Electronic Supplementary Information

for

Dual Fluorescence of Excited State Intra-molecular Proton Transfer of HBFO: Mechanistic Understanding, Substituent and Solvent Effects

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Section 1, Computational method for rate calculation.

Without consideration of rotational degrees of freedom, the standard expression* for the unimolecular rate constant (units s^{-1}) of an isolated molecule with total energy E

$$k(E)=\frac{N(E)}{2\pi\hbar N_0(E)} \qquad \text{(S1)}$$

Within the separable approximation tunneling is accounted for by replacing N(E) in eq S1 by $N_{QM}(E)$

$$N_{QM}(E)=\sum_n P(E-\varepsilon_n^{\neq}) \qquad \text{(S2)}$$

The expression for the unimolecular rate constant which include the effect of tunneling is

$$k(E)=\frac{\sum_n P(E-\varepsilon_n^{\neq})}{2\pi\hbar N_0'(E)} \qquad \text{(S3)}$$

Where N(E) and $N_0(E)$ are the integral densities of states of the transition state and the reactant molecule. The expressions of them are as follows:

$$N(E)=\sum_n h(E-\varepsilon_n^{\neq}) \qquad \text{(S4)}$$

$$N_0(E)=\sum_n h(E-\varepsilon_n) \qquad \text{(S5)}$$

Where h(x) is the usual step-function

$$h(x)=\begin{cases}0, & x<0\\ 1, & x>0\end{cases} \qquad \text{(S6)}$$

And $\varepsilon_n^{\neq}$ and ε_n are the vibrational energy levels of the transition state and the reactant molecule. It is generally to assume the vibrational energy levels are almost given by an oscillator approximation, so the expression can be obtained as follows:

$$\varepsilon_n=\sum_{i=1}^{s}\hbar\omega_i\left(n_i+\frac{1}{2}\right) \qquad \text{(S7)}$$

$$\varepsilon_n^{\neq}=V_0+\sum_{i=1}^{s-1}\hbar\omega_i^{\neq}\left(n_i+\frac{1}{2}\right) \qquad \text{(S8)}$$

Where s is the number of vibrational degrees of freedom of the stable molecule, $\{\omega_i\}$ and $\{\omega_i^{\neq}\}$ are the normal mode vibration frequencies for the transition state and for the reactant molecule, respectively. And V_0 is the energy of the saddle point of the PES relative to the minimum PES of the reactant molecule, the total energy E is based on the relative energy compares to the minimum of the PES.

Next the large sums of the densities of states would be disposed approximately. So the expressions are shown below：

$$N_0(E) = \frac{E^s}{s!\sum_{i=1}^{s}(\hbar\omega_i)} \tag{S9}$$

$$N(E) = \frac{(E-V_0)^{s-1}}{(s-1)!\sum_{i=1}^{s-1}(\hbar\omega_i^{\neq})} \tag{S10}$$

On the basis of above approximates, the expression of the rate constant can be expressed as follow.

$$k(E) = A\left(\frac{E-V_0}{E}\right)^{s-1} \tag{S11}$$

where A is a frequency factor (units s^{-1}).

$$A = \left[\prod_{i=1}^{s}\omega_i\right] \Big/ 2\pi\left[\prod_{i=1}^{s-1}\omega_i^{\neq}\right] \tag{S12}$$

The unit conversion from cm^{-1} for normal mode vibration frequencies and frequency factor A to rate unit s^{-1} is taken by using the following formula

$$c = \frac{\nu}{\tilde{\nu}} \tag{S13}$$

Where ν is the unimolecular vibration frequencies, $\tilde{\nu}$ is the wave number and c is the velocity of light.

Therefore, the expression of frequency factor can be written as follows：

$$A = \frac{\left[\prod_{i=1}^{s}\omega_i\right]\times(3\times10^{10})}{2\pi\left[\prod_{i=1}^{s-1}\omega_i^{\neq}\right]} \tag{S14}$$

So finally the expression of unimolecular rate constant can be expressed as：

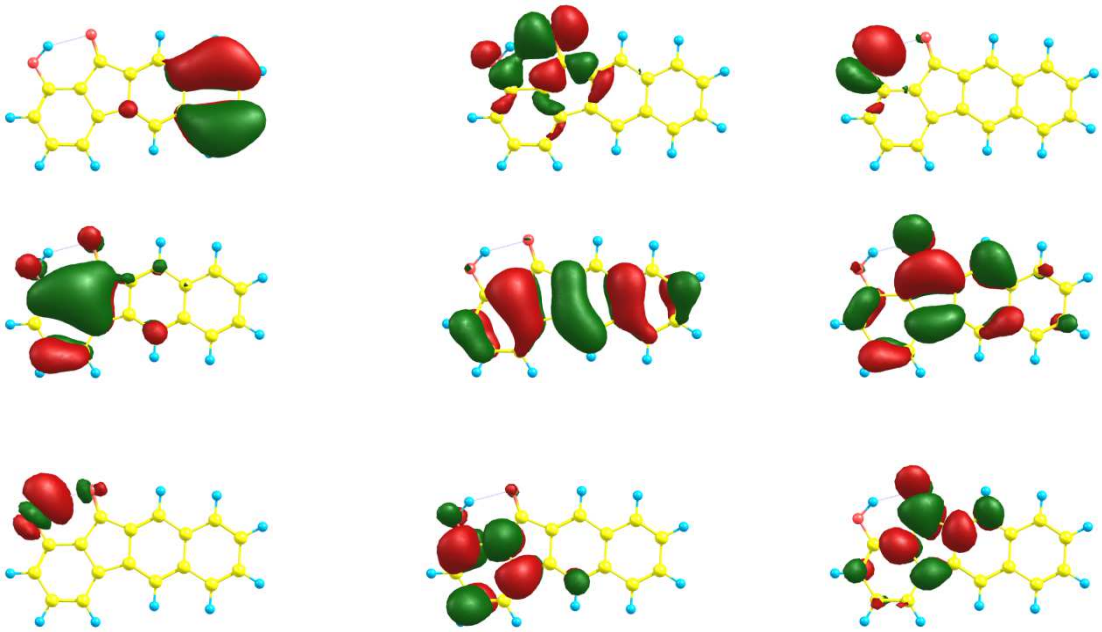
$$k(E)=\frac{\left[\prod_{i=1}^{s}\omega_i\right]\times(3\times10^{10})}{2\pi\left[\prod_{i=1}^{s-1}\omega_i^{\neq}\right]}\left(\frac{E-V_0}{E}\right)^{s-1} \qquad \text{(S15)}$$

Section 2, Test calculations for the choice of most appropriate active space of HBFO at the CASSCF/CASPT2 level of theory.

