Supporting Information for

Atmospheric Chemistry of $(CF_3)_2CHOCH_3$, $(CF_3)_2CHOCHO$, and $CF_3C(O)OCH_3$

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Table S1: Wavenumber ranges of absorption features of reactants and references (cm^{-1}).

Compound	Feature # 1	Feature # 2	Feature # 3	Feature # 4
$(CF_3)_2CHOCH_3$	1080-1125	1175-1215	1350-1400	
$(CF_3)_2CHOCHO$	1105-1150	1760-1795		
$CF_3C(O)OCH_3$	1080-1165			
CH_4	1210-1385	2850-3190		
C_2H_2	650-800			
C_2H_6	2890-2900			
C_3H_8	2860-2910	2950-2975		
C_2H_5Cl	940-995	1260-1300	1440-1450	2920-2965
CH_2F_2	1030-1090	1170-1180	1400-1470	2955-3070
CHF_2CHF_2	1100-1130	1145-1170	1200-1210	1305-1315
$CH_3C(O)OCH_3$	1245-1265	1750-1765	2940-2985	
CD_4	940-1040	2150-2350		

DFT optimization and frequency calculations using Gaussian 09 Revision C.01 were performed to calculate the IR spectra of the three title compounds: $(CF_3)_2CHOCH_3$, $(CF_3)_2CHOCHO$, and $CF_3C(O)OCH_3$ as well as the IR spectrum of $CF_3C(O)OCHO$ for comparison with the experimental spectra. The DFT functional and basis set used was B3LYP/6-31+G(d,p). The IR spectra are shown below in Figures S1-S4 and the coordinates of the optimized structures can be found in Tables S2-S5.

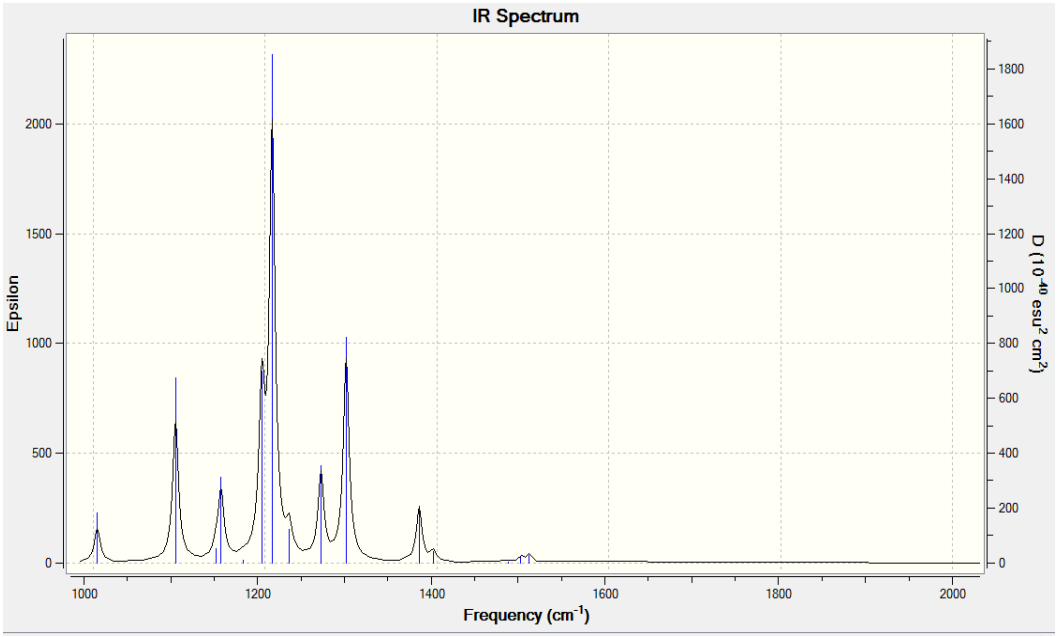

Figure S1: IR spectrum of $(CF_3)_2CHOCH_3$ calculated at the B3LYP/6-31+G(d,p) level. Gaussian 09 Revision C.01.

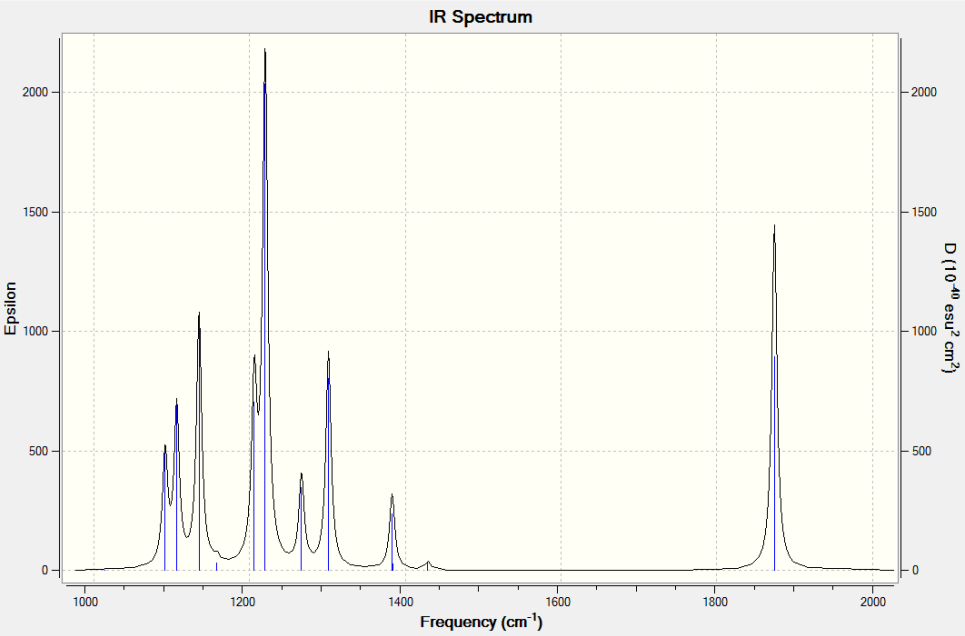

Figure S2: IR spectrum of $(CF_3)_2CHOCHO$ calculated at the B3LYP/6-31+G(d,p) level. Gaussian 09 Revision C.01.

