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Supporting Information for

Theoretical Insights into Photo-Induced Curtius Rearrangement of Chlorodifluoroacetyl Azide

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Curtius Rearrangement on Ground State

To elucidate the mehcanism of thermal Curtius rearrangemement, we have optimized the transition states and intermediates on the reaction paths at B3LYP/6-31+G* level, and the calcualted minimum energy paths (MEPs) are summarized in Fig. S1. We have considered two reaction paths, a concerted one (red dash line) and a stepwise one (blue dash line). On the concerted path, there is only one transition state **TS1** , which has the stretched C_1-C_2 bond of 1.707 Å and stretched N_3-N_8 bond of 1.87 Å, and the energy barrier is 35.5 kcal/mol. For the stepwise path, it is a three steps reaction. The first step is a isomerizaion reaction from ***syn*-1** to ***anti*-1** *via* a transition state **TS2** with a barrier of 10.4 kcal/mol. At **TS2**, the azide group is bent out of plane, resulting in the N_8-N_3-C_2-O_4 dihedral of 94 degree. The second step is a decomposition reaction to produce **nitrene** by elliminating N_2 *via* a transition state **TS3**. This transition state has a highly stretched N_3-N_8 bond of 1.906 Å and it is located higher than **TS1** by 1.6 kcal/mol. The last step is a rearrangement reaction from **nitrene** to **isocyanate** *via* a transition state **TS4**, which has the stretched C_1-C_2 bond of 1.654 Å and the shortened distance of 2.381 Å between C_1 and N_3 atoms. This transition state is located 10.2 kcal/mol higher than **TS1**. Because the overall barrier of the stepwise path (45.7 kcal/mol) is higher than that of the concerted path (35.5 kcal/mol), we can see that the concerted Curtius rearrangement is preferred under the condition of pyrolysis.

