Exploiting the vicinal disubstituent effect in the diastereoselective synthesis of γ and δ lactones

Elisabetta Brenna,[a] Francesco Dalla Santa, [a] Francesco G. Gatti,[*,a] Giuseppe Gatti[b] and Davide Tessaro[a]

a) Dipartimento di Chimica, Materiali ed Ingegneria Chimica "G. Natta", Politecnico di Milano, P.zza Leonardo da Vinci 32, 20133 Milano, Italy

b) Dipartimento di Scienze Biomolecolari Scuola di Farmacia, Università degli Studi di Urbino, P.zza del Rinascimento 6, 61029 Urbino, Italy

SUPPORTING INFORMATION

Index

List of Figures and Tables

Catalytic cycle

In Figure SI.2 we show the complete catalytic cycle for ring closure of γ-hydroxyesters.

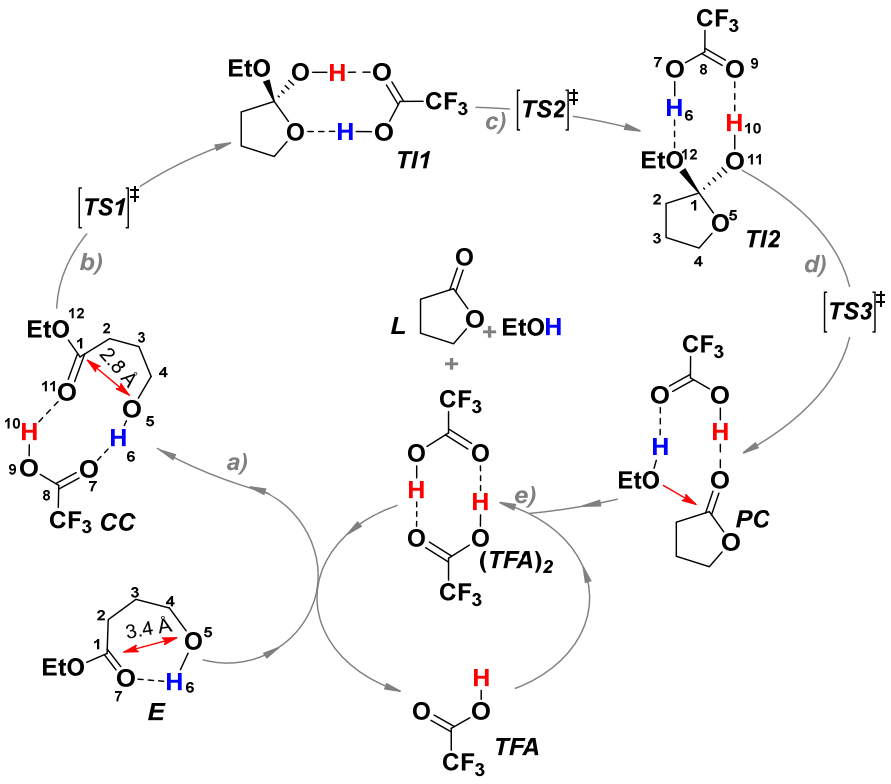


Figure SI.2. Catalytic cycle for the TFA ring closure of the γ-hydroxy ester. For the sake of simplicity we show the reaction for **1a**. Catalytic stages: *a*) H-bonding chelation of ester by TFA to five catalytic complex (***CC***); *b*) addition of alcohol to the activated CO of ester through the transition state ***TS1***‡ to give tetrahedral intermediate (***TI1***); *c*) positional isomerization of ***TI1*** to the spiro intermediate (***TI2***) through transition state ***TS2***‡; *d*) break-down of ***TI2*** to give the lactone·TFA·EtOH product complex trough transition state ***TS3***‡; *e*) Pre-catalyst regeneration (**(TFA)$_2$**).

Stereo conformational analysis

In the following we report the criteria adopted to describe the stereoisomers involved in the RDS (rate determining step) of lactonization reaction. The criteria are based on the values of the τ torsion angles (Figure SI.3) and on the possible stereochemical configurations:

a) τ[O(5)–C(4)–C(3)–C(2)], around +60° or -60°, conventionally described as *gauche* (g^+) or a (g^-), respectively; these two main conformations are present in all species;

b) τ[EtO(12)–C(1)–O(11)–H(10)], with values either around 60° or 180°. For the catalytic complex ***CC*** these conformations are better envisaged as the relative stereochemistry with respect to the C=O double bond, *i.e. Entgegen* (*E*) or *Zusammen* (*Z*), respectively, these conformational descriptors are characterising ***TS1***‡ and ***TI1***species as well, even if for these intermediates the C=O double bond is not anymore present;

c) for the lactonization of *anti*-**1d** there are 3 conformers relative to the *i*-Pr group rotation: τ[O(5)–C(4)–C(13)–H(14)] conventionally described as *gauche* (g'), (g'') and *anti (a')*, respectively; these three main conformations are present in all species;

d) the *Re* or *Si* face of prochiral carbonyl group of ***CC***;

Thus, applying the above criteria, we identified the ensembles for all species involved (Esters, Catalytic Complex (***CC***), Transition State (***TS1***‡) and Tetrahedral Intermediate (***TI1***)) in the RDS of the TFA catalysed ring closure of *anti*-**1c** and *syn*-**1c**.

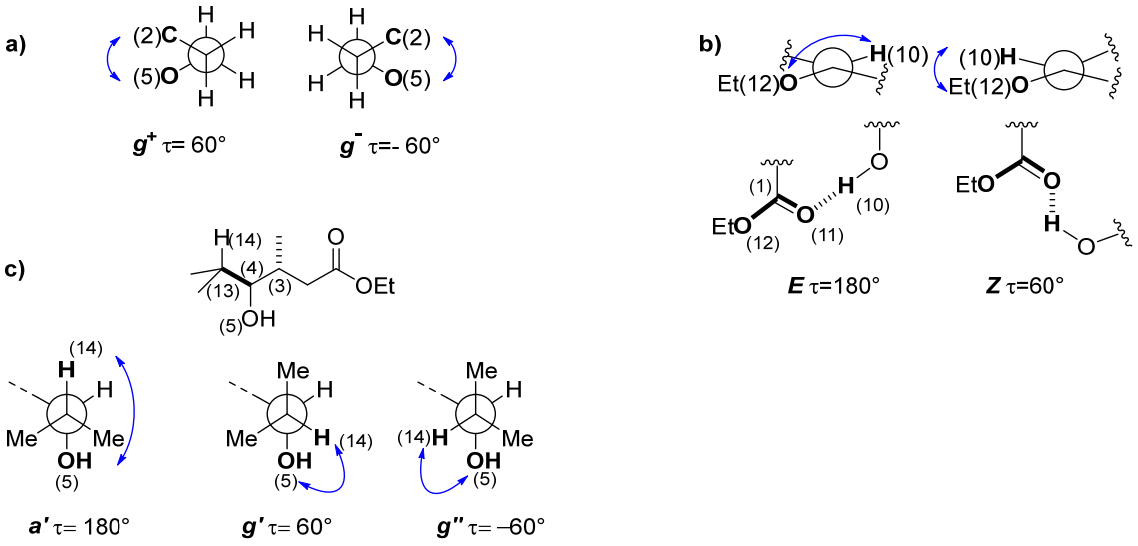
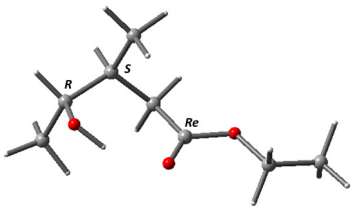


Figure SI.3. Conformational analysis for the determination of the lowest energy stereoisomers involved in the RDS.

The DFT analysis was done with model chemistry B3LYP/6-31G(d), in chloroform solution with the continuum solvation model SCRF=SMD, using Gaussian.09 software. In red is reported the stereochemical configuration of the computed structure.

Esters: (*anti*)-**1c**

1) (1Re,3S,4R, g^+)/ (3R,4S,1Si,g^-) g^+=80.2 °

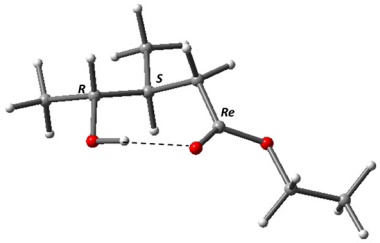


Energy= -540.18775486 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.731900	-1.344721	0.973625
2	6	0	2.568644	-0.185769	-0.015355
3	6	0	1.608323	0.931292	0.478782
4	6	0	0.244150	0.472520	1.049757
5	6	0	-0.748840	-0.130740	0.078227
6	8	0	-0.478791	-0.847455	-0.877202
7	8	0	-2.008973	0.169845	0.414402
8	6	0	-3.065182	-0.415602	-0.397250
9	6	0	1.434746	2.022971	-0.586128
10	1	0	3.514392	-2.024465	0.618852
11	1	0	3.015564	-0.989948	1.973033
12	1	0	1.806486	-1.926012	1.065341
13	8	0	2.251748	-0.672305	-1.317375
14	1	0	2.119198	1.384074	1.340565
15	1	0	0.394627	-0.283728	1.832368
16	1	0	-0.243024	1.320093	1.541705
17	6	0	-4.388076	0.021472	0.195997
18	1	0	-2.941725	-0.069219	-1.427734
19	1	0	-2.949144	-1.503497	-0.387187
20	1	0	2.408868	2.411199	-0.906476
21	1	0	0.929293	1.636210	-1.476730
22	1	0	0.849672	2.864780	-0.196284
23	1	0	1.307410	-0.929398	-1.290516
24	1	0	3.547956	0.297927	-0.131871
25	1	0	-4.484580	1.112384	0.185530
26	1	0	-4.492129	-0.328034	1.228772
27	1	0	-5.208738	-0.401581	-0.393894

2) (1Re,3S,4R,g^-)/ (3R,4S,1Si,g^+) g^-=-67.1 °



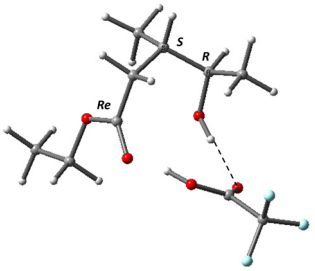
Energy= -540.18562857 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.693062	-0.369570	0.584129
2	6	0	2.365511	-0.449023	-0.167162
3	6	0	1.393729	0.717050	0.159817
4	6	0	0.140322	0.739550	-0.768263
5	6	0	-0.967766	-0.229481	-0.417930
6	8	0	-0.864857	-1.449829	-0.408587
7	8	0	-2.111998	0.398981	-0.128510
8	6	0	-3.256306	-0.435378	0.207713
9	6	0	2.083601	2.087235	0.047159
10	1	0	4.261863	-1.286690	0.396027
11	1	0	4.303219	0.478684	0.260699
12	1	0	3.527266	-0.293366	1.665935
13	8	0	1.819938	-1.721699	0.166938
14	1	0	1.062635	0.579138	1.198829
15	1	0	-0.288315	1.744504	-0.774398
16	1	0	0.450391	0.512671	-1.797696
17	6	0	-4.408462	0.489184	0.541084
18	1	0	-3.479047	-1.078438	-0.649276
19	1	0	-2.983946	-1.074797	1.052559
20	1	0	2.908735	2.185875	0.758229
21	1	0	2.486102	2.249176	-0.961660
22	1	0	1.373495	2.896264	0.253142
23	1	0	0.910905	-1.778308	-0.191142
24	1	0	2.579330	-0.400650	-1.251902
25	1	0	-4.661836	1.128492	-0.311372
26	1	0	-4.166450	1.127981	1.397257
27	1	0	-5.291158	-0.107561	0.796762

Catalytic complex TFA·E: ***CC***-(*anti*)-**1c**

1) (1Re,3S,4R,g^+,*E*)/ (3R,4S,1Si,g^-,*E*) g^+=57.1 ° for this ***CC*** no ***TS1‡*** and ***TI*** were not found

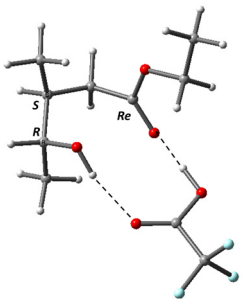


Energy= -1066.99003863 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.130818	2.213026	0.569687
2	6	0	1.863797	0.762280	-1.431776
3	6	0	1.793988	-0.588322	-0.755609
4	8	0	1.000739	1.026408	1.363154
5	8	0	2.973810	-1.026632	-0.332056
6	8	0	0.781940	-1.286823	-0.666631
7	1	0	-0.751422	-0.909341	-0.882278
8	8	0	-1.760162	-0.819347	-0.977653
9	6	0	-2.298218	-0.391233	0.140171
10	6	0	-3.839680	-0.391803	0.040546
11	8	0	-1.733955	-0.037143	1.156859
12	6	0	-0.210918	2.708912	0.031626
13	1	0	1.527566	2.993926	1.235528
14	1	0	2.636309	0.690599	-2.206961
15	1	0	0.908098	0.916637	-1.939810
16	9	0	-4.382211	0.215453	1.100891
17	9	0	-4.299889	-1.656476	-0.008819
18	9	0	-4.248099	0.245247	-1.071682
19	6	0	3.002412	-2.314307	0.350152
20	6	0	4.440709	-2.595869	0.729573
21	1	0	2.349452	-2.248960	1.225038
22	1	0	2.599172	-3.072682	-0.326718
23	1	0	-0.658332	2.006274	-0.680603
24	1	0	-0.920221	2.856509	0.853542
25	1	0	-0.084905	3.669634	-0.480461
26	1	0	0.100993	0.663776	1.262423
27	1	0	4.495541	-3.560621	1.246103
28	1	0	5.081779	-2.644964	-0.157163
29	1	0	4.831233	-1.825061	1.402283
30	6	0	2.197046	1.980398	-0.527680
31	1	0	2.168036	2.851498	-1.197239
32	6	0	3.603484	1.916302	0.084430
33	1	0	3.672090	1.142325	0.853248
34	1	0	4.364735	1.706409	-0.675971
35	1	0	3.852058	2.878026	0.549413

2) (1Re,3S,4R,g^+,*Z*)/ (3R,4S,1Si,g^-,*Z*) g^+=67.5 °

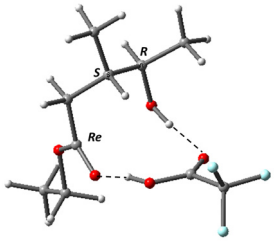


Energy= -1066.98979328 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.991851	-0.320330	1.191745
2	6	0	1.809815	0.593058	0.973545
3	8	0	1.215409	-1.096322	-1.141639
4	8	0	2.101458	1.666797	0.245748
5	8	0	0.703896	0.385345	1.474316
6	1	0	-0.840049	0.616303	1.039500
7	8	0	-1.831819	0.698029	0.866338
8	6	0	-2.260208	-0.271352	0.089068
9	6	0	-3.781018	-0.140016	-0.147892
10	8	0	-1.618028	-1.164495	-0.424728
11	1	0	3.865218	0.295474	1.432402
12	1	0	2.758070	-0.932679	2.065827
13	9	0	-4.039150	0.970677	-0.865548
14	9	0	-4.444236	-0.047763	1.018120
15	9	0	-4.247800	-1.196837	-0.819885
16	6	0	1.024994	2.592629	-0.071049
17	6	0	1.641329	3.780418	-0.779638
18	1	0	0.305528	2.070698	-0.709452
19	1	0	0.527697	2.883985	0.858883
20	1	0	0.315785	-1.285234	-0.818877
21	1	0	0.853791	4.496414	-1.038978
22	1	0	2.369456	4.286985	-0.137384
23	1	0	2.142765	3.471570	-1.702764
24	6	0	3.349009	-1.230100	-0.020211
25	1	0	4.065962	-1.966306	0.369501
26	6	0	2.140370	-2.024666	-0.560541
27	1	0	2.525839	-2.666291	-1.369514
28	6	0	1.468132	-2.929263	0.471626
29	1	0	0.678330	-3.522892	-0.004075
30	1	0	2.192008	-3.627507	0.907832
31	1	0	1.013209	-2.350777	1.282324
32	6	0	4.043338	-0.455304	-1.148879
33	1	0	4.930045	0.072113	-0.777452
34	1	0	4.370038	-1.143261	-1.938348
35	1	0	3.373983	0.281433	-1.600533

3) (1Re,3S,4R,g^-,*E*)/ (3R,4S,1Si,g^-,*E*) g^-=-52.5 °

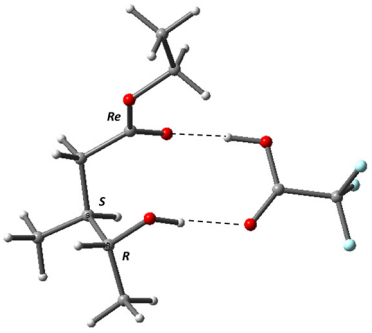


Energy= -1066.99507514

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.176133	2.035140	0.879126
2	6	0	2.109523	0.967405	-1.227567
3	6	0	2.053063	-0.457296	-0.731031
4	8	0	1.223612	0.742147	1.493633
5	8	0	3.223393	-0.892289	-0.280365
6	8	0	1.073325	-1.201400	-0.814120
7	1	0	-0.490264	-0.922258	-0.983270
8	8	0	-1.503363	-0.903466	-1.061698
9	6	0	-2.059355	-0.613682	0.091408
10	6	0	-3.598767	-0.693614	-0.012057
11	8	0	-1.513184	-0.320621	1.137053
12	6	0	0.104106	2.903129	1.540658
13	1	0	2.162525	2.473533	1.082523
14	1	0	3.104827	1.374053	-1.024042
15	1	0	1.992922	0.914512	-2.318167
16	9	0	-3.983446	-1.958327	-0.266295
17	9	0	-4.048881	0.088790	-1.010127
18	9	0	-4.171657	-0.297183	1.128818
19	6	0	3.279322	-2.258054	0.221331
20	6	0	4.687948	-2.498551	0.722102
21	1	0	2.536878	-2.357975	1.018046
22	1	0	3.008615	-2.937743	-0.591947
23	1	0	-0.901849	2.523271	1.321422
24	1	0	0.242119	2.887450	2.627093
25	1	0	0.155599	3.945091	1.208436
26	1	0	0.333792	0.344314	1.415635
27	1	0	4.764221	-3.520013	1.111220
28	1	0	5.420546	-2.383132	-0.083982
29	1	0	4.942277	-1.803916	1.529555
30	6	0	1.022842	1.903662	-0.653598
31	1	0	0.040448	1.455959	-0.858878
32	6	0	1.087632	3.259820	-1.370566
33	1	0	1.040571	3.128314	-2.457833
34	1	0	0.255134	3.909272	-1.082634
35	1	0	2.022537	3.787024	-1.139611

4) (1Re,3S,4R,g^-,*Z*)/ (3R,4S,1Si,g^+,*Z*) g^-=-46.8 °

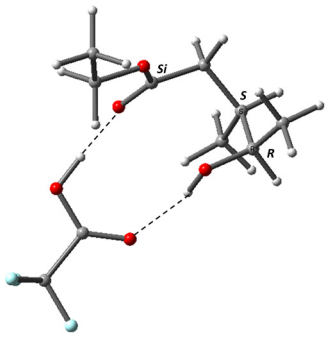


Energy= -1066.99414474 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.034968	0.229403	-0.696415
2	6	0	-1.775376	1.053814	-0.615345
3	8	0	-1.323680	-0.707444	1.338079
4	8	0	-1.909961	2.150995	0.121491
5	8	0	-0.756491	0.777437	-1.250871
6	1	0	0.829555	0.814492	-0.940627
7	8	0	1.831802	0.744578	-0.835392
8	6	0	2.156183	-0.328763	-0.149255
9	6	0	3.691995	-0.467014	-0.059952
10	8	0	1.417600	-1.139164	0.372188
11	1	0	-3.750438	0.583345	0.052391
12	1	0	-3.469081	0.430059	-1.685508
13	9	0	4.223092	0.602188	0.562435
14	9	0	4.231152	-0.544821	-1.290222
15	9	0	4.029196	-1.565856	0.622023
16	6	0	-0.768849	3.048220	0.218353
17	6	0	-1.217381	4.272006	0.989010
18	1	0	0.039502	2.520035	0.733266
19	1	0	-0.434578	3.299068	-0.792762
20	1	0	-0.480030	-0.951007	0.909464
21	1	0	-0.377951	4.970246	1.080442
22	1	0	-2.036017	4.784513	0.472738
23	1	0	-1.552154	4.002033	1.995973
24	6	0	-2.777899	-1.285632	-0.554465
25	1	0	-1.951144	-1.544710	-1.230229
26	6	0	-2.335884	-1.617276	0.890296
27	1	0	-3.189322	-1.426196	1.555530
28	6	0	-1.873679	-3.062808	1.076219
29	1	0	-1.529998	-3.211877	2.105565
30	1	0	-2.677997	-3.779737	0.881363
31	1	0	-1.039613	-3.295786	0.401112
32	6	0	-4.024300	-2.075205	-0.977943
33	1	0	-3.842521	-3.154656	-0.968330
34	1	0	-4.871781	-1.871069	-0.310373
35	1	0	-4.330605	-1.804039	-1.995114

5) (1Re,3R,4S,g^-,*Z*)/ (1Si,3S,4R,g^+,*Z*) g^+=56.2 °

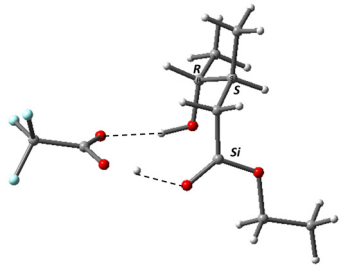


Energy= -1066.99087680 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.314311	-1.707006	0.993410
2	6	0	2.943400	-0.387166	-1.130869
3	6	0	1.832398	0.620344	-0.957652
4	8	0	1.226698	-0.816020	1.263109
5	8	0	2.204659	1.685293	-0.253772
6	8	0	0.722021	0.498701	-1.476819
7	1	0	-0.806522	0.720672	-0.976690
8	8	0	-1.790808	0.793938	-0.765555
9	6	0	-2.200037	-0.229201	-0.048848
10	6	0	-3.725489	-0.149384	0.181848
11	8	0	-1.544508	-1.152504	0.389526
12	6	0	3.482278	-1.228261	1.850345
13	1	0	2.044178	-2.725392	1.317152
14	1	0	3.862137	0.024648	-0.707653
15	1	0	3.098053	-0.506529	-2.209968
16	9	0	-4.073417	1.048395	0.684892
17	9	0	-4.377554	-0.318566	-0.984424
18	9	0	-4.125204	-1.100057	1.032272
19	6	0	1.209882	2.713406	0.004858
20	6	0	1.920055	3.871557	0.673622
21	1	0	0.439675	2.282753	0.652159
22	1	0	0.750256	3.005670	-0.943924
23	1	0	3.743346	-0.189836	1.619316
24	1	0	4.367239	-1.854890	1.692929
25	1	0	3.211632	-1.275078	2.910620
26	1	0	0.404440	-1.170920	0.877900
27	1	0	1.196112	4.663654	0.894495
28	1	0	2.695484	4.287125	0.021332
29	1	0	2.383874	3.557618	1.614540
30	6	0	2.638391	-1.782304	-0.519259
31	1	0	3.571248	-2.355239	-0.613468
32	6	0	1.556297	-2.547454	-1.296848
33	1	0	1.819414	-2.627299	-2.358222
34	1	0	1.453470	-3.565531	-0.901809
35	1	0	0.578132	-2.061825	-1.238929

6) (1Re,3R,4S,g^+,*E*)/ (1Si,3S,4R,g^-,*E*) g^-=-51.1 °

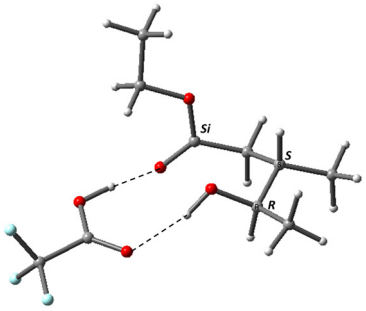


Energy= -1066.99501208 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-1.844793	-1.171837	0.752230
2	6	0	-2.321230	-0.370286	-0.167409
3	6	0	-3.855210	-0.242249	-0.035561
4	8	0	-1.716281	0.226212	-1.038305
5	9	0	-4.188433	0.196313	1.192672
6	9	0	-4.340124	0.616667	-0.937870
7	9	0	-4.441753	-1.438459	-0.225945
8	1	0	-0.836123	-1.307543	0.651181
9	6	0	1.812964	2.996961	-1.501076
10	6	0	1.213664	1.924074	-0.593676
11	6	0	2.052352	1.646379	0.673281
12	6	0	1.496339	0.416869	1.427471
13	6	0	1.612743	-0.891656	0.683960
14	8	0	2.862622	-1.181952	0.347335
15	6	0	3.085029	-2.402719	-0.414371
16	1	0	2.817865	2.703735	-1.828956
17	1	0	1.187958	3.117575	-2.392476
18	1	0	1.882185	3.969085	-1.001511
19	8	0	1.100607	0.708149	-1.349584
20	6	0	2.106202	2.855605	1.617125
21	1	0	0.444263	0.566413	1.691779
22	1	0	2.052961	0.293119	2.365689
23	6	0	4.567907	-2.490213	-0.705968
24	1	0	0.160978	0.447032	-1.353217
25	1	0	0.210042	2.244441	-0.275241
26	1	0	3.073451	1.405074	0.350116
27	1	0	1.100256	3.157142	1.937927
28	1	0	2.686236	2.623364	2.517954
29	1	0	2.577664	3.720098	1.139118
30	8	0	0.685912	-1.681536	0.481132
31	1	0	4.769460	-3.397298	-1.286598
32	1	0	4.906045	-1.627042	-1.288763
33	1	0	5.151227	-2.539005	0.219745
34	1	0	2.488315	-2.344208	-1.329000
35	1	0	2.730907	-3.251560	0.177405

