Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.


# Electronic Supplementary Information

## From prebiotic chemistry to supramolecular oligomers: urea-glyoxal reactions

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## CONTENTS

## 1. EXPERIMENTAL DETAILS

***Isolation of solid phases.*** To a solution of urea (5.00 g, 83.33 mmol) in either acetone or 1,4-dioxane (100 mL) was added glyoxal (40% aqueous solution; amounts gathered in Table S1.1), and the mixture was stirred at room temperature. After 5-6 days an insoluble gel appeared,(*) and the mixture was stirred for three more days. The resulting gel was isolated by decantation and then treated with fresh acetone (100 mL) under stirring for 48 h, which gave rise to a solid that could be filtered and washed repeatedly with acetone, and dried under vacuum for one month. The isolated yields and the corresponding mass efficiencies are shown in Table S1.1.

(*)The 1:2 urea:glyoxal reaction in 1,4-dioxane did not result in gel formation after 8 days. After that time, the solvent was evaporated to ¼ volume and fresh acetone (100 mL) was added under stirring, which caused the precipitation of a white solid.

**Table S1.1.** Oligomeric solids isolated from different urea:glyoxal mixtures

| Urea:glyoxal ratios | Solvent | Glyoxal | Mass isolated (g) | Mass efficiency (%) |
|---|---|---|---|---|
| **1:2** | Acetone | 19.04 ml (166.6 mmol) | 8.82 | 53.2 % |
| **1:1** | Acetone | 9.52 ml (83.3 mmol) | 7.11 | 72.3 % |
| **2:1** | Acetone | 4.76 ml (41.6 mmol) | 4.28 | 57.8 % |
| **1:2** | 1,4-Dioxane | 19.04 ml (166.6 mmol) | 10.2 | 69.6 % |
| **1:1** | 1,4-Dioxane | 9.52 ml (83.3 mmol) | 6.24 | 63.4 % |
| **2:1** | 1,4-Dioxane | 4.76 ml (41.6 mmol) | 3.13 | 42.1 % |

***Sample preparation for $^{1}H/^{13}C$ NMR spectroscopy*.** NMR spectra were recorded in $D_2O/H_2O$ mixtures generated from a solution of urea (0.74 g, 12.0 mmol) in $D_2O$ (5 mL) plus glyoxal (40% aqueous solution, 2.76 mL, 24.0 mmol) (1:2 molar ratio); from urea (0.74 g, 12.0 mmol) and glyoxal (1.38 mL, 12.0 mmol) (1:1 ratio), and urea (0.74 g, 12.0 mmol) and glyoxal (0.69 mL, 6.0 mmol) (2:1 ratio).

***Sample preparation for ESI-MS analysis*.** For a 1:2 molar ratio of reagents: to a solution of urea (0.074 g, 1.2 mmol) in water (5 mL) was added glyoxal (40% aqueous solution, 0.28 mL, 2.4 mmol) and the mixture was kept at room temperature. The same protocol was applied to 1:1 molar ratio starting from urea (0.144 g, 2.4 mmol) and glyoxal (0.28 mL, 2.4 mmol), as well as to 2:1 ratio from urea (0.288 g, 4.8 mmol) and glyoxal (0.28 mL, 2.4 mmol). Aliquots were taken regularly and diluted with distilled water (1/10 v/v) prior to injection.

***Sample preparation for UV spectra recording.*** *To* a solution of urea (0.072 g, 1.2 mmol) in water (5 mL) was added glyoxal (40% aqueous solution, 0.28 mL, 2.4 mmol), and the resulting mixture was kept at room temperature. Aliquots (0.02 mL) were taken at regular intervals and diluted with distilled water (up to 25 mL) before UV-measurements. The same dilution factor was applied to 1:1 molar ratios starting from urea (0.144 g, 2.4 mmol) and glyoxal (0.28 mL, 2.4 mmol), as well as to 2:1 samples from urea (0.288 g, 4.8 mmol) and glyoxal (0.28 mL, 2.4 mmol).

***pH Measurements.*** To a solution of urea (0.072 g, 1.2 mmol) in water (5 mL) was added glyoxal (40% aqueous solution, 0.28 mL, 2.4 mmol), and pH values were estimated at room temperature with a pH meter at a given time. The same procedure was applied to 1:1 urea:glyoxal samples starting from urea (0.144 g, 2.4 mmol) and glyoxal (0.28 mL, 2.4 mmol), and 2:1 molar ratios from urea (0.288 g, 4.8 mmol) and glyoxal (0.28 mL, 2.4 mmol).

***Isolation of glycoluril by-product (7).*** To a solution of urea (0.288 g, 4.8 mmol) in water (5 mL) was added glyoxal (40% aqueous solution, 0.28 mL, 2.4 mmol), and the mixture was kept at room temperature. After *ca*. 20 days, a crystalline solid was observed, which was collected by filtration (0.036 g, 8.4 %), and whose spectroscopic data are coincidental with an authentic sample of glycoluril.

## 2. ADDITIONAL COMPUTATIONAL DETAILS

Because of the multiple nucleophilic sites present in the molecules evaluated through this study, we have calculated the condensed Fukui function[1] for all heteroatoms and compared their corresponding dual descriptor ($\Delta f$).[2] The Fukui function has been widely employed for predicting reactive sites, although it is well known that the dual descriptor should be rather regarded as a local reactivity function for comparative purposes, thus unveiling preferential reaction sites.[3] The higher the value of $\Delta f$, the more electrophilic site is and vice versa. Hirshfeld charges were first chosen as the most suitable charge analysis to estimate the Fukui indicators.[4] In order to calculate the dual descriptor, the condensed Fukui function for either nucleophilic attacks [eq. (1)] or electrophilic attacks [eq. (2)] were obtained, where $f^+$ and $f^-$ denote the condensed Fukui function for the nucleophilic and electrophilic attack respectively, of a given atom A, whereas $q_N$, $q_{N-1}$ and $q_{N+1}$ are the charges of that atom in a molecule in its neutral state, with charge +1 and with charge -1, respectively. Eq. (3) describes the condensed dual descriptor for the atom in question (A).

$$f_A^+ = q_N^A - q_{N+1}^A \quad (1)$$

$$f_A^- = q_{N-1}^A - q_N^A \quad (2)$$

$$\Delta f_A = f_A^+ - f_A^- \quad (3)$$

The isosurfaces of the dual descriptor of the Fukui function ($\Delta f$) based on electron density, were computed with Multiwfn[5] software at the M06-2X/6-31G level of theory. The shape of the molecular orbitals was calculated with Gaussian 09 and the images of the HOMOs and $\Delta f$ were visualized with the Chimera software.[6]

Due to the chiral nature of heterocycles **20**, **21**, **23**, **24**, **25** and **36**, some restrictions have been taken into account, thereby avoiding the cost of computing the formation of all diastereomers. The results obtained for the formation of *cis*- and *trans*-imidazolidin-2-ones, **17** and **18** respectively, demonstrated that the latter is favored with respect to its *cis* counterpart. Accordingly, all substituents in vicinal 1,2 positions display a *trans* relationship. This also applies to the formation of *trans* isomers in heterocycles containing two chiral centers like **25** and **36**.

Figure S2.1 (below) shows the optimized geometries for diastereomeric structures of **20**, **21**, **23** and **24** along with their relative free energies with respect to urea and glyoxal.

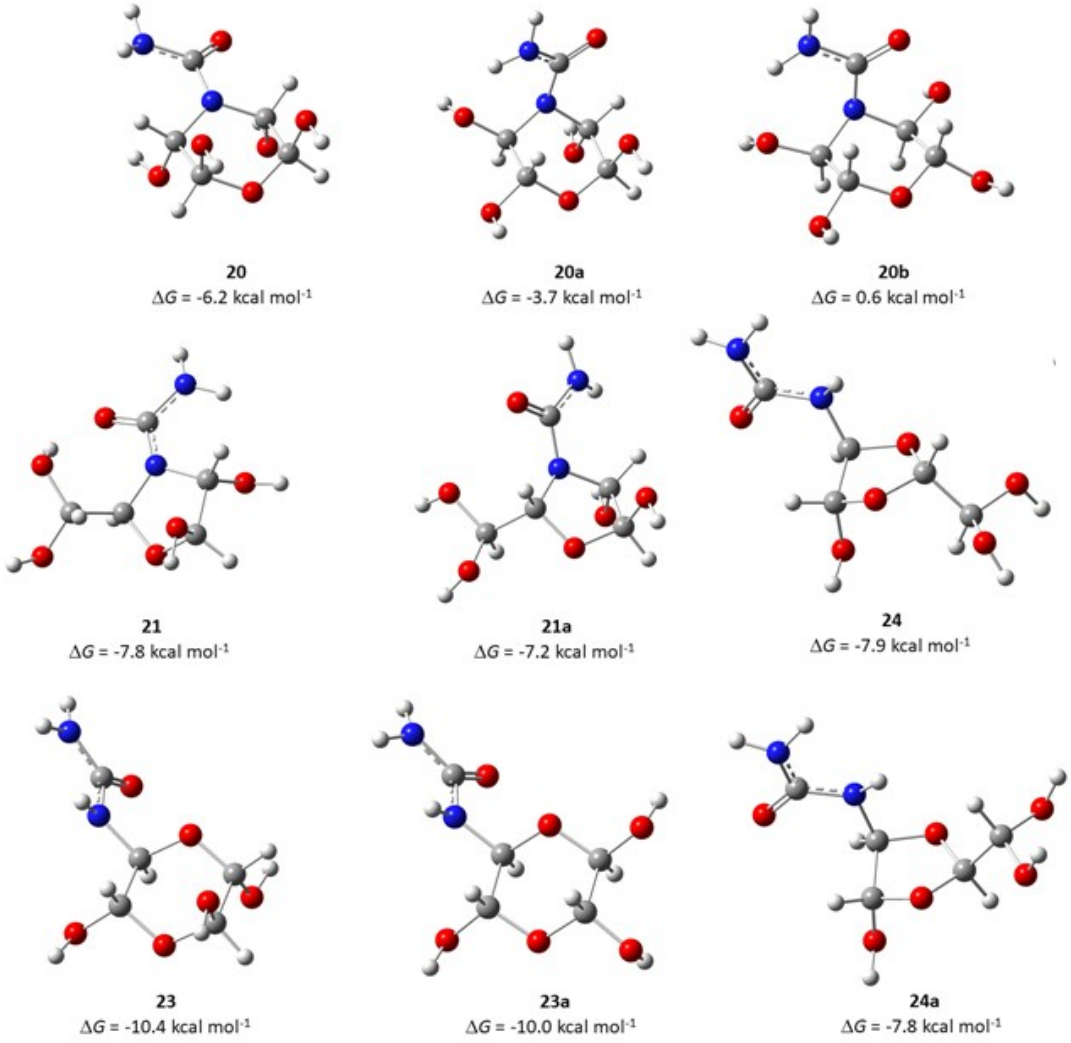


**Figure S2.1** Optimized geometries for compounds **20**, **20a**, **20b**, **21**, **21a**, **23**, **23a**, **24** and **24a** at the M06-2X/6-311+G(d) level of theory in water (SMD). Relative free energies are given with respect to **1** and **3** in kcal $mol^{-1}$.

**Table S2.1.** Relative electronic energy (Δ*E*), enthalpy (Δ*H*), and free energy (Δ*G*) (in kcal $mol^{-1}$) of all the stationary points involved in the reaction of **1** and **3** yielding compound **11**.

| Structure | Δ*E* | Δ*H* | Δ*G* |
|---|---|---|---|
| **1** + **3** | 0.00 | 0.00 | 0.00 |
| **9** | 3.8 | 2.8 | 3.7 |
| **9c** | -5.7 | -5.5 | 5.7 |
| $\mathbf{TS_{9c}}$ | 11.0 | 9.4 | 20.5 |
| $\mathbf{11H^+}$ | -7.4 | -8.5 | -5.4 |
| **11** | -1.2 | -1.5 | 0.4 |
| **9** | 3.8 | 2.8 | 3.7 |
| **10** | 26.0 | 21.7 | 11.0 |
| **10c** | 15.1 | 12.5 | 14.2 |
| $\mathbf{TS_{10c}}$ | 15.9 | 12.3 | 14.4 |
| $\mathbf{11H^+}$ | -7.4 | -8.5 | -5.4 |
| **11** | -1.2 | -1.5 | 0.4 |
| **8** | 15.0 | 11.3 | -0.4 |
| **8c** | 6.4 | 6.0 | 14.8 |
| $\mathbf{TS1_{8c}}$ | 14.3 | 14.1 | 26.1 |
| $\mathbf{I_{8c}}$ | 14.3 | 14.7 | 25.7 |
| $\mathbf{TS2_{8c}}$ | 22.4 | 19.8 | 33.6 |
| **11** | 15.0 | 11.3 | -0.4 |

**Table S2.2.** Relative electronic energy (Δ*E*), enthalpy (Δ*H*), and free energy (Δ*G*) (in kcal $mol^{-1}$) of all the stationary points involved in the reaction of **11** and **1** leading to **15** and **16**.

| Structure | Δ*E* | Δ*H* | Δ*G* |
|---|---|---|---|
| **1** + **3** | 0.00 | 0.00 | 0.00 |
| **12** | 21.5 | 17.9 | 8.3 |
| **12c** | 5.4 | 5.4 | 18.5 |
| $\mathbf{TS1_{12c}}$ | 22.0 | 21.4 | 35.3 |
| $\mathbf{I_{12c}}$ | 18.4 | 19.2 | 33.9 |
| $\mathbf{TS2_{12c}}$ | 26.5 | 23.5 | 40.1 |
| **15** | -6.1 | -6.9 | -2.1 |
| **13** | 1.4 | -0.2 | 2.5 |
| **14** | 9.6 | 5.1 | -3.1 |
| **14c** | 1.8 | -1.0 | 1.6 |
| $\mathbf{TS_{14c}}$ | 3.4 | 0.0 | 5.2 |
| $\mathbf{15H^+}$ | -12.7 | -13.7 | -7.6 |
| **15** | -6.1 | -6.9 | -2.1 |
| **13** | 1.4 | -0.2 | 2.5 |
| **13c** | -7.2 | -6.9 | 8.1 |
| $\mathbf{TS_{13c}}$ | -0.7 | -2.2 | 11.7 |
| $\mathbf{15H^+}$ | -12.7 | -13.7 | -7.6 |
| **15** | -6.1 | -6.9 | -2.1 |
| **16a** | 0.9 | -0.6 | 2.0 |

| | | | |
|---|---|---|---|
| **16ca** | -5.5 | -5.5 | 8.1 |
| **$TS_{16ca}$** | 5.9 | 4.5 | 19.0 |
| **$16H^+$** | -9.6 | -11.1 | -5.4 |
| **16** | -3.7 | -4.6 | 0.1 |
| **16a** | 0.9 | -0.6 | 2.0 |
| **16b** | 10.6 | 7.2 | 10.4 |
| **16cb** | 11.3 | 7.4 | 11.7 |
| **$TS_{16cb}$** | -9.6 | -11.1 | -5.4 |
| **$16H^+$** | -9.6 | -11.1 | -5.4 |
| **16** | -3.7 | -4.6 | 0.1 |

**Table S2.3.** Relative electronic energy (Δ*E*), enthalpy (Δ*H*), and free energy (Δ*G*) (in kcal $mol^{-1}$) of all the stationary points involved in the formation of **17** and **18** from **16b**.

| Structure | Δ*E* | Δ*H* | Δ*G* |
|---|---|---|---|
| **1** + **3** | 0.00 | 0.00 | 0.00 |
| **16b** | 10.6 | 7.2 | 10.4 |
| $\mathbf{TS_{17c}}$ | 28.6 | 23.4 | 16.4 |
| $\mathbf{17H^+}$ | -2.7 | -6.2 | -12.6 |
| **17** | 0.2 | -2.7 | -9.6 |
| **16b** | 10.6 | 7.2 | 10.4 |
| $\mathbf{TS_{18c}}$ | 23.5 | 17.9 | 11.2 |
| $\mathbf{18H^+}$ | -3.0 | -6.4 | -12.8 |
| **18** | 0.6 | -2.4 | -9.9 |

**Table S2.4.** Relative electronic energy (Δ*E*), enthalpy (Δ*H*), and free energy (Δ*G*) (in kcal $mol^{-1}$) of all the stationary points involved in the reaction of **9** and **11** leading to **20** and **21**.

| Structure | Δ*E* | Δ*H* | Δ*G* |
|---|---|---|---|
| **1** + **3** | 0.00 | 0.00 | 0.00 |
| **10** | 26.0 | 21.7 | 11.0 |
| **19c** | 9.2 | 5.6 | 10.1 |
| $\mathbf{TS_{19c}}$ | 15.9 | 11.6 | 16.0 |
| $\mathbf{19H_a^+}$ | -6.9 | -9.4 | -3.8 |
| **19** | 6.4 | 4.9 | 9.4 |
| $\mathbf{19H_b^+}$ | 3.9 | 1.6 | 8.0 |
| $\mathbf{19H_c^+}$ | 25.4 | 19.2 | 13.1 |
| $\mathbf{19H_d^+}$ | 12.7 | 5.9 | 2.1 |
| $\mathbf{TS_{20}}$ | 23.9 | -14.2 | 14.9 |
| $\mathbf{20H^+}$ | 9.8 | 4.5 | 1.0 |
| **20** | 1.5 | -1.9 | -6.2 |
| **19c** | 9.2 | 5.6 | 10.1 |
| $\mathbf{TS_{19c}}$ | 15.9 | 11.6 | 16.0 |
| $\mathbf{19H_a^+}$ | -6.9 | -9.4 | -3.8 |
| **19** | 6.4 | 4.9 | 9.4 |
| $\mathbf{19H_b^+}$ | 3.9 | 1.6 | 8.0 |
| $\mathbf{19H_c^+}$ | 25.4 | 19.2 | 13.1 |
| $\mathbf{19H_d^+}$ | 12.7 | 5.9 | 2.1 |

| | | | |
|---|---|---|---|
| **$TS_{21}$** | 18.1 | 10.3 | 6.2 |
| **$21H^+$** | 12.0 | 6.9 | 3.2 |
| **21** | 0.7 | -3.1 | -7.8 |

**Table S2.5.** Relative electronic energy (Δ*E*), enthalpy (Δ*H*), and free energy (Δ*G*) (in kcal $mol^{-1}$) of all the stationary points involved in the reaction of **13** and **8** leading to **23** and **24**.

| **Structure** | **Δ*E*** | **Δ*H*** | **Δ*G*** |
|---|---|---|---|
| **1** + **3** | 0.00 | 0.00 | 0.00 |
| **14** | 9.6 | 5.1 | -3.1 |
| **22c** | 2.7 | 0.1 | 3.9 |
| **$TS_{22c}$** | 3.0 | -0.4 | 4.7 |
| **$22H_a^+$** | -5.1 | -6.7 | -4.9 |
| **22** | -7.0 | -8.1 | -3.6 |
| **$22H_b^+$** | -2.6 | -4.8 | 0.6 |
| **$22H_c^+$** | 18.5 | 12.5 | 6.3 |
| **$TS_{23}$** | 19.3 | 12.8 | 8.1 |
| **$23H^+$** | 8.3 | 2.4 | -2.4 |

| | | | |
|---|---|---|---|
| **23** | -1.0 | -5.0 | -10.4 |
| **14** | 9.6 | 5.1 | -3.1 |
| **22c** | 2.7 | 0.1 | 3.9 |
| **$TS_{22c}$** | 3.0 | -0.4 | 4.7 |
| **$22H_a^+$** | -5.1 | -6.7 | -4.9 |
| **22** | -7.0 | -8.1 | -3.6 |
| **$22H_b^+$** | -2.6 | -4.8 | 0.6 |
| **$22H_c^+$** | 18.5 | 12.5 | 6.3 |
| **$TS_{24}$** | 18.7 | 12.3 | 6.7 |
| **$24H^+$** | 13.1 | 7.7 | 2.0 |
| **24** | 1.7 | -2.1 | -7.9 |

**Table S2.6.** Relative electronic energy (Δ*E*), enthalpy (Δ*H*), and free energy (Δ*G*) (in kcal $mol^{-1}$) of all the stationary points involved in the formation of **25** evolving from **22** and **26**, which are generated by reaction of **9** and **12**.

| Structure | Δ*E* | Δ*H* | Δ*G* |
|---|---|---|---|
| **1** + **3** | 0.00 | 0.00 | 0.00 |
| **22** | -7.0 | -8.1 | -3.6 |
| **22H$_d^+$** | -6.5 | -10.1 | -5.2 |
| **22H$_e^+$** | 25.1 | 18.7 | 11.7 |
| **TS$_{25a}$** | 29.4 | 22.8 | 17.7 |
| **25H$_a^+$** | 1.5 | -2.4 | -7.2 |
| **25** | 1.2 | -2.2 | -8.0 |
| **10** | 26.0 | 21.7 | 11.0 |
| **26c** | 11.9 | 8.7 | 12.7 |
| **TS$_{26c}$** | 12.8 | 8.6 | 12.9 |
| **26H$_a^+$** | -8.3 | -9.7 | -4.8 |
| **26** | -4.3 | -5.4 | -1.7 |
| **26H$_b^+$** | -2.8 | -5.0 | -0.7 |
| **26H$_c^+$** | 9.0 | 3.9 | -3.3 |
| **TS$_{25b}$** | 20.5 | 14.7 | 10.0 |
| **25H$_b^+$** | 14.3 | 9.0 | 4.3 |
| **25** | 1.2 | -2.2 | -8.0 |

**Table S2.7.** Relative electronic energy (Δ*E*), enthalpy (Δ*H*), and free energy (Δ*G*) (in kcal $mol^{-1}$) of all the stationary points involved in the formation of **33** from **15** and **16**, and the subsequent conversion of **33** into **34**

| Structure | Δ*E* | Δ*H* | Δ*G* |
|---|---|---|---|
| **1** + **3** | 0.00 | 0.00 | 0.00 |
| **15** | -6.1 | -6.9 | -2.1 |
| **33H$_d^+$** | -3.3 | -5.2 | -0.2 |
| **33H$_e^+$** | 18.7 | 13.4 | 6.5 |
| **TS$_{33b}$** | 21.9 | 16.1 | 11.8 |
| **33H$_d^+$** | -4.9 | -9.0 | -13.8 |
| **33** | -2.2 | -5.4 | -10.7 |
| **16** | -3.7 | -4.6 | 0.1 |
| **33H$_a^+$** | -2.9 | -5.0 | -1.0 |
| **33H$_b^+$** | 9.2 | 4.6 | -2.5 |
| **TS$_{33b}$** | 12.6 | 7.1 | 2.7 |
| **33H$_d^+$** | -6.5 | -10.1 | -15.2 |
| **33** | -2.2 | -5.4 | -10.7 |
| **33** | -2.2 | -5.4 | -10.7 |
| **34H$_a^+$** | -2.2 | -5.4 | -10.7 |
| **34H$_b^+$** | 11.5 | 3.9 | -12.0 |
| **TS$_{34}$** | 16.0 | 7.6 | -6.3 |
| **34H$_b^+$** | -2.7 | -8.9 | -23.8 |

| | | | |
|---|---|---|---|
| **34** | 0.7 | -5.4 | -20.8 |

**Table S2.8.** Relative electronic energy (Δ*E*), enthalpy (Δ*H*), and free energy (Δ*G*) (in kcal $mol^{-1}$) of all the stationary points involved in the formation of **36** from **9** and **16**.

| Structure | Δ*E* | Δ*H* | Δ*G* |
|---|---|---|---|
| **1** + **3** | 0.00 | 0.00 | 0.00 |
| **11** | -1.2 | -1.5 | 0.4 |
| **35c** | 8.8 | 4.6 | 9.8 |
| $\mathbf{TS_{35c}}$ | 9.5 | 4.9 | 11.8 |
| $\mathbf{35H_a^+}$ | -12.9 | -15.0 | -7.5 |
| **35** | -9.3 | -11.0 | -5.1 |
| $\mathbf{35H_b^+}$ | -7.9 | -10.3 | -2.7 |
| $\mathbf{35H_c^+}$ | 6.2 | 0.9 | -3.6 |
| $\mathbf{TS_{36}}$ | 18.7 | 12.0 | 9.4 |
| $\mathbf{36H^+}$ | -2.5 | -7.1 | -8.6 |
| **36** | 1.2 | -3.0 | -5.0 |

**References**


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## 3. CHARACTERIZATION METHODS

Reagents and solvents were purchased from commercial suppliers and used as received. IR spectra were recorded in the range of 4000-600 $cm^{-1}$ on an FT-IR Thermo spectrophotometer using KBr (Merck) pellets. Electronic spectra were measured on a Thermo 201 UV-Vis spectrophotometer. NMR spectra were recorded on a Bruker spectrometer operating at 500 MHz and 125 MHz for $^{1}H$ and $^{13}C$ nuclei, respectively. Carbon assignments were facilitated by DEPT (*Distortionless Enhancement by Polarization Transfer*) experiments and isotopic exchange after addition of $D_2O$ for proton resonances. TMS was used as the internal standard (δ = 0.00 ppm). Microanalyses were determined on a Leco CHNS-932 analyzer. The pH measurements of aqueous cyanamide-glyoxal solutions were carried out at 25 ºC by means of a portable CRISON PH25 instrument with a 50 50T electrode.

Electrospray ionization mass spectra were obtained using a 6520 Accurate-Mass Q-TOF LC/MS instrument with DUAL ESI interface (Agilent Technologies) coupled to an Agilent 1200 Liquid Chromatography (LC) apparatus. Solid samples were kept in a vacuum desiccator for 48 h prior to analysis, and then introduced in the system using injector and column switching valve directly to the interface. The mobile phase was milli-Q water containing 1.0% acetic acid with a flow at 0.3 mL/min. The acid imparts a positive charge on some functional groups; all samples were run in positive scan mode only. Mass spectra were recorded from 40 to 1000 *m/z* values in high-resolution mode (at 4 GHz ADC rate for data acquisition) and real-time processing on the mass peaks detected in each transient, weighting the apex data much more heavily than the shoulders. Conditions in the nebulizer were 350 ºC (gas temperature), at a flow rate of 6 mL/min and 60 psi. It should be noted that all collected peaks correspond to normalized signals and had intensities equal to or greater than 10 times the blank/reference (base line), thereby ruling out background noise. All tabulated peaks had intensities >1%, which satisfy the aforementioned criterion.

## 4. FT-IR SPECTRA

### 2:1 STOICHIOMETRY

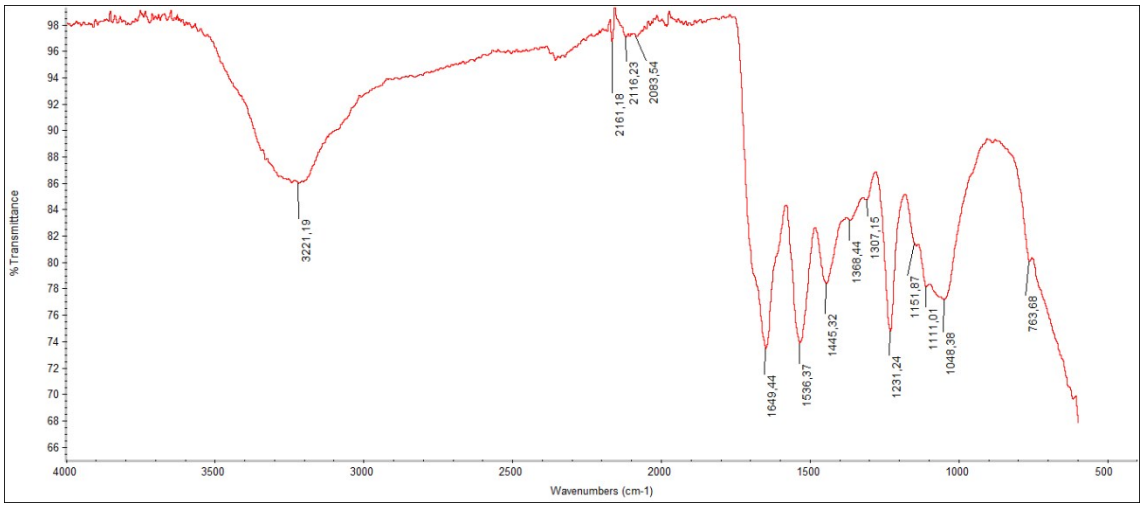


**Figure S4.1**. FT-IR spectrum (ATR) of the 2:1 (urea-glyoxal) solid isolated in acetone.

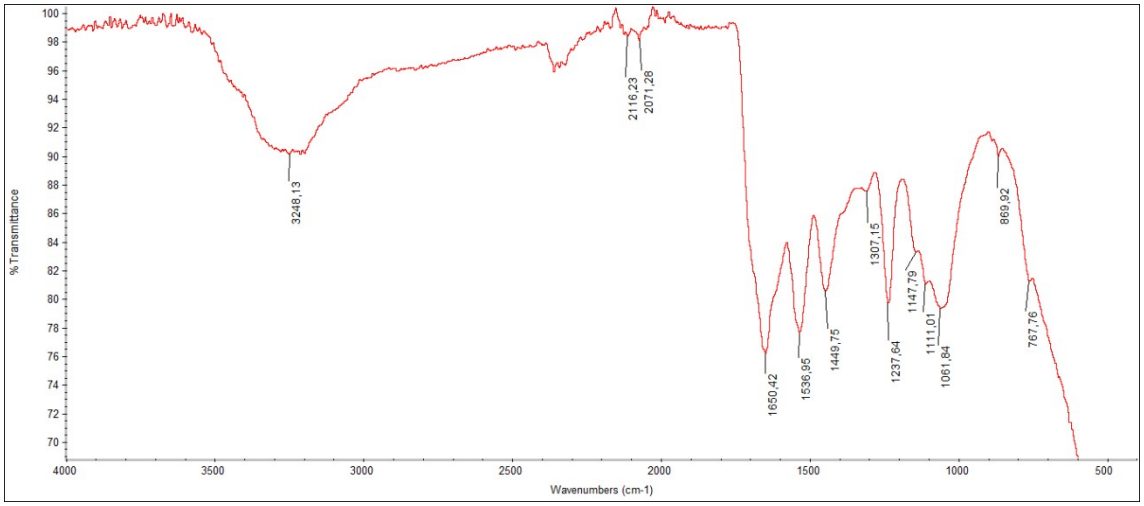


**Figure S4.2**. FT-IR spectrum (ATR) of the 2:1 (urea-glyoxal) solid isolated in 1,4-dioxane.

## 1:1 STOICHIOMETRY

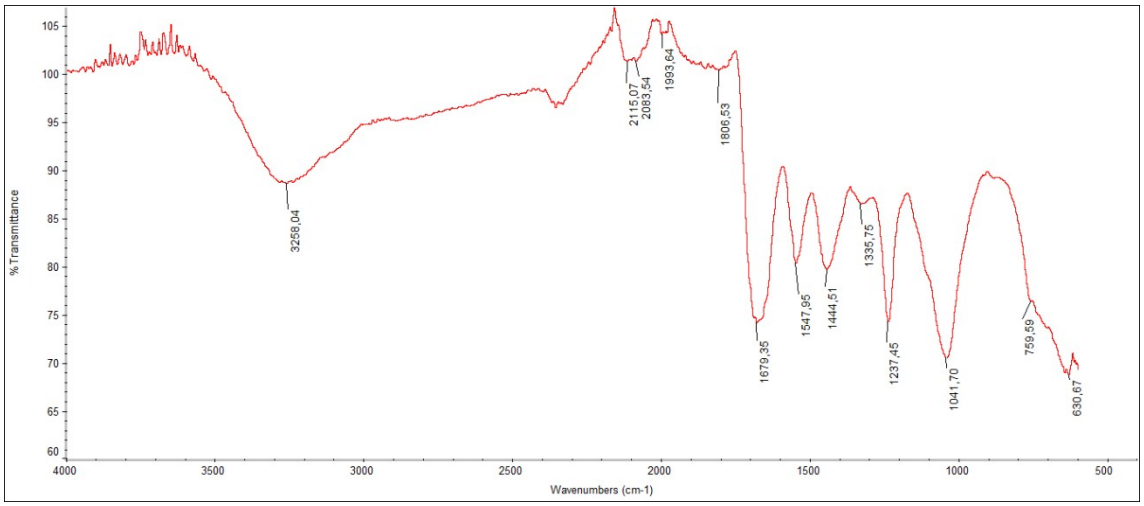


**Figure S4.3**. FT-IR spectrum (ATR) of the 1:1 (urea-glyoxal) solid isolated in acetone.

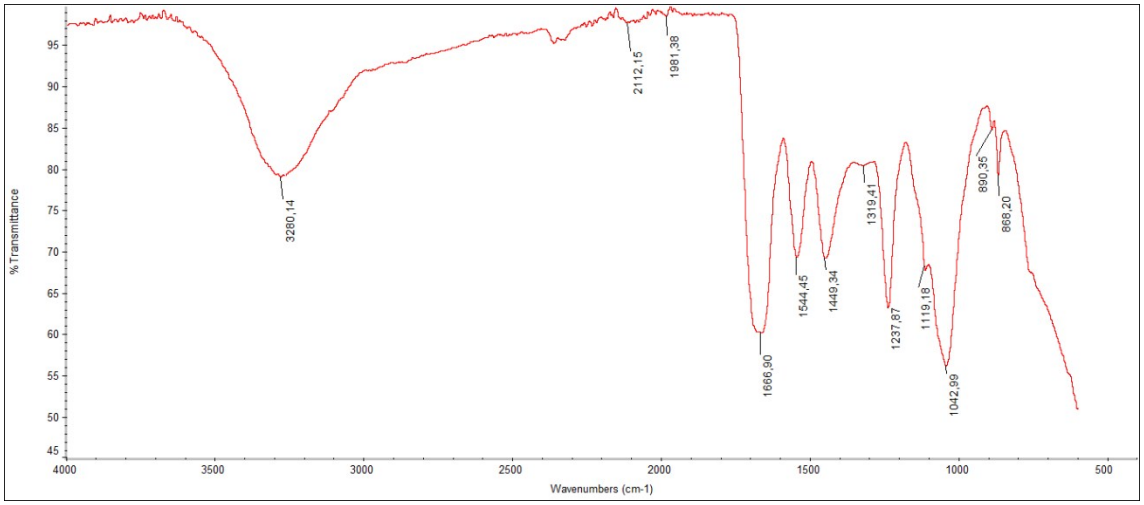


**Figure S4.4**. FT-IR spectrum (ATR) of the 1:1 (urea-glyoxal) solid isolated in 1,4-dioxane.

## 1:2 STOICHIOMETRY

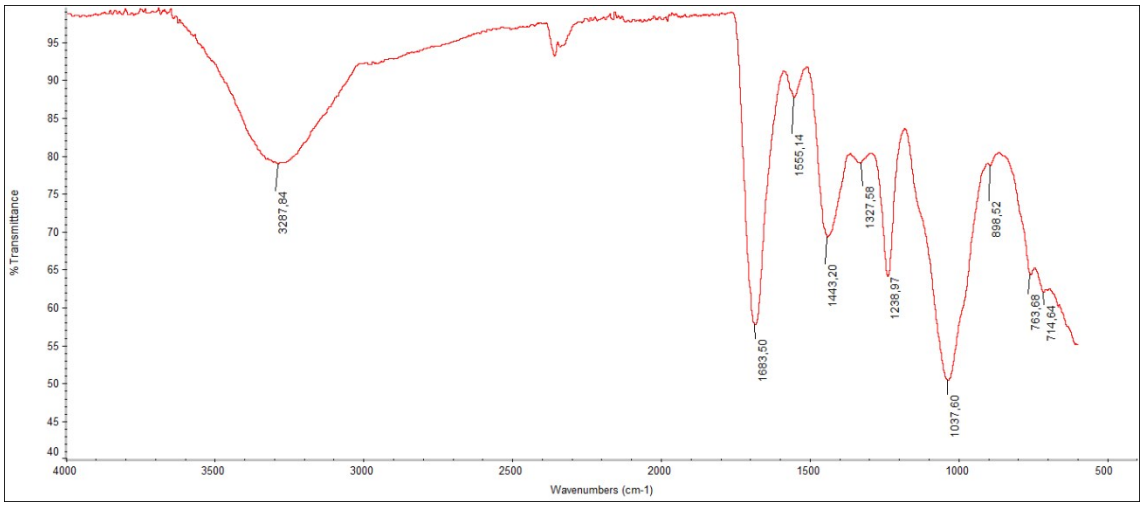


**Figure S4.5**. FT-IR spectrum (ATR) of the 1:2 (urea-glyoxal) solid isolated in acetone.

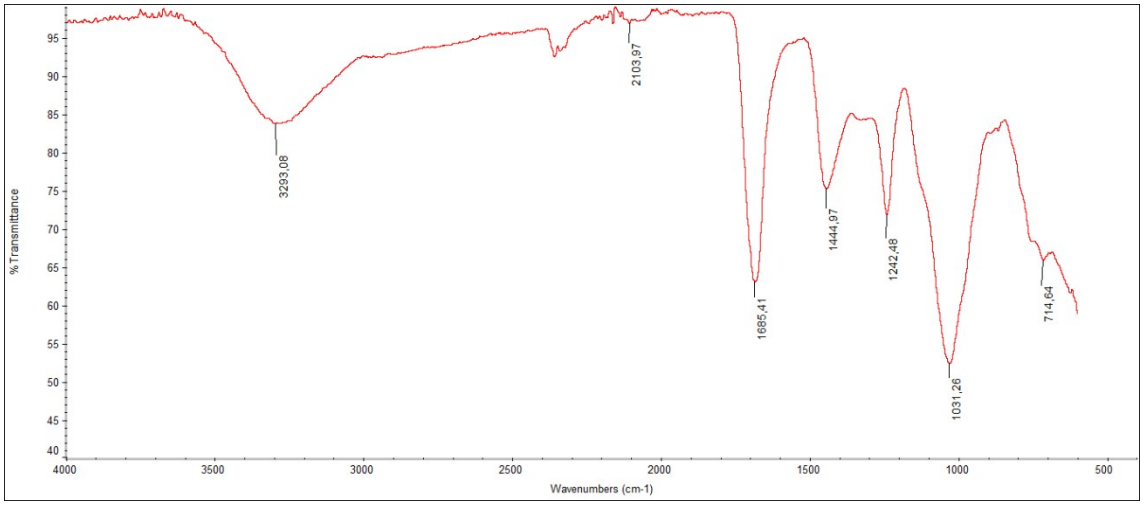


**Figure S4.6**. FT-IR spectrum (ATR) of the 1:2 (urea-glyoxal) solid isolated in 1,4-dioxane.

## 5. MASS SPECTROMETRY DATA

**Table S5.1.** Calculated m/z peaks for $[MH]^+$ compositions of urea-glyoxal oligomers at different stoichiometries for aqueous samples and solids from acetone

| Calculated | | | | | | Observed | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | 1:2 | | | 1:1 | | | 2:1 | | |
| m/z | $[MH]^+$ | U:G[a] | $-H_2O$ | UN[b] | RN[c,d] | Solid | Aq. samples | | Solid | Aq. samples | | Solid | Aq. samples | |
| | | | | | | RI[e] | ΣRI/n | n[f] | RI[e] | ΣRI/n | n[f] | RI[e] | ΣRI/n | n[f] |
| **119.0457** | $C_3H_7N_2O_3$ | 1:1 | 2 | 2 | 1 | 2.1 | 1.7 | 3 | 13.2 | 2.1 | 5 | 2.3 | 2.5 | 5 |
| **143.0569** | $C_4H_7N_4O_2$ | 2:1 | 4 | 4 | 2 | 2.3 | 0.0 | 0 | 100 | 2.7 | 1 | 100 | 2.8 | 5 |
| **183.0518** | $C_6H_7N_4O_3$ | 2:2 | 7 | 6 | 4 | 10.4 | 21.7 | 5 | 43.3 | 23.6 | 5 | 11.5 | 31.3 | 5 |
| **199.0355** | $C_7H_7N_2O_5$ | 1:3 | 8 | 6 | 5 | 6.5 | 96.6 | 5 | 5.8 | 74.0 | 5 | 0.0 | 50.4 | 5 |
| **201.0624** | $C_6H_9N_4O_4$ | 2:2 | 6 | 5 | 3 | 6.4 | 0.0 | 0 | 79.1 | 5.4 | 1 | 17.3 | 2.8 | 5 |
| **217.0461** | $C_7H_9N_2O_6$ | 1:3 | 7 | 5 | 4 | 1.1 | 56.3 | 5 | 0.0 | 56.3 | 5 | 0.0 | 24.7 | 5 |
| **241.0573** | $C_8H_9N_4O_3$ | 2:3 | 9 | 7 | 5 | 11.1 | 28.6 | 5 | 24.5 | 32.8 | 5 | 0.0 | 29.2 | 5 |
| **255.0941** | $C_6H_{15}N_4O_7$ | 2:2 | 3 | 2 | 0 | 100 | 0.0 | 0 | 0.0 | 0.0 | 0 | 0.0 | 0.0 | 0 |
| **259.0679** | $C_8H_{11}N_4O_6$ | 2:3 | 8 | 6 | 4 | 6.3 | 79.7 | 5 | 13.1 | 100 | 5 | 0.0 | 100 | 5 |
| **283.0791** | $C_9H_{11}N_6O_5$ | 3:3 | 10 | 8 | 5 | 3.5 | 1.3 | 2 | 44.5 | 2.2 | 2 | 8.8 | 4.6 | 5 |
| **285.1060** | $C_8H_{13}N_8O_4$ | 4:2 | 8 | 7 | 3 | 0.0 | 0.0 | 0 | 10.8 | 1.3 | 1 | 20.0 | 1.5 | 3 |
| **301.0897** | $C_9H_{13}N_6O_6$ | 3:3 | 9 | 7 | 4 | 0.0 | 9.7 | 4 | 34.1 | 17.4 | 5 | 6.6 | 37.2 | 5 |
| **317.0733** | $C_{10}H_{13}N_4O_8$ | 2:4 | 10 | 7 | 5 | 6.8 | 58.5 | 5 | 15.0 | 58.8 | 5 | 3.7 | 40.7 | 5 |
| **359.0951** | $C_{11}H_{15}N_6O_8$ | 3:4 | 11 | 8 | 5 | 3.7 | 6.8 | 5 | 20.2 | 10.5 | 5 | 3.5 | 13.6 | 5 |
| **361.1220** | $C_{10}H_{17}N_8O_7$ | 4:3 | 9 | 7 | 3 | 0.0 | 1.6 | 5 | 21.0 | 0.0 | 0 | 9.1 | 1.5 | 1 |
| **373.1319** | $C_9H_{21}N_6O_{10}$ | 3:3 | 5 | 3 | 0 | 92.8 | 0.0 | 0 | 0.0 | 0.0 | 0 | 0.0 | 0.0 | 0 |
| **401.1169** | $C_{12}H_{17}N_8O_8$ | 4:4 | 12 | 9 | 5 | 0.0 | 2.5 | 4 | 25.5 | 4.8 | 5 | 4.9 | 7.8 | 5 |
| **419.1275** | $C_{12}H_{19}N_8O_9$ | 4:4 | 11 | 8 | 4 | 0.0 | 3.2 | 3 | 14.5 | 5.5 | 5 | 1.1 | 7.8 | 5 |
| **477.1330** | $C_{14}H_{21}N_8O_{11}$ | 4:5 | 13 | 9 | 5 | 0.0 | 5.4 | 3 | 8.7 | 10.9 | 5 | 0.0 | 14.8 | 5 |
| **507.1534** | $C_{13}H_{27}N_6O_{15}$ | 3:5 | 8 | 4 | 1 | 15.0 | 0.0 | 0 | 0.0 | 0.0 | 0 | 0.0 | 0.0 | 0 |
| **519.1548** | $C_{15}H_{23}N_{10}O_{11}$ | 5:5 | 14 | 10 | 5 | 0.0 | 0.0 | 0 | 12.2 | 1.9 | 4 | 1.1 | 4.8 | 5 |
| **535.1385** | $C_{16}H_{23}N_8O_{13}$ | 4:6 | 15 | 10 | 6 | 0.0 | 4.8 | 3 | 4.0 | 7.8 | 5 | 0.0 | 7.5 | 5 |

| **Table S5.1 cont.** | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **561.1766** | $C_{16}H_{25}N_{12}O_{11}$ | 6:5 | 15 | 11 | 5 | 1.8 | 0.0 | 0 | 10.6 | 0.0 | 0 | 2.4 | 1.7 | 3 |
| **601.1715** | $C_{18}H_{25}N_{12}O_{12}$ | 6:6 | 18 | 13 | 7 | 0.0 | 0.0 | 0 | 10.9 | 0.0 | 0 | 1.8 | 1.4 | 1 |
| **619.1821** | $C_{18}H_{27}N_{12}O_{13}$ | 6:6 | 17 | 12 | 6 | 3.8 | 0.0 | 0 | 12.0 | 0.0 | 0 | 0.0 | 2.0 | 3 |
| **679.2144** | $C_{19}H_{31}N_{14}O_{14}$ | 7:6 | 17 | 12 | 5 | 1.8 | 0.0 | 0 | 8.0 | 0.0 | 0 | 1.3 | 1.2 | 1 |

[a]Urea:glyoxal units affording the molecular formula specified ($MH^+$) after elimination of the corresponding water molecules (4th column); [b]UN = unsaturation number; [c]RN = ring number; [d]Unsaturations other than rings, including minor aromatizations, might be postulated for such formulas. [e]RI = relative intensity; [f]For aqueous samples several aliquots were injected regularly (5 times, between 1 and 40 days), n denotes the number of times the peak in question could be detected with intensities >1% (see ESI for MS protocols and accuracy).

