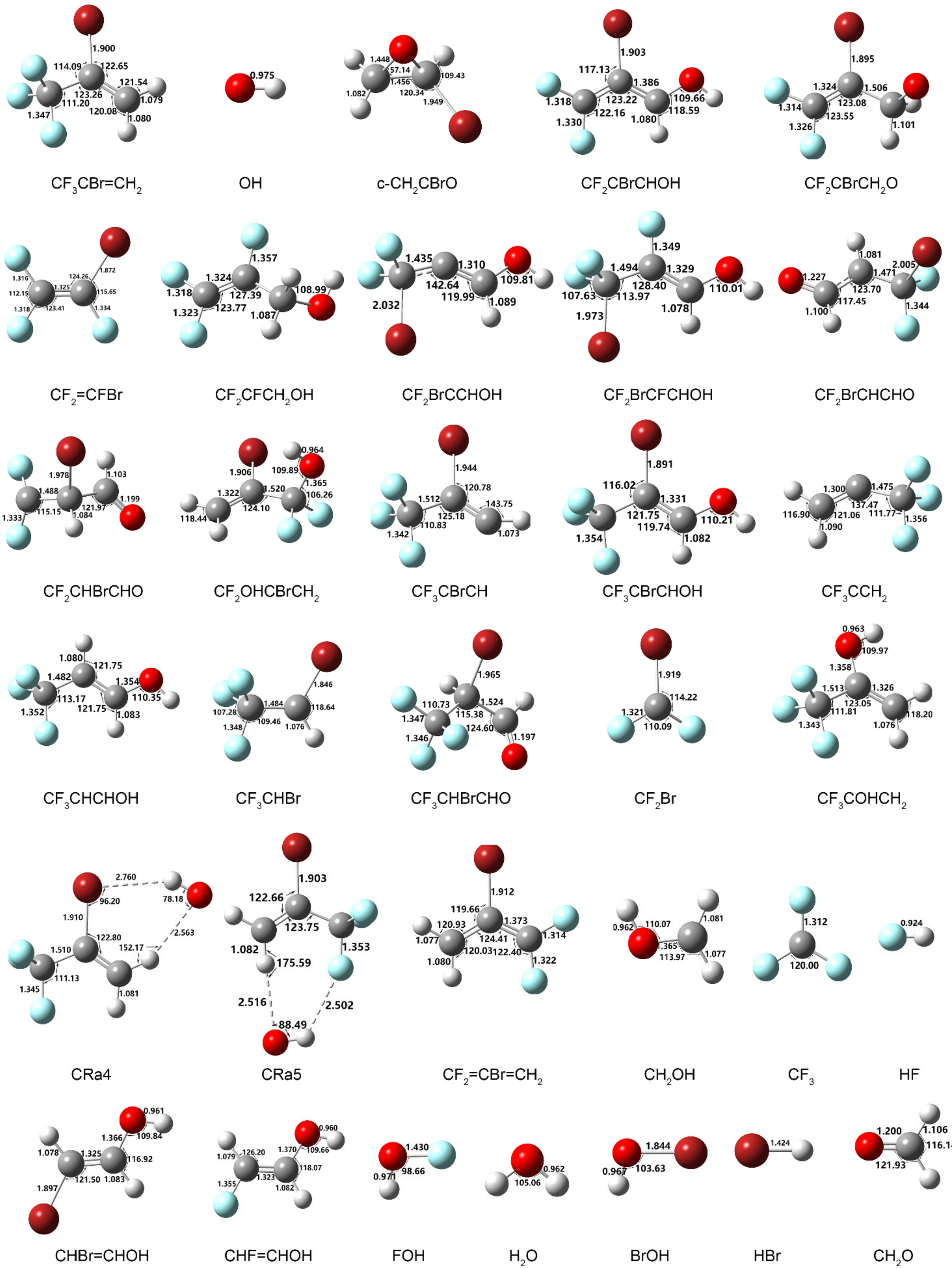
Supplemental Material-I

Theoretical Kinetic and Mechanism Studies on the Reactions of CF_3CBrCH_2 (2-BTP) with OH and H Radicals

