ELECTRONIC SUPPLEMENTARY INFORMATION

Theoretical study on Hammett correlations of excited state lifetimes of Arylchlorodiazirines

Xing-Liang Peng,[a] Annapaola Migani,[b] Quan-Song Li,[a*] Ze-Sheng Li[a] and Lluís Blancafort[c*]

[a]*Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, Key Laboratory of Cluster Science of Ministry of Education, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, 100081 Beijing, China.*

[b]*Departament de Química Biològica i Modelització Molecular, IQAC-CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain*

[c]*Institut de Química Computacional i Catàlisi and Departament de Química, Universitat de Girona, Facultat de Ciències, C/M. A. Campmany 69, 17003 Girona, Spain*

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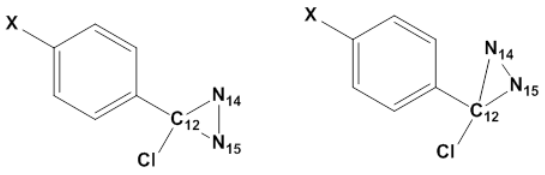
Table ESI1. Mulliken charges on the ACDA diazirine-ring and chlorine atom at $(S_0)_{min}$ and S_0-TS in cyclohexane (CHX) at CASPT2 level.

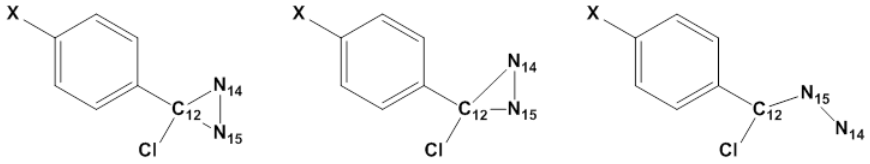


$(S_0)_{min}$ S_0-TS

Substituent group (-X)			*p*-MeO	*p*-Me	*p*-H	*p*-Cl	*p*-NO_2
(S_0)-Min	Cl		-0.1601	-0.1592	-0.1579	-0.1556	-0.1515
	C_{12}		0.1420	0.1430	0.1417	0.1416	0.1426
	N_{14}		-0.0589	-0.0587	-0.0568	-0.0541	-0.0491
	N_{15}		-0.0590	-0.0586	-0.0569	-0.0546	-0.0489
	Dia[a]		0.0241	0.0257	0.0280	0.0329	0.0446
(S_0)-TS	Cl		-0.1612	-0.1561	-0.1542	-0.1520	-0.1464
	C_{12}		0.0438	0.0343	0.0332	0.0347	0.0397
	N_{14}		-0.0557	-0.0360	-0.0325	-0.0289	-0.0179
	N_{15}		-0.0313	-0.0193	-0.0166	-0.0068	-0.0043
	Dia[a]		-0.0432	-0.0210	-0.0159	-0.0010	0.0175

[a] sum of the charges on C_{12}, N_{14} and N_{15}.

Table ESI2. Mulliken charges on ACDA diazirine-ring and chlorine atom in (S_0)-Min, (S_1)-Min, (S_1)-TS and (S_1/S_0)-X in vacuum at CASPT2 level.



$(S_0)_{min}/(S_1)_{min}$ S_1-TS $(S_1/S_0)_x$

Substituent group (-X)			*p*-OMe	*p*-Me	*p*-H	*p*-Cl	*m*-Cl	*p*-CF_3
σ_p^+			-0.78	-0.31	0.00	0.11	0.37	0.53
(S_0)-Min GS[a]	Cl		-0.1592	-0.1579	-0.1563	-0.1539	-0.1524	-0.1529
	C_{12}		0.1480	0.1479	0.1458	0.1458	0.1458	0.1469
	N_{14}		-0.0563	-0.0559	-0.0544	-0.0521	-0.0515	-0.0491
	N_{15}		-0.0563	-0.0559	-0.0544	-0.0521	-0.0515	-0.0491
	Dia[b]		0.0354	0.0361	0.0370	0.0416	0.0428	0.0487
(S_0)-Min ($\pi\pi^*$)	Cl		-0.1406	-0.1387	-0.1350	-0.1331	-0.1320	-0.1323
	C_{12}		0.1821	0.1854	0.1871	0.1900	0.1907	0.1978
	N_{14}		-0.1557	-0.1519	-0.1479	-0.1425	-0.1403	-0.1363
	N_{15}		-0.1557	-0.1519	-0.1479	-0.1425	-0.1403	-0.1363
	Dia[b]		-0.1293	-0.1184	-0.1087	-0.0950	-0.0899	-0.0748
(S_1)-Min ($\pi\pi^*$)	Cl		-0.1224	-0.1196	-0.1164	-0.1137	-0.1116	-0.1114
	C_{12}		0.1731	0.1758	0.1770	0.1803	0.1812	0.1872
	N_{14}		-0.1613	-0.1588	-0.1557	-0.1526	-0.1513	-0.1482
	N_{15}		-0.1613	-0.1588	-0.1557	-0.1526	-0.1513	-0.1482
	Dia[b]		-0.1495	-0.1418	-0.1344	-0.1249	-0.1214	-0.1092
(S_1)-TS ($\pi\pi^*$)	Cl		-0.1326	-0.1302	-0.1273	-0.1248	-0.1225	-0.1227
	C_{12}		0.1407	0.1430	0.1435	0.1473	0.1483	0.1548
	N_{14}		-0.0534	-0.0527	-0.0507	-0.0476	-0.0462	-0.0428
	N_{15}		-0.1468	-0.1449	-0.1431	-0.1436	-0.1429	-0.1438
	Dia[b]		-0.0595	-0.0546	-0.0503	-0.0439	-0.0408	-0.0318
(S_1/S_0)-X GS[a]	Cl		-0.1567	-0.1550	-0.1525	-0.1499	-0.1476	-0.1481
	C_{12}		0.1091	0.1114	0.1125	0.1160	0.1180	0.1228
	N_{14}		0.0740	0.0748	0.0745	0.0723	0.0710	0.0704
	N_{15}		-0.1630	-0.1610	-0.1574	-0.1512	-0.1488	-0.1438
	Dia[b]		0.0201	0.0252	0.0296	0.0371	0.0402	0.0494
(S_1/S_0)-X ($\pi\pi^*$)	Cl		-0.1523	-0.1514	-0.1502	-0.1482	-0.1467	-0.1474
	C_{12}		0.0759	0.0776	0.0770	0.0766	0.0775	0.0764
	N_{14}		0.1180	0.1194	0.1194	0.1185	0.1173	0.1202
	N_{15}		-0.0914	-0.0888	-0.0840	-0.0765	-0.0722	-0.0655
	Dia[b]		0.1025	0.1082	0.1124	0.1186	0.1226	0.1311

[a] on ground state.

[b] sum of the charges on C_{12}, N_{14} and N_{15}.

Table ESI3. TFVC charges on ACDA diazirine-ring and chlorine atom in (S_0)-Min, (S_1)-Min, (S_1)-TS and (S_0)-TS in vacuum at CASPT2 level.

Substituent group (-X)		*p*-OMe	*p*-Me	*p*-H	*p*-Cl	*m*-Cl	*p*-CF_3	*p*-NO_2
σ_p^+		-0.78	-0.31	0.00	0.11	0.37	0.53	0.79
(S_0)-Min GS	C_{12}	0.1480	0.1479	0.1458	0.1458	0.1469	0.1458	
	N_{14}	-0.0563	-0.0559	-0.0544	-0.0521	-0.0491	-0.0515	
	N_{15}	-0.0563	-0.0559	-0.0544	-0.0521	-0.0491	-0.0515	
	Dia[a]	0.0354	0.0361	0.0370	0.0416	0.0487	0.0428	
(S_1)-Min (ππ*)	C_{12}	0.1731	0.1758	0.1770	0.1803	0.1872	0.1812	
	N_{14}	-0.1613	-0.1588	-0.1557	-0.1526	-0.1482	-0.1513	
	N_{15}	-0.1613	-0.1588	-0.1557	-0.1526	-0.1482	-0.1513	
	Dia[a]	-0.1495	-0.1418	-0.1344	-0.1249	-0.1092	-0.1214	
(S_1)-TS (ππ*)	C_{12}	0.1407	0.1430	0.1435	0.1473	0.1548	0.1483	
	N_{14}	-0.0534	-0.0527	-0.0507	-0.0476	-0.0428	-0.0462	
	N_{15}	-0.1468	-0.1449	-0.1431	-0.1436	-0.1438	-0.1429	
	Dia[a]	-0.0595	-0.0546	-0.0503	-0.0439	-0.0318	-0.0408	
(S_0)-TS (ππ*)	C_{12}	0.1407	0.1430	0.1435	0.1473	0.1548	0.1483	
	N_{14}	-0.0534	-0.0527	-0.0507	-0.0476	-0.0428	-0.0462	
	N_{15}	-0.1468	-0.1449	-0.1431	-0.1436	-0.1438	-0.1429	
	Dia[a]	-0.0595	-0.0546	-0.0503	-0.0439	-0.0318	-0.0408	

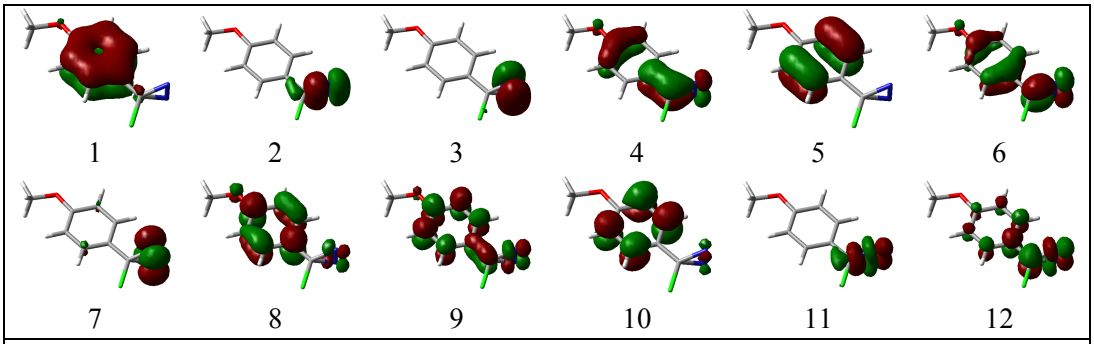
[a]sum of the charges on C_{12}, N_{14} and N_{15}.

