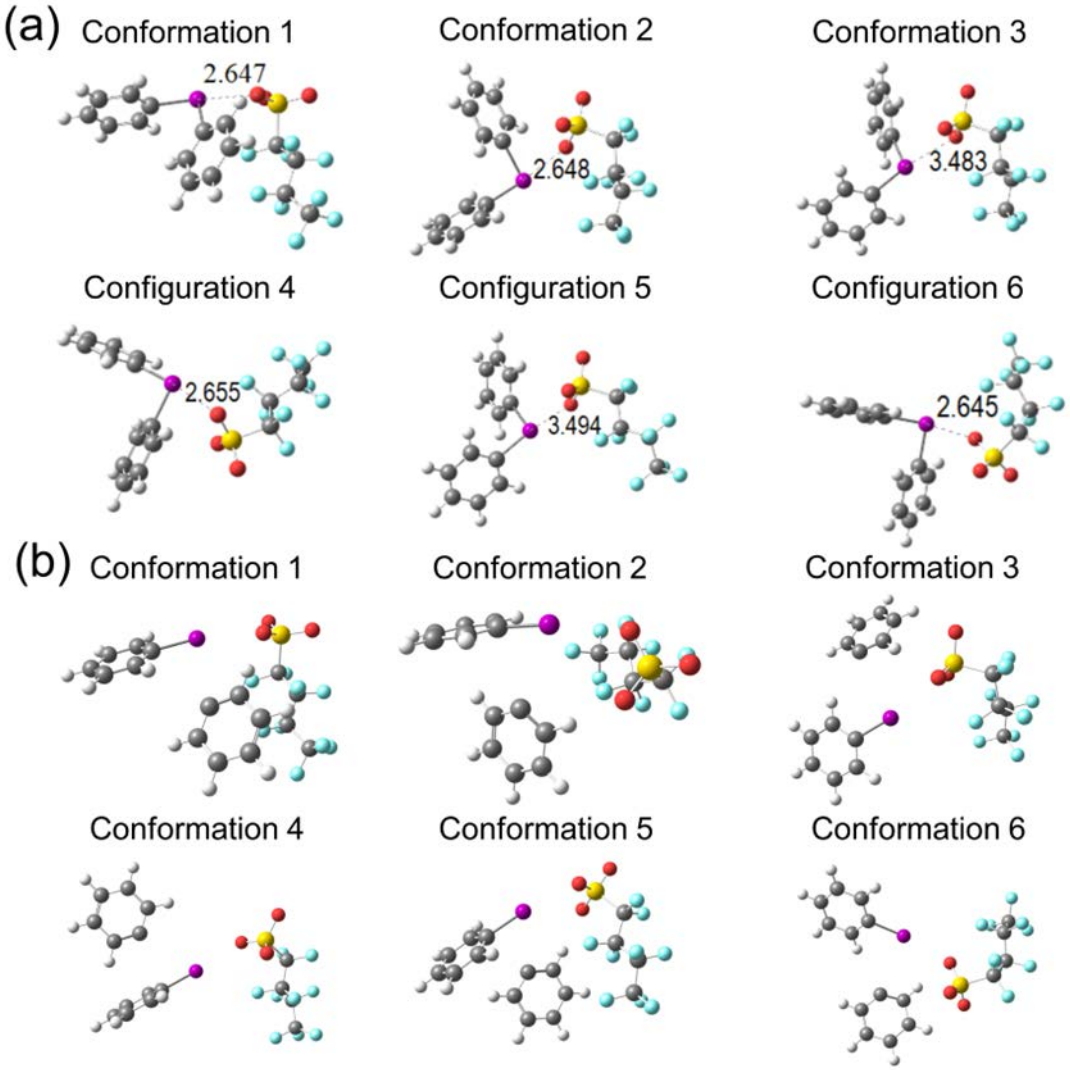


Figure S20. (a) The six different conformations of DPI-Nf before secondary electron attachment. (b) The six different conformations of DPI-Nf after secondary electron attachment.

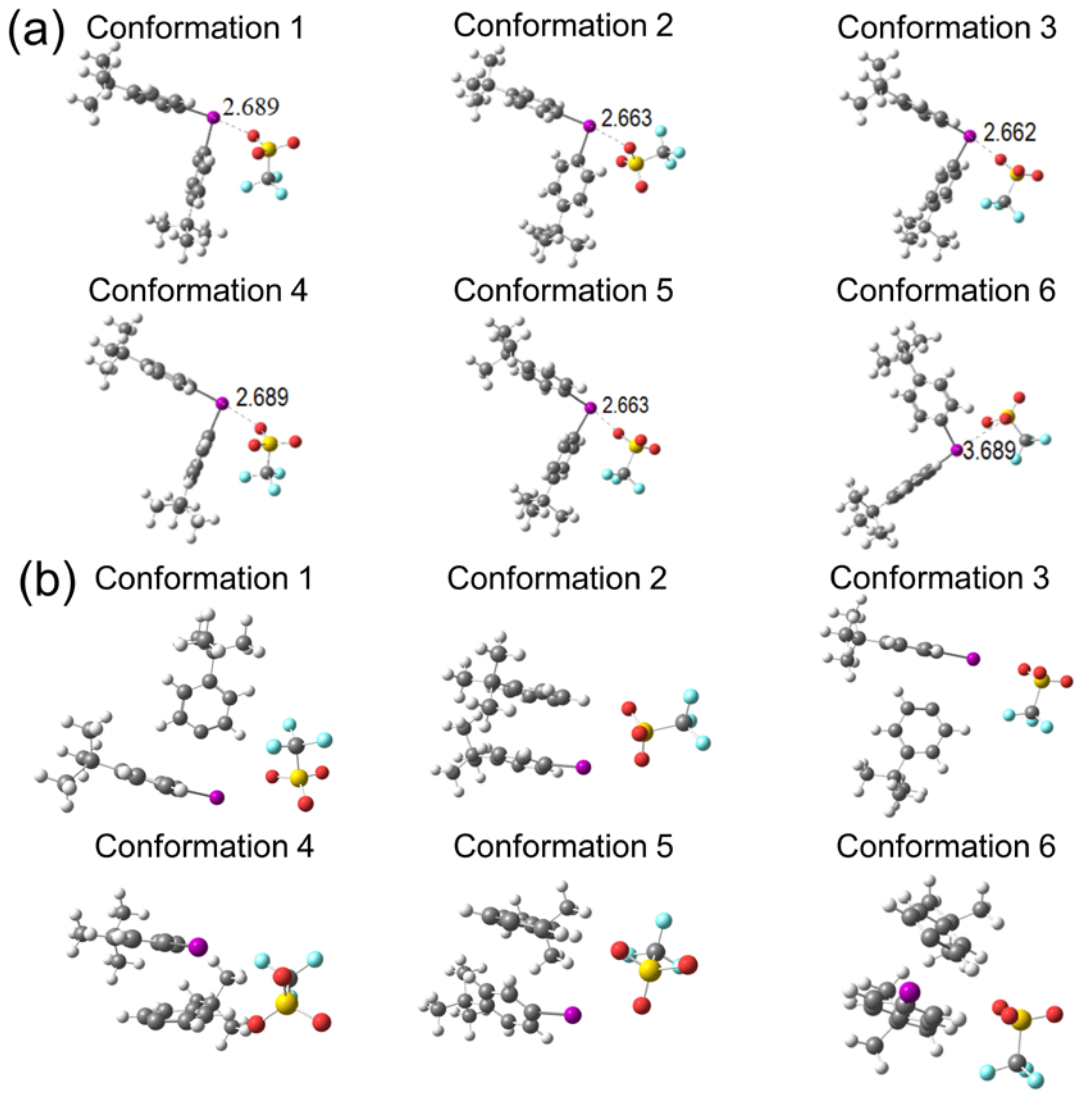


Figure S21. (a) The six different conformations of BBI-Tf before secondary electron attachment. (b) The six different conformations of BBI-Tf after secondary electron attachment.