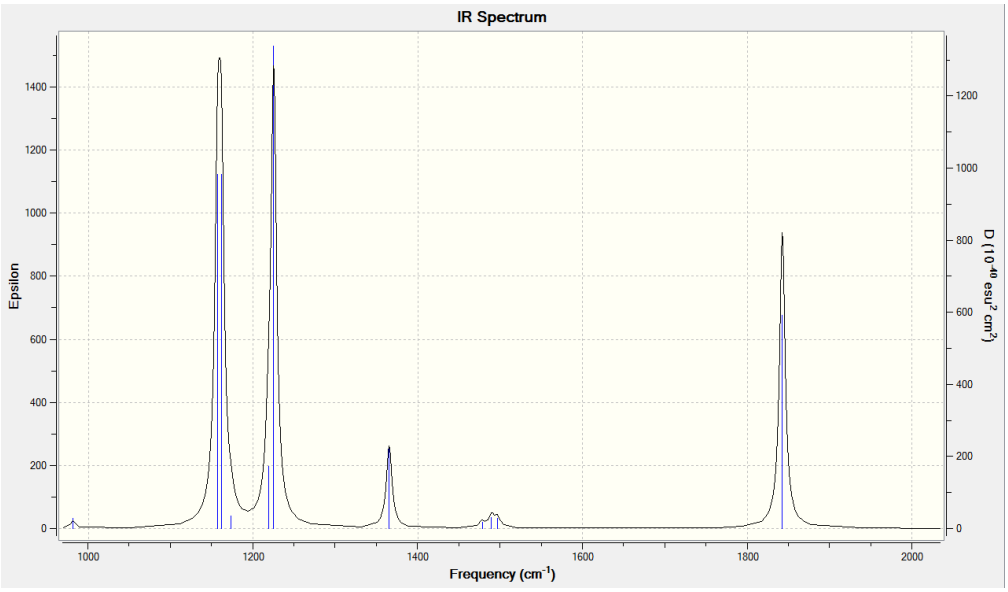

Figure S3: IR spectrum of $CF_3C(O)OCH_3$ calculated at the B3LYP/6-31+G(d,p) level. Gaussian 09 Revision C.01.

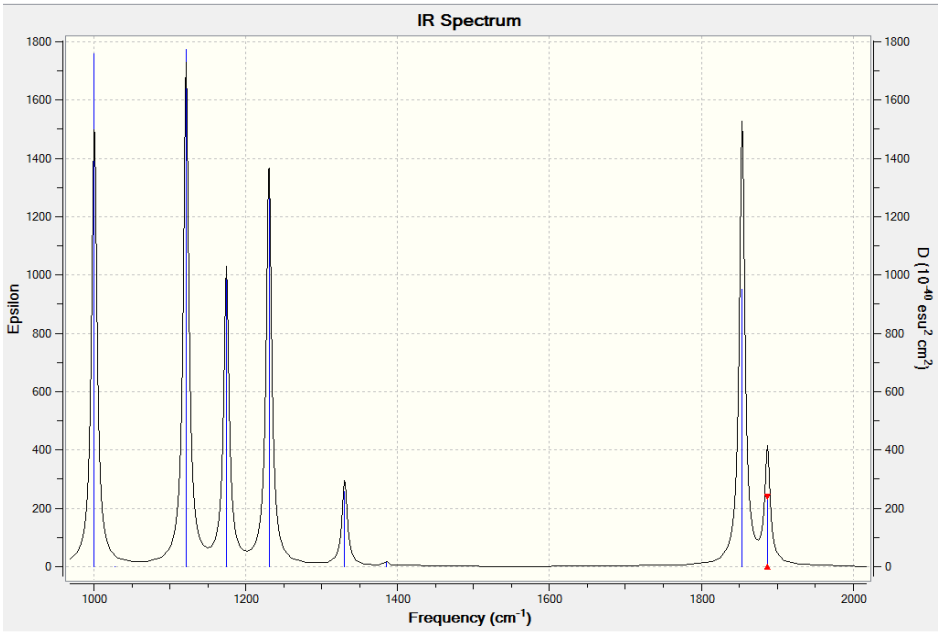

Figure S4: IR spectrum of $CF_3C(O)OCHO$ calculated at the B3LYP/6-31+G(d,p) level. Gaussian 09 Revision C.01.

Table S2: Coordinates for the optimized structure of $(CF_3)_2CHOCH_3$ calculated at the B3LYP/6-31+G(d,p) level (Ångstrøm). Gaussian 09 Revision C.01.

Atom	X	Y	Z
O	-0.17109	1.514353	0.472012
C	1.368391	-0.22118	-0.03559
F	1.573983	-0.48328	1.264322
F	2.305424	0.669604	-0.43323
F	1.571597	-1.36153	-0.73171
C	-0.03027	0.36673	-0.31235
H	-0.06512	0.580366	-1.38864
C	-1.19107	-0.61086	-0.02459
F	-1.14972	-1.68546	-0.84218
F	-2.36637	0.024581	-0.25274
F	-1.20318	-1.0504	1.24401
C	-0.63313	2.683663	-0.21426
H	-1.64294	2.537027	-0.61242
H	-0.64862	3.478533	0.532026
H	0.056199	2.957475	-1.02262

Table S3: Coordinates for the optimized structure of $(CF_3)_2CHOCHO$ calculated at the B3LYP/6-31+G(d,p) level (Ångstrøm). Gaussian 09 Revision C.01.

Atom	X	Y	Z
C	-0.67701	-1.30023	-0.02132
O	1.300163	-0.00154	0.3469
C	2.471545	-0.00178	-0.37061
H	2.310612	-0.00118	-1.46278
F	-1.8375	-1.37164	-0.7031
F	0.085781	-2.35211	-0.39272
F	-0.94404	-1.41759	1.28604
O	3.535062	-0.00262	0.170212
C	0.079974	-0.00025	-0.36191
H	0.235272	-0.00039	-1.4481
C	-0.67431	1.301312	-0.02131
F	0.090427	2.351569	-0.39294
F	-1.83492	1.374902	-0.70283
F	-0.94075	1.419362	1.286092

Table S4: Coordinates for the optimized structure of $CF_3C(O)OCH_3$ calculated at the B3LYP/6-31+G(d,p) level (Ångstrøm). Gaussian 09 Revision C.01.

Atom	X	Y	Z
C	0.475319	0.406646	-0.00047
O	1.30056	-0.63676	-0.00046
C	-0.99478	-0.08963	-8.6E-05
F	-1.24473	-0.83786	1.095526
F	-1.24321	-0.84645	-1.09002
F	-1.84006	0.947009	-0.00475
O	0.776962	1.573879	-0.00023
C	2.715316	-0.32731	0.000173
H	3.216874	-1.29311	0.000148
H	2.970293	0.246971	-0.89269
H	2.969583	0.24658	0.893487

Table S5: Coordinates for the optimized structure of $CF_3C(O)OCHO$ calculated at the B3LYP/6-31+G(d,p) level (Ångstrøm). Gaussian 09 Revision C.01.

