Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Unraveling the regioselectivity of odd electron halogen bond formation using electrophilicity index and chemical hardness parameters

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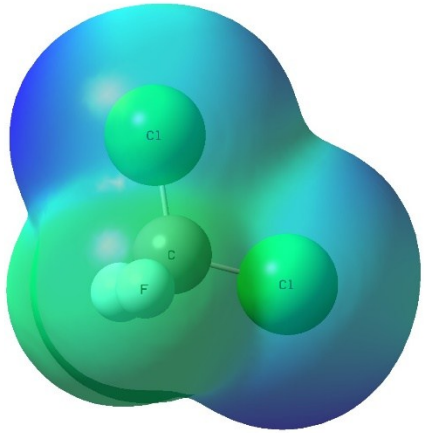
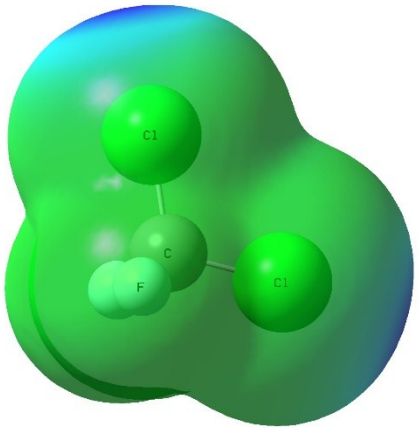
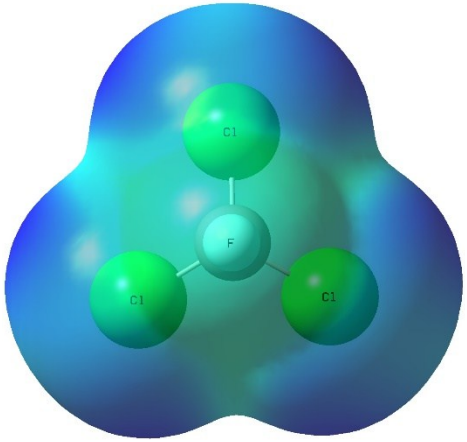
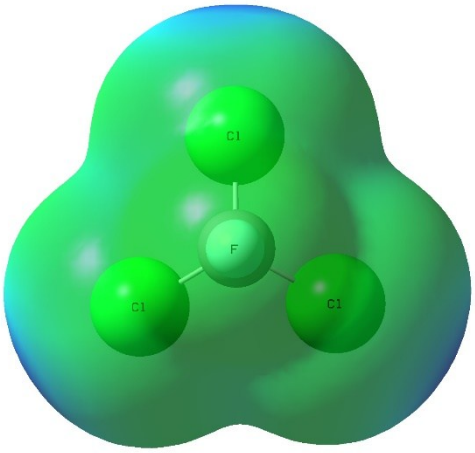
f- Fukui functions over CF_2Cl_2 (blue regions) *f+*



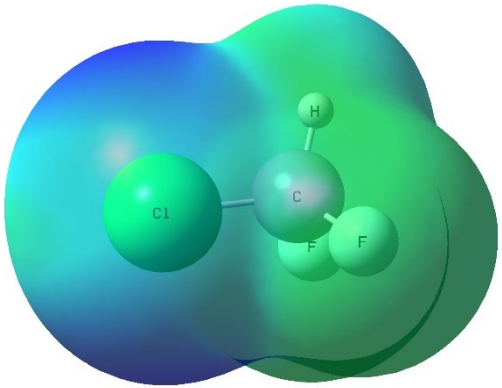


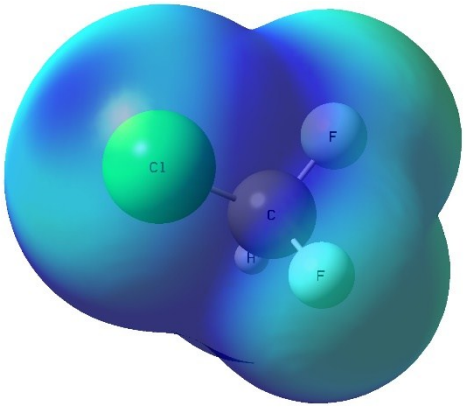
Fukui functions over $CFCl_3$ (blue regions)