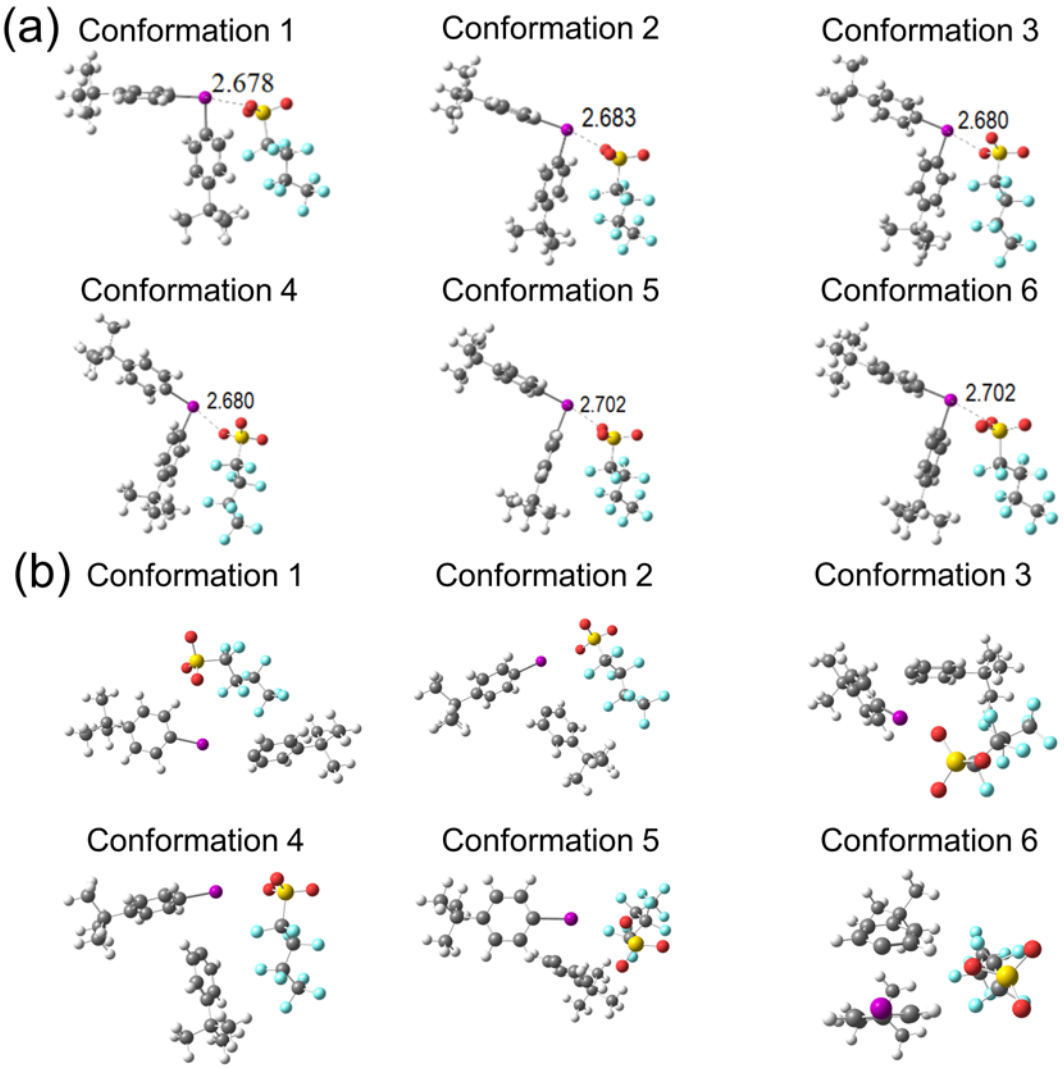


Figure S22. (a) The six different conformations of BBI-Nf before secondary electron attachment. (b) The six different conformations of BBI-Nf after secondary electron attachment.

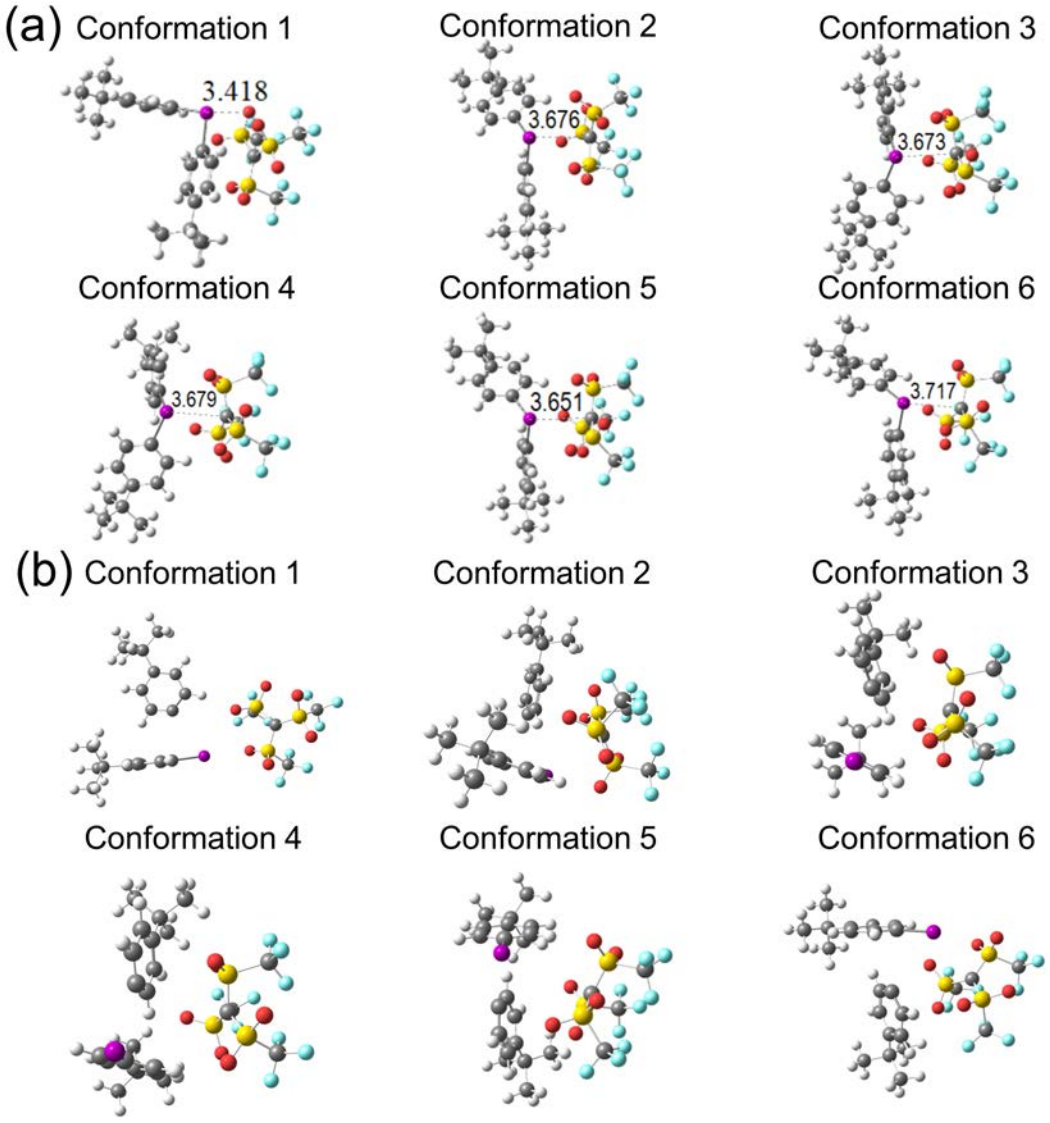


Figure S23. (a) The six different conformations of BBI-TSM before secondary electron attachment. (b) The six different conformations of BBI-TSM after secondary electron attachment.

