CHEMISTRY
A EUROPEAN JOURNAL

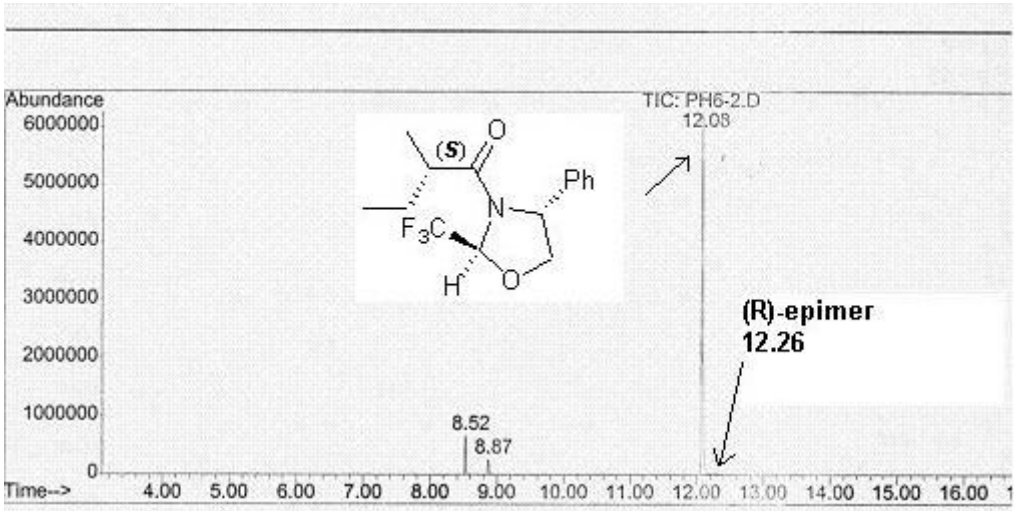
Supporting Information

Fluorine·and p·Alcali Metal Interactions control in the Stereoselective Amide Enolates Alkylation using Fluorinated Oxazolidines (Fox) as Chiral Auxiliary: An experimental and Theoretical Study

Gjergji Sini*, Arnaud Tessier, Julien Pytkowicz, and Thierry Brigaud*

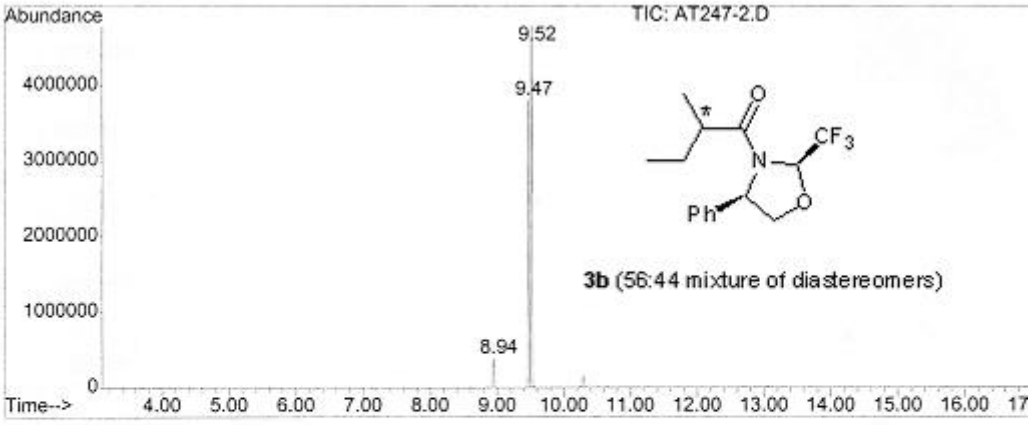
1- Synthesis:

GC/MS of the crude mixture of the benzylation reaction of *trans*-1 in toluene:



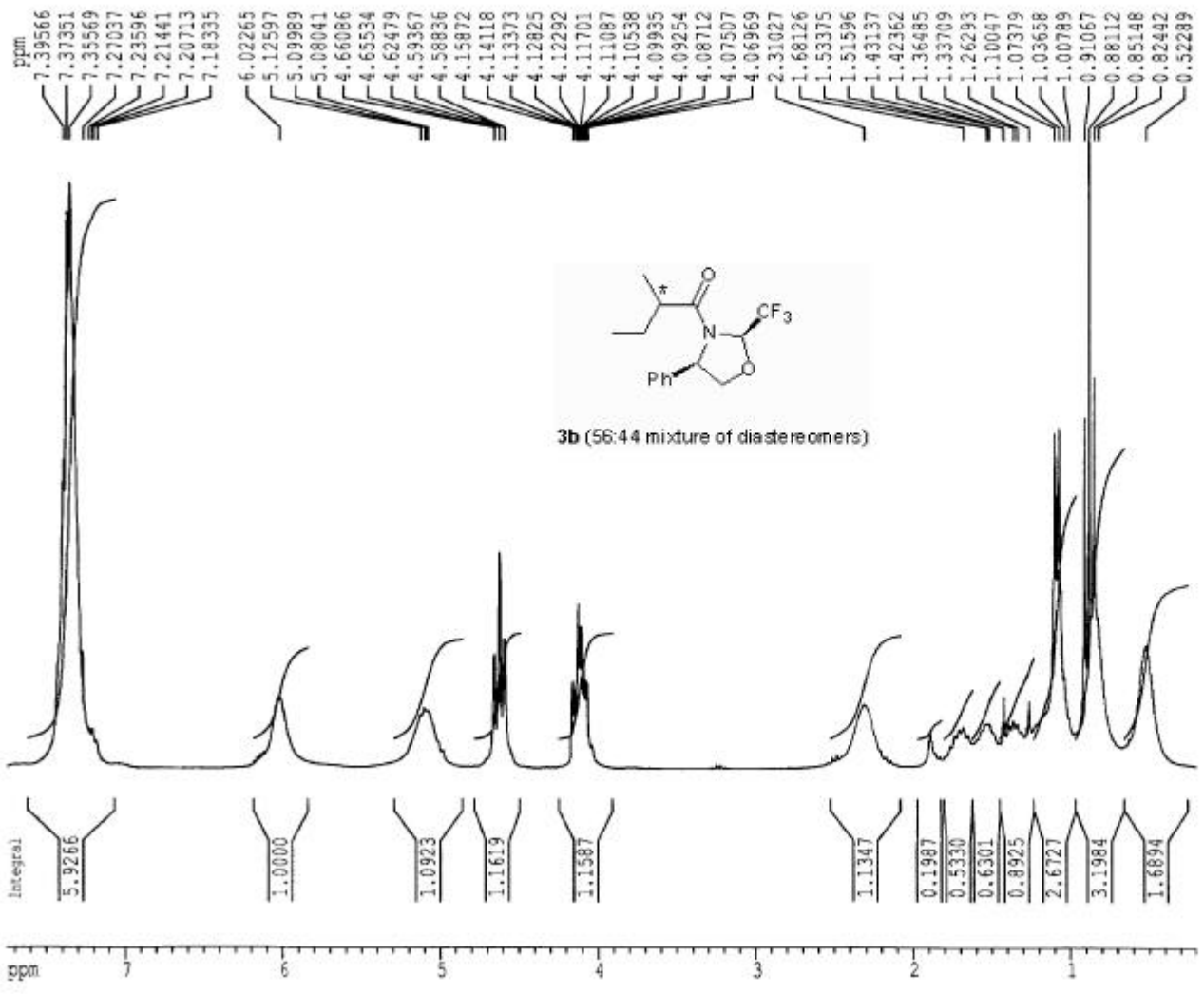
Retention Time	Area	Area %	Ratio %
Total Ion Chromatogram			
8.524	6856666	6.399	7.060
8.869	3178488	2.966	3.273
12.083	97122833	90.635	100.000

