Electronic Supporting Information

Are One-Step Aromatic Nucleophilic Substitutions of Non-Activated Benzenes Concerted Processes?

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*1.BET study of the conversion of dihydroimidazole **2'** yielding fluorobenzene **3** plus imidazolone **4'***

The data related to the topological analysis of the ELF[1] of the structures of the IRC selected by means of the mathematical catastrophe theory[2] are gathered in Table S1 together with other useful parameters. Below is described the electron density rearrangement along the S_NAr reaction in general terms and with a chemically descriptive point of view. From this Boning Evolution Theory (BET) study,[3] the molecular mechanism of this S_NAr reaction can topologically be characterised by fifteen differentiated phases which, in turn, can be reorganised in three *Groups A – C* associated to significant chemical events (see Figure 6 in the manuscript):

Group A, which comprises *Phases I – III*, is related to the rupture of the C2–F1 bond. At the beginning of the reaction, the dihydroimidazole **2'** presents two polarised bonds; the C2–F1 bond, integrating only 0.8 e [V(C2,F1)] while a total of 6.93 e correspond to the non-bonding electron density of the F1 fluorine [V(F1)], and the O3–C4 bond, integrating 1.40 e [V(O3,C4)] while 4.83 e correspond to the non-bonding electron density of the O3 phenoxy oxygen [V(O3)]. Along *Phase I*, the C2–F1 bond is progressively depopulated until it breaks at **S2** leading to the release of a free F1 fluoride anion integrating 7.64 e and the formation of a residual population of 0.10 e at the C2 carbon [V(C2)], which first increases up to 0.31 e and later decreases to 0.19 e along *Phases II* and *III* as being delocalised into the C2–N regions of the dihydroimidazole ring [V(C1,N)].

Group B, which comprises *Phases IV – IX*, is related to the overlapped rupture and formation of the O3–C4 and C4–F1 bonds, respectively. First, the non-bonding electron densities of both F1 fluoride and C4 carbon atoms keep being redistributed, to such an extent that the latter is completely delocalised inside the dihydroimidazole ring at **S4**. At the same time, the O3–C4 bond, somewhat polarised already in dihydroimidazole **2'**, starts experimenting a significant depopulation along *Phases IV* and *V*. Then, the bonding changes are quite symmetric to those occurring along *Group A*. At **S6**, a few non-bonding population of 0.13 e, coming from the benzene framework, appears at the benzene C4 carbon as the fluoride F1 anion approaches [V(C4)]. This non-bonding population remains almost constant along *Phases VI* and *VII*, while the non-bonding electron density of the O3 phenoxy oxygen slightly increases as a consequence of the continued depopulation of the O3–C4 bond. Then, formation of the C4–F1 bond [V(C4,F1)] takes

place at **S8**, with an initial low electron population of 0.41 e, by donation of 0.30 e of the non-bonding electron density of the F1 fluoride anion to the benzene C3 carbon having a non-bonding population of 0.10 e. This trend is kept along *Phase VIII*, in which the new C4–F1 bond reaches 0.56 e as the F1 fluorine is depopulated to 7.11 e. Meanwhile, the depopulation of the O3–C4 bond continues to 0.52 e. Note that at this stage of the reaction, ca. 35 % reaction progress, both O3–C4 and C4–F1 bonds present similar populations. Finally, the rupture of the O3–C4 bond takes place at **S9** leading to a negligible non-bonding electron density of ca. 0.05 e at the benzene C3 carbon and an increase of the non-bonding electron density of the O3 oxygen to 5.72 e.

Finally, Group *C*, which comprises *Phases X – XV*, is related to the molecular relaxation in the two released fluorobenzene and diydroimidazolone molecular frameworks. First, along *Phases X* and *XI*, the C4 non-bonding population is delocalised into the benzene ring, while the O3 oxygen contributes to populate the C2–O3 bonding region to 1.98 e. Next, in the imidazolone **4'** molecule, a negligible non-bonding population of only 0.02 e appears at the C2 carbon in *Phase XII* and subsequently disappears in *Phase XIII* as a consequence of the internal electron density redistribution in the O3–C2–N framework. The most relevant bonding change is that along *Phases XIV* and *XV*, the C2–N bonding regions integrating ca. 2.9 e each one experience a significant depopulation towards the N nitrogen atoms, ending up with 2.23 and 1.68 e, respectively, at imidazolone **4'**. The C2–O3 bonding region experiences very few changes, still being polarised towards the O3 oxygen. On the other hand, the bonding changes in fluorobenzene **3** are less notable. Only an exchange of ca. 0.2 e from the fluoride F1 non-bonding electron density to the C4–F1 bonding region is observed, reaching 6.63 and 1.02 e, respectively, at **3**.

References

1. A. D. Becke and K. E. Edgecombe, *J. Chem. Phys.* 1990, **92**, 5397-5403.
2. (a) R.Thom, *Structural Stability, Morphogenesis: An Outline of a General Theory of Models*, Inc. Reading, MA, **1976**; (b) A. E. R. Woodcock and T. A. Poston, *Geometrical Study of Elementary Catastrophes*, Spinger-Verlag, Berlin, **1974**; (c) R. Gilmore, *Catastrophe Theory for Scientists, Engineers*, Dover, New York, **1981**.
3. X. Krokidis, S. Noury and B. Silvi, *J. Phys. Chem. A* 1997, **101**, 7277-7282.

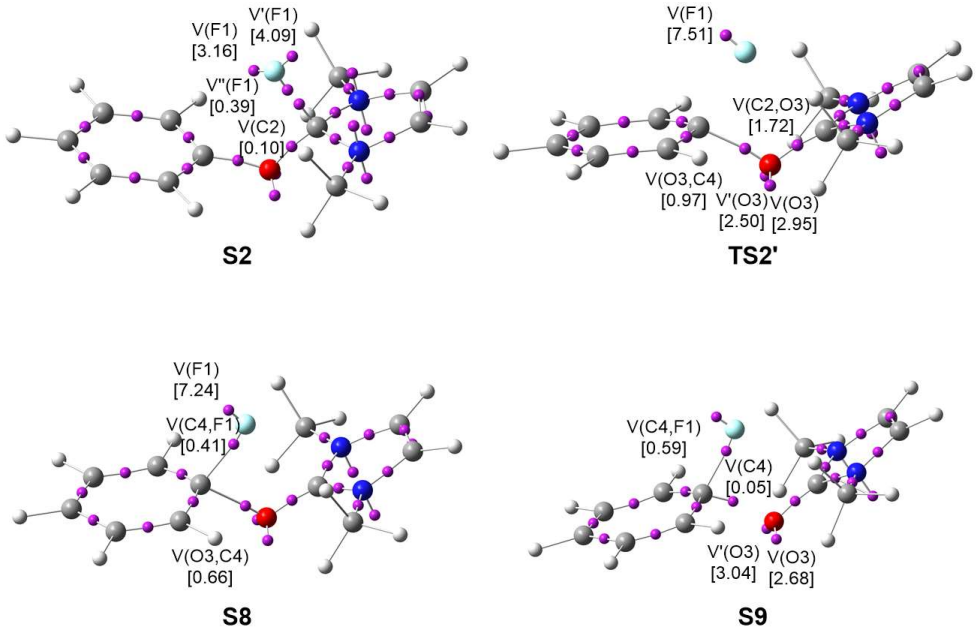
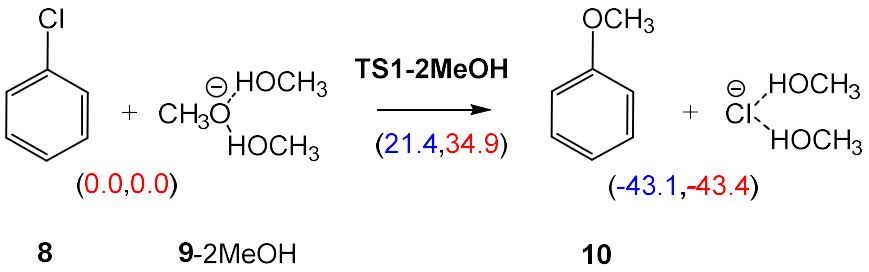