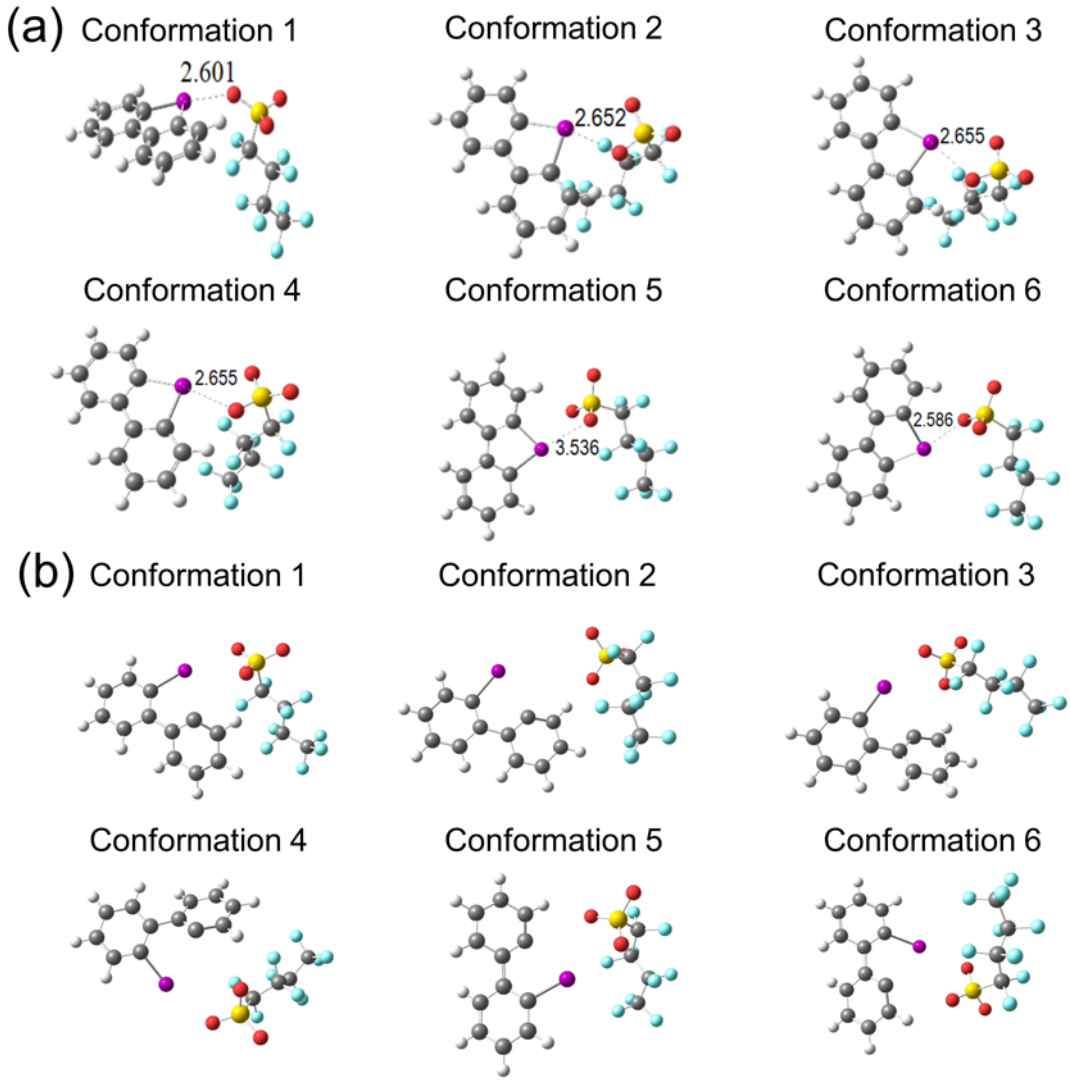


Figure S24. (a) The six different conformations of PAG-8-Nf before secondary electron attachment. (b) The six different conformations of PAG-8-Nf after secondary electron attachment.

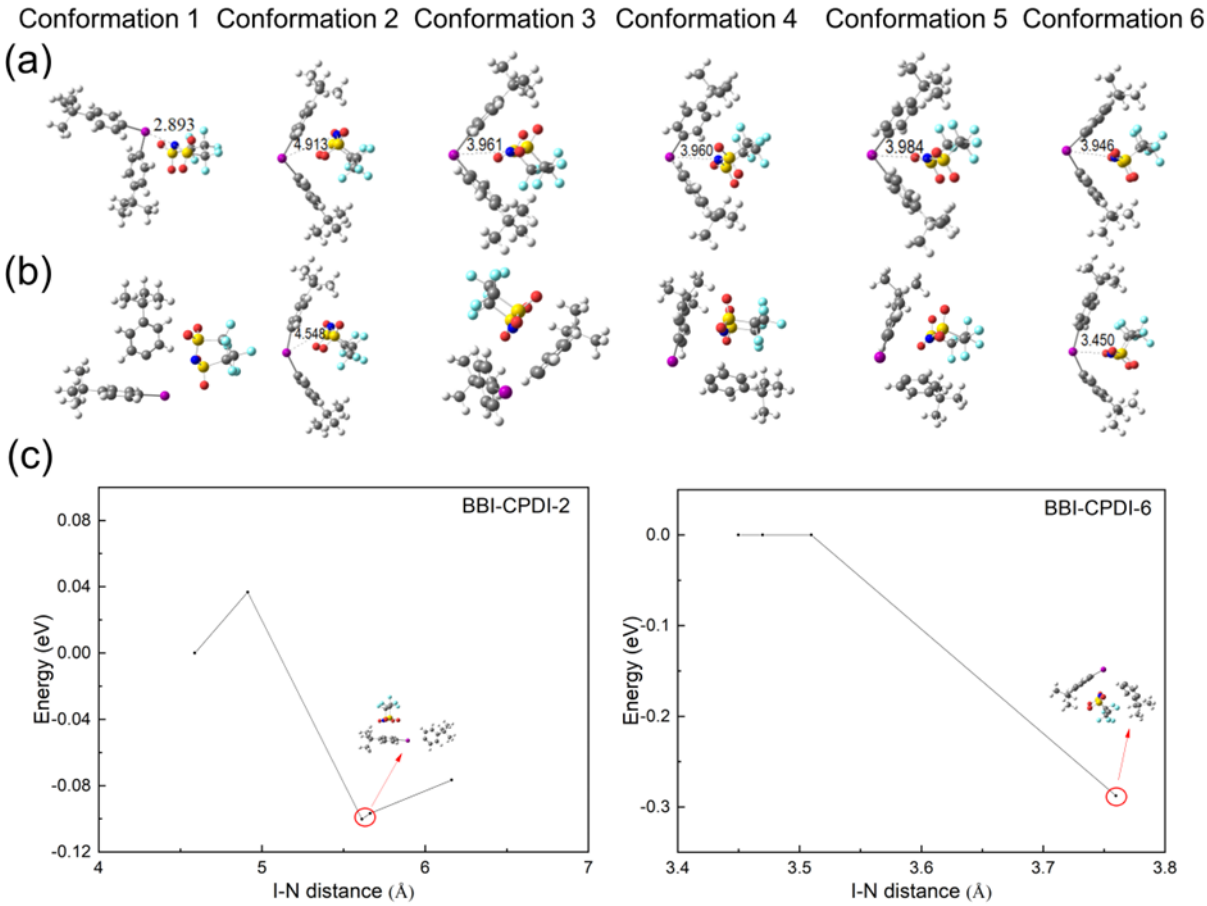


Figure S25. (a) The six different conformations of BBI-CPDI before secondary electron attachment. (b) The six different conformations of BBI-CPDI after secondary electron attachment. (c) The potential energy as a function of the I-N bond length for the Conformation 2 and Conformation 6 of BBI-CPDI after secondary electron attachment.