GC/MS of the crude mixture of the ethylation reaction of *cis*-1 THF:



Retention Time	Area	Area %	Ratio %
Total Ion Chromatogram			
8.944	3711116	3.641	6.947
9.473	44798891	43.952	83.866
9.517	53417008	52.407	100.000

at247-2



3b (56:44 mixture of diastereomers)

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Current Data Parameters
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EXPNO                773
PROCNO                 1

F2 - Acquisition Parameters
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INSTRUM           spect
PROBHD     5 mm QNP  1H
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                  128
DS                    0
SWH           5175.983 Hz
FIDRES        0.078979 Hz
AQ            6.3308277 sec
RG                  128
DW               96.600 usec
DE                6.50 usec
TE               300.0 K
D1            2.00000000 sec

------------ CHANNEL f1 ------------
NUC1                  1H
P1                13.50 usec
PL1               -6.00 dB
SFO1         250.1315447 MHz

F2 - Processing parameters
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SF           250.1300049 MHz
WDW                  EM
SSB                   0
LB                0.30 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P                7.753 ppm
F1              1939.17 Hz
F2P               0.200 ppm
F2                50.03 Hz
PPMCM          0.37763 ppm/cm
HZCM          94.45739 Hz/cm
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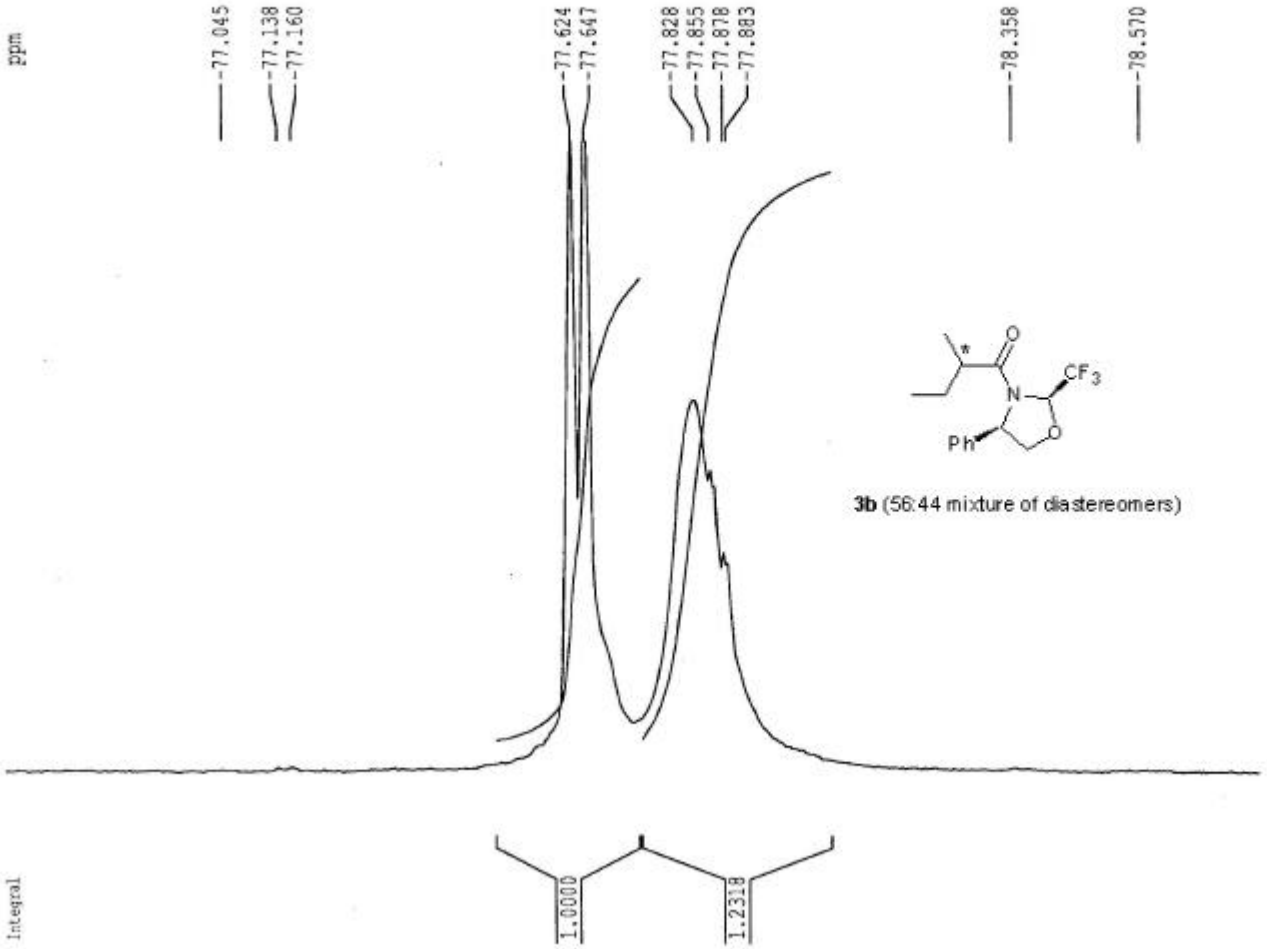
at247-2



3b (56:44 mixture of diastereomers)

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EXPNO                772
PROCNO                 1

F2 - Acquisition Parameters
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TD               131072
SOLVENT            CDCl3
NS                    16
DS                     4
SWH           56497.176 Hz
FIDRES        0.431039 Hz
AQ            1.1600372 sec
RG               2298.8
DW               8.850 usec
DE                6.50 usec
TE               300.0 K
D1            1.00000000 sec

------------ CHANNEL f1 ------------
NUC1                  19F
P1                 9.00 usec
PL1               -6.00 dB
SFO1         235.3339190 MHz

