Electronic Supplementary Information

Can cytosine, uracil and thymine be formed in interstellar regions? A theoretical study.

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Fig.S1 Gas-phase reaction between HNCO and H_2O. CCSD(T)/6-311++G(d,p)//B3LYP/6-311++G(d,p) level of theory. Relative energies in kJ mol^{-1}.
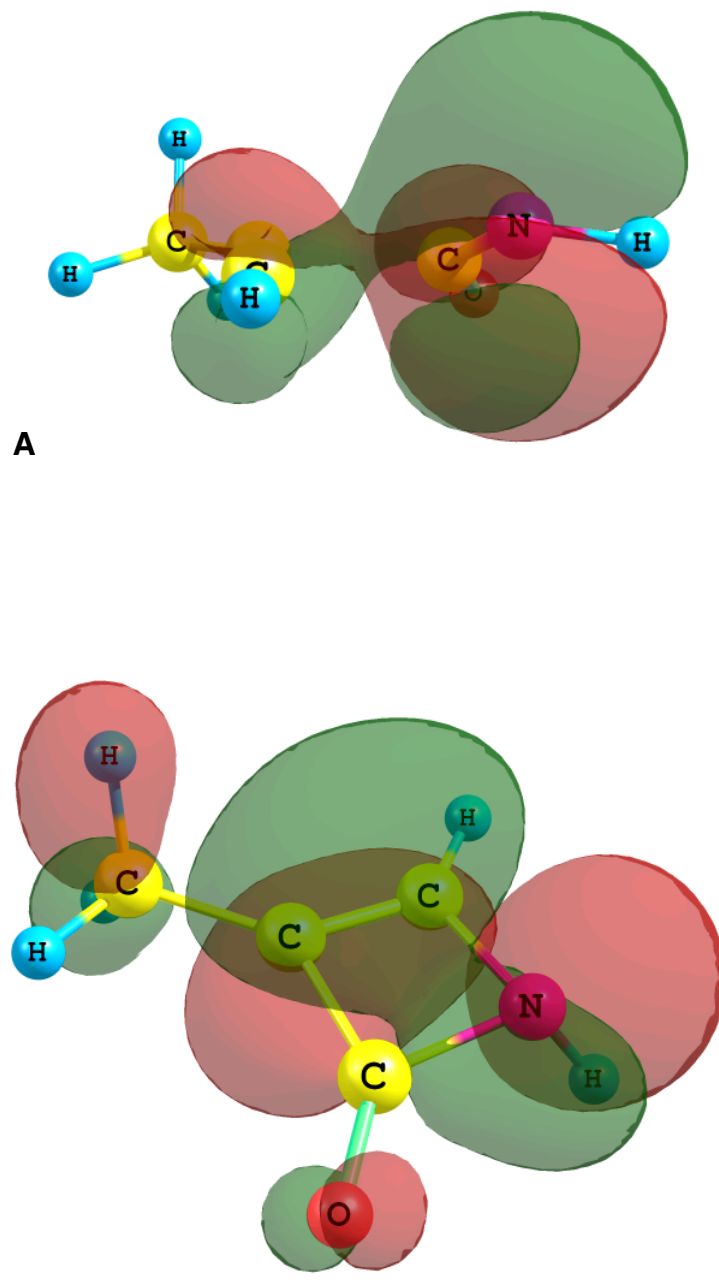
A

B

Fig.S2 A. The HOMO of the transition state for the first step in Scheme 3; B. The HOMO of the product for the first step in **Scheme 3**. Calculated at CCSD(T)/6-311++G(d,p)//B3LYP/6-311++G(d,p) level of theory.

Tunnelling theoretical methods

The tunnelling corrected rate constants evaluated by WKB (Wentzel-Kramers-Brillouin) method for the first steps in Figures 1a and 1b were computed within a reaction-path Hamiltonian model by multiplying the classical rate at which the reactant hits the reaction barrier by the quantum mechanical transmission probability.[48,49] The B3LYP/aug-cc-pVTZ method was employed to map out the intrinsic reaction coordinate (IRC) and to obtain harmonic vibrational frequencies along the pathways. The final potential energy function V along the carbenoid insertion IRC was also constructed at this level of theory with ZPVEs correction. A polynomial expression fit of these points was used to represent V in terms of the arc length s (atomic units) in mass-weighted coordinates along the IRC, as well as to ensure that $V(s)$ extended smoothly all the way to the reactant minimum. A plot of $V(s)$ for the first step (H transfers) in Figure 1a and Figure 1b in kJ mol^{-1} is shown in Supplementary Figures S3 and S5, respectively. The IRC in Figure S3 through the hyperspace of the 33 vibrational degrees of freedom was adopted as the tunnelling route, while for the IRC in Figure S5, the hyperspace contains 30 vibrations. Tunnelling probabilities [$P(\varepsilon)$] were evaluated by computing one-dimensional barrier penetration integrals [$\theta(s)$] numerically along the IRC and invoking the standard WKB formula:

$$\theta(\varepsilon) = \frac{1}{\hbar} \int_{s_1}^{s_2} \sqrt{2\mu(V(s) - \varepsilon)} \, ds \qquad (1)$$

$$P(\varepsilon) = \frac{1}{1 + e^{2\theta(\varepsilon)}} \qquad (2)$$

where ε is the collision energy, μ is the corresponding reduced mass, s is the reaction coordinate, s_1 and s_2 are the turning points where the $V(s) = \varepsilon$, then the tunnelling rate constant at a energy ε is

$$k_{WKB} = \frac{\omega_0}{2\pi} P(\varepsilon) \qquad (3)$$

where ω_0 is the vibrational "reaction" mode of reactants that leads toward **TS 1/2 (TS 5/6).**

The tunnelling contributions to the rate constant were also estimated using Eckart method, in which the cross-section of the potential energy surface is fitted with the Eckart potential,[50,51]

$$V(s) = \frac{A\exp(\frac{s-s_0}{l})}{1+\exp(\frac{s-s_0}{l})} + \frac{B\exp(\frac{s-s_0}{l})}{[1+\exp(\frac{s-s_0}{l})]^2} \qquad (4)$$

The fitting parameters are

$$A = V_f - V_r$$

$$B = (\sqrt{V_f} + \sqrt{V_r})^2$$

$$l = \frac{2\pi}{\omega^*}\sqrt{\frac{2}{\mu}}(\frac{1}{\sqrt{V_f}} + \frac{1}{\sqrt{V_r}})^{-1}$$

while the transmission probability as a function of energy is

$$P(\varepsilon) = \frac{\cosh(\alpha+\beta) - \cosh(\alpha-\beta)}{\cosh(\alpha+\beta) + \cosh\delta} \qquad (5)$$

The parameters are

$$\alpha = \frac{4\pi}{\omega^*}(\frac{1}{\sqrt{V_f}} + \frac{1}{\sqrt{V_r}})^{-1}\sqrt{\varepsilon}$$

$$\beta = \frac{4\pi}{\omega^*}(\frac{1}{\sqrt{V_f}} + \frac{1}{\sqrt{V_r}})^{-1}\sqrt{\varepsilon - V_f + V_r}$$

$$\delta = 4\pi\sqrt{\frac{V_f V_r}{(\omega^*)^2} - \frac{1}{16}}$$

Where ε is the collision energy, V_f and V_r are the energy barriers with ZPEs (excluding the vibration corresponding to reaction mode) in the forward and reverse direction, ω^* is the absolute value of imaginary frequency of the transition state. The rate constant can be calculated by the following equation,

$$k_{Eckart} = \frac{\omega_0}{2\pi}P(\varepsilon) = \frac{\omega_0}{2\pi}\frac{\cosh(\alpha+\beta) - \cosh(\alpha-\beta)}{\cosh(\alpha+\beta) + \cosh\delta} \qquad (6)$$

Eventually, the temperature dependant rate constant expression for WKB and Eckart methods is as follows,

$$k(T) = \frac{\sum_{n=0}^{\infty} k(n\omega_0)e^{-\frac{n\omega_0}{kT}}}{\sum_{n=0}^{\infty} e^{-\frac{n\omega_0}{kT}}} \qquad (7), \text{ in which } T \text{ is the temperature in K.}$$

Process shown in Figure S3	Process shown in Figure S5
Collision frequency (ω_0) = 32 cm^{-1}	Collision frequency (ω_0) = 69 cm^{-1}
Imaginary frequency (ω^*) = 840i cm^{-1}	Imaginary frequency (ω^*) = 1138i cm^{-1}
Turning points (s_1, s_2) = (-20.80, 18.53) amu$^{1/2}$ bohr	Turning points (s_1, s_2) = (-18.42, 17.27) amu$^{1/2}$ bohr
V_f = 10745 cm^{-1}	V_f = 10593 cm^{-1}
V_r = 20745 cm^{-1}	V_r = 22734 cm^{-1}

Comparison of the results of two methods

Some key parameters for carrying out the calculations are collected in the table above. It can be noticed that the widths of both barriers are relatively large, and collision energies are small compared to the overall barrier heights, which would result in low tunnelling probabilities. The tunnelling corrected rate constants at various temperatures determined by WKB and Eckart methods at B3LYP/aug-cc-pVTZ are shown in Figure S4 and S6. The discrepancies between WKB and Eckart results are significant in the low temperature region, caused by the different shape of potential energy curves. The rate constants for reactions above 200K (see Figure S4) and above 250K (see Figure S6) show satisfactory agreement. The WKB estimation of transmission probability at low temperatures gives closer to the exact solution of the Schrödinger equation (5), yielding reasonable results at the low-temperature limit. At room temperature both of these two methods performs well, and they quantitatively coincide as temperature increases.

Conclusion

According to the WKB method described above, it can be seen that the penetration integral $\theta(\varepsilon)$ and hence the tunnelling probability $P(\varepsilon)$ are principally dependant on three factors: the width of the barrier, the square root of the difference between the overall barrier height and the collision energy, and the square root of the effective mass. Moreover, barrier width trumps barrier height because the penetration integral (θ) scales linearly with the former but only as the square root of the latter. The IRC calculations show that the barriers are wide especially at the bottom (see Figs S3 and S5) where the tunnelling may occur at low temperature, as there are extensive geometry variations in theses processes to reach the minimum points, which

make the tunnelling probabilities small. For example, the calculations show that both processes have extremely low tunnelling corrected rate constants at low temperature, $\sim 10^{-40}$ s^{-1} (k_{WKB}) at 125 K for Fig.S4, and $\sim 10^{-32}$ s^{-1} (k_{WKB}) at 150K for Fig.S6, which yield extraordinarily long half-life ($t_{1/2} = (ln2)/k$) for the reactants (c.f. Fig.S1 and S3). It means that the tunnelling effect is negligible for both reactions.
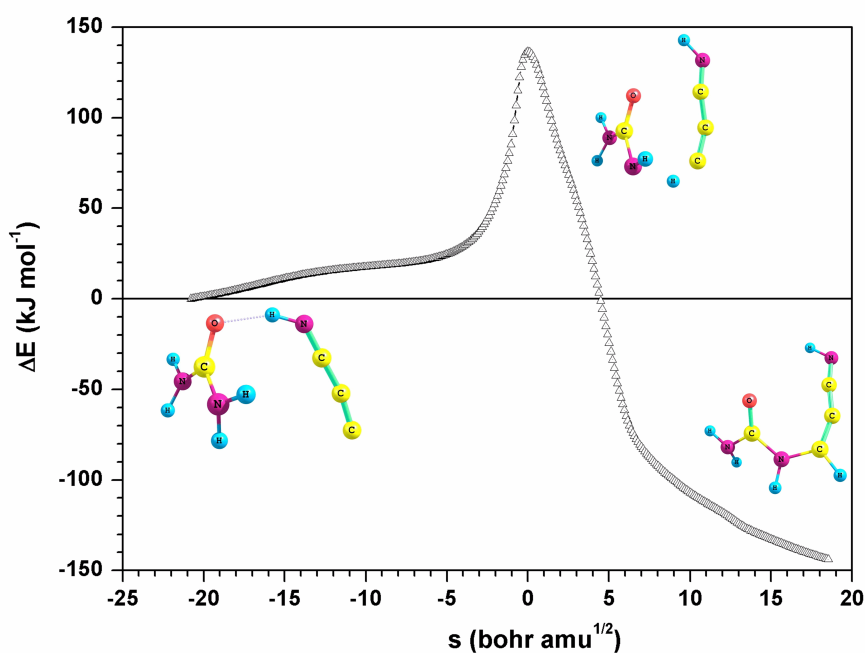

