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Hypervalent Iodine-Mediated Styrene Hetero- and Homodimerizations Initiation Proceed with Two-Electron Reductive Cleavage

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A mechanistic insight into the hetero- and homodimerizations (HETD and HOMD) of styrenes promoted by hypervalent iodine reagents (HVIRs; DMP and PIDA) and facilitated by HFIP to yield all trans cyclobutanes is reported using density functional theory (DFT) calculations. The reaction is initiated with two-electron reductive cleavage of two I—O bond cleavages, affording I(III) (iodinane) and I(I) (iodobenzene) product with DMP and PIDA as oxidant, respectively. The resulting acetate groups are stabilized by the solvent HFIP through strong hydrogen bonding interaction, which promotes the electron transfer process. The initialization involving one-electron transfer was found to be highly unfavored, especially for the PIDA system. At this point, we found that two-electron process is the key initialization process, which is in accordance with literature report on alcohol oxidation. The reaction rate is determined by the initialization step: For I(III), the initiation is thermodynamically endergonic, whereas the endergonicity for I(V) is modest. The difference in reactivity is explained by the difference LUMO energies. Upon initialization, the reaction proceeds through a stepwise [2+2] pathway, involving a radical-cationic π-π stacked intermediate, either hetero- or homodimerized. DFT results supported by quasiclassical molecular dynamics simulations show that HOMD is dynamically competing pathway to HETD although the latter is relatively faster, in accordance with experimental observations.

File list (2)

Electronic Supplementary Information

For

Hypervalent Iodine-Mediated Styrene Hetero- and Homodimerizations Initiation Proceed with Two-Electron Reductive Cleavage

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TABLE OF CONTENTS

1- Computational Details

All mechanical quantum calculations were performed using Gaussian 09. All geometries were fully optimized at the hybrid meta-generalized gradient dispersion-corrected approximation ωB97XD [1] with the basis set 6-31G(d) [2-5] for all atoms except iodine where an effective core potential (ECP) of Hay and Wadt with a double-ξ valence basis set LANL2DZ was used for iodine.[6-8] All minima intermediates were verified by the absence of negative eigenvalues in the vibrational frequency analysis. Transition state (TS) structure was verified by the presence of a single imaginary frequency. Single-point energies of the optimized geometries were evaluated using ωB97XD/6-311+G(d,p)/ECP, and the thermal corrections evaluated from the unscaled vibrational frequencies at the ωB97XD/6-31G(d)/ECP level of theory were then added to the ωB97XD/6-311+G(d,p)/ECP electronic energies to obtain the free energies at 298.15 K. The effect of solvent was included via the solvation model based on density (IEFPCM-SMD) incorporated for all calculations with both implicit and explicit calculations.[9] The solvent 1,1,1,3,3,3-Hexafluoroisopropanol (HFIP) was used as a representative solvent medium with SMD solvation model. Since solvent parametrizations of HFIP are not available in Gaussian 09 database, the parameterizations were added manually using commands, solvent=generic and read, to allow adding solvent requirements: *SolventName = Hexafluoro-2-propanol, EpsInf = 1.275*,[10] *HBondAcidity = 0.771* and *HBondBasicity = 0.730*,[11] *SurfaceTensionAtInterface = 14.7*,[12] *Eps = 15.7*,[13] *CarbonAromaticity = 0.00, ElectronegativeHalogenicity = 0.500*.[14] The explicit solvent HFIP was added to the calculation based on the number of carbonyl groups in iodine reagents; that means two and four HFIP molecules were added to PIDA and DMP, respectively. In order to determine the minimum energy path (MEP) on the potential energy surface (PES), intrinsic reaction coordinate (IRC) calculations were used to confirm the reaction path proceeding in both directions (reactant and product).[15-17] All calculated free energies of activation are quoted relative to infinitely separated reagents. All the calculations of the frontier orbital analysis were performed in gas phase with *w*B97XD/6-31G(d)/LANL2DZ level of theory and the orbital contours were plotted with iso value of 0.02 with cutoff level of 0.0004 was applied.

We carried out a basis set search on Fe and I atoms through running single point energy calculations. For Fc/Fc^+, the combination bases set Def2-TZVPP/6-31G(d,p) level of theory (where Def2-TZVPP [18] used for Fe and 6-31G(d,p) used for C and H atoms) was used (see Table 1). For iodine in **PIDA** and **DMP**, the combination basis set Def2-TZVPP/6-311+G(d,p) (where Def2-TZVPP [18] used for I and 6-311+G(d,p) used for C, H, and O atoms) was used (see Table S1). The presence of non-covalent interactions shown by Reduced Density Gradient (RDG) analysis [19] is performed at the *w*B97xD/6-311+G(d,p) level of theory using the Multiwfn program.[20] To get better insight into the redox step, the activation energy of electron transfer was calculated using Marcus theory.[21] One of the methods most often employed is the four-point method proposed by Nelsen,[22-24] which has been extensively applied for many systems.[25-30] The output of Nelsen calculations is the total reorganization energy which is then applied in the Marcus equation of SEO ($\Delta G^{\ddagger} = (\lambda + \Delta G_r)^2/4\lambda$) (Nelsen's procedure is explained below).

The quasiclassical trajectory molecular dynamics simulations were carried out using the PROGDYN program, [31] a script suite that works in combination with Gaussian 09. The initial geometry for each trajectory was generated by adding displacements that follows a QM-like Gaussian distribution to all vibrational modes higher than 10 cm^{-1} for the input transition state. Each real normal mode was given its zero-point energy plus a random Boltzmann sampling of the thermal energy available at 298.15 K. Trajectories were propagated at *w*B97XD/6-31G(d) level in gas phase in both the forward and backward directions with the Verlet algorithm, until the product formed or starting materials were re-generated. C3−C4 bond lengths were recorded along the whole trajectory. Each trajectory was labelled as "returned to starting materials" and "C−C bond formed" if the C3−C4 distance is longer than 2.5 Å or shorter than 1.6 Å, respectively. The step length for Verlet integration was 1.0 fs.

2- Bases sets search for Fc/Fc^+ and Iodine in PIDA and DMP

All of Fc/Fc+ and **PIDA** were optimized using the *w*B97XD/6-31G(d)/LANL2DZ level of theory, where LANL2DZ used for Fe and I atoms whereas 6-31G(d) used for C, H, O, and F atoms. Following this, many single point energy calculations were performed with different basis sets. For Fc/Fc^+, we found that Def2-TZVPP/6-31G(d,p) level of theory (where Def2-TZVPP used for Fe and 6-31G(d,p) used for C and H atoms) gives the best agreement with the experimental redox potential values of different substituted *trans-β*-methylstyrenes using Cp_2Fe (calculated $E^{1/2}$ = 4.84 V) as reference to calculate their redox potentials. For iodine in **PIDA**, it was found that the basis set Def2-TZVPP for iodine and 6-311+G(d,p) for C, H, and O atoms gave the best agreement with experimental redox potentials. Under explicit protocol, the calculated value for $\mathbf{PIDA_{HFIP}} + e^- \rightarrow \mathbf{PIDA^-_{HFIP}}$ is $E^{1/2}$ = 4.25 V of peak potential for $\mathbf{PIDA_{HFIP}}$ is $E_{p,c} = -0.59$ V versus calculated peak potential Fc/Fc^+ ($E^{1/2}$ = 4.84 V) as a reference, leading to a good agreement with the measured peak potential for **PIDA** is $E_{p,c} = -0.47$ V. Under implicit protocol, the calculated value of non-hydrogen-bonded **PIDA** is $E^{1/2}$ = 4.02 V of peak potential $E_{p,c}$ = −0.82 V versus Fc/Fc^+ with a shifting to more negative value of 230 mV less favorable than explicit $\mathbf{PIDA_{HFIP}}$. The same level of theory used for **PIDA** has been used for **DMP**. Therefore, the *w*B97XD/def2-TZVPP/6-311+G(d) level of theory is used for oxidants whereas the *w*B97XD/def2-TZVPP/6-31G(d,p) level of theory is utilized for Cp_2Fe in order to calculate the redox potentials.

Table S1. Bases sets search for Fc/Fc^{+} and **PIDA** with wB97XD functional and different basis sets.

Level of theory	G (Ha)		
	Fc	**Fc^{+}**	$E^{1/2}$ (V)
LANL2DZ/6-311+G(d,p)	–510.3522055	–510.1559683	5.34
SDD/6-31G(d)	–510.7270892	–510.4709144	6.97
Def2-TZVP/6-31G	–1650.727958	–1650.540789	5.09
Def2-TZVP/6-311+G	–1650.809295	–1650.616485	5.25
Def2-TZVPP/6-31G(d)	–1650.736754	–1650.551259	5.05
Def2-TZVPP/6-31G (d,p)	**–1650.612812**	**–1650.434749**	**4.84**
Def2-QZVPP/6-31G(d,p)	–1650.786539	–1650.60125	5.04
Def2-TZVPP/6-311+G(d,p)	–1650.831558	–1650.641027	5.18
Def2-TZVPP/6-31G(3df,2p)	–1650.776069	–1650.589091	5.09
Level of theory	G (Ha)		
	PIDA	**$PIDA^{-}$**	$E^{1/2}$ (V)
LANL2DZ/6-311+G(d,P)	–699.7428735	–699.9048742	4.40
SDD/6-31G(d)	–699.5535777	–699.6363813	2.25
Def2-TZVP/6-31G	–986.1132191	–986.1705729	1.56
LAN/6-31G	–699.6841958	–699.7458841	1.68
LAN/6-31+G(d)	–699.7201474	–699.7932141	1.99
LAN/6-311G(d,p)	–699.8721771	–699.9420885	1.90
LAN/6-311+G(d)	–699.8757468	–699.9518732	2.07
Def2-TZVPP/6-311+G(d,p)	**–986.1620002**	**–986.3098347**	**4.02**
Level of theory	G (Ha)		
	$PIDA_{HFIP}$	**$PIDA^{-}_{HFIP}$**	$E^{1/2}$ (V)
Def2-TZVPP/6-311+G(d,p)	**–2565.78694**	**–2565.943167**	**4.25**

3- Effect of π-π stacking interactions on for the HETD and HOMD pathways

We have calculated the first C-C bond formation for the HETD and HOMD pathways when both aromatic rings are not π-π stacked (labeled as staggered) and shown in Figure S2. In comparison with the π-π stacked first C-C bond formation (see the main paper), a destabilization has been seen when aromatics rings are unstacked. For HETD pathway, the TS **8$^+$_staggered** less stable than the π-π stacking TS **8$^+$** by 4.8 kcal mol^{-1}, correspondingly this also gave less stable intermediate **9$^+$_staggered** by 5.2 kcal mol^{-1}. For HOMD pathway, a destabilization on the TS **11$^+$_staggered** has been found to be 3.9 kcal mol^{-1} to give an intermediate **12$^+$_staggered** that is less stable than the π-π stacked **12$^+$** by 2.1 kcal mol^{-1}. Overall, this indicates that the π-π stacking interactions in homo- and heterodimerization play important role in controlling the stereochemical outcome that leads to all *trans* cyclobutane.

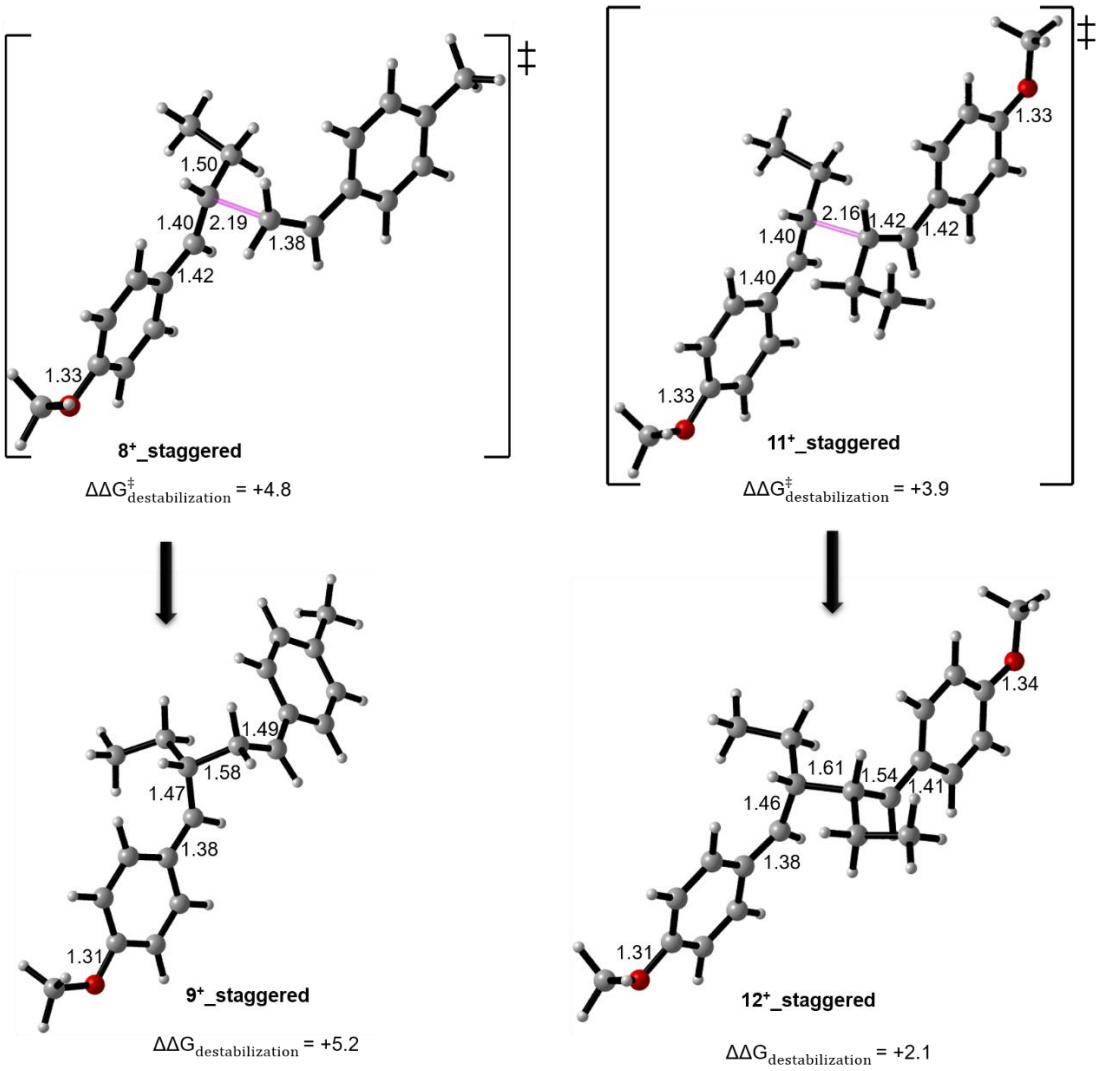


Figure S2. Unstacked optimized TSs and intermediates for the HETD and HOMD pathways. Calculations were performed with SMD (HFIP)-*w*B97XD/6-311+G(d,p)//*w*B97XD/6-31G(d) level of theory.

4- One-electron Reduction Initiation Mechanism

HETD initiated by one-electron reduction. The DFT results of HETD in the presence I(V) **DMP** with and without explicit HFIP molecules have been exploited following one-electron reduction, I(V)→I(IV). Initially, the two-electron reduction explained in the main paper, I(V)→I(III) is more favored over one-electron reduction. Generally, the explicit HFIP molecules decrease the overall energetic pathway for the HETD over the nonexplicit one due to the hydrogen bonding between DMP and HFIP (Figure S3). The decrease is around 5 kcal mol^{-1} for the single electron oxidation (SEO), electron transfer from styrene to iodine reagent, step and single electron reduction (SER) step, when electron return from iodine reagent to cationic cyclobutane ring, and more than 6 kcal mol^{-1} for the stepwise [2+2] cycloaddition steps. In the presence of explicit HFIP the free energy of activation for SEO was found to be 20.2 kcal mol^{-1} to give radical cation $\mathbf{4}^{+}$ and radical anion $\mathbf{DMP}^{-}_{\mathbf{HFIP}}$ as an endergonic step (ΔG_r = 13.8 kcal mol^{-1}). In absence of explicit HIFP the barrier for SEO increased to 25.4 kcal mol^{-1} as a more endergonic process (ΔG_r = 21.8 kcal mol^{-1}). An apparent increased in the I–O bond distances, clearly represented for the perpendicular acetate units to the phenyl iodine. After the electron transfer, the I–O bond distances elongate from 2.08 and 2.15 Å to 2.63 Å and 2.99 Å when HFIP are not involved in calculations explicitly. Elongation is slightly less when HFIP is involved explicitly, where I–O bond length is 2.12 Å is before the SEO and 2.55 Å and 2.77 Å are after the SEO (see $\mathbf{DMP}_{\mathbf{HFIP}}$ and $\mathbf{DMP}^{-}_{\mathbf{HFIP}}$ in the main paper). The increase in distance is reasonably attributed to the repulsions with the single unpaired electron existed on iodine (see spin density contours in Figure S7).

Following cycloaddition, to release the cyclobutane **6**, the radical cation $\mathbf{6}^{+}$ undergoes SER by either the radical anion $\mathbf{DMP}^{-}_{\mathbf{HFIP}}$ or another styrene to propagate the reaction. The SER step to cyclobutane cation $\mathbf{6}^{+}$ by $\mathbf{DMP}^{-}_{\mathbf{HFIP}}$ needs a barrier of 4.3 kcal mol^{-1} as an exergonic step (ΔG_r = −20.4 kcal mol^{-1}) (see Figure S3). Thus, propagation through oxidation of another styrene **4** by $\mathbf{6}^{+}$ is more favored. The oxidation of styrene **4** by $\mathbf{6}^{+}$ is nearly to be barrierless of 1.1 kcal mol^{-1} as an exergonic step (ΔG_r = −6.6 kcal mol^{-1}) (see Figure S5).

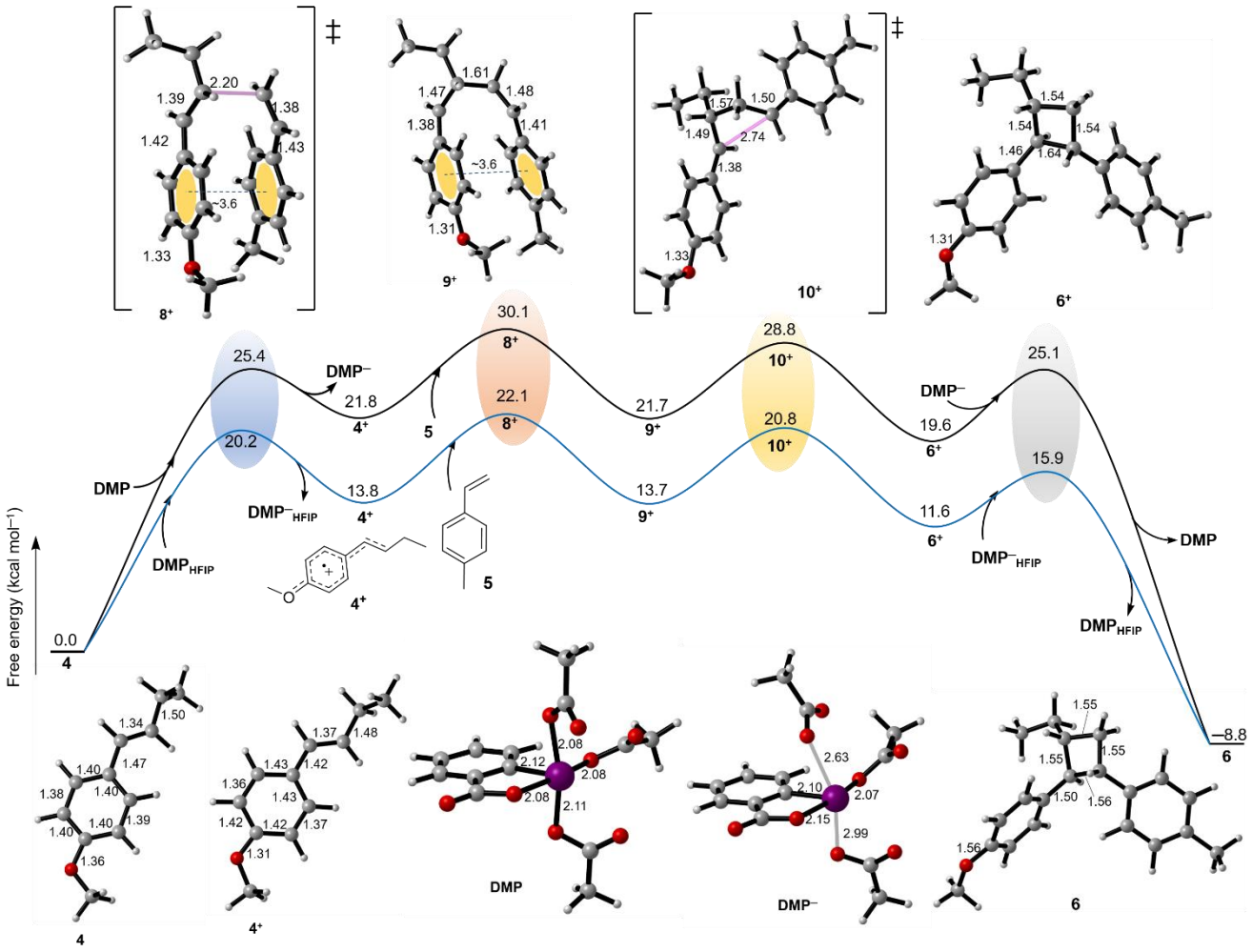


Figure S3. Free energy profile for the catalytic mechanism of **DMP**-mediated heterodimerization of styrenes (**4**) and (**5**) initiated via one-electron reduction, where SEO and SER proceed through only **DMP** to get cyclobutane ring formed, with explicit HFIP (blue pathway) and implicit HFIP (black pathway). Structures of $\mathbf{DMP_{HFIP}}$ and $\mathbf{DMP^{-}_{HFIP}}$ are shown in the main paper. The barriers for one-electron transfer were estimated based on Nelsen four-point method explained below.

HOMD pathway. Following the strategy for one-electron reductive initiated HETD, the one-electron reductive initiated HOMD mechanism, I(III)→I(II), in the presence I(III) **PIDA** with and without explicit HFIP molecules is investigated and shown in Figure S4. Also, as explained in the main paper, the two-electron reductive cleavage-initiated mechanism, I(III)→I(I), is more favored over one-electron reduction one, I(III)→I(II) (see the main paper). As shown above with HETD, the explicit HFIP pathway shows lower energetic level than the nonexplicit pathway. The barrier of SEO, the FRS, was found to be 31.3 kcal mol^{-1} to give radical cation $\mathbf{4}^{+}$ and anion $\mathbf{PIDA^{-}_{HFIP}}$ as an endergonic step (ΔG_r = 28.1 kcal mol^{-1}). The SEO for HOMD is more endergonic than for the HETD. Following the SEO step the bond length of the acetate group to iodine, namely I–O bonds, increases from

2.15 Å to around 2.58 Å for the non-hydrogen bonded **PIDA** (Figure S4) and to longer distances of 2.66 Å and 2.78 Å for the hydrogen-bonded one **PIDA$_{HFIP}$** (see the main paper) for the reason mentioned above for SEO by **DMP$_{HFIP}$** (see the spin density shown in Figure S7). Following the cycloaddition, the release of neutral homodimerized cyclobutane **7** via propagation process (Figure S5) is calculated to be favored over SER by radical anion **PIDA$^{-}_{HFIP}$** (Figure S4). The oxidation of styrene **4** by **7**$^{+}$ is found to be nearly barrierless of 1.5 kcal mol^{-1} as an exergonic step (ΔG_r = −6.3 kcal mol^{-1}) (Figure S5). The SER by **PIDA$^{-}_{HFIP}$** requires higher barrier of 2.5 kcal mol^{-1} as a result of the high exergonicity (ΔG_r = −34.4 kcal mol^{-1}) needed to release the neutral cyclobutane **7** (Figure S4).

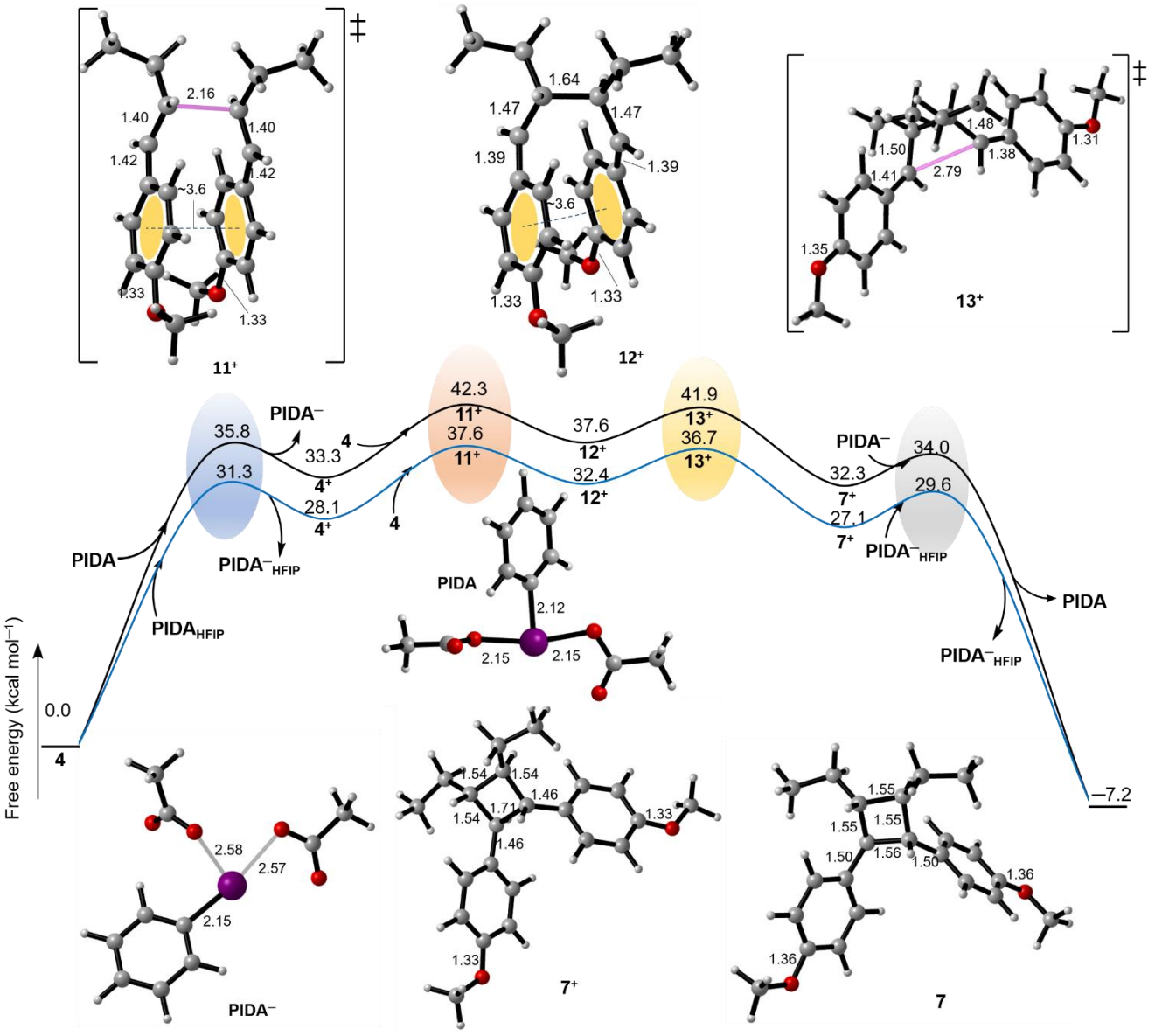


Figure S4. Free energy profile for the catalytic mechanism of **PIDA**-mediated homodimerization of styrenes (**4**) initiated via one-electron reduction, where SEO and SER proceed through only **PIDA** to get cyclobutane ring

formed, with explicit HFIP (blue pathway) and implicit HFIP (black pathway). Structures of **PIDA$_{HFIP}$** and **PIDA$^{-}_{HFIP}$** are shown in the main paper. The barriers for electron transfer were estimated based on Nelsen four-point method explained in below.

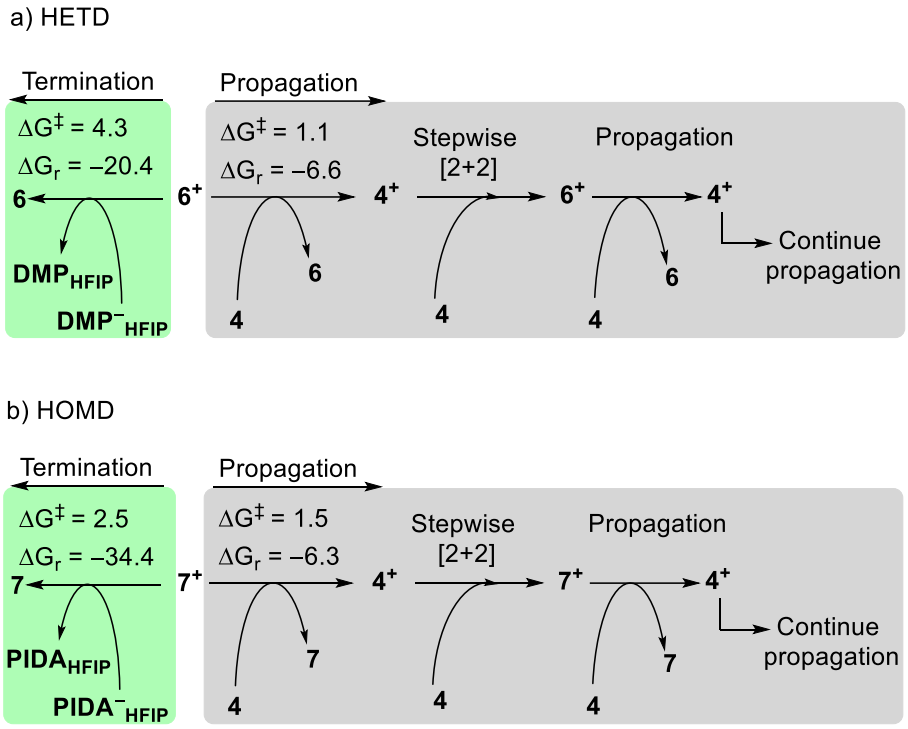


Figure S5. Favored propagation of HOMD and HETD over SER by I(II) and I(IV), respectively.

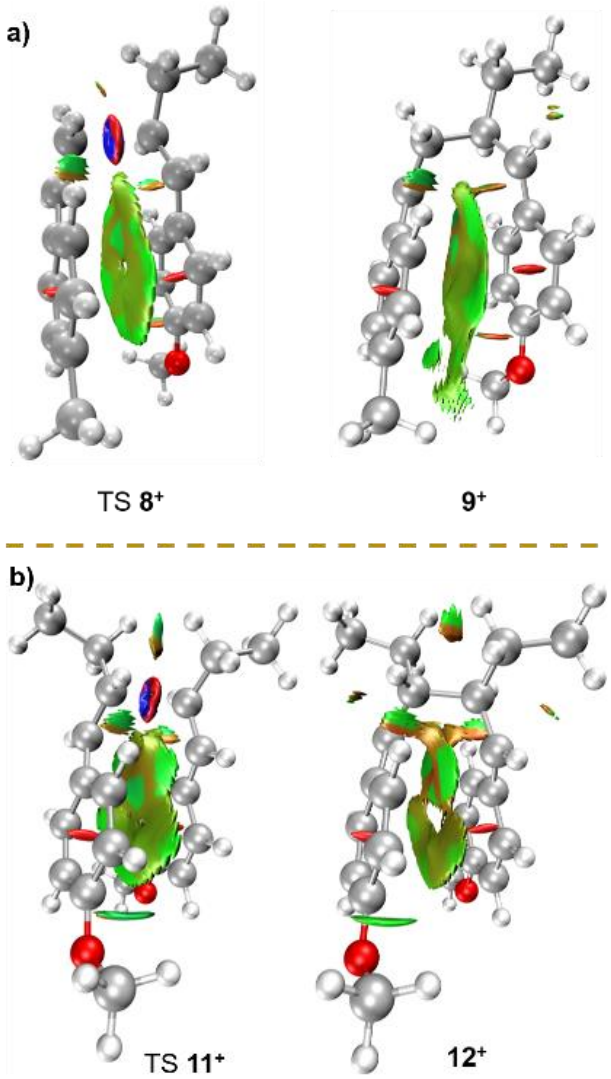


Figure S6. (a) and (b) Reduced Density Gradient (RDG) isosurface (isovalue at 0.5) for TSs $\mathbf{8}^+$ and $\mathbf{11}^+$ and intermediates $\mathbf{9}^+$ and $\mathbf{12}^+$, where attractive π-π stacking interactions are shown in green area, whereas red and blue area indicates steric repulsion and strong interactions, respectively.

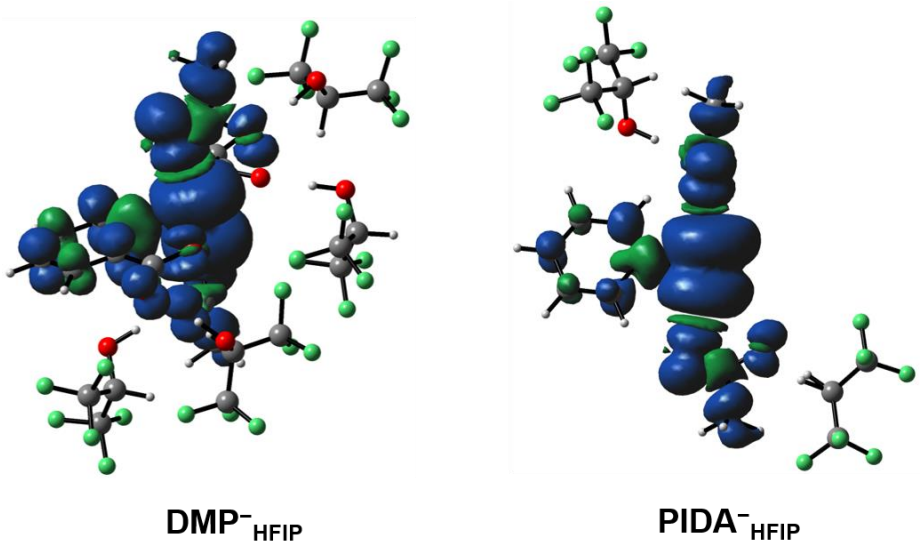


Figure S7. Spin density contour of iodine reagents undergoes single-electron reduction.

5- Quasiclassical trajectory molecular dynamics simulations on unstacked TSs 11^+_staggered and 8^+_staggered

Quasiclassical molecular dynamics simulations were also performed for the less favored unstacked conformation of the two transition states (Figure S8). 64 and 41 trajectories were produced for **11^+_staggered** and **8^+_staggered**, and the timing for C−C bond formation were determined to be 47.0 and 45.0 fs respectively. The results are very similar to those for the stacked conformations, and again timing gap for HETD and HOMD pathways is considerably small. One interesting observation is that a few trajectories recrossed and dissociated to starting materials for the staggered transition states, whereas no recrossing was observed in the presence of π-π stacking. It was shown that the π-π interaction provide extra stabilization in the transition state region and, thus, it may prevent recrossing to starting materials.

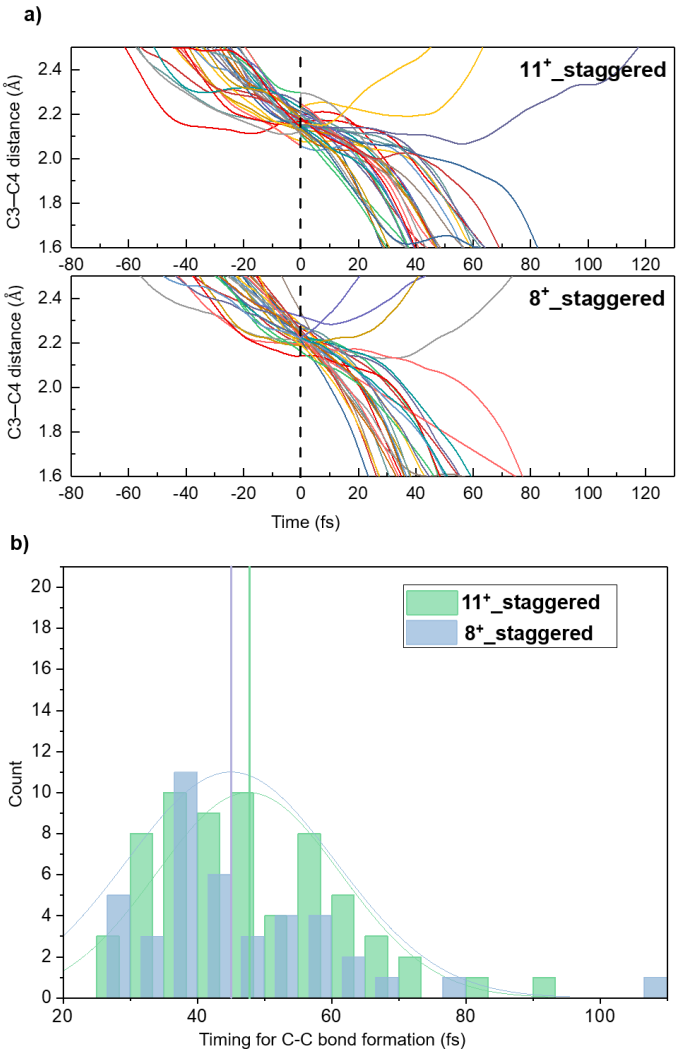


Figure S8. (a) Evolution of the C–C distance corresponding to the first C–C bond formation along quasiclassical trajectories initialized from the higher-energy unstacked conformation of TSs $\mathbf{8}^+$ and $\mathbf{11}^+$ (labelled as staggered). (b) A histogram for the C–C bond formation timing, where the average timing for each reaction is shown by the vertical line.

