Supplementary Information

Determination of the Rotational Isomerization Rate along Carbon–Carbon Single Bonds in Solution

*Seongchul Park, Hojeong Yoon, Juhyang Shin, and Manho Lim**

Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Busan 46241, Korea

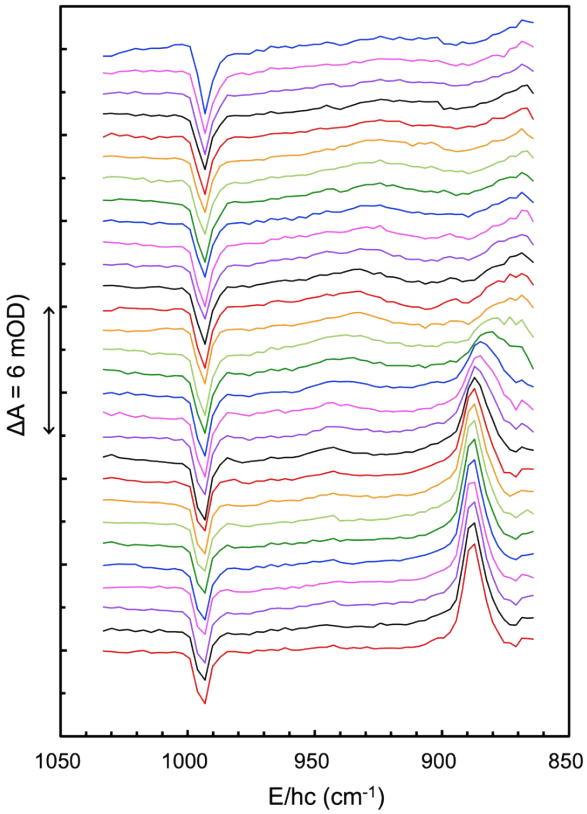

Figure S1. Time-resolved infrared (TRIR) spectra of CF_2BrCF_2I in CCl_4 at 280 K collected over a pump-probe delay range of 0.32–1000 ps following excitation at 267 nm, in the spectral region of 1050–850 cm^{-1}. The pump-probe delay times, from the top of the spectra, are as follows: 0.32, 0.42, 0.56, 0.75, 1.0, 1.3, 1.8, 2.4, 3.2, 4.2, 5.6, 7.5, 10, 13, 18, 24, 32, 42, 56, 75, 100, 130, 180, 240, 320, 420, 560, 750, 1000 ps.