Test 1:

The vertical excitation energy: 3.31 eV (experimental value:3.03 eV)

The diagram of orbitals in active space cas(10,9)



Occupation numbers of these orbitals

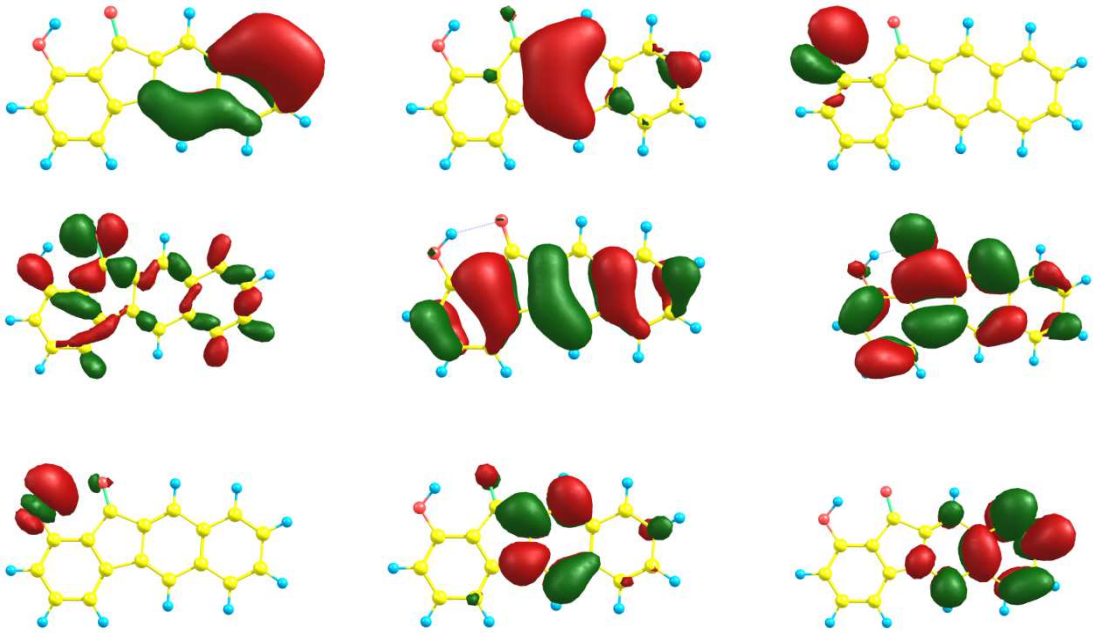
	1	2	3	4	5
1	0.199988D+01				
2	0.321563D-04	0.199989D+01			
3	-0.973261D-07	0.110158D-05	0.198126D+01		
4	-0.228208D-04	0.110198D-05	0.196043D-05	0.195996D+01	
5	0.103917D-04	0.114739D-05	-0.713624D-06	-0.233188D-05	0.193523D+01
6	0.582563D-04	0.101117D-04	0.300263D-06	0.333791D-03	-0.136028D-03
7	0.540031D-07	0.309784D-04	0.154174D-04	0.581731D-06	-0.314053D-06
8	0.379016D-04	-0.443733D-04	0.399573D-06	-0.205618D-03	0.741175D-04
9	0.513347D-05	0.270888D-05	-0.684411D-05	-0.163345D-02	0.487065D-03

	6	7	8	9
6	0.638849D-01			
7	0.596630D-07	0.187869D-01		
8	0.991337D-05	0.551403D-06	0.345485D-01	
9	-0.640363D-05	-0.299211D-06	0.227016D-03	0.655915D-02

Test 2

The vertical excitation energy: 3.97 eV (experimental value:3.03 eV)

The diagram of orbitals in active space cas(10,9)



Occupation numbers of these orbitals

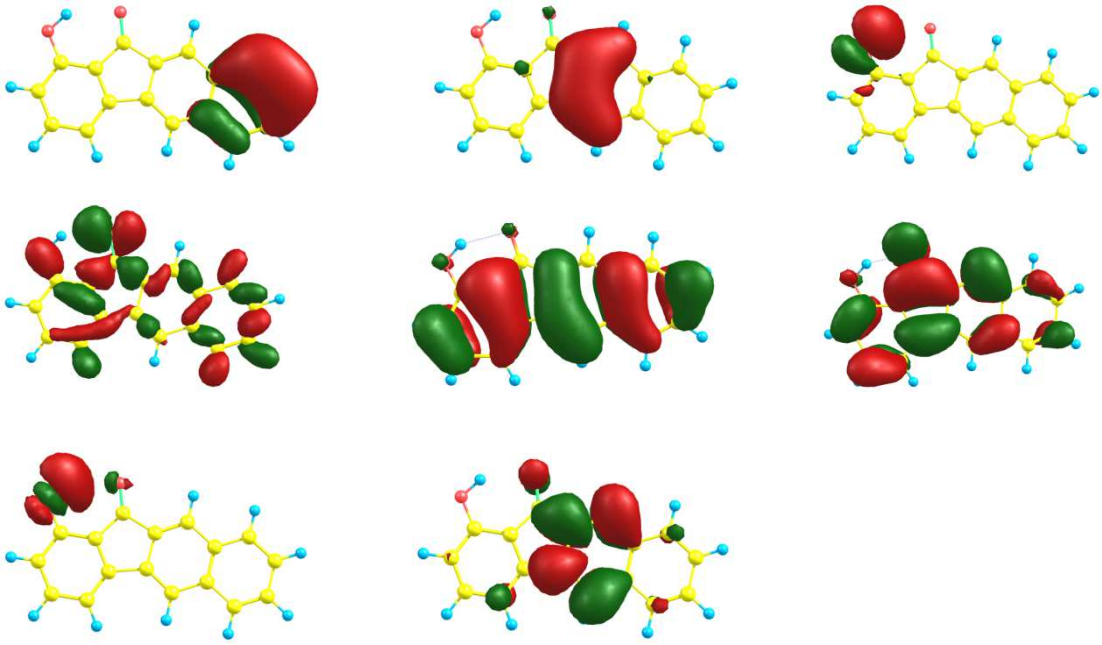
	1	2	3	4	5
1	0.194855D+01				
2	-0.156944D-05	0.194250D+01			
3	-0.882271D-06	-0.112541D-05	0.198138D+01		
4	-0.169157D-06	-0.841250D-07	-0.143827D-05	0.199998D+01	
5	0.948764D-06	0.153291D-07	-0.435568D-06	-0.486922D-06	0.191001D+01
6	0.594017D-06	0.327197D-04	0.726153D-06	-0.688234D-05	-0.292908D-05
7	-0.490469D-05	0.331468D-05	0.171414D-04	-0.336908D-05	-0.110051D-04
8	-0.100885D-04	-0.225938D-04	0.355710D-05	0.176116D-04	-0.253944D-06
9	-0.859608D-05	-0.145292D-04	-0.326979D-05	0.146717D-05	0.190099D-04

	6	7	8	9
6	0.910035D-01			
7	0.129763D-05	0.186236D-01		
8	-0.128525D-05	0.380035D-06	0.578989D-01	
9	-0.182043D-05	0.151963D-06	-0.282292D-07	0.500622D-01

Test 3

The vertical excitation energy: 3.88 eV (experimental value:3.03 eV)

The diagram of orbitals in active space cas(10,8)



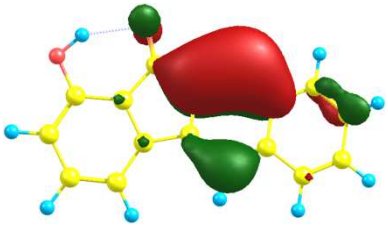
Occupation numbers of these orbitals

	1	2	3	4	5
1	0.199992D+01				
2	0.160922D-04	0.194282D+01			
3	0.324397D-07	-0.238688D-07	0.198139D+01		
4	0.364109D-04	-0.577274D-05	-0.323699D-07	0.199998D+01	
5	0.150811D-04	0.175093D-04	-0.403405D-07	-0.166140D-05	0.191277D+01
6	-0.302331D-03	-0.767787D-03	-0.997503D-06	0.255324D-04	-0.247269D-04
7	-0.121878D-05	-0.898377D-06	-0.114098D-05	-0.318771D-05	0.590908D-06
8	0.515718D-03	0.215390D-03	0.190969D-05	-0.126049D-04	-0.871742D-03

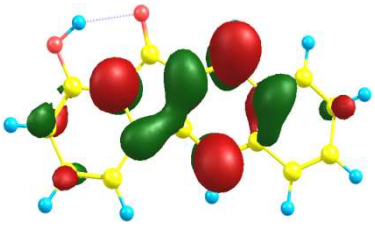
	6	7	8
6	0.867646D-01		
7	-0.151916D-06	0.186215D-01	
8	0.198506D-04	0.116806D-06	0.577370D-01

Section 3, Figures

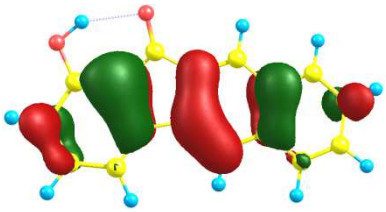
Figure S1. The diagram of selected orbitals in active space for HBFO.



