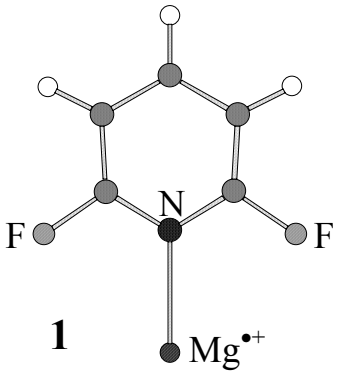
Supplementary Material (ESI) for PCCP

Supporting Information

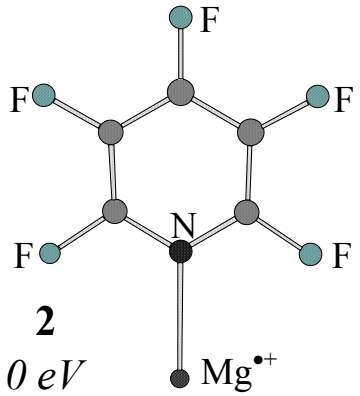
*(All calculations were performed at the B3LYP/6-31+G** level unless otherwise specified.)*

S-1. Geometries and Cartesian coordinates of $Mg^{\bullet+}$(*2,6*-$C_5H_3F_2N$) and $Mg^{\bullet+}(C_5F_5N)$. Relative energies of isomers are also shown for $Mg^{\bullet+}(C_5F_5N)$.



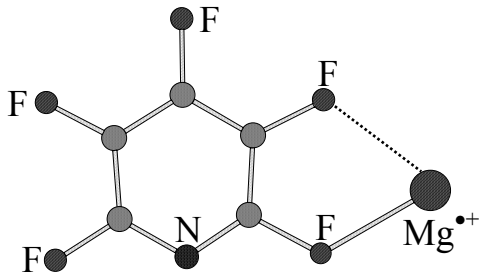
$Mg^{\bullet+}$(*2,6*-$C_5H_3F_2N$)

C	1.139511	-0.130661	0.000000
N	-0.000046	-0.832687	0.000000
C	-1.140396	-0.131989	0.000000
C	-1.217209	1.247482	0.000000
C	-0.001617	1.940170	0.000000
C	1.214706	1.248825	0.000000
F	-2.240555	-0.893860	0.000000
F	2.240555	-0.891251	0.000000
Mg	0.001236	-3.025284	0.000000
H	-2.179382	1.744629	0.000000
H	-0.002213	3.025284	0.000000
H	2.176346	1.746933	0.000000



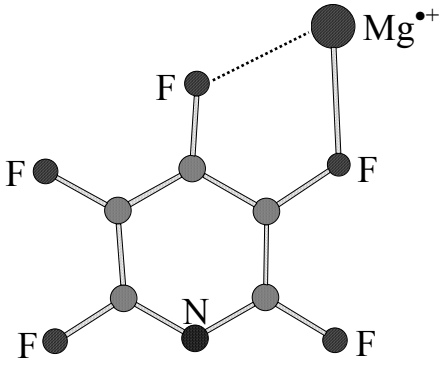
$Mg^{\bullet+}(C_5F_5N)$
$Mg^{\bullet+}$ linked to N

C	1.209427	1.134003	0.133636
C	1.141754	-0.247879	0.027100
N	-0.006622	-0.922821	-0.069427
C	-1.151657	-0.235397	-0.063446
C	-1.212479	1.147141	0.038010
C	0.000168	1.842575	0.138641
F	2.247803	-0.985703	0.015762
F	-2.261261	-0.961151	-0.162292
F	-2.368500	1.788269	0.040024
F	0.003479	3.151733	0.237167
F	2.368515	1.762573	0.227081
Mg	-0.012070	-3.151733	-0.237183



$Mg^{\bullet+}(C_5F_5N)$
$Mg^{\bullet+}$ linked to 2,3- F

C	0.247147	0.068604	-0.015930
C	0.183182	-1.304855	-0.003311
C	-0.958344	0.770584	-0.000839
F	1.472916	0.684036	-0.042435
N	-0.893158	-2.021378	0.021439
C	-2.143097	0.025131	0.026047
F	1.421509	-1.967346	-0.019333
F	-0.979004	2.088928	-0.011536
C	-2.047165	-1.374817	0.036118
F	-3.314697	0.637421	0.041275
Mg	3.314713	-0.883606	-0.061371
F	-3.153427	-2.088928	0.061356