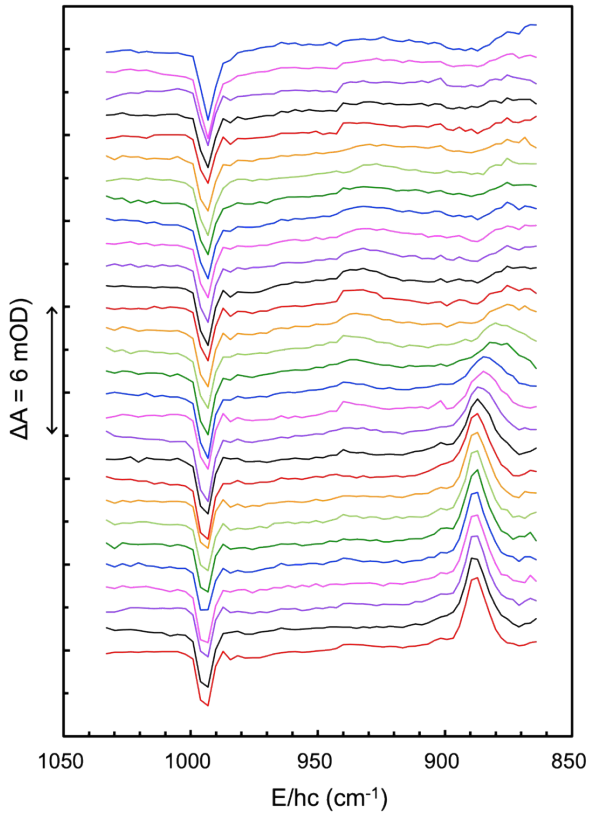

Figure S2. TRIR spectra of CF_2BrCF_2I in CCl_4 at 300 K collected over a pump-probe delay range of 0.32–1000 ps following excitation at 267 nm, in the spectral region of 1050–850 cm^{-1}. The pump-probe delay times, from the top of the spectra, are as follows: 0.32, 0.42, 0.56, 0.75, 1.0, 1.3, 1.8, 2.4, 3.2, 4.2, 5.6, 7.5, 10, 13, 18, 24, 32, 42, 56, 75, 100, 130, 180, 240, 320, 420, 560, 750, 1000 ps.

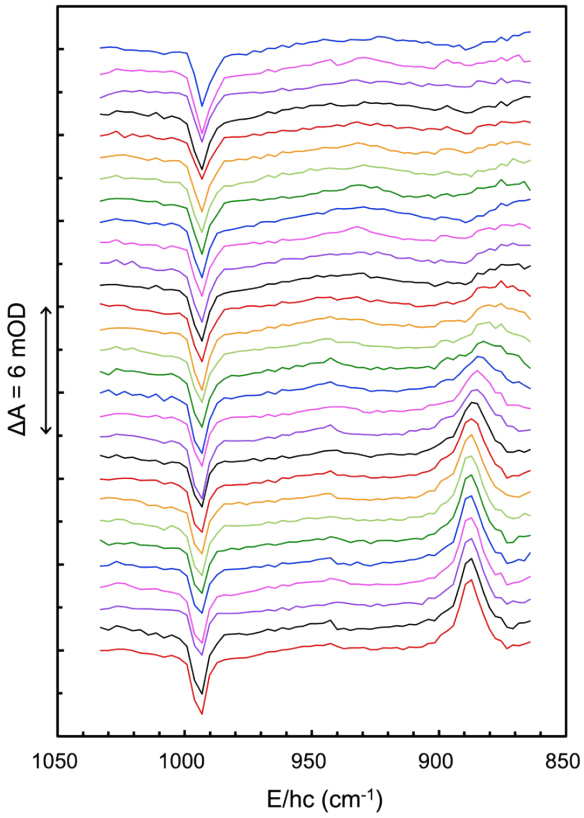

Figure S3. TRIR spectra of CF_2BrCF_2I in CCl_4 at 310 K collected over a pump-probe delay range of 0.32–1000 ps following excitation at 267 nm, in the spectral region of 1050–850 cm^{-1}. The pump-probe delay times, from the top of the spectra, are as follows: 0.32, 0.42, 0.56, 0.75, 1.0, 1.3, 1.8, 2.4, 3.2, 4.2, 5.6, 7.5, 10, 13, 18, 24, 32, 42, 56, 75, 100, 130, 180, 240, 320, 420, 560, 750, 1000 ps.