Figure S1. ELF valence basin attractor positions of **TS2'** and the most relevant structures directly involved in the rupture of the C2–F1 and C4–O3 single bonds and the formation of the C4–F1single bond along the IRC path associated with the S_NAr reaction in dihydroimidazole **2'**. Electron populations, in average number of electrons, e, are given in brackets.

Table S1. ELF valence basin populations, percentage of reaction progress, relative[a] energies and distances of the breaking and forming bonds, of the IRC structures **S1** – **S16** defining the fifteen topological phases along the S_NAr reaction in dihydroimidazole **2'**. Electron populations are given in average number of electrons, e, relative energies in kcal·mol^{-1} and distances in angstroms, Å.

	S1	**S2**	**S3**	**S4**	**S5**	**TS2'**	**S6**	**S7**	**S8**	**S9**	**S10**	**S11**	**S12**	**S13**	**S14**	**S15**	**S16**
Phases	*I*	*II*	*III*	*IV*	*V*	*VI*	*VII*	*VIII*	*IX*	*X*	*XI*	*XII*	*XIII*	*XIV*	*XV*		
d(C1–F1)	1.503	1.581	1.678	1.835	2.241	2.289	2.293	2.307	2.316	2.325	2.333	2.349	2.359	2.366	2.379	2.929	3.273
d(C4–F1)	2.513	2.467	2.442	2.387	1.928	1.775	1.758	1.702	1.662	1.616	1.580	1.512	1.477	1.456	1.426	1.359	1.359
d(O3–C4)	1.400	1.402	1.406	1.415	1.527	1.621	1.634	1.681	1.717	1.762	1.800	1.882	1.933	1.968	2.031	3.162	3.556
ΔE	0.0	1.2	2.8	6.2	21.7	23.6	23.6	22.9	21.9	19.9	17.8	12.6	9.1	6.8	2.9	-31.8	-32.6
% Evolution	0	5	7	12	28	32	32	34	35	37	38	40	41.5	42.5	44	84	100
V(C2,O3)	1.46	1.50	1.52	1.57	1.67	1.72	1.73	1.76	1.78	1.82	1.86	1.92	1.99	2.03	2.11	2.25	2.24
V(O3)	2.45	2.35	2.33	2.35	2.40	2.47	2.49	2.54	2.58	2.68	2.75	2.77	2.77	2.78	2.77	2.76	2.76
V'(O3)	2.38	2.45	2.45	2.43	2.43	2.50	2.51	2.57	2.62	3.04	2.92	2.88	2.86	2.90	2.86	2.86	2.86
V(C2,N)	2.02	2.08	2.15	2.64	2.92	2.95	2.95	2.96	2.96	2.96	2.96	2.95	2.93	2.92	2.91	2.24	2.23
V(N)	1.06	1.01	0.93	1.37	0.85	0.83	0.83	0.84	0.85	0.86	0.88	0.91	0.92	0.93	0.95	0.83	0.84
V'(N)	1.06	1.01	0.93													0.83	0.84
V(C2,F1)	0.80																
V(F1)	2.94	3.16	3.30	3.50	7.58	7.51	7.48	7.32	7.24	7.09	5.17	2.01	2.23	2.36	3.98	3.32	3.32
V'(F1)	1.99	4.09	4.17	4.05				0.21			1.84	1.80	2.00	2.23	2.72	3.30	3.31
V''(F1)	2.04	0.39										3.08	2.58	2.18			
V(O3,C4)	1.40	1.39	1.39	1.38	1.19	0.97	0.93	0.80	0.66								
V(C2)		0.10	0.31										0.02				
V(C4)							0.13	0.10		0.05							
V(C4,F1)									0.41	0.59	0.67	0.81	0.88	0.92	0.98	1.02	1.02

[a] Relative to the first structure of the IRC path, **S1**.



Scheme S1. S_NAr reaction of chlorobenzene **8** with methoxide anion **9** computed in the presence of two explicit molecules of methanol. B3LYP/6-311+G(d) relative enthalpies, in blue, and Gibbs free energies, in red, in methanol at 120 ºC, are given in kcal·mol^{-1}.

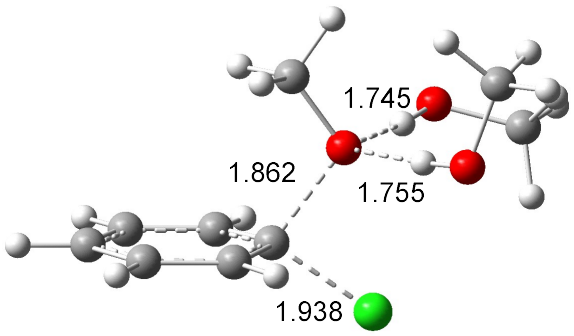


Figure S2. B3LYP/6-311+G(d) geometry of **TS1-2MeOH** hydrogen-bonded to two methanol molecules. Distances are given in angstroms, Å.

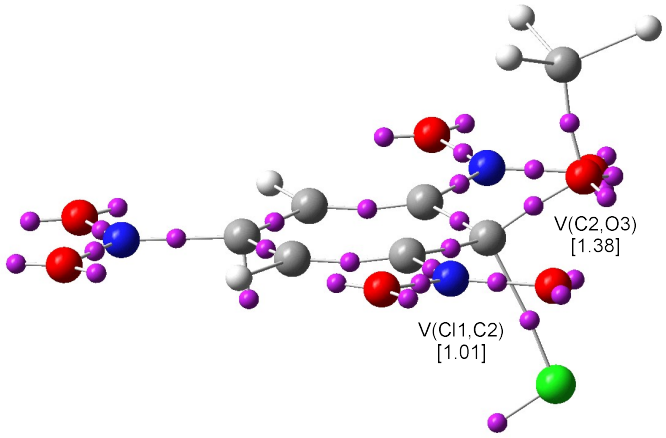


Figure S3. B3LYP/6-311+G(d) ELF valence basin attractor positions of the Meisenheimer intermediate involved in the two-step S_NAr reaction of 2-chloro-1,3,5-trinitrobenzene **11** with anion methoxide **9**. Electron populations, in average number of electrons, e, are given in brackets.