6- IRC plots for TSs 8^+ and 11^+

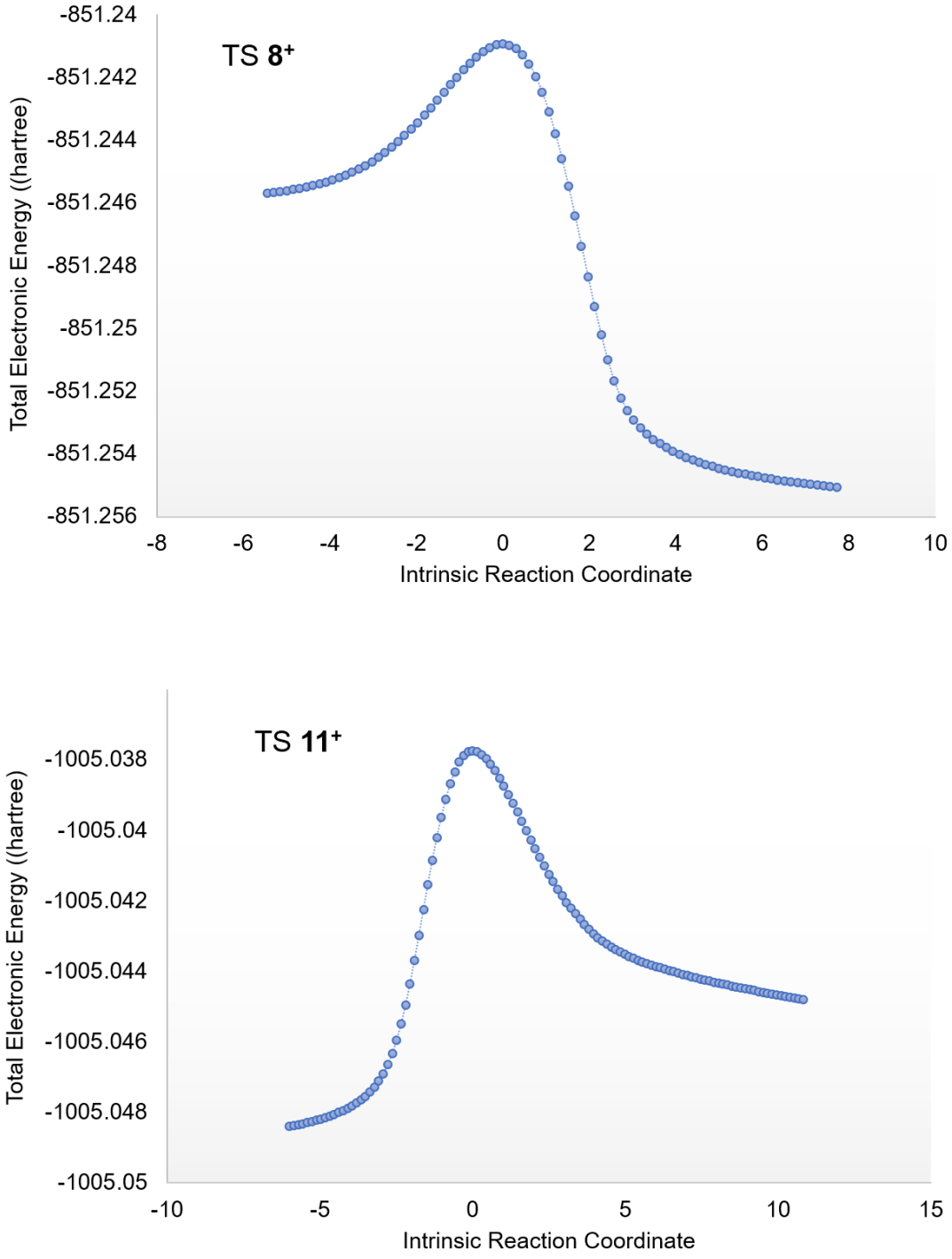


Figure S9. IRC plots for TSs **8**$^+$ and **11**$^+$.

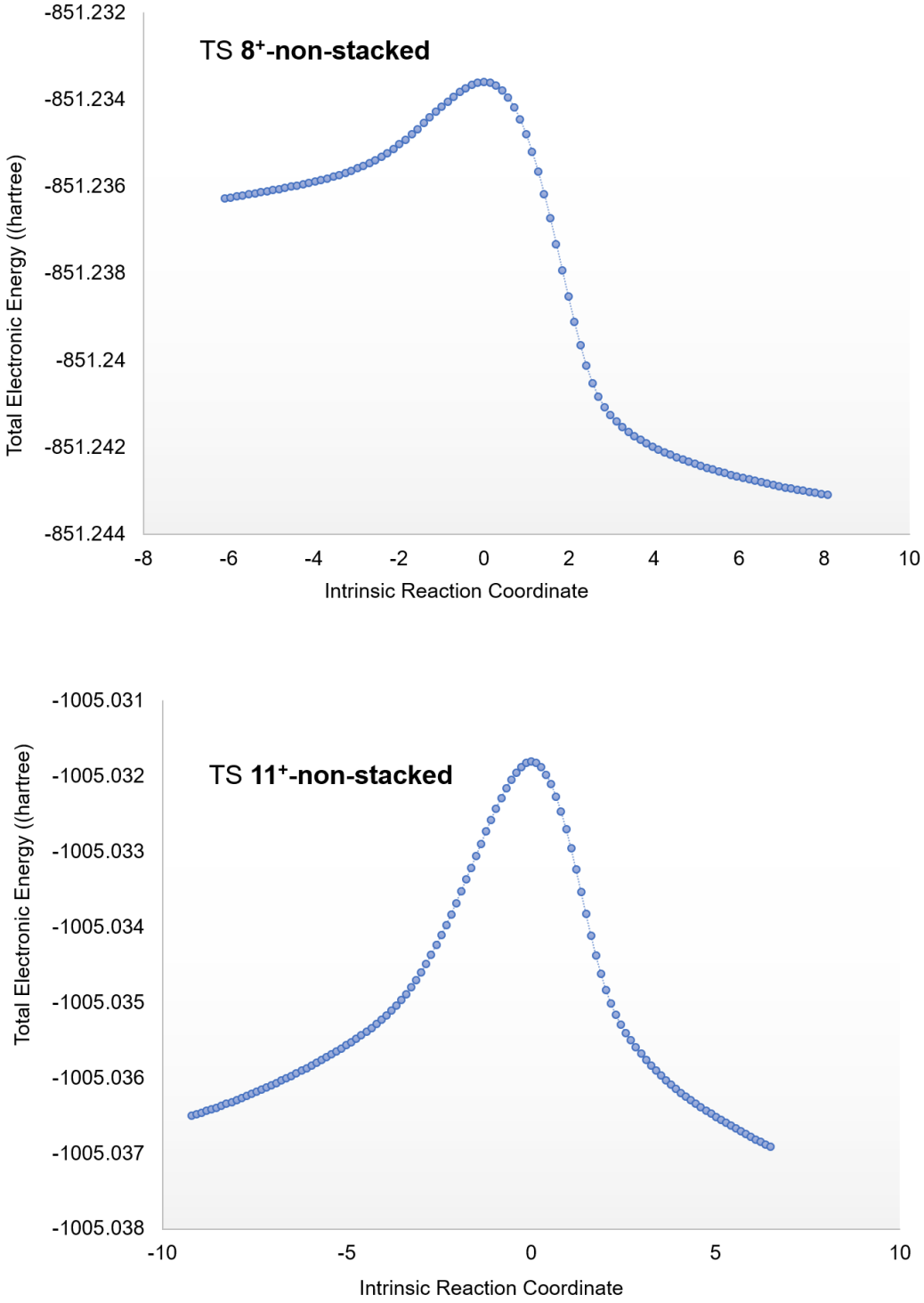


Figure S10. IRC plots for TSs **8$^+$-non-stacked** and **11$^+$-non-stacked**.

7- Frontier molecular orbitals (FMO) analysis of the reacting species in cycloaddition

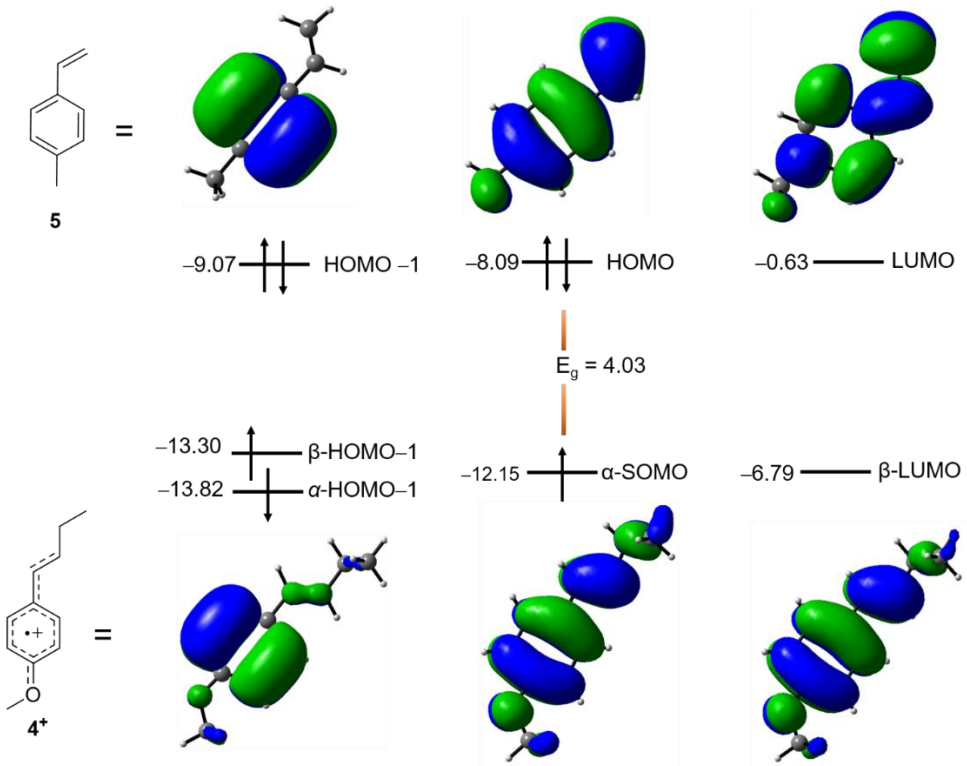


Figure S11. FMOs of radical cation **4**$^{+}$ and styrene **5** in the HETD. Energies are in eV. Calculations were performed in gas phase with *w*B97XD/6-31G(d) level of theory.

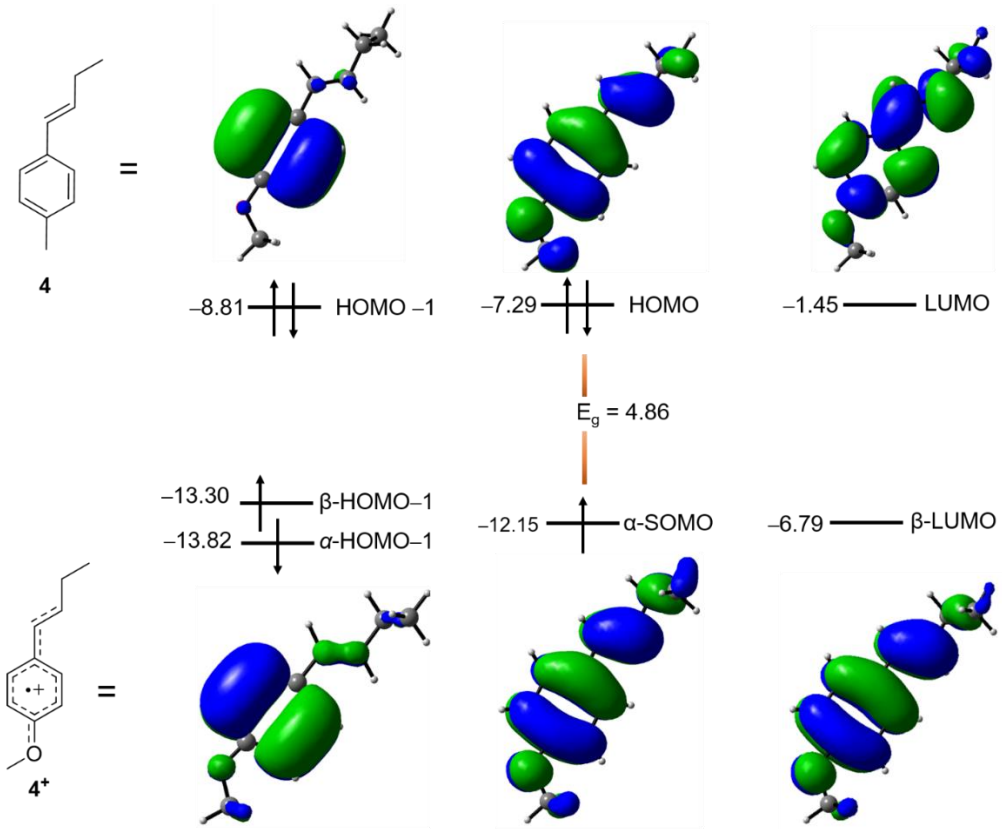


Figure S12. FMOs of radical cation $\mathbf{4}^{+}$ and styrene **4** in the HOMD. Energies are in eV. Calculations were performed in gas phase with *w*B97XD/6-31G(d) level of theory.

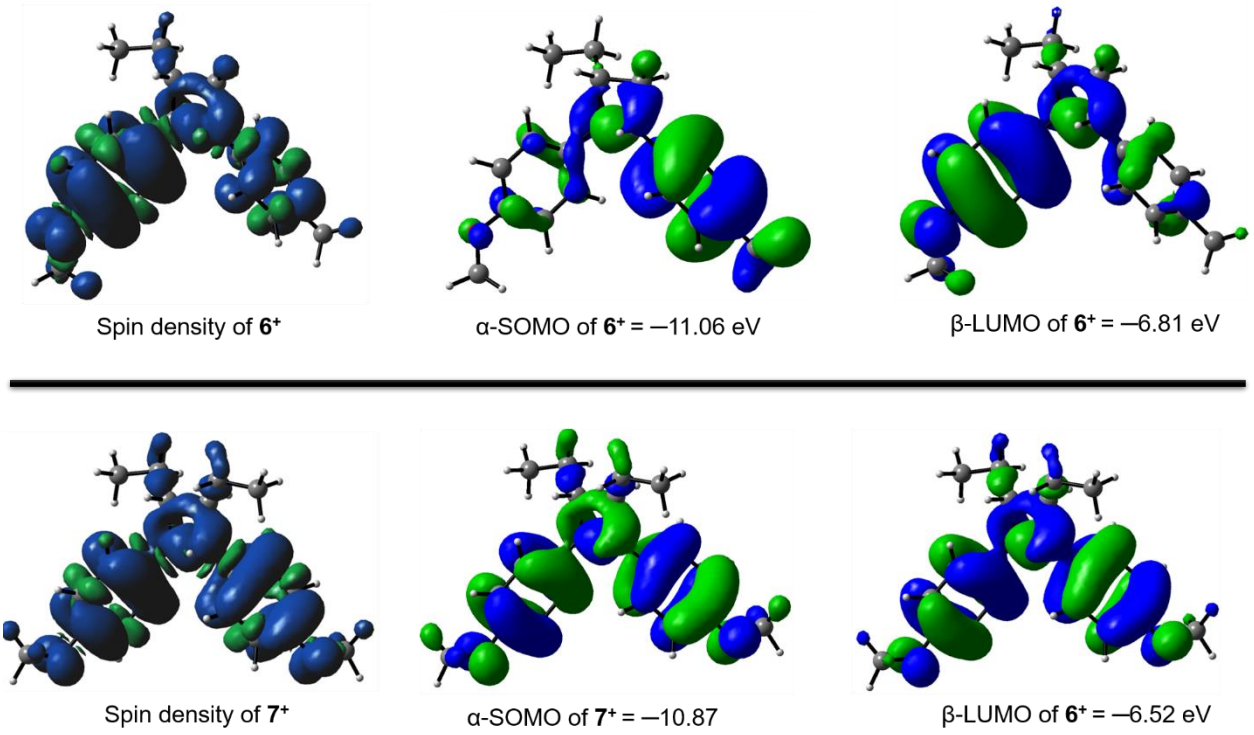


Figure S13. Spin density and SOMO and LUMO of radically-cationic cyclized cyclobutane $\mathbf{6}^{+}$ and $\mathbf{7}^{+}$. Calculations were performed in gas phase with *w*B97XD/6-31G(d) level of theory.

8- FMO analysis of neutral $\mathbf{DMP_{HFIP}}$ and $\mathbf{PIDA_{HFIP}}$

The effect of hydrogen bonding interactions on stability of the HOMOs and LUMOs accounted for neutral HVIRs before electron addition is presented in Figure 9. Two important information can be seen from Figure 14. First, the hydrogen bonding generally lessens the energy of LUMOs and HOMOs of **DMP** and **PIDA**. The impact of lowering the energetic levels of LUMOs is seen to be greater on $\mathbf{DMP_{HFIP}}$ than $\mathbf{PIDA_{HFIP}}$. The LUMO energy of $\mathbf{DMP_{HFIP}}$ decreases by around 1.04 eV (–0.52 → –1.56 eV, Figure 14-a) whereas a lower decrease of 0.82 eV (+0.09 → –73 eV, Figure 14-b) is obtained for $\mathbf{PIDA_{HFIP}}$. LUMO+1, which is in the plane of phenyl ring, and LUMO+2, which is the antibonding orbitals for the phenyl ring, are stabilized by 1.01 eV (–0.27 → –1.28 eV) and 0.81 eV (+0.36 → –0.45 eV) for **DMP**, respectively. For **PIDA**, LUMO+1 and LUMO+2 are stabilized by 0.63 eV (+0.68 → +0.05 eV) and 0.38 (+1.28 → +0.90 eV), respectively. This indicates that hydrogen bonding

makes the iodine more deficient by lowering the energy of antibonding orbitals. Second, stabilization of the HOMOs is also seen but the effect on **DMP** is different. The HOMO orbitals on **PIDA** have similar contours before and after **PIDA** being hydrogen bonded. The HOMO and HOMO-1 that were belong to the axial and equatorial (to the plane of phenyl ring) antibonding orbitals on **DMP** become located on HFIP molecules, specifically on the OH of HFIP, although HFIP is low nucleophilic solvent. This would indicate that the effect of nucleophilicity of acetate groups on iodine decreases substantially when they are hydrogen bonded. This case is not seen in I(III) **PIDA** because **DMP** is already higher oxidation state in which hydrogen bonding makes I(V) more deficient and reactive reagent. Overall, HIFP lowers the HOMOs of acetate groups and, subsequently, the LUMO of the iodine center decreases to a level that makes it a capable species for SEO.

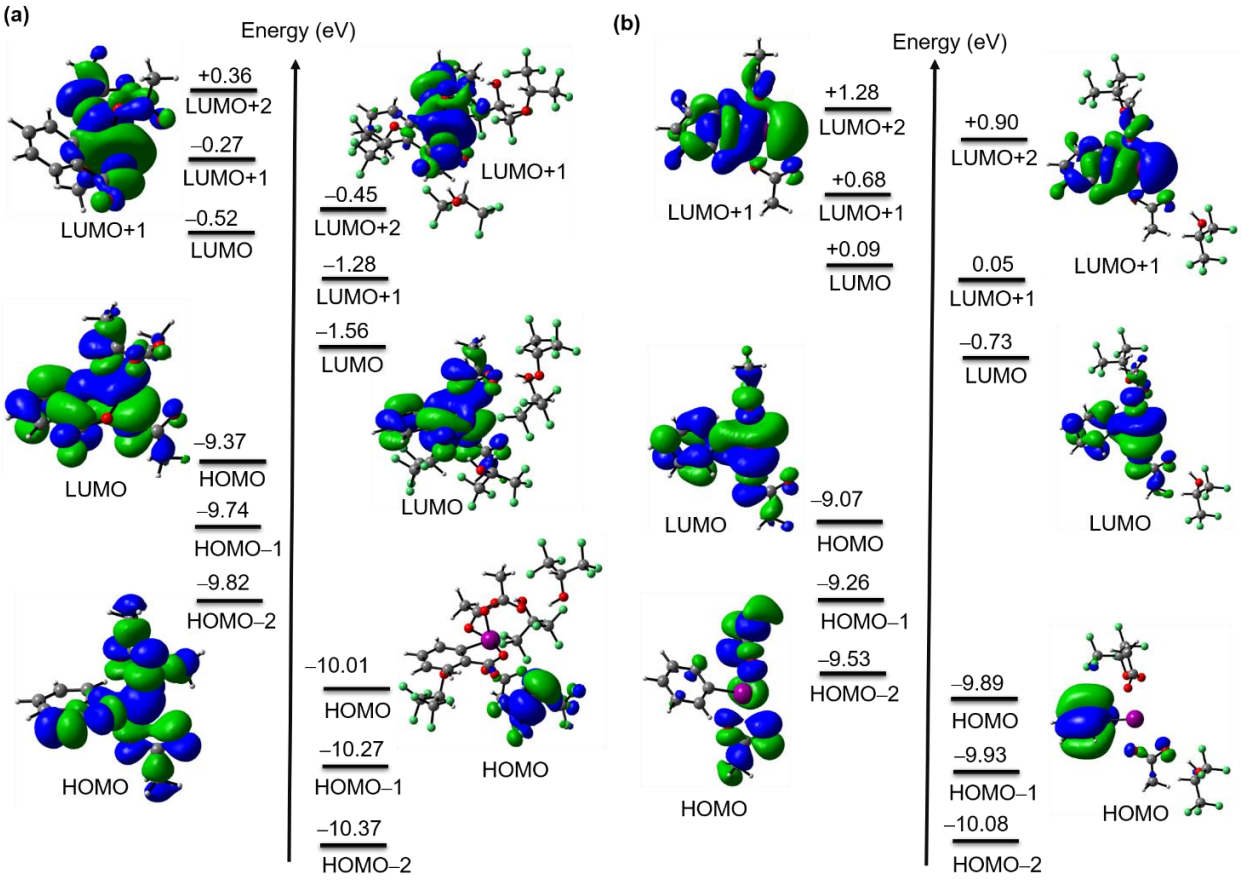


Figure 14. FMOs of the **DMP** (a) and **PIDA** (b) before electron addition, showing the effect of hydrogen bonding interactions on stabilities of the HOMOs and LUMOs of each reagent.

9- Calculation method for free energy barrier of electron transfer using Nelsen's four-point method

To get better insight into the redox step, the free energy of activation for the electron transfer (ET) step was calculated using Nelsen's four-point method [22-24] that has been proposed to adapt Marcus theory computationally [21] which has been extensively applied for many systems.[25-30] The benefit of Nelsen procedure is to calculate the total reorganization energy ($\lambda = \lambda_1 + \lambda_2$) which is then applied in the Marcus equation of ET ($\Delta G^{\ddagger} = (\lambda + \Delta G_r)^2/4\lambda$) in order to calculate the free energy of activation for electron transfer reaction. The Nelsen's four-point method to calculate the total reorganization energy λ for an electron transfer reaction involves four steps. These steps involve the optimization of the reactants and products first, then single point energy calculation for the product based on optimized geometry structure of reactant and vice versa (single point energy calculation of reactant based on optimized geometry structure of product) in order to calculate λ_1 and λ_2.

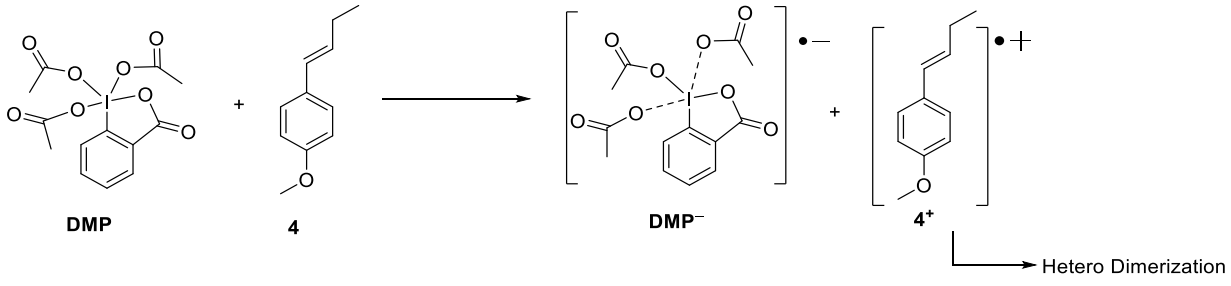
Now, the strategy of Nelsen's four-point method is explained below in detail for the ET step for reaction of **DMP** or **DMP$_{HFIP}$** and **PIDA** or **PIDA$_{HFIP}$** with styrene **4**. Also, this procedure is explained for the electron transfer back (ET-back) step from oxidant to cation cyclobutene after the [2+2] cycloaddition.

6-1 Nelsen's four-point method for the ET step from styrene 4 to DMP or DMP$_{HFIP}$ and PIDA or PIDA$_{HFIP}$

The ET from styrene **4** to iodine catalyst **DMP** or **DMP$_{HFIP}$** and **PIDA** or **PIDA$_{HFIP}$**, the first reaction step, has been calculated with explicit and implicit hydrogen bonding condition calculations.

6-1-1 For reaction of DMP with styrene 4 under implicit and explicit HFIP condition calculations:

a- For reaction of **DMP** with styrene **4** under implicit HFIP condition calculations:



1. Geometry optimization of reactants **DMP** and **4** on a singlet spin state to give their summation free energy:

G_1 = -1905.0612126 Ha (Ha = hartree)

2. Single point energy calculations of the reactants **DMP** and **4** but on a doublet spin state, which means that estimation of the energy of products $\mathbf{DMP}^{-}$ and $\mathbf{4}^{+}$ is based on geometry of reactants **DMP** and **4**, to give their summation free energy:

$$G_2 = -1904.9925487 \text{ Ha}$$

3. Geometry optimization of products $\mathbf{DMP}^{-}$ and $\mathbf{4}^{+}$ on a doublet state to give their summation free energy:

$$G_3 = -1905.0265133 \text{ Ha}$$

4. Finally, single point energy calculations of the products $\mathbf{DMP}^{-}$ and $\mathbf{4}^{+}$ but on a singlet spin state, which means that estimation of the energy of reactants **DMP** and **4** is based on geometry of products $\mathbf{DMP}^{-}$ and $\mathbf{4}^{+}$, to give their summation free energy:

$$G_4 = -1904.9414908 \text{ Ha}$$

So, from the above results the reorganization energy λ_1 and λ_2 of ET step requires subtraction of G_4 from G_1 to give λ_1 and G_2 from G_3 to give λ_2. That means:

$$\lambda_1 = G_4 - G_1 = 75.1 \text{ kcal mol}^{-1}$$

and;

$$\lambda_2 = G_2 - G_3 = 21.3 \text{ kcal mol}^{-1}$$

Now, the average of both λ_1 and λ_2 will give the total reorganisation energy:

$$\lambda = \lambda_1 + \lambda_2/2 = 48.2 \text{ kcal mol}^{-1}$$

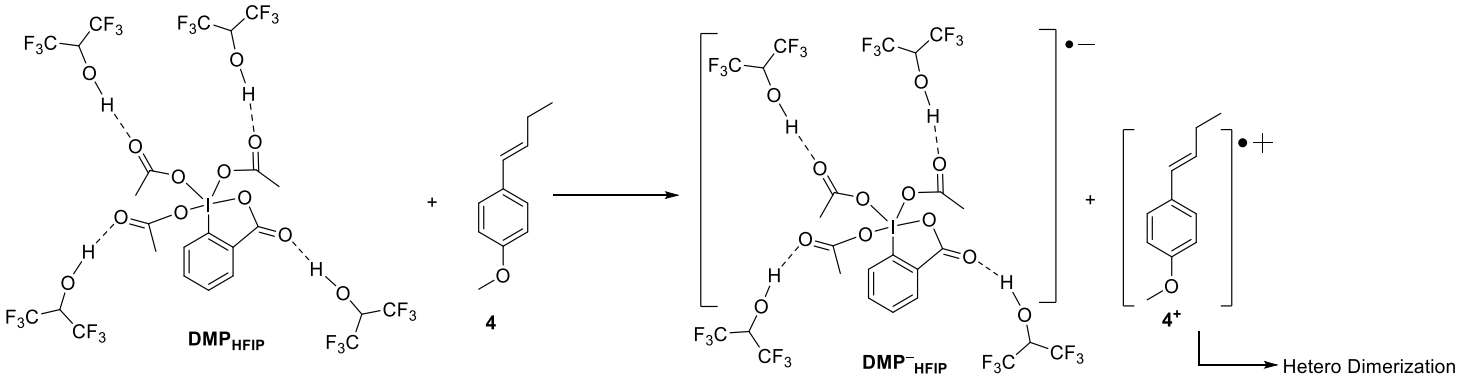
Since the free energy reaction of ET is $\Delta G_r = 21.8$ kcal mol $^{-1}$, which in fact refers to $\Delta G_r = G_3 - G_1$, then by applying the free energy of reoxidation and the calculated reorganization energy in the Marcus theory equation of ET,

$$\Delta G^{\ddagger} = (\lambda + \Delta G_r)^2/4\lambda$$

the free energy of activation for ET step will be:

$$\Delta G^{\ddagger} = 25.4 \text{ kcal mol}^{-1}$$

b- For reaction of $\mathbf{DMP_{HFIP}}$ with styrene **4** under explicit HFIP condition calculations:



1. Geometry optimization of reactants **DMP$_{HFIP}$** and **4** on a singlet spin state to give their summation free energy:

$$G_1 = -5064.3127606 \text{ Ha (Ha = hartree)}$$

2. Single point energy calculations of the reactants **DMP$_{HFIP}$** and **4** but on a doublet spin state, which means that estimation of the energy of products **DMP$^{-}_{HFIP}$** and **4^{+}** is based on geometry of reactants **DMP$_{HFIP}$** and **4**, to give their summation free energy:

$$G_2 = -5064.2491277 \text{ Ha}$$

3. Geometry optimization of products **DMP$^{-}_{HFIP}$** and **4^{+}** on a doublet state to give their summation free energy:

$$G_3 = -5064.2907793 \text{ Ha}$$

4. Finally, single point energy calculations of the products **DMP$^{-}_{HFIP}$** and **4^{+}** but on a singlet spin state, which means that estimation of the energy of reactants **DMP$_{HFIP}$** and **4** is based on geometry of products **DMP$^{-}_{HFIP}$** and **4^{+}**, to give their summation free energy:

$$G_4 = -5064.1976738 \text{ Ha}$$

So,

$$\lambda_1 = G_4 - G_1 = 72.2 \text{ kcal mol}^{-1}$$

and;

$$\lambda_2 = G_2 - G_3 = 26.1 \text{ kcal mol}^{-1}$$

Now, the total reorganisation energy is:

$$\lambda = \lambda_1 + \lambda_2/2 = 49.2 \text{ kcal mol}^{-1}$$

Again, since the free energy reaction of ET step is $\Delta G_r = 13.79$ kcal mol $^{-1}$, which in fact refers to $\Delta G_r = G_3 - G_1$, then by applying the free energy of reoxidation and the calculated reorganization energy in the Marcus theory equation of ET,

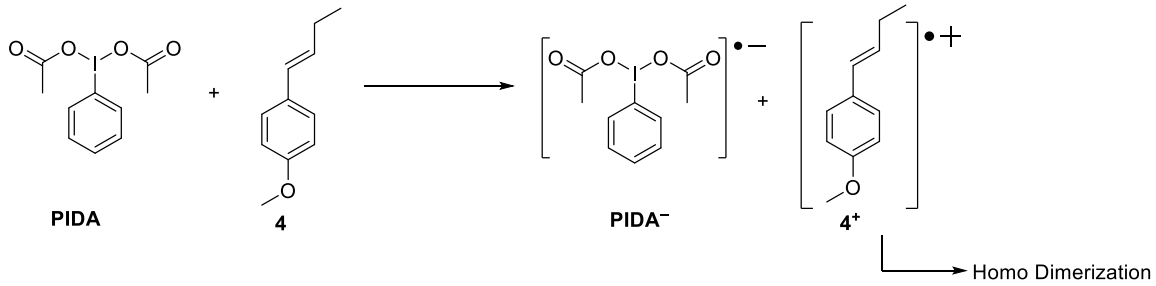
$$\Delta G^{\ddagger} = (\lambda + \Delta G_r)^2/4\lambda$$

the free energy of activation for ET step under explicit HFIP will be:

$$\Delta G^{\ddagger} = 20.2 \text{ kcal mol}^{-1}$$

6-1-2 For reaction of PIDA with styrene 4 under implicit and explicit HFIP condition calculations:

a- For reaction of **PIDA** with styrene **4** under implicit HFIP condition calculations:



1. Geometry optimization of reactants **PIDA** and **4** on a singlet spin state to give their summation free energy:

$$G_1 = -1488.7440728 \text{ Ha (Ha = hartree)}$$

2. Single point energy calculations of the reactants **PIDA** and **4** but on a doublet spin state, which means that estimation of the energy of products **PIDA**$^-$ and **4**$^+$ is based on geometry of reactants **PIDA** and **4**, to give their summation free energy:

$$G_2 = -1488.6501919 \text{ Ha}$$

3. Geometry optimization of products **PIDA**$^{-}$ and **4**$^{+}$ on a doublet state to give their summation free energy:

$$G_3 = -1488.690943 \text{ Ha}$$

4. Finally, single point energy calculations of the products **PIDA**$^{-}$ and **4**$^{+}$ but on a singlet spin state, which means that estimation of the energy of reactants **PIDA** and **4** is based on geometry of products **PIDA**$^{-}$ and **4**$^{+}$, to give their summation free energy:

$$G_4 = -1488.6019709 \text{ Ha}$$

So,

$$\lambda_1 = G_4 - G_1 = 89.2 \text{ kcal mol}^{-1}$$

and;

$$\lambda_2 = G_2 - G_3 = 25.6 \text{ kcal mol}^{-1}$$

Now, the total reorganisation energy:

$$\lambda = \lambda_1 + \lambda_2/2 = 57.4 \text{ kcal mol}^{-1}$$

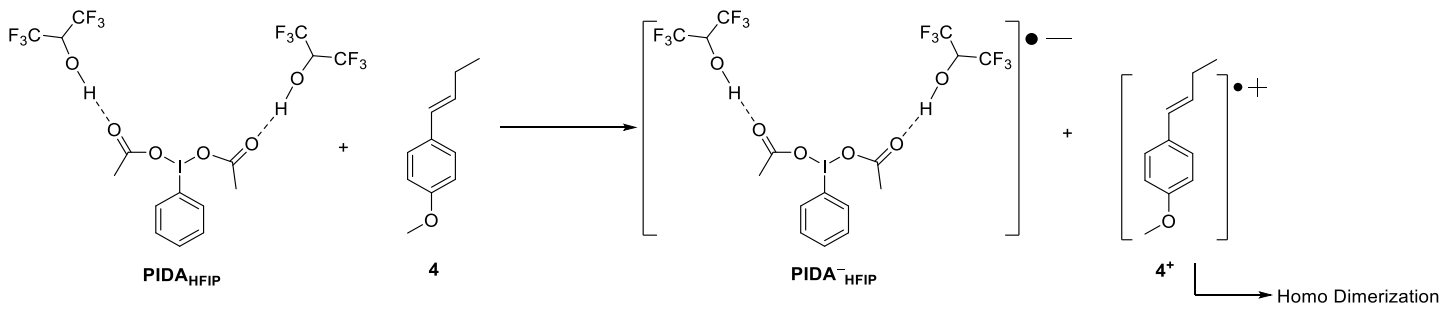
Again, since the free energy reaction of ET step is $\Delta G_r = 33.3$ kcal mol $^{-1}$, which in fact refers to $\Delta G_r = G_3 - G_1$, then by applying the free energy of reoxidation and the calculated reorganization energy in the Marcus theory equation of ET,

$$\Delta G^{\ddagger} = (\lambda + \Delta G_r)^2/4\lambda$$

the free energy of activation for ET step under implicit HFIP will be:

$$\Delta G^{\ddagger} = 35.8 \text{ kcal mol}^{-1}$$

b- For reaction of **PIDA** with styrene **4** under explicit HFIP condition calculations:



1. Geometry optimization of reactants **PIDA$_{HFIP}$** and **4** on a singlet spin state to give their summation free energy:

$$G_1 = -3068.3690126 \text{ Ha (Ha = hartree)}$$

2. Single point energy calculations of the reactants **PIDA$_{HFIP}$** and **4** but on a doublet spin state, which means that estimation of the energy of products **PIDA$^{-}_{HFIP}$** and **4**$^{+}$ is based on geometry of reactants **PIDA$_{HFIP}$** and **4**, to give their summation free energy:

$$G_2 = -3068.2879197 \text{ Ha}$$

3. Geometry optimization of products **PIDA$^{-}_{HFIP}$** and **4**$^{+}$ on a doublet state to give their summation free energy:

$$G_3 = -3068.3242753 \text{ Ha}$$

4. Finally, single point energy calculations of the products **PIDA$^{-}_{HFIP}$** and **4**$^{+}$ but on a singlet spin state, which means that estimation of the energy of reactants **PIDA$_{HFIP}$** and **4** is based on geometry of products **PIDA$^{-}_{HFIP}$** and **4**$^{+}$, to give their summation free energy:

$$G_4 = -3068.2315388 \text{ Ha}$$

So,

$$\lambda_1 = G_4 - G_1 = 86.3 \text{ kcal mol}^{-1}$$

and;

$$\lambda_2 = G_2 - G_3 = 22.8 \text{ kcal mol}^{-1}$$

Now, the total reorganisation energy:

$$\lambda = \lambda_1 + \lambda_2/2 = 54.5 \text{ kcal mol}^{-1}$$

Again, since the free energy reaction of ET step is $\Delta G_r = 28.1$ kcal mol $^{-1}$, which in fact refers to $\Delta G_r = G_3 - G_1$, then by applying the free energy of reoxidation and the calculated reorganization energy in the Marcus theory equation of ET,

$$\Delta G^{\ddagger} = (\lambda + \Delta G_r)^2/4\lambda$$

the free energy of activation for ET step under explicit HFIP will be:

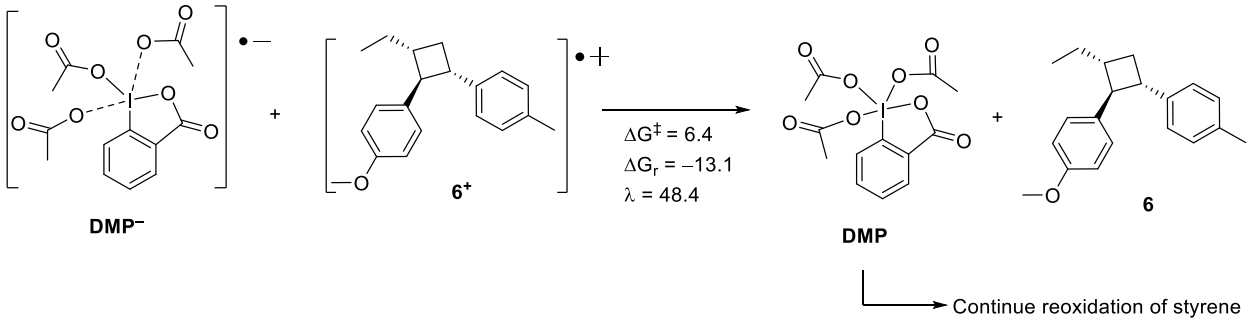
$$\Delta G^{\ddagger} = 31.3 \text{ kcal mol}^{-1}$$

6-2 Nelsen's four-point method for the ET-back step from reduced DMP^{-}_{HFIP} or DMP^{-} to heterodimerized cationic cyclobutane 6^{+} and from reduced $PIDA^{-}$ or $PIDA^{-}_{HFIP}$ to homodimerized cationic cyclobutane 7^{+}

Now, the ET-back step, the fourth reaction step, from the reduced iodine catalyst **DMP**$^{-}$ or **DMP**$^{-}_{\mathbf{HFIP}}$ to heterodimerized cationic cyclobutane **6**$^{+}$ or from the reduced iodine catalyst **PIDA**$^{-}$ or **PIDA**$^{-}_{\mathbf{HFIP}}$ to heterodimerized cationic cyclobutane **7**$^{+}$ under explicit and implicit hydrogen bonding have been calculated.

