*Supporting Information*

# Computational Study with DFT and Kinetic Models on the Mechanism of Photoinitiated Aromatic Perfluoroalkylations

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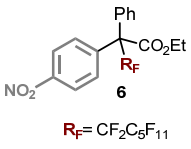
## Table of Contents

*S.1 EXPERIMENTAL PROCEDURES*

**General Procedures.** All reactions were set up under an argon atmosphere in oven-dried glassware using standard Schlenk techniques. Synthesis grade solvents were used as purchased and the reaction mixtures were deoxygenated by three cycles of freeze-pump-thaw. Chromatographic purification of products was accomplished using force-flow chromatography (FC) on silica gel (35-70 mesh). For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 $GF_{254}$, 0.25 mm) were employed, using UV light as the visualizing agent and an acidic mixture of para-anisaldehyde or basic aqueous potassium permangante ($KMnO_4$) stain solutions, and heat as developing agents. Organic solutions were concentrated under reduced pressure on a Büchi rotatory evaporator.

Details of the experimental evaluation of the quantum yield, the synthetic procedures, and the full product characterization of the metal free, photochemical aromatic perfluoroalkylation of α-cyano arylacetates are available in the reported experimental investigations, published in *Angew. Chem. Int. Ed.* **2014**, *53*, 4921–4925; *Angew. Chem.* **2014**, *126*, 5021–5025.

Procedure for the synthesis of product **6** (Figure 1c in the main manuscript). To an oven dried Schlenk tube was added ethyl 2-(4-nitrophenyl)-2-phenylacetate **5** (28.5 mg, 0.1 mmol, 1 eq.), perfluorohexyl iodide **2a** (65 µL, 0.3 mmol, 3 eq.), DMSO (200 µL) and tetramethyl guanidine (23 µL, 0.25 mmol, 2.5 eq.). Upon addition of the base smoke was observed as was a distinct change of colour from pale yellow to dark blue (resultant from the enolate). The tube was sealed and purged of dissolved gases by freeze-pump-thaw cycles (x3) and back-filled with Argon. The reaction was then positioned 10 cm away from a household CFL bulb and stirred for 12 hours. The reaction was then quenched with 1 M HCl solution and extracted with methylene chloride (10 mL x 3). The organic extracts were dried over magnesium sulphate and concentrated *in vacuo* to yield an amorphous residue which was purified by flash chromatography (100% hexanes to 20% ethyl acetate in hexanes) to give a colourless oil (43.4 mg, 0.079 mmol, 79% of theory).



**6**

$R_F = CF_2C_5F_{11}$

$^1$H NMR (500.5 MHz, $CDCl_3$) $\delta$ 8.17 (d, 2 H, $J$ = 8.98 Hz, 3-Nitroaryl-C*H*), 7.61 (d, 2 H, $J$ = 8.98 Hz, 2-Nitroaryl-C*H*), 7.33-7.41 (m, 5 H, Phenyl-C*H*), 4.23-4.34 (m, 2 H, OC$H_2$CH$_3$), 1.22 (t, 3 H, $J$ = 7.16 Hz, OCH$_2$C$H_3$). $^{13}$C NMR $\delta$ (125.9 MHz, $CDCl_3$) 168.1 (CO), 157.3 (1-Nitroaryl- *C*), 155.1 (4-Nitroaryl-*C*), 148.2 (1-Phenyl-*C*), 136.1 (d, $J$ = 9.14 Hz, *C*$F_2$), 132.7 (2-Nitroaryl-*C*H), 130.67 (3-Nitroaryl-*C*H), 129 .8 (*C*$F_2$), 129.5 (3-Phenyl –*C*H), 129.0 (2-Phenyl-*C*H), 128.9 (*C*$F_2$), 126.7 (d, $J$ = 2.85 Hz, *C*$F_2$), 125.1 (d, $J$ = 4.55 Hz, *C*$F_2$), 123.3 (4-Phenyl-*C*H), 119.0 (d, $J$ = 20.87 Hz, *C*$F_3$), 63.6 (O*C*H$_2$CH$_3$), 62.6 (*C*(CF$_2$), 14.1 (OCH$_2$*C*H$_3$). {$^1$H}-$^{19}$F NMR $\delta$ (470.4 MHz) -80.83 (t, 3 F, $J$ = 10.11 Hz, C*F*$_3$), -102.10 (br d, 2 F, $J$ = 75.96 Hz, C*F*$_2$), -113.72 (br s, 2 F, C*F*$_2$), -121.90 (br s, 2 F, C*F*$_2$), -122.53 (br s, 2 F, C*F*$_2$), -126.13 (s, 2 F, C*F*$_2$).

*S.2 COMPUTATIONAL DETAILS*

Electronic structure calculations were carried out with the ωB97XD long-range corrected functional.[1] For the basis set we used that associated to the SDD effective core potential for iodine and 6-31+G(d) for other atoms.[2] For the solvent we used the PCM model with acetonitrile (ε=35.688).[3] Geometry optimizations were carried out in solvent without symmetry constraints. The nature of all minima and transition states was confirmed through frequency calculations. All reported energies are free energies in solution unless noted otherwise. Frequency calculations were carried out assuming a temperature of 298 K and a pressure of 1 atm. $C_3F_7I$ was used as the fluorinated alkyl iodide to avoid conformational issues. All electronic structure calculations were carried out using Gaussian09 software.[4]

The kinetic simulation was carried out with the Acuchem software.[5] All rate constants were calculated using Eyring approximation and transition state theory (for chemical steps), and Marcus theory (for electron transfer steps). For electron transfer rate constants we used the non-equilibrium solvent cage available in Gaussian09 calculations, in a treatment similar to that recently applied by Nelson et al.[6] The rate constant for the transformation from **I** to RF• plus **V** (including photochemical charge transfer and intersystem crossing steps) was adjusted to result in full conversion at 16 hours. Starting concentrations for all species in the simulation were taken from the experimental data.

## References


1 Chai, J.-D. ; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620.

2 (a) Bergner, A.; Dolg, M.; Küchle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431–1441, (b) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724–728, (c) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P.v.R. *J. Comput.. Chem.* **1983**, *4*, 294–301.

3 Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999–3094.

4 Frisch, M. J. *et al.*, Gaussian, Inc., Wallingford, CT, 2009.

5 Braun, W.; Herron, J. T.; Kahaner, D.K. *Int. J. Chem. Kinet.* **1988**, *20*, 51–62.

6 Vaissier, V.; Barnes, P.; Kirkpatrick, J.; Nelson, J. *Phys. Chem. Chem. Phys.* **2013**, *15*, 4804–4814

*S.3 COMPUTATIONAL ESTIMATION OF THE QUANTUM YIELD*

The quantum yield was experimentally determined by the following equation (using a ferrioxalate actinometer):

$$\Phi_{exp} = \frac{\#\ of\ molecules\ of\ product\ formed}{\#\ of\ photons\ absorbed}$$

The number of photons absorbed cannot be determined by DFT methods. Therefore, we made the assumption that all the radical intermediate **V** formed upon light absorption is consumed by the termination step. This is certainly the only possible outcome for **V** in the general reaction mechanism outlined in Scheme 3 of the main text. With this assumption, the number of photons is basically the amount of product formed through the termination step.

In that case, the equation for the quantum yield becomes:

$$\Phi_{calc} = \frac{moles\ of\ product\ formed\ from\ termination\ and\ propagation\ steps}{moles\ of\ product\ formed\ from\ the\ termination\ step}$$

This equation considers the product formed in the termination pathway as different from that formed in the propagation pathway. To account for their relative formations in the reaction time, we labeled them as different products in the kinetic simulation.

*S.4 ESTIMATION OF THE SINGLE ELECTRON TRANSFER ENERGY BARRIER*.

The Marcus theory states the activation energy for an electron transfer reaction as:

$$\Delta G^{\ddagger} = \frac{(\Delta G^{o} + \lambda)^2}{4\lambda}$$

Here λ is the total reorganization energy from the solvent cage around both reacting species. The nuclear reorganization energy of the nuclei was considered the absolute value of $\Delta G^{o}$ (see Figure S1), and the solvent reorganization energy was calculated using the non-equilibrium solvent cage implemented in Gaussian09vD01 (scrf=read keyword with NonEq=write/read input option). This feature allows the user to optimize the solvent cage (SC) for the reactant and use that frozen solvent cage for the energy calculation of the product ($E_{product}$). The solvent reorganization energy is calculated using this equation:

$$\lambda_s = E_{product}(polarized\ SC) - E_{product}(unpolarized\ SC)$$

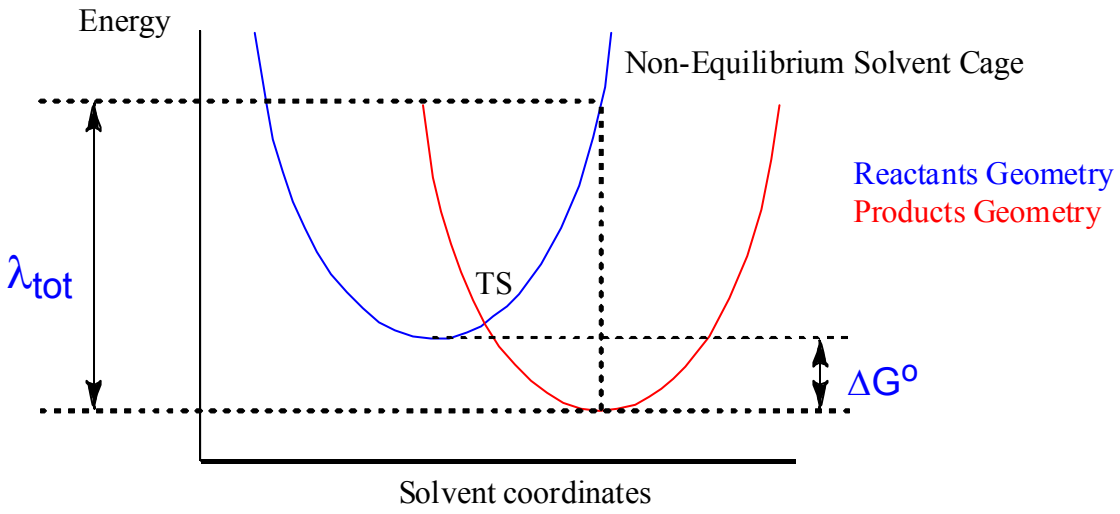



Figure **S1**. Marcus theory diagram for the reorganization energy in SETs.