Huiting Bian[1], Lili Ye[2], Jinhua Sun[1,*]

[1] *State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China*

[2] *Key Laboratory for Power Machinery and Engineering of MOE, Shanghai Jiao Tong University, Shanghai 200240, P. R. China*



$CF_3CBr=CH_2$
OH
c-CH_2CBrO
$CF_2CBrCHOH$
CF_2CBrCH_2O
$CF_2=CFBr$
CF_2CFCH_2OH
$CF_2BrCCHOH$
$CF_2BrCFCHOH$
$CF_2BrCHCHO$
$CF_2CHBrCHO$
$CF_2OHCBrCH_2$
CF_3CBrCH
$CF_3CBrCHOH$
CF_3CCH_2
$CF_3CHCHOH$
CF_3CHBr
$CF_3CHBrCHO$
CF_2Br
CF_3COHCH_2
CRa4
CRa5
$CF_2=CBr=CH_2$
CH_2OH
CF_3
HF
$CHBr=CHOH$
$CHF=CHOH$
FOH
H_2O
BrOH
HBr
CH_2O

Figure S1. Optimized geometries of reactants, products and prereaction complexes involved in the reactions of 2-BTP + OH calculated at B3LYP/aug-cc-pVTZ. Distances and angles are in angstrom and degree, respectively.