6-2-1 Reaction of DMP^{-} with heterodimerized cationic cyclobutane 6^{+} under implicit and explicit HFIP condition calculations

a- For reaction of **DMP**$^{-}$ with heterodimerized cationic cyclobutene **6**$^{+}$ under implicit HFIP condition calculations:



1. Geometry optimization of reactants **DMP**$^{-}$ and **6**$^{+}$ on a doublet spin state to give their summation free energy:

$$G_1 = -2253.833807 \text{ Ha (Ha = hartree)}$$

2. Single point energy calculations of the reactants **DMP**$^{-}$ and **6**$^{+}$ but on a singlet spin state, which means that estimation of the energy of products **DMP** and **6** is based on geometry of reactants **DMP**$^{-}$ and **6**$^{+}$, to give their summation free energy:

$$G_2 = -2253.750546 \text{ Ha}$$

3. Geometry optimization of products **DMP** and **6** on a singlet spin state to give their summation free energy:

$$G_3 = -2253.879032 \text{ Ha}$$

4. Finally, single point energy calculations of the products **DMP** and **6** but on a doublet spin state, which means that estimation of the energy of reactants $\mathbf{DMP}^-$ and $\mathbf{6}^+$ is based on geometry of products **DMP** and **6**, to give their summation free energy:

$$G_4 = -2253.750546 \text{ Ha}$$

So,

$$\lambda_1 = G_4 - G_1 = 52.2 \text{ kcal mol}^{-1}$$

and;

$$\lambda_2 = G_2 - G_3 = 80.6 \text{ kcal mol}^{-1}$$

Now, the total reorganisation energy is:

$$\lambda = \lambda_1 + \lambda_2/2 = 66.4 \text{ kcal mol}^{-1}$$

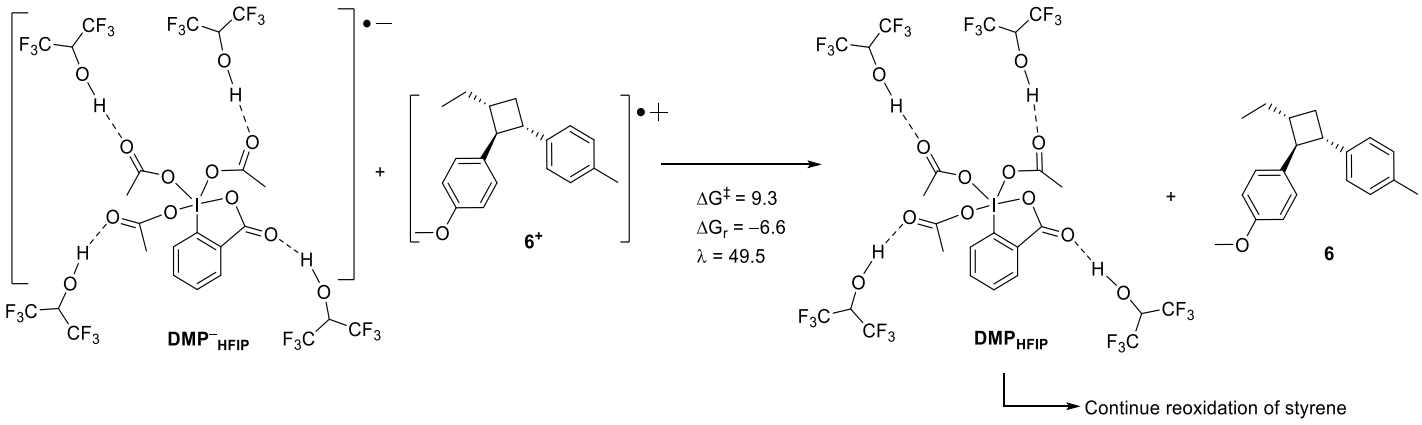
Again, since the free energy reaction of ET step is $\Delta G_r = -28.4$ kcal mol $^{-1}$, which in fact refers to $\Delta G_r = G_3 - G_1$, then by applying the free energy of re-oxidation and the calculated reorganization energy in the Marcus theory equation of ET,

$$\Delta G^{\ddagger} = (\lambda + \Delta G_r)^2/4\lambda$$

the free energy of activation for ET-back step from $\mathbf{6}^+$ under implicit HFIP will be:

$$\Delta G^{\ddagger} = 5.5 \text{ kcal mol}^{-1}$$

b- For reaction of $\mathbf{DMP}^-_{\mathbf{HFIP}}$ with heterodimerized cationic cyclobutene $\mathbf{6}^+$ under explicit HFIP condition calculations:



1. Geometry optimization of reactants $\mathbf{DMP^-_{HFIP}}$ and $\mathbf{6^+}$ on a doublet spin state to give their summation free energy:

$$G_1 = -5413.098073 \text{ Ha (Ha = hartree)}$$

2. Single point energy calculations of the reactants $\mathbf{DMP^-_{HFIP}}$ and $\mathbf{6^+}$ but on a singlet spin state, which means that estimation of the energy of products $\mathbf{DMP_{HFIP}}$ and **6** is based on geometry of reactants $\mathbf{DMP^-_{HFIP}}$ and $\mathbf{6^+}$, to give their summation free energy:

$$G_2 = -5413.006729 \text{ Ha}$$

3. Geometry optimization of products $\mathbf{DMP_{HFIP}}$ and **6** on a singlet spin state to give their summation free energy:

$$G_3 = -5413.13058 \text{ Ha}$$

4. Finally, single point energy calculations of the products $\mathbf{DMP_{HFIP}}$ and **6** but on a doublet spin state, which means that estimation of the energy of reactants $\mathbf{DMP^-_{HFIP}}$ and $\mathbf{6^+}$ is based on geometry of products $\mathbf{DMP_{HFIP}}$ and **6**, to give their summation free energy:

$$G_4 = -5413.063316 \text{ Ha}$$

So,

$$\lambda_1 = G_4 - G_1 = 21.8 \text{ kcal mol}^{-1}$$

and;

$$\lambda_2 = G_2 - G_3 = 77.7 \text{ kcal mol}^{-1}$$

Now, the total reorganisation energy is:

$$\lambda = \lambda_1 + \lambda_2/2 = 49.8 \text{ kcal mol}^{-1}$$

Again, since the free energy reaction of ET step is ΔG_r = -20.4 kcal mol $^{-1}$, which in fact refers to $\Delta G_r = G_3 - G_1$, then by applying the free energy of reoxidation and the calculated reorganization energy in the Marcus theory equation of ET,

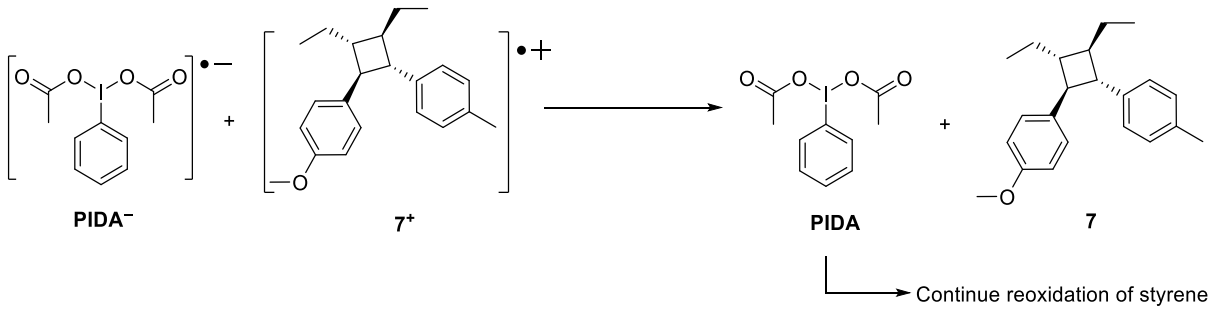
$$\Delta G^{\ddagger} = (\lambda + \Delta G_r)^2/4\lambda$$

the free energy of activation for ET-back step from $\mathbf{6}^+$ under explicit HFIP will be:

$$\Delta G^{\ddagger} = 4.3 \text{ kcal mol}^{-1}$$

6-2-2 Reaction of PIDA$^-$ with homodimerized cationic cyclobutane 7$^+$ under implicit and explicit HFIP condition calculations:

a- For reaction of **PIDA**$^-$ with homodimerized cationic cyclobutane **7**$^+$ under implicit HFIP condition calculations:



1. Geometry optimization of reactants **PIDA**$^-$ and **7**$^+$ on a doublet spin state to give their summation free energy:

   G_1 = -1991.2756927 Ha (Ha = hartree)

2. Single point energy calculations of the reactants **PIDA**$^-$ and **7**$^+$ but on a singelt spin state, which means that estimation of the energy of products **PIDA** and **7** is based on geometry of reactants **PIDA**$^-$ and **7**$^+$, to give their summation free energy:

   G_2 = -1991.1847111 Ha

3. Geometry optimization of products **PIDA** and **7** on a singlet spin state to give their summation free energy:

$$G_3 = -1991.3388762 \text{ Ha}$$

4. Finally, single point energy calculations of the products **PIDA** and **7** but on a doublet spin state, which means that estimation of the energy of reactants $\mathbf{PIDA}^-$ and $\mathbf{7}^+$ is based on geometry of products **PIDA** and **7**, to give their summation free energy:

$$G_4 = -1991.2388822 \text{ Ha}$$

So,

$$\lambda_1 = G_4 - G_1 = 23.1 \text{ kcal mol}^{-1}$$

and;

$$\lambda_2 = G_2 - G_3 = 96.7 \text{ kcal mol}^{-1}$$

Now, the total reorganisation energy:

$$\lambda = \lambda_1 + \lambda_2/2 = 59.9 \text{ kcal mol}^{-1}$$

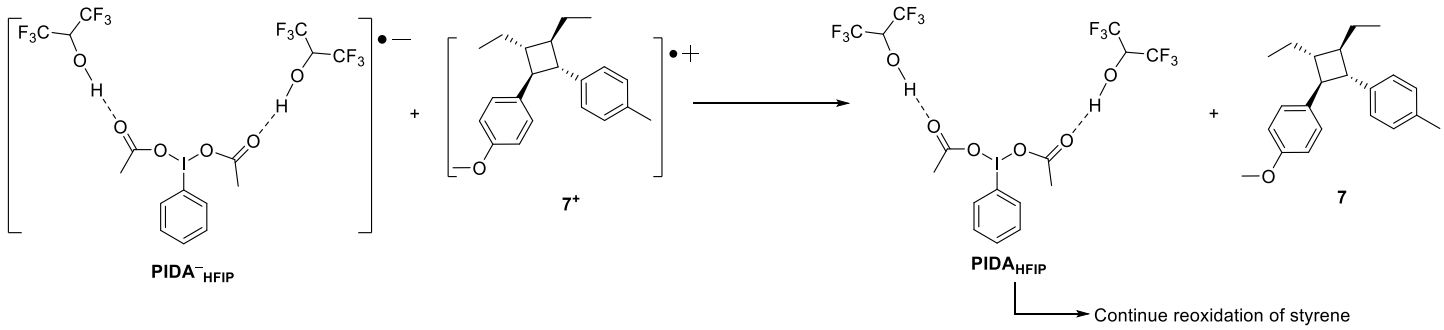
Again, since the free energy reaction of ET-back step is $\Delta G_r = -39.6$ kcal mol $^{-1}$, which in fact refers to $\Delta G_r = G_3 - G_1$, then by applying the free energy of reoxidation and the calculated reorganization energy in the Marcus theory equation of ET,

$$\Delta G^{\ddagger} = (\lambda + \Delta G_r)^2/4\lambda$$

the free energy of activation for ET-back step from $\mathbf{7}^+$ under implicit HFIP will be:

$$\Delta G^{\ddagger} = 1.7 \text{ kcal mol}^{-1}$$

b- For reaction of $\mathbf{PIDA}^-_{\mathbf{HFIP}}$ with homodimerized cationic cyclobutane $\mathbf{7}^+$ under explicit HFIP condition calculations:



1. Geometry optimization of reactants **PIDA$^-_{HFIP}$** and **7**$^+$ on a doublet spin state to give their summation free energy:

$$G_1 = -3570.909025 \text{ Ha (Ha = hartree)}$$

2. Single point energy calculations of the reactants **PIDA$^-_{HFIP}$** and **7**$^+$ but on a singlet spin state, which means that estimation of the energy of products **PIDA$_{HFIP}$** and **7** is based on geometry of reactants **PIDA$^-_{HFIP}$** and **7**$^+$, to give their summation free energy:

$$G_2 = -3570.814279 \text{ Ha}$$

3. Geometry optimization of products **PIDA$_{HFIP}$** and **7** on a singlet spin state to give their summation free energy:

$$G_3 = -3570.963816 \text{ Ha}$$

4. Finally, single point energy calculations of the products **PIDA$_{HFIP}$** and **7** but on a singlet spin state, which means that estimation of the energy of reactants **PIDA$^-_{HFIP}$** and **7**$^+$ is based on geometry of products **PIDA$_{HFIP}$** and **7**, to give their summation free energy:

$$G_4 = -3570.87661 \text{ Ha}$$

So,

$$\lambda_1 = G_4 - G_1 = 20.3 \text{ kcal mol}^{-1}$$

and;

$$\lambda_2 = G_2 - G_3 = 93.8 \text{ kcal mol}^{-1}$$

Now, the total reorganisation energy:

$$\lambda = \lambda_1 + \lambda_2/2 = 57.1 \text{ kcal mol}^{-1}$$

Again, since the free energy reaction of ET-back step is ΔG_r = -34.4 kcal mol $^{-1}$, which in fact refers to $\Delta G_r = G_3 - G_1$, then by applying the free energy of reoxidation and the calculated reorganization energy in the Marcus theory equation of ET,

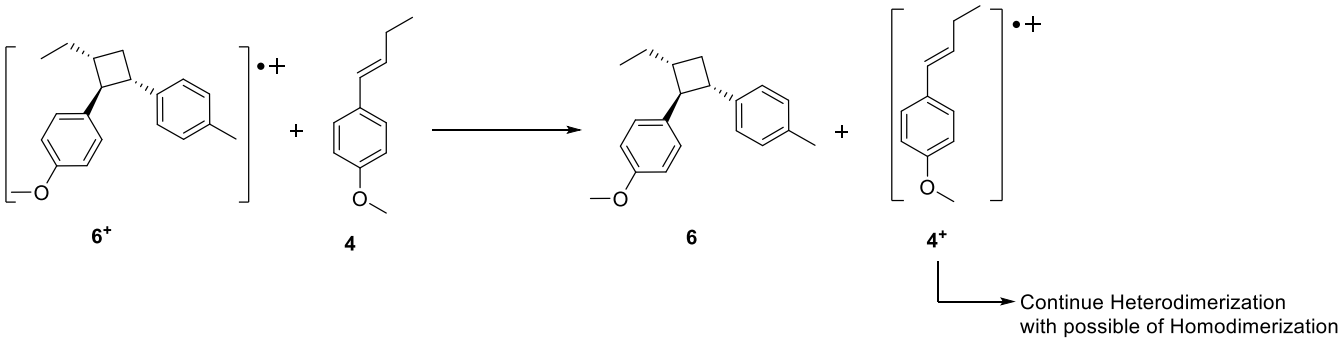
$$\Delta G^{\ddagger} = (\lambda + \Delta G_r)^2/4\lambda$$

the free energy of activation for ET-back step under explicit HFIP will be:

$$\Delta G^{\ddagger} = 2.5 \text{ kcal mol}^{-1}$$

6-3 Nelsen's four-point method for the propagation step of heterodimerized cationic cyclobutane 6^+ and homodimerized cationic cyclobutane 7^+ with styrene 4

a- Reaction of heterodimerized cationic cyclobutane $\mathbf{6}^+$ with styrene **4**



5. Geometry optimization of reactants $\mathbf{6}^+$ (doublet spin state) and **4** (singlet spin state) to give their summation free energy:

$$G_1 = -1353.770475 \text{ Ha}$$

6. Single point energy calculations of the reactants $\mathbf{6}^+$ and **4** but on a singlet spin state for $\mathbf{6}^+$ and doublet spin state for **4**, which means that estimation of the energy of products **6** and $\mathbf{4}^+$ is based on geometry of reactants $\mathbf{6}^+$ and **4**, to give their summation free energy:

$$G_2 = -1352.755392 \text{ Ha}$$

7. Geometry optimization of products **6** (singlet spin state) and $\mathbf{4}^{+}$ (doublet spin state) on a singlet spin state to give their summation free energy:

$$G_3 = -1353.781000 \text{ Ha}$$

8. Finally, single point energy calculations of the products **6** and $\mathbf{4}^{+}$ but on a singlet spin state for **6** and doublet spin state for $\mathbf{4}^{+}$, which means that estimation of the energy of reactants $\mathbf{6}^{+}$ and **4** is based on geometry of products **6** and $\mathbf{4}^{+}$, to give their summation free energy:

$$G_4 = -1353.750259 \text{ Ha}$$

So,

$$\lambda_1 = G_4 - G_1 = 12.7 \text{ kcal mol}^{-1}$$

and;

$$\lambda_2 = G_2 - G_3 = 16.1 \text{ kcal mol}^{-1}$$

Now, the total reorganisation energy is:

$$\lambda = \lambda_1 + \lambda_2/2 = 14.4 \text{ kcal mol}^{-1}$$

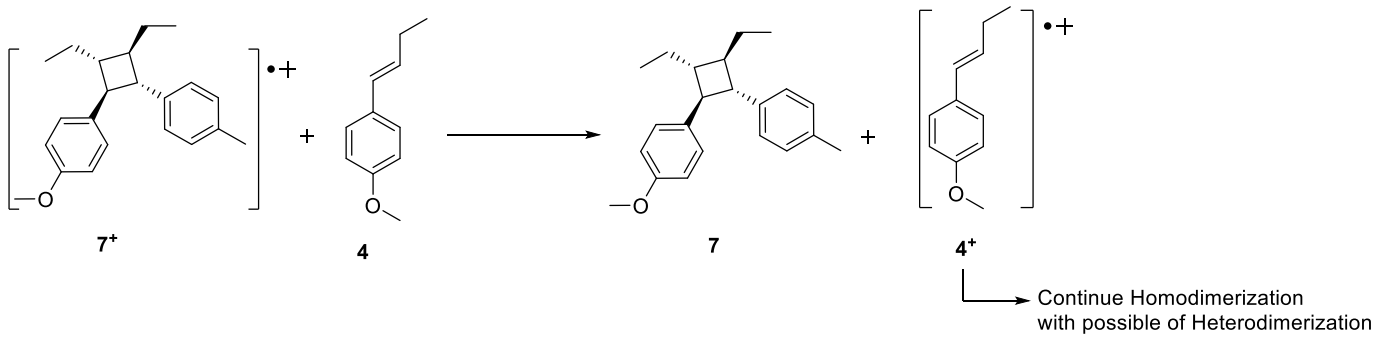
Again, since the free energy reaction of ET step is $\Delta G_r = -6.6$ kcal mol $^{-1}$, which in fact refers to $\Delta G_r = G_3 - G_1$, then by applying the free energy of reoxidation and the calculated reorganization energy in the Marcus theory equation of ET,

$$\Delta G^{\ddagger} = (\lambda + \Delta G_r)^2/4\lambda$$

the free energy of activation for ET-back step of $\mathbf{6}^{+}$ from **4** (activation energy of propagation) will be:

$$\Delta G^{\ddagger} = 1.1 \text{ kcal mol}^{-1}$$

b- Reaction of heterodimerized cationic cyclobutane $\mathbf{7}^{+}$ with styrene **4**



1. Geometry optimization of reactants $\mathbf{7}^+$ (doublet spin state) and **4** (singlet spin state) to give their summation free energy:

$$G_1 = -1507.547931 \text{ Ha}$$

2. Single point energy calculations of the reactants $\mathbf{7}^+$ and **4** but on a singlet spin state for $\mathbf{7}^+$ and doublet spin state for **4**, which means that estimation of the energy of products **7** and $\mathbf{4}^+$ is based on geometry of reactants $\mathbf{7}^+$ and **4**, to give their summation free energy:

$$G_2 = -1507.529894 \text{ Ha}$$

3. Geometry optimization of products **7** (singlet spin state) and $\mathbf{4}^+$ (doublet spin state) on a singlet spin state to give their summation free energy:

$$G_3 = -1057.557984 \text{ Ha}$$

4. Finally, single point energy calculations of the products **7** and $\mathbf{4}^+$ but on a singlet spin state for **7** and doublet spin state for $\mathbf{4}^+$, which means that estimation of the energy of reactants $\mathbf{7}^+$ and **4** is based on geometry of products **7** and $\mathbf{4}^+$, to give their summation free energy:

$$G_4 = -1507.523944 \text{ Ha}$$

So,

$$\lambda_1 = G_4 - G_1 = 15.0 \text{ kcal mol}^{-1}$$

and;

$$\lambda_2 = G_2 - G_3 = 17.6 \text{ kcal mol}^{-1}$$

Now, the total reorganisation energy is:

$$\lambda = \lambda_1 + \lambda_2/2 = 16.3 \text{ kcal mol}^{-1}$$

Again, since the free energy reaction of ET step is $\Delta G_r = -6.3$ kcal mol $^{-1}$, which in fact refers to $\Delta G_r = G_3 - G_1$, then by applying the free energy of reoxidation and the calculated reorganization energy in the Marcus theory equation of ET,

$$\Delta G^{\ddagger} = (\lambda + \Delta G_r)^2/4\lambda$$

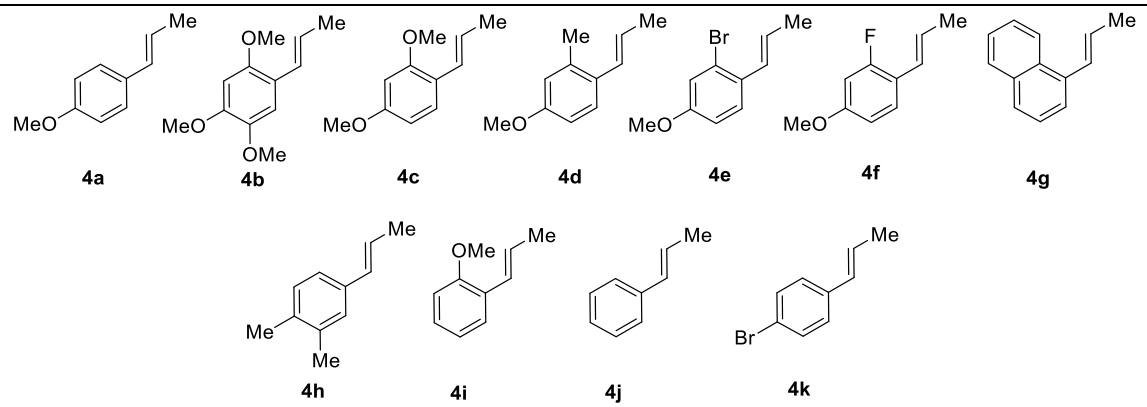
the free energy of activation for ET-back step of $\mathbf{7}^+$ from **4** (activation energy of propagation) will be:

$$\Delta G^{\ddagger} = 1.5 \text{ kcal mol}^{-1}$$

10- Comparison between measured and calculated voltammetric peak potentials (V) for redox species of different substituted *trans-β*-methylstyrenes under explicit and implicit SEO step by PIDA for styrenes 4a ─ 4k

We have compared between measured and calculated voltammetric peak potentials (V) for redox species of different substituted *trans-β*-methylstyrenes **14 ─ 24** againest Fc/Fc^{+} (Table S2). Good agreement between calculated and experimental redox potentials when they DFT calculations conducted with explicit PIDA, however the implicit calculations do not show a good agreement. This gave good support to our DFT calculations that the existence of explicit HFIP in calculations is of prime importance to get accurate results.

Table S2. Comparison between measured and calculated voltammetric peak potentials (V) for redox species of different substituted *trans-β*-methylstyrenes by PIDA and comparison with their redox potential, ($E_m^{0/+}$ in eV), Energies between bracket are calculated with implicit HFIP only.



	Exp. potentials [a] (eV)		Calc. potentials (eV)		
Subs.	$E_{p,a}$	$\Delta E_{p\text{-}p}$	$E_m^{0/+}$	$E_{p,a}$	$\Delta E_{p\text{-}p}$
4a	0.85	−1.31	5.45	0.61	−1.20 (−1.43)
4b	0.63	−1.10	5.13	0.29	−0.88 (−1.11)
4c	0.72	−1.19	5.32	0.48	−1.07 (−1.30)
4d	0.84	−1.31	5.42	0.58	−1.17 (−1.40)
4e	1.07	−1.54	5.62	0.78	−1.37 (−1.60)
4f	1.02	−1.49	5.74	0.90	−1.49 (−1.72)
4g	1.02	−1.49	5.80	0.96	−1.55 (−1.78)
4h	1.03	−1.50	5.59	0.75	−1.34 (−1.57)
4i	1.05	−1.52	5.60	0.76	−1.35 (−1.58)

4j	1.31	−1.78	5.85	1.01	−1.60 (−1.83)
4k	1.37	−1.84	5.97	1.13	−1.72 (−1.95)

[a] The measured results were obtained versus Fc/Fc^+, as measured at 100 mV s^{-1}. The calculated one is $E_m^{0/+} = 4.84$ V. The calculated value for **PIDA**$_{\mathbf{HFIP}}$ + e^- → **PIDA**$^-_{\mathbf{HFIP}}$ is $E_m^{0/+} = 4.25$ V (4.02 V in implicit HFIP, PIDA). Measured and calculated peak potential for **PIDA** is $E_{p,c}$ = −0.47 V and $E_{p,c}$ = −0.59 V (−0.82 eV in implicit HFIP, **PIDA**), respectively.

11- Electrochemical computational methods for redox potentials

The method for the redox potential calculations is summarized below. It consists of three steps;

1- For an oxidized species such as:

$$Fc \rightarrow Fc^+ + e^-$$

or

$$Styrene \rightarrow Styrene^+ + e^-$$

The $E^{1/2}$ will be:

$$E^{1/2} = \text{Neutral} - \text{Oxidized (with the sign is overlapped)}$$

or

$$E^{1/2} = \text{Oxidized} - \text{Neutral (the sign is remained).}$$

2- For a reduced species such as:

$$\mathbf{PIDA} + e^- \rightarrow \mathbf{PIDA}^-$$

or

$$\mathbf{DMP} + e^- \rightarrow \mathbf{DMP}^-$$

The $E^{1/2}$ will be:

$$E^{1/2} = \text{Neutral} - \text{Reduced (with the sign is remained)}$$

or

$$E^{1/2} = \text{Reduced} - \text{Neutral (the sign is overlapped).}$$

3- Then, peak potential will be:

$$E_{\text{p,a or c}} = E^{1/2}_{\text{(oxidized or reduced)}} - E^{1/2}_{\text{Reference}}$$

E_p: peak potential. a is anode and c is cathode.