**Table S5.2.** Calculated m/z peaks for $[MH]^+$ compositions and their temporal evolution for 2:1 urea-glyoxal oligomers in aqueous samples and solids from acetone

| m/z | $[MH]^+$ | U:G[a] | - $H_2O$ | + $NH_3$ | UN[b] | RN[c] | ON[d] | 1 day | | 5 days | | 10 days | | 20 days | | 40 days | | Solid | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) |
| **100.0511** | $C_3H_6N_3O$ | 2:1 | 4 | 1 | 3 | 2 | 3 | | | | | 1.7 | 4.87 | 4.6 | -8.13 | 5.8 | -16.12 | 23.7 | 5.87 |
| **101.0351** | $C_3H_5N_2O_2$ | 1:1 | 3 | | 3 | 2 | 2 | 1.5 | 4.97 | 1.6 | -5.91 | 1.7 | 8.93 | 3.1 | -19.77 | 2.3 | -9.87 | 3.4 | -4.92 |
| **119.0457** | $C_3H_7N_2O_3$ | 1:1 | 2 | | 2 | 1 | 1 | 2.0 | 6.44 | 1.8 | -0.28 | 1.6 | 3.08 | 4.8 | -7.84 | 2.0 | 1.40 | 2.3 | 3.08 |
| **126.0304** | $C_4H_4N_3O_2$ | 2:1 | 4 | -1 | 5 | 3 | 2 | | | | | | | 1.0 | 3.58 | 1.0 | -12.29 | 12.5 | 7.55 |
| **140.0460** | $C_4H_6N_3O_2$ | 1:2 | 7 | 1 | 5 | 4 | 5 | | | | | | | | | | | 3.3 | 2.15 |
| **141.0300** | $C_5H_5N_2O_3$ | 1:2 | 6 | | 5 | 4 | 4 | 13.1 | 19.27 | 16.1 | 17.85 | 19.5 | 24.23 | 20.7 | 11.47 | 21.2 | 6.50 | | |
| **143.0569** | $C_4H_7N_4O_2$ | 2:1 | 4 | | 4 | 2 | 2 | 1.0 | 16.78 | 1.5 | 30.76 | 1.9 | 22.37 | 4.2 | -1.39 | 5.5 | 2.10 | 100.0 | 8.39 |
| **158.0566** | $C_5H_8N_3O_3$ | 1:2 | 6 | 1 | 4 | 3 | 4 | | | | | | | | | | | 3.1 | 0.42 |
| **159.0406** | $C_5H_7N_2O_4$ | | 5 | | 4 | 3 | 3 | | | | | | | 1.0 | 55.85 | | | | |
| **165.0413** | $C_6H_5N_4O_2$ | 2:2 | 8 | | 7 | 5 | 5 | | | | | 1.5 | 30.60 | 2.5 | 19.09 | 4.3 | 8.79 | 4.1 | 19.09 |
| **182.0678** | $C_6H_8N_5O_2$ | 2:2 | 8 | 1 | 6 | 4 | 5 | | | | | | | | | | | 3.7 | 10.43 |
| **183.0518** | $C_6H_7N_4O_3$ | 2:2 | 7 | | 6 | 4 | 4 | 19.5 | 14.29 | 32.9 | 13.19 | 38.4 | 20.30 | 35.0 | 7.73 | 30.6 | 3.91 | 11.5 | 10.46 |
| **199.0355** | $C_7H_7N_2O_5$ | 1:3 | 8 | | 6 | 5 | 5 | 42.9 | 13.04 | 49.4 | 10.53 | 52.6 | 18.07 | 50.2 | 7.02 | 56.9 | 5.51 | | |
| **201.0624** | $C_6H_9N_4O_4$ | 2:2 | 6 | | 5 | 3 | 3 | 2.0 | 13.33 | 2.2 | 23.77 | 1.9 | 39.19 | 4.8 | 11.84 | 3.3 | 16.31 | 17.3 | 11.34 |
| **213.0637** | $C_8H_5N_8$ | 4:2 | 12 | | 11 | 7 | 7 | 4.3 | 20.26 | 6.0 | 15.10 | 6.5 | 24.02 | 7.3 | 13.69 | 9.4 | 2.90 | | |
| **217.0461** | $C_7H_9N_2O_6$ | 1:3 | 7 | | 5 | 4 | 4 | 16.9 | 11.80 | 22.1 | 9.50 | 26.4 | 17.33 | 25.1 | 3.97 | 33.3 | 1.66 | | |
| **219.0729** | $C_6H_{11}N_4O_5$ | 2:2 | 5 | | 4 | 2 | 2 | 1.0 | 31.70 | | | | | 1.4 | 34.89 | 1.5 | 7.51 | 3.1 | -2.99 |
| **223.0467** | $C_8H_7N_4O_4$ | 2:3 | 10 | | 8 | 6 | 6 | | | | | 1.0 | 17.17 | 1.5 | 1.93 | 2.5 | 11.34 | 1.1 | 3.27 |
| **225.0736** | $C_7H_9N_6O_3$ | 3:2 | 8 | | 7 | 4 | 4 | | | 1.3 | 5.83 | 10.5 | 19.61 | 12.5 | 4.50 | 21.6 | 1.39 | 13.8 | 7.61 |
| **241.0573** | $C_8H_9N_4O_5$ | 2:3 | 9 | | 7 | 5 | 5 | 8.4 | 11.59 | 18.4 | 9.10 | 36.1 | 15.33 | 39.1 | 4.95 | 43.8 | 2.47 | | |
| **243.0842** | $C_7H_{11}N_6O_4$ | 3:2 | 7 | | 6 | 3 | 3 | 3.4 | 57.91 | | | | | | | | | 10.1 | 6.49 |
| **255.0941** | $C_6H_{15}N_4O_7$ | 2:2 | 3 | | 2 | 0 | 0 | | | | | | | | | | | | |
| **257.0410** | $C_9H_9N_2O_7$ | 1:4 | 10 | | 7 | 6 | 6 | 3.0 | -0.48 | 3.8 | -4.76 | 4.0 | -5.54 | 4.6 | 4.18 | 5.7 | -13.32 | | |
| **259.0679** | $C_8H_{11}N_4O_6$ | 2:3 | 8 | | 6 | 4 | 4 | 100.0 | 9.49 | 100.0 | 7.56 | 100.0 | 13.35 | 100.0 | 3.32 | 100.0 | -1.70 | | |
| **261.0947** | $C_7H_{13}N_6O_5$ | 3:2 | 6 | | 5 | 2 | 2 | | | | | | | | | | | 11.4 | 4.38 |
| **265.0685** | $C_9H_9N_6O_4$ | 3:3 | 11 | | 9 | 6 | 6 | | | | | | | | | 1.7 | -5.93 | 1.6 | 17.84 |
| **271.0778** | $C_7H_{15}N_2O_9$ | 1:3 | 4 | | 2 | 1 | 1 | | | | | | | | | 4.8 | 32.30 | | |
| **275.0515** | $C_9H_{11}N_2O_8$ | 1:4 | 9 | | 6 | 5 | 5 | 9.2 | 29.23 | 9.8 | 24.51 | 8.9 | 27.41 | 7.0 | 25.60 | 7.3 | 15.42 | | |
| **283.0791** | $C_9H_{11}N_6O_5$ | 3:3 | 10 | | 8 | 5 | 5 | 1.1 | 5.63 | 2.0 | 9.51 | 4.9 | 13.40 | 5.0 | 4.21 | 10.0 | -2.50 | 8.8 | 4.57 |
| **285.1060** | $C_8H_{13}N_8O_4$ | 4:2 | 8 | | 7 | 3 | 3 | | | | | | | | | | | 20.0 | 10.09 |

[a]Urea:glyoxal units affording the molecular formula specified ($MH^+$) after elimination of the corresponding water molecules (4th column); [b]UN = unsaturation number; [c]RN = ring number; [d]ON = oxygen number (not belonging to urea moieties)

**Table S5.2 cont.** Calculated m/z peaks for $[MH]^+$ compositions and their temporal evolution for 2:1 urea-glyoxal oligomers in aqueous samples and solids from acetone

| m/z | $[MH]^+$ | U:G[a] | $-H_2O$ | $+NH_3$ | UN[b] | RN[c] | ON[d] | 1 day | | 5 days | | 10 days | | 20 days | | 40 days | | Solid | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) |
| **293.0621** | $C_9H_{13}N_2O_9$ | 1:4 | 8 | | 5 | 4 | 4 | 2.1 | 13.67 | 2.5 | 10.60 | 2.3 | 16.40 | 1.9 | 1.04 | 1.7 | 5.14 | | |
| **299.0628** | $C_{10}H_{11}N_4O_7$ | 2:4 | 11 | | 8 | 6 | 6 | 1.6 | 8.61 | 3.7 | 4.93 | 7.5 | 12.28 | 11.1 | 1.58 | 14.4 | -0.76 | | |
| **301.0897** | $C_9H_{13}N_6O_6$ | 3:3 | 9 | | 7 | 4 | 4 | 35.0 | 8.83 | 49.6 | 6.17 | 49.4 | 11.48 | 32.3 | 2.18 | 19.6 | 3.51 | 6.6 | 18.12 |
| **303.1165** | $C_8H_{15}N_8O_5$ | 4:2 | 7 | | 6 | 2 | 2 | | | | | | | | | | | 7.4 | 4.75 |
| **307.0903** | $C_{10}H_{11}N_8O_4$ | 4:3 | 12 | | 10 | 6 | 6 | | | | | | | 1.0 | 5.62 | 2.4 | -3.17 | 1.3 | 7.90 |
| **313.0996** | $C_8H_{17}N_4O_9$ | 2:3 | 5 | | 3 | 1 | 1 | | | | | | | | | 2.0 | 27.64 | | |
| **317.0733** | $C_{10}H_{13}N_4O_8$ | 2:4 | 10 | | 7 | 5 | 5 | 20.1 | 10.84 | 33.4 | 6.74 | 48.3 | 11.16 | 49.6 | 2.64 | 52.3 | -1.77 | 3.7 | 29.77 |
| **319.1002** | $C_9H_{15}N_6O_7$ | 3:3 | 8 | | 6 | 3 | 3 | | | | | | | | | | | 2.0 | 17.93 |
| **323.0740** | $C_{11}H_{11}N_6O_6$ | 3:4 | 13 | | 10 | 7 | 7 | | | | | | | | | | | | |
| **325.1009** | $C_{10}H_{13}N_8O_5$ | 4:3 | 11 | | 9 | 5 | 5 | | | | | 4.2 | 14.74 | 5.3 | 3.05 | 9.8 | -3.41 | 9.2 | 11.97 |
| **335.0839** | $C_{10}H_{15}N_4O_9$ | 2:4 | 9 | | 6 | 4 | 4 | 7.1 | 7.17 | 5.8 | 8.07 | 4.0 | 12.54 | 3.0 | 16.12 | 3.3 | 5.38 | | |
| **341.0846** | $C_{11}H_{13}N_6O_7$ | 3:4 | 12 | | 9 | 6 | 6 | | | 1.4 | 10.47 | 2.7 | 10.18 | 3.6 | 7.25 | 5.3 | 4.32 | | |
| **343.1115** | $C_{10}H_{15}N_8O_6$ | 4:3 | 10 | | 8 | 4 | 4 | 1.6 | 15.32 | 3.6 | 9.49 | 5.4 | 15.90 | 5.7 | 4.24 | 7.3 | 3.95 | 7.9 | 7.45 |
| **345.1383** | $C_9H_{17}N_{10}O_5$ | 5:2 | 8 | | 7 | 2 | 2 | | | | | | | | | | | 12.1 | 10.54 |
| **347.0852** | $C_{12}H_{11}N_8O_5$ | | 15 | | 12 | 8 | 8 | | | | | | | | | | | | |
| **355.1214** | $C_9H_{19}N_6O_9$ | 3:3 | 6 | | 4 | 1 | 1 | | | | | | | | | | | | |
| **357.0683** | $C_{12}H_{13}N_4O_9$ | 2:5 | 13 | | 9 | 7 | 7 | | | | | 1.1 | 4.07 | | | 1.3 | 13.87 | | |
| **359.0951** | $C_{11}H_{15}N_6O_8$ | 3:4 | 11 | | 8 | 5 | 5 | 7.1 | 9.85 | 11.1 | 4.00 | 15.2 | 10.68 | 15.7 | 1.49 | 18.8 | -3.24 | 3.5 | 27.39 |
| **361.122** | $C_{10}H_{17}N_8O_7$ | 4:3 | 9 | | 7 | 3 | 3 | | | | | | | | | 2.5 | 15.56 | 9.1 | 3.66 |

| | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **0** | | | | | | | | | | | | | | | | | | | |
| **363.0689** | $C_{13}H_{11}N_6O_7$ | 3:5 | 16 | | 12 | 9 | 9 | | | | | | | | | | | | |
| **365.0958** | $C_{12}H_{13}N_8O_6$ | 4:4 | 14 | | 11 | 7 | 7 | | | | | | | | | 1.1 | -4.66 | | |
| **367.1227** | $C_{11}H_{15}N_{10}O_5$ | 5:3 | 12 | | 10 | 5 | 5 | | | | | 5.2 | 9.78 | 6.1 | 1.33 | 12.3 | -2.48 | 5.0 | 14.68 |
| **373.1319** | $C_9H_{21}N_6O_{10}$ | 3:3 | 5 | | 3 | 0 | 0 | | | | | | | | | | | | |
| **375.0788** | $C_{12}H_{15}N_4O_{10}$ | 2:5 | 12 | | 8 | 6 | 6 | 3.0 | 11.46 | 4.6 | 9.60 | 4.6 | 16.26 | 5.4 | 2.93 | 4.3 | -1.60 | 2.4 | 20.00 |
| **377.1057** | $C_{11}H_{17}N_6O_9$ | 3:4 | 10 | | 7 | 4 | 4 | 5.6 | 9.81 | 6.4 | 5.57 | 6.5 | 10.88 | 6.9 | 3.19 | 8.2 | 1.59 | | |
| **379.1326** | $C_{10}H_{19}N_8O_8$ | 4:3 | 8 | | 6 | 2 | 2 | | | | | | | | | | | 2.3 | 15.26 |
| **383.1064** | $C_{12}H_{15}N_8O_7$ | 4:4 | 13 | | 10 | 6 | 6 | | | | | 1.1 | 10.88 | 1.1 | 11.67 | 3.7 | 5.66 | 4.8 | 22.11 |
| **385.1333** | $C_{11}H_{17}N_{10}O_6$ | 5:3 | 11 | | 9 | 4 | 4 | | | | | | | 1.1 | 18.83 | 2.2 | 18.31 | 8.5 | 10.01 |
| **389.1156** | $C_{10}H_{21}N_4O_{12}$ | 2:4 | 6 | | 3 | 1 | 1 | | | | | | | | | | | | |
| **393.0894** | $C_{12}H_{17}N_4O_{11}$ | 2:5 | 11 | | 7 | 5 | 5 | 3.2 | 10.39 | 4.0 | 3.52 | 5.0 | 10.64 | 4.1 | 3.01 | 4.6 | 3.01 | | |

[a]Urea:glyoxal units affording the molecular formula specified ($MH^+$) after elimination of the corresponding water molecules (4th column); [b]UN = unsaturation number; [c]RN = ring number; [d]ON = oxygen number (not belonging to urea moieties)

**Table S5.2 cont.** Calculated m/z peaks for $[MH]^+$ compositions and their temporal evolution for 2:1 urea-glyoxal oligomers in aqueous samples and solids from acetone

| m/z | $[MH]^+$ | U:G[a] | $-H_2O$ | $+NH_3$ | UN[b] | RN[c] | ON[d] | 1 day | | 5 days | | 10 days | | 20 days | | 40 days | | Solid | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) |
| **399.0901** | $C_{13}H_{15}N_6O_9$ | 3:5 | 14 | | 10 | 7 | 7 | | | | | | | | | 1.5 | 10.65 | | |
| **401.1169** | $C_{12}H_{17}N_8O_8$ | 4:4 | 12 | | 9 | 5 | 5 | 1.8 | 10.06 | 4.8 | 5.07 | 8.4 | 11.55 | 11.2 | 1.83 | 12.9 | -6.15 | 4.9 | 11.30 |
| **403.1438** | $C_{11}H_{19}N_{10}O_7$ | 5:3 | 10 | | 8 | 3 | 3 | | | | | | | 1.2 | 46.68 | 1.6 | 46.18 | 9.9 | 6.49 |

| | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **405.0993** | $C_{11}H_{21}N_2O_{14}$ | 1:5 | 7 | | 3 | 2 | 2 | | | | | | | | | | | | |
| **405.1707** | $C_{10}H_{21}N_{12}O_6$ | 6:2 | 8 | | 7 | 1 | 1 | | | | | | | | | | | 5.0 | 5.19 |
| **407.1176** | $C_{13}H_{15}N_{10}O_6$ | 5:4 | 15 | | 12 | 7 | 7 | | | | | | | | | 1.3 | 4.18 | 1.4 | 6.89 |
| **411.0999** | $C_{12}H_{19}N_4O_{12}$ | 2:5 | 10 | | 6 | 4 | 4 | 1.9 | 10.57 | 1.9 | 2.30 | 2.3 | 10.09 | 2.1 | -2.07 | 2.5 | -5.97 | | |
| **417.1006** | $C_{13}H_{17}N_6O_{10}$ | 3:5 | 13 | | 9 | 6 | 6 | 1.8 | 4.35 | 3.1 | 1.72 | 4.7 | 9.87 | 5.2 | 2.20 | 6.3 | -3.80 | 1.8 | 17.54 |
| **419.1275** | $C_{12}H_{19}N_8O_9$ | 4:4 | 11 | | 8 | 4 | 4 | 6.1 | 9.54 | 8.0 | 5.49 | 7.7 | 9.78 | 8.7 | 1.43 | 8.5 | -0.24 | 1.1 | -0.48 |
| **421.1544** | $C_{11}H_{21}N_{10}O_8$ | 5:3 | 9 | | 7 | 2 | 2 | | | | | | | | | | | 5.5 | -1.23 |
| **423.1013** | $C_{14}H_{15}N_8O_8$ | 4:5 | 16 | | 12 | 8 | 8 | | | | | | | | | | | | |
| **425.1282** | $C_{13}H_{17}N_{10}O_7$ | 5:4 | 14 | | 11 | 6 | 6 | | | | | 1.2 | 13.33 | 1.4 | 2.04 | 8.0 | -1.02 | 3.6 | 18.98 |
| **427.1551** | $C_{12}H_{19}N_{12}O_6$ | 6:3 | 12 | | 10 | 4 | 4 | | | | | | | | | | | 5.2 | 3.40 |
| **431.1374** | $C_{11}H_{23}N_6O_{12}$ | 3:4 | 7 | | 4 | 1 | 1 | | | | | | | | | 1.1 | 14.37 | | |
| **433.0843** | $C_{14}H_{17}N_4O_{12}$ | 2:6 | 14 | | 9 | 7 | 7 | | | | | | | 1.3 | 29.09 | 1.0 | -2.78 | | |
| **435.1112** | $C_{13}H_{19}N_6O_{11}$ | 3:5 | 12 | | 8 | 5 | 5 | 5.1 | 6.85 | 5.7 | 2.02 | 6.2 | 10.07 | 5.8 | 1.56 | 8.0 | -2.34 | | |
| **437.1381** | $C_{12}H_{21}N_8O_{10}$ | 4:4 | 10 | | 7 | 3 | 3 | | | | | | | | | 1.3 | 38.58 | 1.1 | 6.78 |
| **441.1118** | $C_{14}H_{17}N_8O_9$ | 4:5 | 15 | | 11 | 7 | 7 | | | | | | | | | 1.5 | 9.86 | | |
| **443.1275** | $C_{13}H_{19}N_{10}O_8$ | 5:4 | 13 | | 10 | 5 | 5 | | | | | 3.0 | -15.57 | 3.9 | -20.99 | 4.7 | -30.92 | 6.2 | -13.54 |
| **445.1656** | $C_{12}H_{21}N_{12}O_7$ | 6:3 | 11 | | 9 | 3 | 3 | | | | | | | | | | | 8.0 | 6.10 |
| **449.1480** | $C_{11}H_{25}N_6O_{13}$ | 3:4 | 6 | | 3 | 0 | 0 | | | | | | | | | | | | |
| **453.1217** | $C_{13}H_{21}N_6O_{12}$ | 3:5 | 11 | | 7 | 4 | 4 | 1.8 | 6.50 | 2.0 | 6.50 | 1.5 | 9.15 | 1.2 | 7.82 | 1.1 | -14.69 | | |
| **459.1224** | $C_{14}H_{19}N_8O_{10}$ | 4:5 | 14 | | 10 | 6 | 6 | 1.6 | 5.48 | 3.9 | 2.43 | 8.4 | 9.61 | 9.1 | 2.64 | 13.2 | -2.15 | | |
| **461.1493** | $C_{13}H_{21}N_{10}O_9$ | 5:4 | 12 | | 9 | 4 | 4 | 1.5 | 10.62 | 2.4 | 4.76 | 4.3 | 14.52 | 4.2 | 3.03 | 4.9 | 5.85 | 4.7 | 8.02 |

| | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **463.1762** | $C_{12}H_{23}N_{12}O_8$ | 6:3 | 10 | | 8 | 2 | 2 | | | | | | | | | | | 3.6 | 9.03 |
| **465.1231** | $C_{15}H_{17}N_{10}O_8$ | 5:5 | 17 | | 13 | 8 | 8 | | | | | | | | | | | | |
| **467.1500** | $C_{14}H_{19}N_{12}O_7$ | 6:4 | 15 | | 12 | 6 | 6 | | | | | 1.7 | 9.77 | 2.7 | -2.43 | 5.0 | 0.36 | 3.5 | 1.85 |
| **473.1592** | $C_{12}H_{25}N_8O_{12}$ | 4:4 | 8 | | 5 | 1 | 1 | | | | | | | | | | | | |
| **475.1061** | $C_{15}H_{19}N_6O_{12}$ | 3:6 | 15 | | 10 | 7 | 7 | | | 1.0 | -8.00 | 1.6 | 6.10 | 1.6 | 5.47 | 1.9 | -2.32 | | |
| **477.1330** | $C_{14}H_{21}N_8O_{11}$ | 4:5 | 13 | | 9 | 5 | 5 | 8.7 | 6.66 | 15.0 | 3.31 | 15.9 | 7.92 | 16.9 | 0.79 | 17.5 | -4.24 | | |

[a]Urea:glyoxal units affording the molecular formula specified ($MH^+$) after elimination of the corresponding water molecules (4th column); [b]UN = unsaturation number; [c]RN = ring number; [d]ON = oxygen number (not belonging to urea moieties)

**Table S5.2 cont.** Calculated m/z peaks for $[MH]^+$ compositions and their temporal evolution for 2:1 urea-glyoxal oligomers in aqueous samples and solids from acetone

| m/z | $[MH]^+$ | U:G[a] | $-H_2O$ | $+NH_3$ | UN[b] | RN[c] | ON[d] | 1 day | | 5 days | | 10 days | | 20 days | | 40 days | | Solid | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) |
| **479.1599** | $C_{13}H_{23}N_{10}O_{10}$ | 5:4 | 11 | | 8 | 3 | 3 | | | | | | | | | 1.1 | 37.07 | 2.3 | -8.01 |
| **483.1336** | $C_{15}H_{19}N_{10}O_9$ | 5:5 | 16 | | 12 | 7 | 7 | | | | | | | | | 1.7 | -0.11 | 1.6 | 13.76 |
| **485.1605** | $C_{14}H_{21}N_{12}O_8$ | 6:4 | 14 | | 11 | 5 | 5 | | | | | | | | | 1.5 | 6.66 | 4.9 | 9.34 |
| **487.1874** | $C_{13}H_{23}N_{14}O_7$ | 7:3 | 12 | | 10 | 3 | 3 | | | | | | | | | | | 3.5 | 7.01 |
| **489.1429** | $C_{13}H_{25}N_6O_{14}$ | 3:5 | 9 | | 5 | 2 | 2 | | | | | | | | | 1.0 | 26.32 | | |
| **491.1698** | $C_{12}H_{27}N_8O_{13}$ | 4:4 | 7 | | 4 | 0 | 0 | | | | | | | | | 1.0 | 154.04 | | |
| **493.1167** | $C_{15}H_{21}N_6O_{13}$ | 3:6 | 14 | | 9 | 6 | 6 | 1.7 | 5.68 | 2.3 | 2.23 | 2.7 | 7.50 | 2.5 | 2.84 | 2.4 | 2.03 | | |
| **495.1435** | $C_{14}H_{23}N8O_{12}$ | 4:5 | 12 | | 8 | 4 | 4 | 16.6 | 7.56 | 13.1 | 1.30 | 7.7 | 8.77 | 6.4 | 1.30 | 6.6 | -1.93 | | |
| **499.117** | $C_{16}H_{19}N_8O_{11}$ | 4:6 | 17 | | 12 | 8 | 8 | | | | | | | | | | | | |

| | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **3** | $C_{15}H_{21}N_{10}O_{1}$ | | | | | | | | | | | | | | | | | | |
| **501.1442** | $C_{15}H_{21}N_{10}O_{10}$ | 5:5 | 15 | | 11 | 6 | 6 | | | | | 1.3 | 14.79 | 1.8 | 6.41 | 3.7 | -5.16 | 1.9 | 4.01 |
| **503.1711** | $C_{14}H_{23}N_{12}O_{9}$ | 6:4 | 13 | | 10 | 4 | 4 | | | | | | | | | | | 7.8 | 9.13 |
| **507.1534** | $C_{13}H_{27}N_{6}O_{15}$ | 3:5 | 8 | | 4 | 1 | 1 | | | | | | | | | | | | |
| **511.1272** | $C_{15}H_{23}N_{6}O_{14}$ | 3:6 | 13 | | 8 | 5 | 5 | 1.1 | 13.55 | 1.5 | 11.00 | 1.3 | 11.79 | 1.3 | 15.50 | 1.9 | -2.30 | | |
| **517.1279** | $C_{16}H_{21}N_{8}O_{12}$ | 4:6 | 16 | | 11 | 7 | 7 | | | | | 1.4 | -3.88 | 3.0 | 0.37 | 4.3 | -1.56 | | |
| **519.1548** | $C_{15}H_{23}N_{10}O_{11}$ | 5:5 | 14 | | 10 | 5 | 5 | 2.6 | 7.85 | 4.8 | 3.81 | 5.5 | 10.55 | 5.7 | 0.53 | 5.5 | -3.70 | 1.1 | 11.13 |
| **521.1817** | $C_{14}H_{25}N_{12}O_{10}$ | 6:4 | 12 | | 9 | 3 | 3 | | | | | | | | | | | 2.5 | 4.72 |
| **525.1554** | $C_{16}H_{21}N_{12}O_{9}$ | 6:5 | 17 | | 13 | 7 | 7 | | | | | | | | | 2.3 | -1.44 | 1.8 | 5.42 |
| **527.1823** | $C_{15}H_{23}N_{14}O_{8}$ | 7:4 | 15 | | 12 | 5 | 5 | | | | | | | | | | | 3.8 | 15.61 |
| **535.1385** | $C_{16}H_{23}N_{8}O_{13}$ | 4:6 | 15 | | 10 | 6 | 6 | 2.5 | 6.27 | 5.4 | 6.27 | 8.5 | 7.40 | 9.9 | -2.32 | 11.3 | -5.68 | | |
| **537.1653** | $C_{15}H_{25}N_{10}O_{12}$ | 5:5 | 13 | | 9 | 4 | 4 | 6.5 | 7.71 | 6.5 | 3.99 | 4.3 | 11.81 | 3.1 | 3.80 | 2.0 | 11.99 | | |
| **543.1660** | $C_{16}H_{23}N_{12}O_{10}$ | 6:5 | 16 | | 12 | 6 | 6 | | | | | 1.3 | 9.41 | 1.5 | 5.36 | 2.8 | 3.88 | 2.8 | 8.49 |
| **545.1929** | $C_{15}H_{25}N_{14}O_{9}$ | 7:4 | 14 | | 11 | 4 | 4 | | | | | | | | | | | 4.2 | 6.96 |
| **549.1752** | $C_{14}H_{29}N_{8}O_{15}$ | 4:5 | 9 | | 5 | 1 | 1 | | | | | | | | | | | | |
| **553.1490** | $C_{16}H_{25}N_{8}O_{14}$ | 4:6 | 14 | | 9 | 5 | 5 | 6.2 | 8.36 | 6.5 | 4.20 | 6.8 | 9.08 | 4.7 | 3.66 | 5.3 | -1.22 | | |
| **559.1497** | $C_{17}H_{23}N_{10}O_{12}$ | 5:6 | 17 | | 12 | 7 | 7 | | | | | | | | | 1.5 | 6.06 | | |
| **561.1766** | $C_{16}H_{25}N_{12}O_{11}$ | 6:5 | 15 | | 11 | 5 | 5 | | | | | 1.3 | 12.07 | 1.7 | 4.77 | 2.2 | -2.54 | 2.4 | 12.79 |
| **563.2035** | $C_{15}H_{27}N_{14}O_{10}$ | 7:4 | 13 | | 10 | 3 | 3 | | | | | | | | | | | 3.5 | -4.51 |
| **565.1504** | $C_{18}H_{21}N_{12}O_{10}$ | 6:6 | 20 | | 15 | 9 | 9 | | | | | | | | | | | | |
| **567.1772** | $C_{17}H_{23}N_{14}O_{9}$ | 7:5 | | | -4 | -11 | -11 | | | | | | | 1.1 | 15.06 | 3.1 | -3.27 | 1.4 | 6.42 |
| **577.160** | $C_{17}H_{25}N_{10}O$ | 5:6 | 16 | | 11 | 6 | 6 | 1.0 | 12.57 | 1.9 | 3.91 | 3.6 | 10.15 | 3.5 | -0.60 | 4.6 | -2.85 | | |

| | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **3** | $_{13}$ | | | | | | | | | | | | | | | | | | | | |

[a]Urea:glyoxal units affording the molecular formula specified ($MH^+$) after elimination of the corresponding water molecules (4th column); [b]UN = unsaturation number; [c]RN = ring number; [d]ON = oxygen number (not belonging to urea moieties)

**Table S5.2 cont.** Calculated m/z peaks for $[MH]^+$ compositions and their temporal evolution for 2:1 urea-glyoxal oligomers in aqueous samples and solids from acetone

| m/z | $[MH]^+$ | U:G[a] | $-H_2O$ | $+NH_3$ | UN[b] | RN[c] | ON[d] | 1 day | | 5 days | | 10 days | | 20 days | | 40 days | | Solid | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) |
| **579.1871** | $C_{16}H_{27}N_{12}O_{12}$ | 6:5 | 14 | | 10 | 4 | 4 | 1.4 | 9.91 | 2.1 | 4.90 | 1.4 | 11.81 | 1.0 | 16.99 | | | 1.3 | -5.80 |
| **585.1878** | $C_{17}H_{25}N_{14}O_{10}$ | 7:5 | 17 | | 13 | 6 | 6 | | | | | 1.3 | 8.22 | 1.6 | 7.70 | 2.1 | 1.89 | 3.3 | 4.29 |
| **587.2147** | $C_{16}H_{27}N_{16}O_{9}$ | 8:4 | 15 | | 12 | 4 | 4 | | | | | | | | | | | 3.0 | -1.04 |
| **593.1439** | $C_{18}H_{25}N_{8}O_{15}$ | 4:7 | 17 | | 11 | 7 | 7 | | | | | | | 1.9 | 6.64 | 2.4 | 2.93 | | |
| **595.1708** | $C_{17}H_{27}N_{10}O_{14}$ | 5:6 | 15 | | 10 | 5 | 5 | 2.4 | 8.77 | 3.2 | 1.71 | 3.3 | 8.77 | 2.6 | -0.81 | 2.1 | 3.23 | | |
| **601.1715** | $C_{18}H_{25}N_{12}O_{12}$ | 6:6 | 18 | | 13 | 7 | 7 | | | | | | | | | 1.4 | -6.51 | 1.8 | -1.85 |
| **603.1984** | $C_{17}H_{27}N_{14}O_{11}$ | 7:5 | 16 | | 12 | 5 | 5 | | | | | | | | | | | 3.5 | 12.39 |
| **607.1807** | $C_{16}H_{31}N_{8}O_{17}$ | 4:6 | 11 | | 6 | 2 | 2 | | | | | | | | | | | | |
| **611.1545** | $C_{18}H_{27}N_{8}O_{16}$ | 4:7 | 16 | | 10 | 6 | 6 | 1.8 | 8.02 | 2.2 | 4.26 | 2.6 | 8.18 | 2.7 | 4.58 | 3.3 | -10.80 | | |
| **619.1821** | $C_{18}H_{27}N_{12}O_{13}$ | 6:6 | 17 | | 12 | 6 | 6 | | | | | 1.8 | 11.72 | 1.7 | -1.53 | 2.5 | 1.54 | | |
| **621.2089** | $C_{17}H_{29}N_{14}O_{12}$ | 7:5 | 15 | | 11 | 4 | 4 | | | | | | | | | | | 2.0 | 8.11 |
| **635.1657** | $C_{19}H_{27}N_{10}O_{15}$ | 5:7 | 18 | | 12 | 7 | 7 | | | | | | | 1.2 | -1.83 | 2.0 | -0.89 | | |
| **637.1926** | $C_{18}H_{29}N_{12}O_{14}$ | 6:6 | 16 | | 11 | 5 | 5 | 1.0 | 13.06 | 1.4 | 3.95 | 1.7 | 6.93 | 1.0 | -3.27 | 1.6 | 3.01 | | |
| **641.1664** | $C_{20}H_{25}N_{12}O_{13}$ | 6:7 | 21 | | 15 | 9 | 9 | | | | | | | | | | | | |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **643.1933** | $C_{19}H_{27}N_{14}O_{12}$ | 7:6 | 19 | | 14 | 7 | 7 | | | | | | | | | 1.4 | 5.42 | 1.5 | 11.80 |
| **649.2025** | $C_{17}H_{33}N_{10}O_{17}$ | 5:6 | 12 | | 7 | 2 | 2 | | | | | | | | | | | | |
| **661.2039** | $C_{19}H_{29}N_{14}O_{13}$ | | 18 | | 13 | 6 | 6 | | | | | 1.1 | 7.79 | 1.0 | 5.37 | 2.2 | -3.25 | 1.1 | 1.14 |
| **667.2045** | $C_{20}H_{27}N_{16}O_{11}$ | 8:6 | 21 | | 16 | 8 | 8 | | | | | | | | | 1.4 | 3.18 | | |
| **669.1600** | $C_{20}H_{29}N_8O_{18}$ | 4:8 | 18 | | 11 | 7 | 7 | | | | | | | | | | | | |
| **677.1875** | $C_{20}H_{29}N_{12}O_{15}$ | 6:7 | 19 | | 13 | 7 | 7 | | | | | 1.6 | 8.47 | 2.1 | 0.20 | 2.6 | -7.48 | | |
| **679.2144** | $C_{19}H_{31}N_{14}O_{14}$ | 7:6 | 17 | | 12 | 5 | 5 | | | | | | | | | 1.2 | 12.10 | 1.3 | 1.79 |
| **685.2151** | $C_{20}H_{29}N_{16}O_{12}$ | 8:6 | 20 | | 15 | 7 | 7 | | | | | | | | | 1.2 | 9.76 | 1.5 | -0.90 |
| **695.1981** | $C_{20}H_{31}N_{12}O_{16}$ | 6:7 | 18 | | 12 | 6 | 6 | | | 2.0 | 6.18 | 2.4 | 7.91 | 2.3 | 0.57 | 2.4 | -0.15 | | |
| **701.1988** | $C_{21}H_{29}N_{14}O_{14}$ | 7:7 | 21 | | 15 | 8 | 8 | | | | | | | | | 1.0 | 1.52 | | |
| **711.1818** | $C_{21}H_{31}N_{10}O_{18}$ | 5:8 | 19 | | 12 | 7 | 7 | | | | | | | | | | | | |
| **719.2093** | $C_{21}H_{31}N_{14}O_{15}$ | 7:7 | 20 | | 14 | 7 | 7 | | | | | | | | | 1.4 | 1.57 | | |
| **721.2362** | $C_{20}H_{33}N_{16}O_{14}$ | 8:6 | 18 | | 13 | 5 | 5 | | | | | | | | | | | 1.5 | 0.44 |
| **737.2199** | $C_{21}H_{33}N_{14}O_{16}$ | 7:7 | 19 | | 13 | 6 | 6 | | | | | 1.0 | 12.20 | | | 1.3 | 1.76 | | |
| **787.2692** | $C_{22}H_{35}N_{20}O_{13}$ | 10:6 | 21 | | 16 | 6 | 6 | | | | | | | | | | | 2.2 | 3.49 |
| **795.2254** | $C_{23}H_{35}N_{14}O_{18}$ | 7:8 | 21 | | 14 | 7 | 7 | | | | | | | | | 1.1 | 11.29 | | |

[a]Urea:glyoxal units affording the molecular formula specified ($MH^+$) after elimination of the corresponding water molecules (4th column); [b]UN = unsaturation number; [c]RN = ring number; [d]ON = oxygen number (not belonging to urea moieties)

