DFT Investigation the DDQ-Catalytic Mechanism for Constructing C-O Bond

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1.The definition of the relevant parameters of excited states of DDQ.

(1) D(Å): the distance of the centroids between the hole and the electron.

(2) Sr: the geometric mean of overlap function between the hole and the electron.

(3) H(Å): the overall average distribution breadth of electron and hole.

(4) t(Å): the degree of separation of hole and electron.

(5) E_{coul}(eV): exciton binding energy.(Coulomb attraction energy between hole and electron)

(6) HDI: hole delocalization index; EDI: electron delocalization index; the smaller the HDI (EDI) value, the higher the degree of hole (electron) elocalization, that is, the greater the degree of uniformity of distribution.

The website (http://sobereva.com/434) has all the definitions of these parametersThe above related are defined as follows:

$$D_x = |X_{ele} - X_{hole}|$$

$$D_y = |Y_{ele} - Y_{hole}|$$

$$D_z = |Z_{ele} - Z_{hole}|$$

$$D\ index = \sqrt{(D_x)^2 + (D_y)^2 + (D_z)^2}$$

$$S_r(r) = \sqrt{\rho^{hole}(r)\rho^{ele}(r)}$$

$$S_r\ index = \int S_r(r)\mathrm{d}r = \int \sqrt{\rho^{hole}(r)\rho^{ele}(r)}\mathrm{d}r$$

$$\sigma_{hole,x} = \sqrt{\int (x - X_{hole})^2 \rho^{hole}(r)\mathrm{d}r}$$

$$\sigma_{ele,x} = \sqrt{\int (x - X_{ele})^2 \rho^{ele}(r)\mathrm{d}r}$$

$$H\ index = \frac{|\sigma_{ele}| + |\sigma_{hole}|}{2}$$

$$H_{CT} = |H \cdot u_{CT}|$$

$$t\ index = D\ index - H_{CT}$$

$$HDI = 100X\sqrt{\int [\rho^{hole}(r)]^2 \mathrm{d}r}$$

$$EDI = 100X\sqrt{\int [\rho^{ele}(r)]^2 \mathrm{d}r}$$

$$E_C = \iint \frac{\left|\rho^{hole}(r_1)\right| + \left|\rho^{ele}(r_2)\right|}{|r_1 - r_2|} dr_1 dr_2$$

2. The substrate in each of the three schemes is excited at the DDQ coordination of the hole- electron diagram.

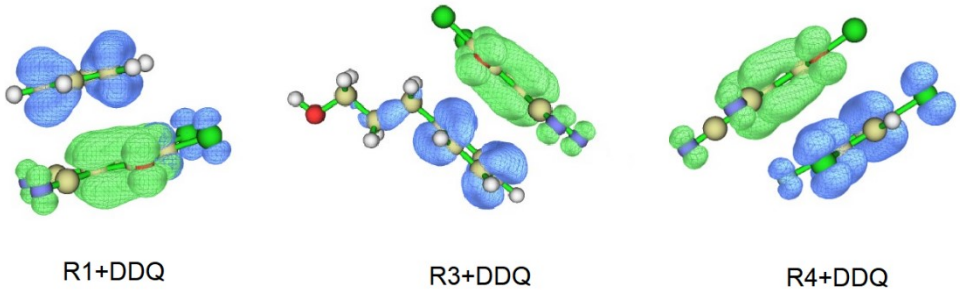

Figure s1. The ρ_{hole}(bule) and ρ_{ele}(green) of R1, R3 and R4+ DDQ.

3. The intersystem crossing process (ISC) from DDQ to ^{3}DDQ*.

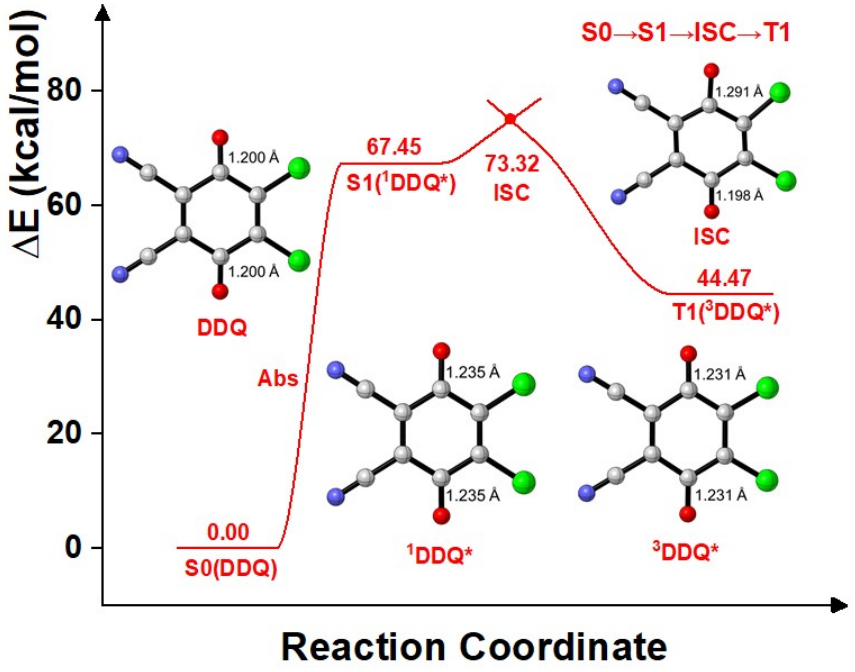

Figure s2. The energy diagram of S0→S1→ISC→T1.

S0(DDQ) is firstly excited to generate S1(^{1}DDQ*) under photocatalysis. As we all know, the triplet excited state T1(^{3}DDQ*) is more stable than the singlet excited state ^{1}DDQ*. There is an energy intersection between the excited singlet state (S1) and the triplet state (T1), where ISC may occur. Therefore, considering that the singlet excited state ^{1}DDQ* occurs intersystem crossing (ISC) and releases part of the energy to transform into the stable triplet excited state ^{3}DDQ*, The calculation results show that the energy of ^{3}DDQ* is 22.98 kcal/mol lower than that of ^{1}DDQ*, indicating that this step is an exothermic reaction. Then, the triplet excited state ^{3}DDQ* with high REDOX potential can participate in the subsequent reaction.

4. The paths a and a1 from IM3a to product P3 in system3.

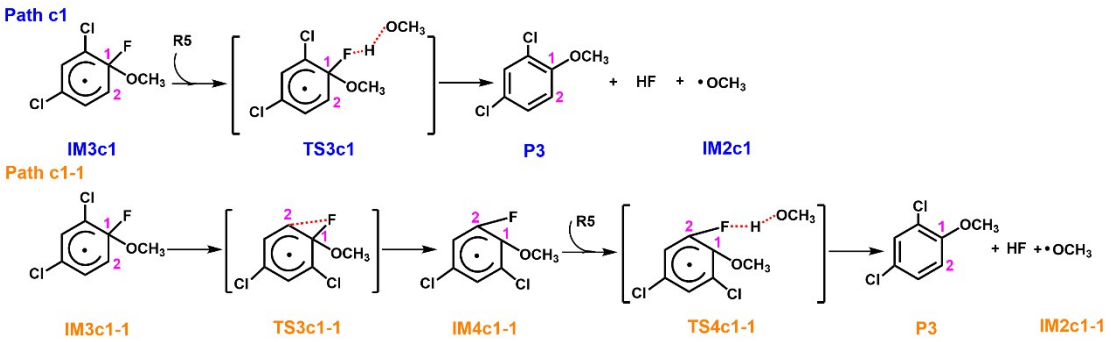

Figure s3. The detailed reaction process from IM3a to P3 in path c1 and c1-1.

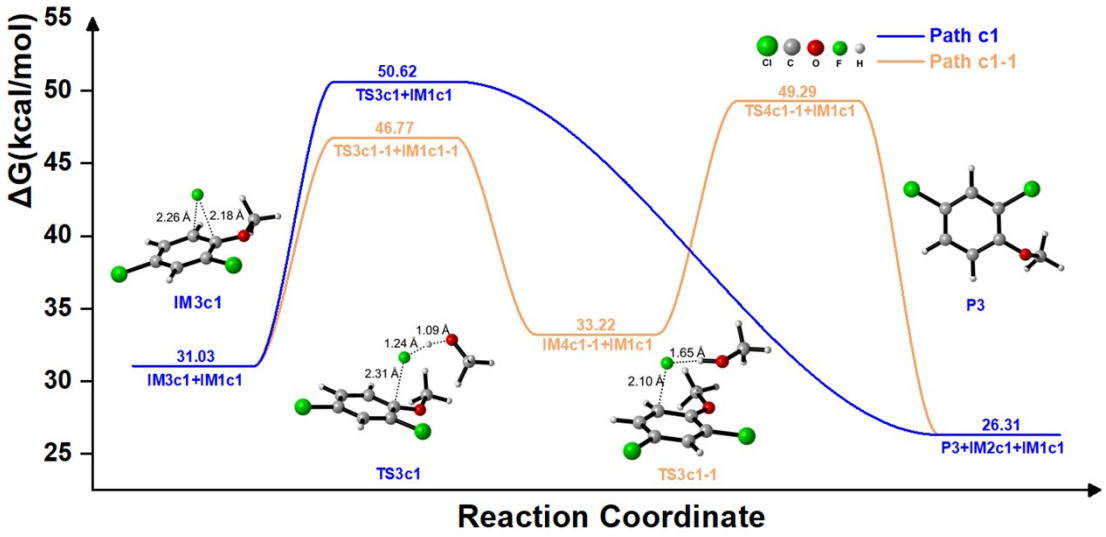

Figure s4. The Gibbs free energy surfaces of Path c1 and c1-1.