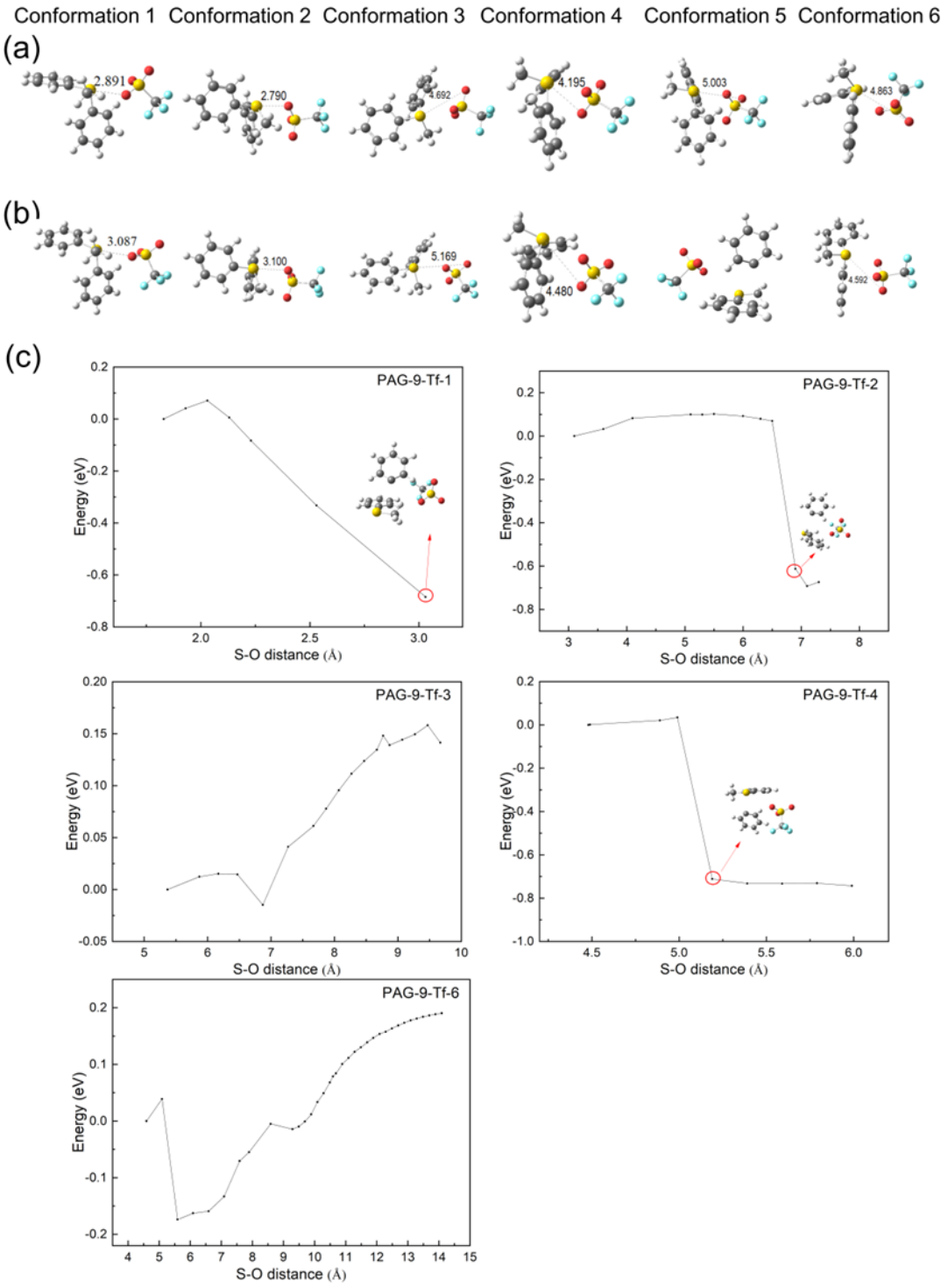


Figure S26. (a) The six different conformations of PAG-9-Tf before secondary electron attachment. (b) The six different conformations of PAG-9-Tf after secondary electron attachment. (c) The potential energy as a function of the S-O bond length for the Conformation 1, Conformation 2, Conformation 3, Conformation 4, and Conformation 6 of PAG-9-Tf after secondary electron attachment.

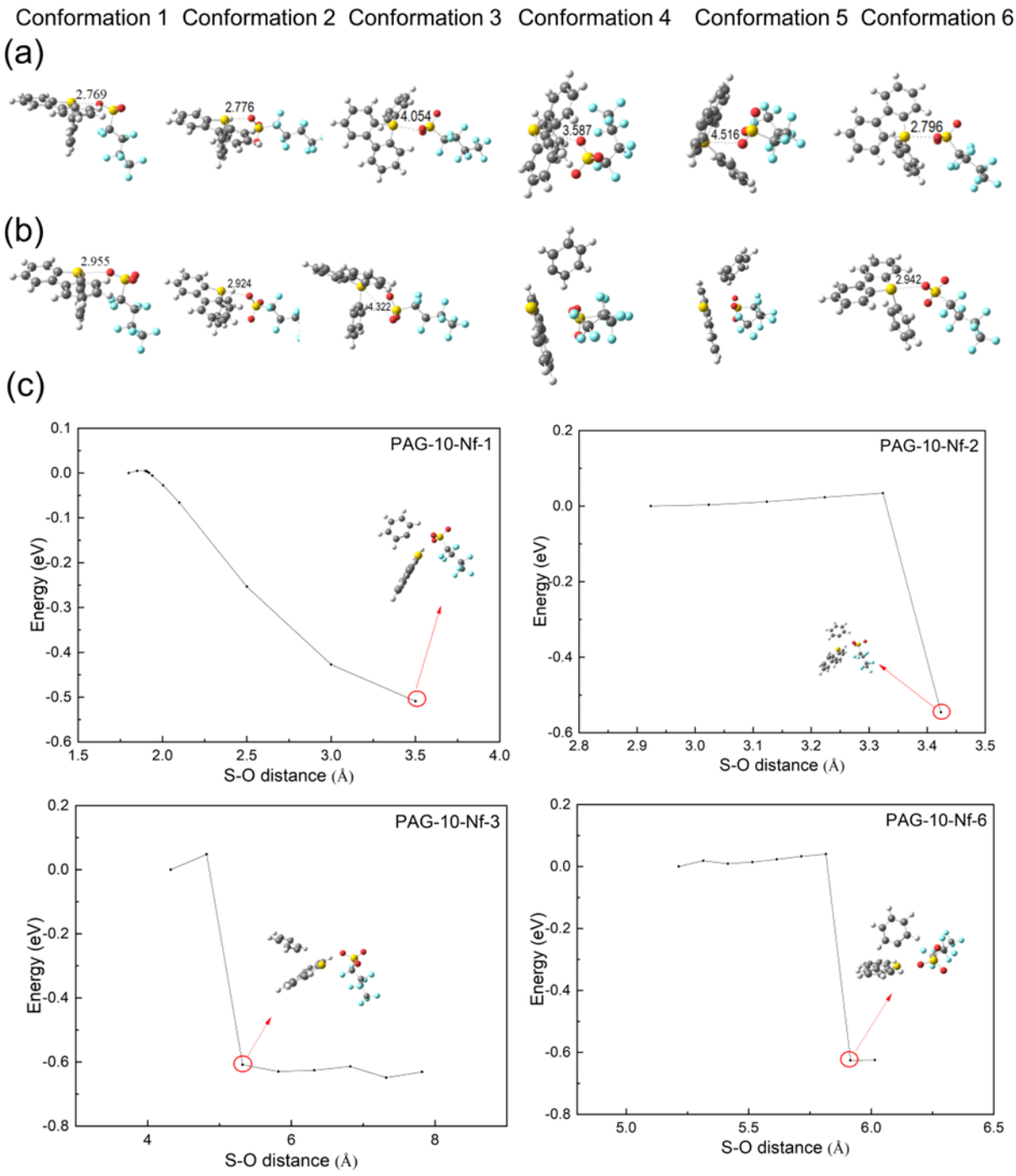


Figure S27. (a) The six different conformations of PAG-10-Nf before secondary electron attachment. (b) The six different conformations of PAG-10-Nf after secondary electron attachment. (c) The potential energy as a function of the S-O bond length for the Conformation 1, Conformation 2, Conformation 3, and Conformation 6 of PAG-10-Nf after secondary electron attachment.

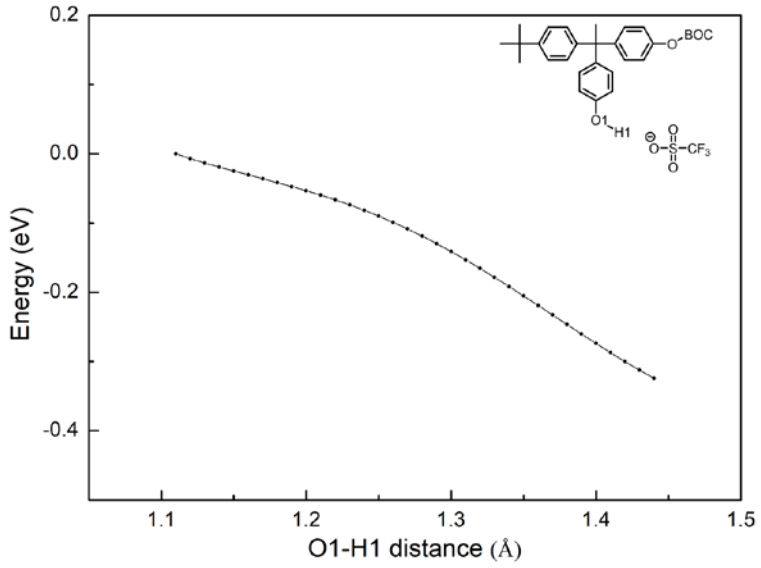


Figure S28. The potential energy as a function of the O1-H1 bond of CR4-BOC^{+}-Tf^{-}.