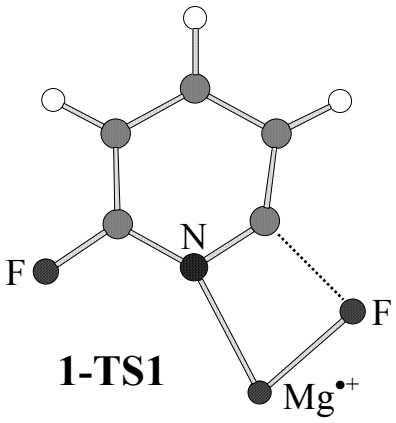
2b *+ 0.64 eV*

$Mg^{\bullet+}(C_5F_5N)$

$Mg^{\bullet+}$ linked to 3,4- F

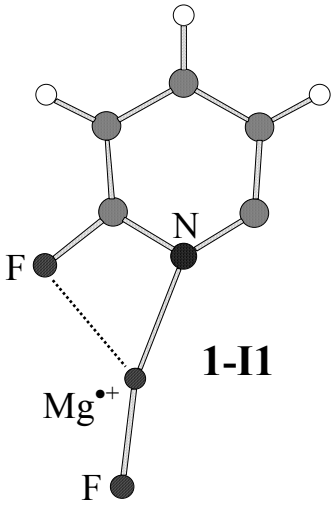
C	0.002182	0.242508	0.001160
C	1.203888	-0.447784	-0.019623
C	-1.205078	-0.436295	0.020416
F	0.074463	1.609085	0.001541
C	1.180267	-1.834244	-0.020828
C	-1.102951	-1.838500	0.017075
F	2.365387	0.313828	-0.038055
F	-2.365372	0.203659	0.040451
N	0.040192	-2.488235	-0.002609
F	2.312988	-2.516037	-0.040436
F	-2.217300	-2.544144	0.034851
Mg	2.273010	2.544159	-0.033951

S-2. Geometries and Cartesian coordinates of selected transition states and intermediates for the complexes **1** and **2**.



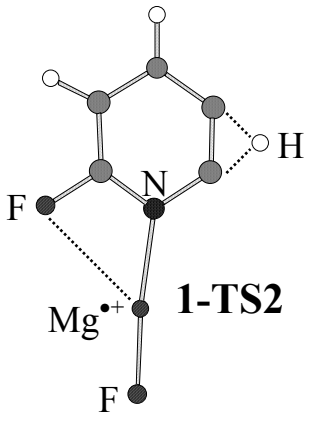
1-TS1

N	-0.080490	-0.958481	0.000732
C	-1.246719	-0.288879	0.000732
C	-1.276886	1.099640	0.000732
C	-0.056900	1.788422	0.000900
C	1.176804	1.102631	0.000992
C	0.995270	-0.249969	0.000641
F	2.345810	-1.634964	-0.000885
Mg	0.922119	-2.875443	-0.001022
F	-2.345810	-1.022873	0.000671
H	-2.229416	1.615936	0.000656
H	-0.057922	2.875443	0.000916
H	2.142273	1.593170	0.001007



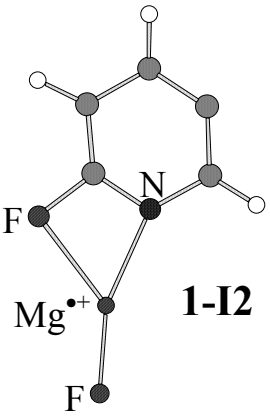
1-I1

C	1.147430	0.612350	0.001358
N	0.026413	-0.086975	0.001358
C	-1.112396	0.621460	0.001358
C	-1.208984	1.990204	0.001297
C	0.016113	2.680634	0.001282
C	1.238495	1.988220	0.001343
Mg	-0.744827	-2.039261	0.001266
F	-0.955490	-3.767044	-0.001419
F	-2.193039	-0.225372	0.001419
H	-2.169907	2.490875	0.001282
H	0.015274	3.767029	0.001236
H	2.193039	2.501282	0.001358