In path c1, IM3c1 directly reacts with R5 via transition state TS3c1 to produce the product P3, which step would overcome the energy barrier of 19.59 kcal/mol. While, in path c1-1, IM3c1 firstly undergoes transition state TS3c1-1 on its own to complete the migration of the F atom to the C2 atom to produce the intermediate IM4c1-1. Then the IM4c1-1 would interact with R5 via transition state TS4c1-1 with overcoming an energy barrier of 16.07 kcal/mol. Path a1 has more steps and during the formation of IM4c1-1 would absorb heat which makes the reaction more difficult. In comparison, path c1 is favorable.

5.The Cartesian coordinates (Angstrom) for the optimized reactants, intermediates, transition states and product obtained at the M06-2X-D3/ ma-def2-SVP level of theory in the solvent of acetonitrile (system1&2) and C_2H_4Cl/TFE(1:1) (system3).

Scheme1

^{3}DDQ*

C	-1.15397800	0.73340800	0.00002300
C	0.08590900	1.49128900	-0.00002100
C	1.31487800	0.68533800	-0.00002300
C	1.31487700	-0.68533800	0.00003200
C	0.08590900	-1.49128900	0.00002900
C	-1.15397800	-0.73340800	-0.00001500
C	2.54497100	-1.42694300	0.00007600
N	3.53091800	-2.02554600	0.00012000
C	2.54497100	1.42694300	-0.00006800
N	3.53091800	2.02554600	-0.00011300
O	0.09835600	-2.72162700	0.00003400
O	0.09835600	2.72162700	-0.00002600
Cl	-2.59222600	-1.57671200	-0.00013700
Cl	-2.59222600	1.57671200	0.00014400

R1

C	-1.33263600	-0.41772500	-0.00000300
C	-0.30439200	-1.36259100	0.00012000
C	1.02790700	-0.94500500	-0.00008700
C	1.33259800	0.41783300	0.00001900
C	0.30450500	1.36256200	0.00008000
C	-1.02798200	0.94492800	-0.00008500
H	-2.37413100	-0.74384300	-0.00007100
H	-0.54238800	-2.42768000	0.00003400
H	1.83098100	-1.68410400	-0.00018500
H	2.37417000	0.74368400	-0.00002000
H	0.54224800	2.42769900	0.00004500
H	-1.83088000	1.68422900	-0.00006500

$DDQ^{\bullet-}$

C	1.10974800	-0.67938100	0.00000000
C	-0.13353600	-1.48154700	-0.00000300
C	-1.35637400	-0.69800000	-0.00000100
C	-1.35637400	0.69800000	-0.00000200
C	-0.13353700	1.48154700	-0.00000200
C	1.10974800	0.67938200	0.00000000
Cl	2.57333000	1.58774100	-0.00000300
Cl	2.57333100	-1.58774100	-0.00000400
O	-0.12264400	2.71108400	0.00001600
O	-0.12264300	-2.71108400	0.00001400
C	-2.57988700	1.43644400	-0.00000300
N	-3.57216700	2.03093600	-0.00000700
C	-2.57988700	-1.43644400	0.00000000
N	-3.57216700	-2.03093700	-0.00000300

IM1a1

C	0.00055600	-1.38191500	0.00000100
C	1.24663400	-0.68320000	0.00000800
C	1.24607200	0.68413300	-0.00000800
C	-0.00056600	1.38191400	0.00000600
C	-1.24662700	0.68320300	-0.00001100
C	-1.24606700	-0.68413600	0.00000600
H	0.00098200	-2.47305900	-0.00003000
H	2.17624200	-1.25240900	0.00000000
H	2.17522000	1.25409000	-0.00001900
H	-0.00095600	2.47305800	0.00004200
H	-2.17625800	1.25237700	-0.00002400
H	-2.17524000	-1.25405200	0.00002100

R2

O	0.00000000	0.00000000	0.12055500
H	0.00000000	0.75423000	-0.48222100
H	0.00000000	-0.75423000	-0.48222100

R2+ DDQ$^{\bullet-}$

C	0.92818500	-0.38129200	0.03453300
C	0.47691600	1.02160100	0.04521700
C	-0.95999700	1.20133300	0.01968900
C	-1.84859900	0.12775900	-0.01005600
C	-1.40453100	-1.25594300	-0.01916900
C	0.06376700	-1.43046100	0.00407300
Cl	0.61487900	-3.06044200	-0.00828000
Cl	2.63534000	-0.61281200	0.06945400
O	-2.18046600	-2.20880800	-0.04389100
O	1.26299400	1.97492800	0.07455900
C	-3.26205800	0.34006800	-0.03292200
N	-4.40499500	0.51492600	-0.05133200
C	-1.43177000	2.55173000	0.02692900
N	-1.81908200	3.64110400	0.03246600
O	4.10195200	2.29543200	-0.09914000
H	4.31688700	1.66658600	-0.79779700
H	3.15061800	2.14533300	0.02791600

TS1a1

C	-0.11740500	1.66885900	0.04928000
C	1.11904200	0.86351500	-0.04899900
C	1.10514700	-0.48815800	-0.17383600
C	-0.13937100	-1.26109100	-0.15838300
C	-1.34898600	-0.49115600	-0.17676000
C	-1.34781700	0.89762500	-0.03259700
Cl	2.55220000	-1.40776200	-0.30682100
Cl	2.59072700	1.75722300	-0.00115300
C	-2.57165500	-1.22400700	-0.30116900
C	-2.56695500	1.63930500	0.00849300
N	-3.56450600	-1.80875400	-0.39679300
N	-3.55568200	2.23889700	0.04268000
O	-0.10019700	2.88967000	0.17780500
O	-0.15559500	-2.52757900	-0.55840000
O	0.06302400	-2.08115000	1.65031100
H	-0.80119200	-1.99852800	2.08290100
H	-0.03710000	-2.83017900	0.47753700

$DDQH^-$

C	-0.11403600	1.37178900	0.00004900
C	-1.34850400	0.67007200	0.00003900
C	-1.37158300	-0.71432200	0.00005300
C	-0.14009100	-1.50491900	0.00015600
C	1.11224900	-0.73040900	0.00003200
C	1.11181600	0.64127300	0.00002200
C	-2.56235200	1.43866800	-0.00000300
N	-3.54076300	2.04893700	-0.00004100
C	-2.60434600	-1.44108100	-0.00000700
N	-3.59671600	-2.03081600	-0.00003200
O	-0.15261500	-2.73044100	-0.00004800
O	-0.16911100	2.68124000	0.00002300
H	0.70905600	3.10826300	0.00000500
Cl	2.57422500	1.55214200	-0.00004500
Cl	2.56272700	-1.62437200	-0.00003400

IM2a1

O	0.00000000	0.00000000	0.10890100
H	0.00000000	0.00000000	-0.87121100

TS2a1

C	1.69929200	0.10069800	0.38792100
C	1.14693300	-1.16270900	0.12020300
C	-0.10770100	-1.26622400	-0.45229800
C	-0.87538700	-0.09755400	-0.71482900
C	-0.26406600	1.17048700	-0.52291200
C	0.99485000	1.26242800	0.05656800
H	2.69058200	0.17657000	0.83873700
H	1.71756900	-2.06329600	0.35462800
H	-0.53801100	-2.24554800	-0.66973200
H	-1.75628200	-0.17256400	-1.35138600
H	-0.80919700	2.07356800	-0.80653800
H	1.44272400	2.24159800	0.23596600
O	-2.01583300	-0.11246200	0.90150100
H	-2.18425400	0.84660800	0.93839200

IM3a1

C	1.12381800	1.24142700	-0.05282500
C	-0.21851000	1.24173900	0.19015100
C	-1.01009800	-0.02104400	0.38072800
C	-0.18212400	-1.25488900	0.19015000
C	1.16045300	-1.21227300	-0.04604700
C	1.84895900	0.02478800	-0.16071900
H	1.65205200	2.18945300	-0.17690400
H	-0.76998900	2.18342700	0.26606200
H	-1.39275600	-0.03118700	1.42616700
H	-0.71158000	-2.20829000	0.25790900
H	1.71723300	-2.14471800	-0.16234300
H	2.92141200	0.03977500	-0.35559100
O	-2.12482800	-0.09244400	-0.50337800
H	-2.75273300	0.59259500	-0.23690100

TS1a2

C	-0.88868900	1.53271900	0.08161100
C	0.55501900	1.25398600	-0.01689300
C	1.01898400	-0.03509200	-0.18874500
C	0.15737300	-1.20443000	-0.18435000
C	-1.25593500	-0.93072100	-0.11046600
C	-1.75044100	0.35773900	0.00858900
Cl	2.68203100	-0.33047700	-0.45046100
Cl	1.59362400	2.59611900	0.04081600
C	-2.13102800	-2.06719100	-0.13009700
C	-3.15860900	0.60583700	0.09437100
N	-2.83724800	-2.97996400	-0.14498000
N	-4.29327100	0.80779200	0.16456700
O	-1.32246400	2.67324200	0.21152800
O	0.61725300	-2.37169800	-0.19165000
O	2.77280900	-2.20995300	1.03302300
H	3.50921800	-2.66707000	0.57219900
H	1.89744400	-2.45345600	0.50733000