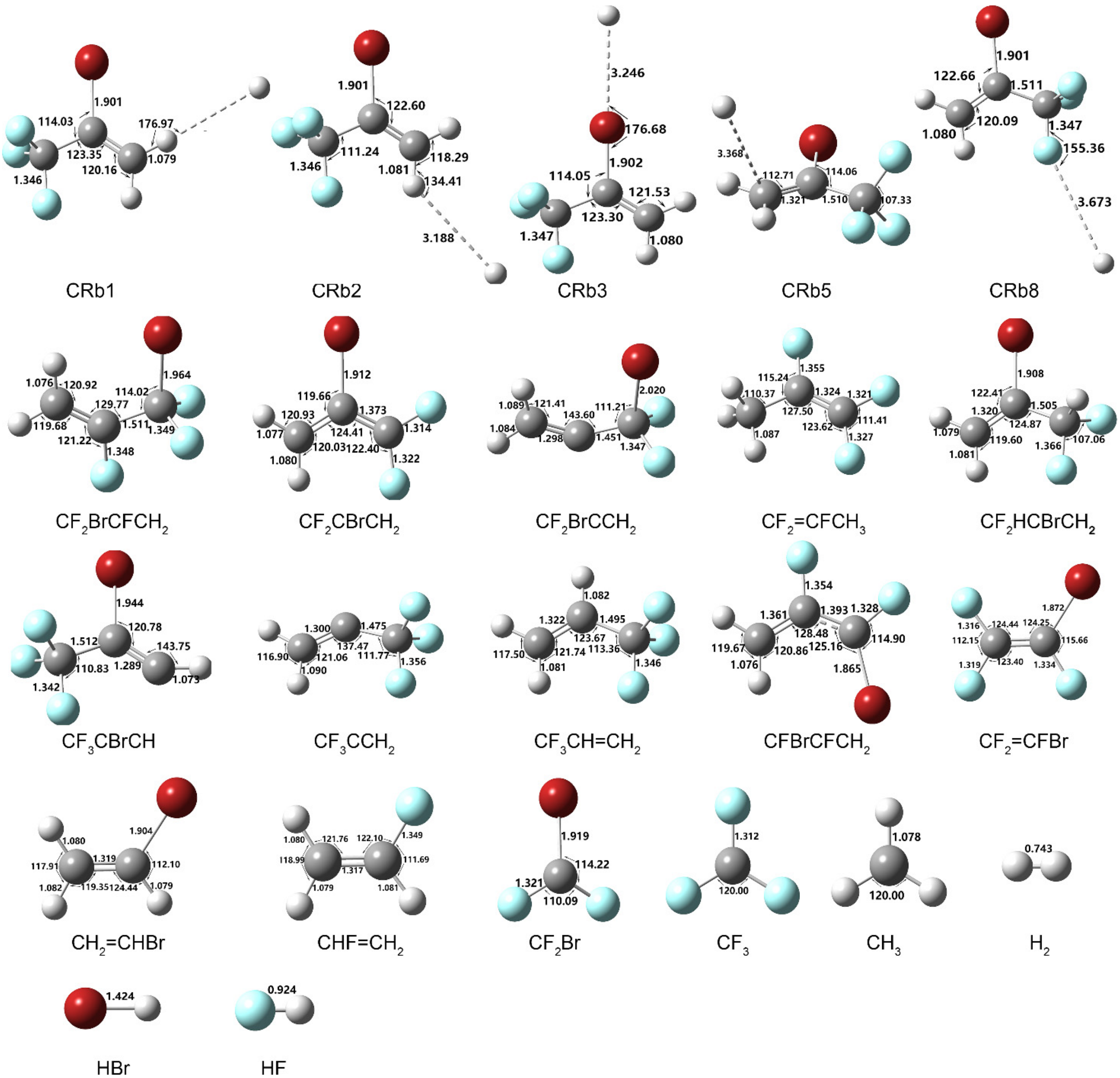


Figure S2. Optimized geometries of reactants, products and prereaction complexes involved in the reactions of 2-BTP + H calculated at B3LYP/aug-cc-pVTZ. Distances and angles are in angstrom and degree, respectively.

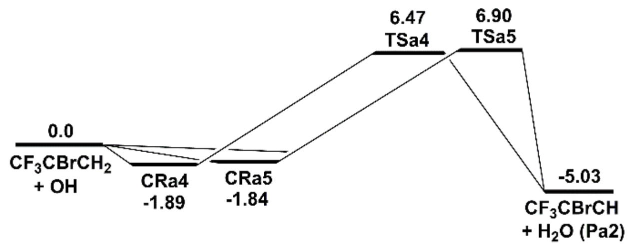


Figure S3. Complete potential energy diagram for channels including prereaction complexes in the reactions of 2-BTP with OH radical at 0 K in kcal/mol at CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ (zero point vibrational energy included).