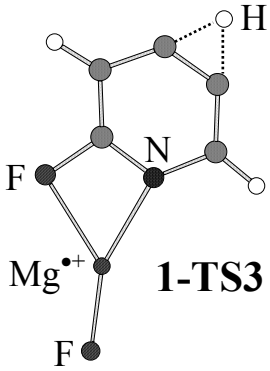
1-TS2

C	-1.061127	0.682419	0.297745
N	0.028671	-0.086319	0.162582
C	1.177429	0.660568	0.202347
C	1.224136	1.982468	0.189377
C	0.076126	2.794525	0.103745
C	-1.113159	2.083405	0.279556
Mg	-0.256180	-2.130615	0.111481
F	-0.313202	-3.865082	-0.027313
F	-2.192551	-0.027023	0.414169
H	0.086456	3.865067	-0.071838
H	-2.081512	2.568878	0.343216
H	2.192566	1.249084	-0.414169



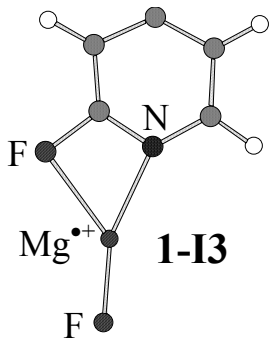
1-I2

C	1.243179	0.557281	-0.000427
C	1.190735	1.928894	-0.000427
C	0.031631	2.680649	-0.000443
C	-1.187286	1.977066	-0.000458
C	-1.058777	0.604706	-0.000488
N	0.056503	-0.114304	-0.000443
Mg	-0.812042	-2.030334	-0.000076
F	-0.938248	-3.767181	0.000488
F	-2.156097	-0.240280	-0.000473
H	2.156952	-0.026230	-0.000412
H	0.043427	3.767166	-0.000443
H	-2.156937	2.461975	-0.000473



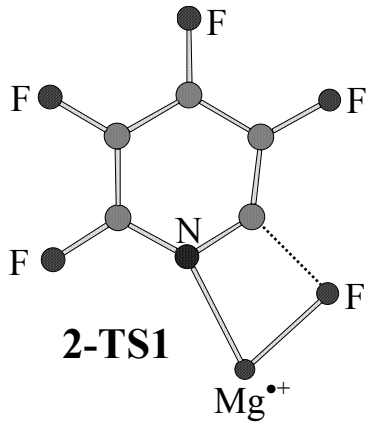
1-TS3

N	0.060730	0.158951	0.006638
C	1.319336	0.672073	0.006638
C	1.367691	2.059555	0.050873
C	0.273651	2.820786	0.072281
C	-1.045288	2.355637	0.064240
C	-0.998062	0.974731	0.034058
F	-2.156418	0.200394	0.025208
Mg	-0.995667	-1.667664	-0.028580
F	-1.221710	-3.393890	-0.077942
H	2.156418	-0.015335	-0.024445
H	-1.961456	2.933640	0.077942
H	1.483658	3.393890	0.053726



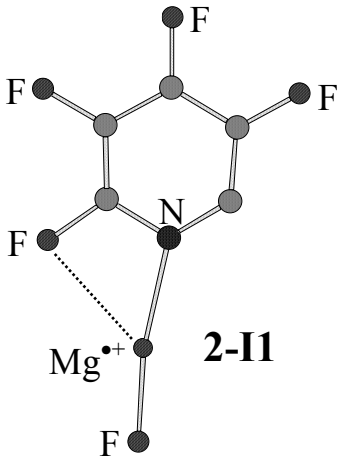
1-I3

C	-1.107819	1.206848	0.006180
N	0.000870	0.475510	0.006180
C	1.196716	1.115097	0.016586
C	1.259903	2.509415	0.026993
C	0.045151	3.165390	0.026062
C	-1.207581	2.583160	0.015762
Mg	-0.885925	-1.428543	-0.013794
F	-1.011215	-3.165390	-0.035339
F	-2.214706	0.374832	-0.005371
H	2.086563	0.494339	0.016373
H	2.214706	3.024734	0.035324
H	-2.154343	3.113144	0.015045