DDQH·

C	0.11357800	1.37314500	-0.00000800
C	1.34801900	0.67242200	0.00000000
C	1.37139200	-0.71336500	-0.00000200
C	0.14150200	-1.50671100	-0.00004400
C	-1.11052600	-0.73099600	-0.00000400
C	-1.11118000	0.64035200	-0.00000100
C	2.56048500	1.44259300	0.00001200
N	3.53748100	2.05532000	0.00001700
C	2.60326400	-1.44038300	0.00001600
N	3.59476600	-2.03175200	-0.00000800
O	0.15481600	-2.73099000	-0.00000500
O	0.16239700	2.68262600	-0.00000700
H	-0.72526100	3.09067300	-0.00001000
Cl	-2.57383500	1.55110700	-0.00000400
Cl	-2.55777600	-1.62705200	0.00001800

TS3a2-1

C	-0.89235000	-1.05965800	0.61093400
C	-0.28550900	0.17425100	0.98708600
C	-0.95920500	1.35749900	0.60496200
C	-2.20316600	1.31833000	-0.04868300
C	-2.79733300	0.09053700	-0.37753800
C	-2.11493600	-1.09963000	-0.04220600
Cl	-2.84983500	-2.59664000	-0.48539100
Cl	-0.04339600	-2.50423500	0.98897000
C	-2.88717700	2.52821000	-0.40384300
C	-0.32841100	2.60776700	0.91156700
O	-3.97247100	0.10733900	-0.99378000
H	-4.30130400	-0.79261100	-1.16478200
O	0.84268400	0.21330900	1.62728800
N	-3.43026400	3.50662500	-0.68629700
N	0.19243800	3.61175900	1.14393300
C	5.25281300	0.26482000	-0.64406600
C	4.73876400	-1.03884800	-0.37860000
C	3.41030600	-1.24920200	-0.17422300
C	2.43438800	-0.12354000	-0.31931400
C	3.03322500	1.23788200	-0.49015600
C	4.37234500	1.38541800	-0.67785400
H	6.32255800	0.40714000	-0.79323500
H	5.43188200	-1.88050600	-0.31638300
H	3.01740500	-2.24067800	0.06468700
H	2.35377800	2.09335100	-0.48830000
H	4.78693200	2.38273900	-0.83878500
O	1.44492400	-0.33612200	-1.25681600
H	1.31088200	-1.29319800	-1.38194800
H	1.76396600	-0.02927600	0.79254100

$DDQH_2$

C	-1.08694100	0.69438600	-0.00002600
C	0.12342000	1.42620300	-0.00004500
C	1.32050200	0.70899100	0.00001300
C	1.32050200	-0.70899100	0.00001300
C	0.12342000	-1.42620300	-0.00004500
C	-1.08694100	-0.69438600	-0.00002600
Cl	-2.56061100	-1.57701500	0.00003500
Cl	-2.56061100	1.57701500	0.00003500
O	0.04299700	2.75535100	-0.00008100
H	0.92203400	3.17281900	-0.00004600
O	0.04299700	-2.75535100	-0.00008100
H	0.92203400	-3.17281900	-0.00004600
C	2.55834100	-1.43024800	0.00003300
N	3.53892100	-2.04050300	0.00003500
C	2.55834100	1.43024800	0.00003300
N	3.53892100	2.04050300	0.00003500

TS3a2-2

C	-0.92662300	-1.51136700	0.34750500
C	0.36118000	-1.16270800	0.78717400
C	1.09419300	0.02977200	0.25975700
C	0.18469400	0.96523300	-0.49818100
C	-1.02456600	0.53798300	-0.99538100
C	-1.62034400	-0.71645600	-0.53970800
H	-1.38203800	-2.43039600	0.72339500
H	0.89141100	-1.80515300	1.49267400
H	1.12630962	0.62807243	1.35383738
H	0.63929100	1.87433800	-0.89662700
H	-1.59038900	1.17754800	-1.67537700
H	-2.60949900	-1.00092900	-0.89908100
O	2.13516600	-0.44880900	-0.60316600
H	2.79531000	0.25143700	-0.70218100
O	1.23848173	1.28598662	2.63254145
H	1.89879088	1.56064702	3.29373048

O_2

O	0.00000000	0.00000000	0.59125500
O	0.00000000	0.00000000	-0.59125500

IM2a2-3

C	1.36667400	-1.65031700	-0.06555100
C	2.26492700	-0.49465600	0.09153200
C	1.77962400	0.75185400	0.01353600
C	0.32817900	0.99650800	-0.30326100
C	-0.52855400	-0.12505100	0.25805700
C	0.03712200	-1.48933800	-0.01824000
H	1.80047800	-2.64388800	-0.19524500
H	3.33016300	-0.67180200	0.25026200
H	2.41881600	1.63457000	0.09025800
H	-0.67571500	0.02711600	1.34277400
H	-0.66094900	-2.32701100	-0.08424200
H	0.22124500	0.96486500	-1.40963600
O	-0.05951400	2.24740300	0.20096300
H	-0.93155100	2.45950200	-0.15770900
O	-1.83209400	0.03281100	-0.35728300
O	-2.73218200	-0.70238300	0.19470800

TS3a2-3

C	1.38328266	-1.64540231	0.10628778
C	2.28153566	-0.48974131	0.26337078
C	1.79623266	0.75676869	0.18537478
C	0.34478766	1.00142269	-0.13142222
C	-0.51194534	-0.12013631	0.42989578
C	0.05373066	-1.48442331	0.15359878
H	1.81708666	-2.63897331	-0.02340622
H	3.34677166	-0.66688731	0.42210078
H	2.43542466	1.63948469	0.26209678
H	-0.65910634	0.03203069	1.51461278
H	-0.64434034	-2.32209631	0.08759678
H	-0.20223413	0.77693309	-1.55831811
O	-0.04290534	2.25231769	0.37280178
H	-0.91494234	2.46441669	0.01412978
O	-1.81548534	0.03772569	-0.18544422
O	-1.34778551	0.26164473	-1.49312007

TS3a2-4

C	-2.35830000	-1.00430500	-0.02407000
C	-2.93285900	0.34387900	-0.29985100
C	-2.05296100	1.50241700	0.02321900
C	-0.82750900	1.32634500	0.59483400
C	-0.31946600	-0.00636400	0.95515600
C	-1.13484400	-1.15950500	0.53810200
O	0.74901100	-0.13812700	1.54850200
O	-4.02908200	0.49652500	-0.78124800
Cl	-0.43759500	-2.69867500	0.82034400
Cl	-3.33170200	-2.32899000	-0.48707900
C	0.08104100	2.41369400	0.82266800
C	-2.54552600	2.80114200	-0.32848800
N	0.85131400	3.26070500	0.96993200
N	-2.93232500	3.85095300	-0.61273000
C	4.73194000	0.94890300	-0.09450400
C	3.38328700	1.13938400	-0.26106800
C	2.49008400	-0.00797200	-0.48285600
C	3.15051600	-1.28154200	-0.80910800
C	4.50048700	-1.43524800	-0.62748900
C	5.29987600	-0.33276100	-0.25317800
H	5.37390500	1.79826700	0.14231900
H	2.91881700	2.12071400	-0.13787400
H	2.07700000	-0.20101600	0.59791600
H	2.50662900	-2.10945300	-1.11218000
H	4.96778500	-2.40572500	-0.80019600
H	6.37380100	-0.46723800	-0.11983400
O	1.29644600	0.25311200	-1.16753300
H	1.50160700	0.57266700	-2.05405500

IM3a2-3

O	1.35502600	-0.89611600	-0.56037100
O	2.62625400	-0.36525300	-0.23782300
C	-2.31016500	0.21844600	-0.31090700
C	-1.33198100	1.22782900	-0.22492500
C	-0.04942700	0.93145500	0.16634200
C	0.41220800	-0.47239100	0.43627900
C	-0.71058400	-1.45987700	0.40244200
C	-1.97312600	-1.12085100	0.02219000
H	-3.32352800	0.46934400	-0.62192900
H	-1.59240800	2.26520200	-0.45307900
H	0.95304800	-0.49448500	1.40163700
H	-0.45540300	-2.49053600	0.65334400
H	-2.74682100	-1.88931700	-0.01984000
O	0.92115600	1.84323800	0.31422500
H	0.59032000	2.71541300	0.06615100
H	3.13375500	-1.17822700	-0.10305200

·HO_2

O	0.24000000	0.37599999	0.00000000
H	-0.08045459	1.28093583	0.00000000
O	1.56000000	0.37599999	0.00000000

P1

C	1.85508600	0.03487600	-0.00006900
C	1.12192400	1.22207300	0.00002000
C	-0.27261100	1.19672800	0.00002000
C	-0.94598000	-0.03011300	-0.00003600
C	-0.21587200	-1.22516600	0.00009200
C	1.17610700	-1.18613700	0.00001000
H	2.94561800	0.05962200	-0.00012500
H	1.63809600	2.18422400	0.00009400
H	-0.84797700	2.12614800	0.00009700
H	-0.75887900	-2.17182000	0.00022300
H	1.73708100	-2.12297400	0.00000800
O	-2.29359600	-0.11543000	-0.00013600
H	-2.67709800	0.77466800	0.00056600