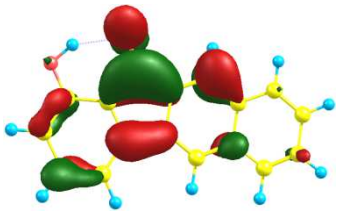
π orbital



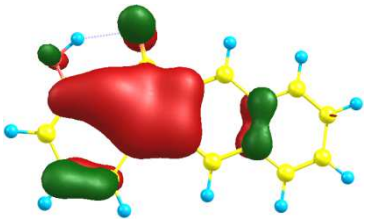
π* orbital



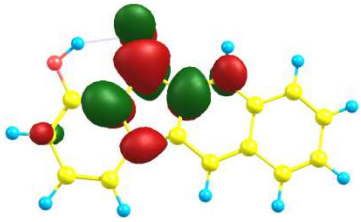
π orbital



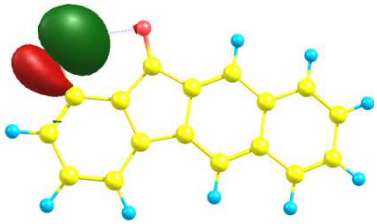
π* orbital



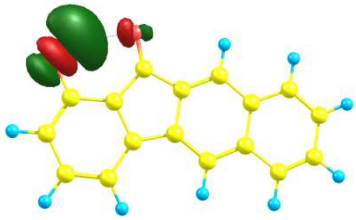
π orbital



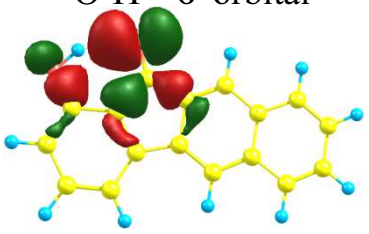
π* orbital



O-H σ orbital

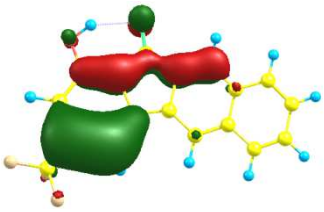


O-H σ* orbital

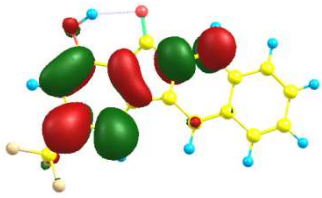


n orbital (C=O)

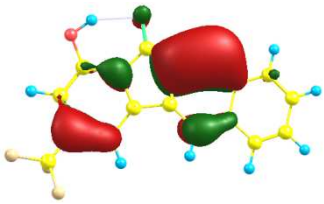
Figure S2. The diagram of selected orbitals in active space for *meta*-CF_3-HBFO.



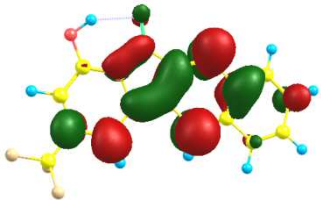
π orbital



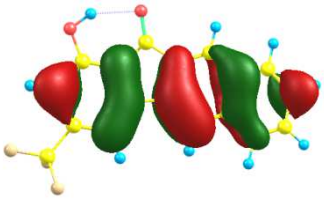
π* orbital



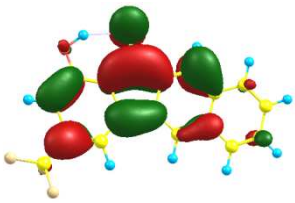
π orbital



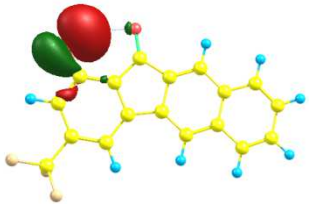
π* orbital



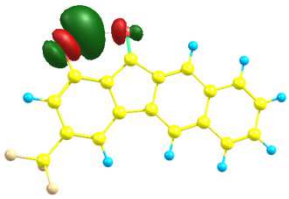
π orbital



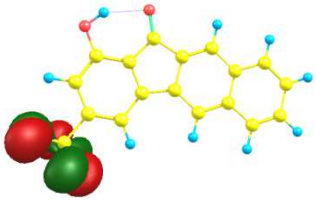
π* orbital



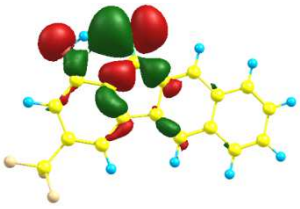
O-H σ orbital



O-H σ* orbital

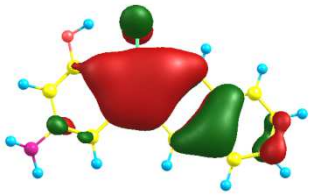


n orbital (F)

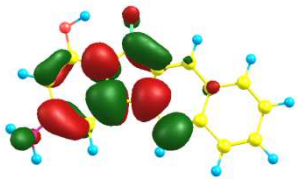


n orbital (C=O)

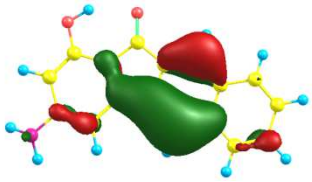
Figure S3. The diagram of selected orbitals in active space for *meta*-NH_2-HBFO.



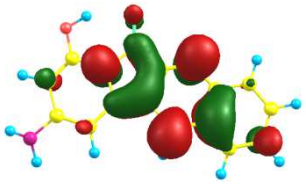
π orbital



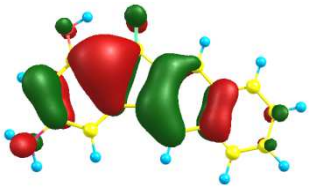
π* orbital



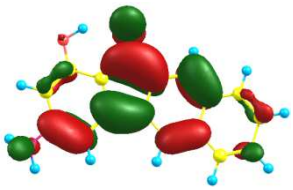
π orbital



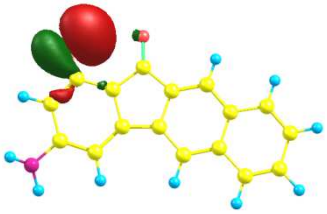
π* orbital



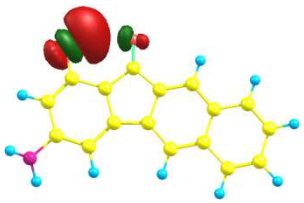
π orbital



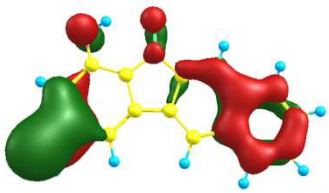
π* orbital



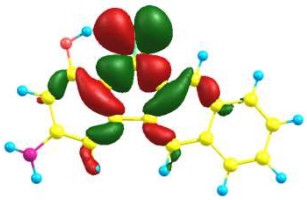
O-H σ orbital



O-H σ* orbital



n orbital (N)



n orbital (C=O)

