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Supporting Information for the manuscript: A qualitative failure of B3LYP for textbook organic reactions.

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Basis set influence

The basis set influence is low, since results obtained with the *aug*-cc-pVTZ one are close from those obtained with the 6-31+G(d,p) one (see Table 1). TS energies are slightly changed, but (**TS-1**)-spiro values remain in the same range.

Table 1: Basis set influence on the Smiles rearrangement and on the Nef reaction

Smiles rearrangement	(**TS-1**)	Spiro	(**TS-2**)	Product
M06-2X/6-31+G(d,p)	10.5	9.1	20.6	-7.0
M06-2X/*aug*-cc-pVTZ	12.3	11.0	21.6	-6.7

Nef reaction	(**TS-1**)	RI	(**TS-2**)	Product
M06-2X/6-31+G(d,p)	11.7	11.5	12.6	-11.7
M06-2X/*aug*-cc-pVTZ	12.1	11.6	12.0	-10.1

Mechanism of the Ugi-Smiles reaction

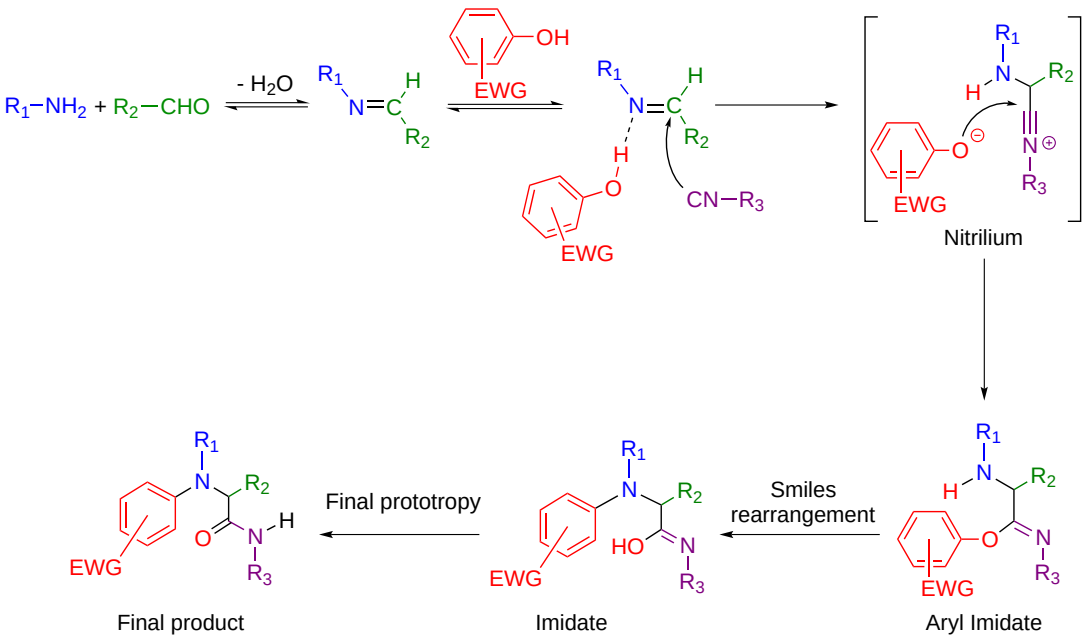

Figure 1: The mechanism of the Ugi-Smiles reaction

Influence of the exact exchange in the spiro stabilisation

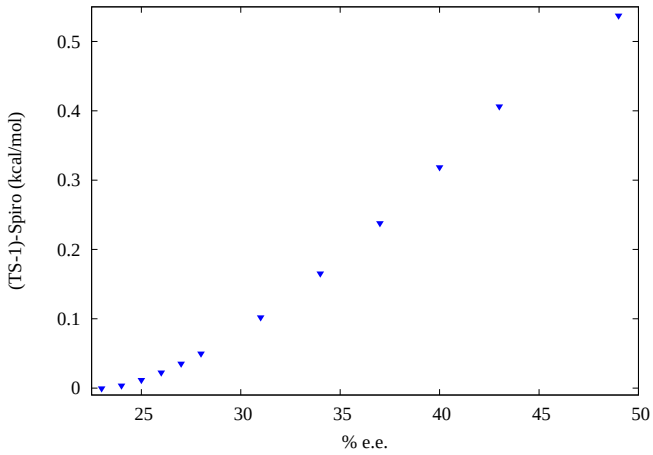

Figure 2: Stabilisation of the spiro structure with respect to (**TS-1**) against amount of exact exchange in the B3LYP functional

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Cartesian coordinates of the structures optimized at the M06-2X/6-31+G(d,p) level of theory in methanol for the Smiles rearrangement

Aryl Imidate: E=-817.707114 u.a.