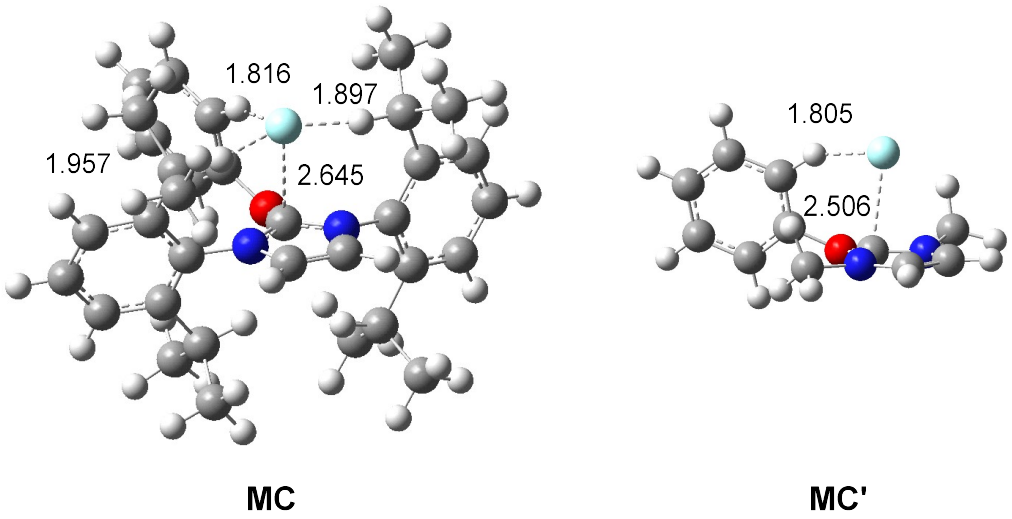


Figure S4. B3LYP/6-311+G(d) geometries of **MC** and **MC'**. Distances are given in angstroms, Å.

Table S2. B3LYP/6-311+G(d) Enthalpies (H, in a.u.), entropies (S, in cal·mol^{-1}·K^{-1}) and Gibbs free energies (G, in au), computed at 120 ºC in methanol, for the S_NAr reaction of chlorobenzene **8** with methoxide anion **9**.

	H	S	G
8	-691.828199	82.9	-691.878804
9	-115.212833	55.2	-115.246540
TS1	-807.013404	102.3	-807.075879
10	-346.715256	90.2	-346.770319
Cl$^-$	-460.409727	37.8	-460.432834

Table S3. B3LYP/6-311+G(d) Enthalpies (H, in a.u.), entropies (S, in cal·mol^{-1}·K^{-1}) and Gibbs free energies (G, in au), computed at 110 ºC in toluene, for the domino reaction of imidazolium **1** with the fluoride anion.

	H	S	G
1	-1466.360494	247.4	-1466.511563
F$^-$	-99.965347	36.0	-99.987343
MC	-1566.385962	270.9	-1566.551435
2	-1566.396710	270.8	-1566.562079
TS1	-1566.360304	274.4	-1566.527773
3	-331.471585	79.9	-331.520373
2	-1234.977575	238.8	-1235.123402

Table S4. B3LYP/6-311+G(d) Enthalpies (H, in a.u.), entropies (S, in cal·mol^{-1}·K^{-1}) and Gibbs free energies (G, in au), computed at 110 ºC in toluene, for the domino reaction of imidazolium **1'** with the fluoride anion.

	H	S	G
1'	-611.426623	124.6	-611.502715
F$^-$	-99.965347	36.0	-99.987343
MC'	-711.457654	137.9	-711.541851
2'	-711.463182	134.1	-711.545077
TS1'	-711.428418	133.2	-711.509796
3'	-331.471585	79.9	-331.520373
4'	-380.042733	97.3	-380.102139
TS3	-811.396729	133.9	-811.478480

B3LYP/6-311+G(d) computed total energies, single imaginary frequencies and cartesian coordinates, in methanol, of the stationary points involved in S_NAr reaction of chlorobenzene **8** with methoxide anion **9**.

8

E(RB3LYP) = -691.928824554 A.U.

C	0.49907300	-0.00014100	-0.00008500
C	-0.17892000	-1.21550400	0.00000500
C	-1.57415000	-1.20682000	0.00010600
C	-2.27341300	0.00008400	0.00011900
C	-1.57393100	1.20695600	0.00010600
C	-0.17877800	1.21540300	0.00000400
H	0.36928700	-2.15003200	-0.00000500
H	-2.11070500	-2.14952800	0.00015500
H	-3.35788500	0.00026200	0.00019200
H	-2.11048900	2.14966400	0.00015700
H	0.36971500	2.14976400	-0.00000700
Cl	2.26592900	0.00000000	-0.00011900

9

E(RB3LYP) = -115.254592218 A.U.

C	0.00000000	0.00000000	-0.56482100
H	0.00000000	1.01974100	-1.02463300
H	0.88312200	-0.50987100	-1.02463300
H	-0.88312200	-0.50987100	-1.02463300
O	0.00000000	0.00000000	0.80785300

TS1

E(RB3LYP) = -807.156663797 A.U.
1 imaginary frequencies -314.3533 cm-1

C	0.34727400	-0.29505100	0.00000900
Cl	2.00277000	-1.14433000	0.00003200
O	1.27849800	1.46216600	-0.00004300
C	-0.37336700	-0.38039900	1.21403900
C	-1.76432900	-0.38737700	1.20113600
C	-2.48347500	-0.38427100	0.00001400
C	-1.76433100	-0.38745000	-1.20110900
C	-0.37336900	-0.38047200	-1.21401500
H	0.16851800	-0.40582600	2.15324500
H	-2.29396100	-0.41697600	2.15034400
H	-3.56818700	-0.40404400	0.00001600

H	-2.29396600	-0.41710800	-2.15031400
H	0.16851400	-0.40595600	-2.15322000
C	0.31852600	2.46279000	-0.00007500
H	0.78885700	3.46132000	-0.00012400
H	-0.34322300	2.42908400	-0.88810300
H	-0.34320400	2.42916100	0.88796900

10

E(RB3LYP) = -346.860070868 A.U.

