

***Electronic Supplementary Information (ESI)***

***Unimolecular photolysis mechanisms of formamide:***

***The effect of thermal energy***

by

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## ***Kinetic and Thermodynamic Properties Calculations:***

In this study, the equations used in the kinetic and thermodynamic analysis are as follows:

### ***The classical rate constant:***

$$k^{\text{Class}}(T) = \frac{k_B T}{h} \frac{Q^\ddagger}{Q^R} e^{-\Delta E^\ddagger/k_B T}. \quad (1)$$

$Q^\ddagger$  and  $Q^R$  are the partition functions of the transition and reactant structures, respectively, and  $\Delta E^\ddagger$  is the potential energy barrier obtained from the relaxed-scan energy curve.  $k_B$  and  $h$  are the Boltzmann and Planck constants, respectively.

### ***The rate constant with quantized vibrations:***

$$k^{\text{Q-vib}}(T) = \frac{k_B T}{h} \frac{Q_{\text{ZPE}}^\ddagger}{Q_{\text{ZPE}}^R} e^{-\Delta E_{\text{ZPE}}^\ddagger/k_B T}. \quad (2)$$

$Q_{\text{ZPE}}^\ddagger$  and  $Q_{\text{ZPE}}^R$  are the partition functions of the transition and reactant structures, respectively, obtained with respect to their zero-point vibrational energies, and based on the harmonic oscillator approximation.  $\Delta E_{\text{ZPE}}^\ddagger$  is the barrier height obtained with the zero-point vibrational energy. <sup>a)</sup>

### ***The crossover temperature:***

The temperature below which the transition states are dominated by quantum mechanical tunneling;

$$T_c = \frac{h\Omega^\ddagger}{2\pi k_B}. \quad (3)$$

$\Omega^\ddagger$  is the imaginary frequency of the transition structure.  $T_c$  is the temperature below which the transition states are dominated by quantum mechanical tunneling.

### ***The rate constants with quantized vibrations and second-order Wigner correction:***

$$k^{\text{S-Wig}}(T) = \kappa^{\text{S-Wig}}(T) k^{\text{Q-vib}}(T). \quad (4)$$

$\kappa^{\text{S-Wig}}$  is the Wigner transmission coefficient,

$$\kappa^{\text{S-Wig}}(T) = 1 + \frac{1}{24} \left( \frac{h\Omega^\ddagger}{k_B T} \right)^2, \quad (5)$$

which is 1 in the classical limit ( $h = 0$ ). <sup>b), c)</sup>

***The activation enthalpy:***

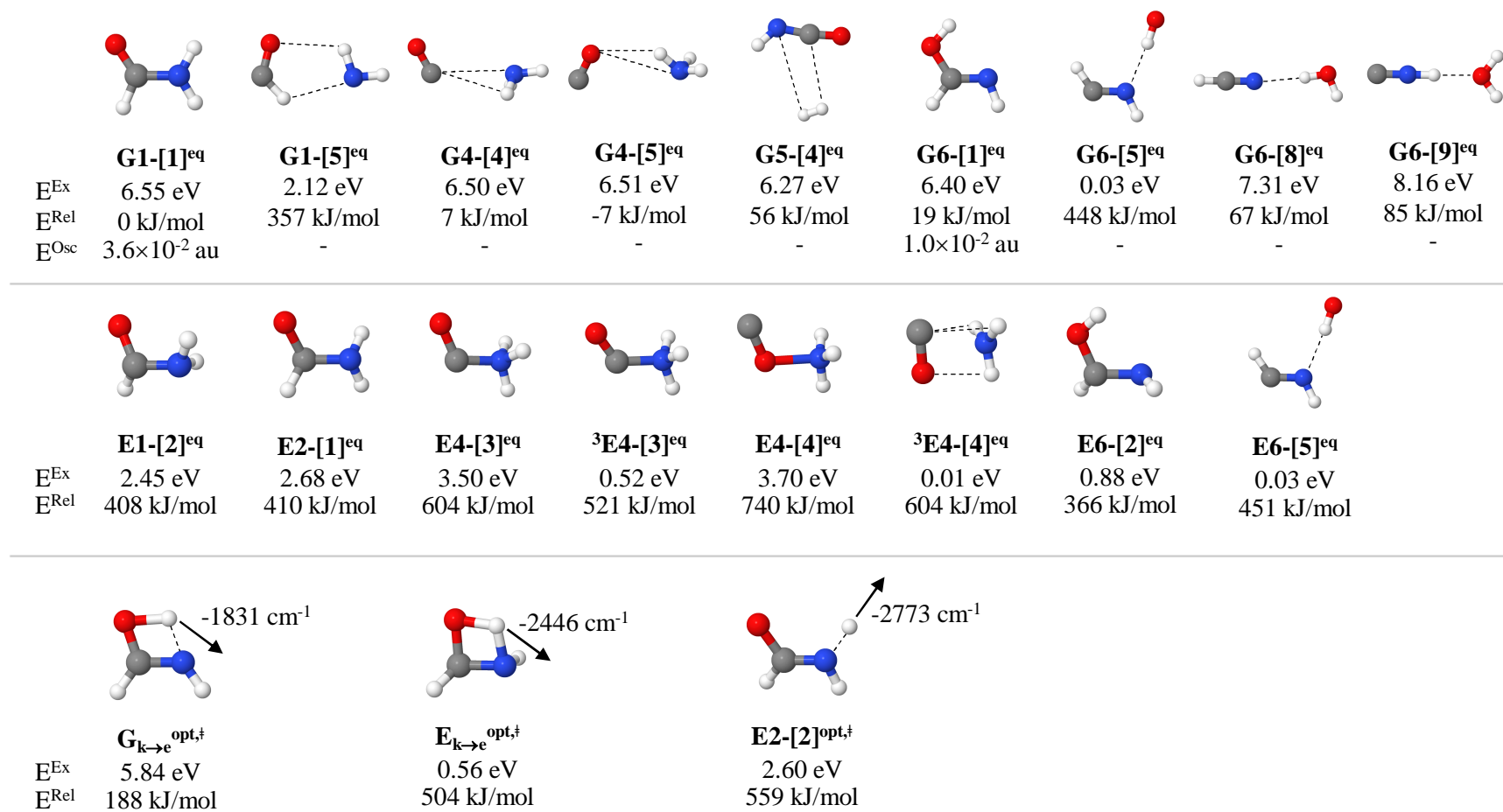
For the reactions with energy barrier higher than  $k_B T$ , the linear relationship between  $\ln k^{\text{Q-vib}}(T)$  and  $1/T$  was used to calculate the activation enthalpy ( $\Delta H^{\circ,\ddagger}$ ) through the Eyring equation,<sup>a)</sup>

$$\ln k^{\text{Q-vib}}(T) = \ln A - \frac{\Delta H^{\circ,\ddagger}}{RT} + \frac{\Delta S^{\circ,\ddagger}}{R}, \quad (6)$$

$\Delta S^{\circ,\ddagger}$  is the activation entropy, and  $R$  is the gas constant.

- a) J. E. House, *Principles of Chemical Kinetics 2<sup>nd</sup> edn*, Elsevier, USA, 2007.
- b) E. Wigner, *Z. Phys. Chem.*, 1932, **15**, 203–216.
- c) E. Wigner, *Trans. Faraday Soc.*, 1938, **34**, 29–41.

**Figure S1<sup>†</sup>** Equilibrium (<sup>eq</sup>) and transition (<sup>opt,†</sup>) structures in the ground ( $S_0$ ) and lowest excited ( $S_1$  and  $T_1$ ) states obtained from the CASPT2(6,9)/aug-cc-pVDZ geometry optimizations.  
→ = vibrational normal mode of the imaginary frequency.



**Figure S1<sup>†</sup>**

**Figure S2<sup>†</sup>**

- a) Potential energy curves for C–N, N–H and C–H dissociations, obtained based on the CASPT2(6,9) methods with the aug-cc-pVDZ, aug-cc-pVTZ and aug-cc-pVQZ basis sets.
- b) Plots of the activation Gibbs free energies of the rate determining process in Channel (1) as a function of temperature (T).
- c) relax-scan potential energy curves for N–H and C–H dissociations in the  $T_1$  states obtained by CASPT2(6,9)/aug-cc-pVDZ calculations.
- d) intramolecular isomerization of the H(6) atom from the C to N atom in Channel (4) computed in the  $S_1$  and  $T_1$  states.

Energies are in kJ/mol unless otherwise specified. Solid lines represent the relax-scan potential energies. The dash lines denote the energies calculated using the geometries on relax-scan potential energy curves.

a)