Fig.S3 Potential energy curve along the intrinsic reaction coordinate (IRC) for the first step in Fig.1a. The geometric structures, zero-point vibrational corrections and energetics along the path were generated at the B3LYP/aug-cc-pVTZ level of theory. The abscissa is the arc length along the path in mass-weighted Cartesian coordinates.
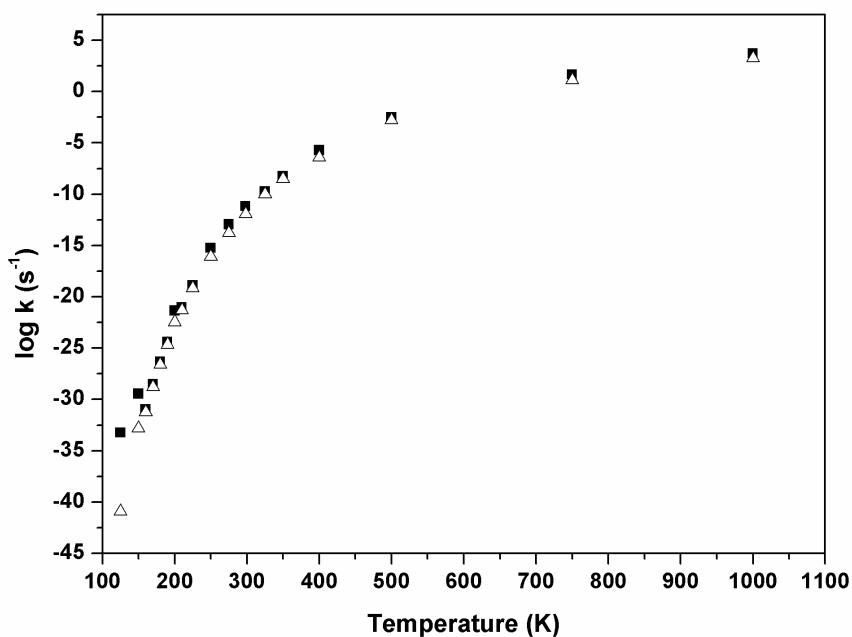
Fig.S4 Temperature dependence of Eckart (solid squares) and WKB (open triangles) tunnelling corrected rate constants for the reaction shown in Fig.S3.
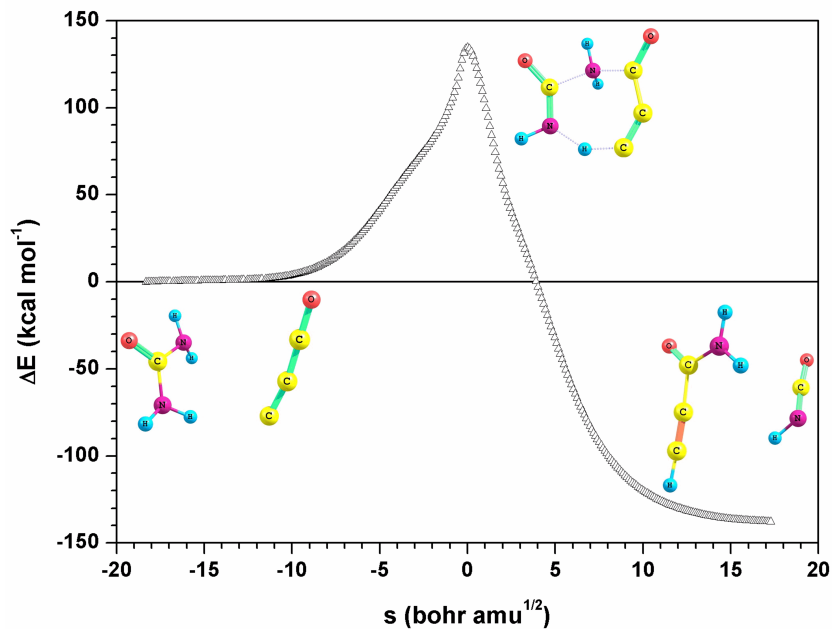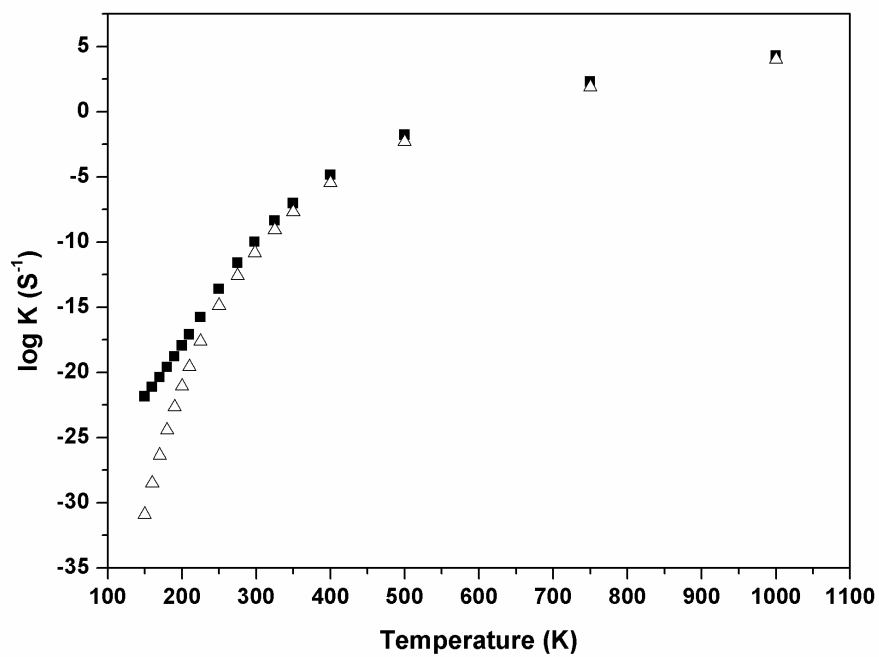

Fig.S5 Potential energy curve along the intrinsic reaction coordinate (IRC) for the first step in Fig.1b. The geometric structures, zero-point vibrational corrections and energetics along the path were generated at the B3LYP/aug-cc-pVTZ level of theory. The abscissa is the arc length along the path in mass-weighted Cartesian coordinates.

Fig.S6 Temperature dependence of Eckart (solid squares) and WKB (open triangles) tunnelling corrected rate constants for the reaction shown in Fig.S5.
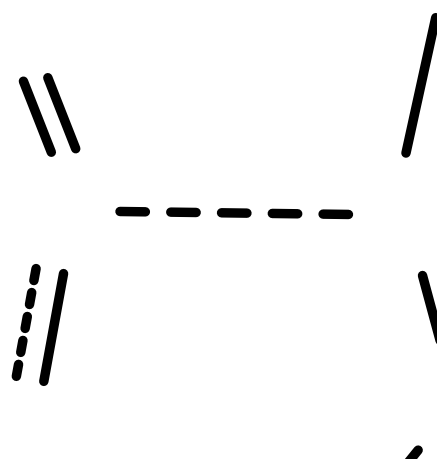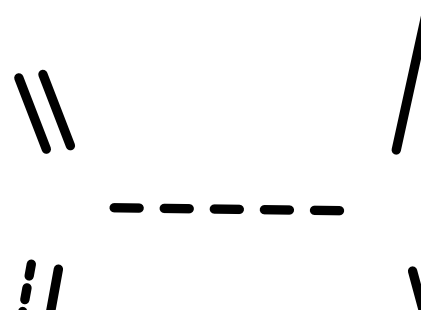
Fig.S7a Reaction coordinate diagram for the reaction between the mono hydrated propional enolate anion and two molecules of isocyanic acid to produce thymine. *Planar (eclipsed)* elimination. CCSD(T)/6-311++G(d,p)//B3LYP/6-311++G(d,p) level of theory, ΔG energies in kJ mol^{-1}.   For full details of energies and geometries of minima and transition states see **Table S7a**.
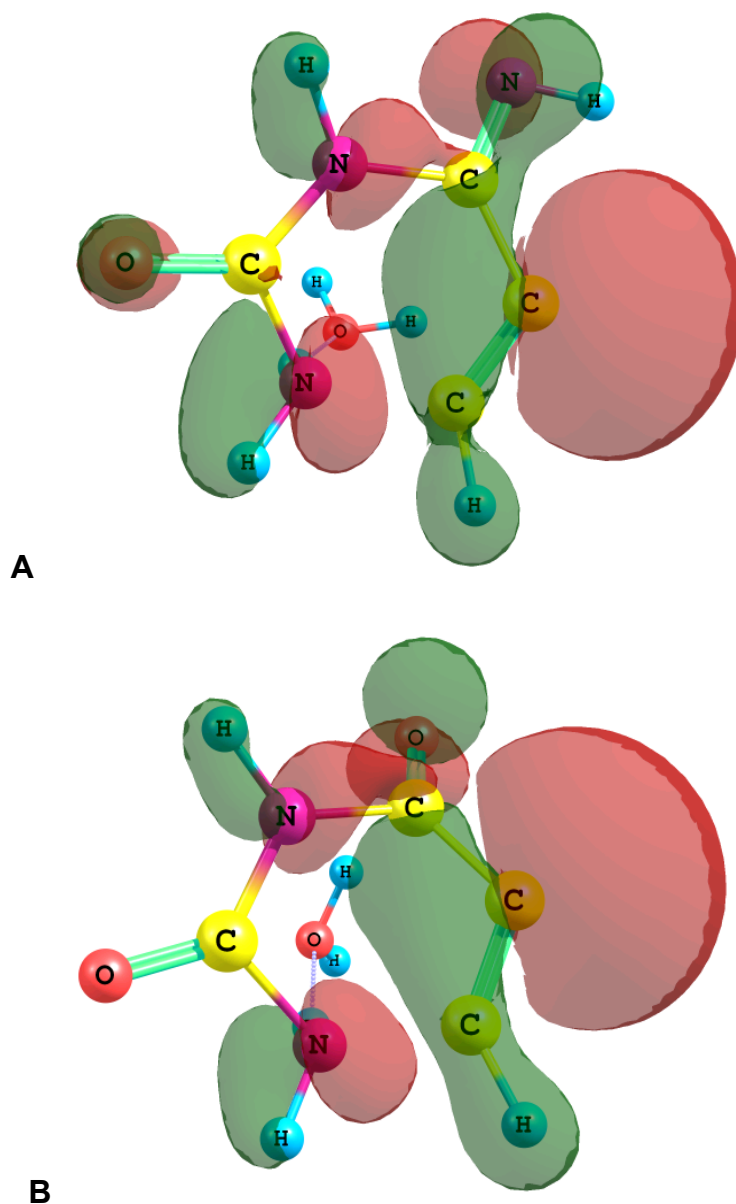
Fig.S8 Reaction coordinate diagram for the reaction between the mono hydrated propional enolate anion and two molecules of isocyanic acid to produce thymine. Anti elimination. CCSD(T)/6-311++G(d,p)//B3LYP/6-311++G(d,p) level of theory, ΔG energies in kJ mol^{-1}. For full details of energies and geometries of minima and transition states see **Table S8**.

Fig.S9 A. The HOMO of the intermediate **19** in **Table S3a**; B. The HOMO of the intermediate **24** in **Table S3b**. (A red orbital indicates δ- charge; a green orbital indicates δ+ charge). Calculated at CCSD(T)/6-311++G(d,p)//B3LYP/6-311++G(d,p) level of theory.

Table S1-7 Energies (0 K), Gibbs free energies (298 K) and selected geometries of reactants and products for reactions in Figs 1 to 7.

Level of theory used CCSD(T)/6-311++G(d,p)//B3LYP/6-311++G(d,p).

A	Energy: -224.73653 Hartree, Gibbs free energy: -224.76284 Hartree Dipole: 4.1709. Symmetry: C_1, State: ^1A. Cartesian Coordinates: C -0.000002 0.143421 -0.000007 O -0.000086 1.360131 0.000003 N -1.161439 -0.609856 0.068289 H -2.002491 -0.072040 -0.076207 H -1.166817 -1.530321 -0.344981 N 1.161518 -0.609747 -0.068313 H 2.002482 -0.071825 0.076305
B	Energy: -169.07439 Hartree, Gibbs free energy: -169.09924 Hartree Dipole: 5.2427. Symmetry: C_1, State: ^1A. Cartesian Coordinates: C 0.497806 0.013092 -0.000009 C -0.804727 0.009716 -0.000822 C -2.072592 0.006946 0.000554 N 1.681229 -0.093598 0.000192 H 2.508474 0.476666 0.000325
C	Energy: -188.96326 Hartree, Gibbs free energy: -188.98687 Hartree Dipole: 1.6740. Symmetry: $C_{\infty h}$, State: $^1\Sigma$. Cartesian Coordinates: C 0.000000 0.000000 -0.758150 C 0.000000 0.000000 0.537142 O 0.000000 0.000000 1.686818 C 0.000000 0.000000 -2.028083
D	Energy: -169.15607 Hartree, Gibbs free energy: -169.17933 Hartree Dipole: 4.1974. Symmetry: $C_{\infty h}$, State: $^1\Sigma$. Cartesian Coordinates: C 0.000000 0.000000 -1.834920 H 0.000000 0.000000 -2.898788 C 0.000000 0.000000 -0.631281 C 0.000000 0.000000 0.737609 N 0.000000 0.000000 1.895763
E	Energy: -76.26525 Hartree, Gibbs free energy: -76.28289 Hartree Dipole: 2.2359. Symmetry: C_{2v}, State: $^1A_1$.

Table S1-7 Continued.

F	Energy: -55.74052 Hartree, Gibbs free energy: -55.75950 Hartree Dipole: 2.0786. Symmetry: C_s, State: ^{2}A".
G	Energy: -75.58801 Hartree, Gibbs free energy: -75.60494 Hartree Dipole: 1.9146. Symmetry: $C_{\infty v}$, Charge: 0, State: $^2\Sigma$.
H	Energy: -75.63732 Hartree, Gibbs free energy: -75.65357 Hartree Dipole: 1.8000. Symmetry: $C_{\infty v}$, Charge: -1, State: $^1\Sigma$.