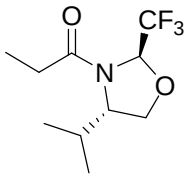
F2 - Processing parameters
SI                 65536
SF           235.3574550 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P              -76.684 ppm
F1             -18048.04 Hz
F2P              -78.766 ppm
F2             -18538.09 Hz
PPMCM            0.10411 ppm/cm
HZCM            24.50243 Hz/cm
```

2-trifluoromethyl-3-propanoyl-4-*iso*propyloxazolidine (4).

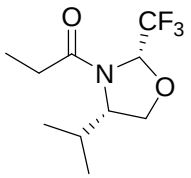
Oxazolidines *trans*-**4** and *cis*-**4** were prepared folowing our previouseley reported procedure[1] from a diastereomeric mixture of (4*S*)-2-trifluoromethyl-4-*iso*propyloxazolidine[2](2.45g, 13.4 mmol). After silicagel chromatography (cyclohexane/ethyl acetate: 90/10), *trans*-**4** (1.356g, 43%) and *cis*-**4** (0.992g, 32%) were obtained.

(2*R*,4*S*)-2-trifluoromethyl-3-propanoyl-4-*iso*-propyloxazolidine (*trans*-4)



^{1}H NMR (400 MHz, $CDCl_3$) **:** δ 0.93 (d, 3H, ^{3}J = 6.4 Hz), 0.97 (d, 3H, ^{3}J = 6.4 Hz),1.12-1.19 (m, 1H), 1.18 (t, 3H, ^{3}J = 6.9 Hz), 1.99 (sep, 1H, J = 6.8 Hz), 2.39 (sep, 1H, J = 7.1 Hz), 2.36-2.46 (m, 1H), 4.06 (bs, 2H), 5.50-5.60 (bs, 1H); ^{19}F NMR (376.2 MHz, $CDCl_3$) : δ -81.55 (d, 3F, $^{3}J_{H-F}$ = 4.8 Hz); ^{13}C NMR (100.5 MHz, $CDCl_3$) : δ 8.8, 18.7, 19.4, 28.1, 30.7, 62.7, 70.6, 85.1 (q, $^{3}J_{C-F}$ = 35.4 Hz), 122.7 (q, $^{2}J_{C-F}$ = 284.7 Hz), 174.7; MS : 239 (M^+, 9), 196 (42), 170 (6), 140 (38), 114 (21), 85 (8), 57 (100); GC R_t = 6.60 min.

(2*S*,4*S*)-2-trifluoromethyl-3-propanoyl-4-*iso*-propyloxazolidine (*cis*-4)



^{1}H NMR (400 MHz, $CDCl_3$) **:**mixture of two conformers (50/50) δ 0.69-1.0 (m, 6H), 1.20 (t, 3H, ^{3}J = 7.3 Hz),2.17 (m, 0.5H), 2.39 (sep, 1H, J = 7.1 Hz), 2.27-2.50 (m, 1H), 2.8 (m, 0.5H), 3.97 (bs, 1H), 4.13 (bs, 1H), 4.22 (bs, 1H), 5.49 (m, 0.5H), 5.81 (m, 1H); ^{19}F NMR (376.2 MHz, $CDCl_3$) : mixture of two conformers δ -81.28 (bs) -81.71 (bs); ^{13}C NMR (100.5 MHz, $CDCl_3$) : mixture of two conformers δ 9.4, 14.1 (0.5C), 14.7 (bs, 0.5C), 19.1, 25.1 (bs, 0.5C), 28.7, 30.9 (bs, 0.5C), 61.1, 67.3 (bs, 0.5C), 68.2 (bs,

[1] A. Tessier, J. Pytkowicz, T. Brigaud, *Angew. Chem.* **2006**, *118*, 3759–3763; *Angew. Chem. Int. Ed.* **2006**, *45*, 3677–3681.

[2]F. Gosselin, A. Roy, P. D. O'Shea, C. Cheng, R. P. Volante, *Org. Lett.* **2004**, *6*, 641–644.

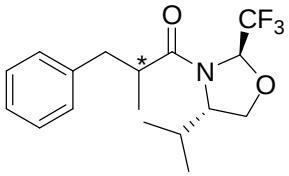
0.5C), 84.4 (q, $^{3}J_{C\text{-}F}$ = 34.5 Hz), 123.3 (q, $^{2}J_{C\text{-}F}$ = 289.4 Hz), 171.5 (bs, 0.5C), 173.5 (bs, 0.5C); MS : 239 (M^{+}, 9), 196 (42), 170 (6), 140 (38), 114 (21), 85 (8), 57 (100); GC R_t = 6.49 min.

Procedure for the benzylation reaction of *trans*-4 or *cis*-4 in THF:

The oxazolidine **4** (0.343 g, 1.43 mmol) was dissolved in THF (10 mL) under argon atmosphere. The solution was cooled down to -78°C and NaHMDS was added dropwise (1.12 mL, 2M in THF, 2.24 mmol). The reaction mixture was stirred for 0.5 hours at this temperature and the benzylbromide (0.233 mL, 2.24 mmol) was added slowly. The reaction mixture was stirred for 4 additional hours at -78°C, quenched with a saturated NH_4Cl solution (15 mL) and extracted with dichloromethane (2x30 mL). The combined organic layers were dried over $MgSO_4$, evaporated under reduced pressure to give a crude mixture (702 mg) which was analyzed by ^{1}H and ^{19}F NMR spectroscopy.

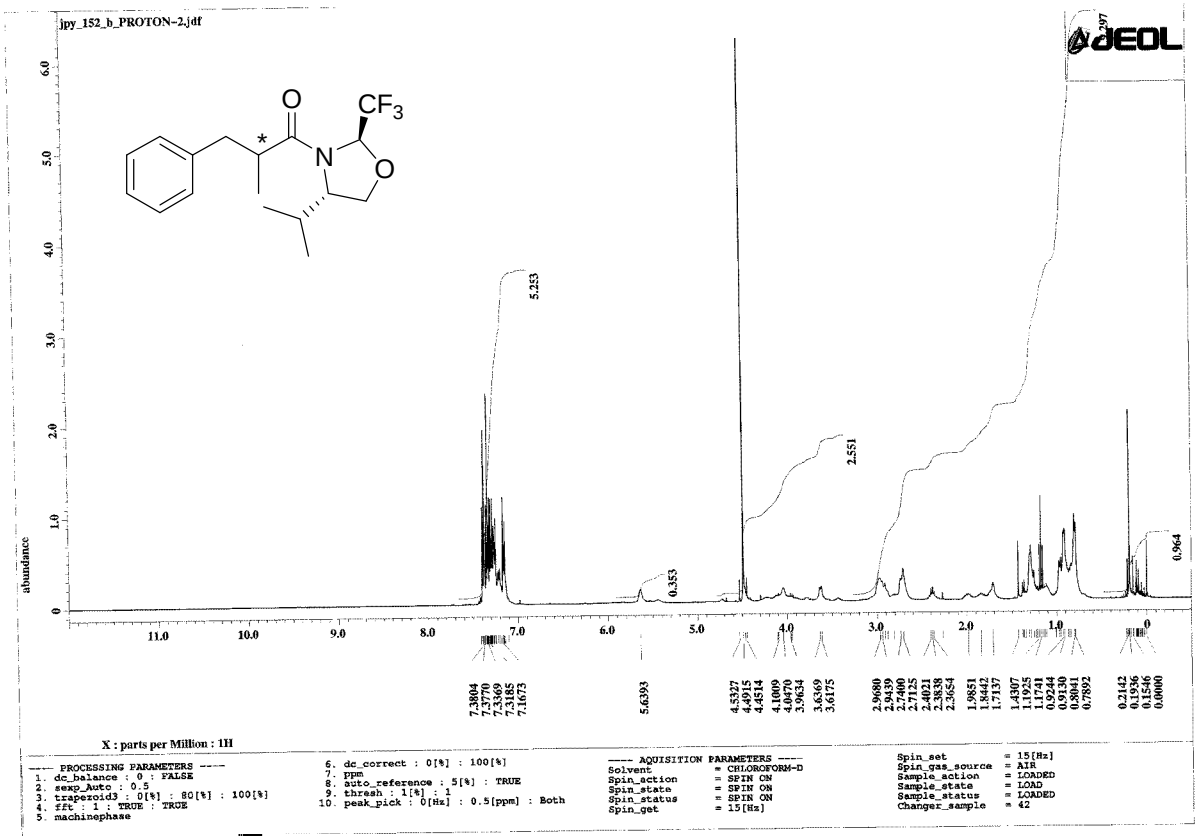