Table ESI4. CASPT2//CASSCF energies of carbenes[a] in cyclohexane relative to each (S_0)-Min.

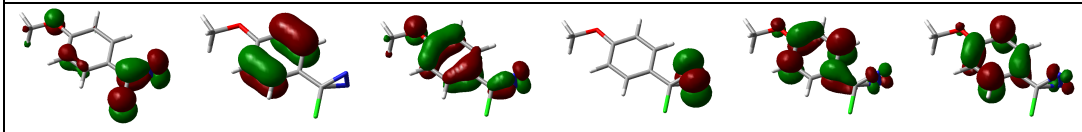
Substitute group	Energy (kcal/mol)
p-CH_3O	9.3
p-CH_3	10.6
p-Cl	12.0
p-H	11.6
p-NO_2	13.9

[a]The two C-N bonds are about 5 Å.

Table ESI5. The CASSCF active space orbitals and TD-CAM-B3LYP orbitals of *p*-CH_3O-ACDA, and the CASPT2/ANO-S and TD-CAM-B3LYP/6-311G** vertical excitations calculated in acetonitrile (PCM model) at (S_0)-Min along with the main configurations, vertical excitation energies (excited wavelength), oscillator strengths (*f*) and the dipole moments (μ).



(a)CASSCF



(b)TD-B3LYP

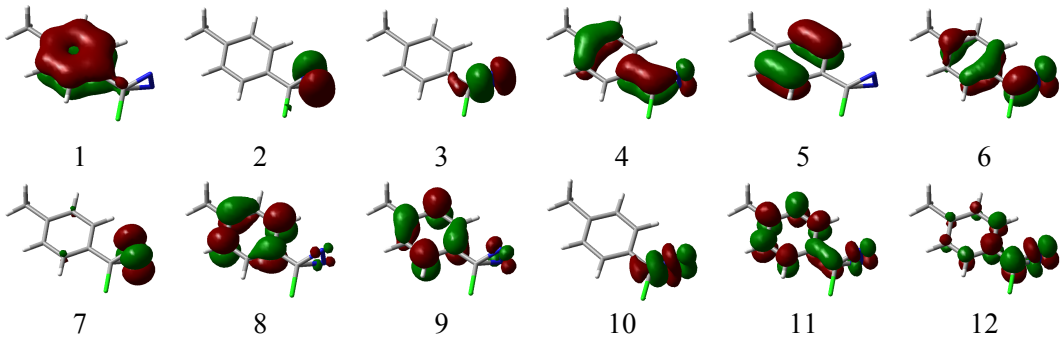
state	CASPT2/ANO-S				TD-CAM-B3LYP/6-311G**		
	Main configurations[a]	Energy [eV][b]	*f*	μ [D][c]	Main configurations[a]	Energy [eV][b]	*f*
S_1	6→7 (0.68)	3.17 (391)	0.005	7.81	47→48 (0.64)	3.22 (385)	0.008
S_2	6→10 (0.28) 5→8 (0.30)	4.40 (282)	0.002	4.25	47→49 (0.32) 47→50 (0.22)	5.00 (248)	0.033
S_3	5→7 (0.41) 4→7 (0.24)	5.00 (248)	0.008	11.4	45→48 (0.22) 47→49 (0.24) 46→48 (0.30) 47→48 (0.22)	5.32 (233)	0.096
S_4	4→7 (0.31) 5→7 (0.29)	5.14 (241)	0.010	11.5	47→50 (0.54)	5.59 (222)	0.079

[a]Transition contribution of leading configurations.

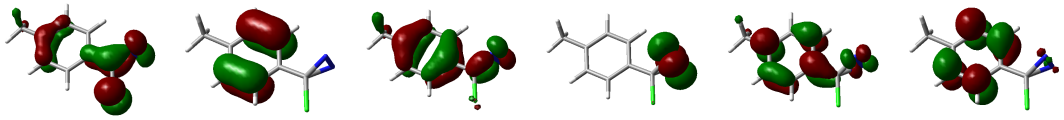
[b]Transition wave length [nm] in parentheses.

[c]Ground-state dipole moment 4.27.

Table ESI6. The CASSCF active space orbitals and TD-CAM-B3LYP orbitals of *p*-CH_3-ACDA, and the CASPT2/ANO-S and TD-CAM-B3LYP/6-311G** vertical excitations calculated in acetonitrile (PCM model) at (S_0)-Min along with the main configurations, vertical excitation energies (excited wavelength), oscillator strengths (*f*) and the dipole moments (μ).



(a)CASSCF



(b)TD-B3LYP

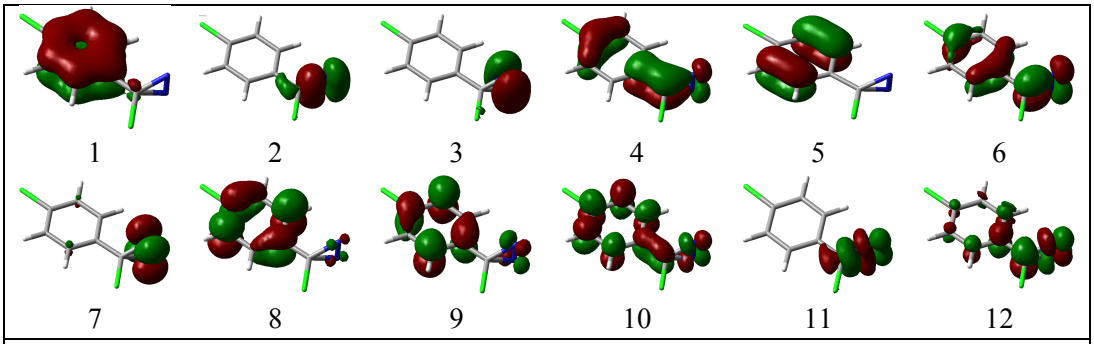
state	CASPT2/ANO-S				TD-CAM-B3LYP/6-311G**		
	Main configurations[a]	Energy [eV][b]	*f*	μ [D][c]	Main configurations[d]	Energy [eV][b]	*f*
S_1	6→7 (0.68)	3.27 (379)	0.007	6.80	43→44 (0.70)	3.31 (375)	0.006
S_2	6→9 (0.23) 5→8 (0.33)	4.41 (281)	0.003	3.81	42→44 (0.24) 42→45 (0.22) 43→46 (0.32)	5.18 (239)	0.002
S_3	5→7 (0.62)	5.03 (247)	0.008	12.0	42→44 (0.54)	5.46 (227)	0.034
S_4	4→7 (0.46)	5.25 (236)	0.012	9.13	41→44 (0.45)	5.73 (216)	0.037

[a]Transition contribution of leading configurations.

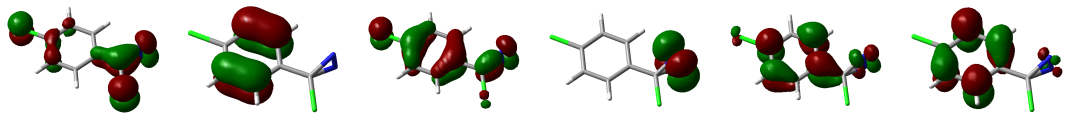
[b]Transition wave length [nm] in parentheses.

[c]Ground-state dipole moment 3.76.

Table ESI7. The CASSCF active space orbitals and TD-CAM-B3LYP orbitals of *p*-Cl-ACDA, and the CASPT2/ANO-S and TD-CAM-B3LYP/6-311G** vertical excitations calculated in acetonitrile (PCM model) at (S_0)-Min along with the main configurations, vertical excitation energies (excited wavelength), oscillator strengths (*f*) and the dipole moments (μ).



(a)CASSCF



(b)TD-B3LYP

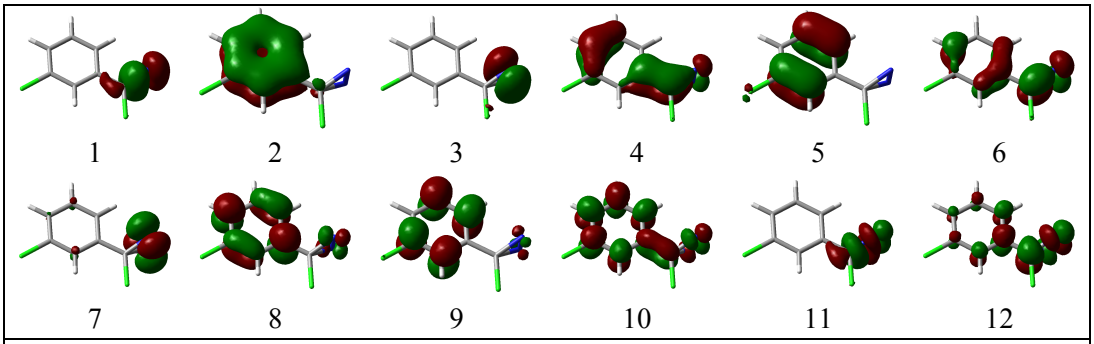
state	CASPT2/ANO-S				TD-CAM-B3LYP/6-311G**		
	Main configurations[a]	Energy [eV][b]	*f*	μ [D][c]	Main configurations[a]	Energy [eV][b]	*f*
S_1	6→7 (0.67)	3.32 (373)	0.004	2.99	47→48 (0.67)	3.37 (368)	0.008
S_2	6→9 (0.21) 5→8 (0.32)	4.38 (283)	0.001	0.66	46→49 (0.24) 47→50 (0.36)	5.17 (240)	0.033
S_3	5→7 (0.61)	5.17 (240)	0.004	8.20	47→49 (0.50)	5.54 (224)	0.096
S_4	4→7 (0.45)	5.45 (227)	0.009	4.72	45→48 (0.34)	5.81 (213)	0.079

[a]Transition contribution of leading configurations.