*S.5 COMPLETE COMPUTED FREE ENERGY PROFILES*

R'-H = ethyl α-cyanophenylacetate

$R_f$ = perfluoropropyl iodide

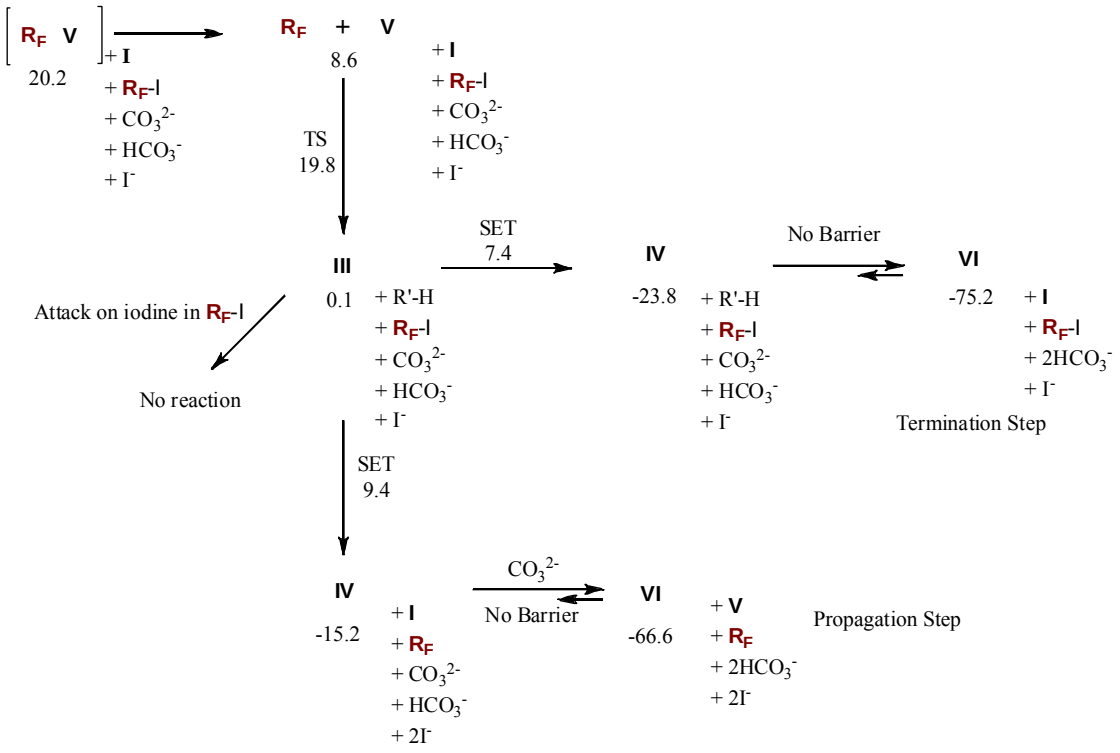



Figure **S2**. Electron transfer mechanism. Energies in kcal.mol$^{-1}$

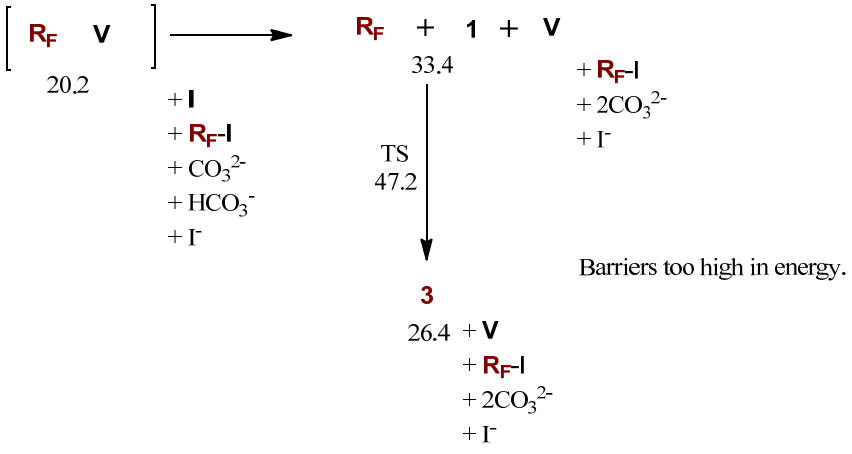



Figure **S3**. Protonation mechanism. Energies in kcal.mol$^{-1}$

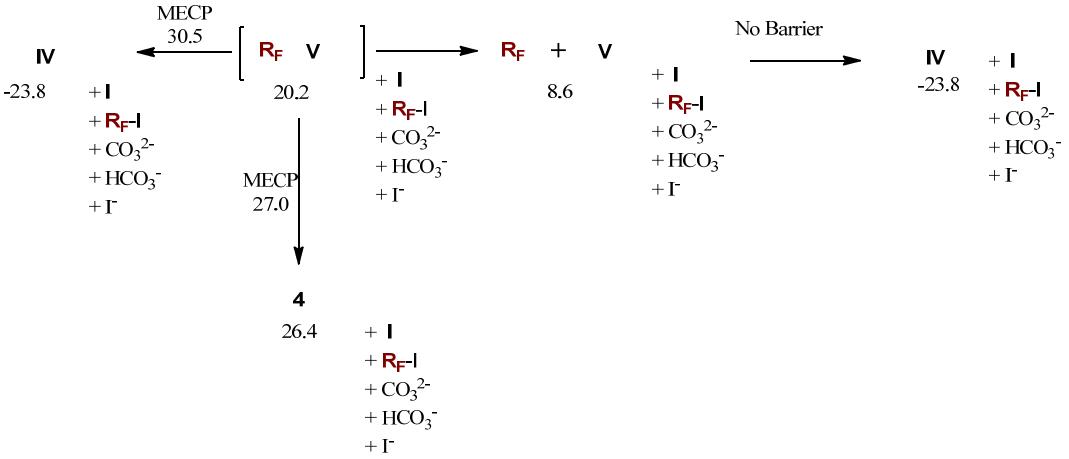



Figure **S4**. Radical-radical mechanism. Energies in kcal.mol$^{-1}$

*S.6 DISTORTION/INTERACTION ANALYSIS ON THE ORIGIN OF REGIOSELECTIVITY*

The origin of the regioselectivity leading to either *para*-**3**, *ortho*-**3** or **4** was investigated by carrying out a distortion/interaction analysis on the corresponding transition states. In this analysis, outlined in Table S1, the transition state energy was dissected in two parts: distortion, required to put the reactants in the transition state geometry; and interaction, the gain of putting the two distorted fragments together. The analysis considers potential energies ($\Delta V^{\ddagger}$), which differ from free energies ($\Delta G^{\ddagger}$) in the entropic term but follow the same trend, as can be seen by inspection of the corresponding columns in Table S1. The decomposition of $\Delta V^{\ddagger}$ in Table S1 clearly indicates that the key factor precluding the attack to the $\alpha$-carbonyl position (to give **4**) is the large cost for the distortion of the anionic fragment **I**. The distortion cost for the attack at the aliphatic carbon is 15.5 kcal.mol$^{-1}$, far above the value (below 4 kcal mol$^{-1}$) for the attack at the aromatic positions. The difference in distortion is apparent from the geometries, depicted in Figure S7, which show an important pyramidalyzation of the aliphatic carbon in the transition state leading to product **4**, while that leading to **3** can be reached with minimal distortion. The preference for the termination reaction (radical coupling between **V** and RF•) could not be analyzed in the same way because of the difficulty in locating radical coupling transition states in DFT, as they are likely to take place in the open-shell singlet surface. However, the same distortion factors should be present as for the anion, thus explaining the preference for the HAS process.