7) (1Re,3R,4S,g^+,*Z*)/ (1Si,3S,4R,g^-,*Z*) g^-=-64.5 °



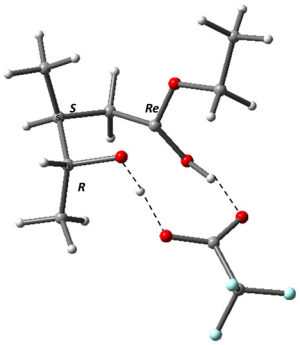
Energy= -1066.99189142 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.832675	0.174982	-1.259591
2	6	0	1.617279	0.994235	-0.902641
3	8	0	1.179824	-0.836755	0.920974
4	8	0	1.879110	1.935209	-0.000331
5	8	0	0.523650	0.850298	-1.450079
6	1	0	-1.007464	0.825486	-0.943532
7	8	0	-2.000127	0.764955	-0.760259
8	6	0	-2.318821	-0.373080	-0.187428
9	6	0	-3.848484	-0.466652	0.006434
10	8	0	-1.583242	-1.268826	0.176006
11	1	0	3.645294	0.865821	-1.512835
12	1	0	2.584211	-0.401136	-2.156295
13	9	0	-4.485277	-0.338534	-1.171591
14	9	0	-4.186454	-1.641625	0.546237
15	9	0	-4.274422	0.516661	0.821879
16	6	0	0.773691	2.750923	0.470872
17	6	0	1.346149	3.794787	1.406491
18	1	0	0.062233	2.096255	0.983742
19	1	0	0.276648	3.203103	-0.392686
20	1	0	0.294306	-1.147147	0.657022
21	1	0	0.535714	4.427525	1.784954
22	1	0	2.068281	4.434659	0.888138
23	1	0	1.844363	3.325047	2.261030
24	6	0	3.317599	-0.776621	-0.134799
25	1	0	3.604173	-0.161175	0.728855
26	6	0	2.171429	-1.693582	0.334736
27	1	0	1.746920	-2.198175	-0.547260
28	6	0	2.590747	-2.752153	1.355647
29	1	0	1.703888	-3.288234	1.712275
30	1	0	3.278325	-3.489788	0.927680
31	1	0	3.074258	-2.285781	2.222971
32	6	0	4.550411	-1.547496	-0.624735
33	1	0	5.010358	-2.127465	0.181283
34	1	0	4.292844	-2.240920	-1.436009
35	1	0	5.311280	-0.857707	-1.008471

Transition States: ***TS1*‡-(*anti*)-1c**

1) (1Re,3R,4S,g^+,*Z*)/ (1Si,3S,4R,g^-,*Z*) g^+= 41°

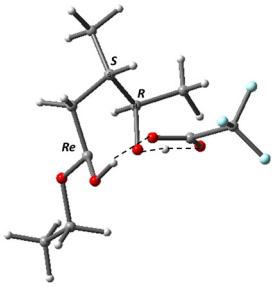


Energy= -1066.96590325 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.918401	-0.415336	1.124562
2	6	0	1.680062	0.395798	0.768835
3	8	0	1.108424	-0.555237	-0.541138
4	8	0	1.989556	1.567538	0.180964
5	8	0	0.720783	0.357808	1.692319
6	1	0	-0.197715	0.654811	1.370943
7	8	0	-1.726439	0.797961	0.940466
8	6	0	-2.087587	-0.039704	0.087311
9	6	0	-3.611869	-0.184659	-0.152709
10	8	0	-1.388819	-0.810059	-0.627293
11	1	0	3.745494	0.267334	1.334874
12	1	0	2.691199	-0.974035	2.035002
13	9	0	-3.910691	-0.002489	-1.456650
14	9	0	-4.331032	0.697798	0.559119
15	9	0	-4.024729	-1.424783	0.189434
16	6	0	0.927309	2.498174	-0.153304
17	6	0	1.579933	3.721630	-0.762760
18	1	0	0.245977	2.015538	-0.861812
19	1	0	0.374380	2.754634	0.755357
20	1	0	0.054178	-0.689095	-0.532850
21	1	0	0.808037	4.453536	-1.024204
22	1	0	2.272415	4.188540	-0.054366
23	1	0	2.131264	3.461665	-1.672526
24	6	0	3.247444	-1.370512	-0.045683
25	1	0	3.773620	-2.248804	0.343441
26	6	0	1.872302	-1.804284	-0.584192
27	1	0	1.932481	-2.077670	-1.642322
28	6	0	1.180383	-2.906593	0.206565
29	1	0	0.171218	-3.087128	-0.177507
30	1	0	1.750083	-3.837229	0.107107
31	1	0	1.103878	-2.659779	1.270358
32	6	0	4.111197	-0.709669	-1.127579
33	1	0	5.073567	-0.390057	-0.711852
34	1	0	4.315313	-1.412235	-1.944049
35	1	0	3.619205	0.172071	-1.551531

2) (1Re,3S,4R,g^+,*E*)/ (1Si,3R,4S,g^-,*E*) g^+= 41°

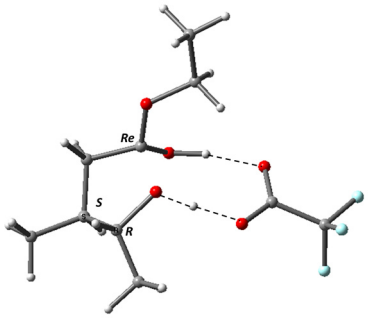


Energy= -1066.97060846 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.297263	1.518855	-0.825459
2	6	0	-1.634262	0.846301	1.476285
3	6	0	-1.693531	-0.444870	0.642144
4	8	0	-1.057683	0.070914	-0.783694
5	8	0	-2.973226	-0.767844	0.358620
6	8	0	-0.952200	-1.505063	0.999186
7	1	0	-0.014018	-1.224164	1.224660
8	8	0	1.581951	-0.797793	1.267134
9	6	0	2.010227	-0.538612	0.130378
10	6	0	3.543778	-0.447023	-0.060982
11	8	0	1.361838	-0.310019	-0.939084
12	6	0	-0.467668	2.161043	-1.922136
13	1	0	-2.364744	1.620436	-1.051256
14	1	0	-2.659869	1.095670	1.763457
15	1	0	-1.060872	0.664810	2.388903
16	9	0	4.214200	-0.802341	1.045025
17	9	0	3.898076	0.819627	-0.371585
18	9	0	3.951293	-1.244205	-1.068437
19	6	0	-3.204461	-2.012681	-0.354019
20	6	0	-4.655354	-2.016430	-0.790185
21	1	0	-2.525622	-2.062647	-1.211137
22	1	0	-2.983504	-2.848847	0.315364
23	1	0	0.604464	2.074378	-1.721122
24	1	0	-0.681148	1.698991	-2.891557
25	1	0	-0.722905	3.223670	-1.992097
26	1	0	0.047496	-0.152852	-0.826664
27	1	0	-4.876503	-2.951375	-1.317093
28	1	0	-5.325242	-1.942889	0.073408
29	1	0	-4.866103	-1.181268	-1.466800
30	6	0	-1.018336	1.969924	0.614458
31	1	0	0.070893	1.962475	0.753654
32	6	0	-1.554182	3.361136	0.950963
33	1	0	-1.365714	3.604495	2.002672
34	1	0	-1.071123	4.134217	0.342864
35	1	0	-2.636735	3.419742	0.781732

3) (1Re,3S,4R,g^-,*Z*)/ (1Si,3R,4S,g^+,*Z*) g^-= -33°

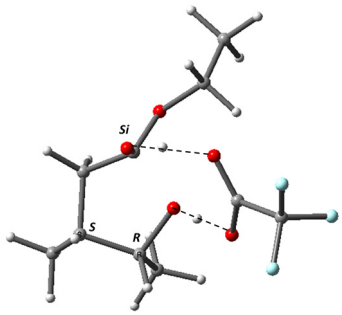


Energy=-1066.96902780 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.085142	0.170391	0.658120
2	6	0	1.713561	0.778328	0.442302
3	8	0	1.161154	-0.266361	-0.738425
4	8	0	1.775403	1.985424	-0.158855
5	8	0	0.901774	0.618784	1.497383
6	1	0	-0.078025	0.765018	1.294660
7	8	0	-1.678713	0.704674	1.036451
8	6	0	-2.000646	-0.128108	0.167414
9	6	0	-3.502609	-0.490510	0.056285
10	8	0	-1.268920	-0.756570	-0.651429
11	1	0	3.776702	0.592297	-0.078467
12	1	0	3.436747	0.430045	1.660452
13	9	0	-4.279438	0.325152	0.786356
14	9	0	-3.706256	-1.753949	0.491428
15	9	0	-3.924619	-0.427161	-1.222934
16	6	0	0.579461	2.800492	-0.244334
17	6	0	0.967953	4.089635	-0.939102
18	1	0	-0.184152	2.259619	-0.813396
19	1	0	0.200601	2.991570	0.764522
20	1	0	0.103468	-0.496584	-0.642926
21	1	0	0.090781	4.741428	-1.015865
22	1	0	1.743091	4.619439	-0.375167
23	1	0	1.342206	3.893733	-1.949323
24	6	0	2.921506	-1.341908	0.458165
25	1	0	2.349121	-1.741682	1.305144
26	6	0	2.045242	-1.445466	-0.800565
27	1	0	2.661663	-1.285655	-1.692535
28	6	0	1.235889	-2.721904	-0.942708
29	1	0	0.591473	-2.885873	-0.073040
30	1	0	0.613628	-2.702436	-1.842876
31	1	0	1.923078	-3.570662	-1.029021
32	6	0	4.244300	-2.097316	0.339890
33	1	0	4.838799	-1.981249	1.252899
34	1	0	4.077557	-3.169916	0.189002
35	1	0	4.841689	-1.724886	-0.501525

4) (1Re,3R,4S,g^-,*Z*)/ (1Si,3S,4R,g^+,*Z*) g^+= 26.8°

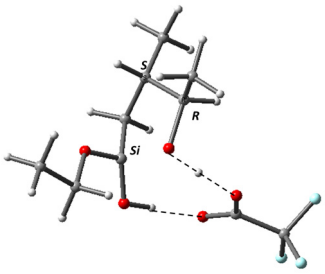


Energy=-1066.96662352 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.962637	-1.583232	0.867126
2	6	0	3.082294	-0.116144	-0.738271
3	6	0	1.758150	0.596485	-0.552957
4	8	0	1.179020	-0.343759	0.756157
5	8	0	1.903786	1.826575	-0.029991
6	8	0	0.890727	0.411299	-1.549223
7	1	0	-0.076883	0.624164	-1.316406
8	8	0	-1.638128	0.659906	-1.003767
9	6	0	-1.987306	-0.154822	-0.123849
10	6	0	-3.509435	-0.376288	0.062492
11	8	0	-1.276132	-0.825297	0.674505
12	6	0	2.683573	-1.570368	2.205256
13	1	0	1.243888	-2.407535	0.830111
14	1	0	3.814441	0.359969	-0.081181
15	1	0	3.410755	0.014584	-1.773450
16	9	0	-4.236105	0.215172	-0.899031
17	9	0	-3.809916	-1.691210	0.056889
18	9	0	-3.910506	0.128606	1.250869
19	6	0	0.755874	2.712771	0.038502
20	6	0	1.236659	4.019219	0.635409
21	1	0	-0.013668	2.248767	0.664214
22	1	0	0.354407	2.858060	-0.969056
23	1	0	3.406408	-0.748537	2.259086
24	1	0	3.221787	-2.514898	2.344658
25	1	0	1.969473	-1.457926	3.027623
26	1	0	0.136781	-0.544974	0.677065
27	1	0	0.397270	4.720147	0.699780
28	1	0	2.015831	4.470107	0.011616
29	1	0	1.638128	3.866469	1.642647
30	6	0	2.890655	-1.601591	-0.371722
31	1	0	3.860800	-2.016856	-0.077563
32	6	0	2.325678	-2.451902	-1.517200
33	1	0	2.234098	-3.499474	-1.206637
34	1	0	2.990064	-2.418358	-2.388436
35	1	0	1.338307	-2.101396	-1.832792

5) (1Re,3R,4S,g^+,*E*)/ (1Si,3S,4R,g^-,*E*) g^-= -28°

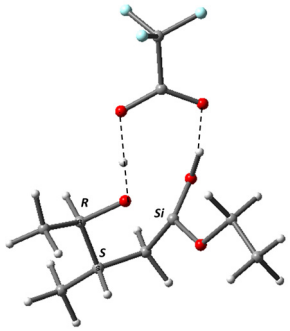


Energy= -1066.97383288 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.572604	0.782448	-1.515414
2	6	0	-1.536266	-0.515708	-0.725829
3	8	0	-0.927551	0.070227	0.689019
4	8	0	-2.783928	-0.937224	-0.436047
5	8	0	-0.717308	-1.511213	-1.095169
6	1	0	0.203649	-1.158896	-1.284930
7	8	0	1.773904	-0.626048	-1.253054
8	6	0	2.164283	-0.384062	-0.099268
9	6	0	3.688465	-0.246421	0.132993
10	8	0	1.480936	-0.206575	0.958800
11	1	0	-2.273097	0.687564	-2.349329
12	1	0	-0.572108	0.976056	-1.918885
13	9	0	3.997851	1.031827	0.443402
14	9	0	4.092221	-1.025210	1.155761
15	9	0	4.396654	-0.589231	-0.953230
16	6	0	-2.918223	-2.187903	0.289647
17	6	0	-4.370459	-2.312877	0.702632
18	1	0	-2.253090	-2.165866	1.158856
19	1	0	-2.613877	-3.010903	-0.362999
20	1	0	0.180477	-0.139018	0.792988
21	1	0	-4.517304	-3.255790	1.241071
22	1	0	-5.029251	-2.311576	-0.172612
23	1	0	-4.665242	-1.489590	1.362205
24	6	0	-1.975397	1.866112	-0.508233
25	1	0	-3.036748	1.732071	-0.266170
26	6	0	-1.147569	1.524997	0.748411
27	1	0	-0.154874	1.984359	0.670213
28	6	0	-1.795613	1.875729	2.074982
29	1	0	-1.982098	2.954680	2.125887
30	1	0	-2.751187	1.352178	2.187255
31	1	0	-1.146527	1.604645	2.914160
32	6	0	-1.751236	3.294531	-1.003490
33	1	0	-2.365490	3.499693	-1.887379
34	1	0	-2.022890	4.028019	-0.235603
35	1	0	-0.701596	3.461491	-1.275105

6) (1Re,3R,4S,g^+,*Z*)/ (1Si,3S,4R,g^-,*Z*) g^-= -41.7°



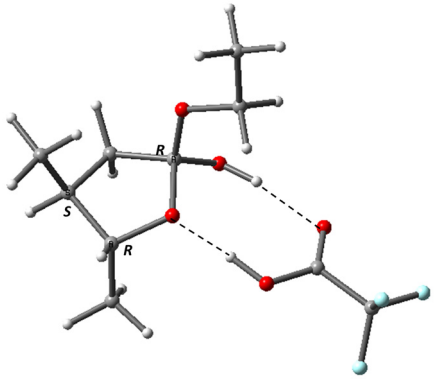
Energy= -1066.96945032 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.816725	-0.017105	-1.218380
2	6	0	1.564435	0.701454	-0.748170
3	8	0	1.042341	-0.427662	0.429800
4	8	0	1.858607	1.790046	-0.011599
5	8	0	0.586428	0.762274	-1.650672
6	1	0	-0.329362	0.972255	-1.265168
7	8	0	-1.853209	0.936410	-0.755389
8	6	0	-2.141827	-0.140743	-0.192899
9	6	0	-3.646594	-0.457747	-0.005220
10	8	0	-1.377730	-1.035667	0.264879
11	1	0	3.586520	0.717484	-1.468396
12	1	0	2.561970	-0.580004	-2.121538
13	9	0	-3.960558	-1.630218	-0.596528
14	9	0	-3.946778	-0.570375	1.307279
15	9	0	-4.441567	0.490141	-0.526507
16	6	0	0.776065	2.632601	0.460778
17	6	0	1.396703	3.748177	1.275960
18	1	0	0.095682	2.026891	1.068061
19	1	0	0.227469	3.027550	-0.400059
20	1	0	0.017288	-0.702405	0.309425
21	1	0	0.606158	4.409017	1.648000
22	1	0	2.084325	4.343497	0.665792
23	1	0	1.945963	3.348477	2.134753
24	6	0	3.260114	-0.970527	-0.095194
25	1	0	3.683253	-0.372039	0.722379
26	6	0	1.946054	-1.580385	0.407524
27	1	0	1.557069	-2.292515	-0.332020
28	6	0	1.977837	-2.206827	1.789517
29	1	0	2.640538	-3.079323	1.789461
30	1	0	0.979498	-2.544253	2.087396
31	1	0	2.342145	-1.489581	2.532914
32	6	0	4.287516	-2.006190	-0.548563
33	1	0	5.191690	-1.514654	-0.924569
34	1	0	4.587037	-2.658158	0.279423
35	1	0	3.889220	-2.637615	-1.352334

Tetrahedral Intermediates: ***TI1***-(*anti*)-**1c**

1) (1R,3S,4R,g^+,*Z*)/ (1S,3R,4S,g^-,*Z*) g^+= 28.9°

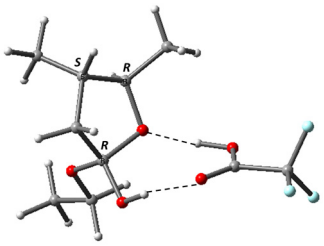


Energy=-1066.97649504 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.070539	-0.367702	1.092381
2	6	0	1.738032	0.315675	0.780361
3	8	0	1.094210	-0.544738	-0.201492
4	8	0	2.004201	1.558528	0.192399
5	8	0	0.938454	0.400048	1.908421
6	1	0	0.000701	0.523543	1.649537
7	8	0	-1.825926	0.492920	1.168971
8	6	0	-2.211705	-0.099839	0.178756
9	6	0	-3.714016	-0.196433	-0.165327
10	8	0	-1.484097	-0.712151	-0.725268
11	1	0	3.845965	0.375039	1.292768
12	1	0	2.934682	-0.979642	1.987791
13	9	0	-3.959521	0.411396	-1.340618
14	9	0	-4.453745	0.389554	0.779998
15	9	0	-4.091890	-1.482541	-0.271869
16	6	0	0.877343	2.360019	-0.189642
17	6	0	1.407888	3.615805	-0.856672
18	1	0	0.237755	1.798887	-0.883643
19	1	0	0.285059	2.617178	0.697581
20	1	0	-0.497800	-0.641605	-0.496934
21	1	0	0.573878	4.262041	-1.153078
22	1	0	2.052218	4.177567	-0.171606
23	1	0	1.988098	3.368166	-1.752412
24	6	0	3.369660	-1.240475	-0.142284
25	1	0	3.932860	-2.132843	0.151945
26	6	0	1.955422	-1.654410	-0.603856
27	1	0	1.891318	-1.704623	-1.696204
28	6	0	1.439505	-2.952146	0.004869
29	1	0	0.394422	-3.125328	-0.275681
30	1	0	2.030117	-3.799552	-0.362390
31	1	0	1.502474	-2.933927	1.098690
32	6	0	4.150302	-0.497418	-1.233283
33	1	0	5.133198	-0.184826	-0.861370
34	1	0	4.312648	-1.141076	-2.106392
35	1	0	3.616255	0.399999	-1.562276

2) (1R,3S,4R,g^-,*E*)/ (1S,3R,4S,g^+,*E*) g^+= - 4.5°

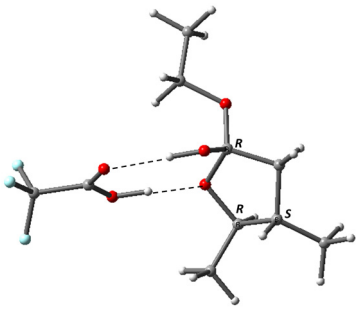


Energy=-1066.97841650 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.592538	1.407906	-0.806909
2	6	0	-1.899681	0.779318	1.538590
3	6	0	-1.568295	-0.439590	0.672476
4	8	0	-0.926358	0.152541	-0.496996
5	8	0	-2.752429	-1.061871	0.312721
6	8	0	-0.699672	-1.371774	1.204163
7	1	0	0.135740	-0.920663	1.450432
8	8	0	1.885848	-0.231202	1.332460
9	6	0	2.331357	-0.178856	0.200651
10	6	0	3.852716	-0.158857	-0.061916
11	8	0	1.663355	-0.129408	-0.927028
12	6	0	-0.596992	2.350093	-1.461498
13	1	0	-2.400897	1.177029	-1.511649
14	1	0	-2.732733	0.559175	2.210852
15	1	0	-1.019460	1.010653	2.146588
16	9	0	4.208073	0.994283	-0.658234
17	9	0	4.202244	-1.174551	-0.870752
18	9	0	4.531376	-0.271771	1.083391
19	6	0	-2.637453	-2.204682	-0.559502
20	6	0	-4.038060	-2.581522	-1.004441
21	1	0	-2.004961	-1.948091	-1.417476
22	1	0	-2.161791	-3.029464	-0.018070
23	1	0	0.225432	2.593388	-0.778927
24	1	0	-0.178043	1.916068	-2.376255
25	1	0	-1.100511	3.284322	-1.734947
26	1	0	0.665035	-0.076886	-0.754015
27	1	0	-3.997413	-3.459315	-1.659460
28	1	0	-4.668884	-2.825789	-0.142555
29	1	0	-4.510249	-1.761129	-1.556425
30	6	0	-2.198872	1.917442	0.537160
31	1	0	-1.662797	2.822558	0.844324
32	6	0	-3.688409	2.250376	0.408179
33	1	0	-4.266911	1.356382	0.149007
34	1	0	-4.084201	2.649392	1.349428
35	1	0	-3.861169	3.004666	-0.369798

3) (1R,3S,4R,g^-,*Z*)/ (1S,3R,4S,g^+,*Z*) g^-= - 32.9°

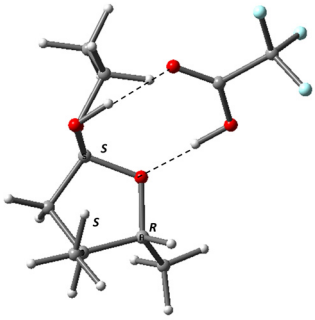


Energy=-1066.97936981 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.235703	0.284456	0.558813
2	6	0	1.783332	0.731305	0.422939
3	8	0	1.171426	-0.258075	-0.461131
4	8	0	1.740319	1.985554	-0.178181
5	8	0	1.146187	0.679644	1.657129
6	1	0	0.188341	0.514013	1.529219
7	8	0	-1.653101	0.169984	1.280964
8	6	0	-2.091802	-0.270797	0.235304
9	6	0	-3.605501	-0.496514	0.031463
10	8	0	-1.418630	-0.599323	-0.842770
11	1	0	3.824028	0.754365	-0.236576
12	1	0	3.642080	0.588535	1.526239
13	9	0	-4.056327	0.273885	-0.975527
14	9	0	-4.281912	-0.186804	1.140881
15	9	0	-3.853116	-1.781257	-0.279210
16	6	0	0.462281	2.630958	-0.282949
17	6	0	0.687484	3.993994	-0.911071
18	1	0	-0.209905	2.029326	-0.909876
19	1	0	0.013095	2.731564	0.712103
20	1	0	-0.425163	-0.455593	-0.695620
21	1	0	-0.268369	4.519607	-1.015899
22	1	0	1.350586	4.604078	-0.288036
23	1	0	1.138303	3.896300	-1.904730
24	6	0	2.091113	-1.362908	-0.726144
25	1	0	2.537684	-1.176780	-1.713135
26	6	0	4.502021	-1.887805	-0.004628
27	1	0	5.234670	-1.755894	0.799751
28	1	0	4.388727	-2.965386	-0.172484
29	1	0	4.922595	-1.446217	-0.916802
30	6	0	1.319292	-2.670245	-0.745132
31	1	0	0.549217	-2.669638	-1.524537
32	1	0	2.002311	-3.500898	-0.956424
33	1	0	0.840312	-2.854953	0.223117
34	6	0	3.170278	-1.235177	0.361320
35	1	0	2.778870	-1.690721	1.280825