C 1.705005 -1.326057 -0.284882
C 0.461532 -0.780345 -0.594016
C -0.685138 -1.528553 -0.297969
C -0.604259 -2.785252 0.299653
C 0.641165 -3.302939 0.624862
C 1.793774 -2.571975 0.326167
N 1.648845 1.431624 1.175441
C 0.238181 1.630554 0.832439
C 0.140954 1.605608 -0.677278
O 0.409917 0.393655 -1.297976
N -2.018310 -1.018029 -0.609831
O -2.192903 0.190935 -0.599684
N -0.089197 2.621227 -1.385420
C -0.118234 2.454642 -2.833673
C -0.393873 2.883541 1.428240
C 1.853913 0.841869 2.493935
O -2.894989 -1.832557 -0.848999
H -0.871507 1.716261 -3.131271
H -1.518845 -3.328984 0.505593
H -0.358690 3.411769 -3.297464
H 0.850215 2.112137 -3.215181
H -0.305299 0.754007 1.207641
H 1.464199 -0.182511 2.487676
H 0.713906 -4.272624 1.103881
H -1.455110 2.945356 1.173442
H 2.925057 0.792158 2.701756
H 1.367783 1.391099 3.313848
H -0.297717 2.858816 2.516940
H 2.134458 2.322829 1.106585
H 0.102940 3.778916 1.046334
H 2.770619 -2.976556 0.569737
H 2.586287 -0.743230 -0.524716

(TS-1): E=-817.690372 u.a.

C 2.023655 -0.822473 -0.290304
C 0.675162 -0.311932 -0.151705
C -0.309022 -1.325342 0.130898
C 0.050112 -2.658572 0.436983
C 1.359362 -3.057867 0.414628
C 2.346691 -2.112215 0.019112
N 0.770986 0.923852 1.284104
C 0.088045 2.127633 0.803090
C -0.030657 1.916357 -0.694893
O 0.369243 0.678760 -1.103484
N -1.676005 -0.978772 0.167589
O -1.982287 0.223216 0.145860
N -0.429978 2.800416 -1.496910
C -0.524394 2.433907 -2.906468
C 0.807149 3.421391 1.161989
C 0.290062 0.342224 2.541237
O -2.532383 -1.865102 0.239218
H -1.187323 1.572566 -3.047264
H -0.748903 -3.345707 0.690355
H -0.919751 3.279423 -3.469754
H 0.457633 2.168574 -3.313907
H -0.923990 2.120418 1.216637
H -0.773293 0.119598 2.441487
H 1.635513 -4.076330 0.658377
H 0.253953 4.268419 0.753281
H 0.841676 -0.581447 2.729028
H 0.442201 1.035353 3.372474

H 0.867340 3.530104 2.247809
H 1.777270 1.089671 1.349572
H 1.817370 3.434622 0.742528
H 3.381970 -2.427332 -0.073647
H 2.774267 -0.119702 -0.639772

Spiro: E=-817.692580 u.a.

C 2.023034 -0.907990 -0.200631
C 0.649770 -0.372902 -0.043374
C -0.338272 -1.450306 0.152196
C 0.033106 -2.814210 0.294701
C 1.334446 -3.211889 0.229225
C 2.331304 -2.218358 -0.048545
N 0.703453 0.714345 1.168018
C 0.030108 1.968122 0.718124
C -0.074043 1.757880 -0.775631
O 0.352658 0.519649 -1.132860
N -1.681185 -1.119694 0.199004
O -1.996874 0.092774 0.215037
N -0.472577 2.634167 -1.585858
C -0.529726 2.256802 -2.995246
C 0.802625 3.217072 1.108565
C 0.242123 0.180694 2.473176
O -2.553678 -2.004755 0.242722
H -1.172359 1.381718 -3.144876
H -0.767812 -3.524963 0.462232
H -0.929807 3.091011 -3.571642
H 0.466225 2.009541 -3.379580
H -0.973123 1.968912 1.146183
H -0.827309 -0.012081 2.408919
H 1.612336 -4.251000 0.353151
H 0.264234 4.086923 0.728802
H 0.789001 -0.739212 2.682400
H 0.449318 0.925409 3.242142
H 0.877307 3.301131 2.195506
H 1.706434 0.909553 1.260076
H 1.805358 3.217048 0.672204
H 3.367546 -2.522513 -0.167233
H 2.783198 -0.174868 -0.459830

(TS-2): E=-817.674252 u.a.