**Table S1 Distortion/Interaction Analysis for TSs Emerging from the Interaction between I/I' and $R_F$•. Relative Potential and Free Energies in kcal·mol$^{-1}$.**

| product | $\Delta V^{\ddagger}$ | $\Delta V^{\ddagger}_{dist}$ (**I**) | $\Delta V^{\ddagger}_{dist}$ ($\mathbf{R_F}$) | $\Delta V^{\ddagger}_{int}$ | $\Delta G^{\ddagger}$ |
|---|---|---|---|---|---|
| *para*-**3** | -1.0 | 3.1 | 2.5 | -6.7 | 11.2 |
| *ortho*-**3** | -1.7 | 3.8 | 2.8 | -8.3 | 11.7 |
| **4** | 6.6 | 15.5 | 6.6 | -15.5 | 20.8 |

*S.7 DISCUSSION OF AN ALTERNATIVE MECHANISM FOR TERMINATION*

The mechanism reported in Scheme 3 of the main manuscript reproduces satisfactorily the experimental results, but we also evaluated computationally an alternative pathway. As depicted in Figure S5, a feasible process can be found in that the cyclohexadienyl radical anion **III** reduces by SET the radical **V** instead of $R_F$-I. This constitutes an additional termination step for the radical chain propagation. The barrier for the corresponding SET process is lower than that of the chain mechanism (7.4 *vs* 9.4 kcal·mol$^{-1}$, compare Scheme 3 of the main manuscript and Figure **S5**). However, the kinetic model discards any role for this alternative mechanism, as it does not produce any significant amount of product. The alternative termination mechanism is much less efficient than the propagation because of the lower concentration of **V** with respect to $R_F$-I, and is much less efficient than the normal termination because of the existence of a measurable barrier compared to the barrierless diffusion-controlled normal termination

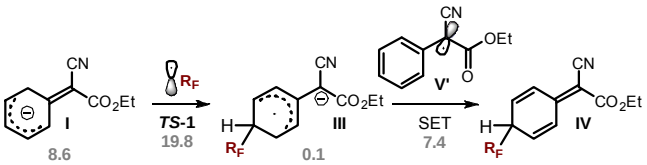



Figure **S5.** An alternative termination pathway. Free energies in kcal.mol$^{-1}$.

## *S.8 COMPARISON OF TRANSITION STATE GEOMETRIES*

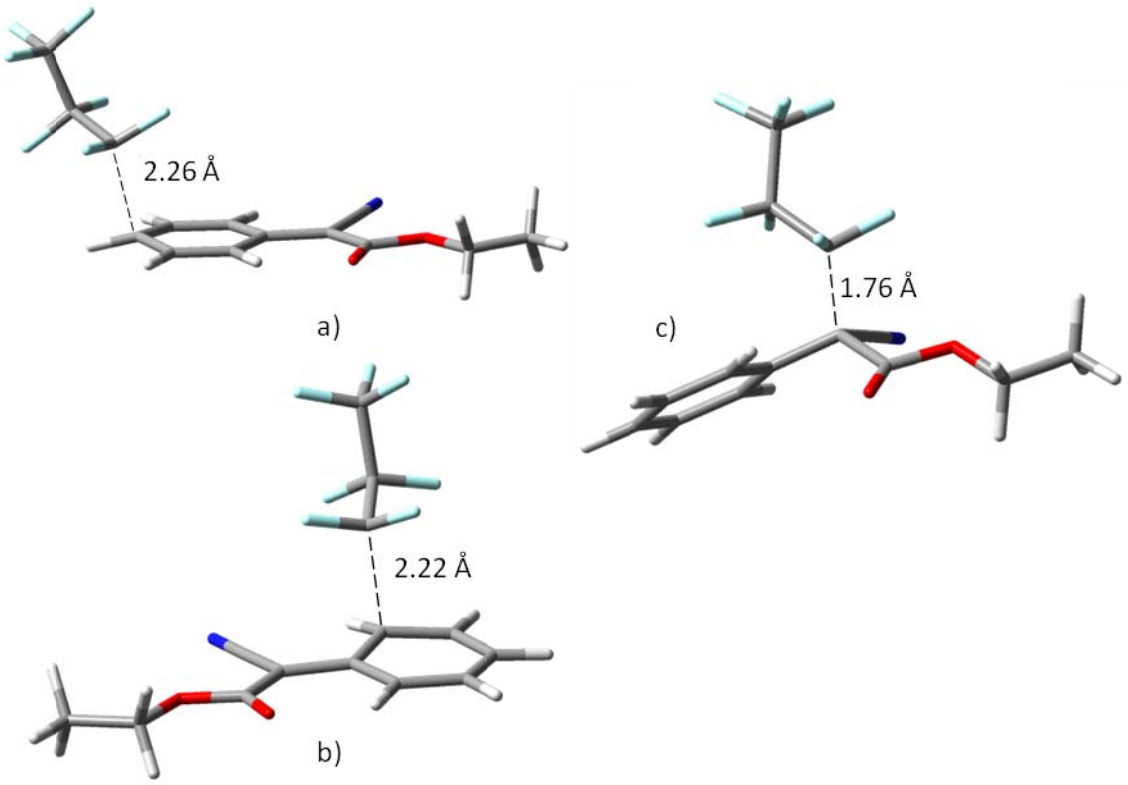



***Figure S6.*** Optimized geometries for the transition states leading to *para*-**III** (a), *ortho*-**III** (b), and **4** (c).

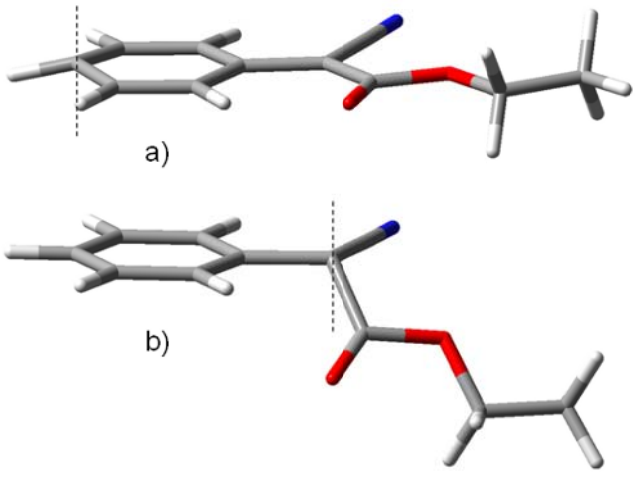



***Figure S7.*** Distorted geometry of the intermediate **I** in the transition state for the formation of the *para*-**3** adduct (HAS pathway, a) and α-carbonyl perfluoroalkylation path leading to product **4** (b). The sums of the angles for the attacking C atoms are 356° and 334°, respectively.

*S.9 TD-DFT DESCRIPTION OF THE EXCITATION OF ADDUCT **II***

*Excitation 1: Energy: 377 nm Oscillator Strength: 0.01*

*HOMO – LUMO Coeff: 0.8*

*Excitation 2: Energy: 277 nm Oscillator Strength: 0.03*

*HOMO-1 – LUMO+1 Coeff: 0.2*

*HOMO – LUMO+1 Coeff: 0.4*

*HOMO – LUMO+2 Coeff: 0.1*

*HOMO – LUMO+3 Coeff: 0.8*

*Excitation 3: Energy: 270 nm Oscillator Strength: 0.51*

*HOMO-1 – LUMO+1 Coeff: 0.6*

*HOMO-1 – LUMO+3 Coeff: 0.4*

*Excitation 4: Energy: 259 nm Oscillator Strength: 0.00*

*HOMO-6 – LUMO Coeff: 0.4*

*HOMO-5 – LUMO Coeff: 0.1*

*HOMO-4 – LUMO Coeff: 0.6*

*Excitation 4: Energy: 258 nm Oscillator Strength: 0.00*

*HOMO-5 – LUMO Coeff: 0.7*

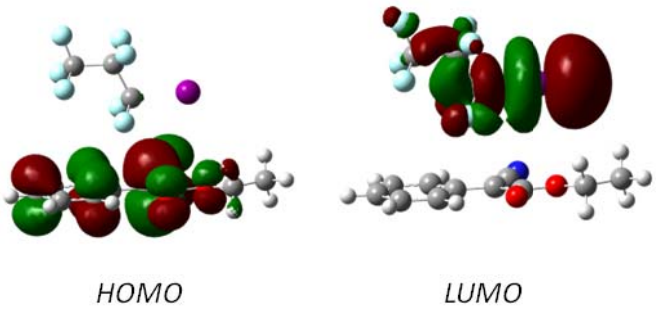



Figure **S8.** HOMO and LUMO of the adduct **II**.

**I**

Total Energy = -630.334978974

Gibbs energy = -630.187895

Number of Negative Frequencies = 0

| | | | |
|---|---|---|---|
| 6 | -4.193678 | 1.019107 | 0.802281 |
| 6 | -3.419407 | 0.013778 | 1.425533 |
| 6 | -3.337340 | -1.227038 | 0.756103 |
| 6 | -3.988210 | -1.438341 | -0.458468 |
| 6 | -4.745672 | -0.432283 | -1.057833 |
| 6 | -4.840479 | 0.800766 | -0.410283 |
| 1 | -4.290605 | 1.992060 | 1.277358 |
| 1 | -2.755382 | -2.024995 | 1.199844 |
| 1 | -3.897400 | -2.408930 | -0.941128 |
| 1 | -5.249075 | -0.602831 | -2.005402 |
| 1 | -5.423486 | 1.605661 | -0.851830 |
| 6 | -2.747256 | 0.281884 | 2.703796 |
| 6 | -1.937288 | -0.656215 | 3.413501 |
| 8 | -1.433045 | -0.139981 | 4.577638 |
| 6 | -2.904074 | 1.557196 | 3.277427 |
| 7 | -3.057947 | 2.630488 | 3.722804 |
| 6 | -0.601625 | -0.998365 | 5.360808 |
| 1 | -1.155195 | -1.906752 | 5.620706 |
| 1 | 0.274486 | -1.293246 | 4.773098 |
| 6 | -0.195190 | -0.228754 | 6.601981 |
| 1 | -1.074046 | 0.061323 | 7.187189 |
| 1 | 0.445790 | -0.855921 | 7.230752 |
| 1 | 0.361397 | 0.676226 | 6.337231 |
| 8 | -1.670288 | -1.820016 | 3.087316 |