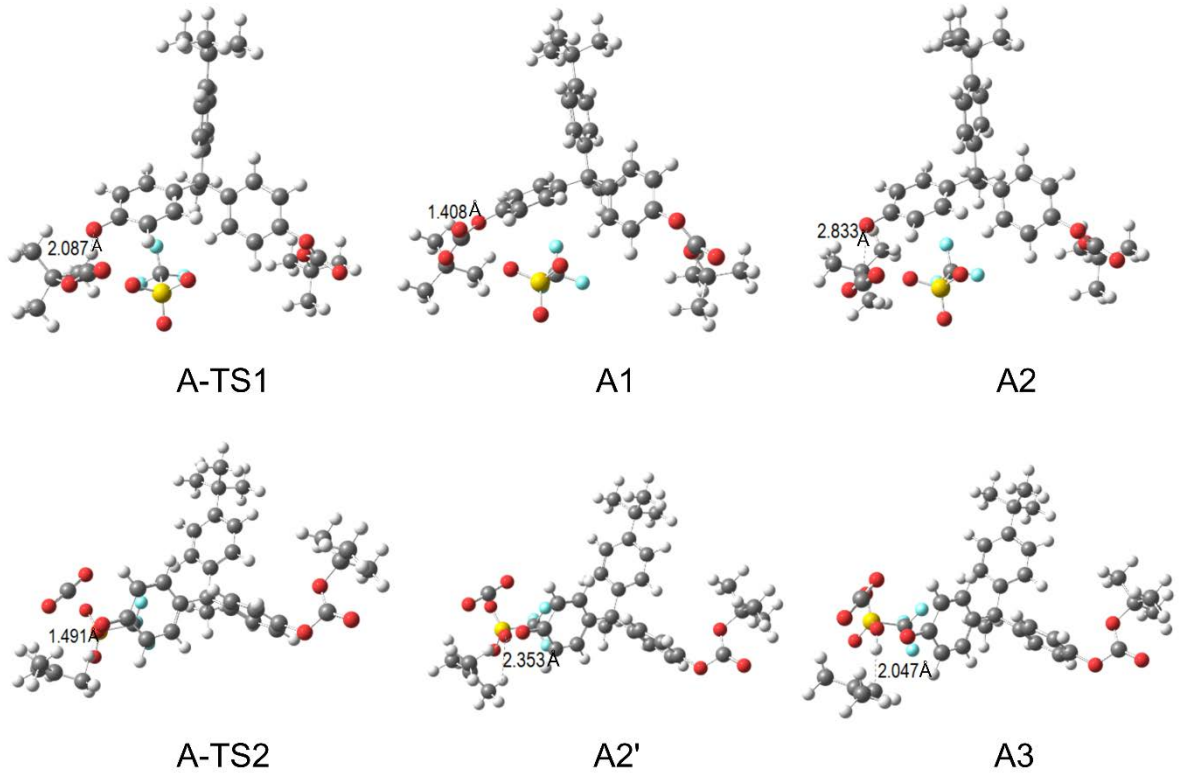


Figure S29. Molecular configurations of the transition state, the reactant, and the product of Pathway A in **Fig. 4**.

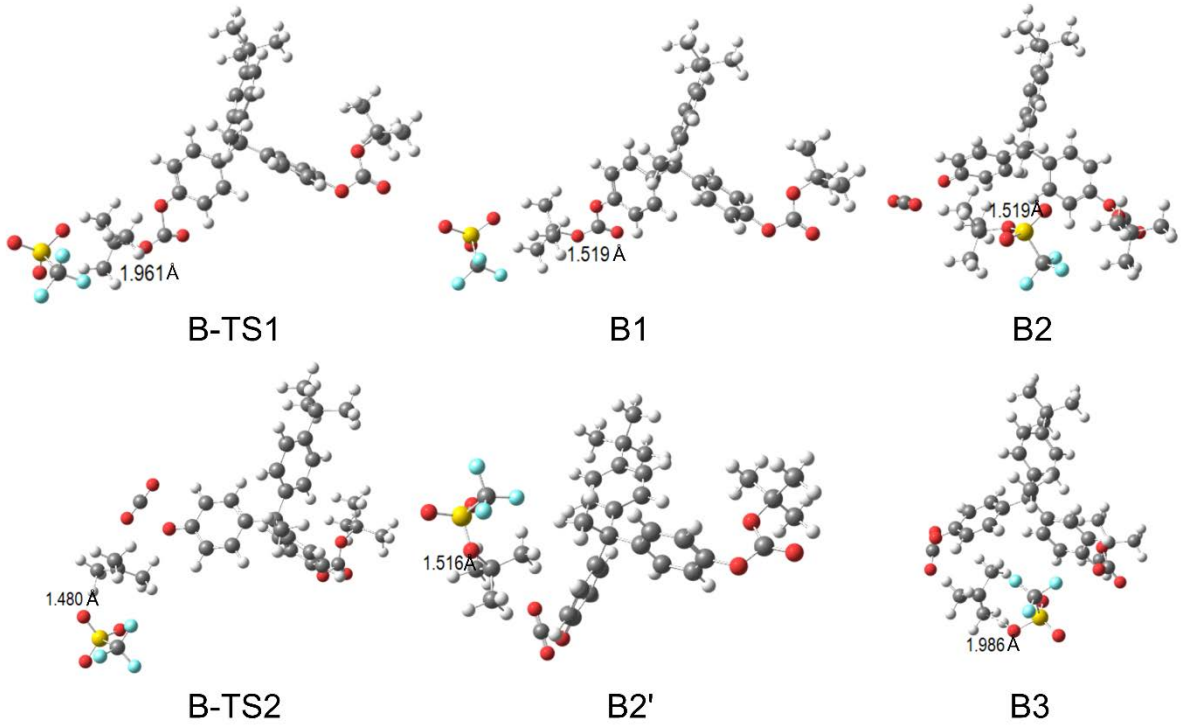


Figure S30. Molecular configurations of the transition state, the reactant, and the product of Pathway B in **Fig. 4**.