12- Cartesian coordinates and absolute energies

Heterodimerization

4

C	2.8080206	0.4604149	-0.2038648
C	2.1359406	1.6853709	-0.1678888
C	0.7534906	1.7191199	-0.2199378
C	-0.0096214	0.5445149	-0.3020348
C	0.6821376	-0.6676351	-0.3530708
C	2.0720236	-0.7220761	-0.3006298
H	2.7199906	2.5972599	-0.0995238
H	0.2462596	2.6803429	-0.1880628
H	0.1324306	-1.5992421	-0.4523338
H	2.5640956	-1.6867891	-0.3478518
C	-1.4788394	0.6377749	-0.3362818
H	-1.8722554	1.6284929	-0.5692558
C	-2.3529634	-0.3435231	-0.0970408
H	-1.9928854	-1.3365591	0.1763152
C	-3.8451184	-0.1858921	-0.1420958
H	-4.2592984	-0.8559061	-0.9084118
H	-4.0988634	0.8356729	-0.4496748
O	4.1635026	0.5256579	-0.1481878
C	4.8847336	-0.6839231	-0.1793828
H	4.6291066	-1.3286791	0.6716382
H	5.9384566	-0.4093451	-0.1171008
H	4.7099886	-1.2348961	-1.1128098
C	-4.5075634	-0.5032791	1.2040002
H	-5.5962314	-0.4073621	1.1385412
H	-4.2783304	-1.5265581	1.5221182
H	-4.1482064	0.1770429	1.9828272

E = -502.770073568

G= -502.582072568

4^+

C	2.7750950	0.5045767	0.1900268
C	2.1080900	1.7637197	0.1780608
C	0.7472260	1.8072827	0.1865598
C	-0.0364890	0.6092727	0.2057798
C	0.6585170	-0.6422693	0.2237068
C	2.0233880	-0.7029493	0.2160838
H	2.7145400	2.6622527	0.1612538
H	0.2378060	2.7656917	0.1750478
H	0.0999470	-1.5710613	0.2440468
H	2.5234590	-1.6635243	0.2312288
C	-1.4528520	0.7214307	0.2047768
H	-1.8562180	1.7325467	0.1960688
C	-2.3510340	-0.3145423	0.2077438
H	-1.9947530	-1.3439173	0.2071868
C	-3.8257720	-0.1438423	0.1819458
H	-4.2397650	-0.6323643	1.0753948
H	-4.0929940	0.9159827	0.2329818
O	4.0819330	0.5636747	0.1739698
C	4.8809850	-0.6297923	0.1755098

H	4.7046530	-1.1997763	1.0910978
H	5.9108330	-0.2819013	0.1444868
H	4.6618480	-1.2312953	-0.7101832
C	-4.4470660	-0.8007093	-1.0664952
H	-4.2111070	-1.8681933	-1.1139702
H	-5.5338330	-0.6964073	-1.0303762
H	-4.0864370	-0.3238843	-1.9819332

E = -502.568073328
G= -502.381108328

5

C	1.6962269	-0.0464188	0.0053096
C	1.1107879	1.2214862	0.0220746
C	-0.2690571	1.3719802	-0.0095254
C	-1.1201421	0.2609552	-0.0518304
C	-0.5315491	-1.0080088	-0.0775634
C	0.8491909	-1.1555888	-0.0463724
H	1.7455529	2.1040012	0.0583446
H	-0.6997121	2.3704722	0.0053166
H	-1.1559711	-1.8949608	-0.1340014
H	1.2792719	-2.1539488	-0.0695094
C	-2.5788341	0.4726822	-0.0712554
H	-2.8874421	1.5047582	-0.2359324
C	3.1957739	-0.2024868	0.0309676
H	3.6544469	0.2395022	-0.8609494
H	3.6312039	0.2979592	0.9030236
H	3.4870349	-1.2562798	0.0692866
C	-3.5268891	-0.4492538	0.1028546
H	-4.5780321	-0.1818258	0.0657216
H	-3.3018611	-1.4950238	0.2940406

E = -348.933917845
G = -348.803594845

6

C	-0.1174690	1.0615025	-0.0042743
C	1.0938650	0.8946265	0.9588557
C	1.3076530	2.4244375	0.8845257
C	-0.1496390	2.5643635	0.3899347
H	0.2492600	0.9778075	-1.0362293
H	0.7189650	0.6297985	1.9564467
H	2.0192750	2.6852825	0.0921837
H	-0.8250020	2.7016295	1.2449597
C	-1.3396050	0.2029465	0.1618987
C	-1.8509820	-0.5363585	-0.9010903
C	-2.0067320	0.1126425	1.3913037
C	-2.9832410	-1.3410685	-0.7666533
H	-1.3554770	-0.4880075	-1.8682153
C	-3.1303980	-0.6791495	1.5473777
H	-1.6382070	0.6728925	2.2473817
C	-3.6288090	-1.4144715	0.4661747
H	-3.3432390	-1.8969005	-1.6249703
H	-3.6429040	-0.7488485	2.5013067
C	2.1998680	-0.0485695	0.5708567

C	1.9040940	-1.3048565	0.0330137
C	3.5406380	0.2925885	0.7418307
C	2.9182640	-2.1855295	-0.3206693
H	0.8658240	-1.5920275	-0.1146323
C	4.5553720	-0.5934815	0.3895617
H	3.7986440	1.2653295	1.1535137
C	4.2632110	-1.8471745	-0.1463753
H	2.6624600	-3.1544785	-0.7439013
H	5.5935230	-0.3016495	0.5313687
C	-0.4766520	3.5817925	-0.6909833
H	-0.3322450	4.5940805	-0.2904983
H	0.2435060	3.4682495	-1.5131163
O	-4.7349250	-2.1612535	0.7208717
C	-5.2720610	-2.9249955	-0.3336323
H	-6.1397910	-3.4405925	0.0796697
H	-5.5939800	-2.2897035	-1.1692433
H	-4.5517270	-3.6672115	-0.7020073
H	1.5911060	2.9476715	1.8019607
C	5.3576690	-2.8194915	-0.5095853
H	5.4661610	-3.5953335	0.2579797
H	5.1436240	-3.3258575	-1.4567143
H	6.3239380	-2.3155285	-0.6082923
C	-1.8996270	3.4307935	-1.2286503
H	-2.0479450	2.4416855	-1.6754123
H	-2.6374320	3.5384535	-0.4254073
H	-2.1188310	4.1839665	-1.9924213

E = -851.744961402
G= -851.399892

6^{+}

C	-0.1196880	1.3210268	-0.1134890
C	1.0139920	0.9834698	1.0225850
C	1.3668860	2.4834658	0.9419390
C	-0.0104230	2.7953118	0.3152140
H	0.3855270	1.1580098	-1.0716230
H	0.4893700	0.7710618	1.9585080
H	2.1771120	2.6735408	0.2320180
H	-0.7284190	3.0223198	1.1124460
C	-1.3116190	0.4883978	-0.0041880
C	-1.2594820	-0.8420492	-0.5224590
C	-2.4981510	0.9085758	0.6589010
C	-2.3248520	-1.6943132	-0.4279510
H	-0.3389040	-1.1767222	-0.9915430
C	-3.5765690	0.0776148	0.7541500
H	-2.5575130	1.9127628	1.0621750
C	-3.5116420	-1.2407362	0.2108630
H	-2.2602040	-2.6976792	-0.8308810
H	-4.5025080	0.3860848	1.2267100
C	1.9680920	-0.1073592	0.6916910
C	1.9263730	-1.3155482	1.3964900
C	2.8847480	0.0130458	-0.3614860
C	2.7831830	-2.3599762	1.0725510
H	1.2201490	-1.4351742	2.2149640
C	3.7374300	-1.0313462	-0.6824520
H	2.9364780	0.9330728	-0.9381880

C	3.7059370	-2.2365462	0.0301970
H	2.7405970	-3.2847542	1.6414230
H	4.4459550	-0.9125712	-1.4976500
C	-0.1081590	3.8361468	-0.7897350
H	0.1483750	4.8175518	-0.3738460
H	0.6482370	3.6163918	-1.5548340
O	-4.5991290	-1.9568922	0.3567600
C	-4.6779280	-3.2968082	-0.1533660
H	-5.6841330	-3.6331522	0.0853300
H	-4.5281820	-3.2957362	-1.2357860
H	-3.9406700	-3.9315442	0.3445120
H	1.6090890	2.9613878	1.8931110
C	4.6594970	-3.3523312	-0.3030630
H	5.6133100	-3.2090402	0.2180450
H	4.2628670	-4.3255702	-0.0008100
H	4.8747430	-3.3862062	-1.3749820
C	-1.4952430	3.8814998	-1.4281510
H	-1.7649230	2.9120618	-1.8654570
H	-2.2622530	4.1439338	-0.6903360
H	-1.5373510	4.6253218	-2.2283070

E = -851.533562028
G= -851.188402

DMP

I	0.4092803	0.6805159	0.5896157
O	-0.9393757	2.6968599	2.1526177
O	2.7584773	1.7820579	-0.7145653
C	-1.8412827	2.0843629	1.6235957
C	3.0451833	0.6114409	-0.5438033
C	4.3609643	-0.0146781	-0.9258523
H	4.8584983	-0.3916611	-0.0275783
H	4.1877193	-0.8671531	-1.5884553
H	4.9902073	0.7264549	-1.4188803
C	-3.2953207	2.4682749	1.6600767
H	-3.5855537	2.8232629	0.6663527
H	-3.9143827	1.6013119	1.9029627
H	-3.4450127	3.2634369	2.3904827
O	2.2060283	-0.2555391	0.0143587
O	-1.6253377	0.9678479	0.9137447
C	-0.2555257	-1.3215391	0.4134477
C	-0.1028437	-2.0007501	1.6034527
C	-0.7772707	-1.8898551	-0.7312573
C	-0.4903397	-3.3353941	1.6687777
C	-1.1632807	-3.2277511	-0.6507373
H	-0.8753857	-1.3214771	-1.6457473
C	-1.0209947	-3.9445331	0.5372137
H	-0.3677937	-3.8678711	2.6059127
H	-1.5787817	-3.7115041	-1.5290233
H	-1.3259427	-4.9851731	0.5781247
C	0.4744163	-1.2766891	2.7814997
O	0.6565933	-1.7945961	3.8540097
O	0.7624093	-0.0000691	2.5224277
C	-0.2760497	2.0265529	-1.8287743
C	-0.3476047	2.1708679	-3.3246833

H	0.6571183	2.0372069	-3.7369923
H	-0.9934707	1.4011999	-3.7549193
H	-0.7182287	3.1643109	-3.5771513
O	-0.4358467	2.9249069	-1.0307563
O	0.0087303	0.7753629	-1.4494983

E = -1402.48002200
G= -1402.479140

DMP_{HFIP}

I	-0.0828558	-0.1110369	-0.8737693
O	2.6128522	0.4703071	-1.5320573
O	-0.1743828	1.2946121	1.6546687
C	2.2540202	-0.2334649	-2.4630643
C	-1.2390068	0.7152501	1.6365837
C	-2.2288268	0.6431011	2.7613747
H	-3.1642288	1.1100451	2.4411427
H	-2.4185108	-0.4060709	3.0067597
H	-1.8344948	1.1682831	3.6297997
C	3.1764952	-0.7964609	-3.5039213
H	3.7442642	-1.6062659	-3.0345443
H	2.6281792	-1.1872349	-4.3607903
H	3.8796942	-0.0233129	-3.8215623
O	-1.6399328	0.0421331	0.5464677
O	0.9797262	-0.5762109	-2.6108863
C	-1.7287508	-0.1120479	-2.2064283
C	-1.9697148	1.1599451	-2.6887863
C	-2.4920468	-1.2138779	-2.5293593
C	-3.0331938	1.3560161	-3.5626133
C	-3.5552488	-0.9988649	-3.4078133
H	-2.3010458	-2.1887879	-2.1052053
C	-3.8213278	0.2680261	-3.9213733
H	-3.2262598	2.3555431	-3.9365353
H	-4.1894958	-1.8368969	-3.6749713
H	-4.6578438	0.4089611	-4.5974173
C	-1.1017508	2.2734181	-2.2246443
O	-1.2440358	3.4268031	-2.5638313
O	-0.1446988	1.8970731	-1.3806293
C	0.5140572	-2.8597129	-0.3184613
C	0.2066342	-4.2705229	0.0882937
H	0.7368072	-4.4768539	1.0217717
H	-0.8648018	-4.4238269	0.2151997
H	0.5921582	-4.9521149	-0.6759353
O	1.6344412	-2.3673779	-0.3048303
O	-0.5381638	-2.1507789	-0.6905803
C	0.8109472	-2.1030119	3.2761177
C	2.3308862	-2.0365389	3.0654577
C	2.8338192	-0.6322769	2.6999367
F	0.4536162	-3.3501519	3.5905627
F	4.1615362	-0.6340679	2.6586467
F	2.3805182	-0.2603819	1.4875697
F	2.4333922	0.2795241	3.5879797
F	0.3912562	-1.2897079	4.2463967
F	0.1209132	-1.7730979	2.1551357
O	2.7535042	-2.9921369	2.1554647
H	2.5662232	-2.7001119	1.2414797

C	-2.0164818	4.1244521	1.0754407
C	-0.5752728	4.4729681	0.6755397
C	0.1420472	5.3007861	1.7443527
F	-2.4974358	3.1751511	0.2340557
F	1.3651712	5.6226401	1.3189387
F	-0.5145138	6.4321511	2.0259437
F	0.2724592	4.6054441	2.8829537
F	-2.1031038	3.6129601	2.3148767
F	-2.8345818	5.1685061	1.0052997
O	-0.5765468	5.2200821	-0.4931163
H	-0.6618688	4.6264331	-1.2605973
C	-5.7182758	-2.5439409	1.1261247
C	-4.7721148	-1.3769349	0.8381027
C	-5.3517158	-0.3664839	-0.1613723
F	-5.2224338	-3.2836629	2.1239177
F	-4.4128618	0.5492641	-0.4500983
F	-5.7305678	-0.9410599	-1.3082883
F	-6.4057958	0.2783001	0.3491817
F	-6.9252688	-2.1002669	1.5000807
F	-5.8734468	-3.3334999	0.0620817
O	-3.5876888	-1.9254639	0.3666187
H	-2.8775698	-1.2656739	0.4709527
C	5.6790502	-1.3231449	-0.5428503
C	5.6999302	0.1962691	-0.7686683
C	7.0957162	0.7981401	-0.5973283
F	4.4010912	-1.7470419	-0.5201073
F	7.9905772	0.1387481	-1.3519763
F	7.0865782	2.0744581	-0.9952933
F	7.5088532	0.7585701	0.6677717
F	6.2878752	-1.9697279	-1.5519333
F	6.2527702	-1.6952679	0.5980227
O	4.8538062	0.8428041	0.1140927
H	3.9613172	0.8065501	-0.2668353
H	-4.6500918	-0.8357619	1.7862217
H	2.7744292	-2.2801559	4.0354297
H	5.4216502	0.3532931	-1.8192563
H	-0.0310088	3.5242831	0.5949227

E = -4561.73354400
G = -4561.730688

DMP_{HFIP} • 2 (styrene **4)**

C	1.6275314	0.6633725	0.2471452
C	0.7161294	1.6812245	0.0258872
C	1.0597684	2.9268315	-0.4418318
C	2.4193954	3.1581955	-0.6566348
C	3.3658354	2.1731115	-0.3979628
C	2.9770614	0.9158645	0.0500442
H	0.3285954	3.6883955	-0.6698688
H	2.7307524	4.1236475	-1.0399168
H	4.4167584	2.3776145	-0.5677038
H	3.6949774	0.1259635	0.2369232
I	-1.2366276	1.0054205	0.4495332
O	-1.6346536	3.2182945	1.1959942
O	-2.6700366	-1.0872865	-0.6222238
C	-2.0827136	3.6207005	0.0870942

O	-2.0337286	2.8265255	-0.9070978
C	-2.0745626	-0.6987585	-1.6299398
O	-1.1897806	0.2662595	-1.5420198
C	-2.5992066	5.0171585	-0.0802028
H	-3.4044156	5.0302505	-0.8149808
H	-2.9409446	5.4087425	0.8778482
H	-1.7811306	5.6456815	-0.4484448
C	-2.3109816	-1.2442315	-3.0022708
H	-2.6551466	-2.2761485	-2.9254218
H	-3.0960436	-0.6333665	-3.4594368
H	-1.4086706	-1.1798945	-3.6120258
H	-4.3761916	-1.3917975	-0.7220268
H	-3.5142886	2.0912165	-1.8184898
O	-5.3498616	-1.4530615	-0.6926308
O	-4.0712556	1.2988635	-1.9320278
C	-5.3366946	1.5063345	-1.3899028
C	-6.0864896	2.5642685	-2.2038248
C	-5.2804946	1.8590255	0.1026492
H	-5.8787896	0.5597185	-1.4535038
C	-5.6959856	-2.4520685	0.2159432
C	-6.4250446	-3.5691785	-0.5329588
C	-6.5359236	-1.8213825	1.3259592
H	-4.8227516	-2.8980635	0.7021322
F	-7.0437026	-2.7447725	2.1523922
F	-6.6372196	-4.6287865	0.2586822
F	-7.6088176	-3.1674385	-1.0129168
F	-5.6807826	-3.9738715	-1.5693408
F	-5.7632976	-1.0009745	2.0540862
F	-7.5488946	-1.0976275	0.8381892
F	-4.3945506	1.0742635	0.7316562
F	-6.4624576	1.7150795	0.6881492
F	-4.8756056	3.1347855	0.3072032
F	-5.3479856	3.6861035	-2.3239988
F	-7.2521206	2.8969345	-1.6414578
F	-6.3267826	2.1101275	-3.4343888
C	1.1141974	-0.6774135	0.6001212
O	1.8029114	-1.6619965	0.7490132
O	-0.2125996	-0.7469525	0.7092112
O	-0.6269526	1.0854815	2.4917852
C	-1.4308676	0.3054865	3.1777522
O	-2.3560366	-0.2860985	2.6277242
C	-1.1075466	0.1941185	4.6388512
H	-2.8238366	-1.9839235	2.2401852
H	-0.2634266	-0.4932905	4.7550072
H	-0.8160416	1.1656885	5.0429012
H	-1.9676436	-0.2083135	5.1743292
O	-2.9556476	-2.9274485	2.0320932
C	-1.8433196	-3.4105705	1.3524022
C	-2.3292016	-4.6055765	0.5312102
C	-0.7263666	-3.7765195	2.3365142
H	-1.4194006	-2.6877015	0.6506292
F	-3.0761966	-5.4398705	1.2483512
F	-1.3011166	-5.3094875	0.0206372
F	-3.0664416	-4.1719265	-0.5010448
F	-0.4269916	-2.7025255	3.0922762
F	0.4017004	-4.1363705	1.6965192

F	-1.0625606	-4.7690415	3.1600002
H	2.1008094	-3.0949625	-0.3019138
O	2.4354874	-3.6532745	-1.0259818
C	1.4255884	-4.4572215	-1.5277378
C	2.1059014	-5.4914825	-2.4246088
C	0.3859454	-3.6200115	-2.2835588
H	0.8775104	-5.0035985	-0.7524478
F	2.8968004	-4.9124045	-3.3320408
F	1.1977564	-6.2331335	-3.0726698
F	2.8564264	-6.3088695	-1.6812718
F	-0.0438576	-2.6335735	-1.4602458
F	-0.6824126	-4.3301805	-2.6454268
F	0.8782724	-3.0248985	-3.3752938
C	3.7876574	1.3318395	-3.7506938
C	3.0360054	0.2732715	-3.2393468
C	1.6458734	0.4460955	-3.1526768
C	1.0404644	1.6364775	-3.5134258
C	1.8149084	2.6971575	-3.9948298
C	3.1943534	2.5367435	-4.1273798
H	4.8611944	1.2146115	-3.8712518
H	1.0329704	-0.3603045	-2.7611128
H	-0.0303896	1.7719985	-3.4033398
H	3.8176294	3.3302005	-4.5246808
O	1.1354684	3.8388465	-4.2917568
C	1.8629604	4.9135405	-4.8369838
H	1.1381754	5.7070915	-5.0243418
H	2.6283394	5.2814445	-4.1392408
H	2.3470044	4.6363085	-5.7823408
C	3.6413084	-0.9736085	-2.7413868
C	4.8427134	-1.0696705	-2.1633378
H	3.0241054	-1.8680325	-2.7953048
H	5.4513234	-0.1700135	-2.0409818
C	5.4021594	-2.3320435	-1.5738298
H	6.4272074	-2.4863995	-1.9368708
H	4.8044694	-3.1872515	-1.9026128
C	5.4072234	-2.2757205	-0.0410888
H	5.8499824	-3.1783275	0.3916292
H	5.9781594	-1.4149295	0.3288132
H	4.3859274	-2.1861865	0.3416932
C	2.4795974	0.8167265	3.5215212
C	3.3797594	1.8406165	3.2162552
C	4.7054554	1.4736515	2.9477312
C	5.0985394	0.1436975	2.9273922
C	4.1685644	-0.8696775	3.1845362
C	2.8523634	-0.5223075	3.5011622
H	1.4527094	1.0699805	3.7583762
H	5.4378844	2.2459085	2.7233242
H	6.1226044	-0.1386745	2.7051942
H	2.1100364	-1.2855685	3.7065612
O	4.6327024	-2.1385535	3.1133542
C	3.7006044	-3.1946515	3.2346292
H	4.2641574	-4.1107275	3.0551192
H	3.2666994	-3.2298335	4.2425022
H	2.8980104	-3.1081405	2.4944842
C	2.9563994	3.2462405	3.0896672
C	1.7120604	3.6500815	2.8144122

H	3.7475434	3.9931905	3.1732632
H	0.9221494	2.9096425	2.6938312
C	1.2808344	5.0723005	2.6135942
H	1.0163604	5.2121295	1.5535032
H	2.1135004	5.7553025	2.8220182
C	0.0603254	5.4359255	3.4659952
H	-0.2507076	6.4711175	3.2882822
H	-0.7816956	4.7790345	3.2221892
H	0.2833354	5.3260525	4.5324542

E = -5567.72031864
G = -5566.899977

DMP^-

I	-0.6900066	-0.2839825	-1.3115164
O	1.4618264	1.0979965	-1.9083424
O	-3.6109276	-0.9008625	-1.2523504
C	1.7377964	2.0179375	-1.0667924
C	-3.2837686	-1.6615155	-0.3368654
C	-4.3546456	-2.4675695	0.4078346
H	-4.1792346	-3.5373175	0.2540306
H	-4.2833386	-2.2740415	1.4825116
H	-5.3482896	-2.1998495	0.0426576
C	3.1198994	2.6508865	-1.2869164
H	3.2080064	3.5778405	-0.7146614
H	3.8886134	1.9462115	-0.9498044
H	3.2908364	2.8419065	-2.3501854
O	-2.0946166	-1.8791285	0.0911976
O	1.0454424	2.4016865	-0.1143954
C	0.7333424	-0.8597155	0.1239696
C	1.6154324	-1.8013895	-0.3652054
C	0.8080474	-0.3314535	1.3984936
C	2.6284504	-2.2624515	0.4710516
C	1.8281974	-0.8024685	2.2213906
H	0.1091844	0.4280365	1.7188316
C	2.7313064	-1.7632865	1.7637496
H	3.3199874	-3.0012605	0.0788876
H	1.9223284	-0.4044645	3.2276806
H	3.5218724	-2.1164945	2.4200376
C	1.4672104	-2.2791155	-1.7836334
O	2.2162234	-3.1092735	-2.2638394
O	0.4641054	-1.7212035	-2.4157574
C	-1.8265036	2.1270075	-0.2998544
C	-1.9883476	3.1345365	0.8099116
H	-2.4714306	2.6872495	1.6821416
H	-0.9750766	3.4448365	1.0851966
H	-2.5556656	3.9953395	0.4520936
O	-1.9650446	2.3768695	-1.4790674
O	-1.4912126	0.9285035	0.1675186

E = -1402.646279
G= -1402.645405

DMP^-_{HFIP}

I	0.3821685	1.1686217	0.4948812

O	2.8939875	1.5449367	1.9702222
O	-0.2995775	-0.2215223	-1.7301888
C	2.6405445	2.7589187	1.8629452
C	-1.3483315	-0.7753413	-1.3401528
C	-1.8848625	-1.9732743	-2.1032208
H	-2.0923085	-2.7760283	-1.3911218
H	-2.8317605	-1.6961233	-2.5773098
H	-1.1740495	-2.3108933	-2.8580888
C	3.6832875	3.7810257	2.2907692
H	3.8597085	3.6681927	3.3645302
H	4.6181225	3.5504377	1.7729142
H	3.3655705	4.8005267	2.0712712
O	-2.0225655	-0.3902573	-0.3279408
O	1.5479185	3.2418317	1.4139012
C	-1.1804255	2.4640277	-0.0413568
C	-2.1864925	2.4767687	0.9091072
C	-1.2499625	3.1581647	-1.2319358
C	-3.3279865	3.2320057	0.6664672
C	-2.4002915	3.9142577	-1.4561268
H	-0.4525545	3.0959907	-1.9598688
C	-3.4288165	3.9527767	-0.5172278
H	-4.1307975	3.2074717	1.3938522
H	-2.4975555	4.4609437	-2.3889088
H	-4.3286675	4.5225207	-0.7241188
C	-2.0416515	1.5931807	2.1017462
O	-2.9262675	1.4404737	2.9310222
O	-0.8900205	0.9737157	2.1735982
C	2.2586945	1.0580917	-1.6531368
C	2.7361905	1.2943837	-3.0569508
H	2.1165405	0.6689777	-3.7085558
H	2.6144685	2.3391397	-3.3459278
H	3.7775705	0.9851437	-3.1480888
O	2.6356305	0.1135707	-0.9647558
O	1.3770805	1.9182287	-1.2194808
C	2.2032875	-3.5748163	-2.0343608
C	3.0756985	-3.1882453	-0.8308018
C	2.2221775	-2.8495653	0.4069372
F	2.9617215	-4.1712233	-2.9684188
F	2.9622325	-2.2090953	1.3168302
F	1.1748455	-2.0757683	0.1043072
F	1.7542715	-3.9720983	0.9719792
F	1.2303675	-4.4341263	-1.6957678
F	1.6383185	-2.5033273	-2.5978238
O	3.9658455	-2.1899463	-1.1801308
H	3.4803155	-1.3423513	-1.2956628
C	-3.9013445	-2.6371883	2.0292422
C	-2.6424805	-1.8332533	2.3617412
C	-1.3785685	-2.6954063	2.3308732
F	-4.9817265	-1.8497743	2.1276332
F	-0.2960105	-1.9307843	2.5162962
F	-1.3763365	-3.6338253	3.2869922
F	-1.2408415	-3.3235743	1.1504412
F	-3.8756615	-3.1115413	0.7661362
F	-4.0887585	-3.6825833	2.8439562
O	-2.7791175	-1.2788453	3.6282762
H	-2.8041125	-0.3062333	3.5346772

C	-6.0229885	-0.5333733	-2.0784018
C	-5.1673305	-0.1193963	-0.8809088
C	-5.9850845	0.5663807	0.2189722
F	-5.2577985	-1.1263623	-3.0070948
F	-5.1970555	0.8147657	1.2704612
F	-6.4914555	1.7397147	-0.1906668
F	-7.0092525	-0.1904933	0.6427192
F	-6.9776725	-1.4110163	-1.7278488
F	-6.6262765	0.5107607	-2.6604568
O	-4.1846595	0.7476147	-1.3224208
H	-3.3303305	0.4312257	-0.9341928
C	6.5659235	-0.9279373	0.8642762
C	5.5052275	0.1615287	0.7018372
C	5.7999735	1.0872237	-0.4828708
F	6.1505315	-1.8387093	1.7531762
F	5.7144275	0.4475007	-1.6624238
F	4.9056575	2.0930467	-0.5112588
F	7.0168045	1.6437437	-0.4147478
F	6.8161095	-1.5641173	-0.2890508
F	7.7283125	-0.4294783	1.3086292
O	5.4719435	0.8963667	1.8776362
H	4.5248985	1.1127547	2.0548302
H	-2.5254405	-1.0998743	1.5554702
H	-4.7588725	-1.0408753	-0.4485198
H	4.5600495	-0.3433423	0.4803452
H	3.6577005	-4.0749683	-0.5636078

E = -4561.912521
G = -4561.909671

Iodinane • 2AcO$^-$$_{HFIP}$

I	-1.5363919	1.7363889	-1.5188155
O	-4.4677129	1.3846269	-1.9562825
O	2.7598531	2.5943379	1.6569105
C	-4.6512759	2.4508309	-1.2879705
C	2.7854131	1.3468259	1.6849385
C	1.6292111	0.6133239	2.3697375
H	1.7046941	-0.4678871	2.2358955
H	1.6339091	0.8459309	3.4414145
H	0.6698231	0.9612619	1.9771275
C	-6.0952869	2.9221609	-1.1140385
H	-6.5450349	3.0885569	-2.0995255
H	-6.6785709	2.1406789	-0.6209065
H	-6.1339169	3.8434969	-0.5290555
O	3.6892131	0.6016929	1.1896845
O	-3.7368879	3.1351239	-0.7853415
C	0.5785391	1.4690439	-1.6981015
C	0.9237711	0.3443119	-2.4319545
C	1.5333021	2.3219559	-1.1720445
C	2.2733611	0.0736789	-2.6647275
C	2.8758691	2.0217829	-1.3873895
H	1.2640361	3.1775529	-0.5717905
C	3.2472681	0.9079859	-2.1329425
H	2.5452441	-0.8166501	-3.2217135
H	3.6290361	2.6415769	-0.9156975
H	4.2982051	0.6766739	-2.2541165

C	-0.1759929	-0.5389251	-2.9285545
O	0.0508311	-1.6523791	-3.4105055
O	-1.3619019	-0.0347981	-2.8129835
C	-1.0227239	3.0699129	1.0635995
C	-0.1847259	4.0255619	1.8710065
H	0.8311431	3.5940279	1.9318675
H	-0.1229149	5.0029439	1.3874395
H	-0.5972849	4.1139999	2.8780305
O	-1.6268029	2.1436979	1.5874495
O	-0.9546869	3.3016959	-0.2310345
C	-2.7410299	-0.8108451	3.3224795
C	-3.1363699	-0.9254101	1.8445055
C	-2.0431789	-1.5781151	0.9870285
F	-3.7321349	-0.2226051	4.0084695
F	-2.4626029	-1.6788241	-0.2766005
F	-0.9046899	-0.8748121	0.9791875
F	-1.7671089	-2.8118871	1.4367415
F	-2.5468849	-2.0267491	3.8696855
F	-1.6306329	-0.0976791	3.5165315
O	-3.5694029	0.2794049	1.3251235
H	-2.8495189	0.9533279	1.3215395
C	3.7053321	-2.9341801	-0.6716365
C	2.2295061	-2.7527571	-1.0222355
C	1.3013181	-3.5885681	-0.1346355
F	4.4563851	-2.0925831	-1.3959985
F	0.0473911	-3.4710761	-0.5864205
F	1.6138391	-4.8952771	-0.1469495
F	1.3254051	-3.1816961	1.1420735
F	3.9438631	-2.6858321	0.6222215
F	4.1389381	-4.1775651	-0.9323195
O	2.0768941	-3.1180031	-2.3517995
H	1.3194551	-2.6169751	-2.7424785
C	7.3229471	0.1583899	1.5051625
C	6.4433961	0.1679009	0.2453275
C	7.2670741	-0.1155891	-1.0112165
F	6.5890571	0.4424109	2.5827895
F	6.4817751	-0.1797021	-2.0969875
F	8.1897691	0.8300269	-1.2501755
F	7.9195621	-1.2929901	-0.9320825
F	7.8964371	-1.0475291	1.7177565
F	8.3211621	1.0581299	1.4484245
O	5.8142291	1.3811129	0.1087205
H	4.8914161	1.2446889	0.5622465
C	-5.4958679	-2.4463431	-1.0310495
C	-5.8298129	-1.0039131	-0.6402165
C	-6.8196339	-0.9428331	0.5240565
F	-4.6335649	-2.4619671	-2.0443135
F	-6.3700479	-1.6031881	1.6136035
F	-7.0340389	0.3249829	0.8977105
F	-8.0145089	-1.4727141	0.2156875
F	-4.9410599	-3.1321191	-0.0070045
F	-6.5850269	-3.1388291	-1.4126265
O	-6.3722089	-0.3452871	-1.7283155
H	-5.6937899	0.3572589	-1.9744595
H	1.9946461	-1.6993291	-0.8187015
H	5.7363401	-0.6649431	0.3579815

H	-4.8998989	-0.5349261	-0.2906765
H	-3.9837359	-1.6149951	1.8142355

E = -4562.51983871
G = -4562.12328671

8^{+}

C	0.1477179	1.9147385	0.9106383
C	0.1698549	-0.9735135	2.2316253
C	0.5794529	0.0738135	3.0301563
C	-0.3026301	1.9242645	2.2284703
H	1.0967769	2.4134505	0.7132373
H	-0.7785591	-1.4497545	2.4742663
H	1.5909229	0.4626715	2.9711823
H	-1.3158451	1.5823895	2.4284633
C	-0.4449071	1.2345165	-0.1818267
C	0.2691309	1.1366365	-1.4081447
C	-1.7095171	0.5975645	-0.1071207
C	-0.2188231	0.4119445	-2.4609257
H	1.2340209	1.6270885	-1.4964557
C	-2.2205811	-0.1206405	-1.1657627
H	-2.3067801	0.6814065	0.7946603
C	-1.4672161	-0.2395545	-2.3499367
H	0.3285259	0.3192165	-3.3921327
H	-3.1936821	-0.5879785	-1.0760647
C	0.8170289	-1.4287315	1.0371053
C	0.1504299	-2.3590595	0.2088053
C	2.0820169	-0.9591695	0.6189843
C	0.7001799	-2.7644815	-0.9890637
H	-0.8180801	-2.7427125	0.5175253
C	2.6312589	-1.3811665	-0.5779067
H	2.6426559	-0.2695245	1.2419403
C	1.9492099	-2.2784025	-1.4102357
H	0.1647239	-3.4702745	-1.6179997
H	3.6072819	-1.0123285	-0.8793617
C	0.2440159	2.9202495	3.2196233
H	0.1247699	2.5433625	4.2399533
H	1.3168519	3.0656455	3.0501223
O	-1.8425931	-0.9368015	-3.4165907
C	-3.1008871	-1.6039345	-3.4171847
H	-3.1726841	-2.0900035	-4.3884517
H	-3.1436541	-2.3573215	-2.6236317
H	-3.9210011	-0.8882635	-3.3031747
C	-0.4917521	4.2627295	3.0897653
H	-1.5674121	4.1414265	3.2516843
H	-0.1175441	4.9684525	3.8363063
H	-0.3437851	4.7013965	2.0983933
H	0.0803109	0.2231145	3.9820913
C	2.5299029	-2.7286915	-2.7204707
H	2.7136269	-3.8087165	-2.7096857
H	1.8324579	-2.5281315	-3.5413857
H	3.4748089	-2.2269215	-2.9414867

E = -851.512960347
G = -851.171492

8^+_staggered

C	-1.2428663	0.7293141	-0.7342022
C	1.2368487	-1.3215519	0.1056398
C	0.3364017	-0.8397879	1.0329528
C	-0.3229033	1.0921341	0.2529128
H	-0.8722833	0.7224211	-1.7597192
H	0.8263427	-1.8717119	-0.7401192
H	0.6890717	-0.4042229	1.9637108
H	-0.7134233	1.3106231	1.2456488
C	-2.5847333	0.3070291	-0.5523092
C	-3.3486403	-0.0694179	-1.6912602
C	-3.2150503	0.2275991	0.7144178
C	-4.6457613	-0.4947059	-1.5734062
H	-2.8911853	-0.0137229	-2.6750022
C	-4.5168333	-0.2029169	0.8472378
H	-2.6748983	0.5152791	1.6110858
C	-5.2496493	-0.5696869	-0.3000862
H	-5.2329513	-0.7801909	-2.4389332
H	-4.9676183	-0.2493319	1.8309588
C	2.6544627	-1.1007049	0.0769248
C	3.3782297	-1.4887369	-1.0693782
C	3.3666697	-0.5025819	1.1400698
C	4.7413237	-1.2712439	-1.1579962
H	2.8540347	-1.9598549	-1.8967342
C	4.7276587	-0.2916119	1.0433188
H	2.8526997	-0.2195039	2.0535088
C	5.4420487	-0.6695259	-0.1050582
H	5.2767067	-1.5727349	-2.0533622
H	5.2587047	0.1662321	1.8728508
C	0.9435727	1.8174111	-0.1081952
H	1.6939997	1.6741271	0.6761758
H	1.3657077	1.3974071	-1.0280152
O	-6.5074463	-0.9944959	-0.2860382
C	-7.2051683	-1.0979649	0.9513308
H	-8.1963283	-1.4686719	0.6964698
H	-6.7081703	-1.8078739	1.6202478
H	-7.2913013	-0.1183889	1.4322918
C	0.6771087	3.3190031	-0.2885622
H	0.2650527	3.7626221	0.6234418
H	1.6098547	3.8383131	-0.5243632
H	-0.0313873	3.5001461	-1.1027492
H	-0.6649853	-1.2565079	1.0595738
C	6.9289457	-0.4676139	-0.1815192
H	7.4479867	-1.3141589	0.2838908
H	7.2728497	-0.3977959	-1.2167102
H	7.2373017	0.4375591	0.3490578

E = -851.502165801

G= -851.163842801

9^+

C	-2.2887263	0.7056861	0.5882518
C	-1.0228263	-1.8354419	-0.7574382
C	-2.2793833	-1.6833529	0.0047898

C	-3.0158893	-0.2747089	-0.2309202
H	-2.6700253	0.8450911	1.6016368
H	-1.1386363	-2.0221719	-1.8239852
H	-2.1541313	-1.8433399	1.0792658
H	-2.9264403	-0.0542039	-1.3001502
C	-1.0883883	1.3105431	0.2864928
C	-0.3359163	1.9321071	1.3425098
C	-0.4554423	1.1620111	-0.9884002
C	0.9802737	2.2275901	1.1799408
H	-0.8194593	2.1076141	2.2990088
C	0.8684137	1.4699991	-1.1631562
H	-1.0275113	0.7962081	-1.8329532
C	1.6162077	1.9410171	-0.0607662
H	1.5820797	2.6483451	1.9771398
H	1.3356317	1.3244691	-2.1282252
C	0.2995777	-1.7642149	-0.2656132
C	1.3847277	-1.9075559	-1.1706602
C	0.6219027	-1.4762269	1.0874028
C	2.6916227	-1.7302949	-0.7583672
H	1.1757237	-2.1549789	-2.2082492
C	1.9318637	-1.2891499	1.4812048
H	-0.1682103	-1.3843559	1.8260138
C	2.9959717	-1.3975489	0.5702708
H	3.4993167	-1.8581189	-1.4749952
H	2.1471357	-1.0580849	2.5211578
C	-4.4995773	-0.3687009	0.1468368
H	-4.9516103	-1.1825249	-0.4302522
H	-4.5856213	-0.6521089	1.2041398
O	2.9110987	2.1667201	-0.0876702
C	3.6665457	1.8839651	-1.2701182
H	4.7013157	2.0940791	-1.0076432
H	3.5525087	0.8314141	-1.5441412
H	3.3520617	2.5373451	-2.0885802
C	-5.2580143	0.9314371	-0.1163612
H	-5.1838913	1.2237831	-1.1693352
H	-6.3179233	0.8144981	0.1235388
H	-4.8701573	1.7586401	0.4894558
H	-3.0066843	-2.4239809	-0.3455452
C	4.4107167	-1.1431769	1.0122488
H	5.1339467	-1.4707039	0.2607608
H	4.5712607	-0.0729569	1.1933258
H	4.6345607	-1.6646589	1.9481338

E = -851.529584200
G = -851.184961

9^{+}_staggered

C	-0.5500784	0.7625926	0.5977757
C	0.5771586	-2.0037264	0.9529707
C	1.3377496	-0.7482984	1.2161057
C	0.8818426	0.5088286	0.3827577
H	-1.1872404	-0.1096784	0.4361437
H	-0.3336114	-2.1543584	1.5303937
H	2.4048916	-0.8695584	1.0026197
H	1.4893796	1.3594216	0.7087977
C	-1.1911314	1.9336626	0.9412357

C	-2.6215864	1.9315306	1.0836167
C	-0.5009384	3.1714886	1.1544347
C	-3.3021374	3.0636536	1.4115247
H	-3.1615864	1.0029016	0.9234417
C	-1.1743664	4.3137936	1.4831707
H	0.5773036	3.2083136	1.0479787
C	-2.5885214	4.2746136	1.6182257
H	-4.3800314	3.0793906	1.5230917
H	-0.6317734	5.2379946	1.6374897
C	0.9320076	-3.0328774	0.0513327
C	0.0750616	-4.1564304	-0.0963123
C	2.1143206	-3.0227304	-0.7370373
C	0.3731856	-5.1797374	-0.9751793
H	-0.8314614	-4.2075204	0.5014937
C	2.3991936	-4.0535264	-1.6099953
H	2.8194046	-2.2021244	-0.6490433
C	1.5370036	-5.1522534	-1.7556843
H	-0.3059674	-6.0235534	-1.0613783
H	3.3147436	-4.0184924	-2.1948463
C	1.1305146	0.2963566	-1.1369083
H	2.1915556	0.0461746	-1.2423443
H	0.5676036	-0.5784324	-1.4787123
O	-3.3255034	5.3111416	1.9303187
C	-2.7317684	6.5947546	2.1700337
H	-3.5645284	7.2514056	2.4111607
H	-2.0413344	6.5411766	3.0157597
H	-2.2217124	6.9513896	1.2714467
C	0.8035336	1.5197146	-1.9888873
H	1.3401256	2.4075216	-1.6341973
H	1.1031936	1.3477056	-3.0259833
H	-0.2674914	1.7494966	-1.9895073
H	1.2617806	-0.4863334	2.2773107
C	1.8560356	-6.2530254	-2.7302053
H	1.2246756	-7.1301994	-2.5658573
H	1.6984436	-5.9168434	-3.7619913
H	2.9020606	-6.5653224	-2.6465613