**$R_F$-I**

Total Energy = -824.427272302

Gibbs energy = -824.427633

Number of Negative Frequencies = 0

| | | | |
|---|---|---|---|
| 53 | -3.209737 | 1.254784 | -0.017543 |
| 6 | -1.035618 | 1.226431 | 0.028435 |
| 6 | -0.435294 | 0.476222 | -1.194853 |
| 6 | 1.123412 | 0.449568 | -1.262084 |
| 9 | -0.857355 | -0.800943 | -1.167717 |

| | | | |
|---|---|---|---|
| 9 | -0.871721 | 1.061434 | -2.325076 |
| 9 | 1.613377 | 1.681824 | -1.388052 |
| 9 | 1.638568 | -0.112390 | -0.169522 |
| 9 | 1.492286 | -0.266688 | -2.325049 |
| 9 | -0.574965 | 2.485762 | 0.036427 |
| 9 | -0.624340 | 0.622718 | 1.152292 |

**$^{1}$II**

Total Energy = -1454.77027632

Gibbs energy = -1454.605281

Number of Negative Frequencies = 0

| | | | |
|---|---|---|---|
| 6 | -4.038283 | 0.863495 | 0.888697 |
| 6 | -3.143051 | -0.065927 | 1.463726 |
| 6 | -2.998452 | -1.301131 | 0.796222 |
| 6 | -3.713437 | -1.583706 | -0.366392 |
| 6 | -4.597281 | -0.654406 | -0.914977 |
| 6 | -4.749322 | 0.575379 | -0.271999 |
| 1 | -4.188909 | 1.827495 | 1.367746 |
| 1 | -2.324681 | -2.042896 | 1.205833 |
| 1 | -3.574309 | -2.549165 | -0.848081 |
| 1 | -5.152614 | -0.881026 | -1.821038 |
| 1 | -5.432620 | 1.320251 | -0.673587 |
| 6 | -2.421219 | 0.267647 | 2.697395 |
| 6 | -1.588427 | -0.634215 | 3.426066 |
| 8 | -1.038748 | -0.059165 | 4.540515 |
| 6 | -2.585572 | 1.559070 | 3.230321 |
| 7 | -2.743486 | 2.644900 | 3.642934 |
| 6 | -0.272797 | -0.909202 | 5.394270 |
| 1 | -0.874908 | -1.779511 | 5.677060 |
| 1 | 0.610490 | -1.270374 | 4.856369 |
| 6 | 0.120485 | -0.096796 | 6.612075 |
| 1 | -0.766499 | 0.251410 | 7.151650 |
| 1 | 0.717214 | -0.715616 | 7.290614 |
| 1 | 0.718298 | 0.774889 | 6.326021 |
| 8 | -1.338648 | -1.816331 | 3.155125 |
| 6 | -5.600826 | -0.933988 | 4.350647 |
| 6 | -7.017080 | -1.507260 | 4.638782 |
| 6 | -7.889112 | -1.781516 | 3.374061 |
| 53 | -4.449416 | -0.629563 | 6.169502 |
| 9 | -4.951231 | -1.789229 | 3.552463 |
| 9 | -5.735643 | 0.234633 | 3.711159 |
| 9 | -6.893605 | -2.675725 | 5.295911 |

| | | | |
|---|---|---|---|
| 9 | -7.694546 | -0.637547 | 5.410750 |
| 9 | -9.072101 | -2.258867 | 3.767201 |
| 9 | -7.311213 | -2.681270 | 2.580047 |
| 9 | -8.091550 | -0.660590 | 2.682863 |

## $^3$II (Dissociation)

Total Energy = -1443.12192784

Gibbs energy = -1442.957827

Number of Negative Frequencies = 0

| | | | |
|---|---|---|---|
| 6 | -4.035215 | 1.041134 | 0.579695 |
| 6 | -3.392899 | -0.045210 | 1.234554 |
| 6 | -3.488716 | -1.331763 | 0.641163 |
| 6 | -4.193135 | -1.509131 | -0.538355 |
| 6 | -4.819040 | -0.427523 | -1.165523 |
| 6 | -4.733176 | 0.848825 | -0.598799 |
| 1 | -3.981166 | 2.036960 | 1.008256 |
| 1 | -3.011615 | -2.175665 | 1.120051 |
| 1 | -4.259179 | -2.500449 | -0.975879 |
| 1 | -5.367248 | -0.576786 | -2.090623 |
| 1 | -5.215351 | 1.693455 | -1.080647 |
| 6 | -2.695708 | 0.188072 | 2.465229 |
| 6 | -1.977814 | -0.842852 | 3.257408 |
| 8 | -1.511410 | -0.327821 | 4.394577 |
| 6 | -2.671738 | 1.502138 | 3.002964 |
| 7 | -2.662062 | 2.588030 | 3.422414 |
| 6 | -0.796357 | -1.219451 | 5.276646 |
| 1 | -1.447801 | -2.064333 | 5.515524 |
| 1 | 0.083641 | -1.595063 | 4.747262 |
| 6 | -0.422239 | -0.426395 | 6.509018 |
| 1 | -1.315260 | -0.052410 | 7.018675 |
| 1 | 0.125968 | -1.073656 | 7.200547 |
| 1 | 0.218561 | 0.421685 | 6.249329 |
| 8 | -1.825728 | -2.005166 | 2.929730 |
| 6 | -5.530880 | -0.717099 | 5.440029 |
| 6 | -6.678032 | -1.433623 | 4.746257 |
| 6 | -6.478465 | -1.757684 | 3.235813 |
| 9 | -4.424747 | -1.425746 | 5.577048 |
| 9 | -5.285593 | 0.504951 | 5.004123 |
| 9 | -6.889557 | -2.602826 | 5.384765 |
| 9 | -7.779833 | -0.661990 | 4.850181 |
| 9 | -7.543879 | -2.402865 | 2.760227 |
| 9 | -5.401564 | -2.528242 | 3.072141 |

| | | | |
|---|---|---|---|
| 9 | -6.314834 | -0.630600 | 2.542019 |

**V**

Total Energy = -630.166310620

Gibbs energy = -630.019724

Number of Negative Frequencies = 0

| | | | |
|---|---|---|---|
| 6 | -4.189145 | 1.034161 | 0.817189 |
| 6 | -3.422677 | 0.003851 | 1.428209 |
| 6 | -3.334481 | -1.246471 | 0.760128 |
| 6 | -3.978465 | -1.441270 | -0.451290 |
| 6 | -4.724534 | -0.413796 | -1.036448 |
| 6 | -4.825829 | 0.824581 | -0.393244 |
| 1 | -4.277923 | 2.001292 | 1.302035 |
| 1 | -2.759840 | -2.047428 | 1.204673 |
| 1 | -3.898837 | -2.403667 | -0.947060 |
| 1 | -5.223716 | -0.575534 | -1.986823 |
| 1 | -5.403185 | 1.626885 | -0.841536 |
| 6 | -2.769843 | 0.257226 | 2.680510 |
| 6 | -1.923131 | -0.712516 | 3.421978 |
| 8 | -1.450282 | -0.172977 | 4.545137 |
| 6 | -2.919206 | 1.532163 | 3.287616 |
| 7 | -3.055784 | 2.583885 | 3.767799 |
| 6 | -0.600480 | -1.005824 | 5.364459 |
| 1 | -1.159841 | -1.904657 | 5.637811 |
| 1 | 0.267160 | -1.301748 | 4.768240 |
| 6 | -0.204969 | -0.192855 | 6.576903 |
| 1 | -1.085913 | 0.102966 | 7.154537 |
| 1 | 0.441455 | -0.799009 | 7.219283 |
| 1 | 0.344905 | 0.706585 | 6.283984 |
| 8 | -1.680452 | -1.851024 | 3.066331 |

**$R_F$**

Total Energy = -812.948939271

Gibbs energy = -812.948638

Number of Negative Frequencies = 0

| | | | |
|---|---|---|---|
| 6 | -0.977181 | 1.231882 | 0.016101 |
| 6 | -0.411449 | 0.487959 | -1.182507 |
| 6 | 1.141668 | 0.423902 | -1.289692 |

| | | | |
|---|---|---|---|
| 9 | -0.863982 | -0.782141 | -1.138768 |
| 9 | -0.867293 | 1.086301 | -2.302330 |
| 9 | 1.646622 | 1.655171 | -1.389541 |
| 9 | 1.653433 | -0.163883 | -0.206222 |
| 9 | 1.498719 | -0.275243 | -2.366703 |
| 9 | -0.730559 | 2.528907 | 0.041438 |
| 9 | -0.754524 | 0.662437 | 1.186508 |

