Electronic Supporting Information

Infrared Spectrum of the 1-Cyanoadamantane Cation: Evidence of Hydrogen Transfer and Cage-Opening upon Ionization

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Table S1. E_0 energies (kJ mol^{-1}) of transition state structures involved in the formation of different AdCN$^+$ isomers (B3LYP-D3BJ/cc-pVTZ).

Tables S2-S20. Cartesian coordinates (Å) and energies (Hartree) calculated at the B3LYP-D3BJ/cc-pVTZ level of **(S2)** AdCN, **(S3) CC(I)**, **(S4) CC(II)**, **(S5) CC(III)**, **(S6) CC(IV)**, **(S7) OC(I)**, **(S8) OC(II)**, **(S9) TS(I)**, **(S10) TS(II)**, **(S11) TS(III)**, **(S12) TS(IV)**, **(S13) TS(V)**, **(S14) TS(VI)**, (**S15) CC(I)N_2(1)**, (**S16) CC(I)N_2(5)**, (**S17) CC(II)N_2(1)**, (**S18) OC(I)N_2(1)**, (**S19) OC(II)N_2(1)**, and **(S20)** N_2.

Table S21. Assignments of major vibrational frequencies (in cm^{-1}) and their IR intensities (in km mol^{-1}) in the mid-IR range (>2000 cm^{-1}) computed for AdCN and various AdCN$^+$ isomers (B3LYP-D3BJ/cc-pVTZ).

Tables S22-S26. Unscaled vibrational frequencies (in cm^{-1}) and their IR intensities (in km mol^{-1}) computed at the B3LYP-D3BJ/cc-pVTZ level for **(S22)** AdCN, **(S23) CC(I)**, **(S24) CC(II)**, **(S25) OC(I)**, and **(S26) OC(II)**.

Figure S1. (a) Typical mass spectrum of the EI ion source for an expansion of AdCN seeded in Ar (15 bar), along with major assignments. Major ions include AdCN$^+$ (*m/z* 161), AdCN$^+$L clusters with L=Ar/N_2 (*m/z* 201/189), and fragment ions F$^+$ of AdCN (*m/z* 27, 39, 53, 69, 93, 104, 119, 134, 146). Some of the F$^+$ ions are blended by other strong ion signals, arising from Ar_n^+ (*m/z* 40, 80, 120, 160), ArN_2^+ (*m/z* 68). Cluster ions of H_2O and O_2 result from H_2O/O_2 impurities in the gas inlet system. Similarly, AdCN$^+N_2$ clusters stem from remaining N_2 carrier gas used before Ar. **(b)** EI mass spectrum of the NIST data base (70 eV) along with major fragment ions. This spectrum agrees well with the EI mass spectrum of our EI ion source, confirming the identification of the *m/z* 161 peak as AdCN.

Figure S2. Collision-induced dissociation (CID) spectra of size-selected AdCN^+L_n clusters with **(a)** L=Ar (n=1) and **(c)** L=N_2 (n=1) obtained by mass-selecting the parent ion with the first quadrupole and scanning the second quadrupole (mode parent $\rightarrow$ x). The exclusive loss of ligands confirms the identity of the parent clusters as AdCN$^+$L. Also shown are the CID spectra obtained by scanning the first quadrupole, while keeping the second quadrupole at the mass of the AdCN$^+$ fragment to identify AdCN^+L_n cluster ions produced in the EI source for **(b)** L=Ar and **(d)** L=N_2 (mode parent x $\rightarrow$ AdCN$^+$). CID spectra **(a)** and **(b)** are obtained at 15 bar Ar carrier gas, while **(c)** and **(d)** are obtained at 12 bar N_2 carrier gas. These CID spectra show the production of AdCN$^+Ar_{n=1-2}$, AdCN$^+(N_2)_{n=1-2}$, and AdCN^+H_2O clusters in the EI source.

Figure S3. Equilibrium structures (in Å and degrees) of all relevant $AdCN^{(+)}$ monomer structures in their ground electronic states (B3LYP-D3BJ/cc-pVTZ). The acidic CH protons of **CC(I)** and **OC(I)** are indicated in red.

Figure S4-S7. Calculated equilibrium structures and associated E_0 and D_0 energies (kJ mol^{-1}, B3LYP-D3BJ/cc-pVTZ) of all N_2 cluster isomers of **(S4) CC(I)** (acidic proton indicated in red), **(S5) CC(II)**, **(S6) OC(I)**, and **(S7) OC(II)**.

Figure S8. Calculated structures (in Å and degrees) of all transition state structures (B3LYP-D3BJ/cc-pVTZ).

Figure S9. NBO charge distributions (in m*e*) of AdCN and the $AdCN^+$ isomers **CC(I)**, **CC(II)**, **OC(I)**, and **OC(II)** in their ground electronic states (B3LYP-D3BJ/cc-pVTZ).

Figure S10. Spin density distributions of the $AdCN^+$ isomers **CC(I)**, **CC(II)**, **OC(I)**, and **OC(II)** in their ground electronic states (B3LYP-D3BJ/cc-pVTZ).

Figure S11. Calculated IR spectrum of neutral AdCN compared with calculated IR spectrum of isomer **CC(I)** of $AdCN^+$ (B3LYP-D3BJ/cc-pVTZ). Computed scaled harmonic stick spectra are convoluted with Gaussian line profiles (FWHM=10 cm^{-1}).

Figure S12. Calculated IR spectra of isomers **CC(II-IV)** (B3LYP-D3BJ/cc-pVTZ). Computed scaled harmonic stick spectra are convoluted with Gaussian line profiles (FWHM=10 cm^{-1}).

Figure S13. Calculated IR spectra of isomers **OC(I)** and **OC(II)** (B3LYP-D3BJ/cc-pVTZ). Computed scaled harmonic stick spectra are convoluted with Gaussian line profiles (FWHM=10 cm^{-1}).

Figure S14. HOMO orbitals of AdCN and various closed-cage and open-cage isomers evaluated at the B3LYP-D3/cc-pVTZ level.

Figure S15. Calculated equilibrium structures (B3LYP-D3BJ/cc-pVTZ) of all closed-cage isomers **CC(I-IV)** with hydrogen groups 1-3 labelled in red for **CC(I)**. Red arrows indicate from which C site the H atom migrates to the N atom of the CN group.

Table S1. E_0 energies (kJ mol^{-1}) of transition states (**TS**) involved in the formation of different AdCN$^+$ isomers (B3LYP-D3BJ/cc-pVTZ, Figure 4).

Start Structure	End Structure	E_0 of **TS** relative to Start Structure	**TS**
CC(I)	**CC(IV)**	+216.75	**TS(VI)**
	CC(III)	+185.95	**TS(V)**
	CC(II)	+148.04	**TS(IV)**
	OC(I)	+83.44	**TS(III)**
OC(I)	**OC(II)**	+47.34	**TS(II)**
CC(II)	**OC(II)**	+6.99	**TS(I)**

Table S2. Cartesian coordinates (Å) and energies (Hartree) of AdCN (B3LYP-D3BJ/cc-pVTZ)

Center Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	6	0	-0.000000	1.448284	1.528911
2	1	0	-0.000000	1.470374	2.620928
3	1	0	-0.000000	2.485769	1.186492
4	6	0	-1.254458	0.724261	1.019286
5	1	0	-2.147609	1.239923	1.376007
6	6	0	1.254458	0.724261	1.019286
7	1	0	2.147609	1.239923	1.376007
8	6	0	1.254251	-0.724142	1.528911
9	1	0	1.273382	-0.735187	2.620928
10	1	0	2.152739	-1.242885	1.186492
11	6	0	-1.254251	-0.724142	1.528911
12	1	0	-2.152739	-1.242885	1.186492
13	1	0	-1.273382	-0.735187	2.620928
14	6	0	0.000000	-1.448523	1.019286
15	1	0	0.000000	-2.479845	1.376007
16	6	0	0.000000	-1.455966	-0.515214
17	1	0	0.878707	-1.978550	-0.896044
18	1	0	-0.878707	-1.978550	-0.896044
19	6	0	-1.260904	0.727983	-0.515214
20	1	0	-1.274121	1.750257	-0.896044
21	1	0	-2.152828	0.228293	-0.896044
22	6	0	1.260904	0.727983	-0.515214
23	1	0	1.274121	1.750257	-0.896044
24	1	0	2.152828	0.228293	-0.896044
25	6	0	0.000000	0.000000	-1.038775
26	6	0	0.000000	0.000000	-2.498439
27	7	0	0.000000	0.000000	-3.649208

Sum of electronic and zero-point Energies= -482.945442
Sum of electronic and thermal Energies= -482.936579
Sum of electronic and thermal Enthalpies= -482.935635
Sum of electronic and thermal Free Energies= -482.977694

Table S3. Cartesian coordinates (Å) and energies (Hartree) of **CC(I)** (B3LYP-D3BJ/cc-pVTZ)

Center Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	6	0	0.779586	-1.532732	1.260175
2	1	0	0.785300	-2.619635	1.268720
3	1	0	1.257511	-1.164819	2.165939
4	6	0	-0.736145	-1.018239	1.251650
5	1	0	-1.178502	-1.415355	2.166612
6	6	0	1.393657	-0.964836	-0.000000
7	1	0	2.458291	-1.315395	-0.000000
8	6	0	0.779586	-1.532732	-1.260175
9	1	0	0.785300	-2.619635	-1.268720
10	1	0	1.257511	-1.164819	-2.165939
11	6	0	-1.391617	-1.580263	-0.000000
12	1	0	-2.451567	-1.292540	-0.000000
13	1	0	-1.368984	-2.669033	-0.000000
14	6	0	-0.736145	-1.018239	-1.251650
15	1	0	-1.178502	-1.415355	-2.166612
16	6	0	-0.736145	0.496619	-1.273788
17	1	0	-0.238871	0.882310	-2.163393
18	1	0	-1.764882	0.868610	-1.318437
19	6	0	-0.736145	0.496619	1.273788
20	1	0	-0.238871	0.882310	2.163393
21	1	0	-1.764882	0.868610	1.318437
22	6	0	1.454162	0.540026	0.000000
23	1	0	1.938091	0.942121	0.887072
24	1	0	1.938091	0.942121	-0.887072
25	6	0	-0.080073	1.059735	0.000000
26	6	0	-0.040750	2.504081	0.000000
27	7	0	0.009308	3.655754	0.000000

Sum of electronic and zero-point Energies= -482.603223
Sum of electronic and thermal Energies= -482.593534
Sum of electronic and thermal Enthalpies= -482.59259
Sum of electronic and thermal Free Energies= -482.637629

Table S4. Cartesian coordinates (Å) and energies (Hartree) of **CC(II)** (B3LYP-D3BJ/cc-pVTZ)

Center Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	6	0	1.255981	1.233203	1.254313
2	1	0	2.282612	1.597311	1.261354
3	1	0	0.755082	1.611499	2.146486
4	6	0	1.255981	-0.324893	1.258508
5	1	0	1.755934	-0.690411	2.155397
6	6	0	0.542832	1.617109	-0.000000
7	6	0	1.255981	1.233203	-1.254313
8	1	0	2.282612	1.597311	-1.261354
9	1	0	0.755082	1.611499	-2.146486
10	6	0	1.970517	-0.837532	-0.000000
11	1	0	1.994271	-1.929160	-0.000000
12	1	0	3.006811	-0.499234	-0.000000
13	6	0	1.255981	-0.324893	-1.258508
14	1	0	1.755934	-0.690411	-2.155397
15	6	0	-0.193650	-0.833777	-1.281428
16	1	0	-0.714764	-0.475111	-2.169279
17	1	0	-0.211751	-1.923301	-1.297071
18	6	0	-0.193650	-0.833777	1.281428
19	1	0	-0.714764	-0.475111	2.169279
20	1	0	-0.211751	-1.923301	1.297071
21	6	0	-0.902602	1.289578	0.000000
22	1	0	-1.418961	1.645446	0.890166
23	1	0	-1.418961	1.645446	-0.890166
24	6	0	-0.921129	-0.322764	0.000000
25	6	0	-2.278699	-0.735783	0.000000
26	7	0	-3.401349	-0.976658	0.000000
27	1	0	-4.373215	-1.223921	0.000000

Sum of electronic and zero-point Energies= -482.613498
Sum of electronic and thermal Energies= -482.603871
Sum of electronic and thermal Enthalpies= -482.602927
Sum of electronic and thermal Free Energies= -482.648017

Table S5. Cartesian coordinates (Å) and energies (Hartree) of **CC(III)** (B3LYP-D3BJ/cc-pVTZ)

Center Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	6	0	1.421312	-1.557880	-0.000000
2	1	0	2.093440	-2.401883	-0.000000
3	6	0	0.760669	-1.085582	1.252707
4	1	0	1.283270	-1.440211	2.139506
5	6	0	0.760669	-1.085582	-1.252707
6	1	0	1.283270	-1.440211	-2.139506
7	6	0	-0.705403	-1.587479	-1.260943
8	1	0	-0.717138	-2.676383	-1.284284
9	1	0	-1.218383	-1.238666	-2.160201
10	6	0	-0.705403	-1.587479	1.260943
11	1	0	-1.218383	-1.238666	2.160201
12	1	0	-0.717138	-2.676383	1.284284
13	6	0	-1.421324	-1.083697	-0.000000
14	1	0	-2.454001	-1.433396	-0.000000
15	6	0	-1.452851	0.451667	0.000000
16	1	0	-1.969467	0.827145	-0.883323
17	1	0	-1.969467	0.827145	0.883323
18	6	0	0.760669	0.457563	1.284225
19	1	0	1.781163	0.837517	1.297358
20	1	0	0.241526	0.824741	2.169985
21	6	0	0.760669	0.457563	-1.284225
22	1	0	1.781163	0.837517	-1.297358
23	1	0	0.241526	0.824741	-2.169985
24	6	0	0.024433	0.957658	0.000000
25	6	0	0.024093	2.384977	0.000000
26	7	0	0.023915	3.529084	0.000000
27	1	0	0.026019	4.533017	0.000000

Sum of electronic and zero-point Energies= -482.611343
Sum of electronic and thermal Energies= -482.601585
Sum of electronic and thermal Enthalpies= -482.600641
Sum of electronic and thermal Free Energies= -482.645968

Table S6. Cartesian coordinates (Å) and energies (Hartree) of **CC(IV)** (B3LYP-D3BJ/cc-pVTZ)

Center Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	6	0	-1.227272	-1.223009	1.260128
2	1	0	-2.252830	-1.593594	1.260715
3	1	0	-0.743706	-1.603339	2.160429
4	6	0	-1.227272	0.311604	1.252854
5	1	0	-1.727794	0.682823	2.147754
6	6	0	-0.492703	-1.745880	-0.000000
7	1	0	-0.473056	-2.833804	-0.000000
8	6	0	-1.227272	-1.223009	-1.260128
9	1	0	-2.252830	-1.593594	-1.260715
10	1	0	-0.743706	-1.603339	-2.160429
11	6	0	-1.944100	0.831077	-0.000000
12	1	0	-1.968728	1.922622	-0.000000
13	1	0	-2.979135	0.489322	-0.000000
14	6	0	-1.227272	0.311604	-1.252854
15	1	0	-1.727794	0.682823	-2.147754
16	6	0	0.213473	0.842318	-1.283041
17	1	0	0.737999	0.495954	-2.172410
18	1	0	0.226949	1.932719	-1.271072
19	6	0	0.213473	0.842318	1.283041
20	1	0	0.737999	0.495954	2.172410
21	1	0	0.226949	1.932719	1.271072
22	6	0	0.898080	-1.216915	0.000000
23	1	0	1.788285	-1.824302	0.000000
24	6	0	0.946190	0.291293	0.000000
25	6	0	2.291926	0.767159	0.000000
26	7	0	3.363236	1.167267	0.000000
27	1	0	4.305247	1.514819	0.000000

Sum of electronic and zero-point Energies= -482.610526
Sum of electronic and thermal Energies= -482.601214
Sum of electronic and thermal Enthalpies= -482.600270
Sum of electronic and thermal Free Energies= -482.644837

Table S7. Cartesian coordinates (Å) and energies (Hartree) of **OC(I)** (B3LYP-D3BJ/cc-pVTZ)

Center Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	6	0	1.080471	0.776156	1.261201
2	1	0	2.123466	1.114346	1.320088
3	1	0	0.559312	1.177695	2.127733
4	6	0	1.080471	-0.772677	1.256645
5	1	0	1.581636	-1.128265	2.154508
6	6	0	0.529213	1.311974	0.000000
7	1	0	0.317820	3.364255	0.000000
8	6	0	1.080471	0.776156	-1.261201
9	1	0	2.123466	1.114346	-1.320088
10	1	0	0.559312	1.177695	-2.127733
11	6	0	1.783347	-1.293017	0.000000
12	1	0	1.780271	-2.383434	0.000000
13	1	0	2.828988	-0.983080	0.000000
14	6	0	1.080471	-0.772677	-1.256645
15	1	0	1.581636	-1.128265	-2.154508
16	6	0	-0.395211	-1.235603	-1.275252
17	1	0	-0.925152	-0.846064	-2.141270
18	1	0	-0.422114	-2.328118	-1.332188
19	6	0	-0.395211	-1.235603	1.275252
20	1	0	-0.925152	-0.846064	2.141270
21	1	0	-0.422114	-2.328118	1.332188
22	6	0	-0.348929	2.484964	0.000000
23	1	0	-0.960207	2.560225	0.896677
24	1	0	-0.960207	2.560225	-0.896677
25	6	0	-1.033983	-0.803448	0.000000
26	6	0	-2.223504	-0.086865	0.000000
27	7	0	-3.180942	0.572351	0.000000