4) (1R,3R,4S,g^-,*Z*)/ (1S,3S,4R,g^+,*Z*) g^+= 27.2°

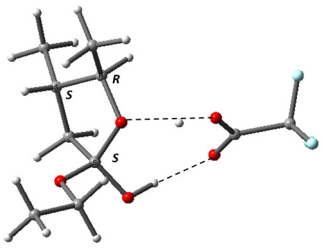


Energy= -1066.97672859 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.936512	-1.492747	0.875951
2	6	0	3.244407	-0.098163	-0.583297
3	6	0	1.847735	0.509753	-0.477460
4	8	0	1.163209	-0.302591	0.520125
5	8	0	1.951048	1.818303	-0.012887
6	8	0	1.173854	0.404593	-1.690063
7	1	0	0.205843	0.387552	-1.532194
8	8	0	-1.649014	0.226925	-1.241132
9	6	0	-2.094584	-0.191662	-0.188760
10	6	0	-3.612738	-0.378294	0.021921
11	8	0	-1.425891	-0.527675	0.888581
12	6	0	2.413183	-1.362829	2.315869
13	1	0	1.249923	-2.342221	0.786689
14	1	0	3.900161	0.427963	0.115537
15	1	0	3.638794	0.029121	-1.594352
16	9	0	-4.284461	-0.080001	-1.093512
17	9	0	-3.887959	-1.649817	0.362736
18	9	0	-4.045562	0.424393	1.011435
19	6	0	0.747692	2.598872	0.045377
20	6	0	1.124204	3.983272	0.540067
21	1	0	0.029951	2.128669	0.731490
22	1	0	0.291031	2.654353	-0.949963
23	1	0	3.118187	-0.531301	2.427324
24	1	0	2.913126	-2.286523	2.630544
25	1	0	1.566555	-1.188192	2.989001
26	1	0	-0.428360	-0.406477	0.735861
27	1	0	0.231423	4.616384	0.595006
28	1	0	1.841441	4.455301	-0.140293
29	1	0	1.574439	3.932561	1.537469
30	6	0	3.064875	-1.573242	-0.177916
31	1	0	3.978270	-1.947153	0.297696
32	6	0	2.708403	-2.489206	-1.355376
33	1	0	2.557505	-3.521149	-1.015697
34	1	0	3.515051	-2.496169	-2.097906
35	1	0	1.794717	-2.154856	-1.857404

5) (1R,3R,4S,g^+,*E*)/ (1S,3S,4R,g^-,*E*) g^-= -27.2°

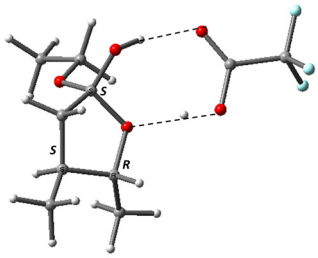


Emergy= -1066.98071699 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	1.880228	-0.104485	-1.340547
2	6	0	2.297154	-0.172849	-0.198323
3	6	0	3.811115	-0.145264	0.104136
4	8	0	1.602223	-0.268074	0.908674
5	9	0	4.519349	-0.092829	-1.027702
6	9	0	4.117072	0.932188	0.851038
7	9	0	4.174208	-1.245263	0.787192
8	1	0	0.115728	-0.726763	-1.589584
9	6	0	-1.744799	1.562266	2.212638
10	6	0	-1.317906	1.452913	0.759629
11	6	0	-2.394151	1.815876	-0.283988
12	6	0	-2.035057	0.889317	-1.451554
13	6	0	-1.606163	-0.404847	-0.760586
14	8	0	-2.739940	-1.129014	-0.442538
15	6	0	-2.538856	-2.355862	0.286908
16	1	0	-2.612049	0.922449	2.409805
17	1	0	-0.932626	1.265925	2.885729
18	1	0	-2.014341	2.598391	2.448939
19	8	0	-0.946459	0.068591	0.467036
20	6	0	-2.438466	3.303485	-0.629718
21	1	0	-1.181348	1.287274	-2.013858
22	1	0	-2.857943	0.707777	-2.146800
23	6	0	-3.901985	-2.845248	0.738382
24	1	0	0.601372	-0.231193	0.712868
25	1	0	-0.418781	2.060757	0.586019
26	1	0	-3.370238	1.507793	0.111802
27	1	0	-1.482182	3.644601	-1.045873
28	1	0	-3.218983	3.508058	-1.371489
29	1	0	-2.657887	3.913230	0.254891
30	8	0	-0.718340	-1.219873	-1.436528
31	1	0	-3.795956	-3.789057	1.285503
32	1	0	-4.382180	-2.115144	1.399387
33	1	0	-4.559346	-3.018679	-0.120884
34	1	0	-1.885122	-2.166505	1.146193
35	1	0	-2.050793	-3.091657	-0.361323

6) (1R,3R,4S,g^+,*Z*)/ (1S,3S,4R,g^-,*Z*) g^-= -29°



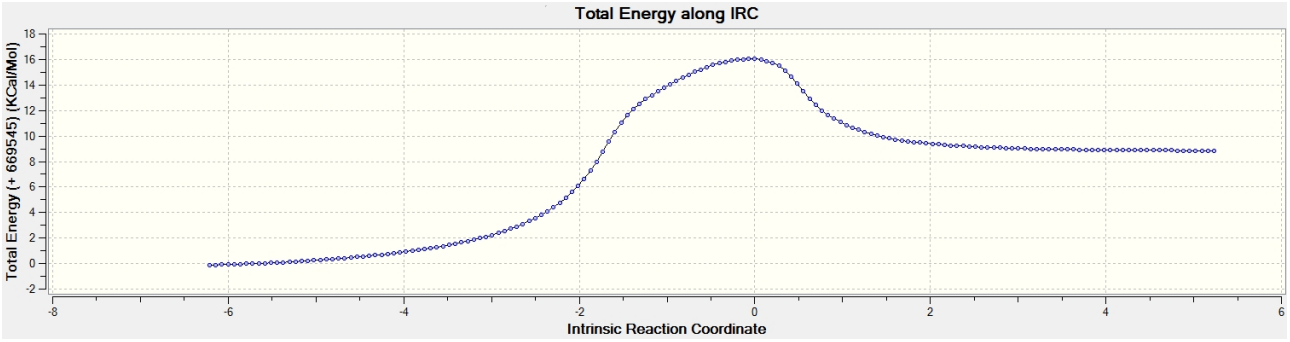
Energy=-1066.97907818 a.u.

Standard orientation:

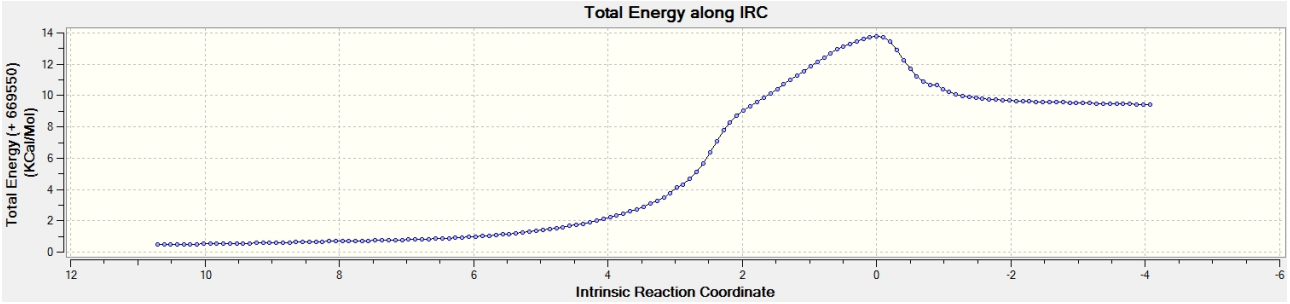
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.742324	-0.358159	-1.361452
2	6	0	1.592733	0.472092	-0.804632
3	8	0	1.000189	-0.374938	0.230593
4	8	0	2.135459	1.609351	-0.200090
5	8	0	0.637056	0.746198	-1.763563
6	1	0	-0.186087	1.070577	-1.339611
7	8	0	-1.951808	1.055026	-0.640670
8	6	0	-2.308741	0.001519	-0.145675
9	6	0	-3.804889	-0.334409	0.034530
10	8	0	-1.554061	-0.973123	0.300376
11	1	0	3.513770	0.278131	-1.800828
12	1	0	2.344598	-1.022952	-2.136026
13	9	0	-4.096068	-0.484785	1.339985
14	9	0	-4.572159	0.639809	-0.462774
15	9	0	-4.106683	-1.483051	-0.596934
16	6	0	1.221355	2.519954	0.429735
17	6	0	2.045974	3.573872	1.145642
18	1	0	0.583220	1.977409	1.138483
19	1	0	0.578168	2.986721	-0.327903
20	1	0	-0.568427	-0.733487	0.215594
21	1	0	1.385361	4.305118	1.624953
22	1	0	2.693307	4.105543	0.439637
23	1	0	2.676348	3.118878	1.917548
24	6	0	3.219858	-1.160567	-0.143313
25	1	0	3.803082	-0.492813	0.503636
26	6	0	1.894791	-1.482546	0.572633
27	1	0	1.453307	-2.390101	0.137729
28	6	0	1.969788	-1.613092	2.083322
29	1	0	2.619233	-2.452906	2.356750
30	1	0	0.979625	-1.803260	2.512368
31	1	0	2.373517	-0.698589	2.531716
32	6	0	4.054959	-2.395035	-0.478864
33	1	0	4.979280	-2.110964	-0.994764
34	1	0	4.339044	-2.944958	0.426219
35	1	0	3.503245	-3.081996	-1.132708

Intrinsic Reaction Coordinates (IRC) for *anti*-1c

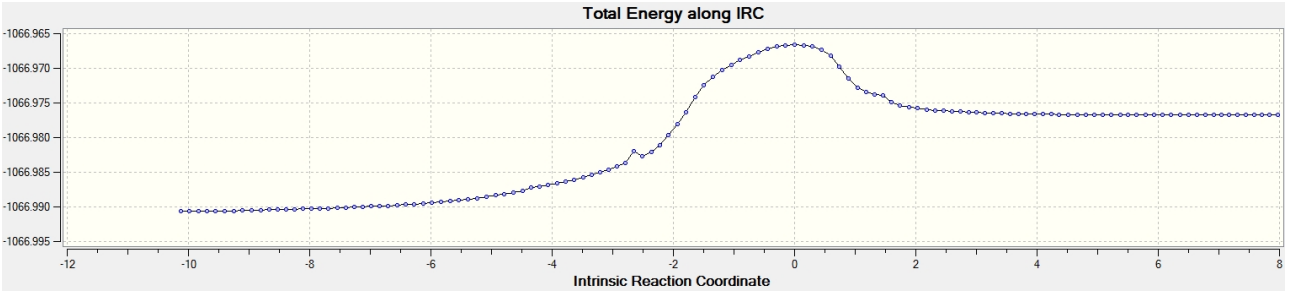
1) (1Re,3S,4R,g^-,*Z*)-***CC***-*anti*-**1c** → (1R,3S,4R,g^-,*Z*)-***TI1***-*anti*-**1c**



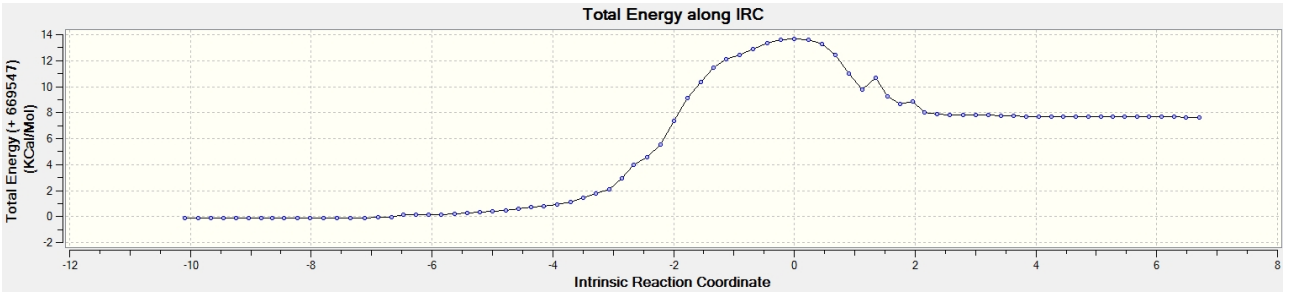
2) (1Si,3S,4R,g^-,*E*)-***CC***-*anti*-**1c** → (1S,3S,4R,g^-,*E*)-***TI1***-*anti*-**1c**



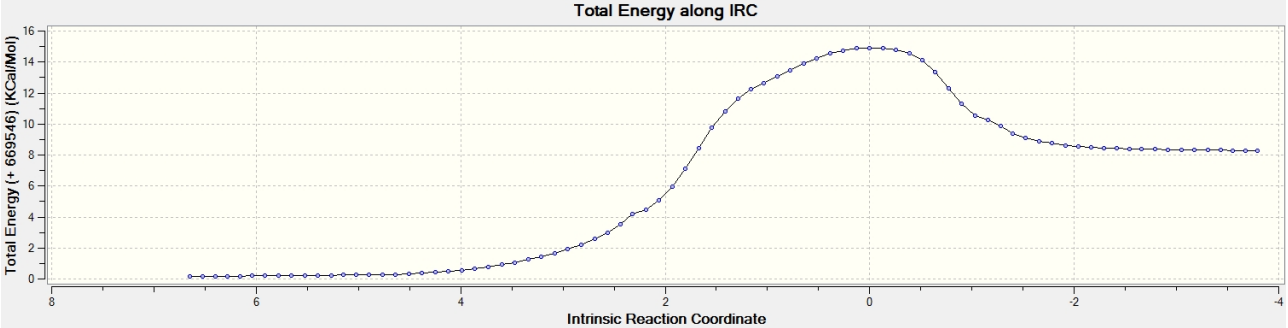
3) (1Si,3S,4R,g^+,*Z*)-***CC***-*anti*-**1c** → (1S,3S,4R,g^+,*Z*)-***TI1***-*anti*-**1c**



4) (1Si,3S,4R,g^-,*Z*)-***CC***-*anti*-**1c** → (1S,3S,4R,g^-,*Z*)-***TI1***-*anti*-**1c**



5) (1Re,3S,4R,g^+,*Z*)-***CC***-*anti*-**1c** → (1R,3S,4R,g^+,*Z*)-***TI1***-*anti*-**1c**



6) (1Re,3S,4R,g^-,*E*)-***CC***-*anti*-**1c** → (1R,3S,4R,g^-,*E*)-***TI1***-*anti*-**1c**

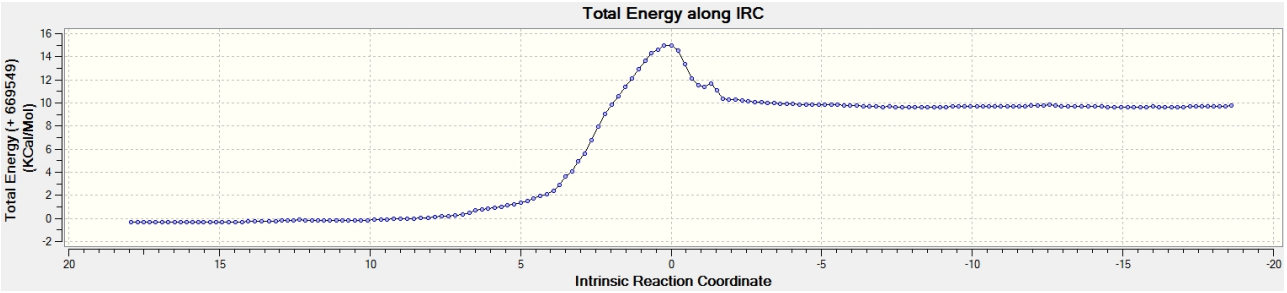


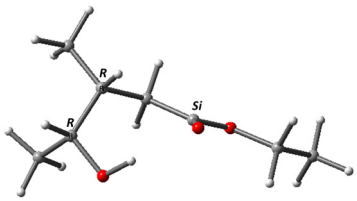
Table SI-3. Winstein-Holness equation applied to the RDS of the *anti*-**1c** lactonization.

Stereochemical descriptor [a]	$\Delta G_i^{\ddagger}$ [b] (kcal mol^{-1})	k_i [c] (s^{-1})	x_i [d] (%)	$k_{(W\text{-}H)i}$ [e] (s^{-1})	**Stereoisomer Contrib.** [g] (%)
(1Re,3S,4R,g^+,*Z*)-***CC***	16.09	16.0	0.2	0.04	<0.01
(1Re,3S,4R,g^-,*E*)-***CC***	15.17	72.8	32.9	24.0	1.4
(1Re,3S,4R,g^-,*Z*)-***CC***	16.53	33.9	14.4	4.9	0.3
(1Re,3R,4S,g^-,*Z*)-***CC***	14.40	262.6	0.8	2.1	0.1
(1Re,3R,4S,g^+,*E*)-***CC***	12.87	3341.7	49.1	1640.2	98
(1Re,3R,4S,g^+,*Z*)-***CC***	14.87	120.2	2.6	3.2	0.2
(1Re,3R,4S,g^-,*E*)-***CC***	-[h]	-[h]	-[h]	-[h]	-[h]
(1Re,3S,4R,g^+,*E*)-***CC***	-[h]	-[h]	-[h]	-[h]	-[h]
Ensemble	**13.28** [c]			**1674.2** [f]	

[a] Arbitrary we chosen 1Re stereochemical configuration;
[b] $H_{TS} - H_{CC}$;
[c] Calculated with Eyring equantion;
[d] Calculated as Boltzman distribution;
[e] $x_i \cdot k_i$;
[f] $\sum k_{(W\text{-}H)i}$;
[g] $k_{(W\text{-}H)i} / k_{W\text{-}H} \cdot 100$;
[h] Not found.

Esters: (*syn*)-**1c**

1) (1Si,3R,4R, g^+)/ (1Re,3S,4S,g^-) g^+=50.0 °



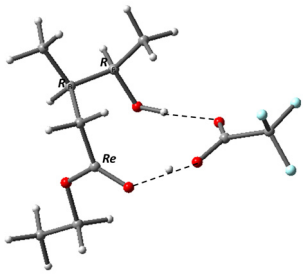
Energy= -540.18588907a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.911458	-0.772834	1.306825
2	6	0	2.332749	-0.690936	-0.103426
3	6	0	1.647809	0.653872	-0.461167
4	6	0	0.304315	0.867501	0.260791
5	6	0	-0.872671	0.142322	-0.362614
6	8	0	-0.838697	-0.552762	-1.366988
7	8	0	-2.002232	0.382965	0.318598
8	6	0	-3.214369	-0.245642	-0.179897
9	6	0	2.586610	1.847767	-0.234911
10	1	0	3.301193	-1.782698	1.476294
11	1	0	3.735896	-0.066251	1.446059
12	1	0	2.150450	-0.577817	2.071401
13	8	0	1.429983	-1.792654	-0.230907
14	1	0	1.429065	0.607762	-1.536905
15	1	0	0.355444	0.581960	1.318170
16	1	0	0.041243	1.933714	0.258347
17	6	0	-4.339278	0.119602	0.766681
18	1	0	-3.400905	0.114079	-1.196570
19	1	0	-3.052122	-1.326681	-0.225901
20	1	0	2.164206	2.759872	-0.672670
21	1	0	2.755903	2.040094	0.831016
22	1	0	3.563282	1.677874	-0.704258
23	1	0	0.829805	-1.599486	-0.974111
24	1	0	3.166932	-0.814526	-0.816247
25	1	0	-4.488385	1.204127	0.804379
26	1	0	-4.133493	-0.239684	1.780618
27	1	0	-5.270683	-0.342643	0.421065

Catalytic complex TFA·E: ***CC***-(*syn*)-**1c**

1) (1Re,3R,4R,g^+,*E*)/ (1Si,3S,4S,g^-,*E*) g^+=53.3 °

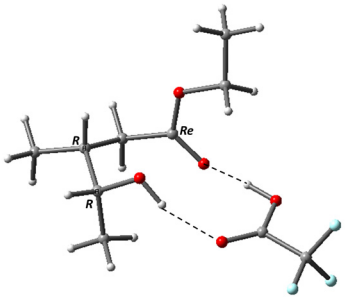


Energy= -1066.99219964 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	1.739849	-0.944128	0.984042
2	6	0	2.275064	-0.415445	-0.090285
3	6	0	3.814343	-0.371154	0.032853
4	8	0	1.712786	-0.005673	-1.087147
5	9	0	4.185403	0.237978	1.173814
6	9	0	4.353383	0.290817	-0.996083
7	9	0	4.314383	-1.621349	0.044843
8	1	0	0.734065	-1.062224	0.870643
9	6	0	-0.107095	2.773732	-0.620536
10	6	0	-1.383697	1.997095	-0.943481
11	6	0	-1.769752	0.692190	1.232311
12	6	0	-1.761980	-0.712398	0.677949
13	8	0	-2.965480	-1.117019	0.291678
14	6	0	-3.072431	-2.447402	-0.291741
15	1	0	0.480473	2.293838	0.170858
16	1	0	-0.335876	3.794902	-0.299606
17	1	0	0.522116	2.838181	-1.515117
18	8	0	-1.096227	0.738694	-1.568639
19	1	0	-0.754852	0.937085	1.559095
20	1	0	-2.402433	0.668174	2.129191
21	6	0	-4.524240	-2.661087	-0.663993
22	1	0	-0.171279	0.491125	-1.381436
23	1	0	-1.953056	2.581880	-1.680050
24	8	0	-0.785911	-1.465441	0.647036
25	1	0	-4.641056	-3.653921	-1.112472
26	1	0	-4.858497	-1.914337	-1.391911
27	1	0	-5.171325	-2.604754	0.217810
28	1	0	-2.412585	-2.489892	-1.162794
29	1	0	-2.723001	-3.177565	0.443777
30	6	0	-2.329303	1.756597	0.259769
31	1	0	-3.255869	1.346824	-0.160007
32	6	0	-2.680956	3.050719	1.004521
33	1	0	-3.015178	3.827354	0.305631
34	1	0	-3.493907	2.878831	1.719649
35	1	0	-1.826115	3.448945	1.563617

2) (1Re,3R,4R,g^+,*Z*)/ (1Si,3S,4S,g^-,*Z*) g^+=67 °

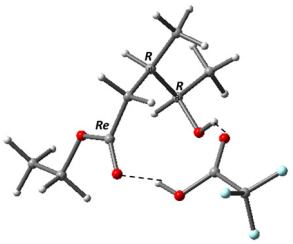


Energy=-1066.99104190 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.000816	0.014850	1.018182
2	6	0	1.734973	0.820899	0.866833
3	8	0	1.217714	-0.763931	-1.265484
4	8	0	1.905269	1.901131	0.111078
5	8	0	0.677346	0.530338	1.426786
6	1	0	-0.890673	0.609478	1.028873
7	8	0	-1.892053	0.604876	0.893137
8	6	0	-2.265263	-0.367093	0.091291
9	6	0	-3.803664	-0.384882	-0.048704
10	8	0	-1.569716	-1.172162	-0.493571
11	1	0	2.859412	-0.673183	1.855784
12	1	0	3.816586	0.700340	1.274623
13	9	0	-4.192295	-1.359570	-0.876529
14	9	0	-4.384123	-0.584307	1.148840
15	9	0	-4.243565	0.790459	-0.536191
16	6	0	0.737634	2.705802	-0.204922
17	6	0	1.219522	3.936739	-0.943778
18	1	0	0.223673	2.963616	0.725747
19	1	0	0.069924	2.097862	-0.823353
20	1	0	0.351154	-1.100048	-0.973215
21	1	0	0.358988	4.559163	-1.212794
22	1	0	1.746665	3.662354	-1.863486
23	1	0	1.892223	4.533057	-0.318106
24	6	0	3.395212	-0.755800	-0.269203
25	1	0	3.579283	-0.006566	-1.050020
26	6	0	2.257040	-1.644489	-0.816945
27	1	0	2.662197	-2.167908	-1.697934
28	6	0	1.723089	-2.698666	0.152551
29	1	0	0.957984	-3.308307	-0.343131
30	1	0	2.518974	-3.375175	0.482538
31	1	0	1.267202	-2.241033	1.037091
32	6	0	4.693935	-1.537825	-0.040347
33	1	0	4.984209	-2.086602	-0.944450
34	1	0	5.517690	-0.861567	0.215892
35	1	0	4.596113	-2.263945	0.775549