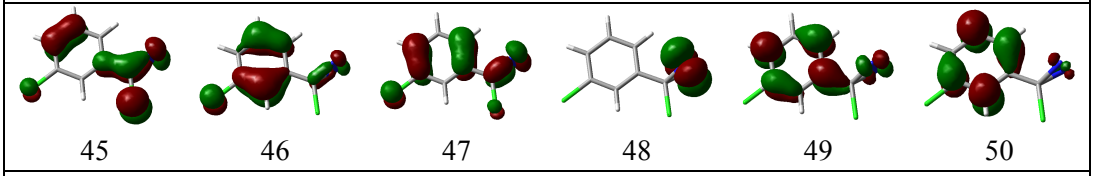
[b]Transition wave length [nm] in parentheses.

[c]Ground-state dipole moment 0.61.

Table ESI8. The CASSCF active space orbitals and TD-CAM-B3LYP orbitals of *m*-Cl-ACDA, and the CASPT2/ANO-S and TD-CAM-B3LYP/6-311G** vertical excitations calculated in acetonitrile (PCM model) at (S_0)-Min along with the main configurations, vertical excitation energies (excited wavelength), oscillator strengths (*f*) and the dipole moments (μ).



(a)CASSCF



(b)TD-B3LYP

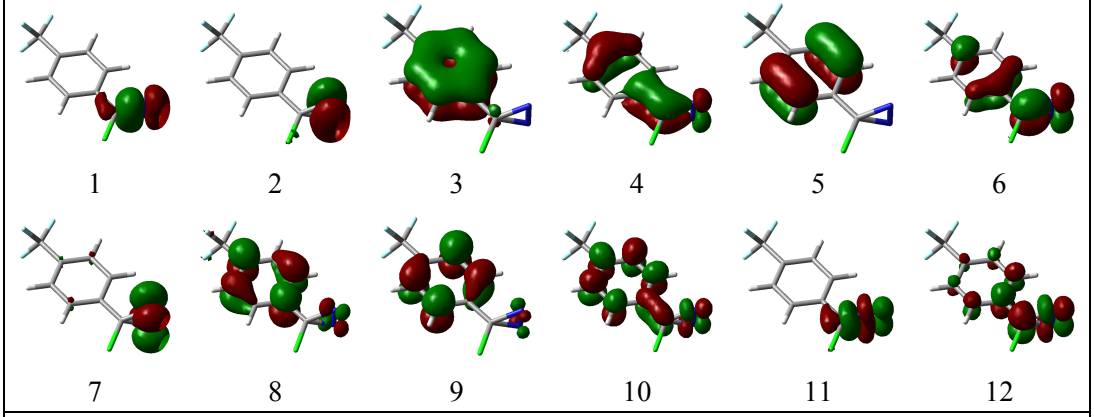
state	CASPT2/ANO-S				TD-CAM-B3LYP/6-311G**		
	Main configurations[a]	Energy [eV][b]	*f*	μ [D][c]	Main configurations[a]	Energy [eV][b]	*f*
S_1	6→7 (0.67)	3.39 (365)	0.005	4.09	47→48 (0.62)	3.41 (364)	0.005
S_2	6→9 (0.19) 5→8 (0.34)	4.37 (284)	0.002	2.46	46→48 (0.26) 46→49 (0.26) 47→50 (0.26)	5.11 (242)	0.010
S_3	5→7 (0.67)	5.11 (242)	0.008	9.78	46→48 (0.38) 47→49 (0.29)	5.51 (225)	0.002
S_4	4→7 (0.48)	5.53 (224)	0.009	5.66	47→49 (0.53)	5.80 (214)	0.225

[a]Transition contribution of leading configurations.

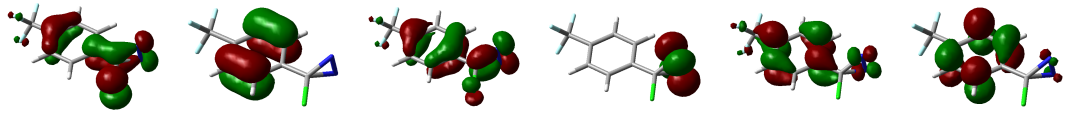
[b]Transition wave length [nm] in parentheses.

[c]Ground-state dipole moment 2.52.

Table ESI9. The CASSCF active space orbitals and TD-CAM-B3LYP orbitals of *p*-CF_3-ACDA, and the CASPT2/ANO-S and TD-CAM-B3LYP/6-311G** vertical excitations calculated in acetonitrile (PCM model) at (S_0)-Min along with the main configurations, vertical excitation energies (excited wavelength), oscillator strengths (*f*) and the dipole moments (μ).



(a)CASSCF



(b)TD-B3LYP

state	CASPT2/ANO-S				TD-CAM-B3LYP/6-311G**		
	Main configurations[a]	Energy [eV][b]	*f*	μ [D][c]	Main configurations[a]	Energy [eV][b]	*f*
S_1	6→7 (0.67)	3.42 (362)	0.003	1.37	55→56 (0.78)	3.43 (362)	0.004
S_2	6→9 (0.17) 5→8 (0.35)	4.38 (283)	0.005	0.61	54→56 (0.21) 54→57 (0.36) 55→58 (0.25)	5.23 (237)	0.007
S_3	5→7 (0.59)	5.28 (235)	0.003	6.30	55→57 (0.55)	5.62 (221)	0.145
S_4	4→7 (0.39)	5.52 (225)	0.006	2.92	54→56 (0.62) 55→57 (0.29)	5.86 (211)	0.263

[a]Transition contribution of leading configurations.

[b]Transition wave length [nm] in parentheses.

[c]Ground-state dipole moment 0.83.

Table ESI10. The barriers for concerted photolytic decomposition of *p*-*R*-ACDA derivatives in vacuum (ΔE^{vac}).

R	ΔE^{vac} [kcal·mol^{-1}]
p-CF_3	15.0
m-Cl	15.5
p-Cl	15.7
p-H	15.5
p-CH_3	12.2
p-CH_3O	16.7

Table ESI11. The excess excitation energy of p-R-ACDA derivatives in vacuum (ΔE^{vac}).

R	ΔE^{vac} [kcal·mol^{-1}]
p-CF_3	4.8
m-Cl	4.7
p-Cl	4.5
p-H	4.4
p-CH_3	3.8
p-CH_3O	3.2

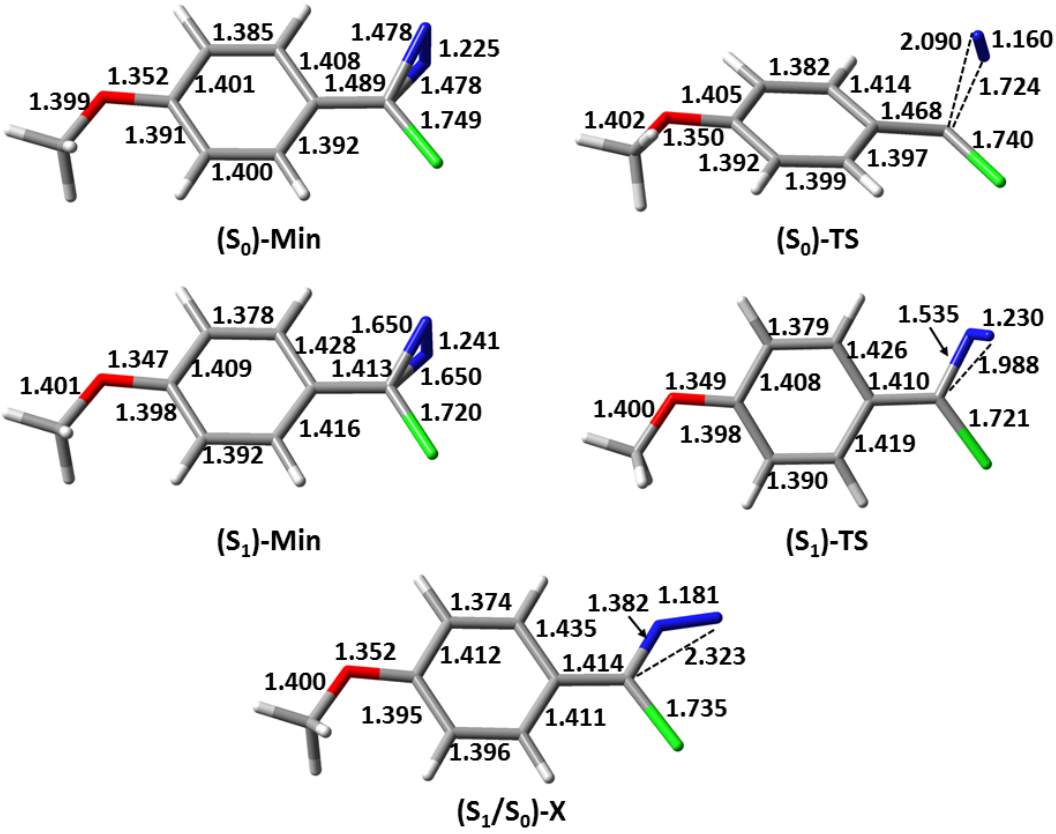


Figure ESI1. The critical structures of *p*-CH_3O-ACDA.