Sum of electronic and zero-point Energies= -482.619117
Sum of electronic and thermal Energies= -482.608299
Sum of electronic and thermal Enthalpies= -482.607355
Sum of electronic and thermal Free Energies= -482.655505

Table S8. Cartesian coordinates (Å) and energies (Hartree) of **OC(II)** (B3LYP-D3BJ/cc-pVTZ)

Center Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	6	0	1.180975	0.941813	1.265071
2	1	0	2.219002	1.279592	1.331777
3	1	0	0.657437	1.326750	2.139257
4	6	0	1.180975	-0.601707	1.255840
5	1	0	1.686821	-0.967189	2.148258
6	6	0	0.572432	1.461785	0.000000
7	6	0	1.180975	0.941813	-1.265071
8	1	0	2.219002	1.279592	-1.331777
9	1	0	0.657437	1.326750	-2.139257
10	6	0	1.888222	-1.120547	0.000000
11	1	0	1.907574	-2.211581	0.000000
12	1	0	2.927423	-0.790450	0.000000
13	6	0	1.180975	-0.601707	-1.255840
14	1	0	1.686821	-0.967189	-2.148258
15	6	0	-0.275183	-1.113816	-1.290799
16	1	0	-0.819989	-0.708979	-2.141790
17	1	0	-0.255759	-2.203482	-1.405002
18	6	0	-0.275183	-1.113816	1.290799
19	1	0	-0.819989	-0.708979	2.141790
20	1	0	-0.255759	-2.203482	1.405002
21	6	0	-0.483620	2.299272	0.000000
22	1	0	-0.917195	2.659243	0.923322
23	1	0	-0.917195	2.659243	-0.923322
24	6	0	-0.970729	-0.800556	0.000000
25	6	0	-2.251729	-0.368199	0.000000
26	7	0	-3.323179	0.125642	0.000000
27	1	0	-4.282026	-0.195329	0.000000

Sum of electronic and zero-point Energies= -482.625631
Sum of electronic and thermal Energies= -482.615178
Sum of electronic and thermal Enthalpies= -482.614234
Sum of electronic and thermal Free Energies= -482.661470

Table S9. Cartesian coordinates (Å) and energies (Hartree) of **TS(I)** (B3LYP-D3BJ/cc-pVTZ)

Center Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	6	0	-1.441091	-1.255232	-0.939340
2	1	0	-2.515181	-1.255730	-1.117240
3	1	0	-1.006582	-2.140763	-1.400233
4	6	0	-1.169831	-1.257864	0.602615
5	1	0	-1.610426	-2.155830	1.033395
6	6	0	-0.798700	0.000704	-1.402144
7	1	0	4.398822	0.000036	0.305163
8	6	0	-1.441344	1.256037	-0.938020
9	1	0	-2.515471	1.256382	-1.115716
10	1	0	-1.007189	2.142129	-1.398155
11	6	0	-1.788118	-0.000661	1.227510
12	1	0	-1.623645	-0.001234	2.306321
13	1	0	-2.867404	-0.000605	1.074391
14	6	0	-1.169909	1.257209	0.603903
15	1	0	-1.610511	2.154734	1.035597
16	6	0	0.344386	1.286060	0.854875
17	1	0	0.802621	2.160373	0.393224
18	1	0	0.530312	1.351626	1.927917
19	6	0	0.344448	-1.286886	0.853647
20	1	0	0.802759	-2.160767	0.391251
21	1	0	0.530306	-1.353434	1.926647
22	6	0	0.593888	0.000969	-1.569137
23	1	0	1.076422	-0.909079	-1.903098
24	1	0	1.076119	0.911646	-1.901838
25	6	0	0.999618	-0.000192	0.331158
26	6	0	2.379822	-0.000079	0.278457
27	7	0	3.488576	0.000017	-0.139824

Sum of electronic and zero-point Energies= -482.610801
Sum of electronic and thermal Energies= -482.60149
Sum of electronic and thermal Enthalpies= -482.600546
Sum of electronic and thermal Free Energies= -482.645108

Table S10. Cartesian coordinates (Å) and energies (Hartree) of **TS(II)** (B3LYP-D3BJ/cc-pVTZ)

Center Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	6	0	0.096766	1.202792	-1.279779
2	1	0	-0.197136	2.243423	-1.466044
3	1	0	0.742079	0.923054	-2.112689
4	6	0	-1.196446	0.360970	-1.248693
5	1	0	-1.767212	0.588487	-2.147821
6	6	0	0.876619	1.223352	0.000295
7	1	0	2.779736	1.459206	0.922918
8	6	0	0.097311	1.201455	1.280717
9	1	0	-0.196314	2.241979	1.468019
10	1	0	0.742904	0.920888	2.113129
11	6	0	-2.009539	0.700954	0.000577
12	1	0	-2.951987	0.152899	0.000551
13	1	0	-2.260940	1.763081	0.001073
14	6	0	-1.196029	0.359848	1.249261
15	1	0	-1.766537	0.586572	2.148754
16	6	0	-0.908036	-1.177943	1.278041
17	1	0	-0.308469	-1.446345	2.144540
18	1	0	-1.862525	-1.703535	1.341254
19	6	0	-0.908378	-1.176820	-1.278994
20	1	0	-0.309202	-1.444544	-2.145963
21	1	0	-1.862963	-1.702226	-1.342153
22	6	0	2.249662	1.250382	-0.000154
23	1	0	2.779030	1.459558	-0.923501
24	1	0	2.438616	-0.216148	0.000215
25	6	0	-0.222873	-1.515443	-0.000717
26	6	0	1.128857	-1.704204	-0.000765
27	7	0	2.279061	-1.454058	-0.000147

Sum of electronic and zero-point Energies= -482.601105
Sum of electronic and thermal Energies= -482.591635
Sum of electronic and thermal Enthalpies= -482.590691
Sum of electronic and thermal Free Energies= -482.635395

Table S11. Cartesian coordinates (Å) and energies (Hartree) of **TS(III)** (B3LYP-D3BJ/cc-pVTZ)

Center Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	6	0	1.291783	0.918959	1.275151
2	1	0	2.354006	1.155413	1.314052
3	1	0	0.811504	1.348807	2.153388
4	6	0	1.113659	-0.623733	1.250930
5	1	0	1.594716	-1.008480	2.148687
6	6	0	0.689212	1.450140	-0.000747
7	1	0	0.626686	2.697238	-0.001325
8	6	0	1.291370	0.917585	-1.276264
9	1	0	2.353549	1.154150	-1.315768
10	1	0	0.810754	1.346439	-2.154804
11	6	0	1.784624	-1.199155	0.000533
12	1	0	1.701617	-2.286564	0.001124
13	1	0	2.849642	-0.963678	0.000354
14	6	0	1.113498	-0.625111	-1.250408
15	1	0	1.594542	-1.010723	-2.147802
16	6	0	-0.373997	-1.037567	-1.290804
17	1	0	-0.893268	-0.580239	-2.132549
18	1	0	-0.416240	-2.120484	-1.459389
19	6	0	-0.373890	-1.035900	1.291885
20	1	0	-0.893074	-0.577431	2.133066
21	1	0	-0.416276	-2.118591	1.461887
22	6	0	-0.627814	1.907635	-0.000716
23	1	0	-1.130897	2.153497	0.927121
24	1	0	-1.131424	2.152210	-0.928604
25	6	0	-1.082671	-0.738287	0.000357
26	6	0	-2.399983	-0.307373	0.000177
27	7	0	-3.481512	0.127897	-0.000000

Sum of electronic and zero-point Energies= -482.571433
Sum of electronic and thermal Energies= -482.561451
Sum of electronic and thermal Enthalpies= -482.560507
Sum of electronic and thermal Free Energies= -482.606956

Table S12. Cartesian coordinates (Å) and energies (Hartree) of **TS(IV)** (B3LYP-D3BJ/cc-pVTZ)

Center Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	6	0	-1.541761	1.395912	-0.429967
2	1	0	-2.626906	1.399214	-0.410399
3	1	0	-1.144452	2.330277	-0.814180
4	6	0	-1.048520	0.188979	-1.407389
5	1	0	-1.466996	0.434790	-2.381235
6	6	0	-0.918638	0.939850	0.792286
7	1	0	-0.416241	4.372173	0.840347
8	6	0	-1.527278	-0.159522	1.507440
9	1	0	-2.612495	-0.147922	1.515775
10	1	0	-1.119879	-0.331814	2.498875
11	6	0	-1.602362	-1.121500	-0.857443
12	1	0	-1.316242	-1.941654	-1.518097
13	1	0	-2.691637	-1.103784	-0.834861
14	6	0	-1.033695	-1.371263	0.535700
15	1	0	-1.441327	-2.272072	0.989898
16	6	0	0.491432	-1.406230	0.524632
17	1	0	0.889885	-1.577557	1.523703
18	1	0	0.835388	-2.232814	-0.097224
19	6	0	0.476275	0.182054	-1.453116
20	1	0	0.863890	1.123706	-1.839470
21	1	0	0.820048	-0.600902	-2.129153
22	6	0	0.523305	1.113400	0.920682
23	1	0	0.891148	2.055442	0.526123
24	1	0	0.903514	0.934247	1.921617
25	6	0	1.041661	-0.085475	-0.045609
26	6	0	2.494338	-0.053694	-0.031527
27	7	0	3.643393	-0.025199	-0.017977

Sum of electronic and zero-point Energies= -482.546835
Sum of electronic and thermal Energies= -482.536367
Sum of electronic and thermal Enthalpies= -482.535423
Sum of electronic and thermal Free Energies= -482.58259

Table S13. Cartesian coordinates (Å) and energies (Hartree) of **TS(V)** (B3LYP-D3BJ/cc-pVTZ)

Center Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	6	0	1.522077	-1.308982	0.004887
2	1	0	2.488439	-1.805533	0.006649
3	1	0	-1.885437	-3.528222	0.009038
4	6	0	0.967218	-0.859313	-1.236579
5	1	0	1.364094	-1.381845	-2.103010
6	6	0	0.967676	-0.849471	1.243052
7	1	0	1.364669	-1.365533	2.113307
8	6	0	1.646278	0.644090	1.230447
9	1	0	2.731476	0.572164	1.258452
10	1	0	1.308041	1.077055	2.170926
11	6	0	1.646044	0.634436	-1.235434
12	1	0	1.307571	1.059956	-2.179220
13	1	0	2.731224	0.562214	-1.263123
14	6	0	1.148118	1.374239	-0.005332
15	1	0	1.586891	2.376098	-0.009312
16	6	0	-0.380888	1.490786	-0.005627
17	1	0	-0.717816	2.046571	0.868428
18	1	0	-0.718023	2.039851	-0.883839
19	6	0	-0.555804	-0.695684	-1.253270
20	1	0	-1.027086	-1.677479	-1.283833
21	1	0	-0.853525	-0.166541	-2.156688
22	6	0	-0.555412	-0.686089	1.258758
23	1	0	-1.026462	-1.667729	1.296800
24	1	0	-0.853120	-0.150227	2.158212
25	6	0	-1.015692	0.079998	-0.000127
26	6	0	-2.470543	0.189889	-0.000375
27	7	0	-3.616482	0.275114	-0.000741

Sum of electronic and zero-point Energies= -482.532394
Sum of electronic and thermal Energies= -482.52176
Sum of electronic and thermal Enthalpies= -482.520816
Sum of electronic and thermal Free Energies= -482.568288

Table S14. Cartesian coordinates (Å) and energies (Hartree) of **TS(VI)** (B3LYP-D3BJ/cc-pVTZ)

Center Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	6	0	-1.614368	-1.389682	0.377069
2	1	0	-2.694276	-1.308249	0.492314
3	1	0	-1.317113	-2.402915	0.639473
4	6	0	-1.014087	-0.330418	1.454470
5	1	0	-1.334889	-0.655421	2.441058
6	6	0	-1.115321	-0.980652	-0.998462
7	1	0	-1.503162	-1.695366	-1.731027
8	6	0	-1.577156	0.437510	-1.359133
9	1	0	-2.666168	0.478635	-1.369131
10	1	0	-1.238726	0.695375	-2.362841
11	6	0	-1.516511	1.076791	1.066390
12	1	0	-1.165113	1.796527	1.805288
13	1	0	-2.604855	1.078594	1.107332
14	6	0	-1.019391	1.434330	-0.335345
15	1	0	-1.350056	2.441301	-0.589473
16	6	0	0.510041	1.411649	-0.358934
17	1	0	0.898613	1.628476	-1.352449
18	1	0	0.933244	2.146318	0.324687
19	6	0	0.394579	-0.520365	1.255487
20	1	0	0.953870	-1.200823	1.890670
21	1	0	4.609529	1.274044	0.600457
22	6	0	0.396654	-1.087327	-1.024023
23	1	0	0.758848	-2.082719	-0.777613
24	1	0	0.850470	-0.776432	-1.963488
25	6	0	1.020827	0.003725	0.063434
26	6	0	2.462471	-0.108863	0.024542
27	7	0	3.614764	-0.156791	-0.021176

Sum of electronic and zero-point Energies= -482.520674
Sum of electronic and thermal Energies= -482.510011
Sum of electronic and thermal Enthalpies= -482.509067
Sum of electronic and thermal Free Energies= -482.556886

Table S15. Cartesian coordinates (Å) and energies (Hartree) of **CC(I)N_2(1)** (B3LYP-D3BJ/cc-pVTZ)

Center Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	6	0	1.276270	-1.941653	1.259860
2	1	0	1.282006	-3.028747	1.268363
3	1	0	1.757640	-1.575372	2.164513
4	6	0	-0.236432	-1.428559	1.251953
5	1	0	-0.681895	-1.823829	2.166197
6	6	0	1.894327	-1.376131	0.000000
7	1	0	2.958629	-1.724477	0.000000
8	6	0	1.276270	-1.941653	-1.259860
9	1	0	1.282006	-3.028747	-1.268363
10	1	0	1.757640	-1.575372	-2.164513
11	6	0	-0.897124	-1.987585	0.000000
12	1	0	-1.955259	-1.696158	0.000000
13	1	0	-0.876479	-3.076475	0.000000
14	6	0	-0.236432	-1.428559	-1.251953
15	1	0	-0.681895	-1.823829	-2.166197
16	6	0	-0.236432	0.085307	-1.273447
17	1	0	0.259056	0.472784	-2.163394
18	1	0	-1.264655	0.459807	-1.309536
19	6	0	-0.236432	0.085307	1.273447
20	1	0	0.259056	0.472784	2.163394
21	1	0	-1.264655	0.459807	1.309536
22	6	0	1.957019	0.127840	0.000000
23	1	0	2.438175	0.531968	0.887077
24	1	0	2.438175	0.531968	-0.887077
25	6	0	0.416388	0.648721	0.000000
26	6	0	0.457873	2.091891	0.000000
27	7	0	0.507160	3.243801	0.000000
28	7	0	-3.450703	3.022863	0.000000
29	7	0	-2.816359	2.135383	0.000000

Sum of electronic and zero-point Energies= -592.171448
Sum of electronic and thermal Energies= -592.157711
Sum of electronic and thermal Enthalpies= -592.156767
Sum of electronic and thermal Free Energies= -592.213900

Table S16. Cartesian coordinates (Å) and energies (Hartree) of **CC(I)N$_2$(5)** (B3LYP-D3BJ/cc-pVTZ)

Center Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	6	0	1.143387	0.463550	1.259177
2	1	0	2.170852	0.818330	1.267396
3	1	0	0.640871	0.799037	2.164210
4	6	0	1.143387	-1.137368	1.251560
5	1	0	1.661779	-1.429034	2.166232
6	6	0	0.409005	0.859006	0.000000
7	1	0	0.403085	1.983682	0.000000
8	6	0	1.143387	0.463550	-1.259177
9	1	0	2.170852	0.818330	-1.267396
10	1	0	0.640871	0.799037	-2.164210
11	6	0	1.885811	-1.580285	0.000000
12	1	0	1.952939	-2.676104	0.000000
13	1	0	2.910079	-1.209899	0.000000
14	6	0	1.143387	-1.137368	-1.251560
15	1	0	1.661779	-1.429034	-2.166232
16	6	0	-0.291446	-1.624965	-1.272700
17	1	0	-0.816435	-1.277399	-2.162070
18	1	0	-0.312557	-2.718413	-1.316882
19	6	0	-0.291446	-1.624965	1.272700
20	1	0	-0.816435	-1.277399	2.162070
21	1	0	-0.312557	-2.718413	1.316882
22	6	0	-1.034700	0.436094	0.000000
23	1	0	-1.570359	0.767120	0.886282
24	1	0	-1.570359	0.767120	-0.886282
25	6	0	-1.034846	-1.181605	0.000000
26	6	0	-2.416047	-1.609562	0.000000
27	7	0	-3.522099	-1.932942	0.000000
28	7	0	0.370008	4.280193	0.000000
29	7	0	0.350139	5.370826	0.000000

Sum of electronic and zero-point Energies= -592.170582
Sum of electronic and thermal Energies= -592.156785
Sum of electronic and thermal Enthalpies= -592.155840
Sum of electronic and thermal Free Energies= -592.214777