I	Energy: -245.47510 Hartree, Gibbs free energy: -245.50390 Hartree Dipole: 2.0558. Symmetry: C_1, State: ^{1}A. Cartesian Coordinates:

C	-1.358844	0.102476	-0.020703
N	-2.394009	-0.395614	-0.115281
C	-0.030469	0.689794	0.097466
H	0.015869	1.286427	1.017563
H	0.176103	1.362885	-0.737708
C	1.085394	-0.361037	0.181409
O	2.198173	-0.142849	-0.208818
H	0.804222	-1.324619	0.648626

J	Energy: -168.31278 Hartree, Gibbs free energy: -168.33566 Hartree Dipole: 2.4807. Symmetry: C_s, State: ^{1}A'. Cartesian Coordinates:

C	0.000000	0.049865	0.000000
O	-0.515817	1.094973	0.000000
N	0.395621	-1.095300	0.000000
H	1.357192	-1.391872	0.000000

K1	Energy: -268.32246 Hartree, Gibbs free energy: -268.35493 Hartree Dipole: 3.9302. Symmetry: C_1, State: ^{1}A. Cartesian Coordinates:

C	-2.706993	-0.496851	0.017744
H	-2.357099	-1.531006	-0.099293
H	-3.321294	-0.475128	0.935169
H	-3.406458	-0.306090	-0.815202
C	-0.235064	0.034979	-0.060281
C	-1.536163	0.447098	0.051529
H	-1.736534	1.512132	0.162860
O	0.844418	0.737805	-0.051302
H	-0.110349	-1.068656	-0.174964
O	3.177257	-0.444544	-0.051964
H	3.360941	-0.388169	0.889313
H	2.266708	-0.000522	-0.125704

Table S1-7 Continued.

	Energy: -268.32476 Hartree, Gibbs free energy: -268.35796 Hartree, Dipole: 2.9183. Symmetry: C_1, State: ^{1}A.

Cartesian Coordinates:

C	-1.926990	1.891692	0.227157
H	-1.020987	2.504903	0.229247
H	-2.577424	2.266711	-0.580760
H	-2.463028	2.091257	1.170392
C	-0.242916	0.025999	-0.065571
C	-1.541953	0.447354	0.056599
H	-2.326099	-0.306233	0.023737
O	0.834117	0.736494	-0.057003
H	-0.118898	-1.072426	-0.187328
O	3.177411	-0.427876	-0.046338
H	3.348580	-0.381521	0.897856
H	2.264658	0.009167	-0.126211

K2

Energy: -152.53634 Hartree, Gibbs free energy: -152.56244 Hartree Dipole: 3.2308. Symmetry: C_1, State: ^{1}A.

Cartesian Coordinates:

H	1.798901	0.767356	-0.299289
O	-1.517976	0.000140	-0.119864
H	-1.891210	-0.000936	0.765824
O	1.374223	-0.000099	0.097988
H	1.798976	-0.766756	-0.300735
H	-0.556648	0.000011	0.009202

L

Energy: -151.94655 Hartree, Gibbs free energy: -151.97057 Hartree Dipole: 2.2031. Symmetry: C_1, Charge: -1, State: ^{1}A.

Cartesian Coordinates:

H	-0.117403	-0.039734	-0.077778
O	1.236343	0.096420	-0.061885
O	-1.233725	-0.100702	-0.049039
H	-1.473728	0.679528	0.458801
H	1.570182	-0.605538	0.506375

M

Energy: -393.96106 Hartree, Gibbs free energy: -393.99198 Hartree Dipole: 7.4392. Symmetry: C_1, State: ^{1}A.

Cartesian Coordinates:

C	1.185736	-0.530651	0.000159
O	2.215502	-1.177460	0.001128
N	1.281479	0.894191	0.000156
H	2.221621	1.263172	0.000831
H	0.394537	2.778180	0.001545
N	-0.081766	-1.048569	0.002373
H	-1.925590	1.815507	-0.005814
C	-1.130192	-0.251642	-0.001497
C	-1.047727	1.185699	0.000330
C	0.202368	1.712056	0.001013
N	-2.355225	-0.841992	-0.028757
H	-2.391304	-1.845105	0.062874
H	-3.195810	-0.310252	0.115110

4

Table S1-7 Continued.
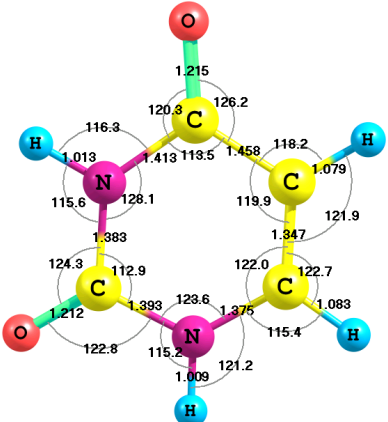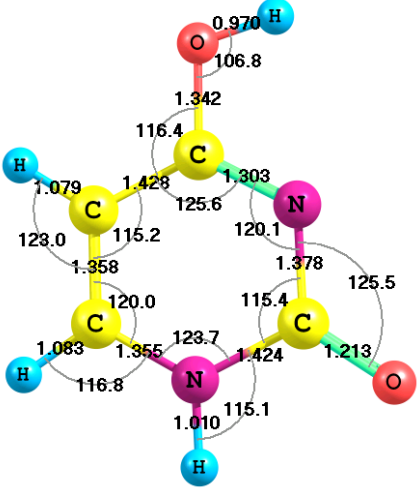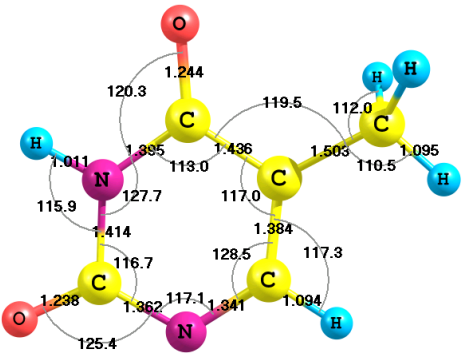
8	Energy: -413.83964 Hartree, Gibbs free energy: -413.87013 Hartree Dipole: 5.0698. Symmetry: C_1, State: ^{1}A. Cartesian Coordinates:

C	-0.363242	1.373763	-1.016098
O	0.834910	1.227329	-1.128083
N	-1.025152	2.526230	-1.434764
H	-0.434954	3.236671	-1.840882
H	-2.756192	3.656407	-1.684949
N	-1.215792	0.432589	-0.467583
H	-4.249852	1.916672	-0.683454
H	-0.776765	-0.422573	-0.148884
C	-2.615605	0.517121	-0.298157
O	-3.228628	-0.403247	0.205172
C	-3.184496	1.771591	-0.776156
C	-2.382247	2.709743	-1.315699

8a

Energy: -413.82191 Hartree, Gibbs free energy: -413.85227 Hartree

Dipole: 5.5725. Symmetry: C_1, State: ^{1}A.

Cartesian Coordinates:

C	-0.422045	1.304179	-0.975966
O	0.779120	1.195366	-1.104172
N	-1.061307	2.497475	-1.417527
H	-0.445584	3.190676	-1.819297
H	-2.762309	3.666209	-1.688767
N	-1.256938	0.355150	-0.426956
H	-4.267563	1.895303	-0.670204
H	-2.725956	-1.103740	0.443874
C	-2.537131	0.582889	-0.338973
O	-3.312062	-0.369951	0.202433
C	-3.201127	1.770351	-0.772460
C	-2.394796	2.717572	-1.317592

39

Energy: -452.49515 Hartree, Gibbs free energy: -452.52756 Hartree

Dipole: 4.5829. Symmetry: C_1, State: ^{1}A, Charge: -1.

Cartesian Coordinates:

C	-1.832882	-2.327827	-0.000031
N	-0.423990	-2.205089	0.000245
C	0.329619	-1.031611	0.000276
C	-0.479477	0.154618	-0.000010
C	-1.852393	-0.021484	-0.000270
N	-2.547362	-1.168508	-0.000294
H	-2.472968	0.879457	-0.000488
O	-2.315946	-3.467366	-0.000013
O	1.572401	-1.083768	0.000534
C	0.184527	1.502481	-0.000012
H	0.828588	1.642721	0.877078
H	0.828924	1.642555	-0.876881
H	-0.566593	2.299873	-0.000232
H	0.095466	-3.072404	0.000440

. **Table S1-7** Continued.
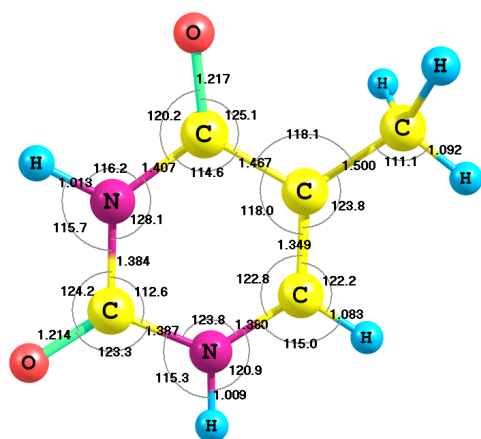
40	Energy: -453.03143 Hartree, Gibbs free energy: -453.06399 Hartree Dipole: 4.9734. Symmetry: C_1, State: ^1A.

Cartesian Coordinates:

C	-1.795962	-2.395693	-0.000002
N	-0.421360	-2.231830	0.000220
C	0.310050	-1.029583	0.000233
C	-0.511769	0.186079	-0.000024
C	-1.853564	0.044682	-0.000241
N	-2.476340	-1.186467	-0.000234
H	-2.523706	0.895880	-0.000438
O	-2.353677	-3.473506	0.000004
O	1.526936	-1.052214	0.000446
C	0.188171	1.512775	-0.000011
H	0.832974	1.612338	0.877150
H	0.833605	1.612011	-0.876741
H	-0.529971	2.335159	-0.000416
H	-3.482525	-1.258524	-0.000397
H	0.122526	-3.085984	0.000395

Table S1a. Energies and selected geometries of transition states, intermediates and product for reaction in Fig.1a. Level of theory used CCSD(T)/6-311++G(d,p)//B3LYP/6-311++G(d,p). Relative energies in kJ mol^{-1} with respect to [**A+B**] (see **Table S1-7**) (0 kJ mol^{-1}).
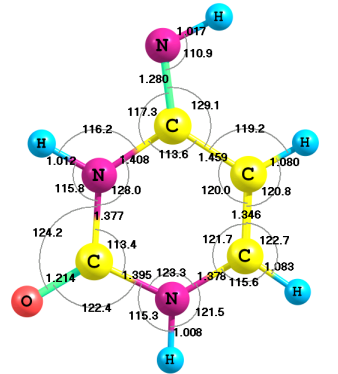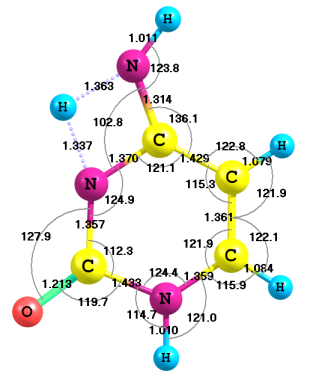
	TS 1/2	2	TS 2/3	3	TS 3/4
Symmetry	C_1	C_1	C_1	C_1	C_1
ΔH (0 K)	87	-200	87	-391	-223
ΔG (298 K)	134	-154	138	-337	-169
Cartesian coordiantes	C -1.221044 -0.434854 -0.229792	C -0.647147 1.562172 -0.587888	C 1.279105 0.575643 0.214887	C -0.046802 1.712432 0.000001	C 0.152178 1.735236 0.000020
	O -0.271197 -1.104123 -0.694175	O 0.512940 1.244055 -0.772524	O 2.412771 0.980255 0.296045	H -0.178836 2.786908 0.000000	H 0.362834 2.798216 0.000096
	N -1.827120 -0.820144 0.950817	N -1.185945 1.884081 0.611861	N 0.153891 1.398332 -0.158613	C 1.165447 1.128413 -0.000003	C -1.118982 1.249278 -0.000022
	H -1.651336 -1.764986 1.252515	H -0.574137 1.859529 1.410673	H -0.587117 0.542228 -0.969016	C 1.275152 -0.326107 0.000000	C -1.227796 -0.175884 -0.000078
	H -2.740243 -0.441674 1.147286	H -2.158580 2.143952 0.707124	H 0.415723 2.374986 -0.293474	N 2.325966 -1.056341 -0.000009	N -2.209300 -1.049932 0.000057
	N -1.664570 0.754312 -0.726377	N -1.528250 1.608733 -1.694642	N 0.852870 -0.727899 0.360351	H -2.114227 1.412501 -0.000003	H 2.172105 1.291801 0.000071
	H -0.932989 1.924175 0.049967	H -3.220184 1.859316 -2.815362	H -0.536502 -2.032306 -0.523630	N -1.207799 0.970960 0.000006	N 1.235375 0.915091 -0.000001
	H -1.219045 0.875107 -1.636078	H -1.050392 1.357226 -2.548232	H 1.585898 -1.422467 0.428725	H 2.066633 1.724129 -0.000004	H -1.978481 1.901611 0.000033
	C 1.856635 0.053825 0.125233	C -4.760522 2.651366 -0.222920	C -1.060373 1.083914 0.655452	C -1.224967 -0.423598 0.000001	C 1.166284 -0.516534 -0.000001
	C 1.185728 1.169859 0.335913	C -3.694428 2.291016 -0.816141	C -1.492043 -0.165125 0.030345	O -2.257885 -1.061451 -0.000014	O 2.189863 -1.168032 0.000046
	C 0.191728 1.916016 0.325617	C -2.860393 1.929309 -1.789004	C -0.456032 -1.056691 -0.050025	N 0.031611 -0.985786 0.000016	N -0.112488 -0.971430 -0.000125
	N 2.659841 -0.826468 0.026891	N -5.812485 3.003775 0.315060	N -1.463291 1.904874 1.519536	H 3.166427 -0.483241 -0.000007	H -3.187865 -0.797394 0.000203
	H 2.457849 -1.742614 -0.361426	H -5.803014 3.159381 1.320394	H -2.336137 1.576671 1.935200	H 0.061653 -1.997351 0.000049	H -1.112709 -1.858658 0.000208

Table S1b. Energies and selected geometries of transition states, intermediates and product for reaction in Fig.1b. Level of theory used CCSD(T)/6-311++G(d,p)//B3LYP/6-311++G(d,p). Relative energies in kJ mol^{-1} with respect to [**A+C**] (see **Table S1-7**) (0 kJ mol^{-1}).