**TS-1-*para-3***

Total Energy = -1443.28552696

Gibbs energy = -1443.118694

Number of Negative Frequencies = 1

| | | | |
|---|---|---|---|
| 6 | -4.340245 | 1.081062 | 0.703841 |
| 6 | -3.322211 | 0.200988 | 1.168339 |
| 6 | -2.818193 | -0.738595 | 0.227836 |
| 6 | -3.325508 | -0.818716 | -1.053886 |
| 6 | -4.418510 | -0.015910 | -1.466126 |
| 6 | -4.846662 | 1.001679 | -0.575119 |
| 1 | -4.720624 | 1.851402 | 1.369233 |
| 1 | -2.010163 | -1.393358 | 0.527946 |
| 1 | -2.907233 | -1.542928 | -1.747899 |
| 1 | -5.610759 | 1.705269 | -0.893333 |
| 6 | -2.833402 | 0.301454 | 2.531388 |
| 6 | -1.787724 | -0.508499 | 3.092599 |
| 8 | -1.544734 | -0.208863 | 4.400402 |
| 6 | -3.424655 | 1.259335 | 3.382301 |
| 7 | -3.938540 | 2.063894 | 4.059461 |
| 6 | -0.514298 | -0.953825 | 5.056388 |
| 1 | -0.753781 | -2.021163 | 5.011468 |
| 1 | 0.434847 | -0.797131 | 4.533395 |
| 6 | -0.440843 | -0.464307 | 6.488727 |
| 1 | -1.391113 | -0.628264 | 7.007015 |
| 1 | 0.342975 | -1.010800 | 7.023719 |
| 1 | -0.202980 | 0.603712 | 6.526124 |
| 8 | -1.139111 | -1.390606 | 2.522660 |
| 1 | -4.661608 | 0.056917 | -2.521794 |
| 6 | -6.051637 | -1.566317 | -1.267452 |
| 6 | -7.419578 | -1.072664 | -1.720246 |
| 6 | -8.576993 | -2.108465 | -1.816774 |
| 9 | -7.831693 | -0.108947 | -0.864130 |
| 9 | -7.289230 | -0.526525 | -2.955827 |
| 9 | -6.079428 | -1.962192 | 0.018124 |

| | | | |
|---|---|---|---|
| 9 | -5.637970 | -2.602531 | -2.030390 |
| 9 | -8.761137 | -2.715151 | -0.640195 |
| 9 | -9.718310 | -1.498786 | -2.157799 |
| 9 | -8.308743 | -3.037782 | -2.737372 |

**TS-1-*ortho-3***

Total Energy = -1443.28666260

Gibbs energy = -1443.117996

Number of Negative Frequencies = 1

| | | | |
|---|---|---|---|
| 6 | -0.241857 | 2.924981 | 0.769343 |
| 6 | 1.074476 | 2.376054 | 0.246069 |
| 6 | 2.101040 | 3.419797 | -0.287106 |
| 9 | 1.681848 | 1.699786 | 1.243323 |
| 9 | 0.810466 | 1.529971 | -0.771541 |
| 9 | 1.571384 | 4.119820 | -1.293557 |
| 9 | 2.450884 | 4.265801 | 0.684549 |
| 9 | 3.198097 | 2.802094 | -0.729286 |
| 9 | -1.003622 | 3.493254 | -0.152778 |
| 9 | -0.128778 | 3.690083 | 1.844198 |
| 6 | -2.918988 | 1.575585 | 2.264098 |
| 6 | -1.765895 | 0.805612 | 2.543065 |
| 6 | -1.306947 | -0.040493 | 1.508874 |
| 6 | -1.972711 | -0.117725 | 0.286887 |
| 6 | -3.112949 | 0.643131 | 0.036024 |
| 6 | -3.575576 | 1.495097 | 1.040720 |
| 1 | -3.307866 | 2.250548 | 3.022343 |
| 1 | -0.420021 | -0.638350 | 1.675353 |
| 1 | -1.583268 | -0.781316 | -0.481756 |
| 1 | -3.625507 | 0.579918 | -0.919722 |
| 1 | -4.459407 | 2.105971 | 0.872863 |
| 6 | -1.094163 | 0.917105 | 3.841673 |
| 6 | -0.017300 | 0.083405 | 4.274127 |
| 8 | 0.445530 | 0.424579 | 5.516610 |
| 6 | -1.541337 | 1.908649 | 4.734196 |
| 7 | -1.942738 | 2.745567 | 5.449939 |
| 6 | 1.517388 | -0.359508 | 6.044401 |
| 1 | 1.194988 | -1.402177 | 6.137488 |
| 1 | 2.365499 | -0.328912 | 5.352618 |
| 6 | 1.888326 | 0.222864 | 7.393556 |
| 1 | 1.040285 | 0.185347 | 8.085019 |
| 1 | 2.712548 | -0.352422 | 7.828409 |
| 1 | 2.210976 | 1.264291 | 7.293537 |

| | | | |
|---|---|---|---|
| 8 | 0.495198 | -0.862129 | 3.662100 |

**TS-1 4**

Total Energy = -1443.27347659

Gibbs energy = -1443.104208

Number of Negative Frequencies = 1

| | | | |
|---|---|---|---|
| 6 | -12.387827 | -0.196091 | -1.286311 |
| 6 | -12.092348 | -1.227560 | -0.371448 |
| 6 | -13.042502 | -1.481102 | 0.638007 |
| 6 | -14.220646 | -0.741247 | 0.718122 |
| 6 | -14.496748 | 0.275508 | -0.195853 |
| 6 | -13.564697 | 0.540858 | -1.199886 |
| 1 | -11.679976 | 0.038493 | -2.076812 |
| 1 | -12.846684 | -2.260950 | 1.362964 |
| 1 | -14.930888 | -0.965072 | 1.510680 |
| 1 | -15.417648 | 0.847918 | -0.127669 |
| 1 | -13.753209 | 1.327559 | -1.926327 |
| 6 | -10.824387 | -1.967376 | -0.480113 |
| 6 | -10.536677 | -3.195881 | 0.212537 |
| 8 | -9.347315 | -3.736257 | -0.170454 |
| 6 | -9.935581 | -1.604734 | -1.515768 |
| 7 | -9.218718 | -1.276341 | -2.379659 |
| 6 | -8.933169 | -4.933802 | 0.493874 |
| 1 | -8.849238 | -4.739574 | 1.568235 |
| 1 | -9.690422 | -5.710549 | 0.346655 |
| 6 | -7.600272 | -5.343424 | -0.099016 |
| 1 | -6.847887 | -4.562536 | 0.051934 |
| 1 | -7.248283 | -6.259963 | 0.385761 |
| 1 | -7.693785 | -5.535233 | -1.172794 |
| 8 | -11.231118 | -3.745951 | 1.069879 |
| 6 | -9.434136 | -0.637596 | 1.459982 |
| 6 | -9.671545 | 0.861500 | 1.376568 |
| 6 | -8.811111 | 1.774347 | 2.298744 |
| 9 | -10.963954 | 1.111389 | 1.682415 |
| 9 | -9.433320 | 1.264017 | 0.106510 |
| 9 | -7.511421 | 1.635853 | 2.024096 |
| 9 | -9.142886 | 3.057941 | 2.123761 |
| 9 | -9.010161 | 1.460038 | 3.582812 |
| 9 | -8.157247 | -0.965863 | 1.216430 |
| 9 | -9.812179 | -1.149030 | 2.639673 |

**III**

Total Energy = -1443.32132505

Gibbs energy = -1443.150078

Number of Negative Frequencies = 0

| | | | |
|---|---|---|---|
| 6 | -4.377229 | 1.002730 | 0.902400 |
| 6 | -3.320984 | 0.141798 | 1.360228 |
| 6 | -2.858477 | -0.831509 | 0.411491 |
| 6 | -3.443703 | -1.020119 | -0.800575 |
| 6 | -4.683816 | -0.279888 | -1.231699 |
| 6 | -4.999453 | 0.855859 | -0.294923 |
| 1 | -4.677964 | 1.837865 | 1.531532 |
| 1 | -1.985421 | -1.420501 | 0.667215 |
| 1 | -3.026077 | -1.742141 | -1.496245 |
| 1 | -5.753213 | 1.575536 | -0.600174 |
| 6 | -2.732306 | 0.326782 | 2.670056 |
| 6 | -1.726576 | -0.520613 | 3.249455 |
| 8 | -1.336941 | -0.097283 | 4.487228 |
| 6 | -3.183281 | 1.405086 | 3.462658 |
| 7 | -3.580554 | 2.307740 | 4.093358 |
| 6 | -0.363999 | -0.894304 | 5.168378 |
| 1 | -0.751323 | -1.911246 | 5.289876 |
| 1 | 0.548815 | -0.947432 | 4.565977 |
| 6 | -0.101881 | -0.241514 | 6.510718 |
| 1 | -1.021203 | -0.182914 | 7.102353 |
| 1 | 0.630722 | -0.832711 | 7.070176 |
| 1 | 0.297225 | 0.769936 | 6.383071 |
| 8 | -1.226687 | -1.533369 | 2.748625 |
| 1 | -4.555239 | 0.098725 | -2.256656 |
| 6 | -5.851131 | -1.286616 | -1.351731 |
| 6 | -7.205459 | -0.694880 | -1.841883 |
| 6 | -8.239353 | -1.717887 | -2.400701 |
| 9 | -7.806429 | -0.050053 | -0.819198 |
| 9 | -6.972795 | 0.201850 | -2.829199 |
| 9 | -6.096927 | -1.905853 | -0.166998 |
| 9 | -5.509777 | -2.268722 | -2.243337 |
| 9 | -8.426749 | -2.723593 | -1.542998 |
| 9 | -9.410141 | -1.098887 | -2.586278 |
| 9 | -7.844347 | -2.217010 | -3.571824 |