3) (1Re,3R,4R,g^-,*E*)/ (1Si,3S,4S,g^+,*E*) g^-=-37.3 °

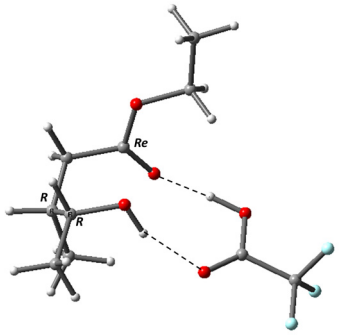


Energy=-1066.98665168 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.928627	1.669859	-0.777451
2	6	0	-1.390543	0.333668	1.353543
3	6	0	-1.649657	-0.942103	0.593111
4	8	0	-0.707404	1.113368	-1.276408
5	8	0	-2.944920	-1.178420	0.397902
6	8	0	-0.780204	-1.728890	0.222673
7	1	0	0.821289	-1.369052	0.118422
8	8	0	1.829102	-1.401542	0.025816
9	6	0	2.387788	-0.214035	0.017161
10	6	0	3.923124	-0.349851	-0.102948
11	8	0	1.859026	0.875686	0.106357
12	6	0	-2.188566	3.050755	-1.381756
13	1	0	-2.697535	0.987644	-1.158153
14	1	0	-1.773350	0.186778	2.371887
15	1	0	-0.307150	0.445494	1.426950
16	9	0	4.257774	-1.074142	-1.185894
17	9	0	4.422068	-0.969254	0.984556
18	9	0	4.497732	0.853603	-0.203829
19	6	0	-3.304350	-2.397598	-0.317689
20	6	0	-4.811114	-2.408650	-0.462941
21	1	0	-2.795434	-2.390937	-1.285444
22	1	0	-2.939468	-3.253112	0.258183
23	1	0	-1.397354	3.761393	-1.117200
24	1	0	-2.217968	2.972258	-2.473925
25	1	0	-3.147215	3.463002	-1.042609
26	1	0	0.048995	1.485252	-0.789531
27	1	0	-5.116352	-3.316131	-0.995604
28	1	0	-5.302680	-2.402775	0.515754
29	1	0	-5.158584	-1.541628	-1.034846
30	6	0	-2.016498	1.629964	0.773258
31	1	0	-3.085661	1.637913	1.020277
32	6	0	-1.357310	2.828185	1.476294
33	1	0	-1.860525	3.768829	1.232375
34	1	0	-1.400044	2.703942	2.564955
35	1	0	-0.299411	2.926506	1.200799

4) (1Re,3R,4R,g^-,*Z*)/ (1Si,3S,4S,g^+,*Z*) g^-=-55.9 °

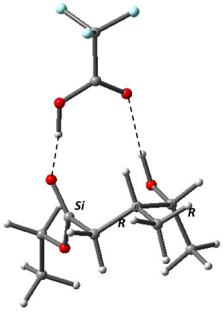


Energy= -1066.99101244 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.101212	-0.048278	-0.922028
2	6	0	-1.925085	0.887004	-0.770705
3	8	0	-1.298395	-0.752735	1.267256
4	8	0	-2.187802	1.922999	0.020517
5	8	0	-0.864864	0.748884	-1.382727
6	1	0	0.696442	0.847281	-0.947839
7	8	0	1.690471	0.865114	-0.771598
8	6	0	2.086802	-0.228367	-0.159253
9	6	0	3.615921	-0.197511	0.060150
10	8	0	1.414421	-1.165373	0.220689
11	1	0	-3.934418	0.340123	-0.329708
12	1	0	-3.397646	-0.014903	-1.978004
13	9	0	4.262080	-0.022488	-1.106573
14	9	0	4.036907	-1.339710	0.612054
15	9	0	3.947175	0.819705	0.878258
16	6	0	-1.132836	2.900591	0.233048
17	6	0	-1.715421	4.020366	1.069596
18	1	0	-0.303738	2.403413	0.745588
19	1	0	-0.781379	3.255064	-0.740662
20	1	0	-0.496874	-1.118141	0.847144
21	1	0	-0.942594	4.773821	1.257403
22	1	0	-2.549923	4.505539	0.552245
23	1	0	-2.071506	3.645710	2.034975
24	6	0	-2.811541	-1.520135	-0.526338
25	1	0	-3.776704	-2.037893	-0.618795
26	6	0	-2.413812	-1.599589	0.968064
27	1	0	-3.239251	-1.162959	1.544770
28	6	0	-2.174010	-3.022080	1.474699
29	1	0	-1.294711	-3.474070	1.000862
30	1	0	-2.001423	-3.007481	2.556276
31	1	0	-3.037369	-3.667945	1.273592
32	6	0	-1.825188	-2.217690	-1.476654
33	1	0	-1.813559	-3.298630	-1.300251
34	1	0	-2.120026	-2.058936	-2.520520
35	1	0	-0.803125	-1.844523	-1.367296

5) (1Re,3S,4S,g^-,*E*)/ (1Si,3R,4R,g^+,*E*) g^+=58.2 °

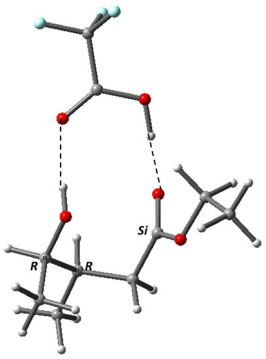


Energy= -1066.99417066 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.305163	1.906599	0.926987
2	6	0	-1.885540	0.816988	-1.340281
3	6	0	-1.815755	-0.596787	-0.812931
4	8	0	-1.160880	0.623617	1.542477
5	8	0	-2.998634	-1.067611	-0.437329
6	8	0	-0.802040	-1.298159	-0.793906
7	1	0	0.751401	-0.931669	-0.904220
8	8	0	1.763301	-0.854753	-0.956608
9	6	0	2.266719	-0.397685	0.165426
10	6	0	3.810277	-0.384470	0.103626
11	8	0	1.675657	-0.027224	1.160983
12	6	0	-2.709296	2.393480	1.270196
13	1	0	-0.578197	2.609303	1.366261
14	1	0	-2.927285	1.147399	-1.337499
15	1	0	-1.556388	0.774126	-2.386427
16	9	0	4.239528	0.256363	-0.998478
17	9	0	4.321324	0.227460	1.176678
18	9	0	4.282435	-1.644892	0.065387
19	6	0	-3.035707	-2.414671	0.115840
20	6	0	-4.473479	-2.714091	0.482988
21	1	0	-2.373559	-2.440440	0.985719
22	1	0	-2.648644	-3.109250	-0.635276
23	1	0	-3.471748	1.705849	0.888167
24	1	0	-2.900071	3.391506	0.862882
25	1	0	-2.822036	2.443029	2.358468
26	1	0	-0.229311	0.346474	1.443346
27	1	0	-4.535976	-3.722530	0.906886
28	1	0	-5.124221	-2.671467	-0.396974
29	1	0	-4.846129	-2.004287	1.228937
30	6	0	-0.986860	1.825295	-0.586423
31	1	0	0.047463	1.463402	-0.661184
32	6	0	-1.039791	3.196774	-1.272582
33	1	0	-0.436328	3.931077	-0.725397
34	1	0	-0.646430	3.138627	-2.294152
35	1	0	-2.063790	3.582915	-1.333833

6) (1Re,3S,4S,g^-,*Z*)/ (1Si,3R,4R,g^+,*Z*) g^+=54.4 °

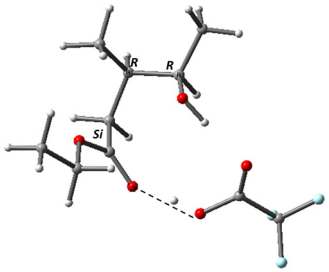


Energy=-1066.99269360 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.232311	-1.647224	0.883076
2	6	0	2.859122	-0.055666	-1.038428
3	6	0	1.678795	0.867370	-0.866761
4	8	0	1.189425	-0.747243	1.272006
5	8	0	1.955238	1.958217	-0.161512
6	8	0	0.588710	0.651944	-1.398365
7	1	0	-0.968863	0.748011	-0.963355
8	8	0	-1.961249	0.715970	-0.782340
9	6	0	-2.278133	-0.363729	-0.102568
10	6	0	-3.808920	-0.455751	0.081566
11	8	0	-1.537503	-1.218773	0.338642
12	6	0	3.408456	-1.367451	1.813713
13	1	0	1.903250	-2.685637	1.050545
14	1	0	3.720425	0.338320	-0.493390
15	1	0	3.109634	-0.041416	-2.107136
16	9	0	-4.296205	0.681150	0.610014
17	9	0	-4.407004	-0.653997	-1.108477
18	9	0	-4.126916	-1.471026	0.890649
19	6	0	0.879464	2.912573	0.059861
20	6	0	1.454396	4.066050	0.854408
21	1	0	0.078713	2.405343	0.606549
22	1	0	0.491555	3.233326	-0.911741
23	1	0	3.764453	-0.336188	1.711697
24	1	0	4.244710	-2.046704	1.619896
25	1	0	3.090788	-1.507421	2.852478
26	1	0	0.358225	-1.024083	0.841272
27	1	0	0.667301	4.803812	1.045104
28	1	0	2.262842	4.559884	0.304975
29	1	0	1.844099	3.722619	1.818377
30	6	0	2.536898	-1.511131	-0.629430
31	1	0	1.612048	-1.787606	-1.154120
32	6	0	3.643562	-2.465675	-1.095247
33	1	0	3.444780	-3.490660	-0.758868
34	1	0	3.707295	-2.482754	-2.189508
35	1	0	4.627199	-2.171102	-0.711038

7) (1Re,3S,4S,g^+,*E*)/ (1Si,3R,4R,g^-,*E*) g^-=-63 °

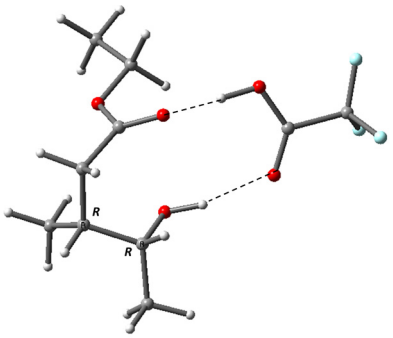


Energy=-1066.99215746 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-1.810935	-1.105648	0.759277
2	6	0	-2.346742	-0.369856	-0.183739
3	6	0	-3.882778	-0.318990	-0.024812
4	8	0	-1.790465	0.218719	-1.091080
5	9	0	-4.216130	0.145194	1.194027
6	9	0	-4.429008	0.480503	-0.946497
7	9	0	-4.408266	-1.550345	-0.161611
8	1	0	-0.802848	-1.200791	0.635261
9	6	0	0.980178	3.444201	-0.753101
10	6	0	0.869624	2.047664	-0.141254
11	6	0	1.643900	0.372709	1.601279
12	6	0	1.693402	-0.839381	0.698798
13	8	0	2.921935	-1.149692	0.303347
14	6	0	3.070150	-2.293505	-0.587852
15	1	0	1.902178	3.547857	-1.334785
16	1	0	0.136432	3.622066	-1.429349
17	1	0	0.967247	4.222385	0.020342
18	8	0	0.969467	1.057118	-1.173942
19	1	0	0.648591	0.394125	2.055960
20	1	0	2.373132	0.208712	2.403650
21	6	0	4.540267	-2.416076	-0.927162
22	1	0	0.079091	0.682795	-1.306174
23	1	0	-0.114256	1.963955	0.343588
24	8	0	0.726018	-1.546301	0.405178
25	1	0	4.686938	-3.274010	-1.592712
26	1	0	4.903816	-1.518899	-1.438981
27	1	0	5.142620	-2.574342	-0.026194
28	1	0	2.455081	-2.116127	-1.474385
29	1	0	2.690719	-3.181785	-0.074597
30	6	0	1.933894	1.745511	0.934052
31	1	0	1.794685	2.483499	1.736484
32	6	0	3.373868	1.879791	0.418722
33	1	0	4.093469	1.564643	1.183184
34	1	0	3.542008	1.270286	-0.472949
35	1	0	3.599008	2.921490	0.166555

8) (1Re,3S,4S,g^+,*Z*)/ (1Si,3R,4R,g^-,*Z*) g^-=-73.2 °



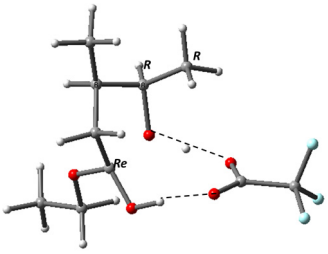
Energy=-1066.98997679 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.939471	0.050123	1.393406
2	6	0	-1.731807	0.867018	1.003808
3	8	0	-1.217613	-1.116271	-0.817875
4	8	0	-1.997718	1.811071	0.106531
5	8	0	-0.623487	0.694488	1.512490
6	1	0	0.904335	0.781410	1.004456
7	8	0	1.895904	0.810340	0.804892
8	6	0	2.285759	-0.265063	0.163711
9	6	0	3.808121	-0.275683	-0.100731
10	8	0	1.612369	-1.202974	-0.217377
11	1	0	-3.800512	0.717842	1.503531
12	1	0	-2.714041	-0.387470	2.369750
13	9	0	4.370287	-1.295859	0.572602
14	9	0	4.031612	-0.466419	-1.412396
15	9	0	4.413351	0.859917	0.270606
16	6	0	-0.891677	2.620589	-0.380319
17	6	0	-1.475009	3.706340	-1.259520
18	1	0	-0.214538	1.967220	-0.939091
19	1	0	-0.355377	3.034362	0.478761
20	1	0	-0.283521	-1.284281	-0.595472
21	1	0	-0.664246	4.332366	-1.648281
22	1	0	-2.160848	4.345077	-0.692991
23	1	0	-2.016002	3.276961	-2.109167
24	6	0	-3.294757	-1.086018	0.387719
25	1	0	-3.981714	-1.747359	0.932454
26	6	0	-2.041493	-1.917134	0.039405
27	1	0	-1.502236	-2.116805	0.977728
28	6	0	-2.353514	-3.258954	-0.624866
29	1	0	-1.423409	-3.808635	-0.810614
30	1	0	-2.991305	-3.882003	0.014747
31	1	0	-2.856632	-3.119392	-1.587580
32	6	0	-4.027557	-0.556720	-0.852901
33	1	0	-4.360347	-1.379039	-1.495745
34	1	0	-4.917886	0.012067	-0.559620
35	1	0	-3.386168	0.098698	-1.447721

Transition States: ***TS1*‡-(*syn*)-1c**

1) (1Re,3R,4R,g^+,*E*)/ (1Si,3S,4S,g^-,*E*) g^+=32.0 °

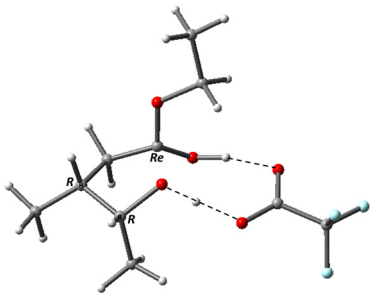


Energy=-1066.96869391 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.279328	1.494709	-1.013738
2	6	0	-1.945742	0.946804	1.254565
3	6	0	-1.673996	-0.421475	0.654464
4	8	0	-0.973932	0.073520	-0.765392
5	8	0	-2.825463	-1.025909	0.301819
6	8	0	-0.798475	-1.259461	1.224354
7	1	0	0.083290	-0.808354	1.398016
8	8	0	1.649294	-0.288679	1.323496
9	6	0	2.074118	-0.372856	0.157689
10	6	0	3.608919	-0.329160	-0.039640
11	8	0	1.419984	-0.445589	-0.928637
12	6	0	-0.005209	2.328447	-0.991855
13	1	0	-1.725006	1.532657	-2.011712
14	1	0	-2.738508	0.866170	2.003293
15	1	0	-1.036688	1.308138	1.747482
16	9	0	4.008626	-1.141389	-1.034957
17	9	0	4.267969	-0.684669	1.074721
18	9	0	3.987883	0.929874	-0.359724
19	6	0	-2.738841	-2.357777	-0.270638
20	6	0	-4.111755	-2.704486	-0.810297
21	1	0	-1.983926	-2.352944	-1.063589
22	1	0	-2.424322	-3.058683	0.507592
23	1	0	0.472063	2.330956	-0.006330
24	1	0	0.715996	1.952523	-1.723163
25	1	0	-0.243705	3.362126	-1.261556
26	1	0	0.116523	-0.184315	-0.817848
27	1	0	-4.093544	-3.715676	-1.231769
28	1	0	-4.864184	-2.679018	-0.014334
29	1	0	-4.414196	-2.007079	-1.598783
30	6	0	-2.334541	1.839155	0.069066
31	1	0	-3.304235	1.486334	-0.300640
32	6	0	-2.460377	3.323799	0.408822
33	1	0	-2.698581	3.916657	-0.482182
34	1	0	-3.270666	3.476836	1.130498
35	1	0	-1.541353	3.725301	0.848911

2) (1Re,3R,4R,g^+,*Z*)/ (1Si,3S,4S,g^-,*Z*) g^+=41.7 °

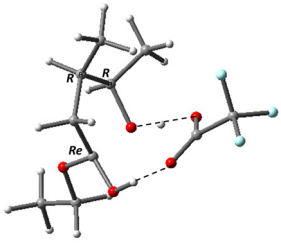


Energy=-1066.96636181 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.963029	-0.021563	0.910079
2	6	0	1.628376	0.653549	0.639604
3	8	0	1.082516	-0.322002	-0.633152
4	8	0	1.792979	1.859761	0.055997
5	8	0	0.733875	0.519155	1.621859
6	1	0	-0.219853	0.730001	1.352080
7	8	0	-1.789088	0.717484	0.969434
8	6	0	-2.091884	-0.178004	0.155613
9	6	0	-3.601189	-0.456119	-0.058849
10	8	0	-1.340697	-0.901404	-0.558718
11	1	0	3.711753	0.738579	1.145997
12	1	0	2.844793	-0.675565	1.778206
13	9	0	-3.876075	-1.767570	0.098266
14	9	0	-3.965452	-0.111278	-1.314094
15	9	0	-4.375679	0.231478	0.795213
16	6	0	0.624669	2.666843	-0.236625
17	6	0	1.110727	3.931915	-0.913875
18	1	0	-0.044063	2.098986	-0.892115
19	1	0	0.099350	2.892522	0.696781
20	1	0	0.047642	-0.600775	-0.550125
21	1	0	0.253165	4.571777	-1.148978
22	1	0	1.788274	4.490856	-0.259640
23	1	0	1.635857	3.700742	-1.846659
24	6	0	3.339243	-0.828282	-0.346224
25	1	0	3.647818	-0.115559	-1.121325
26	6	0	2.008751	-1.443372	-0.819236
27	1	0	2.031489	-1.635558	-1.896301
28	6	0	1.519185	-2.680596	-0.078146
29	1	0	0.517643	-2.957431	-0.422983
30	1	0	2.186082	-3.524649	-0.281567
31	1	0	1.476569	-2.522815	1.004337
32	6	0	4.471373	-1.828662	-0.121983
33	1	0	4.673769	-2.407314	-1.031006
34	1	0	5.394693	-1.303989	0.147756
35	1	0	4.239521	-2.531675	0.685576

3) (1Re,3R,4R,g^-,*E*)/ (1Si,3S,4S,g^-,*E*) g^-=-19.7 °

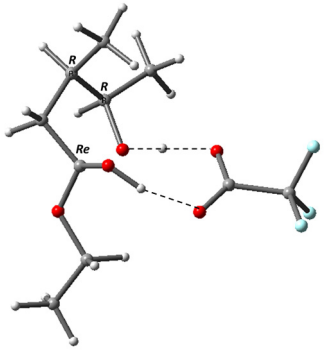


Energy=-1066.96769407 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.447294	1.620007	0.592000
2	6	0	1.261545	0.509967	-1.602974
3	6	0	1.682146	-0.531214	-0.566772
4	8	0	1.129185	0.195308	0.781426
5	8	0	3.026892	-0.560530	-0.429823
6	8	0	1.127158	-1.751670	-0.586559
7	1	0	0.135408	-1.687246	-0.737077
8	8	0	-1.503027	-1.466191	-0.786371
9	6	0	-1.940816	-0.721767	0.106907
10	6	0	-3.470400	-0.494103	0.158819
11	8	0	-1.306090	-0.055071	0.982748
12	6	0	0.692040	2.456437	1.608473
13	1	0	2.517654	1.674776	0.800764
14	1	0	1.955540	0.469455	-2.445881
15	1	0	0.269649	0.233582	-1.972657
16	9	0	-4.144550	-1.410315	-0.551993
17	9	0	-3.757773	0.724265	-0.357126
18	9	0	-3.934817	-0.522959	1.421621
19	6	0	3.583764	-1.545232	0.482266
20	6	0	5.058780	-1.232781	0.633296
21	1	0	3.056978	-1.480547	1.439836
22	1	0	3.426285	-2.543050	0.063560
23	1	0	-0.391180	2.395900	1.476094
24	1	0	0.938434	2.130018	2.624194
25	1	0	0.995056	3.504434	1.509995
26	1	0	0.023816	0.028510	0.870520
27	1	0	5.520952	-1.967496	1.301987
28	1	0	5.570639	-1.279784	-0.334080
29	1	0	5.210841	-0.235581	1.060462
30	6	0	1.215831	1.904946	-0.922445
31	1	0	2.058322	2.512659	-1.269062
32	6	0	-0.081615	2.650465	-1.259494
33	1	0	-0.095653	3.654628	-0.822450
34	1	0	-0.174611	2.763262	-2.345952
35	1	0	-0.968237	2.112459	-0.904588

4) (1Re,3R,4R,g^-,*Z*)/ (1Si,3S,4S,g^+,*Z*) g^-=-39.6 °

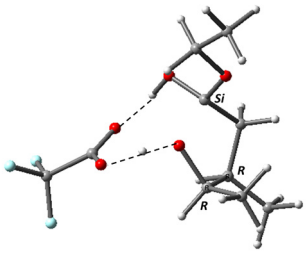


Energy=-1066.96572378 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.083720	-0.363976	-0.768439
2	6	0	-1.876144	0.523119	-0.505089
3	8	0	-1.180162	-0.330876	0.780798
4	8	0	-2.230802	1.705318	0.037277
5	8	0	-0.966353	0.506135	-1.484881
6	1	0	-0.050210	0.847667	-1.214258
7	8	0	1.504698	1.039093	-0.843279
8	6	0	1.916281	0.081224	-0.157082
9	6	0	3.450411	-0.087618	-0.023532
10	8	0	1.255808	-0.791143	0.474846
11	1	0	-3.931751	0.046809	-0.214004
12	1	0	-3.316881	-0.331431	-1.836210
13	9	0	4.131588	0.784737	-0.783208
14	9	0	3.827338	-1.332016	-0.384817
15	9	0	3.832661	0.097462	1.259481
16	6	0	-1.219278	2.729623	0.216955
17	6	0	-1.904007	3.926827	0.843682
18	1	0	-0.428560	2.337789	0.865210
19	1	0	-0.787313	2.983028	-0.756312
20	1	0	-0.150834	-0.566012	0.590416
21	1	0	-1.173561	4.729687	0.991235
22	1	0	-2.703279	4.302960	0.196243
23	1	0	-2.334050	3.668117	1.816997
24	6	0	-2.749031	-1.786689	-0.275444
25	1	0	-3.681466	-2.318750	-0.053814
26	6	0	-2.019708	-1.510888	1.052652
27	1	0	-2.748505	-1.157750	1.789386
28	6	0	-1.185763	-2.625781	1.657487
29	1	0	-0.402245	-2.972878	0.978770
30	1	0	-0.716093	-2.293165	2.588680
31	1	0	-1.840352	-3.472569	1.892346
32	6	0	-1.943182	-2.606615	-1.291177
33	1	0	-1.771287	-3.626189	-0.930202
34	1	0	-2.496811	-2.679428	-2.234255
35	1	0	-0.971755	-2.153102	-1.511488

5) (1Re,3S,4S,g^-,*E*)/ (1Si,3R,4R,g^+,*E*) g^+=39.6 °

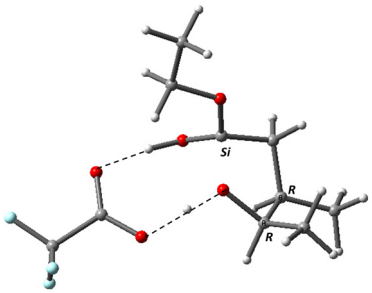


Energy=-1066.96944327 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.971349	0.040243	0.768716
2	6	0	-1.072514	1.493593	0.948387
3	6	0	-0.991060	2.034467	-0.493490
4	6	0	-1.823247	1.032297	-1.312088
5	6	0	-1.647794	-0.359343	-0.694788
6	8	0	-0.782572	-1.227281	-1.245783
7	8	0	-2.839562	-0.918702	-0.413447
8	6	0	-2.840782	-2.277310	0.102226
9	6	0	-4.262256	-2.597563	0.516471
10	6	0	-2.334498	1.806860	1.737230
11	8	0	1.424751	-0.411024	0.968980
12	6	0	2.103697	-0.371075	-0.104963
13	8	0	1.706533	-0.326843	-1.281669
14	6	0	3.631815	-0.359746	0.143129
15	1	0	0.115919	-0.244677	0.818257
16	1	0	0.118021	-0.807547	-1.390923
17	1	0	-0.189487	1.781857	1.526479
18	1	0	-3.241812	1.521241	1.195936
19	1	0	-2.384157	2.877703	1.960363
20	1	0	-2.318797	1.263783	2.687741
21	1	0	-2.886737	1.284814	-1.275480
22	1	0	-1.518597	0.999112	-2.361679
23	1	0	0.056793	1.935763	-0.803770
24	1	0	-2.487949	-2.954778	-0.679959
25	1	0	-2.151546	-2.332001	0.951131
26	1	0	-4.946345	-2.520561	-0.335572
27	1	0	-4.307471	-3.622646	0.900865
28	1	0	-4.607224	-1.918512	1.303494
29	9	0	4.331039	-0.419463	-0.999941
30	9	0	3.999299	-1.404936	0.911221
31	9	0	3.991506	0.770811	0.789665
32	6	0	-1.413228	3.491419	-0.674845
33	1	0	-0.808422	4.157918	-0.048529
34	1	0	-1.274595	3.802673	-1.716286
35	1	0	-2.467411	3.645401	-0.418553