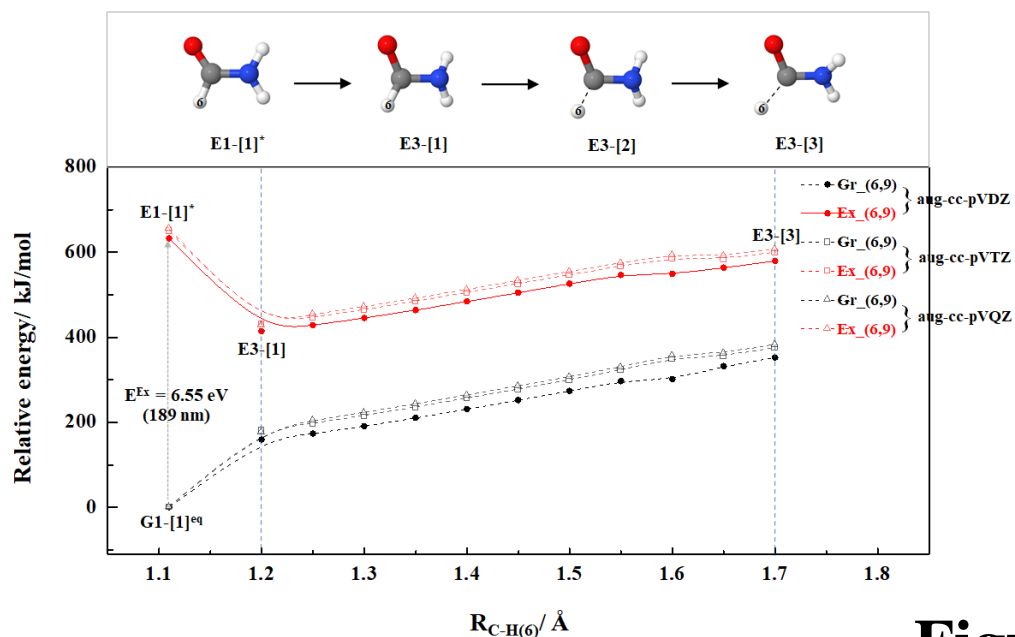
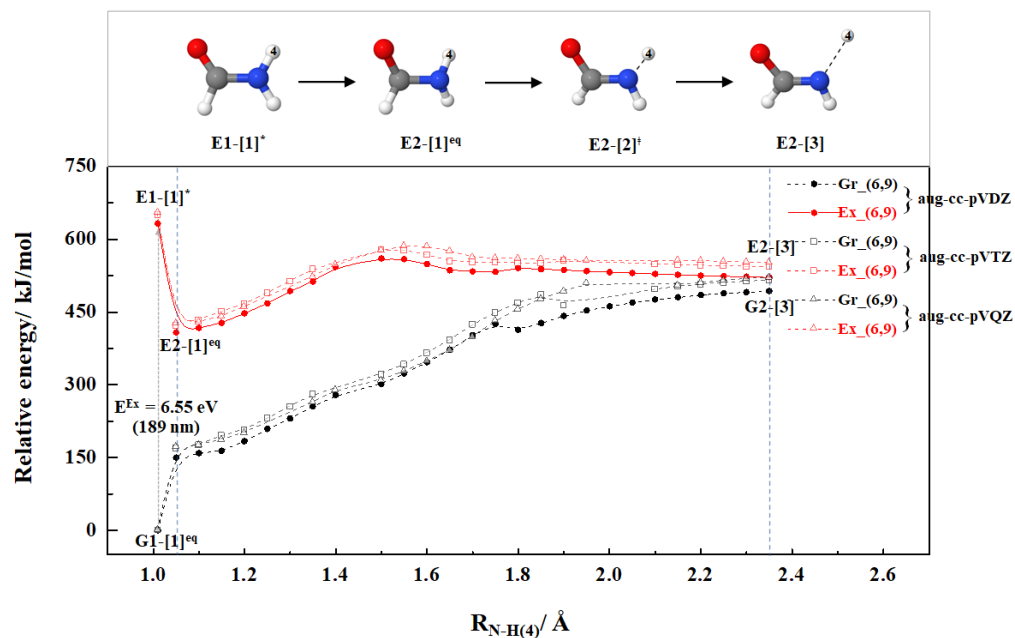
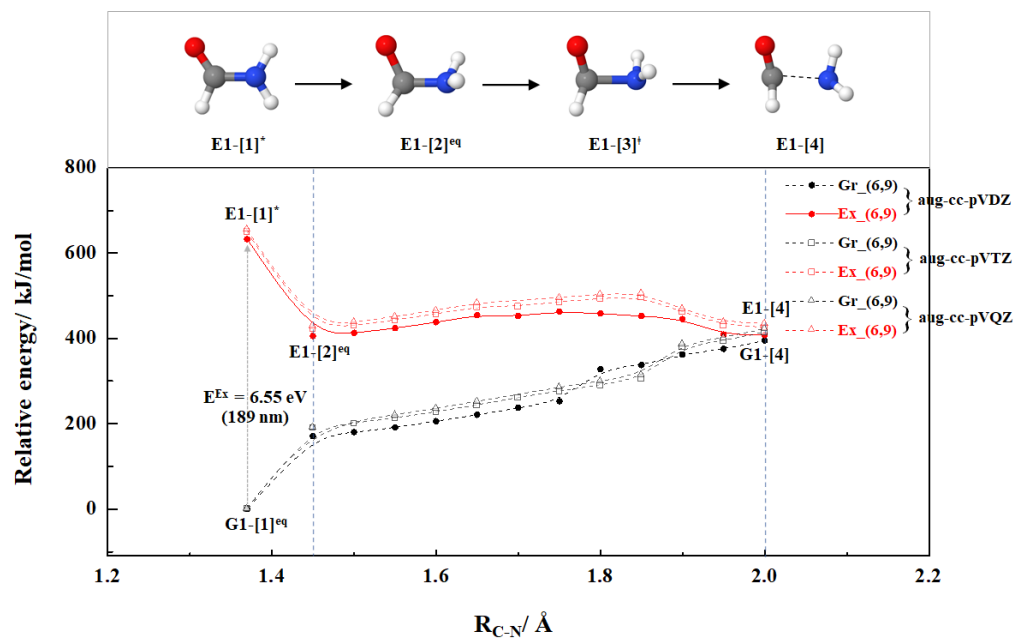
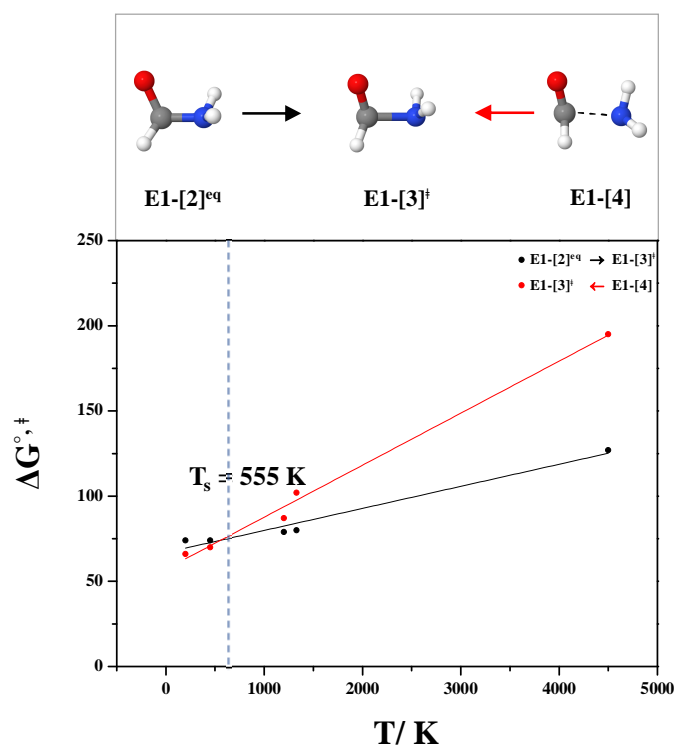


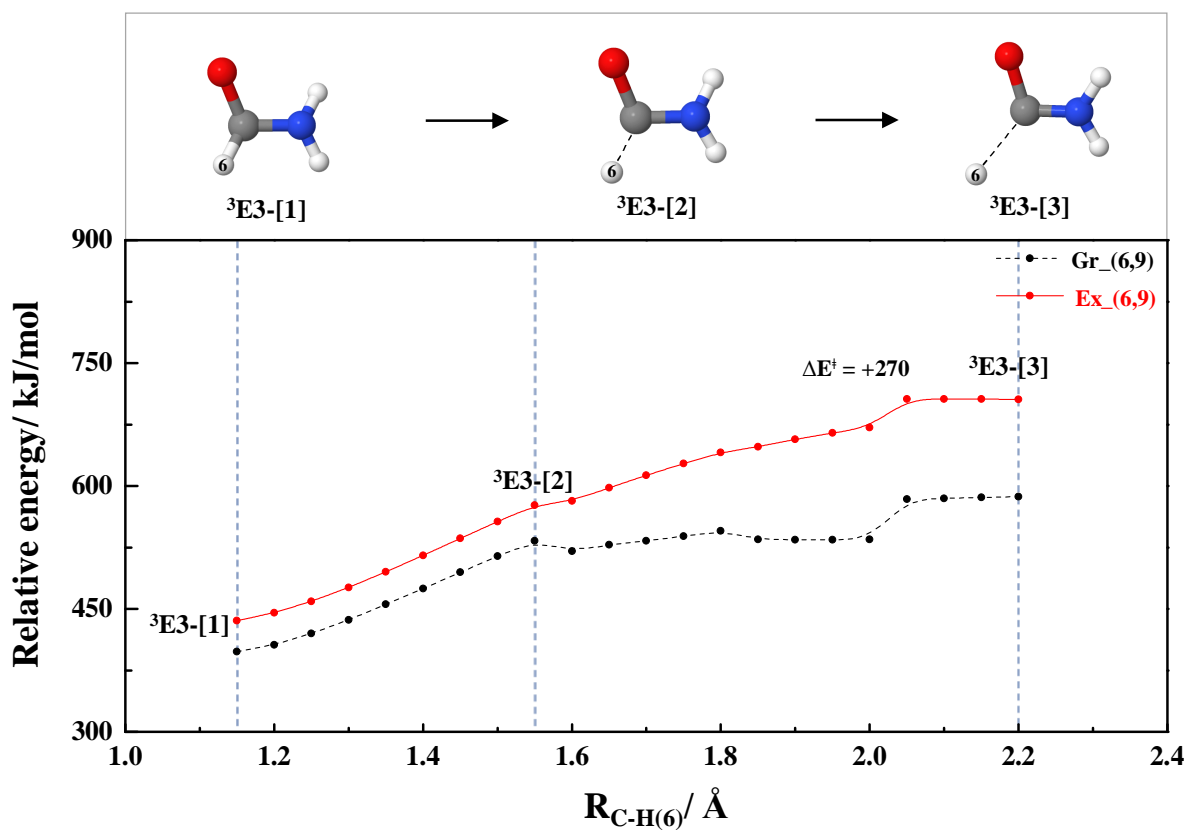
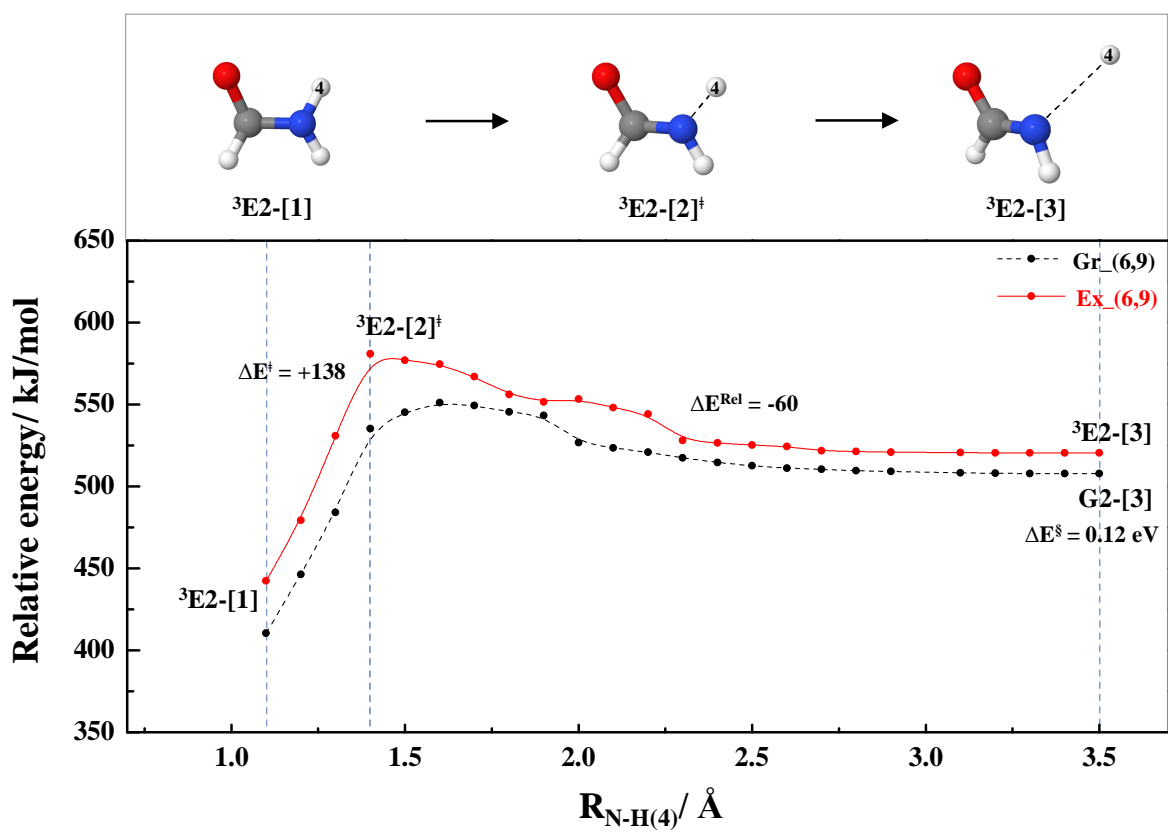
Figure S2a<sup>†</sup>

b)





c)

Figure S2c<sup>†</sup>

d)