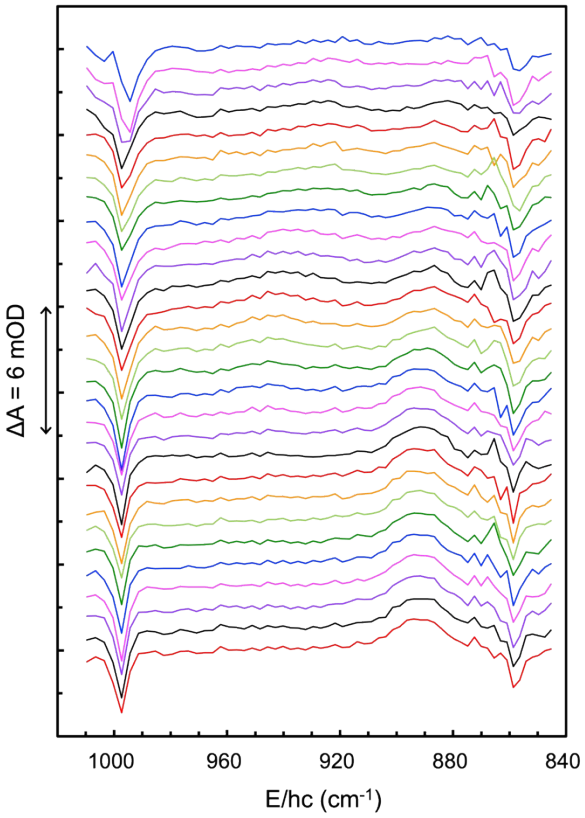

Figure S4. TRIR spectra of CF_2BrCF_2I in DMF at 293 K collected over a pump-probe delay range of 0.32–1000 ps following excitation at 267 nm, in the spectral region of 1050–850 cm^{-1}. The pump-probe delay times, from the top of the spectra, are as follows: 0.32, 0.42, 0.56, 0.75, 1.0, 1.3, 1.8, 2.4, 3.2, 4.2, 5.6, 7.5, 10, 13, 18, 24, 32, 42, 56, 75, 100, 130, 180, 240, 320, 420, 560, 750, 1000 ps.

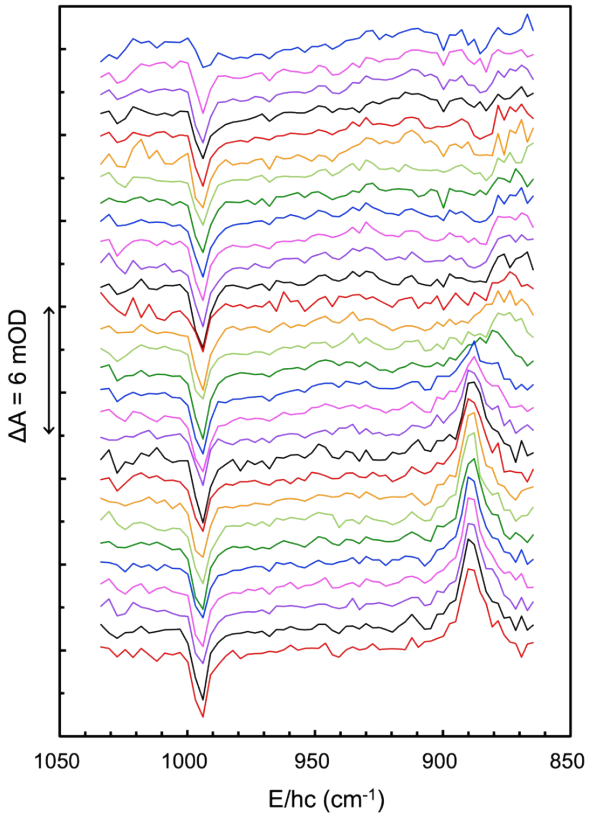

Figure S5. TRIR spectra of CF_2BrCF_2I *n*-hexane at 293 K collected over a pump-probe delay range of 0.32–1000 ps following excitation a t 267 nm, in the spectral region of 1050–850 cm^{-1}. The pump-probe delay times, from the top of the spectra, are as follows: 0.32, 0.42, 0.56, 0.75, 1.0, 1.3, 1.8, 2.4, 3.2, 4.2, 5.6, 7.5, 10, 13, 18, 24, 32, 42, 56, 75, 100, 130, 180, 240, 320, 420, 560, 750, 1000 ps.