C	-0.45241700	-0.27434100	-0.00007300
O	-1.75949200	-0.67281200	-0.00038000
C	-0.03396300	1.06016200	-0.00011700
C	1.33369200	1.35213300	-0.00005600
C	2.28380200	0.33485800	0.00004800
C	1.85582800	-0.99686400	0.00000800
C	0.50027900	-1.30306000	-0.00002400
H	-0.75050400	1.87146500	-0.00026300
H	1.64876500	2.39077800	-0.00008300
H	3.34230400	0.57140600	0.00012200
H	2.58327400	-1.80231800	0.00006600
H	0.15907600	-2.33292600	-0.00003700
C	-2.77828000	0.32571200	0.00043200
H	-3.72284100	-0.21409400	0.00078900
H	-2.71840200	0.95304800	0.89423200
H	-2.71939000	0.95353500	-0.89309800

B3LYP/6-311+G(d) computed total energies, single imaginary frequencies and cartesian coordinates, in methanol, of the stationary points involved in the domino reaction of imidazolium **1** with the fluoride anion.

1

E(RB3LYP) = -1467.08576554 A.U.

C	-0.51216500	-0.76084400	1.89293800
O	0.13285200	0.23825500	1.10947600
C	0.17968100	0.19416400	-0.20601200
C	-0.29341400	-2.10889100	1.65471200
C	-0.86974800	-3.03634000	2.52353800
C	-1.63478600	-2.60809100	3.60640000
C	-1.83151100	-1.24431400	3.82352300
C	-1.26684900	-0.30537800	2.96254200
H	0.31815800	-2.43938000	0.82414200
H	-0.70683500	-4.09474300	2.35351600
H	-2.07316000	-3.33425100	4.28151500
H	-2.42429000	-0.90532500	4.66563600
H	-1.40272600	0.75803400	3.11718800
C	-0.31898700	0.40995800	-2.35480300
H	-0.95625700	0.52481500	-3.21439200
C	1.02864100	0.34572700	-2.24853600
H	1.80027600	0.39006400	-2.99709500
N	-0.84877400	0.32107200	-1.07032300
N	1.33459100	0.20258700	-0.89925300
C	-2.26044700	0.45109800	-0.73296500
C	-3.09296900	-0.67181200	-0.89974500
C	-2.72760800	1.71082400	-0.31151800
C	-4.44564600	-0.50486800	-0.58985600
C	-4.08945600	1.80949900	-0.01162700
C	-4.93664200	0.71595600	-0.14321500
H	-5.12641100	-1.34039900	-0.70079100
H	-4.49662700	2.75814100	0.31858000
H	-5.99029400	0.81891200	0.09373100
C	2.67701900	0.12008000	-0.33989100
C	3.24159000	1.28268100	0.21419100
C	3.35504500	-1.11148700	-0.41648000
C	4.54204200	1.17693700	0.71617200
C	4.65537200	-1.14908900	0.09445100
C	5.24195600	-0.02112800	0.65595000
H	5.01546000	2.04719000	1.15607000
H	5.21804200	-2.07432800	0.05655900
H	6.25159800	-0.07690900	1.04890200
C	-1.84557400	2.95396200	-0.24473300
H	-0.79995300	2.64531700	-0.31926200
C	-2.59444000	-2.00684500	-1.44393000
H	-1.50223800	-2.01867700	-1.37666600
C	2.75104100	-2.36340900	-1.04549800

H	1.67617300	-2.20089500	-1.17640200
C	2.51747500	2.62154000	0.28683000
H	1.54464000	2.51980100	-0.20088500
C	-3.10949200	-3.21137800	-0.63790900
H	-4.18529500	-3.35603700	-0.76308100
H	-2.62204400	-4.12611100	-0.98619000
H	-2.90443200	-3.10301800	0.42829200
C	-2.96935700	-2.16512000	-2.93168300
H	-2.57905800	-3.10838100	-3.32326900
H	-4.05493700	-2.17474700	-3.06126200
H	-2.57208200	-1.35641000	-3.55006200
C	2.91484100	-3.60537900	-0.15109400
H	2.55220200	-3.42839300	0.86423900
H	2.35678400	-4.44610200	-0.57179000
H	3.95882600	-3.91897800	-0.07772200
C	3.34623500	-2.62543600	-2.44312800
H	2.87634000	-3.50068100	-2.89981400
H	3.20248100	-1.77740300	-3.11730300
H	4.42065100	-2.81782200	-2.38267700
C	2.25507300	3.04206700	1.74501400
H	1.66662900	2.29400700	2.27963700
H	1.70850600	3.98928700	1.76727400
C	-2.13063000	3.88089200	-1.44358000
H	-1.98463200	3.36865900	-2.39813000
H	-3.15940600	4.25006700	-1.42017100
H	-1.46555100	4.74852200	-1.42099600
C	-1.98469100	3.72105000	1.08090300
H	-2.97881600	4.15782700	1.20091800
H	-1.79495800	3.07606200	1.94233100
H	-1.26322800	4.54140700	1.11213500
C	3.27819300	3.71884900	-0.47974200
H	3.44839600	3.43750000	-1.52214100
H	2.70525100	4.65009500	-0.47092400
H	4.25115500	3.92931700	-0.02875200
H	3.18938100	3.18947600	2.29301400

MC

E(RB3LYP) = -1567.11425973 A.U.

C	0.25309400	-0.02326800	-0.15633200
F	-0.00467000	-2.65425300	-0.22992700
N	1.42697800	-0.12128500	-0.81303000
C	1.15251000	-0.19798500	-2.17453500
C	-0.18461600	-0.10664900	-2.32488200
N	-0.75261000	0.04182500	-1.05786700
C	-2.16985600	0.30501700	-0.84336600
C	2.75848200	-0.01521900	-0.23459400
C	-2.56232200	1.62680500	-0.53905300
C	-3.92936400	1.87546700	-0.39685900