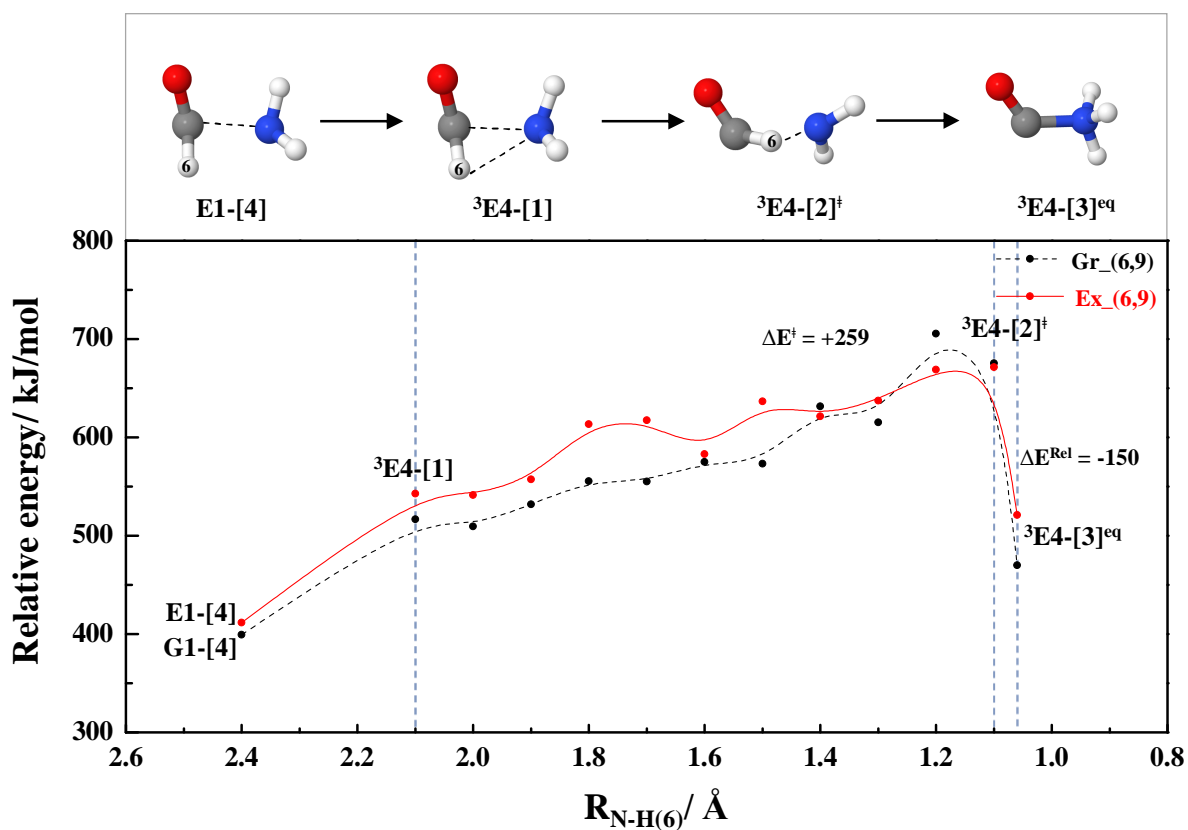
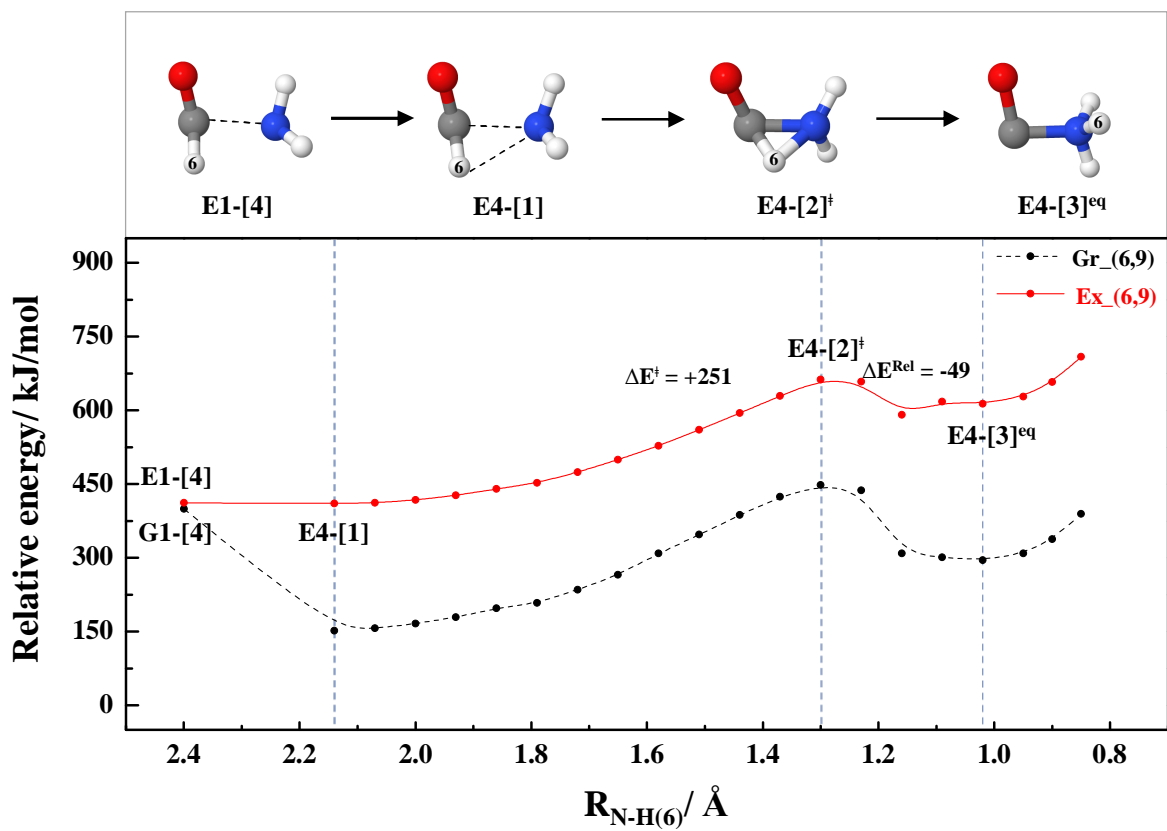
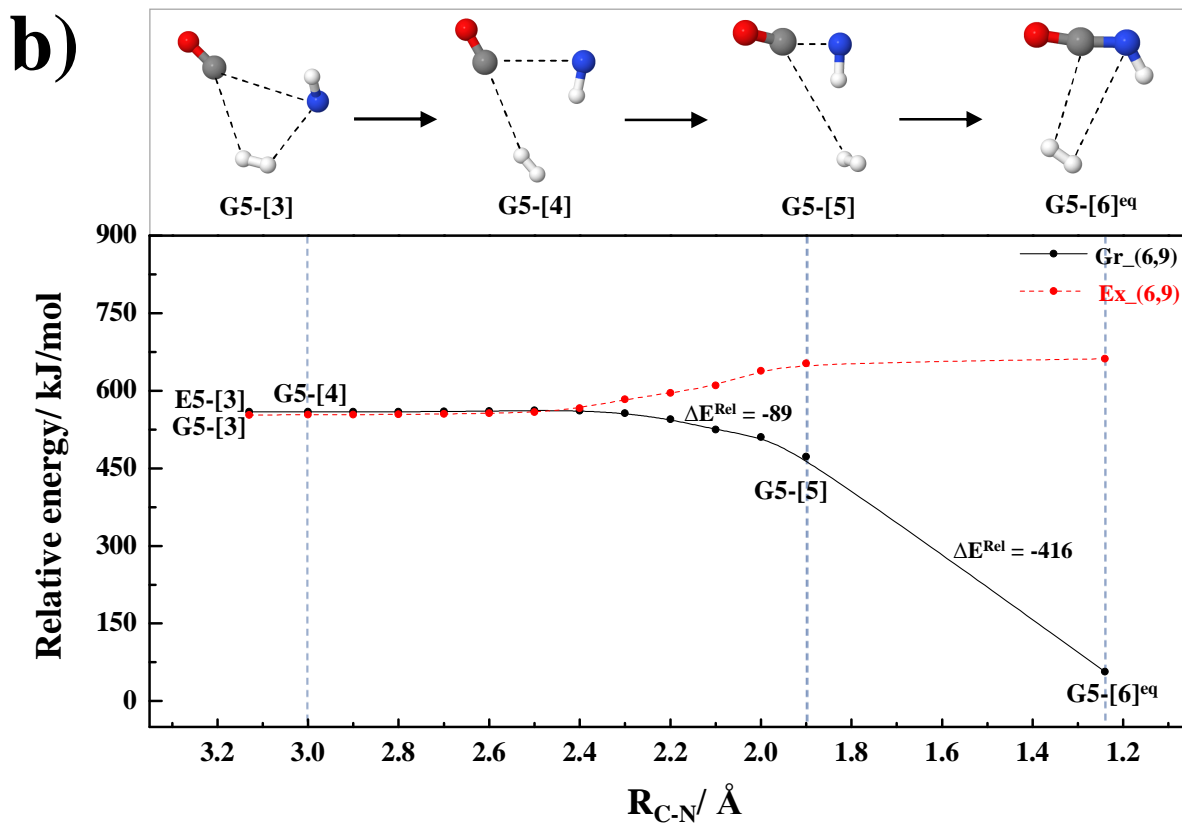
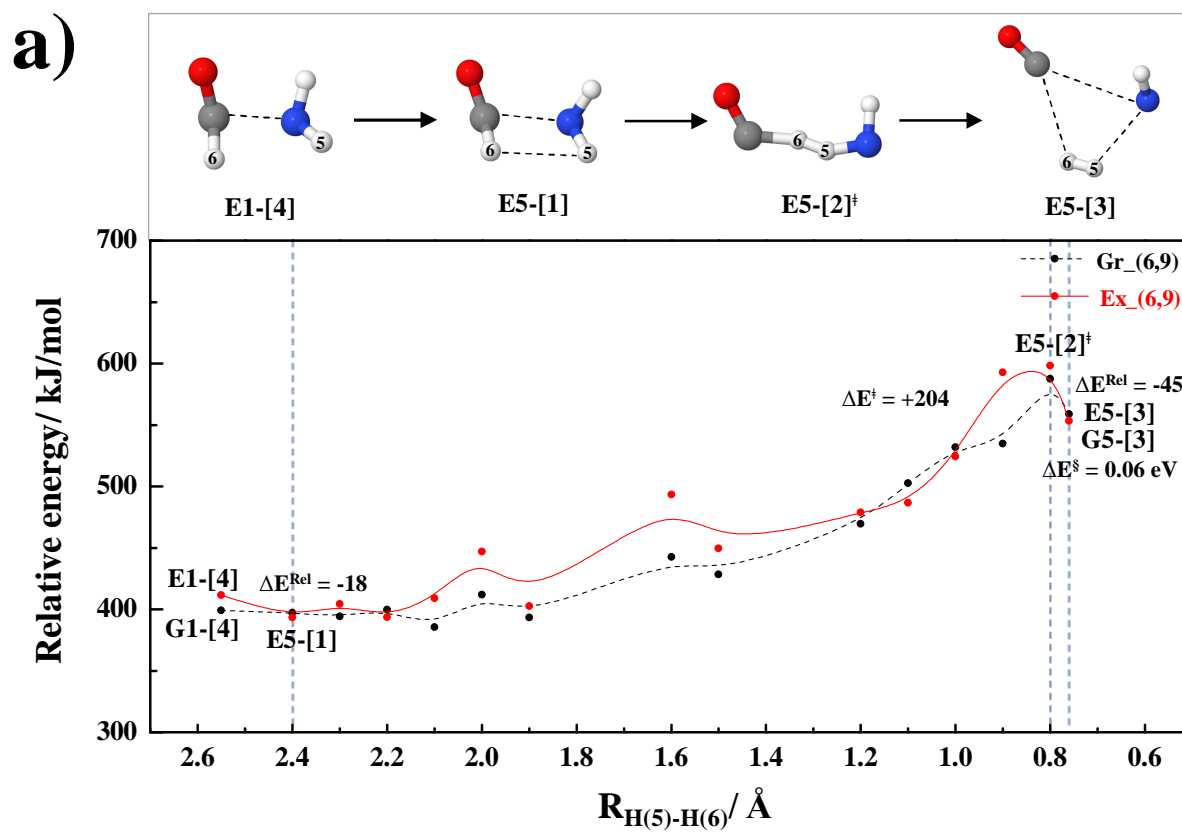