**Table S5.2 cont.** Calculated m/z peaks for $[MH]^+$ compositions and their temporal evolution for 2:1 urea-glyoxal oligomers in aqueous samples and solids from acetone

| m/z | [MH]$^+$ | U:G[a] | - $H_2O$ | + $NH_3$ | UN[b] | RN[C] | ON[d] | 1 day | | 5 days | | 10 days | | 20 days | | 40 days | | Solid | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) |
| **837.2472** | $C_{24}H_{37}N_{16}O_{18}$ | 8:8 | 22 | | 15 | 7 | 7 | | | | | | | | | | | | |
| **855.2577** | $C_{24}H_{39}N_{16}O_{19}$ | 8:8 | 21 | | 14 | 6 | 6 | | | | | | | | | | | | |
| **861.2584** | $C_{25}H_{37}N_{18}O_{17}$ | 9:8 | 24 | | 17 | 8 | 8 | | | | | | | | | | | | |
| **877.2421** | $C_{26}H_{37}N_{16}O_{19}$ | 8:9 | 25 | | 17 | 9 | 9 | | | | | | | | | | | | |
| **879.2690** | $C_{25}H_{39}N_{18}O_{18}$ | 9:8 | 23 | | 16 | 7 | 7 | | | | | | | | | | | | |
| **897.2795** | $C_{25}H_{41}N_{18}O_{19}$ | 9:8 | 22 | | 15 | 6 | 6 | | | | | | | | | | | | |
| **919.2639** | $C_{27}H_{39}N_{18}O_{19}$ | 9:9 | 26 | | 18 | 9 | 9 | | | | | | | | | | | | |
| **937.2745** | $C_{27}H_{41}N_{18}O_{20}$ | 9:9 | 25 | | 17 | 8 | 8 | | | | | | | | | | | | |
| **955.2850** | $C_{27}H_{43}N_{18}O_{21}$ | 9:9 | 24 | | 16 | 7 | 7 | | | | | | | | | | | | |
| **961.2857** | $C_{28}H_{41}N_{20}O_{19}$ | 10:9 | 27 | | 19 | 9 | 9 | | | | | | | | | | | | |
| **1097.3341** | $C_{31}H_{49}N_{22}O_{23}$ | 11:10 | 28 | | 19 | 8 | 8 | | | | | | | | | | | | |

[a]Urea:glyoxal units affording the molecular formula specified ($MH^+$) after elimination of the corresponding water molecules (4th column); [b]UN = unsaturation number; [c]RN = ring number; [d]ON = oxygen number (not belonging to urea moieties)

**Table S5.3.** Calculated m/z peaks for $[MH]^+$ compositions and their temporal evolution for 1:1 urea-glyoxal oligomers in aqueous samples and solids from acetone

| m/z | $[MH]^+$ | U:G[a] | - $H_2O$ | + $NH_3$ | UN[b] | RN[C] | ON[d] | 1 day | | 5 days | | 10 days | | 20 days | | 40 days | | Solid | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) |
| **100.0511** | $C_3H_6N_3O$ | 2:1 | 4 | 1 | 3 | 2 | 3 | | | 1.3 | 4.87 | | | 1.2 | 14.86 | 1.7 | 3.87 | 22.3 | 4.87 |
| **101.0351** | $C_3H_5N_2O_2$ | 1:1 | 3 | | 3 | 2 | 2 | 1.5 | -2.95 | 3.5 | -8.88 | 2.4 | 8.93 | 2.4 | 5.96 | 5.8 | 3.98 | 10.2 | -12.84 |
| **119.0457** | $C_3H_7N_2O_3$ | 1:1 | 2 | | 2 | 1 | 1 | 1.4 | 10.64 | 2.2 | 7.28 | 1.3 | 3.92 | 2.5 | -1.96 | 3.1 | 5.60 | 13.2 | 4.76 |
| **126.0304** | $C_4H_4N_3O_2$ | 2:1 | 4 | -1 | 5 | 3 | 2 | | | | | | | | | 2.1 | 2.79 | 41.9 | 5.17 |
| **140.0460** | $C_4H_6N_3O_2$ | 1:2 | 7 | 1 | 5 | 4 | 5 | | | 1.4 | 39.28 | 1.2 | 42.14 | 1.2 | 37.14 | 1.4 | 17.86 | 25.5 | -2.13 |
| **141.0300** | $C_5H_5N_2O_3$ | 1:2 | 6 | | 5 | 4 | 4 | | | 32.8 | 19.97 | 31.8 | 26.36 | 36.6 | 17.14 | 31.0 | 15.72 | 6.2 | -20.44 |
| **143.0569** | $C_4H_7N_4O_2$ | 2:1 | 4 | | 4 | 2 | 2 | | | | | | | | | 2.7 | 38.45 | 100.0 | 9.79 |
| **158.0566** | $C_5H_8N_3O_3$ | 1:2 | 6 | 1 | 4 | 3 | 4 | | | | | | | | | | | 16.9 | 8.64 |
| **159.0406** | $C_5H_7N_2O_4$ | | 5 | | 4 | 3 | 3 | | | | | | | | | | | 5.6 | -14.58 |
| **165.0413** | $C_6H_5N_4O_2$ | 2:2 | 8 | | 7 | 5 | 5 | | | | | | | | | 1.0 | 28.18 | 13.8 | 2.12 |
| **182.0678** | $C_6H_8N_5O_2$ | 2:2 | 8 | 1 | 6 | 4 | 5 | | | | | | | | | | | 6.1 | 6.59 |
| **183.0518** | $C_6H_7N_4O_3$ | 2:2 | 7 | | 6 | 4 | 4 | 13.6 | 19.20 | 23.0 | 11.55 | 32.9 | 20.30 | 30.5 | 12.10 | 17.8 | 17.02 | 43.3 | 9.92 |
| **199.0355** | $C_7H_7N_2O_5$ | 1:3 | 8 | | 6 | 5 | 5 | 54.1 | 16.56 | 74.7 | 10.53 | 82.0 | 19.07 | 85.4 | 12.54 | 73.6 | 8.02 | 5.8 | 25.10 |
| **201.0624** | $C_6H_9N_4O_4$ | 2:2 | 6 | | 5 | 3 | 3 | | | | | | | | | 5.4 | 47.15 | 79.1 | 7.36 |
| **213.0637** | $C_8H_5N_8$ | 4:2 | 12 | | 11 | 7 | 7 | 6.2 | 21.67 | 13.8 | 15.57 | 12.3 | 25.89 | 12.9 | 15.10 | 11.4 | 12.28 | 4.3 | 7.59 |
| **217.0461** | $C_7H_9N_2O_6$ | 1:3 | 7 | | 5 | 4 | 4 | 46.1 | 14.10 | 49.5 | 9.04 | 49.4 | 16.41 | 44.1 | 11.80 | 92.6 | 5.81 | | |
| **219.0729** | $C_6H_{11}N_4O_5$ | 2:2 | 5 | | 4 | 2 | 2 | | | | | | | | | 4.6 | 206.53 | 7.5 | 12.07 |
| **223.0467** | $C_8H_7N_4O_4$ | 2:3 | 10 | | 8 | 6 | 6 | | | 1.5 | 23.00 | 1.2 | 38.69 | 2.5 | 27.03 | 2.3 | 28.83 | 7.2 | -3.45 |
| **225.0736** | $C_7H_9N_6O_3$ | 3:2 | 8 | | 7 | 4 | 4 | | | 1.3 | 14.72 | 1.9 | 32.05 | 1.5 | 25.38 | | | 15.3 | 12.05 |
| **241.0573** | $C_8H_9N_4O_5$ | 2:3 | 9 | | 7 | 5 | 5 | 10.0 | 14.91 | 20.5 | 9.10 | 44.5 | 13.67 | 50.5 | 9.10 | 38.6 | 4.54 | 24.5 | 7.86 |
| **243.0842** | $C_7H_{11}N_6O_4$ | 3:2 | 7 | | 6 | 3 | 3 | | | | 60.79 | | | | | | | 22.2 | 8.14 |
| **255.0941** | $C_6H_{15}N_4O_7$ | 2:2 | 3 | | 2 | 0 | 0 | | | | | | | | | | | | |
| **257.0410** | $C_9H_9N_2O_7$ | 1:4 | 10 | | 7 | 6 | 6 | 5.5 | -2.82 | 8.5 | -2.82 | 7.9 | 3.02 | 7.6 | 7.69 | 8.2 | -13.32 | 4.5 | 32.20 |
| **259.0679** | $C_8H_{11}N_4O_6$ | 2:3 | 8 | | 6 | 4 | 4 | 100.0 | 13.35 | 100.0 | 3.32 | 100.0 | 15.28 | 100.0 | 6.79 | 100.0 | 6.79 | 13.1 | 5.25 |
| **261.0947** | $C_7H_{13}N_6O_5$ | 3:2 | 6 | | 5 | 2 | 2 | | | | | | | | | | | 15.2 | 7.44 |
| **265.0685** | $C_9H_9N_6O_4$ | 3:3 | 11 | | 9 | 6 | 6 | | | | | | | | | | | 11.7 | 5.76 |
| **271.0778** | $C_7H_{15}N_2O_9$ | 1:3 | 4 | | 2 | 1 | 1 | | | | | | | | | | | | |
| **275.0515** | $C_9H_{11}N_2O_8$ | 1:4 | 9 | | 6 | 5 | 5 | 14.9 | 23.78 | 18.6 | 19.78 | 16.4 | 20.14 | 13.5 | 19.42 | 14.4 | 13.96 | | |
| **283.0791** | $C_9H_{11}N_6O_5$ | 3:3 | 10 | | 8 | 5 | 5 | | | | | 2.4 | 17.28 | 1.9 | 9.51 | | | 44.5 | 5.63 |
| **285.1060** | $C_8H_{13}N_8O_4$ | 4:2 | 8 | | 7 | 3 | 3 | | | | | | | | | | | 10.8 | 44.11 |

[a]Urea:glyoxal units affording the molecular formula specified ($MH^+$) after elimination of the corresponding water molecules (4th column); [b]UN = unsaturation number; [c]RN = ring number; [d]ON = oxygen number (not belonging to urea moieties)

**Table S5.3 cont.** Calculated m/z peaks for $[MH]^+$ compositions and their temporal evolution for 1:1 urea-glyoxal oligomers in aqueous samples and solids from acetone

| m/z | $[MH]^+$ | U:G[a] | - $H_2O$ | + $NH_3$ | UN[b] | RN[c] | ON[d] | 1 day | | 5 days | | 10 days | | 20 days | | 40 days | | Solid | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) |
| **293.0621** | $C_9H_{13}N_2O_9$ | 1:4 | 8 | | 5 | 4 | 4 | 7.7 | 14.01 | 6.2 | 6.84 | 9.9 | 12.64 | 6.4 | 8.89 | 10.4 | 5.48 | | |
| **299.0628** | $C_{10}H_{11}N_4O_7$ | 2:4 | 11 | | 8 | 6 | 6 | 2.6 | 18.97 | 5.4 | 18.64 | 10.4 | 13.62 | 16.1 | 9.61 | 16.2 | 8.27 | 7.5 | 3.92 |
| **301.0897** | $C_9H_{13}N_6O_6$ | 3:3 | 9 | | 7 | 4 | 4 | 16.6 | 12.15 | 23.5 | 7.83 | 19.8 | 16.80 | 17.9 | 14.47 | 9.2 | 17.46 | 34.1 | 8.49 |
| **303.1165** | $C_8H_{15}N_8O_5$ | 4:2 | 7 | | 6 | 2 | 2 | | | | | 1.1 | 100.76 | | | | | 5.2 | 34.11 |
| **307.0903** | $C_{10}H_{11}N_8O_4$ | 4:3 | 12 | | 10 | 6 | 6 | | | | | | | | | | | 1.8 | 4.64 |
| **313.0996** | $C_8H_{17}N_4O_9$ | 2:3 | 5 | | 3 | 1 | 1 | | | | | | | | | | | | |
| **317.0733** | $C_{10}H_{13}N_4O_8$ | 2:4 | 10 | | 7 | 5 | 5 | 29.1 | 12.10 | 47.6 | 6.43 | 69.3 | 12.10 | 74.9 | 5.80 | 73.4 | 2.01 | 15.0 | 23.77 |
| **319.1002** | $C_9H_{15}N_6O_7$ | 3:3 | 8 | | 6 | 3 | 3 | | | | | | | | | 3.3 | 120.41 | 13.6 | 5.08 |
| **323.0740** | $C_{11}H_{11}N_6O_6$ | 3:4 | 13 | | 10 | 7 | 7 | | | | | | | | | | | 6.8 | 8.07 |
| **325.1009** | $C_{10}H_{13}N_8O_5$ | 4:3 | 11 | | 9 | 5 | 5 | | | | | | | | | | | 15.5 | 7.97 |
| **335.0839** | $C_{10}H_{15}N_4O_9$ | 2:4 | 9 | | 6 | 4 | 4 | 7.8 | 10.16 | 5.9 | 6.87 | 4.3 | 11.35 | 3.1 | 11.05 | 5.2 | 6.28 | | |
| **341.0846** | $C_{11}H_{13}N_6O_7$ | 3:4 | 12 | | 9 | 6 | 6 | | | | | | | 3.2 | 15.75 | 5.0 | 21.91 | 19.7 | 6.95 |
| **343.1115** | $C_{10}H_{15}N_8O_6$ | 4:3 | 10 | | 8 | 4 | 4 | 1.6 | 25.23 | 2.2 | 25.23 | 3.8 | 18.52 | 4.3 | 9.78 | 2.4 | 34.55 | 17.3 | 5.41 |
| **345.1383** | $C_9H_{17}N_{10}O_5$ | 5:2 | 8 | | 7 | 2 | 2 | | | | | | | | | | | | |
| **347.0852** | $C_{12}H_{11}N_8O_5$ | | 15 | | 12 | 8 | 8 | | | 1.2 | 20.28 | | | | | 1.3 | 3.86 | 1.8 | 5.59 |
| **355.1214** | $C_9H_{19}N_6O_9$ | 3:3 | 6 | | 4 | 1 | 1 | | | | | | | | | | | 1.3 | 24.36 |
| **357.0683** | $C_{12}H_{13}N_4O_9$ | 2:5 | 13 | | 9 | 7 | 7 | | | 2.1 | 25.91 | | | | | | | | |
| **359.0951** | $C_{11}H_{15}N_6O_8$ | 3:4 | 11 | | 8 | 5 | 5 | 5.1 | 16.81 | 8.6 | 4.00 | 14.1 | 11.52 | 13.8 | 7.62 | 11.1 | 9.57 | 20.2 | 10.68 |
| **361.122** | $C_{10}H_{17}N_8O$ | 4:3 | 9 | | 7 | 3 | 3 | | | | | | | | | | | 21.0 | 2.55 |

| | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **0** | $_{7}$ | | | | | | | | | | | | | | | | | | |
| **363.0689** | $C_{13}H_{11}N_6O_7$ | 3:5 | 16 | | 12 | 9 | 9 | | | | | 1.4 | 20.99 | | | | | | |
| **365.0958** | $C_{12}H_{13}N_8O_6$ | 4:4 | 14 | | 11 | 7 | 7 | | | | | | | | | | | 8.9 | 6.30 |
| **367.1227** | $C_{11}H_{15}N_{10}O_5$ | 5:3 | 12 | | 10 | 5 | 5 | | | | | | | | | | | 2.6 | 9.23 |
| **373.1319** | $C_9H_{21}N_6O_{10}$ | 3:3 | 5 | | 3 | 0 | 0 | | | | | | | | | | | | |
| **375.0788** | $C_{12}H_{15}N_4O_{10}$ | 2:5 | 12 | | 8 | 6 | 6 | 6.8 | 11.20 | 12.5 | 4.80 | 13.7 | 13.60 | 16.0 | 6.93 | 12.8 | 9.33 | | |
| **377.1057** | $C_{11}H_{17}N_6O_9$ | 3:4 | 10 | | 7 | 4 | 4 | 5.9 | 8.22 | 6.9 | 5.31 | 7.1 | 16.44 | 6.7 | 10.88 | 7.6 | 13.26 | 7.8 | 17.50 |
| **379.1326** | $C_{10}H_{19}N_8O_8$ | 4:3 | 8 | | 6 | 2 | 2 | | | | | | | | | | | 4.8 | 14.73 |
| **383.1064** | $C_{12}H_{15}N_8O_7$ | 4:4 | 13 | | 10 | 6 | 6 | | | | | | | | | | | 21.8 | 3.31 |
| **385.1333** | $C_{11}H_{17}N_{10}O_6$ | 5:3 | 11 | | 9 | 4 | 4 | | | | | | | | | | | 7.9 | 28.44 |
| **389.1156** | $C_{10}H_{21}N_4O_{12}$ | 2:4 | 6 | | 3 | 1 | 1 | | | | | | | | | | | | |
| **393.0894** | $C_{12}H_{17}N_4O_{11}$ | 2:5 | 11 | | 7 | 5 | 5 | 7.5 | 10.64 | 9.6 | 6.82 | 9.5 | 10.39 | 10.5 | 4.53 | 13.2 | 1.74 | | |

[a]Urea:glyoxal units affording the molecular formula specified ($MH^+$) after elimination of the corresponding water molecules (4th column); [b]UN = unsaturation number; [c]RN = ring number; [d]ON = oxygen number (not belonging to urea moieties)

**Table S5.3 cont.** Calculated m/z peaks for $[MH]^+$ compositions and their temporal evolution for 1:1 urea-glyoxal oligomers in aqueous samples and solids from acetone

| m/z | $[MH]^+$ | U:G[a] | $-H_2O$ | $+NH_3$ | UN[b] | RN[c] | ON[d] | 1 day | | 5 days | | 10 days | | 20 days | | 40 days | | Solid | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) |
| **399.0901** | $C_{13}H_{15}N_6O_9$ | 3:5 | 14 | | 10 | 7 | 7 | | | | | | | | | | | 4.7 | -0.12 |
| **401.1169** | $C_{12}H_{17}N_8O_8$ | 4:4 | 12 | | 9 | 5 | 5 | 1.5 | 12.55 | 3.3 | 11.55 | 6.5 | 13.80 | 6.9 | 6.32 | 5.7 | 9.06 | 25.5 | 5.82 |
| **403.1438** | $C_{11}H_{19}N_{10}O_7$ | 5:3 | 10 | | 8 | 3 | 3 | | | | | | | | | | | 8.5 | 22.12 |

| | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **405.0993** | $C_{11}H_{21}N_2O_{14}$ | 1:5 | 7 | | 3 | 2 | 2 | | | | | | | | | | | 2.6 | -17.58 |
| **405.1707** | $C_{10}H_{21}N_{12}O_6$ | 6:2 | 8 | | 7 | 1 | 1 | | | | | | | | | | | | |
| **407.1176** | $C_{13}H_{15}N_{10}O_6$ | 5:4 | 15 | | 12 | 7 | 7 | | | | | | | | | | | 3.1 | 16.47 |
| **411.0999** | $C_{12}H_{19}N_4O_{12}$ | 2:5 | 10 | | 6 | 4 | 4 | 6.5 | 8.87 | 6.4 | 4.49 | 6.4 | 11.79 | 5.6 | 2.30 | 12.5 | 0.36 | | |
| **417.1006** | $C_{13}H_{17}N_6O_{10}$ | 3:5 | 13 | | 9 | 6 | 6 | 2.1 | 6.51 | 4.1 | 4.11 | 8.8 | 13.22 | 8.3 | 7.95 | 9.2 | -3.08 | 10.3 | 11.31 |
| **419.1275** | $C_{12}H_{19}N_8O_9$ | 4:4 | 11 | | 8 | 4 | 4 | 5.2 | 9.78 | 6.0 | 5.25 | 6.0 | 10.50 | 4.7 | 5.49 | 5.6 | 11.21 | 14.5 | 3.58 |
| **421.1544** | $C_{11}H_{21}N_{10}O_8$ | 5:3 | 9 | | 7 | 2 | 2 | | | | | | | | | | | 6.4 | 2.33 |
| **423.1013** | $C_{14}H_{15}N_8O_8$ | 4:5 | 16 | | 12 | 8 | 8 | | | | | | | | | | | 5.3 | 10.60 |
| **425.1282** | $C_{13}H_{17}N_{10}O_7$ | 5:4 | 14 | | 11 | 6 | 6 | | | | | | | | | | | 8.7 | 9.80 |
| **427.1551** | $C_{12}H_{19}N_{12}O_6$ | 6:3 | 12 | | 10 | 4 | 4 | | | | | | | | | | | | |
| **431.1374** | $C_{11}H_{23}N_6O_{12}$ | 3:4 | 7 | | 4 | 1 | 1 | | | | | | | | | | | | |
| **433.0843** | $C_{14}H_{17}N_4O_{12}$ | 2:6 | 14 | | 9 | 7 | 7 | 1.3 | 5.77 | 2.5 | -6.93 | 2.2 | 14.31 | 2.0 | 22.62 | 2.6 | 12.46 | 2.8 | 19.85 |
| **435.1112** | $C_{13}H_{19}N_6O_{11}$ | 3:5 | 12 | | 8 | 5 | 5 | 6.1 | 13.29 | 8.9 | 2.48 | 8.3 | 13.51 | 8.2 | 8.69 | 12.0 | -0.27 | 2.0 | 19.03 |
| **437.1381** | $C_{12}H_{21}N_8O_{10}$ | 4:4 | 10 | | 7 | 3 | 3 | | | | | | | | | | | 9.1 | -0.77 |
| **441.1118** | $C_{14}H_{17}N_8O_9$ | 4:5 | 15 | | 11 | 7 | 7 | | | | | | | | | 1.4 | 19.38 | 12.4 | 8.50 |
| **443.1275** | $C_{13}H_{19}N_{10}O_8$ | 5:4 | 13 | | 10 | 5 | 5 | | | | | | | | | | | 14.4 | -13.09 |
| **445.1656** | $C_{12}H_{21}N_{12}O_7$ | 6:3 | 11 | | 9 | 3 | 3 | | | | | | | | | | | 3.5 | 31.26 |
| **449.1480** | $C_{11}H_{25}N_6O_{13}$ | 3:4 | 6 | | 3 | 0 | 0 | | | | | | | | | | | | |
| **453.1217** | $C_{13}H_{21}N_6O_{12}$ | 3:5 | 11 | | 7 | 4 | 4 | 3.8 | 10.47 | 2.3 | 2.97 | 2.6 | 9.59 | 1.6 | 9.81 | 3.4 | 4.07 | | |
| **459.1224** | $C_{14}H_{19}N_8O_{10}$ | 4:5 | 14 | | 10 | 6 | 6 | | | 3.3 | 18.11 | 7.6 | 10.05 | 8.6 | 5.26 | 9.3 | -3.67 | 13.5 | 11.36 |
| **461.1493** | $C_{13}H_{21}N_{10}O_9$ | 5:4 | 12 | | 9 | 4 | 4 | | | | | | | | | 1.2 | 17.34 | 16.4 | 7.80 |

| | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **463.1762** | $C_{12}H_{23}N_{12}O_8$ | 6:3 | 10 | | 8 | 2 | 2 | | | | | | | | | | | 2.1 | 18.31 |
| **465.1231** | $C_{15}H_{17}N_{10}O_8$ | 5:5 | 17 | | 13 | 8 | 8 | | | | | | | | | | | 4.2 | -9.93 |
| **467.1500** | $C_{14}H_{19}N_{12}O_7$ | 6:4 | 15 | | 12 | 6 | 6 | | | | | | | | | | | 3.8 | 2.71 |
| **473.1592** | $C_{12}H_{25}N_8O_{12}$ | 4:4 | 8 | | 5 | 1 | 1 | | | | | | | | | | | | |
| **475.1061** | $C_{15}H_{19}N_6O_{12}$ | 3:6 | 15 | | 10 | 7 | 7 | | | 1.8 | 7.79 | 2.8 | 19.36 | 2.3 | 15.58 | 2.8 | 8.84 | 3.9 | 16.00 |
| **477.1330** | $C_{14}H_{21}N_8O_{11}$ | 4:5 | 13 | | 9 | 5 | 5 | 7.8 | 12.74 | 9.1 | 2.89 | 11.7 | 8.76 | 12.7 | 4.36 | 13.3 | 3.94 | 8.7 | 13.37 |

[a]Urea:glyoxal units affording the molecular formula specified ($MH^+$) after elimination of the corresponding water molecules (4th column); [b]UN = unsaturation number; [c]RN = ring number; [d]ON = oxygen number (not belonging to urea moieties)

**Table S5.3 cont.** Calculated m/z peaks for $[MH]^+$ compositions and their temporal evolution for 1:1 urea-glyoxal oligomers in aqueous samples and solids from acetone

| m/z | $[MH]^+$ | U:G[a] | $-H_2O$ | $+NH_3$ | UN[b] | RN[c] | ON[d] | 1 day | | 5 days | | 10 days | | 20 days | | 40 days | | Solid | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) |
| **479.1599** | $C_{13}H_{23}N_{10}O_{10}$ | 5:4 | 11 | | 8 | 3 | 3 | | | | | | | | | | | 6.8 | 4.72 |
| **483.1336** | $C_{15}H_{19}N_{10}O_9$ | 5:5 | 16 | | 12 | 7 | 7 | | | | | | | | | | | 10.8 | 2.58 |
| **485.1605** | $C_{14}H_{21}N_{12}O_8$ | 6:4 | 14 | | 11 | 5 | 5 | | | | | | | | | | | 6.7 | 7.48 |
| **487.1874** | $C_{13}H_{23}N_{14}O_7$ | 7:3 | 12 | | 10 | 3 | 3 | 1.4 | 159.93 | | | | | | | | | | |
| **489.1429** | $C_{13}H_{25}N_6O_{14}$ | 3:5 | 9 | | 5 | 2 | 2 | | | | | | | | | | | | |
| **491.1698** | $C_{12}H_{27}N_8O_{13}$ | 4:4 | 7 | | 4 | 0 | 0 | | | | | | | | | | | | |
| **493.1167** | $C_{15}H_{21}N_6O_{13}$ | 3:6 | 14 | | 9 | 6 | 6 | 2.8 | 7.10 | 4.2 | 2.64 | 4.7 | 16.43 | 5.5 | 10.95 | 5.9 | 10.14 | 2.3 | 14.20 |
| **495.1435** | $C_{14}H_{23}N8O_{12}$ | 4:5 | 12 | | 8 | 4 | 4 | 11.0 | 11.20 | 7.2 | 2.11 | 6.9 | 9.78 | 5.4 | 3.12 | 5.3 | 5.34 | | |
| **499.117** | $C_{16}H_{19}N_8O_1$ | 4:6 | 17 | | 12 | 8 | 8 | | | | | | | | | | | 3.6 | 2.46 |

| | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **3** | $_{1}$ | | | | | | | | | | | | | | | | | | |
| **501.1442** | $C_{15}H_{21}N_{10}O_{10}$ | 5:5 | 15 | | 11 | 6 | 6 | | | | | | | | | | | 16.9 | 9.00 |
| **503.1711** | $C_{14}H_{23}N_{12}O_{9}$ | 6:4 | 13 | | 10 | 4 | 4 | | | | | | | | | | | 8.3 | 19.27 |
| **507.1534** | $C_{13}H_{27}N_{6}O_{15}$ | 3:5 | 8 | | 4 | 1 | 1 | | | | | | | | | | | | |
| **511.1272** | $C_{15}H_{23}N_{6}O_{14}$ | 3:6 | 13 | | 8 | 5 | 5 | 2.6 | 11.40 | 2.6 | -1.71 | 2.9 | 9.63 | 3.2 | 17.46 | 4.6 | 0.83 | | |
| **517.1279** | $C_{16}H_{21}N_{8}O_{12}$ | 4:6 | 16 | | 11 | 7 | 7 | | | | | 2.2 | 14.30 | 2.9 | 3.27 | 4.4 | 14.49 | 7.1 | 6.56 |
| **519.1548** | $C_{15}H_{23}N_{10}O_{11}$ | 5:5 | 14 | | 10 | 5 | 5 | | | 2.1 | 12.28 | 2.1 | 10.16 | 1.9 | 7.47 | 1.8 | 7.66 | 12.2 | 8.24 |
| **521.1817** | $C_{14}H_{25}N_{12}O_{10}$ | 6:4 | 12 | | 9 | 3 | 3 | | | | | | | | | | | 6.0 | 13.35 |
| **525.1554** | $C_{16}H_{21}N_{12}O_{9}$ | 6:5 | 17 | | 13 | 7 | 7 | | | | | | | | | | | 3.4 | 12.27 |
| **527.1823** | $C_{15}H_{23}N_{14}O_{8}$ | 7:4 | 15 | | 12 | 5 | 5 | | | | | | | | | | | | |
| **535.1385** | $C_{16}H_{23}N_{8}O_{13}$ | 4:6 | 15 | | 10 | 6 | 6 | 2.7 | 17.11 | 4.2 | 6.27 | 9.2 | 15.24 | 9.8 | 8.52 | 13.0 | 2.91 | 4.0 | 7.21 |
| **537.1653** | $C_{15}H_{25}N_{10}O_{12}$ | 5:5 | 13 | | 9 | 4 | 4 | 2.5 | 9.57 | 1.9 | 10.13 | | | | | | | 7.6 | -0.48 |
| **543.1660** | $C_{16}H_{23}N_{12}O_{10}$ | 6:5 | 16 | | 12 | 6 | 6 | | | | | | | | | | | 8.6 | 12.35 |
| **545.1929** | $C_{15}H_{25}N_{14}O_{9}$ | 7:4 | 14 | | 11 | 4 | 4 | | | | | | | | | | | 4.9 | 8.24 |
| **549.1752** | $C_{14}H_{29}N_{8}O_{15}$ | 4:5 | 9 | | 5 | 1 | 1 | | | | | | | | | | | | |
| **553.1490** | $C_{16}H_{25}N_{8}O_{14}$ | 4:6 | 14 | | 9 | 5 | 5 | 5.7 | 10.16 | 5.7 | 0.40 | 5.6 | 7.27 | 5.8 | 7.27 | 6.1 | 2.75 | | |
| **559.1497** | $C_{17}H_{23}N_{10}O_{12}$ | 5:6 | 17 | | 12 | 7 | 7 | | | | | | | | | 1.3 | 1.24 | 11.6 | 10.89 |
| **561.1766** | $C_{16}H_{25}N_{12}O_{11}$ | 6:5 | 15 | | 11 | 5 | 5 | | | | | | | | | | | 10.6 | 5.12 |
| **563.2035** | $C_{15}H_{27}N_{14}O_{10}$ | 7:4 | 13 | | 10 | 3 | 3 | | | | | | | | | | | | |
| **565.1504** | $C_{18}H_{21}N_{12}O_{10}$ | 6:6 | 20 | | 15 | 9 | 9 | | | | | | | | | | | 2.7 | -3.61 |
| **567.1772** | $C_{17}H_{23}N_{14}O_{9}$ | 7:5 | | | -4 | -11 | -11 | | | | | | | | | | | 2.6 | -2.92 |
| **577.160** | $C_{17}H_{25}N_{10}O$ | 5:6 | 16 | | 11 | 6 | 6 | | | | | 2.0 | 14.65 | 1.2 | 16.56 | 2.1 | 16.90 | 6.9 | 7.89 |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **3** | $_{13}$ | | | | | | | | | | | | | | | | | | | | |

[a]Urea:glyoxal units affording the molecular formula specified ($MH^+$) after elimination of the corresponding water molecules (4th column); [b]UN = unsaturation number; [c]RN = ring number; [d]ON = oxygen number (not belonging to urea moieties)

**Table S5.3 cont.** Calculated m/z peaks for $[MH]^+$ compositions and their temporal evolution for 1:1 urea-glyoxal oligomers in aqueous samples and solids from acetone

| m/z | $[MH]^+$ | U:G[a] | $-H_2O$ | $+NH_3$ | UN[b] | RN[c] | ON[d] | 1 day | | 5 days | | 10 days | | 20 days | | 40 days | | Solid | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) |
| **579.1871** | $C_{16}H_{27}N_{12}O_{12}$ | 6:5 | 14 | | 10 | 4 | 4 | | | | | | | | | | | 8.6 | 1.62 |
| **585.1878** | $C_{17}H_{25}N_{14}O_{10}$ | 7:5 | 17 | | 13 | 6 | 6 | | | | | | | | | | | 6.7 | 16.93 |
| **587.2147** | $C_{16}H_{27}N_{16}O_{9}$ | 8:4 | 15 | | 12 | 4 | 4 | | | | | | | | | | | | |
| **593.1439** | $C_{18}H_{25}N_{8}O_{15}$ | 4:7 | 17 | | 11 | 7 | 7 | | | | | | | | | 3.5 | 15.40 | 2.0 | 3.94 |
| **595.1708** | $C_{17}H_{27}N_{10}O_{14}$ | 5:6 | 15 | | 10 | 5 | 5 | 1.1 | 14.82 | 1.6 | 6.59 | 1.4 | 13.48 | 1.4 | 14.99 | | | 3.6 | 3.56 |
| **601.1715** | $C_{18}H_{25}N_{12}O_{12}$ | 6:6 | 18 | | 13 | 7 | 7 | | | | | | | | | | | 10.9 | 6.97 |
| **603.1984** | $C_{17}H_{27}N_{14}O_{11}$ | 7:5 | 16 | | 12 | 5 | 5 | | | | | | | | | | | 8.8 | 11.89 |
| **607.1807** | $C_{16}H_{31}N_{8}O_{17}$ | 4:6 | 11 | | 6 | 2 | 2 | | | | | | | | | | | 1.4 | -9.36 |
| **611.1545** | $C_{18}H_{27}N_{8}O_{16}$ | 4:7 | 16 | | 10 | 6 | 6 | 1.9 | 14.07 | 2.9 | -1.63 | 4.6 | 12.93 | 4.8 | 5.08 | 5.5 | 0.17 | | |
| **619.1821** | $C_{18}H_{27}N_{12}O_{13}$ | 6:6 | 17 | | 12 | 6 | 6 | | | | | | | | | | | 12.0 | -1.20 |
| **621.2089** | $C_{17}H_{29}N_{14}O_{12}$ | 7:5 | 15 | | 11 | 4 | 4 | | | | | | | | | | | 5.8 | 16.16 |
| **635.1657** | $C_{19}H_{27}N_{10}O_{15}$ | 5:7 | 18 | | 12 | 7 | 7 | | | | | | | | | 1.5 | 15.01 | 5.0 | 15.96 |
| **637.1926** | $C_{18}H_{29}N_{12}O_{14}$ | 6:6 | 16 | | 11 | 5 | 5 | | | | | | | | | | | 7.9 | -0.60 |
| **641.1664** | $C_{20}H_{25}N_{12}O_{13}$ | 6:7 | 21 | | 15 | 9 | 9 | | | | | | | | | | | 3.6 | -6.70 |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **643.1933** | $C_{19}H_{27}N_{14}O_{12}$ | 7:6 | 19 | | 14 | 7 | 7 | | | | | | | | | | | 4.8 | -1.73 |
| **649.2025** | $C_{17}H_{33}N_{10}O_{17}$ | 5:6 | 12 | | 7 | 2 | 2 | | | | | | | | | | | | |
| **661.2039** | $C_{19}H_{29}N_{14}O_{13}$ | | 18 | | 13 | 6 | 6 | | | | | | | | | | | 10.8 | 3.56 |
| **667.2045** | $C_{20}H_{27}N_{16}O_{11}$ | 8:6 | 21 | | 16 | 8 | 8 | | | | | | | | | | | 1.5 | -5.81 |
| **669.1600** | $C_{20}H_{29}N_8O_{18}$ | 4:8 | 18 | | 11 | 7 | 7 | 1.2 | 14.32 | 1.7 | 12.52 | 1.7 | 14.77 | 2.3 | 7.89 | | | | |
| **677.1875** | $C_{20}H_{29}N_{12}O_{15}$ | 6:7 | 19 | | 13 | 7 | 7 | | | | | | | | | 2.0 | 8.17 | 8.1 | 4.04 |
| **679.2144** | $C_{19}H_{31}N_{14}O_{14}$ | 7:6 | 17 | | 12 | 5 | 5 | | | | | | | | | | | 8.0 | 9.15 |
| **685.2151** | $C_{20}H_{29}N_{16}O_{12}$ | 8:6 | 20 | | 15 | 7 | 7 | | | | | | | | | | | 3.4 | 15.59 |
| **695.1981** | $C_{20}H_{31}N_{12}O_{16}$ | 6:7 | 18 | | 12 | 6 | 6 | | | | | 1.4 | 6.61 | 1.2 | 10.35 | 1.5 | -3.74 | 4.5 | 10.64 |
| **701.1988** | $C_{21}H_{29}N_{14}O_{14}$ | 7:7 | 21 | | 15 | 8 | 8 | | | | | | | | | | | 5.5 | 2.23 |
| **711.1818** | $C_{21}H_{31}N_{10}O_{18}$ | 5:8 | 19 | | 12 | 7 | 7 | | | | | | | 1.4 | 29.78 | 1.6 | 2.08 | | |
| **719.2093** | $C_{21}H_{31}N_{14}O_{15}$ | 7:7 | 20 | | 14 | 7 | 7 | | | | | | | | | | | 8.5 | 11.03 |
| **721.2362** | $C_{20}H_{33}N_{16}O_{14}$ | 8:6 | 18 | | 13 | 5 | 5 | | | | | | | | | | | 5.4 | 15.13 |
| **737.2199** | $C_{21}H_{33}N_{14}O_{16}$ | 7:7 | 19 | | 13 | 6 | 6 | | | | | | | | | | | 5.2 | 14.92 |
| **787.2692** | $C_{22}H_{35}N_{20}O_{13}$ | 10:6 | 21 | | 16 | 6 | 6 | | | | | | | | | | | | |
| **795.2254** | $C_{23}H_{35}N_{14}O_{18}$ | 7:8 | 21 | | 14 | 7 | 7 | | | | | | | | | | | 4.0 | -0.28 |

[a]Urea:glyoxal units affording the molecular formula specified ($MH^+$) after elimination of the corresponding water molecules (4th column); [b]UN = unsaturation number; [c]RN = ring number; [d]ON = oxygen number (not belonging to urea moieties)

**Table S5.3 cont.** Calculated m/z peaks for $[MH]^+$ compositions and their temporal evolution for 1:1 urea-glyoxal oligomers in aqueous samples and solids from acetone

| m/z | [MH]+ | U:G[a] | -$H_2O$ | +$NH_3$ | UN[b] | RN[c] | ON[d] | 1 day | | 5 days | | 10 days | | 20 days | | 40 days | | Solid | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) |
| **837.2472** | $C_{24}H_{37}N_{16}O_{18}$ | 8:8 | 22 | | 15 | 7 | 7 | | | | | | | | | | | | |
| **855.2577** | $C_{24}H_{39}N_{16}O_{19}$ | 8:8 | 21 | | 14 | 6 | 6 | | | | | | | | | | | | |
| **861.2584** | $C_{25}H_{37}N_{18}O_{17}$ | 9:8 | 24 | | 17 | 8 | 8 | | | | | | | | | | | | |
| **877.2421** | $C_{26}H_{37}N_{16}O_{19}$ | 8:9 | 25 | | 17 | 9 | 9 | | | | | | | | | | | | |
| **879.2690** | $C_{25}H_{39}N_{18}O_{18}$ | 9:8 | 23 | | 16 | 7 | 7 | | | | | | | | | | | | |
| **897.2795** | $C_{25}H_{41}N_{18}O_{19}$ | 9:8 | 22 | | 15 | 6 | 6 | | | | | | | | | | | | |
| **919.2639** | $C_{27}H_{39}N_{18}O_{19}$ | 9:9 | 26 | | 18 | 9 | 9 | | | | | | | | | | | | |
| **937.2745** | $C_{27}H_{41}N_{18}O_{20}$ | 9:9 | 25 | | 17 | 8 | 8 | | | | | | | | | | | | |
| **955.2850** | $C_{27}H_{43}N_{18}O_{21}$ | 9:9 | 24 | | 16 | 7 | 7 | | | | | | | | | | | | |
| **961.2857** | $C_{28}H_{41}N_{20}O_{19}$ | 10:9 | 27 | | 19 | 9 | 9 | | | | | | | | | | | | |
| **1097.3341** | $C_{31}H_{49}N_{22}O_{23}$ | 11:10 | 28 | | 19 | 8 | 8 | | | | | | | | | | | | |

[a]Urea:glyoxal units affording the molecular formula specified ($MH^+$) after elimination of the corresponding water molecules (4th column); [b]UN = unsaturation number; [c]RN = ring number; [d]ON = oxygen number (not belonging to urea moieties)