6) (1Re,3S,4S,g^-,*Z*)/ (1Si,3R,4R,g^+,*Z*) g^+=32.4 °

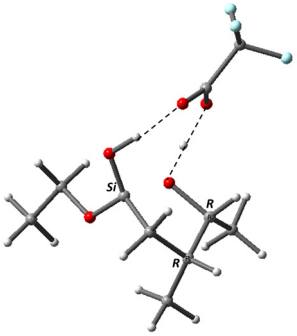


Energy=-1066.96761369 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.943400	0.073123	-0.869106
2	6	0	1.608810	0.727091	-0.580278
3	8	0	1.093362	-0.316957	0.645258
4	8	0	1.732474	1.923754	0.024904
5	8	0	0.729042	0.589003	-1.579044
6	1	0	-0.235371	0.744081	-1.311763
7	8	0	-1.808986	0.684701	-0.951100
8	6	0	-2.092059	-0.202745	-0.121808
9	6	0	-3.588895	-0.577150	0.019088
10	8	0	-1.324970	-0.880195	0.620200
11	1	0	3.690615	0.470442	-0.175703
12	1	0	3.245619	0.320608	-1.890562
13	9	0	-3.829648	-1.748470	-0.612539
14	9	0	-3.939723	-0.731715	1.310886
15	9	0	-4.397110	0.351395	-0.517564
16	6	0	0.559712	2.762694	0.185364
17	6	0	1.012622	4.035996	0.869933
18	1	0	-0.181671	2.229449	0.790067
19	1	0	0.129732	2.970833	-0.799301
20	1	0	0.041444	-0.548507	0.585493
21	1	0	0.153803	4.702934	1.003242
22	1	0	1.764118	4.557447	0.267550
23	1	0	1.440320	3.821597	1.854880
24	6	0	2.731698	-1.435377	-0.672835
25	1	0	2.075692	-1.781081	-1.480704
26	6	0	1.921162	-1.535772	0.640193
27	1	0	1.228861	-2.382239	0.607153
28	6	0	2.714813	-1.561630	1.937060
29	1	0	3.278897	-2.496413	2.020669
30	1	0	2.031587	-1.501970	2.790409
31	1	0	3.417104	-0.723589	2.001232
32	6	0	4.020588	-2.256119	-0.706907
33	1	0	3.818543	-3.319178	-0.530996
34	1	0	4.498327	-2.170493	-1.689369
35	1	0	4.742214	-1.917923	0.044667

7) (1Re,3S,4S,g^+,*E*)/ (1Si,3R,4R,g^-,*E*) g^-=-32.4 °

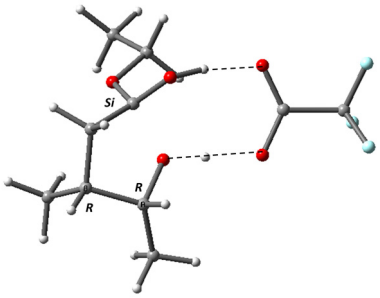


Energy=-1066.96932452 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.663255	0.612036	1.686336
2	6	0	1.493771	-0.547090	0.711708
3	8	0	0.864891	0.284440	-0.569354
4	8	0	2.681397	-1.026808	0.291527
5	8	0	0.613639	-1.522321	0.987726
6	1	0	-0.281048	-1.139590	1.236515
7	8	0	-1.832722	-0.562389	1.261694
8	6	0	-2.219851	-0.273312	0.116619
9	6	0	-3.744437	-0.141660	-0.117846
10	8	0	-1.532640	-0.046381	-0.928255
11	1	0	2.451922	0.371308	2.404222
12	1	0	0.722537	0.728743	2.234109
13	9	0	-4.138925	-0.912297	-1.151027
14	9	0	-4.454951	-0.501803	0.961495
15	9	0	-4.062859	1.137306	-0.415504
16	6	0	2.663144	-2.169409	-0.606091
17	6	0	4.081852	-2.381442	-1.093493
18	1	0	1.980763	-1.956266	-1.435375
19	1	0	2.291287	-3.041613	-0.061883
20	1	0	-0.217677	0.042893	-0.733310
21	1	0	4.112405	-3.251631	-1.758771
22	1	0	4.760889	-2.567626	-0.254396
23	1	0	4.444278	-1.510491	-1.649892
24	6	0	1.960755	1.874890	0.856364
25	1	0	1.665110	2.760282	1.430341
26	6	0	0.978595	1.735578	-0.329566
27	1	0	-0.013655	2.063887	0.000206
28	6	0	1.336239	2.421968	-1.634325
29	1	0	1.419633	3.503142	-1.474160
30	1	0	2.284261	2.053314	-2.036378
31	1	0	0.552541	2.252535	-2.380132
32	6	0	3.439591	2.027109	0.476645
33	1	0	3.610476	2.952727	-0.083191
34	1	0	4.050116	2.076572	1.385709
35	1	0	3.802775	1.188621	-0.123107

8) (1Re,3S,4S,g^+,*Z*)/ (1Si,3R,4R,g^-,*Z*) g^-=-44.4 °



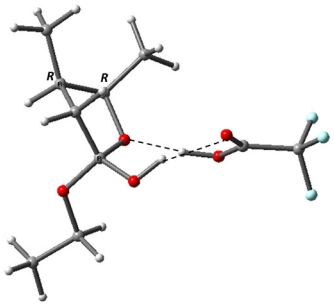
Energy= -1066.96654477 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.833313	-0.135323	-1.407828
2	6	0	1.606840	0.575065	-0.847085
3	8	0	1.084039	-0.628024	0.255469
4	8	0	1.934681	1.605460	-0.044055
5	8	0	0.615280	0.717750	-1.725999
6	1	0	-0.288187	0.941123	-1.316838
7	8	0	-1.803205	0.965419	-0.798289
8	6	0	-2.126505	-0.079702	-0.195166
9	6	0	-3.636089	-0.282128	0.091649
10	8	0	-1.395083	-1.004403	0.254722
11	1	0	3.645470	0.586452	-1.525146
12	1	0	2.561205	-0.517759	-2.394839
13	9	0	-4.407855	0.572268	-0.599497
14	9	0	-4.027780	-1.534408	-0.218381
15	9	0	-3.886437	-0.090946	1.407108
16	6	0	0.883139	2.455880	0.482966
17	6	0	1.545954	3.490106	1.368977
18	1	0	0.177792	1.840118	1.050511
19	1	0	0.353077	2.926824	-0.350810
20	1	0	0.032463	-0.788554	0.208607
21	1	0	0.783088	4.161397	1.778227
22	1	0	2.263633	4.090524	0.799913
23	1	0	2.071110	3.013863	2.203576
24	6	0	3.212453	-1.296206	-0.461358
25	1	0	3.736470	-2.070179	-1.033139
26	6	0	1.843391	-1.848487	-0.032821
27	1	0	1.366783	-2.332803	-0.894087
28	6	0	1.788662	-2.766972	1.173912
29	1	0	2.385879	-3.665455	0.980274
30	1	0	0.758326	-3.083198	1.367731
31	1	0	2.174799	-2.275445	2.071222
32	6	0	4.107433	-0.846775	0.700611
33	1	0	4.390984	-1.691883	1.336736
34	1	0	5.031294	-0.405095	0.310137
35	1	0	3.617226	-0.094534	1.326923

Tetrahedral Intermediates: ***TI*1**-(*syn*)-**1c**

1) (1R,3R,4R,g^+,*E*)/ (1S,3S,4S,g^-,*E*) g^+=27.1 °

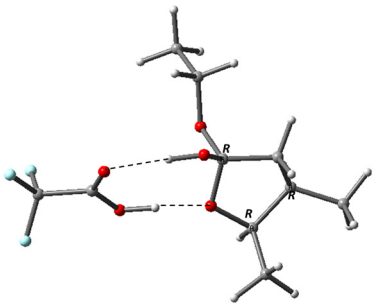


Energy= -1066.97745881 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	1.783403	0.223992	1.293090
2	6	0	2.233108	-0.072148	0.201551
3	6	0	3.755564	-0.156764	-0.042739
4	8	0	1.569234	-0.357165	-0.893924
5	9	0	4.430174	0.161435	1.065888
6	9	0	4.122264	0.687194	-1.024453
7	9	0	4.099837	-1.403841	-0.411651
8	1	0	0.017114	-0.435159	1.573929
9	6	0	-0.452602	2.416971	-0.981426
10	6	0	-1.561143	1.371365	-0.998311
11	6	0	-2.346721	0.853725	1.213624
12	6	0	-1.685611	-0.401007	0.645601
13	8	0	-2.681811	-1.302683	0.313449
14	6	0	-2.264555	-2.521556	-0.331550
15	1	0	-0.070337	2.591204	0.030320
16	1	0	-0.818481	3.368404	-1.381667
17	1	0	0.381904	2.095437	-1.614009
18	8	0	-1.008270	0.088537	-0.558245
19	1	0	-1.607061	1.414867	1.797129
20	1	0	-3.182810	0.593668	1.866775
21	6	0	-3.517986	-3.250558	-0.778668
22	1	0	0.570390	-0.243603	-0.747587
23	1	0	-1.908466	1.228514	-2.027140
24	8	0	-0.742833	-1.037992	1.433159
25	1	0	-3.246795	-4.193467	-1.267028
26	1	0	-4.091956	-2.646377	-1.490030
27	1	0	-4.162469	-3.480604	0.077091
28	1	0	-1.623264	-2.281061	-1.187844
29	1	0	-1.684555	-3.129635	0.371124
30	6	0	-2.761419	1.623511	-0.045861
31	1	0	-3.626277	1.104664	-0.475476
32	6	0	-3.138194	3.086690	0.180814
33	1	0	-3.386719	3.588206	-0.762383
34	1	0	-4.020302	3.153313	0.828235
35	1	0	-2.330829	3.649653	0.662069

2) (1R,3R,4R,g^+,Z)/ (1S,3S,4S,g^-,Z) g^+=28.4 °

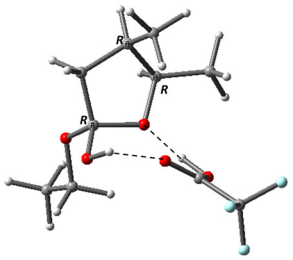


Energy=-1066.97814982 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.980638	0.518785	0.627695
2	6	0	1.454343	0.468443	0.641792
3	8	0	1.130037	-0.824330	0.098200
4	8	0	0.843851	1.362254	-0.268991
5	8	0	0.941264	0.584278	1.915575
6	1	0	-0.031286	0.462098	1.842157
7	8	0	-1.823058	0.120672	1.287527
8	6	0	-2.154411	-0.402207	0.239973
9	6	0	-3.641959	-0.500351	-0.165293
10	8	0	-1.389938	-0.942013	-0.677622
11	1	0	3.357439	0.048631	1.542292
12	1	0	3.359489	1.542950	0.587079
13	9	0	-4.000845	-1.786397	-0.333267
14	9	0	-4.425811	0.039987	0.772852
15	9	0	-3.854796	0.147876	-1.325530
16	6	0	0.767903	2.738942	0.132662
17	6	0	0.186222	3.523204	-1.029560
18	1	0	1.767445	3.115300	0.391261
19	1	0	0.136767	2.835011	1.023657
20	1	0	-0.410980	-0.875045	-0.419088
21	1	0	0.103255	4.582617	-0.761499
22	1	0	-0.812828	3.154116	-1.286840
23	1	0	0.822996	3.439800	-1.917086
24	6	0	3.335450	-0.307554	-0.617062
25	1	0	3.114276	0.310041	-1.495983
26	6	0	2.274125	-1.435054	-0.581087
27	1	0	1.941583	-1.690111	-1.592817
28	6	0	2.648220	-2.706971	0.167719
29	1	0	1.776037	-3.366446	0.236487
30	1	0	3.438450	-3.249703	-0.362628
31	1	0	2.992794	-2.493167	1.185177
32	6	0	4.790734	-0.765295	-0.696096
33	1	0	4.967968	-1.382141	-1.585274
34	1	0	5.459205	0.101160	-0.759776
35	1	0	5.085619	-1.346832	0.184413

3) (1R,3R,4R,g^-,*E*)/ (1S,3S,4S,g^+,*E*) g^-= -36.9 °

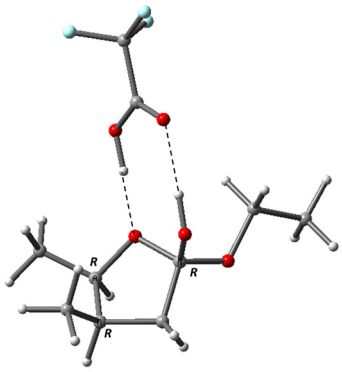


Energy=-1066.97627331 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.675897	1.462424	1.028775
2	6	0	2.377469	1.182745	-1.241401
3	6	0	1.877559	-0.165947	-0.666273
4	8	0	1.150250	0.194692	0.547031
5	8	0	2.984778	-0.937319	-0.356134
6	8	0	1.017886	-0.907412	-1.460216
7	1	0	0.185486	-0.407258	-1.590202
8	8	0	-1.667521	0.008520	-1.314922
9	6	0	-2.083323	-0.276924	-0.207097
10	6	0	-3.588156	-0.510047	0.049079
11	8	0	-1.394084	-0.425464	0.899471
12	6	0	0.747531	2.023097	2.089498
13	1	0	2.654255	1.250041	1.480204
14	1	0	3.467744	1.145053	-1.303336
15	1	0	1.986253	1.321368	-2.253212
16	9	0	-4.283965	-0.391648	-1.085282
17	9	0	-4.055520	0.389554	0.934231
18	9	0	-3.793917	-1.739875	0.552822
19	6	0	2.725441	-2.241892	0.200775
20	6	0	4.045972	-2.787910	0.711062
21	1	0	1.994997	-2.154670	1.013598
22	1	0	2.302482	-2.892478	-0.572153
23	1	0	-0.259840	2.203128	1.701930
24	1	0	0.673577	1.332860	2.936888
25	1	0	1.146429	2.973032	2.462715
26	1	0	-0.411972	-0.230513	0.740951
27	1	0	3.899023	-3.791086	1.127340
28	1	0	4.778795	-2.857145	-0.100679
29	1	0	4.459801	-2.145025	1.495940
30	6	0	1.895043	2.279863	-0.263636
31	1	0	2.686561	3.017209	-0.089076
32	6	0	0.646332	3.008886	-0.774274
33	1	0	0.309666	3.780227	-0.072642
34	1	0	0.866508	3.503903	-1.727266
35	1	0	-0.188204	2.319172	-0.947820

4) (1R,3R,4R,g^-,*Z*)/ (1S,3S,4S,g^+,*Z*) g^-= -38.5 °

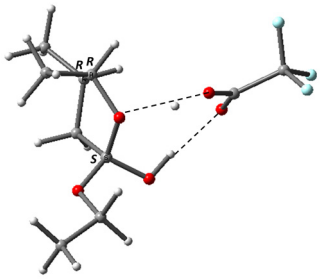


Energy=-1066.97661276 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.333369	0.056438	0.509639
2	6	0	1.904443	0.605350	0.410461
3	8	0	1.212850	-0.295417	-0.501080
4	8	0	1.962071	1.887276	-0.140024
5	8	0	1.263152	0.559049	1.641053
6	1	0	0.293071	0.498766	1.509097
7	8	0	-1.567428	0.287234	1.265551
8	6	0	-2.038768	-0.163551	0.238541
9	6	0	-3.562786	-0.336725	0.061875
10	8	0	-1.395212	-0.546484	-0.839436
11	1	0	3.975095	0.650467	-0.146911
12	1	0	3.701346	0.146336	1.534512
13	9	0	-4.000939	0.432379	-0.951719
14	9	0	-4.209835	0.016868	1.175675
15	9	0	-3.862481	-1.616404	-0.222299
16	6	0	0.738317	2.632621	-0.213618
17	6	0	1.062477	3.984647	-0.822910
18	1	0	0.010041	2.097032	-0.837866
19	1	0	0.313089	2.751587	0.790199
20	1	0	-0.396586	-0.435785	-0.711130
21	1	0	0.151969	4.589648	-0.898849
22	1	0	1.785990	4.525854	-0.203562
23	1	0	1.484739	3.869470	-1.827220
24	6	0	2.154441	-1.250224	-1.076924
25	1	0	2.604269	-0.770760	-1.957383
26	6	0	2.888204	-2.387841	1.130077
27	1	0	2.809240	-3.413756	0.753546
28	1	0	3.674506	-2.376995	1.893944
29	1	0	1.945986	-2.126519	1.623126
30	6	0	1.398827	-2.491873	-1.512610
31	1	0	0.664271	-2.247152	-2.287757
32	1	0	2.099238	-3.219392	-1.938316
33	1	0	0.875957	-2.963838	-0.675204
34	6	0	3.235939	-1.398557	0.011426
35	1	0	4.176829	-1.705515	-0.459389

5) (1R,3S,4S,g^-,*E*)/ (1S,3R,4R,g^+,*E*) g^+= 37.8 °

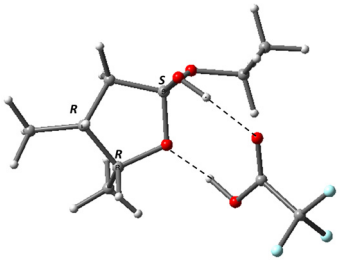


Energy=-1066.97677475 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.981894	0.025553	0.568758
2	6	0	-1.248736	1.411817	0.934365
3	6	0	-1.413277	2.103953	-0.435407
4	6	0	-2.156211	1.032855	-1.249968
5	6	0	-1.676169	-0.318216	-0.684194
6	8	0	-0.776740	-1.026961	-1.466659
7	8	0	-2.775752	-1.112819	-0.428412
8	6	0	-2.514849	-2.429217	0.099765
9	6	0	-3.848305	-3.022711	0.513691
10	6	0	-2.436258	1.483090	1.887112
11	8	0	1.561070	-0.465656	0.924617
12	6	0	2.248564	-0.194601	-0.158237
13	8	0	1.822332	0.072740	-1.267284
14	6	0	3.765412	-0.225600	0.127792
15	1	0	0.561408	-0.371926	0.747600
16	1	0	0.042493	-0.498248	-1.570825
17	1	0	-0.347704	1.759932	1.450501
18	1	0	-3.363474	1.144526	1.413739
19	1	0	-2.580980	2.508517	2.244735
20	1	0	-2.246599	0.845760	2.757511
21	1	0	-3.237943	1.108532	-1.104303
22	1	0	-1.953544	1.087007	-2.322596
23	1	0	-0.402835	2.211379	-0.851786
24	1	0	-2.030800	-3.043096	-0.667063
25	1	0	-1.836348	-2.350483	0.957292
26	1	0	-4.530124	-3.083579	-0.341951
27	1	0	-3.699724	-4.034754	0.907252
28	1	0	-4.323668	-2.415347	1.291872
29	9	0	4.462459	-0.083488	-1.003416
30	9	0	4.118254	-1.385787	0.707137
31	9	0	4.096025	0.778111	0.962674
32	6	0	-2.082577	3.476723	-0.417839
33	1	0	-1.529750	4.181441	0.215351
34	1	0	-2.116720	3.898495	-1.429044
35	1	0	-3.112035	3.420905	-0.046491

6) (1R,3S,4S,g^-,*Z*)/ (1S,3R,4R,g^+,*Z*) g^+= 31.9 °

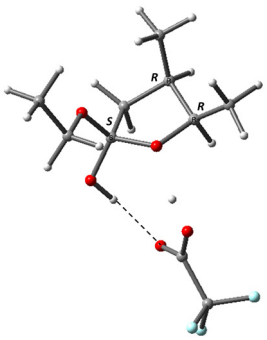


Energy=-1066.97690127 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.111448	0.099777	-0.784787
2	6	0	1.711559	0.653531	-0.543818
3	8	0	1.094164	-0.295698	0.383125
4	8	0	1.796770	1.900112	0.065142
5	8	0	0.990709	0.656846	-1.732012
6	1	0	0.030532	0.599333	-1.540872
7	8	0	-1.806817	0.365252	-1.196834
8	6	0	-2.191674	-0.233050	-0.209175
9	6	0	-3.688822	-0.546219	0.005014
10	8	0	-1.465884	-0.702974	0.776604
11	1	0	3.790265	0.502534	-0.026326
12	1	0	3.474235	0.392495	-1.772859
13	9	0	-3.897587	-1.872661	-0.092751
14	9	0	-4.090705	-0.147871	1.224105
15	9	0	-4.435848	0.071499	-0.914387
16	6	0	0.572144	2.618769	0.278415
17	6	0	0.928626	3.956046	0.901011
18	1	0	-0.084134	2.046258	0.947630
19	1	0	0.053343	2.763380	-0.676713
20	1	0	-0.480468	-0.510766	0.611593
21	1	0	0.018482	4.539738	1.079356
22	1	0	1.582400	4.531443	0.236532
23	1	0	1.443256	3.817530	1.858046
24	6	0	2.925178	-1.414946	-0.626166
25	1	0	2.409051	-1.779155	-1.522914
26	6	0	1.913426	-1.499538	0.539411
27	1	0	1.238538	-2.352906	0.411375
28	6	0	2.490255	-1.516729	1.948974
29	1	0	3.023938	-2.454991	2.136353
30	1	0	1.679790	-1.440820	2.682360
31	1	0	3.179911	-0.682633	2.117162
32	6	0	4.216209	-2.211608	-0.447410
33	1	0	4.010545	-3.279146	-0.303030
34	1	0	4.847280	-2.116271	-1.338459
35	1	0	4.798667	-1.859238	0.411055

7) (1R,3S,4S,g^+,*E*)/ (1S,3R,4R,g^-,*E*) g^-= -33.5 °

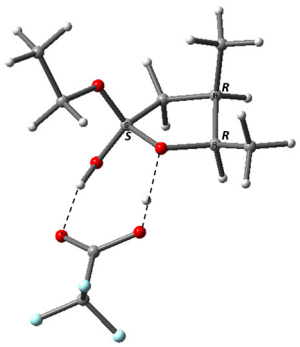


Energy= -1066.97702989 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.112415	0.750335	1.631274
2	6	0	1.590517	-0.399579	0.759787
3	8	0	0.924827	0.278173	-0.358612
4	8	0	2.661230	-1.143010	0.297678
5	8	0	0.678793	-1.257568	1.357940
6	1	0	-0.133927	-0.755086	1.576303
7	8	0	-1.905091	-0.080069	1.354591
8	6	0	-2.307850	-0.118434	0.206146
9	6	0	-3.818399	-0.123364	-0.114596
10	8	0	-1.597181	-0.150679	-0.895345
11	1	0	3.015419	0.446948	2.166207
12	1	0	1.340791	0.997283	2.368860
13	9	0	-4.540919	-0.139030	1.009292
14	9	0	-4.147832	0.975086	-0.819818
15	9	0	-4.140475	-1.203878	-0.847484
16	6	0	2.357263	-2.230064	-0.599411
17	6	0	3.676329	-2.827264	-1.052718
18	1	0	1.783806	-1.849199	-1.452977
19	1	0	1.746554	-2.975017	-0.079081
20	1	0	-0.601857	-0.087089	-0.682399
21	1	0	3.490181	-3.673024	-1.724420
22	1	0	4.254700	-3.190232	-0.195906
23	1	0	4.281031	-2.087934	-1.589531
24	6	0	2.322930	1.924286	0.658296
25	1	0	2.201282	2.879310	1.182241
26	6	0	1.120234	1.727755	-0.291134
27	1	0	0.225726	2.145380	0.191655
28	6	0	1.224381	2.270871	-1.704384
29	1	0	1.353215	3.359144	-1.679666
30	1	0	2.068353	1.829876	-2.242882
31	1	0	0.307619	2.055590	-2.264714
32	6	0	3.698519	1.910164	-0.019469
33	1	0	3.814460	2.754701	-0.707710
34	1	0	4.486462	1.993029	0.738364
35	1	0	3.870559	0.983713	-0.575020

8) (1R,3S,4S,g^+,*Z*)/ (1S,3R,4R,g^-,*Z*) g^-= -38.4 °



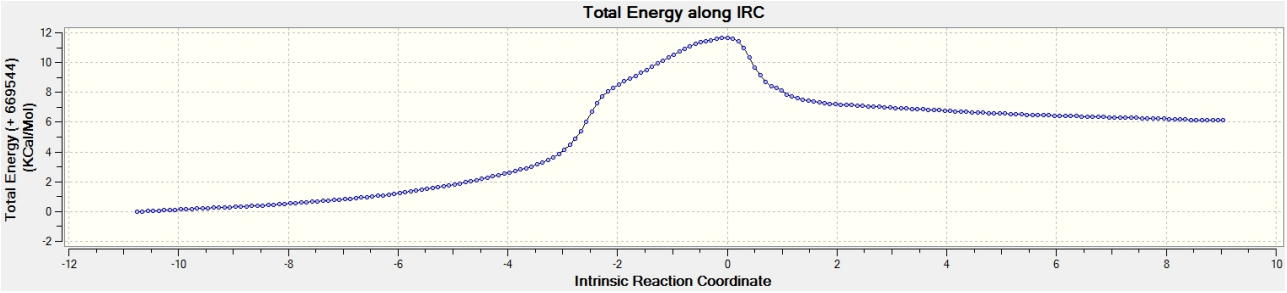
Energy= -1066.97627063 a.u.