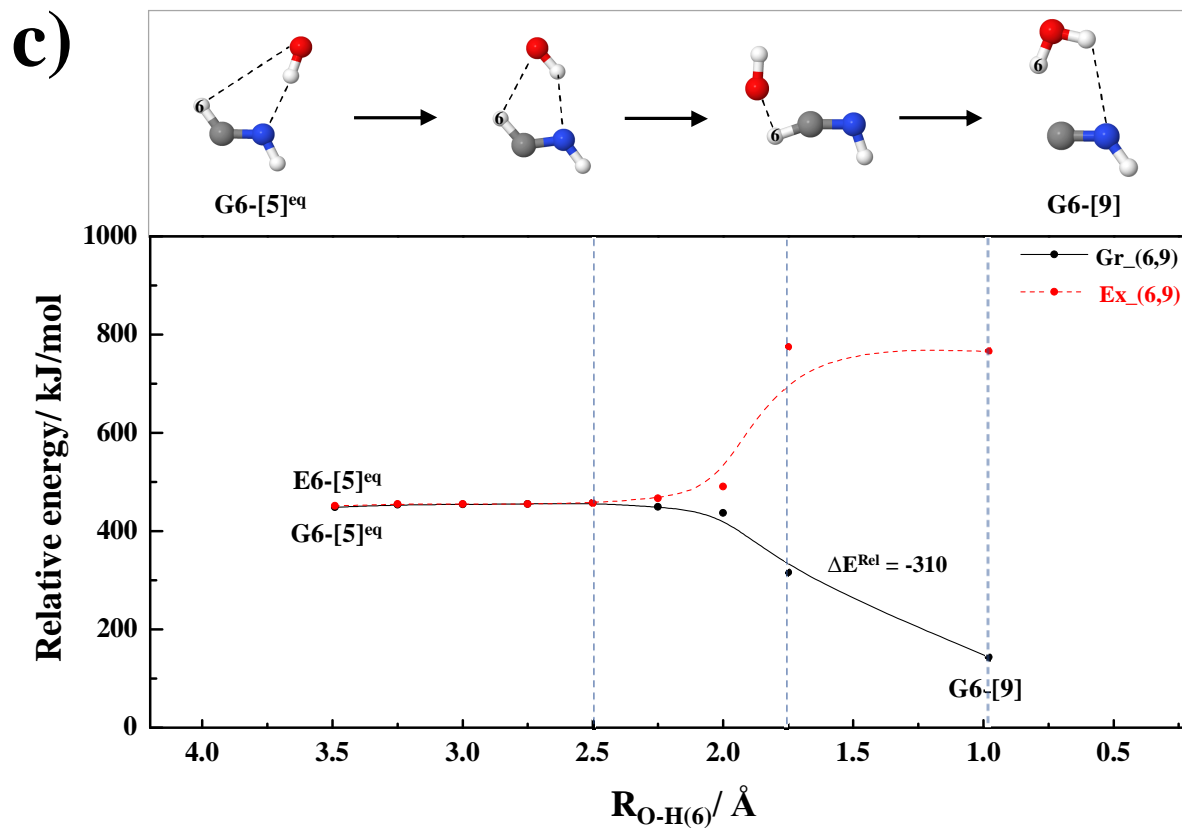
Figure S2d<sup>†</sup>

- Figure S3<sup>†</sup>** Relax-scan potential energy curves obtained by CASPT2(6,9)/aug-cc-pVDZ calculations.
- a) formation of CO–NH–H<sub>2</sub> van der Waals cluster (**E5-[3]**) at the intersection of the S<sub>0</sub> and S<sub>1</sub> states using **E1-[4]** as the precursor.
  - b) formation of the C–N bond in **G5-[3]** to yield the HNC and H<sub>2</sub> products in the S<sub>0</sub> state (**G5-[6]<sup>eq</sup>**).
  - c) formation of the HNC–H<sub>2</sub>O complex in the S<sub>0</sub> state using **G6-[5]<sup>eq</sup>** as the precursor (Channel (6)).

The energies are in kJ/mol unless otherwise specified. The solid lines represent the relax-scan potential energies. The dashed lines denote the energies calculated using the geometries of the relax-scan potential energy curves.



**Figure S3<sup>†</sup>**

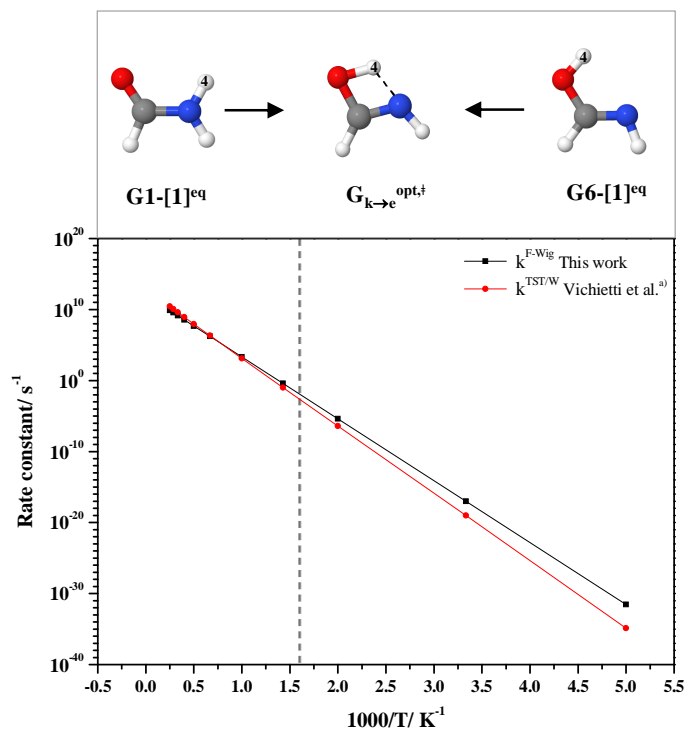


**Figure S3<sup>†</sup>**

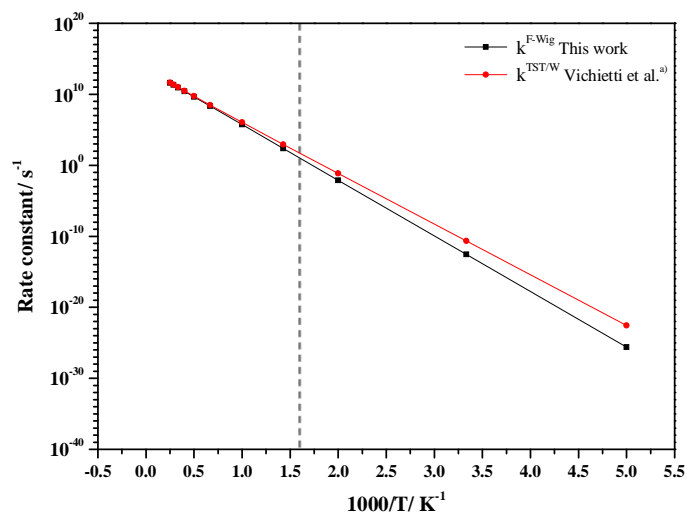
**Figure S4<sup>†</sup>** a)–b) Plots of the rate constants ( $k^{\text{F-Wig}}$  and  $k^{\text{TST/W}}$ ) as functions of  $1000/T$  for the keto-enol tautomerization of  $\text{HCONH}_2$  in the forward and reverse directions, respectively.  
c) Plots of the equilibrium constants ( $K$ ) as functions of  $1000/T$ .

<sup>†</sup>R. M. Vichiatti, A. B. F. da Silva and R. L. A. Haiduke, *Mol. Astrophys.*, 2018, **10**, 1-10.

a)



b)



c)

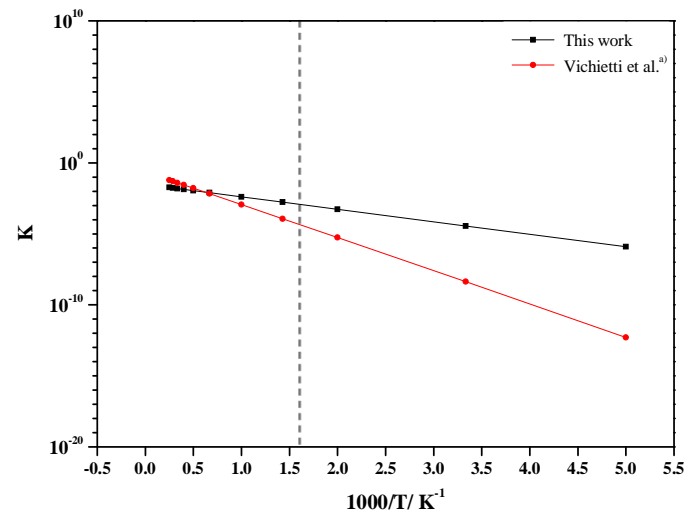
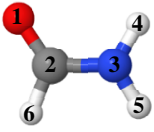
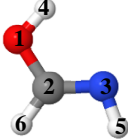


Figure S4<sup>†</sup>

**Table S1a**<sup>†</sup> Equilibrium geometries of HCONH<sub>2</sub> and HCOHNH in the S<sub>0</sub> and S<sub>1</sub> states obtained from CASPT2(6,9)/aug-cc-pVDZ geometry optimizations compared with available theoretical<sup>a), c)</sup> and experimental data.<sup>b)</sup> Distances and angles are in Å and degree, respectively.

S <sub>0</sub>					
	G1-[1] <sup>eq</sup>	CASPT2 <sup>a)</sup>	Exp. <sup>b)</sup>	G6-[1] <sup>eq</sup>	MP2/6-31G <sup>**c)</sup>
R <sub>C-N</sub>	1.370	1.357	1.352	1.280	1.273
R <sub>C-O</sub>	1.223	1.214	1.219	1.360	1.349
R <sub>N-H(4)</sub>	1.013	1.004	1.002	2.303	-
R <sub>N-H(5)</sub>	1.010	1.001	1.002	1.023	1.016
R <sub>C-H(6)</sub>	1.107	1.098	1.098	1.096	1.087
R <sub>O-H(4)</sub>	-	-	-	0.973	0.971
∠ <sub>H(4)NC</sub>	117.7	119.3	118.5	54.5	-
∠ <sub>H(5)NC</sub>	119.4	121.1	120.0	109.6	110.0
∠ <sub>NCO</sub>	124.6	124.7	124.7	121.7	121.6
∠ <sub>NCH(6)</sub>	112.8	112.5	112.7	127.6	128.1
∠ <sub>H(4)NCO</sub>	-11.7	-4.1	0.0	0.0	-

<sup>a)</sup> N. V. Tukachev, V. A. Bataev, A. V. Abramkov, I. A. Godunov, *Comput Theor Chem.* **2016**, 1080, 23-32.

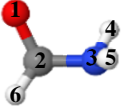
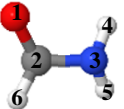

<sup>b)</sup> E. Hirota, R. Sugisaki, C. J. Nielsen, G. O. Sørensen, *J. Mol. Spectrosc.* **1974**, 49, 251-267.

<sup>c)</sup> J. Tortajada, E. Leon, J. P. Morizur, A. Luna, O. Mo, M. Yanez, *J. Phys Chem.* **1995**, 99, 13890-13898.

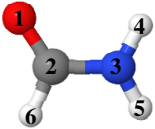
<sup>d)</sup> N. V. Tukachev, V. A. Bataev, A. V. Abramkov, I. A. Godunov, *Comput Theor Chem.* **2016**, 1080, 23-32.



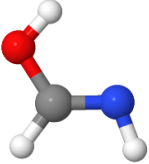
Table S1a<sup>†</sup> (Cont.)