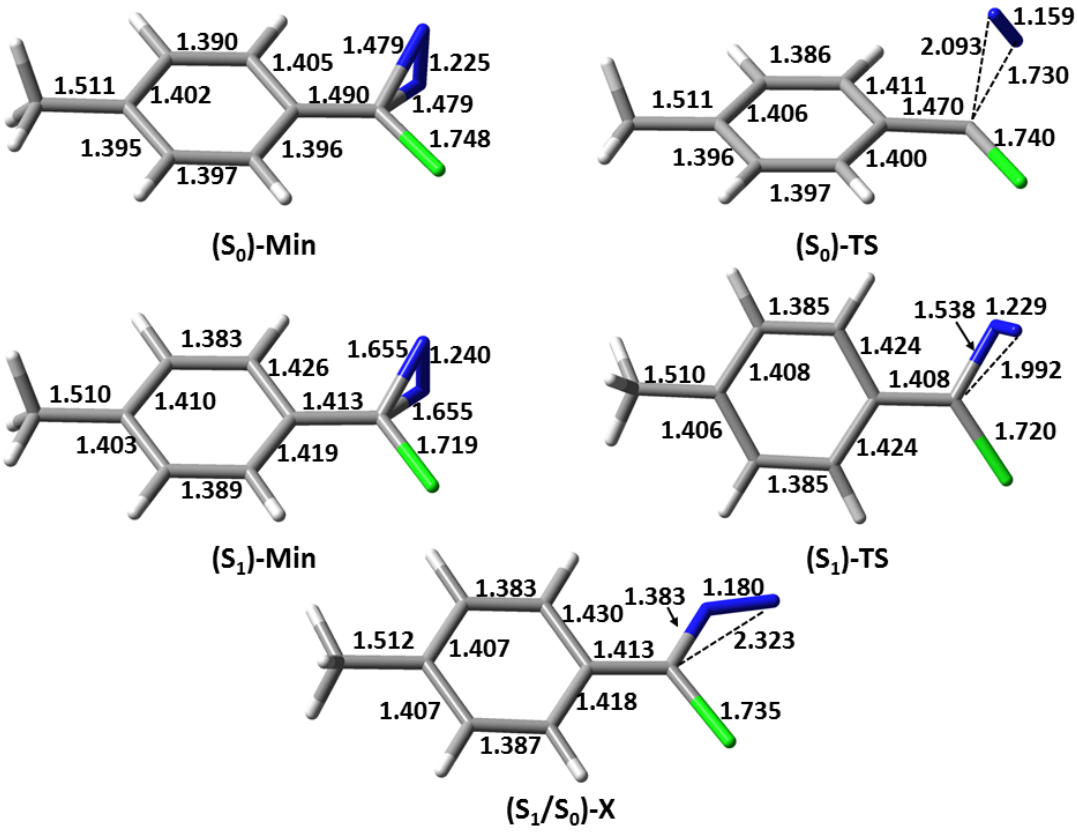


Figure ESI2. The critical structures of *p*-CH_3-ACDA.

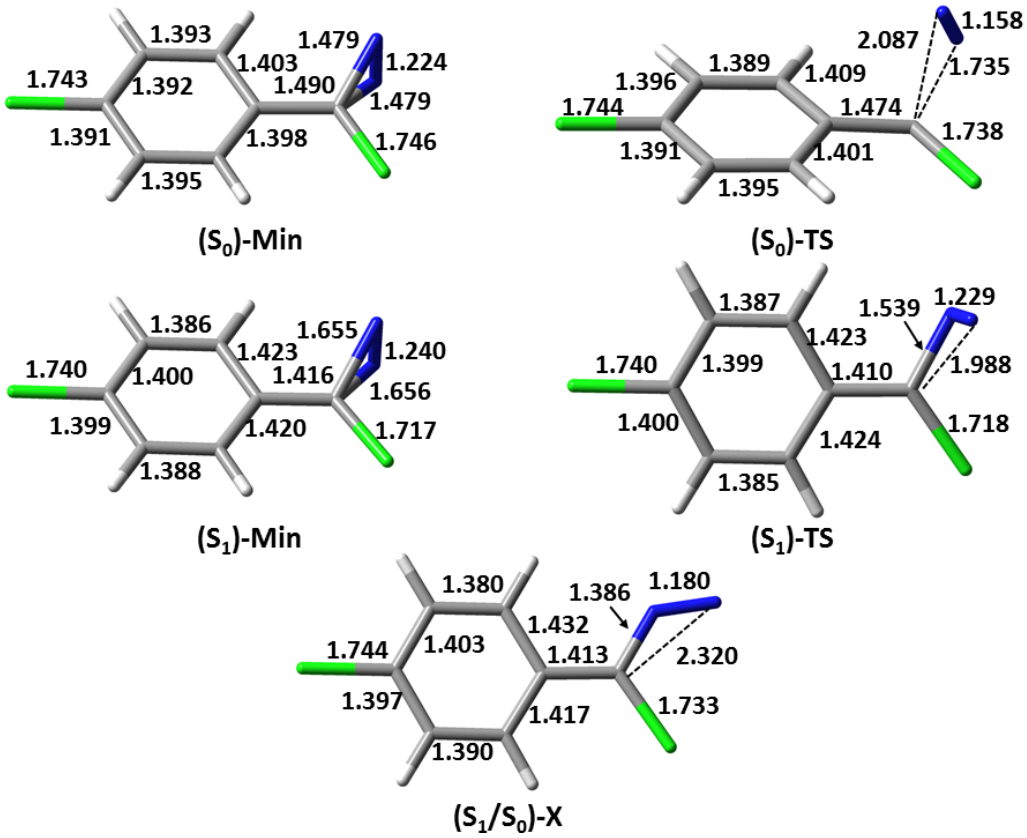


Figure ESI3. The critical structures of *p*-Cl-ACDA.

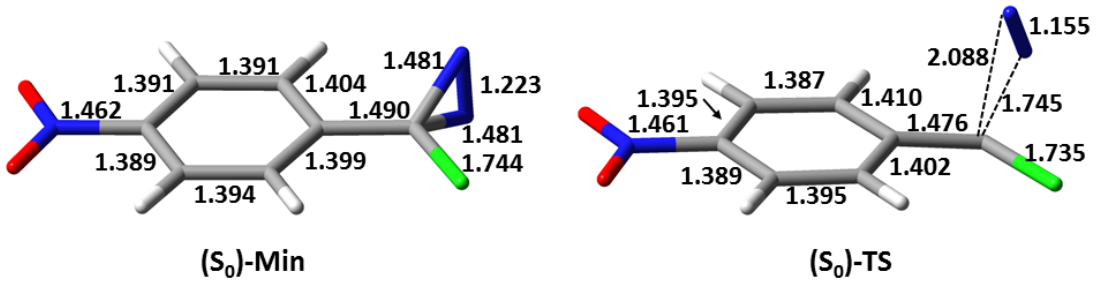


Figure ESI4. The critical structures of *p*-NO_2-ACDA.

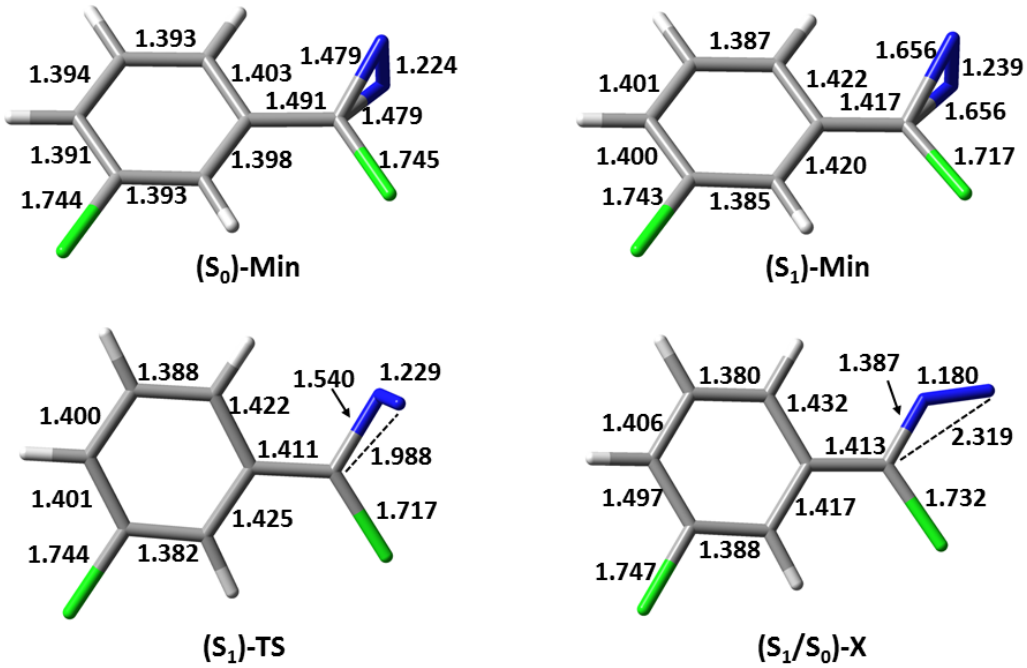


Figure ESI5. The critical structures of *m*-Cl-ACDA.