System 2

R3

C	-0.89390600	0.36167100	-0.12386100
C	-1.48702000	-0.20269100	-1.26750000
C	-2.87384600	-0.39561600	-1.28098100
C	-3.65357300	-0.04085000	-0.18274400
C	-3.05177800	0.50549600	0.94998900
C	-1.66938700	0.71057000	0.99646200
C	0.57965800	0.62649800	-0.12095000
C	1.54190200	-0.35584900	0.17821000
C	2.90827500	-0.06123500	0.08437900
C	3.33346800	1.21301600	-0.27869100
C	2.38774500	2.19639300	-0.56776500
C	1.02767100	1.89949400	-0.49592300
H	-3.34091800	-0.83090400	-2.16737200
H	-4.73410500	-0.19510700	-0.20688600
H	-3.65875600	0.77325400	1.81804600
H	3.63765000	-0.83988600	0.30966700
H	4.39975900	1.43618300	-0.33728600
H	2.70839100	3.19858800	-0.85787500
H	0.28910000	2.66660000	-0.73968400
C	-1.00910500	1.25441600	2.23436500
H	-0.25604600	0.54032000	2.60272200
H	-0.48602100	2.20137600	2.03264500
H	-1.74533700	1.42740200	3.03035800
C	-0.64645300	-0.60829400	-2.45078200
H	-0.04135100	0.23326900	-2.82064300
H	0.05763500	-1.41123400	-2.17929100
H	-1.27778100	-0.97115900	-3.27243900
C	1.12284700	-1.71910900	0.62741600
O	0.10886500	-1.97134500	1.22582300
O	2.02062400	-2.65718000	0.31123300
H	1.71288200	-3.50397000	0.68185300

TS1b1

C	3.16122600	-0.88811300	0.04837400
C	2.92232000	-1.19169600	1.40217000
C	2.32509300	-2.41884200	1.71547400
C	1.97101800	-3.31877800	0.71071500
C	2.21247900	-3.00367200	-0.62348700
C	2.81350600	-1.79071000	-0.97695600
C	3.77806400	0.43188900	-0.28776700
C	2.99359100	1.59920800	-0.38245900
C	3.56010200	2.85834800	-0.60734200
C	4.93840600	2.96655600	-0.74690000
C	5.73570800	1.82166300	-0.65145600
C	5.16311100	0.57274100	-0.40798900
H	2.12801900	-2.66354600	2.76116900
H	1.49664100	-4.26633600	0.97063400
H	1.92851800	-3.70533800	-1.40984800
H	2.91670000	3.73762700	-0.66403000
H	5.39480500	3.94106000	-0.92314300
H	6.81791000	1.90440400	-0.76350700
H	5.79427900	-0.31252900	-0.30990100
C	3.09716200	-1.46145400	-2.41807000
H	2.68188800	-0.48045600	-2.68748200
H	4.18091500	-1.42230600	-2.60693700
H	2.66368000	-2.21619600	-3.08515200
C	3.27632300	-0.21260300	2.49411300
H	4.33365500	0.08512100	2.43776900
H	2.67892700	0.70993800	2.41917300
H	3.09487800	-0.65177600	3.48254800
C	1.51966900	1.46036500	-0.19468900
O	0.97015300	0.65439500	-0.97140300
O	0.93915800	2.11860100	0.71360900
H	-0.17027300	1.96162300	0.75228400
C	-1.96392800	-0.35182900	0.33675900
C	-2.30014700	1.04726200	0.45563900
C	-3.67346900	1.40105100	0.19286800
C	-4.61153500	0.46199200	-0.19722600
C	-4.28086900	-0.95451400	-0.36502100
C	-2.88106800	-1.30484100	-0.08337800
C	-5.96853300	0.84095900	-0.46245400
N	-7.05934200	1.15276300	-0.67628200
C	-4.02077500	2.78892400	0.32642500
N	-4.30091100	3.90341900	0.43070700
O	-5.10179200	-1.79319200	-0.72048400
O	-1.46189400	1.94040900	0.76955200

Cl	-2.45053100	-2.93910000	-0.27078800
Cl	-0.36055700	-0.79617700	0.70321000

IM1b1

C	-0.63353000	-0.59682400	-0.07227700
C	-1.17913600	-1.85501600	-0.34008500
C	-2.56194900	-2.05155700	-0.36154600
C	-3.43182900	-0.98877800	-0.12076800
C	-2.91302400	0.27503600	0.14482000
C	-1.52429000	0.46259700	0.18630700
C	0.84915500	-0.39863500	-0.09882200
C	1.60088200	-0.59747400	1.07370800
C	2.98850100	-0.43238800	1.01733600
C	3.61590500	-0.07357300	-0.17449700
C	2.86005000	0.12909400	-1.32639300
C	1.46908600	-0.02941000	-1.30694200
H	-0.50542900	-2.69110500	-0.54035900
H	-2.96069700	-3.04549300	-0.57231500
H	-4.51131000	-1.14319700	-0.13941500
H	-3.57937200	1.11676500	0.34107100
H	3.57865800	-0.58481100	1.92379900
H	4.69994100	0.05246200	-0.20388800
H	3.34962800	0.41421500	-2.26027800
C	0.65388200	0.19764800	-2.55349800
H	0.08530400	-0.70399800	-2.82761100
H	-0.08089400	1.00444200	-2.40672600
H	1.29944200	0.47086200	-3.39820400
C	0.91631300	-0.95222900	2.36595000
H	0.20892200	-0.15690900	2.64662900
H	0.33985600	-1.88495900	2.27347500
H	1.64630700	-1.07388400	3.17683600
C	-0.99273200	1.82402400	0.50257100
O	-0.16847800	2.12951600	1.32518900
O	-1.56578000	2.71429800	-0.27871500

TS1b2

C	-0.88868900	1.53271900	0.08161100
C	0.55501900	1.25398600	-0.01689300
C	1.01898400	-0.03509200	-0.18874500
C	0.15737300	-1.20443000	-0.18435000
C	-1.25593500	-0.93072100	-0.11046600
C	-1.75044100	0.35773900	0.00858900
Cl	2.68203100	-0.33047700	-0.45046100
Cl	1.59362400	2.59611900	0.04081600
C	-2.13102800	-2.06719100	-0.13009700
C	-3.15860900	0.60583700	0.09437100
N	-2.83724800	-2.97996400	-0.14498000
N	-4.29327100	0.80779200	0.16456700
O	-1.32246400	2.67324200	0.21152800
O	0.61725300	-2.37169800	-0.19165000
O	2.77280900	-2.20995300	1.03302300
H	3.50921800	-2.66707000	0.57219900
H	1.89744400	-2.45345600	0.50733000

IM1b2

O	0.00000000	0.00000000	0.10890100
H	0.00000000	0.00000000	-0.87121100

TS2b2

C	-0.78951500	0.20598100	-0.19097800
C	-1.32587300	-0.38006600	-1.35376200
C	-2.68835700	-0.69342900	-1.38042800
C	-3.50179400	-0.43008800	-0.27967100
C	-2.95943900	0.14953800	0.86630500
C	-1.60141400	0.47454700	0.92838800
C	0.65563000	0.58898300	-0.16042800
C	1.69074000	-0.27758600	0.23771100
C	3.02336800	0.15498700	0.22365500
C	3.34429300	1.44647000	-0.17644300
C	2.32628400	2.31502200	-0.57175800
C	1.00077600	1.88629900	-0.56393500
H	-3.11208600	-1.15013600	-2.27762900
H	-4.56444500	-0.67816500	-0.31466100
H	-3.59510700	0.35299900	1.73105800
H	3.80043400	-0.54358000	0.53510300
H	4.38461800	1.77485000	-0.18003500
H	2.56419900	3.33206700	-0.88859600
H	0.20615400	2.56673000	-0.87780300
C	-1.00641700	1.06874600	2.17639000
H	-0.21660700	0.41408700	2.57693500
H	-0.54095600	2.04551200	1.97552500
H	-1.77205000	1.20161900	2.95183700
C	-0.44306500	-0.68234100	-2.53493300
H	0.36244700	-1.37939700	-2.25458200
H	-1.02164700	-1.13459300	-3.35086400
H	0.04232600	0.22911000	-2.91554800
C	1.46864200	-1.69591800	0.68749200
O	2.39059000	-2.45082600	0.91530800
O	0.20077000	-2.03658000	0.81502600
H	0.09765200	-3.19306500	1.03771300
O	0.39999500	-4.12580500	1.63536800
H	1.36915800	-4.16258700	1.48552800