Atom	X	Y	Z
C	-0.058889	0.579777	0.001155
C	-2.40176	0.158319	-0.001441
H	-2.462593	1.251683	-0.005399
O	-1.079116	-0.318374	0.00144
C	1.291893	-0.185496	-0.000014
F	1.386107	-0.961673	-1.096418
F	1.384103	-0.970588	1.090111
F	2.310011	0.678533	0.004387
O	-0.147104	1.775531	0.001141
O	-3.304638	-0.617623	0.000478

A screening of different possibilities for the nature of the residual in the oxidation of $CF_3C(O)OCH_3$ was performed by DFT optimization and frequency calculations using Gaussian 09 Revision D.01. One calculation was performed with Revision B.01. The DFT functionals and basis sets used were B3LYP/6-31+G(d,p) and WB97XD/cc-pVTZ. The IR spectra are shown below in Figures S5-S18 and the coordinates of the optimized structures can be found in Tables S6-S19. For some molecules more than one conformer was examined.

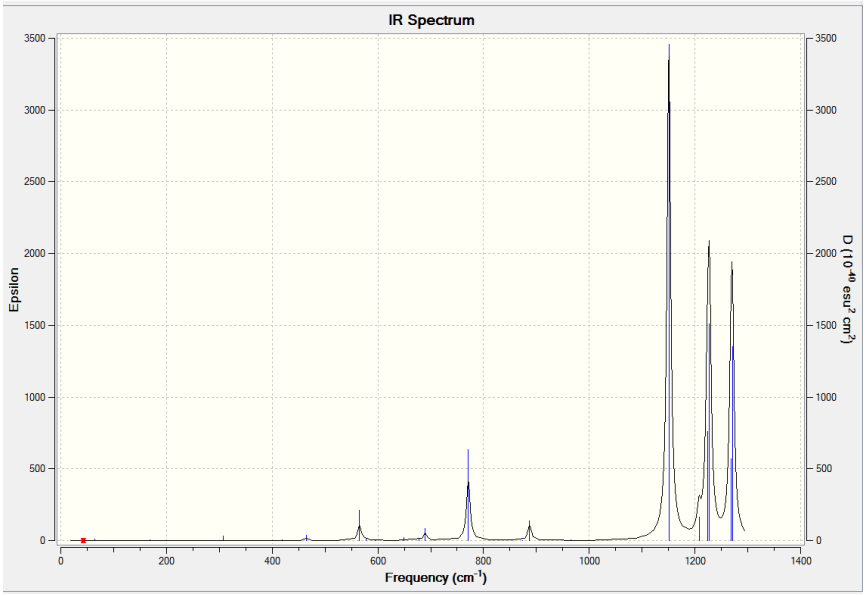

Figure S5: IR spectrum of CF_3OOOCF_3 calculated at the B3LYP/6-31+G(d,p) level.

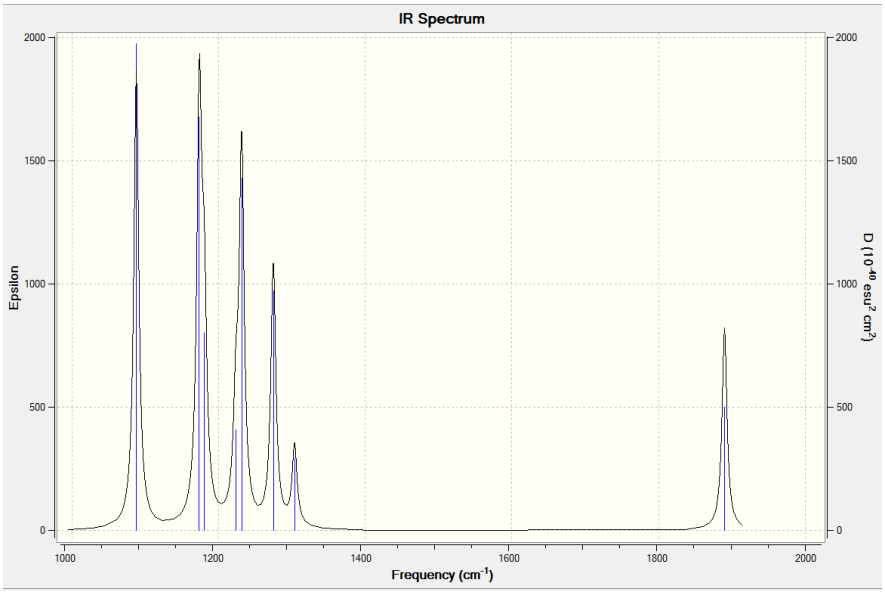

Figure S6: IR spectrum of $CF_3C(O)OOOCF_3$ calculated at the B3LYP/6-31+G(d,p) level.

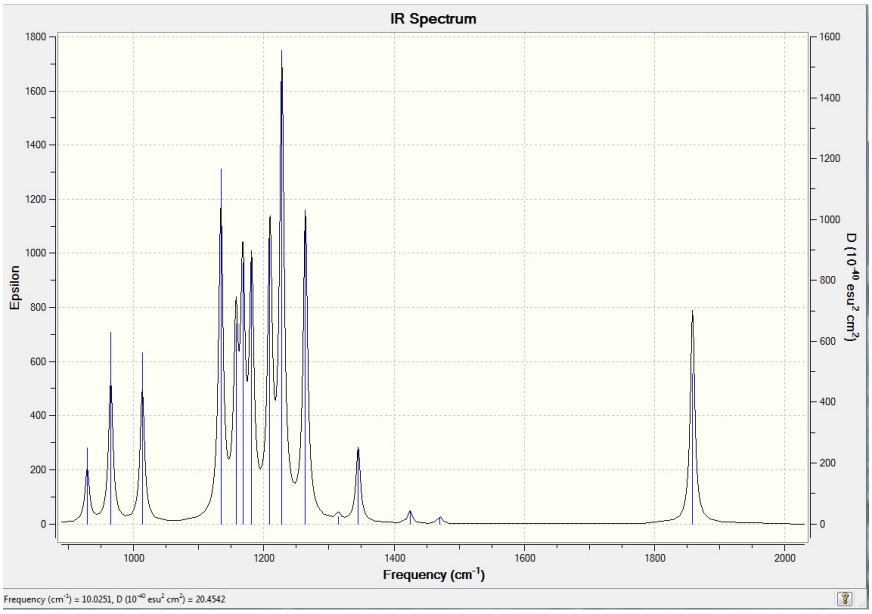

Figure S7: IR spectrum of $CF_3C(O)OCH_2OOOCF_3$ conformer 1 calculated at the B3LYP/6-31+G(d,p) level.