O -2.928975 -2.233593 0.294990
H -1.736704 1.139371 -3.382263
N -2.091366 -1.339877 0.325850
O -2.394717 -0.151785 0.425005
H -1.208732 -3.724915 -0.075436
C -1.144737 2.049294 -3.214713
H -1.605999 2.865975 -3.774648
H -0.146664 1.863857 -3.634232
N -1.086546 2.404371 -1.802158
C -0.387684 -3.020785 -0.019518
C -0.698918 -1.675388 0.237147
H -1.452340 1.878833 0.878130
O -0.037351 0.370377 -1.377333
C -0.545196 1.514952 -1.048708
H -1.279845 0.090150 2.460854
H 1.150818 -4.466475 -0.385903
C -0.455725 1.814522 0.444884
C 0.916227 -3.426186 -0.196912
C 0.300801 -0.665311 0.241296
H -0.163116 3.916341 0.316160
N 0.221856 0.607349 1.066751
C -0.223023 0.345644 2.474046
C 0.357109 3.062760 0.751864
C 1.932176 -2.458646 -0.112121
H 0.374990 -0.469610 2.877875
C 1.636986 -1.136153 0.132735
H -0.060836 1.255506 3.050557
H 0.457055 3.231901 1.827602
H 1.208102 0.878563 1.140296
H 1.352057 3.004588 0.298826
H 2.971894 -2.750151 -0.221718
H 2.443722 -0.411674 0.201192

Imidate: E=-817.718222 u.a.

C 1.877959 -1.129498 0.342003
C 0.660828 -0.509369 0.652171
C -0.498729 -1.224757 0.317402
C -0.468495 -2.446060 -0.353568
C 0.756573 -3.028404 -0.646951
C 1.932366 -2.372782 -0.277769
N -1.826263 -0.767555 0.737232
O -1.935455 -0.300319 1.860743
N 0.718998 0.806219 1.201533
C 0.911555 0.846588 2.655584
O -2.757060 -0.918490 -0.035589
C -0.186333 1.813031 0.630368
C 0.133990 3.207148 1.180398
C 0.006715 1.816042 -0.874244
O 1.295000 1.805182 -1.294658
N -0.974170 1.874529 -1.672161
C -0.658591 1.936786 -3.096024
H -0.062411 1.072409 -3.410896
H -1.403480 -2.935090 -0.603133
H -1.587117 1.949162 -3.667574
H -0.086004 2.839318 -3.339049
H -1.247397 1.617133 0.819283
H -0.039072 0.753390 3.196495
H 0.791843 -3.986758 -1.152598
H -0.449482 3.946560 0.627343
H 1.560617 0.017518 2.941955
H 1.405697 1.776169 2.941088
H -0.137638 3.283284 2.234935
H 1.866315 1.643185 -0.524144
H 1.197390 3.442361 1.072290
H 2.896473 -2.817790 -0.500280
H 2.791027 -0.590862 0.579478

Cartesian coordinates of the structures optimized at the MP4(SDQ)/6-31+G(d,p) level of theory in methanol for the Smiles rearrangement

Aryl Imidate: E=-815.774296 u.a.

C 1.653694 -1.394726 -0.215001
C 0.430912 -0.833763 -0.584336
C -0.737334 -1.574123 -0.374323
C -0.716414 -2.836869 0.216789
C 0.508852 -3.371252 0.613561
C 1.688928 -2.651080 0.393247
N 1.750337 1.552514 1.144486
C 0.305804 1.591622 0.861706
C 0.162993 1.568578 -0.644772
O 0.402640 0.353388 -1.295214
N -2.035536 -1.020562 -0.772041
O -2.260230 0.166578 -0.508013
N -0.069288 2.603564 -1.340522
C -0.128150 2.448538 -2.797104
C -0.448856 2.763035 1.489873
C 2.068647 1.097122 2.502166
O -2.831682 -1.780684 -1.332917
H -0.896690 1.727145 -3.083571
H -1.641897 -3.376183 0.361373
H -0.365560 3.413535 -3.238890
H 0.827171 2.102069 -3.197481
H -0.115743 0.662234 1.252726
H 1.757814 0.056158 2.605361
H 0.541495 -4.343680 1.084725
H -1.511907 2.705104 1.252593
H 3.147769 1.146424 2.643310
H 1.590042 1.682270 3.295410
H -0.335503 2.733705 2.573876
H 2.128184 2.485694 1.001968

H -0.062625 3.711455 1.117150
H 2.641425 -3.071738 0.686784
H 2.555385 -0.828676 -0.397109

(TS-1): E=-815.751519 u.a.