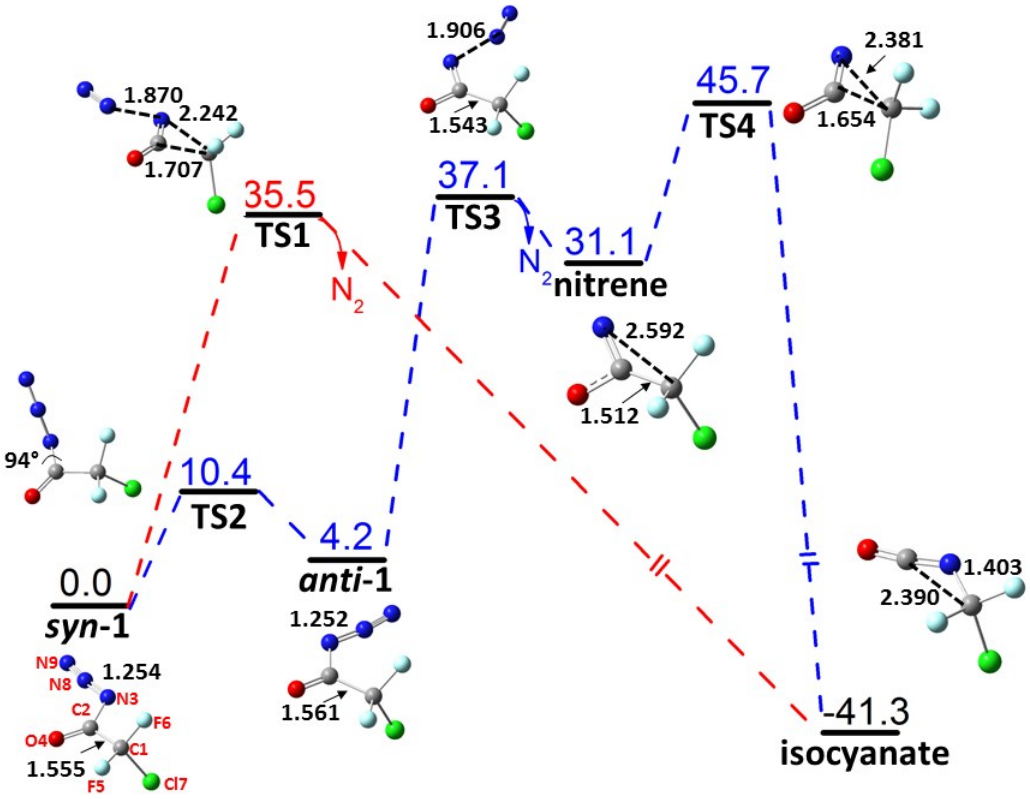

Fig. S1 The ground state potential energy surface for the Curtius rearrangement of ***syn*-1** at B3LYP/6-31+G* level. The red and blue dash lines correspond to the concerted and stepwise rearrangement, respectively. Atomic symbols and labels are exemplified for ***syn*-1**. The selective bond lengths are given in Å, dihedral in degree and energy in kcal/mol.

Table S1 Vertical excitations at ***syn*-2-S_0-Min** and ***syn*-3-S_0-Min** calculated by MS-CASPT2//CASSCF(14,11) along with excitation energy and oscillator strength. ***Syn*-2-S_0-Min** and ***syn*-3-S_0-Min** are re-optimized by CASSCF starting from ***syn*-2** and ***syn*-3**, respectively.

state	***syn*-2-S_0-Min**		***syn*-3-S_0-Min**	
	Excitation Energy kcal/mol(nm)	Oscillator Strength (*f*)	Excitation Energy kcal/mol(nm)	Oscillator Strength (*f*)
S_0	---	---	---	---
S_1	120.4 (237)	0.0004	121.4 (236)	0.0012
S_2	123.1 (232)	0.3222	124.6 (229)	0.3268
S_3	132.6 (216)	0.0006	133.6 (214)	0.0006
S_4	152.1 (188)	0.0642	152.7 (187)	0.0633
S_5	171.1 (167)	0.0005	172.2 (166)	0.0004
S_6	193.8 (148)	0.0948	194.2 (147)	0.0917
S_7	196.6 (145)	0.0000	197.8 (145)	0.0006
S_8	217.8 (131)	0.0126	218.6 (131)	0.0136
S_9	227.6 (126)	0.0001	227.9 (125)	0.0001

Table S2 Vertical excitations at ***syn*-1** calculated by TD-B3LYP/6-31+G* along with excitation energy and oscillator strength.

	Excitation Energy kcal/mol (nm)	Oscillator Strength (*f*)
S_0	---	---
S_1	101.2 (282)	0.0045
S_2	115.0 (249)	0.0009
S_3	118.3 (242)	0.0116
S_4	135.5 (211)	0.0575
S_5	136.7 (209)	0.1233
S_6	140.7 (203)	0.0411
S_7	145.2 (197)	0.0005
S_8	152.4 (188)	0.0067
S_9	155.0 (184)	0.0116

Table S3 The relative energies of critical points.

Structure	state	MS-CASPT2(kcal/mol)
***syn*-S_0-Min**	S_0	0.0
	S_1	121.5
	S_2	124.5
***syn*-S_1-Min**	S_0	47.3
	S_1	79.8
	S_2	90.6
***anti*-S_1-Min**	S_0	46.4
	S_1	79.6
	S_2	99.2
isomer-S_1-TS'	S_0	61.6
	S_1	84.4
	S_2	122.2
***syn*-S_1-TS**	S_0	49.6
	S_1	80.5
	S_2	90.2
***anti*-S_1-TS**	S_0	46.6
	S_1	79.8
	S_2	98.5
nitrene-S_0-Min	S_0	30.9
	S_1	70.1
	S_2	128.2
nitrene-S_0-TS	S_0	50.0
	S_1	64.3
	S_2	76.6
nitrene-S_1/S_0-CI	S_0	56.3
	S_1	58.3
	S_2	66.9
nitrene-S_1-Min	S_0	41.0
	S_1	52.6
	S_2	84.2
nitrene-S_1-TS	S_0	50.7
	S_1	109.8
	S_2	134.7
isocyanate-S_0-Min	S_0	-50.7
	S_1	98.0
	S_2	122.4
ayla-nitrene-S_0[a]	S_0	30.9
	S_1	69.4
	S_2	133.3

[a] The structure is the ground state minimum, which is optimized based on the last point of IRC of ***syn*-S_1-Min** (the N-N dissociation direction), and the relative energy of S_0 of **nitrene-S_0-Min** is set to the same value as the S_0 of this structure.