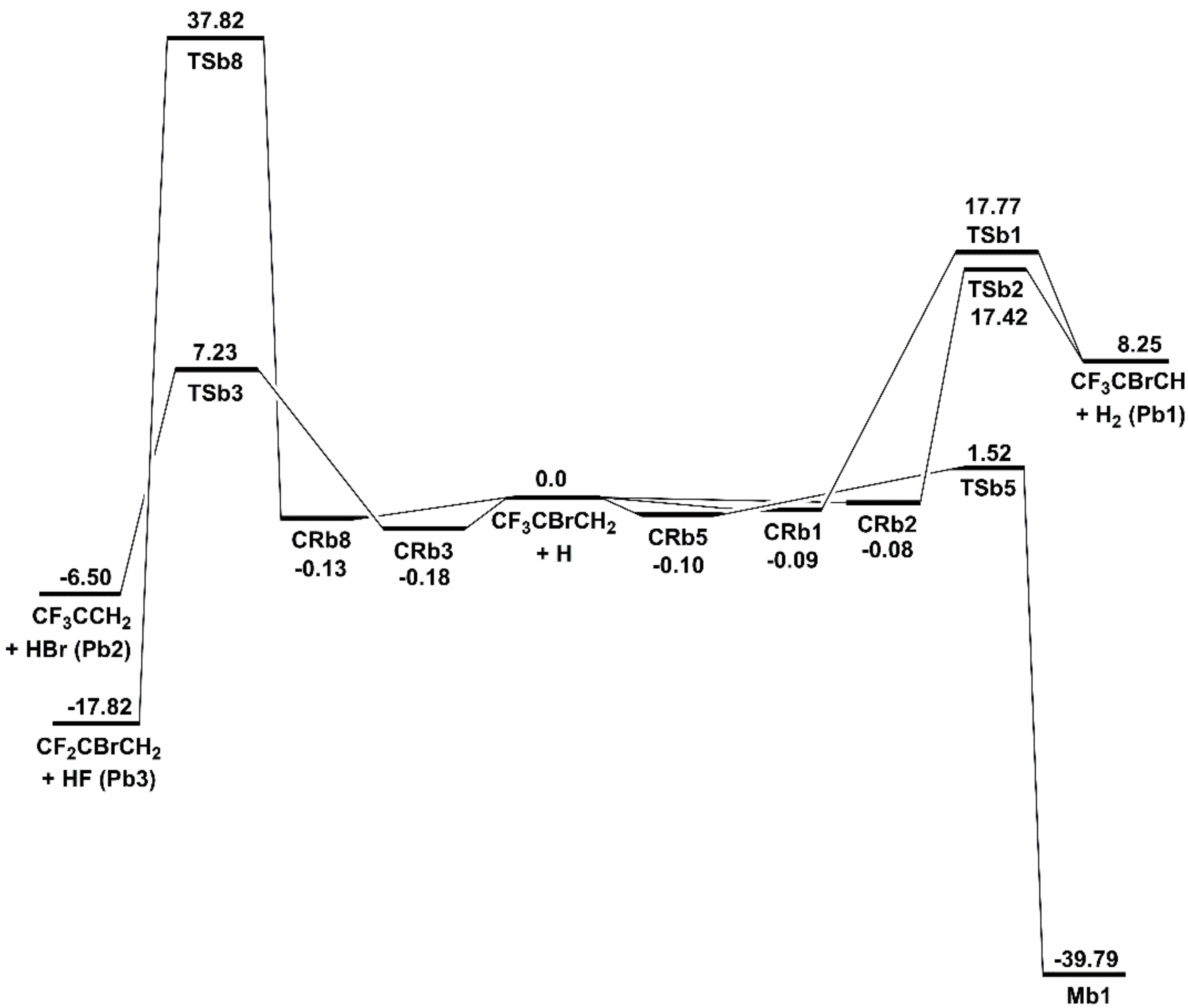


Figure S4. Complete potential energy diagram for channels including prereaction complexes in the reactions of 2-BTP with H radical at 0 K in kcal/mol at CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ (zero point vibrational energy included).

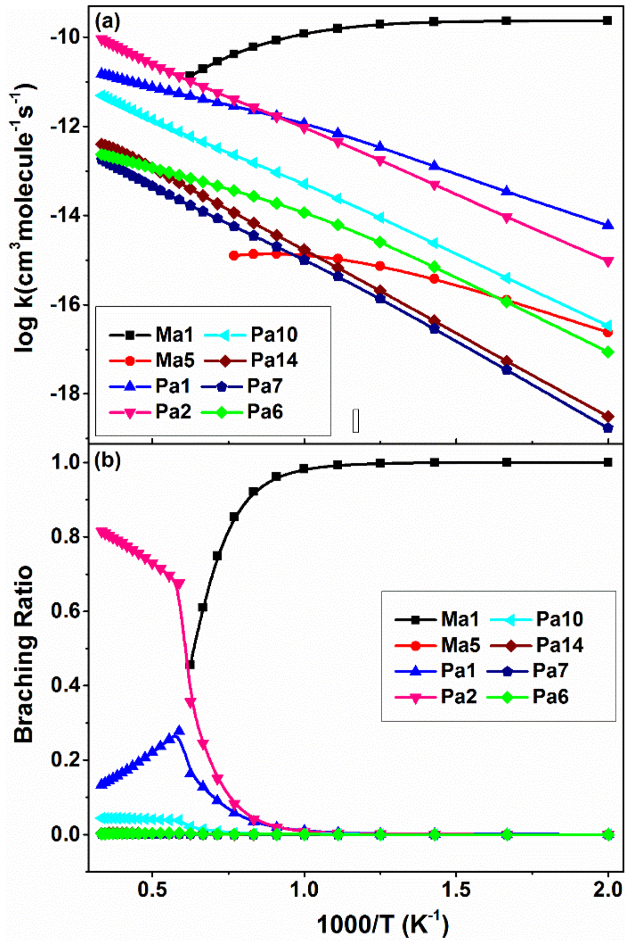


Figure S5. Temperature-dependent rate constants (a) and branching ratios of the major channels for 2-BTP + OH at 100 atm in N2.