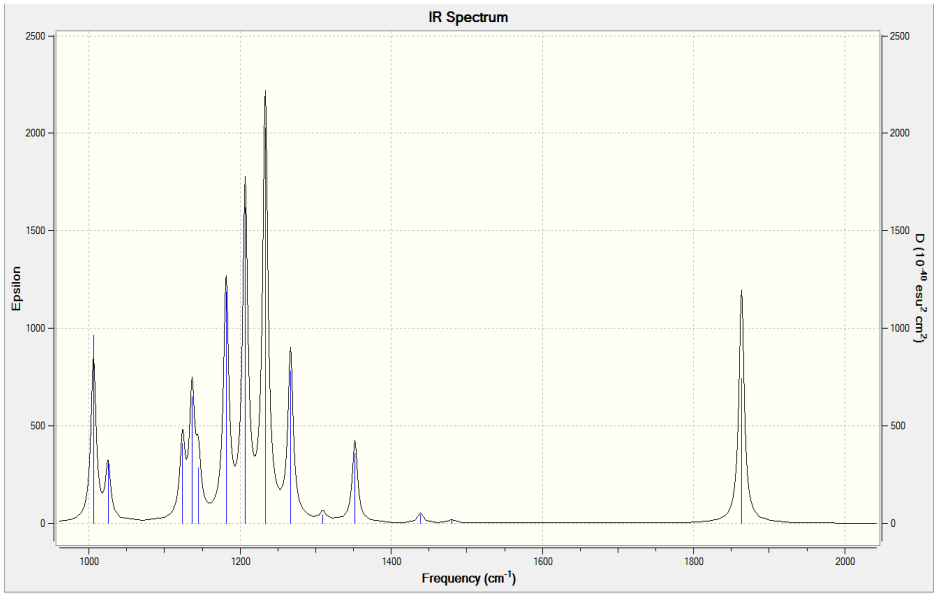

Figure S8: IR spectrum of $CF_3C(O)OCH_2OOOCF_3$ conformer 2 calculated at the B3LYP/6-31+G(d,p) level.

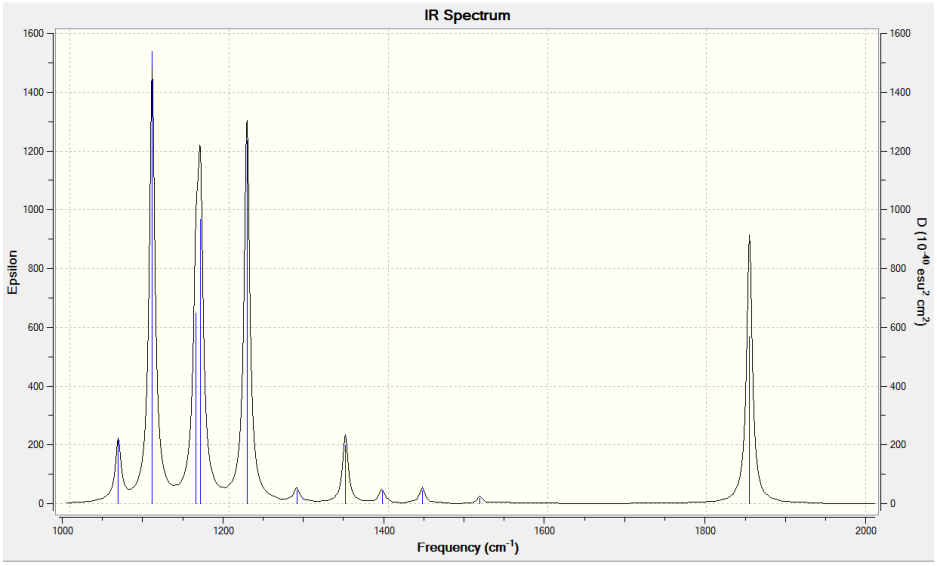

Figure S9: IR spectrum of $CF_3C(O)OCH_2OH$ conformer 1 calculated at the B3LYP/6-31+G(d,p) level.

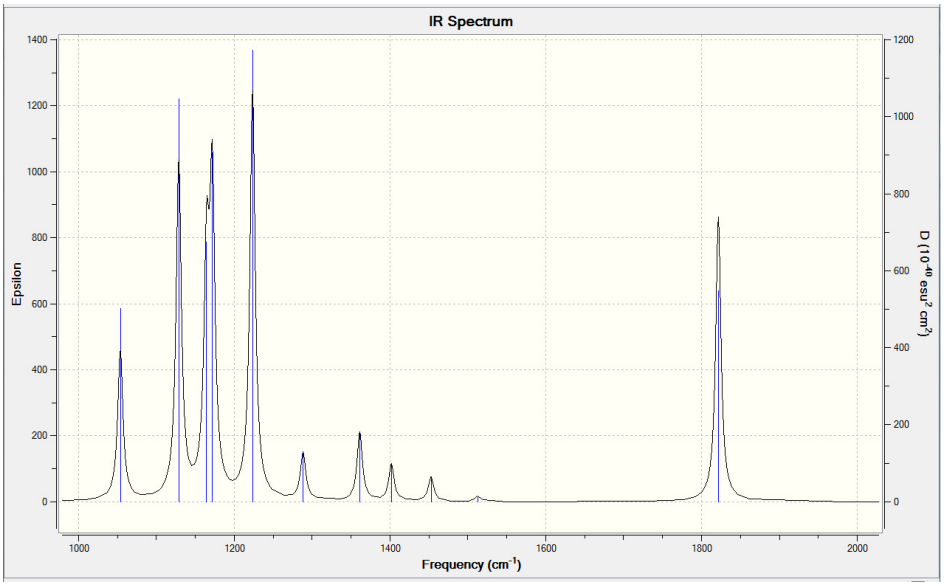

Figure S10: IR spectrum of $CF_3C(O)OCH_2OH$ conformer 2 calculated at the B3LYP/6-31+G(d,p) level.