C 2.027045 -0.834991 -0.291295
C 0.674330 -0.318951 -0.155510
C -0.313670 -1.329965 0.096208
C 0.043266 -2.660369 0.452597
C 1.354663 -3.058889 0.456550
C 2.352072 -2.118634 0.049224
N 0.783105 0.918891 1.280030
C 0.093067 2.128769 0.807246
C -0.039101 1.921750 -0.690235
O 0.388564 0.685391 -1.117318
N -1.686916 -0.986661 0.093798
O -1.998287 0.228632 0.101653
N -0.461653 2.810149 -1.489181
C -0.558853 2.443718 -2.906626
C 0.824220 3.418602 1.166636
C 0.311773 0.344713 2.552143
O -2.548840 -1.890464 0.091468
H -1.208541 1.576349 -3.044294
H -0.752775 -3.344975 0.708536
H -0.972040 3.286197 -3.456075
H 0.423313 2.201611 -3.318907
H -0.908970 2.125680 1.235847
H -0.741562 0.093884 2.453815
H 1.628880 -4.066599 0.733850
H 0.268603 4.270431 0.778947
H 0.886687 -0.556229 2.757522
H 0.443608 1.057203 3.366448
H 0.904797 3.513845 2.249857
H 1.787865 1.087679 1.339837
H 1.824574 3.430414 0.730786
H 3.384426 -2.436059 -0.034146
H 2.778026 -0.137410 -0.641266

Spiro: E=-815.755385 u.a.

C 2.034448 -0.897860 -0.177272
C 0.650493 -0.361783 -0.021126
C -0.347411 -1.443506 0.155349
C 0.034289 -2.821966 0.289359
C 1.336174 -3.210850 0.226526
C 2.345307 -2.208696 -0.041104
N 0.701119 0.704600 1.168302
C 0.032627 1.971344 0.715693
C -0.077697 1.761018 -0.777140
O 0.378175 0.518524 -1.139299
N -1.676417 -1.118539 0.178691
O -2.002388 0.115909 0.193421
N -0.494892 2.636391 -1.591047
C -0.555479 2.248751 -3.005678
C 0.828658 3.207851 1.108370
C 0.228980 0.179296 2.483275
O -2.569685 -2.017403 0.203083
H -1.194099 1.373568 -3.144573
H -0.759955 -3.535829 0.452799
H -0.963898 3.079148 -3.576210
H 0.438335 2.010476 -3.391106
H -0.962670 1.983665 1.151925
H -0.836791 -0.009581 2.415812
H 1.618064 -4.247121 0.345393
H 0.303144 4.085290 0.736283
H 0.775788 -0.733190 2.704327
H 0.436395 0.933747 3.238004
H 0.910361 3.285219 2.192591
H 1.700373 0.902980 1.273199
H 1.827130 3.192075 0.669052
H 3.377565 -2.513795 -0.162881
H 2.790709 -0.161671 -0.427152

(TS-2): E=-815.739970 u.a.

O -2.950328 -2.235972 0.307927

H -1.690198 1.082673 -3.370421
N -2.102765 -1.329786 0.312885
O -2.409056 -0.123321 0.373294
H -1.205736 -3.725207 -0.061913
C -1.138147 2.015552 -3.220076
H -1.636479 2.806566 -3.778683
H -0.135342 1.876230 -3.635386
N -1.091817 2.394510 -1.804381
C -0.391110 -3.017857 -0.019253
C -0.706169 -1.665409 0.248732
H -1.444182 1.899676 0.894000
O -0.006198 0.364373 -1.352392
C -0.543243 1.523922 -1.029836
H -1.282875 0.080409 2.460041
H 1.147430 -4.462002 -0.382299
C -0.452762 1.828827 0.458127
C 0.912356 -3.424664 -0.193486
C 0.286011 -0.645173 0.206754
H -0.153457 3.933784 0.343783
N 0.220831 0.615948 1.071361
C -0.229189 0.331971 2.476782
C 0.366288 3.076668 0.765963
C 1.932649 -2.446840 -0.127357
H 0.365589 -0.489002 2.864718
C 1.635400 -1.125466 0.112051
H -0.064603 1.230173 3.065027
H 0.472976 3.232108 1.840309
H 1.207463 0.876337 1.151317
H 1.356167 3.016714 0.309099
H 2.970243 -2.736221 -0.236735
H 2.435575 -0.395717 0.150447