IM1b3

C	-0.89799300	-0.33916400	0.14362400
C	-1.48962600	0.34235200	1.22322200
C	-2.87580900	0.54258600	1.21329100
C	-3.65645100	0.07917500	0.15585400
C	-3.05658500	-0.59288800	-0.90895800
C	-1.67462000	-0.81207400	-0.92966500
C	0.57409700	-0.61064800	0.16722900
C	1.54883400	0.33853700	-0.19638500
C	2.91217600	0.02967700	-0.08620300
C	3.32066300	-1.22365000	0.36052000
C	2.36181800	-2.17184000	0.71881200
C	1.00584000	-1.86133000	0.62751000
H	-3.34424900	1.06784700	2.04898800
H	-4.73610500	0.24266600	0.16064600
H	-3.66591900	-0.95078600	-1.74226200
H	3.65438200	0.77740000	-0.36735400
H	4.38421200	-1.45712300	0.43078700
H	2.67014200	-3.15638700	1.07590900
H	0.25712100	-2.59923200	0.92461600
C	-1.02591400	-1.51761900	-2.09155900
H	-0.21982900	-0.90311300	-2.52161900
H	-0.57252200	-2.47180600	-1.78125800
H	-1.76002200	-1.72788300	-2.87994100
C	-0.65287800	0.86336800	2.36337400
H	-0.02072900	0.07226500	2.79450200
H	0.02265000	1.66709900	2.02718400
H	-1.29050200	1.27016500	3.15879800
C	1.14814200	1.67766500	-0.72548400
O	0.10310600	1.92563800	-1.27441900
O	2.09437000	2.60769300	-0.54831400
H	1.79140000	3.43736200	-0.95821300

IM2b1

C	1.69382000	0.32026200	0.00008700
C	0.59471300	-0.52318100	0.00001100
C	0.74990600	-1.90452000	-0.00002400
C	2.05407500	-2.40488800	0.00001900
C	3.16664900	-1.54903400	0.00009500
C	2.99983200	-0.16543100	0.00013000
C	1.19783800	1.71743200	0.00011100
H	-0.11302400	-2.57400800	-0.00008100
H	2.21367700	-3.48462900	-0.00000600
H	4.17120900	-1.97464200	0.00012800
H	3.85303000	0.51524200	0.00019000
O	1.81045500	2.74706100	0.00016600
O	-0.15392700	1.67541100	0.00004500
C	-0.68055700	0.31790600	-0.00002100
C	-1.46537600	0.09411900	-1.27404400
C	-1.46549200	0.09404300	1.27391700
C	-2.69133300	-0.50939000	-1.22574000
C	-2.69144700	-0.50946000	1.22546500
C	-3.31224400	-0.85372100	-0.00017600
H	-3.21290800	-0.71140200	-2.16443900
H	-3.21310800	-0.71152500	2.16410400
H	-4.28842200	-1.33846100	-0.00023600
C	-0.81260400	0.52439200	2.54868100
H	-0.66554100	1.61620000	2.56099000
H	-1.42699600	0.24626300	3.41462900
H	0.18454200	0.06796900	2.66710800
C	-0.81236500	0.52452800	-2.54872500
H	-1.42665300	0.24639900	-3.41474700
H	-0.66534100	1.61634200	-2.56098900
H	0.18481000	0.06814500	-2.66705800

IM3b1

C	1.65928900	0.23378300	0.00007800
C	0.50212800	-0.52874600	-0.00001700
C	0.53698900	-1.91466500	-0.00009100
C	1.79802900	-2.51488300	-0.00007000
C	2.97409000	-1.75086900	0.00002200
C	2.91979500	-0.35925100	0.00009900
C	1.30027200	1.66812900	0.00014700
H	-0.37855500	-2.51070000	-0.00015700
H	1.86674500	-3.60371400	-0.00012600
H	3.94052400	-2.25632400	0.00003400
H	3.82254400	0.25367600	0.00016800
O	1.98045200	2.64445800	0.00022700
O	-0.07166900	1.74371500	0.00009300
C	-0.69140900	0.47616500	-0.00000500
C	-1.42274900	0.21050700	-1.28246100
C	-1.42282900	0.21033700	1.28237000
C	-2.53293800	-0.59385900	-1.24185800
C	-2.53300700	-0.59403400	1.24159100
C	-3.06202200	-0.99476100	-0.00017600
H	-3.03909100	-0.87636600	-2.16489400
H	-3.03920600	-0.87668000	2.16456000
H	-3.96265200	-1.61388500	-0.00024100
C	-0.86385100	0.78333300	-2.52573500
H	-1.39647500	0.40936900	-3.40639700
H	-0.94834200	1.88185400	-2.47713400
H	0.21132500	0.55627800	-2.61507000
C	-0.86398000	0.78295800	2.52575900
H	-0.94858100	1.88148000	2.47738200
H	-1.39656700	0.40876700	3.40634700
H	0.21121800	0.55599100	2.61504700

IM4b1

C	1.94550100	0.06022200	0.00091400
C	0.63920100	0.51929900	-0.00743100
C	0.34526400	1.87811400	-0.01898000
C	1.42564700	2.76212100	-0.02234900
C	2.75186500	2.29870800	-0.01395200
C	3.03216100	0.93377900	-0.00218700
C	1.90500700	-1.42221900	0.01408100
H	-0.69314500	2.22257800	-0.02621800
H	1.23866700	3.83747700	-0.03148100
H	3.57077000	3.01965000	-0.01664300
H	4.05718000	0.55899000	0.00461800
O	2.80060100	-2.21628900	0.02393200
O	0.60118300	-1.79835600	0.01401200
C	-0.30131900	-0.67514600	0.00251500
C	-1.12464000	-0.66466400	1.27712300
C	-1.12384900	-0.68966200	-1.27278800
C	-2.38356700	-0.21880400	1.24413800
C	-2.38157400	-0.24078300	-1.25406300
C	-3.07987800	0.22693800	-0.01155400
H	-2.94872700	-0.14113600	2.17885200
H	-2.94323100	-0.17308800	-2.19035300
H	-4.10221300	-0.19307800	-0.01107000
O	-3.16503800	1.64965700	-0.08207400
H	-3.65818000	1.95490300	0.69356400
C	-0.41361800	-1.14150600	-2.51297100
H	-0.16836800	-2.21218400	-2.45205500
H	-1.03672200	-0.97096700	-3.40005800
H	0.53777200	-0.59998500	-2.64281300
C	-0.41531900	-1.08924600	2.52749600
H	-1.04011300	-0.90219700	3.41007100
H	-0.16786700	-2.16048600	2.48864100
H	0.53492600	-0.54348200	2.64804400

OH^-

O	0.00000000	0.00000000	0.10841500
H	0.00000000	0.00000000	-0.86731900

TS2b1

C	-3.50749000	-1.27707800	0.57097100
C	-2.63582200	-0.48923700	-0.16988200
C	-2.13818400	-0.92656100	-1.38994400
C	-2.53449600	-2.19419700	-1.82775700
C	-3.39854500	-2.99667100	-1.06940000
C	-3.90331700	-2.54334600	0.14922300
C	-3.92733000	-0.50774400	1.76109700
H	-1.46180400	-0.31287400	-1.98621700
H	-2.16185800	-2.56813200	-2.78366700
H	-3.68585900	-3.98069800	-1.44320300
H	-4.58903300	-3.14677000	0.74649700
O	-4.66091600	-0.80475400	2.66090200
O	-3.32809000	0.70995100	1.69607500
C	-2.44988800	0.83721900	0.55817800
C	-1.04474200	1.04598300	1.10655700
C	-2.97319500	1.96669000	-0.30472700
C	-0.30699900	2.10100900	0.74303200
C	-2.15143100	2.96479700	-0.74363000
C	-0.70986200	3.05915200	-0.33313300
H	0.67911800	2.24402100	1.19333000
H	-2.52521100	3.73783600	-1.41622200
H	-0.40445000	4.09612800	-0.13307200
O	-0.29057900	2.65799800	-1.60793500
H	0.25691700	1.57159200	-1.67140000
C	-4.43371800	1.98914400	-0.59067000
H	-4.99549500	2.16517500	0.34034300
H	-4.68148900	2.77514500	-1.31234700
H	-4.76243100	1.01238200	-0.98241600
C	-0.55694900	0.01303200	2.07805400
H	0.45605600	0.25845600	2.42159300
H	-1.21792200	-0.05780900	2.95469900
H	-0.53338100	-0.98139400	1.60303800
C	2.98562000	-1.67246100	0.07468800
C	3.91665100	-0.74063500	0.73282200
C	3.71538900	0.66625200	0.40711800
C	2.70407800	1.09167400	-0.44500100
C	1.77512800	0.16755300	-1.02408600
C	1.99433000	-1.24248800	-0.75997300
Cl	0.92348700	-2.34544600	-1.52716600
Cl	3.22038400	-3.33566600	0.41220300
O	0.79555300	0.51785400	-1.76061700
O	4.80472000	-1.11817800	1.49260500
C	2.57830300	2.48244900	-0.77178800

N	2.47763700	3.60372200	-1.02921900
C	4.62659400	1.59897800	0.99565800
N	5.36104500	2.35368000	1.47075300

IM5b1

C	1.91436100	-0.01065700	0.01770100
C	0.63551300	0.52107900	-0.00877700
C	0.42260600	1.89453600	-0.03216400
C	1.55229100	2.71520100	-0.02386900
C	2.84898500	2.17687300	0.00600800
C	3.04935000	0.79824200	0.02645700
C	1.79444500	-1.48822800	0.02725800
H	-0.59076400	2.30369400	-0.05809700
H	1.42597300	3.79916800	-0.04158400
H	3.70769200	2.84975200	0.01177600
H	4.05056100	0.36436700	0.04777200
O	2.64423800	-2.33009200	0.04838100
O	0.47140800	-1.79258700	0.00536500
C	-0.36762900	-0.62297400	-0.01342100
C	-1.20365800	-0.58976800	1.25378200
C	-1.18009000	-0.60283200	-1.29552200
C	-2.44883600	-0.10457000	1.23030900
C	-2.42277500	-0.11284800	-1.28633300
C	-3.10635900	0.39189300	-0.04475900
H	-3.02880600	-0.00847300	2.15040700
H	-2.97936600	-0.03815200	-2.22478400
H	-4.16651300	0.07532300	-0.02787500
O	-3.03121700	1.76443500	0.10149600
C	-0.47701100	-1.08341300	-2.52875800
H	-0.27110100	-2.16183600	-2.46206500
H	-1.08650100	-0.89279600	-3.42095900
H	0.49403800	-0.57629100	-2.65163700
C	-0.53768700	-1.08387400	2.50152600
H	-1.16232900	-0.88333600	3.38065000
H	-0.34826900	-2.16513400	2.43554900
H	0.43892000	-0.59229900	2.64227700