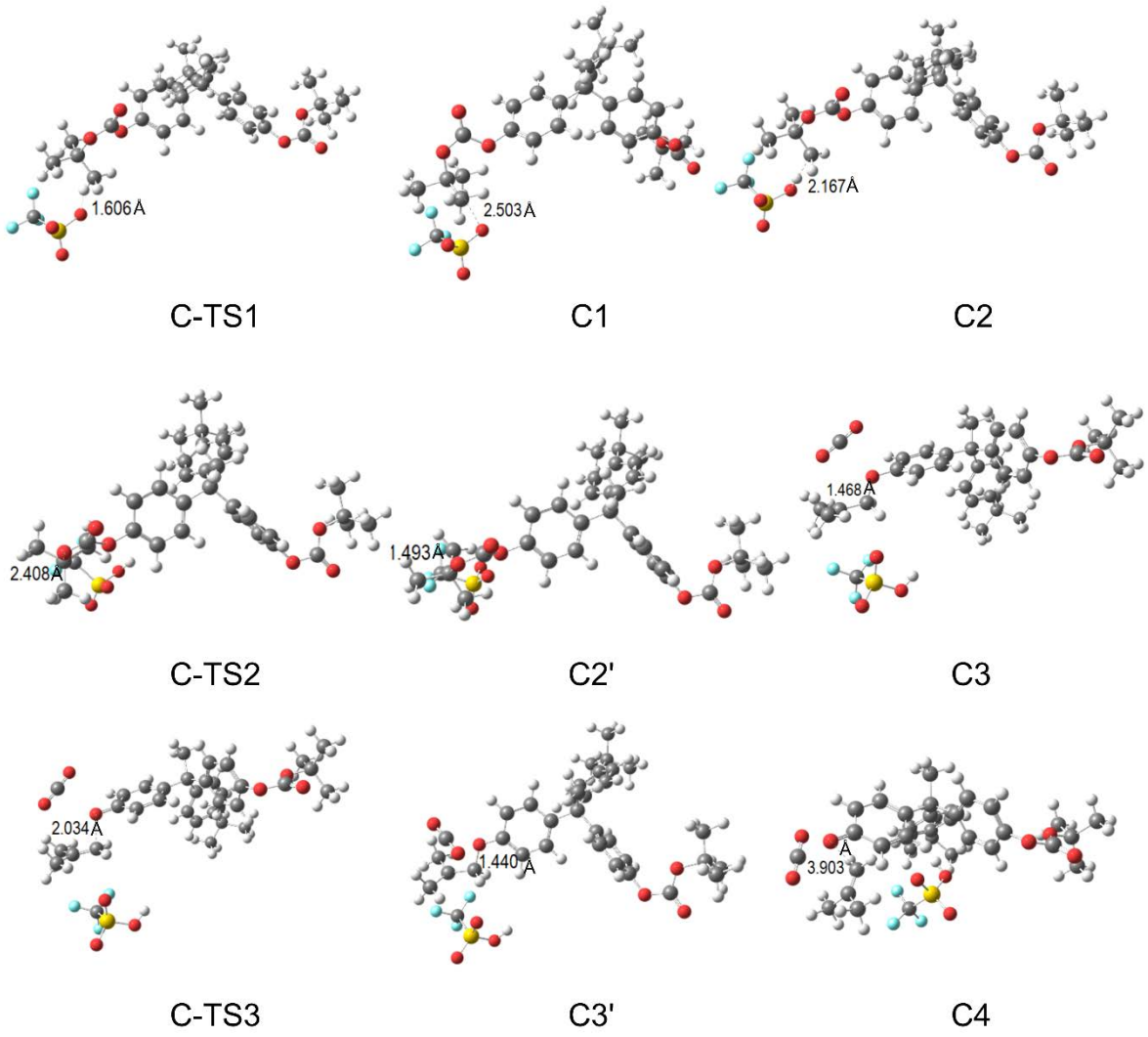


Figure S31. Molecular configurations of the transition state, the reactant, and the product of Pathway C in **Fig. 4**.

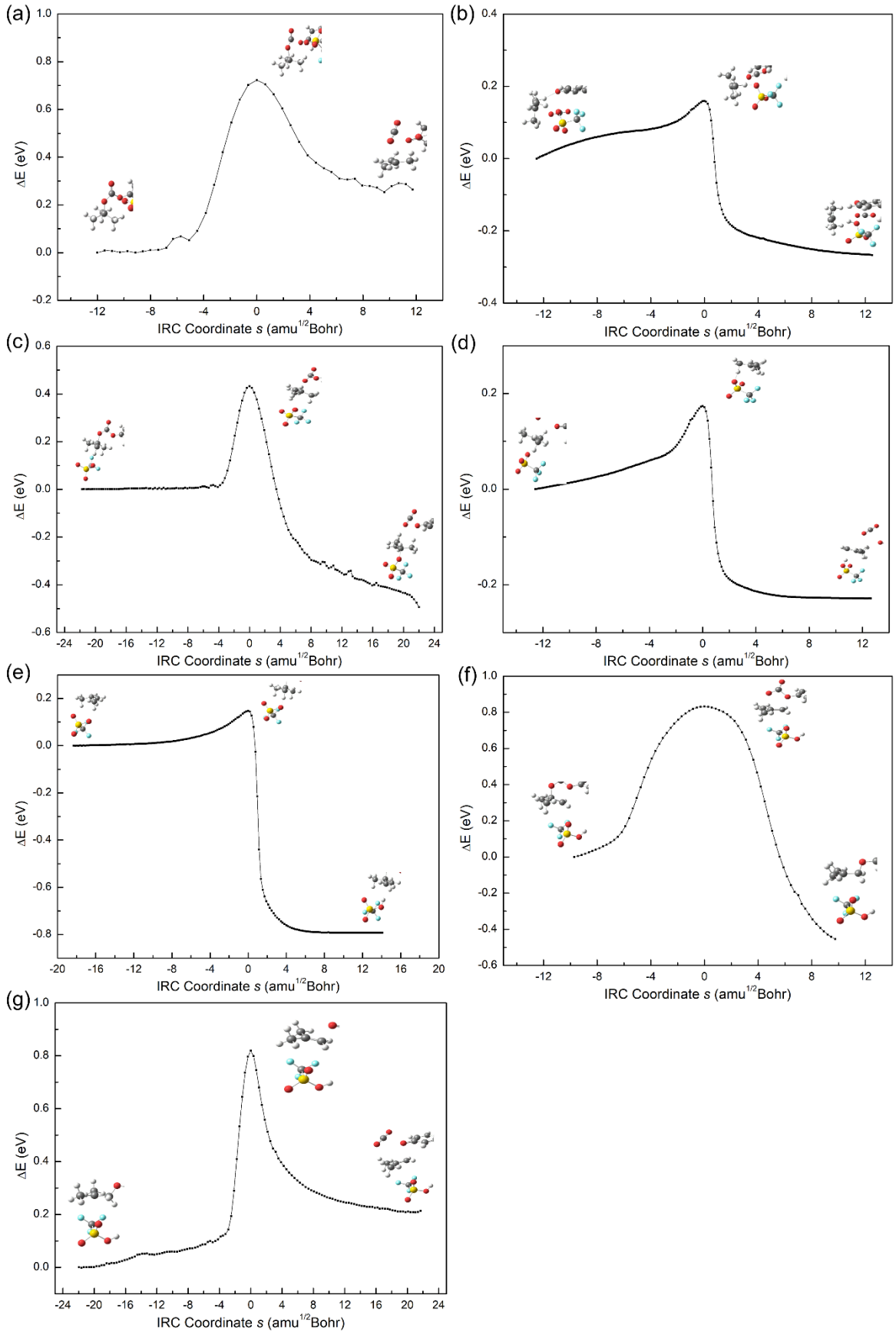


Figure S32. The potential energies along the IRCs for (a) A-TS1, (b) A-TS2, (c) B-TS1, (d) B-TS2, (e) C-TS1, (f) C-TS2, and (g) C-TS3 of Tf^- in **Table 1**.