Conformers were identified by the coalescence of their ^{19}FNMR signals at high-temperature. The ratios of diastereomers were measured by GC-MS and ^{19}FNMR experiments.

(2*R*,4*S*)-2-trifluoromethyl-3-[-2-methyl-3-phenylpropanoyl]-4-*iso*propyloxazolidine

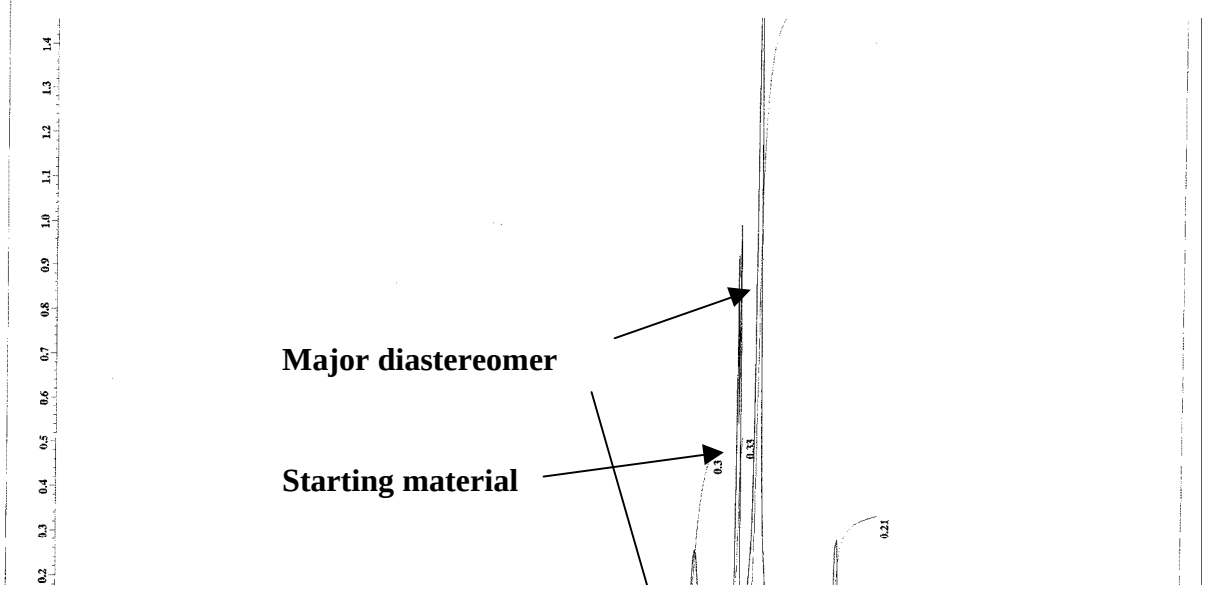


mixture of two diastereomers (80/20) each appearing as a mixture of two conformers (77/23)**:** ^{1}H NMR (400 MHz, $CDCl_3$) **:** δ 0.77-0.96 (m, 6H), 1.06-1.15 (m, 1H), 1.20-1.35 (m, 2H), 1.69-1.89 (m, 1H), 2.65-2.85 (m, 2H), 2.90-3.05 (m, 2H), 3.40-3.50 (m, 0.2H, minor dias), 3.63 (d, 0.8H, ^{3}J = 7.3 Hz, major dia), 3.75-3.83 (m, 0.1H, minor dias), 3.95-4.30 (m, 0.8H), 4.72 (m, 0.1H, minor dias), 5.45 (m, 0.2H, minor dias); 5.64 (m, 0.8H, major dias); ^{19}F NMR (376.2 MHz, $CDCl_3$): δ -81.3 (bs, major dias, minor conformer), -81.46 (bs, minor dias minor conformer), -81.68 (bs, major dias minor conformer), -82.12 (bs, minor dias major conformer); MS : 329 (M^{+}, 35), 188 (3), 147 (45), 119 (98), 91 (100); GC R_t = 10.21min.

^{1}H : Benzylation of *trans*-4 (crude)

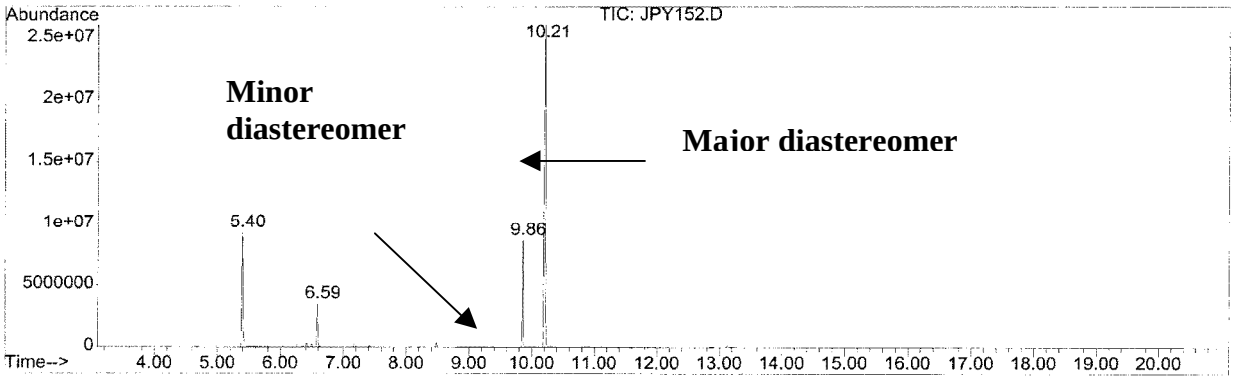


^{19}F : Benzylation of *trans*-4 (crude): 80/20 mixture of diastereomers (two conformers for each compound)



Minor diastereomer

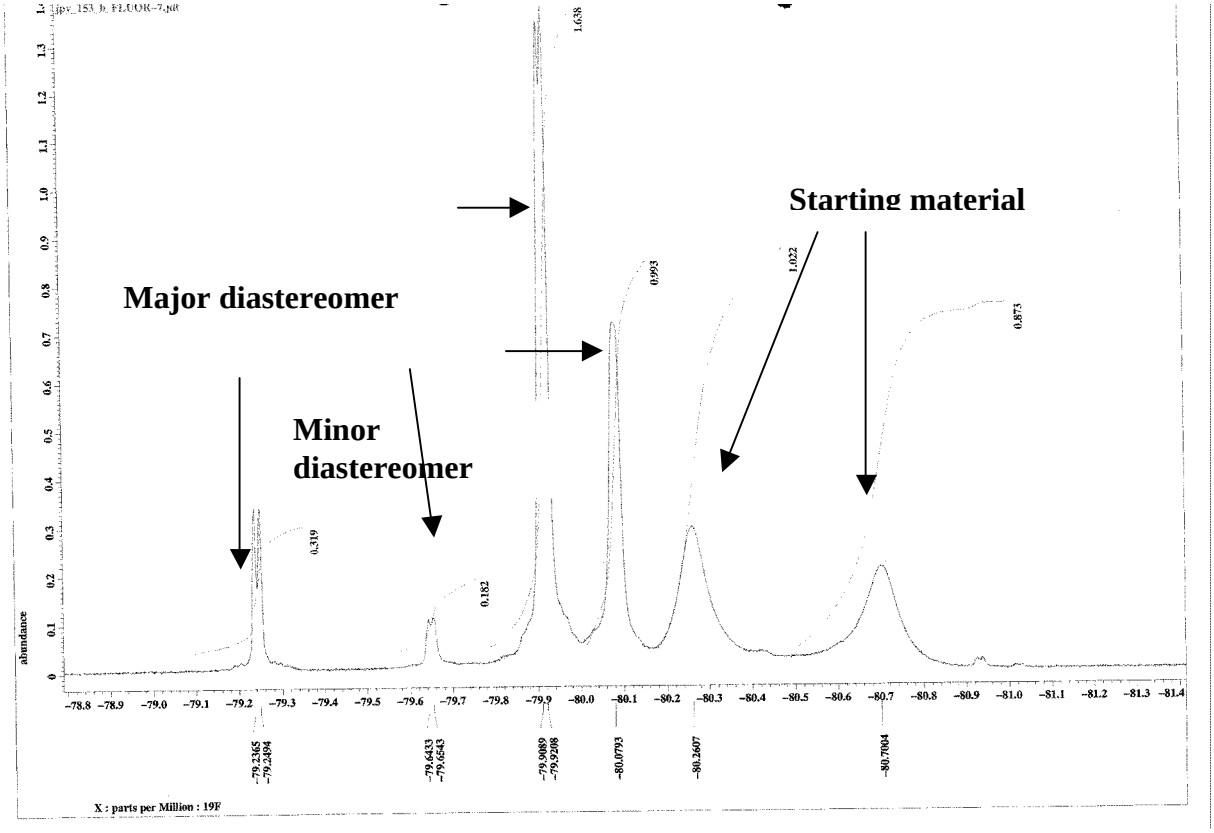
GC/MS of the benzylation of *trans*-4 (crude): 80/20 mixture of diastereomers



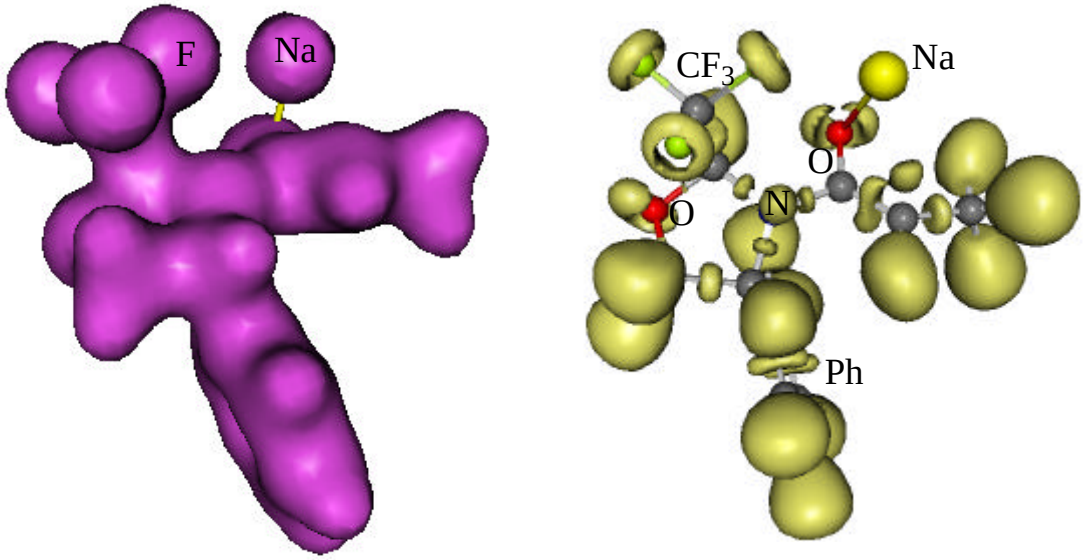
Retention Time	Area	Area %	Ratio %	
Total Ion Chromatogram				
5.398	126780066	20.638	35.260	
6.587	37288301	6.070	10.370	
9.858	90671664	14.760	25.217	20 %
10.207	359562195	58.532	100.000	80 %

^{1}H : Benzylation of *cis*-4

^{19}F : Benzylation of *cis*-4 (crude): 62/38 mixture of diastereomers (two conformers for each compound)



2- Calculations :



a b

Figure 1. Total electronic density surface (a) and ELF representation (b) for the *trans*-EN1 enolate.

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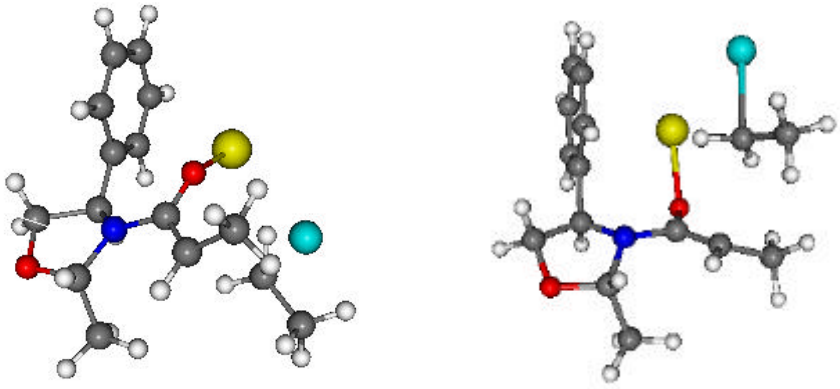

Si-face alkylation Re-face alkylation

Figure 2. Optimised structures of the transition states for the *trans*-oxazolidine chiral auxiliary having a methyl group in place of the trifluoromethyl one.

3- Cartesian coordinates for all the calculated species.

***trans*-TS1**

N	0.114758	-0.404932	-0.154678
C	1.372729	-0.909157	0.425017
C	1.556410	-2.207108	-0.391514
O	0.964096	-1.908082	-1.662371
C	-0.143186	-1.075554	-1.413109
C	-0.375694	0.920013	0.048278
C	-0.061331	1.577913	1.235258
C	-0.222125	3.068252	1.377403
O	-1.160997	1.364715	-0.866380
C	2.576163	0.018001	0.300391
C	2.857341	0.703606	-0.889010
C	4.006966	1.485097	-1.000948
C	4.896641	1.589464	0.071405
C	4.627103	0.907368	1.258357
C	3.473727	0.128034	1.368692
C	-1.400268	-1.975090	-1.381699
F	-1.360283	-2.901320	-0.413797
F	-1.570810	-2.592543	-2.558532
F	-2.554636	-1.246016	-1.164547
Na	-3.252216	0.926291	-0.987321
I	-5.061756	0.730285	1.406037
C	-2.570950	0.962056	2.017027
C	-2.528286	1.056350	3.514733
H	0.622013	1.093714	1.925206
H	1.228363	-1.158677	1.483140
H	-0.272326	-0.374010	-2.242684
H	2.172918	0.631258	-1.728695
H	1.047245	-3.055065	0.081335
H	2.603337	-2.458425	-0.566218
H	-0.935034	3.454715	0.641118
H	0.728026	3.599983	1.212154
H	-0.571148	3.360278	2.378224
H	4.208055	2.015068	-1.928251

H	5.790511	2.200954	-0.017427
H	5.309222	0.985208	2.100936
H	-2.457733	1.861145	1.437236
H	-2.277559	0.035367	1.546813
H	3.266020	-0.396428	2.299596
H	-2.904275	0.144160	3.986118
H	-1.487210	1.198915	3.832274
H	-3.111733	1.905552	3.880344

