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SUPPLEMENTARY INFORMATION

Prediction of Enhanced Solvent-Induced Enantioselectivity in a Ring Opening with a Bifurcating Reaction Path

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Supplementary MM3 parameters for *meso*-2,3-difluoro-2,3-dimethyldiazocyclopropane

```
parameters mm3
bondtype morse
vdwtype mm3-hbond

atom         167     N      "Diazo terminal N"                  7     14.003     1
atom         168     N      "Diazo inner N"                     7     14.003     2
atom         169     C      "Diazocyclopropane C"               6     12.000     3
atom         170     F      "Solute F"                          9     18.998     1
vdw          167                 1.9300      0.0430
vdw          168                 1.9400      0.0440
vdw          169                 1.9400      0.0560
vdw          170                 1.7100      0.0450
bond         170    22           4.7581      1.3595
bond         169   168           1.9870      1.3052
bond         167   168          20.3943      1.1190
bond3         22   169           3.1236      1.5200
angle          1    22   170      0.0010      120.00
angle          1    22    22      0.0100      116.80      114.20        0.00
angle        170    22    22      1.1020      112.00      116.30        0.00
angle        170    22   169      0.6232      112.00      116.30        0.00
angle        167   168   169      0.1922      178.00
angle3        22    22   169      1.8789       56.60
angle3        22   169    22      0.0099       60.00
angle5         1    22   169      0.0003      116.80      114.20        0.00
angle5        22   169   168      0.3314      122.00      117.00        0.00
torsion        1    22    22   170      0.200 0.0 1   0.000 180.0 2   0.0134  0.0 3
torsion        1    22   169    22      0.000 0.0 1   0.000 180.0 2   0.2752  0.0 3
torsion        1    22   169   168      0.000 0.0 1   0.000 180.0 2   0.5401  0.0 3
torsion        5     1    22   170     -0.460 0.0 1   1.190 180.0 2   0.4394  0.0 3
torsion        5     1    22   169      0.000 0.0 1   0.000 180.0 2   0.3227  0.0 3
```

```
torsion     170   22   22  170      0.000 0.0 1   0.000 180.0 2   0.2600  0.0 3
torsion     170   22   22   22      0.200 0.0 1   0.000 180.0 2   0.0100  0.0 3
torsion     170   22   22  169      0.200 0.0 1   0.000 180.0 2   0.2570  0.0 3
torsion     170   22  169   22      0.200 0.0 1   0.000 180.0 2   0.3122  0.0 3
torsion     170   22  169  168      0.000 0.0 1   0.000 180.0 2   0.0110  0.0 3
torsion      22  169  168  167      0.000 0.0 1   0.000 180.0 2   0.0066  0.0 3
torsion     169   22   22    1      0.000 0.0 1   0.000 180.0 2   0.1670  0.0 3
torsion5      1   22   22  169      0.000 0.0 1   0.000 180.0 2   0.1670  0.0 3
torsion5     22   22  169  168      0.000 0.0 1   0.000 180.0 2   0.0001  0.0 3
strbnd        1   22  169    0.0066   0.0066
strbnd       22  169   22    0.9978   0.9978
electneg     22  169  168              -0.0225
electneg      1   22  170              -0.0225
electneg    170   22    1               0.0100
electneg     22   22  170              -0.0225
dipole      170   22         2.2475      0.500
dipole      168  169        -3.4284      0.500
dipole      167  168         2.4223      0.500
hbond        21  170         2.128       8.09
hbond        21   11         2.111       3.95
```