**Table S5.4.** Calculated m/z peaks for $[MH]^+$ compositions and their temporal evolution for 1:2 urea-glyoxal oligomers in aqueous samples and solids from acetone

| m/z | $[MH]^+$ | U:G[a] | $-H_2O$ | $+NH_3$ | UN[b] | RN[c] | ON[d] | 1 day | | 5 days | | 10 days | | 20 days | | 40 days | | Solid | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) |
| **100.0511** | $C_3H_6N_3O$ | 2:1 | 4 | 1 | 3 | 2 | 3 | | | | | | | | | | | | |
| **101.0351** | $C_3H_5N_2O_2$ | 1:1 | 3 | | 3 | 2 | 2 | 1.3 | 6.95 | 2.2 | -1.96 | 1.2 | 5.96 | 2.0 | -2.95 | 2.7 | 6.95 | 3.7 | 9.92 |
| **119.0457** | $C_3H_7N_2O_3$ | 1:1 | 2 | | 2 | 1 | 1 | | | 1.1 | -1.12 | | | 1.7 | 2.24 | 2.3 | -14.56 | 2.1 | -17.08 |
| **126.0304** | $C_4H_4N_3O_2$ | 2:1 | 4 | -1 | 5 | 3 | 2 | | | | | | | | | 1.5 | 9.14 | 10.2 | 7.55 |
| **140.0460** | $C_4H_6N_3O_2$ | 1:2 | 7 | 1 | 5 | 4 | 5 | | | | | | | | | | | 9.4 | 17.15 |
| **141.0300** | $C_5H_5N_2O_3$ | 1:2 | 6 | | 5 | 4 | 4 | 33.9 | 19.97 | 39.5 | 17.85 | | | 50.9 | 13.59 | 39.9 | 12.17 | 7.3 | 0.83 |
| **143.0569** | $C_4H_7N_4O_2$ | 2:1 | 4 | | 4 | 2 | 2 | | | | | | | | | | | 2.3 | 44.04 |
| **158.0566** | $C_5H_8N_3O_3$ | 1:2 | 6 | 1 | 4 | 3 | 4 | | | | | | | | | | | 1.8 | -12.24 |
| **159.0406** | $C_5H_7N_2O_4$ | | 5 | | 4 | 3 | 3 | | | | | | | | | | | 3.4 | 12.46 |
| **165.0413** | $C_6H_5N_4O_2$ | 2:2 | 8 | | 7 | 5 | 5 | | | | | | | | | | | 2.2 | 40.30 |
| **182.0678** | $C_6H_8N_5O_2$ | 2:2 | 8 | 1 | 6 | 4 | 5 | | | | | | | | | | | | |
| **183.0518** | $C_6H_7N_4O_3$ | 2:2 | 7 | | 6 | 4 | 4 | 19.0 | 18.66 | 26.9 | 17.02 | 26.3 | 20.30 | 23.5 | 17.56 | 12.9 | 21.93 | 10.4 | 1.72 |
| **199.0355** | $C_7H_7N_2O_5$ | 1:3 | 8 | | 6 | 5 | 5 | 90.7 | 14.55 | 100.0 | 11.54 | 100.0 | 21.08 | 100.0 | 10.03 | 92.1 | 9.03 | 6.5 | 21.59 |
| **201.0624** | $C_6H_9N_4O_4$ | 2:2 | 6 | | 5 | 3 | 3 | | | | | | | | | | | 6.4 | 13.33 |
| **213.0637** | $C_8H_5N_8$ | 4:2 | 12 | | 11 | 7 | 7 | 9.4 | 23.08 | 9.5 | 19.32 | 12.0 | 25.43 | 9.4 | 16.04 | 6.5 | 11.81 | 1.5 | 30.12 |
| **217.0461** | $C_7H_9N_2O_6$ | 1:3 | 7 | | 5 | 4 | 4 | 50.6 | 12.72 | 47.2 | 9.96 | 47.7 | 17.79 | 35.8 | 9.96 | 100.0 | 3.97 | 1.1 | 30.23 |
| **219.0729** | $C_6H_{11}N_4O_5$ | 2:2 | 5 | | 4 | 2 | 2 | | | | | | | | | | | | |
| **223.0467** | $C_8H_7N_4O_4$ | 2:3 | 10 | | 8 | 6 | 6 | | | 2.3 | 44.52 | 2.6 | 48.11 | 2.0 | 23.90 | 2.5 | 23.45 | 4.5 | 11.34 |
| **225.073** | $C_7H_9N_6O_3$ | 3:2 | 8 | | 7 | 4 | 4 | | | | | | | 1.2 | 23.61 | | | | |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **6** | | | | | | | | | | | | | | | | | | | |
| **241.0573** | $C_8H_9N_4O_5$ | 2:3 | 9 | | 7 | 5 | 5 | 12.4 | 9.52 | 26.2 | 7.44 | 35.2 | 18.64 | 37.8 | 9.10 | 31.3 | 7.03 | 11.1 | 5.78 |
| **243.0842** | $C_7H_{11}N_6O_4$ | 3:2 | 7 | | 6 | 3 | 3 | | | | 64.08 | | | | | | | | |
| **255.0941** | $C_6H_{15}N_4O_7$ | 2:2 | 3 | | 2 | 0 | 0 | | | | | | | | | | | 100.0 | -1.67 |
| **257.0410** | $C_9H_9N_2O_7$ | 1:4 | 10 | | 7 | 6 | 6 | 10.3 | 11.97 | 10.1 | 6.13 | 9.2 | 20.52 | 14.1 | 12.35 | 11.3 | 7.30 | 3.5 | -233.52 |
| **259.0679** | $C_8H_{11}N_4O_6$ | 2:3 | 8 | | 6 | 4 | 4 | 100.0 | 12.58 | 86.4 | 6.79 | 71.7 | 14.12 | 71.8 | 6.79 | 68.5 | 3.32 | 6.3 | 13.35 |
| **261.0947** | $C_7H_{13}N_6O_5$ | 3:2 | 6 | | 5 | 2 | 2 | | | | | | | | | | | | |
| **265.0685** | $C_9H_9N_6O_4$ | 3:3 | 11 | | 9 | 6 | 6 | | | | | | | | | | | | |
| **271.0778** | $C_7H_{15}N_2O_9$ | 1:3 | 4 | | 2 | 1 | 1 | | | | | | | | | | | 16.8 | 6.47 |
| **275.0515** | $C_9H_{11}N_2O_8$ | 1:4 | 9 | | 6 | 5 | 5 | 22.9 | 19.42 | 20.0 | 15.05 | 19.5 | 19.05 | 14.6 | 13.24 | 27.2 | 3.78 | 1.0 | 2.69 |
| **283.0791** | $C_9H_{11}N_6O_5$ | 3:3 | 10 | | 8 | 5 | 5 | | | | | | | 1.4 | 9.86 | 1.1 | 17.28 | 3.5 | 7.04 |
| **285.1060** | $C_8H_{13}N_8O_4$ | 4:2 | 8 | | 7 | 3 | 3 | | | | | | | | | | | | |

[a]Urea:glyoxal units affording the molecular formula specified ($MH^+$) after elimination of the corresponding water molecules (4th column); [b]UN = unsaturation number; [c]RN = ring number; [d]ON = oxygen number (not belonging to urea moieties)

**Table S5.4 cont.** Calculated m/z peaks for $[MH]^+$ compositions and their temporal evolution for 1:2 urea-glyoxal oligomers in aqueous samples and solids from acetone

| m/z | $[MH]^+$ | U:G[a] | $-H_2O$ | $+NH_3$ | UN[b] | RN[c] | ON[d] | 1 day | | 5 days | | 10 days | | 20 days | | 40 days | | Solid | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) |
| **293.0621** | $C_9H_{13}N_2O_9$ | 1:4 | 8 | | 5 | 4 | 4 | 9.5 | 5.48 | 11.3 | 5.82 | 12.5 | 13.67 | 7.1 | 4.11 | 20.8 | 1.04 | | |
| **299.0628** | $C_{10}H_{11}N_4O_7$ | 2:4 | 11 | | 8 | 6 | 6 | 3.7 | 24.99 | 6.8 | 3.92 | 9.9 | 15.96 | 9.4 | 6.93 | 15.0 | 7.60 | | |
| **301.0897** | $C_9H_{13}N_6O_6$ | 3:3 | 9 | | 7 | 4 | 4 | 10.0 | 16.13 | 11.1 | 16.46 | 9.0 | 32.74 | 8.7 | 26.43 | | | | |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **303.1165** | $C_8H_{15}N_8O_5$ | 4:2 | 7 | | 6 | 2 | 2 | | | | | | | | | | | | |
| **307.0903** | $C_{10}H_{11}N_8O_4$ | 4:3 | 12 | | 10 | 6 | 6 | | | | | | | | | | | | |
| **313.0996** | $C_8H_{17}N_4O_9$ | 2:3 | 5 | | 3 | 1 | 1 | | | | | | | | | | | 5.8 | -15.80 |
| **317.0733** | $C_{10}H_{13}N_4O_8$ | 2:4 | 10 | | 7 | 5 | 5 | 40.9 | 9.27 | 57.2 | 5.48 | 65.9 | 10.53 | 64.1 | 6.11 | 64.6 | 0.75 | 6.8 | 14.31 |
| **319.1002** | $C_9H_{15}N_6O_7$ | 3:3 | 8 | | 6 | 3 | 3 | | | | | | | | | | | | |
| **323.0740** | $C_{11}H_{11}N_6O_6$ | 3:4 | 13 | | 10 | 7 | 7 | | | | | | | | | 1.0 | 27.26 | 3.6 | -6.17 |
| **325.1009** | $C_{10}H_{13}N_8O_5$ | 4:3 | 11 | | 9 | 5 | 5 | | | | | | | | | | | | |
| **335.0839** | $C_{10}H_{15}N_4O_9$ | 2:4 | 9 | | 6 | 4 | 4 | 5.0 | 17.62 | 3.5 | 11.35 | 4.0 | 19.71 | 2.0 | 21.50 | 5.1 | 0.90 | 1.2 | -25.36 |
| **341.0846** | $C_{11}H_{13}N_6O_7$ | 3:4 | 12 | | 9 | 6 | 6 | | | 2.0 | 17.80 | | | 2.4 | 23.67 | | | 4.2 | -22.66 |
| **343.1115** | $C_{10}H_{15}N_8O_6$ | 4:3 | 10 | | 8 | 4 | 4 | | | 1.4 | 26.68 | | | 2.0 | 28.14 | | | | |
| **345.1383** | $C_9H_{17}N_{10}O_5$ | 5:2 | 8 | | 7 | 2 | 2 | | | | | | | | | | | | |
| **347.0852** | $C_{12}H_{11}N_8O_5$ | | 15 | | 12 | 8 | 8 | | | | | 1.3 | 26.33 | | | 1.7 | 27.20 | | |
| **355.1214** | $C_9H_{19}N_6O_9$ | 3:3 | 6 | | 4 | 1 | 1 | | | | | | | | | | | 9.9 | -6.61 |
| **357.0683** | $C_{12}H_{13}N_4O_9$ | 2:5 | 13 | | 9 | 7 | 7 | 1.4 | 19.75 | | | 3.0 | 24.23 | 2.2 | 21.15 | | | | |
| **359.0951** | $C_{11}H_{15}N_6O_8$ | 3:4 | 11 | | 8 | 5 | 5 | 5.3 | 6.51 | 7.1 | 5.95 | 7.7 | 10.41 | 7.8 | 10.13 | 6.2 | 23.77 | 3.7 | -8.25 |
| **361.1220** | $C_{10}H_{17}N_8O_7$ | 4:3 | 9 | | 7 | 3 | 3 | | | | | | | | | | | | |
| **363.0689** | $C_{13}H_{11}N_6O_7$ | 3:5 | 16 | | 12 | 9 | 9 | | | | | 1.0 | 22.92 | | | 1.2 | 16.86 | 5.6 | -16.19 |
| **365.0958** | $C_{12}H_{13}N_8O_6$ | 4:4 | 14 | | 11 | 7 | 7 | | | | | | | | | | | | |
| **367.1227** | $C_{11}H_{15}N_{10}O_5$ | 5:3 | 12 | | 10 | 5 | 5 | | | | | | | | | | | | |
| **373.1319** | $C_9H_{21}N_6O_{10}$ | 3:3 | 5 | | 3 | 0 | 0 | | | | | | | | | | | 92.8 | -0.76 |
| **375.0788** | $C_{12}H_{15}N_4O_{10}$ | 2:5 | 12 | | 8 | 6 | 6 | 17.7 | 10.13 | 20.4 | 5.33 | 18.5 | 11.73 | 21.9 | 7.20 | 21.5 | 3.47 | | |

| | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **377.1057** | $C_{11}H_{17}N_6O_9$ | 3:4 | 10 | | 7 | 4 | 4 | | | 5.3 | 16.71 | 4.2 | 19.63 | 3.9 | 16.44 | | | | |
| **379.1326** | $C_{10}H_{19}N_8O_8$ | 4:3 | 8 | | 6 | 2 | 2 | | | | | | | | | | | | |
| **383.1064** | $C_{12}H_{15}N_8O_7$ | 4:4 | 13 | | 10 | 6 | 6 | | | | | | | | | | | | |
| **385.1333** | $C_{11}H_{17}N_{10}O_6$ | 5:3 | 11 | | 9 | 4 | 4 | | | | | | | | | | | 1.7 | -6.61 |
| **389.1156** | $C_{10}H_{21}N_4O_{12}$ | 2:4 | 6 | | 3 | 1 | 1 | | | | | | | | | | | 47.4 | 19.01 |
| **393.0894** | $C_{12}H_{17}N_4O_{11}$ | 2:5 | 11 | | 7 | 5 | 5 | 6.8 | 10.89 | 8.6 | 8.86 | 10.2 | 9.37 | 8.5 | 5.81 | 15.6 | 2.50 | 1.8 | -24.21 |

[a]Urea:glyoxal units affording the molecular formula specified ($MH^+$) after elimination of the corresponding water molecules (4th column); [b]UN = unsaturation number; [c]RN = ring number; [d]ON = oxygen number (not belonging to urea moieties)

**Table S5.4 cont.** Calculated m/z peaks for $[MH]^+$ compositions and their temporal evolution for 1:2 urea-glyoxal oligomers in aqueous samples and solids from acetone

| m/z | $[MH]^+$ | U:G[a] | $-H_2O$ | $+NH_3$ | UN[b] | RN[c] | ON[d] | 1 day | | 5 days | | 10 days | | 20 days | | 40 days | | Solid | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) |
| **399.0901** | $C_{13}H_{15}N_6O_9$ | 3:5 | 14 | | 10 | 7 | 7 | | | | | | | | | 1.9 | 21.43 | | |
| **401.1169** | $C_{12}H_{17}N_8O_8$ | 4:4 | 12 | | 9 | 5 | 5 | 1.6 | 24.52 | 2.2 | 4.08 | 2.9 | 7.57 | 3.4 | 11.80 | | | | |
| **403.1438** | $C_{11}H_{19}N_{10}O_7$ | 5:3 | 10 | | 8 | 3 | 3 | | | | | | | | | | | | |
| **405.0993** | $C_{11}H_{21}N_2O_{14}$ | 1:5 | 7 | | 3 | 2 | 2 | | | | | | | | | | | 4.1 | -14.37 |
| **405.1707** | $C_{10}H_{21}N_{12}O_6$ | 6:2 | 8 | | 7 | 1 | 1 | | | | | | | | | | | | |
| **407.1176** | $C_{13}H_{15}N_{10}O_6$ | 5:4 | 15 | | 12 | 7 | 7 | | | | | | | | | | | | |
| **411.0999** | $C_{12}H_{19}N_4O_{12}$ | 2:5 | 10 | | 6 | 4 | 4 | 6.3 | 7.90 | 6.6 | 5.95 | 6.5 | 10.82 | 3.1 | 1.82 | 16.8 | -0.62 | | |
| **417.1006** | $C_{13}H_{17}N_6O_{10}$ | 3:5 | 13 | | 9 | 6 | 6 | | | 4.9 | 12.74 | 5.2 | 10.11 | 5.0 | 9.63 | 5.9 | 2.44 | | |
| **419.127** | $C_{12}H_{19}N_8O$ | 4:4 | 11 | | 8 | 4 | 4 | 3.4 | 16.22 | 4.2 | 23.62 | | | 1.9 | 22.43 | | | | |

| | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **5** | $_{9}$ | | | | | | | | | | | | | | | | | | |
| **421.1544** | $C_{11}H_{21}N_{10}O_{8}$ | 5:3 | 9 | | 7 | 2 | 2 | | | | | | | | | | | | |
| **423.1013** | $C_{14}H_{15}N_{8}O_{8}$ | 4:5 | 16 | | 12 | 8 | 8 | | | | | | | | | | | 2.1 | -7.60 |
| **425.1282** | $C_{13}H_{17}N_{10}O_{7}$ | 5:4 | 14 | | 11 | 6 | 6 | | | | | | | | | | | | |
| **427.1551** | $C_{12}H_{19}N_{12}O_{6}$ | 6:3 | 12 | | 10 | 4 | 4 | | | | | | | | | | | | |
| **431.1374** | $C_{11}H_{23}N_{6}O_{12}$ | 3:4 | 7 | | 4 | 1 | 1 | | | | | | | | | | | 11.7 | -1.63 |
| **433.0843** | $C_{14}H_{17}N_{4}O_{12}$ | 2:6 | 14 | | 9 | 7 | 7 | 4.2 | 8.07 | 4.6 | 9.46 | 2.5 | 13.15 | 3.1 | 18.23 | 4.5 | 15.69 | | |
| **435.1112** | $C_{13}H_{19}N_{6}O_{11}$ | 3:5 | 12 | | 8 | 5 | 5 | 5.3 | 10.99 | 5.5 | 5.24 | 6.2 | 14.43 | 5.3 | 8.00 | 9.7 | 4.09 | | |
| **437.1381** | $C_{12}H_{21}N_{8}O_{10}$ | 4:4 | 10 | | 7 | 3 | 3 | | | | | | | | | | | | |
| **441.1118** | $C_{14}H_{17}N_{8}O_{9}$ | 4:5 | 15 | | 11 | 7 | 7 | | | | | | | | | | | 1.7 | 0.11 |
| **443.1275** | $C_{13}H_{19}N_{10}O_{8}$ | 5:4 | 13 | | 10 | 5 | 5 | | | | | | | | | | | | |
| **445.1656** | $C_{12}H_{21}N_{12}O_{7}$ | 6:3 | 11 | | 9 | 3 | 3 | | | | | | | | | | | | |
| **449.1480** | $C_{11}H_{25}N_{6}O_{13}$ | 3:4 | 6 | | 3 | 0 | 0 | | | | | | | | | | | 4.1 | 4.81 |
| **453.1217** | $C_{13}H_{21}N_{6}O_{12}$ | 3:5 | 11 | | 7 | 4 | 4 | 2.6 | 10.91 | 2.1 | 14.44 | 1.6 | 10.69 | | | | | | |
| **459.1224** | $C_{14}H_{19}N_{8}O_{10}$ | 4:5 | 14 | | 10 | 6 | 6 | | | | | | | 3.8 | 5.48 | 4.5 | 12.66 | | |
| **461.1493** | $C_{13}H_{21}N_{10}O_{9}$ | 5:4 | 12 | | 9 | 4 | 4 | | | | | | | | | | | | |
| **463.1762** | $C_{12}H_{23}N_{12}O_{8}$ | 6:3 | 10 | | 8 | 2 | 2 | | | | | | | | | | | | |
| **465.1231** | $C_{15}H_{17}N_{10}O_{8}$ | 5:5 | 17 | | 13 | 8 | 8 | | | | | | | | | | | 3.5 | -5.20 |
| **467.1500** | $C_{14}H_{19}N_{12}O_{7}$ | 6:4 | 15 | | 12 | 6 | 6 | | | | | | | | | | | | |
| **473.1592** | $C_{12}H_{25}N_{8}O_{12}$ | 4:4 | 8 | | 5 | 1 | 1 | | | | | | | | | | | 11.1 | -9.52 |
| **475.1061** | $C_{15}H_{19}N_{6}O_{12}$ | 3:6 | 15 | | 10 | 7 | 7 | 1.3 | 17.05 | | | | | 2.2 | 9.05 | | | | |
| **477.133** | $C_{14}H_{21}N_{8}O$ | 4:5 | 13 | | 9 | 5 | 5 | | | 4.8 | 13.37 | | | 5.1 | 6.03 | 6.5 | 12.95 | | |

| | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **0** | $_{11}$ | | | | | | | | | | | | | | | | | | |

[a]Urea:glyoxal units affording the molecular formula specified ($MH^+$) after elimination of the corresponding water molecules (4th column); [b]UN = unsaturation number; [c]RN = ring number; [d]ON = oxygen number (not belonging to urea moieties)

**Table S5.4 cont.** Calculated m/z peaks for $[MH]^+$ compositions and their temporal evolution for 1:2 urea-glyoxal oligomers in aqueous samples and solids from acetone

| m/z | $[MH]^+$ | U:G[a] | - $H_2O$ | + $NH_3$ | UN[b] | RN[c] | ON[d] | 1 day | | 5 days | | 10 days | | 20 days | | 40 days | | Solid | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) |
| **479.1599** | $C_{13}H_{23}N_{10}O_{10}$ | 5:4 | 11 | | 8 | 3 | 3 | | | | | | | | | | | | |
| **483.1336** | $C_{15}H_{19}N_{10}O_{9}$ | 5:5 | 16 | | 12 | 7 | 7 | | | | | | | | | | | | |
| **485.1605** | $C_{14}H_{21}N_{12}O_{8}$ | 6:4 | 14 | | 11 | 5 | 5 | | | | | | | | | | | 1.1 | 14.08 |
| **487.1874** | $C_{13}H_{23}N_{14}O_{7}$ | 7:3 | 12 | | 10 | 3 | 3 | | | | | | | | | | | | |
| **489.1429** | $C_{13}H_{25}N_6O_{14}$ | 3:5 | 9 | | 5 | 2 | 2 | | | | | | | | | | | 8.6 | 10.58 |
| **491.1698** | $C_{12}H_{27}N_8O_{13}$ | 4:4 | 7 | | 4 | 0 | 0 | | | | | | | | | | | 19.7 | 4.60 |
| **493.1167** | $C_{15}H_{21}N_6O_{13}$ | 3:6 | 14 | | 9 | 6 | 6 | 5.1 | 10.14 | | | 5.9 | 6.49 | 6.1 | 5.68 | 7.3 | 5.27 | | |
| **495.1435** | $C_{14}H_{23}N8O_{12}$ | 4:5 | 12.00 | | 8 | 4 | 4 | 7.4 | 11.20 | 3.6 | 10.59 | 2.0 | 6.35 | 2.1 | 3.32 | 2.6 | 13.82 | | |
| **499.1173** | $C_{16}H_{19}N_8O_{11}$ | 4:6 | 17 | | 12 | 8 | 8 | | | | | | | | | | | 2.4 | -6.15 |
| **501.1442** | $C_{15}H_{21}N_{10}O_{10}$ | 5:5 | 15 | | 11 | 6 | 6 | | | | | | | | | | | | |
| **503.1711** | $C_{14}H_{23}N_{12}O_{9}$ | 6:4 | 13 | | 10 | 4 | 4 | | | | | | | | | | | 2.4 | 3.77 |
| **507.1534** | $C_{13}H_{27}N_6O_{15}$ | 3:5 | 8 | | 4 | 1 | 1 | | | | | | | | | | | 15.0 | 12.89 |
| **511.1272** | $C_{15}H_{23}N_6O_{14}$ | 3:6 | 13.00 | | 8 | 5 | 5 | 2.2 | 18.83 | 2.1 | 0.83 | 2.4 | 13.16 | 1.5 | -1.13 | 4.4 | 1.22 | | |
| **517.1279** | $C_{16}H_{21}N_8O_{12}$ | 4:6 | 16 | | 11 | 7 | 7 | | | | | | | | | | | | |

| | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **519.1548** | $C_{15}H_{23}N_{10}O_{11}$ | 5:5 | 14 | | 10 | 5 | 5 | | | | | | | | | | | | |
| **521.1817** | $C_{14}H_{25}N_{12}O_{10}$ | 6:4 | 12 | | 9 | 3 | 3 | | | | | | | | | | | | |
| **525.1554** | $C_{16}H_{21}N_{12}O_{9}$ | 6:5 | 17 | | 13 | 7 | 7 | | | | | | | | | | | | |
| **527.1823** | $C_{15}H_{23}N_{14}O_{8}$ | 7:4 | 15 | | 12 | 5 | 5 | | | | | | | | | | | | |
| **535.1385** | $C_{16}H_{23}N_{8}O_{13}$ | 4:6 | 15 | | 10 | 6 | 6 | | | | | 3.8 | 13.75 | 4.7 | 5.15 | 6.0 | 11.51 | | |
| **537.1653** | $C_{15}H_{25}N_{10}O_{12}$ | 5:5 | 13 | | 9 | 4 | 4 | 1.1 | 7.15 | | | | | | | | | | |
| **543.1660** | $C_{16}H_{23}N_{12}O_{10}$ | 6:5 | 16 | | 12 | 6 | 6 | | | | | | | | | | | | |
| **545.1929** | $C_{15}H_{25}N_{14}O_{9}$ | 7:4 | 14 | | 11 | 4 | 4 | | | | | | | | | | | | |
| **549.1752** | $C_{14}H_{29}N_{8}O_{15}$ | 4:5 | 9 | | 5 | 1 | 1 | | | | | | | | | | | 10.1 | -0.66 |
| **553.1490** | $C_{16}H_{25}N_{8}O_{14}$ | 4:6 | 14 | | 9 | 5 | 5 | 4.0 | 13.78 | 3.5 | 5.28 | 3.1 | 14.68 | 2.7 | 3.29 | 4.1 | 3.29 | | |
| **559.1497** | $C_{17}H_{23}N_{10}O_{12}$ | 5:6 | 17 | | 12 | 7 | 7 | | | | | | | | | | | | |
| **561.1766** | $C_{16}H_{25}N_{12}O_{11}$ | 6:5 | 15 | | 11 | 5 | 5 | | | | | | | | | | | 1.8 | -7.89 |
| **563.2035** | $C_{15}H_{27}N_{14}O_{10}$ | 7:4 | 13 | | 10 | 3 | 3 | | | | | | | | | | | | |
| **565.1504** | $C_{18}H_{21}N_{12}O_{10}$ | 6:6 | 20 | | 15 | 9 | 9 | | | | | | | | | | | 8.4 | -2.37 |
| **567.1772** | $C_{17}H_{23}N_{14}O_{9}$ | 7:5 | | | -4 | -11 | -11 | | | | | | | | | | | | |
| **577.1603** | $C_{17}H_{25}N_{10}O_{13}$ | 5:6 | 16 | | 11 | 6 | 6 | | | | | | | | | | | | |

[a]Urea:glyoxal units affording the molecular formula specified ($MH^+$) after elimination of the corresponding water molecules (4erth column); [b]UN = unsaturation number; [c]RN = ring number; [d]ON = oxygen number (not belonging to urea moieties)

**Table S5.4 cont.** Calculated m/z peaks for $[MH]^+$ compositions and their temporal evolution for 1:2 urea-glyoxal oligomers in aqueous samples and solids from acetone

| m/z | [MH]+ | U:G[a] | -$H_2O$ | +$NH_3$ | UN[b] | RN[c] | ON[d] | 1 day | | 5 days | | 10 days | | 20 days | | 40 days | | Solid | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) |
| **579.1871** | $C_{16}H_{27}N_{12}O_{12}$ | 6:5 | 14 | | 10 | 4 | 4 | | | | | | | | | | | 2.3 | 7.66 |
| **585.1878** | $C_{17}H_{25}N_{14}O_{10}$ | 7:5 | 17 | | 13 | 6 | 6 | | | | | | | | | | | | |
| **587.2147** | $C_{16}H_{27}N_{16}O_{9}$ | 8:4 | 15 | | 12 | 4 | 4 | | | | | | | | | | | | |
| **593.1439** | $C_{18}H_{25}N_{8}O_{15}$ | 4:7 | 17 | | 11 | 7 | 7 | 1.5 | 14.90 | 1.5 | 16.08 | 1.7 | 7.65 | | | | | | |
| **595.1708** | $C_{17}H_{27}N_{10}O_{14}$ | 5:6 | 15 | | 10 | 5 | 5 | | | | | | | | | | | | |
| **601.1715** | $C_{18}H_{25}N_{12}O_{12}$ | 6:6 | 18 | | 13 | 7 | 7 | | | | | | | | | | | | |
| **603.1984** | $C_{17}H_{27}N_{14}O_{11}$ | 7:5 | 16 | | 12 | 5 | 5 | | | | | | | | | | | 1.2 | -5.85 |
| **607.1807** | $C_{16}H_{31}N_{8}O_{17}$ | 4:6 | 11 | | 6 | 2 | 2 | | | | | | | | | | | 3.7 | -7.71 |
| **611.1545** | $C_{18}H_{27}N_{8}O_{16}$ | 4:7 | 16 | | 10 | 6 | 6 | 3.0 | 14.07 | | | | | 4.8 | 3.60 | 6.0 | -5.23 | | |
| **619.1821** | $C_{18}H_{27}N_{12}O_{13}$ | 6:6 | 17 | | 12 | 6 | 6 | | | | | | | | | | | | |
| **621.2089** | $C_{17}H_{29}N_{14}O_{12}$ | 7:5 | 15 | | 11 | 4 | 4 | | | | | | | | | | | | |
| **635.1657** | $C_{19}H_{27}N_{10}O_{15}$ | 5:7 | 18 | | 12 | 7 | 7 | | | | | | | | | | | | |
| **637.1926** | $C_{18}H_{29}N_{12}O_{14}$ | 6:6 | 16 | | 11 | 5 | 5 | | | | | | | | | | | | |
| **641.1664** | $C_{20}H_{25}N_{12}O_{13}$ | 6:7 | 21 | | 15 | 9 | 9 | | | | | | | | | | | | |
| **643.1933** | $C_{19}H_{27}N_{14}O_{12}$ | 7:6 | 19 | | 14 | 7 | 7 | | | | | | | | | | | | |
| **649.2025** | $C_{17}H_{33}N_{10}O_{17}$ | 5:6 | 12 | | 7 | 2 | 2 | | | | | | | | | | | 4.2 | -1.21 |
| **661.2039** | $C_{19}H_{29}N_{14}O_{13}$ | | 18 | | 13 | 6 | 6 | | | | | | | | | | | | |
| **667.2045** | $C_{20}H_{27}N_{16}O_{11}$ | 8:6 | 21 | | 16 | 8 | 8 | | | | | | | | | | | 7.3 | -3.12 |
| **669.1600** | $C_{20}H_{29}N_{8}O_{18}$ | 4:8 | 18 | | 11 | 7 | 7 | | | | | | | 1.8 | 6.25 | 3.7 | 14.77 | | |
| **677.187** | $C_{20}H_{29}N_{12}O$ | 6:7 | 19 | | 13 | 7 | 7 | | | | | | | | | | | | |

| | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **5** | $_{15}$ | | | | | | | | | | | | | | | | | | |
| **679.2144** | $C_{19}H_{31}N_{14}O_{14}$ | 7:6 | 17 | | 12 | 5 | 5 | | | | | | | | | | | 1.8 | -7.19 |
| **685.2151** | $C_{20}H_{29}N_{16}O_{12}$ | 8:6 | 20 | | 15 | 7 | 7 | | | | | | | | | | | | |
| **695.1981** | $C_{20}H_{31}N_{12}O_{16}$ | 6:7 | 18 | | 12 | 6 | 6 | | | | | | | | | | | | |
| **701.1988** | $C_{21}H_{29}N_{14}O_{14}$ | 7:7 | 21 | | 15 | 8 | 8 | | | | | | | | | | | | |
| **711.1818** | $C_{21}H_{31}N_{10}O_{18}$ | 5:8 | 19 | | 12 | 7 | 7 | | | | | | | | | 1.0 | -5.23 | | |
| **719.2093** | $C_{21}H_{31}N_{14}O_{15}$ | 7:7 | 20 | | 14 | 7 | 7 | | | | | | | | | | | | |
| **721.2362** | $C_{20}H_{33}N_{16}O_{14}$ | 8:6 | 18 | | 13 | 5 | 5 | | | | | | | | | | | | |
| **737.2199** | $C_{21}H_{33}N_{14}O_{16}$ | 7:7 | 19 | | 13 | 6 | 6 | | | | | | | | | | | | |
| **787.2692** | $C_{22}H_{35}N_{20}O_{13}$ | 10:6 | 21 | | 16 | 6 | 6 | | | | | | | | | | | | |
| **795.2254** | $C_{23}H_{35}N_{14}O_{18}$ | 7:8 | 21 | | 14 | 7 | 7 | | | | | | | | | | | | |

[a]Urea:glyoxal units affording the molecular formula specified ($MH^+$) after elimination of the corresponding water molecules (4th column); [b]UN = unsaturation number; [c]RN = ring number; [d]ON = oxygen number (not belonging to urea moieties)

**Table S5.4 cont.** Calculated m/z peaks for $[MH]^+$ compositions and their temporal evolution for 1:2 urea-glyoxal oligomers in aqueous samples and solids from acetone

| m/z | $[MH]^+$ | U:G[a] | $-H_2O$ | $+NH_3$ | UN[b] | RN[c] | ON[d] | 1 day | | 5 days | | 10 days | | 20 days | | 40 days | | Solid | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) | Intensity (%) | Error (ppm) |
| **837.2472** | $C_{24}H_{37}N_{16}O_{18}$ | 8:8 | 22 | | 15 | 7 | 7 | | | | | | | | | | | 4.1 | 10.48 |
| **855.2577** | $C_{24}H_{39}N_{16}O_{19}$ | 8:8 | 21 | | 14 | 6 | 6 | | | | | | | | | | | 3.2 | -2.29 |
| **861.2584** | $C_{25}H_{37}N_{18}O_{17}$ | 9:8 | 24 | | 17 | 8 | 8 | | | | | | | | | | | 5.2 | -0.57 |
| **877.2421** | $C_{26}H_{37}N_{16}O_{19}$ | 8:9 | 25 | | 17 | 9 | 9 | | | | | | | | | | | 3.8 | 3.63 |

| | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **879.2690** | $C_{25}H_{39}N_{18}O_{18}$ | 9:8 | 23 | | 16 | 7 | 7 | | | | | | | | | | | 5.6 | 6.79 |
| **897.2795** | $C_{25}H_{41}N_{18}O_{19}$ | 9:8 | 22 | | 15 | 6 | 6 | | | | | | | | | | | 4.7 | 9.29 |
| **919.2639** | $C_{27}H_{39}N_{18}O_{19}$ | 9:9 | 26 | | 18 | 9 | 9 | | | | | | | | | | | 3.9 | 8.58 |
| **937.2745** | $C_{27}H_{41}N_{18}O_{20}$ | 9:9 | 25 | | 17 | 8 | 8 | | | | | | | | | | | 4.5 | 3.36 |
| **955.2850** | $C_{27}H_{43}N_{18}O_{21}$ | 9:9 | 24 | | 16 | 7 | 7 | | | | | | | | | | | 3.9 | 9.96 |
| **961.2857** | $C_{28}H_{41}N_{20}O_{19}$ | 10:9 | 27 | | 19 | 9 | 9 | | | | | | | | | | | 3.6 | 6.43 |
| **1097.3341** | $C_{31}H_{49}N_{22}O_{23}$ | 11:10 | 28 | | 19 | 8 | 8 | | | | | | | | | | | 3.2 | 8.19 |

[a]Urea:glyoxal units affording the molecular formula specified ($MH^+$) after elimination of the corresponding water molecules (4th column); [b]UN = unsaturation number; [c]RN = ring number; [d]ON = oxygen number (not belonging to urea moieties)

## 6. $^{1}H$ and $^{13}C$ NMR DATA AND SPECTRA

**Table S6.1.** $^{13}C$ NMR monitoring of 2:1 urea-glyoxal mixtures in aqueous solution[a,b]

| **$^{13}C$ range (ppm) and tentative assignment** | **1 day** | **3 days** | **10 days** |
|---|---|---|---|
| 169-154<br>N-CO-N | 169.0 (2); 165.4 (14); 165.2 (13); 165.0 (2); 163.0 (3); 162.8 (3); 162.7 (3) | 168.9 (3); 166.3 (3); 165.4 (11); 165.3 (4); 165.2 (14); 165.0 (2); 163.1 (2); 163.0 (5); 162.9 (2); 162.8 (4); 162.7 (7); 162.7 (3) | 168.8 (5); 166.3 (6); 165.8 (5); 165.4 (10); 165.3 (8); 165.3 (8); 165.2 (18); 165.1 (5); 165.0 (3); 163.0 (5); 162.7 (10); 162.7 (9); 162.1 (3); 162.0 (3); 160.2 (3) |
| 108-91<br>O-CHR-O | 107.0 (3); 101.8 (3); 101.2 (3); 93.2 (30); 92.5 (3); 92,0 (2); 92.0 (9); 91.6 (7); 91.4 (1) | 96.0 (3); 93.2 (4); 92.0 (6); 91.6 (4) | 96,0 (8); 93.2 (3); 91.9 (5); 90.7 (2) |
| 91-75<br>O-CHR-N | 87.9 (5); 87.7 (2); 86.3 (7); 86.1 (100); 85.2 (6); 84.4 (3); 84.2 (3); 84.1 (6); 84.0 (6); 84.0 (2); 80.7 (2); 80.3 (6); 80.0 (11); 79.9 (10); 79.6 (1); 79.6 (2); 79.3 (2); 79.1 (3); 79.0 (2); 78.8 (2); 78.3 (2) | 89.2 (2); 88.0 (3); 87.9 (4); 87.8 (2); 87.7 (2); 86.3 (5); 86.1 (100); 85.2 (10); 84.4 (4); 84.3 (3); 84.1 (5); 84.0 (5); 80.4 (3); 80.3 (4); 80.0 (11); 79.9 (8); 79.6 (2); 79.3 (2); 79.1 (5); 79.0 (2); 78.0 (2); 78.8 (2); 78.3 (3) | 89.2 (6); 88.0 (6); 88.0 (3); 86.7 (3); 86.4 (5); 86.3 (5); 86.7 (100); 85.2 (16); 84.3 (7); 84.2 (9); 84.0 (5); 83.7 (3); 80.5 (3); 80.4 (8); 80.3 (3); 80.0 (12); 79.1 (7) |
| 75-62<br>N-CHR-N | 70.4 (4); 65.3[c] (16); 65.0 (2) | 73.0 (2); 71.7 (2); 71.6 (2); 70.4 (7); 69.0 (3); 68.9 (3); 68.6 (5); 65.3[c] (20); 65.0 (3) | 73.0 (5); 71.8 (2); 71.7 (4); 71.6 (3); 70.4 (13); 69.0 (11); 68.6 (8); 65.3[c] (28); 65.0 (6) |

[a]Numbers in parentheses indicate relative intensities. [b]Underlined signals correspond to those of glyoxal itself or its oligomers, as well as urea (165.4 ppm). [c]The secondary carbon at 65.3 ppm is attributed to the $CH_2OH$ group, also detected in aqueous glyoxal solutions.

**Table S6.2.** $^{13}C$ NMR monitoring of 1:1 urea-glyoxal mixtures in aqueous solution[a,b]

| **$^{13}C$ range (ppm) and tentative assignment** | **1 day** | **3 days** | **10 days** |
|---|---|---|---|
| 169-154<br>N-CO-N | 169.0 (2); 165.4 (14); 165.2 (13); 165.0 (2); 163.0 (3); 162.8 (3); 162.7 (3) | 168.9 (3); 166.3 (3); 165.4 (11); 165.3 (4); 165.2 (14); 165.0 (2); 163.1 (2); 163.0 (5); 162.9 (2); 162.8 (4); 162.7 (7); 162.7 (3) | 168.8 (5); 166.3 (6); 165.8 (5); 165.4 (10); 165.3 (8); 165.3 (8); 165.2 (18); 165.1 (5); 165.0 (3); 163.0 (5); 162.7 (10); 162.7 (9); 162.1 (3); 162.0 (3); 160.2 (3) |
| 108-91<br>O-CHR-O | 107.0 (3); 101.8 (3); 101.2 (3); 93.2 (30); 92.5 (3); 92,0 (2); 92.0 (9); 91.6 (7); 91.4 (1) | 96.0 (3); 93.2 (4); 92.0 (6); 91.6 (4) | 96,0 (8); 93.2 (3); 91.9 (5); 90.7 (2) |
| 91-75<br>O-CHR-N | 87.9 (5); 87.7 (2); 86.3 (7); 86.1 (100); 85.2 (6); 84.4 (3); 84.2 (3); 84.1 (6); 84.0 (6); 84.0 (2); 80.7 (2); 80.3 (6); 80.0 (11); 79.9 (10); 79.6 (1); 79.6 (2); 79.3 (2); 79.1 (3); 79.0 (2); 78.8 (2); 78.3 (2) | 89.2 (2); 88.0 (3); 87.9 (4); 87.8 (2); 87.7 (2); 86.3 (5); 86.1 (100); 85.2 (10); 84.4 (4); 84.3 (3); 84.1 (5); 84.0 (5); 80.4 (3); 80.3 (4); 80.0 (11); 79.9 (8); 79.6 (2); 79.3 (2); 79.1 (5); 79.0 (2); 78.0 (2); 78.8 (2); 78.3 (3) | 89.2 (6); 88.0 (6); 88.0 (3); 86.7 (3); 86.4 (5); 86.3 (5); 86.7 (100); 85.2 (16); 84.3 (7); 84.2 (9); 84.0 (5); 83.7 (3); 80.5 (3); 80.4 (8); 80.3 (3); 80.0 (12); 79.1 (7) |
| 75-62<br>N-CHR-N | 70.4 (4); 65.3[c] (16); 65.0 (2) | 73.0 (2); 71.7 (2); 71.6 (2); 70.4 (7); 69.0 (3); 68.9 (3); 68.6 (5); 65.3[c] (20); 65.0 (3) | 73.0 (5); 71.8 (2); 71.7 (4); 71.6 (3); 70.4 (13); 69.0 (11); 68.6 (8); 65.3[c] (28); 65.0 (6) |

[a]Numbers in parentheses indicate relative intensities. [b]Underlined signals correspond to those of glyoxal itself or its oligomers, as well as urea (165.4 ppm). [c]The secondary carbon at 65.3 ppm is attributed to the $CH_2OH$ group, also detected in aqueous glyoxal solutions.