S <sub>1</sub>						
	E1-[2] <sup>eq</sup>	CASPT2 <sup>d)</sup>	E2-[1] <sup>eq</sup>	CASPT2 <sup>d)</sup>	E6-[2] <sup>eq</sup>	CASPT2 <sup>d)</sup>
R <sub>C-N</sub>	1.415	1.412	1.423	1.411	1.280	1.442
R <sub>C-O</sub>	1.385	1.360	1.374	1.372	1.360	1.394
R <sub>N-H(4)</sub>	1.023	1.012	1.020	1.01	2.303	2.295
R <sub>N-H(5)</sub>	1.019	1.017	1.018	1.012	1.023	1.038
R <sub>C-H(6)</sub>	1.095	1.083	1.100	1.088	1.096	1.077
R <sub>O-H(4)</sub>	-	-	-	-	0.973	0.967
∠ <sub>H(4)NC</sub>	113.0	110.3	111.4	111.3	54.2	56.5
∠ <sub>H(5)NC</sub>	111.1	112.2	109.8	109.8	106.9	107.2
∠ <sub>H(4)NH(5)</sub>	108.6	107.9	108.3	108.5	101.3	109.3
∠ <sub>NCO</sub>	113.1	112.2	111.4	111.6	114.2	113.3
∠ <sub>NCH(6)</sub>	117.8	118.3	115.2	115.3	116.2	115.9
∠ <sub>H(4)NCO</sub>	-78.1	-50.2	-57.9	-56.7	12.5	-0.6
∠ <sub>H(5)NCO</sub>	44.2	70.2	-177.8	-176.9	104.4	-102.7
∠ <sub>H(4)NCH</sub>	-178.7	171.6	172.7	173.7	144.9	-134.8
∠ <sub>H(5)NCH</sub>	59.0	-68.1	52.8	53.4	123.3	-123.1

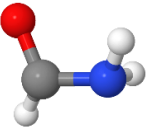
**Table S1b**<sup>†</sup> The equilibrium and transition structures (Z-matrices), as well as the vibrational frequencies and vertical excitation energies ( $E^{\text{Ex}}$ ), obtained based on CASPT2(6,9) geometry optimizations using the aug-cc-pVDZ and aug-cc-pVTZ basis sets. Distances, angles and vibrational frequencies are in Å, degree and  $\text{cm}^{-1}$ , respectively. The scaling factor for the vibrational frequencies is 0.9434. → = vibrational normal mode of the imaginary frequency.

Structures	Z-matrix							Vibrational frequencies	
								aug-cc-pVDZ	aug-cc-pVTZ
<b>G1-[1]<sup>eq</sup></b> 	aug-cc-pVDZ		$E^{\text{Ex}} = 6.55 \text{ eV (189 nm)}$				292	210	
	O						525	533	
	C	1	1.223				572	586	
	N	2	1.370	1	124.6		957	988	
	H(4)	3	1.013	2	117.6	1	-11.8	1006	1009
	H(5)	3	1.010	2	119.4	1	-165.9	1203	1214
	H(6)	2	1.107	1	122.6	3	177.8	1334	1352
	aug-cc-pVTZ		$E^{\text{Ex}} = 6.74 \text{ eV (184 nm)}$				1533	1536	
	O						1668	1694	
	C	1	1.214				2889	2885	
	N	2	1.359	1	124.8		3390	3416	
	H(4)	3	1.006	2	118.5	1	-8.3	3534	3554
	H(5)	3	1.002	2	120.3	1	-170.4		
	H(6)	2	1.097	1	122.6	3	178.4		

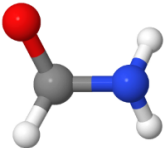
**Table S1b<sup>†</sup>** (Cont.)

Structures	Z-matrix						Vibrational frequencies		
							aug-cc-pVDZ	aug-cc-pVTZ	
<p><b>G6-[1]<sup>eq</sup></b></p> 	aug-cc-pVDZ $E^{\text{Ex}} = 6.40 \text{ eV (191 nm)}$						547	554	
	O						571	582	
	C	1	1.360				782	794	
	N	2	1.279	1	121.7			976	1002
	H(4)	1	0.973	2	105.8	3	-0.1	1008	1017
	H(5)	3	1.023	2	109.6	1	-180.0	1127	1126
	H(6)	2	1.096	1	110.7	3	-180.0	1292	1298
	aug-cc-pVTZ $E^{\text{Ex}} = 6.37 \text{ eV (194 nm)}$						1311	1320	
	O						1585	1603	
	C	1	1.344				3018	3018	
	N	2	1.270	1	121.9			3323	3376
	H(4)	1	0.969	2	106.3	3	0.1	3535	3548
	H(5)	3	1.013	2	110.1	1	179.9		
	H(6)	2	1.084	1	110.6	3	179.9		

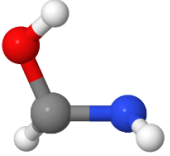
**Table S1b<sup>†</sup>** (Cont.)

Structures	Z-matrix						Vibrational frequencies		
							aug-cc-pVDZ	aug-cc-pVTZ	
<p><b>E1-[2]<sup>eq</sup></b></p> 	aug-cc-pVDZ						206	198	
	O						361	365	
	C	1	1.385					694	668
	N	2	1.415	1	113.0			733	708
	H(4)	3	1.024	2	113.0	1	-78.1	987	1012
	H(5)	3	1.019	2	111.2	1	44.2	1072	1077
	H(6)	2	1.094	1	114.4	3	-138.6	1117	1126
	aug-cc-pVTZ						1244	1263	
	O						1534	1550	
	C	1	1.370					3014	3021
	N	2	1.403	1	113.3			3276	3300
	H(4)	3	1.015	2	113.9	1	-82.1	3402	3423
	H(5)	3	1.010	2	111.9	1	42.8		
	H(6)	2	1.083	1	114.8	3	-140.0		

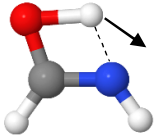
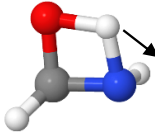
**Table S1b<sup>†</sup>** (Cont.)

Structures	Z-matrix							Vibrational frequencies	
								aug-cc-pVDZ	aug-cc-pVTZ
<p><b>E2-[1]<sup>eq</sup></b></p> 	aug-cc-pVDZ							225	223
	O							416	420
	C 1 1.373							715	700
	N 2 1.423 1 111.5							834	821
	H(4) 3 1.020 2 111.4 1 -57.8							980	989
	H(5) 3 1.018 2 109.8 1 -177.8							1077	1090
	H(6) 2 1.100 1 112.3 3 130.9							1114	1130
	aug-cc-pVTZ							1285	1302
	O							1528	1546
	C 1 1.367							2952	2962
	N 2 1.405 1 111.7							3321	3346
	H(4) 3 1.011 2 112.3 1 -55.3							3430	3450
	H(5) 3 1.009 2 110.8 1 -178.1								
	H(6) 2 1.088 1 112.5 3 132.3								

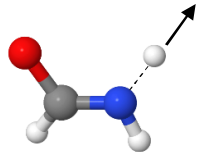
**Table S1b<sup>†</sup>** (Cont.)

Structures	Z-matrix						Vibrational frequencies		
							aug-cc-pVDZ	aug-cc-pVTZ	
<p><b>E6-[2]<sup>eq</sup></b></p> 	aug-cc-pVDZ						232	224	
	O						422	428	
	C	1	1.387				762	749	
	N	2	1.441	1	114.2		957	967	
	H(4)	1	0.969	2	108.3	3	-26.8	1054	1067
	H(5)	3	1.034	2	107.0	1	104.3	1150	1163
	H(6)	2	1.094	1	111.7	3	-134.5	1158	1175
	aug-cc-pVTZ						1298	1304	
	O						1733	1652	
	C	1	1.374				3020	3028	
	N	2	1.428	1	114.6		3155	3195	
	H(4)	1	0.965	2	108.6	3	-24.1	3575	3586
	H(5)	3	1.025	2	107.5	1	103.7		
	H(6)	2	1.082	1	112.3	3	-136.0		

**Table S1b<sup>†</sup>** (Cont.)

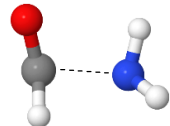
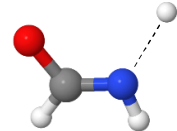
Structures	Z-matrix	Vibrational frequencies
<p><math>G_{k \rightarrow e}^{opt,\ddagger}</math></p> 	<p>aug-cc-pVDZ</p> <p>C</p> <p>O 1 1.307</p> <p>N 1 1.316 2 108.4</p> <p>H(4) 2 1.315 1 74.7 3 0.0</p> <p>H(5) 3 1.005 1 124.8 2 -179.9</p> <p>H(6) 1 1.099 2 125.6 3 -179.8</p>	<p>-1831</p> <p>255</p> <p>807</p> <p>970</p> <p>1052</p> <p>1086</p> <p>1169</p> <p>1323</p> <p>1547</p> <p>1977</p> <p>3048</p> <p>3450</p>
<p><math>E_{k \rightarrow e}^{opt,\ddagger}</math></p> 	<p>aug-cc-pVDZ</p> <p>C</p> <p>N 1 1.423</p> <p>O 1 1.403 2 91.7</p> <p>H(4) 1 1.096 3 119.9 2 130.6</p> <p>H(5) 2 1.032 1 106.0 3 -89.5</p> <p>H(6) 2 1.250 1 81.7 3 7.0</p>	<p>-2446</p> <p>587</p> <p>791</p> <p>838</p> <p>963</p> <p>1060</p> <p>1099</p> <p>1171</p> <p>1246</p> <p>1993</p> <p>2998</p> <p>3235</p>

**Table S1b<sup>†</sup>** (Cont.)

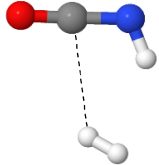
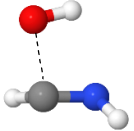
Structures	Z-matrix	Vibrational frequencies
<p><b>E2-[2]<sup>opt,‡</sup></b></p> 	<p>aug-cc-pVDZ</p> <p>C</p> <p>O 1 1.352</p> <p>N 1 1.277 2 119.5</p> <p>H(4) 3 1.479 1 116.0 2 -64.3</p> <p>H(5) 3 1.024 1 110.6 2 -177.4</p> <p>H(6) 1 1.104 3 129.0 2 171.2</p>	<p>-2773</p> <p>376</p> <p>523</p> <p>607</p> <p>874</p> <p>950</p> <p>986</p> <p>1126</p> <p>1297</p> <p>1578</p> <p>2930</p> <p>3335</p>



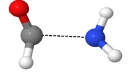
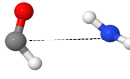
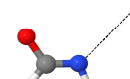
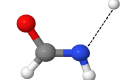
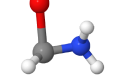
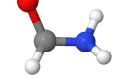
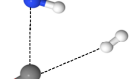
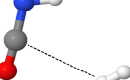
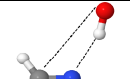
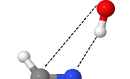
**Table S1b<sup>†</sup>** (Cont.)

Structures	Z-matrix						
<p style="text-align: center;"><b>E1-[4]</b></p> 	<p style="text-align: center;">aug-cc-pVDZ</p> <p>O</p> <p>C    1        1.204</p> <p>N    2        2.000    1        101.1</p> <p>H(4) 3        1.033    2        126.9    1        95.8</p> <p>H(5) 3        1.031    2        100.5    1       -21.5</p> <p>H(6) 2        1.114    1        128.1    3        89.3</p>						
<p style="text-align: center;"><b>E2-[3]</b></p> 	<p style="text-align: center;">aug-cc-pVDZ</p> <p>O</p> <p>C    1        1.335</p> <p>N    2        1.281    1        123.1</p> <p>H(4) 3        2.350    2        115.4    1       -64.5</p> <p>H(5) 3        1.023    2        108.4    1       -178.4</p> <p>H(6) 2        1.105    1        108.3    3       -179.1</p>						

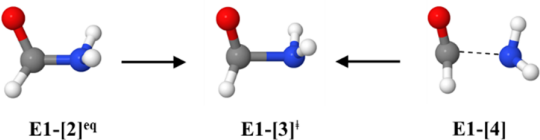
**Table S1b<sup>†</sup>** (Cont.)