Standard orientation:

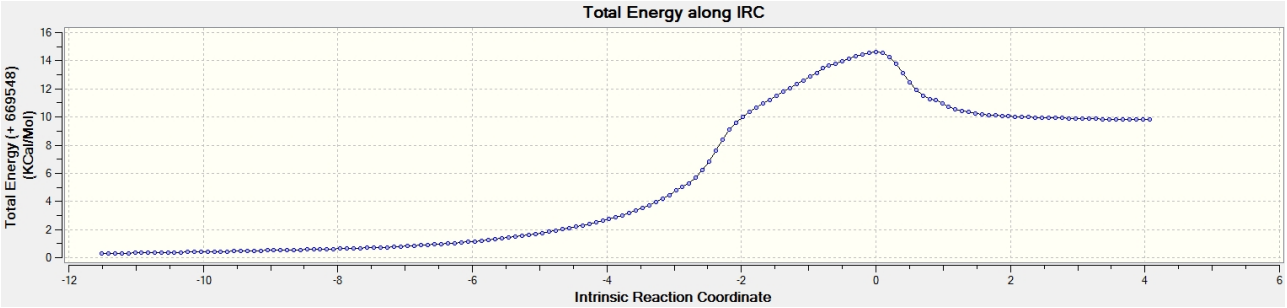
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.995885	-0.154055	1.355520
2	6	0	-1.695683	0.467301	0.829760
3	8	0	-1.104887	-0.556616	-0.029841
4	8	0	-2.010757	1.576242	0.041403
5	8	0	-0.834751	0.751790	1.877734
6	1	0	0.071025	0.915486	1.538739
7	8	0	1.864269	0.860799	0.971017
8	6	0	2.224216	-0.029915	0.223413
9	6	0	3.718856	-0.257775	-0.092338
10	8	0	1.474350	-0.895227	-0.414834
11	1	0	-3.788470	0.596201	1.398851
12	1	0	-2.806366	-0.522806	2.367426
13	9	0	4.480859	0.611512	0.577174
14	9	0	4.086174	-1.505080	0.251412
15	9	0	3.945552	-0.102056	-1.409478
16	6	0	-0.923591	2.284160	-0.573610
17	6	0	-1.519337	3.401223	-1.410690
18	1	0	-0.339719	1.599320	-1.202380
19	1	0	-0.261096	2.696859	0.197726
20	1	0	0.487692	-0.737836	-0.221814
21	1	0	-0.719144	3.978503	-1.887457
22	1	0	-2.110305	4.080369	-0.786562
23	1	0	-2.169564	2.997996	-2.194705
24	6	0	-3.300802	-1.318659	0.393133
25	1	0	-3.833705	-2.119736	0.918042
26	6	0	-1.873071	-1.796270	0.064536
27	1	0	-1.484097	-2.359302	0.924683
28	6	0	-1.659406	-2.599235	-1.205176
29	1	0	-2.239190	-3.528245	-1.159486
30	1	0	-0.604465	-2.872266	-1.319886
31	1	0	-1.967569	-2.037752	-2.092048
32	6	0	-4.126711	-0.882921	-0.823269
33	1	0	-4.318818	-1.720570	-1.502806
34	1	0	-5.098747	-0.496686	-0.494764
35	1	0	-3.628039	-0.087956	-1.387033

Intrinsic Reaction Coordinates (IRC) for *syn*-1c

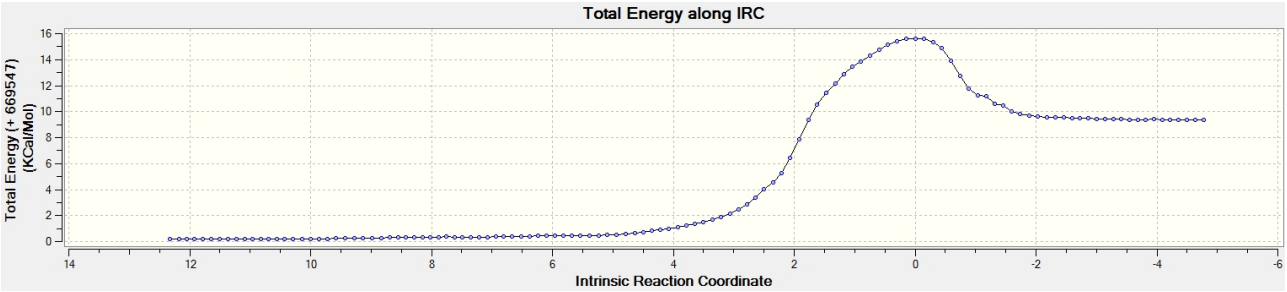
1) (1Re,3R,4R,g^-,*E*)-***CC***-*syn*-**1c** ⟶ (1Re,3R,4R,g^-,*E*)-***TI*1**-*syn*-**1c**



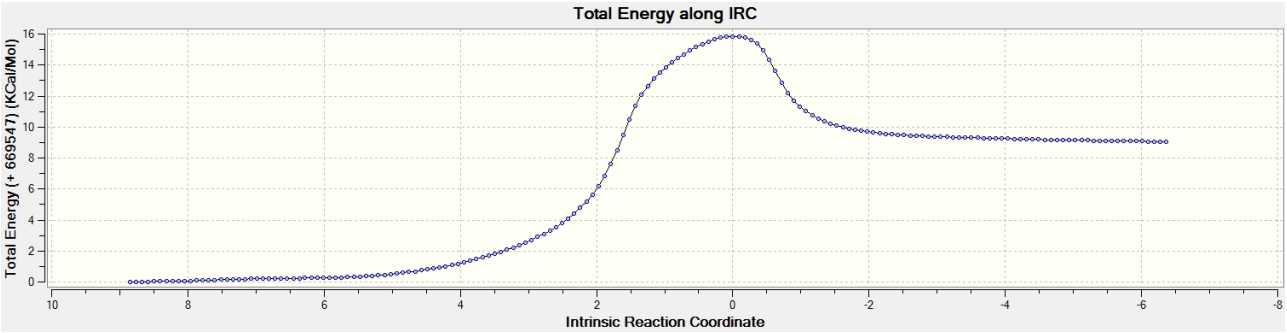
2) (1Si,3R,4R,g^-,*E*)-***CC***-*syn*-**1c** ⟶ (1Si,3R,4R,g^-,*E*)-***TI*1**-*syn*-**1c**



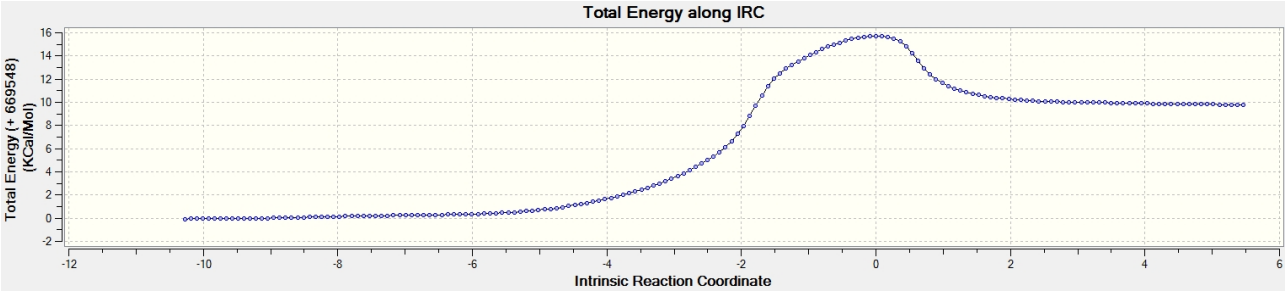
3) (1Re,3R,4R,g^+,*Z*)-***CC***-*syn*-**1c** ⟶ (1Re,3R,4R,g^+,*Z*)-***TI*1**-*syn*-**1c**



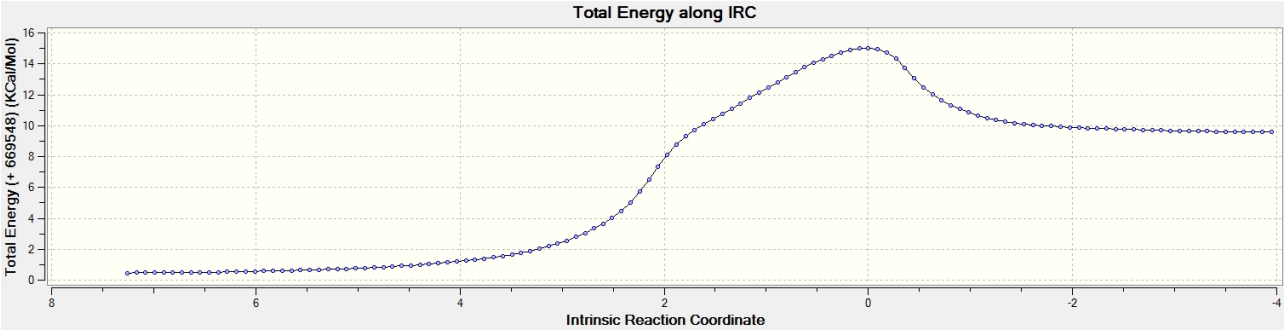
4) (1Re,3R,4R,g^-,*Z*)-***CC***-*syn*-**1c** ⟶ (1Re,3R,4R,g^-,*Z*)-***TI*1**-*syn*-**1c**



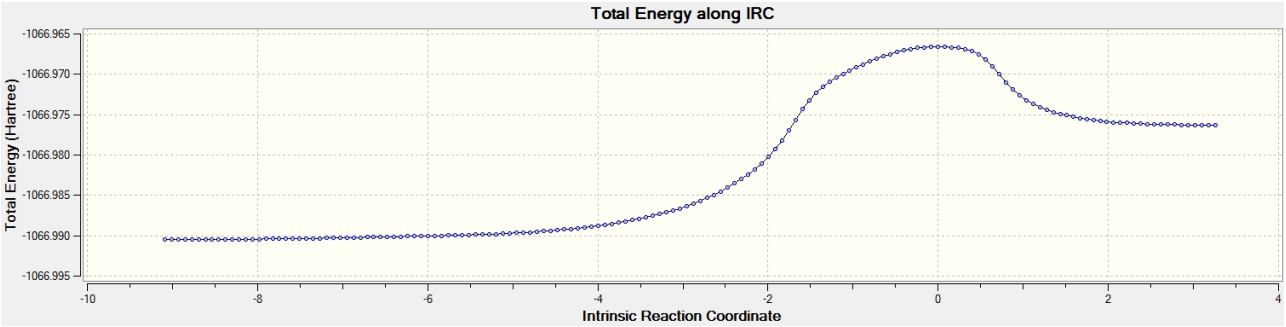
5) (1Si,3R,4R,g^+,*Z*)-***CC***-*syn*-**1c** ⟶ (1Si,3R,4R,g^+,*Z*)-***TI*1**-*syn*-**1c**



6) (1Re,3R,4R,g^+,*E*)-***CC***-*syn*-**1c** ⟶ (1Re,3R,4R,g^+,*E*)-***TI*1**-*syn*-**1c**



7) (1Si,3R,4R,g^-,*E*)-***CC***-*syn*-**1c** ⟶ (1Re,3R,4R,g^-,*E*)-***TI*1**-*syn*-**1c**



8) (1Re,3R,4R,g^-,*Z*)-***CC***-*syn*-**1c** ⟶ (1Si,3R,4R,g^-,*Z*)-***TI*1**-*syn*-**1c**

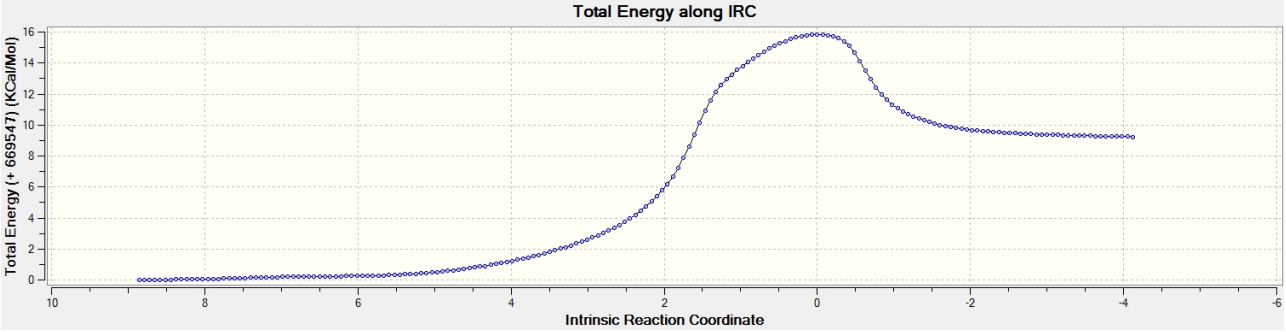


Table SI-4. Winstein-Holness equation applied to the RDS of the *syn*-**1c** lactonization.

Stereochemical descriptor [a]	$\Delta G_i^{\ddagger}$ [b] (kcal mol^{-1})	k_i [c] (s^{-1})	x_i [d] (%)	$k_{(W\text{-}H)i}$ [e] (s^{-1})	**Stereoisomer Contrib.** [g] (%)
(1Re,3R,4R,g^+,*E*)-**CC**	15.18	71.5	3.5	2.5	3.8
(1Re,3R,4R,g^+,*Z*)-**CC**	15.49	43.3	1.8	0.8	1.2
(1Re,3R,4R,g^-,*E*)-**CC**	13.61	972.5	0.4	4.0	4.6
(1Re,3R,4R,g^-,*Z*)-**CC**	16.12	15.1	0.9	0.1	0.2
(1Re,3S,4S,g^-,*E*)-**CC**	15.99	18.8	76.5	14.4	21.8
(1Re,3S,4S,g^-,*Z*)-**CC**	16.33	10.6	13.8	1.5	2.2
(1Re,3S,4S,g^+,*E*)-**CC**	13.38	1437.3	3.0	42.8	65.2
(1Re,3S,4S,g^+,*Z*)-**CC**	14.25	338.6	0.2	0.6	1.0
Ensemble	**15.23** [c]			**65.7** [f]	

[a] Arbitrary we chosen 1*Re* stereochemical configuration;
[b] $G_{TS1} - G_{CC}$;
[c] Calculated with Eyring equantion;
[d] Calculated as Boltzman distribution;
[e] $x_i \cdot k_i$;
[f] $\sum k_{(W\text{-}H)i}$;
[g] $k_{(W\text{-}H)i} / k_{W\text{-}H} \cdot 100$

Table SI-5. Winstein-Holness equation applied to the RDS of the **1b**[3] and *anti*-**1c** lactonization, but calculated with $\Delta H^{\ddagger}$.

Stereochemical descriptor [a]	$\Delta H^{\ddagger}$ [b] (kcal mol^{-1})	k_i [c] (s^{-1})	x_i [d] (%)	$k_{(W\text{-}H)i}$ [e] (s^{-1})	**Stereoisomer Contrib.** [g] (%)
(1Re,g^+,*E*)-***CC***	12.30	8574.8	0.70	5990.3	51.7
(1Re,g^-,*Z*)-***CC***	13.15	2091.5	0.09	199.3	1.7
(1Re,g^-,*E*)-***CC***	8.73	3.21 x10^5	0.01	5074.0	43.8
(1Re,g^-,*Z*)-***CC***	13.3	1630.5	0.20	333.5	2.9
Ensemble	**12.12** [c]			**11597.1** [f]	
(1Re,3S,4R,g^+,*Z*)-***CC***	12.87	3328.9	0.2	0.04	<0.01
(1Re,3S,4R,g^-,*E*)-***CC***	12.53	5853.5	32.9	24.0	1.4
(1Re,3S,4R,g^-,*Z*)-***CC***	13.11	2235.0	14.4	4.9	0.3
(1Re,3R,4S,g^-,*Z*)-***CC***	13.15	2091.5	0.8	2.1	0.1
(1Re,3R,4S,g^+,*E*)-***CC***	10.59	1.46 x10^5	49.1	1640.2	98
(1Re,3R,4S,g^+,*Z*)-***CC***	11.96	1.51 x10^4	2.6	3.2	0.2
(1Re,3R,4S,g^-,*E*)-***CC***	- [h]	- [h]	- [h]	- [h]	- [h]
(1Re,3S,4R,g^+,*E*)-***CC***	- [h]	- [h]	- [h]	- [h]	- [h]
Ensemble	**11.03** [c]			**71081.4** [f]	

[a] Arbitrary we chosen 1Re stereochemical configuration;
[b] $H_{TS1} - H_{CC}$;
[c] Calculated with Eyring equantion;
[d] Calculated as Boltzman distribution;
[e] $x_i \cdot k_i$;
[f] $\sum k_{(W\text{-}H)i}$;
[g] $k_{(W\text{-}H)i} / k_{W\text{-}H} \cdot 100$;
[h] Not found.

Plot of differential computed Gibbs energy barriers ($\delta\Delta G^{\ddagger}_{Comp.}$) *vs.* differential experimental Gibbs activation energies ($\delta\Delta G^{\ddagger}_{Exp.}$) for compounds 1a-c.

Ester	$\delta\Delta G^{\ddagger}_{Comp.}$ (kcalmol^{-1})	$\delta\Delta G^{\ddagger}_{Exp.}$ (kcalmol^{-1})	$\Delta G^{\ddagger}_{ensemble}$ (kcalmol^{-1})
1a[a]	0	0	16.16
1b[a]	-1.08	-0.88	15.08
syn-**1c**	-0.93	-1.00	15.23
anti-**1c**	-2.88	-2.77	13.28

a) For compound **1a-b** the energies have computed in ref. [3]

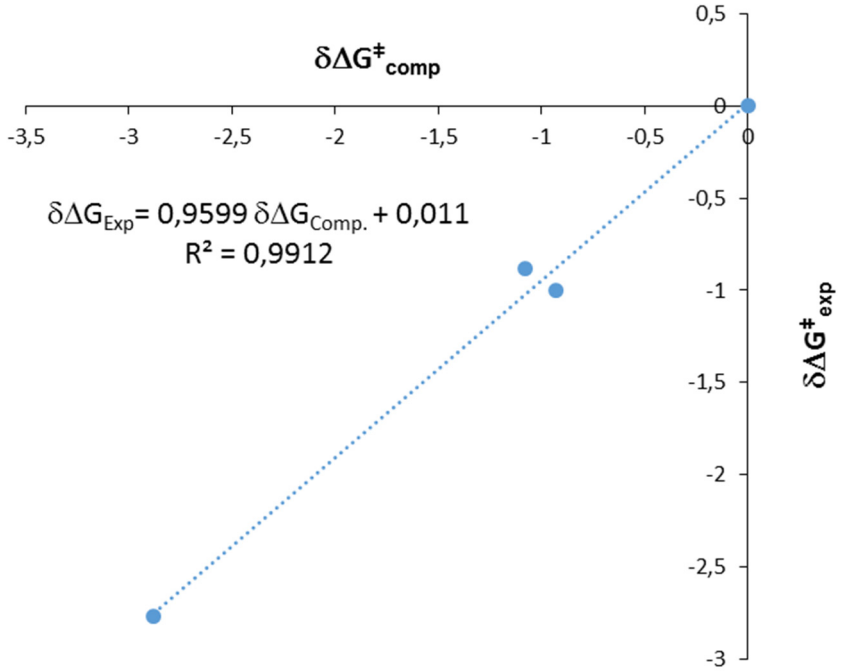
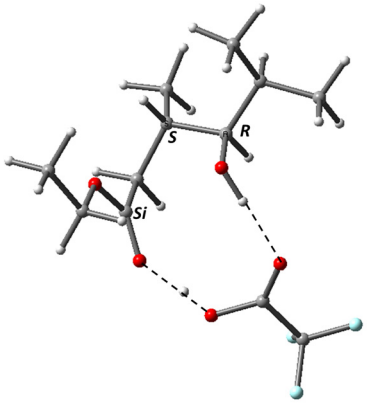


Figure SI-4. Correlation between the experimental Gibbs energy barrier $\delta\Delta G^{\ddagger}_{Exp.}$ with respect to **1a** and the corresponding computed barriers $\delta\Delta G^{\ddagger}_{Exp.}$ of the RDS of the ring closure of esters **1a-c**. The energies are in kcal mol^{-1}.

Catalytic complex TFA·E: ***CC***-(*anti*)-**1d**

1) (1Re,3R,4S,g^+,*E*,*a'*)/ (1Si,3S,4R,g^-,*E*,*a'*) g^-=-53.3 °



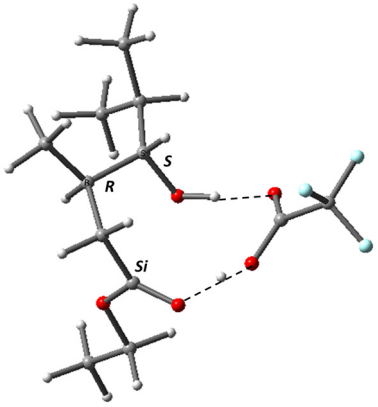
Energy= -1145.62210910 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-2.175740	-1.449027	0.475942
2	6	0	-2.529428	-0.408315	-0.236220
3	6	0	-4.040222	-0.127882	-0.074345
4	8	0	-1.836056	0.295248	-0.946473
5	9	0	-4.339069	0.099575	1.218811
6	9	0	-4.403944	0.942877	-0.787224
7	9	0	-4.762731	-1.183872	-0.490712
8	1	0	-1.185809	-1.677920	0.353361
9	6	0	1.728041	2.831641	-0.323789
10	6	0	1.133952	1.496760	0.183000
11	6	0	1.924938	0.799403	1.310636
12	6	0	1.242888	-0.542187	1.670174
13	6	0	1.274339	-1.582112	0.576727
14	8	0	2.507893	-1.894249	0.202003
15	6	0	2.657491	-2.862187	-0.875439
16	1	0	1.775277	3.511977	0.537549
17	8	0	1.019690	0.571317	-0.909679
18	6	0	2.056794	1.668067	2.568680
19	1	0	0.198256	-0.380646	1.956859
20	1	0	1.755762	-0.981783	2.535421
21	6	0	4.140408	-3.023285	-1.134311
22	1	0	0.070659	0.438481	-1.089878
23	1	0	0.127276	1.712756	0.573957
24	1	0	2.928206	0.565576	0.935800
25	1	0	1.072411	1.962867	2.955773
26	1	0	2.576864	1.122884	3.365092
27	1	0	2.625841	2.582121	2.372034
28	8	0	0.289145	-2.173512	0.125203
29	1	0	4.290415	-3.745511	-1.944480
30	1	0	4.592911	-2.071911	-1.433246
31	1	0	4.658975	-3.393725	-0.243441
32	1	0	2.125280	-2.479687	-1.751043
33	1	0	2.188341	-3.800808	-0.566767
34	6	0	3.144139	2.672950	-0.895983

35	1	0	3.152154	1.942210	-1.712790
36	1	0	3.506881	3.627688	-1.295747
37	1	0	3.864124	2.340923	-0.139019
38	6	0	0.789770	3.463816	-1.362764
39	1	0	-0.221531	3.602853	-0.959188
40	1	0	1.161002	4.446057	-1.679027
41	1	0	0.710283	2.830164	-2.253259

2) (1Re,3R,4S,g^+,*E*,*g*'')/ (1Si,3S,4R,g^-,*E*,*g*') g^+= 54.0 °



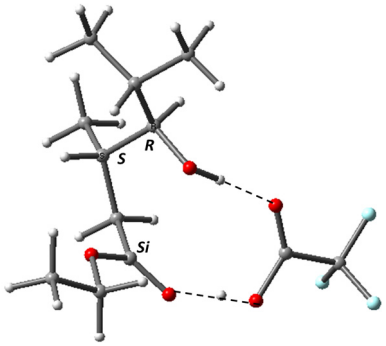
Energy= -1145.61731072 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	2.304657	-1.271594	0.608923
2	6	0	2.610595	-0.305566	-0.220314
3	6	0	4.110685	0.047891	-0.111689
4	8	0	1.885230	0.284752	-0.998635
5	9	0	4.422043	0.398416	1.150185
6	9	0	4.418808	1.065390	-0.922352
7	9	0	4.868209	-1.011785	-0.449679
8	1	0	1.325591	-1.556498	0.524341
9	6	0	-1.828725	2.591303	-0.895584
10	6	0	-1.207904	1.409115	-0.103113
11	6	0	-2.012947	0.806118	1.070998
12	6	0	-1.253475	-0.424349	1.626050
13	6	0	-1.156464	-1.597768	0.681805
14	8	0	-2.346480	-2.050067	0.305706
15	6	0	-2.374602	-3.162008	-0.632951
16	1	0	-1.221024	2.617220	-1.810905
17	8	0	-0.979961	0.331953	-1.030769
18	6	0	-2.290863	1.788529	2.216834
19	1	0	-0.239002	-0.146244	1.930698
20	1	0	-1.774325	-0.788184	2.521251
21	6	0	-3.827588	-3.459102	-0.937563
22	1	0	-0.019071	0.273448	-1.187753
23	1	0	-0.238922	1.748285	0.294800
24	1	0	-2.971112	0.447246	0.676998
25	1	0	-1.366758	2.252125	2.585403
26	1	0	-2.760100	1.269236	3.061009

27	1	0	-2.970284	2.588391	1.911979
28	8	0	-0.112988	-2.173691	0.359782
29	1	0	-3.886430	-4.292978	-1.645883
30	1	0	-4.320561	-2.590562	-1.386884
31	1	0	-4.372127	-3.740487	-0.029742
32	1	0	-1.818418	-2.866095	-1.527021
33	1	0	-1.866699	-4.015998	-0.175483
34	6	0	-1.666510	3.968295	-0.231716
35	1	0	-2.329499	4.109251	0.627646
36	1	0	-1.902125	4.760074	-0.953630
37	1	0	-0.636083	4.131244	0.109071
38	6	0	-3.278917	2.330413	-1.324214
39	1	0	-3.375412	1.353964	-1.812041
40	1	0	-3.613215	3.094498	-2.036752
41	1	0	-3.969348	2.355822	-0.471804

3) (1Re,3R,4S,g^{+},*E*,*g'*)/ (1Si,3S,4R,g^{-},*E*,*g''*) g^{-}=-24.0 °



Energy= -1145.61840048 a.u.