C	-4.86687400	0.86470900	-0.57329500
C	-4.45238700	-0.41709900	-0.90364800
C	-3.09680800	-0.73662800	-1.04913600
C	3.49121500	-1.18723900	0.03272500
C	4.78169100	-1.02275800	0.55117300
C	5.31615900	0.23597900	0.79068300
C	4.57232900	1.37345300	0.50227800
C	3.28129900	1.27685600	-0.02371100
C	3.16191700	-3.53639700	0.93844200
C	3.61994200	-3.16130800	-1.52149800
C	2.52589700	2.55646700	-0.36466000
C	3.22848900	3.33798300	-1.49065200
C	2.31349900	3.44371700	0.87476000
C	-2.69884500	-2.15100900	-1.45234500
C	-3.41564800	-3.22278800	-0.61206000
C	-2.97686900	-2.39083900	-2.94987500
C	-1.57449100	2.78670600	-0.44700100
C	-1.41621500	3.46768700	-1.82167200
C	-1.94485900	3.82579400	0.62362300
H	1.94021700	-0.31487600	-2.89781200
H	-0.79940000	-0.13326500	-3.20633700
H	-4.26916800	2.87535100	-0.15534000
H	-5.92443600	1.08183400	-0.46000100
H	-5.19465600	-1.19325600	-1.04983900
H	5.37666600	-1.90181200	0.77094500
H	6.31805900	0.33227500	1.19748100
H	5.00425900	2.35200400	0.68206300
H	2.71880500	-3.12803700	1.85027400
H	4.21611300	-3.75472100	1.14084000
H	2.66404600	-4.48673400	0.73069400
H	3.45269700	-2.52300500	-2.39443400
H	4.70286000	-3.28206500	-1.40379100
H	3.19609200	-4.14383300	-1.74848900
H	1.53840700	2.28515600	-0.74221000
H	3.34772500	2.72586600	-2.38854300
H	4.22244700	3.67723200	-1.18633000
H	2.64577200	4.22331400	-1.76181000
H	1.79658000	2.90100100	1.66950000
H	3.26266300	3.80334500	1.28110100
H	1.71505000	4.32236900	0.61663400
H	-1.63074800	-2.28571200	-1.25412500
H	-2.98870800	-4.20373300	-0.83657500
H	-4.48997800	-3.27593200	-0.81763900
H	-3.28276600	-3.04406300	0.45658300
H	-2.63116800	-3.38736600	-3.23952000
H	-4.04677700	-2.32928100	-3.17766000
H	-2.46641600	-1.66756400	-3.59195600
H	-0.59885900	2.38777000	-0.16614100
H	-0.67998000	4.27540400	-1.76837100
H	-2.36476900	3.90112600	-2.15185900
H	-1.08660300	2.76419400	-2.58993000

H	-1.12394800	4.53676700	0.74993400
H	-2.82863800	4.40674700	0.34750900
H	-2.13945000	3.35910200	1.59167600
O	0.24365500	0.24056700	1.13245100
C	-0.73892800	-0.18982500	2.06644000
C	-1.20637200	-1.49402100	2.07688600
C	-1.08816700	0.75092300	3.02646600
C	-2.09226300	-1.84762300	3.09733900
H	-0.86087500	-2.18810900	1.30198700
C	-1.97019000	0.37270800	4.03691000
H	-0.66961900	1.74982600	2.98800600
C	-2.47679400	-0.92669300	4.07160400
H	-2.47288400	-2.86342900	3.13343400
H	-2.25530100	1.09363200	4.79590000
H	-3.16156500	-1.22123100	4.86015900
C	2.96216200	-2.58457200	-0.25276400
H	1.87956500	-2.53643000	-0.41433100

2

E(RB3LYP) = -1567.12393629 A.U.

N	1.11115800	-0.10401400	-1.12417600
C	0.67010600	-0.08658400	-2.46030500
C	-0.67137000	-0.08626900	-2.46005700
N	-1.11192300	-0.10343400	-1.12375800
C	-2.48116400	0.00795800	-0.70575200
C	2.48051100	0.00777000	-0.70666900
C	-3.03343500	1.29174800	-0.50045300
C	-4.36727400	1.37586600	-0.08896400
C	-5.13454400	0.23251100	0.10227800
C	-4.58405500	-1.02077100	-0.13627200
C	-3.25506800	-1.16230400	-0.54997800
C	3.25442400	-1.16239400	-0.55015700
C	4.58353000	-1.02057000	-0.13693100
C	5.13412500	0.23289700	0.10040600
C	4.36684700	1.37612100	-0.09159600
C	3.03288200	1.29171500	-0.50261800
C	2.77385500	-3.47798400	0.37583400
C	3.44188000	-3.18329100	-2.05457400
C	2.24664200	2.57234800	-0.75833700
C	2.78467700	3.30555300	-2.00210000
C	2.22811800	3.50629100	0.46300500
C	-2.71292700	-2.55405200	-0.85374800
C	-2.77441000	-3.47873200	0.37387000
C	-3.44309800	-3.18187700	-2.05609200
C	-2.24719800	2.57257100	-0.75522800
C	-2.78563700	3.30702100	-1.99807600
C	-2.22814700	3.50529300	0.46703500
H	1.37260400	-0.07648800	-3.27640700

H	-1.37416400	-0.07584800	-3.27589800
H	-4.81567100	2.34945100	0.07923200
H	-6.16729500	0.31947500	0.42607300
H	-5.19945600	-1.90469500	-0.00399900
H	5.19893400	-1.90440400	-0.00405900
H	6.16696500	0.32010700	0.42384700
H	4.81534100	2.34982600	0.07564100
H	2.22293000	-3.05218000	1.21689200
H	3.80334000	-3.65881500	0.70012700
H	2.32868100	-4.44975600	0.14158000
H	3.37435700	-2.54773300	-2.94202200
H	4.50317100	-3.34869600	-1.84555500
H	2.99944100	-4.15285800	-2.30289600
H	1.21417100	2.29172500	-0.96656100
H	2.75822000	2.66444400	-2.88736300
H	3.81909200	3.63335900	-1.86026300
H	2.18183500	4.19407600	-2.21380500
H	1.82022800	3.00315700	1.34194200
H	3.22813700	3.87119100	0.71528900
H	1.60487600	4.38224900	0.25943100
H	-1.66308000	-2.45128800	-1.12491700
H	-2.32925800	-4.45028900	0.13868400
H	-3.80381400	-3.65988100	0.69824500
H	-2.22331800	-3.05363800	1.21518200
H	-3.00086700	-4.15130200	-2.30533800
H	-4.50436000	-3.34728800	-1.84692700
H	-3.37571100	-2.54559000	-2.94302700
H	-1.21482700	2.29206400	-0.96409500
H	-2.18284400	4.19573800	-2.20910900
H	-3.81999500	3.63471000	-1.85556600
H	-2.75949700	2.66678500	-2.88398200
H	-1.60487400	4.38138400	0.26412900
H	-3.22803700	3.87004800	0.72004300
H	-1.82000500	3.00120900	1.34531100
C	-0.00027000	-0.21465200	-0.25611500
O	-0.00010100	0.69424200	0.81589800
C	0.00088800	0.29054100	2.15482500
C	1.21198100	0.14548900	2.82461000
C	-1.20930900	0.14513000	2.82617300
C	1.20847700	-0.15834300	4.18540200
H	2.14098600	0.26672700	2.27971700
C	-1.20395900	-0.15869500	4.18695600
H	-2.13905500	0.26612000	2.28247000
C	0.00272600	-0.31181200	4.86981000
H	2.15141100	-0.27366300	4.71021900
H	-2.14617700	-0.27430000	4.71299400
H	0.00344000	-0.54761600	5.92894600
C	2.71209900	-2.55436500	-0.85257000
H	1.66218700	-2.45173300	-1.12355300
F	-0.00036700	-1.53359400	0.40511300