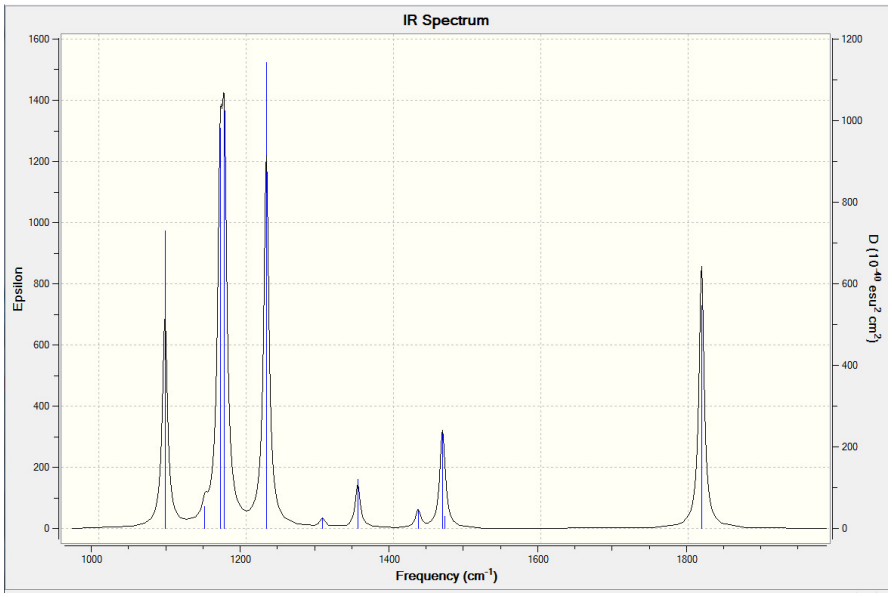

Figure S11: IR spectrum of $CF_3C(O)OCH_2OOH$ calculated at the B3LYP/6-31+G(d,p) level.

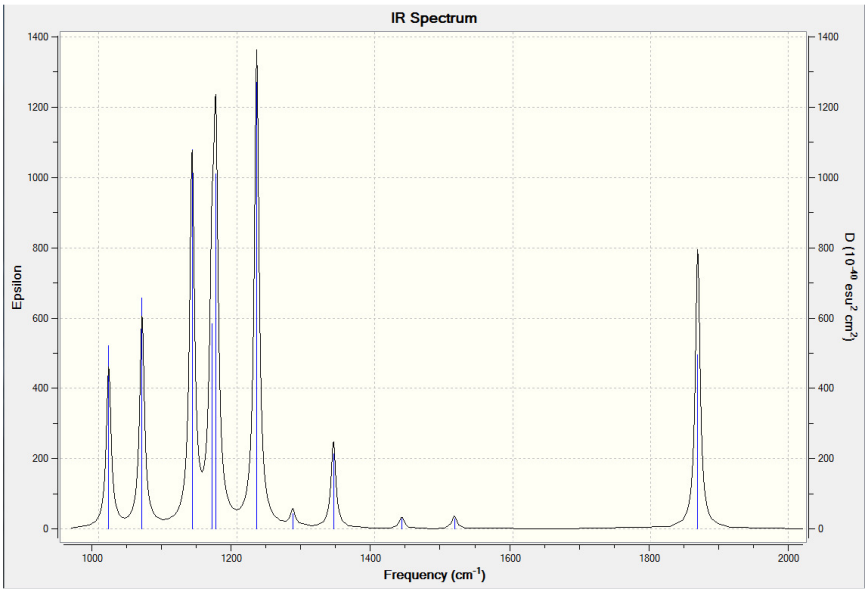

Figure S12: IR spectrum of $CF_3C(O)OCH_2OCl$ conformer 1 calculated at the B3LYP/6-31+G(d,p) level.

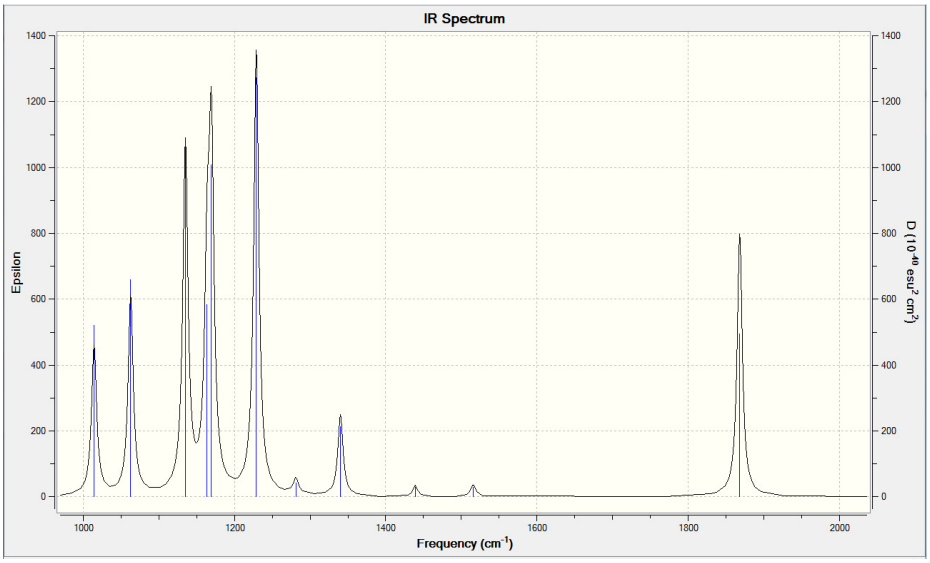

Figure S13: IR spectrum of $CF_3C(O)OCH_2OCl$ conformer 2 calculated at the B3LYP/6-31+G(d,p) level.

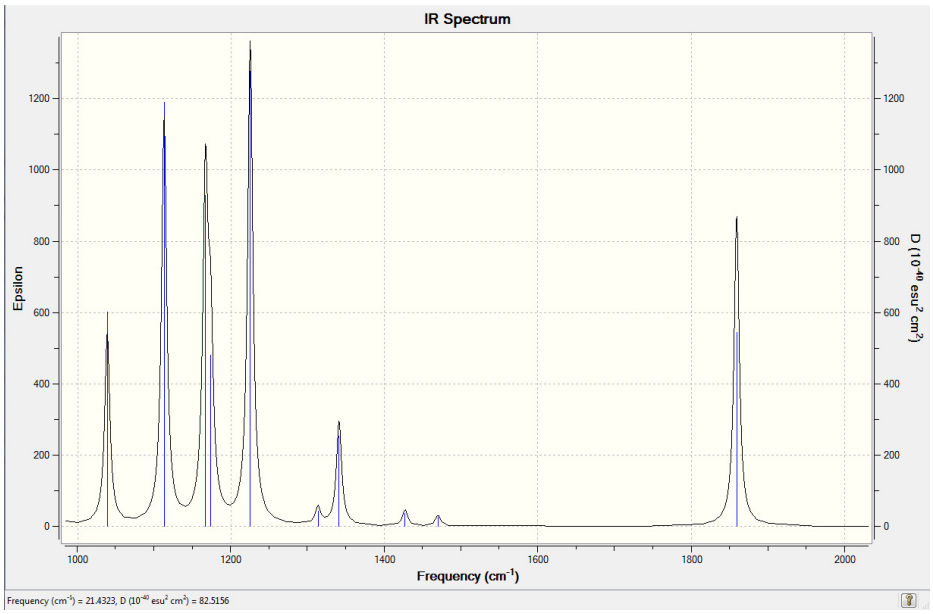

Figure S14: IR spectrum of $CF_3C(O)OCH_2OCl$ conformer 3 calculated at the B3LYP/6-31+G(d,p) level.