Supplementary MM3 parameters for 2,4-difluoropenta-2,3-diene + N_2

```
parameters mm3
bondtype morse
vdwtype mm3-hbond

atom        165    C     "Allene terminal C"                 6    12.000    4
atom        166    C     "Allene central C"                  6    12.000    2
atom        170    F     "Solute F"                          9    18.998    1
vdw         165              1.9600     0.0560
vdw         166              1.9400     0.0560
vdw         170              1.7100     0.0450
bond          1  165         4.9309     1.4874
bond         10   10        27.8918     1.0867
bond        170  165         1.1065     1.3535
bond3       165  166         3.5783     1.3000
bond3       165  165          0.0001     2.6266
angle         1  165  170    1.0376     111.90     115.00       0.00
angle         5    1  165    0.5871     109.50     109.31     110.40
angle       170  165  165    0.1902     120.50     119.00       0.00
angle       170  165  166    0.8758     120.50     119.00       0.00
angle3      165  166  165    0.0142     180.0
angle3      165  165  166    0.0977     0.0001
angle5        1  165  165    0.0024     127.50
angle5        1  165  166    0.0002     127.50
torsion       1  165  165    1     0.000  0.0 1   5.9777   0.0 2   0.000 0.0 3
0.00   0.0 4
torsion       1  165  165  170     0.000  0.0 1   0.1054   0.0 2   0.000 0.0 3
0.00   0.0 4
torsion       1  165  165  166     0.0001 0.0 1   0.0001 180.0 2   0.000 0.0 3
torsion       1  165  166  165     0.0001 0.0 1   0.0001 180.0 2   0.000 0.0 3
torsion       5    1  165  170     0.000  0.0 1   0.000  180.0 2   0.540 0.0 3
torsion       5    1  165  165     0.000  0.0 1   0.0000 180.0 2  -0.090 0.0 3
torsion       5    1  165  166     0.000  0.0 1   0.0000 180.0 2  -0.090 0.0 3
torsion     170  165  165  170     0.000  0.0 1  23.2050   0.0 2   0.000 0.0 3
0.00   0.0 4
torsion     170  165  165  166     0.0001 0.0 1   0.0001 180.0 2   0.000 0.0 3
torsion     170  165  166  165     0.0001 0.0 1   0.0000 180.0 2   0.000 0.0 3
torsion5      1  165  165  166     0.0001 0.0 1   0.0001 180.0 2   0.000 0.0 3
electneg      1  165  170              -0.0225
electneg    170  165    1               0.0100
dipole        1  165          0.7500      0.500
dipole      170  165          2.6500      0.500
hbond        21  170          2.098       8.11
hbond        21   11          2.111       3.95
```

Solvent Box Dimensions

$CHCl_3$: Cubic box, 40.69 Å on a side, 508 solvent molecules, density 1.4801 g/cc.

CHFClBr: Cubic box, 41.53 Å on a side, 508 solvent molecules, density 1.7210 g/cc.

TFIPA: Cubic box, 33.76 Å on a side, 255 solvent molecules, density 1.2608 g/cc.

Empirical Valence Bond H_{12} Function

The best-fit parameters for the EVB off-diagonal coupling term were: $H_{12}=26.442e^{-17.007(r-1.745)^2}$ where r is the length of the breaking C–C bond.
The offsets for the diagonal terms were: ε_1= 42.0316, ε_2= -3.5452

OH•••F Hydrogen-Bonded Complexes

The geometries and strengths of the OH•••F hydrogen bonds included in the supplementary parameter set for TFIPA came from M06-2X/cc-pVTZ calculations. The optimized geometries of the complexes are reported below:

TFIPA•••TFIPA

O	1.617577	1.503056	-0.944049
C	2.507550	0.960357	-0.005905
C	2.513705	-0.554139	-0.140249
C	2.191673	1.373653	1.419576
F	2.813255	-0.945576	-1.377530
F	1.311085	-1.071427	0.159709
F	3.406204	-1.116543	0.686027
H	0.715348	1.361977	-0.637352
H	3.505923	1.292677	-0.293584
H	1.206804	1.004198	1.708231
H	2.189509	2.459742	1.478134
H	2.928533	0.980524	2.117415
O	-3.673501	0.892139	-0.891827
C	-3.297491	0.157971	0.243201
C	-1.782998	0.029870	0.266632
C	-3.952223	-1.208956	0.315957
F	-1.183693	1.235034	0.275287
F	-1.335017	-0.612060	-0.818976
F	-1.351737	-0.626668	1.344616
H	-3.512891	0.356577	-1.675734
H	-3.568673	0.764616	1.107757
H	-3.643796	-1.822183	-0.531963
H	-5.031949	-1.083741	0.284162
H	-3.680314	-1.727636	1.233098

E= -984.240075752 hartree

TFIPA•••Reactant

C	1.814672	0.087890	0.494204
C	2.030324	-0.772097	-0.716678
C	3.090939	0.185462	-0.283644
C	1.761858	-0.403775	1.903905
C	2.221225	-2.253845	-0.712913
F	0.900474	1.085511	0.274482
F	1.247750	-0.378468	-1.783777
H	2.837889	-2.548674	0.132235
H	2.720367	-2.561755	-1.631028
H	1.248873	-2.739392	-0.642044
H	2.514246	-1.172115	2.062513
H	0.771111	-0.808819	2.103208
H	1.958576	0.422481	2.585997
N	3.388745	1.246857	-0.980411
N	3.720494	2.144111	-1.550953
O	-0.838933	-1.263771	-0.069624
C	-2.186123	-1.087964	0.285656
C	-2.362446	0.277962	0.929642
C	-3.129374	-1.258167	-0.891557