	TS 5/6	6	TS 6/7	7	TS 7/8
Symmetry	C_1	C_1	C_1	C_1	C_1
ΔH (0 K)	106	-161	43	-195	87
ΔG (298 K)	151	-130	90	-150	138
Cartesian coordinates	C -0.002623 -0.108751 0.118516 O 0.280097 -0.194173 1.282035 N 1.385855 -0.087807 -0.821582 H 2.136252 -0.068302 -0.127784 H 1.372235 0.797140 -1.332163 N -1.064609 0.045173 -0.624545 H -1.140893 -0.452410 -1.935000 H -1.908200 0.025186 -0.057013 C 1.741445 -1.227907 -1.850202 C 0.685076 -1.310099 -2.770943 C -0.520235 -1.065508 -2.843848 O 2.770561 -1.800195 -1.664756	C -0.671615 0.204387 -0.274726 O -1.615875 0.667570 0.221886 N 3.546439 -0.316182 -0.613918 H 4.261101 0.103293 -0.039070 H 2.571464 -0.121746 -0.426000 N 0.389474 -0.209512 -0.696506 H 1.329427 -2.698556 -3.772096 H 0.507983 -0.834974 -1.483888 C 3.945172 -1.129166 -1.625753 C 2.854486 -1.703997 -2.420897 C 2.027809 -2.221597 -3.126353 O 5.106003 -1.387895 -1.887175	C -0.436004 0.730600 0.134083 O -0.252981 1.236037 1.199913 N 1.139808 0.548874 -0.691802 H 1.824510 0.659324 0.05652₄ H 1.185039 1.336873 -1.336944 N -1.316621 0.283126 -0.681939 H -1.751576 -0.432541 -2.908388 H -2.263604 0.307819 -0.316594 C 1.330449 -0.760830 -1.401421 C 0.406977 -0.873328 -2.481265 C -0.796934 -0.518319 -2.433252 O 2.122385 -1.538885 -0.941776	C 1.852634 0.171959 -0.000167 O 3.053915 -0.012783 -0.000310 N 1.229094 1.366941 0.00031₇ H 1.808986 2.190166 -0.000191 H 0.214314 1.426926 0.000251 N 0.996039 -0.972444 0.000082 H -0.677193 -2.125360 0.000018 H 1.539410 -1.825022 0.000342 C -2.526115 0.082653 -0.000155 C -1.242704 -0.062118 0.000408 C -0.358341 -1.082321 0.000104 O -3.655701 0.376630 -0.000234	C 1.155039 -0.342542 0.004837 O 2.162296 -0.994415 -0.130793 N 0.000684 -0.766287 0.733501 H -0.461124 0.407796 1.340586 H 0.102300 -1.706539 1.114623 N 0.971569 0.958458 -0.455184 H 0.091115 2.729009 0.256399 H 1.808299 1.411807 -0.800376 C -1.318507 -0.322390 -0.035774 C -1.304189 1.072873 0.338680 C -0.124504 1.689018 0.021543 O -2.011471 -1.101714 -0.598603
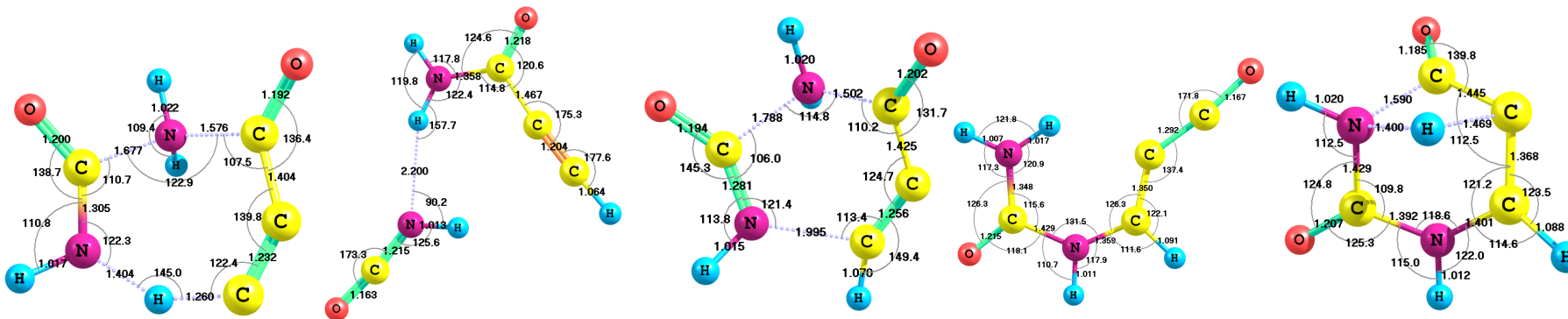
Table S2a. Energies and selected geometries of transition states, intermediates and product for reaction in Fig.2a. Level of theory used CCSD(T)/6-311++G(d,p)//B3LYP/6-311++G(d,p). Relative energies in kJ mol^{-1} with respect to [**A+C+E**] (see **Table S1-7**) (0 kJ mol^{-1}).

	TS 9/10	10	TS 10/11	11	TS 11/12
Symmetry	C_1	C_1	C_1	C_1	C_1
ΔH (0 K)	83	-102	-75	-425	-362
ΔG (298 K)	159	-13	20	-335	-267

	TS 9/10			10			TS 10/11			11			TS 11/12		
	C -1.362755	-0.654001	-0.250063	C -0.759471	-0.382395	0.150832	C 0.514927	1.376468	0.055788	C -2.065262	-0.337006	-0.427215	C 0.465277	1.396073	0.028517
	O -0.789097	-1.563063	-0.879383	O -1.291069	-1.456651	0.040566	O 0.192341	2.504770	0.345379	H -2.680087	0.054877	-1.227592	O 0.292567	2.518812	0.453588
	N -1.785879	-0.840780	1.047066	N 0.681583	-0.323527	0.623472	N -0.329925	0.233088	0.411102	C -1.047137	0.357833	0.115432	N -0.522761	0.479543	-0.215929
	H -1.763156	-1.790727	1.400138	H 1.149541	-1.234940	0.419357	H -1.282857	0.562808	0.567465	C -0.261448	-0.232227	1.188640	H -1.701769	0.643391	-0.067510
	H -2.497901	-0.222383	1.400074	H 0.666901	-0.189659	1.638113	H 0.165245	-0.553171	1.415950	N 0.734285	0.297644	1.812075	H -2.373737	-0.900467	-0.541591
	N -1.586553	0.609704	-0.735101	N -1.251463	0.846975	-0.052463	N 1.647877	0.988352	-0.592303	H -3.148456	-2.119029	-0.396496	N 1.770508	0.932540	-0.256670
	H -0.855910	1.824313	0.087841	H -1.163812	2.922465	0.260445	H 3.094251	-0.543352	-0.689578	N -2.386098	-1.598442	0.009471	H 3.081978	-0.549164	-0.901621
Cartesian	H -1.238165	0.630546	-1.693422	H -2.221555	0.878625	-0.339105	H 2.292313	1.733543	-0.819222	H -0.803468	1.350197	-0.234764	H 2.508491	1.599901	-0.086305
coordinates	C 2.551311	0.636728	0.208899	C 1.488827	0.885366	0.006617	C -0.258007	-0.843439	-0.613657	C -1.694871	-2.256601	1.031478	C -0.305414	-0.787468	-0.679538
	C 1.359836	1.163994	0.192850	C 0.840064	2.129818	0.154276	C 1.103403	-1.379696	-0.655102	O -2.001707	-3.371162	1.397842	C 1.045626	-1.209596	-0.947262
	C 0.243779	1.710859	0.238970	C -0.494802	2.077095	0.132694	C 2.017896	-0.395158	-0.695654	N -0.658464	-1.520927	1.561958	C 2.038905	-0.318044	-0.723788
	N 3.598579	0.059936	0.153304	H 3.145073	-2.835354	0.068821	H 1.044198	-1.890987	0.935121	H 0.942076	1.226985	1.458803	H 1.253240	-2.202652	-1.317325
	H 4.496403	0.309470	0.551755	O 2.466995	-2.237215	-0.256444	O 0.639841	-1.540700	1.877964	H -0.115808	-1.968528	2.307228	O -2.949364	0.212816	-0.193041
	H -0.756001	-3.093759	0.075822	H 2.893737	-1.386963	-0.504534	H 1.364026	-1.371735	2.495304	H 1.480938	-0.905885	3.079605	H -3.489516	0.213291	0.602317
	O -0.901663	-3.690333	0.843286	N 2.592403	0.489719	-0.499626	N -1.346725	-1.153415	-1.179512	O 1.464939	-1.803501	3.478356	N -1.383179	-1.526104	-0.843574
	H -1.260458	-4.505194	0.482043	H 3.114740	1.300178	-0.829701	H -1.192107	-1.946681	-1.803680	H 1.527962	-1.689915	4.430602	H -1.264754	-2.463062	-1.198816

Table S2b. Energies and selected geometries of transition states, intermediates and product for reaction in Fig.2b. Level of theory used CCSD(T)/6-311++G(d,p)//B3LYP/6-311++G(d,p). Relative energies in kJ mol^{-1} with respect to [**A+C+E**] (see **Table S1-7**) (0 kJ mol^{-1}).
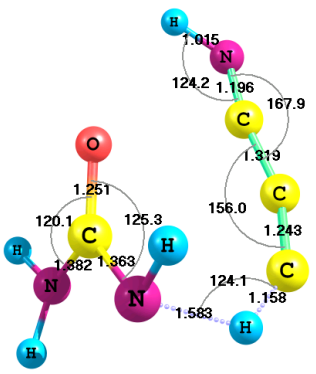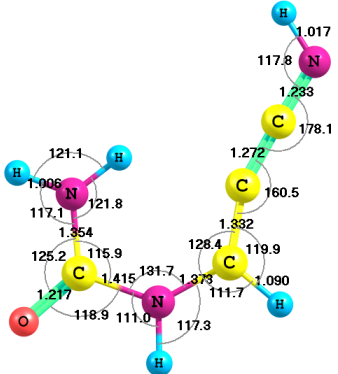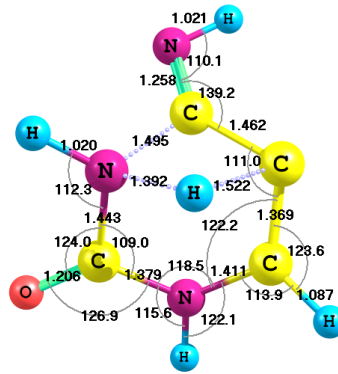

	TS 9/10	10	TS 10/11
Symmetry	C$_1$	C$_1$	C$_1$
ΔH (0 K)	82	-193	17
ΔG (298 K)	162	-126	97
Cartesian coordiantes	C 0.050115 -0.134905 0.036139	C -0.145336 0.628730 0.096131	C -0.365861 0.749606 0.057618
	O 0.321536 -0.270600 1.213529	O -0.286212 1.032259 1.181164	O -0.185917 1.264218 1.137988
	N 1.413141 -0.094734 -0.861274	N 2.602852 0.101889 -2.946227	N 1.167189 0.529390 -0.713245
	H 2.163444 -0.087510 -0.167103	H 3.099206 0.956616 -3.148526	H 1.845330 0.641850 0.041272
	H 1.408591 0.792254 -1.368705	H 1.904017 0.098696 -2.210853	H 1.242611 1.302826 -1.374027
	N -1.019184 0.051437 -0.679571	N 0.120734 0.259915 -1.026646	N -1.278548 0.336054 -0.732524
	H -1.115624 -0.436214 -2.021428	H 1.117983 -4.175581 -2.932467	H -1.690916 -0.468811 -2.984740
	H -1.851934 0.013413 -0.086482	H -0.495257 -0.248893 -1.672388	H -2.210833 0.433074 -0.326598
	C 1.776250 -1.238043 -1.911771	C 2.887120 -0.982090 -3.709365	C 1.365785 -0.800596 -1.403771
	C 0.722090 -1.311838 -2.831958	C 2.128477 -2.192351 -3.367806	C 0.458935 -0.928503 -2.492437
	C -0.478463 -1.044022 -2.900142	C 1.579902 -3.239433 -3.139510	C -0.736801 -0.566227 -2.513670
	O 2.811342 -1.795647 -1.727408	O 3.702016 -0.998339 -4.615173	O 2.156254 -1.563781 -0.921750
	O -2.452697 -0.326226 1.939543	O -1.143877 -1.327688 -3.003672	O -3.072606 1.319618 1.490275
	H -1.506386 -0.346161 2.149807	H -1.641393 -1.037263 -3.774865	H -2.163331 1.468714 1.790887
	H -2.896389 0.048720 2.705238	H -0.383777 -1.823801 -3.340532	H -3.577836 1.081274 2.272712
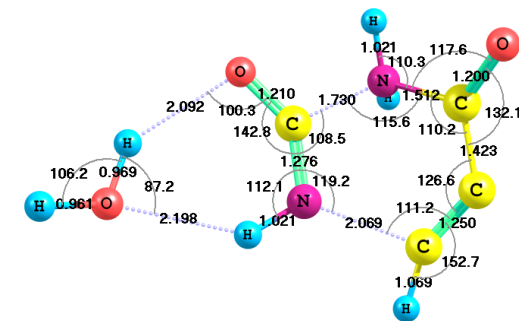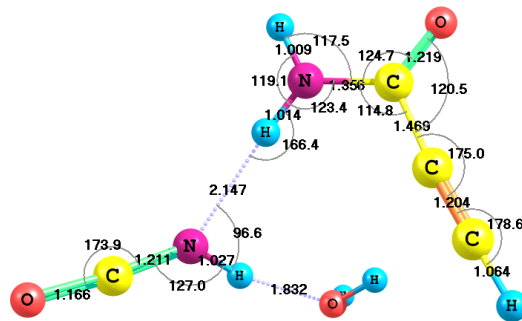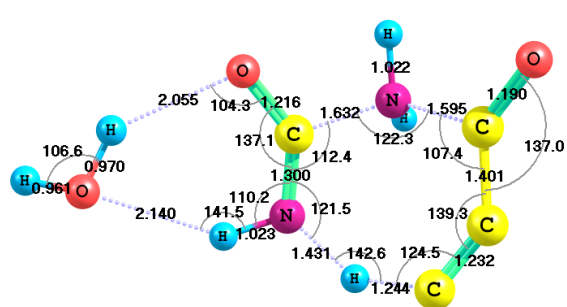
Table S2b Continued.