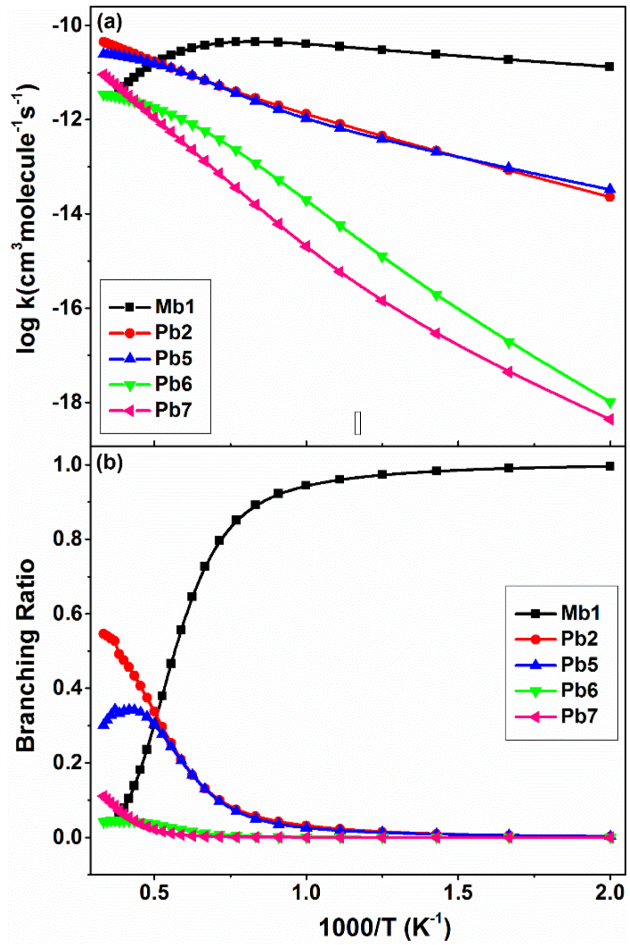


Figure S6. Temperature-dependent rate constants (a) and branching ratios (b) of the major channels for 2-BTP + H at 100 atm in N2.

Table S1. Relative energies of all the stationary points involved in 2-BTP + OH reaction at 0 K in kcal/mol by using the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ method.