**Table S6.3.** $^{13}C$ NMR monitoring of 1:2 urea-glyoxal mixtures in aqueous solution[a,b]

| **$^{13}C$ range (ppm) and tentative assignment** | **1 day** | **6 days** | **14 days** |
|---|---|---|---|
| 169-154<br>N-CO-N | 168.8 (1); 165.4 (4); 165.0 (1); 163.0 (3); 162.9 (2) | 168.8 (2); 165.6 (1); 165.4 (3); 163.0 (4); 162.9 (2); 162.6 (1); 160.9 (1); 160.9 (1) | 168.8 (3); 165.6 (2); 165.4 (3); 163.0 (6); 160.9 (2); 160.9 (2) |
| 108-91<br>O-CHR-O | 107.1 (10); 103.0 (1); 102.6 (1); 102.5 (1); 101.8 (9); 101.2 (9); 99.5 (1); 99.5 (1); 96.9 (3); 96.5 (1); 95.2 (2); 94.9 (2); 93.2 (100); 92.5 (11); 92.0 (1); 91.9 (7); 91.6 (5); 91.5 (2); 91.4 (1); 90.7 (1) | 107.6 (1); 107.1 (5); 103.0 (1); 102.6 (2); 102.5 (3); 101.8 (5); 101.2 (5); 99.5 (1); 99.5 (1); 97.5 (1); 96.9 (2); 96.5 (1); 96.0 (1); 95.1 (2); 94.9 (1); 93.2 (100); 92.5 (1); 92.5 (6); 92.4 (1); 92.0 (2); 91.9 (14); 91.9 (4); 91.9 (5); 91.6 (9); 91.5 (3); 91.4 (2); 90.7 (1) | 107.6 (1); 107.1 (5); 102.5 (4); 101.8 (4); 101.2 (4); 99.5 (2); 97.6 (1); 96.9 (2); 95.1 (3); 93.2 (100); 92.5 (6); 92.4 (2); 92.0 (3); 91.9 (15); 91.9 (5); 91.9 (7); 91.5 (9); 91.5 (5); 91.3 (2); 90.7 (1), 90.6 (4). |
| 91-75<br>O-CHR-N | 89.3 (1); 88.0 (1); 87.9 (4); 86.3 (7); 86.1 (30); 84.7 (1); 84.6 (1); 84.1 (4); 84.1 (5); 80.7 (2); 80.5 (1); 80.4 (1); 80.3 (5); 80.2 (1); 80.0 (5); 80.0 (7) | 89.5 (1); 89.4 (1); 89.3 (2); 88.0 (3); 87.9 (7); 86.4 (2); 86.3 (13); 86.1 (20); 84.7 (3); 84.6 (4); 84.1 (6); 84.0 (8); 83.2 (2); 81.8 (1); 80.7 (3); 80.7 (4); 80.5 (4); 80.4 (3); 80.4 (2); 80.3 (9); 80.2 (2); 80.0 (13) | 89.3 (2); 88.4 (2); 88.3 (2); 88.0 (6); 87.9 (8); 86.4 (4); 86.3 (15); 86.1 (20); 84.7 (5); 84.6 (6); 84.1 (9); 84.1 (10); 80.7 (4); 80.7 (4); 80.6 (2); 80.5 (6); 80.4 (4); 80.3 (9); 80.2 (2); 80.0 (4); 79.9 (13) |
| 75-62<br>N-CHR-N | 65.3[c] (6); 64.7[d] (2); 63.9[d] (1); 63.4[d] (1) | 65.3[c] (9); 64.6[d] (2); 63.4[d] (1) | 65.3[c] (11); 64.7[d] (2) |

[a]Numbers in parentheses indicate relative intensities. [b]Underlined signals correspond to those of glyoxal itself or its oligomers, as well as urea (165.4 ppm). [c]The secondary carbon at 65.3 ppm is attributed to the $CH_2OH$ group, also detected in aqueous glyoxal solutions. [d]Secondary carbon atoms (as inferred from DEPT spectra).

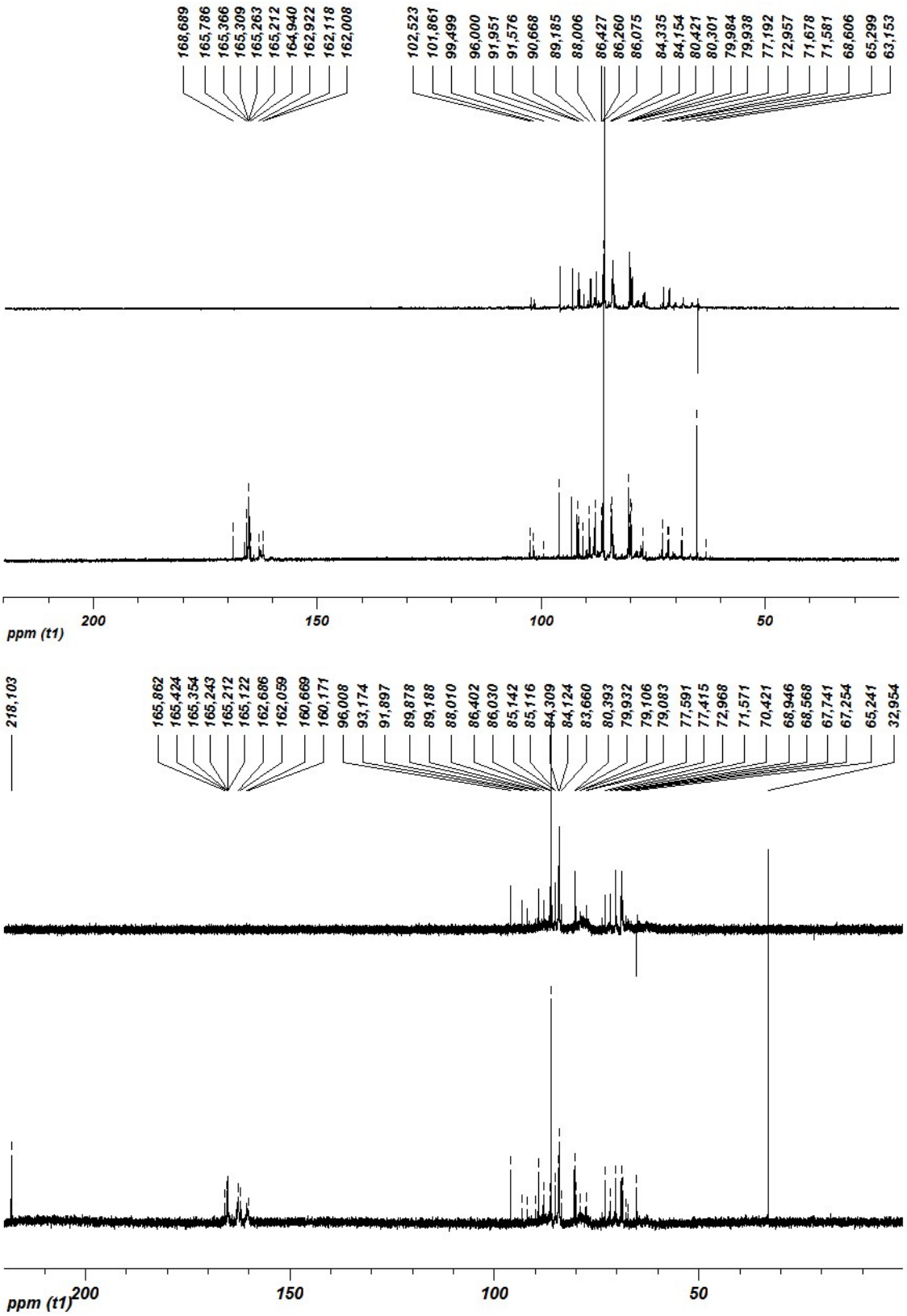


**Figure S6.1.** Decoupled $^{13}C$ NMR and DEPT spectra of aqueous 1:1 urea:glyoxal mixture after 20 days at room temperature (above) and oligomers isolated from acetone (below), both recorded in $D_2O$ solution.

## UREA-GLYOXAL OLIGOMERIZATION CARRRIED OUT IN $D_2O$ SOLUTION

### 2:1 STOICHIOMETRY

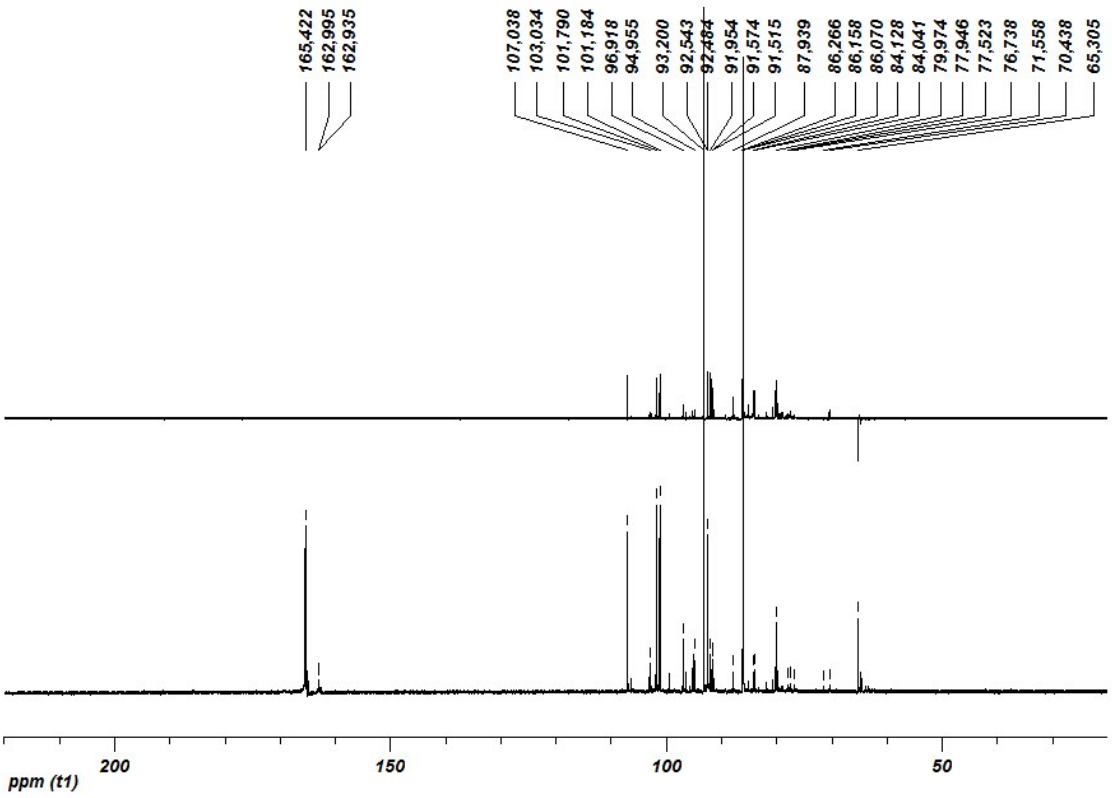


**Figure S6.2.** $^{13}C$ NMR spectra (top: DEPT) of the 2:1 reaction mixture recorded in $D_2O$ (after 2 h).

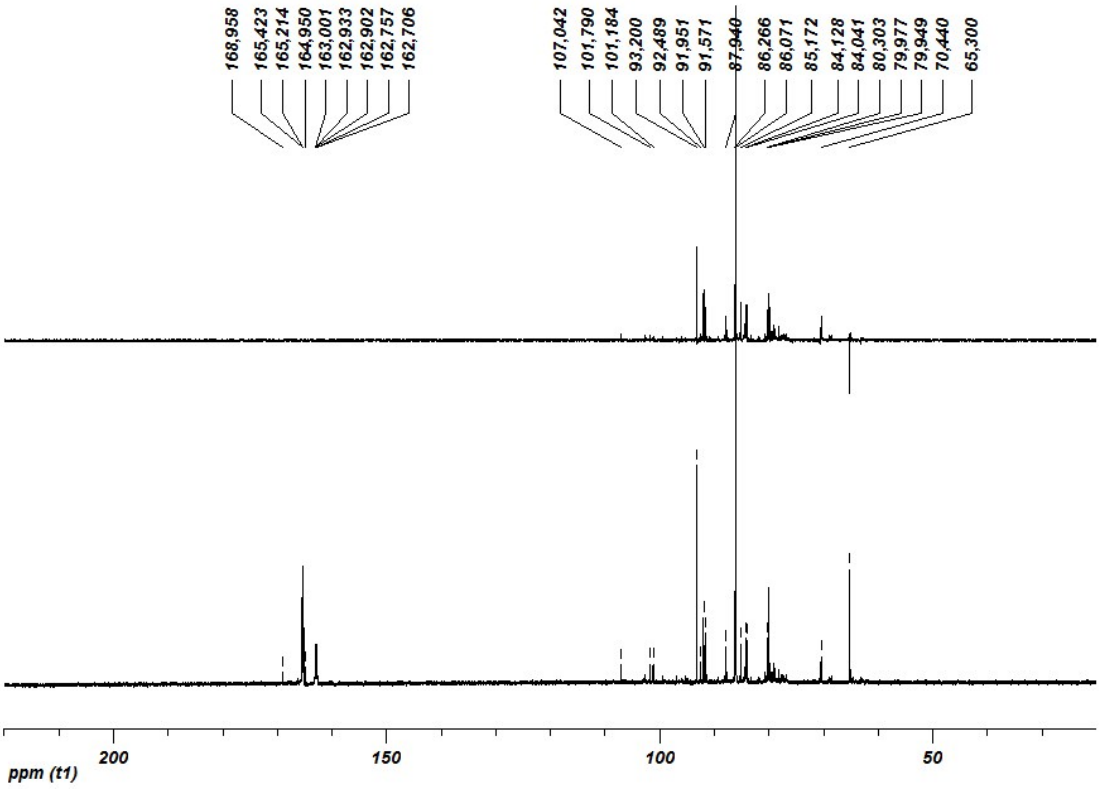


**Figure S6.3.** $^{13}C$ NMR spectra (top: DEPT) of the 2:1 reaction mixture recorded in $D_2O$ (after 1 d).

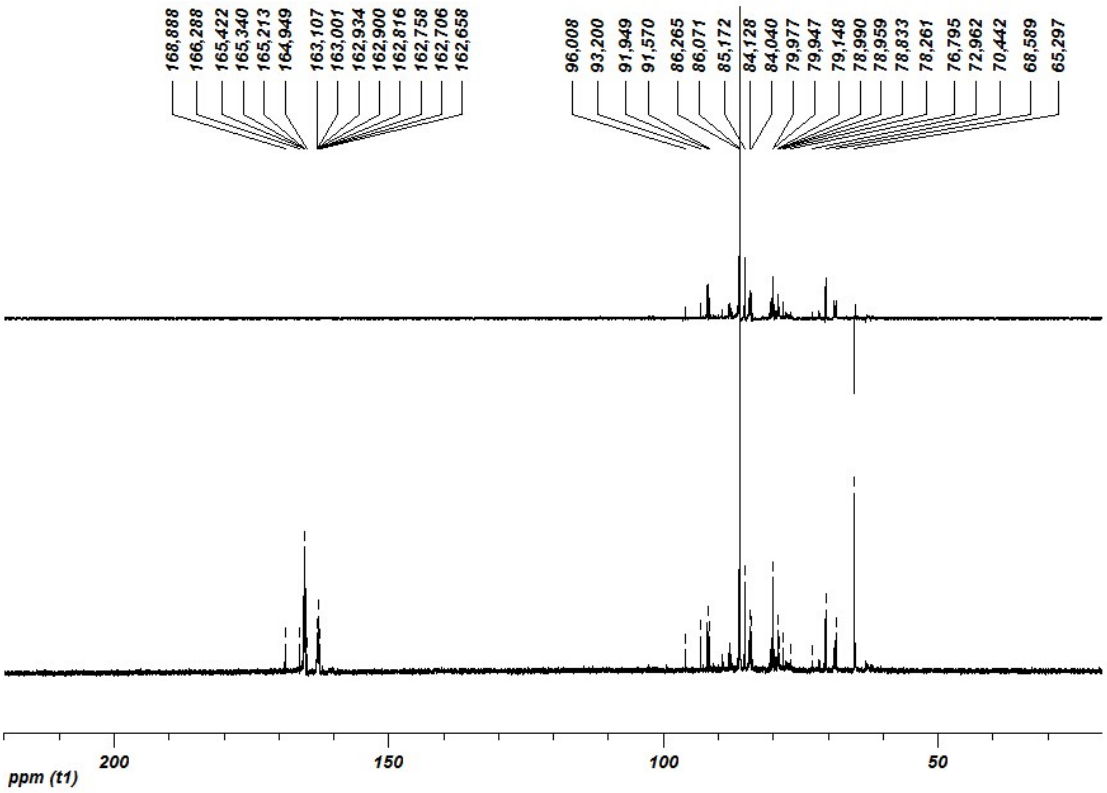


**Figure S6.4.** $^{13}C$ NMR spectra (top: DEPT) of the 2:1 reaction mixture recorded in $D_2O$ (after 3 d).

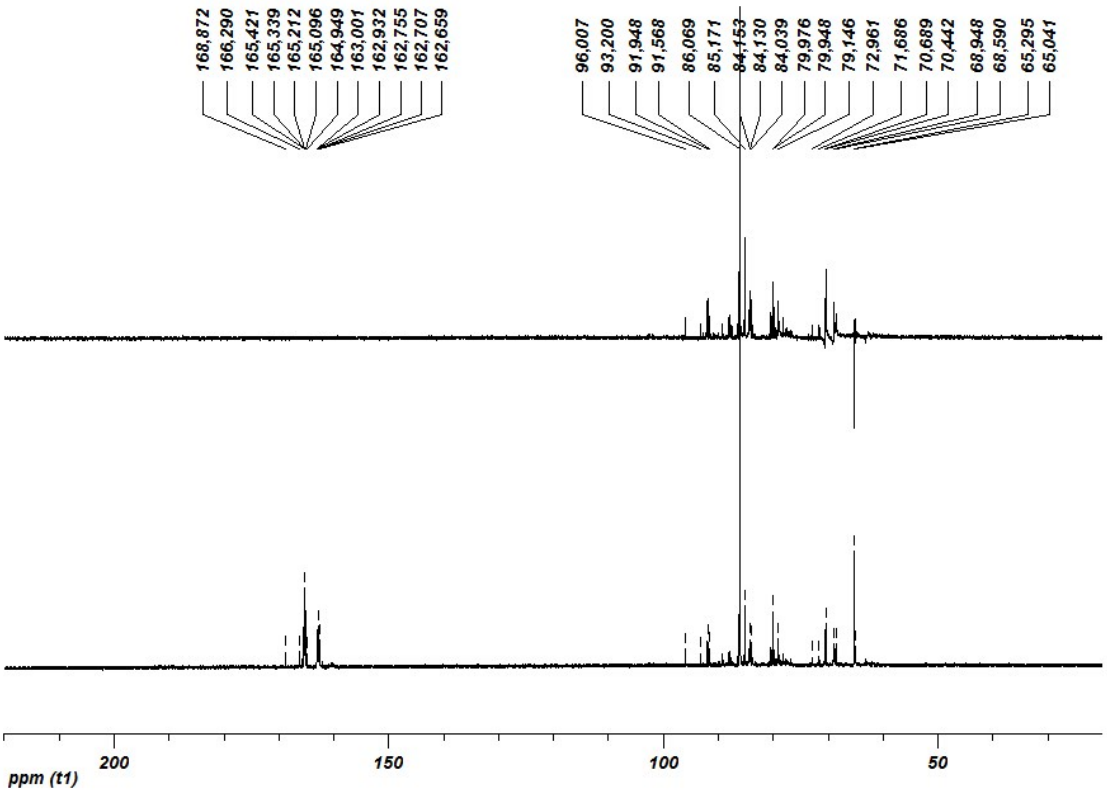


**Figure S6.5.** $^{13}C$ NMR spectra (top: DEPT) of the 2:1 reaction mixture recorded in $D_2O$ (after 4 d).

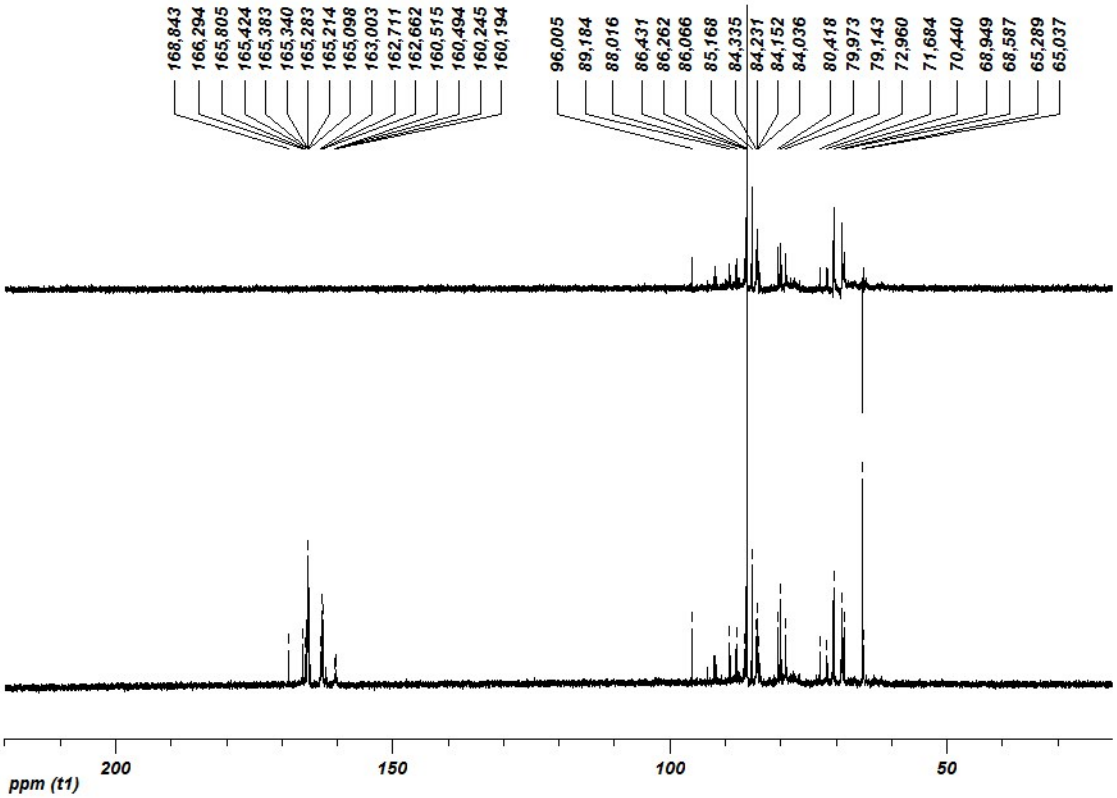


**Figure S6.6.** $^{13}C$ NMR spectra (top: DEPT) of the 2:1 reaction mixture recorded in $D_2O$ (after 10 d).

**Table S6.4.** $^{13}C$ NMR monitoring of 2:1 urea-glyoxal mixtures in aqueous solution.[a, b]

| $^{13}C$ NMR range | 2 h | | 1 day | | 3 days | | 4 days | | 10 days | |
|---|---|---|---|---|---|---|---|---|---|---|
| | ppm | I (%) | Ppm | I (%) | ppm | I (%) | ppm | I (%) | Ppm | I (%) |
| 168-154 | | | **169.0** | 1.7 | **168.9** | 3.4 | **168.9** | 3.3 | **168.8** | 5.1 |
| | **165.4** | 22.4 | **165.4** | 14.1 | **166.3** | 3.4 | **166.3** | 3.4 | **166.3** | 5.9 |
| | **165.2** | 5.7 | **165.2** | 12.9 | **165.4** | 11.0 | **165.8** | 2.1 | **165.8** | 4.6 |
| | **164.9** | 1.7 | **164.9** | 2.4 | **165.3** | 4.2 | **165.4** | 11.2 | **165.4** | 10.2 |
| | | | **163.0** | 3.1 | **165.2** | 14.3 | **165.3** | 5.0 | **165.3** | 7.8 |
| | | | **162.9** | 3.5 | **164.9** | 2.3 | **165.2** | 15.7 | **165.3** | 8.0 |
| | | | **162.8** | 2.5 | **163.1** | 2.2 | **165.1** | 2.0 | **165.2** | 17.5 |
| | | | **162.7** | 3.4 | **163.0** | 4.5 | **164.9** | 2.4 | **165.1** | 5.3 |
| | | | | | **162.9** | 2.9 | **163.1** | 2.2 | **165.0** | 3.2 |
| | | | | | **162.9** | 2.0 | **163.0** | 4.7 | **163.0** | 4.9 |
| | | | | | **162.8** | 4.0 | **162.9** | 2.6 | **162.7** | 10.3 |
| | | | | | **162.7** | 6.6 | **162.8** | 4.2 | **162.7** | 9.1 |
| | | | | | **162.7** | 3.3 | **162.7** | 8.2 | **162.1** | 2.7 |
| | | | | | | | **162.7** | 5.1 | **162.0** | 3.0 |
| | | | | | | | | | **160.2** | 2.6 |
| 108 - 91 | **107.0** | 21.7 | **107.0** | 2.8 | **96.0** | 2.8 | **96.0** | 3.8 | **96.0** | 8.0 |
| | **106.8** | 1.3 | **101.8** | 2.8 | **93.2** | 4.3 | **93.2** | 3.0 | **93.2** | 3.0 |
| | **106.8** | 1.2 | **101.2** | 2.8 | **91.9** | 5.9 | **91.9** | 5.7 | **91.9** | 4.5 |
| | **106.4** | 1.8 | **93.2** | 29.9 | **91.6** | 4.2 | **91.6** | 4.0 | **90.7** | 1.9 |
| | **106.3** | 2.0 | **92.5** | 3.1 | | | | | | |
| | **103.2** | 1.5 | **92.0** | 2.0 | | | | | | |
| | **103.0** | 4.0 | **92.0** | 9.1 | | | | | | |
| | **102.0** | 2.5 | **91.6** | 7.0 | | | | | | |
| | **101.8** | 3.5 | **91.4** | 1.4 | | | | | | |
| | **101.8** | 25.2 | | | | | | | | |
| | **101.3** | 2.8 | | | | | | | | |
| | **101.2** | 25.5 | | | | | | | | |
| | **99.5** | 2.7 | | | | | | | | |
| | **99.5** | 1.2 | | | | | | | | |
| | **96.9** | 7.2 | | | | | | | | |
| | **96.5** | 2.9 | | | | | | | | |
| | **95.7** | 0.9 | | | | | | | | |
| | **95.7** | 1.1 | | | | | | | | |
| | **95.2** | 3.4 | | | | | | | | |
| | **95.0** | 1.0 | | | | | | | | |
| | **95.0** | 5.2 | | | | | | | | |
| | **94.9** | 1.0 | | | | | | | | |
| | **93.3** | 2.2 | | | | | | | | |
| | **93.2** | 100.0 | | | | | | | | |
| | **92.5** | **5.5** | | | | | | | | |

[a] Peaks assigned to glyoxal are highlighted in green. [b] The secondary carbon at 65.3 ppm is attributed to the $CH_2OH$ group, also detected in aqueous glyoxal solutions.

**Table S6.4 cont.** $^{13}C$ NMR monitoring of 2:1 urea-glyoxal mixtures in aqueous solution.[a,b]

| $^{13}C$ NMR range | 2 h | | 1 day | | 3 days | | 4 days | | 10 days | |
|---|---|---|---|---|---|---|---|---|---|---|
| | ppm | I (%) | ppm | I (%) | ppm | I (%) | ppm | I (%) | ppm | I (%) |
| 108 - 91 | **92.5** | 21.2 | | | | | | | | |
| | **92.0** | 2.3 | | | | | | | | |
| | **92.0** | 5.2 | | | | | | | | |
| | **91.6** | 4.1 | | | | | | | | |
| | **91.5** | 4.6 | | | | | | | | |
| | **91.4** | 2.1 | | | | | | | | |
| 91 - 75 | **87.9** | 2.9 | **87.9** | 5.2 | **89.2** | 2.2 | **89.2** | 3.0 | **89.2** | 6.1 |
| | **86.3** | 3.5 | **87.7** | 1.8 | **88.0** | 2.7 | **88.0** | 3.5 | **88.0** | 6.0 |
| | **86.2** | 6.6 | **86.3** | 7.2 | **87.9** | 3.5 | **87.9** | 3.2 | **87.9** | 3.3 |
| | **86.1** | 50.2 | **86.1** | 100.0 | **87.8** | 1.9 | **87.8** | 2.1 | **86.6** | 2.8 |
| | **85.2** | 1.6 | **85.2** | 5.6 | **87.7** | 2.2 | **87.7** | 2.2 | **86.4** | 5.2 |
| | **84.2** | 1.0 | **84.4** | 2.5 | **86.3** | 5.2 | **87.6** | 2.0 | **86.3** | 5.4 |
| | **84.1** | 3.0 | **84.2** | 3.0 | **86.1** | 100.0 | **86.4** | 3.4 | **86.1** | 100.0 |
| | **84.0** | 3.2 | **84.1** | 6.3 | **85.2** | 10.4 | **86.3** | 6.6 | **85.2** | 16.3 |
| | **81.8** | 1.5 | **84.0** | 6.1 | **84.4** | 3.8 | **86.1** | 100.0 | **84.3** | 7.0 |
| | **80.7** | 1.9 | **84.0** | 2.1 | **84.2** | 3.1 | **85.2** | 12.0 | **84.2** | 9.3 |
| | **80.4** | 1.9 | **80.7** | 1.8 | **84.1** | 5.4 | **84.4** | 3.6 | **84.0** | 4.8 |
| | **80.3** | 3.6 | **80.3** | 6.4 | **84.0** | 4.7 | **84.3** | 3.1 | **83.7** | 3.4 |
| | **80.1** | 1.6 | **80.0** | 11.1 | **80.4** | 2.9 | **84.2** | 3.3 | **80.5** | 2.8 |
| | **80.0** | 9.5 | **79.9** | 10.3 | **80.3** | 4.1 | **84.2** | 5.6 | **80.4** | 8.1 |
| | | | **79.6** | 1.4 | **80.0** | 10.9 | **84.0** | 4.6 | **80.3** | 3.3 |
| | | | **79.6** | 1.7 | **79.9** | 7.6 | **83.7** | 1.6 | **80.0** | 11.8 |
| | | | **79.3** | 1.8 | **79.6** | 1.9 | **80.4** | 4.3 | **79.1** | 7.2 |
| | | | **79.1** | 3.0 | **79.3** | 2.0 | **80.3** | 3.7 | | |
| | | | **79.0** | 2.3 | **79.1** | 5.0 | **80.0** | 11.1 | | |
| | | | **78.8** | 2.3 | **79.0** | 2.4 | **79.6** | 1.7 | | |
| | | | **78.3** | 2.0 | **79.0** | 2.2 | **79.3** | 1.9 | | |
| | | | | | **78.8** | 2.3 | **79.1** | 5.7 | | |
| | | | | | **78.3** | 2.9 | **79.0** | 2.1 | | |
| | | | | | | | **78.8** | 2.4 | | |
| | | | | | | | **78.3** | 2.7 | | |
| 75 - 62 | **70.4** | 1.2 | **70.4** | 3.9 | **73.0** | 1.5 | **73.0** | 2.0 | **73.0** | 4.8 |
| | **65.3**[a] | 10.2 | **65.3**[a] | 15.8 | **71.7** | 1.6 | **71.7** | 2.2 | **71.8** | 2.1 |
| | **64.7*** | 2.9 | **65.0** | 2.1 | **71.6** | 1.5 | **71.6** | 1.5 | **71.7** | 4.4 |
| | | | | | **70.4** | 7.2 | **70.4** | 8.6 | **71.6** | 3.4 |
| | | | | | **69.0** | 3.0 | **69.0** | 4.7 | **70.4** | 13.3 |
| | | | | | **68.9** | 3.0 | **68.6** | 4.5 | **68.9** | 10.6 |
| | | | | | **68.6** | 4.7 | **65.3**[a] | 22.9 | **68.6** | 8.0 |
| | | | | | **65.3**[a] | 20.3 | **65.0** | 4.1 | **65.3**[a] | 27.6 |
| | | | | | **65.0** | 3.5 | | | **65.0** | 5.7 |

[a] Peaks assigned to glyoxal are highlighted in green. [b] The secondary carbon at 65.3 ppm is attributed to the $CH_2OH$ group, also detected in aqueous glyoxal solutions.