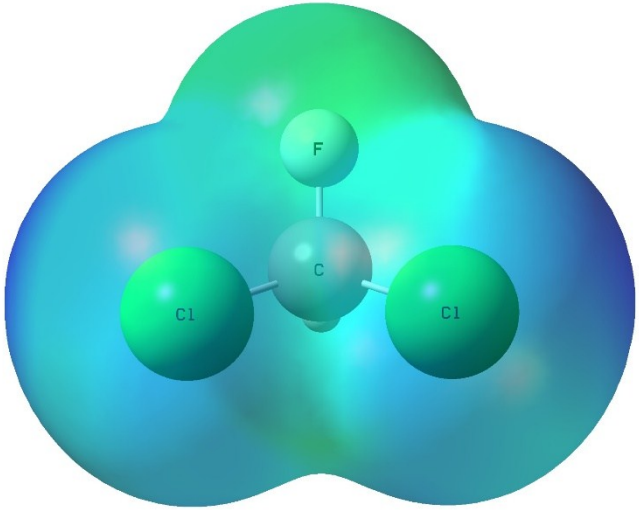


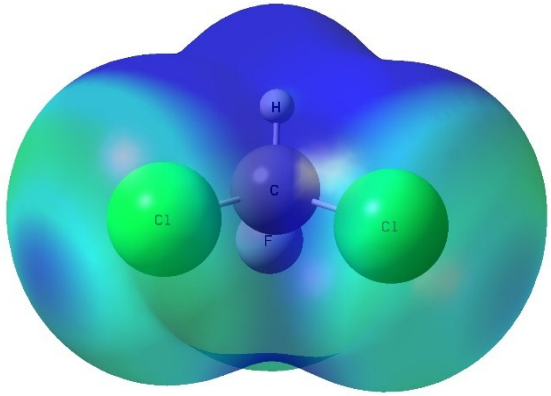
f- Fukui functions over CHF_2Cl (blue regions) *f+*





Fukui functions over $CHFCl_2$ (blue regions)





2. **Table S1:** BSSE and ZPE corrected Interaction energy (ΔE, kcal mol-1); Bond length (Å), total van der Waal radii of complexation atoms radii (Å), Bond angle (°) and coordinates of optimized complexes for Freon...Cl• Complexes**.**

Complex	ΔE	Bond length	van der Waal radii	Bond Angle (C-Cl...Cl•)
CF_3Cl...Cl	-1.90	3.128	4.1	90.64
CF_2Cl_2...Cl	-2.38	3.120	4.1	91.69
$CFCl_3$...Cl	-2.77	3.117	4.1	93.02
CHF_2Cl...Cl	-2.40	3.083	4.1	92.11
$CHFCl_2$...Cl	-2.87	3.081	4.1	93.13

CF3Cl+•Cl

C	0.72659	-0.78980	0.00000
F	1.17801	-2.03143	0.00000
Cl	-1.03989	-0.79673	0.00000
F	1.17801	-0.17053	1.07433
F	1.17801	-0.17053	-1.07433
Cl	-1.08752	2.33151	0.00000

CF2Cl2+•Cl

C	0.96768	-0.13257	-0.22814
F	2.22556	-0.55225	-0.19467
Cl	0.86105	1.46601	0.49347
Cl	-0.04418	-1.31322	0.62397
F	0.58750	-0.07644	-1.49622
Cl	-2.64767	0.22684	-0.14175

CFCl3+•Cl

C	-0.93151	0.00000	0.13731
F	-2.18027	0.00000	0.60583
Cl	0.16271	0.00002	1.53957
Cl	-0.69872	1.45414	-0.83150
Cl	-0.69872	-1.45417	-0.83146
Cl	2.71776	-0.00000	-0.24580

CHF2Cl+•Cl

C	-1.39179	-0.20044	0.00015
Cl	-0.43716	1.29883	0.00009
F	-1.08662	-0.91763	1.08111
F	-1.08730	-0.91729	-1.08123
H	-2.44780	0.05805	0.00053
Cl	2.22327	-0.26007	-0.00012

CHFCl2+•Cl

C	1.19932	-0.38722	-0.27071
Cl	1.32627	1.20560	0.46987
F	0.84536	-0.25650	-1.55608
H	2.15989	-0.88760	-0.20160
Cl	-0.00272	-1.40271	0.55393
Cl	-2.32143	0.52178	-0.09259