TS3b1

C	5.15461300	0.08141500	0.63682900
C	3.80615100	-0.20667900	0.76744800
C	3.28370300	-0.71781700	1.94850400
C	4.17672000	-0.93056200	3.00087100
C	5.54402200	-0.64044100	2.86981400
C	6.05547700	-0.12696600	1.67933000
C	5.37933500	0.60554100	-0.73136600
H	2.21833100	-0.94145400	2.04474600
H	3.80504200	-1.33058200	3.94590000
H	6.21240600	-0.82061800	3.71302300
H	7.11579300	0.10329600	1.56225800
O	6.38518600	0.97410500	-1.26157900
O	4.17736400	0.61458500	-1.37009400
C	3.10743900	0.13220300	-0.54216100
C	2.52141100	-1.12638200	-1.15450400
C	2.10708400	1.24835200	-0.31043800
C	1.20832500	-1.37179600	-1.07926100
C	0.79595700	0.98689200	-0.23070700
C	0.23457700	-0.36593300	-0.55805900
H	0.79234500	-2.31575500	-1.43848900
H	0.07708200	1.76815900	0.02717500
H	-0.55302900	-0.11432800	-1.48485200
O	-0.52854400	-0.77626700	0.46053700
C	2.67090200	2.62133900	-0.11815800
H	3.12970400	2.97501700	-1.05339900
H	1.88616500	3.32590400	0.18275900
H	3.46116100	2.61502200	0.64991300
C	3.50057100	-2.08576500	-1.75712900
H	3.00496500	-3.02471600	-2.03238100
H	3.95610800	-1.64580700	-2.65682700
H	4.31836300	-2.30630800	-1.05265100
C	-4.70755800	0.15356700	0.84358500
C	-4.15854500	1.37780900	0.42541000
C	-3.13821600	1.41073600	-0.53669900
C	-2.65301000	0.22309500	-1.14821200
C	-3.20306200	-1.01236700	-0.67299300
C	-4.20407900	-1.04267300	0.28242900
C	-4.65939800	2.58793300	1.01060400
N	-5.05511000	3.56748000	1.47508400
C	-2.55798900	2.65377600	-0.95259700
N	-2.07762300	3.65236600	-1.27702200
O	-1.75220200	0.25465700	-2.06200600
O	-5.66877600	0.18086100	1.75453900

H	-5.98887300	-0.71352800	1.96821800
Cl	-4.86824900	-2.53345200	0.84397700
Cl	-2.54335300	-2.45645500	-1.31269700

P2

C	-1.95238000	-0.08651900	0.00000400
C	-0.71763700	0.54192100	-0.00001300
C	-0.61220500	1.92691000	-0.00003100
C	-1.80216200	2.65801600	-0.00003600
C	-3.05333100	2.02226700	-0.00001800
C	-3.14625600	0.63205200	0.00000300
C	-1.72416700	-1.55050600	0.00001300
H	0.36004900	2.42481800	-0.00004000
H	-1.75920200	3.74849900	-0.00004900
H	-3.96102000	2.62745000	-0.00001800
H	-4.10993700	0.11994900	0.00001500
O	-2.50588600	-2.45452000	0.00000900
O	-0.37857200	-1.75545700	0.00001900
C	0.36814700	-0.52983500	0.00000000
C	1.17176000	-0.42700300	-1.28300800
C	1.17173700	-0.42696200	1.28302000
C	2.40780800	0.09361500	-1.25877500
C	2.40777900	0.09366600	1.25878700
C	3.08828700	0.46478400	0.00000700
H	2.97332900	0.24616300	-2.18102400
H	2.97330200	0.24626400	2.18102600
O	4.17724600	1.00869700	0.00001300
C	0.48045600	-0.86427000	2.53460800
H	0.29882600	-1.94919800	2.50467300
H	1.08832300	-0.62815600	3.41631400
H	-0.50160000	-0.37548400	2.63784900
C	0.48049200	-0.86431700	-2.53460300
H	1.08838100	-0.62822800	-3.41630100
H	0.29883600	-1.94924000	-2.50465900
H	-0.50155100	-0.37550700	-2.63786800

System 3

R4

C	1.44728300	0.03013200	-0.00000900
C	0.38425300	-0.87036700	-0.00001500
C	-0.91924000	-0.38083900	0.00000100
C	-1.14575000	0.99664100	-0.00002000
C	-0.08042500	1.88669900	-0.00001400
C	1.22627600	1.40615900	0.00001400
H	0.56117200	-1.94497300	-0.00001100
H	-0.29417200	2.95576400	-0.00001000
H	2.07364700	2.09062500	0.00002700
F	-2.38823800	1.45612000	0.00001300
Cl	-2.26794800	-1.45775400	0.00000300
Cl	3.07260200	-0.57854300	0.00000500

^{3}DDQ*

C	1.34878500	-0.68459500	-0.01183100
C	1.34878800	0.68618500	0.01173800
C	0.11887600	1.49299400	0.00884900
C	-1.12022800	0.73426000	-0.01852600
C	-1.12020900	-0.73245000	0.01883600
C	0.11890800	-1.49120800	-0.00872200
C	2.57910400	1.42744700	0.03097600
C	2.57934400	-1.42621400	-0.03096500
N	3.54794300	2.01382100	0.04853900
N	3.56591900	-2.02373900	-0.04863300
Cl	-2.55773200	1.57452400	-0.11441500
Cl	-2.55769500	-1.57269700	0.11499800
O	0.13123400	2.72282900	0.01043300
O	0.13127600	-2.72115600	-0.01027600

IM1c1

C	-0.36863600	-0.92207300	0.00000400
C	-1.44538700	-0.01566300	0.00001000
C	-1.24011400	1.41002600	0.00000600
C	0.03321000	1.91391700	0.00000000
C	1.11356700	1.00968600	0.00000000
C	0.91706200	-0.42254300	-0.00000200
H	-0.54692500	-1.99795700	0.00000400
H	-2.11156600	2.06685500	0.00000700
H	0.24361800	2.98471700	-0.00000400
F	2.31736300	1.45633800	-0.00001300
Cl	2.28450500	-1.40829900	-0.00001000
Cl	-3.01977600	-0.59174600	0.00001000

DDQ$^{\bullet-}$

C	-0.13366800	-1.48585700	-0.00002300
C	-1.35734100	-0.69806000	-0.00001200
C	-1.35734000	0.69806200	-0.00001300
C	-0.13366800	1.48585700	-0.00004700
C	1.10742000	0.67983400	-0.00001000
C	1.10742000	-0.67983400	-0.00000300
C	-2.58510000	1.43670800	0.00000500
C	-2.58510100	-1.43670500	-0.00000100
N	-3.57846600	2.02920300	0.00003500
N	-3.57846400	-2.02920500	0.00000400
Cl	2.57623300	1.58758400	0.00000500
Cl	2.57623300	-1.58758500	0.00001500
O	-0.11682200	2.71456100	0.00000200
O	-0.11682300	-2.71456200	0.00000000

R5

C	-0.04649800	0.65091700	0.00000000
H	-1.09328700	0.98356800	0.00000000
H	0.43902300	1.08177600	0.89458800
H	0.43902300	1.08177600	-0.89458800
O	-0.04649800	-0.74990100	0.00000000
H	0.86622000	-1.05341400	0.00000000

TS1c1

C	-0.09095500	-1.10335100	-0.55592000
C	-1.38519600	-0.55957000	-0.34393500
C	-1.58052500	0.78775800	-0.04652500
C	-0.46893100	1.73222800	0.05725700
C	0.85434300	1.13061000	-0.18766300
C	1.01474100	-0.18857800	-0.51160900
C	-2.89306000	1.31392200	0.17482800
C	-2.49744200	-1.46771000	-0.42831800
N	-3.95503400	1.73792300	0.34822800
N	-3.40078800	-2.18370200	-0.49905200
Cl	2.20007800	2.20180500	-0.06024500
Cl	2.57854600	-0.86119700	-0.80188400
O	-0.61933400	2.91960600	0.32207100
O	0.06698000	-2.36602800	-0.94316000
C	1.35936600	-1.64272900	2.23021700
H	1.52206700	-0.54485500	2.07977500
H	1.06959400	-1.76114000	3.29728100
H	2.36796600	-2.09696000	2.10191500
O	0.42834500	-2.12360000	1.36441700
H	0.41254200	-2.72224500	-0.04362000