Section 4, Tables

Table S1 The vertical excitation energies ($E_{\perp}$, eV), wavelengths (λ_{cal}, nm), experimental wavelength (λ_{exp}, nm), oscillator strengths (*f*), dipole moments (D.M., Debye) and the character of singly occupied orbitals in the $S_{CT}(^1\pi\pi^*)$ state for the Franck-Condon structures of HBFO at the CASPT2//CAS(10,9)/6-31G* and for *meta*-CF_3-HBFO, *meta*-NH_2-HBFO, *para*-CF_3-HBFO, *para*-NH_2-HBFO at the CASPT2//CAS(12,10)/6-31G* level of theory

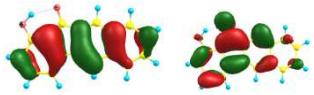
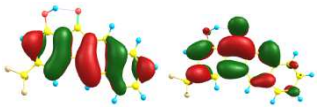
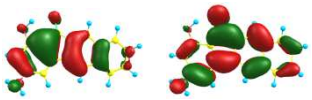
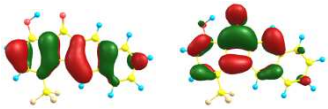
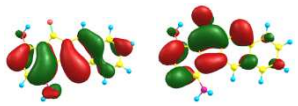
Fluorescers	Singly occupied orbitals	D.M.	*f*	$E_{\perp}$	λ_{cal}	λ_{exp}
HBFO		6.21	2.51E-02	3.13	395	409
meta-CF_3-HBFO		5.55	1.53E-01	3.31	375	
meta-NH_2-HBFO		6.20	2.58E-01	3.43	361	
para-CF_3-HBFO		4.56	1.55E-01	3.36	368	
para-NH_2-HBFO		6.23	2.59E-01	3.47	357	

Table S2 The absolute energy (A.E.) in Hartree for the optimized structures of enol (E)/keto(K) forms and maxima of five fluorescers, HBFO, *meta*-CF_3-HBFO, *meta*-NH_2-HBFO, *para*-CF_3-HBFO, *para*-NH_2 -HBFO in gas phase, cyclohexane and acetonitrile solvents along ESIPT pathways in the $S_{CT}(^1\pi\pi^*)$ state obtained at CASPT2//CASSCF/6-31+G* or CASPT2//CASSCF/PCM/6-31+G*level of theory

fluorescers	Solvents	critical points	A.E.
HBFO	Gas	S_{CT}-E	-801.7735
		S_{CT}-1.26-maximum	-801.7570
		S_{CT}-K	-801.7692
	Cyclohexane	S_{CT}-E	-801.7797
		S_{CT}-1.26-maximum	-801.7627
		S_{CT}-K	-801.7760
	Acetonitrile	S_{CT}-E	-801.7907
		S_{CT}-1.26-maximum	-801.7744
		S_{CT}-K	-801.7873

meta-CF_3-HBFO	Gas	S_{CT}-E	-1138.0648
		S_{CT}-1.20-maximum	-1138.0575
		S_{CT}-K	-1138.0666
	Cyclohexane	S_{CT}-E	-1137.9960
		S_{CT}-1.20-maximum	-1137.9882
		S_{CT}-K	-1137.9918
	Acetonitrile	S_{CT}-E	-1137.9960
		S_{CT}-1.20-maximum	-1137.9785
		S_{CT}-K	-1137.9903
meta-NH_2-HBFO	Gas	S_{CT}-E	-856.9698
		S_{CT}-1.28-maximum	-856.9464
		S_{CT}-K	-856.9596
	Cyclohexane	S_{CT}-E	-856.9848
		S_{CT}-1.28-maximum	-856.9683
		S_{CT}-K	-856.9737
	Acetonitrile	S_{CT}-E	-857.0001
		S_{CT}-1.28-maximum	-856.9754
		S_{CT}-K	-856.9932
para-CF_3-HBFO	Gas	S_{CT}-E	-1137.9748
		S_{CT}-1.22-maximum	-1137.9616
		S_{CT}-K	-1137.9746
	Cyclohexane	S_{CT}-E	-1137.9830
		S_{CT}-1.22-maximum	-1137.9704
		S_{CT}-K	-1137.9766
	Acetonitrile	S_{CT}-E	-1137.9920
		S_{CT}-1.22-maximum	-1137.9746
		S_{CT}-K	-1137.9882
para-NH_2-HBFO	Gas	S_{CT}-E	-856.9847
		S_{CT}-1.28-maximum	-856.9671
		S_{CT}-K	-856.9768
	Cyclohexane	S_{CT}-E	-856.9946
		S_{CT}-1.28-maximum	-856.9795
		S_{CT}-K	-856.9848
	Acetonitrile	S_{CT}-E	-857.0106
		S_{CT}-1.28-maximum	-856.9923
		S_{CT}-K	-857.0037

Table S3 The comparisons between transition states (maxima) structure and the absolute energy (A.E.) in Hartree at CASPT2 level for HBFO, *meta*-CF_3-HBFO, *meta*-NH_2-HBFO in the $S_{CT}(^1\pi\pi^*)$ state are obtained by constraint geometry method and traditional TS optimizations, respectively.

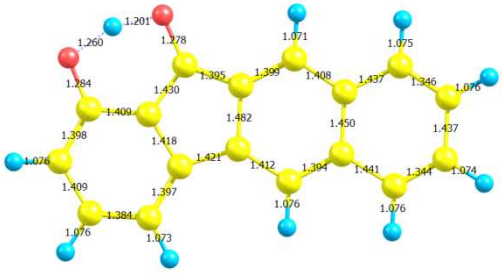
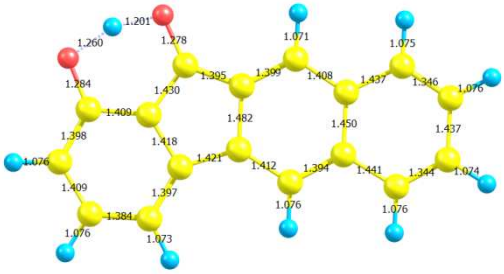
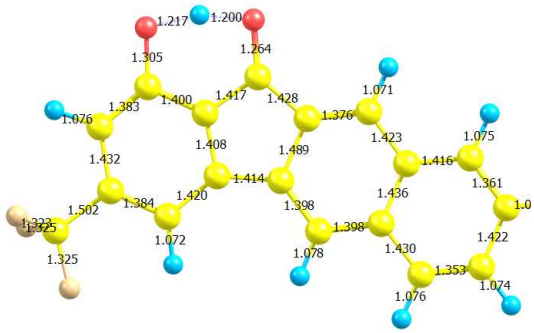
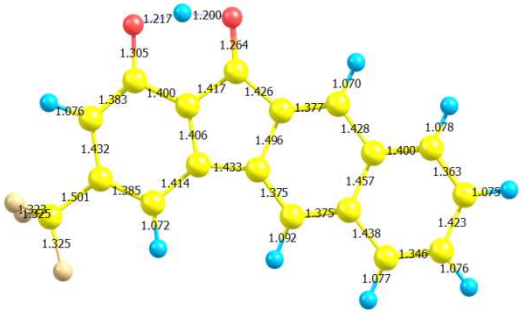
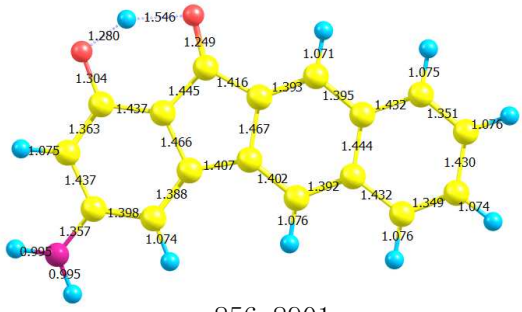
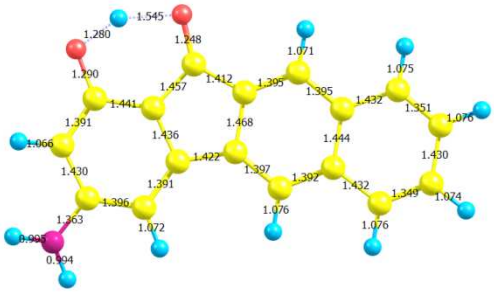
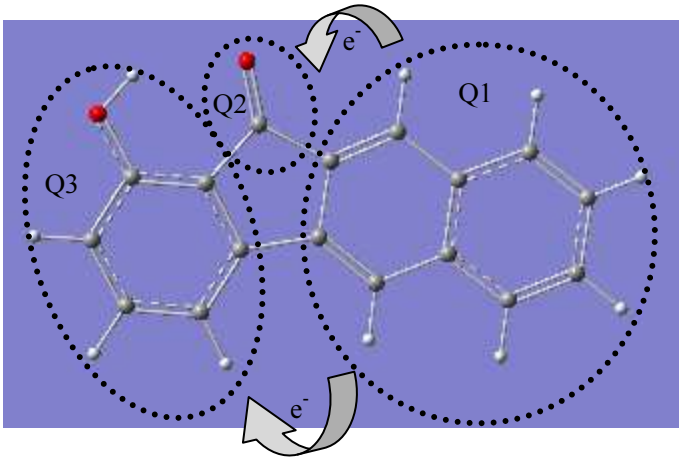
	Constraint method	TS optimization
HBFO	 −801. 7071	 −801. 7070
***meta*-CF_3-HBFO**	 −1137. 9698	 −1137. 9705
***meta*-NH_2-HBFO**	 −856. 8901	 −856. 8899