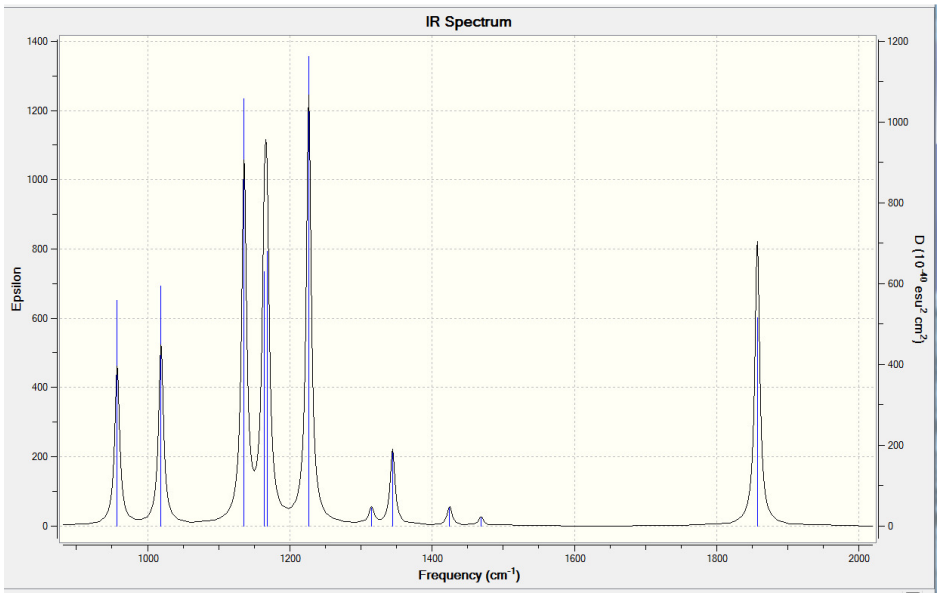

Figure S15: IR spectrum of $CF_3C(O)OCH_2OOCl$ calculated at the B3LYP/6-31+G(d,p) level.

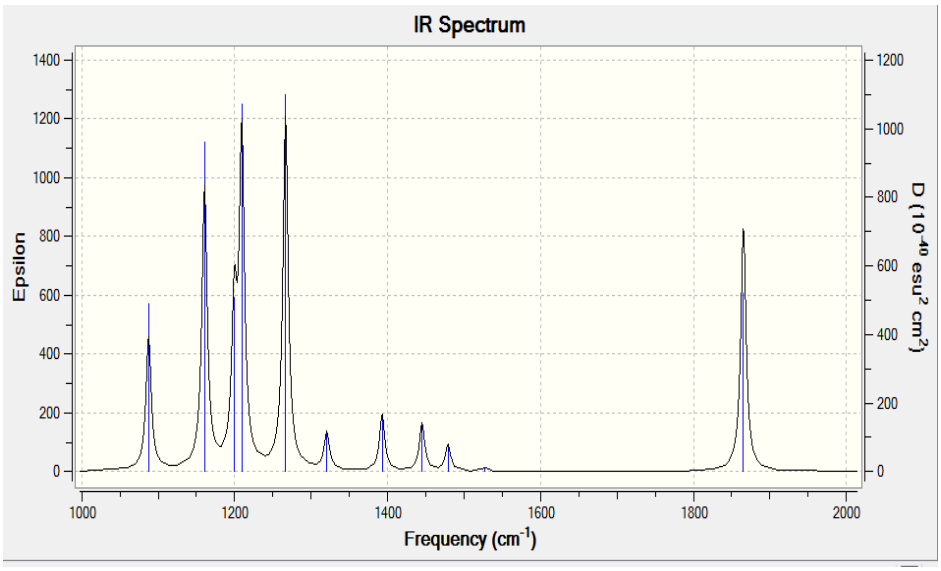

Figure S16: IR spectrum of $CF_3C(O)OCH_2OH$ conformer 2 calculated at the WB97XD/cc-pVTZ level.

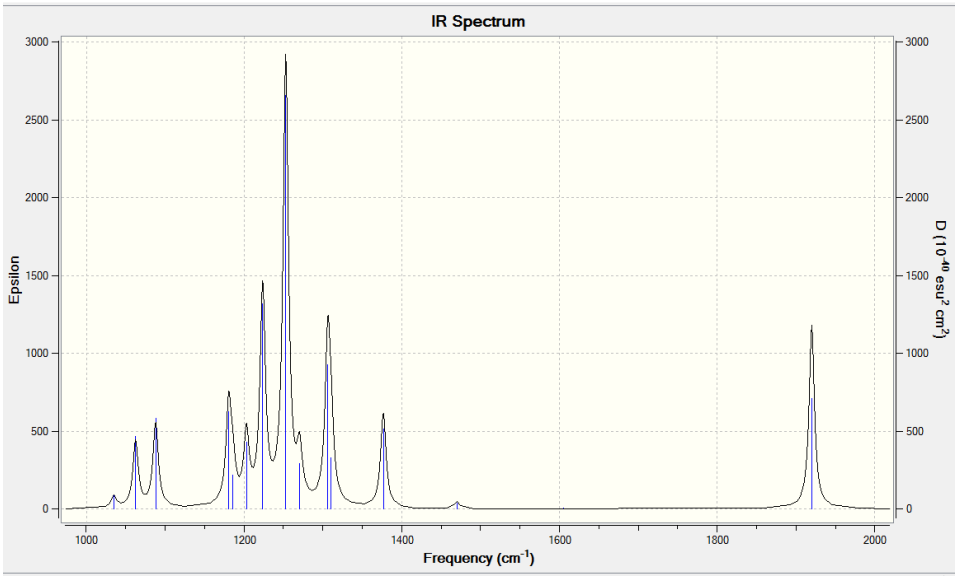

Figure S17: IR spectrum of $CF_3C(O)OCH_2OOOCF_3$ conformer 2 calculated at the WB97XD/cc-pVTZ level. Gaussian 09 Revision B.01.