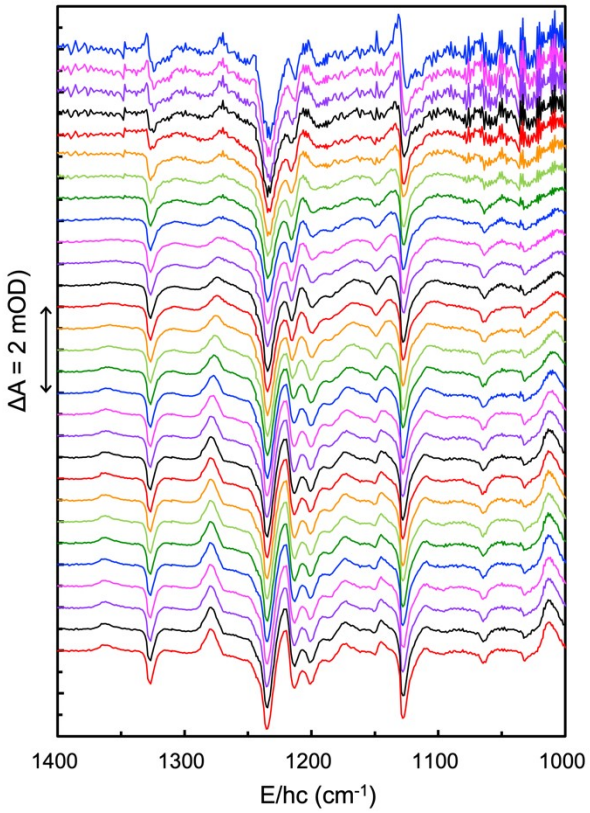

Figure S6. TRIR spectra of $CF_3CF_2CF_2I$ in CCl_4 at 293 K collected over a pump-probe delay range of 0.32–1000 ps following excitation at 267 nm, in the spectral region of 1400–1000 cm^{-1}. The pump-probe delay times, from the top of the spectra, are as follows: 0.32, 0.42, 0.56, 0.75, 1.0, 1.3, 1.8, 2.4, 3.2, 4.2, 5.6, 7.5, 10, 13, 18, 24, 32, 42, 56, 75, 100, 130, 180, 240, 320, 420, 560, 750, 1000 ps.

Table S1. Coordinates of *anti*-CF_2BrCF_2• and *gauche*-CF_2BrCF_2• in CCl_4 calculated by DFT using ωB97XD/aug-cc-pVTZ at 298 K.

	anti-CF_2BrCF_2•				*gauche*-CF_2BrCF_2•		
	Coordinates (Angstroms)				Coordinates (Angstroms)		
	X	Y	Z		X	Y	Z
C	-1.532099	-0.140761	0.000016	C	-1.333363	-0.470176	-0.360446
C	-0.279117	0.695933	0.000007	C	-0.27999	0.51847	0.100203
F	-1.742525	-0.840001	1.087546	F	-2.549472	0.030811	-0.41002
F	-1.742551	-0.839988	-1.087516	F	-1.315464	-1.634884	0.244965
F	-0.259948	1.46765	1.084127	F	-0.46451	0.85952	1.38743
F	-0.259972	1.467663	-1.084104	F	-0.386807	1.628307	-0.629916
Br	1.34035	-0.41797	-0.000018	Br	1.489325	-0.23553	-0.107734

Table S2. Coordinates of *anti*-CF_2BrCF_2• and *gauche*-CF_2BrCF_2• in CCl_4 calculated by DFT using APFD/aug-cc-pVTZ at 298 K.

	anti-CF_2BrCF_2•				*gauche*-CF_2BrCF_2•		
	Coordinates (Angstroms)				Coordinates (Angstroms)		
	X	Y	Z		X	Y	Z
C	0.283045	0.523968	0.096664	C	-1.530535	-0.145586	0.000016
C	1.333728	-0.473103	-0.358778	C	-0.284029	0.702068	0.000008
F	0.466295	0.871259	1.384741	F	-1.735644	-0.844263	1.090635
F	0.388592	1.630813	-0.641213	F	-1.735661	-0.844259	-1.090601
F	1.297182	-1.641699	0.241405	F	-0.261182	1.472335	1.087337
F	2.555431	0.020033	-0.399247	F	-0.261209	1.472353	-1.087309
Br	-1.487661	-0.23511	-0.105671	Br	1.338019	-0.418411	-0.00002

Table S3. Coordinates of *anti*-CF_2BrCF_2• and *gauche*-CF_2BrCF_2• in CCl_4 calculated by DFT using B3LYP/aug-cc-pVTZ at 298 K.