DDQH$^-$

C	-0.11403600	1.37178900	0.00004900
C	-1.34850400	0.67007200	0.00003900
C	-1.37158300	-0.71432200	0.00005300
C	-0.14009100	-1.50491900	0.00015600
C	1.11224900	-0.73040900	0.00003200
C	1.11181600	0.64127300	0.00002200
C	-2.56235200	1.43866800	-0.00000300
N	-3.54076300	2.04893700	-0.00004100
C	-2.60434600	-1.44108100	-0.00000700
N	-3.59671600	-2.03081600	-0.00003200
O	-0.15261500	-2.73044100	-0.00004800
O	-0.16911100	2.68124000	0.00002300
H	0.70905600	3.10826300	0.00000500
Cl	2.57422500	1.55214200	-0.00004500
Cl	2.56272700	-1.62437200	-0.00003400

IM2c1(IM1c2)

C	0.56970900	-0.00008100	0.01292500
H	0.86984900	0.00308600	-1.05844300
H	1.01155300	-0.91227100	0.45593400
H	1.01137600	0.90988200	0.46073000
O	-0.78887900	-0.00002700	0.00802900

TS2cc1

C	0.65712600	-1.09607700	2.07185100
H	0.70954500	-0.03593100	2.38659000
H	0.97277000	-1.72790000	2.92399600
H	-0.40252100	-1.36153200	1.87184800
O	1.48470800	-1.40327300	1.01996600
C	-1.64113900	0.08746300	-0.23403400
C	-0.64172300	1.03801900	0.00161500
C	0.67530300	0.71313300	-0.27020100
C	1.01819900	-0.60050000	-0.68779000
C	-0.01974500	-1.50239700	-1.02230600
C	-1.33457300	-1.17990100	-0.74976000
H	-0.89315100	2.02637600	0.38493200
H	0.26704700	-2.46905000	-1.43597400
H	-2.13903500	-1.88705600	-0.94920000
F	2.22280000	-0.81279000	-1.18209700
Cl	1.95216600	1.81685300	0.04299200
Cl	-3.28617800	0.49126100	0.11234400

IM3c1

C	-1.87187700	-0.06574400	-0.02707000
C	-1.50029100	-1.40687900	0.27320500
C	-0.19587500	-1.72786400	0.44505000
C	0.92855500	-0.75255900	0.24551300
C	0.41262200	0.66756600	0.11701500
C	-0.90701300	0.96423800	-0.06479700
H	-2.28171200	-2.16047700	0.37128200
H	0.12482000	-2.74488900	0.67475600
H	-1.22123400	1.99928500	-0.19653600
F	1.76320200	-0.79433200	1.34418300
O	1.63159400	-1.21677300	-0.84919500
C	2.83230900	-0.56244900	-1.21820200
H	3.39273400	-1.27626700	-1.83331300
H	2.63242000	0.34340400	-1.81033700
H	3.42826700	-0.29592200	-0.33415100
Cl	1.57445700	1.93541300	0.24165700
Cl	-3.52666000	0.31871600	-0.28872000

R5+ DDQ$^{\bullet-}$

C	-0.13327800	1.47843700	0.00074000
C	-1.35753800	0.69732400	0.00035600
C	-1.35753800	-0.69732400	0.00036500
C	-0.13327800	-1.47843700	0.00078200
C	1.11069000	-0.68003700	0.00017800
C	1.11069000	0.68003700	0.00017100
C	-2.58328500	-1.43428600	-0.00000200
C	-2.58328500	1.43428600	-0.00000200
N	-3.57777400	-2.02495800	-0.00025800
N	-3.57777500	2.02495700	-0.00025800
Cl	2.57753200	-1.58573200	-0.00033800
Cl	2.57753200	1.58573200	-0.00034500
O	-0.12414400	-2.71040000	-0.00003900
O	-0.12414400	2.71040000	0.00000000
C	0.29957687	-2.59400017	3.90650331
H	0.47117035	-3.09047911	4.87086019
H	1.03639978	-1.77996282	3.80207118
H	-0.71152387	-2.15360951	3.92072498
O	0.43926860	-3.56866480	2.89507578
H	0.29189504	-3.15143138	2.03796156

IM2c1+R4

C	-2.44983934	2.54808166	1.30990004
C	-2.36956339	3.42904145	0.20927300
C	-2.22430548	2.96903121	-1.14261011
C	-2.15949541	1.62603046	-1.39147491
C	-2.23892924	0.74127451	-0.29833343
C	-2.38472884	1.20131510	1.05909513
H	-2.56013490	2.92790170	2.32690312
H	-2.16758865	3.69709144	-1.95313479
H	-2.04944583	1.21738985	-2.39694938
F	-2.18066353	-0.53095720	-0.50186798
Cl	-2.46986133	0.03658996	2.29800534
Cl	-2.44627515	5.09156788	0.48115698
C	0.93087459	1.19590662	-0.08631415
H	1.46539104	0.78064011	0.82246819
H	1.03279296	2.31582976	0.05122961
H	1.65679093	0.97712701	-0.92820652
O	-0.31978466	0.75022399	-0.27304720

TS1c2

C	-1.90308800	-1.10751500	0.69094100
C	-2.49347800	-0.90940500	-0.62998600
C	-2.93119500	0.43251700	-0.93329600
C	-2.71218300	1.49247300	-0.06999500
C	-2.03729000	1.33528700	1.21248500
C	-1.66240000	-0.04598300	1.55819000
C	-3.12119900	2.82180100	-0.41343600
C	-3.55192700	0.63191100	-2.21128500
N	-3.45025100	3.89373900	-0.68955600
N	-4.05385000	0.79383100	-3.23818100
Cl	-0.96219200	-0.28726100	3.08563000
Cl	-1.57459100	-2.72098900	1.14450300
O	-1.80928400	2.27931000	1.96713000
O	-2.52121300	-1.83316300	-1.47384000
C	0.43801102	-1.25889621	-1.17855677
H	-0.03780202	-0.82273479	-0.32517223
H	0.12448752	-0.47080184	-1.83086827
O	-0.05700598	-2.50043021	-1.33674077
H	-1.04495198	-2.44861421	-1.54500177
H	1.14507393	-1.05996878	-0.40048870

DDQH·

C	1.10692300	0.63698100	-0.00008900
C	-0.11629000	1.36524200	0.00001800
C	-1.35180900	0.66805600	-0.00002100
C	-1.37351200	-0.71956100	0.00003500
C	-0.13950100	-1.51307500	-0.00006300
C	1.11537800	-0.73689200	0.00006900
O	-0.14716700	-2.73464300	-0.00046300
O	-0.15252300	2.68227700	0.00006200
H	0.74634700	3.05080400	0.00025700
Cl	2.56246500	-1.62487800	0.00018800
Cl	2.56914300	1.55847700	-0.00008400
C	-2.60858600	-1.44073900	0.00010100
C	-2.56410900	1.44005700	-0.00002000
N	-3.60731800	-2.02011400	0.00020000
N	-3.53512800	2.06247400	-0.00005500

TS1c3

C	-1.47622700	-1.43766900	0.05525200
C	-1.90648000	-0.08217100	-0.05929800
C	-0.97646700	0.98235800	-0.05830700
C	0.36193700	0.71071100	0.05022000
C	0.82325000	-0.66121400	0.22905300
C	-0.14969900	-1.72481600	0.16772800
H	-2.22175400	-2.23315000	0.02770200
H	-1.32087700	2.01362800	-0.14442400
H	0.22210900	-2.74792400	0.23790300
F	1.58125800	-0.68291400	1.70499700
C	2.61040300	-0.69442300	-1.57848000
H	3.56353200	-1.22253600	-1.67162900
H	2.73661600	0.38743200	-1.68752700
H	1.87987000	-1.09760600	-2.28863700
O	2.12658400	-1.00653100	-0.24589700
H	2.45312900	-0.86178600	0.85588200
Cl	1.53844400	1.94858800	0.11697700
Cl	-3.55473300	0.25163300	-0.20780600

HF

F	-0.24760383	0.06389776	0.00000000
H	-1.12760383	0.06389776	0.00000000

IM1c3

C	-1.71309700	-0.19768400	0.00001300
C	-0.91757900	0.96013600	-0.00001300
C	0.45493100	0.83141900	-0.00001700
C	1.06453800	-0.48968400	0.00000700
C	0.23027600	-1.64706700	0.00003400
C	-1.12955500	-1.50340500	0.00003700
H	-1.37722600	1.94878500	-0.00003100
H	0.67547800	-2.64144900	0.00005300
H	-1.78685800	-2.37374600	0.00005700
O	2.35384400	-0.52018900	0.00000100
C	3.09447600	-1.75135400	0.00001700
H	4.14682500	-1.45800500	0.00000000
H	2.85581300	-2.32276500	0.90658900
H	2.85579400	-2.32280000	-0.90652800
Cl	1.46978700	2.18461900	-0.00005200
Cl	-3.39358300	-0.06007000	0.00001600

DDQ

C	1.15594600	-0.67373300	0.00002000
C	-0.11818900	-1.45820900	0.00025000
C	-1.40257400	-0.67387400	0.00004700
C	-1.40257400	0.67387400	-0.00000700
C	-0.11818900	1.45820900	0.00013200
C	1.15594600	0.67373300	-0.00001400
O	-0.13684500	2.65830000	0.00054500
O	-0.13684500	-2.65830000	0.00022100
Cl	2.58976800	1.60062000	-0.00018400
Cl	2.58976700	-1.60062000	-0.00014400
C	-2.61258400	1.44865700	-0.00011100
C	-2.61258400	-1.44865700	-0.00004500
N	-3.58098300	2.07389500	-0.00021100
N	-3.58098300	-2.07389500	-0.00010200