Table S4 (a)The fragment of charge translocation from the moieties of naphthalene (Q1) to carbonyl group (Q2) and benzene (Q3) (b)The sum of Mulliken charge distribution of the different fragment upon $S_0 \rightarrow S_{CT}(^1\pi\pi^*)$ FC excitation of HBFO.



(a)

	S_0	$S_{CT}(^1\pi\pi^*)$
Q1	-0.037	0.0776
Q2	-0.2733	-0.2844
Q3	0.2985	0.1837

(b)

Table S5 The test computations of single energy calculation at the CASPT2/6-31+G* level of theory along the selective stationary points that are adjacent to maxima of HBFO, *meta*-CF_3-HBFO and *meta*-NH_2-HBFO to confirm the reliability of the maxima searching.

		A.E.	**R.E.**
HBFO	**S_{CT}-1.17**	-801.7625	3.05
	S_{CT}-1.26(Barrier)	-801.7570	3.21
	S_{CT}-1.36	-801.7577	3.18
***meta*-CF_3-HBFO**	**S_{CT}-1.17**	-1138.0639	2.49
	S_{CT}-1.20(Barrier)	-1138.0575	2.66
	S_{CT}-1.26	-1138.0640	2.48
***meta*-NH_2-HBFO**	**S_{CT}-1.23**	-856.9515	3.27
	S_{CT}-1.28(Barrier)	-856.9464	3.49
	S_{CT}-1.33	-856.9603	3.11

Section 5-1, Cartesian coordinates of the optimized structures for HBFO along the ESIPT reaction pathway in $S_{CT}(^1\pi\pi^*)$ state at the CAS(10e/9o)/6-31G* level of theory.

$S_{CT}(^1\pi\pi^*)$-*E*

8	-1.644070000	-2.625807000	-0.004356000
8	-4.211458000	-1.404652000	0.004905000
6	-1.252869000	-1.449187000	0.004568000
6	0.069292000	-0.895611000	0.001163000
6	1.313285000	-1.497418000	-0.002803000
6	2.479491000	-0.693948000	-0.001244000
6	3.775334000	-1.283186000	-0.004259000
6	4.892712000	-0.515811000	-0.002252000
6	4.808734000	0.908897000	0.002890000
6	3.601873000	1.514281000	0.005474000
6	2.393648000	0.745916000	0.003656000
6	1.146785000	1.366072000	0.005769000
6	-0.013889000	0.581335000	0.004031000
6	-1.370507000	0.950634000	0.001738000
6	-2.039929000	2.189259000	-0.001158000
6	-3.406966000	2.162073000	-0.005070000
6	-4.156878000	0.954347000	-0.006424000
6	-3.529383000	-0.260259000	-0.001937000
6	-2.118493000	-0.275463000	0.001077000
1	-3.558766000	-2.132211000	0.016147000
1	1.392104000	-2.566766000	-0.005444000
1	3.851213000	-2.356107000	-0.008045000
1	5.862236000	-0.984089000	-0.004345000
1	5.712337000	1.490270000	0.004428000
1	3.524806000	2.587717000	0.009049000
1	1.078735000	2.441849000	0.007539000
1	-1.502397000	3.118492000	-0.001242000
1	-3.951868000	3.088037000	-0.007479000
1	-5.231216000	0.982241000	-0.007971000

$S_{CT}(^1\pi\pi^*)$-1.26(maximum)

8	-1.765855000	-2.527538000	-0.002608000
8	-3.974479000	-1.548442000	0.004922000
6	-1.253999000	-1.356152000	-0.005186000
6	0.051971000	-0.864836000	-0.006118000
6	1.307138000	-1.483175000	-0.002079000
6	2.474246000	-0.695499000	-0.000169000
6	3.779336000	-1.297811000	0.004914000
6	4.893802000	-0.542232000	0.007134000
6	4.813929000	0.892424000	0.004466000

6	3.619820000	1.510070000	0.000159000
6	2.394463000	0.752229000	-0.002239000
6	1.153016000	1.385372000	-0.005662000
6	-0.029556000	0.614545000	-0.007712000
6	-1.393738000	1.012809000	-0.006422000
6	-2.119315000	2.207014000	-0.001008000
6	-3.498415000	2.087846000	0.006345000
6	-4.200944000	0.866937000	0.008687000
6	-3.512791000	-0.349899000	0.003053000
6	-2.110758000	-0.210878000	-0.005330000
1	-2.938340000	-2.265383000	0.001274000
1	1.375939000	-2.552320000	-0.000635000
1	3.845913000	-2.371016000	0.006945000
1	5.861319000	-1.012173000	0.011164000
1	5.721409000	1.467731000	0.006099000
1	3.559459000	2.583997000	-0.001915000
1	1.101280000	2.460405000	-0.006648000
1	-1.652116000	3.173488000	-0.002252000
1	-4.083576000	2.990246000	0.010525000
1	-5.276508000	0.872638000	0.015074000

$S_{CT}(^1\pi\pi^*)$-*K*

8	1.574508000	2.655254000	0.002846000
8	4.158244000	1.452929000	-0.000164000
6	1.235305000	1.388279000	-0.000540000
6	-0.111746000	0.865428000	-0.002141000
6	-1.325520000	1.464762000	-0.002011000
6	-2.503611000	0.655434000	-0.000468000
6	-3.800542000	1.243923000	0.000385000
6	-4.917035000	0.476278000	0.001386000
6	-4.810969000	-0.941686000	0.001758000
6	-3.577511000	-1.533813000	0.001033000
6	-2.391505000	-0.743845000	-0.000016000
6	-1.094253000	-1.350864000	-0.000350000
6	0.002506000	-0.566104000	-0.001406000
6	1.450277000	-0.898936000	-0.001410000
6	2.114097000	-2.194891000	-0.000673000
6	3.455024000	-2.175259000	0.000408000
6	4.218038000	-0.930389000	0.001375000
6	3.590008000	0.355220000	0.001006000
6	2.166074000	0.274792000	-0.001374000
1	2.554324000	2.698431000	0.005625000
1	-1.414873000	2.535311000	-0.001569000
1	-3.879971000	2.316759000	-0.000087000

1	-5.888601000	0.936549000	0.001929000
1	-5.701023000	-1.543971000	0.002710000
1	-3.491149000	-2.605993000	0.001332000
1	-1.023086000	-2.425233000	-0.000052000
1	1.552677000	-3.108366000	-0.001672000
1	4.006449000	-3.099534000	0.000733000
1	5.292132000	-0.964825000	0.003250000

Section 5-2, Cartesian coordinates of the optimized structures for *meta*-CF_3-HBFO along ESIPT reaction pathway in $S_{CT}(^1\pi\pi^*)$ state at the CAS(12e/10o)/6-31G* level of theory.