***trans*-TS2**

C	1.387578	1.360370	-1.445944
H	2.367455	1.267598	-0.989923
C	1.342784	2.107626	-2.753856
H	1.669388	3.153259	-2.657115
H	2.000440	1.646685	-3.507884
H	0.329741	2.105062	-3.169652
C	0.409361	0.420055	-1.116855
O	-0.781440	0.394280	-1.592190
N	0.668119	-0.548881	-0.104248
C	1.957761	-0.904943	0.443338
H	2.523053	-0.032934	0.787935
C	2.875897	-1.698970	-0.521944
F	3.321899	-0.947543	-1.544803
F	3.952511	-2.158889	0.143286
F	2.230075	-2.764471	-1.052143
O	1.665522	-1.715766	1.555263
C	0.487623	-2.465559	1.232165
H	-0.050806	-2.640450	2.165750
H	0.754766	-3.428825	0.785785
C	-0.312671	-1.585332	0.227212
H	-0.575666	-2.173277	-0.660231
C	-1.599012	-1.047299	0.835084
C	-1.568939	-0.136157	1.902109
H	-0.607576	0.198373	2.282900

C	-2.754324	0.349850	2.460255
H	-2.712878	1.068387	3.273286
C	-3.992576	-0.075635	1.965475
H	-4.913425	0.304397	2.398006
C	-4.034569	-0.997642	0.913805
H	-4.990606	-1.345082	0.530453
C	-2.844381	-1.479976	0.355676
H	-2.879714	-2.186671	-0.470267
C	-0.127719	3.199624	-0.159097
H	-0.428851	2.912660	-1.150889
H	-0.108654	2.412367	0.580038
I	-2.453389	4.056354	0.453298
Na	-2.529309	1.189804	-0.595039
C	0.799445	4.368718	0.010963
H	0.847893	4.698158	1.052609
H	0.494446	5.215954	-0.609142
H	1.808982	4.069249	-0.299053

***trans*-TS3**

I	-1.316998	3.584450	-2.450785
C	0.305854	2.840741	-0.501392
C	1.434238	3.821223	-0.491979
N	-0.284250	-0.585316	0.459456
C	0.824720	-1.497067	0.752619
C	0.252806	-2.792472	0.146600
O	-0.524536	-2.329216	-0.965975
C	-1.148959	-1.135739	-0.562645
C	-0.537576	0.657467	1.078491
C	0.487271	1.322267	1.749889
C	0.209468	2.429932	2.729242
O	-1.717233	1.121935	0.884417
C	2.175677	-1.111523	0.159465
C	2.310377	-0.757328	-1.190736
C	3.563271	-0.451211	-1.722286

C	4.702156	-0.496402	-0.913509
C	4.579183	-0.851924	0.429995
C	3.323230	-1.157443	0.959467
C	-2.620546	-1.450408	-0.111742
F	-2.773895	-1.573299	1.206229
F	-3.059906	-2.577723	-0.690043
F	-3.490449	-0.465533	-0.550820
Na	-2.990990	1.846950	-0.632939
H	1.080700	4.844838	-0.340705
H	2.102417	3.570861	0.344502
H	1.468050	0.860457	1.787533
H	1.433690	-0.733632	-1.831272
H	3.650572	-0.178392	-2.770710
H	5.676894	-0.254606	-1.328460
H	5.457827	-0.887661	1.068680
H	3.232838	-1.428076	2.009650
H	0.932059	-1.594544	1.839148
H	-1.240421	-0.492607	-1.449802
H	2.022329	3.779864	-1.412748
H	-0.499395	2.935428	0.202986
H	-0.387468	-3.318107	0.868577
H	1.009325	-3.474978	-0.242281
H	-0.811227	2.807576	2.609452
H	0.901072	3.277499	2.612652
H	0.309859	2.093514	3.773615
H	0.455897	1.868752	-0.943889

***trans*-RC1**

N	-0.184146	0.342109	-0.070550
C	-1.183302	0.389015	0.996238
C	-1.123384	1.892143	1.365860
O	-0.735680	2.552326	0.155195
C	0.106072	1.671192	-0.547687
C	0.025681	-0.773632	-0.953007

C	0.098509	-2.037112	-0.397366
C	0.022710	-3.291358	-1.235420
O	0.251018	-0.460488	-2.188574
C	-2.583077	-0.065631	0.598876
C	-3.074316	0.103489	-0.701318
C	-4.385963	-0.257413	-1.013303
C	-5.225386	-0.788519	-0.031579
C	-4.741888	-0.964991	1.266159
C	-3.428479	-0.607776	1.574803
C	1.576124	2.054382	-0.263570
F	1.892294	2.000620	1.046432
F	1.873830	3.278874	-0.715069
F	2.449788	1.186346	-0.895659
Na	2.307799	-1.008265	-1.896368
I	4.756886	-1.818151	-0.098682
C	3.325306	-1.302900	1.513067
C	3.723065	-1.930310	2.833948
H	-0.108981	-2.139784	0.665752
H	-0.861295	-0.201640	1.864636
H	-0.050594	1.779493	-1.624771
H	-2.421575	0.492958	-1.476304
H	-0.383516	2.075404	2.155275