TS2

E(RB3LYP) = -1567.08543249 A.U.
1 imaginary frequencies -427.7216 cm-1

N	1.09084800	0.32236500	-1.12089000
C	0.67064500	0.38110200	-2.44598400
C	-0.68081400	0.38154000	-2.44473500
N	-1.09832200	0.31603100	-1.11908900
C	-2.48111100	0.30872900	-0.68795800
C	2.47430300	0.31668400	-0.69240100
C	-3.04135900	1.50642600	-0.20579000
C	-4.38741600	1.47951500	0.17165500
C	-5.14248500	0.31891700	0.05896200
C	-4.56415500	-0.84532800	-0.43263600
C	-3.21924700	-0.88455800	-0.81375900
C	3.21847800	-0.87052300	-0.83765500
C	4.56445100	-0.82983400	-0.46039200
C	5.13818300	0.33000700	0.04643200
C	4.37684600	1.48442800	0.17949200
C	3.02934700	1.50978900	-0.19275100
C	2.90600200	-3.37383100	-0.50366400
C	3.14294700	-2.41290500	-2.83553300
C	2.24013200	2.80676400	-0.05519600
C	2.81752000	3.91375400	-0.95659200
C	2.15759300	3.26678100	1.41095500
C	-2.62502200	-2.17566600	-1.36709600
C	-2.92153200	-3.39063900	-0.47237400
C	-3.11303700	-2.43031000	-2.80689800
C	-2.25751700	2.80862800	-0.08988200
C	-2.85633400	3.90849400	-0.98584700
C	-2.15123200	3.27564200	1.37255500
H	1.37509200	0.42997200	-3.25785700
H	-1.38684300	0.42821300	-3.25537000
H	-4.85261500	2.38142600	0.55433500
H	-6.18662100	0.32147000	0.35557200
H	-5.16644300	-1.74282700	-0.51586000
H	5.17100500	-1.72302100	-0.55875100
H	6.18335700	0.33404500	0.33933500
H	4.83848600	2.38302300	0.57405800
H	2.51454500	-3.21173500	0.50109400
H	3.97293300	-3.60555700	-0.43323100
H	2.40708900	-4.25675500	-0.91334800
H	2.92335500	-1.57757600	-3.50670000
H	4.22612300	-2.56835400	-2.85015000
H	2.67414800	-3.30855900	-3.25377200
H	1.21776200	2.62431800	-0.39197300
H	2.84729100	3.60379300	-2.00487700
H	3.83495700	4.18543600	-0.66186800
H	2.20376400	4.81689600	-0.88966900

H	1.71590900	2.49364200	2.04221300
H	3.14516600	3.51038000	1.81288100
H	1.53936000	4.16566000	1.49229600
H	-1.54036600	-2.06886800	-1.38209800
H	-2.40752900	-4.27182300	-0.86656000
H	-3.98898500	-3.62729000	-0.43239800
H	-2.56105900	-3.22745800	0.54390000
H	-2.64116800	-3.32898100	-3.21512400
H	-4.19662400	-2.58035200	-2.84010600
H	-2.87737800	-1.59757100	-3.47562600
H	-1.24073300	2.62966400	-0.44534600
H	-2.24368500	4.81348600	-0.93640900
H	-3.86825500	4.17985200	-0.67255500
H	-2.90611000	3.59235900	-2.03151700
H	-1.53970500	4.18037700	1.43886500
H	-3.13361300	3.51184300	1.79135000
H	-1.69138200	2.50876300	1.99843000
C	-0.00291600	0.27021100	-0.31309900
O	-0.00269300	0.35298400	0.97337100
C	0.00824300	-0.95694000	1.92981200
C	1.22351400	-1.10582700	2.61355500
C	-1.20355900	-1.12144800	2.61606100
C	1.21365300	-1.52873900	3.93955800
H	2.15479300	-0.91582100	2.09425300
C	-1.18557700	-1.54407800	3.94207000
H	-2.13806900	-0.94262500	2.09859400
C	0.01617500	-1.76109200	4.62021000
H	2.16408100	-1.66564900	4.44843600
H	-2.13309000	-1.69294200	4.45303300
H	0.01930600	-2.08390300	5.65571600
C	2.63024800	-2.15852600	-1.40446800
H	1.54640600	-2.04872300	-1.43980900
F	0.01438100	-1.95598600	0.50554000

3

E(RB3LYP) = -331.573031035 A.U.

C	1.20741200	-1.13489500	0.00000000
C	1.21648300	0.26007900	0.00000000
C	0.00000000	0.92465600	0.00000000
C	-1.21647900	0.26008100	0.00000000
C	-1.20741100	-1.13489700	0.00000000
C	0.00000000	-1.83376900	0.00000000
H	2.14905100	-1.67345000	0.00000000
H	2.14186100	0.82455400	0.00000000
H	-2.14185700	0.82455400	0.00000000
H	-2.14905100	-1.67344900	0.00000000
H	-0.00000300	-2.91828800	0.00000000
F	-0.00000300	2.28539400	0.00000000

4

E(RB3LYP) = -1235.60157036 A.U.

N	-1.10181100	-0.02320400	0.56369400
C	-0.67385600	-0.01458300	1.89553200
C	0.67385100	0.01462300	1.89552800
N	1.10179900	0.02328600	0.56368800
C	2.46988600	0.05247600	0.12474200
C	-2.46990000	-0.05246500	0.12475800
C	3.07437900	1.29635600	-0.14001000
C	4.41031800	1.29784800	-0.55233200
C	5.11903700	0.11049100	-0.69516300
C	4.50021700	-1.10604200	-0.43205700
C	3.16469600	-1.16339200	-0.02214600
C	-3.07433100	-1.29637400	-0.13999400
C	-4.41027500	-1.29793300	-0.55229600
C	-5.11905700	-0.11061100	-0.69511000
C	-4.50029600	1.10595300	-0.43201200
C	-3.16477100	1.16336900	-0.02212000
C	-2.11766500	-3.27130100	-1.39095200
C	-3.00250900	-3.57945400	0.97118200
C	-2.51136400	2.51514900	0.23947600
C	-3.18568900	3.25664900	1.40771100
C	-2.48702800	3.38497400	-1.03026200
C	2.51123100	-2.51513700	0.23948500
C	2.48699800	-3.38507500	-1.03017300
C	3.18543400	-3.25654300	1.40785400
C	2.31956500	2.61391200	-0.01324900
C	3.00266000	3.57937300	0.97129100
C	2.11790300	3.27142600	-1.39090200
H	-1.37456900	-0.02984400	2.71339100
H	1.37456800	0.02990100	2.71338400
H	4.90278800	2.24011800	-0.76889500
H	6.15567500	0.13302700	-1.01681500
H	5.06312200	-2.02566100	-0.55335300
H	-4.90269900	-2.24022800	-0.76885600
H	-6.15570000	-0.13320000	-1.01674300
H	-5.06325100	2.02554300	-0.55329600
H	-1.59622400	-2.59798900	-2.07471000
H	-3.07352700	-3.54392200	-1.84866300
H	-1.52423700	-4.18575600	-1.29485500
H	-3.12076000	-3.12689200	1.95965400
H	-3.99455100	-3.88204000	0.62398000
H	-2.40529700	-4.48880000	1.08744000
H	-1.47346800	2.33546100	0.52712800
H	-3.17150800	2.65905500	2.32339600
H	-4.22940300	3.49717300	1.18496400
H	-2.66726100	4.19805800	1.61350400