2-TS1

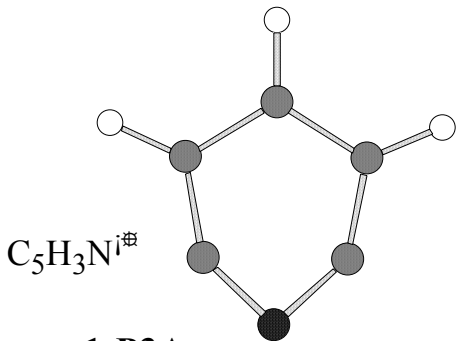
N	-0.049881	-1.069031	-0.015808
C	-1.216400	-0.413666	0.035217
C	-1.230103	0.979691	0.059326
C	-0.008621	1.676224	0.028732
C	1.210052	0.970230	-0.025146
C	1.049759	-0.386978	-0.042221
F	2.344467	-1.692657	-0.109787
Mg	0.938019	-2.990845	-0.082672
F	2.371796	1.596298	-0.054733
F	-0.016907	2.990829	0.050934
F	-2.371796	1.643295	0.109787
F	-2.327286	-1.119873	0.061400



2-I1

C	1.207291	1.894638	0.085373
C	1.089859	0.524017	0.066162
N	-0.043457	-0.148849	-0.016296
C	-1.185287	0.556183	-0.088013
C	-1.224258	1.939896	-0.079315
C	0.003387	2.622818	0.009598
Mg	-0.511200	-2.197647	-0.064835
F	-0.604767	-3.932098	-0.085403
F	-2.285507	-0.206314	-0.168961
F	-2.363495	2.598618	-0.151245
F	0.016205	3.932083	0.021210
F	2.363495	2.520218	0.168961

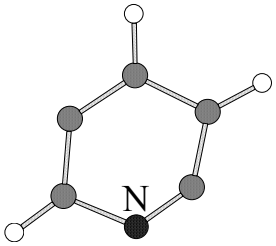
S-3. Geometries and Cartesian coordinates of isomers of $C_5H_3N^{\bullet+}$ and $C_5F_3N^{\bullet+}$ for the complexes **1** and **2**, respectively. Relative energies of isomers are also shown for $C_5H_3N^{\bullet+}$.



1-P3A

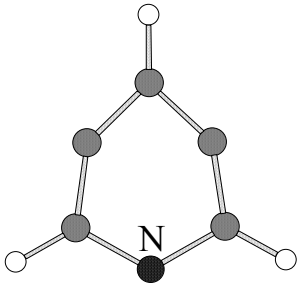
0.00eV

C	0.000000	0.000000	0.000000
N	0.000000	1.297762	0.000000
C	1.293115	1.407474	0.000000
C	2.446986	0.688028	-0.000737
C	2.176378	-0.701541	-0.001074
C	0.814621	-1.088829	-0.000497
H	3.438867	1.126127	-0.001180
H	2.978472	-1.438172	-0.001604
H	0.461870	-2.114176	-0.000631



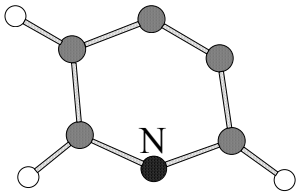
1-P3B *-0.18 eV*

C	-0.051132	0.844100	0.000168
C	1.226593	0.203537	0.000168
C	0.947998	-1.136642	0.000168
N	-0.036300	-1.830627	0.000900
C	-1.309357	-1.293091	-0.000137
C	-1.198807	0.072678	0.000427
H	-0.078659	1.932709	-0.000656
H	2.181519	0.712219	-0.000610
H	-2.181503	-1.932693	-0.000885



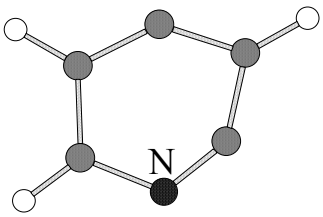
1-P3C *+0.36 eV*

C	-0.027130	0.937241	0.002426
C	0.960709	0.003418	0.002426
C	1.166306	-1.345947	0.002426
N	0.001343	-2.023895	0.000275
C	-1.176331	-1.368469	-0.001450
C	-0.996445	-0.015396	-0.000183
H	-0.036697	2.023911	0.002655
H	2.114624	-1.869537	0.003906
H	-2.114624	-1.909683	-0.003922