Structures	Z-matrix						
<p><b><sup>3</sup>E5-[3]</b></p> 	<p>aug-cc-pVDZ</p> <p>O</p> <p>C    1        1.205</p> <p>N    2        1.383    1      169.2</p> <p>H(4) 3        1.050    2      113.7   1     107.5</p> <p>H(5) 3        3.261    2      86.0    1     102.7</p> <p>H(6) 2        2.931    1      102.1   3     102.3</p>						
<p><b>E6-[4]</b></p> 	<p>aug-cc-pVDZ</p> <p>O</p> <p>C    1        1.900</p> <p>N    2        1.363    1      103.1</p> <p>H(4) 1        0.979    2      95.6    3      1.4</p> <p>H(5) 3        1.035    2      108.3   1     106.0</p> <p>H(6) 2        1.093    1      100.8   3    -129.9</p>						

**Table S2<sup>†</sup>** Structures and energetic of the species obtained from the conical intersection optimizations using the SA-CPMCSCF method with the 6-31G(d) basis set.  $(S_0/S_1)^{opt}$  and  $(S_0/T_1)^{opt}$  = conical intersections of the  $S_0$  and  $S_1$  and  $S_0$  and  $T_1$ , respectively (minimum energy crossing point); (...) = dissociation channels;  $(S_0/S_1)^{sp}$  and  $(S_0/T_1)^{sp}$  = single point calculation using the structures obtained from the relax-scan potential energy curves and the SA-CPMCSCF/6-31G(d) method.

SA-CPMCSCF/6-31G(d)						
Channel	Structure	R/ Å	Intersection (§)	E <sup>Tot</sup> / au		ΔE <sup>§</sup> / eV
				S <sub>0</sub> state	S <sub>1</sub> or T <sub>1</sub> state	
(1)	 <b>E1-[4]§</b>	R <sub>C-N</sub> =2.22	(S <sub>0</sub> /S <sub>1</sub> ) <sup>opt</sup>	-168.8385655	-168.8383818	0.0050
	 <b><sup>3</sup>E1-[4]§</b>	R <sub>C-N</sub> =3.44	(S <sub>0</sub> /T <sub>1</sub> ) <sup>opt</sup>	-168.8353159	-168.8347231	0.0161
(2)	 <b>E2-[3]§</b>	R <sub>N-H(4)</sub> =3.85	(S <sub>0</sub> /S <sub>1</sub> ) <sup>opt</sup>	-168.8267912	-168.8266744	0.0032
	 <b><sup>3</sup>E2-[3]§</b>	R <sub>N-H(4)</sub> =3.74	(S <sub>0</sub> /T <sub>1</sub> ) <sup>opt</sup>	-168.8299766	-168.8299381	0.0010
(3)	 <b>E3-[3]§</b>	R <sub>C-H(6)</sub> =1.09	(S <sub>0</sub> /S <sub>1</sub> ) <sup>opt</sup>	-168.8149178	-168.8148806	0.0010
	 <b><sup>3</sup>E3-[3]§</b>	R <sub>C-H(6)</sub> =1.08	(S <sub>0</sub> /T <sub>1</sub> ) <sup>opt</sup>	-168.9615585	-168.8824506	2.1526
(5)	 <b>E5-[3]§</b>	R <sub>C-H(6)</sub> =3.09	(S <sub>0</sub> /S <sub>1</sub> ) <sup>sp</sup>	-169.1728445	-169.1742238	0.0375
	 <b><sup>3</sup>E5-[3]§</b>	R <sub>C-H(6)</sub> =3.22	(S <sub>0</sub> /T <sub>1</sub> ) <sup>sp</sup>	-169.1583382	-169.1600598	0.0468
(6)	 <b>E6-[5]§</b>	R <sub>C-O</sub> =3.68 R <sub>N-O</sub> =3.03	(S <sub>0</sub> /S <sub>1</sub> ) <sup>sp</sup>	-169.2068081	-169.205497	0.0357
	 <b><sup>3</sup>E6-[5]§</b>	R <sub>C-O</sub> =3.76 R <sub>N-O</sub> =3.06	(S <sub>0</sub> /T <sub>1</sub> ) <sup>opt</sup>	-168.8382159	-168.8383788	0.0044

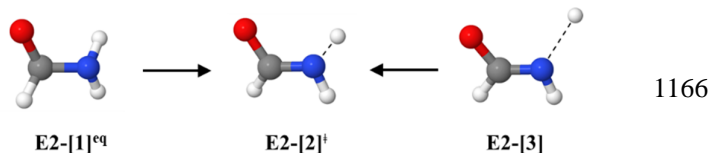
**Table S3<sup>†</sup>** Rate constants (k), enthalpies of activation ( $\Delta H^{\circ\dagger}$ ) and Gibbs free energy barriers ( $\Delta G^{\circ\dagger}$ ) for the C–N dissociation in the S<sub>1</sub> state (Channel (1)), obtained based on the transition state theory and potential energy curves. Energies, rate constants and temperatures are in kJ mol<sup>-1</sup>, s<sup>-1</sup> and K, respectively.

Channel (1)	$\Delta E^\ddagger$	$\Delta H^{\circ\dagger}$	$T_c$	$T_s$	T	$k^{\text{Class}}$	$k^{\text{Q-vib}}$	$k^{\text{S-Wig}}$	$k^{\text{F-Wig}}$	$\Delta G^{\circ\dagger}$
					200	$1.86 \times 10^{-8}$	$2.08 \times 10^{-7}$	$2.28 \times 10^{-7}$	$2.29 \times 10^{-7}$	74
					450	$1.07 \times 10^4$	$2.15 \times 10^4$	$2.18 \times 10^4$	$2.18 \times 10^4$	74
<b>E1-[2]<sup>eq</sup> → E1-[3]<sup>‡</sup></b>	58	76	48		1200	$8.08 \times 10^9$	$9.19 \times 10^9$	$9.21 \times 10^9$	$9.21 \times 10^9$	79
					1328	$1.77 \times 10^{10}$	$1.97 \times 10^{10}$	$1.97 \times 10^{10}$	$1.97 \times 10^{10}$	80
				555	4500	$3.12 \times 10^{12}$	$3.16 \times 10^{12}$	$3.16 \times 10^{12}$	$3.16 \times 10^{12}$	127
					200	$3.85 \times 10^{-8}$	$2.69 \times 10^{-5}$	$3.71 \times 10^{-5}$	$4.07 \times 10^{-5}$	66
					450	$6.65 \times 10^3$	$6.36 \times 10^4$	$6.83 \times 10^4$	$6.86 \times 10^4$	70
<b>E1-[3]<sup>‡</sup> ← E1-[4]</b>	55	65	96		1200	$2.76 \times 10^9$	$4.28 \times 10^9$	$4.32 \times 10^9$	$4.33 \times 10^9$	87
					1328	$1.99 \times 10^9$	$2.71 \times 10^9$	$2.72 \times 10^9$	$2.72 \times 10^9$	102
					4500	$5.01 \times 10^{11}$	$5.16 \times 10^{11}$	$5.16 \times 10^{11}$	$5.16 \times 10^{11}$	195

$T_c$  = crossover temperature; <sup>eq</sup> = equilibrium structure;  $k^{\text{Class}}$  = rate constant obtained from classical TST;  $k^{\text{Q-vib}}$  = rate constant obtained with quantized vibrations including the zero-point vibrational energy;  $k^{\text{S-Wig}}$  = rate constant obtained with quantized vibrations and tunneling correction through the simplified Wigner correction to the second order;  $k^{\text{F-Wig}}$  = full Wigner-corrected rate constant at T above  $T_c$ ;  $T_s$  = temperature at which the forward is spontaneous;  $\Delta E^\ddagger$  = energy barrier with respect to the precursor.

**Table S4<sup>†</sup>** Rate constants (k), enthalpies of activation ( $\Delta H^{\ddagger}$ ) and Gibbs free energy barriers ( $\Delta G^{\ddagger}$ ) for the N–H dissociation in the  $S_1$  state (Channel (2)), obtained based on the transition state theory and potential energy curves. Energies, rate constants and temperatures are in  $\text{kJ mol}^{-1}$ ,  $\text{s}^{-1}$  and K, respectively.

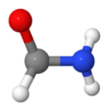
Channel (2)	$\Delta E^{\ddagger}$	$\Delta H^{\circ,\ddagger}$	$T_c$	$T_s$	T	$k^{\text{Class}}$	$k^{\text{Q-vib}}$	$k^{\text{S-Wig}}$	$k^{\text{F-Wig}}$	$\Delta G^{\circ,\ddagger}$
					200	$1.03 \times 10^{-23}$	$1.62 \times 10^{-19}$	$1.05 \times 10^{-18}$	-	120
					450	$2.59 \times 10^{-3}$	$7.32 \times 10^{-2}$	$1.52 \times 10^{-1}$	$3.36 \times 10^{-1}$	122
<b>E2-[1]<sup>eq</sup> → E2-[2]<sup>‡</sup></b>	153	123	365		1200	$4.11 \times 10^7$	$8.22 \times 10^7$	$9.48 \times 10^7$	$9.62 \times 10^7$	126
					1328	$1.15 \times 10^8$	$2.05 \times 10^8$	$2.89 \times 10^8$	$3.21 \times 10^8$	130
					4500	$1.34 \times 10^{12}$	$1.42 \times 10^{12}$	$1.47 \times 10^{12}$	$1.47 \times 10^{12}$	157
					200	$3.68 \times 10^3$	$8.58 \times 10^2$	$5.26 \times 10^3$	-	37
					450	$3.48 \times 10^6$	$2.44 \times 10^6$	$4.91 \times 10^6$	$9.62 \times 10^6$	57
<b>E2-[2]<sup>‡</sup> ← E2-[3]</b>	38	23	353		1200	$1.07 \times 10^8$	$1.01 \times 10^8$	$1.16 \times 10^8$	$1.17 \times 10^8$	124
					1328	$6.14 \times 10^7$	$5.88 \times 10^7$	$8.28 \times 10^7$	$9.20 \times 10^7$	144
					4500	$4.47 \times 10^8$	$4.45 \times 10^8$	$4.61 \times 10^8$	$4.61 \times 10^8$	459



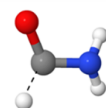
$T_c$  = crossover temperature; <sup>eq</sup> = equilibrium structure;  $k^{\text{Class}}$  = rate constant obtained from classical TST;  $k^{\text{Q-vib}}$  = rate constant obtained with quantized vibrations including the zero-point vibrational energy;  $k^{\text{S-Wig}}$  = rate constant obtained with quantized vibrations and tunneling correction through the simplified Wigner correction to the second order;  $k^{\text{F-Wig}}$  = full Wigner-corrected rate constant at T above  $T_c$ ;  $T_s$  = temperature at which the forward is spontaneous;  $\Delta E^{\ddagger}$  = energy barrier with respect to the precursor.

**Table S5<sup>†</sup>** Rate constants (k), enthalpies of activation ( $\Delta H^{\circ,\ddagger}$ ) and Gibbs free energy barriers ( $\Delta G^{\circ,\ddagger}$ ) for the C–H dissociation in the S<sub>1</sub> state (Channel (3)), obtained based on the transition state theory and potential energy curves. Energies, rate constants and temperatures are in kJ mol<sup>-1</sup>, s<sup>-1</sup> and K, respectively.