C 1.852106 -1.114536 0.202839
C 0.654486 -0.514242 0.620250
C -0.516847 -1.261764 0.415465
C -0.523943 -2.510839 -0.207608
C 0.686013 -3.079005 -0.600737
C 1.878049 -2.381692 -0.380440
N -1.822508 -0.790334 0.902327
O -1.892402 -0.413425 2.078220
N 0.739741 0.814721 1.161353
C 0.942074 0.850712 2.621498
O -2.777443 -0.829669 0.119540
C -0.203366 1.793897 0.589049
C -0.001686 3.183975 1.202852
C 0.061236 1.849935 -0.904705
O 1.382169 1.922455 -1.256214
N -0.885547 1.880024 -1.756083
C -0.498012 1.991652 -3.167126
H 0.184127 1.188813 -3.456194
H -1.461697 -3.029498 -0.351571
H -1.394481 1.931619 -3.779844
H -0.001526 2.944564 -3.364988
H -1.255783 1.528605 0.714761
H 0.009728 0.730563 3.179461
H 0.695291 -4.053050 -1.069930
H -0.616436 3.899266 0.656522
H 1.615665 0.037154 2.884941
H 1.417061 1.788021 2.901871
H -0.312876 3.196974 2.246130
H 1.897856 1.732311 -0.453021
H 1.041554 3.497827 1.139538
H 2.823500 -2.811085 -0.684023
H 2.769549 -0.555669 0.337531

Imidate: E=-815.786357 u.a.

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Cartesian coordinates of the structures optimized at the M06-2X/6-31+G(d,p) level of theory in methanol for the Nef reaction

Reactants: E=-1043.661066 u.a.

F -1.027009 -0.365647 1.344735
Cl -1.716611 0.749390 -1.275630
H 3.408030 -2.953530 -1.886438
O 0.526157 1.939450 -0.699122
C -0.347182 1.246876 -0.304732
H 2.726850 -3.933219 -0.561187
C -0.470012 0.827746 1.180569
C 2.487378 -3.306647 -1.420950
F -1.246529 1.735675 1.792634
N 1.720423 -2.186758 -0.987314
C 1.092747 -1.268672 -0.634219
F 0.723893 0.840588 1.757467
H 1.906985 -3.880714 -2.143914

(TS-1): E=-1043.642469 u.a.

F 0.577528 1.677906 2.511581
Cl 0.058331 2.378028 -0.337566
H 4.716614 -0.383685 -0.745109
O 2.389334 3.640860 0.229252
C 1.659478 2.773167 0.663971
H 3.976815 -1.444953 0.492743
C 1.205074 2.800482 2.143211
C 3.781808 -0.771159 -0.341061
F 0.400782 3.834985 2.362479
N 3.007846 0.329231 0.136436
C 2.370378 1.210912 0.511535
F 2.285674 2.929831 2.924905
H 3.211483 -1.279836 -1.117968

RI: E=-1043.642805 u.a.

F -0.890634 -0.519660 1.495916
Cl -1.473228 0.138456 -1.363223
H 3.148005 -2.634971 -1.640553
O 0.891415 1.501434 -0.768252
C 0.218951 0.580059 -0.328795
H 2.200821 -3.639931 -0.498571
C -0.303194 0.626149 1.127337
C 2.148427 -2.938488 -1.330627
F -1.150436 1.629358 1.304048
N 1.443984 -1.775976 -0.893083
C 0.852527 -0.850914 -0.560483
F 0.747287 0.809767 1.943663
H 1.599564 -3.373608 -2.165587

(TS-2): E=-1043.640944 u.a.