E = -851.518599631

G = -851.176627631

10^{+}

C	-0.8541006	0.4704163	-0.3534057
C	1.1589634	-0.5472007	1.2073383
C	0.5161254	0.7379033	1.6488613
C	-0.1966916	1.5086973	0.4861913
H	-0.2006906	0.0013473	-1.0903507
H	0.5443894	-1.4436987	1.2668013
H	1.2346624	1.4264343	2.1070783
H	-0.9386476	2.1847963	0.9256453
C	-2.1524446	0.0144543	-0.3005197
C	-2.5711146	-1.0260927	-1.1995787
C	-3.1178946	0.5278983	0.6259473
C	-3.8437586	-1.5074217	-1.1780807
H	-1.8516356	-1.4266047	-1.9078747
C	-4.3968536	0.0493093	0.6585933
H	-2.8299166	1.3096983	1.3202273

C	-4.7790346	-0.9753707	-0.2496257
H	-4.1790746	-2.2874797	-1.8516437
H	-5.1090536	0.4506973	1.3686273
C	2.4841434	-0.7041977	0.7451693
C	2.9261744	-1.9816757	0.3038943
C	3.4326554	0.3522073	0.6989163
C	4.2103354	-2.1776897	-0.1610477
H	2.2329634	-2.8185007	0.3416433
C	4.7168924	0.1383853	0.2341173
H	3.1601314	1.3430793	1.0490583
C	5.1356124	-1.1230937	-0.2121987
H	4.5148774	-3.1682007	-0.4888387
H	5.4220124	0.9653183	0.2208833
C	0.7686864	2.3400733	-0.3760727
H	1.2867074	3.0428013	0.2857263
H	1.5369964	1.6804783	-0.7965307
O	-5.9790016	-1.4950377	-0.3078677
C	-7.0253396	-1.0413107	0.5625493
H	-7.8982086	-1.6285127	0.2860853
H	-6.7619486	-1.2324207	1.6060353
H	-7.2219946	0.0209413	0.3964133
C	0.0561644	3.1047963	-1.4905987
H	-0.7042856	3.7817723	-1.0859547
H	0.7664654	3.7063763	-2.0633737
H	-0.4408286	2.4272253	-2.1962887
H	-0.2374376	0.5106903	2.4112313
C	6.5240624	-1.3363507	-0.7499287
H	6.8884844	-2.3436467	-0.5278317
H	6.5405464	-1.2149427	-1.8400487
H	7.2319054	-0.6163487	-0.3293737

E = -851.516786261
G= -851.173619

Homodimerization

7

C	0.5873171	0.7076408	0.4057395
C	-0.6267459	0.7348038	-0.5725585
C	-0.8196319	2.2306158	-0.2222235
C	0.6396631	2.2528978	0.2915695
H	0.2162161	0.4412828	1.4040175
H	-0.2443669	0.6670138	-1.6011005
H	-1.5014029	2.3369388	0.6333355
H	1.3110221	2.5396838	-0.5306765
C	1.7859991	-0.1346502	0.0770525
C	2.2392091	-1.1158482	0.9542435
C	2.4819951	0.0262938	-1.1290195
C	3.3470861	-1.9127022	0.6629915
H	1.7173801	-1.2691312	1.8958945
C	3.5819981	-0.7538112	-1.4386765
H	2.1558561	0.7785978	-1.8433715
C	4.0253531	-1.7312202	-0.5407135
H	3.6621621	-2.6621542	1.3799675
H	4.1181461	-0.6264532	-2.3734775

C	-1.6987379	-0.3010192	-0.3721415
C	-1.3995949	-1.6468122	-0.6355135
C	-2.9717169	-0.0040102	0.0993965
C	-2.3339969	-2.6459392	-0.4331725
H	-0.4092719	-1.9081292	-1.0011415
C	-3.9308569	-0.9984372	0.3061465
H	-3.2434309	1.0260728	0.3097495
C	-3.6117979	-2.3276512	0.0416115
H	-2.1010469	-3.6864152	-0.6355275
H	-4.9124139	-0.7171392	0.6707955
C	-1.2124779	3.1974358	-1.3287625
H	-0.4943869	3.0937418	-2.1543105
H	-1.1089789	4.2265218	-0.9588555
C	0.9843231	3.0557218	1.5350955
H	0.8159051	4.1230848	1.3378125
H	0.2906931	2.7758978	2.3401175
O	5.1140061	-2.4443672	-0.9324665
C	5.5994831	-3.4361522	-0.0580405
H	6.4642181	-3.8795502	-0.5533675
H	5.9142311	-3.0077272	0.9025905
H	4.8486521	-4.2161732	0.1244375
O	-4.4596349	-3.3779212	0.2086255
C	-5.7472509	-3.1087102	0.7100385
H	-6.2491059	-4.0739882	0.7890875
H	-5.7036099	-2.6419162	1.7029715
H	-6.3186129	-2.4592382	0.0336195
C	2.4246781	2.8315008	1.9956235
H	2.6060821	1.7732068	2.2128435
H	3.1360571	3.1307238	1.2175915
H	2.6499421	3.4072088	2.8993425
C	-2.6292089	2.9762948	-1.8567035
H	-2.7535239	1.9553598	-2.2344535
H	-3.3727689	3.1283938	-1.0654665
H	-2.8631019	3.6703318	-2.6705665

E = -1005.58168794

G= -1005.176876

7^{+}

C	0.6056458	0.7560017	0.6004997
C	-0.6056562	0.7560027	-0.6004803
C	-0.7099362	2.2595367	-0.3031993
C	0.7098968	2.2595427	0.3032157
H	0.0600438	0.5860607	1.5329957
H	-0.0600432	0.5860667	-1.5329713
H	-1.4354322	2.4396067	0.5000747
H	1.4353948	2.4396207	-0.5000543
C	1.6503578	-0.2362883	0.3937197
C	1.5238418	-1.5112563	0.9988177
C	2.7596647	-0.0124043	-0.4501733
C	2.4596627	-2.4924973	0.7963977
H	0.6665608	-1.7103513	1.6359347
C	3.7172447	-0.9834783	-0.6571653
H	2.8825857	0.9500697	-0.9354403
C	3.5759707	-2.2395643	-0.0343103

H	2.3760317	-3.4678713	1.2624047
H	4.5684657	-0.7701443	-1.2922603
C	-1.6503373	-0.2363133	-0.3936893
C	-1.5236933	-1.5113443	-0.9986363
C	-2.7597493	-0.0123903	0.4500587
C	-2.4594893	-2.4926053	-0.7962143
H	-0.6663272	-1.7104663	-1.6356303
C	-3.7173083	-0.9834843	0.6570457
H	-2.8827673	0.9501297	0.9352077
C	-3.5759073	-2.2396303	0.0343377
H	-2.3757623	-3.4680263	-1.2621083
H	-4.5686153	-0.7701223	1.2920157
C	-1.0119912	3.1663497	-1.4873233
H	-0.8930402	4.2079397	-1.1644253
H	-0.2607573	2.9967037	-2.2702183
C	1.0119438	3.1663527	1.4873447
H	0.8929858	4.2079417	1.1644477
H	0.2607087	2.9967007	2.2702367
O	4.4287807	-3.2480763	-0.1653873
C	5.5920347	-3.0935723	-0.9739943
H	6.1159207	-4.0455423	-0.9121963
H	5.3186028	-2.8897393	-2.0141063
H	6.2310777	-2.2945733	-0.5852423
C	2.4139178	2.9495797	2.0537507
H	3.1796387	3.1317957	1.2912977
H	2.6081337	3.6277007	2.8890937
H	2.5427718	1.9244147	2.4194787
C	-2.4139653	2.9495687	-2.0537283
H	-2.6081833	3.6276817	-2.8890773
H	-2.5428163	1.9244007	-2.4194493
H	-3.1796873	3.1317897	-1.2912773
O	-4.4286853	-3.2481643	0.1654217
C	-5.5920423	-3.0936333	0.9738787
H	-6.1158873	-4.0456273	0.9120977
H	-5.3187383	-2.8897033	2.0140047
H	-6.2310663	-2.2946893	0.5849827

E = -1005.36734932

G= -1004.96585832

PIDA

I	0.6161774	1.2770852	0.2940237
O	-1.3216286	1.9584222	0.9151557
O	3.3201574	2.1818892	-0.0193983
C	-2.1973836	2.2535742	-0.0292493
C	3.4190644	0.9834352	-0.2384093
C	4.7197044	0.2958672	-0.5834913
H	4.9335894	-0.4839898	0.1530127
H	4.6311124	-0.1880938	-1.5602463
H	5.5283694	1.0269462	-0.6000953
C	-3.4637946	2.8520262	0.5456107
H	-4.1638656	3.0797192	-0.2589013
H	-3.9166796	2.1467802	1.2484877
H	-3.2242336	3.7621582	1.1028607
O	2.3911974	0.1643312	-0.1973243
O	-2.0279796	2.0640902	-1.2210033

C	-0.2238516	-0.6678618	0.1456697
C	0.2212864	-1.6441608	1.0266687
C	-1.1809736	-0.9120198	-0.8280413
C	-0.3272136	-2.9194398	0.9278167
H	0.9852064	-1.4277868	1.7642097
C	-1.7204106	-2.1946858	-0.9060553
H	-1.5107826	-0.1219098	-1.4931173
C	-1.2969906	-3.1926838	-0.0338243
H	0.0056334	-3.6967498	1.6082197
H	-2.4729966	-2.4081488	-1.6583603
H	-1.7227136	-4.1887928	-0.1042173

E = -986.3108582
G= -986.1620002

PIDA^{-}

I	-0.7790505	-0.7379278	-0.1140317
O	0.0510135	1.6886862	-0.4140567
O	-3.0642985	0.4359312	-0.0307267
C	0.4429765	2.2701352	0.6697683
C	-3.9770405	-0.4471498	-0.0958697
C	-5.4085555	0.1261202	-0.0585967
H	-6.1498315	-0.6715518	-0.1610027
H	-5.5692145	0.6563502	0.8872123
H	-5.5375165	0.8584202	-0.8635257
C	0.5234705	3.7916162	0.4689203
H	1.0307215	4.2439312	1.3239813
H	1.0518205	4.0332472	-0.4576737
H	-0.4919645	4.1920212	0.3886693
O	-3.8302095	-1.6772648	-0.1795887
O	0.7314665	1.7701692	1.7519053
C	1.2757115	-1.3613448	-0.2148367
C	1.6547975	-2.3455698	-1.1273317
C	2.2303325	-0.8085128	0.6382343
C	2.9760655	-2.7859638	-1.1803797
H	0.9172545	-2.7737278	-1.8013577
C	3.5511365	-1.2478698	0.5791313
H	1.9314925	-0.0247488	1.3302423
C	3.9286125	-2.2379278	-0.3256357
H	3.2601405	-3.5565448	-1.8931547
H	4.2905225	-0.8112588	1.2463003
H	4.9601465	-2.5792658	-0.3665957

E = -986.4511907
G= -986.3098347

PIDA$_{HFIP}$

I	-0.4408093	0.4063151	0.6620058
O	1.1264897	0.9623891	2.0341978
O	-2.7392283	-1.3100599	0.3677878
C	2.2524217	0.3014301	1.9641038
C	-2.7931923	-0.6299469	-0.6621432
C	-3.8696613	-0.7835159	-1.7055082
H	-4.5534313	0.0689831	-1.6378372
H	-3.4278903	-0.7749139	-2.7043482

H	-4.4276433	-1.7054239	-1.5400762
C	3.2924807	0.7864231	2.9452018
H	3.9924137	-0.0206559	3.1698008
H	3.8409817	1.6095071	2.4767808
H	2.8283357	1.1592241	3.8592278
O	-1.9186223	0.3003071	-0.9133222
O	2.4664157	-0.6098549	1.1692318
C	0.3247147	1.9375561	-0.5927152
C	-0.4469323	3.0757091	-0.7850252
C	1.5677437	1.7554901	-1.1774622
C	0.0632497	4.0779951	-1.6042602
H	-1.4203313	3.1824671	-0.3209232
C	2.0630957	2.7772421	-1.9848862
H	2.1568847	0.8607301	-1.0194332
C	1.3146517	3.9299101	-2.1988372
H	-0.5198013	4.9778271	-1.7716532
H	3.0399697	2.6568971	-2.4391022
H	1.7079407	4.7184951	-2.8324392
C	-5.7333043	-2.8274699	2.5939828
C	-5.6572023	-2.4965559	1.0974768
H	-5.4936783	-1.4123609	1.0314238
C	-6.9595023	-2.7887069	0.3511728
F	-7.9995563	-2.1691159	0.9278928
F	-7.2287743	-4.0911129	0.2934298
F	-6.8645013	-2.3296379	-0.9082152
F	-6.6156363	-2.0376789	3.2253458
F	-6.0760063	-4.0965299	2.8200878
F	-4.5303163	-2.6161109	3.1471408
O	-4.6491813	-3.2297829	0.4917038
H	-3.8396693	-2.6769439	0.5122668
O	4.0245847	-0.6490299	-1.0006332
H	3.4081757	-0.8466759	-0.2688462
C	5.2271237	-0.2608879	-0.4244132
H	5.2543857	-0.4461159	0.6563018
C	5.4189977	1.2469631	-0.6110922
C	6.3537757	-1.0921529	-1.0454022
F	4.4227887	1.9009341	0.0199638
F	6.5721327	1.6761111	-0.0889972
F	5.3796417	1.6089431	-1.8970532
F	7.5415767	-0.7712979	-0.5108132
F	6.4321477	-0.9178329	-2.3659932
F	6.1317517	-2.3874769	-0.8050942

E = -2566.03358

G= -2565.786940

PIDA^{-}$_{HFIP}$

I	-0.6427083	-0.2476489	-0.0372161
O	1.5350397	-0.1722409	1.6850369
O	-3.4588723	-1.4276079	-0.2431341
C	2.6737427	-0.6313369	1.4383649
C	-3.6390663	-0.5690469	-1.1424221
C	-5.0251673	-0.4386139	-1.7725671
H	-5.6071863	0.2831131	-1.1884601
H	-4.9483293	-0.0671879	-2.7962991

H	-5.5569463	-1.3917849	-1.7454881
C	3.6478207	-0.6628119	2.6243769
H	4.4090307	-1.4360909	2.4833169
H	4.1442037	0.3124951	2.6929919
H	3.1109267	-0.8281059	3.5613849
O	-2.7670433	0.2416761	-1.5599121
O	3.0976647	-1.0397199	0.3212279
C	0.2918917	1.2994891	-1.1602711
C	-0.4983223	2.2923131	-1.7275561
C	1.6715167	1.2730661	-1.2959181
C	0.1362077	3.3008111	-2.4496091
H	-1.5771913	2.2604391	-1.6326321
C	2.2862447	2.2927791	-2.0193531
H	2.2532157	0.4729931	-0.8506041
C	1.5224457	3.3057391	-2.5918941
H	-0.4631423	4.0857491	-2.9030101
H	3.3665127	2.2779141	-2.1216841
H	2.0070347	4.0991761	-3.1544641
C	-5.6155153	-2.8492339	2.7794319
C	-5.9366643	-2.1923409	1.4307229
H	-5.4742873	-1.1960859	1.4566809
C	-7.4370503	-1.9800649	1.2258949
F	-7.9876533	-1.2859989	2.2390709
F	-8.1058013	-3.1318779	1.1143679
F	-7.6501513	-1.2769139	0.1024249
F	-5.9765463	-2.0647549	3.8129219
F	-6.2328993	-4.0280629	2.9354669
F	-4.2995603	-3.0593039	2.8740229
O	-5.4531273	-2.9675779	0.3972119
H	-4.6305673	-2.4980789	0.0732269
O	4.9232287	0.0741571	-1.1413531
H	4.2004097	-0.4333839	-0.6760171
C	5.7981037	0.4640751	-0.1495081
H	5.6679647	-0.1134339	0.7751579
C	5.5562187	1.9312371	0.2232429
C	7.2276177	0.2054981	-0.6257941
F	4.2902637	2.0896151	0.6273509
F	6.3541297	2.3321921	1.2299679
F	5.7599687	2.7614411	-0.8097791
F	8.1321267	0.5677011	0.3040949
F	7.5208227	0.8664721	-1.7512121
F	7.3994457	-1.1008309	-0.8617991

E = -2566.183959
G= -2565.943167

PIDA$_{HFIP}$ • 2 (styrene **4)**

C	-2.4893353	-0.9269077	0.4020597
C	-1.1095903	-1.0271597	0.4746647
C	-0.4504983	-2.1602357	0.9249717
C	-1.2273853	-3.2414577	1.3344787
C	-2.6172883	-3.1725747	1.2794927
C	-3.2454453	-2.0207767	0.8121207
H	-2.9632103	-0.0276347	0.0304037
H	0.6329437	-2.2080187	0.9406837

H	-0.7366653	-4.1423137	1.6889197
H	-3.2136213	-4.0220387	1.5989267
H	-4.3282413	-1.9612197	0.7723717
I	0.0553257	0.6311743	-0.1364503
O	1.0266837	0.6342413	1.7628887
O	0.1714917	1.8501943	-2.9996583
C	2.1470227	-0.0257787	1.9266147
O	2.5337197	-0.9163357	1.1734517
C	-0.8854653	1.2237553	-2.9024183
O	-1.2795273	0.5795763	-1.8471853
C	2.9365607	0.4408183	3.1242307
H	3.6529297	1.1916563	2.7770237
H	2.2835947	0.8964973	3.8695257
H	3.5027967	-0.3885417	3.5496777
C	-1.8450823	1.1417883	-4.0680383
H	-2.1129353	2.1549603	-4.3809613
H	-1.3352203	0.6623633	-4.9090543
H	-2.7405283	0.5761323	-3.8096243
C	0.9635847	-3.5859217	-1.7630843
C	0.6291037	-2.4866577	-2.5549113
C	1.6133527	-1.5081907	-2.7630163
C	2.8577737	-1.6007517	-2.1651183
C	3.1631887	-2.6961617	-1.3527093
C	2.2148917	-3.7005047	-1.1623873
H	0.2324417	-4.3752827	-1.6124803
H	1.3832807	-0.6350797	-3.3694493
H	3.5975037	-0.8168627	-2.2886403
H	2.4357517	-4.5716137	-0.5561003
C	-4.1840823	1.1758003	2.3880847
C	-3.0355963	1.8908193	2.0418707
C	-1.8640053	1.6329553	2.7695767
C	-1.8188983	0.6430783	3.7351077
C	-2.9635133	-0.1045347	4.0267327
C	-4.1599363	0.1863843	3.3673877
H	-5.1215313	1.3886103	1.8810257
H	-0.9572653	2.1868693	2.5440867
H	-0.8971133	0.4172213	4.2599207
H	-5.0733953	-0.3489137	3.6008377
O	-2.8161093	-1.0759727	4.9629107
O	4.4034037	-2.6998907	-0.8004263
C	-3.9054853	-1.9370347	5.1937827
H	-3.5587603	-2.6771637	5.9162277
H	-4.7662813	-1.4010117	5.6148307
H	-4.2136933	-2.4460547	4.2704027
C	4.7166957	-3.7059547	0.1410247
H	5.7054197	-3.4583557	0.5248527
H	3.9997717	-3.7014257	0.9710587
H	4.7350197	-4.6974517	-0.3285863
C	-0.7235063	-2.2998027	-3.1062743
C	-1.8484273	-2.6699167	-2.4911333
H	-0.7905433	-1.7495137	-4.0460633
H	-1.7831753	-3.1679767	-1.5229583
C	-2.9851853	2.8119813	0.8936827
C	-3.7441003	2.7180583	-0.2035253
H	-2.2052163	3.5718683	0.9254407
H	-4.4970093	1.9292413	-0.2673093

C	-3.6567143	3.6263993	-1.3942993
H	-3.3997873	3.0266963	-2.2791313
H	-2.8423543	4.3440943	-1.2535523
C	-3.2370243	-2.3812237	-2.9762643
H	-3.2053863	-2.0095277	-4.0081613
H	-3.6503133	-1.5677437	-2.3608233
H	1.3858227	2.5711033	-1.9624793
H	4.3140327	-1.0703997	1.2434307
O	1.9522817	2.7524443	-1.1800333
O	5.2492867	-0.9495267	1.5176287
C	5.9766207	-0.4154477	0.4640467
C	7.4521377	-0.5860117	0.8160847
C	5.5805077	1.0448223	0.2169747
H	5.8079967	-0.9517627	-0.4779653
C	2.0054037	4.1072393	-0.8971723
C	3.1672867	4.3069803	0.0807077
C	0.6695747	4.6116633	-0.3307353
H	2.2204567	4.7232703	-1.7804783
F	0.6415217	5.9427563	-0.2300793
F	3.2151827	5.5777483	0.5063547
F	3.0550797	3.5149153	1.1481977
F	4.3228977	4.0335083	-0.5285063
F	-0.3212693	4.2412493	-1.1613523
F	0.3939547	4.0964343	0.8755937
F	4.2753757	1.0859243	-0.1021133
F	6.2641707	1.5852243	-0.7982313
F	5.7574837	1.8144003	1.2968447
F	7.7801367	0.0293263	1.9540017
F	8.2401057	-0.1080417	-0.1572463
F	7.7335197	-1.8910347	0.9592007
C	-4.1628793	-3.5965357	-2.8774533
H	-5.1789343	-3.3504477	-3.2032703
H	-3.7952203	-4.4210207	-3.4973453
H	-4.2172603	-3.9544487	-1.8423473
C	-4.9713303	4.3686193	-1.6609913
H	-4.8927013	4.9994853	-2.5524973
H	-5.7966023	3.6645943	-1.8188733
H	-5.2344383	5.0072243	-0.8114503

E = -3571.616440650
G = -3570.947324

Iodobenzene • $2AcO^-_{HFIP}$

I	-1.8939647	5.5763324	0.3130953
O	-6.3064337	2.8345104	0.2950393
O	5.0710243	0.7201294	-1.3836207
C	-6.0736237	1.6207714	0.3278743
C	3.8635643	0.6471204	-0.9598787
C	3.4937603	-0.6457926	-0.2110387
H	4.2757333	-0.9210676	0.5029413
H	2.5346123	-0.5374786	0.3015173
H	3.4173633	-1.4690776	-0.9322927
C	-5.4512957	1.0350614	1.6135683
H	-6.1774847	0.3676654	2.0980303
H	-4.5584687	0.4427524	1.3885523

H	-5.1839427	1.8324104	2.3112633
O	2.9934013	1.5093004	-1.1281037
O	-6.3247347	0.7819184	-0.6047797
C	-1.6678707	3.4912294	-0.1754967
C	-0.3860107	2.9905354	-0.3680247
C	-2.8066527	2.7039354	-0.2953717
C	-0.2314047	1.6412374	-0.6868487
H	0.4924983	3.6200134	-0.2798097
C	-2.6349187	1.3570064	-0.6204907
H	-3.8051037	3.1027094	-0.1386997
C	-1.3585167	0.8304604	-0.8081257
H	0.7812043	1.2680444	-0.8424367
H	-3.5097437	0.7230644	-0.7316677
H	-1.2480407	-0.2228206	-1.0493507
C	8.8804783	0.0300754	-0.6516077
C	7.5171333	-0.2140546	0.0075063
H	7.0719263	0.7791954	0.1749723
C	7.6646143	-0.8634376	1.3865973
F	8.4296563	-0.1256186	2.2224113
F	8.2168613	-2.0850226	1.3289073
F	6.4656033	-0.9932916	1.9706993
F	9.6670313	0.8523774	0.0801773
F	9.5763723	-1.1036306	-0.8417287
F	8.7186933	0.6060064	-1.8477057
O	6.7399193	-1.0020476	-0.7954057
H	5.9575993	-0.3622526	-1.1144597
O	-5.0521857	-1.3063596	-1.0110027
H	-5.5877627	-0.4173756	-0.8427147
C	-5.2911697	-2.1345816	0.0489973
H	-5.7787487	-1.6276996	0.8961283
C	-3.9604817	-2.6741636	0.5827813
C	-6.2448007	-3.2649386	-0.3613157
F	-3.1759957	-1.6645006	0.9772983
F	-4.1380767	-3.4813936	1.6520453
F	-3.2841287	-3.3773576	-0.3347817
F	-6.5539997	-4.0750426	0.6771433
F	-5.7471157	-4.0454226	-1.3312257
F	-7.3963717	-2.7494356	-0.8095617

E = -2566.38563136
G = -2566.154839

11^{+}

C	-1.0022772	-0.5120072	-1.4617749
C	-1.0022232	0.5119268	1.4618591
C	-2.2712202	0.6108528	0.8894821
C	-2.2712862	-0.6110212	-0.8894489
H	-0.8889982	0.2015118	-2.2780319
H	-0.8889422	-0.2014892	2.2782041
H	-2.4882312	1.4883178	0.2825911
H	-2.4883163	-1.4885232	-0.2826179
C	0.1848608	-1.1611482	-1.0381269
C	1.4205158	-0.8152852	-1.6489029
C	0.2170228	-2.1007732	0.0189051
C	2.6059888	-1.3441322	-1.2118899
H	1.4207288	-0.1002292	-2.4663899

C	1.4038358	-2.6445042	0.4670931
H	-0.7074382	-2.4137562	0.4935891
C	2.6146068	-2.2595632	-0.1377589
H	3.5532948	-1.0772982	-1.6666039
H	1.3906048	-3.3671672	1.2739801
C	0.1848968	1.1611098	1.0381881
C	1.4205728	0.8152918	1.6489381
C	0.2170088	2.1007238	-0.0188509
C	2.6060248	1.3441428	1.2118671
H	1.4208248	0.1002638	2.4664501
C	1.4037988	2.6444668	-0.4670919
H	-0.7074782	2.4137098	-0.4934849
C	2.6145958	2.2595558	0.1377211
H	3.5533488	1.0773328	1.6665581
H	1.3905268	3.3671108	-1.2739949
C	-3.4452392	0.0533958	1.6627451
H	-4.2625432	-0.2200912	0.9892241
H	-3.1386972	-0.8657122	2.1766411
C	-3.4453092	-0.0534732	-1.6626419
H	-4.2626482	0.2198028	-0.9890769
H	-3.1388162	0.8657728	-2.1763209
O	3.8158488	-2.7029462	0.2267611
C	3.9236838	-3.6451602	1.2870311
H	4.9887798	-3.8413712	1.3971611
H	3.5288758	-3.2295252	2.2204411
H	3.4021198	-4.5750512	1.0383431
C	-3.9647883	-1.0730532	-2.6848289
H	-4.2825652	-1.9976572	-2.1921369
H	-4.8255942	-0.6651362	-3.2217529
H	-3.1927972	-1.3279502	-3.4172959
C	-3.9648073	1.0731758	2.6846891
H	-4.8257542	0.6654248	3.2215121
H	-3.1929212	1.3280958	3.4172591
H	-4.2823942	1.9977438	2.1918061
O	3.8158218	2.7029608	-0.2268419
C	3.9236038	3.6452088	-1.2870859
H	4.9886828	3.8415498	-1.3971509
H	3.5288958	3.2295428	-2.2205249
H	3.4019188	4.5750348	-1.0384159

E = -1005.34940858
G = -1004.94878258

11^{+}_staggered

C	-1.2389659	-1.0415177	0.5159840
C	1.2391741	1.0428983	0.5157320
C	0.3632451	0.9815053	-0.5741940
C	-0.3630609	-0.9805907	-0.5740040
H	-0.7897279	-1.3070467	1.4740030
H	0.7902811	1.3095523	1.4735950
H	0.8136781	0.8355933	-1.5564990
H	-0.8134009	-0.8350847	-1.5564060
C	-2.6253819	-0.7292617	0.5489390
C	-3.2783239	-0.6337787	1.8060590
C	-3.4082689	-0.5182857	-0.6105970

C	-4.6106339	-0.3198357	1.8997960
H	-2.7072809	-0.8075837	2.7139840
C	-4.7494959	-0.2057437	-0.5307770
H	-2.9610099	-0.6261817	-1.5936640
C	-5.3652549	-0.0977487	0.7302660
H	-5.1106169	-0.2398237	2.8583920
H	-5.3174409	-0.0604347	-1.4416350
C	2.6255141	0.7302273	0.5486570
C	3.2789441	0.6368763	1.8056900
C	3.4078261	0.5165113	-0.6107670
C	4.6111851	0.3226563	1.8995070
H	2.7083421	0.8126663	2.7135120
C	4.7489451	0.2035293	-0.5308720
H	2.9602141	0.6225163	-1.5938780
C	5.3652261	0.0978933	0.7301170
H	5.1115191	0.2443373	2.8580600
H	5.3163911	0.0560193	-1.4416850
C	-0.8711089	1.8509403	-0.5804750
H	-1.6023719	1.4621673	-1.2970020
H	-1.3501949	1.8264013	0.4043660
C	0.8713951	-1.8499147	-0.5798400
H	1.6018611	-1.4622577	-1.2977900
H	1.3514521	-1.8234937	0.4044770
O	-6.6495859	0.1956323	0.9224530
C	-7.4958639	0.4131333	-0.1998940
H	-8.4807149	0.6212493	0.2146950
H	-7.1547049	1.2725123	-0.7867730
H	-7.5447009	-0.4803207	-0.8312120
C	0.5177871	-3.2960247	-0.9489420
H	0.0411031	-3.3514727	-1.9331060
H	1.4216941	-3.9109627	-0.9779350
H	-0.1694099	-3.7317337	-0.2168330
C	-0.5175559	3.2963523	-0.9523810
H	-1.4214119	3.9113343	-0.9819830
H	0.1700731	3.7332933	-0.2214170
H	-0.0414109	3.3499913	-1.9369060
O	6.6495411	-0.1955517	0.9223480
C	7.4951291	-0.4161917	-0.1999080
H	8.4801701	-0.6234347	0.2146680
H	7.1534031	-1.2770597	-0.7842650
H	7.5438051	0.4755443	-0.8336610

E = -1005.34051106

G = -1004.942619

12^{+}

C	0.9569018	-0.1486014	1.4678389
C	0.9568668	0.1485866	-1.4678201
C	2.2534158	0.2616196	-0.7757111
C	2.2534398	-0.2616024	0.7757059
H	0.8490348	0.6393026	2.2117199
H	0.8490008	-0.6393244	-2.2116931
H	2.5173278	1.3233356	-0.6831641
H	2.5173768	-1.3233134	0.6831519

C	-0.1556052	-0.9477634	1.2148459
C	-1.4188612	-0.6149074	1.7979639
C	-0.1282042	-2.0069164	0.2659789
C	-2.5654252	-1.2454564	1.4108379
H	-1.4599552	0.1776216	2.5393849
C	-1.2834552	-2.6524804	-0.1270321
H	0.8188648	-2.3423464	-0.1434541
C	-2.5156502	-2.2618634	0.4250179
H	-3.5309372	-0.9899654	1.8326369
H	-1.2283622	-3.4608134	-0.8460551
C	-0.1556472	0.9477406	-1.2148231
C	-1.4189032	0.6148706	-1.7979311
C	-0.1282472	2.0069016	-0.2659681
C	-2.5654702	1.2454186	-1.4108071
H	-1.4599972	-0.1776664	-2.5393431
C	-1.2835002	2.6524616	0.1270429
H	0.8188208	2.3423396	0.1434619
C	-2.5156972	2.2618336	-0.4249981
H	-3.5309812	0.9899186	-1.8326021
H	-1.2284092	3.4608006	0.8460599
C	3.3623798	-0.4671234	-1.5494711
H	4.2706188	-0.5094264	-0.9400921
H	3.0517988	-1.5089674	-1.7094631
C	3.3624038	0.4671656	1.5494419
H	4.2706278	0.5094926	0.9400419
H	3.0517998	1.5090026	1.7094409
O	-3.6901042	-2.7946464	0.1045229
C	-3.7482202	-3.8429604	-0.8567211
H	-4.8036582	-4.0899844	-0.9558901
H	-3.3562802	-3.5075474	-1.8228141
H	-3.1949502	-4.7208824	-0.5084021
C	3.6845628	-0.1960834	2.8873919
H	4.0140258	-1.2303974	2.7416689
H	4.4865108	0.3405806	3.4016209
H	2.8147028	-0.2142924	3.5534329
C	3.6844938	0.1961316	-2.8874301
H	4.4864468	-0.3405114	-3.4016731
H	2.8146198	0.2143146	-3.5534531
H	4.0139298	1.2304556	-2.7417151
O	-3.6901512	2.7946176	-0.1045061
C	-3.7482672	3.8429466	0.8567229
H	-4.8037062	4.0899726	0.9558869
H	-3.3563292	3.5075476	1.8228209
H	-3.1949972	4.7208636	0.5083919

E = -1005.35968126

G =-1004.957450

12^{+}_staggered

C	-1.3335004	0.5312573	-0.5033795
C	1.3742846	-0.8661757	-0.5381575
C	0.4542346	-0.8069507	0.6237775

C	-0.4426164	0.5281423	0.6553975
H	-0.8226324	0.6150373	-1.4651425
H	0.9394146	-1.2173657	-1.4747595
H	1.0240066	-0.7301587	1.5572105
H	-1.0070914	0.4826103	1.5925995
C	-2.7108794	0.4073013	-0.5554745
C	-3.3584534	0.3583793	-1.8344625
C	-3.5328134	0.3086083	0.6104015
C	-4.7089854	0.2086233	-1.9406055
H	-2.7531104	0.4381113	-2.7327675
C	-4.8894874	0.1560113	0.5151275
H	-3.0779364	0.3599283	1.5931525
C	-5.4963554	0.1007043	-0.7656915
H	-5.2113114	0.1660193	-2.9000045
H	-5.4888054	0.0847183	1.4142265
C	2.7468056	-0.5451407	-0.5657505
C	3.4594046	-0.6443617	-1.7973155
C	3.4919556	-0.1229627	0.5652565
C	4.7936926	-0.3390767	-1.8886045
H	2.9270676	-0.9731447	-2.6859935
C	4.8377486	0.1868103	0.4806785
H	3.0098226	-0.0426597	1.5342845
C	5.5048286	0.0836673	-0.7488025
H	5.3279606	-0.4180387	-2.8291685
H	5.3639166	0.5010393	1.3743875
C	-0.4419124	-2.0536057	0.7136045
H	-1.2070614	-1.8974677	1.4861925
H	-0.9796124	-2.1843207	-0.2356215
C	0.4463756	1.7902243	0.6719495
H	1.1687006	1.6744553	1.4873145
H	1.0299196	1.8355023	-0.2539775
O	-6.7864484	-0.0454907	-0.9663605
C	-7.6897214	-0.1717967	0.1374045
H	-8.6732574	-0.2891457	-0.3123395
H	-7.4446344	-1.0561147	0.7321365
H	-7.6677754	0.7306713	0.7545755
C	-0.3546914	3.0755263	0.8665325
H	-0.9399084	3.0433623	1.7925955
H	0.3139776	3.9383383	0.9263815
H	-1.0498614	3.2509363	0.0372125
C	0.3559796	-3.3162237	1.0294815
H	-0.3006324	-4.1889417	1.0863145
H	1.1113866	-3.5064207	0.2604185
H	0.8741566	-3.2213307	1.9898725
O	6.8041486	0.3583833	-0.9433905
C	7.5886036	0.7746303	0.1605965
H	8.5913206	0.9351043	-0.2336525
H	7.2091196	1.7112433	0.5854995
H	7.6206636	0.0015493	0.9368385