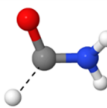
Channel (3)	$\Delta E^{\ddagger}$	$\Delta H^{\circ,\ddagger}$	T <sub>c</sub>	T	k <sup>Class</sup>	k <sup>Q-vib</sup>	k <sup>S-Wig</sup>	k <sup>F-Wig</sup>	$\Delta G^{\circ,\ddagger}$
				200	$7.03 \times 10^{-36}$	$4.63 \times 10^{-32}$	$1.85 \times 10^{-31}$	-	168
				450	$1.55 \times 10^{-8}$	$2.66 \times 10^{-7}$	$4.23 \times 10^{-7}$	$5.27 \times 10^{-7}$	168
<b>E3-[1] → E3-[3]</b>	166	171	269	1200	$7.30 \times 10^5$	$1.25 \times 10^6$	$1.35 \times 10^6$	$1.36 \times 10^6$	168
				1328	$2.86 \times 10^7$	$4.55 \times 10^7$	$4.77 \times 10^7$	$4.78 \times 10^7$	147
				4500	$7.30 \times 10^5$	$1.25 \times 10^6$	$1.35 \times 10^6$	$1.36 \times 10^6$	146



**E3-[1]**



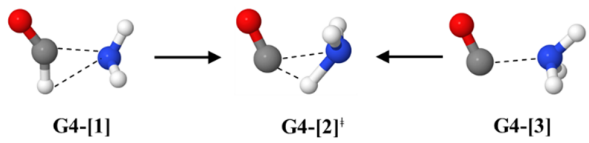
**E3-[2]**



**E3-[3]**

T<sub>c</sub> = crossover temperature; k<sup>Class</sup> = rate constant obtained from classical TST; k<sup>Q-vib</sup> = rate constant obtained with quantized vibrations including the zero-point vibrational energy; k<sup>S-Wig</sup> = rate constant obtained with quantized vibrations and tunneling correction through the simplified Wigner correction to the second order; k<sup>F-Wig</sup> = full Wigner-corrected rate constant at T above T<sub>c</sub>;  $\Delta E^{\ddagger}$  = energy barrier with respect to the precursor.

**Table S6<sup>†</sup>** Rate constants ( $k$ ), enthalpies of activation ( $\Delta H^{\ddagger}$ ) and Gibbs free energy barriers ( $\Delta G^{\ddagger}$ ) for the unimolecular isomerization of the C–N dissociated structure in the  $S_0$  state (Channel (4)), obtained based on the transition state theory and potential energy curves. Energies, rate constants and temperatures are in  $\text{kJ mol}^{-1}$ ,  $\text{s}^{-1}$  and K, respectively.

Channel (4)	$\Delta E^{\ddagger}$	$\Delta H^{\ddagger}$	$T_c$	T	$k^{\text{Class}}$	$k^{\text{Q-vib}}$	$k^{\text{S-Wig}}$	$k^{\text{F-Wig}}$	$\Delta G^{\ddagger}$
				200	$3.33 \times 10^{-12}$	$1.27 \times 10^{-10}$	$8.72 \times 10^{-10}$	-	86
				450	$2.20 \times 10^2$	$7.16 \times 10^2$	$1.54 \times 10^3$	$3.88 \times 10^3$	87
<b>G4-[1] <math>\rightarrow</math> G4-[2]<sup>‡</sup></b>	95	88	377	1200	$1.78 \times 10^9$	$2.26 \times 10^9$	$2.63 \times 10^9$	$2.68 \times 10^9$	93
				1328	$4.47 \times 10^9$	$5.45 \times 10^9$	$6.17 \times 10^9$	$6.25 \times 10^9$	94
				4500	$1.96 \times 10^{12}$	$1.99 \times 10^{12}$	$2.02 \times 10^{12}$	$2.02 \times 10^{12}$	144
				200	$4.30 \times 10^{-48}$	$5.64 \times 10^{-45}$	$4.09 \times 10^{-44}$	-	218
				450	$4.02 \times 10^{-16}$	$5.46 \times 10^{-15}$	$1.22 \times 10^{-14}$	$3.65 \times 10^{-14}$	235
<b>G4-[2]<sup>‡</sup> <math>\leftarrow</math> G4-[3]</b>	209	207	389	1200	$3.88 \times 10^0$	$6.86 \times 10^0$	$8.05 \times 10^0$	$8.21 \times 10^0$	289
				1328	$8.24 \times 10^1$	$1.32 \times 10^2$	$1.49 \times 10^2$	$1.51 \times 10^2$	288
				4500	$4.57 \times 10^7$	$4.79 \times 10^7$	$4.85 \times 10^7$	$4.85 \times 10^7$	542

$T_c$  = crossover temperature;  $k^{\text{Class}}$  = rate constant obtained from classical TST;  $k^{\text{Q-vib}}$  = rate constant obtained with quantized vibrations including the zero-point vibrational energy;  $k^{\text{S-Wig}}$  = rate constant obtained with quantized vibrations and tunneling correction through the simplified Wigner correction to the second order;  $k^{\text{F-Wig}}$  = full Wigner-corrected rate constant at T above  $T_c$ ;  $\Delta E^{\ddagger}$  = energy barrier with respect to the precursor.



**Table S7<sup>†</sup>** Rate constants (k), enthalpies of activation ( $\Delta H^{\circ\dagger}$ ) and Gibbs free energy barriers ( $\Delta G^{\circ\dagger}$ ) for formation HNCO and H<sub>2</sub> (structure **G5-[3]**) (Channel (5)), obtained based on the transition state theory and potential energy curves. Energies, rate constants and temperatures are in kJ mol<sup>-1</sup>, s<sup>-1</sup> and K, respectively.

Channel (5)	$\Delta E^{\ddagger}$	$\Delta H^{\circ\dagger}$	$T_c$	$T_s$	T	$k^{\text{Class}}$	$k^{\text{Q-vib}}$	$k^{\text{S-Wig}}$	$k^{\text{F-Wig}}$	$\Delta G^{\circ\dagger}$
					200	$1.33 \times 10^{-64}$	$1.35 \times 10^{-61}$	$6.14 \times 10^{-61}$	-	281
					450	$2.35 \times 10^{-21}$	$2.74 \times 10^{-20}$	$4.67 \times 10^{-20}$	$6.36 \times 10^{-20}$	280
<b>G5-[1] → G5-[2]<sup>‡</sup></b>	293	285	294		1200	$9.86 \times 10^0$	$1.74 \times 10^1$	$1.90 \times 10^1$	$1.91 \times 10^1$	279
					1328	$2.36 \times 10^2$	$3.72 \times 10^2$	$4.02 \times 10^2$	$4.04 \times 10^2$	276
					4500	$2.96 \times 10^{10}$	$3.10 \times 10^{10}$	$3.12 \times 10^{10}$	$3.12 \times 10^{10}$	300
				206	200	$6.85 \times 10^{-61}$	$6.51 \times 10^{-61}$	$2.95 \times 10^{-61}$	-	283
					450	$2.57 \times 10^{-21}$	$1.81 \times 10^{-21}$	$3.07 \times 10^{-21}$	$4.10 \times 10^{-21}$	290
<b>G5-[2]<sup>‡</sup> ← G5-[3]</b>	297	278	292		1200	$1.58 \times 10^{-1}$	$1.66 \times 10^{-1}$	$1.82 \times 10^{-1}$	$1.83 \times 10^{-1}$	326
					1328	$1.69 \times 10^{-1}$	$1.75 \times 10^{-1}$	$1.89 \times 10^{-1}$	$1.90 \times 10^{-1}$	360
					4500	$3.09 \times 10^7$	$3.12 \times 10^7$	$3.14 \times 10^7$	$3.14 \times 10^7$	558

$T_c$  = crossover temperature;  $k^{\text{Class}}$  = rate constant obtained from classical TST;  $k^{\text{Q-vib}}$  = rate constant obtained with quantized vibrations including the zero-point vibrational energy;  $k^{\text{S-Wig}}$  = rate constant obtained with quantized vibrations and tunneling correction through the simplified Wigner correction to the second order;  $k^{\text{F-Wig}}$  = full Wigner-corrected rate constant at T above  $T_c$ ;  $T_s$  = temperature at which the forward is spontaneous;  $\Delta E^{\ddagger}$  = energy barrier with respect to the precursor.

**Table S8<sup>†</sup>** Rate constants (k), enthalpies of activation ( $\Delta H^{\ddagger}$ ) and Gibbs free energy barriers ( $\Delta G^{\ddagger}$ ) for formation HNCO and H<sub>2</sub> (structure <sup>3</sup>E5-[3]) in the T<sub>1</sub> state (Channel (5)), obtained based on the transition state theory and potential energy curves. Energies, rate constants and temperatures are in kJ mol<sup>-1</sup>, s<sup>-1</sup> and K, respectively.

Channel (5)	$\Delta E^{\ddagger}$	$\Delta H^{\ddagger}$	T <sub>c</sub>	T <sub>s</sub>	T	k <sup>Class</sup>	k <sup>Q-vib</sup>	k <sup>S-Wig</sup>	k <sup>F-Wig</sup>	$\Delta G^{\ddagger}$
					200	$4.42 \times 10^{-46}$	$3.36 \times 10^{-46}$	$2.74 \times 10^{-41}$	-	207
					450	$5.25 \times 10^{-11}$	$8.06 \times 10^{-10}$	$1.95 \times 10^{-9}$	$1.04 \times 10^{-8}$	190
<b>E1-[4] → <sup>3</sup>E5-[2]<sup>‡</sup></b>	236	225	417		1200	$1.81 \times 10^7$	$2.95 \times 10^7$	$3.54 \times 10^7$	$3.63 \times 10^7$	136
					1328	$1.87 \times 10^7$	$2.79 \times 10^8$	$3.25 \times 10^8$	$3.31 \times 10^8$	127
					4500	$9.42 \times 10^{14}$	$9.78 \times 10^{14}$	$9.91 \times 10^{14}$	$9.92 \times 10^{14}$	-87
				1577	200	$6.01 \times 10^{-4}$	$1.11 \times 10^{-3}$	$9.07 \times 10^{-3}$	-	60
					450	$5.43 \times 10^4$	$8.22 \times 10^4$	$2.12 \times 10^5$	$3.80 \times 10^6$	66
<b><sup>3</sup>E5-[2]<sup>‡</sup> ← <sup>3</sup>E5-[3]</b>	55	56	417		1200	$8.26 \times 10^7$	$1.04 \times 10^8$	$1.53 \times 10^8$	$1.76 \times 10^8$	77
					1328	$3.22 \times 10^9$	$3.61 \times 10^9$	$4.20 \times 10^9$	$4.27 \times 10^9$	99
					4500	$1.26 \times 10^{11}$	$1.27 \times 10^{11}$	$1.29 \times 10^{11}$	$1.29 \times 10^{11}$	247

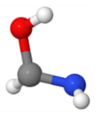
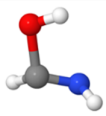
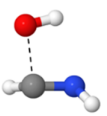
T<sub>c</sub> = crossover temperature; k<sup>Class</sup> = rate constant obtained from classical TST; k<sup>Q-vib</sup> = rate constant obtained with quantized vibrations including the zero-point vibrational energy; k<sup>S-Wig</sup> = rate constant obtained with quantized vibrations and tunneling correction through the simplified Wigner correction to the second order; k<sup>F-Wig</sup> = full Wigner-corrected rate constant at T above T<sub>c</sub>; T<sub>s</sub> = temperature at which the forward is spontaneous;  $\Delta E^{\ddagger}$  = energy barrier with respect to the precursor.

**Table S9<sup>†</sup>** Rate constants (k), enthalpies of activation ( $\Delta H^{\ddagger}$ ) and Gibbs free energy barriers ( $\Delta G^{\ddagger}$ ) for formation of CO–NH–H<sub>2</sub> van der Waals cluster (structure **E5-[3]**) (Channel (5)), obtained based on the transition state theory and potential energy curves. Energies, rate constants and temperatures are in kJ mol<sup>-1</sup>, s<sup>-1</sup> and K, respectively.