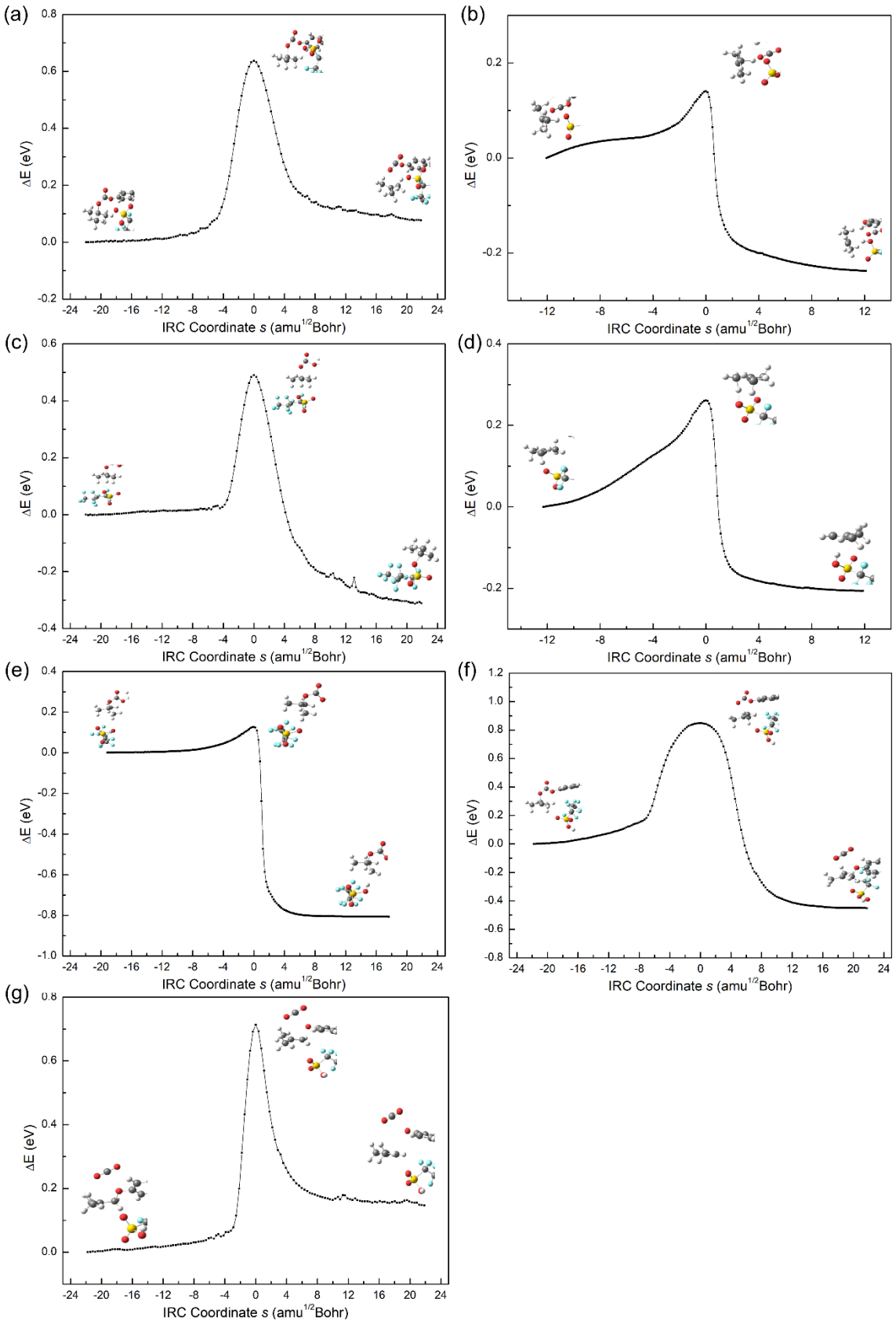


Figure S33. The potential energies along the IRCs for (a) A-TS1, (b) A-TS2, (c) B-TS1, (d) B-TS2, (e) C-TS1, (f) C-TS2, and (g) C-TS3 of Nf^- in **Table 1**.

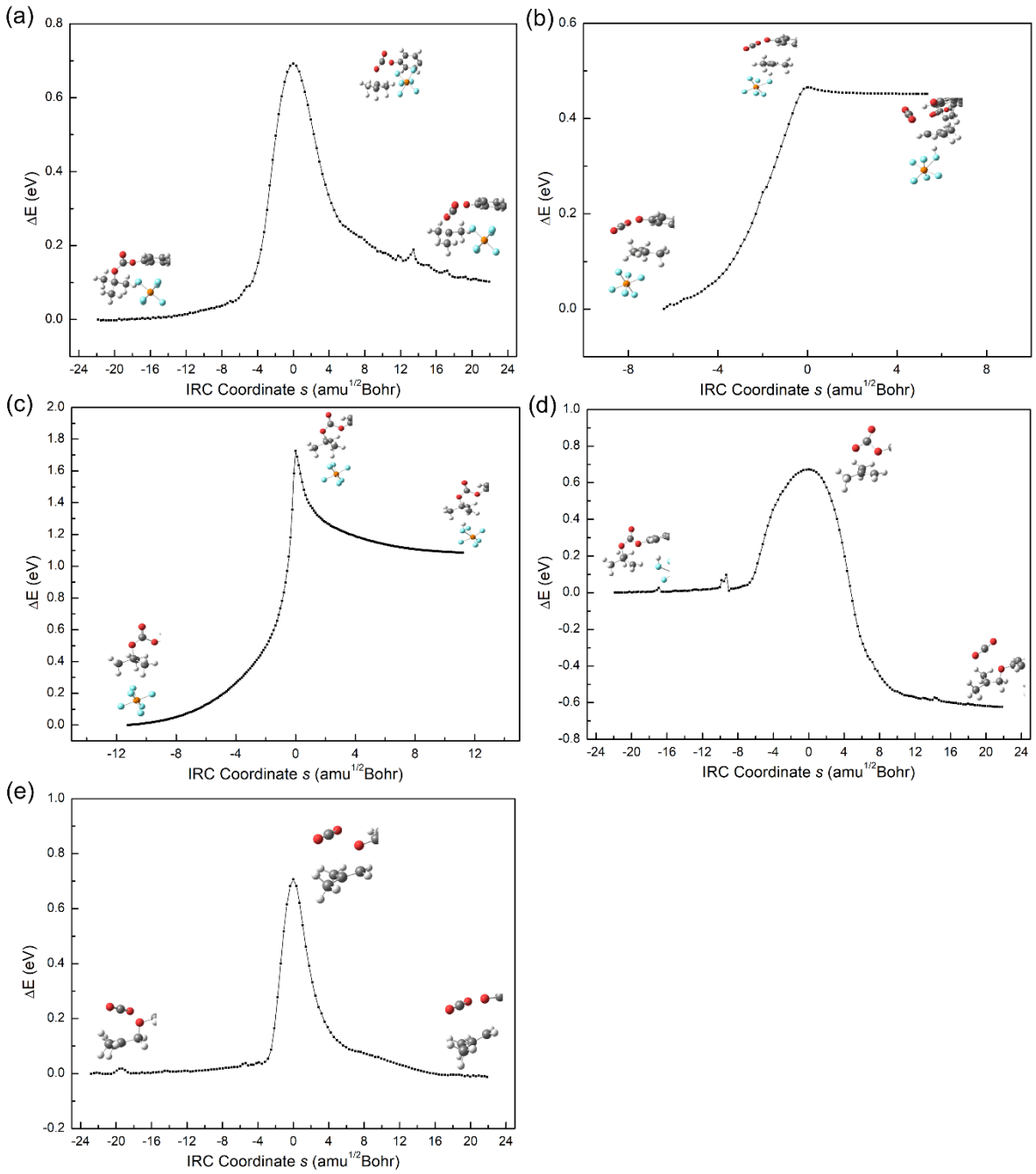


Figure S34. The potential energies along the IRCs for (a) A-TS1, (b) A-TS2, (c) C-TS1, (d) C-TS2, and (e) C-TS3 of PF_6^- in **Table 1**.

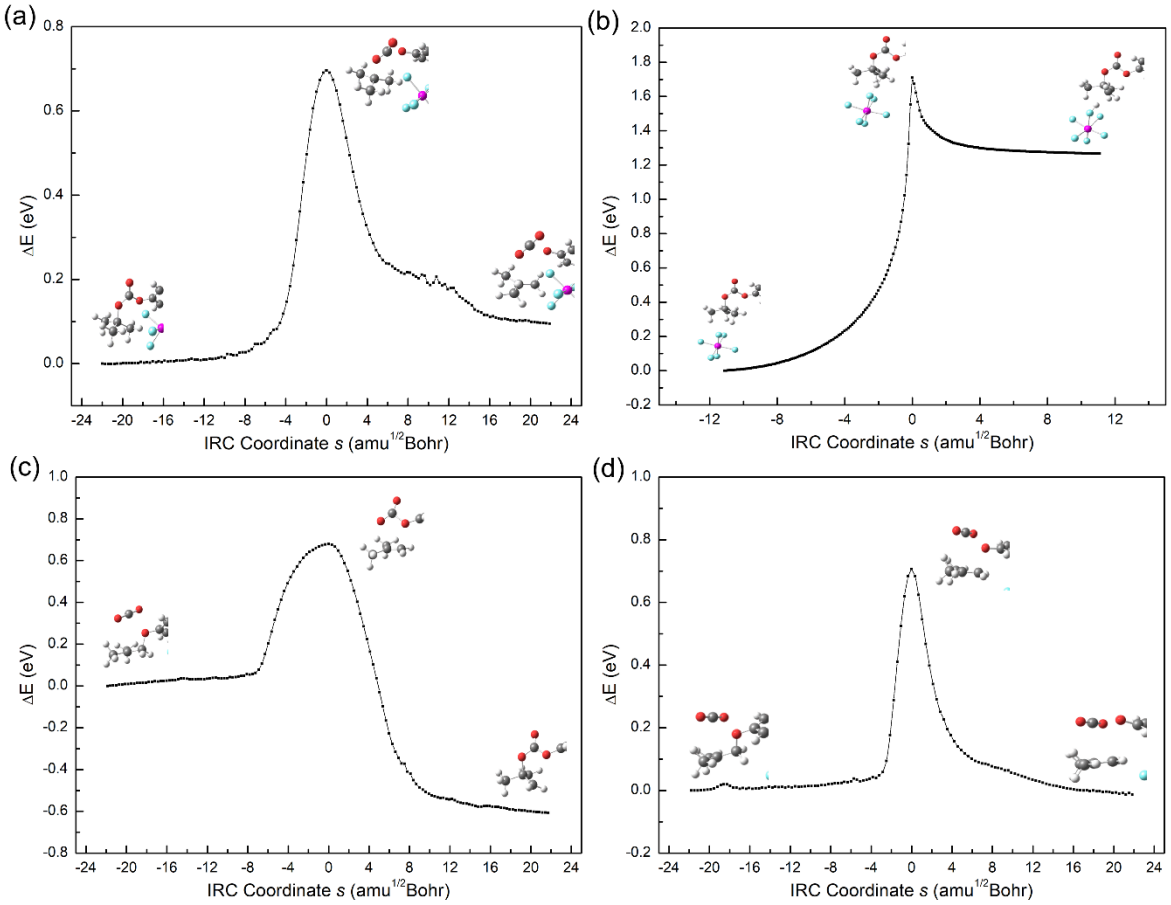


Figure S35. The potential energies along the IRCs for (a) A-TS1, (b) C-TS1, (c) C-TS2, and (d) C-TS3 of SbF_6^- in **Table 1**.