**1:1 STOICHIOMETRY**

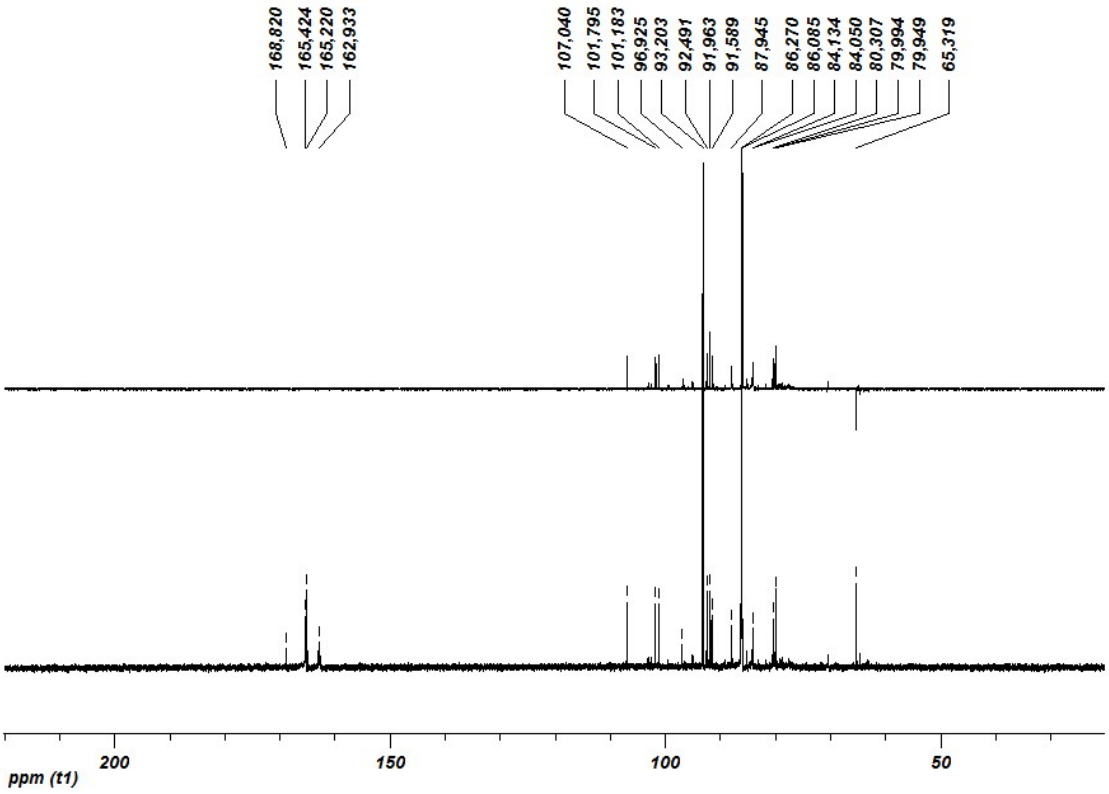


**Figure S6.7.** $^{13}C$ NMR spectra (top: DEPT) of the 1:1 reaction mixture recorded in $D_2O$ (after 2 h).

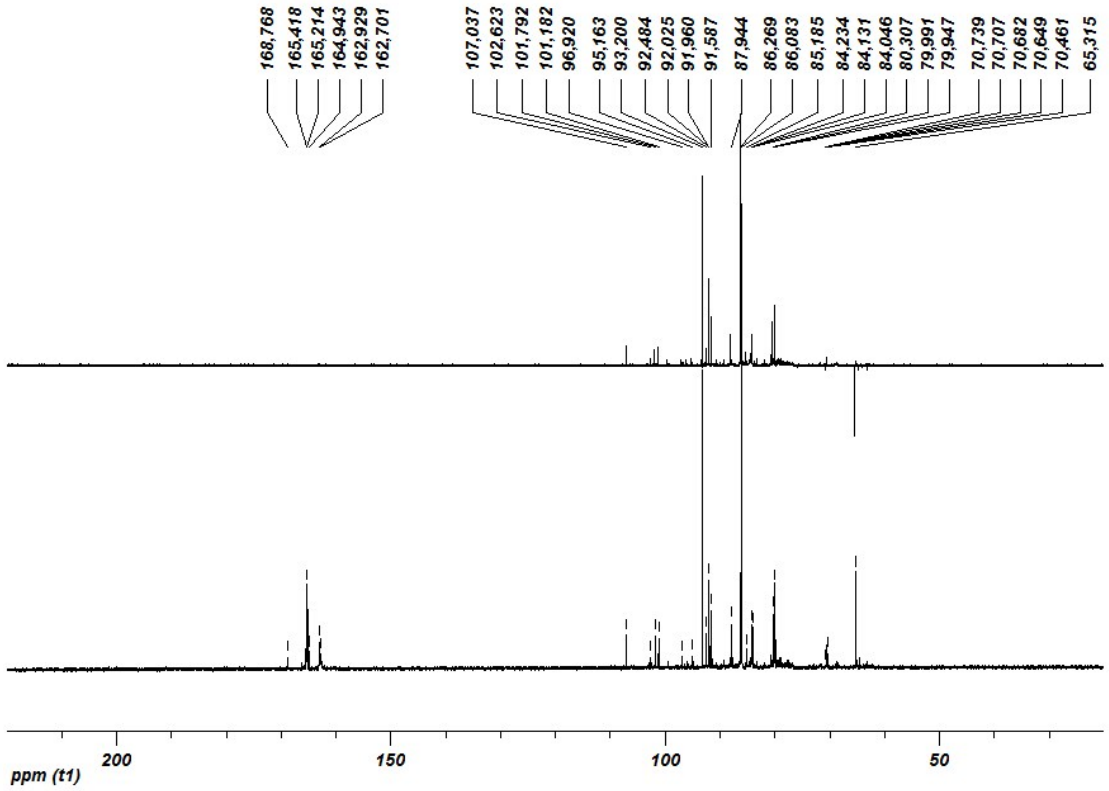


**Figure S6.8.** $^{13}C$ NMR spectra (top: DEPT) of the 1:1 reaction mixture recorded in $D_2O$ (after 1 d).

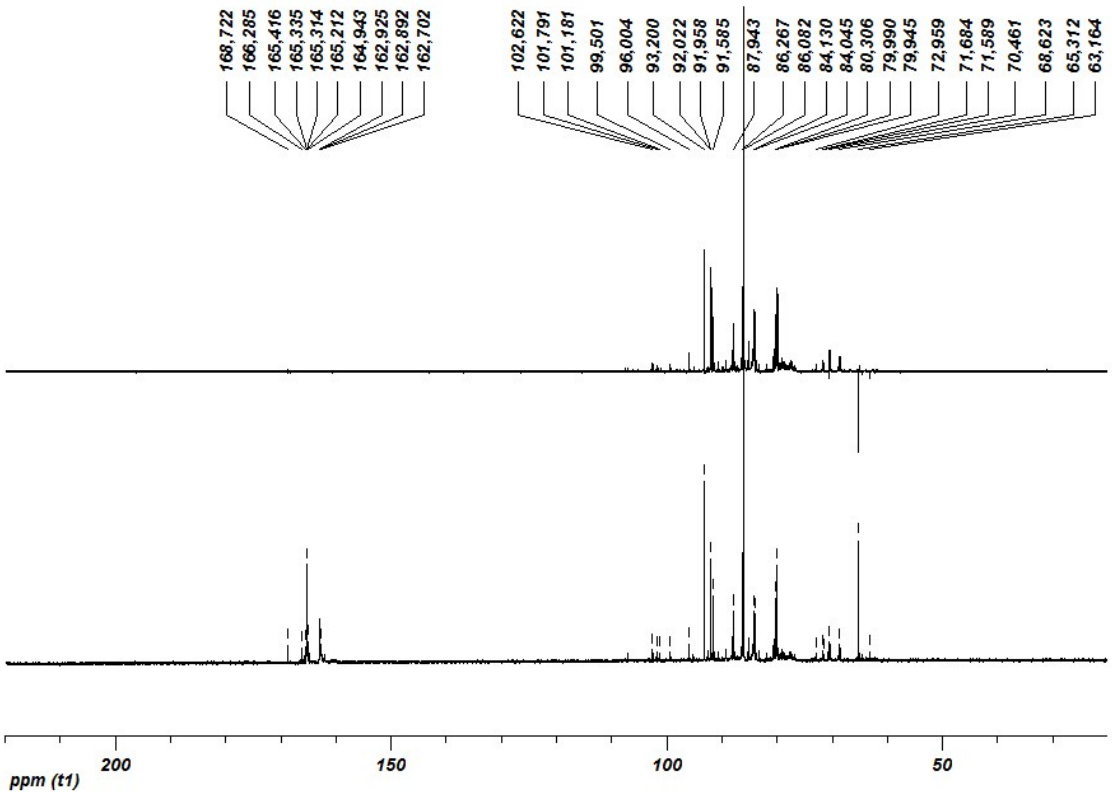


**Figure S6.9.** $^{13}C$ NMR spectra (top: DEPT) of the 1:1 reaction mixture recorded in $D_2O$ (after 2 d).

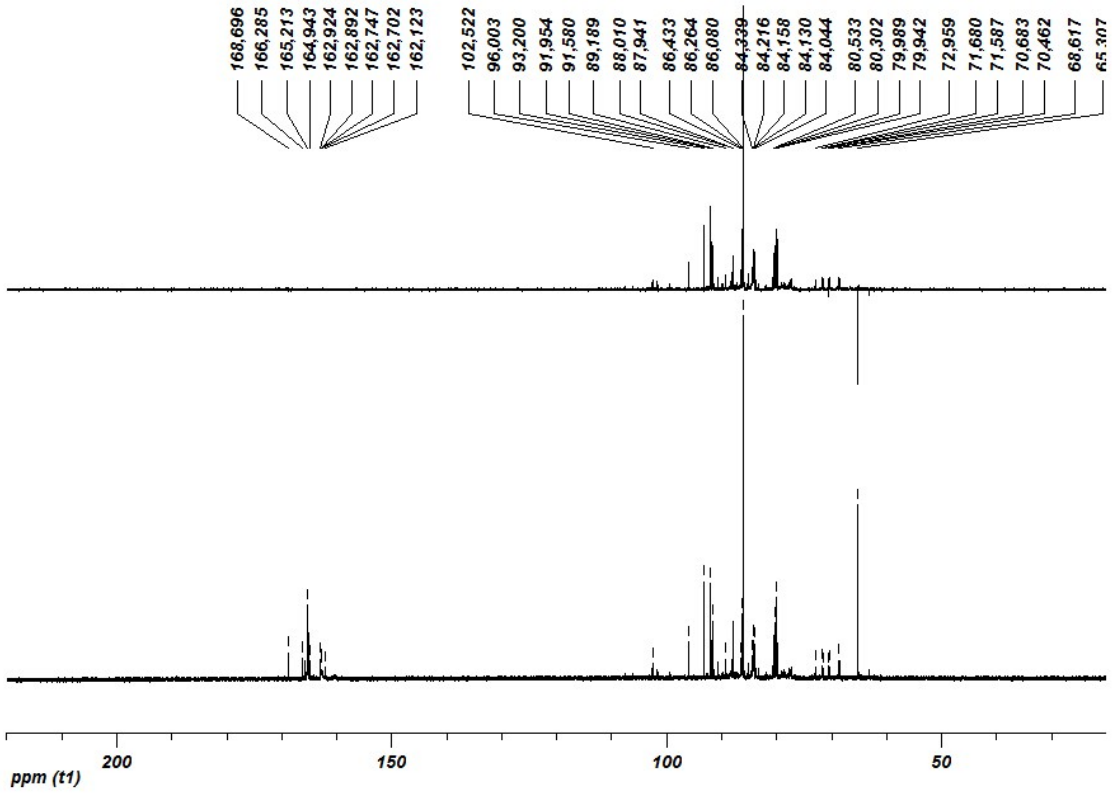


**Figure S6.10.** $^{13}C$ NMR spectra (top: DEPT) of the 1:1 reaction mixture recorded in $D_2O$ (after 5 d).

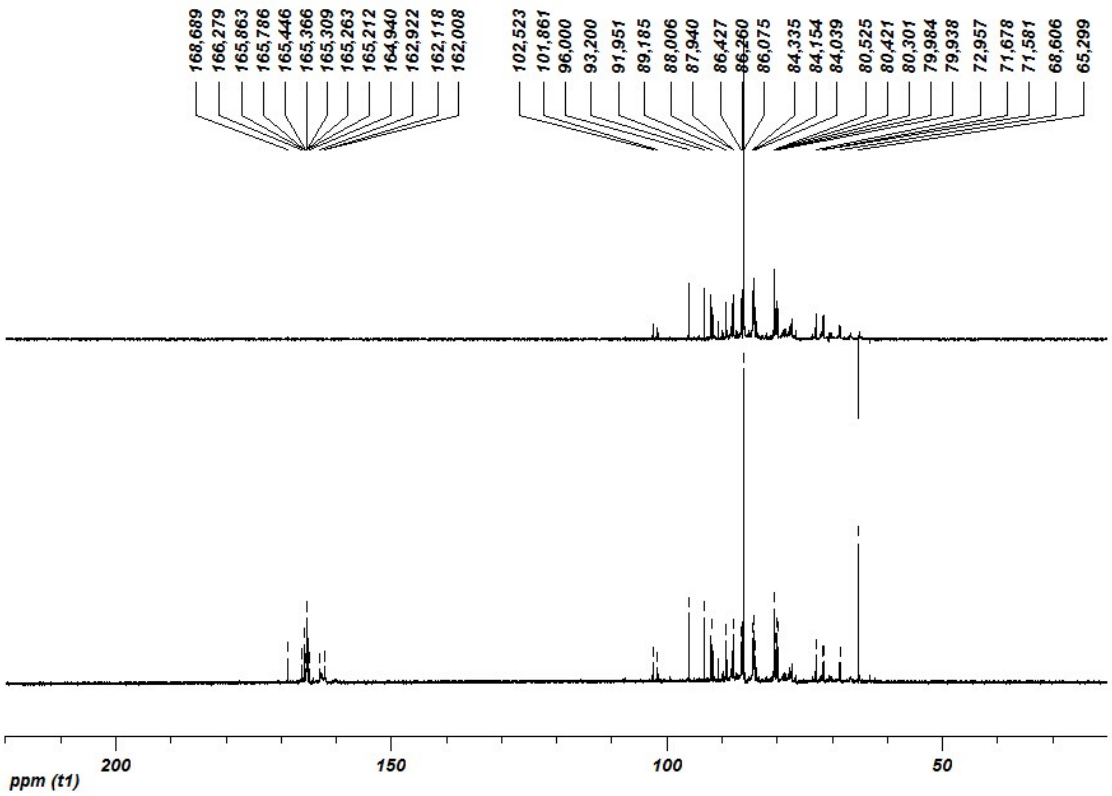


**Figure S6.11.** $^{13}C$ NMR spectra (top: DEPT) of the 1:1 reaction mixture recorded in $D_2O$ (after 23 d).

**Table S6.5.** $^{13}C$ NMR monitoring of 1:1 urea-glyoxal mixtures in aqueous solution.[a, b]

| $^{13}C$ NMR range | 2 h | | 1 day | | 2 days | | 5 days | | 22 days | |
|---|---|---|---|---|---|---|---|---|---|---|
| | ppm | % | Ppm | % | ppm | % | ppm | % | ppm | % |
| 168-154 | **168.8** | 4.4 | **168.8** | 2.7 | **168.7** | 3.4 | **168.7** | 7.3 | **168.7** | 8.1 |
| | **165.4** | 11.5 | **165.4** | 7.0 | **166.3** | 2.9 | **166.3** | 5.9 | **166.3** | 6.0 |
| | **165.2** | 17.2 | **165.2** | 18.5 | **165.2** | 19.6 | **165.8** | 5.4 | **165.9** | 6.0 |
| | **164.9** | 4.1 | **164.9** | 3.7 | **164.9** | 4.2 | **165.3** | 4.0 | **165.8** | 12.5 |
| | **162.9** | 5.9 | **162.9** | 6.0 | **162.9** | 5.6 | **165.2** | 20.3 | **165.4** | 6.2 |
| | | | **162.7** | 3.2 | **162.9** | 3.8 | **164.9** | 5.1 | **165.3** | 8.1 |
| | | | | | **162.7** | 3.6 | **162.9** | 5.6 | **165.3** | 13.0 |
| | | | | | | | **162.9** | 3.8 | **165.2** | 21.0 |
| | | | | | | | **162.9** | 2.4 | **164.9** | 4.8 |
| | | | | | | | **162.7** | 2.9 | **162.9** | 4.7 |
| | | | | | | | **162.7** | 2.8 | **162.8** | 3.2 |
| | | | | | | | **162.5** | 2.3 | **162.7** | 3.1 |
| | | | | | | | **162.1** | 3.3 | **162.7** | 2.7 |
| | | | | | | | **162.0** | 2.3 | **162.7** | 3.2 |
| | | | | | | | | | **162.6** | 2.8 |
| | | | | | | | | | **162.5** | 3.3 |
| | | | | | | | | | **162.5** | 3.0 |
| | | | | | | | | | **162.1** | 5.1 |
| | | | | | | | | | **162.0** | 5.5 |
| 108 - 91 | **107.0** | 14.6 | **107.0** | 7.4 | **102.6** | 2.5 | **107.6** | 1.6 | **102.6** | 2.7 |
| | **101.8** | 14.3 | **102.6** | 2.7 | **101.2** | 1.9 | **106.2** | 1.6 | **102.5** | 6.7 |
| | **101.2** | 14.2 | **101.8** | 7.4 | **99.5** | 2.0 | **102.5** | 4.3 | **101.9** | 5.0 |
| | **96.9** | 5.2 | **101.2** | 6.9 | **96.0** | 3.7 | **101.9** | 2.6 | **101.6** | 3.3 |
| | **95.2** | 3.0 | **96.9** | 2.8 | **93.2** | 36.3 | **101.6** | 1.9 | **99.5** | 2.3 |
| | **94.9** | 2.9 | **95.2** | 2.9 | **92.5** | 2.2 | **99.5** | 2.1 | **96.0** | 22.3 |
| | **93.2** | 89.1 | **93.2** | 65.7 | **92.0** | 3.7 | **96.0** | 10.4 | **93.2** | 21.3 |
| | **92.5** | 3.9 | **92.5** | 8.0 | **92.0** | 20.8 | **93.2** | 27.0 | **92.0** | 15.4 |
| | **92.5** | 16.9 | **92.0** | 4.0 | **91.6** | 13.4 | **92.0** | 4.3 | **91.6** | 10.5 |
| | **92.0** | 4.5 | **92.0** | 20.0 | **91.4** | 2.1 | **92.0** | 26.4 | **90.7** | 8.2 |
| | **92.0** | 17.1 | **91.6** | 13.0 | | | **91.6** | 16.3 | | |
| | **91.6** | 11.7 | | | | | **91.4** | 2.6 | | |
| | **91.5** | 3.7 | | | | | **90.7** | 4.7 | | |
| | **91.4** | 3.4 | | | | | | | | |

[a] Peaks assigned to glyoxal are highlighted in green. [b] The secondary carbon at 65.3 ppm is attributed to the $CH_2OH$ group, also detected in aqueous glyoxal solutions

**Table S6.5 cont.** $^{13}C$ NMR monitoring of 1:1 urea-glyoxal mixtures in aqueous solution.[a, b]

| $^{13}C$ NMR range | 2 h | | 1 day | | 2 days | | 5 days | | 22 days | |
|---|---|---|---|---|---|---|---|---|---|---|
| | ppm | % | ppm | % | ppm | % | ppm | % | ppm | % |
| 91- 75 | **87.9** | 9.5 | **87.9** | 10.2 | **89.3** | 2.7 | **89.3** | 2.4 | **89.9** | 3.8 |
| | **86.3** | 14.9 | **86.3** | 17.9 | **89.2** | 2.6 | **89.3** | 2.9 | **89.3** | 5.7 |
| | **86.1** | **100.0** | **86.1** | **100.0** | **88.0** | 5.1 | **89.2** | 5.7 | **89.2** | 13.7 |
| | **85.2** | 4.0 | **85.2** | 4.2 | **87.9** | 10.3 | **88.0** | 9.8 | **88.3** | 4.8 |
| | **84.2** | 4.2 | **84.2** | 4.1 | **86.5** | 2.3 | **87.9** | 11.8 | **88.3** | 3.5 |
| | **84.1** | 8.9 | **84.1** | 9.4 | **86.4** | 3.1 | **86.4** | 5.8 | **88.1** | 3.9 |
| | **84.0** | 8.6 | **84.0** | 8.8 | **86.3** | 16.8 | **86.3** | 18.1 | **88.0** | 15.7 |
| | **80.7** | 3.1 | **80.3** | 12.5 | **86.1** | **100.0** | **86.1** | **100.0** | **87.9** | 10.1 |
| | **80.3** | 11.0 | **80.0** | 15.3 | **85.2** | 4.9 | **85.2** | 4.5 | **87.5** | 3.4 |
| | **80.0** | 14.2 | **79.9** | 18.5 | **84.4** | 2.8 | **84.4** | 4.4 | **87.3** | 3.2 |
| | **79.9** | 16.7 | | | **84.4** | 2.6 | **84.3** | 6.4 | **86.4** | 13.2 |
| | | | | | **84.3** | 3.7 | **84.2** | 4.7 | **86.3** | 14.8 |
| | | | | | **84.2** | 4.6 | **84.2** | 4.8 | **86.1** | **100.0** |
| | | | | | **84.1** | 10.2 | **84.2** | 10.7 | **85.8** | 3.4 |
| | | | | | **84.0** | 9.6 | **84.1** | 10.4 | **85.1** | 2.4 |
| | | | | | **83.7** | 1.9 | **84.0** | 9.9 | **84.4** | 7.6 |
| | | | | | **83.2** | 2.2 | **84.0** | 2.2 | **84.3** | 14.4 |
| | | | | | **81.8** | 1.7 | **83.7** | 3.1 | **84.2** | 7.4 |
| | | | | | **80.7** | 3.4 | **83.2** | 3.0 | **84.2** | 7.4 |
| | | | | | **80.4** | 4.5 | **81.8** | 1.9 | **84.2** | 16.7 |
| | | | | | **80.4** | 2.9 | **80.5** | 5.1 | **84.0** | 8.7 |
| | | | | | **80.3** | 12.8 | **80.4** | 12.0 | **83.7** | 5.1 |
| | | | | | **80.0** | 15.5 | **80.3** | 15.5 | **83.2** | 2.3 |
| | | | | | **79.9** | 19.5 | **80.0** | 16.1 | **81.8** | 2.4 |
| | | | | | | | **79.9** | 22.6 | **80.7** | 4.1 |
| | | | | | | | **78.6** | 2.8 | **80.5** | 10.0 |
| | | | | | | | **77.6** | 2.9 | **80.4** | 24.0 |
| | | | | | | | **77.5** | 2.7 | **80.3** | 11.0 |
| | | | | | | | **77.2** | 3.5 | **80.0** | 16.0 |
| | | | | | | | | | **79.9** | 14.8 |
| | | | | | | | | | **79.0** | 3.0 |
| | | | | | | | | | **78.9** | 3.1 |
| | | | | | | | | | **78.6** | 3.4 |
| | | | | | | | | | **78.5** | 3.2 |
| | | | | | | | | | **78.5** | 3.1 |
| | | | | | | | | | **77.9** | 3.2 |
| | | | | | | | | | **77.6** | 5.0 |
| | | | | | | | | | **77.5** | 4.2 |
| | | | | | | | | | **77.2** | 6.5 |
| | | | | | | | | | **76.6** | 2.9 |

[a] Peaks assigned to glyoxal are highlighted in green. [b] The secondary carbon at 65.3 ppm is attributed to the $CH_2OH$ group, also detected in aqueous glyoxal solutions

**Table S6.5 cont.** $^{13}C$ NMR monitoring of 1:1 urea-glyoxal mixtures in aqueous solution.[a, b]

| $^{13}C$ NMR range | 2 h | | 1 day | | 2 days | | 5 days | | 22 days | |
|---|---|---|---|---|---|---|---|---|---|---|
| | ppm | % | ppm | % | ppm | % | ppm | % | ppm | % |
| 75 - 62 | | | **70.5** | 3.4 | **73.0** | 1.7 | **73.0** | 3.6 | **73.6** | 2.3 |
| | **65.3**[a] | 18.9 | **65.3**[a] | 21.4 | **71.7** | 2.2 | **71.7** | 3.9 | **73.1** | 3.8 |
| | | | | | **70.7** | 2.3 | **71.6** | 3.0 | **73.0** | 9.1 |
| | | | | | **70.5** | 4.1 | **70.7** | 3.0 | **72.1** | 2.8 |
| | | | | | **68.6** | 3.5 | **70.5** | 2.4 | **71.8** | 2.7 |
| | | | | | **65.3**[a] | 24.7 | **70.5** | 3.6 | **71.7** | 6.8 |
| | | | | | **65.1** | 1.8 | **68.6** | 5.3 | **71.6** | 7.1 |
| | | | | | **63.2** | 2.2 | **65.3**[a] | 47.9 | **70.7** | 2.9 |
| | | | | | | | **63.2** | 2.9 | **70.4** | 2.5 |
| | | | | | | | | | **70.1** | 2.4 |
| | | | | | | | | | **68.6** | 6.6 |
| | | | | | | | | | **66.7** | 2.4 |
| | | | | | | | | | **66.6** | 2.5 |
| | | | | | | | | | **65.3**[a] | 44.8 |
| | | | | | | | | | **65.1** | 2.1 |
| | | | | | | | | | **65.0** | 2.8 |
| | | | | | | | | | **63.2** | 2.9 |
| | | | | | | | | | **62.1** | 1.8 |

[a] Peaks assigned to glyoxal are highlighted in green. [b] The secondary carbon at 65.3 ppm is attributed to the $CH_2OH$ group, also detected in aqueous glyoxal solutions

**1:2 STOICHIOMETRY**

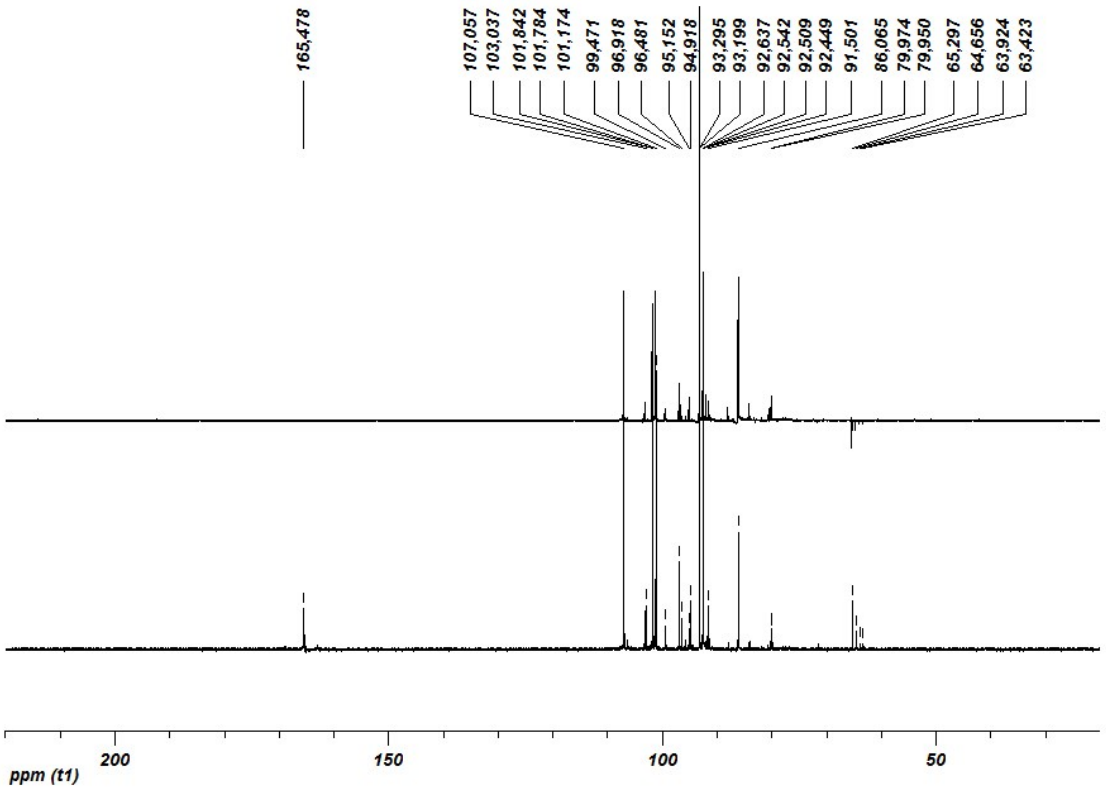


**Figure S6.12.** $^{13}C$ NMR spectra (top: DEPT) of the 1:2 reaction mixture recorded in $D_2O$ (after 2 h).

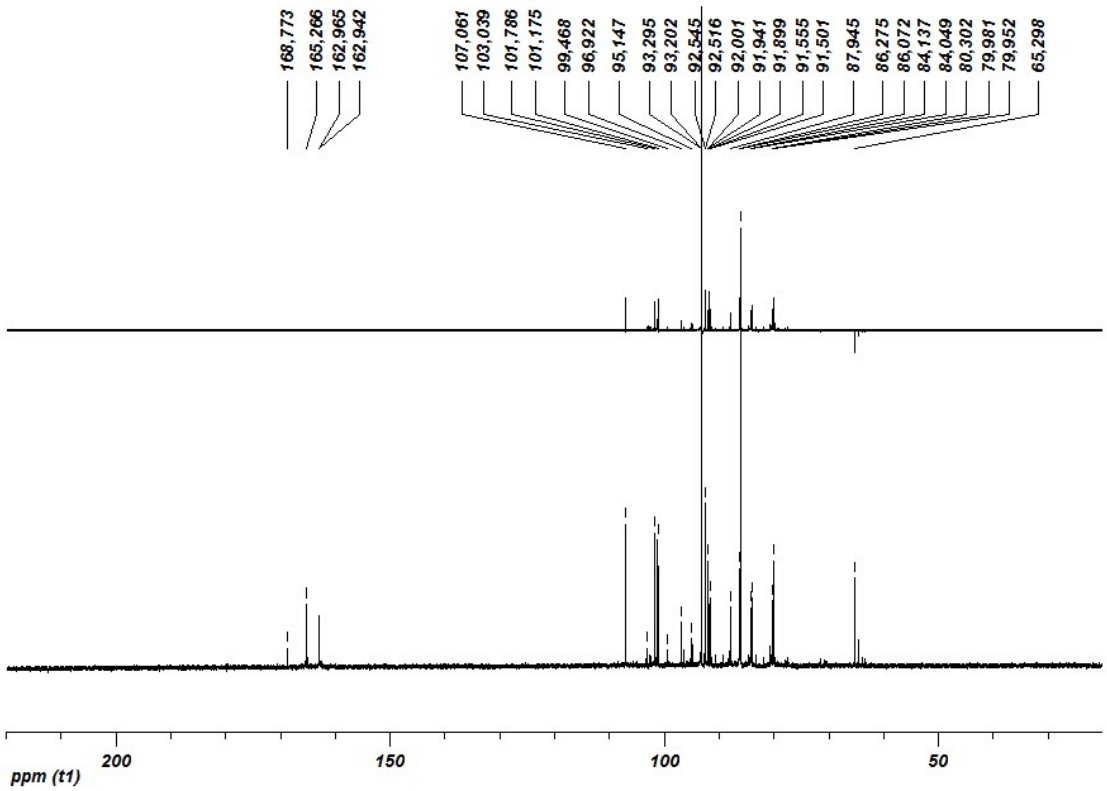


**Figure S6.13.** $^{13}C$ NMR spectra (top: DEPT) of the 1:2 reaction mixture recorded in $D_2O$ (after 1 d).

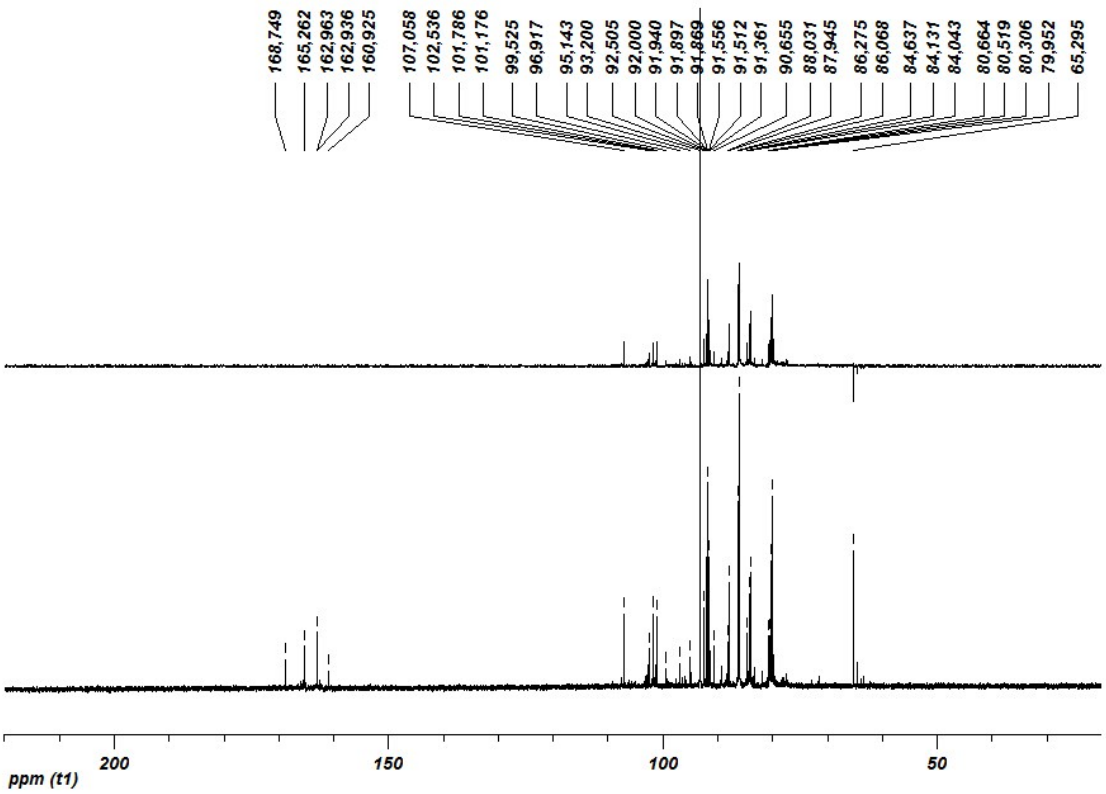


**Figure S6.14.** $^{13}C$ NMR spectra (top: DEPT) of the 1:2 reaction mixture recorded in $D_2O$ (after 6 d).

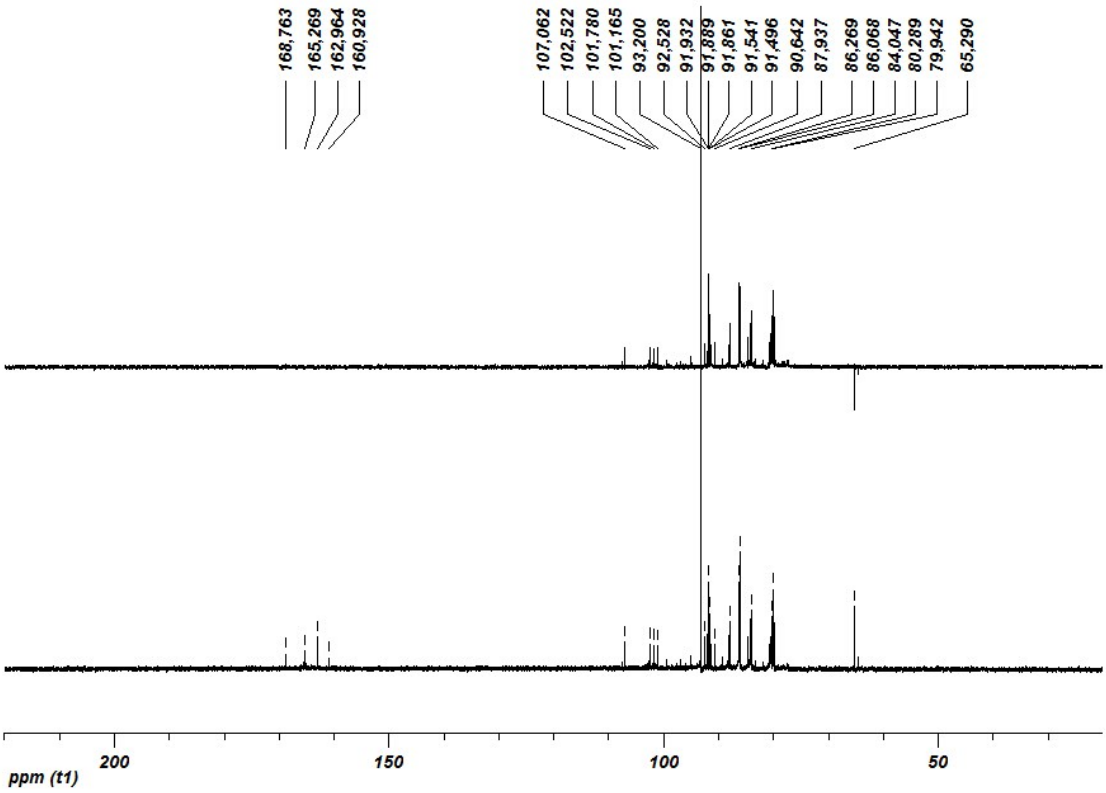


**Figure S6.15.** $^{13}C$ NMR spectra (top: DEPT) of the 1:2 reaction mixture recorded in $D_2O$ (after 14 d).

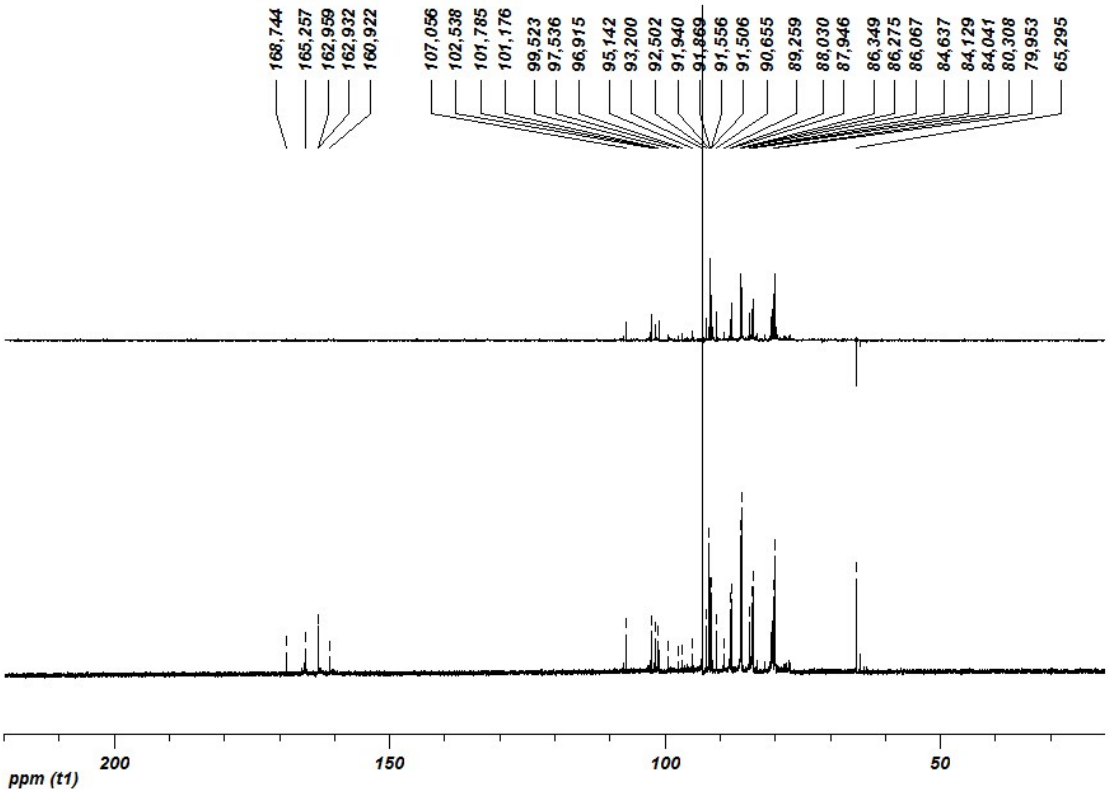


**Figure S6.16.** $^{13}C$ NMR spectra (top DEPT) of the 1:2 reaction mixture recorded in $D_2O$ (after 21 d).

**Table S6.6.** $^{13}C$ NMR monitoring of 1:2 urea-glyoxal mixtures in aqueous solution.[a, b]

| $^{13}C$ NMR range | 2 h | | 1 day | | 6 days | | 14 days | | 21 days | |
|---|---|---|---|---|---|---|---|---|---|---|
| | ppm | % | ppm | % | ppm | % | ppm | % | ppm | % |
| 168-154 | | | 168.8 | 1.4 | 168.7 | 2.0 | 168.8 | 2.8 | 168.7 | 2.6 |
| | 165.5 | 3.9 | 165.3 | 4.3 | 165.6 | 0.7 | 165.6 | 1.6 | 165.5 | 1.4 |
| | | | 165.0 | 0.8 | 165.3 | 2.9 | 165.3 | 3.3 | 165.3 | 3.0 |
| | | | 163.0 | 2.5 | 163.0 | 3.8 | 163.0 | 5.7 | 163.0 | 5.2 |
| | | | 162.9 | 1.9 | 162.9 | 2.4 | 160.9 | 2.2 | 162.9 | 3.8 |
| | | | | | 162.6 | 0.6 | 160.8 | 1.9 | 160.9 | 2.0 |
| | | | | | 160.9 | 1.3 | | | | |
| | | | | | 160.8 | 0.8 | | | | |
| 108 - 91 | 107.1 | 27.3 | 107.1 | 9.7 | 107.6 | 0.8 | 107.6 | 1.4 | 107.1 | 4.6 |
| | 106.8 | 1.5 | 103.0 | 1.4 | 107.1 | 5.1 | 107.1 | 4.8 | 102.6 | 1.6 |
| | 106.8 | 1.5 | 102.6 | 0.9 | 103.0 | 1.0 | 102.5 | 4.4 | 102.5 | 5.0 |
| | 106.4 | 0.9 | 102.5 | 0.9 | 102.6 | 1.7 | 101.8 | 4.2 | 101.9 | 1.3 |
| | 106.3 | 1.0 | 101.8 | 9.1 | 102.5 | 2.7 | 101.2 | 4.1 | 101.8 | 4.2 |
| | 103.3 | 1.8 | 101.2 | 8.6 | 101.8 | 5.1 | 99.5 | 1.9 | 101.2 | 3.8 |
| | 103.0 | 4.3 | 99.5 | 1.0 | 101.2 | 4.9 | 97.6 | 1.2 | 99.5 | 2.0 |
| | 101.9 | 1.2 | 99.5 | 1.2 | 99.5 | 1.4 | 96.9 | 1.9 | 97.5 | 1.5 |
| | 101.8 | 26.8 | 96.9 | 3.1 | 99.5 | 1.1 | 95.1 | 2.5 | 96.9 | 1.6 |
| | 101.5 | 1.5 | 96.5 | 1.3 | 97.5 | 0.7 | | | 95.1 | 2.4 |
| | 101.4 | 1.5 | 95.1 | 2.0 | 96.9 | 1.8 | | | | |
| | 101.3 | 1.6 | 94.9 | 1.6 | 96.5 | 0.8 | | | | |
| | 101.2 | 26.1 | | | 96.0 | 0.9 | | | | |
| | 99.5 | 2.4 | | | 95.1 | 2.2 | | | | |
| | 96.9 | 8.2 | | | 94.9 | 1.2 | | | | |
| | 96.5 | 3.0 | | | | | | | | |
| | 95.7 | 0.8 | | | | | | | | |
| | 95.7 | 1.0 | | | | | | | | |
| | 95.2 | 2.1 | | | | | | | | |
| | 94.9 | 4.7 | | | | | | | | |
| | 93.3 | 3.6 | | | | | | | | |
| | 93.2 | 100.0 | 93.2 | 100.0 | 93.2 | 100.0 | 93.2 | 100.0 | 93.2 | 100.0 |
| | 92.6 | 2.6 | 92.5 | 11.1 | 92.5 | 1.4 | 92.5 | 5.6 | 92.5 | 5.7 |
| | 92.5 | 7.4 | 92.0 | 1.4 | 92.5 | 5.5 | 92.4 | 1.7 | 91.9 | 15.3 |
| | 92.5 | 30.1 | 91.9 | 7.2 | 92.4 | 1.3 | 92.0 | 3.3 | 91.9 | 6.1 |
| | 91.9 | 1.2 | 91.6 | 4.8 | 92.0 | 2.4 | 91.9 | 14.7 | 91.9 | 7.5 |
| | 91.6 | 1.1 | 91.5 | 2.2 | 91.9 | 13.7 | 91.9 | 5.2 | 91.6 | 9.5 |
| | 91.5 | 4.0 | 91.4 | 0.8 | 91.9 | 3.8 | 91.9 | 6.7 | 91.5 | 5.6 |
| | | | 90.7 | 0.9 | 91.9 | 4.8 | 91.5 | 9.4 | 90.7 | 5.1 |
| | | | | | 91.6 | 8.9 | 91.5 | 5.2 | | |
| | | | | | 91.5 | 3.4 | 91.3 | 1.7 | | |
| | | | | | 90.7 | 2.9 | 90.6 | 4.3 | | |

[a] Peaks assigned to glyoxal are highlighted in green. [b] The secondary carbon at 65.3 and 64.7 ppm is attributed to the $CH_2OH$ group, also detected in aqueous glyoxal solutions

**Table S6.6 cont.** $^{13}C$ NMR monitoring of 1:2 urea-glyoxal mixtures in aqueous solution.[a, b]

| $^{13}C$ NMR range | 2 h | | 1 day | | 6 days | | 14 days | | 21 days | |
|---|---|---|---|---|---|---|---|---|---|---|
| | ppm | % | ppm | % | ppm | % | ppm | % | ppm | % |
| 91 - 75 | **87.9** | 0.7 | **89.3** | 0.9 | **89.5** | 0.7 | **89.3** | 2.4 | **89.3** | 2.3 |
| | **86.3** | 1.2 | **88.0** | 1.2 | **89.4** | 0.8 | **88.4** | 1.8 | **88.0** | 7.6 |
| | **86.1** | 11.0 | **87.9** | 4.1 | **89.3** | 1.6 | **88.3** | 1.6 | **87.9** | 8.8 |
| | **84.1** | 0.8 | **86.3** | 6.7 | **88.0** | 3.2 | **88.0** | 5.8 | **86.3** | 16.2 |
| | **84.0** | 0.8 | **86.1** | 29.5 | **87.9** | 7.2 | **87.9** | 8.1 | **86.1** | 19.5 |
| | **80.7** | 0.6 | **84.7** | 0.9 | **86.3** | 2.0 | **86.3** | 3.5 | **84.6** | 6.1 |
| | **80.4** | 0.5 | **84.6** | 0.9 | **86.3** | 12.5 | **86.3** | 14.6 | **84.1** | 8.4 |
| | **80.3** | 0.9 | **84.1** | 4.1 | **86.1** | 19.7 | **86.1** | 19.5 | **84.0** | 10.2 |
| | **80.0** | 2.1 | **84.0** | 4.7 | **84.7** | 2.8 | **84.7** | 4.5 | **80.7** | 4.4 |
| | **80.0** | 1.7 | **80.7** | 1.5 | **84.6** | 3.7 | **84.6** | 5.6 | **80.7** | 4.9 |
| | | | **80.5** | 0.9 | **84.1** | 6.4 | **84.1** | 8.6 | **80.5** | 6.2 |
| | | | **80.4** | 0.6 | **84.0** | 7.8 | **84.0** | 10.0 | **80.4** | 4.7 |
| | | | **80.3** | 4.6 | **83.2** | 1.5 | **80.7** | 4.0 | **80.3** | 9.1 |
| | | | **80.2** | 1.1 | **81.8** | 1.3 | **80.7** | 4.3 | **80.2** | 2.4 |
| | | | **80.0** | 4.5 | **80.7** | 2.7 | **80.6** | 2.3 | **80.0** | 13.8 |
| | | | **80.0** | 7.2 | **80.7** | 3.6 | **80.5** | 5.6 | | |
| | | | | | **80.5** | 3.6 | **80.4** | 4.4 | | |
| | | | | | **80.4** | 2.8 | **80.3** | 9.0 | | |
| | | | | | **80.4** | 1.8 | **80.2** | 2.4 | | |
| | | | | | **80.3** | 8.6 | **80.0** | 3.9 | | |
| | | | | | **80.2** | 1.8 | **79.9** | 13.4 | | |
| | | | | | **80.0** | 12.9 | | | | |
| 75 - 62 | **65.3**[a] | 4.7 | **65.3**[a] | 6.1 | **65.3**[a] | 9.3 | **65.3**[a] | 10.6 | **65.3**[a] | 11.2 |
| | **64.7**[a] | 1.9 | **64.7**[a] | 1.9 | **64.7**[a] | 1.8 | **64.7**[a] | 2.3 | **64.7**[a] | 2.4 |
| | **63.9*** | 0.7 | **63.9*** | 0.8 | **63.4*** | 0.9 | | | | |
| | **63.4*** | 0.7 | **63.4*** | 0.7 | | | | | | |

[a] Peaks assigned to glyoxal are highlighted in green. [b] The secondary carbon at 65.3 and 64.7 ppm is attributed to the $CH_2OH$ group, also detected in aqueous glyoxal solutions