3. **Table S2:** BSSE and ZPE corrected Interaction energy (ΔE, kcal mol-1); Bond length (Å), total van der Waal radii of complexation atoms radii (Å), Bond angle (°) and coordinates of optimized complexes for Freon...•OCl Complexes**.**

Complex	ΔE	Bond length	van der Waal radii	Bond Angle (C-Cl...O•)	Bond Angle(Cl-O•...Cl)
CF_3Cl...OCl	-1.15	2.972	3.76	166.9	99.9
CF_2Cl_2...OCl	-1.25	2.947	3.76	168.4	101.6
$CFCl_3$...OCl	-1.27	2.942	3.76	167.3	99.2
CHF_2Cl...OCl	-0.77	3.021	3.76	167.5	98.5
$CHFCl_2$...OCl	-1.28	3.440	3.76	109.7	78.9

CF3Cl+•OCl

C	1.85322	0.09701	0.00018
F	2.31692	0.18142	1.23775
Cl	0.21907	-0.54100	-0.00116
F	1.87790	1.30674	-0.53936
F	2.65873	-0.68896	-0.69696
O	-2.72255	-0.97101	0.00109
Cl	-3.22030	0.54060	-0.00017

CF2Cl2+•OCl

C	3.91796	-3.32968	1.50044
F	4.19009	-3.56643	2.78025
Cl	2.30904	-3.94871	1.12910
Cl	5.16026	-4.06322	0.49378
F	3.92833	-2.01174	1.32452

O	7.61117	-4.93790	-0.89053
Cl	8.71016	-3.99901	-0.22488

CFCl3+•OCl

C	1.38099	-0.01053	0.26998
F	1.72096	-0.01506	1.56180
Cl	-0.25797	0.62682	0.12887
Cl	1.46056	-1.67686	-0.32149
Cl	2.53261	1.01274	-0.59755
O	-3.16022	1.06367	-0.08532
Cl	-3.64655	-0.45157	-0.09180

CHF2Cl+•OCl

C	-2.07487	0.22535	-0.35491
Cl	-0.47187	-0.32137	0.14065
F	-2.54222	1.11122	0.53255
F	-2.91652	-0.81425	-0.38131
H	-2.01813	0.68201	-1.33996
O	2.47750	-0.73550	0.64911
Cl	3.04692	0.39062	-0.32209

CHFCl2+•OCl

C	-1.54459	-0.25204	0.34550
Cl	-1.53021	1.17817	-0.69585
F	-1.08111	0.08951	1.56061
H	-2.56779	-0.60185	0.43412
Cl	-0.55104	-1.55350	-0.30996
O	2.72781	-0.52921	-0.49719
Cl	2.06612	0.70134	0.26610

4. **Table S3:** BSSE and ZPE corrected Interaction energy (ΔE, kcal mol-1); Bond length (Å), total van der Waal radii of complexation atoms radii (Å), Bond angle (°) and coordinates of optimized complexes for Freon...•NO Complexes**.**

Complex	ΔE	Bond length	van der Waal radii	Bond Angle (C-Cl...N•)	Bond Angle(O-N•...Cl)
CF_3Cl...NO	-0.40	3.182	3.84	164.5	99.2
CF_2Cl_2...NO	-0.61	3.163	3.84	167.7	103.9
$CFCl_3$...NO	-0.67	3.126	3.84	169.9	105.1
CHF_2Cl...NO	-0.39	3.238	3.84	166.6	98.7
$CHFCl_2$...NO	-0.56	3.189	3.84	169.1	101.1

CF3Cl+•NO

C	-1.40532	0.06590	-0.00034
F	-1.80540	0.34241	1.23038
Cl	0.27955	-0.43190	0.00218
F	-2.16949	-0.89970	-0.48504
F	-1.56557	1.14553	-0.74813
O	3.66399	0.63256	0.00059
N	3.46169	-0.48681	-0.00208

CF2Cl2+•NO

C	-1.09244	-0.35852	-0.00001
F	-1.27835	-1.11953	-1.07287
Cl	-2.27990	0.94339	0.00009
Cl	0.56041	0.25266	-0.00011
F	-1.27821	-1.11957	1.07284
O	4.11812	-0.36101	0.00015
N	3.69286	0.69403	-0.00009

CFCl3+•NO

C	0.94088	-0.00864	0.25622
F	1.02245	0.03268	1.58826
Cl	-0.75771	-0.21949	-0.18589
Cl	1.91055	-1.37154	-0.31341
Cl	1.56929	1.51553	-0.38088
O	-4.27015	0.34657	0.33044
N	-3.86580	-0.30220	-0.51186