TS4c1

C	2.42235000	-0.22451500	0.08032700
C	1.70378700	0.97490500	0.10434400
C	0.39719800	0.97878000	-0.34300800
C	-0.21964900	-0.21803800	-0.81721400
C	0.53430500	-1.42151600	-0.80041300
C	1.84257600	-1.41980100	-0.36812900
H	2.16058000	1.89160800	0.47467900
H	2.42287400	-2.34138100	-0.34958500
O	-1.42811700	-0.09878700	-1.30948200
C	-2.22278500	-1.24890000	-1.56901000
H	-3.17063800	-0.87057400	-1.96276700
H	-1.74135900	-1.89108400	-2.32005400
H	-2.38982300	-1.78600100	-0.62220500
H	0.06306900	-2.35209200	-1.10948600
F	-1.10936200	-1.03150800	1.15531400
C	-3.65869700	0.34952900	1.08901900
H	-3.46740300	1.09327100	1.88700600
H	-2.99650500	0.64943100	0.23709800
H	-4.70022700	0.43894700	0.73924600
O	-3.39009000	-0.93716600	1.48635100
H	-2.30035400	-1.04177300	1.50670800
Cl	-0.53715400	2.41774100	-0.31007500
Cl	4.05804800	-0.23196600	0.63072700

TS3c1-1

C	1.78928700	-0.18108900	-0.13088200
C	1.02881500	1.00210000	0.00107800
C	-0.34067200	0.94418900	-0.07240500
C	-1.01010100	-0.30430200	-0.25888400
C	-0.21258600	-1.47808900	-0.36952100
C	1.18439700	-1.40604400	-0.32713400
H	1.52641800	1.95852300	0.15528300
H	-0.69496600	-2.43439500	-0.55755900
H	1.78571000	-2.30842000	-0.42409500
F	-0.94018800	-1.29167800	1.58705800
O	-2.31455100	-0.26339000	-0.42439500
C	-3.04334300	-1.47865000	-0.40420500
H	-4.10092700	-1.19869500	-0.38401300
H	-2.84175500	-2.06996600	-1.31093700
H	-2.77190000	-2.04074000	0.49845700
Cl	-1.29394800	2.37049500	0.07146500
Cl	3.51163800	-0.06242300	-0.04168800

IM4c1-1

C	1.76468400	-0.13103400	-0.08600900
C	1.02594900	1.08183700	0.05715300
C	-0.36564400	1.02828600	0.02206500
C	-1.04931700	-0.17078400	-0.13788700
C	-0.31367400	-1.47855600	-0.17497700
C	1.16772500	-1.33704400	-0.23669800
H	1.53872200	2.03237000	0.18491100
H	1.75769300	-2.24570300	-0.35247800
O	-2.37727000	-0.14351700	-0.19241300
C	-3.11798300	-1.33386900	-0.39182000
H	-4.17033500	-1.05674800	-0.27398000
H	-2.96470200	-1.72377000	-1.41018600
H	-2.84468100	-2.09805000	0.34648200
H	-0.67515400	-2.08993100	-1.02143800
F	-0.66840800	-2.21412500	0.96886300
Cl	-1.27906700	2.49433700	0.15277100
Cl	3.49799900	-0.00586200	-0.09187400

TS4c1-1

C	1.73890197	-0.18498789	-0.08726773
C	1.00168597	1.02460811	0.07523627
C	-0.38940803	0.96095311	0.03215527
C	-1.07296403	-0.23789489	-0.13313673
C	-0.32588303	-1.53774089	-0.14429073
C	1.15209797	-1.39643789	-0.23681873
H	1.51201297	1.97748911	0.20868327
H	1.73714597	-2.30505989	-0.38464973
O	-2.39475403	-0.22174589	-0.20068073
C	-3.12939303	-1.41365089	-0.47823573
H	-4.18533903	-1.13124389	-0.41934073
H	-2.90439703	-1.77503489	-1.49198873
H	-2.91154103	-2.19257489	0.26377727
H	-0.70645603	-2.20577489	-0.93185573
F	-0.69255561	-2.31463068	1.25376015
Cl	-1.31080903	2.43383911	0.16214627
Cl	3.48312097	-0.05078389	-0.12794373
C	-2.47575659	-4.15120091	3.21867624
H	-2.60753361	-4.65441417	4.18580141
H	-3.24295528	-3.36349118	3.13270866
H	-2.64158635	-4.89253823	2.41905736
O	-1.16728234	-3.62255844	3.18862872
H	-0.99223125	-3.04657220	2.10204794

P3

C	1.74120800	-0.13290200	0.00919000
C	1.33588700	-1.45507200	-0.15844300
C	-0.02018900	-1.73547000	-0.29734600
C	-0.97366900	-0.71659200	-0.27893600
C	-0.53793200	0.60610200	-0.10917500
C	0.81374800	0.90601600	0.03260100
H	2.07985200	-2.25074300	-0.17950800
H	-0.37188500	-2.75854200	-0.43702600
H	1.13577000	1.93927100	0.15474200
O	-2.28602700	-1.01124800	-0.44900700
C	-3.04344300	-1.07492700	0.74532900
H	-4.07496800	-1.30732600	0.45751000
H	-2.66142200	-1.86826500	1.40859300
H	-3.02477900	-0.11273900	1.28049000
Cl	-1.70572500	1.88789800	-0.11037700
Cl	3.42996000	0.23359600	0.18378500

6. The number of imaginary frequencies and Electronic Energy + Thermal Free Energy Correction for the optimized reactants, product and transition states obtained at the M06-2X-D3/ ma-def2-SVP level in the processes.

Table 1. The number of imaginary frequencies and the relative Gibbs free energy of transition states in the reaction of R1+R2 to P1.

Transition states	Imaginary frequency (cm^{-1})	Electronic Energy + Thermal Free Energy Correction (a.u)
TS1a1	-654.94	-1560.637882
TS2a1	-474.12	-307.547061
TS1a2	-709.65	-1560.424226
TS3c2-1	-1581.00	-1792.329308
TS3c2-2	-676.25	-383.220968
TS3c2-3	-2075.61	-457.714411
TS3c2-4	-521.32	-1791.721126

Table 2. The number of imaginary frequencies and the relative Gibbs free energy of transition states in the reaction of R3+R2 to P2.

Transition states	Imaginary frequency (cm^{-1})	Electronic Energy + Thermal Free Energy Correction (a.u)
TS1b1	-1023.77	-2213.603338
TS2b1	-432.96	-2288.715115
TS3b1	-1894.97	-2288.697836
TS1b2	-709.65	-1560.424226
TS2b2	-2585.68	-805.135511

Table 3. The number of imaginary frequencies and the relative Gibbs free energy of transition states in the reaction of R4+R5 to P3.

Transition states	Imaginary frequency (cm^{-1})	Electronic Energy + Thermal Free Energy Correction (a.u)
TS1c1	-911.40	-1599.871448
TS2c1	-602.16	-1364.858035
TS3c1	-2077.59	-1480.421611
TS1c2	-993.66	-1599.667057
TS1c3	-956.60	-1365.232254
TS3c1-1	-147.36	-1364.868023
TS4c1-1	-188.01	-1480.423725

Table 4. The relative Gibbs free energy of reactants, intermediates and product in the reaction of R1+R2 to P1.

Names	Electronic Energy + Thermal Free Energy Correction (a.u)
^{3}DDQ*	-1484.119263
R1	-231.907771
$DDQ^{\bullet-}$	-1484.377980
IM1a1	-231.656831
R2	-76.342752
R2+ $DDQ^{\bullet-}$	-1560.714215
$DDQH^{-}$	-1484.983802
IM2a1	-75.658605
IM3a1	-307.576144
DDQH·	-1484.789778
O_2	-150.169596
IM2a2-3	-457.749423
$DDQH_2$	-1485.420437
IM3a2-3	-457.774041
$\cdot HO_2$	-150.748207
P1	-307.057089

Table 5. The relative Gibbs free energy of reactants, intermediates and product in the reaction of R3+R2 to P2.

Names	Electronic Energy + Thermal Free Energy Correction (a.u)
R3	-729.496600
IM1b1	-728.820981
IM2b1	-728.848525
IM3b1	-728.670801
IM4b1	-804.600948
IM5b1	-803.938590
IM1b2	-75.658605
IM1b3	-729.263143
P2	-803.431908

Table 6. The relative Gibbs free energy of reactants, intermediates and product in the reaction of R4+R5 to P3.

Names	Electronic Energy + Thermal Free Energy Correction (a.u)
^{3}DDQ*	-1484.123743
R4	-1249.986414
IM1c1	-1249.726528
$DDQ^{\bullet-}$	-1484.382554
R5	-115.559718
R5+ $DDQ^{\bullet-}$	-1599.934581
$DDQH^{-}$	-1484.987202
IM2c1	-114.900905
IM3c1	-1364.893106
IM4c1-1	-1364.889612
IM1c3	-1264.976238
DDQ	-1484.192874
HF	-100.351323
P3	-1265.207635