Table S17. Cartesian coordinates (Å) and energies (Hartree) of **CC(II)N_2(1)** (B3LYP-D3BJ/cc-pVTZ)

Center Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	6	0	-0.683570	2.551703	1.254411
2	1	0	-0.687520	3.641097	1.262848
3	1	0	-1.205990	2.203707	2.146702
4	6	0	0.786331	2.036443	1.258601
5	1	0	1.297398	2.387083	2.155254
6	6	0	-1.284860	2.007475	0.000000
7	6	0	-0.683570	2.551703	-1.254411
8	1	0	-0.687520	3.641097	-1.262848
9	1	0	-1.205990	2.203707	-2.146702
10	6	0	1.506397	2.541705	0.000000
11	1	0	2.544428	2.202823	0.000000
12	1	0	1.529943	3.631646	0.000000
13	6	0	0.786331	2.036443	-1.258601
14	1	0	1.297398	2.387083	-2.155254
15	6	0	0.786331	0.500828	-1.280367
16	1	0	0.276094	0.127983	-2.168831
17	1	0	1.808490	0.122696	-1.296015
18	6	0	0.786331	0.500828	1.280367
19	1	0	0.276094	0.127983	2.168831
20	1	0	1.808490	0.122696	1.296015
21	6	0	-1.446817	0.531726	0.000000
22	1	0	-1.955636	0.162261	0.888809
23	1	0	-1.955636	0.162261	-0.888809
24	6	0	0.062316	-0.016407	-0.000000
25	6	0	0.010145	-1.438796	-0.000000
26	7	0	-0.113330	-2.578878	-0.000000
27	1	0	-0.201675	-3.595432	-0.000000
28	7	0	-0.470443	-6.564037	-0.000000
29	7	0	-0.372022	-5.478597	-0.000000

Sum of electronic and zero-point Energies= -592.185849
Sum of electronic and thermal Energies= -592.172873
Sum of electronic and thermal Enthalpies= -592.171929
Sum of electronic and thermal Free Energies= -592.227364

Table S18. Cartesian coordinates (Å) and energies (Hartree) of **OC(I)N_2(1)** (B3LYP-D3BJ/cc-pVTZ)

Center Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	6	0	0.310448	-1.705436	-0.044763
2	1	0	0.876172	-2.623597	0.162014
3	1	0	-0.729265	-1.985718	-0.193689
4	6	0	0.915752	-1.047843	-1.309967
5	1	0	0.868218	-1.758052	-2.132875
6	6	0	0.471244	-0.832940	1.135858
7	1	0	-0.475817	-1.554208	2.819255
8	6	0	1.819671	-0.290626	1.399765
9	1	0	2.455102	-1.143151	1.673709
10	1	0	1.816236	0.396499	2.243330
11	6	0	2.361701	-0.623631	-1.041420
12	1	0	2.782847	-0.160391	-1.934246
13	1	0	2.975135	-1.498776	-0.823854
14	6	0	2.417679	0.361810	0.128907
15	1	0	3.443844	0.659455	0.334415
16	6	0	1.572901	1.617878	-0.187327
17	1	0	1.567040	2.315508	0.646891
18	1	0	2.012497	2.132018	-1.047597
19	6	0	0.049051	0.187408	-1.649203
20	1	0	-0.990376	-0.087328	-1.805717
21	1	0	0.421662	0.636187	-2.575176
22	6	0	-0.599963	-0.704176	2.126610
23	1	0	-1.591534	-0.801060	1.691625
24	1	0	-0.519220	0.199027	2.727435
25	6	0	0.194732	1.175440	-0.543250
26	6	0	-0.917896	1.724965	0.080334
27	7	0	-1.846337	2.134369	0.647064
28	7	0	-3.304371	-0.771208	-0.412660
29	7	0	-4.347072	-0.492233	-0.571374

Sum of electronic and zero-point Energies= -592.187103
Sum of electronic and thermal Energies= -592.172138
Sum of electronic and thermal Enthalpies= -592.171193
Sum of electronic and thermal Free Energies= -592.231737

Table S19. Cartesian coordinates (Å) and energies (Hartree) of **OC(II)N_2(1)** (B3LYP-D3BJ/cc-pVTZ)

Center Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	6	0	-0.254626	2.337590	1.265327
2	1	0	-0.225381	3.428608	1.335308
3	1	0	-0.792156	1.971665	2.139429
4	6	0	1.198326	1.820688	1.255774
5	1	0	1.712950	2.175154	2.147815
6	6	0	-0.953678	1.942027	0.000000
7	6	0	-0.254626	2.337590	-1.265327
8	1	0	-0.225381	3.428608	-1.335308
9	1	0	-0.792156	1.971665	-2.139429
10	6	0	1.924400	2.313457	0.000000
11	1	0	2.959191	1.966819	0.000000
12	1	0	1.960007	3.403294	0.000000
13	6	0	1.198326	1.820688	-1.255774
14	1	0	1.712950	2.175154	-2.147815
15	6	0	1.198326	0.276693	-1.291263
16	1	0	0.632081	-0.101757	-2.140561
17	1	0	2.232328	-0.066481	-1.410714
18	6	0	1.198326	0.276693	1.291263
19	1	0	0.632081	-0.101757	2.140561
20	1	0	2.232328	-0.066481	1.410714
21	6	0	-2.102660	1.244129	0.000000
22	1	0	-2.591417	0.962940	0.923291
23	1	0	-2.591417	0.962940	-0.923291
24	6	0	0.676921	-0.277299	0.000000
25	6	0	-0.158743	-1.345896	0.000000
26	7	0	-0.961394	-2.200510	0.000000
27	1	0	-1.085413	-3.211463	0.000000
28	7	0	-1.408290	-5.175880	0.000000
29	7	0	-1.600650	-6.248906	0.000000

Sum of electronic and zero-point Energies= -592.195791
Sum of electronic and thermal Energies= -592.181571
Sum of electronic and thermal Enthalpies= -592.180627
Sum of electronic and thermal Free Energies= -592.239303

Table S20. Cartesian coordinates (Å) and energies (Hartree) of N_2 (B3LYP-D3BJ/cc-pVTZ)

Center Number	Atomic Number	Atomic Type	Coordinates (Å)		
			X	Y	Z
1	7	0	0.000000	0.000000	0.545733
2	7	0	0.000000	0.000000	-0.545733

Sum of electronic and zero-point Energies= -109.563602
Sum of electronic and thermal Energies= -109.561241
Sum of electronic and thermal Enthalpies= -109.560297
Sum of electronic and thermal Free Energies= -109.582027

Table S21. Vibrational frequencies (in cm^{-1}) computed for AdCN and various $AdCN^+$ isomers (B3LYP-D3BJ/cc-pVTZ). Computed harmonic frequencies are scaled by 0.953. IR intensities in km mol^{-1} are listed in parentheses.

Mode	AdCN	CC(I)	CC(II)	OC(I)	OC(II)
ν_{CN}	2235 (21)	2193 (324)	2176 (703)	2081 (31)	2066 (703)
ν_{CH}, ν_{CH2}^{s}	2876 (21) 2877(13) 2892 (45) 2901 (107)	2601* (246) 2829 (67) 2863 (28)	2896 (15) 2901 (13) 2903 (14) 2905 (9) 2906 (5) 2913 (11) 2924 (33) 2925 (9)	2815* (40) 2850 (7) 2862 (6) 2907 (5)	2889 (2) 2902 (11)
ν_{CH}, ν_{CH2}^{a}	2910 (13) 2914 (95) 2931 (45)	2896 (15) 2908 (7) 2932 (4) 2939 (8) 2940 (8) 2945 (8) 2986 (11)	2936 (10) 2948 (7) 2949 (13) 2952 (13) 2952 (27) 2966 (11)	2942 (5) 2948 (5) 2949 (6) 2957 (6) 2959 (5) 2966 (9)	2934 (10) 2935 (15) 2937 (11) 2942 (16) 2950 (20)
ν_{CC}/ν_{CH2}^{s}					2993 (8)
ν_{CN}			3555 (1333)		3421 (545)

*Acidic CH stretching frequency

Table S22. AdCN

Wavenumber / cm^{-1}	IR Intensity / km mol^{-1}
138.6381	4.9583
138.6388	4.9584
314.5305	0.3451
314.5307	0.345
386.9889	0.0265
407.777	0.1762
407.779	0.176
440.7672	0.0692
440.7678	0.0693
502.5922	0.3603
559.0053	0.0454
559.0059	0.0454
658.2757	0.1111
658.2758	0.1111
704.6405	1.7425
775.5785	0.4344
818.6847	0.6425
818.6868	0.6427
898.5685	0.0161
898.5693	0.016
909.1175	0.0072
942.8444	0.184
942.845	0.184
988.3505	1.7007
988.3512	1.7007
994.7283	2.0824
1047.9582	0.0026
1047.9589	0.0026
1118.6377	3.7885
1124.851	2.6678
1153.7733	0.3513
1211.4101	0.2949
1211.4106	0.2944
1285.3334	0.0176
1285.3343	0.0177
1317.038	0.0567
1317.0383	0.0568
1347.779	3.3222
1350.2357	0.0328
1350.2362	0.0328
1383.4048	0.6957
1383.4048	0.6959
1399.5821	0.4071
1401.3404	0.0779
1401.3442	0.0775
1486.3973	0.0012
1486.3973	0.0012
1498.9526	11.1298
1498.9527	11.1307
1500.3328	14.2751
1522.2511	0.3027
2345.6827	21.3265
3018.4006	21.3495
3018.4007	21.3506
3018.7157	13.3127
3032.1448	0.1395
3032.145	0.1393

3035.8088	45.2565
3044.5571	107.129
3044.5575	107.1252
3052.001	7.9259
3053.1628	12.8766
3053.1628	12.8744
3058.3522	94.43
3076.211	45.2401
3076.211	45.2436

Table S23. CC(I)

Wavenumber / cm^{-1}	IR Intensity / km mol^{-1}
127.863	13.5446
135.826	4.9909
276.7519	78.7793
299.2598	47.8915
311.7139	76.9395
330.7959	2.5534
361.5279	80.9434
407.959	0.9275
438.4488	7.6168
448.9667	7.8261
491.6683	96.7699
529.373	4.8967
545.4422	132.574
547.6861	177.7328
557.4164	778.7614
641.9001	67.4839
664.3452	19.2934
682.0949	50.946
701.9106	138.1357
768.1417	85.1609
799.7162	14.5376
844.3993	25.327
848.1226	21.8587
849.6106	29.9496
881.2296	10.4908
893.0156	37.4815
906.3342	52.779
912.2377	0.03
951.5972	3.1309
964.0641	56.7286
964.7999	10.7905
982.6538	12.0407
1028.0298	29.6706
1063.8309	2.8378
1083.3024	17.0071
1086.9957	12.2799
1098.2994	42.7267
1131.29	294.7065
1134.0377	53.7998
1142.7016	11.6023
1162.611	33.1967
1223.4937	10.3295
1252.6863	0.6186
1287.1413	0.189
1288.9177	1.5128
1306.8486	6.6268
1315.1502	2.1679
1332.7401	0.8696
1341.7029	3.4692
1363.634	6.9841
1377.2337	2.5164
1392.8326	5.8216
1433.6279	9.415
1440.8481	22.6852
1467.3476	24.9422
1492.5385	2.8372
1492.9171	6.3995

1524.0561	4.3809
2301.4537	324.8384
2729.7849	246.1526
2968.2793	67.0633
3003.7601	27.6125
3020.418	3.3762
3038.3151	13.778
3051.8121	7.4486
3075.0518	1.5886
3075.6628	3.863
3078.2945	0.972
3083.4502	7.5316
3085.0221	7.612
3089.8974	7.9407
3129.5903	0.1666
3133.5693	11.0235
3134.8245	2.5064

Table S24. CC(II)

Wavenumber / cm^{-1}	IR Intensity / km mol^{-1}
115.2382	5.1356
117.955	3.4882
302.9343	0.3825
312.2267	4.7721
324.911	0.0093
348.9279	119.5626
378.6292	2.8147
393.6239	0.2768
399.8431	1.7605
434.447	1.4176
446.0533	0.0772
505.0949	0.2295
511.5501	125.6612
550.8231	34.2637
579.7925	1.019
639.0056	3.0834
645.912	1.6238
649.1939	33.2714
757.131	62.5237
776.9972	10.762
811.9886	0.0192
831.0051	11.364
899.7344	1.6119
902.5104	26.7556
907.9729	0.0434
919.778	3.1922
926.8241	4.7491
952.6039	0.2343
979.9499	13.1672
985.7222	4.9918
1029.6061	0.3654
1039.8728	4.513
1051.1263	0.0635
1125.6153	2.2442
1132.2368	5.3345
1140.17	0.1718
1163.3227	4.8489
1183.8363	0.7371
1222.8905	1.2967
1224.3914	11.1484
1269.108	8.1143
1289.9485	0.0007
1299.7269	9.4123
1303.5685	1.4025
1309.0286	0.6375
1316.7148	3.1434
1341.5619	2.9005
1350.5752	0.0129
1369.18	1.736
1379.1303	0.6963
1382.1244	2.1707
1392.552	4.6606
1484.509	0.2354
1486.2785	0.579
1496.6891	27.2486
1498.1553	13.6199
1500.6767	18.1798

1521.485	2.1845
2283.3132	702.5285
3038.3221	14.6288
3043.9675	13.2147
3045.8023	13.7599
3048.1977	9.1234
3049.2301	5.247
3057.004	11.0596
3067.8706	32.7642
3069.5174	8.589
3081.0321	9.9541
3091.8915	1.0006
3093.8458	6.6518
3094.294	12.6175
3097.4787	27.4629
3112.0684	10.7639
3730.2954	1333.3094

Table S25. OC(I)

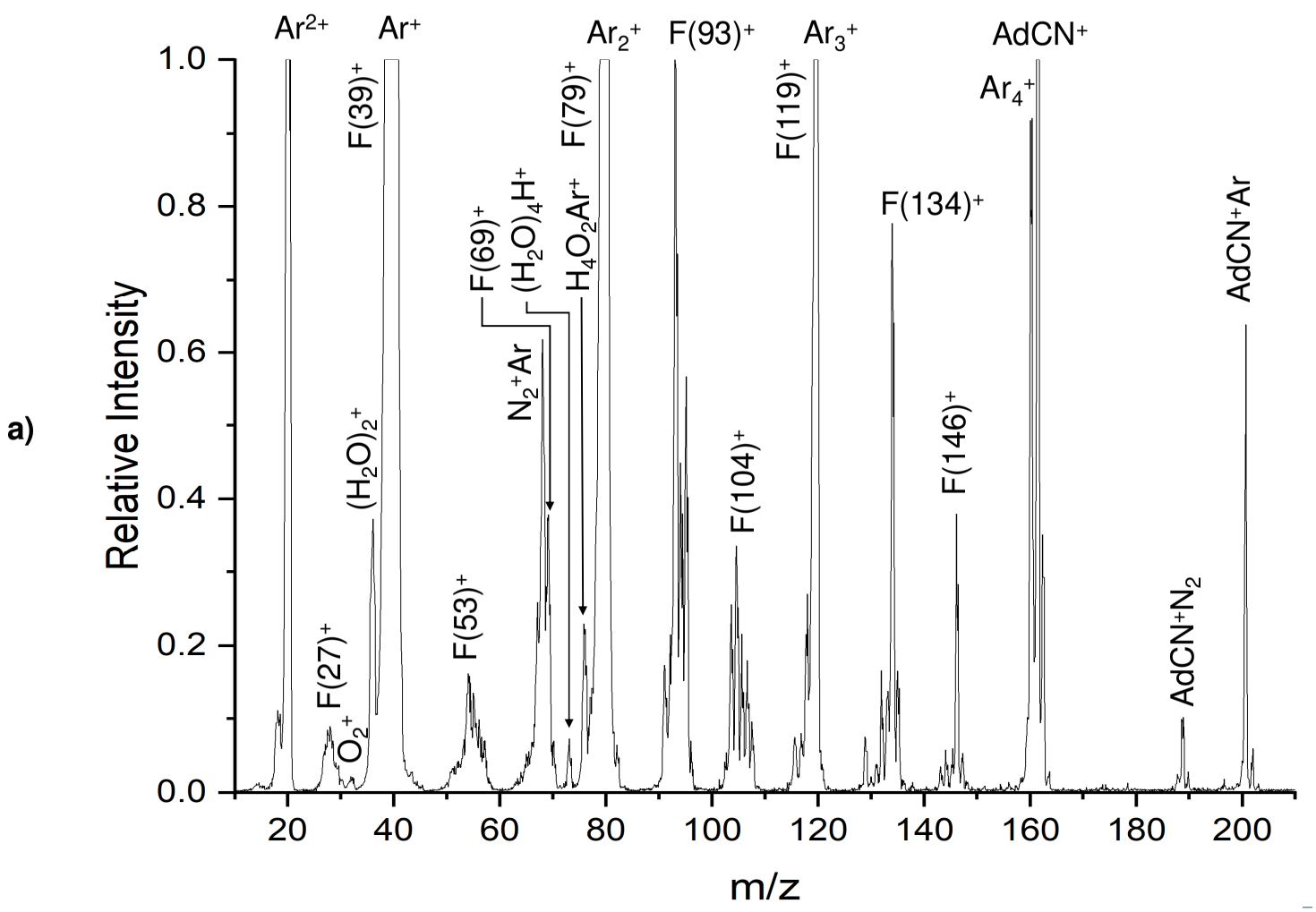
Wavenumber / cm^{-1}	IR Intensity / km mol^{-1}
84.8674	2.3076
109.38	4.505
119.31	0.2035
138.1762	6.4049
209.2083	2.3412
262.7976	7.4394
338.9819	2.4578
349.9208	0.1366
375.3358	0.0036
396.7794	5.9289
397.1029	0.0067
416.1448	0.0111
475.0014	1.4792
508.4194	5.3682
573.5705	18.0775
580.7492	0.0074
634.5921	3.5316
706.1649	2.9036
769.8506	3.5158
803.9875	7.997
806.1281	2.029
839.302	0.3076
843.2342	14.4297
895.0847	3.8699
897.5445	0.0202
916.6219	11.1022
928.9839	0.0254
954.8734	1.4323
1003.831	16.2626
1009.7478	0.6596
1028.8683	16.9026
1049.0127	2.0594
1080.5986	26.0226
1138.5215	3.4463
1151.5377	50.7898
1160.2819	5.2964
1171.7206	87.0477
1210.7927	15.9523
1221.2743	31.3636
1262.6598	0.1075
1269.345	7.3064
1305.283	16.0281
1323.7999	2.864
1328.7397	10.3487
1338.2564	39.0177
1365.4239	1.832
1370.9102	39.9934
1380.179	9.4255
1382.746	1.2356
1399.4408	7.4863
1430.3304	29.3102
1438.0148	0.3289
1451.7452	15.6042
1473.3718	20.0898
1473.4844	0.2162
1485.4028	5.9139
1491.4512	15.6907