$S_{CT}(^1\pi\pi^*)$-*E*

8	-0.415401000	3.437656000	-0.017403000
8	2.374462000	3.175858000	-0.001046000
6	-0.380972000	2.204527000	-0.005196000
6	-1.455560000	1.239770000	0.004733000
6	-2.821671000	1.393512000	0.006556000
6	-3.658540000	0.240774000	0.006372000
6	-5.068987000	0.363192000	0.016243000
6	-5.868836000	-0.737805000	0.012811000
6	-5.313586000	-2.047943000	-0.001741000
6	-3.971640000	-2.211410000	-0.010286000
6	-3.094030000	-1.080400000	-0.004761000
6	-1.710175000	-1.247189000	-0.006853000
6	-0.878873000	-0.113714000	-0.004104000
6	0.525070000	0.003954000	-0.004110000
6	1.574771000	-0.944058000	-0.021847000
6	2.869857000	-0.456593000	-0.041512000
6	3.147744000	0.942216000	-0.035177000
6	2.131390000	1.866686000	-0.013242000
6	0.811368000	1.396123000	-0.003948000
1	1.507156000	3.628292000	0.027278000
1	-3.254783000	2.374400000	0.011910000
1	-5.499853000	1.348324000	0.025742000
1	-6.938725000	-0.621121000	0.019284000
1	-5.967906000	-2.900253000	-0.004033000
1	-3.540164000	-3.197174000	-0.019498000
1	-1.286870000	-2.238080000	-0.015063000
1	1.384836000	-2.000558000	-0.025384000
1	4.166378000	1.284707000	-0.048725000
6	4.017983000	-1.420818000	0.003992000
9	3.732530000	-2.553482000	-0.622684000
9	5.106652000	-0.922675000	-0.556597000
9	4.341682000	-1.746553000	1.248015000

$S_{CT}(^1\pi\pi^*)$-1.20(ESIPT)

8	-0.229863000	3.374445000	0.006864000
8	2.146353000	3.162723000	-0.000203000
6	-0.347690000	2.116277000	0.006183000
6	-1.451850000	1.211274000	0.006452000
6	-2.816905000	1.388106000	0.007725000
6	-3.672354000	0.251208000	0.004048000
6	-5.080298000	0.399563000	0.007053000
6	-5.900239000	-0.686524000	-0.001330000
6	-5.368564000	-2.004958000	-0.011726000
6	-4.028695000	-2.192809000	-0.013480000
6	-3.132079000	-1.079385000	-0.007751000
6	-1.748187000	-1.275227000	-0.008917000
6	-0.893061000	-0.168695000	-0.003763000
6	0.518810000	-0.085600000	-0.000607000
6	1.602359000	-1.002829000	-0.008534000
6	2.873739000	-0.456081000	-0.017252000
6	3.131364000	0.952746000	-0.014146000
6	2.086277000	1.858639000	-0.001766000
6	0.806125000	1.292879000	0.002051000
1	0.966894000	3.462527000	0.003231000
1	-3.235158000	2.374446000	0.013402000
1	-5.492774000	1.392415000	0.014429000
1	-6.967738000	-0.550279000	-0.000094000
1	-6.037658000	-2.845648000	-0.017894000
1	-3.615517000	-3.186253000	-0.020771000
1	-1.347474000	-2.275601000	-0.014725000
1	1.458756000	-2.065387000	-0.011657000
1	4.148298000	1.304248000	-0.025422000
6	4.072049000	-1.360731000	-0.001674000
9	3.742983000	-2.632023000	-0.175084000
9	4.934917000	-1.045850000	-0.954261000
9	4.727717000	-1.282959000	1.146750000

$S_{CT}(^1\pi\pi^*)$-*K*

8	0.503703000	3.420911000	0.023617000
8	-2.307921000	3.172664000	0.023426000
6	0.405861000	2.122851000	-0.004065000
6	1.477912000	1.193509000	-0.005896000
6	2.835942000	1.353934000	-0.010232000
6	3.672542000	0.207306000	-0.008384000
6	5.095733000	0.335063000	-0.009422000
6	5.899082000	-0.776863000	-0.003261000
6	5.320225000	-2.071503000	0.002338000

6	3.953505000	-2.216717000	0.006371000
6	3.101164000	-1.078284000	0.005226000
6	1.673830000	-1.224638000	0.007254000
6	0.895190000	-0.125593000	0.001365000
6	-0.572482000	0.048418000	-0.004491000
6	-1.656917000	-0.909898000	0.006376000
6	-2.924295000	-0.408799000	-0.014584000
6	-3.206060000	0.979105000	-0.017260000
6	-2.161544000	1.942856000	-0.003376000
6	-0.837775000	1.383436000	-0.007808000
1	-0.406467000	3.787456000	0.006470000
1	3.276130000	2.334495000	-0.015178000
1	5.528788000	1.319345000	-0.014323000
1	6.968495000	-0.669487000	-0.004383000
1	5.953556000	-2.939562000	0.004536000
1	3.513661000	-3.197993000	0.010027000
1	1.255103000	-2.216256000	0.008241000
1	-1.470922000	-1.966960000	0.013399000
1	-4.217634000	1.332521000	-0.029067000
6	-4.064230000	-1.399190000	0.005434000
9	-4.001775000	-2.182455000	1.071551000
9	-5.245093000	-0.811763000	0.017702000
9	-4.029609000	-2.194691000	-1.053038000

Section 5-3, Cartesian coordinates of the optimized structures for *meta*-NH_2-HBFO along ESIPT reaction pathway in $S_{CT}(^1\pi\pi^*)$ state at the CAS(12e/10o)/6-31G* level of theory.