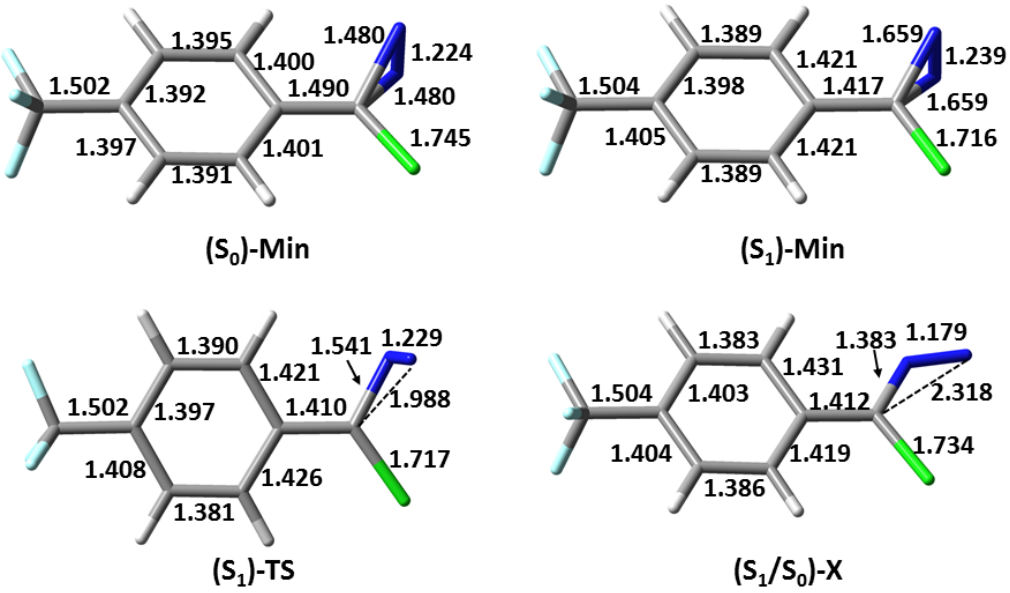


Figure ESI6. The critical structures of *p*-CF_3-ACDA.

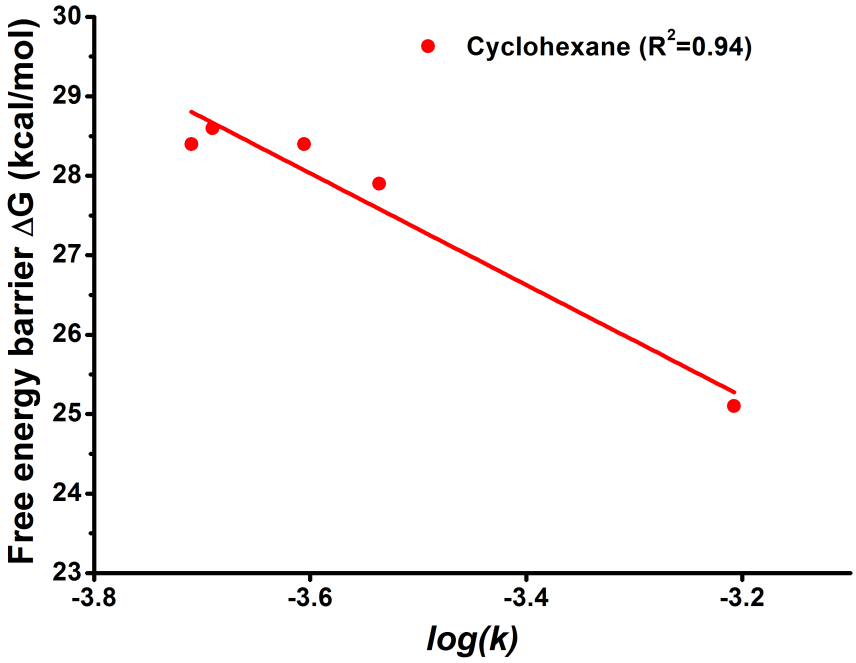


Figure ESI7. Linear correlation plot of free energy barriers for thermal decomposition of *p*-*R*-ACDA derivatives in cyclohexane *vs.* logarithm of experimental rate constants.

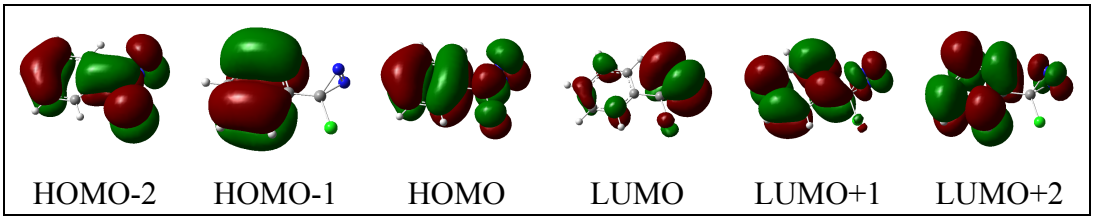


Figure ESI8. TD-CAM-B3LYP orbitals at *p*-H-ACDA (S_0)-Min.

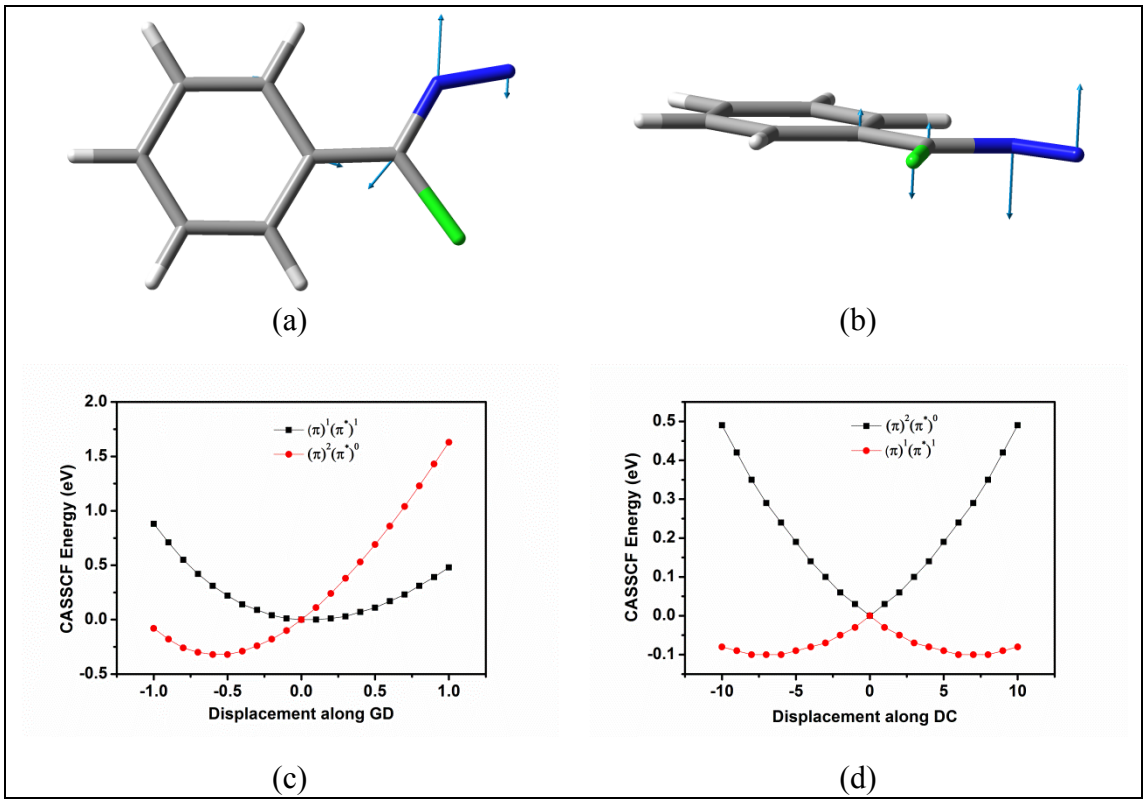


Figure ESI9. The models of (a) gradient difference (GD) and (b) derivative coupling (DC) vectors at ACDA-*p*-H (S_1/S_0)-X, and the CASSCF energy plots along the positive and negative (c) GD and (d) DC vectors. The energy at (S_1/S_0)-X is set as zero.

Coordinates of ACDAs's critical points optimized by CASSCF in vacuum.

_p_-H-ACDA (S_0)-Min

C	-2.43968200	-0.91954400	0.00000000
C	-1.04844000	-1.02947600	0.00000000
C	-0.24970300	0.11891000	0.00000000
C	-0.86842200	1.37903400	0.00000000
C	-2.25787700	1.48215700	0.00000000
C	-3.04965600	0.33336300	0.00000000
H	-3.03846800	-1.81217800	0.00000000
H	-0.59798200	-2.00206200	0.00000000
H	-0.27941400	2.27640300	0.00000000
H	-2.71535500	2.45479300	0.00000000
H	-4.12144400	0.41459600	0.00000000
C	1.23910600	0.04660300	0.00000000
Cl	2.02582900	-1.51441600	0.00000000
N	2.02582900	1.13908800	0.61217800
N	2.02582900	1.13908800	-0.61217800

_p_-H-ACDA (S_0)-TS

C	-2.41324100	-0.91651000	0.19976700
C	-1.03180400	-1.02893700	0.03627300
C	-0.25761400	0.11015600	-0.22596100
C	-0.89636900	1.36257700	-0.32554900
C	-2.26988500	1.47005700	-0.14479000
C	-3.03475800	0.32837800	0.11653300
H	-2.99546000	-1.79771800	0.39921000
H	-0.56566200	-1.99179600	0.10963000
H	-0.31351000	2.23864000	-0.54258800
H	-2.74342900	2.43211300	-0.21813300
H	-4.09828400	0.41075400	0.24868700
C	1.18091900	0.06483600	-0.54172000
Cl	2.00004400	-1.46894800	-0.54852000
N	1.91973300	0.86122100	1.24220600
N	2.15671800	1.29470400	0.19495600