Species	ΔE	ΔE + ΔE_{ZPVE}	Species	ΔE	ΔE + ΔE_{ZPVE}
Ra: $CF_3CBr{=}CH_2$ + OH	0.0	0.0	TSa3	35.91	6.47
Pa1: CF_3COHCH_2 + Br	-27.28	-23.59	TSa4	8.97	6.47
Pa2: CF_3CBrCH + H_2O	-4.45	-5.03	TSa5	9.37	6.90
Pa3: CF_3CCH_2 + BrOH	31.74	31.87	TSa6	73.99	75.17
Pa4: $CF_2OHCBrCH_2$ + F	15.28	17.38	TSa7	74.35	75.59
Pa5: CF_2CBrCH_2 + FOH	70.51	70.24	TSa8	75.82	75.60
Pa6: CF_3CHBr + CH_2O	-11.51	-11.88	Ma1-TS1	8.56	7.35
Pa7: $CF_3CHBrCHO$ + H	-0.12	-2.73	Ma1-TS2	13.10	14.06
Pa8: cCH_2CHBrO + CF_3	12.91	14.56	Ma1-TS3	14.21	17.62
Pa9: CF_2CBrCH_2O + HF	7.51	7.11	Ma1-TS4	31.73	32.22
Pa10: $CF_3CBrCHOH$ + H	5.45	3.35	Ma1-TS5	5.34	6.65
Pa11: $CF_2CBrCHOH$ + HF	-11.37	-9.90	Ma1-TS6	18.32	17.87
Pa12: CF_2CFCH_2OH + Br	-1.26	2.82	Ma2-TS1	-2.46	-1.07
Pa13: $CF_2{=}CFBr$ + CH_2OH	22.06	22.52	Ma2-TS2	2.49	4.57
Pa14: $CF_3CHCHOH$ + Br	-28.98	-24.99	Ma2-TS3	10.00	13.74
Pa15: $CF_2CHBrCHO$ + HF	-13.61	-13.48	Ma2-TS4	25.46	28.46
Pa16: CHBr=CHOH + CF_3	1.15	2.24	Ma3-TS1	-6.16	-2.37
Pa17: $CF_2BrCH{=}CHO$ + HF	-21.82	-22.20	Ma3-TS2	25.89	27.30
Pa18: $CF_2BrCCHOH$ + HF	5.52	5.41	Ma4-TS1	3.54	6.34
Pa19: CHF=CHOH + CF_2Br	13.45	14.38	Ma4-TS2	13.84	15.64
Pa20: $CF_2BrCFCHOH$ + H	23.75	21.21	Ma4-TS3	27.08	25.53
Ma1	-31.91	-28.01	Ma4-TS4	26.04	26.23
Ma2	-38.55	-34.20	Ma5-TS1	4.40	2.59
Ma3	-16.88	-12.72	Ma5-TS2	-6.06	-4.24
Ma4	-23.41	-19.89	Ma5-TS3	41.71	44.51
Ma5	-26.33	-22.95	CRa4	-2.73	-1.89
TSa1	-0.05	1.52	CRa5	-2.68	-1.84
TSa2	0.27	1.80			

Table S2. Relative energies of all the stationary points involved in 2-BTP + H at 0 K in kcal/mol by using the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ method.

Species	ΔE	ΔE + ΔE_{ZPVE}	Species	ΔE	ΔE + ΔE_{ZPVE}
Rb: $CF_3CBr{=}CH_2$ + H	0.0	0.0	TSb6	68.16	70.49
Pb1: CF_3CBrCH + H_2	10.56	8.25	TSb7	35.95	36.23
Pb2: CF_3CCH_2 + HBr	-7.67	-6.50	TSb8	37.47	37.82
Pb3: CF_2CBrCH_2 + HF	-19.91	-17.82	Mb1-TS1	0.95	3.99
Pb4: $CF_2HCBrCH_2$ + F	17.98	23.23	Mb1-TS2	2.55	7.97
Pb5: CF_3CHCH_2 + Br	-34.00	-27.81	Mb1-TS3	21.92	25.11
Pb6: CF_2CFCH_3 + Br	-13.99	-7.90	Mb2-TS1	-37.38	-31.42
Pb7: $CHBr{=}CH_2$ + CF_3	-6.86	-3.47	Mb2-TS2	-3.91	0.36
Pb8: $CF_2{=}CFBr$ + CH_3	15.39	16.54	Mb2-TS3	23.80	28.61
Pb9: $CFBrCFCH_2$ + HF	-17.10	-15.00	Mb3-TS1	-21.76	-15.76
Pb10: CF_2BrCCH_2 + HF	-2.59	-0.89	Mb3-TS2	21.03	23.72
Pb11: $CHF{=}CH_2$ + CF_2Br	1.39	5.36	Mb4-TS1	4.05	8.14
Pb12: $CF_2BrCFCH_2$ + H	14.46	14.09	Mb4-TS2	19.26	19.84
Mb1	-45.91	-39.79	Mb4-TS3	21.00	23.76
Mb2	-42.44	-36.61	Mb4-TS4	46.70	47.60
Mb3	-29.46	-23.15	CRb1	-0.22	-0.09
Mb4	-27.01	-21.76	CRb2	-0.18	-0.08
TSb1	19.36	17.77	CRb3	-0.36	-0.18
TSb2	18.92	17.42	CRb5	-0.29	-0.10
TSb3	6.89	7.23	CRb8	-0.13	-0.13
TSb4	5.55	6.51			
TSb5	0.98	1.52			