11
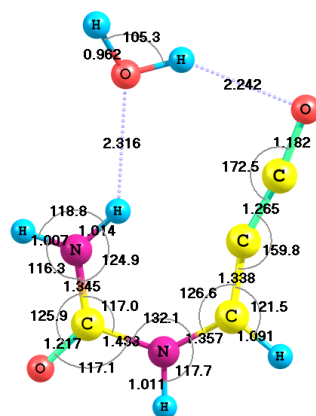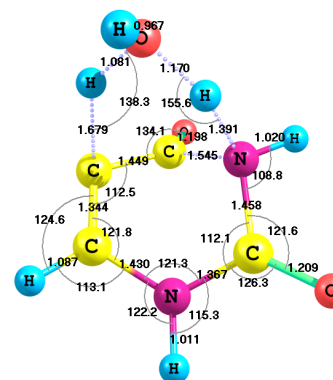
TS 11/12

|	11	TS 11/12
Symmetry	C_1	C_1
ΔH (0 K)	-207	-30
ΔG (298 K)	-131	62
Cartesian coordiantes	C -1.283105 0.848554 -0.029782	C 0.510239 1.383976 0.055912
	O -2.387944 1.358124 -0.063912	O 0.194204 2.520420 0.321558
	N -0.110547 1.506808 -0.026356	N -0.327089 0.251180 0.431951
	H 0.802246 1.065041 -0.001571	H -1.274118 0.587093 0.606499
	H -0.161829 2.511308 -0.080222	H 0.180066 -0.568846 1.434518
	N -1.225040 -0.582862 0.015302	N 1.642029 0.991801 -0.602360
	H -0.516098 -2.489636 0.044224	H 3.082608 -0.546487 -0.661021
	H -2.159336 -0.970102 0.025159	H 2.282236 1.736133 -0.843204
	C 2.374867 -1.279607 -0.022917	C -0.266161 -0.858012 -0.642403
	C 1.118112 -1.135466 -0.006503	C 1.089702 -1.368710 -0.661965
	C -0.182321 -1.450772 0.018466	C 2.008000 -0.387838 -0.693431
	O 3.556179 -1.259032 -0.041208	H 1.024047 -1.895000 0.931248
	H 3.511165 2.393603 0.544795	O 0.637307 -1.549653 1.879436
	O 3.010078 1.765216 0.016517	H 1.365249 -1.395783 2.496770
	H 3.573405 0.982760 -0.052546	O -1.283375 -1.171151 -1.191273

Table S3a. Energies and selected geometries of transition states, intermediates and product for reaction in Fig.3a. Level of theory used CCSD(T)/6-311++G(d,p)//B3LYP/6-311++G(d,p). Relative energies in kJ mol^{-1} with respect to [**A+B+E**] (see **Table S1-7**) (0 kJ mol^{-1}).
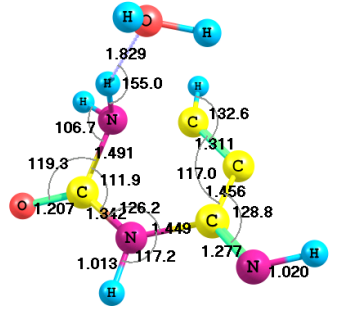
	TS 17/18	18	TS 18/19	19
Symmetry	C_1	C_1	C_1	C_1
ΔH (0 K)	-16	-244	-110	-110
ΔG (298 K)	73	-163	-25	-26
Cartesian coordinates	C -1.641522 -0.329311 -0.136158	C 1.663753 0.189183 0.106307	C 1.256142 -0.664453 -0.156771	C 0.548800 -0.856157 -0.405780
	O -2.197920 -1.284049 -0.628067	O 2.864605 0.019425 0.212716	O 2.342379 -1.138621 -0.394054	O 1.530402 -1.389503 -0.862481
	N -2.161073 0.584387 0.700690	N 1.017901 1.349163 0.413408	N 1.147584 0.629831 0.533877	N 0.683198 0.467377 0.267064
	H -3.157743 0.531924 0.848569	H 0.170298 1.624738 -0.073844	H 0.902999 1.372526 -0.144060	H 0.422331 1.209793 -0.410762
	H -1.666968 1.475691 0.783692	H 1.637288 2.095656 0.689664	H 2.052272 0.828895 0.960285	H 1.667400 0.571015 0.518500
	N -0.193058 -0.188855 -0.395902	N 0.862838 -0.868710 -0.374307	N 0.050688 -1.179270 -0.480419	N -0.726679 -1.273367 -0.440218
	H 2.207445 -1.425396 0.320727	H -2.667530 0.455665 2.272504	H 0.113522 1.287089 2.428908	H 0.160552 1.268783 2.245990
	H -0.053373 -0.511945 -1.354971	H 1.409058 -1.596207 -0.818166	H 0.065768 -2.014032 -1.054231	H -0.913374 -2.112616 -0.976735
	C 0.617066 1.059036 -0.194533	C -0.465924 -1.223323 -0.189819	C -1.237098 -0.774198 0.028951	C -1.839655 -0.685957 0.277079
	C 1.980155 0.732247 -0.316484	C -1.270332 -0.494797 0.761610	C -1.251743 -0.000778 1.261669	C -1.528544 0.119101 1.449879
	C 2.964163 -0.005202 -0.142993	C -2.027432 0.002243 1.554128	C -0.191655 0.655964 1.609563	C -0.334039 0.656211 1.504249
	H 1.319753 -2.186066 1.474060	H -2.187473 1.547201 -0.769353	H -1.070895 2.434336 -0.649122	H -1.474512 2.456875 -0.598560
	O 1.334137 -1.970057 0.532326	O -1.494564 2.162846 -1.033511	O -0.200876 2.546988 -1.052317	O -0.692280 2.448726 -1.164922
	H 0.514784 -1.180503 0.208204	H -1.617528 2.316056 -1.975908	H -0.351704 2.599996 -2.001899	H -1.017605 2.471828 -2.070988
	N 0.005434 2.132428 0.119692	N -0.913566 -2.238015 -0.836134	N -2.228675 -1.185387 -0.661877	N -2.982850 -0.989022 -0.204499
	H 0.668074 2.892792 0.255293	H -1.875036 -2.438182 -0.572651	H -3.085047 -0.931173 -0.170459	H -3.696022 -0.612016 0.419546

Table S3a Continued.
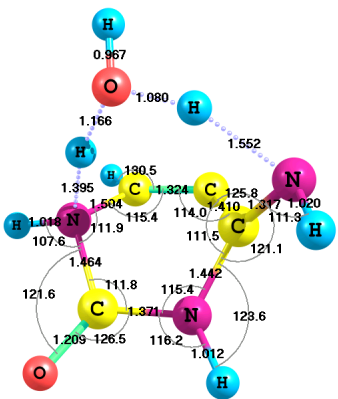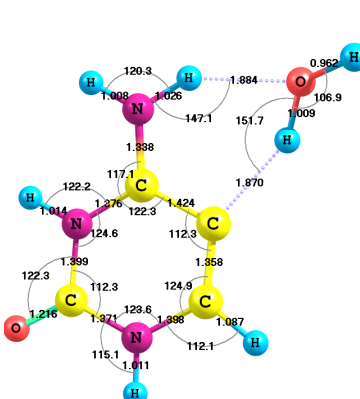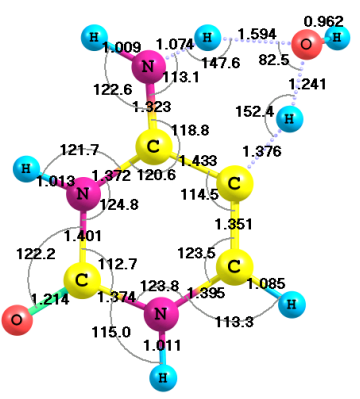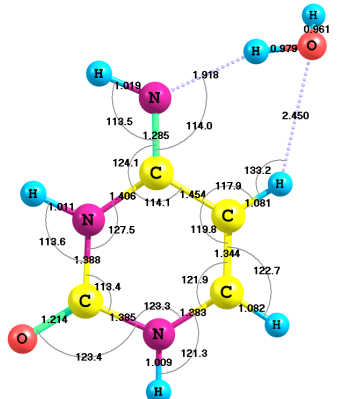
	TS 19/20	20	TS 20/21	21
Symmetry	C_1	C_1	C_1	C_1
ΔH (0 K)	-38	-267	-253	-412
ΔG (298 K)	58	-177	-159	-326
Cartesian coordinates	C -0.680081 -0.814654 0.191303	C -0.824768 -0.047759 0.199753	C -1.209212 -0.652544 -0.001120	C -1.960539 -0.216934 -0.018997
	O -1.664759 -1.376448 0.610320	O -1.535507 -1.029429 0.294842	O -2.237140 -1.297642 -0.013440	O -3.079900 -0.685617 -0.033581
	N -0.710986 0.593586 -0.206974	N 0.560046 -0.142136 0.028333	N 0.052910 -1.260089 -0.000664	N -0.811687 -0.994656 0.017830
	H 0.010875 1.313892 0.744550	H 2.519767 3.280939 -0.147222	H 2.612500 1.177983 0.011054	H 1.667535 1.304163 0.024745
	H -1.687243 0.865468 -0.302039	H 0.894047 -1.098944 -0.004978	H 0.014358 -2.272571 -0.013523	H -0.995867 -1.989114 0.030760
	N 0.580981 -1.343673 0.091753	N -1.255011 1.253317 0.243850	N -1.137546 0.719620 0.014291	N -1.702835 1.143729 -0.036993
	H -0.316964 1.403168 -2.195224	H -0.938768 3.296871 0.190401	H -0.081295 2.509895 0.032591	H -0.372958 2.755697 -0.042423
	H 0.726805 -2.239246 0.540995	H -2.251333 1.371693 0.368934	H -2.029759 1.194082 0.010730	H -2.517604 1.737398 -0.066234
	C 1.635574 -0.389170 -0.147136	C 1.409823 0.934951 -0.082561	C 1.247654 -0.584829 0.009180	C 0.522437 -0.551280 0.038747
	C 1.396096 0.362273 -1.316410	C 0.943857 2.279677 -0.038541	C 1.276829 0.848249 0.026402	C 0.667279 0.895278 0.015110
	C 0.171646 0.859381 -1.395199	C -0.401505 2.354271 0.128660	C 0.059928 1.434239 0.025996	C -0.426272 1.675212 -0.021706
	H 1.057309 2.673250 1.143308	H 3.717504 4.005621 -0.885575	H 4.365501 1.333819 0.574777	H 4.617990 0.021216 0.490595
	O 0.845521 1.770970 1.417663	O 3.524179 3.352094 -0.207192	O 3.816169 0.889090 -0.077296	O 3.894632 0.289531 -0.082082
	H 1.706332 1.144709 1.234939	H 3.339940 1.479779 -0.305060	H 3.251961 -0.599200 0.011233	H 3.226966 -0.424425 -0.020571
	N 2.516766 -0.100556 0.787856	N 2.712115 0.670766 -0.238151	N 2.393664 -1.245476 0.003561	N 1.540732 -1.334387 0.074618
	H 2.458238 -0.755735 1.567163	H 3.086758 -0.264646 -0.237320	H 2.441122 -2.252481 -0.030754	H 1.292801 -2.322332 0.077630

Table S3b. Energies and selected geometries of transition states, intermediates and product for reaction in Fig.3b. Level of theory used CCSD(T)/6-311++G(d,p)//B3LYP/6-311++G(d,p). Relative energies in kJ mol^{-1} with respect to [**A+C+E**] (see **Table S1-7**) (0 kJ mol^{-1}).