$S_{CT}(^1\pi\pi^*)$-*E*

8	1.009474000	2.952298000	0.011678000
8	3.728616000	2.088265000	-0.004045000
6	0.790206000	1.738397000	0.006667000
6	-0.439280000	1.007767000	0.003606000
6	-1.749195000	1.475298000	0.002990000
6	-2.805145000	0.571413000	0.001793000
6	-4.167195000	1.023967000	0.000399000
6	-5.195214000	0.150010000	-0.002950000
6	-4.961176000	-1.262117000	-0.002681000
6	-3.699159000	-1.737544000	0.000194000
6	-2.572644000	-0.852819000	0.000281000
6	-1.269354000	-1.338800000	0.001193000
6	-0.192097000	-0.435333000	-0.000984000
6	1.189507000	-0.653974000	-0.002349000
6	2.028275000	-1.763445000	0.004129000
6	3.403283000	-1.550869000	-0.000164000

6	4.005629000	-0.240944000	-0.007360000
6	3.226783000	0.867443000	-0.003873000
6	1.800537000	0.694741000	-0.000282000
1	2.992651000	2.738545000	0.005318000
1	-1.937464000	2.531026000	0.003352000
1	-4.350540000	2.083402000	0.000694000
1	-6.208201000	0.512175000	-0.004996000
1	-5.798398000	-1.935162000	-0.004008000
1	-3.515018000	-2.797579000	0.001299000
1	-1.092977000	-2.400495000	-0.001031000
1	1.643280000	-2.766360000	0.002432000
1	5.075778000	-0.148791000	-0.022321000
7	4.253582000	-2.610645000	-0.031020000
1	3.896594000	-3.514409000	0.188514000
1	5.207339000	-2.465178000	0.216252000

$S_{CT}(^1\pi\pi^*)$-1.28(maximum)

8	1.072493000	2.924015000	-0.018046000
8	3.660171000	2.104588000	0.013172000
6	0.798737000	1.705365000	-0.008477000
6	-0.434033000	1.009108000	-0.002290000
6	-1.743561000	1.484585000	-0.000171000
6	-2.806404000	0.581201000	0.000893000
6	-4.164855000	1.035624000	0.004543000
6	-5.194403000	0.161144000	0.004288000
6	-4.962357000	-1.249831000	0.000085000
6	-3.700635000	-1.727804000	-0.002611000
6	-2.573610000	-0.844360000	-0.001899000
6	-1.270846000	-1.333372000	-0.003328000
6	-0.191697000	-0.437984000	-0.001762000
6	1.195594000	-0.672949000	0.001310000
6	2.040650000	-1.774038000	0.006376000
6	3.419233000	-1.543856000	0.008885000
6	4.010147000	-0.234224000	0.012953000
6	3.220409000	0.877011000	0.009511000
6	1.799635000	0.663241000	0.001719000
1	2.616071000	2.844714000	-0.008480000
1	-1.930303000	2.539193000	-0.001181000
1	-4.346951000	2.095194000	0.007540000
1	-6.207335000	0.524310000	0.006905000
1	-5.801085000	-1.921215000	-0.000851000
1	-3.516557000	-2.787740000	-0.005545000
1	-1.098131000	-2.395107000	-0.003802000
1	1.667311000	-2.781214000	0.000300000

1	5.080089000	-0.135506000	0.007509000
7	4.272949000	-2.598504000	-0.021023000
1	3.922947000	-3.511470000	0.164006000
1	5.232798000	-2.453406000	0.196321000

$S_{CT}(^1\pi\pi^*)$-*K*

8	0.978745000	2.980212000	0.004328000
8	3.730296000	2.061828000	-0.010912000
6	0.812622000	1.669473000	0.002520000
6	-0.456069000	1.005657000	0.001436000
6	-1.739552000	1.469679000	0.002169000
6	-2.811679000	0.543621000	0.001535000
6	-4.176699000	0.993478000	0.001383000
6	-5.211815000	0.101147000	0.000384000
6	-4.949315000	-1.302302000	-0.001199000
6	-3.658622000	-1.756814000	-0.001716000
6	-2.554366000	-0.840386000	-0.000857000
6	-1.211844000	-1.305468000	-0.000577000
6	-0.194973000	-0.406085000	-0.000825000
6	1.257054000	-0.573006000	-0.002310000
6	2.031466000	-1.759373000	-0.001963000
6	3.392816000	-1.606225000	-0.002642000
6	4.004466000	-0.268144000	-0.008053000
6	3.232286000	0.938529000	0.013876000
6	1.812512000	0.714465000	0.004610000
1	1.937897000	3.146148000	0.006382000
1	-1.945006000	2.523627000	0.003048000
1	-4.368566000	2.051647000	0.002095000
1	-6.228059000	0.451145000	0.000511000
1	-5.771013000	-1.994428000	-0.002177000
1	-3.451062000	-2.812454000	-0.003274000
1	-1.025658000	-2.365371000	-0.002285000
1	1.573396000	-2.727946000	-0.002070000
1	5.081657000	-0.180419000	-0.041059000
7	4.250563000	-2.649603000	-0.032707000
1	3.900029000	-3.571096000	0.117800000
1	5.211307000	-2.511709000	0.189706000

Section 5-4, Cartesian coordinates of the optimized structures for *para*-CF_3-HBFO along ESIPT reaction pathway in $S_{CT}(^1\pi\pi^*)$ state at the CAS(12e/10o)/6-31G* level of theory.

$S_{CT}(^1\pi\pi^*)$-*E*

8	-0.592431446	3.599647928	-0.000282693
8	-3.380818091	3.024846218	-0.000171593
6	-0.496428301	2.367270804	-0.000199439
6	0.668924181	1.536181297	-0.000151116
6	2.004067475	1.875469714	-0.000201368
6	2.984784812	0.853990266	-0.000132941
6	4.371695436	1.159066782	-0.000180320
6	5.304430674	0.173237161	-0.000111144
6	4.921639897	-1.201059372	0.000011050
6	3.614421086	-1.536576280	0.000059722
6	2.593960368	-0.528757761	-0.000009854
6	1.248628380	-0.883804017	0.000043429
6	0.262181601	0.118945864	-0.000025809
6	-1.154847239	0.066628065	0.000011172
6	-2.125427562	-0.979240144	0.000123561
6	-3.440753754	-0.636898713	0.000142812
6	-3.879941465	0.718896172	0.000048043
6	-2.966662005	1.758943397	-0.000071370
6	-1.596612529	1.427295950	-0.000086979
1	-2.595771609	3.609176723	-0.000266059
1	2.290374423	2.908593877	-0.000291791
1	4.668579822	2.192568026	-0.000271660
1	6.350839472	0.424544796	-0.000147927
1	5.682219414	-1.960063111	0.000064044
1	3.312477189	-2.569207234	0.000152506
1	0.983843854	-1.922801354	0.000139256
1	-4.183947428	-1.409834847	0.000228721
1	-4.932450724	0.939481973	0.000063217
6	-1.739016529	-2.427494874	0.000226277
9	-2.788222944	-3.226755068	0.000332008
9	-1.008091867	-2.741034405	1.064346213
9	-1.008178007	-2.741208065	-1.063901593

$S_{CT}(^1\pi\pi^*)$-1.22(maximum)

8	-0.614087993	3.591863186	0.000069926
8	-3.316589870	3.054304547	-0.000411367
6	-0.491597702	2.353213528	-0.000072358
6	0.674206614	1.531315004	-0.000043792
6	2.010334738	1.868928353	-0.000077720
6	2.989172813	0.842717547	-0.000060920

6	4.374891111	1.144828448	-0.000255866
6	5.306203418	0.155093609	-0.000306649
6	4.920058308	-1.215213477	-0.000100303
6	3.609642526	-1.546852976	0.000071095
6	2.595736784	-0.536342007	0.000048696
6	1.245700125	-0.890203442	0.000100732
6	0.263282852	0.113500672	-0.000005250
6	-1.154933553	0.063180005	-0.000044834
6	-2.136797226	-0.974503336	0.000048120
6	-3.448074975	-0.615035321	-0.000010016
6	-3.874549932	0.747695745	-0.000165679
6	-2.945331050	1.780810652	-0.000262650
6	-1.589210742	1.421856860	-0.000161340
1	-2.279382559	3.696644959	-0.000273554
1	2.301481350	2.900278217	-0.000060166
1	4.675802383	2.177026810	-0.000401974
1	6.352805577	0.405177936	-0.000499914
1	5.676654533	-1.978110294	-0.000102652
1	3.305983824	-2.578948207	0.000191979
1	0.981094551	-1.929271604	0.000167324
1	-4.203460702	-1.376073688	0.000120258
1	-4.924300701	0.980840667	-0.000179417
6	-1.761946843	-2.426706738	0.000292072
9	-2.818057915	-3.216616164	0.000422178
9	-1.033286059	-2.745770123	1.063690997
9	-1.033320345	-2.746125423	-1.063023217