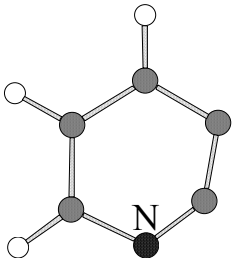
1-P3D *+0.64 eV*

C	0.022995	1.298111	0.000137
C	1.133789	0.653381	0.000137
C	1.331894	-0.699646	0.000137
N	0.067810	-1.157028	-0.000229
C	-1.146744	-0.606735	0.000092
C	-1.265976	0.796921	0.000198
H	2.201126	-1.344574	-0.000092
H	-1.989243	-1.295059	0.000229
H	-2.201126	1.344589	0.000229



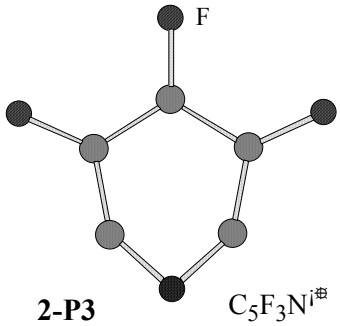
1-P3E *-0.45 eV*

C	-0.037537	1.293289	0.000000
C	1.269073	0.858261	0.000000
C	0.977325	-0.485336	0.000000
N	0.037857	-1.255737	0.000000
C	-1.224777	-0.732849	0.000000
C	-1.270035	0.671936	0.000000
H	2.209991	1.395340	0.000000
H	-2.082596	-1.395355	0.000000
H	-2.209976	1.215134	0.000000



1-P3F *+0.05 eV*

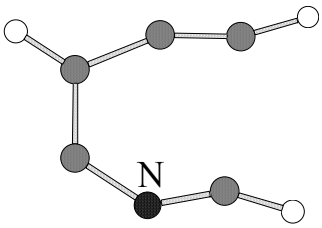
C	0.472855	0.839203	0.000000
C	-0.737793	0.102509	0.000000
C	-0.748169	-1.296890	0.000000
N	0.488770	-1.887344	0.000000
C	1.455353	-1.158127	0.000015
C	1.686615	0.143219	0.000015
H	0.464981	1.928848	0.000000
H	-1.686600	0.631378	-0.000015
H	-1.627304	-1.928833	-0.000015



2-P3 $C_5F_3N^{i\oplus}$

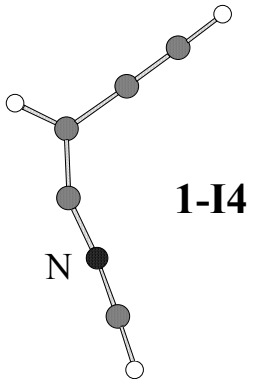
C	-1.222397	-0.000107	0.090286
C	-0.910706	-1.337814	0.104004
N	0.102356	-1.983612	0.058075
C	1.294968	-1.399750	-0.028885
C	1.278915	-0.010025	-0.061905
C	0.027924	0.677567	-0.002487
F	2.375427	0.700806	-0.146118
F	0.015381	1.983627	-0.033676
F	-2.375427	0.589172	0.146118

S-4. Geometries and Cartesian coordinates of transition states and intermediate involved in the decomposition of $C_5H_3N^{\bullet+}$.



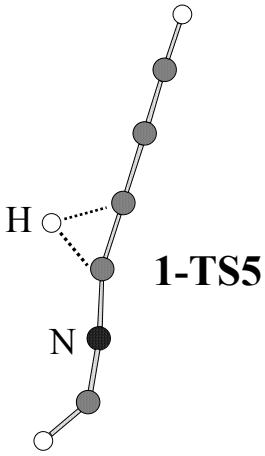
1-TS4

C	-0.028900	1.216202	-0.034897
C	-1.324753	0.683044	0.063293
C	-1.328476	-0.672897	0.160660
N	-0.217285	-1.391907	0.160660
C	0.957047	-1.182755	0.091782
C	1.203186	1.192917	-0.090469
H	-2.233597	1.278275	0.062286
H	1.994141	-1.486908	0.066666
H	2.233612	1.486893	-0.160660