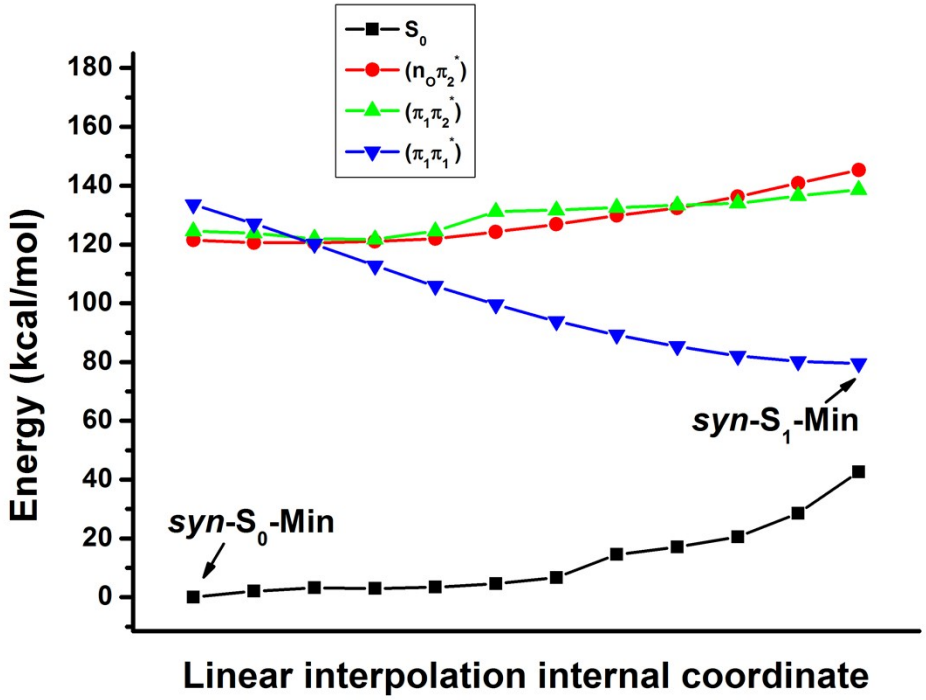

Fig. S2 The MS-CASPT2 energy plot from ***syn*-S$_0$-Min** to ***syn*-S$_1$-Min**.