E = -1005.35251024

G= -1004.95408024

13^{+}

C	1.0682584	-0.0006572	-0.8840085

C	-1.1115756	-0.0320152	0.8494245
C	-0.3438836	-1.3108772	0.6558045
C	0.4461634	-1.3319132	-0.7133555
H	0.3834534	0.7729888	-1.2346025
H	-0.5676776	0.7826168	1.3292245
H	-1.0343566	-2.1609552	0.5901865
H	1.2058504	-2.1185782	-0.6477875
C	2.3627854	0.3951988	-0.6276055
C	2.7273504	1.7708448	-0.8277105
C	3.3723194	-0.5034182	-0.1513155
C	3.9892244	2.2112878	-0.5711645
H	1.9742804	2.4652598	-1.1885965
C	4.6417884	-0.0713492	0.1110335
H	3.1261744	-1.5467982	0.0098575
C	4.9672474	1.2959088	-0.0971275
H	5.3887214	-0.7680752	0.4703075
C	-2.4636906	0.2009188	0.5250375
C	-3.0409556	1.4742898	0.7763005
C	-3.3235886	-0.7812132	-0.0485705
C	-4.3612916	1.7595438	0.4807225
H	-2.4233366	2.2494968	1.2230535
C	-4.6369976	-0.5033682	-0.3435465
H	-2.9473076	-1.7783372	-0.2534125
C	-5.1771306	0.7698208	-0.0864475
H	-4.7522606	2.7473388	0.6955775
C	-0.4694246	-1.6319532	-1.9151975
H	-0.9583936	-2.5939592	-1.7262815
H	-1.2649096	-0.8788422	-1.9597595
C	0.5995104	-1.5753712	1.8396865
H	1.1822624	-2.4835812	1.6357325
H	1.3197814	-0.7494402	1.9305565
O	6.1519454	1.8098158	0.1202205
O	-6.4713026	0.9321768	-0.4154525
C	-7.0871436	2.1790798	-0.1510835
H	-6.6040746	2.9888858	-0.7108305
H	-8.1198316	2.0761338	-0.4826565
H	-7.0698256	2.4098378	0.9206105
C	7.2355394	0.9970608	0.5920855
H	8.0795844	1.6770388	0.6830225
H	6.9941534	0.5689048	1.5683985
H	7.4644094	0.2123798	-0.1336425
H	4.2824734	3.2445588	-0.7157635
H	-5.2874636	-1.2578742	-0.7731825
C	-0.1496856	-1.7424442	3.1605995
H	-0.7067936	-0.8365492	3.4180295
H	-0.8665876	-2.5681062	3.1018555
H	0.5465604	-1.9582342	3.9759195
C	0.2874104	-1.6895052	-3.2414215
H	1.0803634	-2.4449362	-3.2135025
H	-0.3891796	-1.9465272	-4.0604355
H	0.7510554	-0.7265082	-3.4887875

E = -1005.35199498
G = -1004.949927

Redox calculations

Fc

C	1.0847970	-0.5569030	-1.6473239
C	0.8660010	0.8506090	-1.6522829
C	-0.5403010	1.0774070	-1.6595149
C	-1.1905470	-0.1900150	-1.6586309
C	-0.1860470	-1.2000090	-1.6502159
Fe	-0.0001510	0.0009910	-0.0000029
C	0.8522280	0.8582620	1.6554871
C	1.0713610	-0.5492030	1.6586651
C	-0.1993260	-1.1926090	1.6540191
C	-1.2040790	-0.1828420	1.6496411
C	-0.5541340	1.0847370	1.6501571
H	-0.3707720	-2.2598020	1.6190161
H	2.0333070	-1.0423710	1.6275501
H	-1.0284850	2.0419210	-1.6301319
H	-2.2587280	-0.3560850	-1.6275189
H	-0.3580440	-2.2669960	-1.6118139
H	2.0463310	-1.0501330	-1.6060909
H	1.6322280	1.6128480	-1.6162419
H	-1.0422660	2.0489860	1.6124221
H	1.6185600	1.6205250	1.6223011
H	-2.2719320	-0.3493190	1.6105091

E = -1650.474613
G = -1650.612812

Fc^+

C	1.0863810	-0.5576010	-1.6682069
C	0.8671650	0.8518650	-1.6718819
C	-0.5409860	1.0789220	-1.6780639
C	-1.1920980	-0.1902400	-1.6778969
C	-0.1861810	-1.2016970	-1.6721509
Fe	-0.0000530	-0.0002340	0.0000021
C	0.8531790	0.8596570	1.6750861
C	1.0728040	-0.5497430	1.6795621
C	-0.1995700	-1.1942110	1.6759641
C	-1.2057780	-0.1830530	1.6688961
C	-0.5550390	1.0863010	1.6686881
H	-0.3712020	-2.2617090	1.6437261
H	2.0349560	-1.0431630	1.6504661
H	-1.0291360	2.0437150	-1.6484529
H	-2.2605070	-0.3562430	-1.6479119
H	-0.3584050	-2.2689910	-1.6365139
H	2.0481070	-1.0511500	-1.6289919
H	1.6336740	1.6142190	-1.6364039
H	-1.0431950	2.0507980	1.6307261
H	1.6197440	1.6220820	1.6424631
H	-2.2738590	-0.3495240	1.6308951

E = -510.291641769
G = -1650.434749

4a

C	-1.1521362	-1.8346468	-0.2492025
C	0.2400108	-1.8712708	-0.3029735

C	0.9613448	-0.6848738	-0.1831725
C	0.3367718	0.5499782	-0.0044355
C	-1.0676252	0.5608852	0.0347765
C	-1.8002402	-0.6049118	-0.0815875
H	0.7735758	-2.8052738	-0.4377955
H	2.0472278	-0.7281408	-0.2253955
H	-1.5989592	1.5012632	0.1476545
H	-2.8850052	-0.5926688	-0.0533865
C	1.1593558	1.7638292	0.1285515
H	2.2163248	1.6283862	-0.1057375
C	0.7523168	2.9767612	0.5124105
H	-0.2923412	3.1400252	0.7758055
C	1.6460748	4.1749112	0.6234915
H	1.3062788	4.9836852	-0.0356235
H	1.6444898	4.5759962	1.6446125
H	2.6791178	3.9310532	0.3558005
O	-1.9618022	-2.9195558	-0.3547535
C	-1.3558492	-4.1811168	-0.5155435
H	-0.7104002	-4.4295258	0.3370345
H	-2.1717752	-4.9028038	-0.5699045
H	-0.7667552	-4.2319848	-1.4406255

E = -463.463125511
G = -463.296539

4a^{+}

C	-1.1274063	-1.8164818	-0.2514116
C	0.2917347	-1.8721638	-0.2919216
C	1.0033417	-0.7161918	-0.1319576
C	0.3633407	0.5470812	0.0749624
C	-1.0690083	0.5718542	0.1109864
C	-1.7917113	-0.5698298	-0.0466116
H	0.8058117	-2.8128228	-0.4468476
H	2.0882427	-0.7498938	-0.1616696
H	-1.5943013	1.5071652	0.2652044
H	-2.8756503	-0.5718888	-0.0225206
C	1.1809437	1.6984692	0.2320094
H	2.2565947	1.5386362	0.1831184
C	0.7414387	2.9807012	0.4376754
H	-0.3258053	3.1853172	0.4934844
C	1.6367457	4.1510292	0.5954974
H	1.4061507	4.9017582	-0.1714306
H	1.4460047	4.6380562	1.5605324
H	2.6941667	3.8863762	0.5308274
O	-1.9157903	-2.8502948	-0.3910506
C	-1.3834003	-4.1679758	-0.6033436
H	-0.7683643	-4.4668568	0.2490444
H	-2.2533853	-4.8157788	-0.6815766
H	-0.8096943	-4.1962658	-1.5330006

E = -463.255329695
G = -463.096169

4b

C	-1.1653777	-1.4056225	-0.0228029
C	0.2033973	-1.4881595	0.2192631

C	1.0077413	-0.3500695	0.1946251
C	0.4500453	0.9155475	-0.0929529
C	-0.9288227	0.9612285	-0.3225559
C	-1.7436147	-0.1620265	-0.2862539
H	0.6078773	-2.4712225	0.4253961
H	-1.4029817	1.9147965	-0.5371899
O	-1.9020187	-2.5573695	0.0489361
C	-2.5247747	-2.9399825	-1.1713789
H	-1.7716887	-3.1008035	-1.9528789
H	-3.0422977	-3.8791175	-0.9676979
H	-3.2411547	-2.1843105	-1.5071139
O	2.3452183	-0.3964985	0.4291701
O	-3.0889307	-0.0228325	-0.5300509
C	1.1892333	2.1859655	-0.1560399
H	0.5513743	3.0340455	-0.4109379
C	2.4856053	2.4426765	0.0542361
H	3.1650413	1.6389365	0.3123371
C	3.0762223	3.8177135	-0.0386599
H	3.5204833	4.1185175	0.9187511
H	3.8810373	3.8520235	-0.7837979
H	2.3257443	4.5659465	-0.3143129
C	-3.8993077	-0.2139795	0.6207891
H	-3.6324267	0.5057395	1.4050321
H	-4.9299497	-0.0410925	0.3046391
H	-3.7990837	-1.2316405	1.0143591
C	2.9350023	-1.6404735	0.7267321
H	2.8270683	-2.3472525	-0.1058269
H	3.9943813	-1.4387305	0.8905951
H	2.5069563	-2.0819525	1.6355891

E = -692.486607138
G = -692.266343

4b^{+}

C	-0.9246816	-1.7288676	-0.1858168
C	0.4680134	-1.6930496	-0.0634268
C	1.1536554	-0.4983146	0.0586222
C	0.4342004	0.7648574	0.0670632
C	-0.9667066	0.7040544	-0.0647778
C	-1.6644586	-0.4806746	-0.1856838
H	0.9771534	-2.6476166	-0.0719458
H	-1.5104416	1.6408864	-0.0624878
O	-1.4348886	-2.9326336	-0.2930798
C	-2.8285996	-3.2646146	-0.4381718
H	-3.2320756	-2.8248866	-1.3497948
H	-2.8336406	-4.3509456	-0.5029598
H	-3.3919076	-2.9306776	0.4326912
O	2.4703804	-0.4242806	0.1656542
O	-2.9850256	-0.5812746	-0.3025168
C	1.0295654	2.0649274	0.1934022
H	0.3165794	2.8852104	0.1236052
C	2.3295654	2.4027694	0.4002572
H	3.0828454	1.6300984	0.4929082
C	2.7953804	3.8099054	0.5253172
H	3.2546544	3.9647374	1.5097182
H	3.5792834	4.0147424	-0.2139118

H	1.9886934	4.5354714	0.3953062
C	-3.7828316	0.6027324	-0.3040228
H	-3.5171166	1.2426574	-1.1508518
H	-4.8100476	0.2587034	-0.4078278
H	-3.6652076	1.1443734	0.6394312
C	3.2579884	-1.6169236	0.1499482
H	3.1243294	-2.1495406	-0.7959508
H	4.2892044	-1.2823436	0.2439012
H	2.9961384	-2.2594836	0.9954022

E = -692.297374270
G = -692.077959

4c

C	-1.4726367	-1.6461122	-0.3708229
C	-0.1810507	-1.6089622	0.1638291
C	0.5079673	-0.4074542	0.2654791
C	-0.0787257	0.8073658	-0.1686209
C	-1.3655567	0.7197808	-0.6984259
C	-2.0767837	-0.4728272	-0.8091719
H	0.2495813	-2.5472442	0.4901861
H	-1.8395087	1.6357238	-1.0428269
O	-2.0424657	-2.8777762	-0.4154979
C	-3.3450627	-2.9783492	-0.9434839
H	-3.3817917	-2.6508462	-1.9905509
H	-3.6129817	-4.0342042	-0.8877839
H	-4.0639837	-2.3916322	-0.3571099
O	1.7626353	-0.3303152	0.7747151
C	0.5535363	2.1339618	-0.1126829
H	-0.0596037	2.9135688	-0.5691599
C	1.7272883	2.5155148	0.4046301
H	2.3762653	1.7864528	0.8758241
C	2.2152843	3.9333218	0.3766101
H	3.1767123	4.0093378	-0.1470339
H	1.5029643	4.5972758	-0.1245469
H	2.3786253	4.3143608	1.3928531
C	2.3980223	-1.5158332	1.1946091
H	2.5105693	-2.2263722	0.3661201
H	3.3850723	-1.2152042	1.5484611
H	1.8504743	-1.9976362	2.0144191
H	-3.0748477	-0.4658952	-1.2300179

E = -577.976572484
G = -577.786120

4c^{+}

C	-1.4647856	-1.6312972	-0.3756199
C	-0.1659536	-1.6073262	0.1616911
C	0.5204124	-0.4168822	0.2768651
C	-0.0921306	0.8302548	-0.1572019
C	-1.4148596	0.7456348	-0.6955059
C	-2.0964216	-0.4280982	-0.8110279
H	0.2590274	-2.5521002	0.4742061
H	-1.8869036	1.6662288	-1.0239629
O	-2.0255956	-2.8168722	-0.4391419

C	-3.3492076	-2.9808842	-0.9665749
H	-3.3853316	-2.6624192	-2.0115969
H	-3.5514146	-4.0475532	-0.8978939
H	-4.0717426	-2.4260792	-0.3624779
O	1.7451424	-0.3215882	0.7736151
C	0.4975704	2.1167068	-0.0965619
H	-0.1335376	2.9203088	-0.4736699
C	1.7395664	2.4878948	0.3656451
H	2.4143794	1.7341568	0.7531271
C	2.2159534	3.8915108	0.3625491
H	3.1424294	3.9690978	-0.2212939
H	1.4805224	4.5909308	-0.0414929
H	2.4784964	4.1980108	1.3834941
C	2.4224194	-1.4974982	1.2248701
H	2.5566574	-2.2012312	0.3983411
H	3.3918034	-1.1534852	1.5797951
H	1.8698754	-1.9648142	2.0450661
H	-3.0963706	-0.4426062	-1.2252419

E = -577.780020778
G = -577.590542

4d

C	-1.3055547	-1.8722729	-0.3345596
C	-0.0056427	-1.8264929	0.1721004
C	0.6599533	-0.6265639	0.3953234
C	0.0012253	0.5899551	0.0977284
C	-1.3114947	0.5206671	-0.3784436
C	-1.9728377	-0.6803559	-0.6074706
H	0.4795173	-2.7711419	0.4006834
H	-1.8373707	1.4490861	-0.5885206
O	-1.8286617	-3.1134439	-0.5098836
C	-3.1428427	-3.2078749	-1.0082366
H	-3.2321587	-2.7496379	-2.0018596
H	-3.3611217	-4.2738299	-1.0842136
H	-3.8667317	-2.7383589	-0.3291746
C	0.5712693	1.9401311	0.2745344
H	-0.1761387	2.7141891	0.4596424
C	1.8442543	2.3379831	0.1822894
H	2.6275463	1.6204321	-0.0473016
C	2.2911563	3.7595491	0.3517504
H	2.8097053	4.1195701	-0.5454816
H	1.4447683	4.4260221	0.5464594
H	2.9975133	3.8560171	1.1858074
H	-2.9888867	-0.6691659	-0.9847546
C	2.0512223	-0.6864809	0.9759394
H	2.8185553	-0.5715139	0.2013134
H	2.2108493	0.1049921	1.7145394
H	2.2219053	-1.6514609	1.4617894

E = -502.769970785
G = -502.581645

4d^{+}

C	-1.3317477	-1.8379849	-0.3208216
C	0.0122973	-1.8188769	0.1417654

C	0.7117593	-0.6557229	0.3201254
C	0.0458363	0.5973461	0.0210654
C	-1.3218507	0.5441741	-0.4185706
C	-2.0056947	-0.6210039	-0.5987626
H	0.4674673	-2.7800789	0.3560314
H	-1.8252737	1.4831391	-0.6268936
O	-1.8598507	-3.0282459	-0.4494286
C	-3.2127387	-3.1915909	-0.9034156
H	-3.3251297	-2.7792129	-1.9091636
H	-3.3788137	-4.2662359	-0.9201566
H	-3.9046587	-2.7162609	-0.2037036
C	0.5871153	1.9103261	0.1143794
H	-0.1308877	2.7054511	-0.0810966
C	1.8653793	2.3349881	0.3814764
H	2.6656243	1.6257161	0.5535684
C	2.2476393	3.7674951	0.4301114
H	3.0266893	3.9710411	-0.3160906
H	1.4033233	4.4379791	0.2557804
H	2.6956963	4.0011391	1.4044634
H	-3.0323807	-0.6098129	-0.9428096
C	2.1233513	-0.7445719	0.8292474
H	2.8410543	-0.4208449	0.0677384
H	2.2662823	-0.1328099	1.7252934
H	2.3695113	-1.7755419	1.0898674

E = -502.568803919
G = -502.382483

4e

C	-1.0230224	-1.9531362	-0.1783119
C	0.2022476	-1.9093982	0.4913121
C	0.8157166	-0.6918332	0.7308391
C	0.2641336	0.5300918	0.3178461
C	-0.9763494	0.4420288	-0.3257749
C	-1.6226674	-0.7609422	-0.5832359
H	0.6490066	-2.8382882	0.8241201
H	-1.4486054	1.3659018	-0.6491659
O	-1.5410664	-3.1898932	-0.3691619
C	-2.7865324	-3.2909252	-1.0223889
H	-2.7425774	-2.8798402	-2.0390509
H	-3.0128654	-4.3563262	-1.0749849
H	-3.5783084	-2.7805502	-0.4590179
C	0.8442876	1.8765458	0.5075231
H	0.1245116	2.6460498	0.7892021
C	2.1129906	2.2352458	0.3035151
H	2.8374816	1.4878728	-0.0129709
C	2.6347736	3.6277528	0.4851891
H	3.0852646	4.0028238	-0.4418959
H	1.8421756	4.3196648	0.7872151
H	3.4188766	3.6501658	1.2518891
H	-2.5784524	-0.7510092	-1.0935599
Br	2.4789816	-0.7820012	1.7608681

E = -476.020132875
G = -475.872206

4e$^+$

C	-1.0282405	-1.9360610	-0.1945100
C	0.2674555	-1.9187580	0.3913870
C	0.9173315	-0.7395090	0.6149900
C	0.3214665	0.5200840	0.2466890
C	-1.0143055	0.4524200	-0.2817010
C	-1.6764375	-0.7169500	-0.5174700
H	0.7074735	-2.8696080	0.6682540
H	-1.5022915	1.3889740	-0.5323600
O	-1.5370725	-3.1267770	-0.3732400
C	-2.8476525	-3.2962960	-0.9378410
H	-2.8811035	-2.8734320	-1.9449740
H	-2.9996045	-4.3723660	-0.9777280
H	-3.5978635	-2.8344240	-0.2912060
C	0.8721935	1.8285320	0.3186640
H	0.1481825	2.6264510	0.1612700
C	2.1783335	2.2325990	0.4699540
H	2.9751955	1.5004500	0.5323910
C	2.5852585	3.6559680	0.5064050
H	3.2857615	3.8636920	-0.3134740
H	1.7410415	4.3460010	0.4435940
H	3.1436055	3.8533930	1.4311800
H	-2.6719225	-0.7041840	-0.9434390
Br	2.6131945	-0.8801980	1.5231640

E = -475.807528368
G = -475.661255

4f

C	-0.9922015	-1.9578960	-0.2161006
C	0.3297805	-1.8963460	0.2313084
C	0.9475565	-0.6700620	0.3563614
C	0.3207805	0.5480120	0.0562384
C	-1.0001705	0.4392170	-0.3902876
C	-1.6637195	-0.7756870	-0.5300466
H	0.8664285	-2.8049850	0.4772974
H	-1.5340205	1.3528660	-0.6390906
O	-1.5223755	-3.2009840	-0.3096316
C	-2.8560265	-3.3179570	-0.7528916
H	-2.9787915	-2.9221220	-1.7691196
H	-3.0794715	-4.3852350	-0.7536836
H	-3.5509475	-2.8034680	-0.0770126
C	0.9329855	1.8796360	0.1679514
H	0.2827275	2.6846220	-0.1779876
C	2.1431485	2.2163140	0.6274054
H	2.8224975	1.4509060	0.9863944
C	2.6434405	3.6277820	0.6864444
H	3.5631815	3.7418770	0.0993384
H	1.9038685	4.3375000	0.3015894
H	2.8885605	3.9147580	1.7166584
H	-2.6887755	-0.7845260	-0.8805366
F	2.2215435	-0.6742230	0.7894014

E = -562.697034680
G = -562.546437

4f^{+}

C	-0.9902486	-1.9275578	-0.2094888
C	0.3443834	-1.8744178	0.2649942
C	0.9559704	-0.6662568	0.3933802
C	0.3092074	0.5751892	0.0679502
C	-1.0385506	0.4678322	-0.4070298
C	-1.6808636	-0.7276438	-0.5473088
H	0.8619744	-2.7916938	0.5194852
H	-1.5603376	1.3846122	-0.6630268
O	-1.5018156	-3.1268258	-0.3026788
C	-2.8461096	-3.3283648	-0.7696408
H	-2.9479856	-2.9618888	-1.7940388
H	-2.9955796	-4.4052148	-0.7422728
H	-3.5551306	-2.8346338	-0.1005968
C	0.8830504	1.8647672	0.1761512
H	0.2319574	2.6859912	-0.1189768
C	2.1492644	2.1996332	0.6042302
H	2.8400894	1.4219272	0.9097662
C	2.6404584	3.5936522	0.6751062
H	3.5434374	3.6984322	0.0591642
H	1.8988424	4.3282082	0.3543162
H	2.9545504	3.8218682	1.7023232
H	-2.7003926	-0.7598638	-0.9102808
F	2.2038274	-0.6377518	0.8384722

E = -562.490271443

G = -562.340059

4g

C	1.3977745	0.9941437	0.4310686
H	0.9765635	1.7262727	1.1204506
C	2.5718265	1.2614877	-0.1458614
H	2.9792165	0.5480267	-0.8625054
C	3.3875805	2.4931677	0.1042706
H	3.5461755	3.0565757	-0.8232354
H	2.9038425	3.1551967	0.8294026
H	4.3805545	2.2326817	0.4909876
C	0.6245375	-0.2464893	0.2186676
C	-0.7993515	-0.2042423	0.0525386
C	1.2634635	-1.4677873	0.1988616
C	-1.5284455	1.0146217	0.0250996
C	-1.5170345	-1.4231293	-0.1135034
C	0.5509135	-2.6728833	0.0145966
H	2.3372065	-1.5034063	0.3584626
C	-2.8909565	1.0228357	-0.1319934
H	-0.9946025	1.9554547	0.1117926
C	-2.9268895	-1.3819603	-0.2720864
C	-0.8099265	-2.6536503	-0.1306414
H	1.0908975	-3.6150713	0.0057566
C	-3.6020965	-0.1897543	-0.2769054
H	-3.4285645	1.9662747	-0.1517474
H	-3.4638515	-2.3194603	-0.3935884
H	-1.3681775	-3.5774843	-0.2586114
H	-4.6806555	-0.1714213	-0.4012764

E = -502.558125160

G = -502.389295

4g$^+$

C	1.3656575	1.0569086	0.0019306
H	0.8228645	1.9899966	-0.1055134
C	2.7133505	1.1602616	0.1822066
H	3.3193795	0.2681276	0.3234606
C	3.4480645	2.4479736	0.2286296
H	4.2393285	2.4539216	-0.5316494
H	2.7982595	3.3120956	0.0746246
H	3.9571145	2.5510786	1.1955166
C	0.6143225	-0.1613354	-0.0399464
C	-0.8363585	-0.1490594	-0.0408714
C	1.2781265	-1.4195054	-0.1070334
C	-1.5995565	1.0248376	0.0585256
C	-1.5355405	-1.3923894	-0.1284194
C	0.5868055	-2.6086694	-0.1849184
H	2.3607505	-1.4509574	-0.1254364
C	-2.9896835	0.9800646	0.0530516
H	-1.1261985	1.9944126	0.1516746
C	-2.9467535	-1.4131634	-0.1323904
C	-0.8106445	-2.6012084	-0.1987924
H	1.1254925	-3.5476684	-0.2448904
C	-3.6687265	-0.2364984	-0.0453864
H	-3.5499725	1.9058876	0.1295606
H	-3.4593165	-2.3679864	-0.2016264
H	-1.3538565	-3.5398274	-0.2638184
H	-4.7529085	-0.2572974	-0.0484884

E = -502.350568814
G = -502.176198

4h

C	-0.9795306	-1.8714759	0.0361778
C	0.3899874	-1.8688939	0.3033338
C	0.4997504	0.5393681	0.1196718
C	-0.8760836	0.5319921	-0.1349772
C	-1.6233166	-0.6423569	-0.1835222
H	0.8943954	-2.8150149	0.4858808
H	-1.3809356	1.4808221	-0.3089032
C	1.2186824	1.8255181	0.1342048
H	0.5810834	2.7105701	0.1524968
C	2.5420394	2.0037811	0.1044888
H	3.2017944	1.1377591	0.0584498
C	3.2196924	3.3402741	0.1199578
H	3.8436034	3.4759931	-0.7721492
H	2.4936064	4.1586391	0.1550798
H	3.8832894	3.4360151	0.9884248
C	-1.7516556	-3.1650119	-0.0062522
H	-2.2512256	-3.3029919	-0.9728262
H	-1.0943296	-4.0239279	0.1558838
H	-2.5336176	-3.1919309	0.7626258
C	-3.1017706	-0.5911779	-0.4738082
H	-3.3465726	-1.1269199	-1.3992142
H	-3.6867226	-1.0576129	0.3279618

H	-3.4477716	0.4403551	-0.5837262
C	1.1226434	-0.6907919	0.3501648
H	2.1829644	-0.7329809	0.5805768

E = -427.569232611
G = -427.386710

4h$^+$

C	-0.9601274	-1.8549999	0.0168927
C	0.4407556	-1.8617839	0.2158727
C	0.5059346	0.5536011	0.0215937
C	-0.9061864	0.5463841	-0.1801983
C	-1.6432184	-0.6128439	-0.1863323
H	0.9426436	-2.8119099	0.3673377
H	-1.4079784	1.4980961	-0.3325393
C	1.1816036	1.8011471	0.0157667
H	0.5690546	2.6861811	-0.1468553
C	2.5321886	1.9912101	0.1974057
H	3.1804336	1.1333511	0.3633547
C	3.1929946	3.3145121	0.1850037
H	3.9707706	3.3321301	-0.5900223
H	2.4963356	4.1377141	0.0151107
H	3.7178786	3.4743931	1.1362587
C	-1.7188474	-3.1393139	0.0163277
H	-2.2139544	-3.2910169	-0.9511503
H	-1.0740314	-3.9969879	0.2134357
H	-2.5147204	-3.1185199	0.7706767
C	-3.1302034	-0.5861219	-0.3961213
H	-3.4206204	-1.1946469	-1.2591953
H	-3.6579974	-0.9873129	0.4761707
H	-3.4857394	0.4319811	-0.5659603
C	1.1657066	-0.7015379	0.2208547
H	2.2373246	-0.7437049	0.3763117

E = -427.360772711
G = -427.181180

4i

C	-2.3622910	-1.9597033	-0.2342398
C	-0.9853770	-2.0759493	-0.0597518
C	-0.7527660	0.3523367	-0.0962488
C	-2.1396710	0.4236567	-0.2676158
C	-2.9468430	-0.7060813	-0.3388218
H	-0.5468450	-3.0634663	0.0209292
H	-2.5942880	1.4079847	-0.3480078
C	-0.0114680	1.6224657	-0.0359098
H	-0.6649370	2.4954877	-0.0842748
C	1.3028860	1.8550787	0.0596292
H	2.0006670	1.0273857	0.1062062
C	1.8924960	3.2330557	0.1036012
H	2.5852920	3.3907017	-0.7326578
H	1.1208270	4.0085397	0.0573562
H	2.4704640	3.3827727	1.0243462
C	-0.1823660	-0.9372043	0.0094532
H	-4.0188120	-0.6031213	-0.4738108

H	-2.9688820	-2.8589293	-0.2866248
O	1.1640930	-0.9974013	0.1813022
C	1.7741600	-2.2592163	0.3197352
H	1.3896280	-2.7989893	1.1943272
H	1.6357510	-2.8755433	-0.5776288
H	2.8382810	-2.0638593	0.4587062

E = -463.454911071
G = -463.294680

4i^{+}

C	-2.3409978	-1.9484093	-0.2389548
C	-0.9805868	-2.0862293	-0.0636268
C	-0.7615858	0.3802037	-0.0924218
C	-2.1785528	0.4506997	-0.2649178
C	-2.9516148	-0.6719143	-0.3387738
H	-0.5474178	-3.0750813	0.0121882
H	-2.6338188	1.4326747	-0.3425708
C	-0.0563458	1.6094237	-0.0452288
H	-0.6887888	2.4927467	-0.1198168
C	1.2979622	1.8411257	0.0679012
H	1.9838172	1.0046427	0.1302632
C	1.8841472	3.1995417	0.1015642
H	2.6032192	3.3121337	-0.7208398
H	1.1364612	3.9927417	0.0368542
H	2.4666332	3.3275727	1.0237852
C	-0.1697988	-0.9438993	0.0177042
H	-4.0244438	-0.5967803	-0.4742308
H	-2.9575598	-2.8395783	-0.3000228
O	1.1339682	-0.9920643	0.1983442
C	1.8091032	-2.2526753	0.3277472
H	1.4298522	-2.7953393	1.1971082
H	1.6889082	-2.8401763	-0.5857928
H	2.8574402	-2.0013603	0.4737382

E = -463.247651615
G = -463.088859

4j

C	-1.9077615	-2.4813152	-0.2439006
C	-0.5256915	-2.5432932	-0.0767106
C	-0.4009275	-0.1217252	0.0371094
C	-1.7915585	-0.0772232	-0.1194726
C	-2.5386585	-1.2415202	-0.2614886
H	-0.0250215	-3.5069822	-0.0497466
H	-2.2915435	0.8883868	-0.1363546
C	0.3435935	1.1438498	0.1665854
H	-0.2736585	2.0236788	0.3530804
C	1.6638185	1.3121428	0.0558724
H	2.3023895	0.4556318	-0.1584076
C	2.3649935	2.6290918	0.1953444
H	2.9214475	2.8773158	-0.7168126
H	1.6586215	3.4409978	0.3948844
H	3.0942165	2.6024758	1.0145764

C	0.2178735	-1.3790332	0.0667584
H	-3.6160935	-1.1798632	-0.3845796
H	-2.4872665	-3.3930332	-0.3537306
H	1.2912265	-1.4495832	0.2169934

E = -348.935683638
G = -348.805502

4j^{+}

C	-1.8877536	-2.4553950	-0.1988166
C	-0.4829446	-2.5256190	-0.1384636
C	-0.3948456	-0.0977530	-0.0223876
C	-1.8245196	-0.0583580	-0.0851096
C	-2.5550366	-1.2184030	-0.1718056
H	0.0086974	-3.4917200	-0.1608086
H	-2.3239576	0.9055120	-0.0631366
C	0.2982454	1.1340320	0.0657954
H	-0.3097526	2.0369970	0.0802034
C	1.6701714	1.2968890	0.1350754
H	2.3186224	0.4234460	0.1231954
C	2.3410464	2.6082390	0.2265654
H	3.0408744	2.7222300	-0.6129566
H	1.6442254	3.4482690	0.2352814
H	2.9637344	2.6400920	1.1313784
C	0.2572444	-1.3730420	-0.0517286
H	-3.6376226	-1.1859130	-0.2192936
H	-2.4647126	-3.3724080	-0.2673366
H	1.3382834	-1.4370950	-0.0056506

E = -348.719267945
G = -348.590670

4k

C	-1.8664544	-2.4278778	-0.2358169
C	-0.4911814	-2.5106348	-0.0558909
C	-0.3782284	-0.0827518	0.0484591
C	-1.7674304	-0.0422838	-0.1206409
C	-2.5183554	-1.2038408	-0.2666509
H	0.0018256	-3.4755018	-0.0194559
H	-2.2731084	0.9193982	-0.1472289
C	0.3640456	1.1829472	0.1815831
H	-0.2500214	2.0587712	0.3938251
C	1.6819096	1.3533382	0.0438091
H	2.3146996	0.5004082	-0.2007359
C	2.3856176	2.6678332	0.1908251
H	2.9181866	2.9339462	-0.7304289
H	1.6837676	3.4743312	0.4252091
H	3.1358636	2.6237672	0.9900071
C	0.2411236	-1.3390718	0.0896921
H	-3.5929734	-1.1528478	-0.4011989
H	1.3118776	-1.4126098	0.2535011
Br	-2.9011634	-4.0673208	-0.4388619

E = -361.505088002
G = -361.388428

4k$^+$

C	-1.8596744	-2.4186999	-0.1967729
C	-0.4510534	-2.4924299	-0.1364219
C	-0.3716784	-0.0610639	-0.0198589
C	-1.8004874	-0.0280059	-0.0827779
C	-2.5351984	-1.1820969	-0.1697469
H	0.0408706	-3.4579169	-0.1589829
H	-2.3063424	0.9322381	-0.0609229
C	0.3217486	1.1732001	0.0689331
H	-0.2877704	2.0749761	0.0834901
C	1.6893386	1.3346341	0.1382661
H	2.3383056	0.4611581	0.1264841
C	2.3617526	2.6470641	0.2303751
H	3.0603396	2.7638031	-0.6096129
H	1.6626086	3.4855461	0.2388211
H	2.9825756	2.6812121	1.1362041
C	0.2779986	-1.3360049	-0.0496679
H	-3.6176614	-1.1519759	-0.2172709
H	1.3588636	-1.4038379	-0.0037409
Br	-2.8645354	-4.0217989	-0.3167969

E = -361.284639313

G = -361.169174

13- Input file for quasi-classical direct dynamics simulations

The following PROGDYN configuration file, progdyn.conf, is used for all trajectories.

```
#This is the configuration file for PROGDYN.  This file is read by progdynstarterHP and
# the awk programs proggenHP, prog1stpoint, prog2ndpoint, and progdynb.
#The programs won't read anything past the first blank line,
#and this file must end with a blank line.
#The program has a number of default values but they are unlikely to be what you want.
#Do not delete lines - rather, comment out lines for unwanted options.
#The values here are read repeatedly and most can be changed in the middle of running jobs
#***The keywords are case sensitive.  The following keywords should always be defined:***
#***method, charge, multiplicity, memory, processors, title
#*** method --The following word is copied exactly to the gaussian input file.
method wb97xd/6-31G(d)
#To do a nonstandard route, make nonstandard 1.  For normal calcs, use nonstandard 0 or else leave it
out.
#Then make a file called "nonstandard" containing the nonstandard route with no extra lines.
nonstandard 0
# NMRoptions As is NMRtype=1 will add a section for an NMR calc at every NMRevery intervals.  If
you want to combine the two use nonstandard
#NMRtype 1
#NMRmethod2 B97D/6-31G*
#NMRmethod LC-wPBE/6-31G*
#NMRmethod3 B3LYP/cc-pvtz
#NMRevery 4
#NMRrand 1
#NMRcc 1
#loadlimit 10.0
#geometry linear
rotationmode 1
#*** method2 --The options here are restricted, unrestricted, and read. restricted is the default
#If the method is U..., put unrestricted here and the .com files will have in them guess=mix.
#If you put read here, the .com files will contain guess=tcheck, which sometimes makes things faster,
sometimes not.
#The use of read requires a specifically defined checkpoint file name using the keyword checkpoint.
method2 restricted
charge 1
multiplicity 2
#oniomchargemult 1 1
processors 18
#*** memory --The following "word" is copied exactly to the gaussian input file after %mem=.
memory 24gb
#*** killcheck and checkpoint -- You can use a specifically defined checkpoint file name by putting
#the name after the keyword checkpoint.  This is necessary if you use the read option with method2.
#Defined checkpoint names are an unnecessary modest hastle and if you do not want to bother, use
killcheck 1
killcheck 0
checkpoint g09.chk
#*** diagnostics -- 0 prints out nothing extra, 1 (default) prints out extra stuff to a
#file "diagnostics", 2 adds more stuff, 3 adds velocities to a file "vellist"
```