H	-1.98751100	2.86942900	-1.85361100
H	-3.49659800	3.64639000	-1.36103100
H	-1.95124900	4.32004800	-0.84074200
H	1.47330900	-2.33540300	0.52701600
H	1.95115400	-4.32010800	-0.84062800
H	3.49658900	-3.64657500	-1.36081200
H	1.98759300	-2.86958100	-1.85362100
H	2.66698000	-4.19793200	1.61368000
H	4.22916700	-3.49708800	1.18522000
H	3.17117100	-2.65886900	2.32348400
H	1.32799700	2.39506700	0.38845200
H	2.40550800	4.48875500	1.08757500
H	3.99474000	3.88190700	0.62415300
H	3.12083200	3.12674400	1.95974200
H	1.52451900	4.18590500	-1.29477500
H	3.07380200	3.54402700	-1.84854600
H	1.59646100	2.59818500	-2.07473000
C	-0.00000900	0.00006000	-0.29093200
O	-0.00001400	0.00004500	-1.51489000
C	-2.31943600	-2.61388700	-0.01326700
H	-1.32790100	-2.39499800	0.38849300

B3LYP/6-311+G(d) computed total energies, single imaginary frequencies and cartesian coordinates, in methanol, of the stationary points involved in the domino reaction of imidazolium **1'** with the fluoride anion.

1'

E(RB3LYP) = -611.673339249 A.U.

C	1.19435100	-0.27919700	-0.36067800
O	-0.08041700	-0.46089400	-0.97292500
C	-1.17854500	-0.06671300	-0.35518600
C	1.34171200	-0.21641500	1.01744300
C	2.63034300	-0.07624600	1.53661500
C	3.73187400	-0.01351100	0.68630400
C	3.55026400	-0.09078400	-0.69489700
C	2.27140500	-0.22373800	-1.23186000
H	0.48846300	-0.28330600	1.68413300
H	2.76532500	-0.02446700	2.61115400
H	4.72907000	0.09125800	1.09805600
H	4.40445900	-0.04681900	-1.36100800
H	2.10853500	-0.28735500	-2.30141300
C	-2.81697600	1.16789200	0.46611100
H	-3.32617000	2.06973100	0.76103000
C	-3.19519000	-0.13198000	0.54654100
H	-4.10062600	-0.58147200	0.91749700
N	-1.55607400	1.19978600	-0.11070600
N	-2.15845500	-0.89687200	0.03353600
C	-0.76813600	2.40273700	-0.40228100
C	-2.14147600	-2.35916500	-0.08922700
H	-2.34591500	-2.80175800	0.88396100
H	-2.89682800	-2.67318100	-0.80854100
H	-1.15974100	-2.67077900	-0.43492600
H	-1.45311200	3.21102100	-0.64829600
H	-0.16536400	2.67626100	0.46324900
H	-0.12081700	2.21033700	-1.25460400

MC'

E(RB3LYP) = -711.707159318 A.U.

C	1.28767100	-0.36813600	-0.40115900
O	-0.02494500	-0.62996800	-0.87388900
C	-1.10894700	-0.02259900	-0.42375000
F	-1.02857200	-0.71462400	1.98362900
C	1.56687100	-0.34575300	0.95705100
C	2.89701300	-0.14825800	1.33459600
C	3.90226800	0.00236000	0.37846700
C	3.58419300	-0.04404000	-0.97956300
C	2.26231900	-0.23182500	-1.38161700
H	0.73252700	-0.49114500	1.65585000

H	3.14656600	-0.12575300	2.39061000
H	4.93183700	0.14792700	0.68875500
H	4.36140900	0.06394800	-1.72878000
H	1.99028500	-0.27617400	-2.43045400
C	-2.66269300	1.46677500	0.07120200
H	-3.05869700	2.43068600	0.34008300
C	-3.26935600	0.27006900	-0.08801700
H	-4.30063500	-0.01705000	0.02342000
N	-1.30542300	1.28588300	-0.18310400
N	-2.29377000	-0.64855500	-0.43978000
C	-0.28993200	2.32900100	-0.06110400
C	-2.43597600	-2.10182500	-0.42114200
H	-3.48238100	-2.34770700	-0.59181800
H	-1.82982500	-2.54185600	-1.21069600
H	-2.10657600	-2.45699000	0.55527700
H	-0.78578000	3.29313000	-0.15694600
H	0.20372700	2.26317300	0.90800500
H	0.44802900	2.23326600	-0.85445000

2’

E(RB3LYP) = -711.711320348 A.U.

C	1.27564300	-0.44638000	-0.37420800
O	-0.05380700	-0.75795500	-0.65312400
C	-1.10398800	-0.16145600	0.04846600
F	-0.91854400	-0.63212800	1.44327900
C	1.92253000	-0.95720900	0.75011600
C	3.27585300	-0.67996300	0.93873500
C	3.97891700	0.08846200	0.01020000
C	3.32344600	0.57897500	-1.11881600
C	1.96926100	0.31150700	-1.31539300
H	1.36877500	-1.55522700	1.46187700
H	3.78347700	-1.07426400	1.81313400
H	5.03287800	0.29645900	0.16196500
H	3.86495100	1.16951800	-1.85067300
H	1.44299500	0.67958900	-2.18875700
C	-2.56975700	1.57897700	-0.13290800
H	-2.89953100	2.60487900	-0.10532400
C	-3.24222400	0.46096300	-0.43639200
H	-4.26936800	0.32430600	-0.73390600
N	-1.20404600	1.25887900	0.05450700
N	-2.33619000	-0.61333900	-0.45818300
C	-0.39720900	2.07033600	0.96375200
C	-2.73075500	-2.00715800	-0.34398000
H	-3.53135900	-2.20716200	-1.05765400
H	-1.88314800	-2.64258400	-0.59731700
H	-3.07810400	-2.26024700	0.66364900
H	-0.50782300	3.11623000	0.67346900
H	-0.70934600	1.95318200	2.00634400

H	0.65430700	1.80700500	0.87697100

TS2’