H	-2.089779	2.297883	1.669908
H	0.123796	-3.047848	-2.299976
H	-0.944316	-3.807182	-1.122486
H	0.795485	-4.032946	-0.980773
H	-4.750761	-0.127024	-2.028830
H	-6.245698	-1.070634	-0.277812
H	-5.382879	-1.387711	2.035738
H	2.369829	-1.662092	1.121859
H	3.334521	-0.213729	1.526153
H	-3.053530	-0.756935	2.586145
H	4.703455	-1.585397	3.175331
H	2.979749	-1.637853	3.588255
H	3.735172	-3.022493	2.778069

***trans*-RC3**

I	5.516169	-1.043989	-0.314924
C	3.914110	-2.322495	-1.194060
C	4.043666	-3.759537	-0.735259
N	-0.498488	0.416822	-0.001633
C	-1.824115	0.682015	0.539220
C	-2.087676	2.105756	-0.019788
O	-1.202566	2.232739	-1.140540
C	-0.047526	1.512846	-0.807891
C	0.419172	-0.565450	0.489977
C	0.027781	-1.450052	1.449161
C	0.920947	-2.546312	1.957510
O	1.597756	-0.475085	-0.083010
C	-2.888792	-0.323923	0.117362
C	-2.856934	-0.929604	-1.143816
C	-3.878370	-1.793006	-1.540296
C	-4.947363	-2.061974	-0.681615
C	-4.985389	-1.464406	0.579274
C	-3.960562	-0.601930	0.973717
C	0.974069	2.493002	-0.087254
F	1.205512	2.183198	1.225506
F	0.595245	3.771957	-0.119518
F	2.217504	2.439214	-0.680055
Na	3.143786	0.712992	0.687998
H	3.927439	-3.850564	0.348194
H	3.233518	-4.333583	-1.206208
H	-1.001646	-1.448601	1.790539
H	-2.016851	-0.730814	-1.802264
H	-3.838134	-2.260829	-2.520831
H	-5.740655	-2.737650	-0.990627
H	-5.807386	-1.674367	1.258968
H	-3.989590	-0.145625	1.961718
H	-1.794721	0.717460	1.638769

H	0.455541	1.195647	-1.724809
H	4.995822	-4.211203	-1.029326
H	2.993484	-1.828737	-0.864728
H	-1.856910	2.875937	0.730444
H	-3.105922	2.252001	-0.383052
H	1.950510	-2.398047	1.610999
H	0.608764	-3.547752	1.615501
H	0.945090	-2.593002	3.057074
H	4.072249	-2.193150	-2.264872

***trans*-EN1**

C	-3.173973	-0.602829	-1.187268
C	-2.080146	-0.522656	-0.317088
C	-2.314280	-0.275186	1.041224
C	-3.616825	-0.117118	1.516186
C	-4.703010	-0.206812	0.642513
C	-4.478104	-0.449213	-0.713664
C	-0.677140	-0.775862	-0.854910
N	0.386410	-0.044739	-0.169487
C	1.194894	-0.934204	0.621895
O	0.585105	-2.199601	0.561792
C	-0.200610	-2.236393	-0.637060
C	0.376378	1.353064	0.140038
O	0.921885	1.667048	1.269778
C	2.629771	-1.049390	0.050688
F	3.248151	0.196753	-0.017538
C	-0.042406	2.241709	-0.839211
C	-0.417366	3.670096	-0.511036
F	2.663136	-1.538668	-1.198440
F	3.418970	-1.805896	0.823103
Na	2.509438	2.409220	-0.006557
H	-0.441595	1.829662	-1.762996
H	-0.675146	-0.561592	-1.932162
H	1.287600	-0.608679	1.661458

H	-1.474519	-0.183422	1.723232
H	0.407453	-2.583167	-1.481380
H	-1.023813	-2.933166	-0.470339
H	-0.013733	3.962135	0.466122
H	-1.509407	3.808214	-0.451437
H	-0.059183	4.392633	-1.259048
H	-3.782703	0.081298	2.571898
H	-5.716339	-0.080777	1.014697
H	-5.315233	-0.510380	-1.404452
H	-3.003391	-0.781522	-2.247578

***trans*-EN2**

C	-2.683466	-0.896508	-1.176426
C	-1.558366	-1.051267	-0.351303
C	-1.750942	-1.073736	1.041652
C	-3.031602	-0.924571	1.591256
C	-4.141931	-0.752049	0.757226
C	-3.962956	-0.748888	-0.633513
C	-0.156942	-1.086346	-0.956524
N	0.690647	0.027710	-0.490899
C	1.592365	-0.455447	0.536086
O	1.319960	-1.833264	0.702847
C	0.688088	-2.285094	-0.502783
C	0.116133	1.340557	-0.500712
O	-0.756162	1.512813	-1.433197
C	3.067216	-0.272603	0.134706
F	3.373355	-0.958554	-0.985377
C	0.403755	2.255268	0.506503
C	0.097375	3.727737	0.327315
F	3.354610	1.024602	-0.080098
F	3.875416	-0.715363	1.120814
Na	-2.209586	1.649989	0.196831
H	1.194133	2.033128	1.215141
H	-0.277341	4.203477	1.245786

H	0.989109	4.302957	0.027733