**IV**

Total Energy = -1443.19458916

Gibbs energy = -1443.020075

Number of Negative Frequencies = 0

| | | | |
|---|---|---|---|
| 6 | -4.393679 | 0.977643 | 0.960442 |
| 6 | -3.316766 | 0.096968 | 1.412887 |
| 6 | -2.884281 | -0.937960 | 0.477179 |
| 6 | -3.517190 | -1.140911 | -0.686141 |
| 6 | -4.705489 | -0.340197 | -1.131740 |
| 6 | -5.037675 | 0.783767 | -0.196921 |
| 1 | -4.671496 | 1.819969 | 1.585488 |
| 1 | -2.031821 | -1.546892 | 0.743966 |
| 1 | -3.167111 | -1.918851 | -1.357086 |
| 1 | -5.814674 | 1.480281 | -0.493740 |
| 6 | -2.753691 | 0.275001 | 2.654044 |
| 6 | -1.660081 | -0.554932 | 3.232162 |
| 8 | -1.325058 | -0.116552 | 4.444807 |
| 6 | -3.239551 | 1.329326 | 3.494348 |
| 7 | -3.646389 | 2.189184 | 4.160654 |
| 6 | -0.277959 | -0.830857 | 5.136977 |
| 1 | -0.584349 | -1.875173 | 5.241845 |
| 1 | 0.628013 | -0.791805 | 4.526052 |
| 6 | -0.085477 | -0.160028 | 6.478975 |
| 1 | -1.003124 | -0.202632 | 7.073440 |
| 1 | 0.707220 | -0.677000 | 7.028834 |
| 1 | 0.206872 | 0.886984 | 6.354609 |
| 8 | -1.130425 | -1.508867 | 2.693597 |
| 1 | -4.486170 | 0.082972 | -2.122454 |
| 6 | -5.890328 | -1.301149 | -1.353777 |
| 6 | -7.191908 | -0.644767 | -1.903244 |
| 6 | -8.238543 | -1.624537 | -2.515201 |
| 9 | -7.805259 | 0.016250 | -0.899786 |
| 9 | -6.865367 | 0.245535 | -2.865482 |
| 9 | -6.213679 | -1.933709 | -0.198506 |
| 9 | -5.520336 | -2.260661 | -2.247229 |
| 9 | -8.503612 | -2.622266 | -1.670393 |
| 9 | -9.369493 | -0.955376 | -2.751768 |
| 9 | -7.803797 | -2.133894 | -3.666456 |

**4**

Total Energy = -1443.21187855

Gibbs energy = -1442.610862

Number of Negative Frequencies = 0

| | | | |
|---|---|---|---|
| 6 | -11.726190 | -0.673312 | -1.249412 |

| | | | |
|---|---|---|---|
| 6 | -11.353332 | -1.254669 | -0.038424 |
| 6 | -12.329098 | -1.785115 | 0.810088 |
| 6 | -13.671523 | -1.720590 | 0.450411 |
| 6 | -14.046580 | -1.130614 | -0.756471 |
| 6 | -13.072181 | -0.611893 | -1.605651 |
| 1 | -10.978667 | -0.263736 | -1.921837 |
| 1 | -12.053048 | -2.247438 | 1.753229 |
| 1 | -14.423518 | -2.132330 | 1.116146 |
| 1 | -15.094884 | -1.079199 | -1.034237 |
| 1 | -13.353846 | -0.155416 | -2.549311 |
| 6 | -9.881278 | -1.306284 | 0.403335 |
| 6 | -9.554293 | -2.752338 | 0.907294 |
| 8 | -9.637166 | -3.586315 | -0.108359 |
| 6 | -8.959933 | -1.052197 | -0.717535 |
| 7 | -8.218077 | -0.888895 | -1.588949 |
| 6 | -9.415085 | -4.994631 | 0.169734 |
| 1 | -8.419192 | -5.099932 | 0.606726 |
| 1 | -10.161226 | -5.312036 | 0.902248 |
| 6 | -9.547548 | -5.733800 | -1.141211 |
| 1 | -8.801930 | -5.387881 | -1.862994 |
| 1 | -9.387743 | -6.801897 | -0.964987 |
| 1 | -10.545504 | -5.599571 | -1.568705 |
| 8 | -9.296464 | -3.039997 | 2.048974 |
| 6 | -9.582549 | -0.275278 | 1.538931 |
| 6 | -9.950607 | 1.210985 | 1.209283 |
| 6 | -9.270639 | 2.271757 | 2.130519 |
| 9 | -11.281073 | 1.367521 | 1.333016 |
| 9 | -9.601017 | 1.506897 | -0.059438 |
| 9 | -7.967070 | 2.361346 | 1.873665 |
| 9 | -9.829915 | 3.460596 | 1.898198 |
| 9 | -9.441406 | 1.964376 | 3.417148 |
| 9 | -8.259939 | -0.316831 | 1.836564 |
| 9 | -10.271890 | -0.593544 | 2.651621 |

**Ia orientation 1**

Total Energy = -742.569151200

Gibbs energy = -742.362818

Number of Negative Frequencies = 0

| | | | |
|---|---|---|---|
| 6 | -4.639771 | 0.323702 | 1.368544 |
| 6 | -3.248477 | 0.174533 | 1.357224 |
| 6 | -2.644363 | -0.377638 | 0.222445 |
| 6 | -3.408329 | -0.765122 | -0.878007 |

| | | | |
|---|---|---|---|
| 6 | -4.794692 | -0.607034 | -0.856677 |
| 6 | -5.409295 | -0.061779 | 0.271280 |
| 1 | -5.120172 | 0.746759 | 2.247531 |
| 1 | -1.564439 | -0.504309 | 0.205184 |
| 1 | -2.922424 | -1.192550 | -1.751107 |
| 1 | -5.392278 | -0.909412 | -1.712452 |
| 1 | -6.488736 | 0.062004 | 0.297596 |
| 6 | -2.431141 | 0.568889 | 2.539202 |
| 6 | -2.187937 | -0.441905 | 3.544636 |
| 8 | -1.446924 | -0.093627 | 4.611120 |
| 6 | -1.215806 | -1.117453 | 5.589356 |
| 1 | -2.176074 | -1.456624 | 5.990576 |
| 1 | -0.727969 | -1.971249 | 5.109002 |
| 6 | -0.343067 | -0.517182 | 6.672470 |
| 1 | -0.838717 | 0.334602 | 7.149134 |
| 1 | -0.141128 | -1.272073 | 7.439549 |
| 1 | 0.613283 | -0.178973 | 6.261091 |
| 8 | -2.639895 | -1.585781 | 3.432007 |
| 7 | -1.975067 | 1.852130 | 2.581067 |
| 8 | -1.281601 | 2.296915 | 3.533855 |
| 8 | -2.264094 | 2.626832 | 1.617888 |

**Ia orientation 2**

Total Energy = -742.569151200

Gibbs energy = -742.417812

Number of Negative Frequencies = 0

| | | | |
|---|---|---|---|
| 6 | -4.266017 | 1.045045 | 0.787359 |
| 6 | -3.218689 | 0.409642 | 1.486769 |
| 6 | -3.063717 | -0.982270 | 1.293054 |
| 6 | -3.905992 | -1.698421 | 0.451282 |
| 6 | -4.939033 | -1.054280 | -0.232170 |
| 6 | -5.106672 | 0.317323 | -0.054390 |
| 1 | -4.412475 | 2.108694 | 0.913764 |
| 1 | -2.270576 | -1.520149 | 1.805826 |
| 1 | -3.752832 | -2.767333 | 0.329219 |
| 1 | -5.598976 | -1.613597 | -0.889054 |
| 1 | -5.905592 | 0.837925 | -0.576706 |
| 6 | -2.297091 | 1.083365 | 2.394914 |
| 6 | -1.207994 | 0.302458 | 3.061846 |
| 8 | -1.584754 | -0.170083 | 4.252810 |
| 6 | -0.621059 | -0.950017 | 4.987789 |
| 1 | -0.343846 | -1.819712 | 4.384319 |

| | | | |
|---|---|---|---|
| 1 | 0.272936 | -0.339909 | 5.146653 |
| 6 | -1.266955 | -1.354403 | 6.295304 |
| 1 | -2.168824 | -1.948639 | 6.118100 |
| 1 | -0.564564 | -1.959233 | 6.877613 |
| 1 | -1.536698 | -0.473892 | 6.886788 |
| 8 | -0.122939 | 0.058426 | 2.565014 |
| 7 | -2.294177 | 2.376105 | 2.726130 |
| 8 | -1.403945 | 2.791709 | 3.557112 |
| 8 | -3.131177 | 3.208978 | 2.250628 |