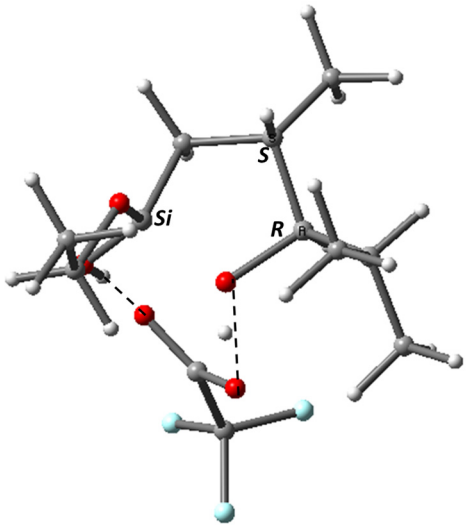
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-2.550308	-1.299010	0.236607
2	6	0	-2.740412	-0.069674	-0.169700
3	6	0	-4.245067	0.281975	-0.156557
4	8	0	-1.910726	0.748889	-0.520674
5	9	0	-4.748156	0.145575	1.084636
6	9	0	-4.441619	1.542081	-0.557335
7	9	0	-4.926836	-0.538604	-0.976416
8	1	0	-1.561950	-1.562015	0.215191
9	6	0	2.882455	1.857427	-0.771944
10	6	0	1.603844	1.394953	-0.036175
11	6	0	1.870059	0.693141	1.334633
12	6	0	0.872167	-0.456719	1.585303
13	6	0	0.900811	-1.581367	0.579641
14	8	0	2.127304	-2.015576	0.319023
15	6	0	2.264417	-3.095980	-0.647846
16	1	0	3.413273	0.933388	-1.047859
17	8	0	0.932524	0.505302	-0.940162
18	6	0	1.787413	1.675505	2.513783

19	1	0	-0.153157	-0.079223	1.641260
20	1	0	1.097552	-0.908197	2.561568
21	6	0	3.744081	-3.375300	-0.804759
22	1	0	-0.030973	0.607713	-0.823282
23	1	0	0.960519	2.270881	0.144624
24	1	0	2.874318	0.252311	1.310197
25	1	0	0.770180	2.075666	2.615959
26	1	0	2.046947	1.180597	3.457489
27	1	0	2.463877	2.525270	2.389581
28	8	0	-0.097357	-2.138851	0.113839
29	1	0	3.885299	-4.185167	-1.529080
30	1	0	4.274664	-2.490002	-1.171020
31	1	0	4.191127	-3.683318	0.146599
32	1	0	1.803792	-2.772712	-1.585576
33	1	0	1.717677	-3.966900	-0.274954
34	6	0	2.518646	2.602888	-2.064713
35	1	0	2.008593	3.549966	-1.840348
36	1	0	3.419492	2.842634	-2.642834
37	1	0	1.855978	2.002602	-2.693935
38	6	0	3.832148	2.712631	0.078441
39	1	0	4.208793	2.179603	0.957497
40	1	0	4.703061	3.007309	-0.519658
41	1	0	3.345558	3.635204	0.420909

Transition States: ***TS*1‡-(*anti*)-1d**

1) (1Re,3R,4S,g^+,*E*,*a'*)/ (1Si,3S,4R,g^-,*E*,*a'*) g^-=-59.7 °



Energy= -1145.60046640 a.u.

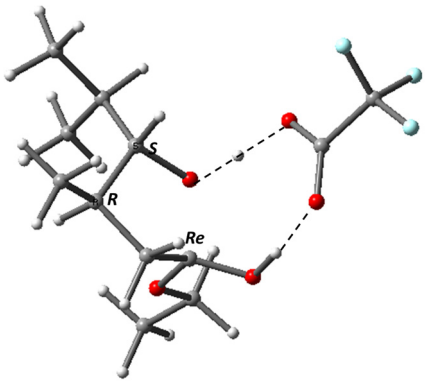
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.324618	-0.331574	1.961711
2	6	0	1.269029	-1.135943	0.673296
3	8	0	0.781700	0.058831	-0.349450

4	8	0	2.506972	-1.486482	0.269469
5	8	0	0.373260	-2.126063	0.535500
6	1	0	-0.536050	-1.822967	0.831754
7	8	0	-2.076714	-1.209105	0.970952
8	6	0	-2.369235	-0.492250	0.000368
9	6	0	-3.862865	-0.152956	-0.221063
10	8	0	-1.600314	0.050577	-0.856356
11	1	0	1.977997	-0.832720	2.680917
12	1	0	0.314915	-0.278113	2.384720
13	9	0	-4.095751	1.135302	0.116631
14	9	0	-4.212286	-0.307494	-1.512193
15	9	0	-4.669283	-0.925201	0.522220
16	6	0	2.618267	-2.324076	-0.911391
17	6	0	4.090814	-2.421659	-1.255152
18	1	0	2.042112	-1.869930	-1.724125
19	1	0	2.193554	-3.307117	-0.690091
20	1	0	-0.325585	-0.027860	-0.601066
21	1	0	4.218669	-3.061669	-2.135271
22	1	0	4.656920	-2.860769	-0.426403
23	1	0	4.511485	-1.436013	-1.480604
24	6	0	1.820606	1.063863	1.562877
25	1	0	2.886809	0.991654	1.322768
26	6	0	1.029032	1.369551	0.274760
27	1	0	0.041640	1.757096	0.557647
28	6	0	1.667864	2.334212	-0.736211
29	1	0	1.894321	3.241959	-0.157366
30	6	0	1.624213	2.123349	2.647832
31	1	0	2.195695	1.867044	3.547093
32	1	0	1.965603	3.108389	2.309480
33	1	0	0.568138	2.209973	2.932196
34	6	0	0.667330	2.717114	-1.838214
35	1	0	1.098394	3.472788	-2.505002
36	1	0	0.400031	1.847627	-2.450673
37	1	0	-0.258412	3.128434	-1.418217
38	6	0	2.976280	1.814114	-1.347715
39	1	0	3.727024	1.568415	-0.589152
40	1	0	2.797763	0.918267	-1.952090
41	1	0	3.409907	2.577512	-2.003939

---

2) (1Re,3R,4S,g^+,*E*,*g''*)/ (1Si,3S,4R,g^-,*E*,*g'*) g^+= 28.6 °

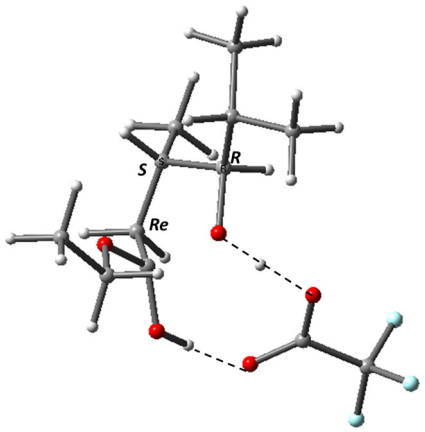


Energy= -1145.59828253 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.261746	-0.218701	1.901184
2	6	0	-1.154995	-1.173137	0.725704
3	8	0	-0.726723	-0.086865	-0.432234
4	8	0	-2.368553	-1.639118	0.366549
5	8	0	-0.204798	-2.120754	0.711487
6	1	0	0.686212	-1.733722	0.965767
7	8	0	2.189587	-1.031949	1.031832
8	6	0	2.451273	-0.410834	-0.011776
9	6	0	3.928312	-0.029340	-0.275217
10	8	0	1.663873	-0.011174	-0.926675
11	1	0	-1.897122	-0.655435	2.676377
12	1	0	-0.259229	-0.066706	2.317652
13	9	0	4.074442	1.313669	-0.252564
14	9	0	4.326282	-0.463419	-1.487862
15	9	0	4.756716	-0.548882	0.642823
16	6	0	-2.422809	-2.635552	-0.688884
17	6	0	-3.885499	-2.884918	-0.996066
18	1	0	-1.883443	-2.255895	-1.562990
19	1	0	-1.927267	-3.546275	-0.342078
20	1	0	0.372368	-0.140120	-0.669959
21	1	0	-3.968938	-3.647705	-1.778245
22	1	0	-4.414708	-3.245516	-0.107240
23	1	0	-4.379716	-1.973560	-1.349038
24	6	0	-1.817164	1.099752	1.342618
25	1	0	-2.881147	0.958431	1.124271
26	6	0	-1.045124	1.283875	0.015614
27	1	0	-0.079180	1.757971	0.230485
28	6	0	-1.706172	2.025640	-1.161043
29	1	0	-1.008971	1.890953	-2.000022
30	6	0	-1.652365	2.259012	2.329384
31	1	0	-2.151477	2.023280	3.276457
32	1	0	-2.088179	3.188003	1.950826
33	1	0	-0.593150	2.444981	2.546409
34	6	0	-3.059265	1.438563	-1.581943
35	1	0	-3.398068	1.910236	-2.511707
36	1	0	-3.833787	1.613931	-0.825681
37	1	0	-2.992309	0.360497	-1.757961
38	6	0	-1.810996	3.535920	-0.897769
39	1	0	-0.857688	3.959014	-0.558495
40	1	0	-2.573283	3.766749	-0.145177
41	1	0	-2.095659	4.055781	-1.819721

3) (1Re,3R,4S,g^+,*E*,*g'*)/ (1Si,3S,4R,g^-,*E*,*g''*) g^-=-17.8 °



Energy= -1145.60045170 a.u.

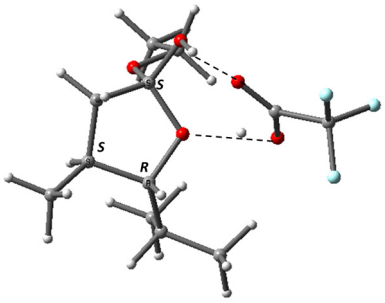
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.102468	-0.382382	1.908612
2	6	0	1.138461	-1.239935	0.657881
3	8	0	0.760762	-0.074500	-0.437593
4	8	0	2.398581	-1.621342	0.364516
5	8	0	0.235196	-2.213612	0.480183
6	1	0	-0.684803	-1.891011	0.726124
7	8	0	-2.199392	-1.240800	0.845941
8	6	0	-2.441293	-0.417581	-0.053362
9	6	0	-3.913433	0.018202	-0.251228
10	8	0	-1.638506	0.159193	-0.851358
11	1	0	1.653922	-0.875177	2.713924
12	1	0	0.057774	-0.272924	2.220429
13	9	0	-4.066734	1.310496	0.113902
14	9	0	-4.278628	-0.087530	-1.543950
15	9	0	-4.762246	-0.719056	0.480429
16	6	0	2.585919	-2.497705	-0.778894
17	6	0	4.078638	-2.641585	-0.994994
18	1	0	2.092067	-2.052748	-1.648913
19	1	0	2.117566	-3.462517	-0.566172
20	1	0	-0.341846	-0.045791	-0.635463
21	1	0	4.261617	-3.313783	-1.840695
22	1	0	4.562932	-3.065488	-0.108538
23	1	0	4.542927	-1.674614	-1.216661
24	6	0	1.700882	0.978568	1.522608
25	1	0	2.792744	0.881643	1.498651
26	6	0	1.200579	1.237528	0.074335
27	1	0	0.298101	1.860728	0.094041
28	6	0	2.223554	1.821328	-0.911428
29	1	0	3.054815	1.103979	-0.961003
30	6	0	1.312721	2.079828	2.513679
31	1	0	1.668354	1.831768	3.520539
32	1	0	1.743447	3.047696	2.239712
33	1	0	0.223078	2.197079	2.562400

34	6	0	2.777467	3.168347	-0.423219
35	1	0	3.482743	3.569718	-1.159977
36	1	0	1.976339	3.908065	-0.297742
37	1	0	3.312413	3.079786	0.528032
38	6	0	1.618014	1.965578	-2.315167
39	1	0	1.244829	1.009561	-2.695944
40	1	0	0.782288	2.677701	-2.312521
41	1	0	2.370175	2.338484	-3.020121

Tetrahedral Intermediate: ***TI*1**-(*anti*)-**1d**

1) (1R,3R,4S,g^+,*E*,*a'*)/ (1S,3S,4R,g^-,*E*,*a'*) g^-=- 28.5 °



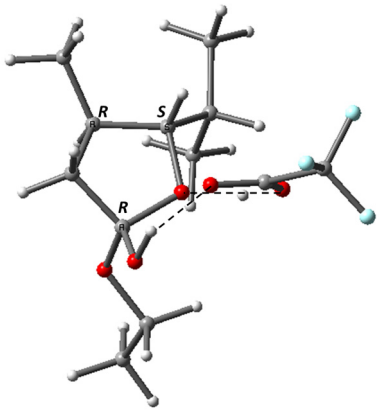
Energy= -1145.60687139 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	2.133750	0.682351	1.319620
2	6	0	2.473960	0.319958	0.207552
3	6	0	3.963346	0.121447	-0.148501
4	8	0	1.707893	0.047121	-0.819835
5	9	0	4.743035	0.414551	0.896293
6	9	0	4.192493	-1.155010	-0.508576
7	9	0	4.308477	0.915519	-1.177738
8	1	0	0.432135	1.489012	1.353422
9	6	0	-1.685949	-2.154671	-1.028487
10	6	0	-1.213458	-1.369961	0.206375
11	6	0	-2.219884	-1.206577	1.363927
12	6	0	-1.755727	0.107555	2.001915
13	6	0	-1.352371	0.970482	0.806695
14	8	0	-2.483617	1.575284	0.294365
15	6	0	-2.298279	2.436513	-0.846835
16	1	0	-2.042311	-3.117373	-0.632045
17	8	0	-0.818299	-0.009187	-0.158732
18	6	0	-2.252135	-2.401479	2.316354
19	1	0	-0.870724	-0.061349	2.628005
20	1	0	-2.518833	0.607107	2.603256
21	6	0	-3.675395	2.813775	-1.359962
22	1	0	0.720010	0.117857	-0.570690
23	1	0	-0.309828	-1.859232	0.599660
24	1	0	-3.221849	-1.051273	0.948682

25	1	0	-1.267329	-2.576076	2.767910
26	1	0	-2.968398	-2.231569	3.128525
27	1	0	-2.553563	-3.319716	1.798440
28	8	0	-0.380481	1.928943	1.024143
29	1	0	-3.580821	3.485962	-2.220451
30	1	0	-4.236194	1.926636	-1.674027
31	1	0	-4.251724	3.329199	-0.583489
32	1	0	-1.720483	1.909517	-1.615074
33	1	0	-1.734861	3.325896	-0.545229
34	6	0	-0.517922	-2.449589	-1.983185
35	1	0	-0.842650	-3.103134	-2.801323
36	1	0	-0.128372	-1.528514	-2.433103
37	1	0	0.310984	-2.948261	-1.465886
38	6	0	-2.843949	-1.487683	-1.783740
39	1	0	-3.710120	-1.294804	-1.141873
40	1	0	-2.529089	-0.534488	-2.221661
41	1	0	-3.179396	-2.135644	-2.602017

2) (1R,3R,4S,g^+,*E*,*g*′′)/ (1S,3S,4R,g^-,*E*,*g*′) g^+= 28.5 °



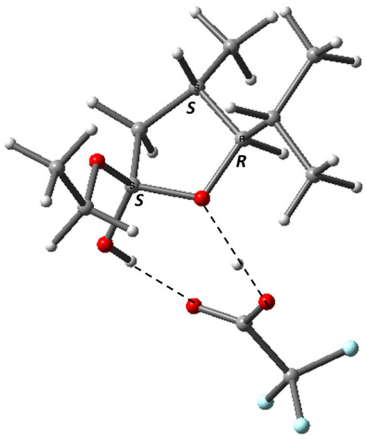
Energy= -1145.60529284 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.737185	-0.141462	1.941756
2	6	0	-1.253454	-1.058226	0.820851
3	8	0	-0.751468	-0.119120	-0.192557
4	8	0	-2.332325	-1.766450	0.325101
5	8	0	-0.233879	-1.940744	1.131297
6	1	0	0.554624	-1.428380	1.409841
7	8	0	2.216080	-0.543165	1.287283
8	6	0	2.538919	-0.238702	0.153076
9	6	0	4.015259	0.023908	-0.215325
10	8	0	1.761495	-0.081105	-0.890225
11	1	0	-2.502809	-0.632412	2.547081
12	1	0	-0.883476	0.100099	2.587256
13	9	0	4.172080	1.292727	-0.636938
14	9	0	4.405626	-0.797938	-1.205688

15	9	0	4.809411	-0.173894	0.840908
16	6	0	-2.062957	-2.689659	-0.749194
17	6	0	-3.397610	-3.219447	-1.239309
18	1	0	-1.523863	-2.172408	-1.551747
19	1	0	-1.430047	-3.503795	-0.381119
20	1	0	0.780658	-0.195202	-0.630655
21	1	0	-3.236737	-3.941264	-2.048233
22	1	0	-3.935715	-3.725202	-0.429786
23	1	0	-4.030075	-2.409856	-1.619973
24	6	0	-2.229068	1.119057	1.216814
25	1	0	-3.213307	0.905815	0.785021
26	6	0	-1.194848	1.251655	0.076254
27	1	0	-0.316212	1.792544	0.458216
28	6	0	-1.608035	1.890246	-1.263432
29	1	0	-0.755742	1.706695	-1.934016
30	6	0	-2.330064	2.337592	2.136763
31	1	0	-3.007953	2.127109	2.972449
32	1	0	-2.715211	3.219649	1.616024
33	1	0	-1.350618	2.595369	2.559215
34	6	0	-2.845681	1.244984	-1.899801
35	1	0	-2.978630	1.613394	-2.923869
36	1	0	-3.760643	1.485514	-1.345142
37	1	0	-2.751883	0.155498	-1.942783
38	6	0	-1.771585	3.413392	-1.147622
39	1	0	-0.904761	3.882045	-0.665552
40	1	0	-2.665612	3.684212	-0.574505
41	1	0	-1.877405	3.857140	-2.144430

3) (1R,3R,4S,g^{+},*E*,*g'*)/ (1S,3S,4R,g^{-},*E*,*g''*) g^{-}=- 16.6 °



Energy=-1145.60739076 a.u.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.504204	-0.296503	1.993724
2	6	0	1.251691	-1.128018	0.740773

3	8	0	0.767059	-0.126782	-0.221826
4	8	0	2.453186	-1.663263	0.313934
5	8	0	0.304445	-2.127775	0.822775
6	1	0	-0.546908	-1.737420	1.116140
7	8	0	-2.242699	-0.942552	1.114625
8	6	0	-2.546879	-0.344947	0.097587
9	6	0	-4.015669	0.024815	-0.202415
10	8	0	-1.753461	0.081045	-0.853919
11	1	0	2.192000	-0.803836	2.674344
12	1	0	0.547099	-0.149150	2.508880
13	9	0	-4.165608	1.362988	-0.190466
14	9	0	-4.380710	-0.426676	-1.414744
15	9	0	-4.833159	-0.502288	0.713661
16	6	0	2.411374	-2.485873	-0.869406
17	6	0	3.844621	-2.764922	-1.281684
18	1	0	1.867085	-1.960598	-1.662708
19	1	0	1.878833	-3.416735	-0.647263
20	1	0	-0.775157	-0.098849	-0.622847
21	1	0	3.857903	-3.409869	-2.167767
22	1	0	4.388696	-3.274079	-0.478283
23	1	0	4.374512	-1.836606	-1.522607
24	6	0	2.037377	1.039528	1.457135
25	1	0	3.109075	0.929280	1.251534
26	6	0	1.293320	1.201184	0.102935
27	1	0	0.414318	1.848628	0.233293
28	6	0	2.130494	1.713389	-1.080496
29	1	0	2.948702	0.992965	-1.220639
30	6	0	1.825970	2.201077	2.431591
31	1	0	2.347609	2.009250	3.376831
32	1	0	2.203034	3.147955	2.032065
33	1	0	0.760500	2.332541	2.659064
34	6	0	2.743641	3.091552	-0.790502
35	1	0	3.307582	3.442574	-1.662630
36	1	0	1.966790	3.838211	-0.579784
37	1	0	3.434093	3.070268	0.059111
38	6	0	1.296218	1.760181	-2.369296
39	1	0	0.877893	0.779730	-2.617939
40	1	0	0.462690	2.469102	-2.273730
41	1	0	1.912543	2.086264	-3.215505

BEP (Bronsted-Evans-Polany) Plots

First, we plotted $\Delta E^{\ddagger}$ *vs.* ΔE_{rxn} relative to the RDS of the ring closure of esters **1a-d** (Figure SI.5), however the correlation was poor (R^2=0.65). Conversely, if the BEP plot is repeated for subset of conformers the correlations significantly improves. We have arbitrary chosen to compare all esters that give the tetrahedral intermediate with *R* stereochemical absolute configuration at C(1) stereogenic center. Then, we classified all esters on the basis of the conformational descriptors g^+, g^-, *E* and *Z*. In Table SI-6 we show the partition in four different subsets: (g^+,*E*), (g^-,*Z*), (g^+,*Z*) and (g^-,*E*).

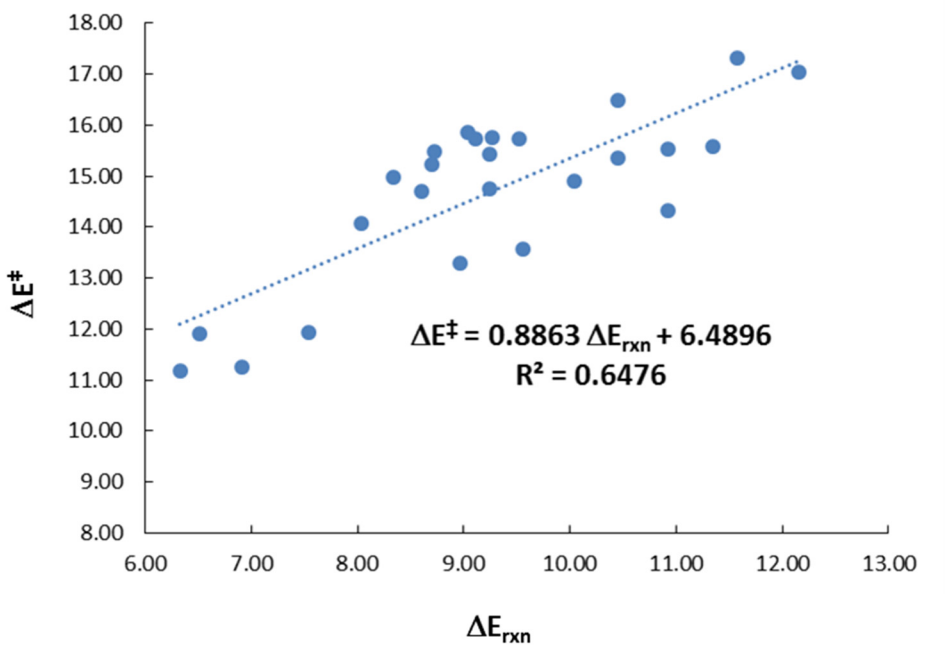


Figure SI-5. Correlation between the energy barrier $\Delta E^{\ddagger}$ without thermal correction and the reaction energy ΔE_{rxn} of the RDS of ring closure of esters **1a-d**. The energies are in kcal mol^{-1}.

Table SI-6. Energy barriers $\Delta E^{\ddagger}$ and reaction energies ΔE_{rxn} of the RDS of the TFA catalyzed lactonization of esters **1a-d** (the *E* are electronic energies without thermal corrections).