$S_{CT}(^1\pi\pi^*)$-*K*

8	0.480579635	3.594735502	0.014529937
8	3.228556218	3.064392983	0.004903050
6	0.437335714	2.289493120	0.003188458
6	-0.721569311	1.482856883	0.003646644
6	-2.053256707	1.809783440	0.003034055
6	-3.021605510	0.781444637	0.001868775
6	-4.423823745	1.079135331	-0.003202388
6	-5.351033621	0.072066219	-0.006035161
6	-4.929402028	-1.286380425	-0.004204856
6	-3.592787807	-1.593422940	0.000209781
6	-2.607574680	-0.561614804	0.001679676
6	-1.214945671	-0.886202217	0.001592794
6	-0.295943276	0.105805149	-0.000675062
6	1.191752505	0.116706804	-0.008788074
6	2.210480591	-0.936581214	-0.010541311

6	3.516913182	-0.551042255	-0.010794052
6	3.922120993	0.802016937	-0.011344467
6	2.965744909	1.857492415	-0.010711529
6	1.593424136	1.418942194	-0.013587252
1	1.421962611	3.867724466	0.010241407
1	-2.360752557	2.839267472	0.003352604
1	-4.734026401	2.108651913	-0.004719237
1	-6.400483654	0.303441221	-0.010476026
1	-5.663013826	-2.071250405	-0.004774923
1	-3.270428368	-2.619068733	0.003574860
1	-0.940436646	-1.921406840	-0.001130139
1	4.278135475	-1.308235292	-0.006509306
1	4.964819295	1.064092801	0.000293789
6	1.844794214	-2.382993374	0.003625315
9	2.905929205	-3.168425256	0.019939301
9	1.121521190	-2.719383319	-1.060392465
9	1.106704497	-2.694555857	1.064999276

Section 5-5, Cartesian coordinates of the optimized structures for *para*-NH_2-HBFO along ESIPT reaction pathways in $S_{CT}(^1\pi\pi^*)$ state at the CAS(12e/10o)/6-31G* level of theory.

$S_{CT}(^1\pi\pi^*)$-*E*

8	1.396564140	-2.892266859	0.063714285
8	4.073390844	-1.804841612	-0.095347877
6	1.104537770	-1.700506248	0.060377721
6	-0.197369465	-1.072751532	0.063692413
6	-1.466623382	-1.623302780	0.072278722
6	-2.616093180	-0.772229550	0.026937834
6	-3.922632411	-1.308583448	0.033029881
6	-5.018074190	-0.496064253	-0.025644061
6	-4.871209231	0.905591811	-0.096668941
6	-3.625813351	1.454655673	-0.104168590
6	-2.468923653	0.636866867	-0.037811658
6	-1.174552164	1.212318878	-0.041658742
6	-0.036670077	0.370226589	0.030950577
6	1.334709368	0.666116610	0.039930581
6	2.067939798	1.886174938	0.040172675
6	3.468497057	1.797501950	-0.067655691
6	4.112050624	0.554075425	-0.124133659
6	3.408917731	-0.645018964	-0.062091657
6	2.029045456	-0.592960967	0.028319477
1	3.419067039	-2.529554993	-0.051619409
1	-1.588998055	-2.687876661	0.102667691

1	-4.042453433	-2.376145011	0.082959060
1	-6.004362309	-0.925765640	-0.020536745
1	-5.742950177	1.531910418	-0.146337910
1	-3.504153936	2.522653024	-0.160152231
1	-1.063873055	2.277817771	-0.135480060
1	4.053616745	2.695527505	-0.081384501
1	5.185529404	0.510197303	-0.196946621
7	1.416713844	3.119344855	0.118134980
1	2.051061240	3.892793746	0.120052461
1	0.794459635	3.197230385	0.897760850

$S_{CT}(^1\pi\pi^*)$-1.28(maximum)

8	1.432492306	-2.869969410	0.060726894
8	3.983765766	-1.849585470	-0.097936039
6	1.094998234	-1.672407343	0.061022849
6	-0.215224043	-1.062397402	0.066599956
6	-1.472204990	-1.617342053	0.073207227
6	-2.622828320	-0.765178036	0.027456088
6	-3.929657202	-1.298539637	0.032346747
6	-5.022507796	-0.481805479	-0.025647989
6	-4.867007982	0.917639658	-0.094984437
6	-3.618023952	1.462099631	-0.101976390
6	-2.466606846	0.640416424	-0.037749377
6	-1.163058339	1.209504734	-0.042985719
6	-0.050583020	0.381775586	0.028562353
6	1.338493610	0.665197424	0.036087729
6	2.114090003	1.889740556	0.038488720
6	3.506597856	1.777657745	-0.067915986
6	4.134541329	0.519998338	-0.125581298
6	3.406624071	-0.667873775	-0.058631786
6	2.011311356	-0.575107628	0.038036056
1	2.996999816	-2.662466548	-0.035350670
1	-1.592922412	-2.682352119	0.102067722
1	-4.052614964	-2.365934885	0.081888227
1	-6.010751965	-0.906658770	-0.020642149
1	-5.735071521	1.549261066	-0.143428305
1	-3.492772513	2.529622558	-0.157026398
1	-1.054319437	2.275450127	-0.132803506
1	4.107913331	2.665282629	-0.078812487
1	5.205900786	0.457677369	-0.201445438
7	1.472619791	3.123972246	0.113484863
1	2.107602565	3.895914653	0.152586466
1	0.807909448	3.192564788	0.858237199

$S_{CT}(^1\pi\pi^*)$-*K*

8	1.341339112	-2.853153210	0.041363103
8	4.093851657	-1.828433038	-0.057452191
6	1.088758456	-1.680310299	0.031729110
6	-0.253460883	-1.031023461	0.043264857
6	-1.483560250	-1.606149811	0.047478099
6	-2.651247726	-0.760239521	0.018354170
6	-3.953869659	-1.301150926	0.026819430
6	-5.050838623	-0.489610165	-0.009970328
6	-4.888845481	0.906135022	-0.058942148
6	-3.637694550	1.452326198	-0.068288599
6	-2.487476242	0.635491292	-0.028314477
6	-1.162728964	1.214190054	-0.033105132
6	-0.074101414	0.396147997	0.012371848
6	1.389720312	0.665672472	0.009561378
6	2.103514332	1.845432899	0.020253874
6	3.500503189	1.736524448	-0.023884809
6	4.161517716	0.527862067	-0.066100744
6	3.436516320	-0.662842760	-0.039579802
6	2.060331822	-0.566873312	0.003404826
1	3.456794122	-2.559206340	-0.034296362
1	-1.590123996	-2.676020143	0.065538785
1	-4.069922574	-2.370212998	0.062525857
1	-6.039711349	-0.911268581	-0.002904909
1	-5.756220672	1.540993233	-0.089665516
1	-3.514161545	2.520435189	-0.107264737
1	-1.064377175	2.280812745	-0.096947610
1	4.086619550	2.640010589	-0.025284983
1	5.234081158	0.489280982	-0.103530357
7	1.459138858	3.103712366	0.039596283
1	2.108727077	3.862314856	0.010033283
1	0.870567109	3.220070696	0.863025947