CHF2Cl+•NO

C	-1.62685	-0.08153	0.38134
Cl	0.04154	0.16567	-0.14720
F	-2.13778	-1.15095	-0.23706
F	-2.36451	0.98171	0.04616
H	-1.64871	-0.22699	1.45846
O	3.54889	-0.28641	0.48168
N	3.26186	0.24489	-0.48279

CHFCl2+•NO

C	-1.33864	0.40218	0.37806
Cl	-1.99700	-1.21095	0.08519
F	-1.65292	1.19852	-0.65707
H	-1.78074	0.79670	1.28705
Cl	0.41724	0.37006	0.56986
O	3.69847	-0.35209	-0.68609
N	3.58860	0.11323	0.34621

5. **Table S4:** BSSE and ZPE corrected Interaction energy (ΔE, kcal mol-1); Bond length (Å), total van der Waal radii of complexation atoms radii (Å), Bond angle (°) and coordinates of optimized complexes for Freon...•OH Complexes.

Complex	ΔE	Bond length	van der Waal radii	Bond Angle (C-Cl...O•)	Bond Angle(H-O•...Cl)
CF_3Cl...OH	-0.94	2.967	3.76	179.7	129.0
CF_2Cl_2...OH	-0.85	2.957	3.76	179.8	127.5
$CFCl_3$...OH	-0.68	2.933	3.76	173.7	116.9
CHF_2Cl...OH	-0.39	3.025	3.76	179.9	118.2
$CHFCl_2$...OH	-0.56	2.97	3.76	90.6	81.7

CF3Cl+•OH

C	1.02193	0.00542	-0.00014
F	1.48266	0.29259	1.20885
Cl	-0.72973	-0.02921	0.00096
F	1.46884	0.92385	-0.84503
F	1.51149	-1.17020	-0.36502
O	-3.69655	-0.07752	-0.00035
H	-4.32074	0.66803	-0.00186

CF2Cl2+•OH

C	-0.75818	-0.35210	0.00723
F	-1.12854	-1.07490	-1.04539
Cl	-1.64219	1.17663	-0.00667
Cl	0.98173	-0.11188	-0.02641
F	-1.09199	-1.03363	1.09983

O	3.91065	0.29623	-0.07699
H	4.47653	0.61883	0.64497

CFCl3+•OH

C	-0.59080	0.00135	0.25986
F	-0.78178	0.00821	1.58389
Cl	1.14407	-0.01315	-0.04816
Cl	-1.34143	1.45959	-0.40543
Cl	-1.36454	-1.44926	-0.39449
O	4.07079	-0.03537	-0.24261
H	4.56696	0.24882	0.54412

CHF2Cl+•OH

C	1.25136	0.00002	0.33078
Cl	-0.50484	-0.00013	0.18355
F	1.75597	1.08206	-0.27614
F	1.75616	-1.08189	-0.27621
H	1.53282	0.00001	1.38092
O	-3.52004	0.00009	-0.06923
H	-3.90767	-0.00009	-0.96098

CHFCl2+•OH

C	0.76902	-0.52413	0.03241
Cl	1.02919	1.19757	0.38006
F	0.75314	-0.70058	-1.29391
H	1.58929	-1.08358	0.47018
Cl	-0.74861	-1.10221	0.72192
O	-2.26124	0.98788	-0.76914
H	-1.63561	1.57163	-0.30590

6. **Table S5:** BSSE and ZPE corrected Interaction energy (ΔE, kcal mol-1); Bond length (Å), total van der Waal radii of complexation atoms radii (Å), Bond angle (°) and coordinates of optimized complexes for Freon...Ph• Complexes.