H	-0.643361	3.882667	-0.467624
H	1.455995	0.034503	1.508277
H	0.100095	-3.171258	-0.254802
H	1.440353	-2.540400	-1.257530
H	-0.246492	-1.057282	-2.045051
H	-0.895778	-1.212169	1.695525
H	-3.159576	-0.951300	2.670356
H	-5.135954	-0.642258	1.182534
H	-4.819001	-0.629360	-1.292558
H	-2.544434	-0.851421	-2.252779

***trans*-EN3**

N	-0.195251	-0.024329	-0.639659
C	-1.338773	-0.774784	-1.080015
H	-1.723925	-0.400748	-2.039485
C	-2.579213	-0.809613	-0.139961
F	-2.277314	-1.181331	1.149302
F	-3.178638	0.422710	-0.008410
F	-3.520452	-1.644323	-0.582271
O	-0.932818	-2.123967	-1.181184
C	0.413163	-2.231546	-0.686033
H	1.106830	-2.299777	-1.532096
H	0.485484	-3.141991	-0.083612
C	0.657742	-0.942731	0.118263
H	0.312064	-1.077324	1.154846
C	2.117507	-0.537112	0.151946
C	2.710119	0.144933	-0.918421
C	4.070590	0.453319	-0.892113
C	4.858139	0.080228	0.199551
C	4.274043	-0.596691	1.271662
C	2.911170	-0.897243	1.247112
H	2.456450	-1.414076	2.090148
H	4.876014	-0.883949	2.130072

H	5.917572	0.322676	0.218103
H	4.516025	0.991377	-1.725105
H	2.091230	0.449590	-1.755721
C	-0.362008	1.359713	-0.160452
O	-0.469348	1.504687	1.130674
C	-0.396376	2.312952	-1.126160
C	-0.629476	3.768351	-0.839980
H	-0.218755	2.007677	-2.154037
H	-1.498868	4.173466	-1.381938
H	0.231133	4.392038	-1.127553
H	-0.795114	3.920692	0.232062
Na	-2.238562	1.066612	2.086910

***trans*-TS-(EN1-EN3)**

C,0,-3.3900025727,0.3358305823,-0.1198905721
C,0,-2.1857298028,0.0726934591,0.5424773351
C,0,-2.0392687628,0.516117018,1.8659050426
C,0,-3.0696207859,1.2087287005,2.5013668105
C,0,-4.266676712,1.4672756443,1.8282086635
C,0,-4.4249926248,1.0265880228,0.513978999
C,0,-1.096475921,-0.7298889804,-0.1691192253
N,0,0.2344510318,-0.1281669039,-0.3219663167
C,0,1.0916002707,-0.5763341141,0.7421832619
O,0,0.3563401267,-1.5356635343,1.47366375
C,0,-0.7082084545,-1.9890242114,0.6188848045
C,0,0.5307720044,1.0577371279,-1.131646474
O,0,1.5916703619,0.941462318,-1.8771170371
Na,0,2.9723120407,-0.4457991984,-2.3989484458
C,0,2.4067294745,-1.2874440805,0.295222252
F,0,3.3975444243,-0.4107310202,-0.0635545191
C,0,-0.3020873059,2.1280403139,-1.0715599334
C,0,-0.1410074296,3.3214589439,-1.9699842973
F,0,2.2368349673,-2.0975226083,-0.8035887791
F,0,2.9136035225,-2.0456894498,1.2682429261

H,0,-5.0674461878,2.009100679,2.3246222877
H,0,-5.3502874501,1.2241781778,-0.0212405758
H,0,-3.5138717605,0.0055078405,-1.1490936732
H,0,-1.1070355975,2.1433998766,-0.3482957065
H,0,-1.4735582215,-0.9986919032,-1.1631607831
H,0,1.4198064849,0.2194396516,1.4316373737
H,0,-1.1178306781,0.3110232984,2.4022200717
H,0,-0.3483270312,-2.7840480279,-0.0484781843
H,0,-1.4976662941,-2.3774910447,1.2640748372
H,0,0.622729571,3.124065291,-2.7287942349
H,0,-1.078841999,3.5803491876,-2.4857728139
H,0,0.1675503897,4.2252077913,-1.4199315738
H,0,-2.937929297,1.5473455691,3.5259797403

***Cis*-TS1**

N	0.087138	-0.332257	-0.085216
C	-0.582261	0.838884	0.348082
O	-1.274893	1.419369	-0.560473
C	-0.524160	1.226787	1.686703
H	0.075489	0.632249	2.368247
C	-0.830722	2.634883	2.120602
H	0.088738	3.209722	2.312606
H	-1.416875	2.670370	3.050362
H	-1.391224	3.168282	1.346034
C	-3.646345	0.470985	2.987086
H	-2.823225	0.687959	3.683176
H	-4.385475	1.270040	3.091494
H	-4.102493	-0.475390	3.290209
C	-3.096196	0.409425	1.598364
H	-2.860907	1.309351	1.062663
H	-2.643233	-0.503621	1.246780
I	-5.185473	0.051097	-0.015055
Na	-2.992150	1.150414	-1.770748
H	0.518904	-1.485244	1.646616

C	1.009881	-1.129625	0.726669