#4 adds the apparent temperature to vellist, but this is meaningless with quasiclassical calculations
diagnostics 0
#*** title -- the title keyword must be followed by exactly four words
title vinylfuran cpdienone 298.15 2XPSdis4
#*** initialdis -- 0 (default) turns off displacement of the normal modes, so that all trajectories start from the same place
and only the energies and signs of the motion in the modes are randomized
1 gives a flat distribution of displacements where all of the possible values are equally likely
2 gives a QM-like gaussian distribution of displacements, so that displacements in the middle are more likely that those at the end by 1/e.
4 a QM-correct distribution bounded by the classical limits of the wavefunction
initialdis 4
#*** timestep -- this is the time between points in the trajectory. Typical values would be 1E-15 or 0.5E-15 or 0.25E-15
timestep 1E-15
#*** scaling -- this lets you scale the gaussian frequencies by a constant
scaling 1.0
temperature 298.15
#*** thermostat 1 puts in a damping factor so as to bring the classical temperature toward the desired temperature.
#*** use a thermostatmult between 0.95 and 1, typically 0.995, so the damping happens slowly - otherwise there will be
#*** overadjustment in response to random variation
#*** the thermostat is not exact. The second traj point ignores this, so it only applies to later points handled by progdynb.
#thermostat 1
#thermostatmult 0.995
#*** method3, method4, method5, and method6 -- These keywords let you add extra lines to the gaussian input file.
#method3 and method4 add lines at the top of the input after the lines defining the method, and
#this is useful to implement things like the iop for mPW1k
#method5 and method6 add lines after the geometry, after a blank line of course
#only a single term with no spaces can be added, one per method line. Here are some examples to uncomment if needed
#method3 empiricaldispersion=gd3bj
#method3 scrf=(solvent=chloroform)
#add the line below with big structures to get it to put out the distance matrix and the input orientation
#method4 empiricaldispersion=gd3
#method4 scf=(conver=5)
#method4 iop(3/124=3)
#method4 scrf=(pcm,solvent=dmso,read)
#method5 radii=bondi
#method6
#*** methodfile -- This keyword lets you add more complicated endings to gaussian input files
#such as a gen basis set. Put after the keyword the number of lines in a file you create called
#methodfile that contains the test you want to add to the end of the gaussian input
#methodfile 15
#*** numimag --This tells the program the number of imaginary frequencies in the starting structure.
#if 0, treats as ground state and direction of all modes is random
#if 1, motion along the reaction coordinate will start out in the direction defined by searchdir
#if 2, only lowest freq will go direction of searchdir and other imag mode will go in random direction

```
numimag 1
#*** searchdir -- This keyword says what direction to follow the mode associated with the imaginary frequency.
#The choices are "negative" and "positive".  Positive moves in the direction defined in the gaussian frequency calculation
#for the imaginary frequency, while negative moves in the opposite direction.  The correct choice can be made either
#by a careful inspection of the normal modes and standard orientation geometry, or by trial and error.
searchdir positive
#*** classical --  for quassiclassical dynamics, the default, use 0.  for classical dynamics, use 1
#if there are no normal modes and the velocities are to be generated from scratch, use classical 2
classical 0
#*** DRP, saddlepoint, and maxAtomMove --to run a DRP use 'DRP 1' in the line below, otherwise leave it at 0 or comment it out
#the treatment of starting saddlepoints is not yet implemented so use saddlepoint no
#if DRP shows oscillations then decrease maxAtomMove
#DRP 1
#saddlepoint no
#maxAtomMove 0.01
#*** cannonball -- The program can "fire" a trajectory from a starting position toward a particular target, such as toward
#a ts.  To use this, make a file cannontraj with numAtom lines and three numbers per line that defines the vector
#for firing the trajectory, relative to the starting geometry's standard orientation.  The number following cannonball sets
#the extra energy being put into the structure in kcal/mol
#cannonball 10
#*** keepevery --This tells the program how often to write the gaussian output file to file dyn, after the first two points.
#Use 1 for most dynamics to start with, but use a higher number to save on disk space or molden loading time.
keepevery 9999
#*** highlevel --For ONIOM jobs, the following line states the number of highlevel atoms,
#which must come before the medium level atoms.  Use some high value such as 999 if not using ONIOM
highlevel 9999
#*** fixedatom1, fixedatom2, fixedatom3, and fixedatom4 - These fix atoms in space.
#Fixing one atom serves no useful purpose and messes things up, while fixing two atoms
#fixes one distance and fixing three has the effect of fixing three distances, not just two
#in current form fixed atoms only are meant to work with no displacements, that is, initialdis=0
#fixedatom1 16
#fixedatom2 1
#fixedatom3 4
#fixedatom4 20
#applyforce 1 lets one push atoms together or appart - a positive force pushes them together
#format is applyforce force     - with the units on force the same as in the Gaussian output file
#applyforce 2 or 3 or 4 applys a polynomical force centered at dist0.  2 is just harmonic, 3 is second order, 4 is third order
#format is applyforce 4 forcecoefficient dist0 forcecoefficient2 forcecoefficient3
#then use afatoms to chose the atoms with format afatoms firstatom secondatom [additional atoms]
#applyforce 2 0.1 2.0
```

#afatoms 24 29
#applyforceB 2 0.1 2.6
#afatomsB 6 9
#applyforceC 2 0.01 5.2
#afatomsC 8 15
#zeroatom pushes the numbered atom toward the origin with a small harmonic potential - good with boxon when you want to keep the reaction in the center
#zeroatom 16
#*** boxon and boxsize - With boxon 1, a cubic box is set such that atoms that reach the edge
#are reflected back toward the middle. Useful for dynamics with solvent molecules. This is a crude
#implementation that is ok for a few thousand femtoseconds but will not conserve energy long term.
#Set the box size so as to fit the entire initial molecule but not have too much extra room.
#The dimensions of the box are two times the boxsize, e.g. boxsize 7.5 leads to a box that is 15 x 15 x 15 angstroms
#boxon 1
#boxsize 11.2
#*** sphereon and spheresize and sphereforce - uses a force to push atoms within a sphere. notice that if the atom is far outside of
#the sphere then the force is large unless sphereforce is set small
#sphereon 1
#spheresize 12.9
#sphereforce .01
#setting a value for empiricaldispersion sets its s6 value with the Grimme 2006 algorithm. Default is 0, with no empiricaldispersion
#empiricaldispersion 1.0
#*** displacements -- This keyword lets you set the initialdis of particular modes by using a series of lines of the format
displacements NumberOfMode InitialDisForThatMode, as in the example below. You should be able to do as many of these as you like
you might consider this for rotations where a straight-line displacement goes wrong at large displacements
The choices for InitialDisForThatMode are 0, 1, 2, and 10, where 10 does the same thing as 0 but is maintained for now because
a previous version of the program had a bug that made 0 not work.
#displacements 2 0
#displacements 3 0
#*** etolerance --This sets the allowable difference between the desired energy in a trajectory and the actual
#energy, known after point 1 from the potential energy + the kinetic energy in the initial velocities.
#The unit is kcal/mol and 1 is a normal value for mid-sized organic systems. For very large and floppy molecules, a larger value
#may be needed, but the value must stay way below the average thermal energy in the molecule (not counting zpe).
#If initialdis is not 0 and few trajectories are being rejected, decrease the value.
etolerance 5
#*** controlphase --It is sometimes useful to set the phase of particular modes in the initialization of trajectories.
#The format is controlphase numberOfModeToControl positive or controlphase numberOfModeToControl negative.
#controlphase 2 positive

#*** damping -- The damping keyword lets you add or subtract energy from the system at each point, by multiplying the velocities
#by the damping factor. A damping of 1 has no effect, and since you mostly want to change the energy slowly, normal values range
#from 0.95 to 1.05. The use of damping lets one do simulated annealing - you add energy until the structure is moving enough
#to sample the kinds of possibilities you are interested in, then you take away the energy slowly.
damping 1.000
#at a damping of .9995, the energy is cut in half in 693 points
#*** reversetraj --This keyword sets the trajectories so that both directions from a transition state are explored.
reversetraj true

#updated Aug 9, 2007 to include the possibility of classical dynamics by the keyword classical
#updated Jan 2008 to include fixed atoms, ONIOM jobs, keepevery, and box size
#update Feb 2008 to include methodfile parameter
updated Nov 2008 to allow for start without an initial freq calc using classical = 2
update Aug 2010 to include etolerance, damping controlphase and reversetraj

14- References

1. Chai, J.-D.; Head-Gordon, M., Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections. *PCCP* **2008,** *10* (44), 6615-6620.

2. Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. V. R., Efficient diffuse function-augmented basis sets for anion calculations. III. The 3-21+G basis set for first-row elements, Li–F. *Journal of Computational Chemistry* **1983,** *4* (3), 294-301.

3. Frisch, M. J.; Pople, J. A.; Binkley, J. S., Self-consistent molecular orbital methods 25. Supplementary functions for Gaussian basis sets. *The Journal of Chemical Physics* **1984,** *80* (7), 3265-3269.

4. Binning, R. C.; Curtiss, L. A., Compact contracted basis sets for third-row atoms: Ga–Kr. *Journal of Computational Chemistry* **1990,** *11* (10), 1206-1216.

5. McGrath, M. P.; Radom, L., Extension of Gaussian-1 (G1) theory to bromine-containing molecules. *The Journal of Chemical Physics* **1991,** *94* (1), 511-516.

6. Hay, P. J.; Wadt, W. R., Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. *The Journal of Chemical Physics* **1985,** *82* (1), 270-283.

7. Wadt, W. R.; Hay, P. J., Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi. *The Journal of Chemical Physics* **1985,** *82* (1), 284-298.

8. Hay, P. J.; Wadt, W. R., Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. *The Journal of Chemical Physics* **1985,** *82* (1), 299-310.

9. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G., Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *The Journal of Physical Chemistry B* **2009,** *113* (18), 6378-6396.

10. Sigma-Aldrich, 1,1,1,3,3,3-Hexafluoro-2-propanol. https://www.sigmaaldrich.com/catalog/product/aldrich/105228

11. Abraham, M. H.; Gola, J. M. R.; Cometto-Muñiz, J. E.; Acree, W. E., Hydrogen Bonding between Solutes in Solvents Octan-1-ol and Water. *The Journal of Organic Chemistry* **2010,** *75* (22), 7651-7658.

12. ChemSpider, Hexafluoroisopropanol. http://www.chemspider.com/Chemical-Structure.12941.html

13. Colomer, I.; Chamberlain, A. E. R.; Haughey, M. B.; Donohoe, T. J., Hexafluoroisopropanol as a highly versatile solvent. *Nature Reviews Chemistry* **2017,** *1* (11), 0088.

14. Richmond, E.; Yi, J.; Vuković, V. D.; Sajadi, F.; Rowley, C. N.; Moran, J., Ring-opening hydroarylation of monosubstituted cyclopropanes enabled by hexafluoroisopropanol. *Chemical Science* **2018,** *9* (30), 6411-6416.

15. Hratchian, H. P.; Schlegel, H. B., Accurate reaction paths using a Hessian based predictor–corrector integrator. *The Journal of Chemical Physics* **2004,** *120* (21), 9918-9924.

16. Collins, M. A., Molecular potential-energy surfaces for chemical reaction dynamics. *Theoretical Chemistry Accounts* **2002,** *108* (6), 313-324.

17. Fukui, K., The path of chemical reactions - the IRC approach. *Acc. Chem. Res.* **1981,** *14* (12), 363-368.

18. Weigend, F.; Ahlrichs, R., Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Physical Chemistry Chemical Physics* **2005,** *7* (18), 3297-3305.

19. Johnson, E. R.; Keinan, S.; Mori-Sánchez, P.; Contreras-García, J.; Cohen, A. J.; Yang, W., Revealing Noncovalent Interactions. *Journal of the American Chemical Society* **2010,** *132* (18), 6498-6506.

20. Lu, T.; Chen, F., Multiwfn: A multifunctional wavefunction analyzer. *Journal of Computational Chemistry* **2012,** *33* (5), 580-592.

21. Marcus, R. A., Chemical and Electrochemical Electron-Transfer Theory. *Annual Review of Physical Chemistry* **1964,** *15* (1), 155-196.

22. Nelsen, S. F.; Blackstock, S. C.; Kim, Y., Estimation of inner shell Marcus terms for amino nitrogen compounds by molecular orbital calculations. *Journal of the American Chemical Society* **1987,** *109* (3), 677-682.

23. Vaissier, V.; Barnes, P.; Kirkpatrick, J.; Nelson, J., Influence of polar medium on the reorganization energy of charge transfer between dyes in a dye sensitized film. *Physical Chemistry Chemical Physics* **2013,** *15* (13), 4804-4814.

24. Manke, F.; Frost, J. M.; Vaissier, V.; Nelson, J.; Barnes, P. R. F., Influence of a nearby substrate on the reorganization energy of hole exchange between dye molecules. *Physical Chemistry Chemical Physics* **2015,** *17* (11), 7345-7354.

25. Wu, Q.; Van Voorhis, T., Constrained Density Functional Theory and Its Application in Long-Range Electron Transfer. *Journal of Chemical Theory and Computation* **2006,** *2* (3), 765-774.

26. Extracting electron transfer coupling elements from constrained density functional theory. *The Journal of Chemical Physics* **2006,** *125* (16), 164105.

27. Nelsen, S. F.; Adamus, J.; Wolff, J. J., Comparison of Intramolecular Electron Transfer Rate Constant with Hush Theory for an Organic Intervalence Compound. *Journal of the American Chemical Society* **1994,** *116* (4), 1589-1590.

28. Blomgren, F.; Larsson, S.; Nelsen, S. F., Electron transfer in bis(hydrazines), a critical test for application of the Marcus model. *Journal of Computational Chemistry* **2001,** *22* (6), 655-664.

29. Zhang, W.; Zhu, W.; Liang, W.; Zhao, Y.; Nelsen, S. F., Ab Initio Calculations on the Intramolecular Electron Transfer Rates of a Bis(hydrazine) Radical Cation. *The Journal of Physical Chemistry B* **2008,** *112* (35), 11079-11086.

30. López-Estrada, O.; Laguna, H. G.; Barrueta-Flores, C.; Amador-Bedolla, C., Reassessment of the Four-Point Approach to the Electron-Transfer Marcus–Hush Theory. *ACS Omega* **2018,** *3* (2), 2130-2140.

31. Singleton, D. A.; Hang, C.; Szymanski, M. J.; Greenwald, E. E., A New Form of Kinetic Isotope Effect. Dynamic Effects on Isotopic Selectivity and Regioselectivity. *Journal of the American Chemical Society* **2003,** *125* (5), 1176-1177.

Hypervalent Iodine-Mediated Styrene Hetero- and Homodimerizations Initiation Proceed with Two-Electron Reductive Cleavage

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Abstract

A mechanistic insight into the hetero- and homodimerizations (HETD and HOMD) of styrenes promoted by hypervalent iodine reagents (HVIRs; **DMP** and **PIDA**) and facilitated by HFIP to yield all *trans* cyclobutanes is reported using density functional theory (DFT) calculations. The reaction is initiated with two-electron reductive cleavage of two I─O bond cleavages, affording I(III) (iodinane) and I(I) (iodobenzene) product with DMP and PIDA as oxidant, respectively. The resulting acetate groups are stabilized by the solvent HFIP through strong hydrogen bonding interaction, which promotes the electron transfer process. The initialization involving one-electron transfer was found to be highly unfavored, especially for the PIDA system. At this point, we found that two-electron process is the key initialization process, which is in accordance with literature report on alcohol oxidation. The reaction rate is determined by the initialization step: For I(III), the initiation is thermodynamically endergonic, whereas the endergonicity for I(V) is modest. The difference in reactivity is explained by the difference LUMO energies. Upon initialization, the reaction proceeds through a stepwise [2+2] pathway, involving a radical-cationic π-π stacked intermediate, either hetero- or homodimerized. DFT results supported by quasiclassical molecular dynamics simulations show that HOMD is dynamically competing pathway to HETD although the latter is relatively faster, in accordance with experimental observations.

Introduction

Stereoselective approaches to substituted cyclobutanes have been captivated by organic chemists to be of high interest despite of its challenging requirements.[1, 2] Due to the fact that these cyclobutane rings exist in many bioactive natural products (Figure 1-a),[3-5] the need for such efficient, reliable, and benign synthesis methods is still under developing strategies to get a purely chiral strained carbocycle. Regardless the many different synthetic methodologies appeared in literatures to access cyclobutanes,[6-11] the olefin dimerization via oxidative manners, which involves an active radical cation intermediate formation, represents a helpful and promising tactic to reach. The olefin dimerization was firstly reported by Ledwith[12, 13] and Bauld,[14-16]. In this regard, metal complexes[17] and organic [18, 19] photoredox catalysis have been applied to promote such a nice cyclization.[20-28] Recently, a major contribution to this field has been exploited by using catalytic amounts of HVIR [29, 30] in HFIP to investigate a stereoselective functionalization of alkenes.[31-33] The HFIP has been shown to be a unique solvent due its significant role of hydrogen bonding [34-36] that enables the HVIR to act as single electron oxidants.[37-40] Based on the utility of the HVIR/HFIP, Donohoe and co-workers have developed a diastereoselective [2+2] cycloaddition of alkenes with remarkable results (Figure 1-b).[41, 42] The mechanism proposed involves a SEO of styrene **1** to a radical cation $\mathbf{1}^{+}$ by HVIR followed by either HOMD, where dimerization proceeds with another molecule of styrene **1** in the presence of I(III) **PIDA**, or HETD, where dimerization proceeds with a different alkene **2** in the presence of I(V) **DMP**, to give the all *trans* cyclobutane product **3** after the re-addition of an electron to the product. The presence of a *p*-methoxy group plays an important role in the success of a styrene toward dimerization.

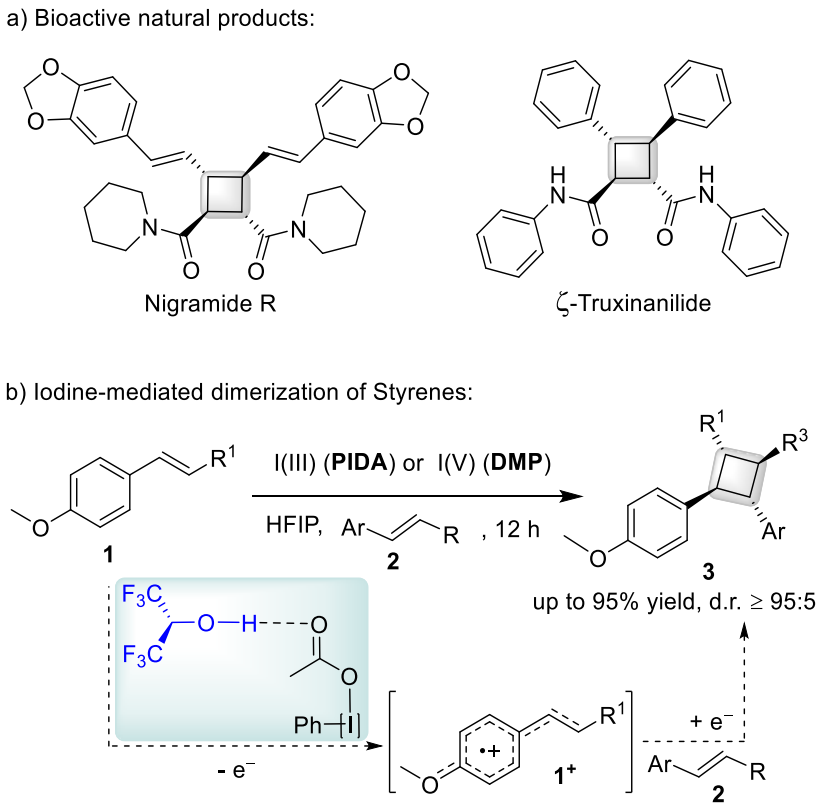


Figure 1. a) Examples of bioactive natural products containing cyclobutane ring. b) HOMD or HETD of styrenes with phenyliodine(III) diacetate (**PIDA**) or Dess-Martin periodinane (**DMP**), respectively .

The existence of hydrogen bonding interactions between the HFIP and **PIDA** has been proposed to be essential and the physical origin of the enhanced oxidative strength for the iodine reagent.[43] In addition to the almost disappearance of HO signals from NMR experiments, the voltammetric peak potential experiments measured versus Fc/Fc^{+} demonstrated a shift in reduction potentials for **PIDA** ($E_{p,c}$ in ACN = −1.32 V, $E_{p,c}$ in HFIP = −0.47 V). The possibility of ligand exchange between HFIP and **PIDA** has been excluded and any altered reactivity to the oxidants is ruled out as the HFIP is a low nucleophilic solvent.[43-47] All of the above-mentioned study concerns the first step of the reaction, the SEO step, and seems to us in need for further understandings despite the subsequent steps that lead to the all *trans* cyclobutane ring are not considered, at least to the best of our knowledge, by other workers under these conditions.[26, 48-50] An important question that should be raised is the number of electrons to be transferred to the iodine reagent to initiate the reaction. At this point, the reaction mechanism and reactivity of HVIR-mediate dimerization exclusively appears incomplete and warrants further attentions (Figure 2). Therefore, we herein interpret DFT simulations on the HOMD and HETD that gives all

trans cyclobutane under HVIRs with **PIDA** and **DMP**, respectively, featuring (1) the nature of initiation whether one or two electron reduction, (2) the effect of HFIP on reactivity of this protocol, and (3) realizing the dynamical nature of homo- and heterodimerization via quasiclassical trajectory molecular dynamics (QCTMD) simulations.

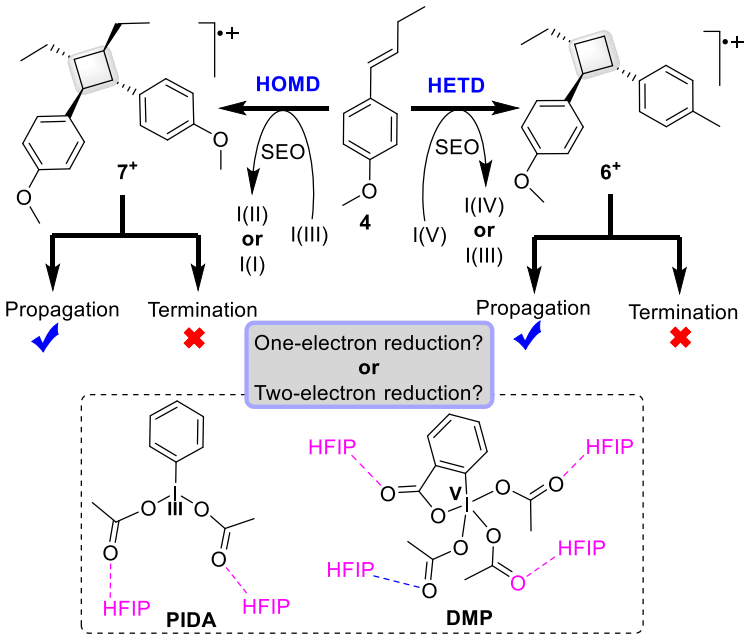


Figure 2. General representation of the HVIR [2+2] cycloaddition considered in this study, where iodine reagents are hydrogen bonded to HFIP explicitly.

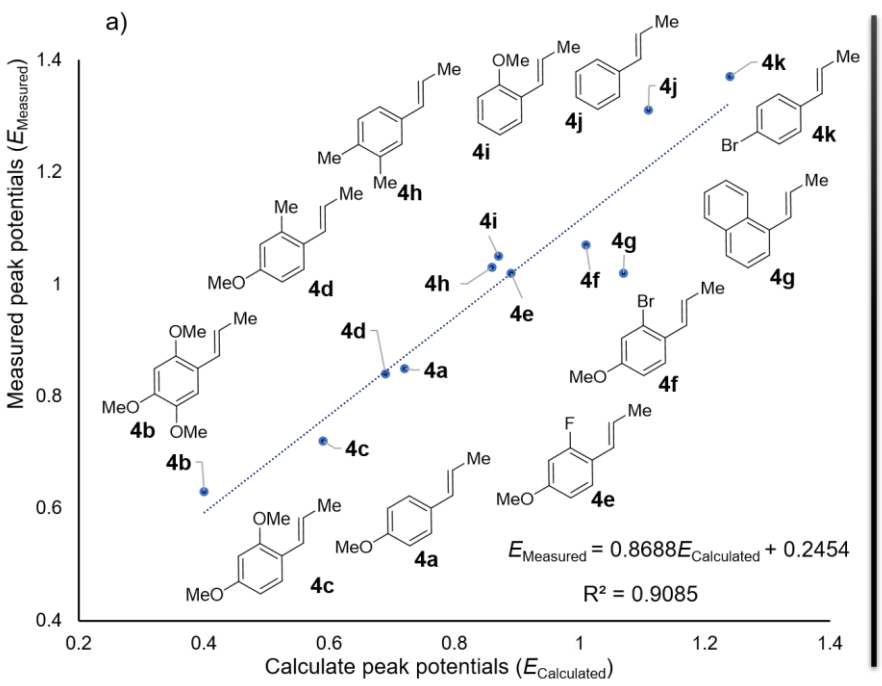
Results and Discussion

To explore our HVIR-mediated dimerization of styrenes, we have divided our discussions into five distinct sections with the following order: validation of our strategy, mechanism of dimerization, molecular dynamics of HOMD and HETD.

Validation of strategy and level of theory

The calculations were conducted in explicit and implicit HFIP. The explicit HFIP protocol means that every single acetate groups in **PIDA** and **DMP** is hydrogen bonded to one HFIP molecule to match the experimental conditions, whereas the implicit protocol is performed only with continuum solvation model based on density

(IEFPCM-SMD). All structures were initially calculated using the *w*B97XD/6-311+G(d,p)/LANL2DZ//6-31G(d)/LANL2DZ level of theory, however we found inconsistencies with the experimental results because of Fe and I atoms. Therefore, we carried out a basis set search on Fe and I atoms through running single point energy calculations on optimized structure by 6-31G(d)/LANL2DZ through comparison between measured and calculated voltammetric peak potentials for redox species of different substituted *trans-β*-methylstyrenes toward **PIDA** (Figure 10, see below). For Fc/Fc^+, as shown in SI, the cyclopentadienyl group in Fc was tested with a basis set of triple- ζ quality (6-31G(d,p)) to be consistent with the valence basis sets used for iron. We found that Def2-TZVPP/6-31G(d,p) level of theory gives the best agreement with the experimental redox potential values of different substituted *trans-β*-methylstyrenes using Cp_2Fe (calculated $E^{1/2}$ = 4.84 V) as reference to calculate their redox potentials (see Figure 10). For iodine in **PIDA**, it was found that the basis set Def2-TZVPP for iodine and 6-311+G(d,p) for C, H, and O atoms gave the best agreement with experimental redox potentials (see SI). Importantly, and under explicit protocol, the calculated value for $\mathbf{PIDA_{HFIP}} + e^- \rightarrow \mathbf{PIDA^-_{HFIP}}$ is $E^{1/2}$ = 4.25 V of peak potential for $\mathbf{PIDA_{HFIP}}$ is $E_{p,c} = -0.59$ V versus calculated peak potential Fc/Fc^+ ($E^{1/2}$ = 4.84 V) as a reference, leading to a good agreement with the measured peak potential for **PIDA** is $E_{p,c} = -0.47$ V. Under implicit protocol, the calculated value of non-hydrogen-bonded **PIDA** is $E^{1/2}$ = 4.02 V of peak potential $E_{p,c} = -0.82$ V versus Fc/Fc^+ with a shifting to more negative value of 230 mV less favorable than explicit $\mathbf{PIDA_{HFIP}}$. Using this strategy, a good agreement between the measured and calculated peak potential have been achieved as shown in Figure 10. Therefore, the *w*B97XD/def2-TZVPP/6-311+G(d) level of theory is used for oxidants whereas the *w*B97XD/def2-TZVPP/6-31G(d,p) level of theory is utilized for Cp_2Fe in order to calculate the redox potentials. Comparison between calculated and measured redox potentials of different substituted *trans-β*-methylstyrenes **4a** – **4k** is indicated in Figure 3. Our strategic DFT simulations present a very good agreement with the experimental redox potentials and free energy of reoxidation accordingly. The explicit-involved HFIP calculations are consistent with experimental results than inexplicit calculations (for comparison see SI). The calculated results appeared in Figure 3-b indicate a deviation from experimental values of around 0.12 eV which is in agreement with the mean absolute error in ionization energy (2.74 kcal mol^{-1}) reported for *w*B97XD.[51]



b)

	Measured		Calculated	
Subs.	$\Delta E_{p\text{-}p}$	$\Delta G°$	$\Delta E_{p\text{-}p}$	$\Delta G°$
4a	−1.31	30.2	−1.20	27.7
4b	−1.10	25.4	−0.88	20.3
4c	−1.19	27.4	−1.07	24.7
4d	−1.31	30.2	−1.17	27.0
4e	−1.49	34.4	−1.37	31.6
4f	−1.54	35.5	−1.49	34.4
4g	−1.49	34.4	−1.55	35.7
4h	−1.50	34.6	−1.34	30.9
4i	−1.52	35.1	−1.35	31.1
4j	−1.78	41.0	−1.60	36.9
4k	−1.84	42.4	−1.72	39.7

Figure 3. (a) Agreement between measured and calculated voltammetric peak potentials (in V) for redox species of different substituted *trans-β*-methylstyrenes **4a** – **4k**. (b) Differences in the reduction and oxidation peak potentials (in V) and their Gibbs free energies (in kcal mol^{-1}) for styrenes **4a** – **4k**. Styrenes **4g** – **4k** did not undergo **PIDA** [2+2] cycloaddition. The measured results were obtained versus Fc/Fc^{+}, as measured at 100 mV s^{-1}.[43] The calculated Fc/Fc^{+} is $E^{1/2}$ = 4.84 V in HFIP. The calculated value for **PIDA$_{HFIP}$** + e^{-} → **PIDA$^{-}_{HFIP}$** is $E^{1/2}$ = 4.25 V. Measured peak potential for **PIDA** is $E_{p,c}$ = −0.47 V.[43] Th calculated peak potential for **PIDA$_{HFIP}$** $E_{p,c}$ = −0.59 V.

Mechanism of dimerization

General Considerations. Our DFT investigations with the exploration of the HETD and HOMD facilitated by **DMP** and **PIDA**, respectively, are considered. Firstly, the cyclobutane ring formation is investigated based on the SEO and single electron reduction (SER). When the SEO and SER are initiated and terminated, respectively, through only HVIR to get cyclobutane ring formed, this is a catalytic mechanism. The more plausible scenario is that the HVIR only initiates the reaction to get the styrene molecule radicalized by SEO and propagation of the reaction proceeds without HVIR and this is an initiated or propagated mechanism as the HVIR serves as an initiator. Secondly, to account better knowledge about the height barrier of SEO, free energy of activation for

the SEO was calculated using four-point method proposed by Nelsen (see SI).[52-54] We are convinced that this method result in a reasonable estimation of the electron transfer (ET) activation barrier. Thirdly, it has been reported that HFIP plays a critical role with oxidizing agent rather than with the radical cation formed.[43] The effect of explicit hydrogen bonding in our calculations is considered only on the SEO steps, whereas the cyclization steps are proceeded with an implicit HFIP protocol.

HETD pathway. The DFT results of HETD in the presence I(V) **DMP** with and without explicit HFIP molecules have been exploited (for comparison between explicit and implicit HFIP see SI). Initially, the iodine catalyst undergoes either one-electron reduction to give I(IV) or two-electron reduction to give I(III), namely iodinane. Both pathways are investigated and shown in Figure 4. On one hand, when the initiation proceeds with a one-electron process, single electron transfer from one styrene to I(V), the free energy of activation for SEO for the FRS was found to be 20.2 kcal mol^{-1} to give radical cation $\mathbf{4}^{+}$ and radical anion $\mathbf{DMP}^{-}_{\mathbf{HFIP}}$ as an endergonic step (ΔG_r = 13.8 kcal mol^{-1}) (Figure 4). In absence of explicit HIFP the barrier for SEO increased to 25.4 kcal mol^{-1} as a more endergonic process (ΔG_r = 21.8 kcal mol^{-1}) (See SI). An apparent increased in the I–O bond distances, clearly represented for the perpendicular acetate units to the phenyl iodine. After the ET, the I–O bond distances elongate from 2.08 and 2.15 Å to 2.63 Å and 2.99 Å when HFIP are not involved in calculations explicitly (see **DMP** and **DMP**$^{-}$ in Figure xx). Elongation is slightly less when HFIP is involved explicitly, where I–O bond length is 2.12 Å is before the SEO and 2.55 Å and 2.77 Å are after the SEO (see $\mathbf{DMP}_{\mathbf{HFIP}}$ and $\mathbf{DMP}^{-}_{\mathbf{HFIP}}$ in Figure 4). On the other hand, a lower and more favored energetic pathway was found when a two-electron reduction process is involved, accompanying by two I─O bond cleavages, occurring through two SEOs from two styrenes give iodinane I(III) and two acetate groups stabilized by strong hydrogen bonding interactions (see $\mathbf{Iodinane \bullet 2AcO}^{-}_{\mathbf{HFIP}}$ in Figure 4). This pathway is lower than one-electron pathway by more than 7.0 kcal mol^{-1}. Here, addition of two electrons from two styrenes found to need only 5.4 kcal mol^{-1} as a free energy of reduction. Similarly, the change in oxidation state I(V)→I(III) has been reported for oxidation of alcohols to give iodinane and two acetic acid molecules.[55-57]

All trails to find a concerted [2+2] cycloaddition TS for the cation cyclobutane formation $\mathbf{6}^{+}$ are unsuccessful and, therefore, a two-step mechanism have been taken through the stepwise cycloaddition. For the first C-C bond formation, the head-to-head first C–C bond formation was found to have a barrier of 8.3 kcal mol^{-1} via

TS $\mathbf{8}^+$ with bond length of 2.20 Å along the TS is established, giving uncyclized intermediate $\mathbf{9}^+$ with C–C bond being formed at 1.58 Å as a thermoneutral step of 0.1 kcal mol^{-1} (Figure 3).[58] The TS $\mathbf{8}^+$ shows a π-π stacking interaction of 3.6 Å. A higher barrier TS of 13.1 kcal mol^{-1} was found without π-π stacking (see Figure SIxx). It seems that the favorable π-π stacking plays an important role in controlling the configurations of the product to be all *trans* cyclobutane. The presence of non-covalent interaction, π-π stacking, for TS $\mathbf{8}^+$ and intermediate $\mathbf{9}^+$ is shown by Reduced Density Gradient (RDG) analysis (see Figure SIxx).[59] Attractive π-π interaction is clearly seen in the green areas between the two phenyl rings. The nature of interaction between $\mathbf{4}^+$ and **5** through TS $\mathbf{8}^+$ has a radical character due to SOMO-HOMO overlapping. The SOMO orbitals located on radical styrene $\mathbf{4}^+$ is overlapped with the HOMOs of **5** with an energy gap if 4.03 eV (see Figure SIxx). The radical cation intermediate $\mathbf{9}^+$ cyclizes to the cationic cyclobutane $\mathbf{6}^+$ in a low barrier step of $\Delta G^{\ddagger}$ = 7.1 kcal mol^{-1} with a long C—C bond of 2.74 Å along TS $\mathbf{10}^+$ but in a slightly exergonic step (ΔG_r = −2.1 kcal mol^{-1}). Noticeably, the new C–C bond formed in cyclobutane $\mathbf{6}^+$ is 1.64 Å whereas all other C–C bonds in the ring are 1.54 Å, and this is attributed to radical character as indicated by the partial delocalization shown by spin density and β-LUMO contours (see Figure SIxx). To release the cyclobutane **6**, the radical cation $\mathbf{6}^+$ undergoes SER by or another styrene to propagate the reaction. The oxidation of styrene **4** by $\mathbf{6}^+$ is nearly to be barrierless of 1.1 kcal mol^{-1} as an exergonic step (ΔG_r = −6.6 kcal mol^{-1}) (Figure 4).