Complex	ΔE	Bond length	van der Waal radii	Bond Angle (C-Cl...C•)
CF_3Cl...Ph	-1.70	3.120	4.01	176.8
CF_2Cl_2...Ph	-1.84	3.097	4.01	176.9
$CFCl_3$...Ph	-1.86	3.076	4.01	175.4
CHF_2Cl...Ph	-1.22	3.165	4.01	178.4
$CHFCl_2$...Ph	-1.64	3.121	4.01	172.7

CF3Cl+•Ph

C	-2.41839	1.82918	-1.51917
C	-2.91293	1.19125	-2.62976
C	-3.32439	2.00692	-3.68805
C	-3.22296	3.39219	-3.58495
C	-2.71248	3.98296	-2.43161
C	-2.29485	3.18743	-1.36047
H	-2.98416	0.11181	-2.69159
H	-3.72304	1.55629	-4.58984
H	-3.54429	4.01628	-4.41002
H	-2.63736	5.06208	-2.36059
H	-1.89492	3.62804	-0.45463
C	-0.81678	-0.30254	2.56326
F	-1.83752	-0.73708	3.28562
Cl	-1.38730	0.41265	1.06268
F	-0.14820	0.59120	3.27564
F	-0.01434	-1.32497	2.31185

$CF_2Cl_2^{+\bullet}Ph$

C	2.67512	-0.08827	-0.31694
F	3.12338	-1.28040	-0.69586
Cl	3.46624	0.37456	1.18922
Cl	0.92071	-0.15011	-0.15342
F	2.99808	0.78495	-1.26527
C	-2.17183	-0.14176	0.01462
C	-2.64795	1.13653	-0.14168
C	-4.03646	1.29547	-0.10612
C	-4.86305	0.18997	0.07908
C	-4.32151	-1.08410	0.23125
C	-2.93588	-1.26734	0.19913
H	-1.98774	1.98387	-0.28535
H	-4.46723	2.28322	-0.22424
H	-5.93787	0.32241	0.10508
H	-4.97307	-1.93854	0.37470
H	-2.49595	-2.25069	0.31542

$CFCl_3^{+\bullet}Ph$

C	-2.42416	-0.12018	0.07121
C	-2.91608	1.14649	-0.12514
C	-4.30470	1.26800	-0.23112
C	-5.11541	0.13946	-0.13781
C	-4.55782	-1.12119	0.06176
C	-3.17187	-1.26734	0.17120
H	-2.26725	2.01196	-0.19386
H	-4.74849	2.24506	-0.38597
H	-6.19058	0.24338	-0.22131
H	-5.19736	-1.99388	0.13149
H	-2.71874	-2.23963	0.32564
C	2.43340	-0.04762	0.25218
F	2.82001	-0.26350	1.51234

Cl	3.03961	1.53861	-0.24162
Cl	0.66640	-0.09030	0.19863
Cl	3.12236	-1.32367	-0.75941

CHF2Cl+•Ph

C	1.55331	-0.10458	0.11471
C	2.05611	1.16283	-0.04841
C	3.44292	1.27420	-0.18378
C	4.24350	0.13488	-0.15013
C	3.67653	-1.12617	0.01777
C	2.29196	-1.26147	0.15512
H	1.41586	2.03699	-0.07332
H	3.89342	2.25153	-0.31640
H	5.31744	0.23051	-0.25665
H	4.30764	-2.00751	0.04089
H	1.83227	-2.23430	0.28494
C	-3.37724	-0.10203	0.26541
Cl	-1.60940	-0.10696	0.24255
F	-3.84030	-0.89774	-0.70510
F	-3.82475	1.13688	0.03173
H	-3.73107	-0.44953	1.23295

CHFCl2+•Ph

C	-0.30408	-2.71176	-4.73883
C	0.84463	-3.25756	-4.22000
C	1.75131	-3.80303	-5.13361
C	1.47152	-3.77717	-6.49760
C	0.28986	-3.21015	-6.96823
C	-0.63071	-2.65921	-6.07190
H	1.04648	-3.26926	-3.15537
H	2.67378	-4.24653	-4.77606
H	2.17948	-4.20198	-7.19881
H	0.08015	-3.19436	-8.03183

H	-1.55500	-2.21406	-6.42100
C	-3.45143	-0.82325	-1.62131
Cl	-3.86101	-1.95404	-0.32850
F	-4.57295	-0.48734	-2.28076
H	-3.01161	0.06466	-1.17920
Cl	-2.29743	-1.51569	-2.76437

7. Table S6: BSSE and ZPE corrected Interaction energy (ΔE, kcal mol^{-1}); Bond length (Å), total van der Waal radii of complexation atoms radii (Å), Bond angle (°) and coordinates of optimized complexes for Freon...Ph• Complexes at M06-2X-D3/6-311++G(d,p) level.