1-I4

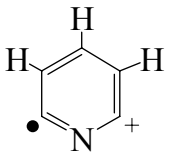
C	-0.016510	-2.370392	0.043594
N	-0.419846	-1.263306	0.015366
C	-0.965591	-0.120834	-0.015839
C	-0.997009	1.213806	-0.038971
C	0.153595	2.020370	-0.026260
C	1.124863	2.749115	-0.017715
H	0.306152	-3.396927	0.069077
H	-1.977570	1.694595	-0.069077
H	1.977570	3.396912	-0.008636



1-TS5

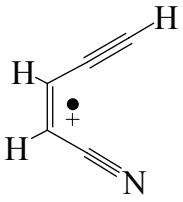
C	0.951248	2.905106	0.086075
C	0.586945	1.740829	0.075638
C	0.189819	0.455658	0.064697
C	-0.201385	-0.753600	0.052231
N	-0.250549	-2.036758	0.089645
C	-0.447495	-3.225250	0.103516
H	1.277176	3.926865	0.096069
H	-1.277176	-3.926865	0.012390
H	-1.129883	0.076553	-0.103531

S-5. Relative energies of the chain and cyclic forms of $C_5H_3N^{\bullet+}$ and $C_5F_3N^{\bullet+}$.



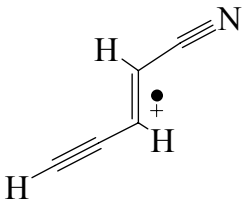
0.00eV

1-P3A



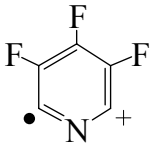
-0.35eV

1-P3G



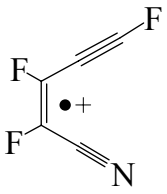
-0.38eV

1-P3H



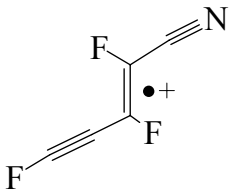
0.99eV

2-P3



0.01eV

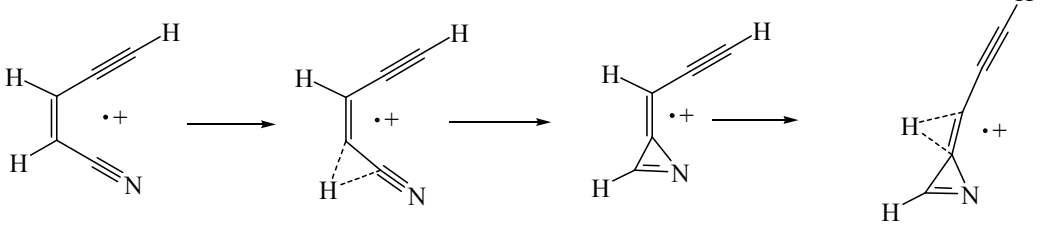
2-P3A



0.00eV

2-P3B

S-6. Energetics of H- and F-transfer in 1-**P3G** and **2**, respectively.

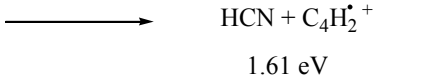


1-P3G
-0.35 eV relative to **1-P3A**

1-TS3G
2.53 eV above **1-P3A** (5.28 eV above **1**)

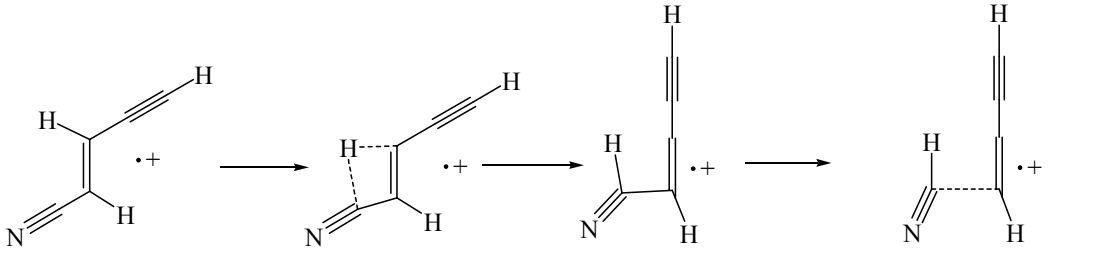
1-I3G
0.34 eV above **1-P3A**

1-TS3G2
2.57 eV above **1-P3A** (5.32 eV above **1**)