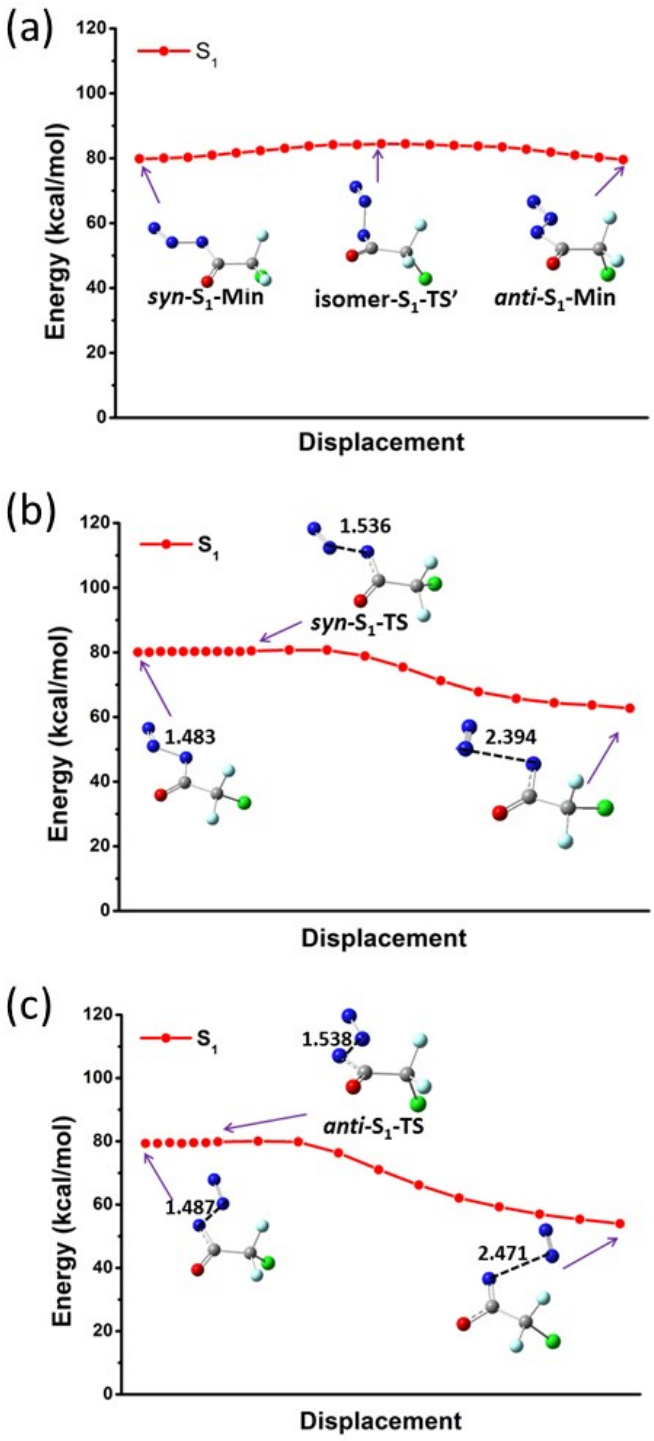

Fig. S3 The MS-CASPT2//CASSCF energy plot for the decomposition of $F_2ClCC(O)N_3$ on S_1 state. The selective bond lengths are given in Å. (a) The isomerization reaction from ***syn*-S_1-Min** to ***anti*-S_1-Min**. (b) The eliminating of N_2 from ***syn*-S_1-Min**. (c) The eliminating of N_2 from ***anti*-S_1-Min**.

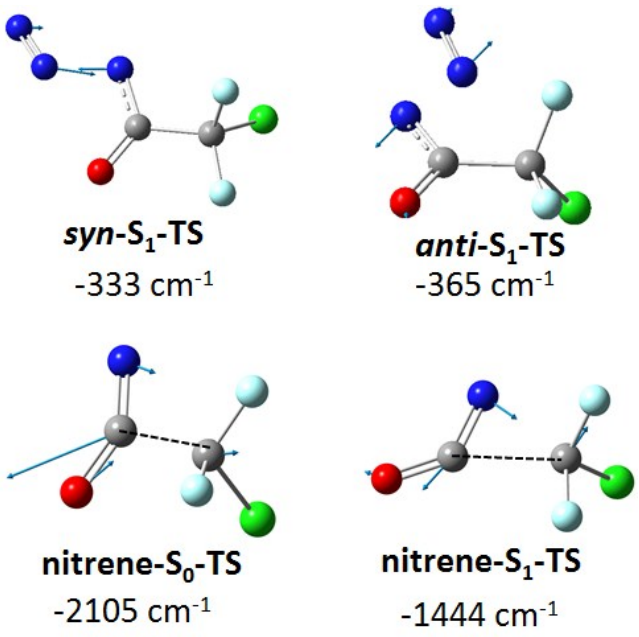

Fig. S4 The imaginary frequency vibrational modes of ***syn*-S_1-TS**, ***anti*-S_1-TS**, **nitrene-S_0-TS**, and **nitrene-S_1-TS**.