Channel (5)	$\Delta E^{\ddagger}$	$\Delta H^{\ddagger}$	$T_c$	$T_s$	T	$k^{\text{Class}}$	$k^{\text{Q-vib}}$	$k^{\text{S-Wig}}$	$k^{\text{F-Wig}}$	$\Delta G^{\ddagger}$
					200	$1.87 \times 10^{-39}$	$2.63 \times 10^{-42}$	$1.52 \times 10^{-41}$	-	207
					450	$3.58 \times 10^{-9}$	$9.51 \times 10^{-11}$	$1.85 \times 10^{-10}$	$3.27 \times 10^{-10}$	198
<b>E5-[1] → E5-[2]<sup>‡</sup></b>	204	219	340		1200	$4.95 \times 10^6$	$1.23 \times 10^6$	$1.39 \times 10^6$	$1.41 \times 10^6$	167
					1328	$3.07 \times 10^7$	$1.08 \times 10^7$	$1.20 \times 10^7$	$1.21 \times 10^7$	162
					4500	$2.27 \times 10^{13}$	$1.90 \times 10^{13}$	$1.92 \times 10^{13}$	$1.92 \times 10^{13}$	60
				990	200	$3.65 \times 10^{-4}$	$1.35 \times 10^{-15}$	$7.80 \times 10^{-15}$	-	105
					450	$9.61 \times 10^2$	$6.07 \times 10^{-2}$	$1.17 \times 10^{-1}$	$2.08 \times 10^{-1}$	122
<b>E5-[2]<sup>‡</sup> ← E5-[3]</b>	45	92	340		1200	$1.56 \times 10^6$	$1.27 \times 10^5$	$1.44 \times 10^5$	$1.45 \times 10^5$	190
					1328	$2.36 \times 10^6$	$2.75 \times 10^5$	$3.05 \times 10^5$	$3.07 \times 10^5$	203
					4500	$3.98 \times 10^7$	$3.06 \times 10^7$	$3.09 \times 10^7$	$3.09 \times 10^7$	559

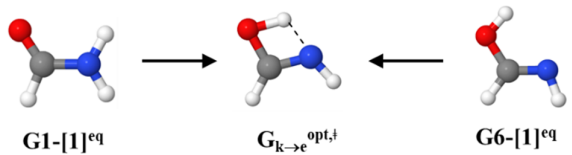
$T_c$  = crossover temperature;  $k^{\text{Class}}$  = rate constant obtained from classical TST;  $k^{\text{Q-vib}}$  = rate constant obtained with quantized vibrations including the zero-point vibrational energy;  $k^{\text{S-Wig}}$  = rate constant obtained with quantized vibrations and tunneling correction through the simplified Wigner correction to the second order;  $k^{\text{F-Wig}}$  = full Wigner-corrected rate constant at T above  $T_c$ ;  $T_s$  = temperature at which the forward is spontaneous;  $\Delta E^{\ddagger}$  = energy barrier with respect to the precursor.

**Table S10<sup>†</sup>** Rate constants (k), enthalpies of activation ( $\Delta H^{\circ,\ddagger}$ ) and Gibbs free energy barriers ( $\Delta G^{\circ,\ddagger}$ ) for the dissociation of the C–O bond in formamidic acid (HCOHNH) in the S<sub>1</sub> state (Channel (6)), obtained based on the transition state theory and potential energy curves. Energies, rate constants and temperatures are in kJ mol<sup>-1</sup>, s<sup>-1</sup> and K, respectively.

Channel (6)	$\Delta E^{\ddagger}$	$\Delta H^{\circ,\ddagger}$	T <sub>c</sub>	T	k <sup>Class</sup>	k <sup>Q-vib</sup>	k <sup>S-Wig</sup>	k <sup>F-Wig</sup>	$\Delta G^{\circ,\ddagger}$
				200	$1.29 \times 10^{-22}$	$4.54 \times 10^{-22}$	$1.22 \times 10^{-21}$	-	130
				450	$7.33 \times 10^{-3}$	$7.23 \times 10^{-3}$	$9.63 \times 10^{-3}$	$1.03 \times 10^{-2}$	130
<b>E6-[2]<sup>eq</sup> → E6-[4]</b>	133	133	202	1200	$5.52 \times 10^7$	$5.09 \times 10^7$	$5.33 \times 10^7$	$5.33 \times 10^7$	131
				1328	$2.05 \times 10^8$	$1.91 \times 10^8$	$1.99 \times 10^8$	$1.99 \times 10^8$	131
				4500	$1.22 \times 10^{12}$	$1.21 \times 10^{12}$	$1.22 \times 10^{12}$	$1.22 \times 10^{12}$	162
									

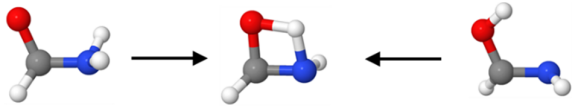
T<sub>c</sub> = crossover temperature; <sup>eq</sup> = equilibrium structure; k<sup>Class</sup> = rate constant obtained from classical TST; k<sup>Q-vib</sup> = rate constant obtained with quantized vibrations including the zero-point vibrational energy; k<sup>S-Wig</sup> = rate constant obtained with quantized vibrations and tunneling correction through the simplified Wigner correction to the second order; k<sup>F-Wig</sup> = full Wigner-corrected rate constant at T above T<sub>c</sub>;  $\Delta E^{\ddagger}$  = energy barrier with respect to the precursor.

**Table S11<sup>†</sup>** Rate constants (k), enthalpies of activation ( $\Delta H^{\circ,\ddagger}$ ) and Gibbs free energy barriers ( $\Delta G^{\circ,\ddagger}$ ) for the keto-enol tautomerism of HCONH<sub>2</sub> in the S<sub>0</sub> state (structure **G1-[1]<sup>eq</sup>** → **G6-[1]<sup>eq</sup>**), obtained based on the transition state theory and the optimize transition geometry (**G<sub>k→e</sub><sup>opt,‡</sup>**). Energies, rate constants and temperatures are in kJ mol<sup>-1</sup>, s<sup>-1</sup> and K, respectively.

	$\Delta E^{\ddagger}$	$\Delta H^{\circ,\ddagger}$	T <sub>c</sub>	T	k <sup>Class</sup>	k <sup>Q-vib</sup>	k <sup>S-Wig</sup>	k <sup>F-Wig</sup>	$\Delta G^{\circ,\ddagger}$
				200	$2.92 \times 10^{-36}$	$2.19 \times 10^{-33}$	$1.87 \times 10^{-32}$	-	173
				450	$7.38 \times 10^{-11}$	$1.05 \times 10^{-9}$	$2.79 \times 10^{-9}$	-	179
<b>G1-[1]<sup>eq</sup> → G<sub>k→e</sub><sup>opt,‡</sup></b>	188	141	306	1200	$1.07 \times 10^0$	$3.30 \times 10^0$	$4.93 \times 10^0$	$5.75 \times 10^0$	189
				1328	$1.29 \times 10^5$	$2.05 \times 10^5$	$2.40 \times 10^5$	$2.46 \times 10^5$	207
				4500	$1.55 \times 10^{10}$	$1.62 \times 10^{10}$	$1.65 \times 10^{10}$	$1.65 \times 10^{10}$	324
				200	$3.61 \times 10^{-30}$	$2.81 \times 10^{-27}$	$2.39 \times 10^{-26}$	-	150
				450	$3.36 \times 10^{-7}$	$4.06 \times 10^{-6}$	$1.08 \times 10^{-5}$	-	150
<b>G<sub>k→e</sub><sup>opt,‡</sup> ← G6-[1]<sup>eq</sup></b>	169	124	255	1200	$5.16 \times 10^2$	$1.44 \times 10^3$	$2.15 \times 10^3$	$2.51 \times 10^3$	150
				1328	$2.03 \times 10^7$	$3.07 \times 10^7$	$3.59 \times 10^7$	$3.66 \times 10^7$	151
				4500	$7.95 \times 10^{11}$	$8.27 \times 10^{11}$	$8.40 \times 10^{11}$	$8.40 \times 10^{11}$	177

T<sub>c</sub> = crossover temperature; <sup>eq</sup> = equilibrium structure; k<sup>Class</sup> = rate constant obtained from classical TST; k<sup>Q-vib</sup> = rate constant obtained with quantized vibrations including the zero-point vibrational energy; k<sup>S-Wig</sup> = rate constant obtained with quantized vibrations and tunneling correction through the simplified Wigner correction to the second order; k<sup>F-Wig</sup> = full Wigner-corrected rate constant at T above T<sub>c</sub>;  $\Delta E^{\ddagger}$  = energy barrier with respect to the precursor.

**Table S12<sup>†</sup>** Rate constants (k), enthalpies of activation ( $\Delta H^{\circ,\ddagger}$ ) and Gibbs free energy barriers ( $\Delta G^{\circ,\ddagger}$ ) for the keto-enol tautomerism of HCONH<sub>2</sub> in the S<sub>1</sub> state (structure **E1-[2]<sup>eq</sup>** → **E6-[2]<sup>eq</sup>**), obtained based on the transition state theory and the optimize transition geometry (**E<sub>k→e</sub><sup>opt,‡</sup>**). Energies, rate constants and temperatures are in kJ mol<sup>-1</sup>, s<sup>-1</sup> and K, respectively.

	$\Delta E^{\ddagger}$	$\Delta H^{\circ,\ddagger}$	T <sub>c</sub>	T	k <sup>Class</sup>	k <sup>Q-vib</sup>	k <sup>S-Wig</sup>	k <sup>F-Wig</sup>	$\Delta G^{\circ,\ddagger}$
				200	$2.91 \times 10^{-19}$	$8.42 \times 10^{-17}$	$1.31 \times 10^{-15}$	-	110
				450	$9.95 \times 10^{-2}$	$8.59 \times 10^{-1}$	$3.32 \times 10^0$	-	112
<b>E1-[2]<sup>eq</sup> → E<sub>k→e</sub><sup>opt,‡</sup></b>	94	111	594	1200	$5.82 \times 10^7$	$9.49 \times 10^7$	$1.33 \times 10^8$	$1.48 \times 10^8$	125
				1328	$1.87 \times 10^7$	$2.81 \times 10^8$	$3.74 \times 10^8$	$4.01 \times 10^8$	127
				4500	$4.19 \times 10^{11}$	$4.36 \times 10^{11}$	$4.49 \times 10^{11}$	$4.49 \times 10^{11}$	201
				200	$3.43 \times 10^{-22}$	$2.17 \times 10^{-20}$	$3.63 \times 10^{-19}$	-	124
				450	$4.22 \times 10^{-3}$	$2.16 \times 10^{-2}$	$8.87 \times 10^{-2}$	-	126
<b>E<sub>k→e</sub><sup>opt,‡</sup> ← E6-[2]<sup>eq</sup></b>	138	150	594	1200	$1.48 \times 10^7$	$2.19 \times 10^7$	$3.14 \times 10^7$	$3.55 \times 10^7$	139
				1328	$6.96 \times 10^6$	$1.17 \times 10^7$	$1.55 \times 10^7$	$1.66 \times 10^7$	162
				4500	$2.46 \times 10^{11}$	$2.59 \times 10^{11}$	$2.67 \times 10^{11}$	$2.67 \times 10^{11}$	220

T<sub>c</sub> = crossover temperature; <sup>eq</sup> = equilibrium structure; k<sup>Class</sup> = rate constant obtained from classical TST; k<sup>Q-vib</sup> = rate constant obtained with quantized vibrations including the zero-point vibrational energy; k<sup>S-Wig</sup> = rate constant obtained with quantized vibrations and tunneling correction through the simplified Wigner correction to the second order; k<sup>F-Wig</sup> = full Wigner-corrected rate constant at T above T<sub>c</sub>;  $\Delta E^{\ddagger}$  = energy barrier with respect to the precursor.