1502.0095	8.0076
2183.1225	31.399
2954.0453	40.1887
2990.094	6.9014
3002.3208	5.7038
3022.1522	0.6863
3028.262	0.1585
3050.6973	5.3792
3083.8019	1.1304
3087.4474	5.3427
3093.8399	4.9086
3094.3421	5.6465
3102.8331	6.2342
3104.671	4.5861
3112.0971	8.9411
3112.5846	0.9952
3145.8972	0.0898

Table S26. OC(II)

Wavenumber / cm^{-1}	IR Intensity / km mol^{-1}
83.4181	2.8279
108.6679	0.1336
119.697	1.6646
200.3678	0.7033
292.6726	9.6764
321.4998	6.3756
345.2053	1.3363
376.7801	0.2184
404.7048	35.0667
405.0441	0.4024
420.4223	0.0002
471.9553	19.9632
508.7636	16.9691
591.9708	43.8164
598.8136	10.1606
608.6977	544.1453
610.3694	7.6412
626.1091	50.7406
693.9118	2.5411
716.6079	2.7166
793.9246	1.1651
810.4408	2.9153
817.9987	0.4285
865.489	0.0313
895.3403	1.4929
920.9814	5.0769
922.2635	0.1102
944.4711	6.1955
945.6451	0.2033
973.0692	16.8455
990.7693	0.2147
1003.8897	0.5156
1057.2985	19.6098
1091.242	2.5667
1126.1199	0.1327
1143.9735	2.8012
1167.953	0.0207
1179.485	2.3052
1217.5379	6.5494
1231.7764	7.176
1256.6457	0.566
1258.2402	57.6987
1302.0506	16.0266
1310.2124	0.6454
1318.759	0.0599
1345.7172	62.9156
1361.4345	0.0289
1371.9461	5.395
1383.9573	3.8815
1388.4268	0.0451
1414.2758	10.7576
1457.5271	7.9139
1459.1926	7.8095
1473.0371	14.4052
1477.7573	17.4157
1491.2725	22.3352
1505.814	3.9338

1626.7729	296.9044
2168.0125	703.1366
3002.9903	0.987
3007.7892	0.2843
3025.6712	0.6552
3031.0427	1.8111
3045.0821	10.8327
3079.2333	9.828
3080.0221	14.6901
3082.3277	10.6198
3087.4467	16.0278
3089.2257	2.944
3095.8897	19.3704
3096.0835	2.3799
3140.2982	8.0123
3230.5188	1.4727
3589.3648	544.6227


a)
Relative Intensity
m/z
Ar2+
Ar+
F(39)+
(H2O)2+
O2+
F(27)+
F(53)+
F(69)+
(H2O)4H+
N2+Ar
H4O2Ar+
F(79)+
Ar2+
F(93)+
F(104)+
Ar3+
F(119)+
F(134)+
F(146)+
AdCN+
Ar4+
AdCN+N2
AdCN+Ar

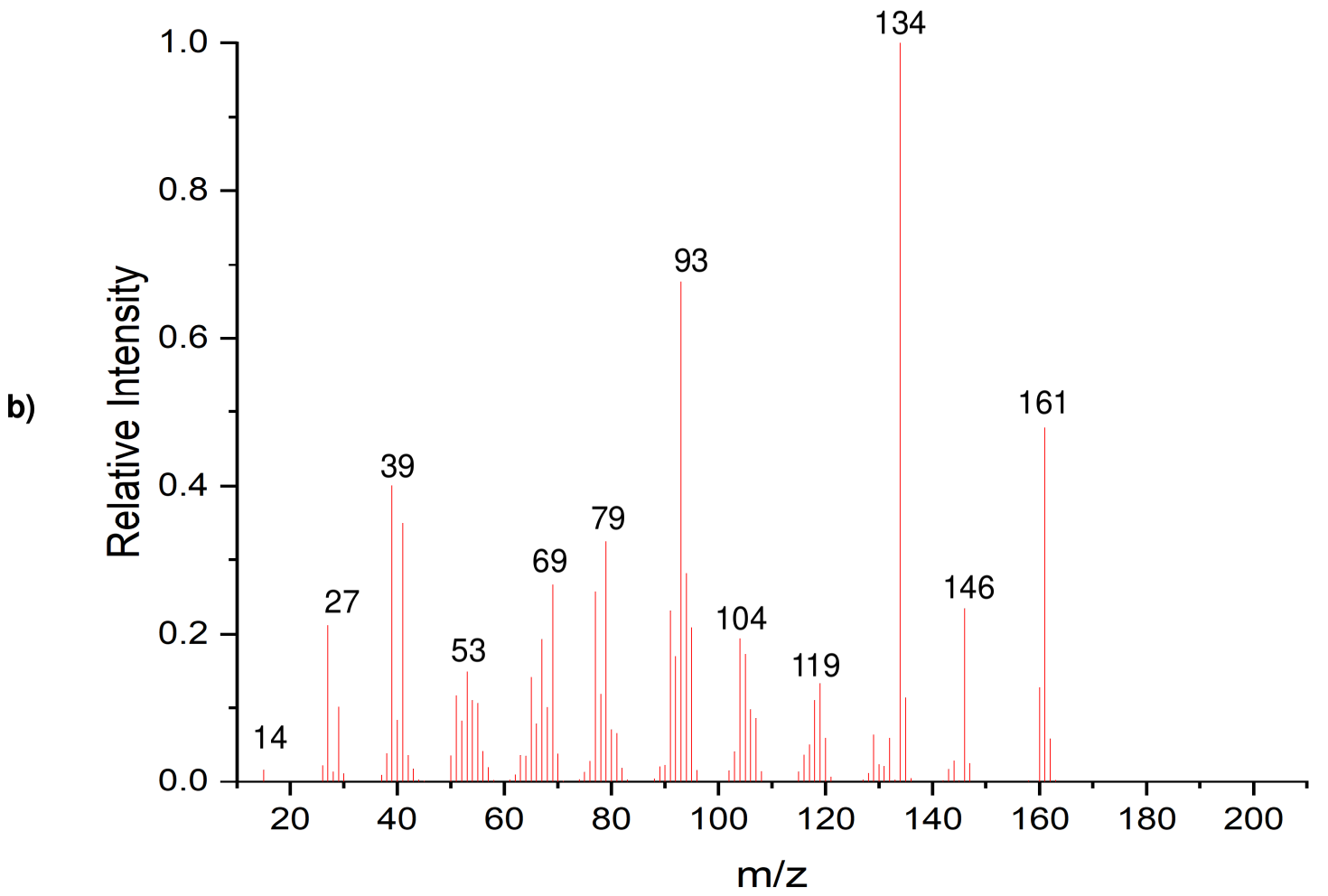

b)
Relative Intensity
m/z
14
27
39
53
69
79
93
104
119
134
146
161

Figure S1

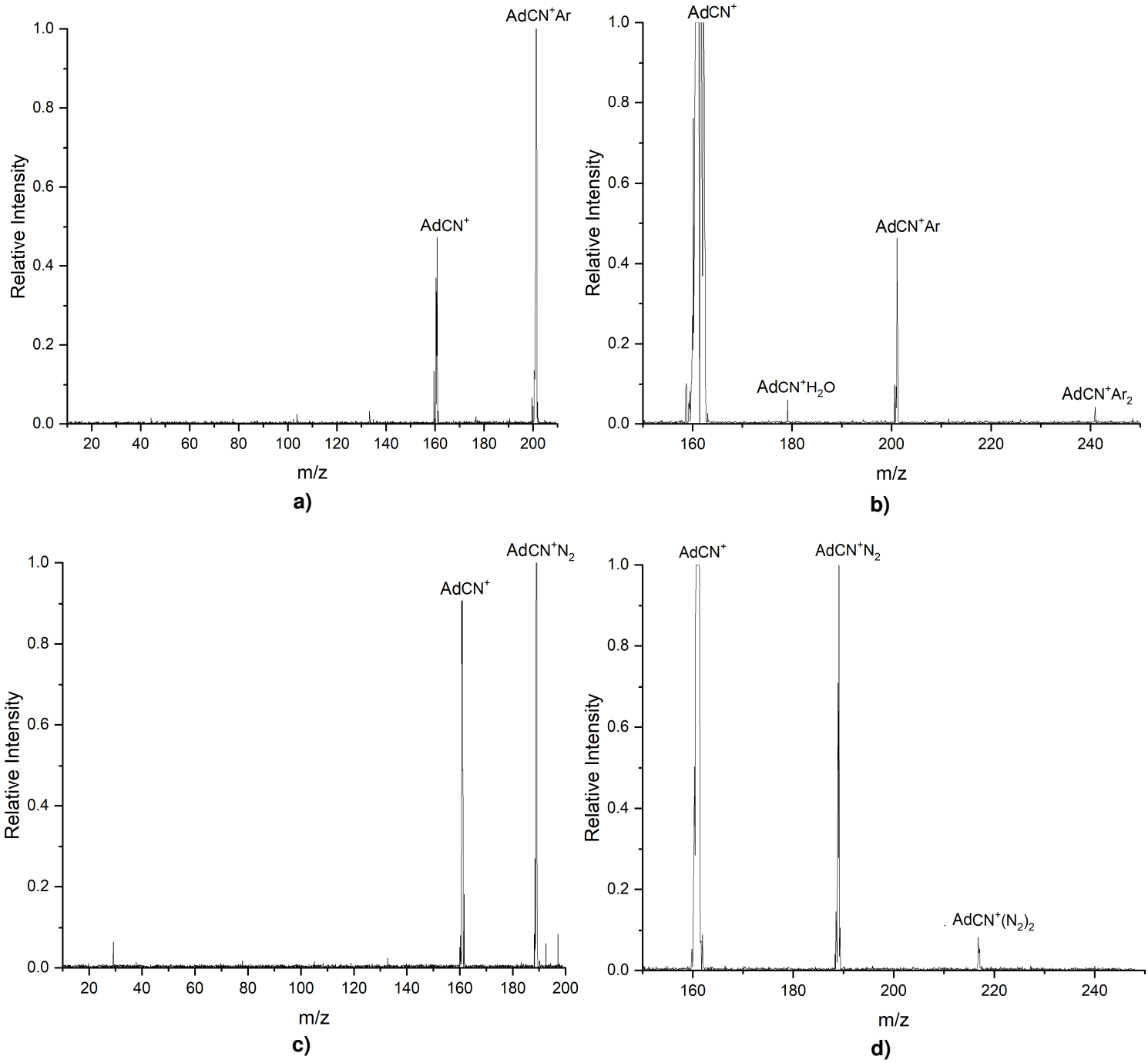
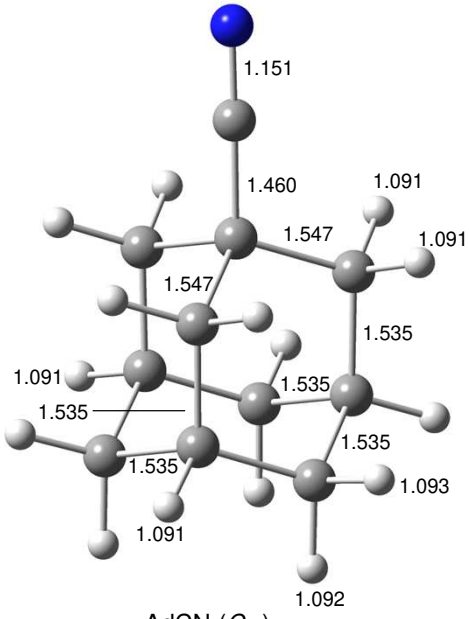
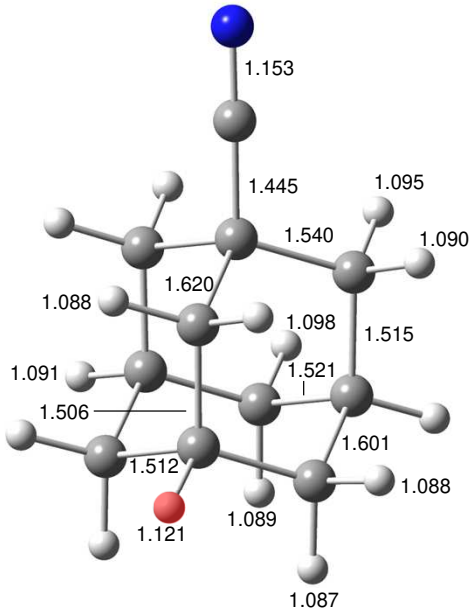

AdCN+Ar
AdCN+
Relative Intensity
m/z
a)
AdCN+
AdCN+Ar
AdCN+H2O
AdCN+Ar2
b)
AdCN+N2
AdCN+
c)
AdCN+
AdCN+N2
AdCN+(N2)2
d)

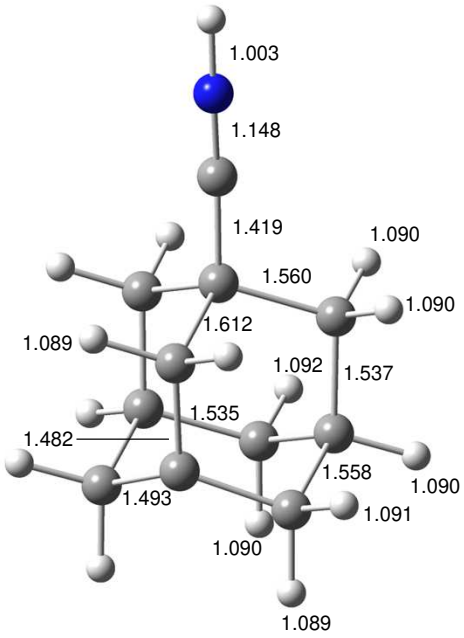
Figure S2



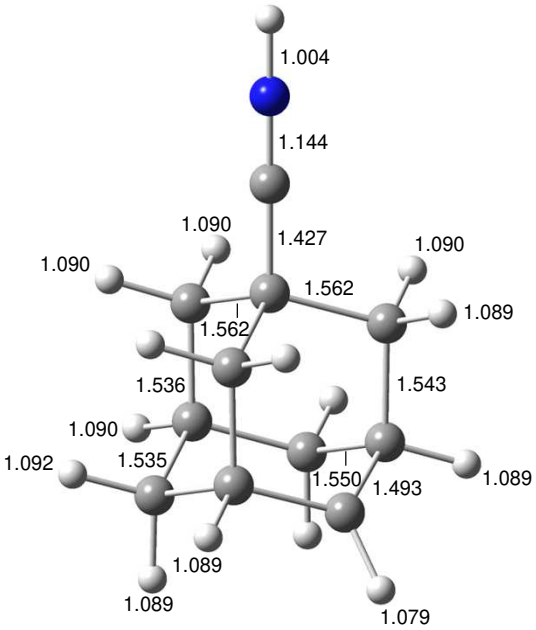
AdCN (C_{3v})



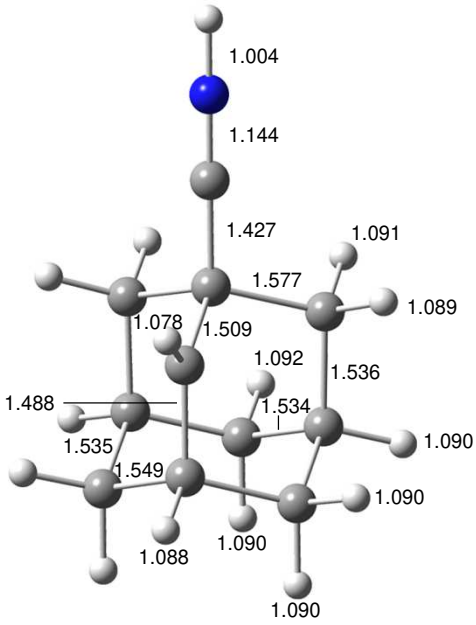
CC(I) (C_s)