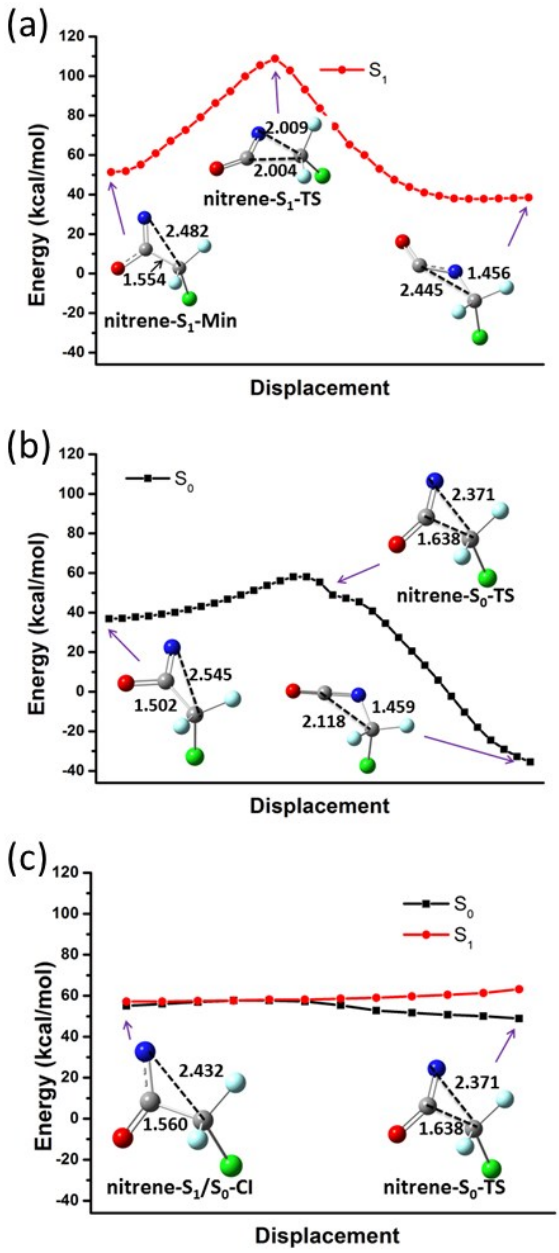

Fig. S5 The MS-CASPT2//CASSCF energy plot for the corresponding reactions from nitrene to isocyanate. (a) The rearrangement from nitrene to isocyanate on S_1 state. (b) The rearrangement from nitrene to isocyanate on S_0 state. (c) The decay from **nitrene-S_1/S_0-CI** to **nitrene-S_0-TS**.

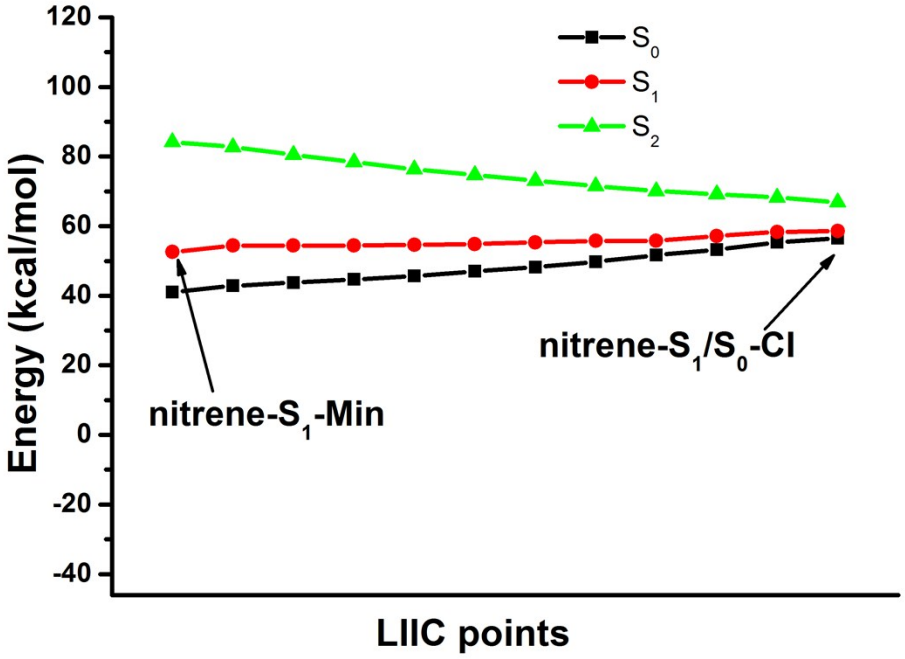

Fig. S6 The MS-CASPT2 energy plot of LIIC path from **nitrene-S_1-Min** to **nitrene-S_1/S_0-CI**.