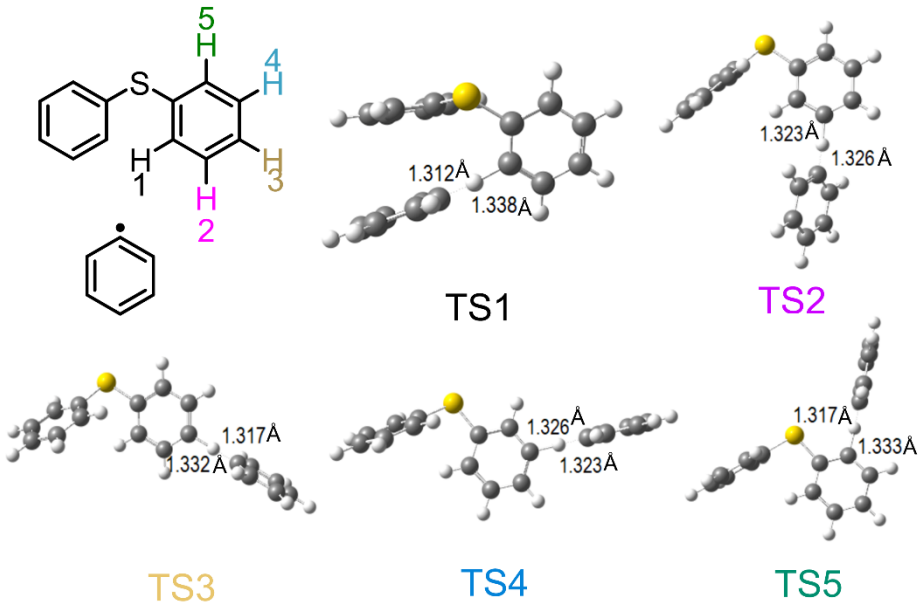


Figure S36. The geometries of the transition state for phenyl radical reacting with the DPS in **Fig. 6**.

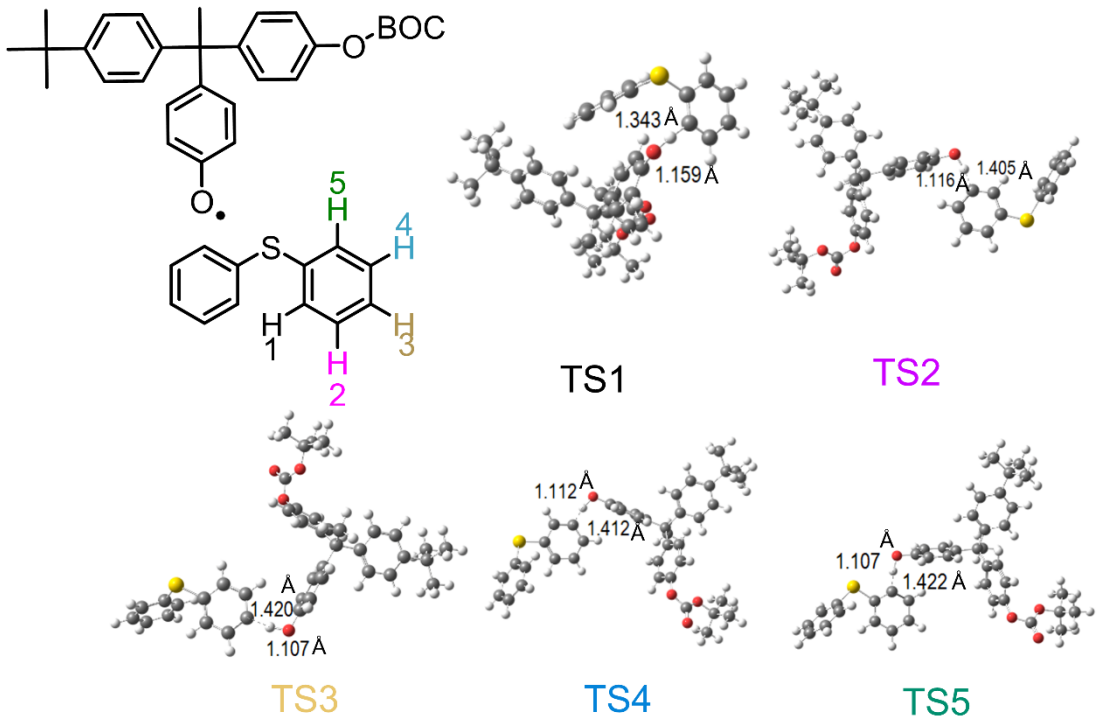


Figure S37. The geometries of the transition state for oxygen free radical reacts with the DPS in **Fig. 6**.

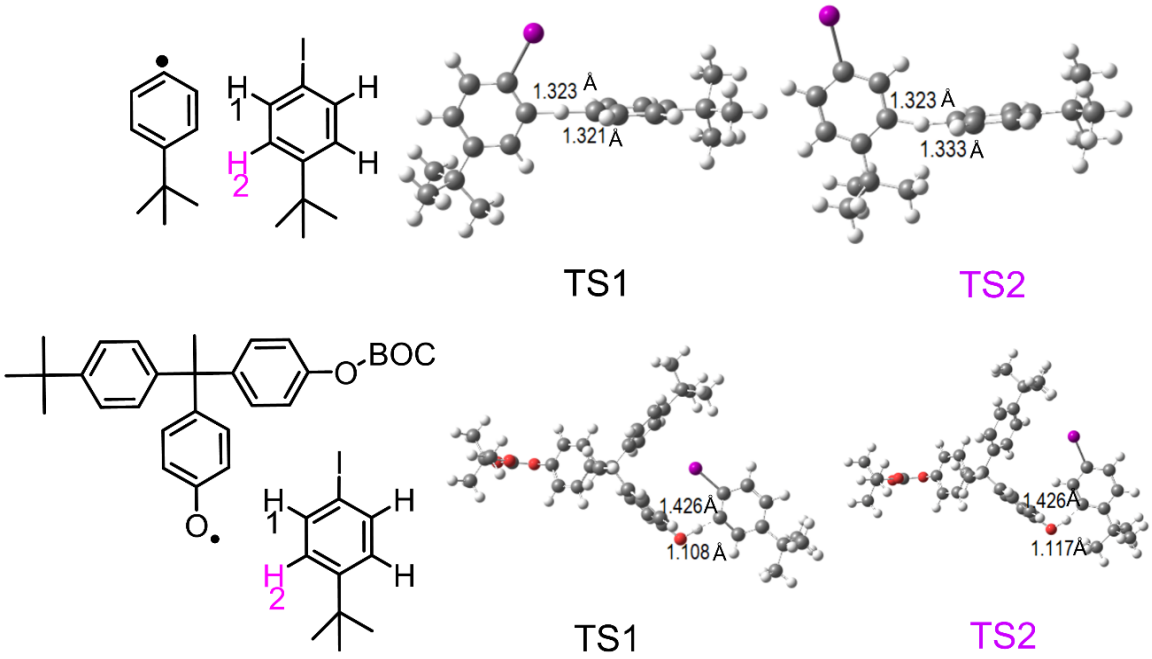


Figure S38. The geometries of the transition state for phenyl radical and oxygen-free radical react with the TIB in **Fig. 6**.