	anti-CF_2BrCF_2•				*gauche*-CF_2BrCF_2•		
	Coordinates (Angstroms)				Coordinates (Angstroms)		
	X	Y	Z		X	Y	Z
C	-1.536222	-0.151556	0.000016	C	-1.336455	-0.473164	-0.359803
C	-0.297361	0.697085	0.000011	C	-0.288739	0.518231	0.101179
F	-1.751788	-0.852689	1.093675	F	-2.562317	0.02581	-0.418634
F	-1.75178	-0.852712	-1.093629	F	-1.319172	-1.64479	0.248835
F	-0.279356	1.473408	1.090986	F	-0.472593	0.862163	1.397802
F	-0.279388	1.473439	-1.090941	F	-0.399242	1.636096	-0.631216
Br	1.358923	-0.412749	-0.000028	Br	1.500888	-0.233826	-0.109124

Table S4. Coordinates of *anti*-$CF_3CF_2CF_2$• and *gauche*-$CF_3CF_2CF_2$• in CCl_4 calculated by DFT using ωB97XD/aug-cc-pVTZ at 298 K.

	anti-$CF_3CF_2CF_2$•				*gauche*-$CF_3CF_2CF_2$•		
	Coordinates (Angstroms)				Coordinates (Angstroms)		
	X	Y	Z		X	Y	Z
C	-0.117554	0.672297	-0.000085	C	0.192188	-0.493104	0.130236
C	-1.528444	0.10867	-0.000029	C	1.371961	0.330759	-0.351712
C	1.033468	-0.38043	0.000056	C	-1.178997	0.200245	-0.104806
F	-1.882474	-0.533185	1.08897	F	2.512157	-0.320025	-0.36077
F	-1.882443	-0.533475	-1.088867	F	1.49044	1.520403	0.193105
F	0.031365	1.433511	1.094822	F	0.297383	-0.765339	1.450168
F	0.031387	1.433241	-1.095176	F	0.19304	-1.655588	-0.536614
F	2.210419	0.231281	-0.000021	F	-2.157279	-0.627858	0.234612
F	0.950047	-1.149059	1.080287	F	-1.281071	1.30381	0.625008
F	0.950051	-1.149339	-1.079976	F	-1.311438	0.51933	-1.387989

Table S5. Coordinates of *anti*-CF_2BrCF_2I and *gauche*-CF_2BrCF_2I in CCl_4 calculated by DFT using ωB97XD/aug-cc-pVTZ at 298 K.

	anti-CF_2BrCF_2I				*gauche*-CF_2BrCF_2I		
	Coordinates (Angstroms)				Coordinates (Angstroms)		
	X	Y	Z		X	Y	Z
C	0.897288	-0.564835	0.000073	C	1.132962	0.65986	0.382842
C	-0.113579	0.618228	0.000076	C	-0.206175	0.954422	-0.366392
F	0.703428	-1.316129	-1.081132	F	0.911288	0.650724	1.695058
F	0.703561	-1.316042	1.081363	F	1.976173	1.658916	0.113631
F	0.092645	1.369412	-1.082419	F	0.02934	0.972334	-1.679184
F	0.092536	1.369333	1.082648	F	-0.596314	2.182001	-0.00258
I	-2.157817	-0.082445	-0.000052	I	-1.781358	-0.443974	0.081787
Br	2.723787	0.088288	-0.000065	Br	1.94191	-1.009453	-0.159307

Table S6. Coordinates of *anti*-$CH_3CH_2CH_2CH_3$ and *gauche*-$CH_3CH_2CH_2CH_3$ in CCl_4 calculated by DFT using ωB97XD/aug-cc-pVTZ at 298 K.