$HCN + C_4H_2^{\bullet +}$

1.61 eV relative to **1-P3A**

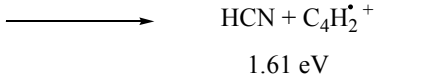


1-P3H
-0.38 eV relative to **1-P3A**

1-TS3H1
2.44eV above **1-P3A** (5.19 eV above **1**)

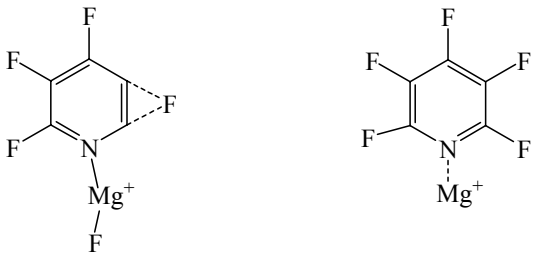
1-I3H
1.34 eV above **1-P3A**

1-TS3H2
1.64eV above **1-P3A** (4.39 eV above **1**)



$HCN + C_4H_2^{\bullet +}$

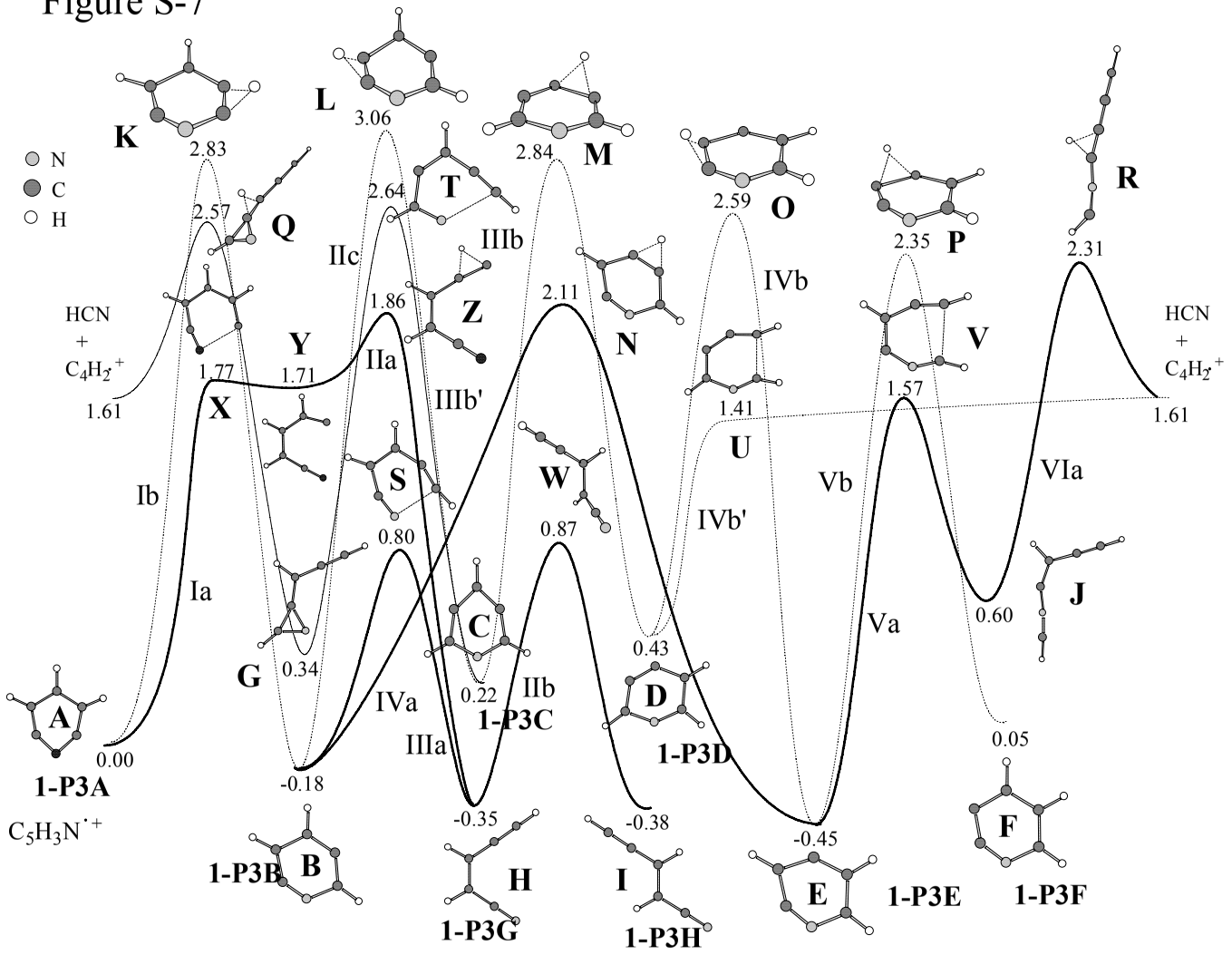
1.61 eV relative to **1-P3A**



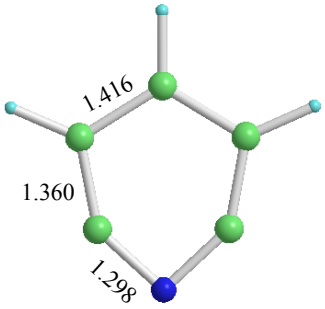
2-TS2
3.75eV above **2**

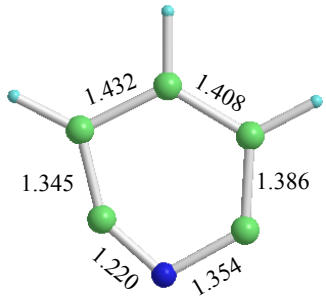
2
0.00eV

Figure S-7



S-8. Artificial asymmetric structures of the pyridyne radical cations: Comparison of calculations using B3LYP and other pure DFT, such as BLYP, BP86 and BPW91.

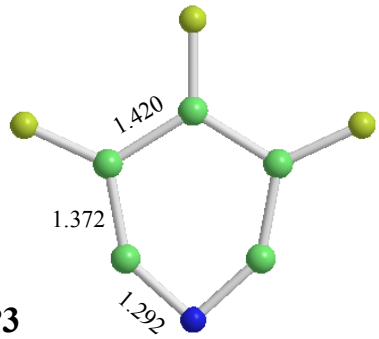


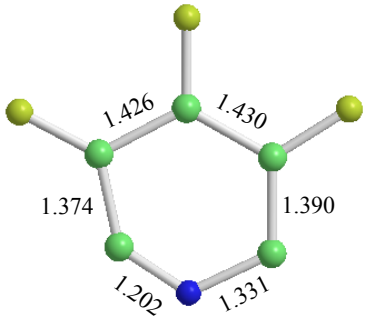


1-P3A

B3LYP: 0.000eV
BLYP: 0.000eV
BP86: 0.000eV
BPW91: 0.000eV

B3LYP: -0.068eV
BLYP: 0.018eV
BP86: 0.001eV
BPW91: 0.001eV





2-P3

B3LYP: 0.000eV
BLYP: 0.000eV
BP86: 0.000eV
BPW91: 0.000eV

B3LYP: -0.131eV
BLYP: No
BP86: No
BPW91: No

The bond lengths shown in the figure are optimized with B3LYP. No asymmetric **2-P3** was located with pure DFT method.

The two structures lie on a very flat potential surface, in which the symmetry-breaking problems may easily occur. In this case, the symmetry-breaking problem is caused by the hybrid B3LYP method. The artificial asymmetric structures can be ruled out based on evidence of the pure DFT calculation. Because no other symmetric structures are involved in the reaction pathway, we still believe that B3LYP is reliable on the ground-state calculation of this system.