_p_-H-ACDA (S_1)-Min

C	-2.45169500	-0.94595100	0.00000000
C	-1.07023400	-1.07955600	0.00000000
C	-0.24050500	0.07403800	0.00000000
C	-0.85573300	1.35917800	0.00000000
C	-2.23801700	1.47071600	0.00000000
C	-3.04526600	0.32391600	0.00000000
H	-3.06739500	-1.82715800	0.00000000
H	-0.62828000	-2.05695700	0.00000000
H	-0.23982400	2.23687900	0.00000000
H	-2.68879200	2.44658100	0.00000000
H	-4.11640900	0.41853000	0.00000000
C	1.17060400	-0.02551000	0.00000000
Cl	2.03631500	-1.51026200	0.00000000
N	2.03631500	1.24254200	0.61993200
N	2.03631500	1.24254200	-0.61993200

_p_-H-ACDA (S_1)-TS

C	-2.46923400	-0.94833000	0.04357500
C	-1.09069500	-1.08098200	0.01813000
C	-0.25864400	0.07458400	-0.04340800
C	-0.87801700	1.35624300	-0.05614700
C	-2.26118400	1.46593100	-0.03989200
C	-3.06712500	0.32074100	0.00922400
H	-3.08305700	-1.82963700	0.08881000
H	-0.64742500	-2.05715200	0.03863900
H	-0.26479000	2.23518800	-0.08378200
H	-2.71332600	2.44079700	-0.06160400
H	-4.13773200	0.41328200	0.02506700
C	1.14421300	-0.02907900	-0.13648200
Cl	2.02170500	-1.50705000	-0.08291300
N	2.38004100	1.27592300	0.71815600
N	1.96267000	1.23906700	-0.43737300

p-H-ACDA (S_1/S_0)-X

C	-1.51314700	2.24796900	0.00000000
C	-1.31349300	0.87149200	0.00000000
C	0.00000000	0.33855500	0.00000000
C	1.10090100	1.25539700	0.00000000
C	0.88434300	2.61908800	0.00000000
C	-0.42598900	3.13041200	0.00000000
H	-2.51919100	2.63025200	0.00000000
H	-2.16205300	0.21322800	0.00000000
H	2.10557800	0.86825100	0.00000000
H	1.72507200	3.29077700	0.00000000
H	-0.59378200	4.19328900	0.00000000
C	0.25990600	-1.05088700	0.00000000
Cl	-0.99510900	-2.24851200	0.00000000
N	1.55414900	-1.54420500	0.00000000
N	1.93243600	-2.66197300	0.00000000

p-H-ACDA (S_0)-diazo

C	-1.33028400	2.33672500	0.00000000
C	-1.24812000	0.94358500	0.00000000
C	0.00000000	0.30721900	0.00000000
C	1.16219800	1.09987300	0.00000000
C	1.07158700	2.48834900	0.00000000
C	-0.17580200	3.11650700	0.00000000
H	-2.29797700	2.80509000	0.00000000
H	-2.14942700	0.36222600	0.00000000
H	2.13430300	0.64095700	0.00000000
H	1.97246500	3.07501000	0.00000000
H	-0.24332600	4.18914400	0.00000000
C	0.10369000	-1.15706600	0.00000000
Cl	-1.26846600	-2.21674900	0.00000000
N	2.26791300	-2.27409000	0.00000000
N	1.25327000	-1.75431500	0.00000000

p-H-ACDA (S_0)-TS'

C	-1.16816600	2.14593000	-0.37567700
C	-1.00364500	0.78126600	-0.15270700
C	0.21893900	0.28522000	0.32620100
C	1.26580400	1.18130300	0.57547000
C	1.09963200	2.54997900	0.35340500
C	-0.11754400	3.03319500	-0.12321600
H	-2.10832800	2.51642400	-0.74269700
H	-1.81785100	0.10773900	-0.34185000
H	2.19834100	0.80154900	0.95081500
H	1.90934200	3.22750400	0.55580300
H	-0.25066800	4.08643700	-0.29347500
C	0.52936000	-1.15538900	0.61761100
Cl	-0.91622100	-2.11055000	1.04371900
N	1.68398700	-2.33156000	-1.52407500
N	0.97941700	-1.80620200	-0.86932500

p-H-ACDA (S_0)-carbene

C	-1.18998100	2.13206400	-0.34431600
C	-1.11964300	0.80378300	0.05311700
C	0.09136000	0.27637800	0.55130200
C	1.21479900	1.11694500	0.63387400
C	1.14085400	2.45273300	0.23713700
C	-0.06160500	2.95804600	-0.25185100
H	-2.11391600	2.52899200	-0.72386400
H	-1.98716000	0.17800700	-0.02015000
H	2.13286600	0.70734600	1.01151800
H	2.00637900	3.08571100	0.30810400
H	-0.12648300	3.98595100	-0.56045700
C	0.36113800	-1.08893900	1.01299500
Cl	-1.04809900	-2.11743100	0.95572600
N	2.31898900	-2.61372900	-2.90681200
N	1.58596900	-2.10969500	-2.27917000

p-CH_3O-ACDA (S_0)-Min

C	0.51514500	-1.76517000	0.00000000
C	0.92686300	-0.42685200	0.00000000
C	-0.00091100	0.61119500	0.00000000
C	-1.37045200	0.28479700	0.00000000
C	-1.78218000	-1.03797000	0.00000000
C	-0.84042900	-2.07521700	0.00000000
H	1.97757000	-0.21500000	0.00000000
H	-2.11630200	1.05667300	0.00000000
H	-2.82597100	-1.28953800	0.00000000
C	0.40442500	2.04411500	0.00000000
Cl	2.10435300	2.45409700	0.00000000
N	-0.47983800	3.05807100	0.61252600
N	-0.47983800	3.05807100	-0.61252600
H	1.26304400	-2.53365600	0.00000000
O	-1.34754000	-3.32838200	0.00000000
C	-0.47983800	-4.42573800	0.00000000
H	0.14770300	-4.43669600	0.88516900
H	-1.10542200	-5.30562700	0.00000000
H	0.14770300	-4.43669600	-0.88516900

C	-0.28449100	-4.46368300	-0.01975300
H	0.32950600	-4.46102800	0.87467400
H	-0.88145400	-5.36292800	-0.03617000
H	0.35542100	-4.44621800	-0.89569600

p-CH_3O-ACDA (S_1)-Min

C	0.62788200	-1.75417700	0.00000000
C	0.99511600	-0.41151400	0.00000000
C	0.01732800	0.61222900	0.00000000
C	-1.35768900	0.22788500	0.00000000
C	-1.71078200	-1.10393900	0.00000000
C	-0.72405300	-2.11032900	0.00000000
H	2.03726900	-0.15740200	0.00000000
H	-2.11599800	0.98582400	0.00000000
H	-2.74329000	-1.39958700	0.00000000
C	0.36540100	1.98149100	0.00000000
Cl	1.98331300	2.56491200	0.00000000
N	-0.72405300	3.05426500	0.62060400
N	-0.72405300	3.05426500	-0.62060400
H	1.39875200	-2.50016300	0.00000000
O	-1.18662300	-3.37566400	0.00000000
C	-0.28821200	-4.45040600	0.00000000
H	0.33870000	-4.44396600	0.88537700
H	-0.89068200	-5.34608500	0.00000000
H	0.33870000	-4.44396600	-0.88537700

p-CH_3O-ACDA (S_1)-TS

C	0.63502900	-1.73619300	0.00344700
C	1.02395300	-0.40175000	-0.02168900
C	0.06231700	0.64036500	-0.06560800
C	-1.31579800	0.27541100	-0.05816500
C	-1.69061900	-1.05198600	-0.04224900
C	-0.72210300	-2.07309200	-0.01458300
H	2.06959700	-0.16474100	-0.01547300
H	-2.06299700	1.04403800	-0.07105600
H	-2.72760400	-1.33073200	-0.04711300
C	0.43619500	1.99660900	-0.16679600
Cl	2.06259400	2.55996800	-0.14224300
N	-0.56326600	3.47721400	0.70523300
N	-0.65232400	3.04327000	-0.44249000
H	1.39392700	-2.49348700	0.03428000
O	-1.20226200	-3.33370700	-0.00352200
C	-0.31606000	-4.41684900	0.03986100
H	0.28096300	-4.40498200	0.94571900
H	-0.92726500	-5.30656000	0.03105200
H	0.34014600	-4.42923700	-0.82401300

p-CH_3O-ACDA (S_0)-TS

C	0.61879200	-1.77055100	0.01629200
C	0.98268700	-0.41951700	0.04883100
C	0.01524600	0.58705000	0.04777600
C	-1.34637100	0.20886300	0.01119000
C	-1.71004200	-1.12365000	-0.00103000
C	-0.72606100	-2.12664200	-0.00138900
H	2.02434100	-0.16599700	0.06991400
H	-2.10743300	0.96683800	-0.00572500
H	-2.74251100	-1.41721200	-0.02431400
C	0.32124200	2.02031600	-0.05392800
Cl	1.98221100	2.52968800	-0.14299900
N	-0.13119700	2.59899300	1.89975600
N	-0.60642100	3.07108800	0.95325500
H	1.39160800	-2.51392600	0.01354400
O	-1.18806300	-3.39461400	-0.02403000

p-CH_3O-ACDA (S_1/S_0)-X

C	0.57945100	-1.83295100	0.00000000
C	0.96242200	-0.49067200	0.00000000
C	0.00000000	0.54108600	0.00000000
C	-1.38299000	0.15877900	0.00000000
C	-1.75252600	-1.16446300	0.00000000
C	-0.77124500	-2.18012300	0.00000000
H	1.34675100	-2.58375600	0.00000000
H	2.00958000	-0.25353600	0.00000000
H	-2.13952600	0.92469200	0.00000000
H	-2.78914400	-1.44920200	0.00000000
C	0.34426800	1.91264900	0.00000000
Cl	1.98790100	2.46946000	0.00000000
N	-0.49865400	4.07703700	0.00000000
N	-0.62034300	2.90282500	0.00000000
O	-1.23827600	-3.44877700	0.00000000