**IIa orientation 1**

Total Energy = -1567.00384856

Gibbs energy = -1566.834669

Number of Negative Frequencies = 0

| | | | |
|---|---|---|---|
| 6 | -4.351535 | -0.396330 | 0.915256 |
| 6 | -3.015004 | -0.081823 | 1.186375 |
| 6 | -2.081865 | -0.189303 | 0.149585 |
| 6 | -2.470974 | -0.596214 | -1.126800 |
| 6 | -3.807303 | -0.900853 | -1.385287 |
| 6 | -4.747788 | -0.798790 | -0.358700 |
| 1 | -5.087259 | -0.315827 | 1.709311 |
| 1 | -1.038833 | 0.044808 | 0.348906 |
| 1 | -1.730336 | -0.673487 | -1.918400 |
| 1 | -4.114139 | -1.216570 | -2.378826 |
| 1 | -5.791363 | -1.034893 | -0.549811 |
| 6 | -2.579184 | 0.333715 | 2.548435 |
| 6 | -1.874119 | -0.644291 | 3.348628 |
| 8 | -1.345788 | -0.228427 | 4.512759 |
| 6 | -0.680622 | -1.222798 | 5.302894 |
| 1 | -1.389327 | -2.022462 | 5.541455 |
| 1 | 0.140719 | -1.657398 | 4.724589 |
| 6 | -0.174898 | -0.538076 | 6.555921 |
| 1 | -1.002332 | -0.102987 | 7.125690 |
| 1 | 0.336443 | -1.268130 | 7.191959 |
| 1 | 0.533493 | 0.258667 | 6.307353 |
| 8 | -1.742314 | -1.813624 | 2.974120 |
| 6 | -5.634988 | -0.801005 | 4.944505 |
| 6 | -7.134868 | -1.132477 | 5.187948 |
| 6 | -8.024580 | -1.157641 | 3.905902 |
| 53 | -4.496200 | -0.748142 | 6.793559 |
| 9 | -5.115009 | -1.729818 | 4.130069 |
| 9 | -5.549910 | 0.389915 | 4.336076 |

| | | | |
|---|---|---|---|
| 9 | -7.225493 | -2.345986 | 5.762229 |
| 9 | -7.658913 | -0.211754 | 6.017510 |
| 9 | -9.273522 | -1.466045 | 4.259675 |
| 9 | -7.588371 | -2.072893 | 3.041320 |
| 9 | -8.033217 | 0.032652 | 3.308279 |
| 7 | -2.859348 | 1.610429 | 2.934276 |
| 8 | -2.562094 | 2.056444 | 4.073811 |
| 8 | -3.448996 | 2.375918 | 2.110787 |

**IIa orientation 2**

Total Energy = -1567.00120068

Gibbs energy = -1566.833066

Number of Negative Frequencies = 0

| | | | |
|---|---|---|---|
| 6 | -4.039203 | 0.874982 | 0.796298 |
| 6 | -2.920567 | 0.308989 | 1.441055 |
| 6 | -2.710415 | -1.078352 | 1.272189 |
| 6 | -3.568661 | -1.856008 | 0.504164 |
| 6 | -4.671892 | -1.279258 | -0.127854 |
| 6 | -4.894380 | 0.087074 | 0.028103 |
| 1 | -4.230880 | 1.932629 | 0.911652 |
| 1 | -1.862094 | -1.564128 | 1.747532 |
| 1 | -3.372614 | -2.919758 | 0.398326 |
| 1 | -5.343251 | -1.885870 | -0.729044 |
| 1 | -5.751589 | 0.554693 | -0.449935 |
| 6 | -1.985233 | 1.049655 | 2.279077 |
| 6 | -0.851897 | 0.327934 | 2.937693 |
| 8 | -1.195062 | -0.188036 | 4.120602 |
| 6 | -0.189909 | -0.950125 | 4.817988 |
| 1 | 0.140483 | -1.765418 | 4.167466 |
| 1 | 0.665723 | -0.298010 | 5.016779 |
| 6 | -0.811018 | -1.468207 | 6.096638 |
| 1 | -1.685974 | -2.090141 | 5.882313 |
| 1 | -0.077935 | -2.076607 | 6.635948 |
| 1 | -1.119022 | -0.643150 | 6.745816 |
| 8 | 0.245202 | 0.158443 | 2.435720 |
| 7 | -1.996264 | 2.358558 | 2.535336 |
| 8 | -1.115968 | 2.828842 | 3.348919 |
| 8 | -2.836271 | 3.155608 | 2.008271 |
| 6 | -5.172867 | 0.517523 | 4.899095 |
| 6 | -6.726990 | 0.575660 | 4.880935 |
| 6 | -7.381898 | 0.435959 | 3.471983 |
| 9 | -4.694155 | 1.518951 | 4.154101 |

| | | | |
|---|---|---|---|
| 9 | -4.776805 | -0.643999 | 4.360300 |
| 9 | -7.211904 | -0.421095 | 5.645020 |
| 9 | -7.124642 | 1.755297 | 5.391947 |
| 9 | -8.707896 | 0.513043 | 3.610513 |
| 9 | -7.080801 | -0.738469 | 2.921142 |
| 9 | -6.982346 | 1.413609 | 2.662004 |
| 53 | -4.375847 | 0.685329 | 6.916089 |

**Ib**

Total Energy = -973.536671764

Gibbs energy = -973.312077

Number of Negative Frequencies = 0

| | | | |
|---|---|---|---|
| 6 | -3.119163 | 0.674392 | 0.324294 |
| 6 | -3.404002 | 0.096246 | 1.567956 |
| 6 | -4.424346 | -0.861357 | 1.629420 |
| 6 | -5.135336 | -1.233182 | 0.488567 |
| 6 | -4.840385 | -0.645698 | -0.742542 |
| 6 | -3.828322 | 0.311483 | -0.821045 |
| 1 | -2.334555 | 1.425103 | 0.259880 |
| 1 | -4.659641 | -1.319902 | 2.587212 |
| 1 | -5.921992 | -1.979871 | 0.560673 |
| 1 | -5.394429 | -0.930975 | -1.632810 |
| 1 | -3.591163 | 0.776629 | -1.774431 |
| 6 | -2.651372 | 0.502872 | 2.797377 |
| 6 | -1.646380 | -0.448485 | 3.198177 |
| 8 | -0.989817 | -0.170539 | 4.355645 |
| 6 | 0.007169 | -1.103174 | 4.783592 |
| 1 | -0.455067 | -2.084797 | 4.929465 |
| 1 | 0.771566 | -1.200129 | 4.006098 |
| 6 | 0.595008 | -0.572295 | 6.075901 |
| 1 | -0.177218 | -0.475046 | 6.846018 |
| 1 | 1.361233 | -1.263619 | 6.442269 |
| 1 | 1.059854 | 0.407018 | 5.921981 |
| 8 | -1.366692 | -1.477653 | 2.568804 |
| 6 | -2.980851 | 1.721784 | 3.429555 |
| 6 | -2.299647 | 2.297690 | 4.564922 |
| 6 | -4.088097 | 2.505679 | 2.931498 |
| 6 | -2.674318 | 3.496999 | 5.114098 |
| 1 | -1.458870 | 1.774624 | 4.996108 |
| 6 | -4.464449 | 3.701125 | 3.483483 |
| 1 | -4.655013 | 2.132399 | 2.086151 |

| | | | |
|---|---|---|---|
| 6 | -3.762208 | 4.226173 | 4.589042 |
| 1 | -2.127321 | 3.894432 | 5.961989 |
| 1 | -5.307953 | 4.246687 | 3.075305 |
| 7 | -4.140991 | 5.451641 | 5.156450 |
| 8 | -5.102397 | 6.080135 | 4.672014 |
| 8 | -3.511448 | 5.895644 | 6.136470 |

**IIb**

Total Energy = -1797.95226059

Gibbs energy = -1797.729006

Number of Negative Frequencies = 0

| | | | |
|---|---|---|---|
| 6 | -4.263516 | 0.301571 | 1.082885 |
| 6 | -2.886202 | 0.230908 | 1.330375 |
| 6 | -2.049450 | -0.145993 | 0.271741 |
| 6 | -2.568309 | -0.444552 | -0.988036 |
| 6 | -3.942767 | -0.366267 | -1.217188 |
| 6 | -4.790323 | 0.010401 | -0.174708 |
| 1 | -4.927739 | 0.599201 | 1.889895 |
| 1 | -0.977352 | -0.208740 | 0.442733 |
| 1 | -1.897744 | -0.735441 | -1.792669 |
| 1 | -4.349625 | -0.594875 | -2.198505 |
| 1 | -5.862837 | 0.075741 | -0.339500 |
| 6 | -2.338563 | 0.550365 | 2.685170 |
| 6 | -1.819764 | -0.597469 | 3.387588 |
| 8 | -1.206744 | -0.338079 | 4.572347 |
| 6 | -0.773936 | -1.459490 | 5.346182 |
| 1 | -1.612150 | -2.150429 | 5.482674 |
| 1 | 0.018406 | -1.989268 | 4.806900 |
| 6 | -0.277760 | -0.923232 | 6.674172 |
| 1 | -1.081864 | -0.407880 | 7.210595 |
| 1 | 0.076952 | -1.750276 | 7.298031 |
| 1 | 0.549126 | -0.220296 | 6.529541 |
| 8 | -1.887798 | -1.763323 | 2.977818 |
| 6 | -6.144678 | -1.056940 | 4.505541 |
| 6 | -7.273696 | -1.857488 | 5.214959 |
| 6 | -8.342158 | -2.482533 | 4.264816 |
| 53 | -4.727370 | -0.204905 | 5.905091 |
| 9 | -5.501069 | -1.875145 | 3.660754 |
| 9 | -6.705553 | -0.070126 | 3.786947 |
| 9 | -6.719490 | -2.866011 | 5.912536 |
| 9 | -7.925241 | -1.040582 | 6.062883 |
| 9 | -9.225985 | -3.157237 | 5.002663 |

| | | | |
|---|---|---|---|
| 9 | -7.779174 | -3.324782 | 3.399859 |
| 9 | -8.989223 | -1.534803 | 3.588049 |
| 6 | -2.401018 | 1.879405 | 3.160050 |
| 6 | -2.080241 | 2.310724 | 4.499702 |
| 6 | -2.828488 | 2.937632 | 2.274308 |
| 6 | -2.195673 | 3.617602 | 4.897827 |
| 1 | -1.752742 | 1.579600 | 5.223433 |
| 6 | -2.934589 | 4.244786 | 2.669160 |
| 1 | -3.064637 | 2.696115 | 1.244124 |
| 6 | -2.625456 | 4.613575 | 3.995873 |
| 1 | -1.961700 | 3.890430 | 5.921045 |
| 1 | -3.249599 | 5.003181 | 1.961056 |
| 7 | -2.739074 | 5.948572 | 4.409194 |
| 8 | -3.129883 | 6.810911 | 3.597892 |
| 8 | -2.448872 | 6.254777 | 5.582491 |