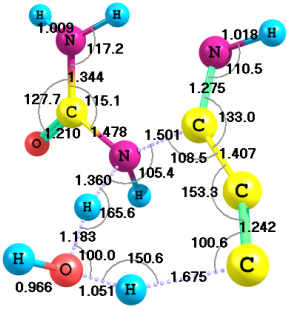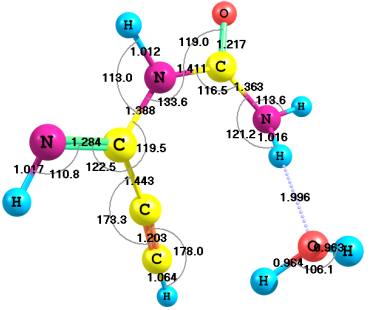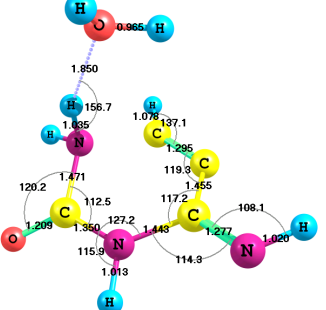|	TS 22/23	23	TS 23/24	24
Symmetry	C_1	C_1	C_1	C_1
ΔH (0 K)	31	-210	-62	-66
ΔG (298 K)	116	-133	20	19
Cartesian coordinates	C -0.041955　0.404052　-0.033567	C　1.641115　0.230911　0.114645	C　1.396060　-0.261424　-0.209698	C -1.116430　-0.800227　0.163104
	O　0.973314　-0.098592　-0.455142	O　2.837636　0.058614　0.235661	O　2.555936　-0.358042　-0.526546	O -2.111504　-1.336427　0.570883
	N -0.271339　0.843809　1.220309	N　0.977819　1.368858　0.433356	N　0.916021　0.941432　0.496339	N -1.222910　0.603274　-0.408964
	H 0.438189　0.619597　1.901770	H　0.092021　1.614015　0.001356	H　0.376804　1.540032　-0.154797	H -0.899057　1.246374　0.344332
	H -1.233590　0.955176　1.523628	H　1.559843　2.120868　0.767692	H　1.731151　1.443971　0.846403	H -2.212452　0.764884　-0.601358
	N -1.126244　0.675700　-0.989755	N　0.846947　-0.823470　-0.425506	N　0.397088　-1.141912　-0.453214	N　0.160876　-1.217506　0.164937
	H -1.809229　2.499520　-2.996680	H -2.685298　0.330403　2.298315	H -0.057155　1.143167　2.529295	H -0.804094　1.268944　-2.454546
	H -1.070231　-0.058199　-1.698369	H　1.407151　-1.508237　-0.919691	H　0.616696　-1.907593　-1.079549	H　0.375982　-2.036581　0.721849
	C -2.602657　0.854357　-0.588258	C -0.450514　-1.249557　-0.212971	C -0.970549　-1.062545　0.065346	C　1.252469　-0.332245　-0.301380
	O -2.927112　0.716334　0.566800	O -0.893796　-2.225114　-0.791097	C -1.085573　-0.430552　1.364153	C　0.942272　0.309023　-1.538053
	C -3.302527　1.265361　-1.729924	C -1.270021　-0.540186　0.757498	C -0.254773　0.505558　1.682725	C -0.274978　0.791332　-1.640345
	C -3.372474　1.995378　-2.734071	C -2.031364　-0.084971　1.569233	H -1.898967　1.868384　-0.588147	H 0.531974　2.710355　1.895582
	H -0.569420　3.405117　-2.410343	H -2.259822　1.515208　-0.877172	O -1.108911　2.223167　-1.014927	O 0.330202　1.810333　1.621970
	O -0.803687　2.509823　-2.689172	O -1.523903　2.116727　-1.036191	H -1.296597　2.223007　-1.959510	H 1.184654　1.363764　1.503252
	H -0.844490　1.721599　-1.805229	H -1.582045　2.371015　-1.962865	O -1.843860　-1.541852　-0.622367	O 2.228313　-0.230699　0.423600

Table S3b. Continued.

TS 24/25	25	TS 25/16
C$_1$	C$_1$	C$_1$
-13	-202	-203
80	-113	-111

TS 24/25	25	TS 25/16
C -0.677046 -0.773695 0.190680	C -1.880755 -0.219269 0.000817	C -1.184104 -0.671031 0.010922
O -1.640108 -1.321263 0.671740	O -2.996097 -0.695566 -0.001569	O -2.193381 -1.342500 0.011953
N -0.734436 0.602110 -0.285802	N -0.718989 -0.992474 0.004857	N 0.099336 -1.222338 0.007076
H 0.028593 1.310282 0.767827	H 2.659775 0.853571 -0.044157	H 2.755532 1.199408 -0.025340
H -1.710785 0.865281 -0.391807	H -0.857999 -1.997495 0.001093	H 0.145319 -2.235596 0.000225
N 0.600060 -1.281216 0.120285	N -1.596326 1.130756 0.000108	N -1.156393 0.709221 0.013808
H -0.341034 1.385069 -2.274781	H -0.302327 2.737909 -0.001338	H -0.177536 2.532814 0.010524
H 0.794383 -2.076586 0.717409	H -2.406659 1.736309 -0.005342	H -2.065352 1.152145 0.013601
C 1.633081 -0.335268 -0.209872	C 0.547468 -0.480956 0.005874	C 1.256177 -0.496166 0.002897
C 1.376012 0.361150 -1.390333	C 0.829297 0.902095 0.006315	C 1.256150 0.927029 0.006758
C 0.146727 0.854072 -1.464885	C -0.310008 1.651127 0.001760	C 0.008679 1.463105 0.010391
H 1.100247 2.549501 1.263222	O 1.473023 -1.411311 0.006791	O 2.347359 -1.191080 -0.004373
O 0.828046 1.645025 1.471657	H 4.057019 0.469528 0.633277	H 4.337360 1.057106 0.647315
H 1.653040 0.996966 1.295185	O 3.468657 0.240569 -0.093289	O 3.797986 0.770494 -0.097043
O 2.492002 -0.071283 0.677702	H 2.376723 -0.955324 -0.002353	H 3.162765 -0.472459 -0.016607

Table S4. Energies and Selected Geometries of Transition States, Intermediates and Product for Reaction in Fig.4. Level of theory used CCSD(T)/6-311++G(d,p)//B3LYP/6-311++G(d,p). Relative energies in kJ mol^{-1} with respect to [**A+D+E**] (see **Table S1-7**) (0 kJ mol^{-1}).

	TS 26/27	27	TS 27/28
Symmetry	C_1	C_1	C_1
ΔH (0 K)	99	-132	46
ΔG (298 K)	177	-65	121
Cartesian coordinates	C -1.877397 -0.451087 0.156931	C 1.482333 1.267519 0.414344	C -1.615008 -0.612525 -0.057750
	H -2.755248 0.121680 -0.093665	H 2.305095 1.628342 1.023673	H -2.042465 0.380165 0.030658
	C -0.608354 -0.484227 0.150654	C 1.710805 0.265271 -0.479373	C -0.440801 -0.811469 -0.670149
	C 0.398168 0.370398 -0.254291	C 2.995754 -0.305767 -0.640919	C 0.309474 0.271015 -1.205152
	N 1.301054 1.032804 -0.570645	N 4.034073 -0.803268 -0.776062	N 0.934975 1.136825 -1.647323
	H -3.666541 -1.818039 0.896653	H 0.206380 2.522603 1.394846	H -3.363993 -1.470444 0.510729
	N -2.652259 -1.916381 0.867545	N 0.303107 1.898326 0.612244	N -2.362194 -1.650298 0.548629
	H -2.277816 -1.918915 1.814268	H -0.555574 1.512111 0.234013	H -2.037555 -2.181455 1.615972
	C -2.347758 -3.170620 0.158964	C -3.215742 -0.107682 -0.368269	C -2.032722 -3.220177 0.222658
	O -3.266275 -3.801384 -0.330045	O -4.305784 -0.035638 -0.776263	O -2.070128 -3.670948 -0.894971
	N -1.040949 -3.451273 0.157202	N -2.069064 -0.058105 0.019579	N -1.784275 -3.539478 1.465809
	H -0.758208 -4.245050 -0.416202	H -1.531034 -0.814866 0.459906	H -1.542931 -4.510538 1.657107
	H -0.399465 -2.667635 0.305940	H 0.928078 -0.072527 -1.150274	H -0.025014 -1.805435 -0.789717
	H -1.509250 -6.212213 -2.299916	H -0.008036 -2.741619 1.222090	H -1.632476 -5.656008 -0.522573
	O -1.535002 -5.791319 -1.436088	O -0.161024 -1.791780 1.196041	O -1.444807 -6.286277 0.189571
	H -2.421180 -5.410607 -1.332519	H 0.673840 -1.389421 0.912498	H -0.957401 -7.010616 -0.212374

Table S4 Continued.
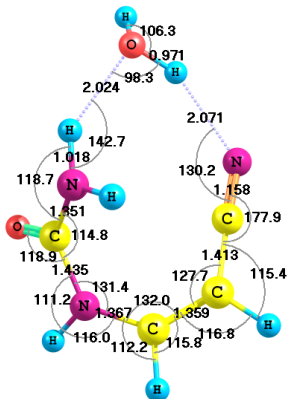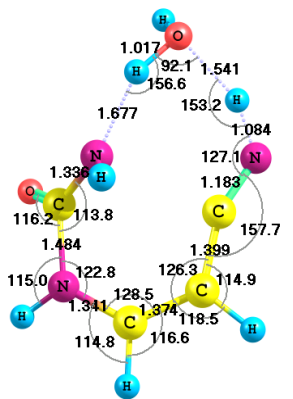
	28	TS 28/3
Symmetry	C_1	C_1
ΔH (0 K)	-156	30
ΔG (298 K)	-77	116
Cartesian coordinates	C -1.719528 -0.855035 -0.312514	C -1.824126 -0.903976 -0.334829
	H -2.207137 -0.698418 -1.269610	H -2.409006 -0.615403 -1.202383
	C -0.896678 0.143971 0.102695	C -0.937501 0.028376 0.147645
	C -0.248616 0.265745 1.352478	C -0.157889 -0.089612 1.303204
	N 0.287799 0.406330 2.369511	N 0.537509 0.258031 2.195009
	H -2.956935 -2.436306 -0.048980	H -2.937427 -2.581519 -0.169192
	N -2.080222 -2.041464 0.262702	N -2.084410 -2.131960 0.136832
	H -0.759163 0.977255 -0.574772	H -0.877128 0.990209 -0.348081
	C -1.594574 -2.715447 1.433358	C -1.540881 -2.630247 1.424687
	O -2.384935 -3.296524 2.146403	O -2.350602 -3.095942 2.204116
	N -0.251001 -2.706912 1.575064	N -0.229319 -2.422916 1.573740
	H 0.143607 -2.845081 2.502847	H 0.669006 -2.218642 2.975175
	H 0.327416 -2.204844 0.921627	H 0.244699 -2.397735 0.674136
	H 1.022401 -1.000467 3.700509	H 0.956303 -0.363859 2.977309
	O 1.209393 -1.919415 3.953428	O 1.234472 -1.718908 3.656215
	H 1.150064 -1.952386 4.912469	H 0.872830 -1.908973 4.528049

Table S5. Energies and selected geometries of transition states, intermediates and product for reaction in Fig.5. Level of theory used CCSD(T)/6-311++G(d,p)//B3LYP/6-311++G(d,p). Relative energies in kJ mol^{-1} with respect to [**A+E+I**] (see **Table S1-7**) (0 kJ mol^{-1}).
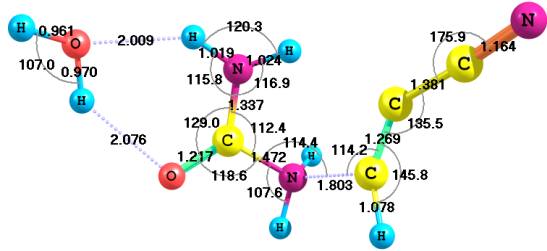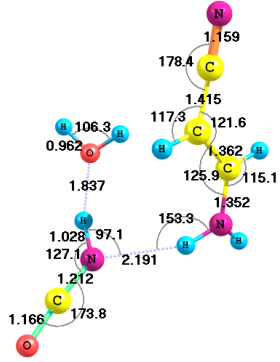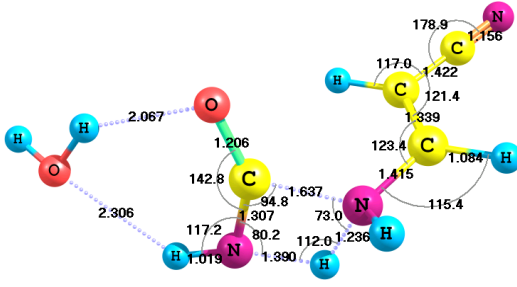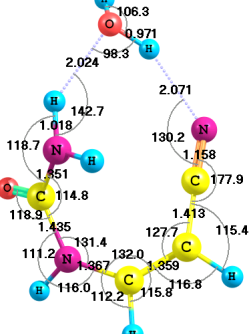