	anti-$CH_3CH_2CH_2CH_3$				*gauche*-$CH_3CH_2CH_2CH_3$		
	Coordinates (Angstroms)				Coordinates (Angstroms)		
	X	Y	Z		X	Y	Z
C	-1.948541	0.120163	0.000187	C	1.559838	-0.56025	0.123041
H	-2.090371	0.749404	-0.880579	H	2.570346	-0.474768	-0.276949
H	-2.090312	0.748294	0.881753	H	1.14502	-1.503655	-0.232888
H	-2.733652	-0.636297	-0.000243	H	1.634594	-0.619426	1.210927
C	-0.563335	-0.513119	-0.000219	C	0.702167	0.626882	-0.301006
H	-0.456857	-1.161873	0.874008	H	1.206809	1.552583	-0.015567
H	-0.457153	-1.161492	-0.87476	H	0.621828	0.645476	-1.391832
C	0.563335	0.513119	-0.000215	C	-0.702167	0.626882	0.301006
H	0.45685	1.161875	0.874008	H	-0.621828	0.645476	1.391832
H	0.457159	1.16149	-0.87476	H	-1.206809	1.552583	0.015567
C	1.948541	-0.120163	0.00019	C	-1.559838	-0.56025	-0.123041
H	2.090399	-0.749324	-0.880629	H	-1.14502	-1.503655	0.232888
H	2.733652	0.636298	-0.000158	H	-2.570346	-0.474768	0.276949
H	2.090284	-0.748373	0.881703	H	-1.634594	-0.619426	-1.210927
C	-1.948541	0.120163	0.000187	C	1.559838	-0.56025	0.123041

Table S7. Coordinates of *anti*-$CH_3CH_2CH{\bullet}CH_3$ and *gauche*-$CH_3CH_2CH{\bullet}CH_3$ in CCl_4 calculated by DFT using ωB97XD/aug-cc-pVTZ at 298 K.

	anti-$CH_3CH_2CH{\bullet}CH_3$				*gauche*-$CH_3CH_2CH{\bullet}CH_3$		
	Coordinates (Angstroms)				Coordinates (Angstroms)		
	X	Y	Z		X	Y	Z
C	1.929559	0.164897	-0.04802	C	1.588182	0.541362	-0.144243
H	2.734412	-0.568418	-0.001735	H	2.560158	0.492815	0.348082
H	2.075843	0.875179	0.767209	H	1.141432	1.509067	0.086373
H	2.024239	0.711758	-0.986905	H	1.749436	0.494371	-1.221746
C	0.563995	-0.504211	0.055467	C	0.679183	-0.608234	0.323471
H	0.449333	-1.242615	-0.747529	H	1.173868	-1.557622	0.110368
H	0.520254	-1.09439	0.983719	H	0.574951	-0.541823	1.411709
C	-0.576604	0.44779	0.016274	C	-0.668657	-0.582226	-0.307074
H	-0.388496	1.494593	0.221684	H	-0.82408	-1.134845	-1.225399
C	-1.976053	-0.043584	-0.039029	C	-1.684455	0.421175	0.102424
H	-2.273751	-0.525647	0.902855	H	-1.463199	1.418494	-0.303415
H	-2.685391	0.761046	-0.228269	H	-2.68299	0.15452	-0.243412
H	-2.101824	-0.80086	-0.819183	H	-1.715096	0.532567	1.189969
C	1.929559	0.164897	-0.04802	C	1.588182	0.541362	-0.144243
H	2.734412	-0.568418	-0.001735	H	2.560158	0.492815	0.348082

Table S8. Coordinates of CH_3CH_3 and $CH_3CH_2{\bullet}$ in CCl_4 calculated by DFT using ωB97XD/aug-cc-pVTZ at 298 K.

	CH_3CH_3				$CH_3CH_2{\bullet}$		
	Coordinates (Angstroms)				Coordinates (Angstroms)		
	X	Y	Z		X	Y	Z
C	0.000000	0.000000	0.761362	C	-0.690977	0.000003	-0.002054
H	0.508176	0.880189	1.15612	H	-1.101227	-0.884676	-0.491072
H	0.508178	-0.880188	1.15612	H	-1.101224	0.884843	-0.490777
H	-1.016354	-0.000001	1.15612	H	-1.085203	-0.000176	1.023514
C	0.000000	0.000000	-0.761362	C	0.79047	0.000000	-0.018155
H	-0.508178	-0.880188	-1.15612	H	1.345355	0.925306	0.039796
H	-0.508176	0.880189	-1.15612	H	1.345341	-0.925315	0.039794
H	1.016354	-0.000001	-1.15612	C	-0.690977	0.000003	-0.002054