Conformational Sub-set	Stereo. Config.	ΔE_{rxn} (kcal mol^{-1})	$\Delta E^{\ddagger}$ (kcal mol^{-1})
g*$^{+}$,*E	(1Re)-**1a** [a]	11.35	15.58
	(1Re,3S,4S)-**1c**	9.49	14.33
	(1Re)-**1b** [a]	10.04	14.90
	(1Re,3R,4R)-**1c**	9.45	14.75
	(1Re,3R,4S)-**1c**	8.97	13.29
	(1Re,3R,4S,*a'*)-**1d**	9.56	13.58
	(1Re,3R,4S,*g''*)-**1d**	7.54	11.94
	(1Re,3R,4S,*g'*)-**1d**	6.91	11.26
g*$^{-}$,*E	(1Re)-**1a** [a]	12.15	17.04
	(1Re,3S,4S)-**1c**	10.92	15.52
	(1Re,3S,4R)-**1c**	10.45	15.35
	(1Re,3R,4R)-**1c**	6.51	11.90
	(1Re)-**1b** [a]	6.33	11.17
g*$^{+}$,*Z	(1Re)-**1a** [a]	10.45	16.50
	(1Re,3R,4R)-**1c**	8.73	15.49
	(1Re)-**1b** [a]	9.24	15.43
	(1Re,3S,4R)-**1c**	8.34	14.99
	(1Re,3S,4S)-**1c**	8.60	14.70
	(1Re,3R,4S)-**1c**	8.04	14.08
g*-,*Z	(1Re)-**1a** [a]	11.57	17.31
	(1Re,3R,4R)-**1c**	9.04	15.87
	(1Re,3S,4R)-**1c**	9.27	15.76
	(1Re,3S,4S)-**1c**	9.11	15.74
	(1Re)-**1b** [a]	9.52	15.73
	(1Re,3R,4S)-**1c**	8.70	15.22

a) For compound **1a-b** the energies have computed in ref. [3]

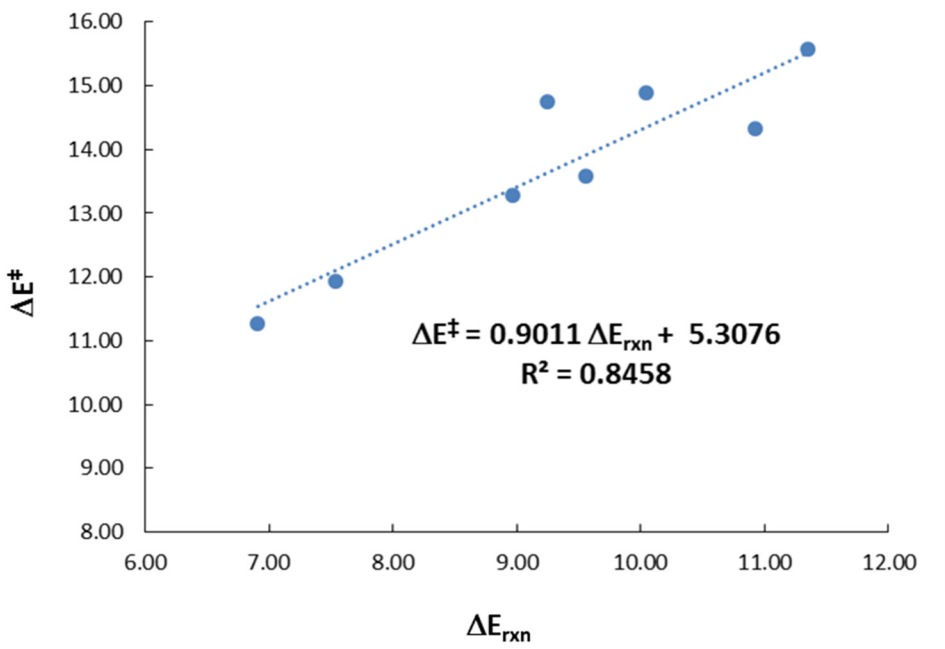


Figure SI.6. BEP plot for (g^+,*E*) conformers, the energies are in kcal mol^{-1}.

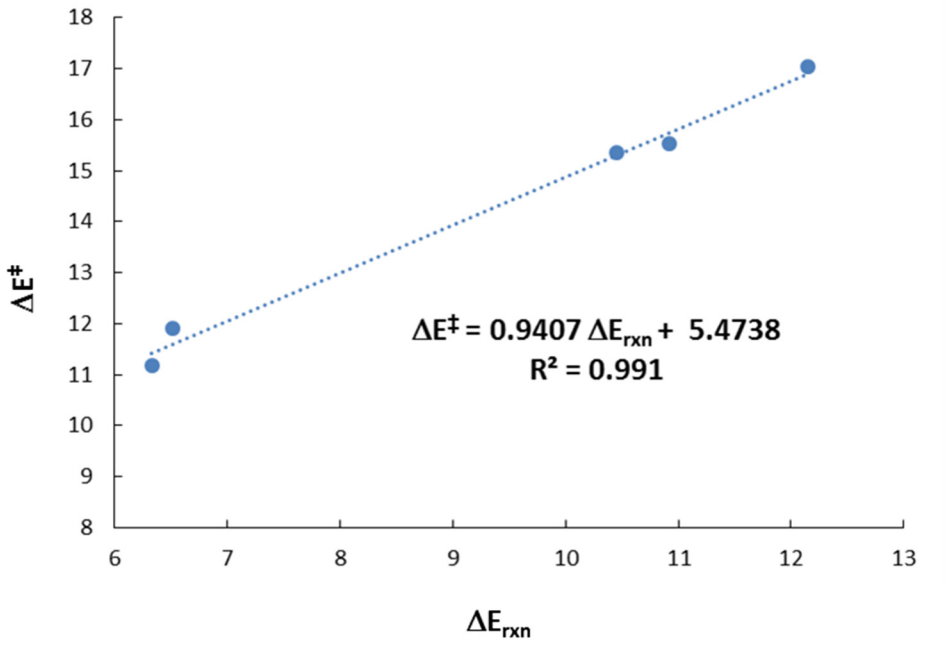


Figure SI.7. BEP plot for (g^-,*E*) conformers, the energies are expressed in kcal mol^{-1}.

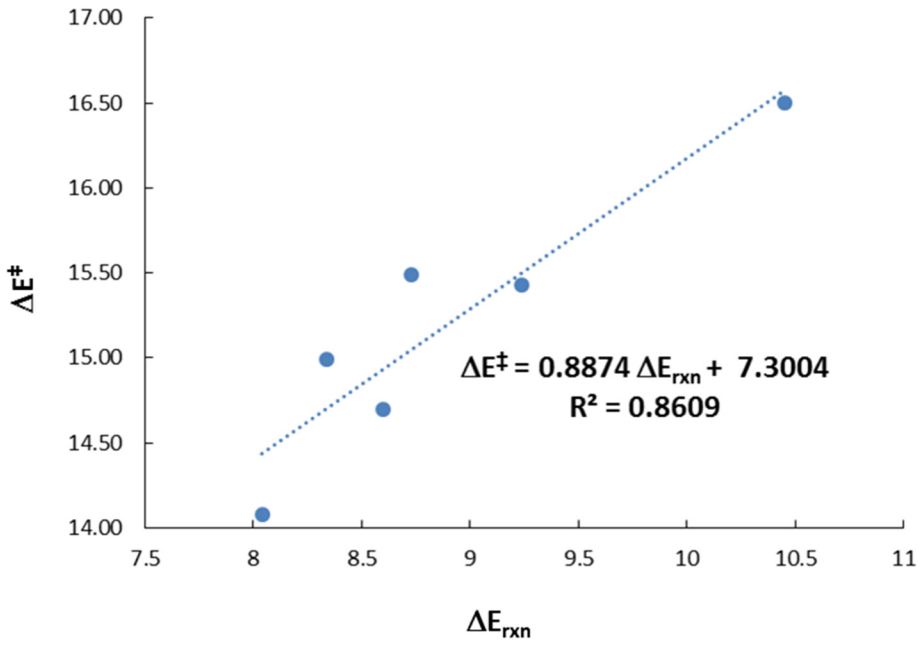


Figure SI.8. BEP plot for (g^+,*Z*) conformers, the energies are in kcal mol^{-1}.

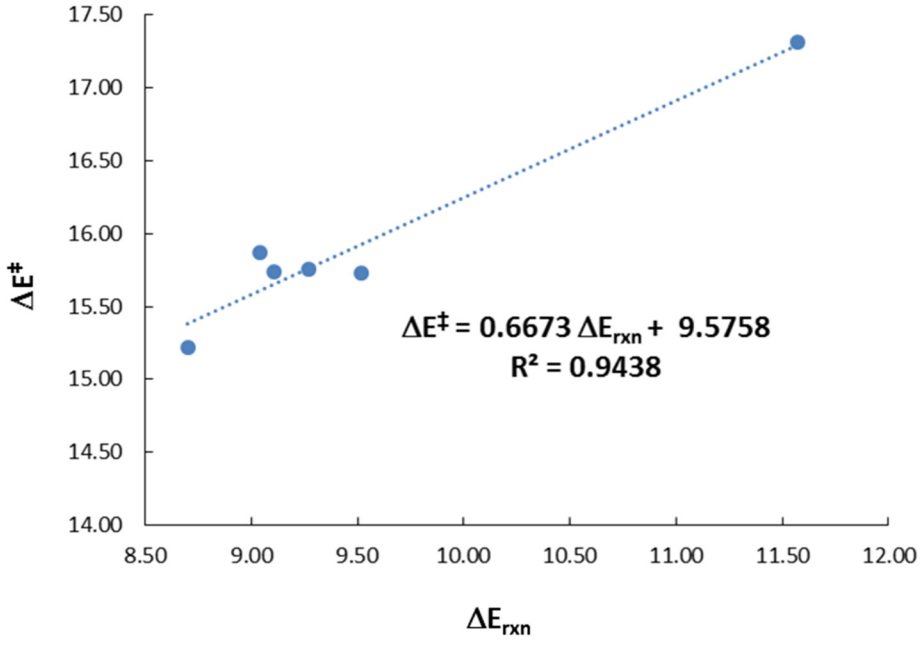


Figure SI.9. BEP plot for (g^-,*Z*) conformers, the energies are in kcal mol^{-1}.

Distortion interaction activation strain model (D/I-ASM) analysis of energy barrier

In Figure SI-10, we report the strategy adopted to decompose the energy barrier of unimolecular reactions.

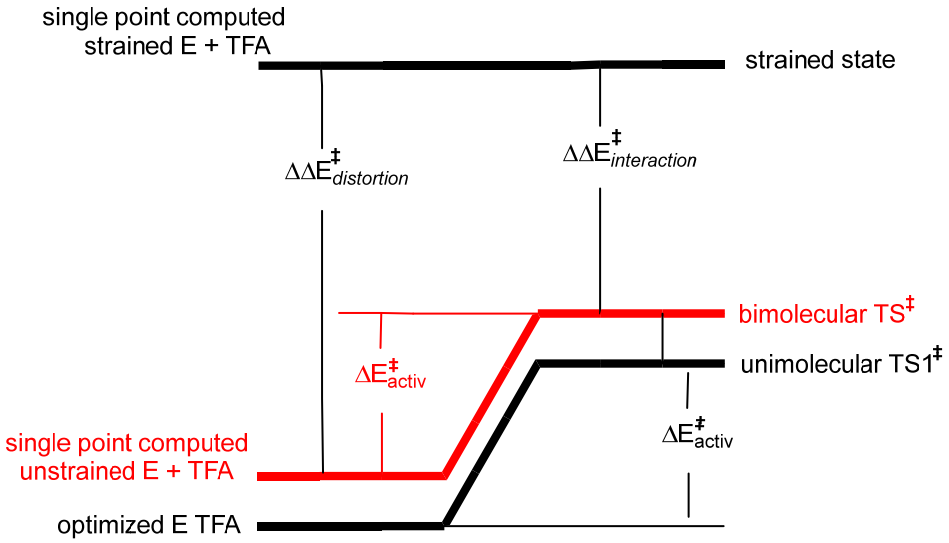


Figure SI.10. Distortion/interaction activation strain model analysis of unimolecular reactions.

Thus, according to the Bickelhaupt's decomposition of intramolecular transformations, the total distortion energy $\Delta E^{\ddagger}_{\text{dist}}$ is the difference between the energies of ester and TFA fragments calculated as single-point in the ***CC*** with the energies of the same fragments, but calculated with the distorted geometries adopted in the $\boldsymbol{TS_1}^{\ddagger}$:

$\Delta E^{\ddagger}_{dist} = \Delta E^{\ddagger}_{dist,\mathrm{E}} + \Delta E^{\ddagger}_{dist,\mathrm{TFA}}$, where $\Delta E^{\ddagger}_{dist,\mathrm{E}} = E_{\mathrm{E}}^{\boldsymbol{TS1}} - E_{\mathrm{E}}^{\boldsymbol{CC}}$ and $\Delta E^{\ddagger}_{dist,\mathrm{TFA}} = E_{\mathrm{TFA}}^{\boldsymbol{TS1}} - E_{\mathrm{TFA}}^{\mathbf{CC}}$

Table SI-7. Energy barriers $\Delta E^{\ddagger}$ and distortion energies of ester and TFA, $\Delta E_{dist,\mathrm{E}}{}^{\ddagger}$ and $\Delta E_{dist,\mathrm{TFA}}{}^{\ddagger}$, together with interaction energy $\Delta E_{inter}{}^{\ddagger}$ of the RDS of the TFA catalyzed lactonization of esters **1a-d** (the *E* are electronic energies without thermal corrections).

Ester	$\Delta E^{\ddagger}$ (kcal mol^{-1})	$\Delta E_{dist,\mathrm{E}}{}^{\ddagger}$ (kcal mol^{-1})	$\Delta E_{dist,\mathrm{TFA}}{}^{\ddagger}$ (kcal mol^{-1})	$\Delta E_{dist}{}^{\ddagger}$ (kcal mol^{-1})	$\Delta E_{inter}{}^{\ddagger}$ (kcal mol^{-1})
1Re,g^+,*E*-**1a** [a)]	15.58	52.96	77.11	130.07	-114.49
1Re,g^+,*E*-**1b** [a)]	14.90	50.32	76.58	126.90	-112.00
1Re,3R,4S,g^+,*E-anti*-**1c**	13.29	49.98	76.65	126.63	-113.34
1Re,3R,4R,g^+,*E-syn*-**1c**	14.75	49.24	75.81	125.05	-110.30
1Re,3S,4S,g^+,*E-syn*-**1c**	14.33	49.82	76.40	126.23	-111.90
1Re,3R,4S,g^+,*E*,*a'-anti*-**1d**	13.58	50.79	77.39	128.18	-114.59
1Re,3R,4S,g^+,*E*,*g''-anti*-**1d**	11.94	47.72	76.51	124.23	-112.29
1Re,3R,4S,g^+,*E*,*g'-anti*-**1d**	11.27	46.72	75.60	122.32	-111.05
1Re,g^-,*E*-**1a** [a)]	17.04	53.63	77.19	130.82	-113.78
1Re,g^-,*E*-**1b** [a)]	11.17	47.39	74.82	122.21	-111.04
1Re,3S,4R,g^-,*E-anti*-**1c**	15.35	52.07	75.83	127.90	-112.55
1Re,3S,4S,g^-,*E-syn*-**1c**	15.52	51.95	77.13	129.08	-113.57
1Re,3R,4R,g^-,*E-syn*-**1c**	11.90	49.15	76.17	125.32	-113.34
1Re,g^+,*Z*-**1a** [a)]	16.50	44.27	72.75	117.02	-100.51
1Re,g^+,*Z*-**1b** [a)]	15.43	42.73	71.78	114.51	-99.08
1Re,3S,4R,g^+,*Z-anti*-**1c**	14.99	40.23	69.23	109.46	-94.47
1Re,3R,4S,g^+,*Z-anti*-**1c**	14.08	39.05	70.59	109.65	-95.57
1Re,3R,4R,g^+,*Z-syn*-**1c**	15.49	43.04	71.24	114.59	-99.10
1Re,3S,4S,g^+,*Z-syn*-**1c**	14.70	40.01	69.36	109.37	-94.67
1Re,g^-,*Z*-**1a** [a)]	17.31	48.36	73.11	121.47	-104.16

1Re,g^-,*Z*-**1b** [a)]	15.73	43.20	72.23	115.43	-99.70
1Re,3S,4R,g^-,*Z-anti*-**1c**	15.77	46.18	72.34	120.18	-104.41
1Re,3R,4S,g^-,*Z-anti*-**1c**	15.22	40.81	68.92	109.73	-94.51
1Re,3R,4R,g^-,*Z-syn*-**1c**	15.87	43.59	70.73	114.32	-98.45
1Re,3S,4S,g^-,*Z-syn*-**1c**	15.74	44.77	71.72	116.49	-100.75

a) For compound **1a-b** the energies have been computed starting from **CC** and **TS1**‡ reported in ref. [3]

b)

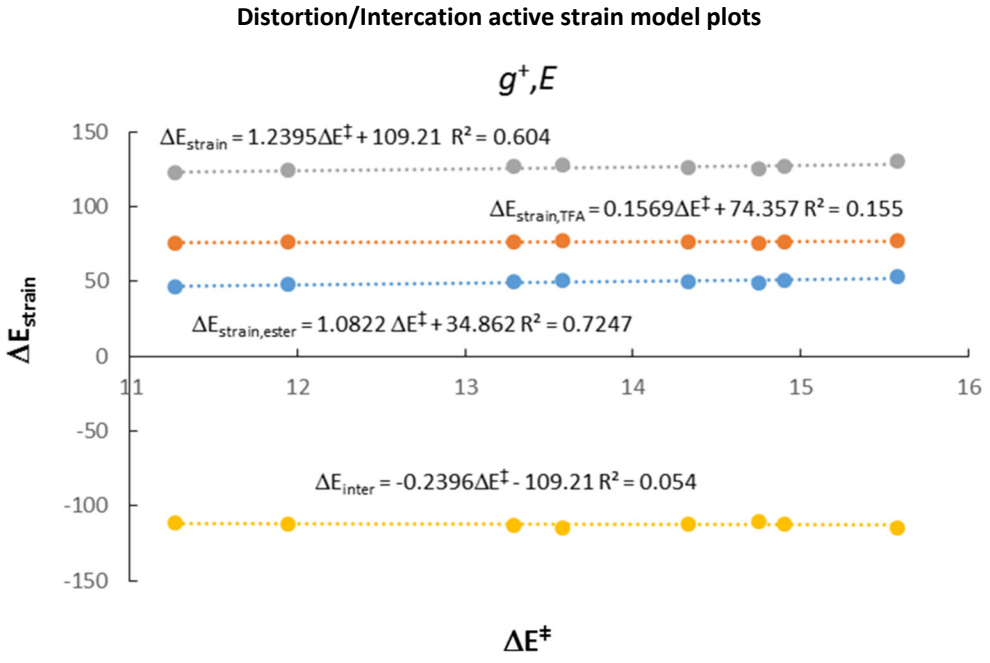


Figure SI.11. D/I-A strain model plot for (g^+,*E*) conformers, the energies are in kcal mol^{-1}.

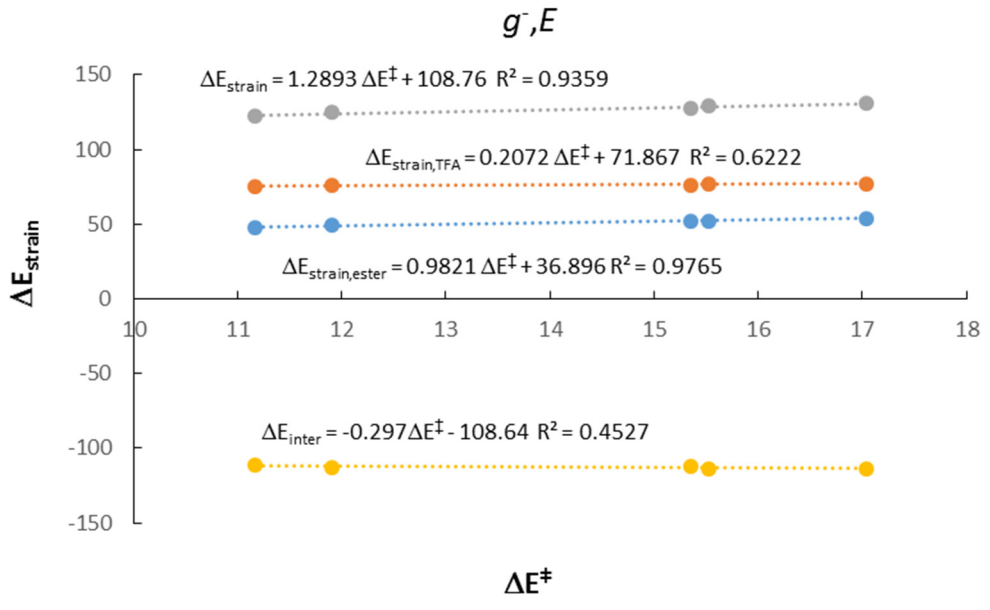


Figure SI.12. D/I-A strain model plot for (g^-,*E*) conformers, the energies are in kcal mol^{-1}.

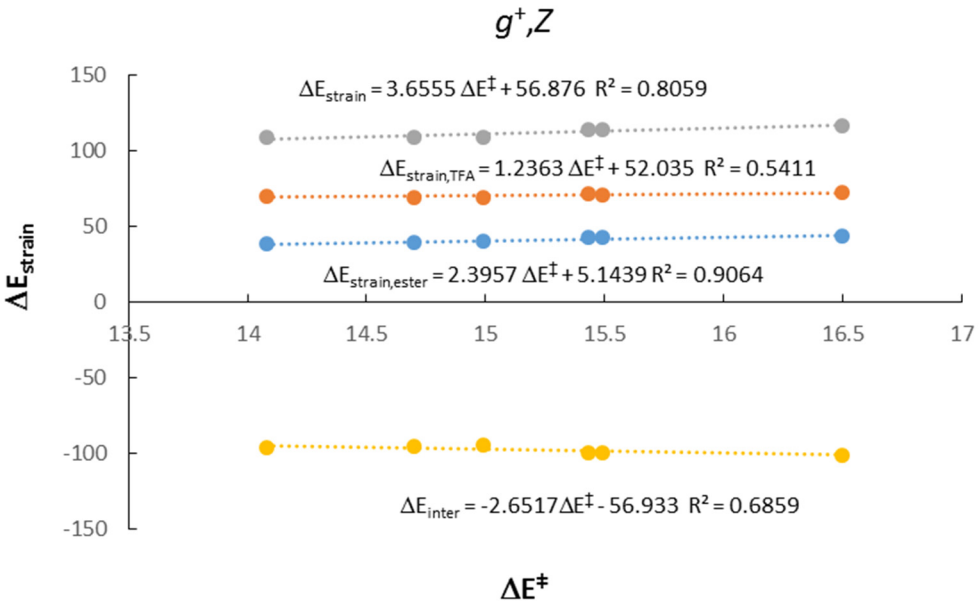


Figure SI.13. D/I-A strain model plot for (g^+,*Z*) conformers, the energies are in kcal mol^{-1}.

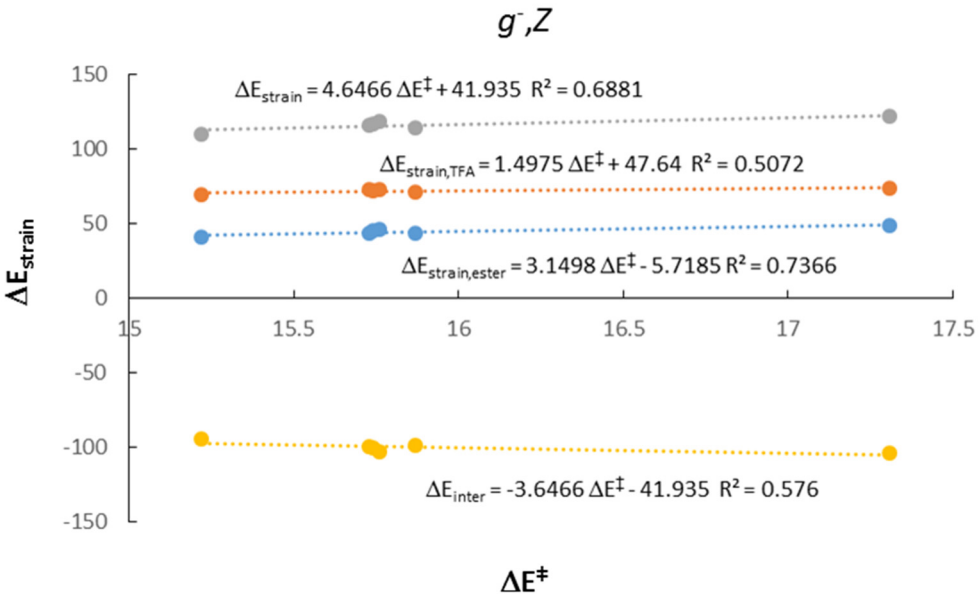


Figure SI.14. D/I-A strain model plot for (g^-,*Z*) conformers, the energies are in kcal mol^{-1}.