	TS 29/30	30	TS 30/31	31
Symmetry	C_1	C_1	C_1	C_1
ΔH (0 K)	51	-48	167	-15 [**26+E**]
ΔG (298 K)	145	35	256	33 [**26+E**]
Cartesian coordinates	C 0.225274 -0.732570 0.304462 N 1.084072 -1.469122 0.535428 H -3.567107 -1.911368 0.911907 N -2.348543 -2.013970 0.666060 H -1.784252 -1.871318 1.501238 C -2.123684 -3.310984 0.059829 O -2.948787 -3.761867 -0.703008 N -0.984395 -3.942531 0.450456 H -0.787345 -4.815158 -0.017364 H -0.185499 -3.410844 0.772700 C -0.951828 0.087511 0.059122 H -0.749097 0.816429 -0.728962 H -1.206030 0.649402 0.962543 C -2.210282 -0.721678 -0.380731 O -3.291404 0.016290 -0.340490 H -2.013074 -1.250942 -1.327098 H -5.318001 -1.981498 0.374364 O -4.727285 -1.427962 0.898508 H -4.269670 -0.639626 0.246752	C 1.271859 -1.825157 0.069872 N 1.434897 -2.924827 -0.237136 H -0.641471 1.647699 0.709068 N -1.002267 -0.232384 -1.038292 H -1.334275 0.234427 -1.873551 C -2.118277 -0.635726 -0.288521 O -3.247895 -0.364962 -0.645945 N -1.843044 -1.350067 0.866828 H -2.686327 -1.713697 1.290037 H -1.097796 -2.032624 0.813474 C 1.028344 -0.447985 0.483340 H 1.982447 0.066869 0.623803 H 0.517621 -0.457863 1.449772 C 0.214902 0.374997 -0.540341 O 0.005309 1.691798 -0.006801 H 0.844083 0.543410 -1.413946 H 1.794681 2.482005 0.342544 O 2.729233 2.303138 0.526416 H 3.209190 3.110188 0.321138	C 2.067298 -1.349397 -0.129454 N 2.942377 -2.027910 -0.469433 H -0.462084 2.307783 -0.306670 N -1.156840 -0.086059 -0.902105 H -1.555856 0.396347 -1.698720 C -2.178416 -0.305355 0.063050 O -3.236283 0.277875 -0.048135 N -1.897751 -1.202973 1.051942 H -2.682230 -1.438460 1.641367 H -1.212510 -1.925608 0.894819 C 1.022219 -0.475546 0.312798 H 1.694613 0.638270 0.841601 H 0.492805 -0.835821 1.187389 C 0.208495 0.088071 -0.764115 O 0.375154 1.947808 -0.627717 H 0.697661 0.114388 -1.729103 H 1.213954 2.081460 0.212969 O 1.982766 1.793801 1.100444 H 2.908475 1.977730 0.903117	See **Table S4**

Table S5 Continued.
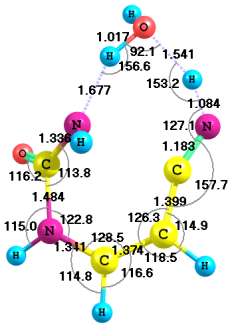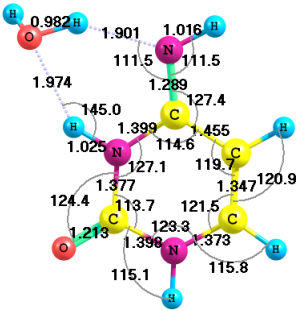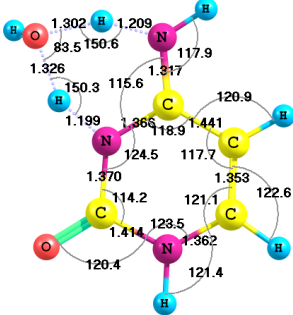
	TS 31/32	32	TS 32/33
Symmetry	C_1	C_1	C_1
ΔH (0 K)	171 [**TS 26/3 + E**]	-69 [**3+E**]	-6 [**TS 3/4 + E**]
ΔG (298 K)	226 [**TS 26/3 + E**]	-15 [**3+E**]	53 [**TS 3/4 + E**]
Cartesian coordinates	See **Table S4**	See **Table S4**	See **Table S4**

Table S6. Energies and selected geometries of transition states, intermediates and product for reaction in Fig.6. Level of theory used CCSD(T)/6-311++G(d,p)//B3LYP/6-311++G(d,p). Relative energies in kJ mol^{-1} with respect to [**F+8a**] (see **Table S1-7**) (0 kJ mol^{-1}).

	TS 34/35	35	TS 35/36
Symmetry	C_1	C_1	C_1
ΔH (0 K)	57	14	65
ΔG (298 K)	99	55	108
Cartesian coordinates	C -0.607206 1.080406 -1.391877	C -0.522352 1.188524 -1.333868	C -0.505813 1.191837 -1.143291
	O 0.534078 0.893755 -1.769624	O 0.652735 1.030986 -1.625203	O 0.706197 1.104592 -1.195411
	N -1.257807 2.294404 -1.692713	N -1.180267 2.380719 -1.619896	N -1.140298 2.424418 -1.332795
	H -0.692366 2.978664 -2.173226	H -0.609686 3.106190 -2.026935	H -0.527097 3.202422 -1.524943
	H -2.893425 3.588119 -1.521897	H -2.839199 3.650555 -1.421044	H -2.868941 3.582415 -1.533479
	N -1.325578 0.174170 -0.631570	N -1.245639 0.201801 -0.666020	N -1.323587 0.081536 -0.947116
	H -4.281046 1.866806 -0.290994	H -4.274934 1.868665 -0.387773	H -4.386503 1.655040 -1.006088
	H -2.516561 -0.983626 0.898335	H -2.327138 -0.767412 1.036456	H -1.737568 -0.262103 1.279992
	C -2.637446 0.392281 -0.380095	C -2.675347 0.320489 -0.513311	C -2.671223 0.273196 -0.728709
	O -3.159496 -0.300216 0.660774	O -3.029390 -0.163922 0.759424	O -2.289713 0.501937 1.046055
	C -3.271878 1.684149 -0.624892	C -3.257041 1.690288 -0.701044	C -3.311750 1.555065 -1.027421
	C -2.535206 2.594741 -1.283534	C -2.494502 2.639873 -1.244032	C -2.504379 2.588618 -1.307632
	N -3.188810 -0.653540 -1.880005	N -3.191098 -0.593072 -1.550512	N -3.433195 -0.861617 -0.895128
	H -2.927208 -0.169739 -2.744895	H -3.206906 -0.179393 -2.477373	H -4.373439 -0.820287 -0.529680
	H -2.611802 -1.500740 -1.851655	H -2.688292 -1.477346 -1.558307	H -2.948054 -1.725162 -0.692926

Table S7. Energies and selected geometries of transition states, intermediates and product for reaction in Fig.7 (Gauche Elimination).

Level of theory used CCSD(T)/6-311++G(d,p)//B3LYP/6-311++G(d,p). Relative energies in kJ mol^{-1} with respect to [2***J+K1**] (see **Table S1-7**) (0 kJ mol^{-1}).
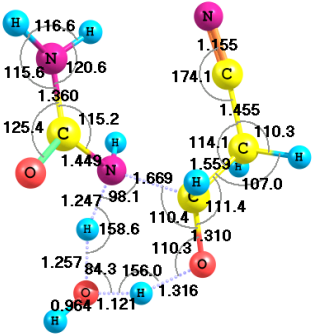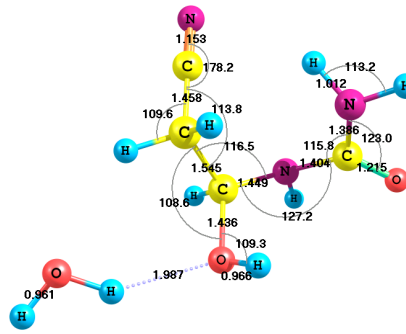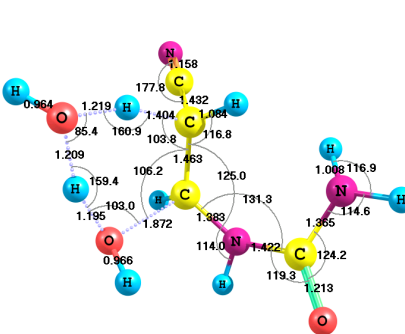

	TS 37/38	38	TS 38/39
Symmetry	C_1	C_1	C_1
ΔH (0 K)	7	-123	-103
ΔG (298 K)	47	-75	-15
Cartesian coordinates	N 2.437203 0.989345 -2.135762	N -0.422682 -1.428623 0.259791	C -0.254417 -0.290043 0.762653
	C 2.443622 1.018121 -0.906366	C 0.780003 -1.008663 -0.091483	N 1.604015 0.591083 -0.511540
	O 2.574753 0.819313 0.249298	O 1.833265 -1.660252 -0.280860	C 2.421016 1.635942 -0.514442
	H 2.684218 0.096361 -2.555892	H -0.383085 -2.444940 0.364404	N -0.871162 0.754428 0.998559
	C 1.643570 3.689244 0.844121	C 2.147654 1.104256 0.324968	O 0.137944 -1.391415 0.679237
	H 0.701855 3.410887 1.333731	H 2.097689 1.060281 1.419032	O 3.669560 1.665068 -0.460741
	H 2.425805 3.057246 1.286987	H 2.984232 0.478667 0.007165	H -1.740085 0.605665 1.504697
	H 1.864493 4.726973 1.144551	H 2.329023 2.143764 0.030473	H 2.175672 -0.254139 -0.455100
	C 0.310934 3.283285 -1.265096	C -0.342361 1.225955 0.263098	C 1.530267 3.604632 0.821223
	C 1.526916 3.524024 -0.646677	C 0.864584 0.544548 -0.307283	H 0.845622 2.984993 1.405649
	H 2.353181 3.862037 -1.268886	H 0.876988 0.723393 -1.387816	H 2.501893 3.617701 1.321665
	O 0.029162 3.312224 -2.504312	O -1.161584 1.870471 -0.366753	H 1.140901 4.628983 0.794726
	H -0.512652 3.012355 -0.561883	H -0.447926 1.125487 1.363415	C 0.390993 2.897929 -1.294770
	O -2.180531 2.168683 -3.426189	O -3.160251 -0.660783 0.060329	C 1.705787 3.028339 -0.596990
	H -1.798147 1.320462 -3.665940	H -2.211996 -0.944239 0.134239	H 2.351067 3.682034 -1.188898
	H -1.389624 2.667737 -3.058953	H -3.076877 0.265887 -0.186978	O 0.131359 3.422242 -2.373167
			H -0.361207 2.283429 -0.776947
			O -2.257461 2.651424 -3.650584
			H -2.131384 1.699547 -3.601209
			H -1.448911 3.009657 -3.227179

Table S7 Continued.

	39	TS 39/40	40
Symmetry	C_1	C_1	C_1
ΔH (0 K)	-238	-130	
ΔG (298 K)	-138	-21	
Cartesian coordinates	C -1.186619 1.483967 0.075856 N -1.878683 0.376724 -0.479605 C -1.463542 -0.942899 -0.533541 N 0.087671 1.212267 0.383251 O -1.786879 2.547628 0.231408 O -2.195198 -1.797440 -1.016005 H 0.651297 1.965313 0.748812 H -2.824213 0.571767 -0.778413 C -0.221610 -1.630964 1.536956 H -0.706860 -0.849975 2.128965 H -0.795141 -2.556401 1.639150 H 0.787222 -1.769580 1.929975 C 0.879698 -0.012312 -0.118162 C -0.096737 -1.219521 0.061371 H 0.320601 -2.057749 -0.502583 O 2.030227 -0.115634 0.514430 H 0.975527 0.155790 -1.219300 O 4.288476 0.156424 -0.804288 H 4.552670 1.024590 -0.489284 H 3.415834 -0.004141 -0.322079	C -1.266289 1.607762 0.036581 N -1.892718 0.542860 -0.617359 C -1.575882 -0.841794 -0.410245 N -0.014507 1.303410 0.497095 O -1.814952 2.699519 0.169199 O -2.498008 -1.648186 -0.521696 H 0.554994 2.104613 0.733109 H -2.863267 0.719673 -0.841478 C -0.085821 -1.864295 1.287862 H -0.319955 -1.238090 2.160954 H -0.786445 -2.702886 1.276516 H 0.921217 -2.263836 1.429850 C 0.645369 0.165913 -0.156513 C -0.192181 -1.104322 -0.040555 H 0.638806 -1.825725 -0.874660 O 1.940493 0.031344 0.383799 H 0.738727 0.406851 -1.228821 O 1.758794 -2.143038 -1.352163 H 1.860462 -3.093878 -1.245277 H 2.289655 -0.752903 -0.094807	C -0.920892 1.125387 0.406878 N 0.220050 1.536834 -0.204320 C 1.483645 0.820951 -0.266071 N -0.807146 -0.094882 1.042141 O -1.977608 1.772392 0.417768 O 2.449870 1.481558 -0.710018 H -1.702644 -0.449061 1.348190 H 0.220786 2.459729 -0.611324 C 2.672932 -1.347767 0.200193 H 2.660851 -2.189437 -0.509937 H 3.532706 -0.722993 -0.052289 H 2.854097 -1.785631 1.195283 C 0.148092 -1.087801 0.600098 C 1.428922 -0.501769 0.167466 H -3.149036 0.012346 -0.560687 O -0.514863 -1.919114 -0.478035 H 0.267904 -1.819565 1.404642 O -3.315185 -0.910609 -0.800978 H -2.436329 -1.327955 -0.764374 H -0.049171 -1.659842 -1.283709

Table S7 Continued.