**UREA-GLYOXAL OLIGOMERS ISOLATED FROM ACETONE SOLUTIONS**

**2:1 STOICHIOMETRY**

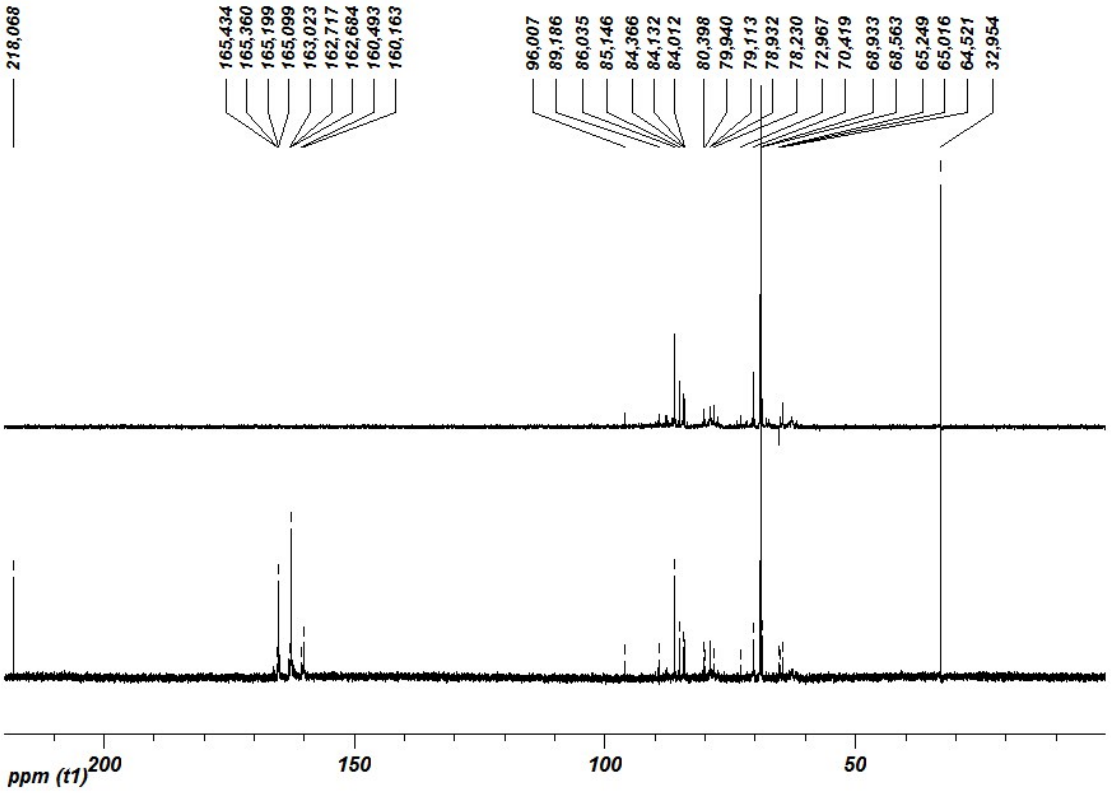


**Figure S6.17.** $^{13}C$ NMR spectra (top: DEPT) of the 2:1 oligomers from acetone, recorded in $D_2O$.

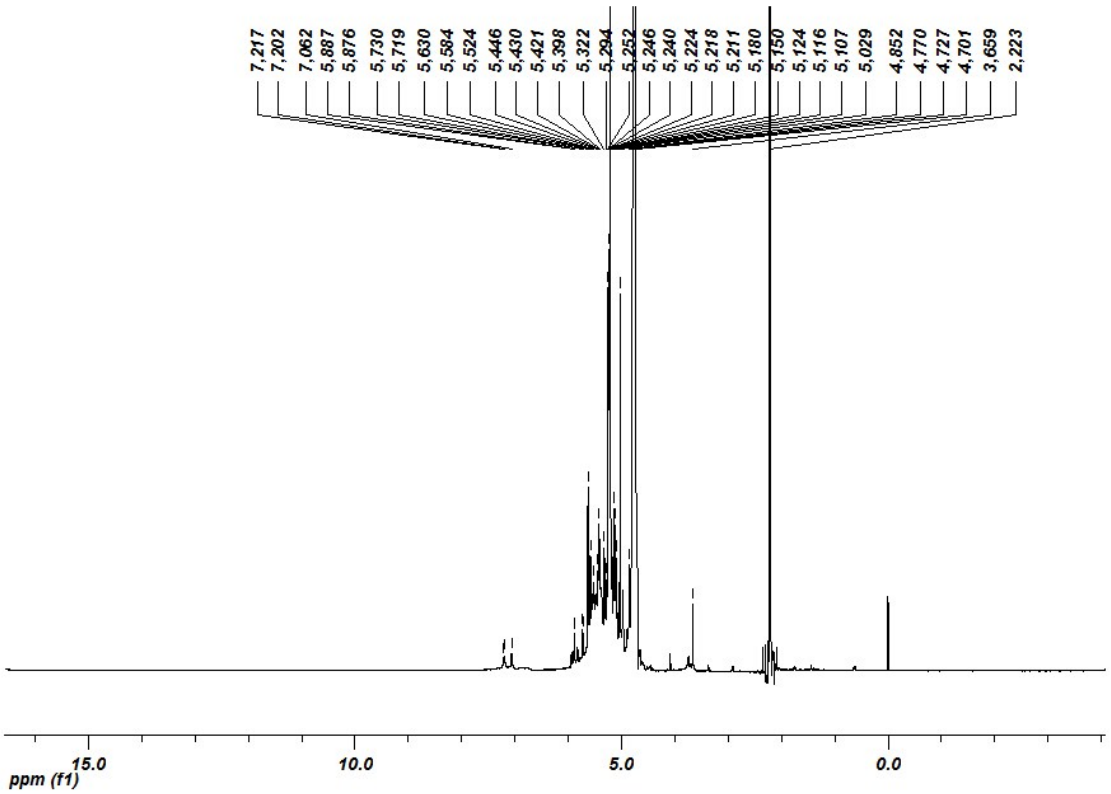


**Figure S6.18.** $^{1}H$ NMR spectrum of the 2:1 oligomers from acetone, recorded in $D_2O$.

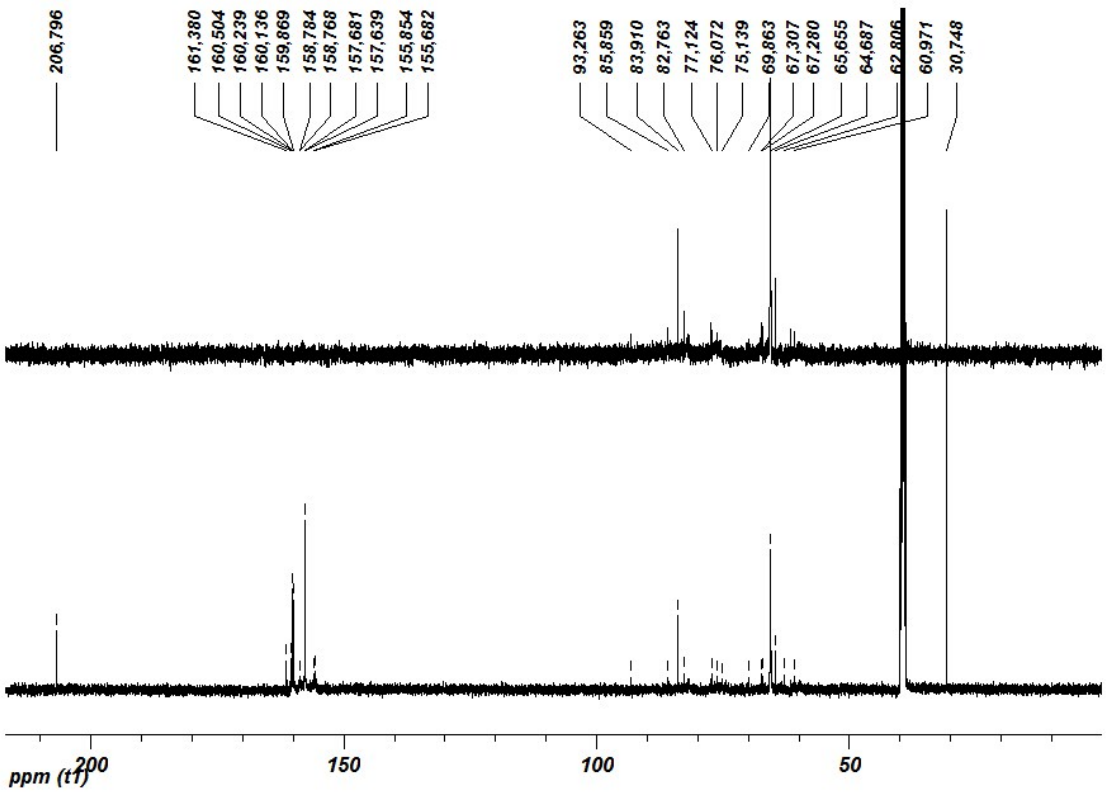


**Figure S6.19.** $^{13}C$ NMR spectra (top: DEPT) of the 2:1 oligomers from acetone, recorded in DMSO-$d_6$.

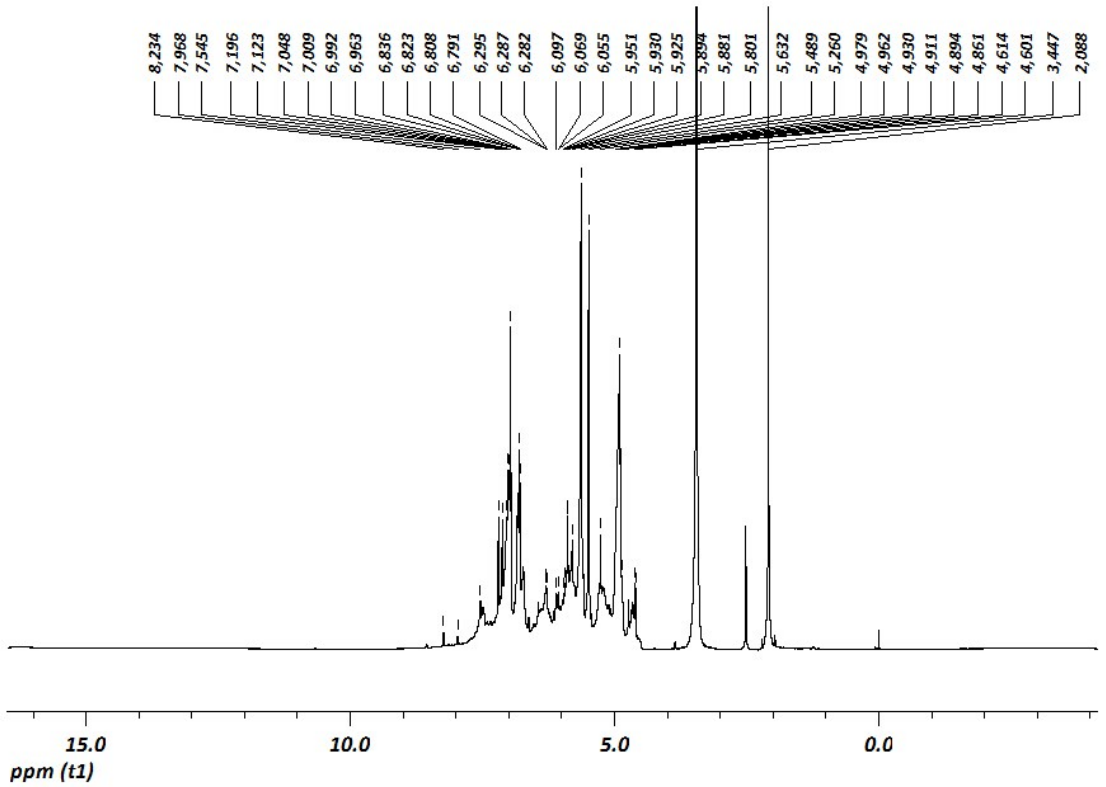


**Figure S6.20.** $^{1}H$ NMR spectrum of the 2:1 oligomers from acetone, recorded in DMSO-$d_6$.

**1:1 STOICHIOMETRY**

**Figure S6.21.** $^{13}C$ NMR spectra (top: DEPT) of the 1:1 oligomers from acetone, recorded in $D_2O$.

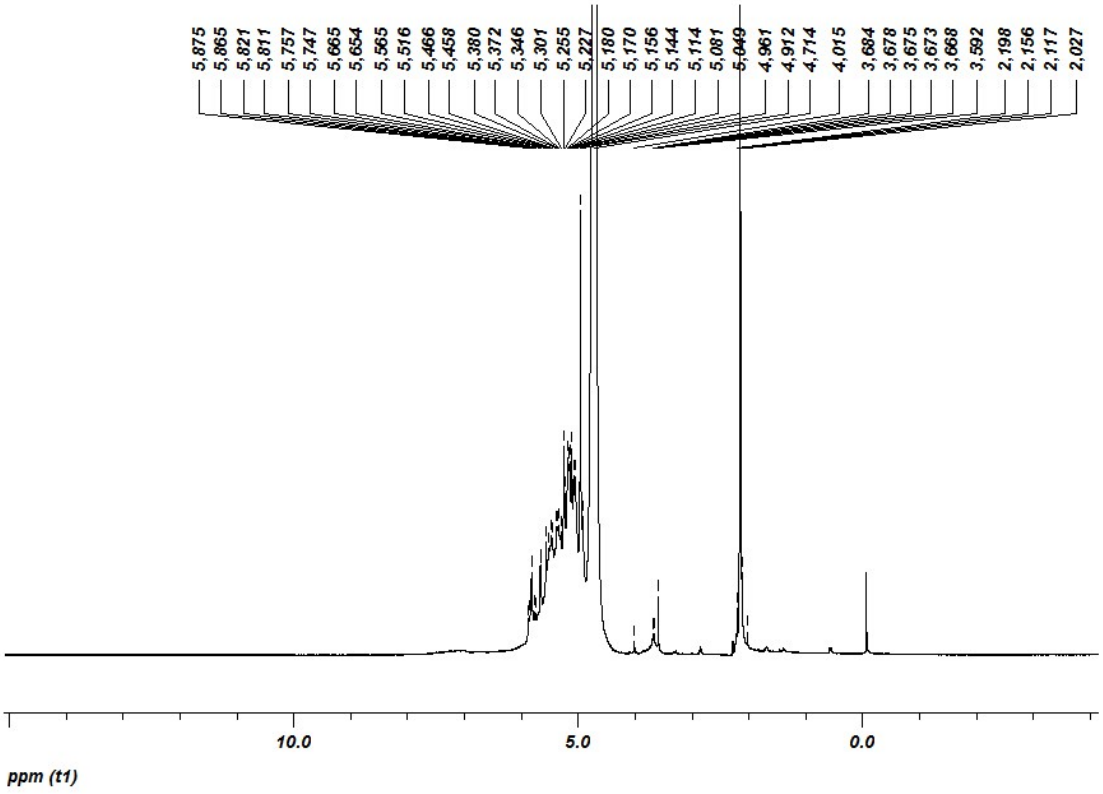


**Figure S6.22.** $^{1}H$ NMR spectrum of the 1:1 oligomers from acetone, recorded in $D_2O$.

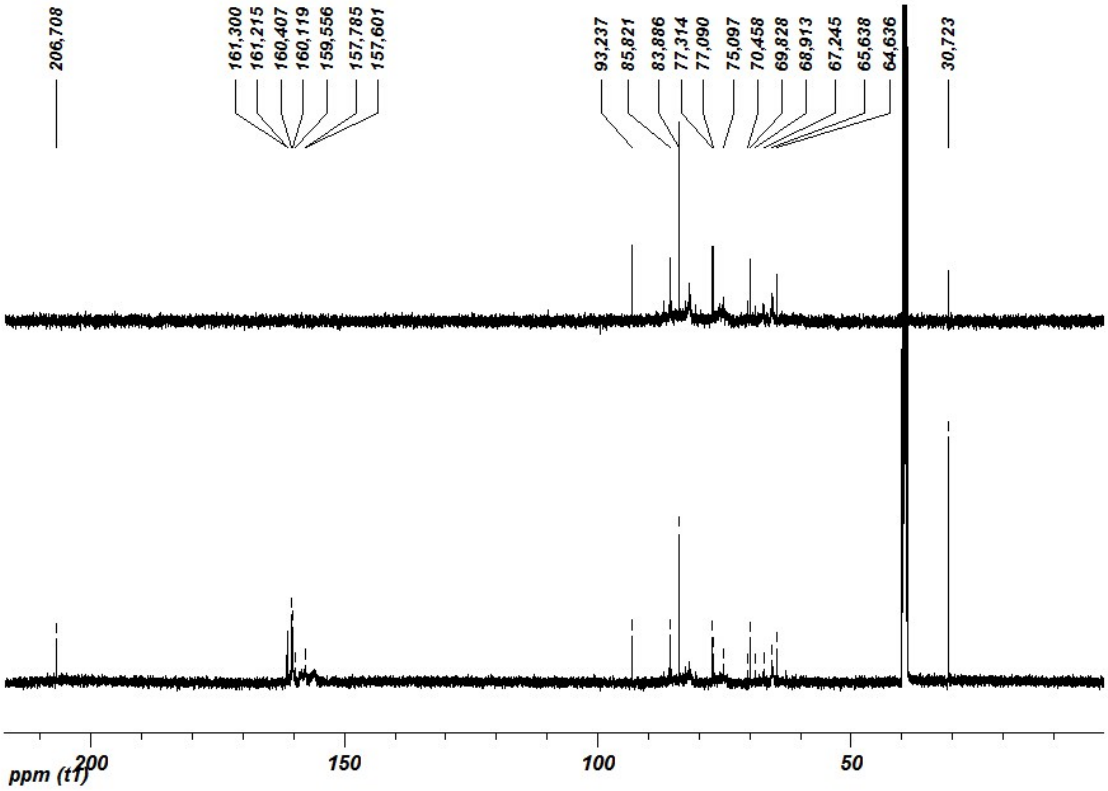


**Figure S6.23.** $^{13}C$ NMR spectra (top: DEPT) of the 1:1 oligomers from acetone recorded in DMSO-$d_6$.

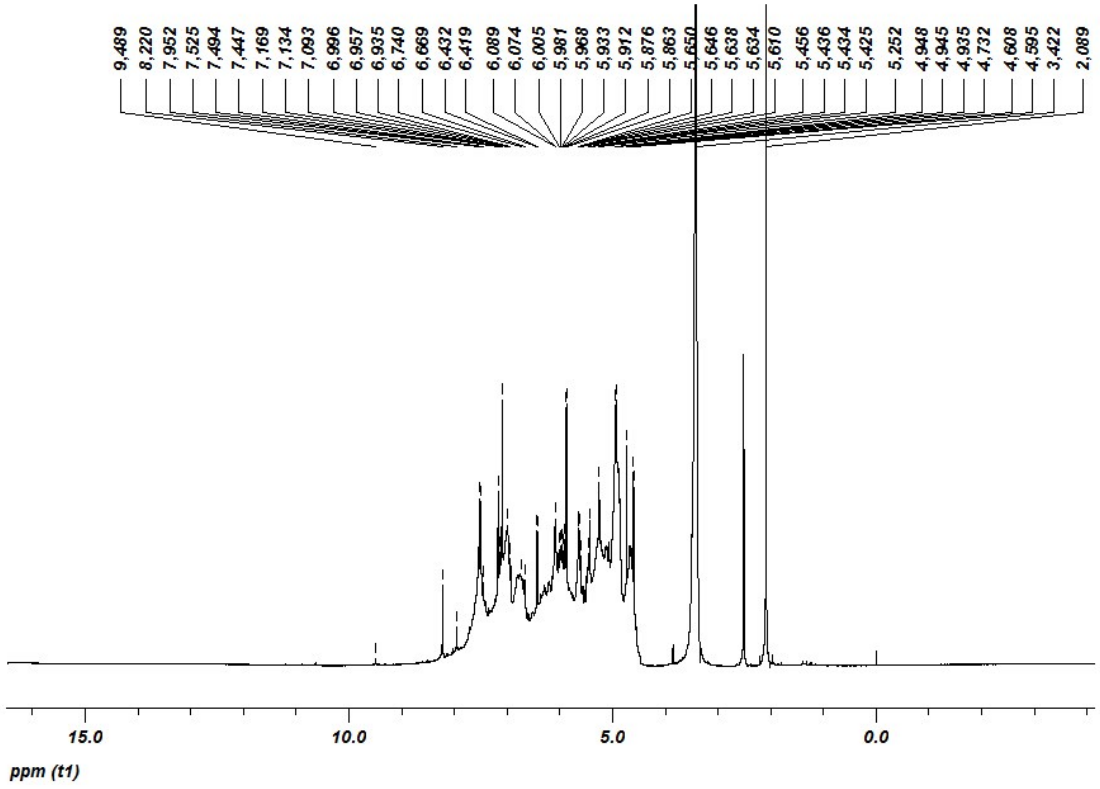


**Figure S6.24.** $^{1}H$ NMR spectrum of the 1:1 oligomers from acetone, recorded in DMSO-$d_6$.

**1:2 STOICHIOMETRY**

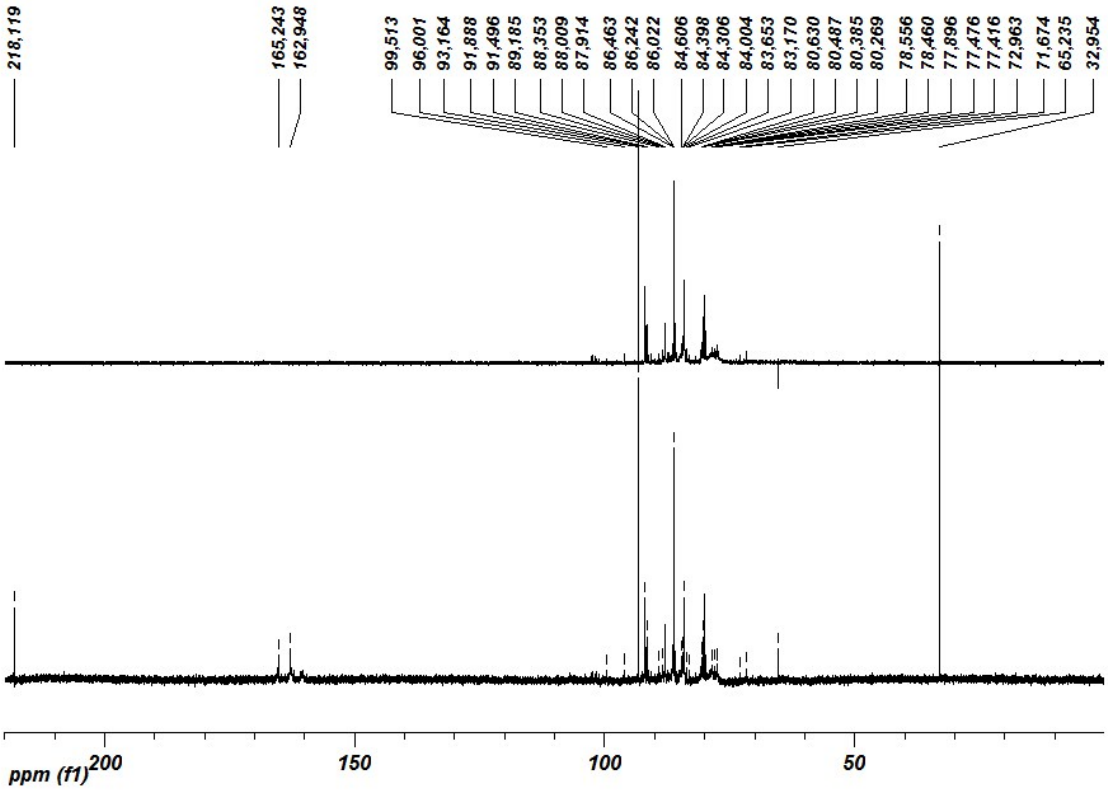


**Figure S6.25.** $^{13}C$ NMR spectra (top: DEPT) of the 1:2 oligomers from acetone, recorded in $D_2O$.

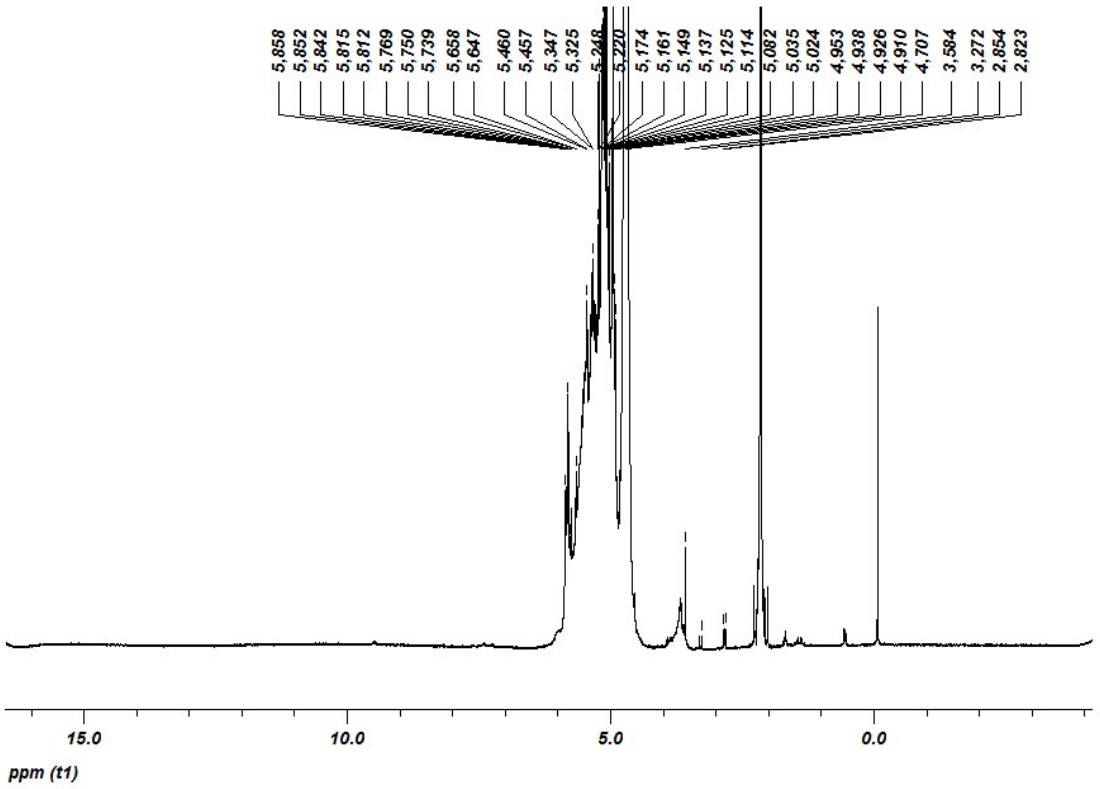


**Figure S6.26.** $^{1}H$ NMR spectrum of the 1:2 oligomers from acetone, recorded in $D_2O$.

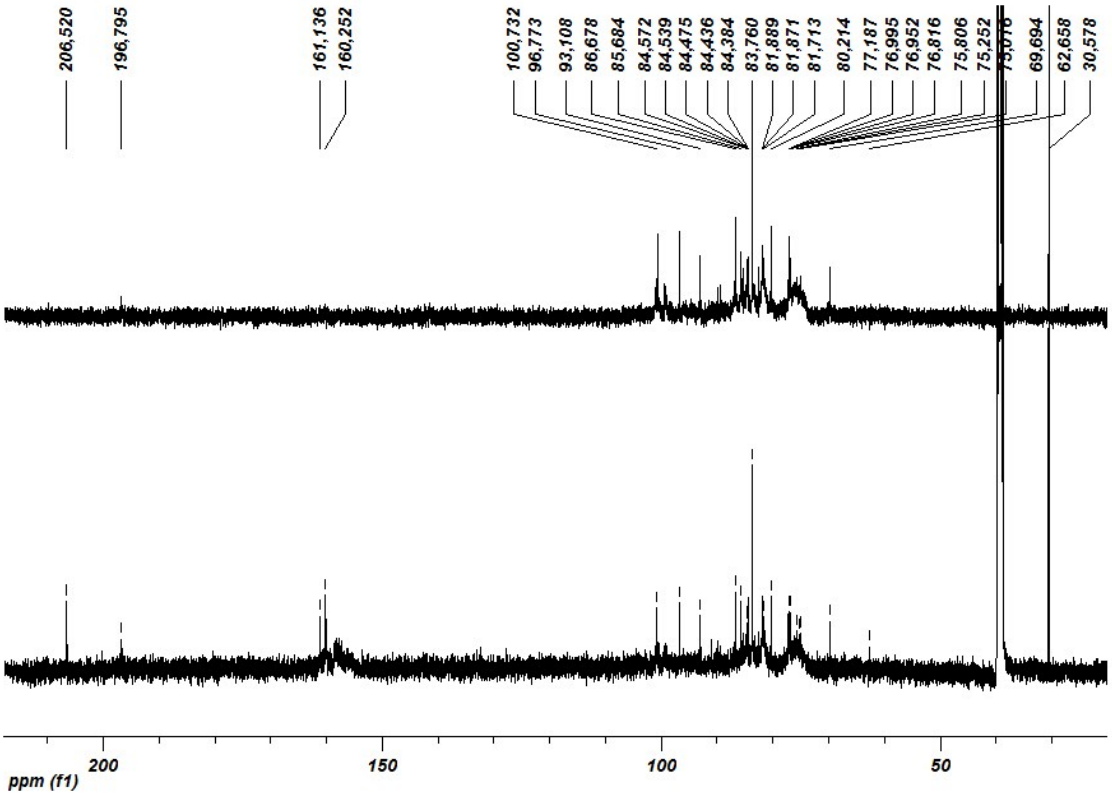


**Figure S6.27.** $^{13}C$ NMR spectra (top: DEPT) of the 1:2 oligomers from acetone, recorded in DMSO-$d_6$. The resonance at 196.8 ppm is assigned to the aldehyde group.