**Vb**

Total Energy = -973.383532037

Gibbs energy = -973.159543

Number of Negative Frequencies = 0

| | | | |
|---|---|---|---|
| 6 | -3.875490 | 1.028131 | 0.533257 |
| 6 | -3.386366 | 0.071467 | 1.449876 |
| 6 | -3.649728 | -1.291572 | 1.188937 |
| 6 | -4.381201 | -1.673053 | 0.072055 |
| 6 | -4.856361 | -0.712140 | -0.823599 |
| 6 | -4.596094 | 0.639219 | -0.589044 |
| 1 | -3.663754 | 2.081238 | 0.691269 |
| 1 | -3.292074 | -2.049507 | 1.877276 |
| 1 | -4.583142 | -2.725840 | -0.101590 |
| 1 | -5.422123 | -1.015064 | -1.699656 |
| 1 | -4.949530 | 1.391858 | -1.287427 |
| 6 | -2.634281 | 0.485006 | 2.623016 |
| 6 | -1.592180 | -0.423563 | 3.153391 |
| 8 | -1.381865 | -0.255155 | 4.462381 |
| 6 | -0.328450 | -1.032553 | 5.065180 |
| 1 | -0.557942 | -2.093663 | 4.933557 |
| 1 | 0.606945 | -0.813243 | 4.542002 |
| 6 | -0.262833 | -0.644030 | 6.526019 |
| 1 | -1.206103 | -0.867847 | 7.033548 |
| 1 | 0.535863 | -1.209744 | 7.016027 |
| 1 | -0.048105 | 0.423265 | 6.637742 |
| 8 | -0.986786 | -1.244208 | 2.481323 |

| | | | |
|---|---|---|---|
| 6 | -2.874404 | 1.771232 | 3.270000 |
| 6 | -1.818730 | 2.517996 | 3.835776 |
| 6 | -4.179402 | 2.302633 | 3.338495 |
| 6 | -2.050415 | 3.743277 | 4.436691 |
| 1 | -0.802622 | 2.143543 | 3.787376 |
| 6 | -4.426682 | 3.522900 | 3.946856 |
| 1 | -5.011709 | 1.738799 | 2.931039 |
| 6 | -3.355490 | 4.229649 | 4.486619 |
| 1 | -1.234141 | 4.318415 | 4.856217 |
| 1 | -5.432932 | 3.918663 | 4.010846 |
| 7 | -3.606853 | 5.517350 | 5.125334 |
| 8 | -4.753767 | 5.950486 | 5.126341 |
| 8 | -2.659864 | 6.108090 | 5.632453 |

**TS-5**

Total Energy = -1786.48357474

Gibbs energy = -1786.238644

Number of Negative Frequencies = 1

| | | | |
|---|---|---|---|
| 6 | -4.258096 | 1.076935 | 0.716705 |
| 6 | -2.969646 | 0.826130 | 1.249674 |
| 6 | -1.923916 | 0.620477 | 0.316785 |
| 6 | -2.148856 | 0.630039 | -1.044904 |
| 6 | -3.463573 | 0.771591 | -1.559880 |
| 6 | -4.498160 | 1.088632 | -0.642567 |
| 1 | -5.081985 | 1.264501 | 1.400343 |
| 1 | -0.913561 | 0.475846 | 0.686087 |
| 1 | -1.318720 | 0.494772 | -1.732468 |
| 1 | -5.499290 | 1.286993 | -1.013971 |
| 6 | -2.736365 | 0.790264 | 2.701184 |
| 6 | -1.868007 | -0.262856 | 3.177283 |
| 8 | -1.445785 | -0.115478 | 4.461804 |
| 6 | -0.645106 | -1.164527 | 5.012107 |
| 1 | -1.160574 | -2.121416 | 4.882983 |
| 1 | 0.305322 | -1.217442 | 4.470445 |
| 6 | -0.427094 | -0.846469 | 6.478024 |
| 1 | -1.380787 | -0.804320 | 7.014225 |
| 1 | 0.191894 | -1.625232 | 6.935743 |
| 1 | 0.082933 | 0.114694 | 6.599221 |
| 8 | -1.479089 | -1.231037 | 2.513845 |
| 1 | -3.602945 | 0.977212 | -2.617155 |
| 6 | -3.862868 | -1.401593 | -1.991651 |
| 6 | -5.194554 | -1.637833 | -2.693812 |
| 6 | -5.524431 | -3.085417 | -3.161825 |

| | | | |
|---|---|---|---|
| 9 | -6.192374 | -1.265131 | -1.859797 |
| 9 | -5.236978 | -0.853473 | -3.799077 |
| 9 | -3.807414 | -2.049386 | -0.817251 |
| 9 | -2.831619 | -1.802325 | -2.762372 |
| 9 | -5.514448 | -3.926754 | -2.124216 |
| 9 | -6.737865 | -3.124077 | -3.723350 |
| 9 | -4.632729 | -3.507659 | -4.061773 |
| 6 | -3.360034 | 1.755239 | 3.557958 |
| 6 | -3.615240 | 1.550842 | 4.952683 |
| 6 | -3.792054 | 3.018479 | 3.036557 |
| 6 | -4.237763 | 2.496556 | 5.732858 |
| 1 | -3.333322 | 0.612452 | 5.410409 |
| 6 | -4.408011 | 3.972245 | 3.810853 |
| 1 | -3.599414 | 3.250768 | 1.994635 |
| 6 | -4.643205 | 3.721408 | 5.173787 |
| 1 | -4.434822 | 2.293671 | 6.779578 |
| 1 | -4.695000 | 4.924653 | 3.379645 |
| 7 | -5.282281 | 4.695330 | 5.977660 |
| 8 | -5.664371 | 5.755109 | 5.456234 |
| 8 | -5.447587 | 4.469197 | 7.186920 |

**TS-5 6**

Total Energy = -1786.49564063

Gibbs energy = -1786.249285

Number of Negative Frequencies = 1

| | | | |
|---|---|---|---|
| 6 | -12.512267 | -0.280680 | 0.691317 |
| 6 | -12.006190 | -1.070154 | -0.348195 |
| 6 | -12.869948 | -1.374028 | -1.412872 |
| 6 | -14.175656 | -0.888882 | -1.451469 |
| 6 | -14.655758 | -0.088707 | -0.414702 |
| 6 | -13.817052 | 0.208080 | 0.659800 |
| 1 | -11.876464 | -0.053562 | 1.537605 |
| 1 | -12.511748 | -2.001829 | -2.225183 |
| 1 | -14.819185 | -1.141888 | -2.290075 |
| 1 | -15.671536 | 0.296194 | -0.442042 |
| 1 | -14.177982 | 0.825569 | 1.478346 |
| 6 | -10.622918 | -1.638866 | -0.331545 |
| 6 | -10.388999 | -2.575491 | 0.760577 |
| 8 | -9.206317 | -3.223487 | 0.723244 |
| 6 | -8.887234 | -4.066093 | 1.835501 |
| 1 | -8.904047 | -3.467640 | 2.752028 |
| 1 | -9.646961 | -4.848782 | 1.925318 |

| | | | |
|---|---|---|---|
| 6 | -7.513450 | -4.650847 | 1.578887 |
| 1 | -6.760387 | -3.860365 | 1.499242 |
| 1 | -7.234640 | -5.311332 | 2.406501 |
| 1 | -7.504293 | -5.236446 | 0.653650 |
| 8 | -11.182022 | -2.779658 | 1.681612 |
| 6 | -8.988558 | 0.092128 | 0.909130 |
| 6 | -9.361063 | 1.090023 | 2.000344 |
| 6 | -8.229551 | 1.928121 | 2.663873 |
| 9 | -9.967942 | 0.420003 | 3.016634 |
| 9 | -10.243414 | 1.983934 | 1.487572 |
| 9 | -7.542819 | 2.613589 | 1.743593 |
| 9 | -8.747027 | 2.807247 | 3.534208 |
| 9 | -7.377384 | 1.143328 | 3.329664 |
| 9 | -8.496284 | 0.773519 | -0.160548 |
| 9 | -7.986996 | -0.709321 | 1.368504 |
| 6 | -9.823676 | -1.517201 | -1.527986 |
| 6 | -8.729309 | -2.357120 | -1.884833 |
| 6 | -10.113767 | -0.457198 | -2.439315 |
| 6 | -8.013867 | -2.168931 | -3.050407 |
| 1 | -8.449862 | -3.174536 | -1.236937 |
| 6 | -9.403910 | -0.258075 | -3.600702 |
| 1 | -10.907346 | 0.241301 | -2.200702 |
| 6 | -8.346476 | -1.121892 | -3.917335 |
| 1 | -7.199192 | -2.838894 | -3.300504 |
| 1 | -9.649131 | 0.566792 | -4.259589 |
| 7 | -7.605653 | -0.929665 | -5.124238 |
| 8 | -7.933489 | -0.013412 | -5.886328 |
| 8 | -6.658721 | -1.684234 | -5.372535 |