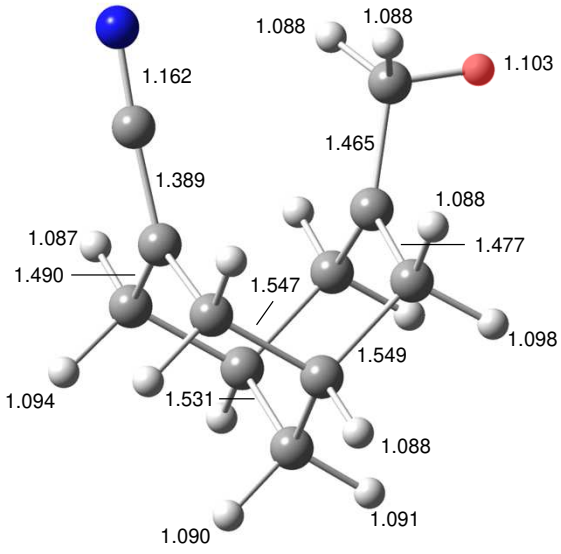
CC(II) (C_s)



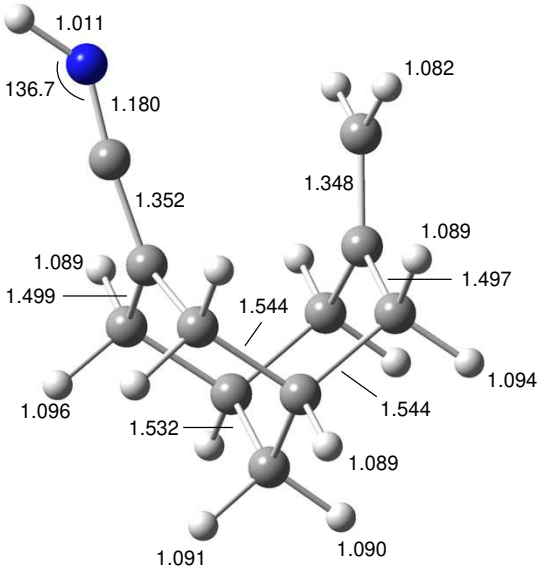
CC(III) (C_S)



CC(IV) (C_S)

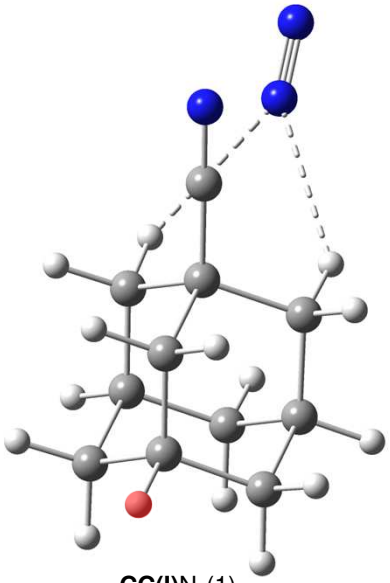


OC(I) (C_s)

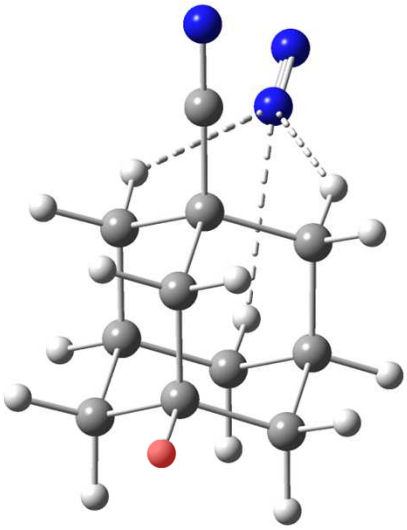


OC(II) (C_s)

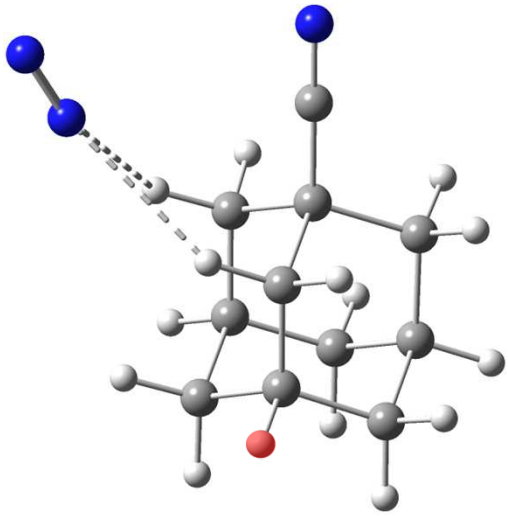
Figure S3



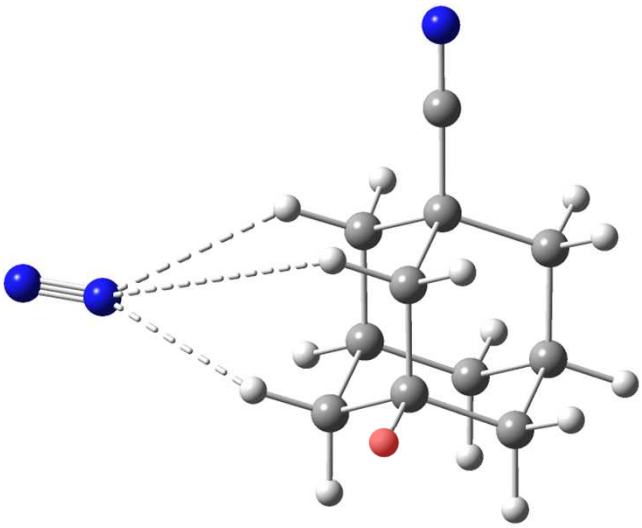
CC(I)N_2(1)
E_0=0.00
D_0=12.14



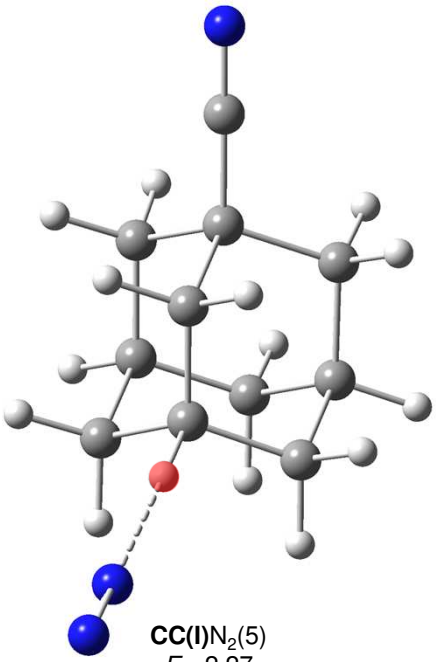
CC(I)N_2(2)
E_0=0.57
D_0=11.57



CC(I)N_2(3)
E_0=0.98
D_0=11.15



CC(I)N_2(4)
E_0=2.22
D_0=9.92



CC(I)N_2(5)
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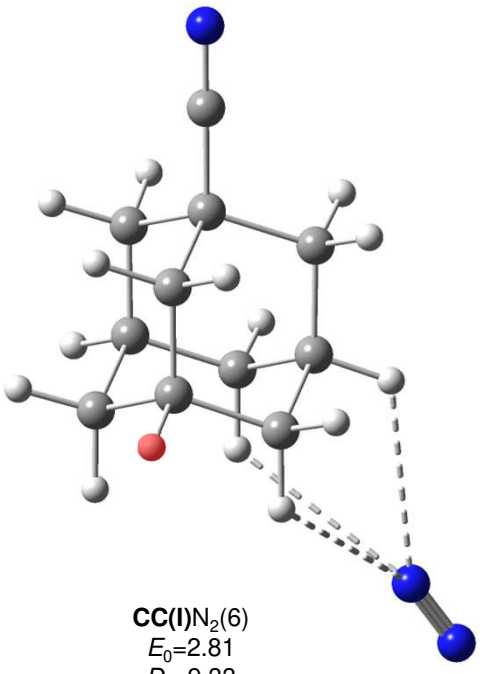
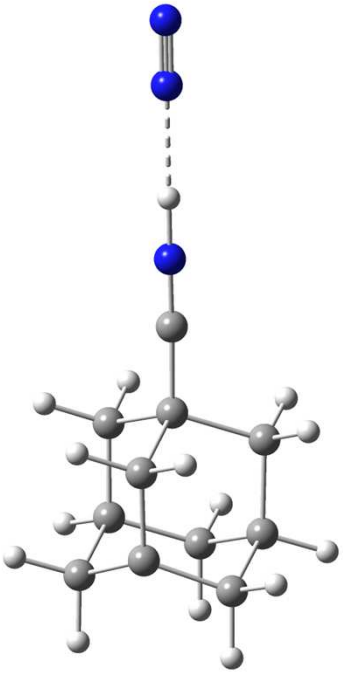
D_0=9.86