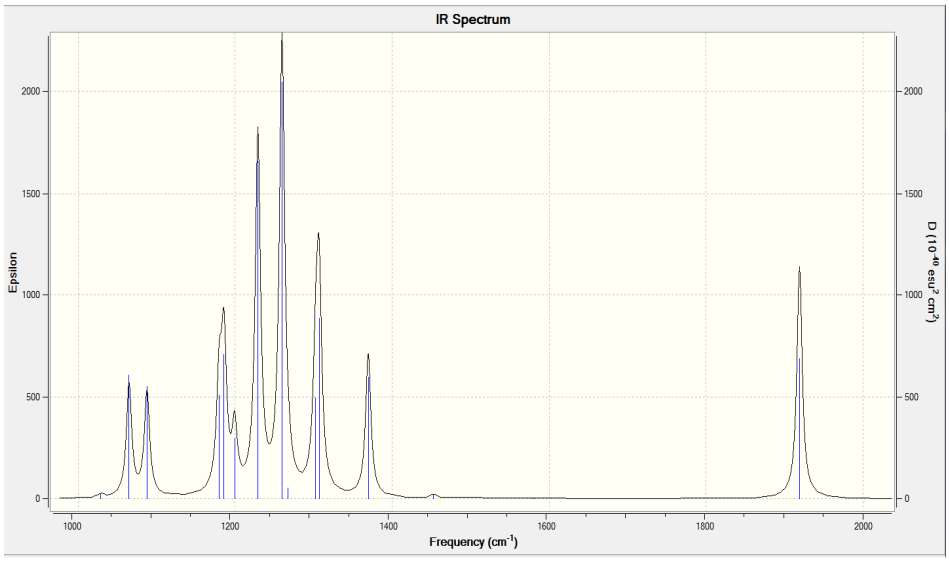

Figure S18: IR spectrum of $CF_3C(O)OCH_2OOOCF_3$ conformer 2 calculated at the WB97XD/cc-pVTZ level.

Table S6: Coordinates for the optimized structure of CF_3OOOCF_3 calculated at the B3LYP/6-31+G(d,p) level (Ångstrøm).

Atom	X	Y	Z
O	0.888011	0.065311	0.740791
O	0.000043	0.915926	-0.000129
O	-0.887982	0.064336	-0.740334
C	-2.066242	-0.077143	-0.002707
F	-2.655599	1.100666	0.224896
F	-2.852115	-0.834873	-0.767431
F	-1.859494	-0.678804	1.172174
C	2.066162	-0.077219	0.002773
F	2.655730	1.100257	-0.225749
F	1.859033	-0.679162	-1.171727
F	2.852434	-0.834574	0.767501

Table S7: Coordinates for the optimized structure of $CF_3C(O)OOOCF_3$ calculated at the B3LYP/6-31+G(d,p) level (Ångstrøm).

Atom	X	Y	Z
C	-2.19842	-0.44511	-0.04904
C	-1.55939	0.97741	-0.00948
O	-2.15569	1.968868	-0.30118
O	-0.25795	1.10617	0.423849
O	0.370178	-0.16932	0.719362
O	1.198496	-0.47911	-0.39972
C	2.506624	-0.07316	-0.10197
F	-3.46897	-0.32912	-0.44223
F	-1.55644	-1.24738	-0.91644
F	-2.17955	-1.01113	1.171875
F	2.978064	-0.68994	0.984773
F	2.59515	1.244822	0.086052
F	3.216952	-0.43033	-1.1702

Table S8: Coordinates for the optimized structure of $CF_3C(O)OCH_2OOOCF_3$ conformer 1 calculated at the B3LYP/6-31+G(d,p) level (Ångstrøm).

Atom	X	Y	Z
C	-1.6969	-0.20017	-0.43313
O	0.84286	1.803641	0.228496
O	1.262068	0.650426	0.989922
C	0.039402	1.385348	-0.84269
H	-0.04709	2.277051	-1.46614
H	0.459496	0.531331	-1.37103
O	2.697733	0.593546	0.887367
C	3.060262	-0.43329	0.028262
F	2.684553	-0.19578	-1.24422
F	4.39116	-0.47996	0.087339
F	2.547152	-1.61075	0.393523
O	-1.28823	1.080522	-0.38167
C	-3.12499	-0.30104	0.166214
F	-3.98015	0.486073	-0.51864
F	-3.12387	0.094985	1.454229
F	-3.56651	-1.56058	0.106583
O	-1.0957	-1.14305	-0.87212

Table S9: Coordinates for the optimized structure of $CF_3C(O)OCH_2OOOCF_3$ conformer 2 calculated at the B3LYP/6-31+G(d,p) level (Ångstrøm).

Atom	X	Y	Z
C	2.337207	0.681849	-0.40243
O	-0.79957	1.933911	0.483637
O	-1.31467	1.256883	-0.6877
C	0.320744	1.2366	0.949541
H	0.512948	1.681241	1.929142
H	0.130012	0.168749	1.011132
O	-2.66248	0.870337	-0.36757
C	-2.70235	-0.48887	-0.09852
F	-2.01502	-0.81273	1.015569
F	-3.99073	-0.77016	0.086788
F	-2.2157	-1.22351	-1.10375
O	1.439642	1.550004	0.10049
C	2.290657	-0.79249	0.100259
F	1.163593	-1.41067	-0.3276
F	2.295118	-0.83667	1.45698
F	3.339752	-1.47596	-0.34416
O	3.172886	1.025721	-1.18983

Table S10: Coordinates for the optimized structure of $CF_3C(O)OCH_2OH$ conformer 1 calculated at the B3LYP/6-31+G(d,p) level (Ångstrøm).

Atom	X	Y	Z
C	0.063425	0.492211	0.115274
C	2.342252	-0.09936	0.537906
H	2.73148	-0.80118	1.279502
H	2.410207	0.934428	0.872587
O	0.93435	-0.47469	0.432424
C	-1.35096	-0.12624	-0.04822
F	-1.74509	-0.71958	1.098941
F	-1.35052	-1.0596	-1.02371
F	-2.24472	0.815979	-0.36499
O	0.284136	1.66661	-0.01956
O	2.974653	-0.18585	-0.68992
H	3.047959	-1.11265	-0.95759

Table S11: Coordinates for the optimized structure of $CF_3C(O)OCH_2OH$ conformer 2 calculated at the B3LYP/6-31+G(d,p) level (Ångstrøm).

Atom	X	Y	Z
C	0.130686	0.312723	-0.17841
C	2.324113	-0.54673	-0.38419
H	2.402514	-0.07994	-1.37097
H	2.744737	-1.54961	-0.37314
O	0.888678	-0.77627	-0.14268
C	-1.35858	-0.05536	0.05478
F	-1.51837	-0.63643	1.260656
F	-1.78412	-0.91973	-0.89027
F	-2.12676	1.037944	0.004453
O	0.50462	1.448954	-0.36079
O	2.915466	0.190817	0.617281
H	2.668595	1.121741	0.506925

Table S12: Coordinates for the optimized structure of $CF_3C(O)OCH_2OOH$ calculated at the B3LYP/6-31+G(d,p) level (Ångstrøm).