Cartesian coordinates of critical points

***syn*-1**

C	-1.02191600	0.25933300	0.24574700
C	0.45298100	0.47206600	-0.18232800
N	1.29366900	-0.44003500	0.47590600
O	0.77386000	1.31192400	-0.98709400
F	-1.73063900	1.36040500	-0.04665800
F	-1.10901500	0.04613500	1.57721200
Cl	-1.72262500	-1.14081500	-0.62016300
N	2.50280200	-0.35787700	0.15241400
N	3.61254500	-0.37703300	-0.05437100

***syn*-2**

C	-0.91657100	-0.38021500	0.00418900
C	0.46123500	0.30363100	0.00204000
N	1.46530700	-0.64967300	-0.01269500
O	0.60237900	1.49169100	0.01606800
F	-1.01605000	-1.14271600	1.08452200
F	-1.00978900	-1.17382500	-1.05329700
Cl	-2.23972400	0.76110700	-0.01670600
N	2.61406800	-0.10849500	-0.00686900
N	3.66646100	0.24902900	-0.00371400

***syn*-3**

C	1.20677300	0.19864900	0.32325300
C	-0.28889000	0.30702200	0.00265800
N	-1.02878700	-0.64423300	0.68054700
O	-0.69900200	1.12841400	-0.76487500
F	1.38950600	0.03476900	1.62330700
F	1.81079400	1.31345100	-0.03189000
Cl	1.94253300	-1.15053300	-0.53558700
N	-2.26069200	-0.57063600	0.37716500
N	-3.35610300	-0.59961400	0.19237900

***anti*-1**

C	-1.12579600	0.34409500	0.19239500
C	0.40114200	0.44008100	-0.11793000
N	1.27373300	-0.45786700	0.51554300
O	0.81027200	1.26694400	-0.88918700
F	-1.74473300	1.44833700	-0.23187800
F	-1.31878100	0.24609300	1.53623000
Cl	-1.84937400	-1.08727100	-0.60318600
N	0.83976500	-1.32910400	1.30341000
N	0.63697300	-2.17229100	2.03102300

***anti*-2**

C	-0.76879000	-0.02841000	0.32527400
C	0.04386200	1.15688800	-0.23421500
N	1.41856900	0.98425100	-0.39519100
O	-0.47123400	2.19079200	-0.52317100
F	-0.26816200	-0.35949500	1.51411400
F	-0.58828000	-1.07883200	-0.47297900
Cl	-2.46832600	0.30004400	0.47971600
N	1.94988800	-0.09655200	-0.09362700
N	2.63578900	-0.96373700	0.10574000

***anti*-3**

C	0.77077200	-0.04367600	0.33642000
C	-0.05490200	1.13009100	-0.22051800
N	-1.43692300	1.00653500	-0.34325500
O	0.49632200	2.13236600	-0.55177200
F	0.18794900	-0.51826500	1.43442000
F	1.96829500	0.37466200	0.66595600
Cl	0.91173300	-1.34625200	-0.83953600
N	-2.00587200	-0.04386600	-0.00816300
N	-2.72455600	-0.87676900	0.22106100

TS1

C	0.10613200	0.00374600	-0.04651100
C	0.10400700	-0.01936200	1.65987600
N	1.38465900	0.01906800	1.79470500
O	-0.96135100	-0.05513900	2.22643600
F	-0.74434900	-0.98265200	-0.35922000
F	1.25559400	-0.23346800	-0.69864200
Cl	-0.55136300	1.57260400	-0.53865500
N	1.63821600	0.02965100	3.64776900
N	2.29282600	0.03236200	4.53933300