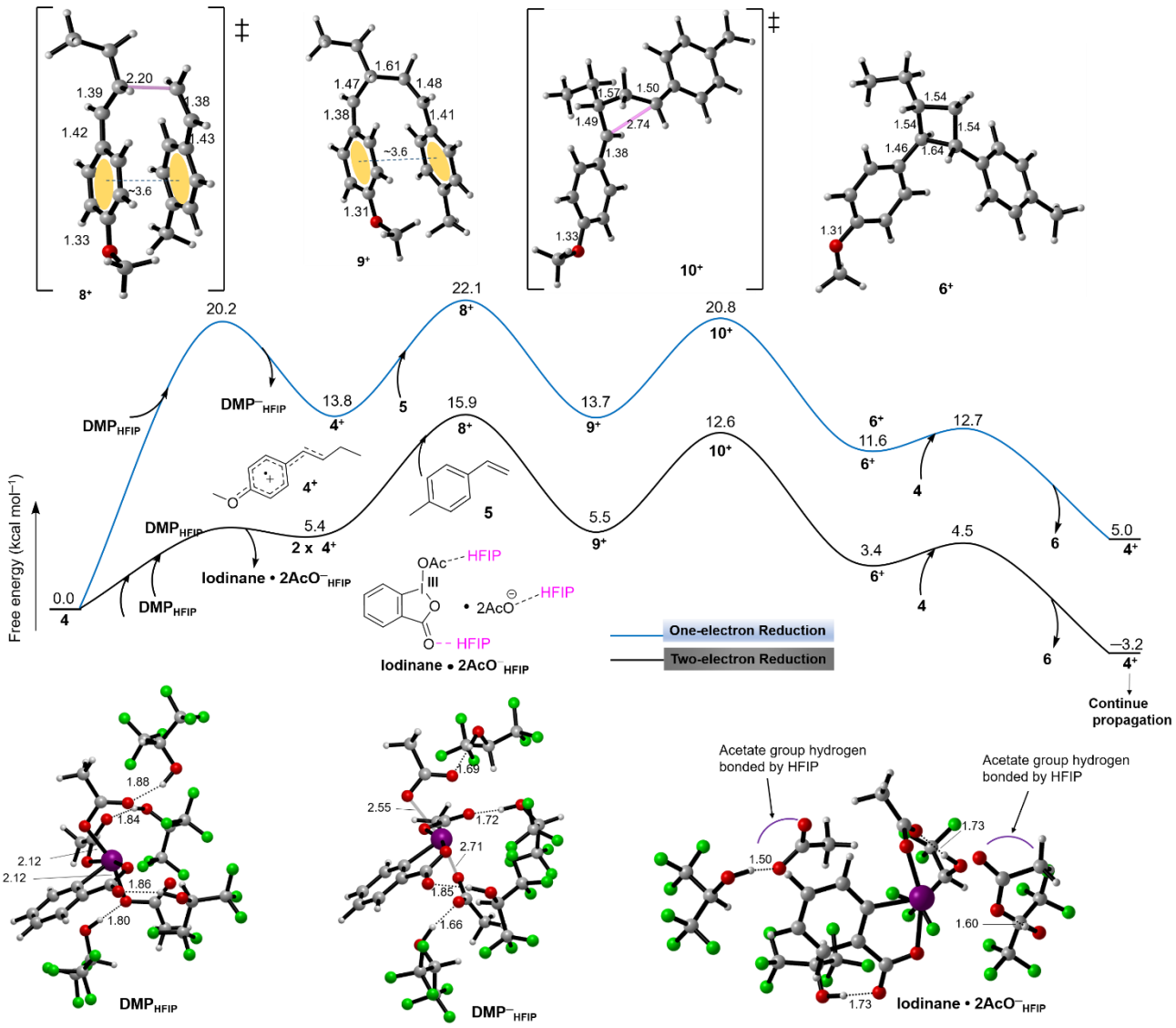


Figure 4. Free energy profile for the mechanism of **DMP**-mediated heterodimerization of styrenes (**4**) and (**5**) to yield cyclobutane **6** under one-electron reduction (blue pathway) and two-electron reduction (black pathway) hydrogen-bonded with HFIP.

HOMD pathway. Following the same strategy for HETD, the HOMD mechanism in the presence I(III) **PIDA** is investigated and shown in Figure 5. Under single electron reductive initiation, the barrier of SEO, the FRS, was found to be 31.3 kcal mol^{-1} to give radical cation **4**$^{+}$ and anion **PIDA**$^{-}_{\mathbf{HFIP}}$ as an endergonic step (ΔG_r = 28.1 kcal mol^{-1}). The SEO for HOMD is more endergonic than for the HETD. The calculated endergonicity for initiation by **PIDA$_{\mathbf{HFIP}}$** is in excellent agreement with that measured for *trans* anethol **14** (see Figure 3).[43] Following the SEO step the bond length of the acetate group to iodine, namely I–O bonds, increases from 2.15

Å to around 2.58 Å for the non-hydrogen bonded **PIDA** (Figure SIxx) and to longer distances of 2.66 Å and 2.78 Å for the hydrogen-bonded one $\mathbf{PIDA_{HFIP}}$ (Figure 5) for the reason mentioned above for SEO by $\mathbf{DMP_{HFIP}}$. However, when a reductive cleavage process, two-electron reduction, iodobenzene and two acetate groups stabilized by HFIP ($\mathbf{Iodobenzene \bullet 2AcO^{-}_{HFIP}}$) as well as two cationic styrenes are produced in a less endergonicity step of 21.4 kcal mol^{-1}. Comparison of one and two electron process initiations, the impact is substantially effective for **PIDA**-HOMD protocol in comparison to **DMP**-HETD protocol. The synthetic utility with **PIDA**/HFIP is considered to be mild conditions and the one-electron reduction would be highly unlikely and, therefore, two-electron process is required to initiate the radically-cationic [2+2] cycloaddition reaction. Reported literatures have shown that I(III), PIDA, undergoes a reductive cleavage of their I-O bonds under to yield the corresponding I(I), namely iodobenzene.[60] This has been also reported for oxidative of alcohols.[44]

The process for $\mathbf{4^{+}}\rightarrow\mathbf{12^{+}}$ has a reasonable barrier of 9.5 kcal mol^{-1} via π-π stacked head-to-head TS $\mathbf{11^{+}}$ with bond length of 2.16 Å to give the cationic uncyclized intermediate $\mathbf{12^{+}}$ as an endergonic step of 4.3 kcal mol^{-1} (Figure 5).[58] The favorable non-covalent interaction that represents the π-π stacking interaction between the two phenyl rings is shown in Figure SIxx. A higher barrier TS of 12.9 kcal mol^{-1} was found for the first C-C bond formation when aromatic rings are not stacked (Figure SIxx). Likely to TS $\mathbf{8^{+}}$, TS $\mathbf{11^{+}}$ has a radical character with an energy gap of 4.86 eV (see Figure SIxx) which is higher than for the HETD ($\mathbf{4^{+}}$ and **5**). The first C–C bond formation in $\mathbf{12^{+}}$ is longer than for that found for the uncyclized heterodimerized intermediate $\mathbf{9^{+}}$. The cyclization, TRS, is a low barrier step of 4.3 kcal mol^{-1} through TS $\mathbf{13^{+}}$ with C—C bond at 2.16 Å is seen to give the cationic homodimerized cyclobutane $\mathbf{7^{+}}$ as an exergonic step ($\mathbf{12^{+}}\rightarrow\mathbf{7^{+}}$, $\Delta G_r = -5.3$ kcal mol^{-1}, Figure 5). Upon formation of $\mathbf{7^{+}}$, the unpaired electron has totally delocalized over the entire system of $\mathbf{7^{+}}$ (see Figure SIxx) and resulted in an increase in the new C–C bond to be 1.71 Å, being longer than for $\mathbf{6^{+}}$. The release of neutral homodimerized cyclobutane **7** via propagation process (Figure 5) is calculated to be kinetically and thermodynamically favored. The oxidation of styrene **4** by $\mathbf{7^{+}}$ is found to be nearly barrierless of 1.5 kcal mol^{-1} as an exergonic step ($\Delta G_r = -6.3$ kcal mol^{-1}) in order to propagate the reaction.

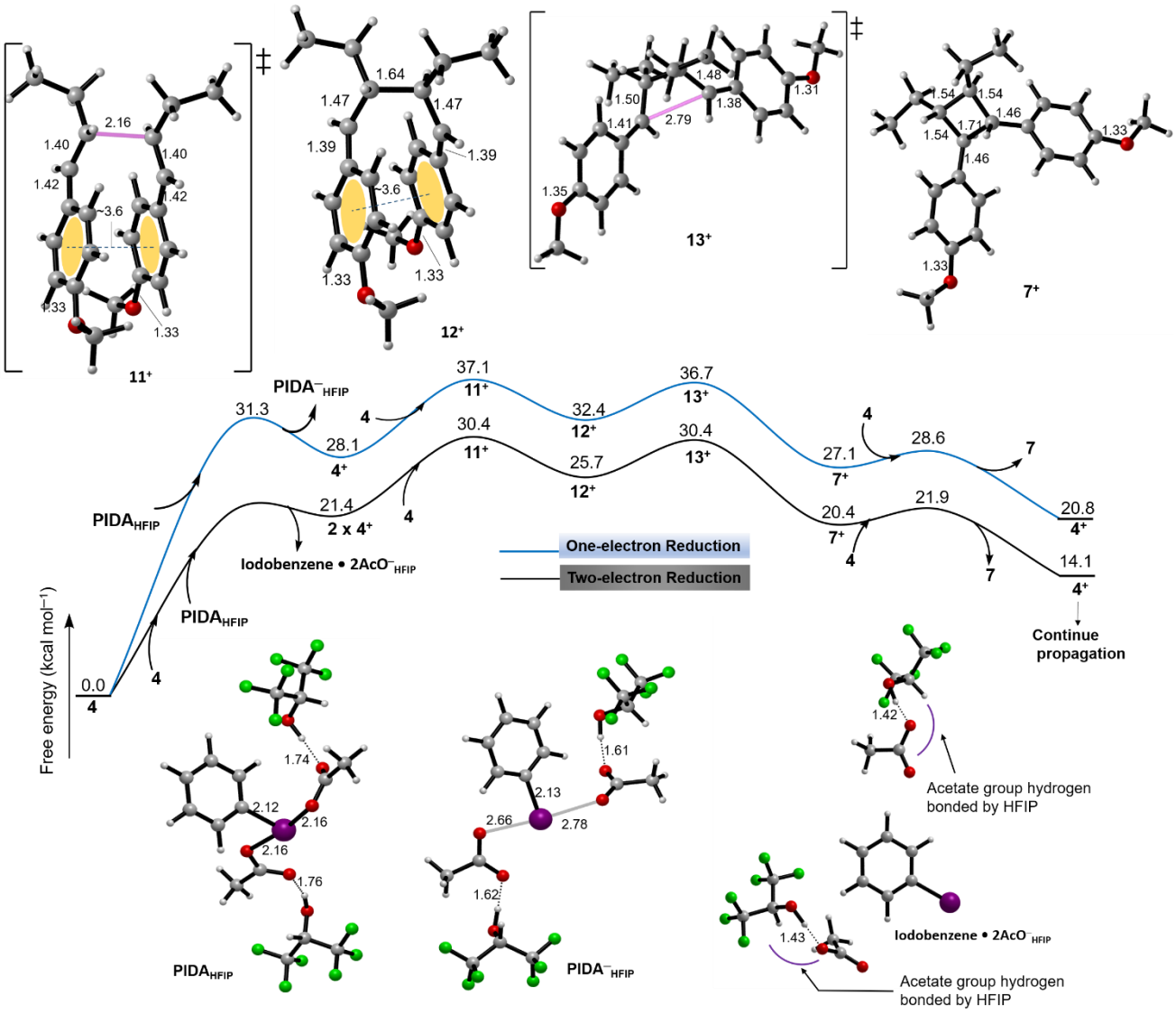


Figure 5. Free energy profile for the mechanism of **PIDA**-mediated heterodimerization of styrenes (**4**) to yield cyclobutane **7** under one-electron reduction (blue pathway) and two-electron reduction (black pathway) hydrogen-bonded with HFIP.

Molecular dynamics of HETD and HOMD

In general, the initiative SEO step from styrene **4** is shown to be more reactive with **DMP** catalyst since the SEO occurs with the more deficient catalyst I(V) (LUMO = –1.56 eV) over less deficient one I(III) (LUMO = –0.73 eV) (see Figure SIxx), apparently indicating that the initiation in HETD is faster than HOMD under **DMP** conditions. However, and from a synthetically perspective point of view, there is a relative competition between

both processes which is experimentally seen (see SI for ref 41).[41] The calculations indicate that once the radical cation $\mathbf{4}^+$ is formed, entering homo [2+2] cycloaddition is relatively possible. The results above (Figure 4 and 5) reveal that the HOMD starts with a barrier of 9.5 kcal mol^{-1} via TS $\mathbf{11}^+$ whereas HETD starts with lower barriers of 8.3 kcal mol^{-1} via TS $\mathbf{8}^+$, implying a barrier difference of $\Delta\Delta G^{\ddagger}$ = 1.2 kcal mol^{-1}. This refers to that the HETD is comparingly predominant. This is in general good agreement with the experimental findings, in which the HETD reaction proceeds an equivalent ratio of styrenes **5** to **4** of 2:1. A further evidence for the competition between HOMD and HETD is emerged form QCT molecular dynamics of the first C–C bond formation (shown below).

Quasiclassical trajectory molecular dynamics (QCTMD) simulations were utilized to understand the chronological character for formation of first C–C bonds in the HETD and HOMD (Figure 7).[61-67] The QCTMD simulations were carried out using the PROGDYN program, [68] a script suite that works in combination with Gaussian 09. 44 and 63 trajectories were generated starting from the TSs $\mathbf{8}^+$ and $\mathbf{11}^+$, respectively, in which forward and backward propagations (t = 0 fs) are initiated showing the typical reactive bonds toward either cationic uncyclized intermediates ($\mathbf{9}^+$ and $\mathbf{12}^+$) or reactants (styrene $\mathbf{4}^+$, **4** and **5**). No recrossing is observed in our simulation. The C3–C4 distance is rapidly shortened to ~1.6 Å in most trajectories, and the bond remains in the whole trajectory once formed although for a small proportion of trajectories the C3–C4 distance oscillates in the range between 1.6 Å and 2.0 Å. By recording the timing for the C3–C4 distance to be shortened below 1.6 Å, we obtained the average timing for the first C–C bond formation at 43.0 and 47.0 fs for HETD $\mathbf{8}^+$ and HOMD $\mathbf{11}^+$, respectively. It is interesting that although the average timing is similar, there are more trajectories exhibiting larger timing for C–C bond formation for the HOMD pathway, which may indicate a flatter potential energy surface in the post-transition state period. Comparison of the average time for the first C–C bond formation through TS $\mathbf{8}^+$ and TS $\mathbf{11}^+$ reveals a short timing gap of 4.0 fs. Also, the timing for first C–C bond formation for the unstacked TSs were obtained and shown a short timing gap where 46 fs for HOMD, derived from 24 trajectories, and 44 fs for HETD, derived from 20 trajectories (see Figure SIxx in SI). Overall, the very small timing gap between both pathways explains that HETD and HOMD are dynamically competitive.

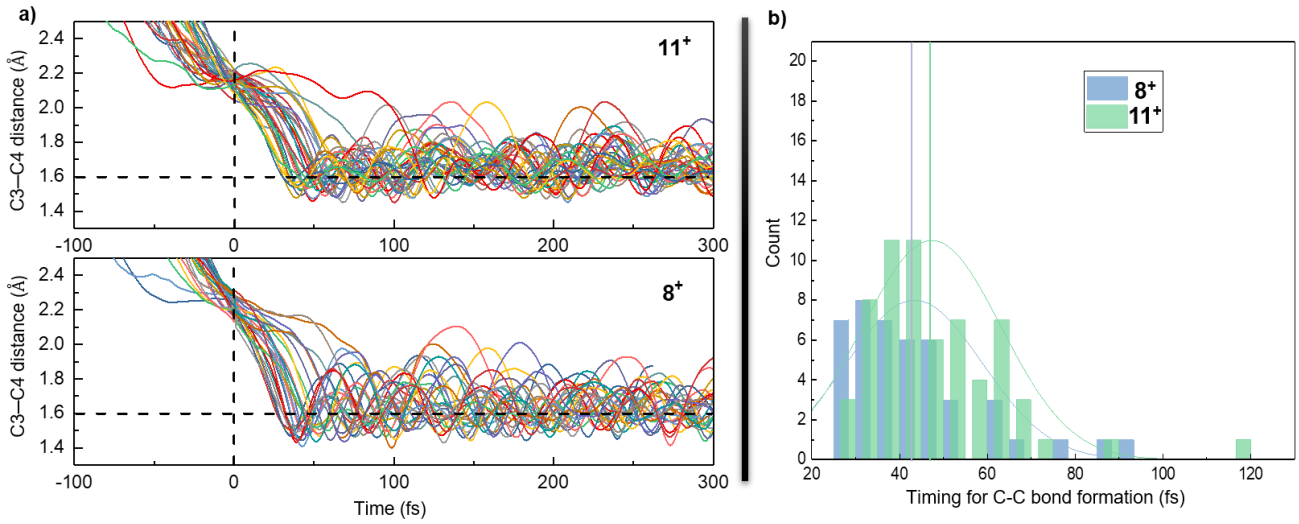


Figure 7. (a) Evolution of the C–C distance corresponding to the first C–C bond formation along quasiclassical trajectories initialized from TSs $\mathbf{8}^{+}$ and $\mathbf{11}^{+}$ calculated by the *w*B97XD/6-31G(d) level of theory. All trajectories start from the initial geometry (t = 0 fs) generated by adding a random displacement to the transition state, and both directions are shown in positive and negative part of the horizontal axis. (b) A histogram for the C–C bond formation timing, where the average timing for each reaction is shown by the vertical line.

Conclusions

DFT calculations at the (SMD)-*w*B97XD/Def2-TZVPP,6-311+G(d,p)//*w*B97XD/6-31G(d),LANL2DZ level of theory were exploited to provide mechanistic insights into the HVIR-promoted hetero- and homodimerizations of styrenes facilitated by HFIP. The computational level was validated through comparison between calculated and measured redox potentials of different substituted *trans*-*β*-methylstyrenes. The findings achieved in this study can be summarized as follows.

First, the hypervalent iodine-mediated hetero- and homodimerizations of styrenes initiated with two-electron reductive cleavage of two I─O bond cleavages giving iodinane I(III) and iodobenzene I(I) when **DMP** and **PIDA** are used, respectively, plus two acetate groups stabilized by strong hydrogen bonding interactions provided by HFIP. Accordingly, the propagation of the reaction is accomplished by radically-cationic hetero- and homodimerized cyclic intermediates. However, a disfavored initiation via a one-electron reduction was found, especially for the HOMD in the presence of **PIDA** where initiation become highly unlikely to take place.

This is agreement with the mild experimental conditions and, therefore, two-electron process is required to initiate the radically-cationic [2+2] cycloaddition reaction. Also, the change in oxidation state reported here, I(V)→I(III) and I(III)→I(I), are commensurate with the oxidation of alcohols by hypervalent iodine reagents.

Second. the mechanism of HETD and HOMD is a radically-characterized π-π stacked head-to-head stepwise [2+2] cycloaddition initiated via SEO by **DMP** and **PIDA**, respectively. DFT results supported by quasiclassical molecular dynamics simulations show that HOMD is dynamically competing pathway to HETD although the latter is relatively faster, in accordance with experimental observations.

Third, the rate-determining step was evaluated to be critical with I(III) to initiate the reaction as a thermodynamically endergonic whereas endergonicity from I(V) initiation showed to be very modest. The initiative SEO step was computed to be more reactive with **DMP** catalyst as the SEO occurs with the more deficient catalyst I(V) (lower LUMO) over less deficient one I(III) (higher LUMO).

Overall, this mechanistic study brings significantly important insights into a such influential synthetic utility and opens possibilities toward advancing an efficient protocol for stereoselective approaches of simple and complex hetero- and homodimerizations. We envision that using DFT simulations on catalyzed SEO will enhance and warrant further attentions toward developing various oxidants to synthetically access a wide range of substrates used for bioactive and synthetic cyclobutane-containing products in a more efficiently-controlled fashion.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Further computational results, absolute energies and cartesian coordinates (PDF)

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Notes

The authors declare no competing financial interest.

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References

1. Xu, Y.; Conner, M. L.; Brown, M. K., Cyclobutane and Cyclobutene Synthesis: Catalytic Enantioselective 2+2 Cycloadditions. *Angewandte Chemie-International Edition* **2015,** *54* (41), 11918-11928.
2. Margaretha, P., Retrospective View on Recent Developments in Cyclobutane Synthesis via [2+2] Photocycloaddition of Unsaturated Ketones to Acyclic Dienes. *Helvetica Chimica Acta* **2014,** *97* (7), 1027-1035.

3. Dembitsky, V. M., Naturally occurring bioactive Cyclobutane-containing (CBC) alkaloids in fungi, fungal endophytes, and plants. *Phytomedicine* **2014,** *21* (12), 1559-1581.
4. Dembitsky, V. M., Bioactive cyclobutane-containing alkaloids. *Journal of Natural Medicines* **2008,** *62* (1), 1-33.
5. Cretton, S.; Bartholomeusz, T. A.; Jeannerat, D.; Munoz, O.; Christen, P.; Hostettmann, K., New cyclobutane-containing tropane alkaloids from the aerial parts of Schizanthus grahamii. *Planta Medica* **2009,** *75* (9), 916-916.
6. Ito, H.; Toyoda, T.; Sawamura, M., Stereospecific Synthesis of Cyclobutylboronates through Copper(I)-Catalyzed Reaction of Homoallylic Sulfonates and a Diboron Derivative. *Journal of the American Chemical Society* **2010,** *132* (17), 5990-5992.
7. Noucti, N. N.; Alexanian, E. J., Stereoselective Nickel- Catalyzed 2+2 Cycloadditions of EneAllenes. *Angewandte Chemie-International Edition* **2015,** *54* (18), 5447-5450.
8. Gulías, M.; Collado, A.; Trillo, B.; López, F.; Oñate, E.; Esteruelas, M. A.; Mascareñas, J. L., Ruthenium-Catalyzed (2 + 2) Intramolecular Cycloaddition of Allenenes. *Journal of the American Chemical Society* **2011,** *133* (20), 7660-7663.
9. Luzung, M. R.; Mauleón, P.; Toste, F. D., Gold(I)-Catalyzed [2 + 2]-Cycloaddition of Allenenes. *Journal of the American Chemical Society* **2007,** *129* (41), 12402-12403.
10. Chiba, K.; Miura, T.; Kim, S.; Kitano, Y.; Tada, M., Electrocatalytic Intermolecular Olefin Cross-Coupling by Anodically Induced Formal [2+2] Cycloaddition between Enol Ethers and Alkenes. *Journal of the American Chemical Society* **2001,** *123* (45), 11314-11315.
11. Rath, B. B.; Kole, G. K.; Morris, S. A.; Vittal, J. J., Rotation of a helical coordination polymer by mechanical grinding. *Chemical Communications* **2020**.
12. Ledwith, A., Cation radicals in electron transfer reactions. *Accounts of Chemical Research* **1972,** *5* (4), 133-139.
13. Bell, F. A.; Crellin, R. A.; Fujii, H.; Ledwith, A., Cation-radicals: metal-catalysed cyclodimerisation of aromatic enamines. *Journal of the Chemical Society D: Chemical Communications* **1969,** (6), 251-252.
14. Bauld, N. L.; Bellville, D. J.; Harirchian, B.; Lorenz, K. T.; Pabon, R. A.; Reynolds, D. W.; Wirth, D. D.; Chiou, H. S.; Marsh, B. K., Cation radical pericyclic reactions. *Accounts of Chemical Research* **1987,** *20* (10), 371-378.
15. Bauld, N. L.; Bellville, D. J.; Pabon, R.; Chelsky, R.; Green, G., Theory of cation-radical pericyclic reactions. *Journal of the American Chemical Society* **1983,** *105* (8), 2378-2382.
16. Bauld, N. L.; Pabon, R., Cation radical catalyzed olefin cyclodimerization. *Journal of the American Chemical Society* **1983,** *105* (3), 633-634.
17. Ischay, M. A.; Ament, M. S.; Yoon, T. P., Crossed intermolecular [2 + 2] cycloaddition of styrenes by visible light photocatalysis. *Chemical Science* **2012,** *3* (9), 2807-2811.
18. Riener, M.; Nicewicz, D. A., Synthesis of cyclobutane lignans via an organic single electron oxidant–electron relay system. *Chemical Science* **2013,** *4* (6), 2625-2629.
19. Jiang, Y.; Wang, C.; Rogers, C. R.; Kodaimati, M. S.; Weiss, E. A., Regio- and diastereoselective intermolecular [2+2] cycloadditions photocatalysed by quantum dots. *Nature Chemistry* **2019,** *11* (11), 1034-1040.
20. Ischay, M. A.; Lu, Z.; Yoon, T. P., [2+2] Cycloadditions by Oxidative Visible Light Photocatalysis. *Journal of the American Chemical Society* **2010,** *132* (25), 8572-8574.
21. Lu, Z.; Yoon, T. P., Visible Light Photocatalysis of [2+2] Styrene Cycloadditions by Energy Transfer. *Angewandte Chemie International Edition* **2012,** *51* (41), 10329-10332.
22. Hurtley, A. E.; Lu, Z.; Yoon, T. P., [2+2] Cycloaddition of 1,3-Dienes by Visible Light Photocatalysis. *Angewandte Chemie International Edition* **2014,** *53* (34), 8991-8994.
23. Fleming, S. A.; Ward, S. C., Stereocontrolled photochemical [2 + 2] cycloaddition. *Tetrahedron Letters* **1992,** *33* (8), 1013-1016.
24. Ward, S. C.; Fleming, S. A., [2 + 2] Photocycloaddition of Cinnamyloxy Silanes. *The Journal of Organic Chemistry* **1994,** *59* (21), 6476-6479.
25. Horibe, T.; Katagiri, K.; Ishihara, K., Radical-Cation-Induced Crossed [2+2] Cycloaddition of Electron-Deficient Anetholes Initiated by Iron(III) Salt. *Advanced Synthesis & Catalysis* **2020,** *362* (4), 960-963.
26. Zhao, L.-M.; Lei, T.; Liao, R.-Z.; Xiao, H.; Chen, B.; Ramamurthy, V.; Tung, C.-H.; Wu, L.-Z., Visible-Light-Triggered Selective Intermolecular [2+2] Cycloaddition of Extended Enones: 2-Oxo-3-enoates and 2,4-Dien-1-ones with Olefins. *The Journal of Organic Chemistry* **2019,** *84* (14), 9257-9269.
27. Li, R.; Ma, B. C.; Huang, W.; Wang, L.; Wang, D.; Lu, H.; Landfester, K.; Zhang, K. A. I., Photocatalytic Regioselective and Stereoselective [2 + 2] Cycloaddition of Styrene Derivatives Using a Heterogeneous Organic Photocatalyst. *ACS Catalysis* **2017,** *7* (5), 3097-3101.
28. Amjaour, H.; Wang, Z.; Mabin, M.; Puttkammer, J.; Busch, S.; Chu, Q. R., Scalable preparation and property investigation of a cis-cyclobutane-1,2-dicarboxylic acid from β-trans-cinnamic acid. *Chemical Communications* **2019,** *55* (2), 214-217.
29. Yoshimura, A.; Zhdankin, V. V., Advances in Synthetic Applications of Hypervalent Iodine Compounds. *Chemical Reviews* **2016,** *116* (5), 3328-3435.

30. Li, Y.; Hari, D. P.; Vita, M. V.; Waser, J., Cyclic Hypervalent Iodine Reagents for Atom-Transfer Reactions: Beyond Trifluoromethylation. *Angewandte Chemie International Edition* **2016,** *55* (14), 4436-4454.
31. Colomer, I.; Chamberlain, A. E. R.; Haughey, M. B.; Donohoe, T. J., Hexafluoroisopropanol as a highly versatile solvent. *Nature Reviews Chemistry* **2017,** *1* (11), 0088.
32. Zhu, Y.; Colomer, I.; Thompson, A. L.; Donohoe, T. J., HFIP Solvent Enables Alcohols To Act as Alkylating Agents in Stereoselective Heterocyclization. *Journal of the American Chemical Society* **2019,** *141* (16), 6489-6493.
33. Colomer, I.; Barcelos, R. C.; Christensen, K. E.; Donohoe, T. J., Orthogonally Protected 1,2-Diols from Electron-Rich Alkenes Using Metal-Free Olefin syn-Dihydroxylation. *Organic Letters* **2016,** *18* (22), 5880-5883.
34. Raheem, I. T.; Thiara, P. S.; Peterson, E. A.; Jacobsen, E. N., Enantioselective Pictet−Spengler-Type Cyclizations of Hydroxylactams: H-Bond Donor Catalysis by Anion Binding. *Journal of the American Chemical Society* **2007,** *129* (44), 13404-13405.
35. Lv, H.; Zhan, J.-H.; Cai, Y.-B.; Yu, Y.; Wang, B.; Zhang, J.-L., π–π Interaction Assisted Hydrodefluorination of Perfluoroarenes by Gold Hydride: A Case of Synergistic Effect on C–F Bond Activation. *Journal of the American Chemical Society* **2012,** *134* (39), 16216-16227.
36. Doyle, A. G.; Jacobsen, E. N., Small-Molecule H-Bond Donors in Asymmetric Catalysis. *Chemical Reviews* **2007,** *107* (12), 5713-5743.
37. Nicolaou, K. C.; Baran, P. S.; Zhong, Y.-L.; Vega, J. A., Novel IBX-Mediated Processes for the Synthesis of Amino Sugars and Libraries Thereof. *Angewandte Chemie International Edition* **2000,** *39* (14), 2525-2529.
38. Nicolaou, K. C.; Baran, P. S.; Zhong, Y. L.; Barluenga, S.; Hunt, K. W.; Kranich, R.; Vega, J. A., Iodine(V) Reagents in Organic Synthesis. Part 3. New Routes to Heterocyclic Compounds via o-Iodoxybenzoic Acid-Mediated Cyclizations: Generality, Scope, and Mechanism. *Journal of the American Chemical Society* **2002,** *124* (10), 2233-2244.
39. Nicolaou, K. C.; Baran, P. S.; Kranich, R.; Zhong, Y.-L.; Sugita, K.; Zou, N., Mechanistic Studies of Periodinane-Mediated Reactions of Anilides and Related Systems. *Angewandte Chemie International Edition* **2001,** *40* (1), 202-206.
40. Janza, B.; Studer, A., Stereoselective Cyclization Reactions of IBX-Generated Alkoxyamidyl Radicals. *The Journal of Organic Chemistry* **2005,** *70* (17), 6991-6994.
41. Colomer, I.; Coura Barcelos, R.; Donohoe, T. J., Catalytic Hypervalent Iodine Promoters Lead to Styrene Dimerization and the Formation of Tri- and Tetrasubstituted Cyclobutanes. *Angewandte Chemie International Edition* **2016,** *55* (15), 4748-4752.
42. Zhu, Y.; Colomer, I.; Donohoe, T. J., Hypervalent iodine initiated intramolecular alkene dimerisation: a stereodivergent entry to cyclobutanes. *Chemical Communications* **2019,** *55* (69), 10316-10319.
43. Colomer, I.; Batchelor-McAuley, C.; Odell, B.; Donohoe, T. J.; Compton, R. G., Hydrogen Bonding to Hexafluoroisopropanol Controls the Oxidative Strength of Hypervalent Iodine Reagents. *Journal of the American Chemical Society* **2016,** *138* (28), 8855-8861.
44. Farshadfar, K.; Chipman, A.; Yates, B. F.; Ariafard, A., DFT Mechanistic Investigation into BF3-Catalyzed Alcohol Oxidation by a Hypervalent Iodine(III) Compound. *ACS Catalysis* **2019,** *9* (7), 6510-6521.
45. Ganji, B.; Ariafard, A., DFT mechanistic investigation into phenol dearomatization mediated by an iodine(iii) reagent. *Organic & Biomolecular Chemistry* **2019,** *17* (14), 3521-3528.
46. Kaur, A.; Ariafard, A., Mechanistic investigation into phenol oxidation by IBX elucidated by DFT calculations. *Organic & Biomolecular Chemistry* **2020,** *18* (6), 1117-1129.
47. De Munari, S.; Frigerio, M.; Santagostino, M., Hypervalent Iodine Oxidants: Structure and Kinetics of the Reactive Intermediates in the Oxidation of Alcohols and 1,2-Diols by o-Iodoxybenzoic Acid (IBX) and Dess−Martin Periodinane. A Comparative 1H-NMR Study. *The Journal of Organic Chemistry* **1996,** *61* (26), 9272-9279.
48. O'Nei, L. L.; Wiest, O., Acyclic or Long-Bond Intermediate in the Electron-Transfer-Catalyzed Dimerization of 4-Methoxystyrene. *The Journal of Organic Chemistry* **2006,** *71* (23), 8926-8933.
49. Guo, C.; Cui, L.; Chen, B.; Yuan, J.; Tian, Z., A theoretical study on the stereoconvergency of the intramolecular radical cation [2+2] cycloadditions of bis(styrenes). *RSC Advances* **2012,** *2* (26), 9932-9937.
50. Li, Y.; Guo, C.; Chen, B.-Z., A theoretical study on intermolecular [2+2] radical cation cycloaddition reactions and the competition between concerted and stepwise mechanisms. *Computational and Theoretical Chemistry* **2016,** *1078*, 163-172.
51. Chai, J.-D.; Head-Gordon, M., Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections. *PCCP* **2008,** *10* (44), 6615-6620.
52. Nelsen, S. F.; Blackstock, S. C.; Kim, Y., Estimation of inner shell Marcus terms for amino nitrogen compounds by molecular orbital calculations. *Journal of the American Chemical Society* **1987,** *109* (3), 677-682.
53. Vaissier, V.; Barnes, P.; Kirkpatrick, J.; Nelson, J., Influence of polar medium on the reorganization energy of charge transfer between dyes in a dye sensitized film. *Physical Chemistry Chemical Physics* **2013,** *15* (13), 4804-4814.

54. Manke, F.; Frost, J. M.; Vaissier, V.; Nelson, J.; Barnes, P. R. F., Influence of a nearby substrate on the reorganization energy of hole exchange between dye molecules. *Physical Chemistry Chemical Physics* **2015,** *17* (11), 7345-7354.
55. Meyer, S. D.; Schreiber, S. L., Acceleration of the Dess-Martin Oxidation by Water. *The Journal of Organic Chemistry* **1994,** *59* (24), 7549-7552.
56. Dess, D. B.; Martin, J. C., A useful 12-I-5 triacetoxyperiodinane (the Dess-Martin periodinane) for the selective oxidation of primary or secondary alcohols and a variety of related 12-I-5 species. *Journal of the American Chemical Society* **1991,** *113* (19), 7277-7287.
57. Dess, D. B.; Martin, J. C., Readily accessible 12-I-5 oxidant for the conversion of primary and secondary alcohols to aldehydes and ketones. *The Journal of Organic Chemistry* **1983,** *48* (22), 4155-4156.
58. Demaille, C.; Bard, A. J., Kinetics and mechanism of the anodic dimerization of trans-anethole studied by cyclic voltammetry and scanning electrochemical microscopy. *Acta Chemica Scandinavica* **1999,** *53* (10), 842-848.
59. Johnson, E. R.; Keinan, S.; Mori-Sánchez, P.; Contreras-García, J.; Cohen, A. J.; Yang, W., Revealing Noncovalent Interactions. *Journal of the American Chemical Society* **2010,** *132* (18), 6498-6506.
60. Kokkinidis, G.; Hatzigrigoriou, E.; Sazou, D.; Varvoglis, A., Electrochemical reduction of some hypervalent iodine compounds. *Electrochimica Acta* **1991,** *36* (9), 1391-1395.
61. Burns, J. M.; Boittier, E. D., Pathway Bifurcation in the (4 + 3)/(5 + 2)-Cycloaddition of Butadiene and Oxidopyrylium Ylides: The Significance of Molecular Orbital Isosymmetry. *The Journal of Organic Chemistry* **2019**.
62. Villar López, R.; Faza, O. N.; Silva López, C., Dynamic Effects Responsible for High Selectivity in a [3,3] Sigmatropic Rearrangement Featuring a Bispericyclic Transition State. *The Journal of Organic Chemistry* **2017,** *82* (9), 4758-4765.
63. Patel, A.; Chen, Z.; Yang, Z. Y.; Gutierrez, O.; Liu, H. W.; Houk, K. N.; Singleton, D. A., Dynamically Complex 6+4 and 4+2 Cycloadditions in the Biosynthesis of Spinosyn A. *Journal of the American Chemical Society* **2016,** *138* (11), 3631-3634.
64. Xu, L.; Doubleday, C. E.; Houk, K. N., Dynamics of Carbene Cycloadditions. *Journal of the American Chemical Society* **2011,** *133* (44), 17848-17854.
65. Xu, L.; Doubleday, C. E.; Houk, K. N., Dynamics of 1,3-Dipolar Cycloadditions: Energy Partitioning of Reactants and Quantitation of Synchronicity. *Journal of the American Chemical Society* **2010,** *132* (9), 3029-3037.
66. Black, K.; Liu, P.; Xu, L.; Doubleday, C.; Houk, K. N., Dynamics, transition states, and timing of bond formation in Diels-Alder reactions. *Proceedings of the National Academy of Sciences of the United States of America* **2012,** *109* (32), 12860-12865.
67. Patel, A.; Chen, Z.; Yang, Z.; Gutiérrez, O.; Liu, H.-w.; Houk, K. N.; Singleton, D. A., Dynamically Complex [6+4] and [4+2] Cycloadditions in the Biosynthesis of Spinosyn A. *Journal of the American Chemical Society* **2016,** *138* (11), 3631-3634.
68. Singleton, D. A.; Hang, C.; Szymanski, M. J.; Greenwald, E. E., A New Form of Kinetic Isotope Effect. Dynamic Effects on Isotopic Selectivity and Regioselectivity. *Journal of the American Chemical Society* **2003,** *125* (5), 1176-1177.