F 0.073424 1.957208 1.009948
Cl 2.230925 3.345649 -0.632078
H 4.478483 -1.038924 -0.131942
O 3.155052 3.063416 2.267554
C 2.321133 2.547840 1.567112
H 2.787457 -1.553938 -0.391803
C 0.810154 2.677665 1.860007
C 3.499709 -0.736668 -0.503664
F 0.409508 3.937649 1.847603
N 3.045308 0.363932 0.282655
C 2.668693 1.364616 0.712708
F 0.600321 2.183077 3.090648
H 3.560984 -0.415746 -1.544344

Product: E=-1043.679735 u.a.

F -1.967465 -0.058173 0.285006
Cl 0.237981 0.055547 -1.908810
H 2.823463 -2.481841 -1.718615
O 1.033393 -0.230783 1.825061
C 0.339844 -0.160527 0.852643
H 1.579314 -3.699398 -1.438403
C -1.003918 0.612057 0.930074

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C 1.745544 -2.634566 -1.606772
F -0.894155 1.826920 0.381752
N 1.325470 -1.917786 -0.422537
C 0.710375 -0.833232 -0.456103
F -1.370180 0.759182 2.198027
H 1.236936 -2.308662 -2.517949

Cartesian coordinates of the structures optimized at the MP4(SDQ)/6-31+G(d,p) level of theory in methanol for the Nef reaction

Reactants: E=-1041.878940 u.a.

F -1.068349 -0.308611 1.388317
Cl -1.833194 0.882820 -1.198571
H 3.498550 -2.997830 -1.834075
O 0.512218 1.935724 -0.714045
C -0.405864 1.299534 -0.281679
H 2.740564 -4.014463 -0.585926
C -0.501852 0.892314 1.206472
C 2.556739 -3.377807 -1.447282
F -1.268943 1.814939 1.836766
N 1.736689 -2.273312 -1.045859
C 1.067582 -1.360808 -0.714655
F 0.710868 0.893178 1.772264
H 2.040113 -3.941141 -2.219829

(TS-1): E=-1041.853872 u.a.

F 0.478008 1.702276 2.490665
Cl 0.007632 2.509462 -0.334624
H 4.702689 -0.340321 -0.786071
O 2.397799 3.620267 0.220211
C 1.606184 2.774778 0.638477
H 4.088044 -1.372042 0.536875
C 1.203628 2.783842 2.131289
C 3.818260 -0.770737 -0.325960
F 0.495752 3.886755 2.420524
N 2.978813 0.306740 0.121627
C 2.284058 1.170077 0.475046
F 2.322016 2.785083 2.891799
H 3.258262 -1.360409 -1.045448

RI: E=-1041.854526 u.a.

F -0.912386 -0.482654 1.548548
Cl -1.595164 0.184953 -1.278108
H 3.228575 -2.632454 -1.369186
O 0.820355 1.453144 -0.866037
C 0.121510 0.545779 -0.378370
H 2.049038 -3.720991 -0.578897
C -0.273980 0.630490 1.115267
C 2.187332 -2.934887 -1.314707
F -1.046010 1.694906 1.359385
N 1.414843 -1.794383 -0.899254
C 0.762246 -0.890455 -0.584964
F 0.855490 0.744760 1.856525
H 1.821639 -3.246532 -2.288413

(TS-2): E=-1041.851315 u.a.

F 0.064800 1.978232 0.973478
Cl 2.238853 3.390733 -0.652166
H 4.485149 -1.042808 -0.147601
O 3.163184 3.088096 2.260143
C 2.321641 2.563785 1.550415
H 2.795929 -1.571329 -0.374384
C 0.813838 2.674790 1.851123
C 3.498670 -0.752721 -0.496138
F 0.400954 3.941522 1.891278
N 3.047787 0.344205 0.320110
C 2.671703 1.372371 0.712305
F 0.608297 2.121979 3.073751

H 3.530345 -0.413079 -1.527908

Product: E=-1041.893342 u.a.

F -1.886685 -0.212240 0.208991
Cl 0.477739 0.202695 -1.917589
H 2.760062 -2.629034 -1.645519
O 1.189841 0.082848 1.742565
C 0.417530 -0.045603 0.817888
H 1.376143 -3.703023 -1.444092
C -1.017350 0.528228 0.931518
C 1.671922 -2.666520 -1.586942
F -1.058643 1.796541 0.470923
N 1.267810 -1.917502 -0.404158
C 0.777808 -0.759418 -0.468928
F -1.423573 0.529577 2.209135
H 1.243998 -2.277811 -2.510419