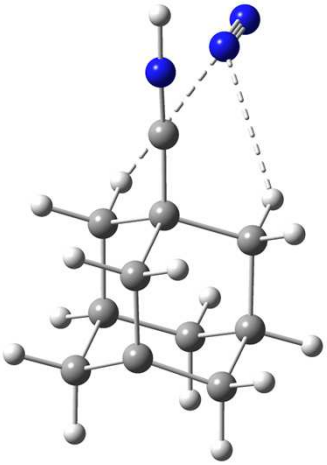


CC(I)N_2(6)
E_0=2.81
D_0=9.33

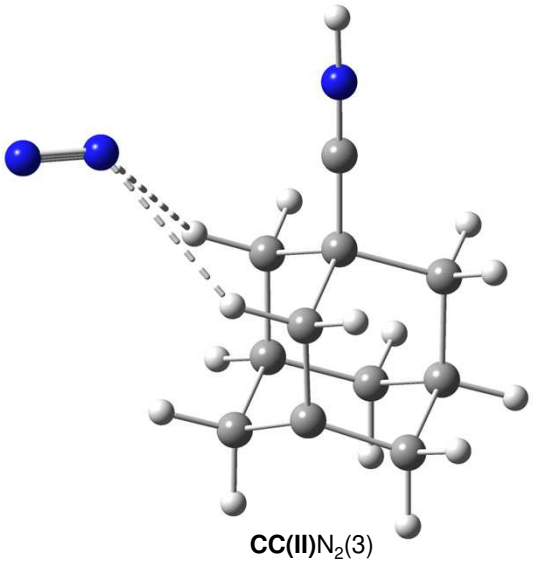
Figure S4



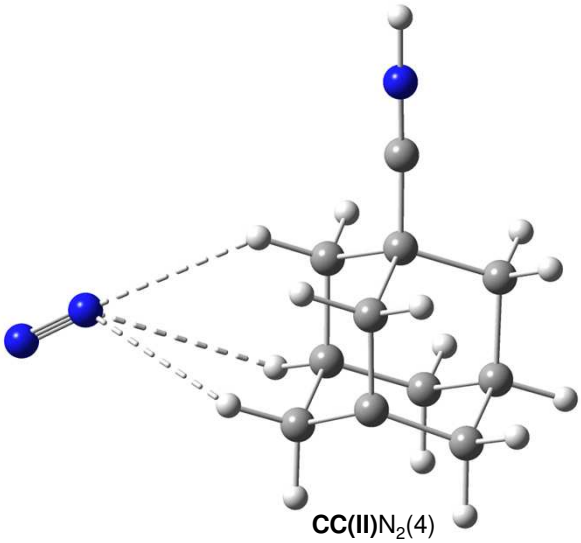
CC(II)N_2(1)
E_0=0.00
D_0=22.96



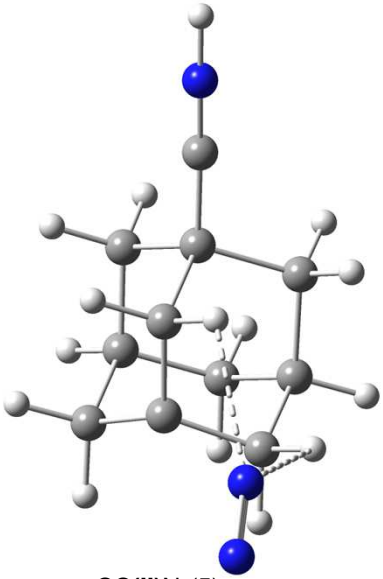
CC(II)N_2(2)
E_0=12.68
D_0=10.28



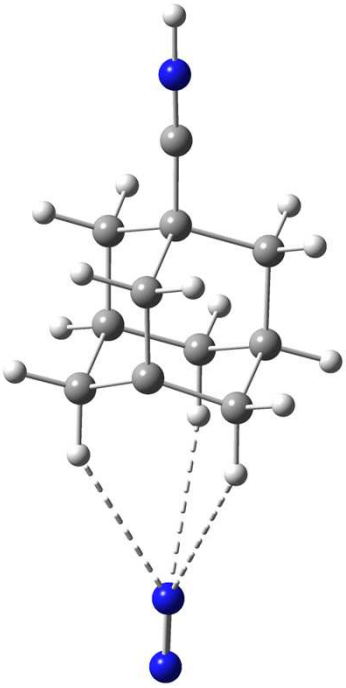
CC(II)N_2(3)
E_0=13.19
D_0=9.77



CC(II)N_2(4)
E_0=15.58
D_0=7.38

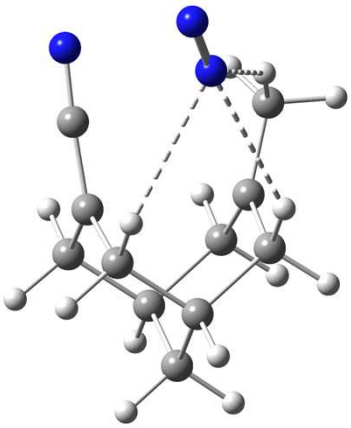


CC(II)N_2(5)
E_0=15.97
D_0=6.99

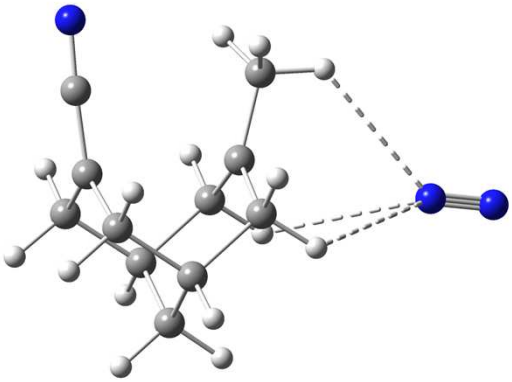


CC(II)N_2(6)
E_0=16.34
D_0=6.62

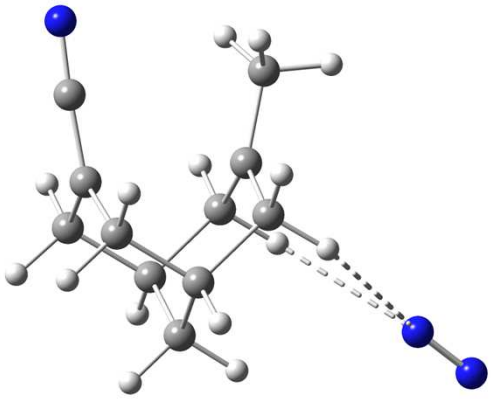
Figure S5



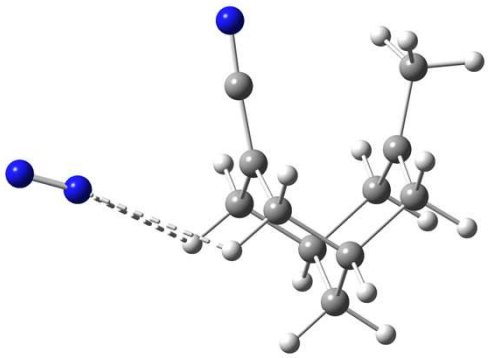
OC(I)N_2(1)
E_0=0.00
D_0=11.51



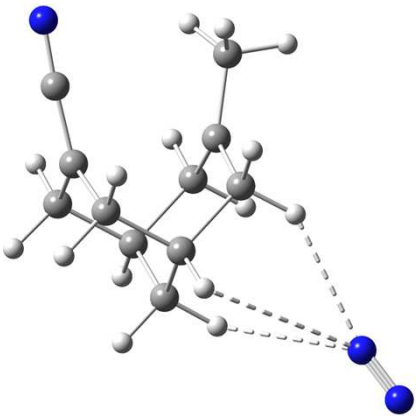
OC(I)N_2(2)
E_0=0.20
D_0=11.31



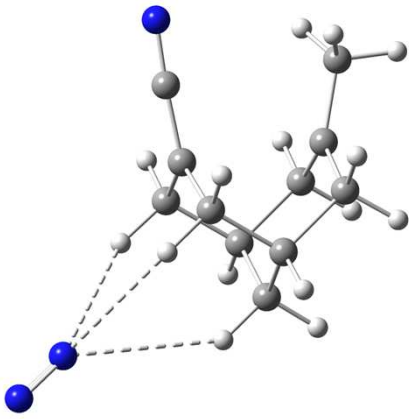
OC(I)N_2(3)
E_0=0.72
D_0=10.79



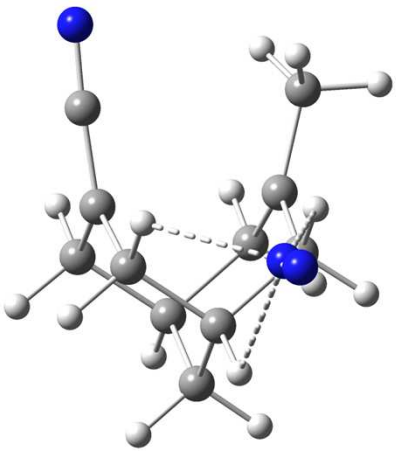
OC(I)N_2(4)
E_0=1.60
D_0=9.91



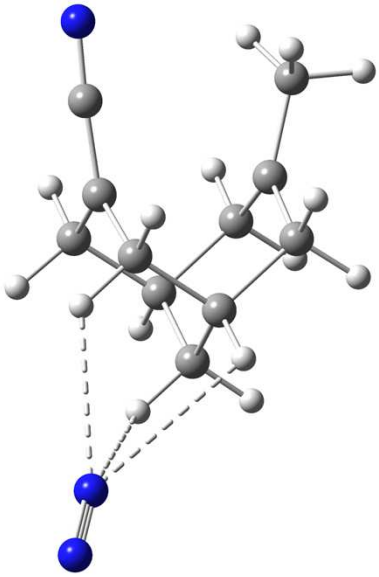
OC(I)N_2(5)
E_0=2.10
D_0=9.41



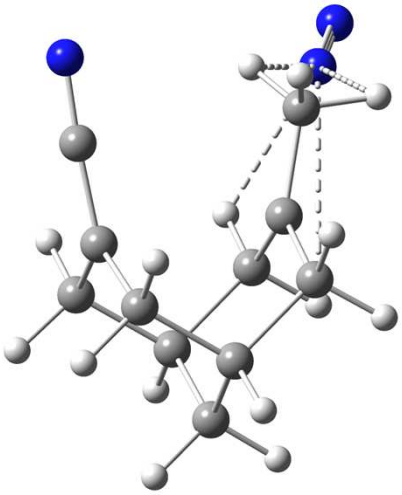
OC(I)N_2(6)
E_0=2.26
D_0=9.25



OC(I)N_2(7)
E_0=2.45
D_0=9.06

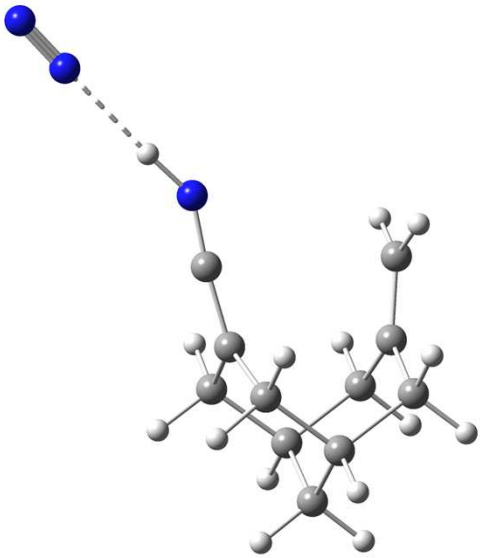


OC(I)N_2(8)
E_0=2.96
D_0=8.55

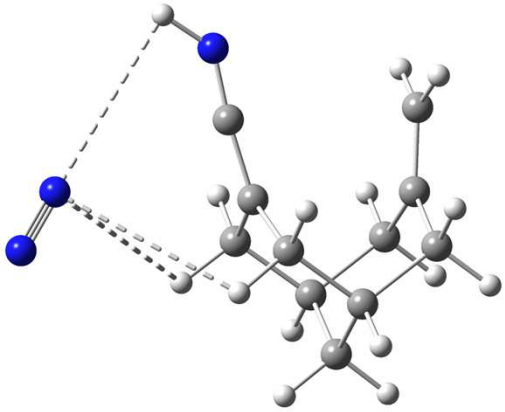


OC(I)N_2(9)
E_0=2.97
D_0=8.54

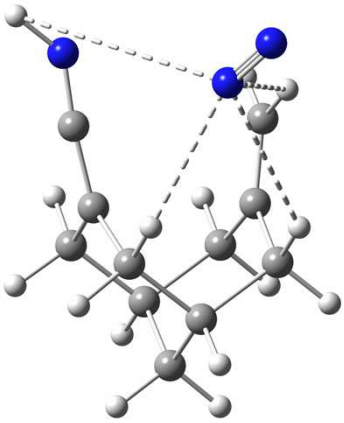
Figure S6



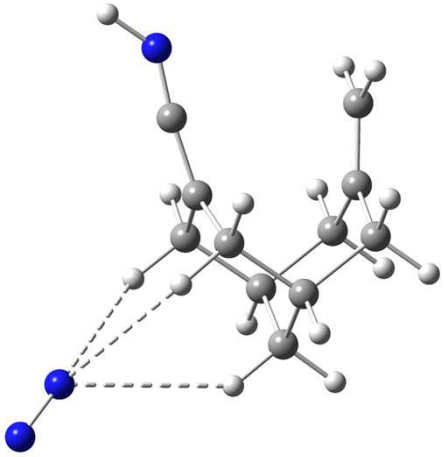
OC(II)N_2(1)
E_0=0.00
D_0=17.24



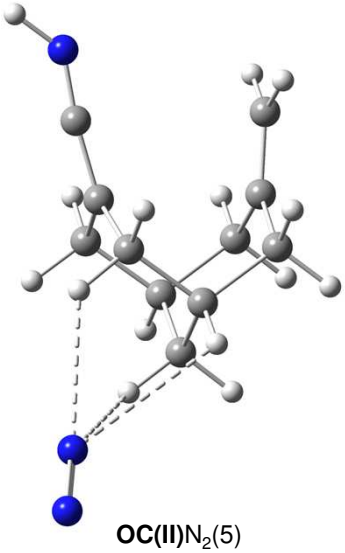
OC(II)N_2(2)
E_0=7.80
D_0=9.44



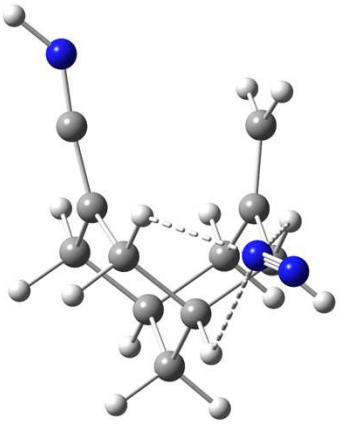
OC(II)N_2(3)
E_0=8.21
D_0=9.03



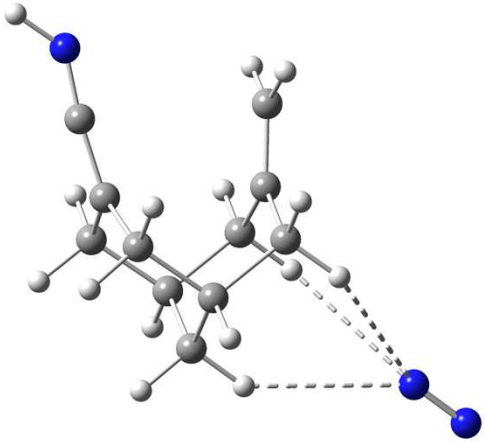
OC(II)N_2(4)
E_0=8.21
D_0=9.03



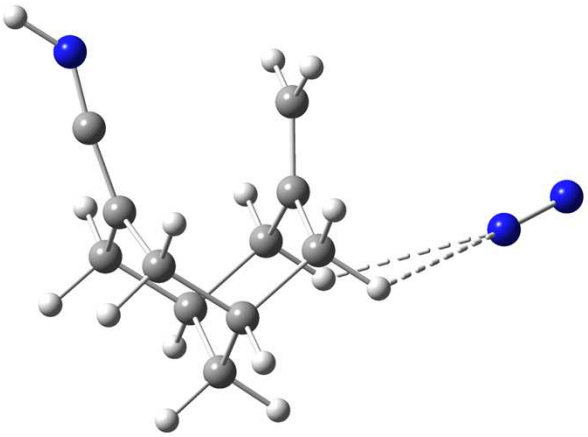
OC(II)N_2(5)
E_0=8.66
D_0=8.58



OC(II)N_2(6)
E_0=9.43
D_0=7.81

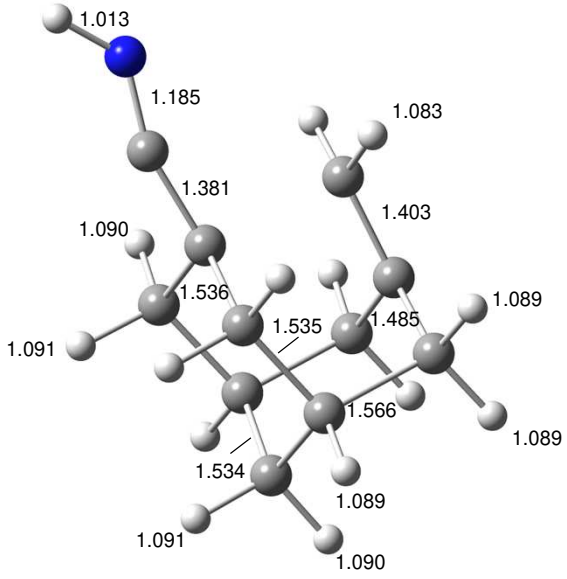


OC(II)N_2(7)
E_0=9.48
D_0=7.76

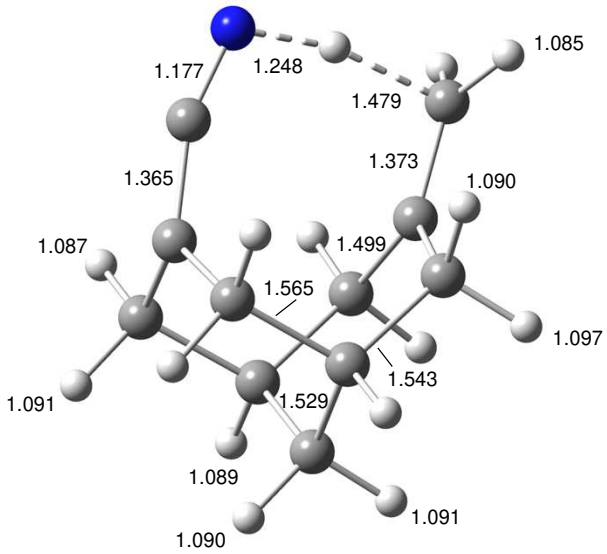


OC(II)N_2(8)
E_0=9.71
D_0=7.53

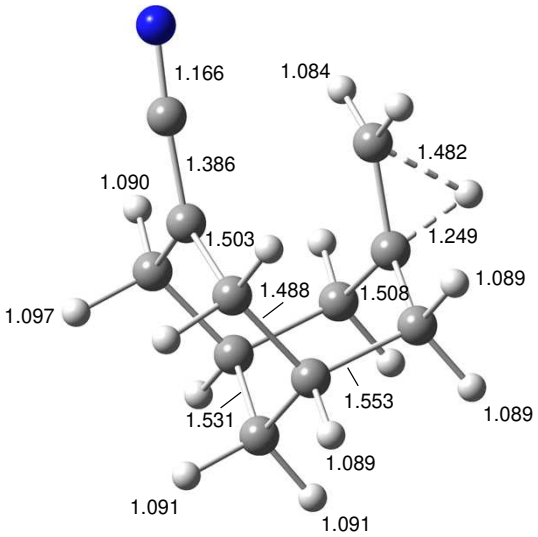
Figure S7



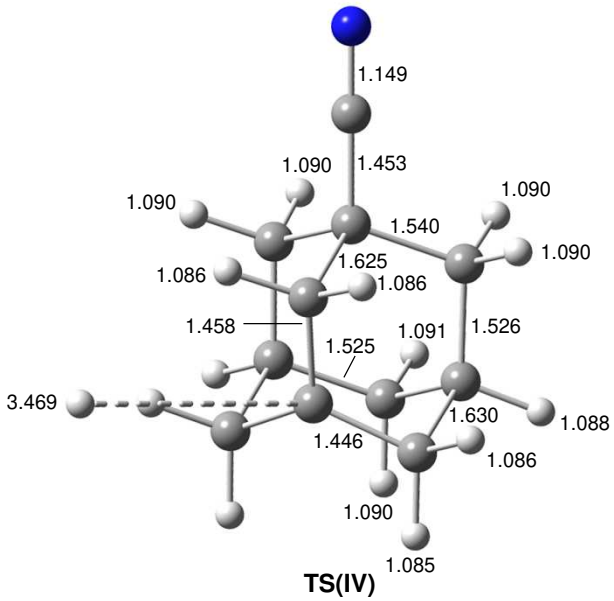
TS(I)



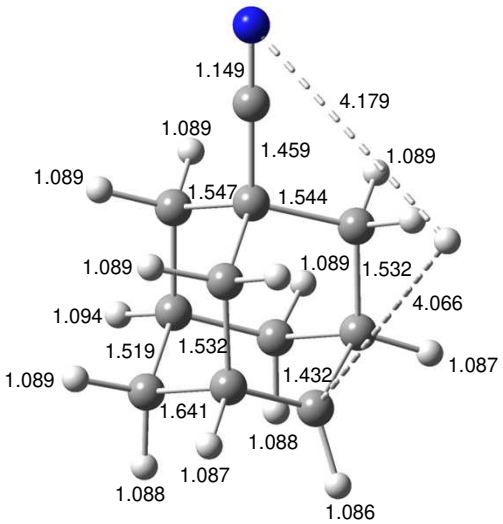
TS(II)



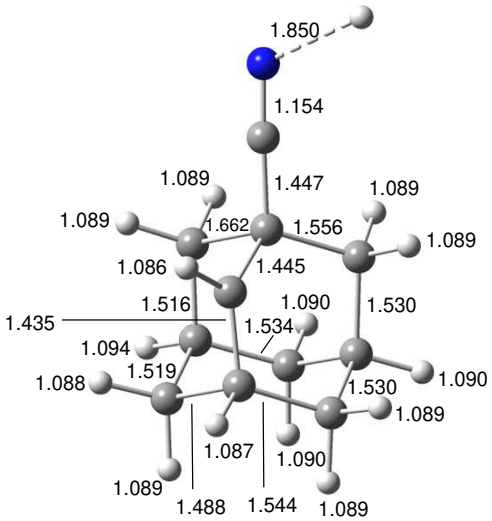
TS(III)



TS(IV)

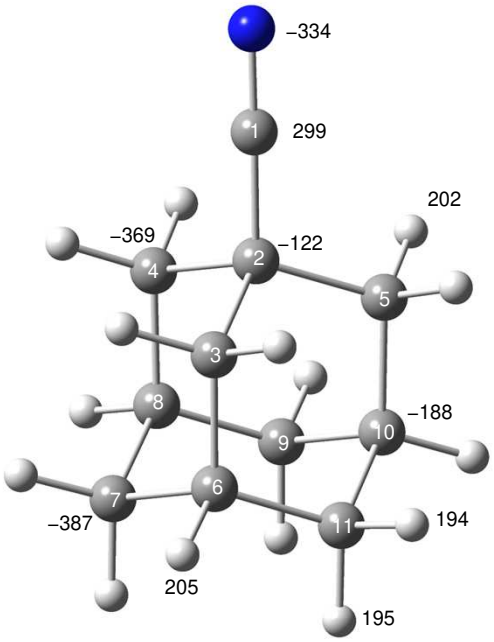


TS(V)

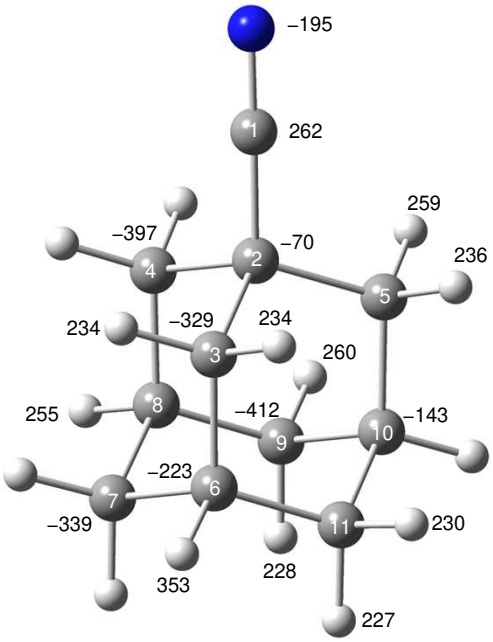


TS(VI)

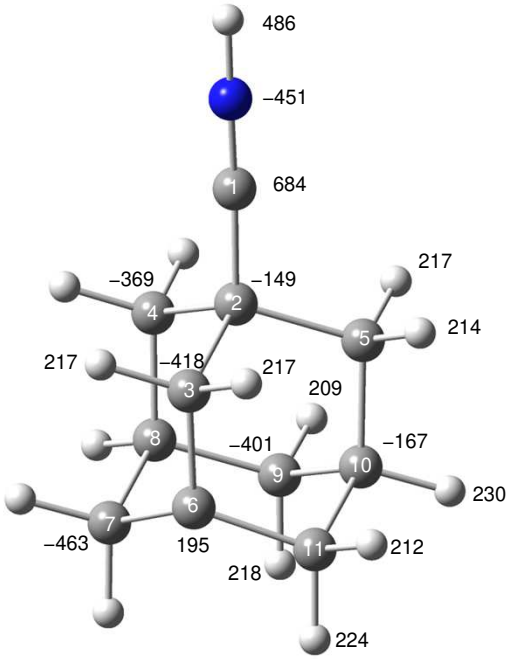
Figure S8



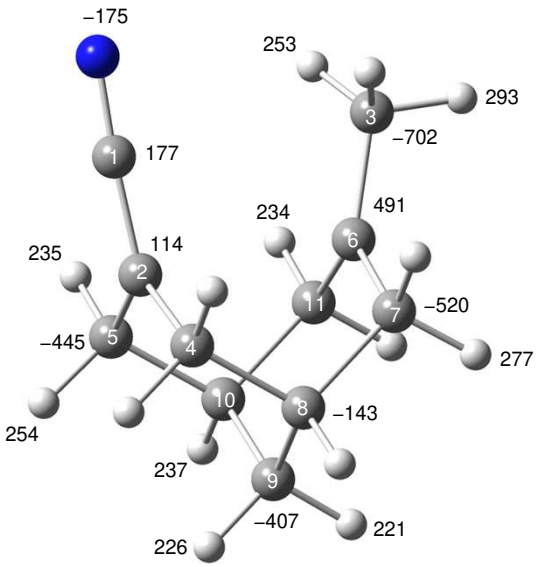
AdCN (C_{3v})