Table S9. Coordinates of *anti*-$CF_2ICF_2{\bullet}$ and *gauche*-$CF_2ICF_2{\bullet}$ in CCl_4 calculated by DFT using ωB97XD/aug-cc-pVTZ at 298 K.

	anti-$CF_2ICF_2{\bullet}$				*gauche*-$CF_2ICF_2{\bullet}$		
	Coordinates (Angstroms)				Coordinates (Angstroms)		
	X	Y	Z		X	Y	Z
C	-1.844433	-0.304541	0.000024	C	-1.663204	-0.521522	-0.360038
C	-0.746438	0.718842	0.000018	C	-0.697706	0.546903	0.108704
F	-1.950923	-1.027147	1.087559	F	-2.911473	-0.113881	-0.464412
F	-1.950917	-1.027166	-1.087498	F	-1.584323	-1.67088	0.272352
F	-0.852505	1.486932	1.086113	F	-0.945769	0.891834	1.388522
F	-0.852542	1.486957	-1.086055	F	-0.877542	1.638201	-0.641613
I	1.245419	-0.203057	-0.000025	I	1.340329	-0.12943	-0.065767

Table S10. Coordinates of *anti*-CH_2ClCF_2Cl and *gauche*-CH_2ClCF_2Cl in CCl_4 calculated by DFT using ωB97XD/aug-cc-pVTZ at 298 K.

	anti-CH_2ClCF_2Cl				*gauche*- CH_2ClCF_2Cl		
	Coordinates (Angstroms)				Coordinates (Angstroms)		
	X	Y	Z		X	Y	Z
C	0.622398	-0.856901	0.000001	C	-0.591939	-0.405792	0.020483
C	-0.425096	0.238723	0.000009	C	0.730802	-0.656192	-0.682759
F	-0.327589	1.021937	-1.077837	F	-0.540793	-0.766503	1.306383
F	-0.327598	1.021916	1.077871	F	-1.523672	-1.171899	-0.573105
H	0.503695	-1.464707	-0.890594	Cl	2.077639	0.232716	0.053649
H	0.503712	-1.464707	0.890598	Cl	-1.127106	1.290612	-0.07082
Cl	2.267833	-0.174224	-0.000016	H	0.643569	-0.359672	-1.722475
Cl	-2.049864	-0.517317	-0.000006	H	0.944384	-1.719383	-0.611461

Table S11. Coordinates of *anti*-CH_2FCH_2NCO and *gauche*- CH_2FCH_2NCO in CCl_4 calculated by DFT using ωB97XD/aug-cc-pVTZ at 298 K.

	anti-CH_2FCH_2NCO				*gauche*- CH_2FCH_2NCO		
	Coordinates (Angstroms)				Coordinates (Angstroms)		
	X	Y	Z		X	Y	Z
C	-1.616306	0.505492	0.000264	C	1.654537	-0.038182	0.312446
H	-1.591626	1.133699	0.890794	H	2.692733	0.132313	0.025781
H	-1.592498	1.133909	-0.890143	H	1.570239	-0.078629	1.398441
C	-0.465748	-0.483526	-0.000454	C	0.77586	1.046108	-0.265369
H	-0.52816	-1.117605	0.884405	H	1.148384	2.009273	0.080365
H	-0.529317	-1.117536	-0.885283	H	0.840341	1.033238	-1.354313
F	-2.805566	-0.204237	0.000777	F	1.267869	-1.273767	-0.186336
N	0.77187	0.24988	-0.001351	N	-0.598549	0.919232	0.144065
C	1.94744	0.042005	-0.000134	C	-1.471543	0.107135	0.037689
O	3.112037	-0.040914	0.000579	O	-2.403224	-0.59466	0.001211