TS2

C	-1.06120600	0.28284900	0.21933400
C	0.42534300	0.54099100	-0.15323300
N	1.33124800	-0.37300800	0.47095400
O	0.74101600	1.35762600	-0.96885700
F	-1.81977100	1.31390100	-0.17869100
F	-1.16590100	0.18345200	1.57010300
Cl	-1.65056700	-1.22114600	-0.53251000
N	1.82964300	-0.07036000	1.56298700
N	2.35896600	0.09354400	2.55457400

TS3

C	-1.22350100	0.39598300	0.15257600
C	0.30785100	0.35170300	-0.03016300
N	1.20848900	-0.43288800	0.50941000
O	0.93097900	1.12741400	-0.78211800
F	-1.67644900	1.55601800	-0.34455200
F	-1.54479900	0.35019100	1.46873300
Cl	-2.01913700	-0.96010900	-0.69440800
N	0.37605100	-1.68996400	1.67552900
N	0.51148800	-2.53070400	2.38218700

TS4

C	-0.07668000	-0.53077500	1.09371400
C	1.48888000	-0.02143200	0.93476000
N	2.20097600	-0.65223800	1.77630800
O	1.79759400	0.87232700	0.13060800
F	-0.62909300	0.10469300	2.13873200
F	-0.16919600	-1.85507000	1.30477500
Cl	-0.85918800	-0.06867800	-0.40897500

nitrene

C	-0.30543600	0.34838100	0.22688800
C	1.08717800	-0.19776500	0.00372500
N	1.99719000	-0.75401600	0.67409700
O	1.82891500	-0.25985400	-1.05960200
F	-0.33048900	1.64836900	-0.13277300
F	-0.60002700	0.26145000	1.53952900
Cl	-1.49296900	-0.56154600	-0.72758100

isocyanate

C	0.52130300	0.46483500	0.08660900
C	-1.72822800	-0.02136100	-0.55841200
N	-0.62220700	0.46762500	-0.72688500
O	-2.81971500	-0.43323300	-0.52736700
F	0.22004200	0.75878600	1.36837400
F	1.37729600	1.38823700	-0.36065800
Cl	1.36818100	-1.13842800	0.07529100

***syn*-S_0-Min**

C	-1.11073200	0.19204600	0.28158600
C	0.34855800	0.42738900	-0.12498700
N	1.20304500	-0.48164500	0.48578500
O	0.65057600	1.29412700	-0.88925300
F	-1.82187700	1.25883600	-0.01453300
F	-1.19507200	-0.00473500	1.58727300
Cl	-1.78481500	-1.20085800	-0.55594300
N	2.41403400	-0.32880000	0.13112100
N	3.51353400	-0.31780000	-0.07714900

***syn*-S_1-Min**

C	-1.14139600	0.14308400	0.28969000
C	0.30042800	0.48174900	-0.11336000
N	1.23204000	-0.49386800	0.20387400
O	0.54559000	1.54365000	-0.64569200
F	-1.93114200	1.12515600	-0.08435400
F	-1.19572900	0.05682300	1.61319000
Cl	-1.71596100	-1.35918800	-0.41148900
N	2.57897700	0.06715500	-0.03791300
N	3.49683900	-0.65075800	0.02559000

***anti*-S_1-Min**

C	-1.09892000	0.07659200	0.34348500
C	0.35028000	0.37827000	-0.09246100
N	1.43373100	-0.39840500	0.26622400
O	0.56363200	1.36059400	-0.77884400
F	-1.84251400	1.12515700	0.06461200
F	-1.15206400	-0.10702700	1.65509700
Cl	-1.77327300	-1.32594000	-0.47722600
N	1.00246200	-1.58526100	1.03174700
N	1.82066600	-2.27201200	1.50428900

isomer-S_1-TS'

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.53902652
N	1.20851564	0.00000000	2.21173665
O	-1.05903969	-0.01733595	2.13441553
F	-1.24024398	-0.11785911	-0.42075628
F	0.67410677	-1.05547519	-0.43704350
Cl	0.69699177	1.46183037	-0.68136263
N	1.71549856	-1.38452410	2.31226684
N	2.65992083	-1.58403964	2.96907835