	TS 40/41	41	42
Symmetry	C_1	C_1	C_1
ΔH (0 K)	-169	[**39+L**]	-79 [**40+M**]
ΔG (298 K)	-66	[**39+L**]	-22 [**40+M**]
Cartesian coordinates	C 0.431033 1.574097 -0.180787 N -0.874302 1.522240 0.239762 C -1.757336 0.398918 0.185333 N 0.888442 0.389368 -0.710714 O 1.122246 2.590269 -0.109933 O -2.933836 0.588622 0.538311 H 1.896929 0.332926 -0.815666 H -1.275510 2.384521 0.577466 C -2.005929 -2.045102 -0.377452 H -2.080534 -2.574690 0.582508 H -3.026750 -1.803706 -0.687520 H -1.579335 -2.750895 -1.098531 C 0.205173 -0.829587 -0.580455 C -1.171238 -0.796679 -0.291136 H 2.740281 -1.191357 0.481241 O 1.214336 -1.714576 0.778901 H 0.574296 -1.595218 -1.251092 O 3.580931 -0.769742 0.120355 H 3.808996 -0.092382 0.763325 H 0.763011 -1.456909 1.590847	See **Table S1-7**.	See **Table S1-7**.
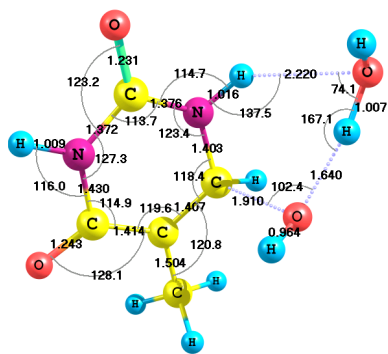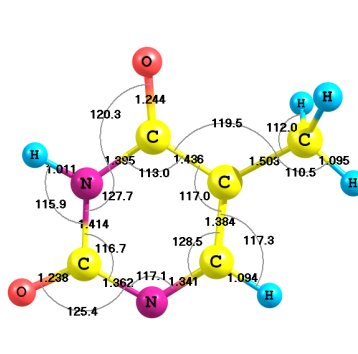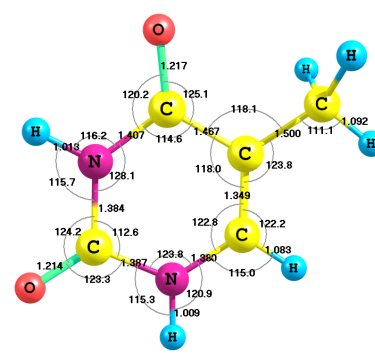
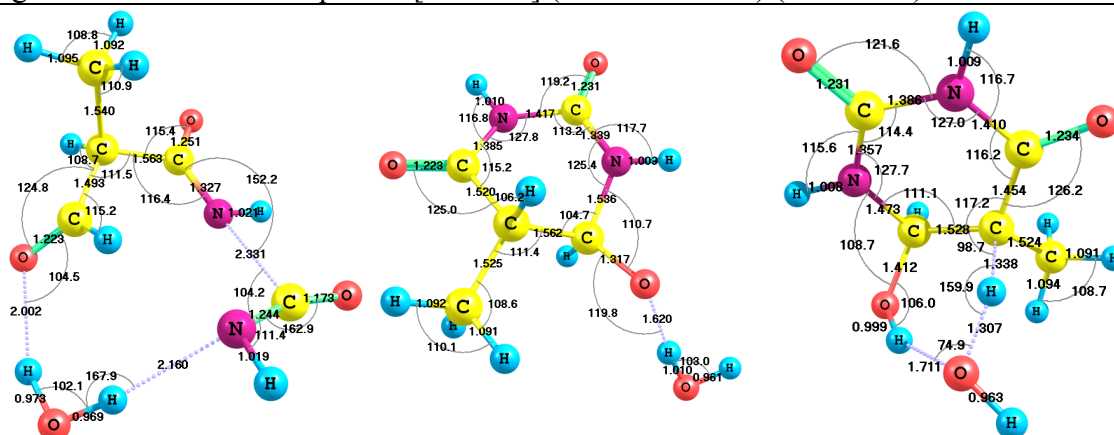**Table S7a**. Energies and selected geometries of transition states, intermediates and product for reaction in Fig.S7a (Planar elimination).
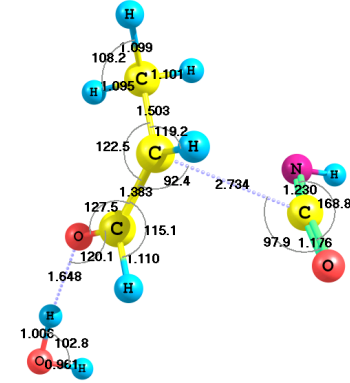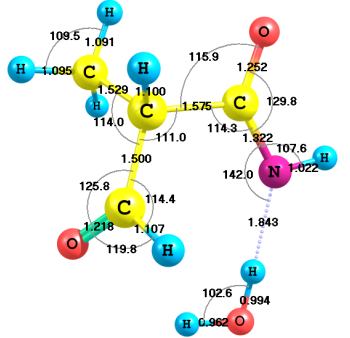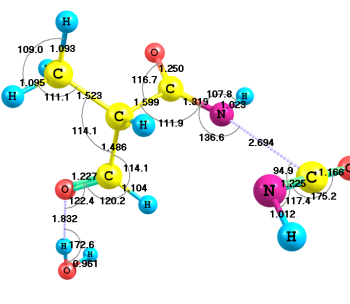Level of theory used CCSD(T)/6-311++G(d,p)//B3LYP/6-311++G(d,p). Relative energies in kJ mol^{-1} with respect to [2***J**+**K1**] (see **Table S1-7**) (0 kJ mol^{-1}).

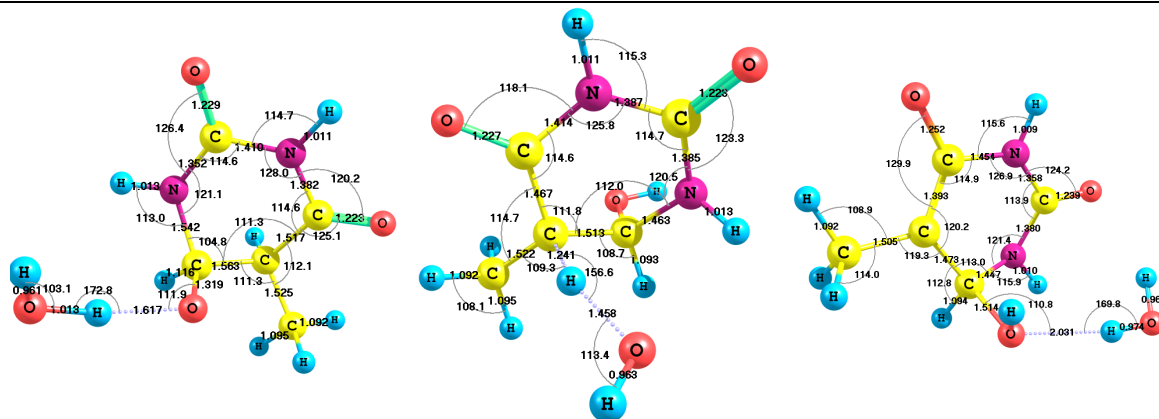|			
Symmetry	C_1	C_1	C_1
ΔH (0 K)	-102	-240	-170
ΔG (298 K)	-8	-140	-62
	C -0.217413 -0.565721 0.029962	C -1.182879 1.474893 0.138490	C -1.392311 1.511511 -0.687561
	N 1.719433 0.647412 -0.431049	N -1.886075 0.409314 -0.476762	N -2.103209 0.330234 -0.546812
	C 2.467752 1.740768 -0.350623	C -1.478409 -0.906658 -0.617027	C -1.611166 -0.906004 -0.080194
	N -1.141912 0.214913 -0.257177	N 0.097060 1.181325 0.400656	N -0.133664 1.472618 -0.182726
	O 0.384863 -1.512685 0.371978	O -1.775555 2.527178 0.377043	O -1.894961 2.508900 -1.205587
	O 3.675317 1.829909 -0.037136	O -2.223948 -1.722127 -1.142262	O -2.415210 -1.836251 0.022233
	H -2.048154 -0.169581 0.005641	H 0.671201 1.906266 0.804713	H 0.423793 2.298408 -0.336675
	H 2.309976 -0.147952 -0.184551	H -2.835344 0.623750 -0.748802	H -3.055580 0.341896 -0.879763
	C 1.566439 3.911996 0.593284	C 0.874901 -0.008310 -0.182580	C 0.241203 -2.104568 1.094124
Cartesian	H 0.858757 3.418185 1.266985	C -0.101409 -1.220435 -0.056052	H 1.322315 -2.260142 1.041406
coordinates	H 2.527056 3.993397 1.106543	O 2.030425 -0.155825 0.431910	H -0.015700 -1.895871 2.144182
	H 1.193370 4.919417 0.378865	H 0.963474 0.221175 -1.275876	H -0.259258 -3.033179 0.813874
	C 0.457227 2.866732 -1.385978	O 4.284529 0.248623 -0.856157	C 0.546173 0.333404 0.458060
	C 1.762053 3.092068 -0.695841	H 4.562369 1.069587 -0.442015	C -0.178625 -0.977896 0.157844
	H 2.429316 3.630783 -1.374233	H 3.411714 0.043049 -0.390755	H 0.389470 -1.258061 -1.020195
	O 0.199368 3.227276 -2.526187	C 0.497849 -2.483405 -0.666152	O 1.268536 -1.269325 -1.987028
	H -0.300566 2.327893 -0.794394	H -0.162027 -3.343136 -0.532785	H 1.616799 -2.163383 -2.068093
	O -2.142341 1.531631 -2.895464	H 0.665032 -2.352856 -1.740336	H 0.591119 0.529601 1.541477
	H -1.791673 1.013892 -2.155646	H 1.461868 -2.674852 -0.192848	O 1.894677 0.317305 0.038822
	H -1.457820 2.212957 -3.010800	H -0.235469 -1.363358 1.026023	H 1.912580 -0.208009 -0.810265

Table S8. Energies and selected geometries of transition states, intermediates and product for reaction in Fig.S8 (Anti elimination).
Level of theory used CCSD(T)/6-311++G(d,p)//B3LYP/6-311++G(d,p). Relative energies in kJ mol^{-1} with respect to [2*J+K2] (see **Table S1-7**) (0 kJ mol^{-1}).

Symmetry	C_1	C_1	C_1
ΔH (0 K)	4	-116	-102
ΔG (298 K)	45	-66	-19

	Cartesian coordinates		
	N 3.107614 0.718391 -1.635819	N -0.461769 -1.455420 0.269998	C 0.034028 -0.102379 1.632247
	C 2.273286 0.641282 -0.735328	C 0.698900 -1.019631 -0.189332	N 1.647065 0.347009 -0.478195
	O 1.555199 0.354390 0.151106	O 1.739387 -1.656618 -0.470501	C 2.285596 1.379205 -0.993712
	H 3.556922 -0.154808 -1.900204	H -0.391559 -2.469850 0.376537	N -0.222939 1.080172 1.822228
	C 2.767863 3.976810 -1.647740	C -0.476280 1.206607 0.102092	O 0.237330 -1.246669 1.537656
	H 2.336205 4.446934 -2.536922	C 0.764880 0.538287 -0.411064	O 3.369619 1.456787 -1.610437
	H 3.288871 4.752220 -1.068026	O -1.262333 1.857199 -0.563512	H -0.948762 1.297813 2.492659
	H 3.530633 3.263617 -1.995814	H -0.655235 1.069623 1.186093	H 2.204795 -0.490151 -0.663420
	C 0.423717 3.066601 -1.367490	O -3.187176 -0.698223 0.490508	C 0.286498 2.668933 -1.663024
	C 1.683555 3.308043 -0.850636	H -2.233908 -0.973673 0.428605	C 1.480831 2.744748 -0.781835
	H 1.828605 3.152845 0.214484	H -3.184157 0.165164 0.065208	O 0.031374 3.431638 -2.589372
	O 0.011691 3.298001 -2.555915	C 1.097865 0.878667 -1.863767	H -0.379509 1.814596 -1.448217
	H -0.297045 2.611509 -0.657042	H 0.281340 0.575488 -2.524043	O -2.099765 2.925496 -4.346070
	O -2.403682 2.506946 -3.304495	H 1.253900 1.953559 -2.001273	H -1.756586 2.132848 -4.767770
	H -2.186829 1.608652 -3.567253	H 2.000264 0.339227 -2.156071	H -1.393446 3.172199 -3.711766
	H -1.516313 2.869778 -2.998751	H 1.585577 0.867622 0.243966	H 1.100438 2.660733 0.242489
			C 2.327957 3.993044 -0.987413
			H 2.760740 4.000224 -1.988056
			H 1.729625 4.901592 -0.860407
			H 3.153348 4.008344 -0.271563

Table S8 Continued.

Symmetry	C_1	C_1	C_1
ΔH (0 K)	-235	-124	-196
ΔG (298 K)	-131	-15	-92
Cartesian coordinates	C -1.112730 1.456972 0.088724 N -1.927536 0.341792 -0.196717 C -1.534121 -0.962526 -0.429564 N 0.201795 1.171488 0.228241 O -1.637901 2.560834 0.219852 O -2.348866 -1.792987 -0.805320 H 0.777849 2.003433 0.184006 H -2.896560 0.562946 -0.378995 C 0.834104 -0.039491 -0.487375 C -0.079367 -1.249419 -0.108338 O 2.372533 2.330271 -2.239036 H 1.683245 2.897042 -2.596039 H 1.895974 1.446566 -2.103299 C 0.409891 -2.538354 -0.760582 H -0.252891 -3.376048 -0.533503 H 0.457701 -2.401121 -1.841852 H 1.418078 -2.773723 -0.404887 H -0.044503 -1.346526 0.987898 H 1.780489 -0.173452 0.089273 O 0.996327 0.141384 -1.783471	C -1.231437 1.598570 0.028979 N -1.958990 0.579600 -0.567178 C -1.583622 -0.782960 -0.620998 N 0.131927 1.369496 0.104190 O -1.762622 2.628048 0.421838 O -2.427271 -1.600445 -0.975809 H 0.498068 1.655085 1.004773 H -2.946046 0.763691 -0.682606 C 0.338430 -2.409062 -0.585295 H 1.270871 -2.610290 -0.047936 H -0.371266 -3.202407 -0.340760 H 0.541315 -2.458392 -1.661001 C 0.703641 0.116813 -0.389791 C -0.219220 -1.059180 -0.156819 O 0.228491 -0.521279 2.391763 H -0.095358 -1.063380 3.118365 H 1.622613 -0.041837 0.179363 O 1.022145 0.258486 -1.791156 H 1.377120 1.148456 -1.895867	See **Table S7** 38.