E(RB3LYP) = -711.674963186 A.U.
1 imaginary frequencies -414.3663 cm-1

C	-1.22847300	-0.01114900	0.03913000
O	0.08364700	0.00235800	-0.91053600
C	1.27731700	0.00332800	-0.40766400
F	-0.19036700	-0.07366200	1.43554600
C	-1.91837600	1.21104700	0.03012000
C	-3.30995800	1.21589400	0.02180500
C	-4.04124200	0.02736600	-0.02570900
C	-3.34072900	-1.17936500	-0.07558200
C	-1.94939900	-1.21041200	-0.06768400
H	-1.36495300	2.14108300	0.06808600
H	-3.82617500	2.17181600	0.04375100
H	-5.12553700	0.04189000	-0.03938000
H	-3.88110900	-2.12039500	-0.13189000
H	-1.41866200	-2.15352100	-0.10884400
C	3.28182600	-0.67275800	0.29383700
H	4.05029400	-1.37523000	0.56828500
C	3.28381400	0.68235800	0.28707500
H	4.05501800	1.38533100	0.55216900
N	2.04093200	-1.08607000	-0.16216900
N	2.04248500	1.09415700	-0.17115200
C	1.56655600	-2.46164400	-0.23681700
C	1.58148400	2.47224300	-0.28016900
H	2.41919900	3.10513200	-0.56952500
H	0.80965200	2.52626700	-1.04461400
H	1.17433700	2.81092300	0.67339600
H	0.84653400	-2.54533600	-1.04811700
H	2.41321400	-3.11591100	-0.43846300
H	1.09147400	-2.74601700	0.70272200

4’

E(RB3LYP) = -380.187654119 A.U.

O	-0.00000800	-1.89933800	-0.00022200
C	-0.00000200	-0.66896500	-0.00030700
C	0.67542200	1.50565500	0.00001000
H	1.37378500	2.32618600	0.00024400
C	-0.67541500	1.50565800	-0.00015000
H	-1.37377400	2.32619200	-0.00007300
N	1.09819600	0.17809200	-0.00012600
N	-1.09819500	0.17809700	-0.00038500
C	2.47063100	-0.28979900	0.00036500

C	-2.47062900	-0.28979300	0.00049100
H	-3.00328100	0.06512200	-0.88515100
H	-2.45283300	-1.37806800	-0.00913300
H	-2.99759000	0.04919600	0.89583600
H	2.45281600	-1.37810700	-0.00446600
H	3.00191400	0.06115600	-0.88769800
H	2.99897800	0.05317600	0.89334700

TS3

E(RB3LYP) = -811.644399361 A.U.
1 imaginary frequencies -242.8246 cm-1

C	-1.26315900	0.00049800	0.75017300
O	0.17519200	0.00071500	1.21577000
C	1.13111200	0.00005500	0.28812700
F	2.52254100	0.00074900	1.48246300
C	-1.71733200	-1.21229700	0.14718100
F	-1.77175900	0.00156000	2.33757900
C	-2.66208600	-1.19784700	-0.86830400
C	-3.15708900	-0.00041700	-1.39995400
C	-2.66167500	1.19745800	-0.86966700
C	-1.71713800	1.21277200	0.14596500
H	-1.36174800	-2.15229400	0.55390400
H	-3.01044900	-2.14937900	-1.26608400
H	-3.88354200	-0.00075400	-2.20640600
H	-3.00976800	2.14863900	-1.26853000
H	-1.36138100	2.15312200	0.55171200
C	2.10317800	-0.67552900	-1.62899300
H	2.48640700	-1.37643800	-2.35243300
C	2.10336200	0.67326400	-1.62972500
H	2.48673100	1.37328100	-2.35395600
N	1.41380400	-1.10117900	-0.49449700
N	1.41398200	1.10036900	-0.49576500
C	1.48211100	2.44825900	0.03732200
H	2.52144400	2.73751900	0.21444000
H	1.01401500	3.15207500	-0.65469600
H	0.95258300	2.47674800	0.98565000
C	1.48046600	-2.44880300	0.03942100
H	1.00947900	-3.15232300	-0.65093900
H	2.51963400	-2.73994500	0.21440200
H	0.95301000	-2.47554600	0.98895100

B3LYP/6-311+G(d) computed total energies, single imaginary frequencies and cartesian coordinates, in methanol, of the stationary points **TS1-2MeOH** and Meisenheimer intermediate.

TS1-2MeOH

E(RB3LYP) = -1038.70426550 A.U.
1 imaginary frequencies -401.3594 cm-1

C	-1.05964300	-0.17597300	0.39132800
Cl	-0.00284200	-0.82591100	1.88041300
O	0.51019700	0.17085000	-0.54847400
C	-1.71694700	1.04932100	0.65115600
C	-3.00313500	1.26914000	0.16904200
C	-3.69723300	0.28397700	-0.54246200
C	-3.06401200	-0.94579600	-0.75169800
C	-1.77770200	-1.19179900	-0.28142000
H	-1.20218800	1.81889000	1.21561000
H	-3.47433700	2.22851900	0.36820700
H	-4.70371800	0.46245900	-0.90532800
H	-3.58336400	-1.74119000	-1.28057600
H	-1.31037100	-2.15781400	-0.43691500
C	0.16981700	0.70244800	-1.80834400
H	1.07741200	0.82219300	-2.41195400
H	-0.51325000	0.03826600	-2.35633200
H	-0.31122100	1.68700700	-1.72151800
H	1.49288800	-1.25010800	-0.79092000
O	2.06212200	-2.02604200	-1.02193300
C	3.20213900	-2.04505500	-0.17745200
H	3.80041500	-2.91980100	-0.44105100
H	3.82673000	-1.15175600	-0.30797900
H	2.92624300	-2.12091700	0.88139400
H	1.54971700	1.30203900	0.29990200
O	2.15267800	1.96841300	0.71343300
C	3.06484200	2.44640500	-0.26257000
H	3.72849700	3.16522100	0.22229500
H	3.68125400	1.64027900	-0.68102100
H	2.55488000	2.95541700	-1.09053500

Meisenheimer intermediate

E(RB3LYP) = -1420.88985815 A.U.

C	-0.08579600	-0.00217200	0.02821100
O	0.06196700	-0.00363500	1.42066200
Cl	1.74849000	-0.00229600	-0.57183800
C	-0.75076700	-1.23145200	-0.52816900
C	-1.64981300	-1.21104100	-1.55938200
C	-2.08379700	0.00189200	-2.10908900

C	-1.64941900	1.21284100	-1.55517600
C	-0.75010600	1.22918100	-0.52422500
H	-2.03462500	-2.14545000	-1.94094200
H	-2.03421900	2.14869700	-1.93319700
C	-1.15348500	-0.00541800	2.15518300
H	-0.85816200	-0.00565800	3.20380100
H	-1.75837300	0.88561400	1.95029000
H	-1.75635400	-0.89757200	1.94938400
N	-3.01450600	0.00392700	-3.19613000
O	-3.39894700	1.09347900	-3.64430100
O	-3.39996100	-1.08390300	-3.64757900
N	-0.37901700	2.53680400	-0.00638300
O	0.55821000	2.62121000	0.78144400
O	-1.03536600	3.51962800	-0.38318600
N	-0.37992400	-2.54101400	-0.01525800
O	0.55417100	-2.62782200	0.77607900
O	-1.03294200	-3.52307700	-0.39964200