***syn*-S_1-TS**

C	-1.14796100	0.17324800	0.26550900
C	0.31699300	0.44753200	-0.10764400
N	1.20525100	-0.55342400	0.21980900
O	0.60994400	1.50725000	-0.63039500
F	-1.89504300	1.15045100	-0.19935000
F	-1.24584500	0.18087400	1.58981100
Cl	-1.75062600	-1.35527500	-0.34798500
N	2.61847300	0.01522500	0.01927000
N	3.50606400	-0.72732300	0.01487400

***anti*-S_1-TS**

C	-1.09373200	0.07360900	0.34462000
C	0.35021800	0.38653800	-0.10102300
N	1.43672300	-0.38101800	0.22899300
O	0.55058700	1.39181100	-0.76843600
F	-1.84810800	1.11552300	0.07014000
F	-1.13560900	-0.10832700	1.65730700
Cl	-1.76611100	-1.33506900	-0.46771500
N	0.99395000	-1.62198300	1.02197900
N	1.81457400	-2.26514100	1.52570400

nitrene-S_0-Min

C	-0.44350300	0.07599600	1.01043500
C	1.08700100	-0.04087400	0.96249900
N	1.90014100	-0.96234500	1.21041200
O	1.93462700	0.86320100	0.62828600
F	-0.77025200	1.06258500	1.82547300
F	-0.92677200	-1.04969200	1.49744800
Cl	-1.11083300	0.38111600	-0.57633000

isocyanate-S_0-Min

C	0.52014000	0.44459300	0.07731000
C	-1.71055000	-0.02272000	-0.52420100
N	-0.59740100	0.42910200	-0.76866800
O	-2.80549600	-0.37744600	-0.50043300
F	0.18011400	0.72691100	1.32579400
F	1.34177300	1.38219900	-0.33415200
Cl	1.38809200	-1.09617900	0.08130100

nitrene-S_0-TS

C	-0.57099300	0.00056600	0.94577400
C	1.06588800	-0.05023500	0.89772200
N	1.43458400	-1.21432100	0.59206600
O	1.45494700	1.13118700	1.14576200
F	-0.92298300	0.67502700	2.01520700
F	-1.07293600	-1.20341900	1.05252500
Cl	-1.17653100	0.77287100	-0.49466900

nitrene-S_1-Min

C	-0.39223500	0.06149700	1.01111900
C	1.15610000	-0.05385200	0.95566300
N	1.77987900	-1.11171600	1.26367500
O	1.80489900	1.04521600	0.57987800
F	-0.70469400	1.05893700	1.82270400
F	-0.90932000	-1.04691800	1.50241600
Cl	-1.06422000	0.37682300	-0.57723200

nitrene-S_1/S_0-CI

C	-0.33817700	0.06753200	0.98514300
C	1.21997500	0.00003400	0.96124200
N	1.72394100	-1.10585300	1.52133400
O	1.70765400	0.99073900	0.38121900
F	-0.71337900	0.96443600	1.90297200
F	-0.87458700	-1.07882600	1.36941500
Cl	-1.05501900	0.49192600	-0.56310200

nitrene-S_1-TS

C	-0.57113000	0.15275200	1.01496900
C	1.42519800	0.30656300	1.11287600
N	1.10796800	-0.92738200	0.78850500
O	2.50452000	0.85504700	1.29588300
F	-0.84279800	1.33812200	1.52172600
F	-1.11832900	-0.72747100	1.81066100
Cl	-1.18159900	0.06726000	-0.60669400

ayla-nitrene-S_0

C	-1.128744	0.213759	0.205312
C	0.211109	0.688249	-0.297810
N	1.378913	0.413336	-0.031139
O	0.416563	1.582031	-1.227611
F	-1.824962	1.263539	0.604011
F	-0.936631	-0.581371	1.237636
Cl	-2.008356	-0.629099	-1.049531
N	4.761572	-1.049196	0.962924
N	5.190860	-0.151671	1.437770