C	2.305954	-0.429632	1.092347
C	2.912117	-0.692157	2.325780
H	2.417337	-1.349533	3.038088
C	4.140786	-0.114332	2.652604
H	4.597792	-0.325428	3.615749
C	4.773813	0.737508	1.746670
H	5.727217	1.193214	2.000123
C	4.172222	1.006610	0.514174
H	4.657178	1.673885	-0.193503
C	2.947457	0.425947	0.186853
H	2.473957	0.639913	-0.766584
C	-0.548132	-1.176563	-1.081308
H	-1.638433	-1.240347	-0.958871
C	-0.309480	-0.707075	-2.557913
F	0.722987	0.127227	-2.706365
F	-0.127857	-1.749737	-3.376309
F	-1.431179	-0.052605	-3.042639
O	-0.020595	-2.465683	-0.898725
C	1.228528	-2.324514	-0.217841
H	1.434956	-3.261038	0.303792
H	2.039857	-2.117056	-0.928691

***Cis*-TS2**

N	-0.319045	-0.913207	0.462598
C	-1.057333	0.031850	1.257511
O	-0.328798	0.815455	1.961791
C	-2.443864	0.120541	1.133526
H	-2.962817	-0.552420	0.460188
C	-3.277734	0.842846	2.158078
H	-2.657937	1.525050	2.748569
H	-4.091298	1.425703	1.702347
H	-3.755718	0.147220	2.865545
H	-3.963803	1.848682	-0.732979

C	-3.225653	2.625696	-0.973839
H	-3.151953	2.692836	-2.062582
H	-3.600959	3.576456	-0.586432
C	-1.913733	2.254941	-0.351481
H	-1.764036	2.407681	0.702953
H	-1.297243	1.514501	-0.837000
Na	0.988856	2.292705	1.037362
I	-0.296943	4.218641	-0.920345
C	1.051871	-1.223379	0.911132
H	1.065163	-1.299306	2.004899
C	2.093093	-0.199119	0.496366
C	2.140813	0.303257	-0.814120
H	1.423681	-0.055516	-1.545578
C	3.083232	1.271733	-1.171658
H	3.096886	1.659042	-2.186158
C	3.996647	1.751307	-0.226710
H	4.723882	2.508555	-0.504963
C	3.968005	1.246252	1.077697
H	4.679448	1.603877	1.817485
C	3.022705	0.277606	1.433743
H	2.990839	-0.098920	2.453422
C	-1.222431	-2.062467	-1.540011
F	-0.092648	-1.888325	-2.268186
F	-2.047616	-1.032142	-1.826469
F	-1.810764	-3.192434	-1.967702
C	-0.931109	-2.137102	-0.029760
H	-1.878218	-2.358145	0.474547
O	-0.028618	-3.190183	0.221917
C	1.276995	-2.616290	0.290504
H	1.726939	-2.547746	-0.706794
H	1.894440	-3.261609	0.919423

***Cis*-TS3**

N	0.201871	-0.403244	-0.901946

C	0.518205	0.927571	-1.351176
O	1.770903	1.163137	-1.500555
C	-0.496440	1.873228	-1.471811
C	-0.265033	3.192741	-2.158285
H	-1.525416	1.569399	-1.317725
H	-0.633366	3.187973	-3.195936
H	0.803464	3.427370	-2.200779
H	-0.780274	4.021485	-1.651481
C	0.313826	2.645076	0.934657
H	0.218291	1.582555	1.092439
H	0.956488	2.978727	0.138759
C	-0.765841	3.555161	1.434762
H	-1.174006	3.209918	2.388025
H	-0.406950	4.581115	1.552100
H	-1.584732	3.566360	0.702534
I	2.271939	2.841354	2.663701
Na	3.059855	1.276516	0.225502
C	-1.165437	-0.942234	-1.050779
C	-2.111564	-0.639341	0.098275
C	-3.447438	-0.317344	-0.168068
H	-3.784966	-0.242668	-1.199898
C	-4.347898	-0.083623	0.873890
H	-5.380907	0.167467	0.648255
C	-3.918740	-0.164528	2.199152
H	-4.615302	0.022426	3.011902
C	-2.586702	-0.485413	2.475019
H	-2.244075	-0.551440	3.504295
C	-1.690819	-0.725099	1.432848
H	-0.658915	-0.981759	1.651165
C	1.971877	-1.965703	-0.075894
F	1.214677	-2.479574	0.907841
F	2.721851	-0.960693	0.507284
F	2.846329	-2.900648	-0.466504
C	1.150066	-1.443833	-1.272993
H	1.867057	-1.087955	-2.016904

O	0.412015	-2.523498	-1.796551
C	-0.894902	-2.452437	-1.221120
H	-0.927280	-2.975031	-0.258407
H	-1.592094	-2.930084	-1.912886
H	-1.600497	-0.549005	-1.979585

C_2H_5I

C	-0.678594	0.853961	0.710111
H	-1.331925	1.230971	-0.082119
H	-1.246349	0.138086	1.311577
H	-0.402441	1.699005	1.355865
C	0.585721	0.230739	0.143555
H	1.239147	-0.173067	0.917113
H	1.151480	0.921420	-0.482006
I	0.163753	-1.475133	-1.164558