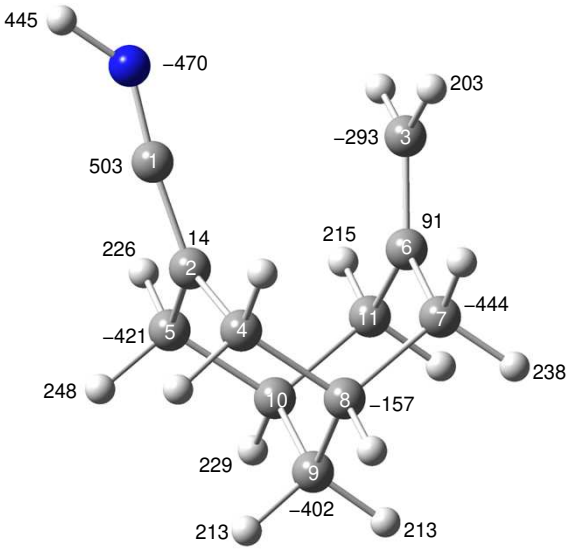
CC(I) (C_s)



CC(II) (C_s)

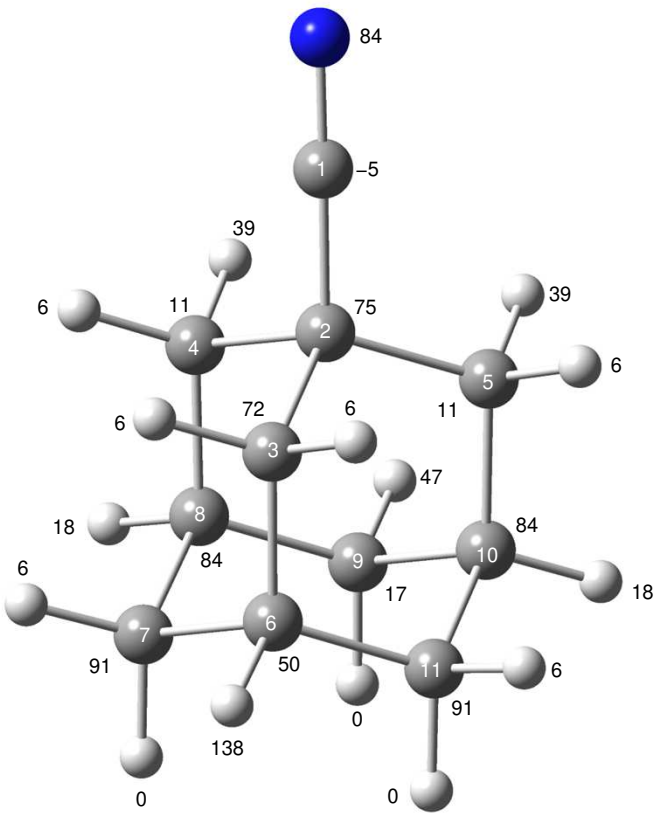


OC(I) (C_s)

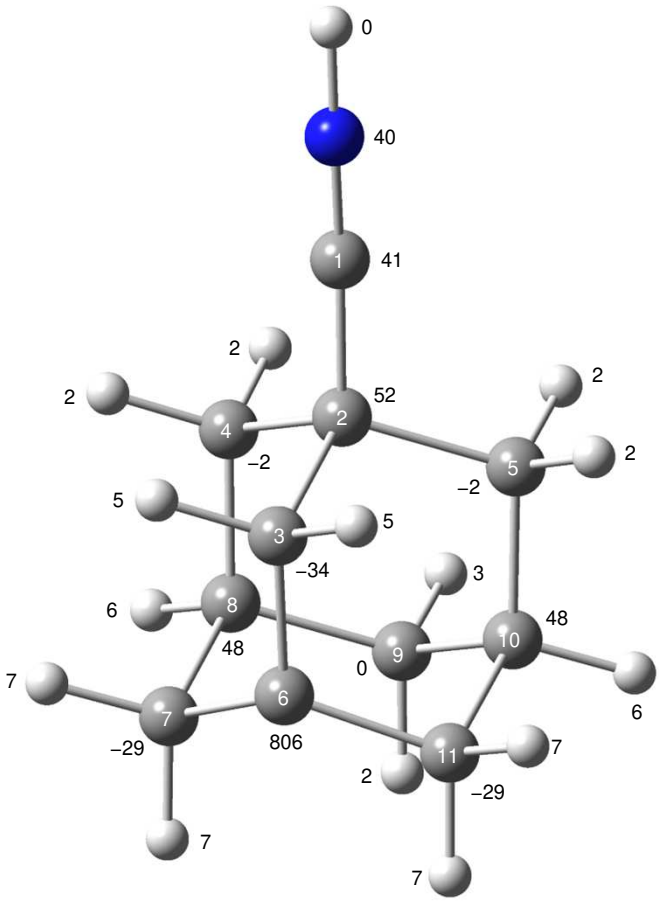


OC(II) (C_s)

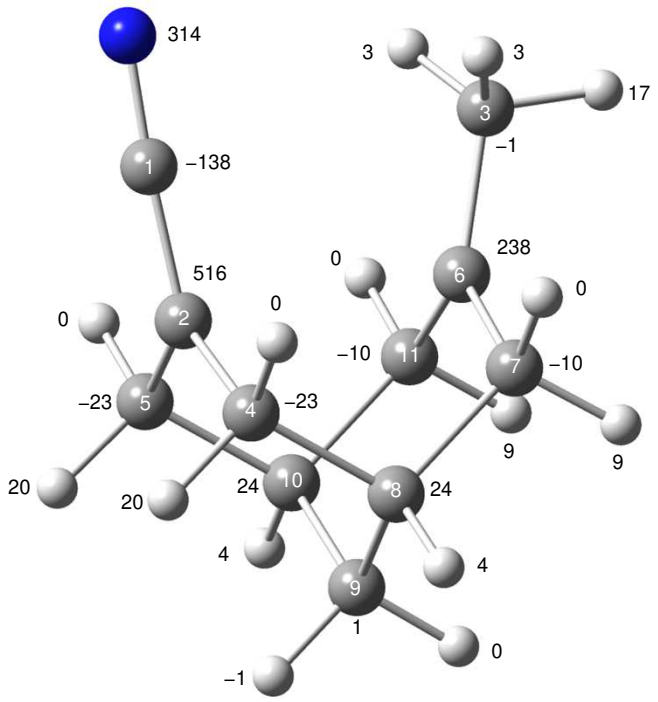
Figure S9



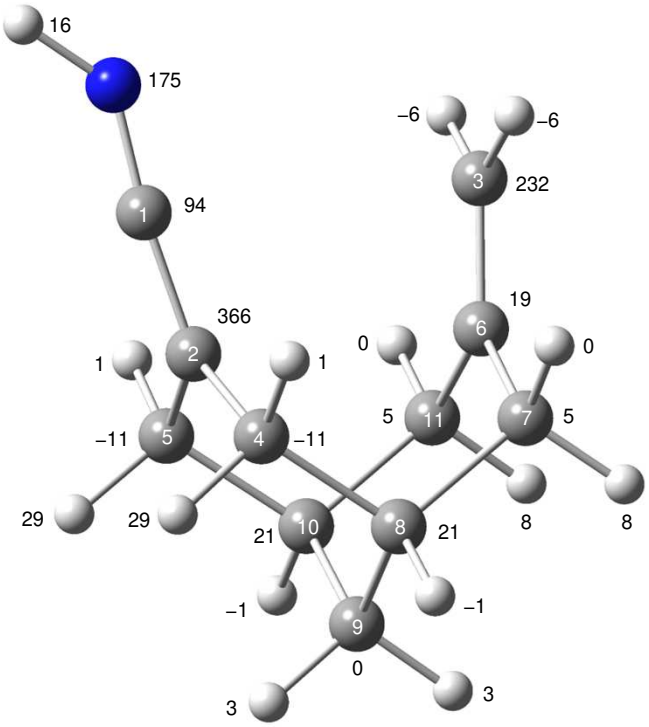
CC(I) (C_S)



CC(II) (C_S)



OC(I) (C_S)



OC(II) (C_S)

Figure S10

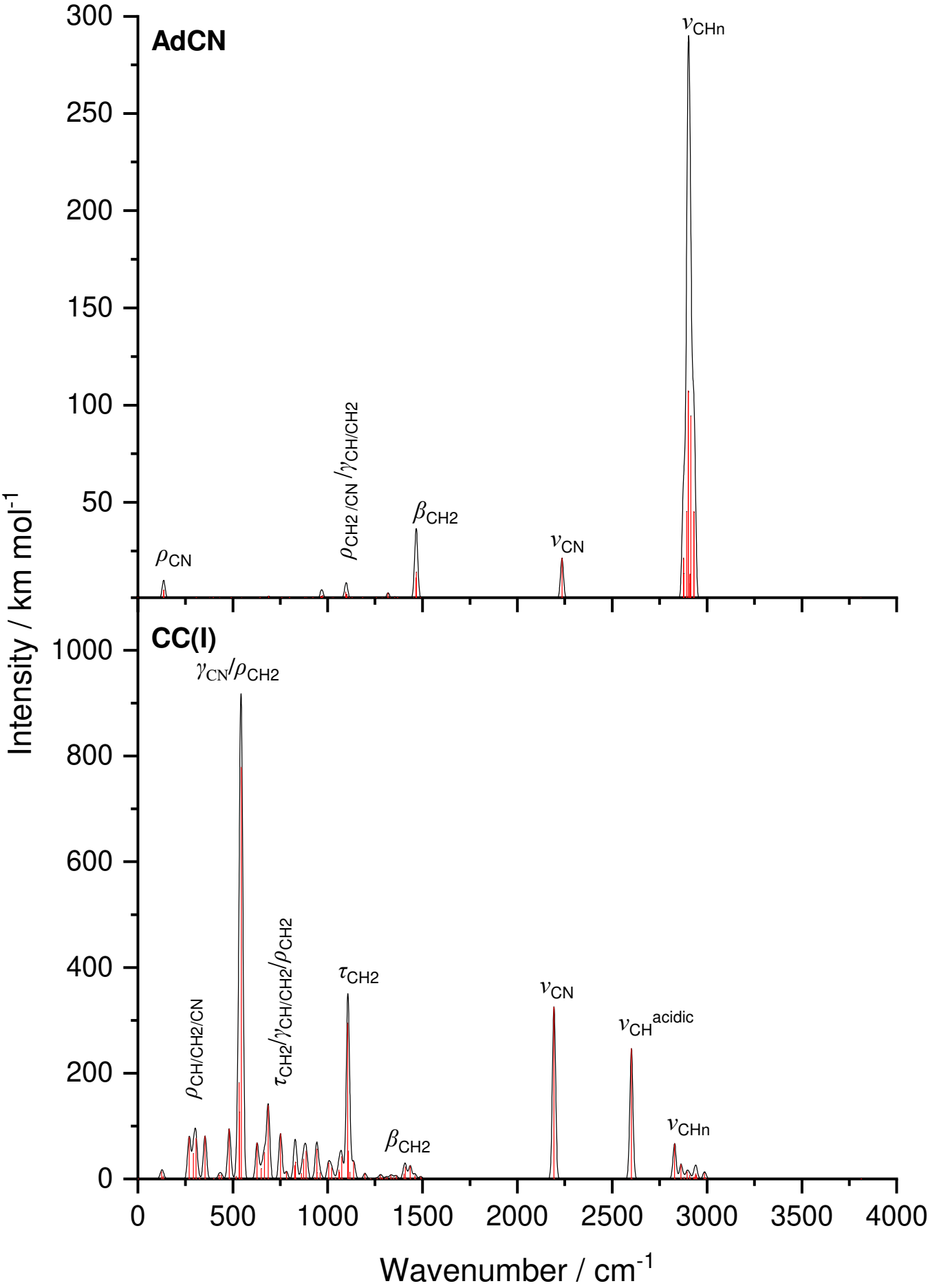

AdCN
CC(I)
Intensity / km mol-1
Wavenumber / cm-1
ρCN
ρCH2 /CN /γCH/CH2
βCH2
νCN
νCHn
γCN/ρCH2
ρCH/CH2/CN
τCH2/γCH/CH2/ρCH2
τCH2
νCH acidic

Figure S11

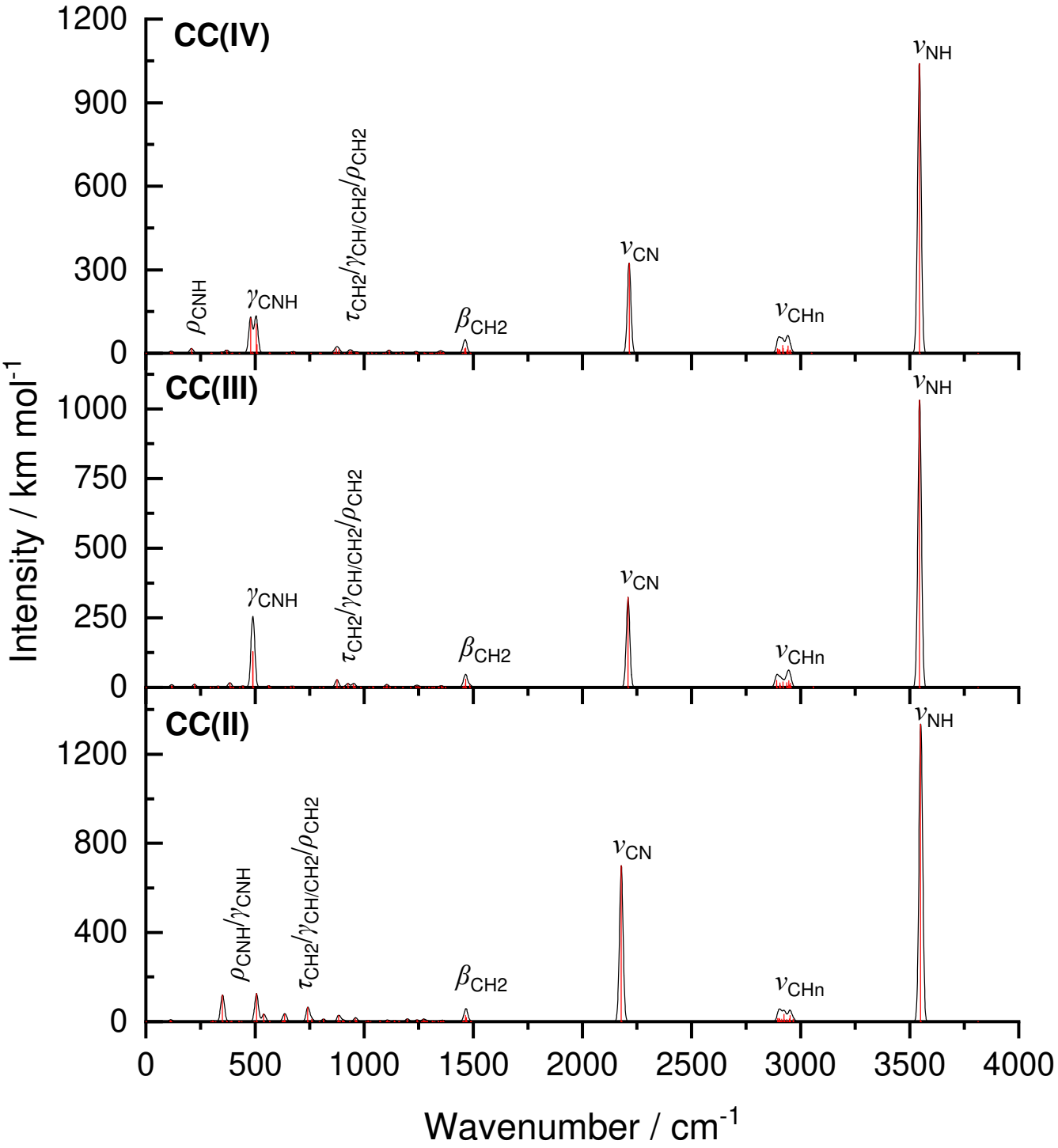

CC(IV)
CC(III)
CC(II)
Intensity / km mol-1
Wavenumber / cm-1
ρCNH
γCNH
τCH2/γCH/CH2/ρCH2
βCH2
νCN
νCHn
νNH
ρCNH/γCNH