Atom	X	Y	Z
C	0.164655	0.215975	-0.10761
C	-1.89657	-1.07115	-0.31386
H	-2.0756	-2.1238	-0.0947
H	-2.10702	-0.80543	-1.35154
O	-0.4362	-0.96285	-0.09917
C	1.699181	0.023226	0.03887
F	2.18119	-0.67994	-1.00734
F	1.986895	-0.64949	1.169818
F	2.319144	1.206325	0.076578
O	-0.33436	1.314918	-0.20821
O	-2.65136	-0.32628	0.564408
O	-3.05178	0.923243	-0.05805
H	-2.21642	1.436691	-0.00154

Table S13: Coordinates for the optimized structure of $CF_3C(O)OCH_2OCl$ conformer 1 calculated at the B3LYP/6-31+G(d,p) level (Ångstrøm).

Atom	X	Y	Z
C	-0.75666	0.438281	0.226104
C	1.398343	-0.33857	0.803363
H	1.753864	-1.17922	1.402827
H	1.493852	0.620907	1.317759
O	0.043447	-0.61738	0.491947
C	-2.17394	-0.08051	-0.13274
F	-2.71175	-0.72662	0.923581
F	-2.12183	-0.93597	-1.17065
F	-2.97261	0.939897	-0.45811
O	-0.46485	1.600173	0.275543
O	2.049637	-0.30186	-0.46847
Cl	3.716212	0.088228	-0.24391

Table S14: Coordinates for the optimized structure of $CF_3C(O)OCH_2OCl$ conformer 2 calculated at the B3LYP/6-31+G(d,p) level (Ångstrøm).

Atom	X	Y	Z
C	-0.75659	0.438024	-0.22665
C	1.398333	-0.33921	-0.80345
H	1.494023	0.620157	-1.31802
H	1.753735	-1.17993	-1.40288
O	0.043337	-0.61783	-0.49213
C	-2.17385	-0.08032	0.132834
F	-2.12177	-0.93375	1.172436
F	-2.71131	-0.72856	-0.92238
F	-2.97274	0.940565	0.456044
O	-0.4645	1.599832	-0.27631
O	2.049415	-0.3024	0.468398
Cl	3.715956	0.088686	0.24411

Table S15: Coordinates for the optimized structure of $CF_3C(O)OCH_2OCl$ conformer 3 calculated at the B3LYP/6-31+G(d,p) level (Ångstrøm).

Atom	X	Y	Z
C	-0.762	0.68505	-0.05508
C	1.464352	0.998119	0.714029
H	1.919096	0.782117	1.681396
H	1.230743	2.056617	0.575563
O	0.254928	0.218223	0.691565
C	-1.93367	-0.33162	-0.0179
F	-2.31525	-0.57068	1.253809
F	-1.55692	-1.50083	-0.57302
F	-2.9844	0.142613	-0.69406
O	-0.80463	1.721562	-0.66067
O	2.305877	0.698096	-0.35898
Cl	3.052809	-0.86418	-0.1976

Table S16: Coordinates for the optimized structure of $CF_3C(O)OCH_2OOCl$ calculated at the B3LYP/6-31+G(d,p) level (Ångstrøm).

Atom	X	Y	Z
C	-0.81652	-0.52378	0.470702
C	1.145127	-1.70881	-0.20441
H	1.130748	-2.60261	-0.83126
H	1.160615	-1.93108	0.862871
O	-0.03733	-0.9573	-0.53529
C	-2.02212	0.255569	-0.11975
F	-2.79261	-0.57538	-0.85443
F	-1.60659	1.259333	-0.91499
F	-2.76915	0.769737	0.861703
O	-0.66387	-0.70786	1.648187
O	2.300982	-1.0291	-0.60773
O	2.688474	-0.11429	0.429399
Cl	2.239927	1.516525	-0.01282

Table S17: Coordinates for the optimized structure of $CF_3C(O)OCH_2OH$ conformer 2 calculated at the WB97XD/cc-pVTZ level (Ångstrøm).

Atom	X	Y	Z
C	0.132664	0.313268	-0.18386
C	2.300346	-0.53205	-0.38674
H	2.38648	-0.04186	-1.35806
H	2.729642	-1.52759	-0.40635
O	0.885064	-0.7673	-0.15508
C	-1.35121	-0.05664	0.055752
F	-1.4967	-0.63314	1.247922
F	-1.77219	-0.9104	-0.87794
F	-2.10885	1.02524	0.012415
O	0.500498	1.438547	-0.3623
O	2.883802	0.17699	0.627547
H	2.63788	1.100801	0.530665

Table S18: Coordinates for the optimized structure of $CF_3C(O)OCH_2OOOCF_3$ conformer 2 calculated at the WB97XD/cc-pVTZ level (Ångstrøm). Gaussian 09 Revision B.01.

Atom	X	Y	Z
C	2.587979	0.666073	0.09749
O	-0.25217	1.522972	-0.64445
O	-1.62195	1.437257	-0.59535
C	0.284575	1.202594	0.642864
H	-0.13847	1.866971	1.392078
H	0.089672	0.16117	0.881634
O	-1.96123	0.073427	-0.92884
C	-2.79458	-0.40021	0.051935
F	-3.89271	0.328613	0.171955
F	-3.10936	-1.62571	-0.31369
F	-2.20531	-0.43953	1.24825
O	1.640506	1.511457	0.545958
C	2.225026	-0.84105	-0.06226
F	1.241477	-1.01949	-0.94401
F	1.828678	-1.34705	1.114426
F	3.280973	-1.51163	-0.4681
O	3.686971	1.047446	-0.119

Table S19: Coordinates for the optimized structure of $CF_3C(O)OCH_2OOOCF_3$ conformer 2 calculated at the WB97XD/cc-pVTZ level.

Atom	X	Y	Z
C	-2.49259	-0.54168	-0.42836
O	0.401813	-1.47299	-0.30703
O	1.627749	-1.50676	0.343269
C	-0.60911	-1.58484	0.695271
H	-0.51607	-2.53957	1.207102
H	-0.53422	-0.75326	1.393215
O	1.911317	-0.19114	0.803943
C	2.716803	0.435137	-0.12925
F	2.128542	0.551503	-1.30643
F	2.948804	1.632759	0.37309
F	3.860791	-0.2069	-0.2972
O	-1.81302	-1.62517	-0.00765
C	-2.11575	0.849778	0.164362
F	-0.86151	1.190256	-0.1304
F	-2.24119	0.82948	1.499015
F	-2.9245	1.769712	-0.31481
O	-3.39589	-0.64882	-1.18526