C	-0.33554000	-4.51881000	0.00000000	H	-1.48281900	-4.31797300	0.87568400
H	0.29314600	-4.51087600	0.88473400	H	-1.48281900	-4.31797300	-0.87568400
H	-0.93211500	-5.41906800	0.00000000				
H	0.29314600	-4.51087600	-0.88473400				

p-CH_3-ACDA (S_0)-Min

C	0.05538200	-2.21228800	0.00000000
C	0.72862300	-0.98811400	0.00000000
C	0.01470200	0.21102800	0.00000000
C	-1.38920100	0.15683600	0.00000000
C	-2.04760600	-1.06750100	0.00000000
C	-1.33797800	-2.27645900	0.00000000
H	0.63146300	-3.12060700	0.00000000
H	1.80063000	-0.98159600	0.00000000
H	-1.97084600	1.05915200	0.00000000
H	-3.12366700	-1.08117800	0.00000000
C	0.68903700	1.53937600	0.00000000
Cl	2.43554600	1.61678000	0.00000000
N	0.01470200	2.70446400	0.61233200
N	0.01470200	2.70446400	-0.61233200
C	-2.07185800	-3.59747400	0.00000000
H	-1.38085100	-4.43225900	0.00000000
H	-2.70673100	-3.69184700	0.87557700
H	-2.70673100	-3.69184700	-0.87557700

p-CH_3-ACDA (S_0)-TS

C	0.66804900	-2.07466500	-0.43227900
C	0.96799200	-0.71090900	-0.47887600
C	0.01230900	0.23672100	-0.09667200
C	-1.25352800	-0.21811600	0.32989100
C	-1.53254800	-1.57435400	0.38873900
C	-0.57563200	-2.53055000	0.00534900
H	1.41924700	-2.78294300	-0.73371200
H	1.93666500	-0.39608700	-0.81433100
H	-2.00601200	0.49493800	0.61236200
H	-2.50283600	-1.89807900	0.72295600
C	0.19487000	1.68873000	-0.24370600
Cl	1.70552400	2.29697200	-0.85400300
N	0.38787000	2.19750000	1.77503300
N	-0.39434500	2.66488900	1.05950600
C	-0.90251300	-4.00412700	0.06668700
H	-1.15280800	-4.30594200	1.07905900
H	-1.75335300	-4.24150000	-0.56452400
H	-0.06551500	-4.60827500	-0.26278400

p-CH_3-ACDA (S_1)-Min

C	0.74610900	-2.10808300	0.00000000
C	1.04092400	-0.75071700	0.00000000
C	-0.00335900	0.20954500	0.00000000
C	-1.35003700	-0.25922700	0.00000000
C	-1.61585800	-1.61632200	0.00000000
C	-0.57832600	-2.57121000	0.00000000
H	1.55614700	-2.81593300	0.00000000
H	2.06473400	-0.43004300	0.00000000
H	-2.15386300	0.45051200	0.00000000
H	-2.64000500	-1.94713000	0.00000000
C	0.25811700	1.59768500	0.00000000
Cl	1.83345600	2.28557500	0.00000000
N	-0.90078300	2.60306100	0.62010800
N	-0.90078300	2.60306100	-0.62010800
C	-0.90078300	-4.04669300	0.00000000
H	0.00011200	-4.64894500	0.00000000

p-CH_3-ACDA (S_1)-TS

C	0.73323400	-2.09118000	-0.18680800
C	1.04502700	-0.74183400	-0.22309700
C	0.02237200	0.23787000	-0.07918500
C	-1.31159500	-0.21503100	0.12756100
C	-1.59663200	-1.57006700	0.14907500
C	-0.58758400	-2.53855700	-0.00985000
H	1.52471100	-2.81046700	-0.30306500
H	2.06204100	-0.43541700	-0.37083200
H	-2.09621400	0.50413500	0.25739600
H	-2.61527200	-1.88570300	0.29261000
C	0.29243100	1.61579800	-0.18734600
Cl	1.86155900	2.29083900	-0.39119400
N	-0.66889900	2.99941900	0.87460800
N	-0.88885400	2.59760700	-0.26591500
C	-0.91747000	-4.01129300	0.03937700
H	-0.11538200	-4.60888500	-0.37825800

H	-1.07776100	-4.34144100	1.06197500
H	-1.82126300	-4.22886900	-0.51998400

p-CH_3-ACDA (S_1/S_0)-X

C	-0.25498300	-2.28518500	0.00000000
C	-0.82240100	-1.01963700	0.00000000
C	0.00000000	0.13556600	0.00000000
C	1.41645000	-0.05771700	0.00000000
C	1.95938500	-1.32959900	0.00000000
C	1.13906600	-2.47287000	0.00000000
H	-0.90582300	-3.14383400	0.00000000
H	-1.89170400	-0.92073100	0.00000000
H	2.06440500	0.80242400	0.00000000
H	3.03049800	-1.44135700	0.00000000
C	-0.52529500	1.44750400	0.00000000
Cl	-2.22815200	1.78162000	0.00000000
N	0.02146200	3.70556300	0.00000000
N	0.29880100	2.55840600	0.00000000
C	1.71445200	-3.87132400	0.00000000
H	2.79855700	-3.85714500	0.00000000
H	1.39038700	-4.42755600	0.87520500
H	1.39038700	-4.42755600	-0.87520500

p-Cl-ACDA (S_0)-Min

C	0.83894100	-1.71176900	0.00000000
C	1.07897700	-0.33779200	0.00000000
C	0.01691700	0.57174400	0.00000000
C	-1.29677000	0.07880200	0.00000000
C	-1.54327000	-1.29183100	0.00000000
C	-0.47064200	-2.17930700	0.00000000
H	1.65897200	-2.40369600	0.00000000
H	2.09249100	0.01006700	0.00000000
H	-2.13421700	0.74962000	0.00000000
H	-2.55051200	-1.66147700	0.00000000
C	0.23735000	2.04534300	0.00000000
Cl	1.86803900	2.66978400	0.00000000
N	-0.77394900	2.93483900	0.61201200
N	-0.77394900	2.93483900	-0.61201200
Cl	-0.77394900	-3.89527800	0.00000000

p-Cl-ACDA (S_1)-Min

C	1.09598900	-1.59281200	0.00000000
C	1.16831200	-0.20714100	0.00000000
C	-0.01493600	0.57711800	0.00000000
C	-1.27311700	-0.08850700	0.00000000
C	-1.33739900	-1.47332800	0.00000000
C	-0.15394300	-2.22078200	0.00000000
H	1.99268200	-2.18249100	0.00000000
H	2.12863300	0.27010800	0.00000000
H	-2.17756700	0.48702700	0.00000000
H	-2.28785400	-1.97168600	0.00000000
C	0.02925100	1.99205100	0.00000000
Cl	1.47877900	2.91256900	0.00000000
N	-1.27311700	2.80441200	0.61979600
N	-1.27311700	2.80441200	-0.61979600
Cl	-0.23861400	-3.95870600	0.00000000

p-Cl-ACDA (S_0)-TS

C	1.08252600	-1.57903900	0.04372200
C	1.17607600	-0.18711100	0.03284000
C	0.02074300	0.60474200	-0.00590100
C	-1.23661100	-0.02971400	-0.03912800
C	-1.33682200	-1.41450400	-0.01073200
C	-0.17087600	-2.18154000	0.02854300
H	1.96967000	-2.18186200	0.07254600
H	2.14535000	0.27030800	0.05158900
H	-2.13097100	0.56300400	-0.08662000
H	-2.29657400	-1.89366100	-0.03110800
C	0.03970600	2.07133300	-0.15341600
Cl	1.56796400	2.89325100	-0.22717000
N	-0.55559500	2.57642600	1.78044800
N	-1.09832400	2.94256100	0.82617600
Cl	-0.29036900	-3.91882900	0.05222500

***p*-Cl-ACDA (S_1)-TS**

C	1.08576800	-1.57683000	0.04150800
C	1.18361300	-0.19628000	0.00203100
C	0.01277600	0.61256000	-0.05805300
C	-1.25478200	-0.03352200	-0.05421100
C	-1.34332800	-1.41721800	-0.02391600
C	-0.17545200	-2.18531400	0.02230700
H	1.97140200	-2.18128000	0.08499400
H	2.15247800	0.26244300	0.01081800
H	-2.14822100	0.55791200	-0.08114200
H	-2.30221200	-1.89873400	-0.03299800
C	0.08743400	2.01633900	-0.16323300
Cl	1.54662500	2.92232700	-0.13826700
N	-1.23974100	3.22238400	0.69430800
N	-1.20141600	2.80356300	-0.46068300
Cl	-0.28939200	-3.92079200	0.06270300

***p*-Cl-ACDA (S_1/S_0)-X**

C	1.03111000	-1.70409200	0.00000000
C	1.15150300	-0.31900900	0.00000000
C	0.00000000	0.50625500	0.00000000
C	-1.28328200	-0.12964900	0.00000000
C	-1.39802200	-1.50514000	0.00000000
C	-0.23628600	-2.29170900	0.00000000
H	1.91118800	-2.32002400	0.00000000
H	2.13190200	0.11869300	0.00000000
H	-2.17168600	0.47801900	0.00000000
H	-2.36522500	-1.97228200	0.00000000
C	0.07026100	1.91756000	0.00000000
Cl	1.56888900	2.78881400	0.00000000
N	-1.18269800	3.87034100	0.00000000
N	-1.07655700	2.69547500	0.00000000
Cl	-0.37495500	-4.03060200	0.00000000