Figure S12

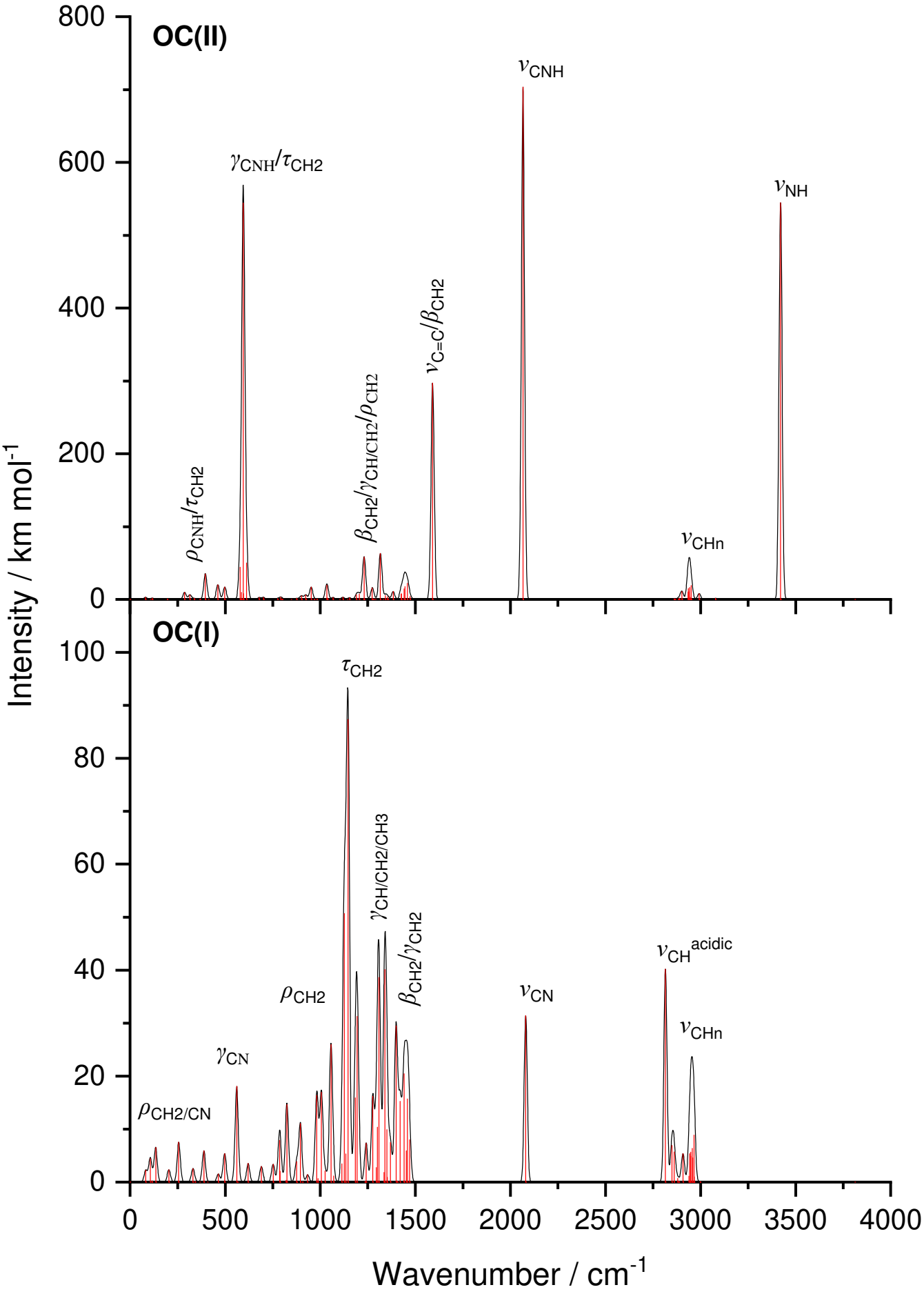
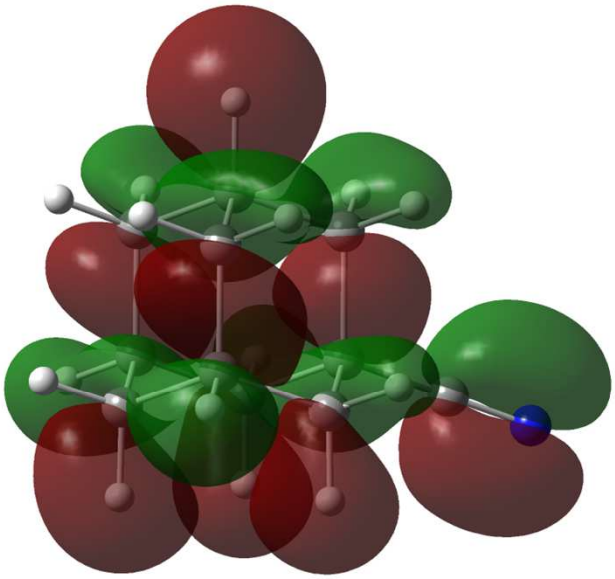
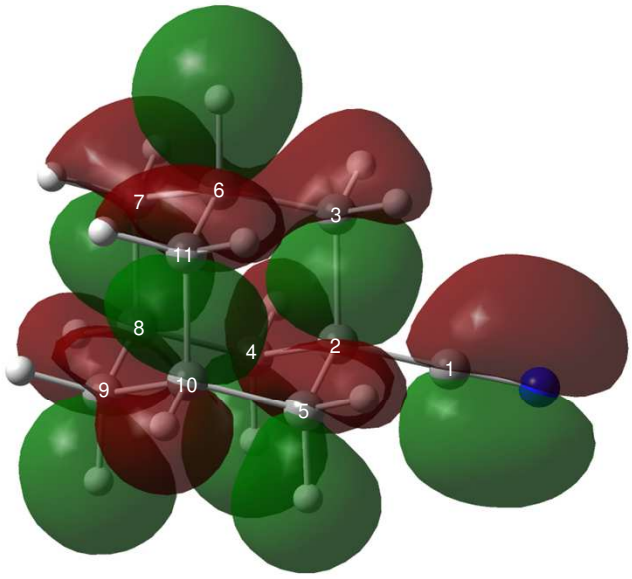

OC(II)
OC(I)
Intensity / km mol-1
Wavenumber / cm-1
νCNH
γCNH/τCH2
νNH
νC=C/βCH2
βCH2/γCH/CH2/ρCH2
ρCNH/τCH2
νCHn
τCH2
γCH/CH2/CH3
βCH2/γCH2
ρCH2
νCN
νCH acidic
νCHn
γCN
ρCH2/CN
0
20
40
60
80
100
0
200
400
600
800
0
500
1000
1500
2000
2500
3000
3500
4000

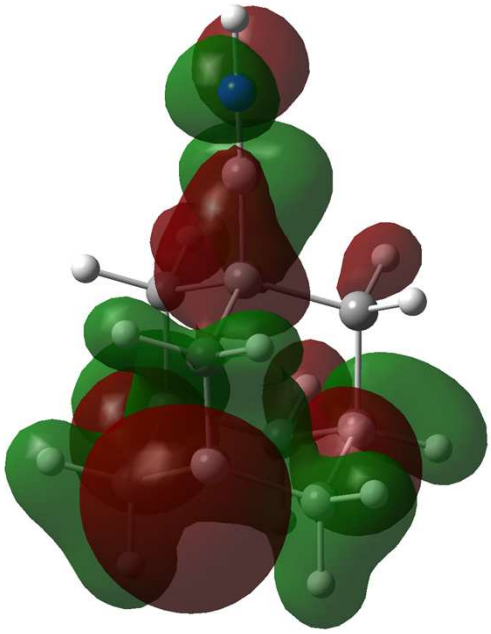
Figure S13



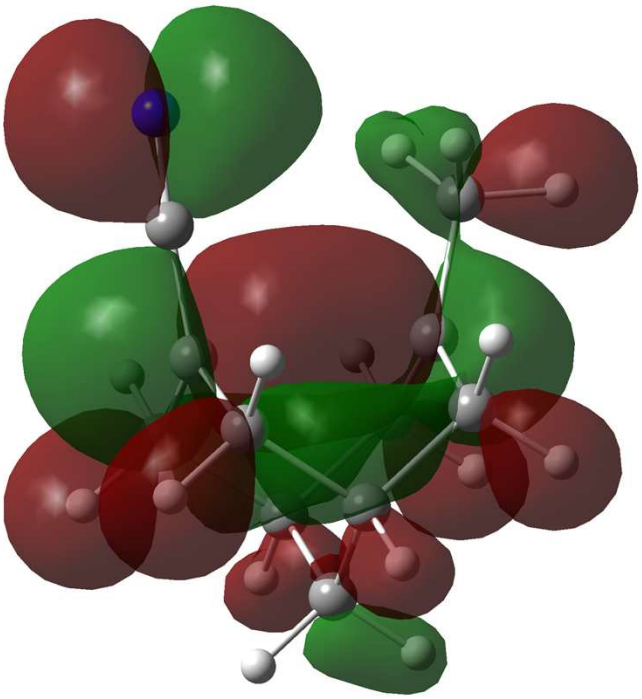
AdCN (C_{3v})



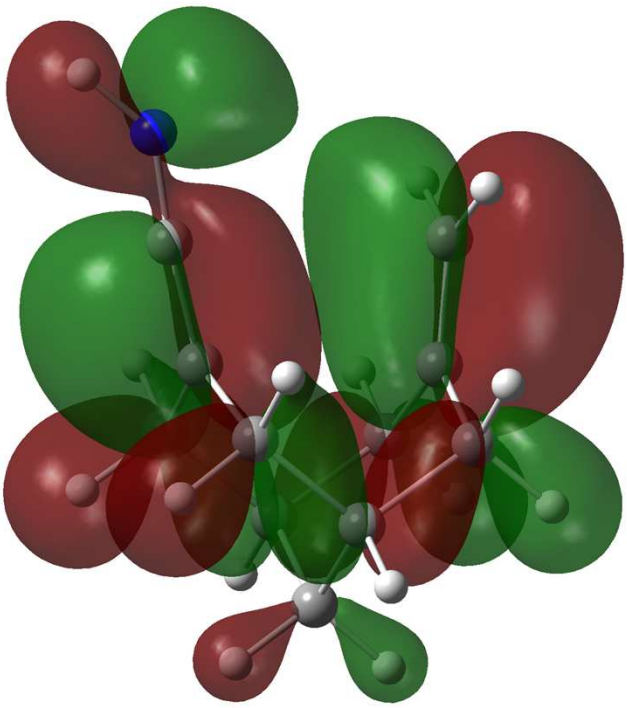
AdCN$^+$ **CC(I)** (C_s)



CC(II) (C_s)

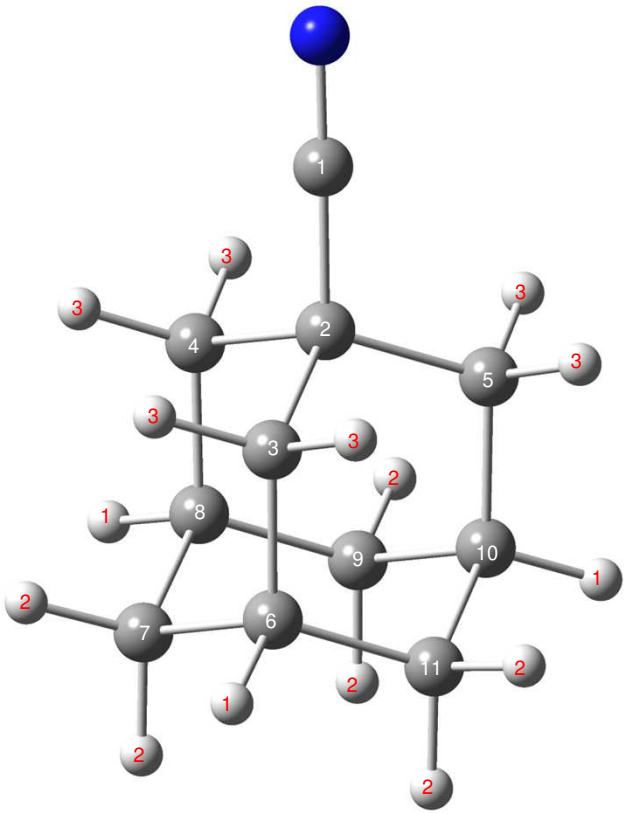


OC(I) (C_s)

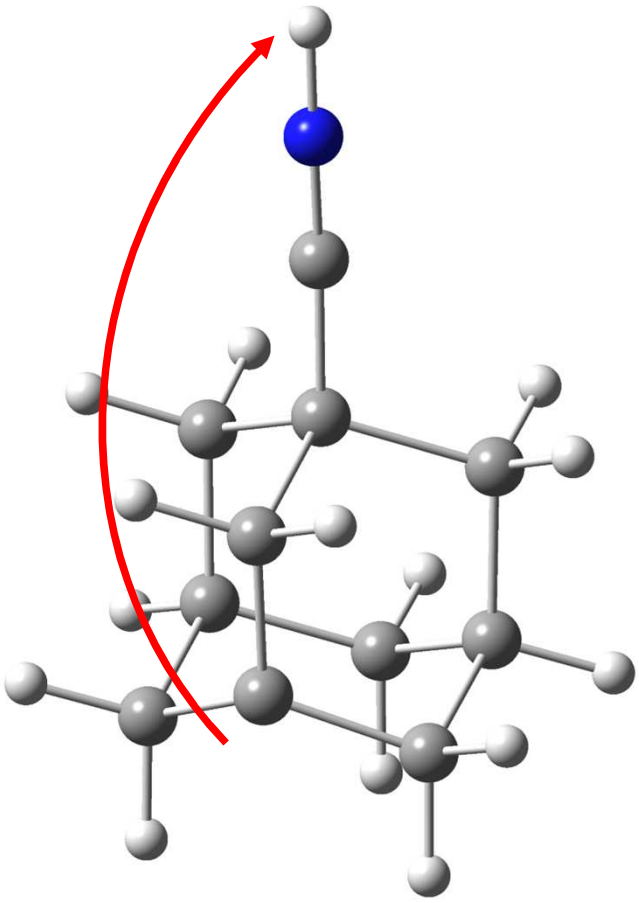


OC(II) (C_s)

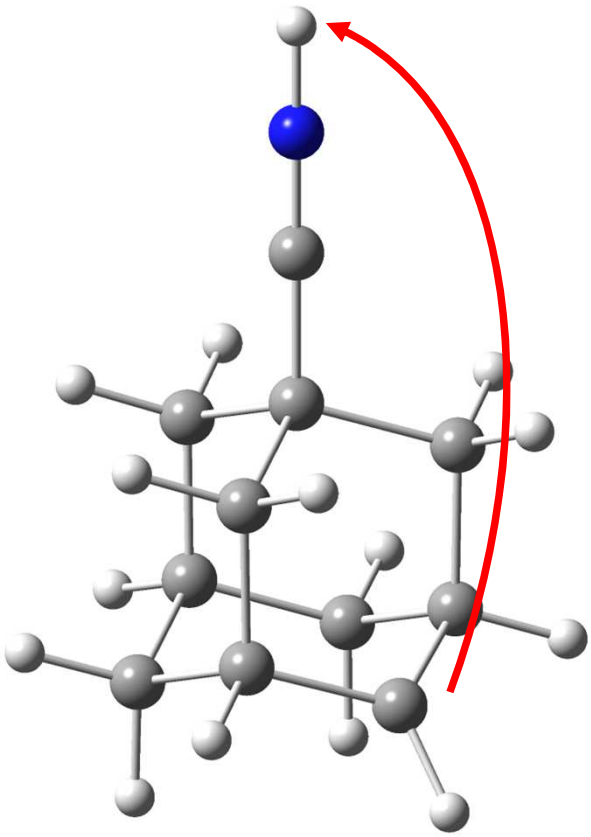
Figure S14



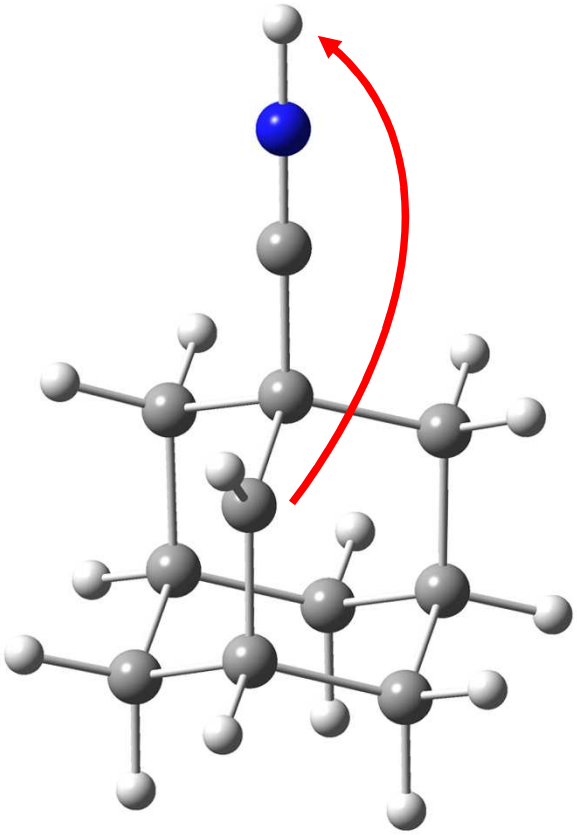
CC(I) (C_S)



CC(II) (C_S)



CC(III) (C_S)



CC(IV) (C_S)

Figure S15