Complex	ΔE	Bond length	van der Waal radii	Bond Angle (C-Cl...C•)
CF_3Cl...Ph	-1.88	3.116	4.01	175.6
CF_2Cl_2...Ph	-2.04	3.089	4.01	176.1
$CFCl_3$...Ph	-2.11	3.071	4.01	174.9
CHF_2Cl...Ph	-1.38	3.161	4.01	178.3
$CHFCl_2$...Ph	-1.84	3.115	4.01	170.4

CF3Cl+•Ph

C	-2.30771	2.20768	-1.33000
C	-2.90851	1.34635	-2.21462
C	-3.39362	1.90554	-3.40062
C	-3.25585	3.27094	-3.63831
C	-2.63606	4.09569	-2.70258
C	-2.14339	3.55889	-1.50938
H	-3.00588	0.28627	-2.01111
H	-3.87748	1.27153	-4.13488
H	-3.63451	3.69577	-4.56007
H	-2.53346	5.15733	-2.89659
H	-1.65831	4.18472	-0.76970
C	-0.88184	-0.51977	2.44472
F	-1.63847	-1.60538	2.49160
Cl	-1.39869	0.53105	1.13435
F	-0.97662	0.10902	3.60579

F	0.37649	-0.89194	2.26975

CF2Cl2+•Ph

C	-2.66916	0.08103	-0.31925
F	-3.13857	1.25547	-0.72660
Cl	-3.45586	-0.36245	1.19497
Cl	-0.91674	0.17938	-0.15243
F	-2.97254	-0.81963	-1.24820
C	2.16800	0.17784	0.02527
C	2.60635	-1.11395	-0.13058
C	3.99004	-1.31219	-0.10525
C	4.84905	-0.23003	0.07000
C	4.34504	1.05940	0.22233
C	2.96498	1.28185	0.20032
H	1.92091	-1.94241	-0.26637
H	4.39160	-2.31215	-0.22356
H	5.91988	-0.39273	0.08811
H	5.02173	1.89540	0.35794
H	2.55427	2.27772	0.31689

CFCl3+•Ph

C	-2.42416	-0.12018	0.07121
C	-2.91608	1.14649	-0.12514
C	-4.30470	1.26800	-0.23112
C	-5.11541	0.13946	-0.13781
C	-4.55782	-1.12119	0.06176
C	-3.17187	-1.26734	0.17120
H	-2.26725	2.01196	-0.19386
H	-4.74849	2.24506	-0.38597
H	-6.19058	0.24338	-0.22131
H	-5.19736	-1.99388	0.13149
H	-2.71874	-2.23963	0.32564
C	2.43340	-0.04762	0.25218

F	2.82001	-0.26350	1.51234
Cl	3.03961	1.53861	-0.24162
Cl	0.66640	-0.09030	0.19863
Cl	3.12236	-1.32367	-0.75941

CHF2Cl+•Ph

C	1.55237	-0.10831	0.11578
C	2.05275	1.16001	-0.04789
C	3.43929	1.27383	-0.18402
C	4.24192	0.13592	-0.15057
C	3.67732	-1.12613	0.01790
C	2.29307	-1.26389	0.15604
H	1.41083	2.03297	-0.07266
H	3.88800	2.25193	-0.31706
H	5.31563	0.23348	-0.25768
H	4.31003	-2.00634	0.04086
H	1.83520	-2.23753	0.28629
C	-3.37438	-0.09976	0.26489
Cl	-1.60661	-0.10682	0.24290
F	-3.83789	-0.89394	-0.70665
F	-3.82024	1.13994	0.03225
H	-3.72908	-0.44781	1.23190

CHFCl2+•Ph

C	-0.30408	-2.71176	-4.73883
C	0.84463	-3.25756	-4.22000
C	1.75131	-3.80303	-5.13361
C	1.47152	-3.77717	-6.49760
C	0.28986	-3.21015	-6.96823
C	-0.63071	-2.65921	-6.07190
H	1.04648	-3.26926	-3.15537
H	2.67378	-4.24653	-4.77606
H	2.17948	-4.20198	-7.19881

H	0.08015	-3.19436	-8.03183
H	-1.55500	-2.21406	-6.42100
C	-3.45143	-0.82325	-1.62131
Cl	-3.86101	-1.95404	-0.32850
F	-4.57295	-0.48734	-2.28076
H	-3.01161	0.06466	-1.17920
Cl	-2.29743	-1.51569	-2.76437