F	-3.628394	0.467462	1.324109
F	-2.056962	1.256236	0.068177
F	-1.583423	0.429555	2.002397
H	-0.596927	-0.622256	-0.751258
H	-2.401251	-1.823190	1.061819
H	-2.968552	-2.239574	-1.331547
H	-2.929986	-0.498547	-1.648102
H	-4.168523	-1.173347	-0.579551

E = -995.343175830 hartree

TFIPA•••Product

C	1.441674	1.505975	-0.083916
C	2.071369	0.374175	-0.022823
C	2.606997	-0.812238	0.003794
C	1.440084	2.539753	-1.147858
C	2.009461	-2.082385	-0.481675
F	3.835767	-0.985650	0.526589
F	0.623641	1.855157	0.957772
H	2.091921	2.239995	-1.962667
H	1.781605	3.491840	-0.740372
H	0.424834	2.673019	-1.522970
H	1.023395	-1.903754	-0.898485
H	1.920153	-2.777232	0.354092
H	2.663114	-2.529988	-1.231287
O	-0.556680	-0.922870	1.277516
C	-1.889007	-0.638382	0.944400
C	-1.992098	-0.399070	-0.553686
C	-2.456976	0.534603	1.721447
F	-1.519260	-1.432717	-1.255621
F	-1.294933	0.684672	-0.932061
F	-3.261707	-0.207132	-0.930966
H	-0.059851	-0.096202	1.315331
H	-2.463003	-1.546078	1.138678
H	-1.888679	1.438953	1.501991
H	-2.378681	0.321992	2.785310
H	-3.501958	0.706857	1.470739

E= -885.887361053 hartree

TFIPA

O	-1.310847	-1.349609	-0.068945
C	-0.817041	-0.099842	-0.477145
C	0.627198	0.037103	-0.022126
C	-1.658482	1.059086	0.024806
F	1.401580	-0.923787	-0.521095
F	0.712980	-0.035781	1.317101
F	1.148571	1.211963	-0.393851
H	-1.379650	-1.354762	0.891299
H	-0.794176	-0.118954	-1.567100
H	-1.646447	1.090727	1.115302
H	-2.683906	0.919928	-0.309325
H	-1.287271	2.010296	-0.351227

E= -492.116889226 hartree

Reactant

C	-0.273420	-0.405459	0.750446
C	-0.273420	-0.405459	-0.750446
C	0.948869	0.028695	-0.000000
C	-0.273420	-1.625396	1.616496
C	-0.273420	-1.625396	-1.616496
F	-1.044592	0.586169	1.291240
F	-1.044592	0.586169	-1.291240
H	0.343132	-2.403843	-1.175341

```
H      0.132493    -1.375922    -2.596018
H     -1.291603    -1.993771    -1.738714
H      0.343132    -2.403843     1.175341
H     -1.291603    -1.993771     1.738714
H      0.132493    -1.375922     2.596018
N      1.322686     1.279669     0.000000
N      1.720669     2.319492     0.000000

E= -503.213386495 hartree
```

Product

```
C      0.000000     0.000000     0.062869
C      0.000000     1.299642     0.031021
C     -0.000000    -1.299642     0.031021
C     -0.835144     2.195301    -0.812921
C      0.835144    -2.195301    -0.812921
F      0.826519     1.997653     0.839530
F     -0.826519    -1.997653     0.839530
H     -1.488006     1.612996    -1.455699
H      1.488006    -1.612996    -1.455699
H     -0.191983     2.830545    -1.422894
H      0.191983    -2.830545    -1.422894
H     -1.436834     2.842943    -0.174386
H      1.436834    -2.842943    -0.174386

E= -393.757552161 hartree
```

M06-2X/cc-pVTZ calculations were performed with GAMESS-US, Version 11-August, 2011, R1 (M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, *J. Comput. Chem*. 1993, **14**, 1347-1363.)

Residuals plot for fit of the EVB potential to M06-2X/cc-pVTZ direct-dynamics trajectory points.