***p*-NO_2-ACDA (S_0)-Min**

C	-2.47222100	-0.80673400	-0.13564500
C	-1.08728100	-0.96101400	-0.13806300
C	-0.24592100	0.14932900	-0.00797800
C	-0.81401900	1.42627700	0.12678400
C	-2.19514500	1.59319500	0.13127600
C	-3.00410700	0.46944800	-0.00097700
H	-3.11986100	-1.65320700	-0.23562800
H	-0.67663000	-1.94476200	-0.24170300
H	-0.19309400	2.29477100	0.22845200
H	-2.63280300	2.56469200	0.23401400
C	1.23775800	0.01550300	-0.01073900
Cl	1.95904400	-1.56392200	-0.17527000
N	2.05932700	1.00994200	0.71633900
N	2.06730200	1.14057000	-0.49934000
N	-4.45638500	0.63699600	0.00214500
O	-4.88233300	1.74326300	0.13046600
O	-5.12399300	-0.34274900	-0.12368100

***p*-NO_2-ACDA (S_0)-TS**

C	-2.50396900	-0.82511300	0.13774400
C	-1.12075500	-1.00431500	0.14893900
C	-0.25882700	0.09272900	0.01501400
C	-0.80945100	1.38198100	-0.14016100
C	-2.18294900	1.57444100	-0.13447800
C	-3.01157500	0.46032400	0.00355500
H	-3.16797200	-1.65847000	0.24085200
H	-0.72529800	-1.99393100	0.25936100
H	-0.16047600	2.22770000	-0.26517200
H	-2.60700000	2.55091400	-0.24617600
C	1.20335300	-0.04453700	-0.13054100
Cl	1.92573000	-1.61134600	0.04178000
N	1.74443800	0.81459300	1.69207400
N	2.15358700	1.17877300	0.67524200
N	-4.46102400	0.65289700	0.00097700
O	-5.14601800	-0.31742600	0.10399600
O	-4.86690800	1.76909300	-0.10351400

***m*-Cl-ACDA (S_0)-Min**

C	-1.20736800	-1.48336200	0.00000000
C	-0.00867200	-0.77448500	0.00000000
C	-0.03625500	0.62367500	0.00000000
C	-1.27304400	1.28608700	0.00000000
C	-2.45973900	0.55712700	0.00000000
C	-2.43874600	-0.83718700	0.00000000
H	0.91825100	-1.30977600	0.00000000
H	-1.31926300	2.35793300	0.00000000
H	-3.40103900	1.07493600	0.00000000
H	-3.34863900	-1.40567500	0.00000000
C	1.21815400	1.42879300	0.00000000
Cl	2.76269200	0.61578700	0.00000000
N	1.21815400	2.77577700	0.61192100
N	1.21815400	2.77577700	-0.61192100
Cl	-1.15501300	-3.22650300	0.00000000

***m*-Cl-ACDA (S_1)-TS**

C	-1.22312500	-1.45683100	0.03850800
C	0.00704500	-0.82881900	-0.00817100
C	0.06509300	0.59336700	-0.06720000
C	-1.15181200	1.32882100	-0.05747000
C	-2.36894800	0.66335600	-0.02073400
C	-2.42371800	-0.73461600	0.02715700
H	0.90492200	-1.41244600	-0.00446700
H	-1.11928900	2.39967000	-0.08426600
H	-3.28265500	1.22841400	-0.02563000
H	-3.36309100	-1.25185800	0.05948900
C	1.29836400	1.26994600	-0.17454500
Cl	2.83755000	0.50926400	-0.15809300
N	1.62078900	3.03115800	0.68920500
N	1.28612100	2.78144800	-0.46681600
Cl	-1.28308600	-3.19779600	0.11284700

***m*-Cl-ACDA (S_1)-Min**

C	-1.23413100	-1.47756700	0.00000000
C	-0.01293200	-0.82392500	0.00000000
C	0.01650700	0.59544300	0.00000000
C	-1.21252600	1.31162400	0.00000000
C	-2.41753100	0.62415900	0.00000000
C	-2.44533400	-0.77635900	0.00000000
H	0.89569100	-1.39148900	0.00000000
H	-1.19804900	2.38341700	0.00000000
H	-3.34148900	1.17252100	0.00000000
H	-3.37630100	-1.31085300	0.00000000
C	1.24291800	1.30552400	0.00000000
Cl	2.79023200	0.56211600	0.00000000
N	1.24291800	2.84147300	0.61961900
N	1.24291800	2.84147300	-0.61961900
Cl	-1.26096900	-3.22021000	0.00000000

***m*-Cl-ACDA (S_1/S_0)-X**

C	-1.42461100	-1.39753400	0.00000000
C	-0.15057000	-0.84783900	0.00000000
C	0.00000000	0.56113800	0.00000000
C	-1.18032100	1.37245100	0.00000000
C	-2.43290200	0.79334600	0.00000000
C	-2.57594200	-0.60548500	0.00000000
H	0.70501600	-1.49436200	0.00000000
H	-1.07981400	2.44396000	0.00000000
H	-3.30998100	1.41593600	0.00000000
C	1.26825200	1.18439700	0.00000000
Cl	2.75829100	0.30073800	0.00000000
N	2.36508600	3.22747200	0.00000000
N	1.38758800	2.56673700	0.00000000
H	-3.54652400	-1.06547400	0.00000000
Cl	-1.58540000	-3.13734800	0.00000000

F	0.41301100	3.60352600	1.06245700
F	0.41301100	3.60352600	-1.06245700

p-CF_3-ACDA (S_0)-Min

C	-0.84549900	1.16510000	0.00000000
C	-1.20735300	-0.17777800	0.00000000
C	-0.22421600	-1.17610900	0.00000000
C	1.12481800	-0.79994300	0.00000000
C	1.48701100	0.54717800	0.00000000
C	0.50275400	1.53135700	0.00000000
H	-1.60904700	1.92067400	0.00000000
H	-2.24633000	-0.43931800	0.00000000
H	1.90064100	-1.54094500	0.00000000
H	2.52482900	0.81726200	0.00000000
C	-0.57234600	-2.62513600	0.00000000
Cl	-2.25005100	-3.10684100	0.00000000
N	0.35991900	-3.59810100	0.61175700
N	0.35991900	-3.59810100	-0.61175700
C	0.85442500	2.99197900	0.00000000
F	2.16064400	3.19312200	0.00000000
F	0.35991900	3.60855800	1.06258200
F	0.35991900	3.60855800	-1.06258200

p-CF_3-ACDA (S_1)-TS

C	0.73130300	0.82708800	-1.18130200
C	0.47365500	-0.52737900	-1.25383000
C	-0.03720200	-1.22515000	-0.11939300
C	-0.29429900	-0.48893100	1.06808600
C	-0.02041000	0.87237000	1.12843300
C	0.49405000	1.53607900	0.01144700
H	1.11826100	1.34156500	-2.04130600
H	0.66528000	-1.05626000	-2.16628000
H	-0.69617800	-0.99281700	1.92432200
H	-0.20740500	1.41021800	2.03723900
C	-0.24896300	-2.61867600	-0.14384500
Cl	-0.01660800	-3.62166500	-1.51745200
N	-1.74638000	-3.47614600	0.84398100
N	-0.57201600	-3.33988500	1.17907000
C	0.80380300	3.00564500	0.04387900
F	0.55931200	3.54424700	1.22485800
F	0.08831600	3.66940800	-0.85082500
F	2.07661700	3.23420500	-0.24082200

p-CF_3-ACDA (S_1)-Min

C	-0.85659800	1.19687400	0.00000000
C	-1.25729800	-0.12793600	0.00000000
C	-0.28926400	-1.16866500	0.00000000
C	1.08808900	-0.81936400	0.00000000
C	1.47561800	0.51497900	0.00000000
C	0.50976200	1.52623600	0.00000000
H	-1.59583900	1.97643400	0.00000000
H	-2.30280800	-0.36594700	0.00000000
H	1.82975500	-1.59328300	0.00000000
H	2.51899500	0.76363400	0.00000000
C	-0.66635400	-2.53432300	0.00000000
Cl	-2.28936400	-3.09107300	0.00000000
N	0.41301100	-3.63171600	0.61944200
N	0.41301100	-3.63171600	-0.61944200
C	0.89640000	2.97936400	0.00000000
F	2.20562000	3.14944200	0.00000000

p-CF_3-ACDA (S_1/S_0)-X

C	-1.02515300	-1.09725000	0.00000000
C	-1.20078700	0.27738700	0.00000000
C	-0.07682800	1.14323400	0.00000000
C	1.22741500	0.55423500	0.00000000
C	1.38947300	-0.81887000	0.00000000
C	0.26304500	-1.65505100	0.00000000
H	-1.88788800	-1.73913300	0.00000000
H	-2.19554100	0.68068200	0.00000000
H	2.09277700	1.19458100	0.00000000
H	2.37728200	-1.24003000	0.00000000
C	-0.19989400	2.54999200	0.00000000
Cl	-1.72971400	3.36551000	0.00000000
N	0.97239800	4.54955700	0.00000000
N	0.91838000	3.37140300	0.00000000
C	0.38598200	-3.15391500	0.00000000
F	1.64462500	-3.55590900	0.00000000

F	-0.19989400	-3.68621600	1.06218300
F	-0.19989400	-3.68621600	-1.06218300