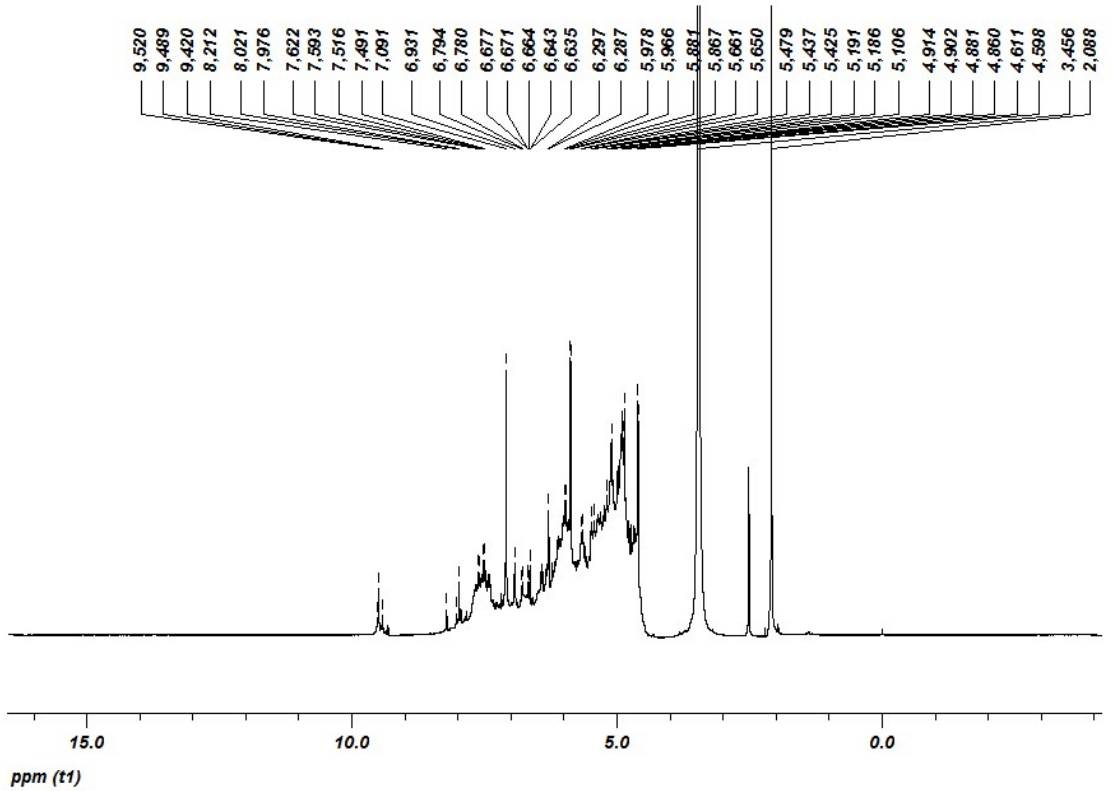


**Figure S6.28.** $^{1}H$ NMR spectrum of the 1:2 oligomers from acetone, recorded in DMSO-$d_6$.

**UREA-GLYOXAL OLIGOMERS ISOLATED FROM 1,4-DIOXANE SOLUTIONS**

**2:1 STOICHIOMETRY**

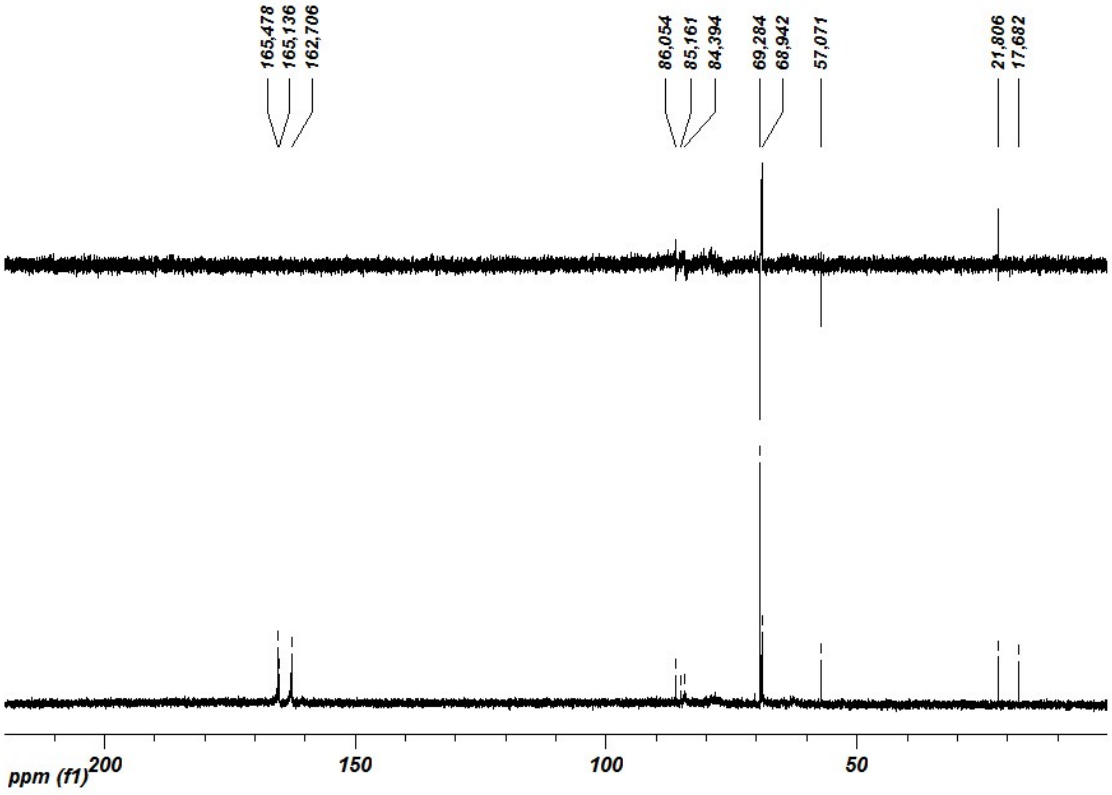


**Figure S6.29.** $^{13}C$ NMR spectra (top: DEPT) of the 2:1 oligomers from 1,4-dioxane, recorded in $D_2O$.

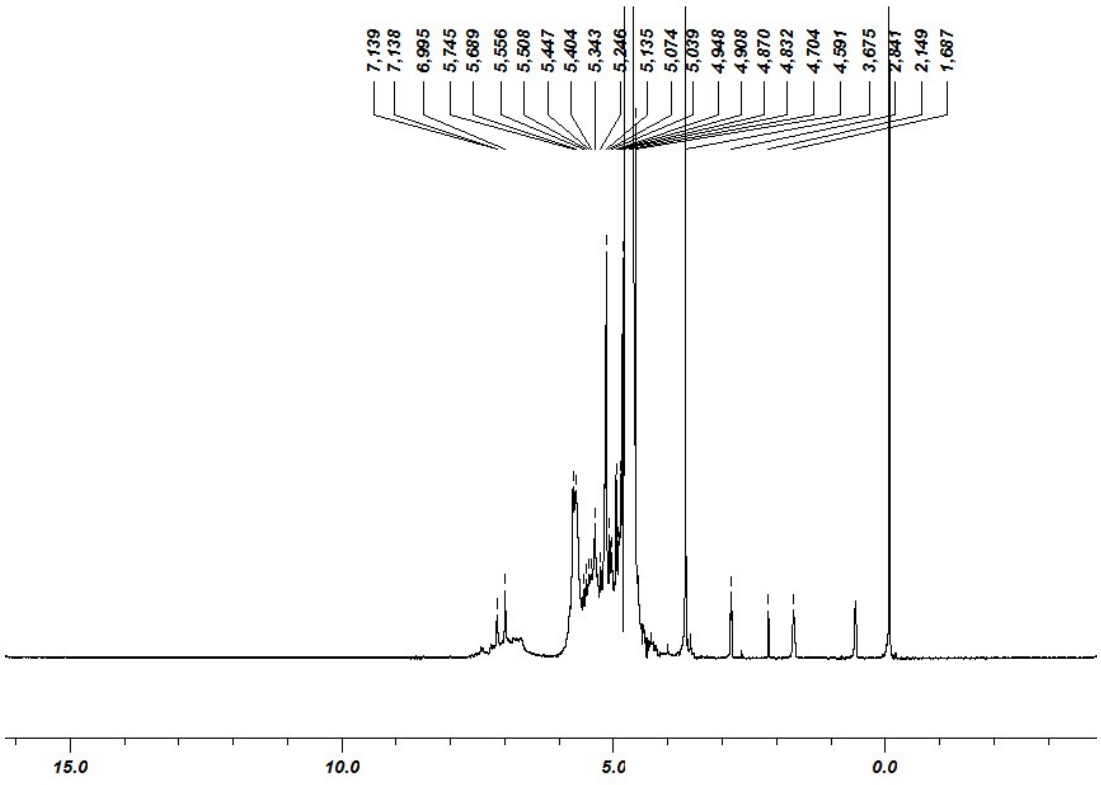


**Figure S6.30.** $^{1}H$ NMR spectrum of the 2:1 oligomers from 1,4-dioxane, recorded in $D_2O$.

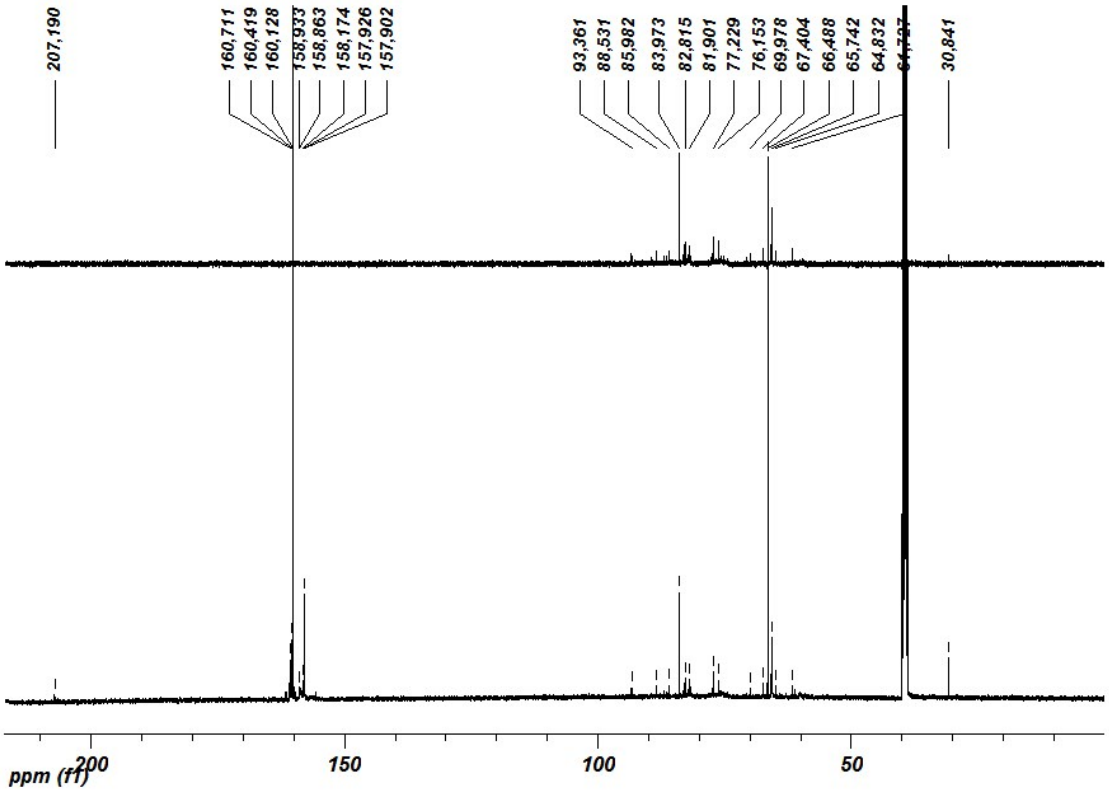


**Figure S6.31.** $^{13}C$ NMR spectra (top: DEPT) of the 2:1 oligomers from 1,4-dioxane, recorded in DMSO-$d_6$.

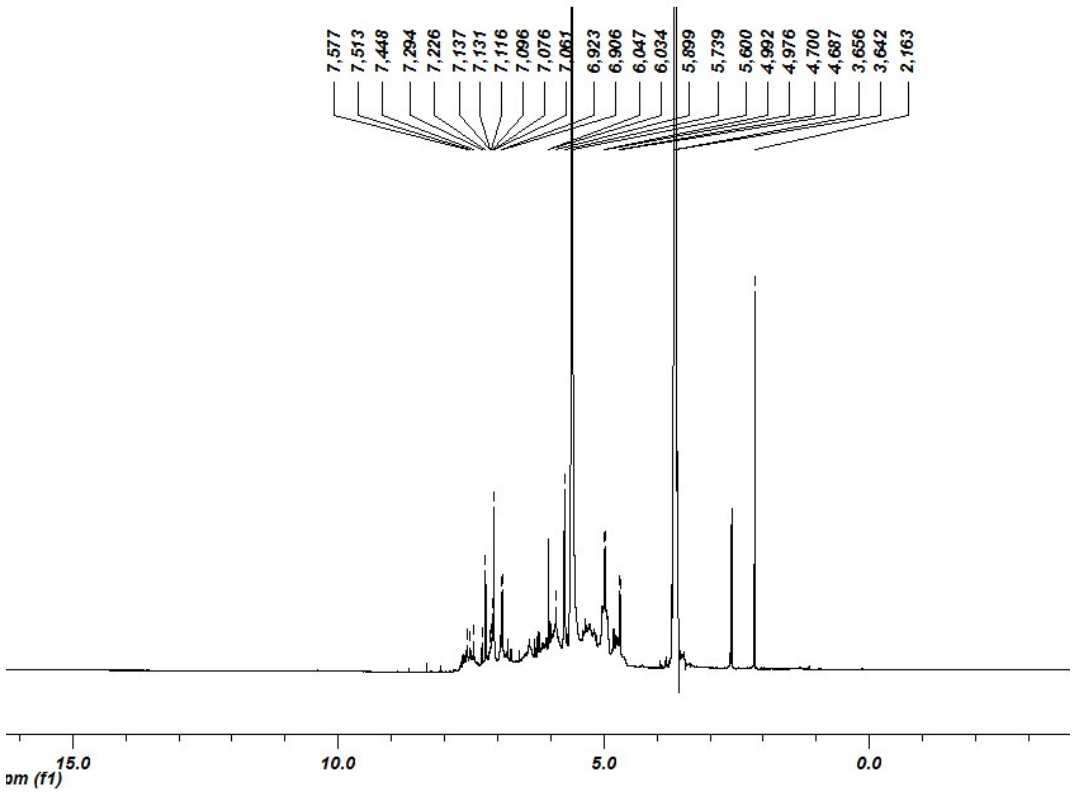


**Figure S6.32.** $^{1}H$ NMR spectrum of the 2:1 oligomers from 1,4-dioxane, recorded in DMSO-$d_6$.

**1:1 STOICHIOMETRY**

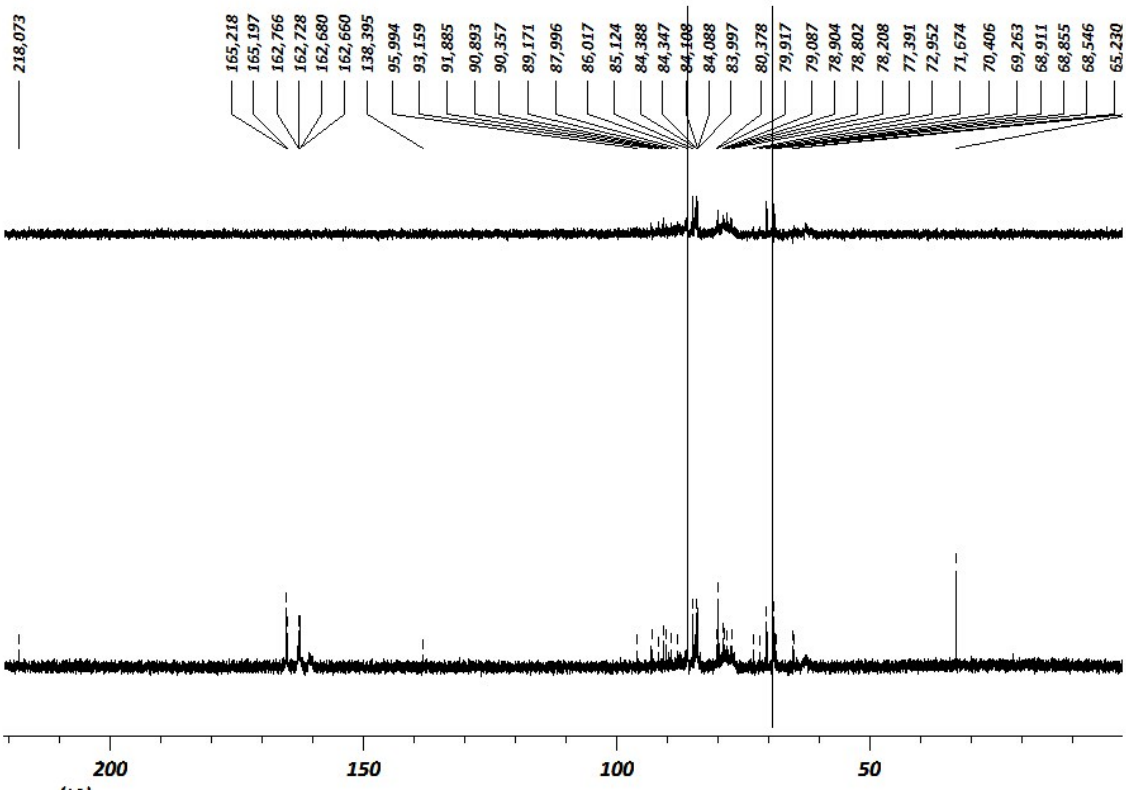


**Figure S6.33.** $^{13}C$ NMR spectra (top: DEPT) of the 1:1 oligomers from 1,4-dioxane, recorded in $D_2O$.

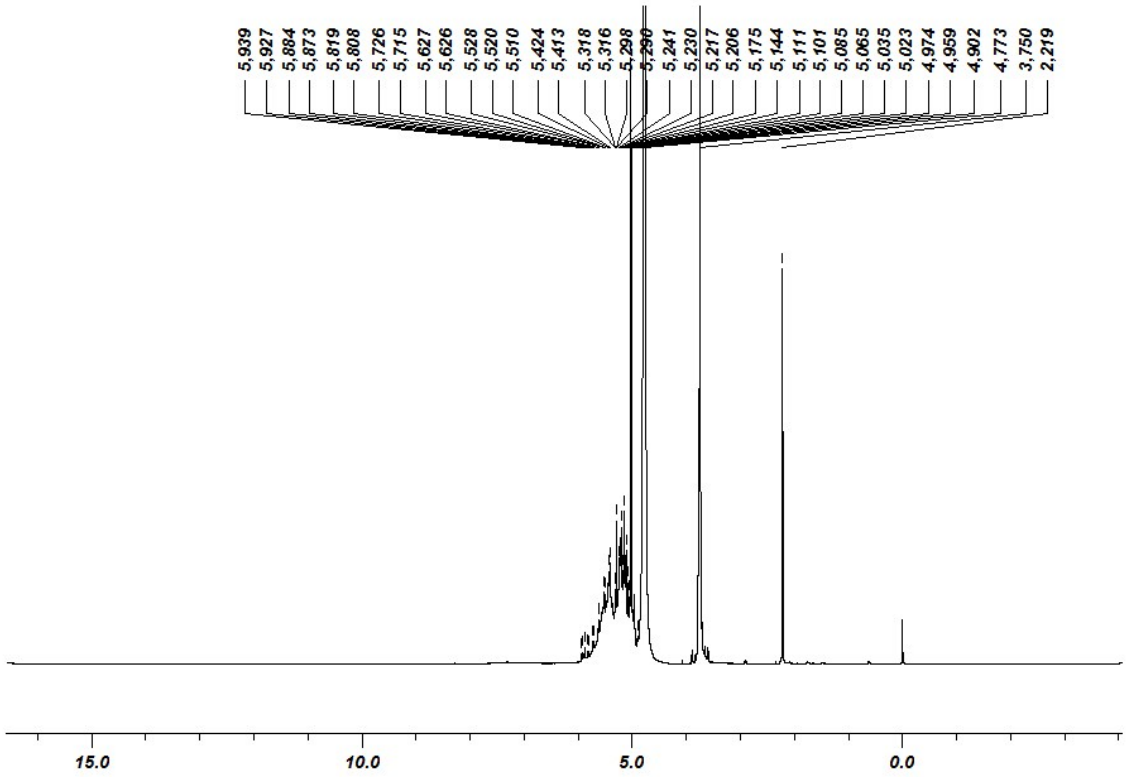


**Figure S6.34.** $^{1}H$ NMR spectrum of the 1:1 oligomers from 1,4-dioxane, recorded in $D_2O$.

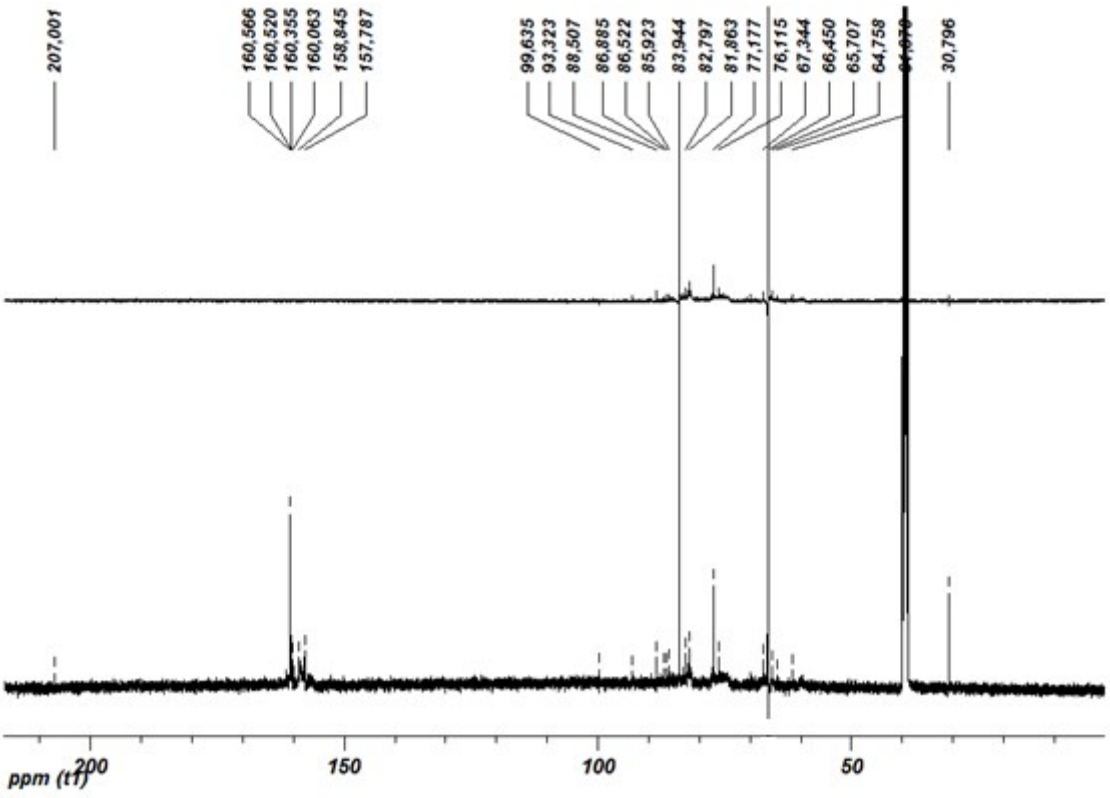


**Figure S6.35.** $^{13}$C NMR spectra (top: DEPT) of the 1:1 oligomers from 1,4-dioxane, recorded in DMSO-$d_6$.

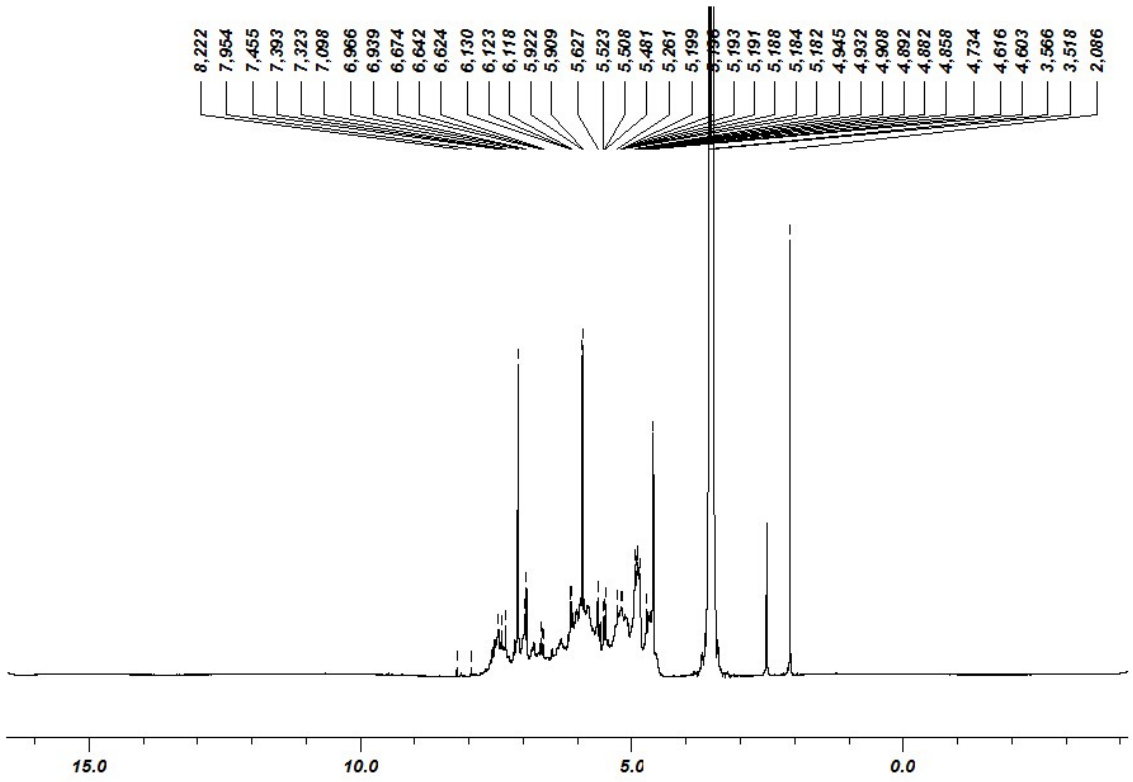


**Figure S6.36.** $^{1}$H NMR spectrum of the 1:1 oligomers from 1,4-dioxane, recorded in DMSO-$d_6$.

**1:2 STOICHIOMETRY**

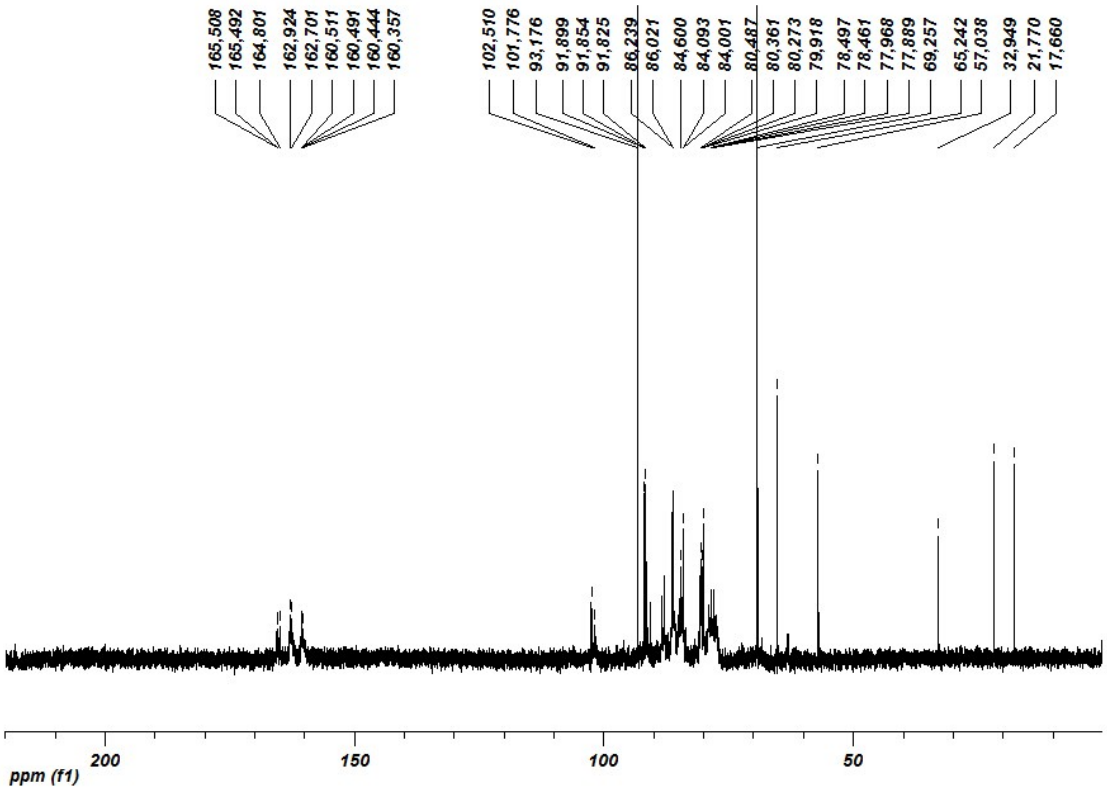


**Figure S6.37.** $^{13}C$ NMR spectra of the 1:2 oligomers from 1,4-dioxane, recorded in $D_2O$.

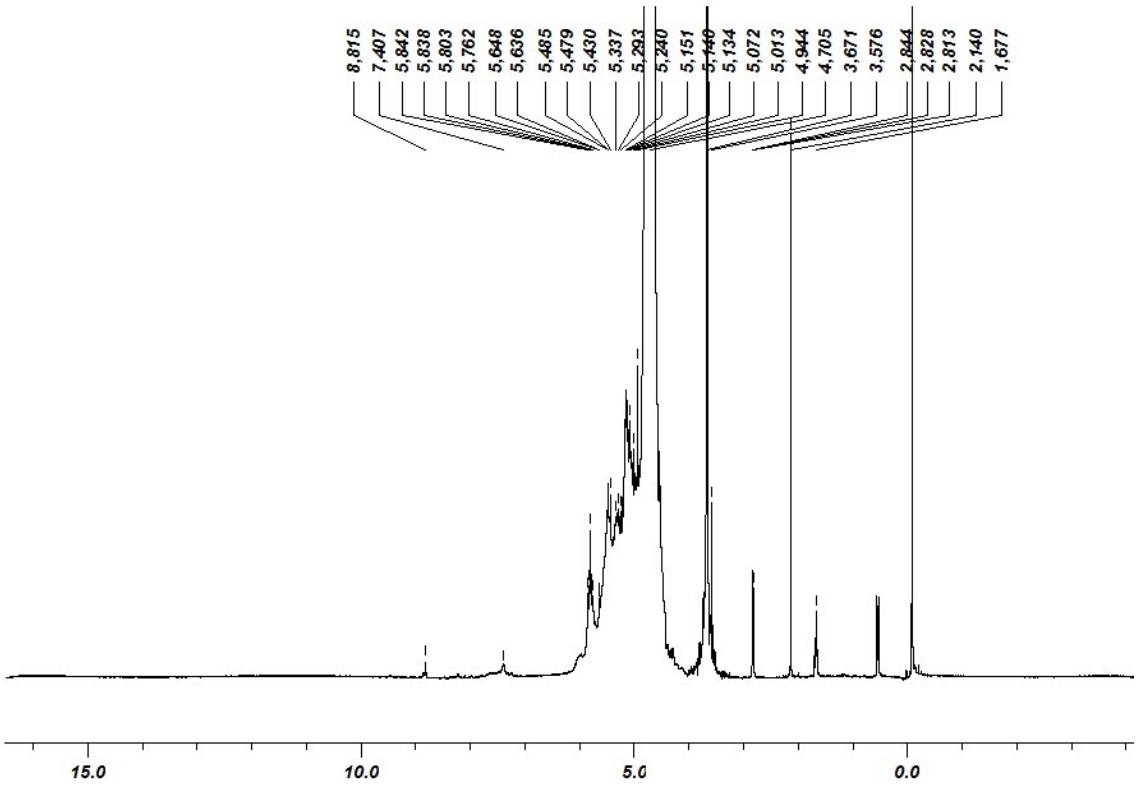


**Figure S6.38.** $^{1}H$ NMR spectrum of the 1:2 oligomers from 1,4-dioxane, recorded in $D_2O$.

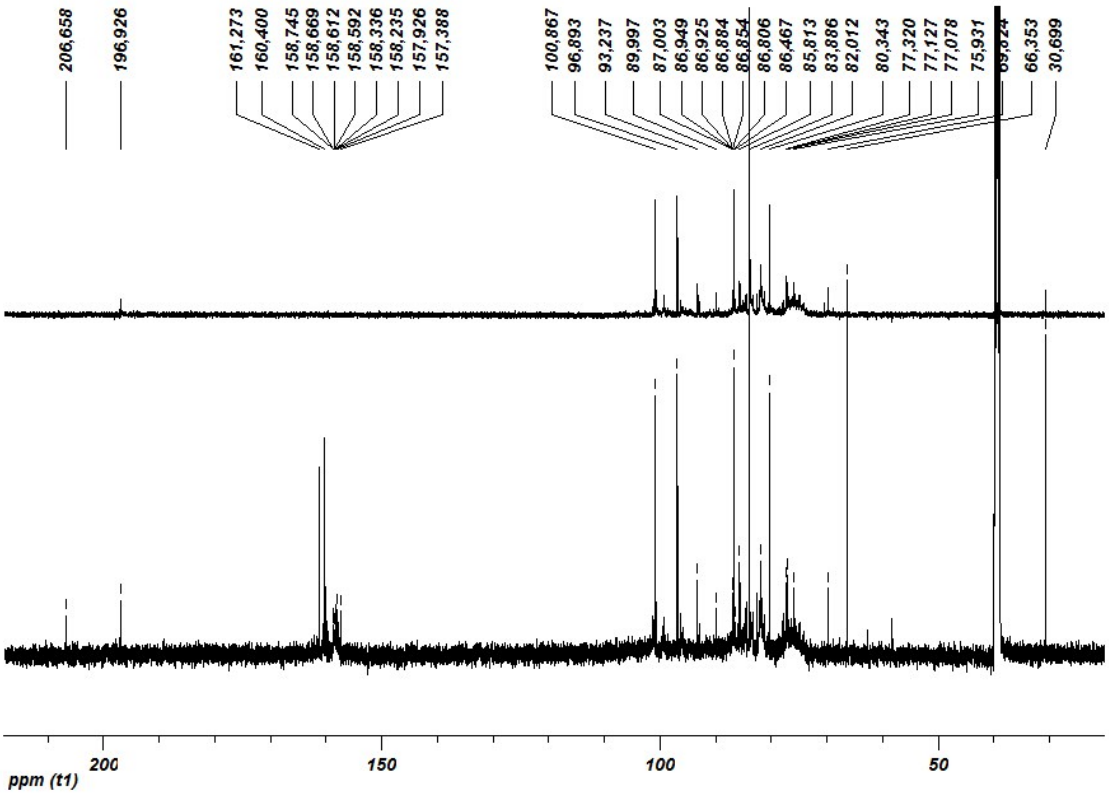


**Figure S6.39.** $^{13}$C NMR spectra (top: DEPT) of the 1:2 oligomers from 1,4-dioxane, recorded in DMSO-$d_6$. The resonance at 196.9 ppm is assigned to the aldehyde group.

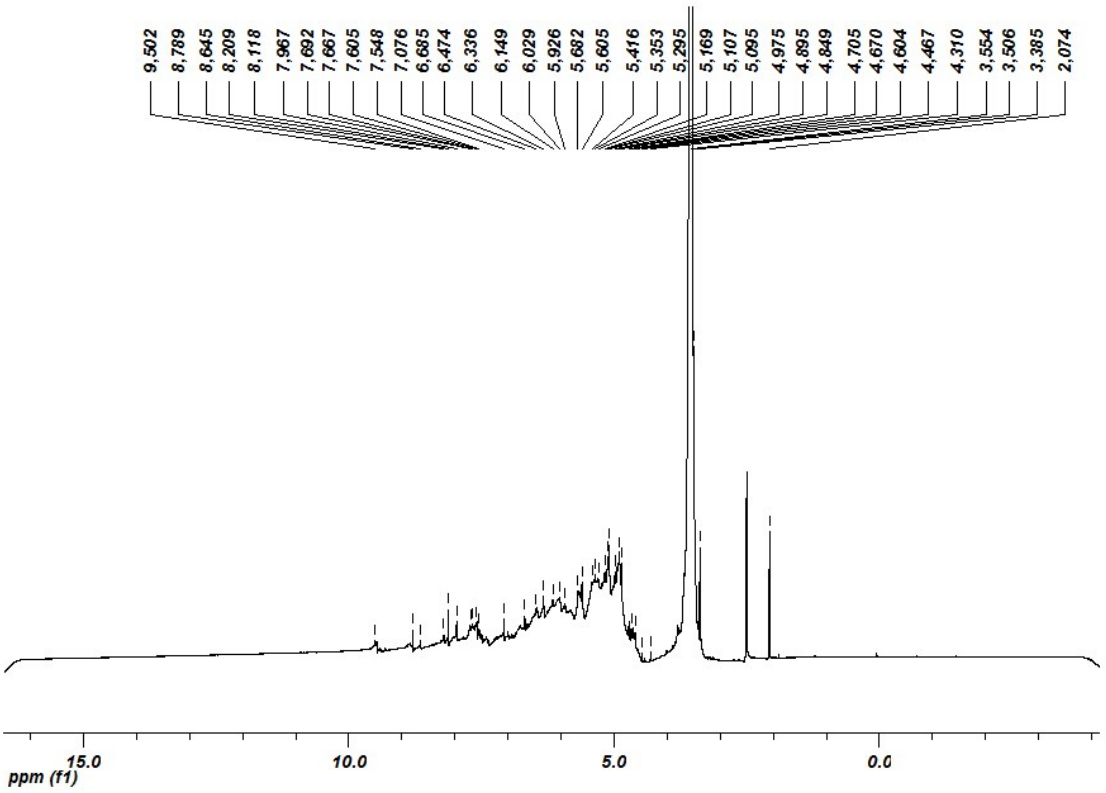


**Figure S6.40.** $^{1}$H NMR spectrum of the 1:2 oligomers from 1,4-dioxane, recorded in DMSO-$d_6$.

## 7. UV-VIS SPECTROPHOTOMETRY

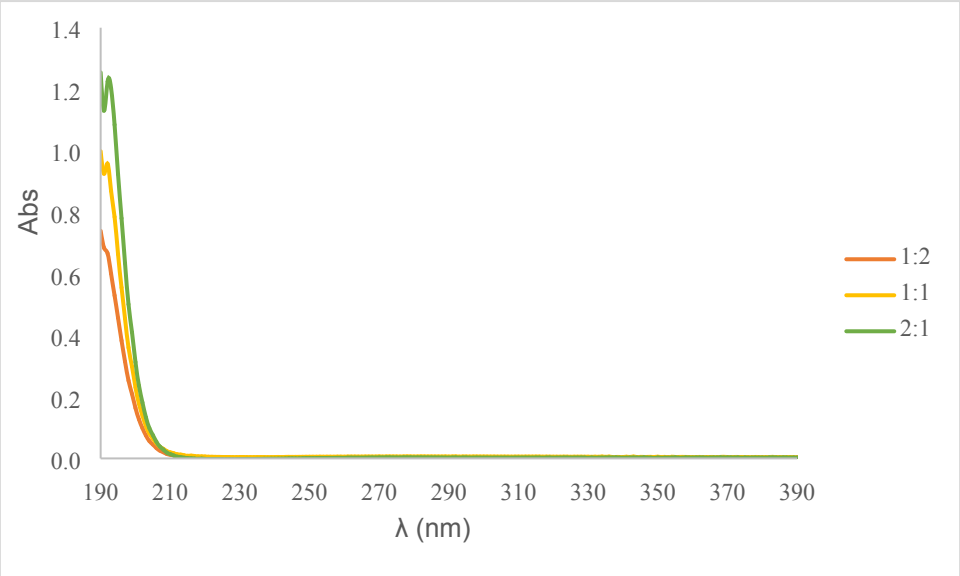


**Figure S7.1**. UV spectra of urea-glyoxal oligomerizations in aqueous solution (after 7 days); total masses: 0.03, 0.05 and 0.07 g/L for 1:2, 1:1 and 2:1 ratios, respectively.

.

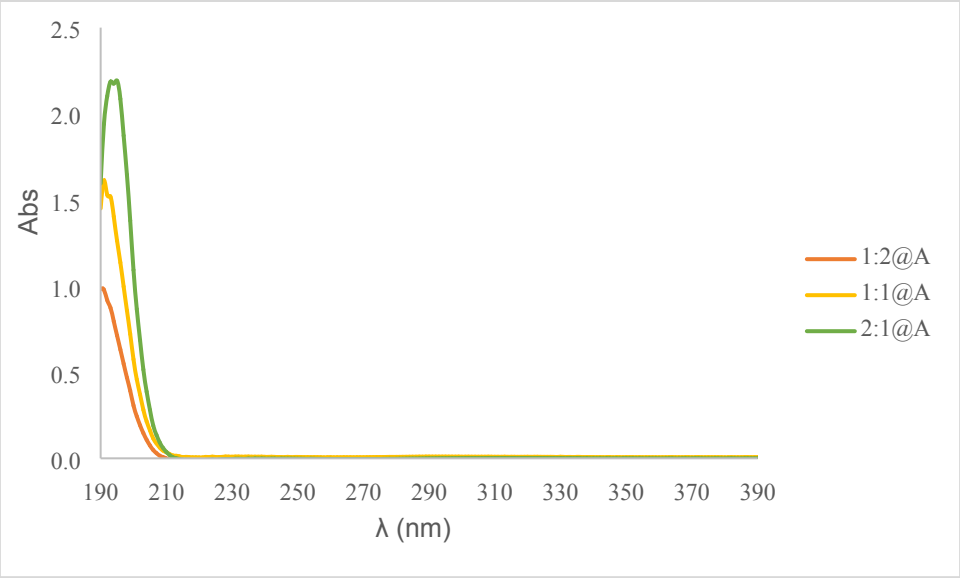


**Figure S7.2.** UV spectra (recorded in water) of urea-glyoxal oligomers isolated from acetone: 1:2 (0.03 g/L); 1:1 (0.05 g/L); 2:1 (0.07 g/L).

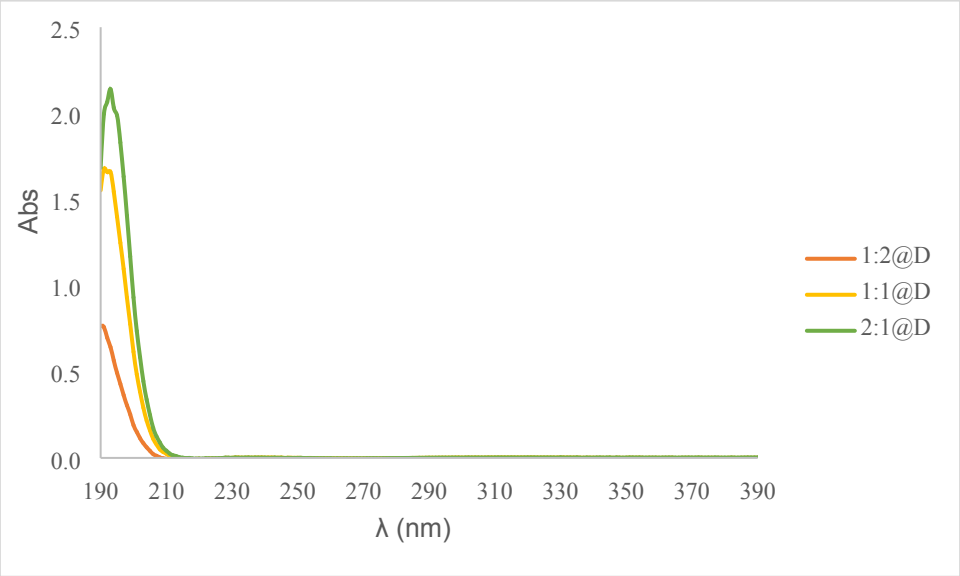


**Figure S7.3.** UV spectra (recorded in water) of urea-glyoxal oligomers isolated from 1,4-dioxane: 1:2 (0.03 g/L); 1:1 (0.05 g/L); 2:1 (0.07 g/L).

## 8. FUKUI INDEXES FOR COMPOUNDS 20, 21, 23-25.

It is well known that Fukui indices should be interpreted with caution in terms of reactivity trends.[1] Taking this premise into account, a surprising result is obtained concerning the indices at the unsubstituted nitrogen atoms. All of them show positive values of the dual descriptor with the sole exception of **24**. Given the structural similarity of **23** and **24**, we performed iterative conformational optimizations of such structures, all affording similar Fukui indices, either positive or negative, at the nitrogen atoms. This unexpected result can be understood through the visualization of the shape of their HOMO orbitals. Positive and negative parts of the Fukui functions can be roughly equal to their frontier molecular orbitals,[2] i.e. [$f^{-}(r) = \rho_N(r) - \rho_{N-1}(r) \sim \rho^{LUMO}(r)$ and $f^{+}(r) = \rho_{N+1}(r) - \rho_N(r) \sim \rho^{HOMO}(r)$; where $\rho(r)$ denotes electron density and $N$ the number of electrons of the system]. Since we are assessing the nucleophilic character of these compounds, attention was focused on the HOMO orbitals only. As shown in Figure S8.1, the HOMOs of **20**, **21** and **23** show a high electron delocalization through the whole system. In stark contrast, the HOMO of **24** shows a higher localization across the urea moiety, thus accounting for the nucleophilic character of the $NH_2$ functionality.

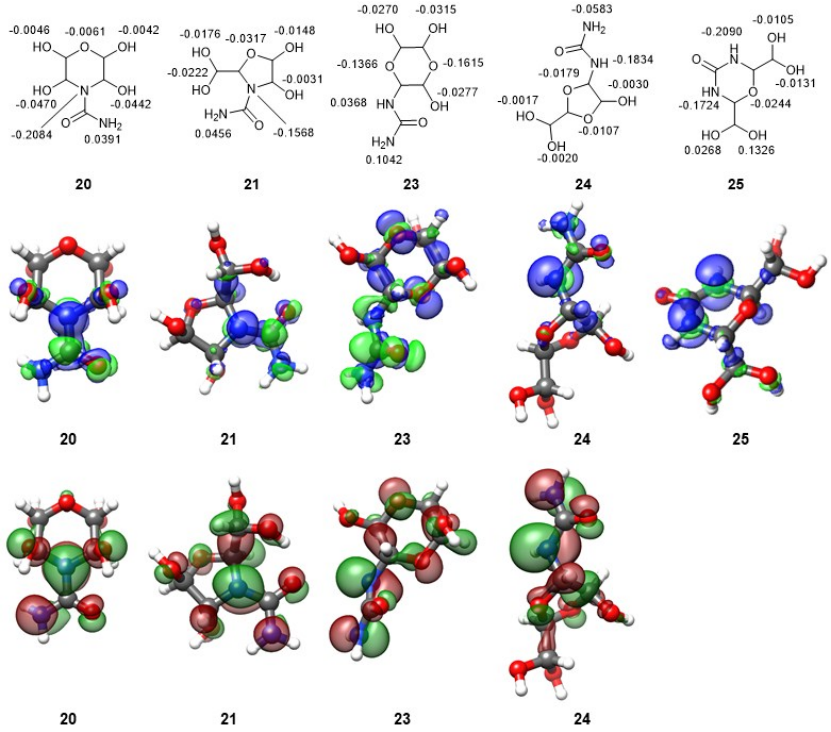


**Figure S8.1.** Heterocyclic fragments as potential growing units for higher oligomerization displaying values of dual descriptor of the Fukui function at heteroatoms positions (top). Dual descriptor ($\Delta f$) isosurfaces are based on electron density. Negative and positive values of $\Delta f$ are denoted in blue and green, respectively, with an isovalue of 0.005 (middle). The bottom line shows the isosurfaces with an isovalue of 0.02 for the HOMOs of heterocycles containing a pendant $NH_2$ group.

**References**

1. (a) T. Mineva, V. Parvanov, I. Petrov, N. Neshev and N. Russo, *J. Phys. Chem. A,* 2001, **105**, 1959-1967; (b) A. Cerda-Monje, R. Ormazábal-Toledo, C. Cárdenas, P. Fuentealba and R. Contreras, *J. Phys. Chem. B,* 2014, **118**, 3696-3701; (c) L. R. Domingo, M. Ríos-Gutiérrez and P. Pérez, *Molecules,* 2016, **21**, 748 (doi: 10.3390/molecules21060748).
2. R. G. Parr and W. Yang, *J. Am. Chem. Soc.*, 1984, **106**, 4049-4050.

## 9. REACTION PROFILES FOR THE FORMATION OF GLYCOLURIL 7 AND TRIAZINONE 36.

Figure S9.1 shows the energy profile accounting for the simplest glycoluril (**7**). Because of its formation involves the formal condensation of 2:1 urea:glyoxal units, both **15** and **16** (whose generation was discussed earlier, Figures 3 and 4) have been evaluated as putative precursors. Such diureas may lead to a common imidazolidin-2-one derivative (**33**), which would further evolve to **7**. Although the resulting protonated intermediates (**33H$_a$**$^+$ and **33H$_c$**$^+$) exhibit similar stability, in stark contrast the associated energies of the corresponding saddle points that lead to protonated heterocycles **33H$_b$**$^+$ and **33H$_d$**$^+$ are markedly different. The distinctive element between such transition structures lie in the electrophilic carbon partner, i.e. a nitrogen atom in **TS$_{33b}$** attacking an electrophilic carbon bearing a hydroxyl group, which contrasts with a electrophilic carbon linked to the ureido nitrogen in **TS$_{33a}$**. This scenario mirrors those highlighted previously in Figures 2 and 3, where the formation of **15** proceeding via **TS$_{14c}$** (Fig 3) is favored with respect to **11** proceeding via **TS$_{10c}$** (Fig. 2). That the reaction pathway occurs more easily on a electrophilic carbon attached to nitrogen, rather than oxygen, also arises from the carbonium-like character of such carbons (nearly planar) in the transition structures, and hence stabilized by the less electron-withdrawing atom. Compound **33** evolves into glycoluril **7** in following the same route as postulated for imidazolidin-2-ones (Figure 5). It should be pointed out that formation of glycoluril **7** is the most favored transformation in thermodynamic terms, of all computed reactions

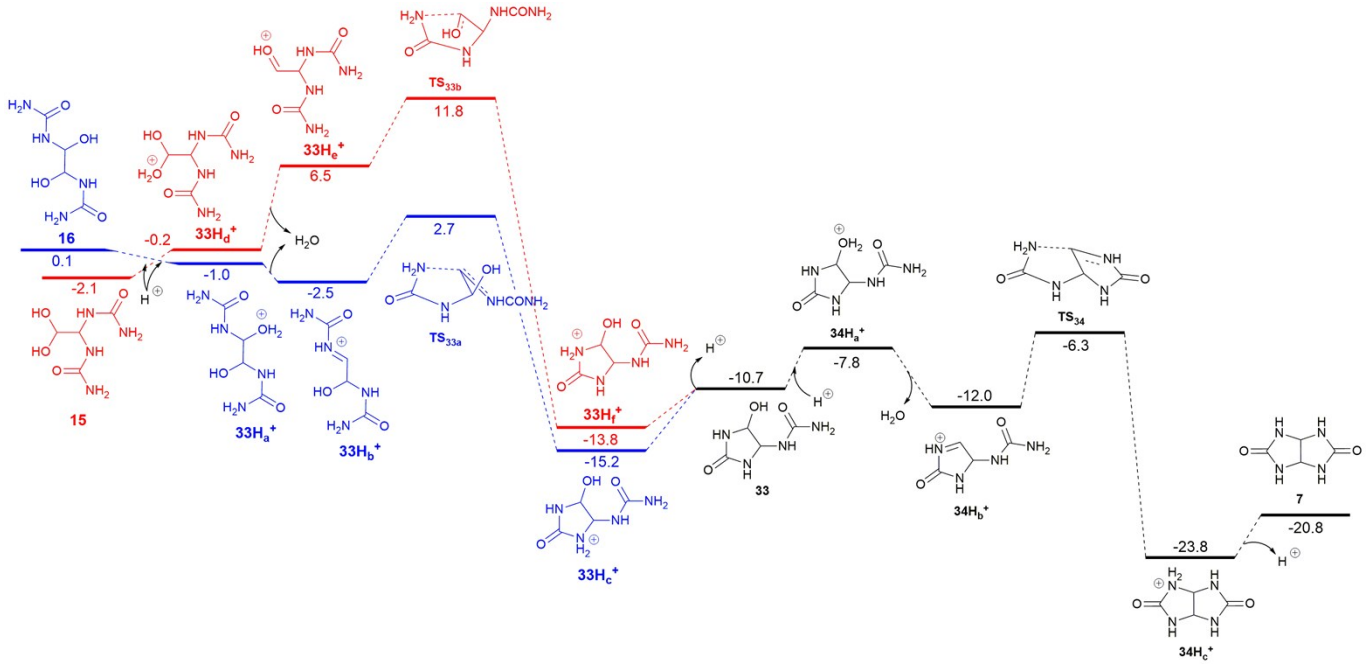


**Figure S9.1.** Energy profile showing the formation glycoluril rings from acyclic and cyclic intermediates generated by condensation of urea and glyoxal dihydrate. The label "c" in numbering denotes the corresponding complexes (not shown) generated from their preceding reagents. Relative electronic energies are referred to **1** and **3** and given in kcal mol$^{-1}$.

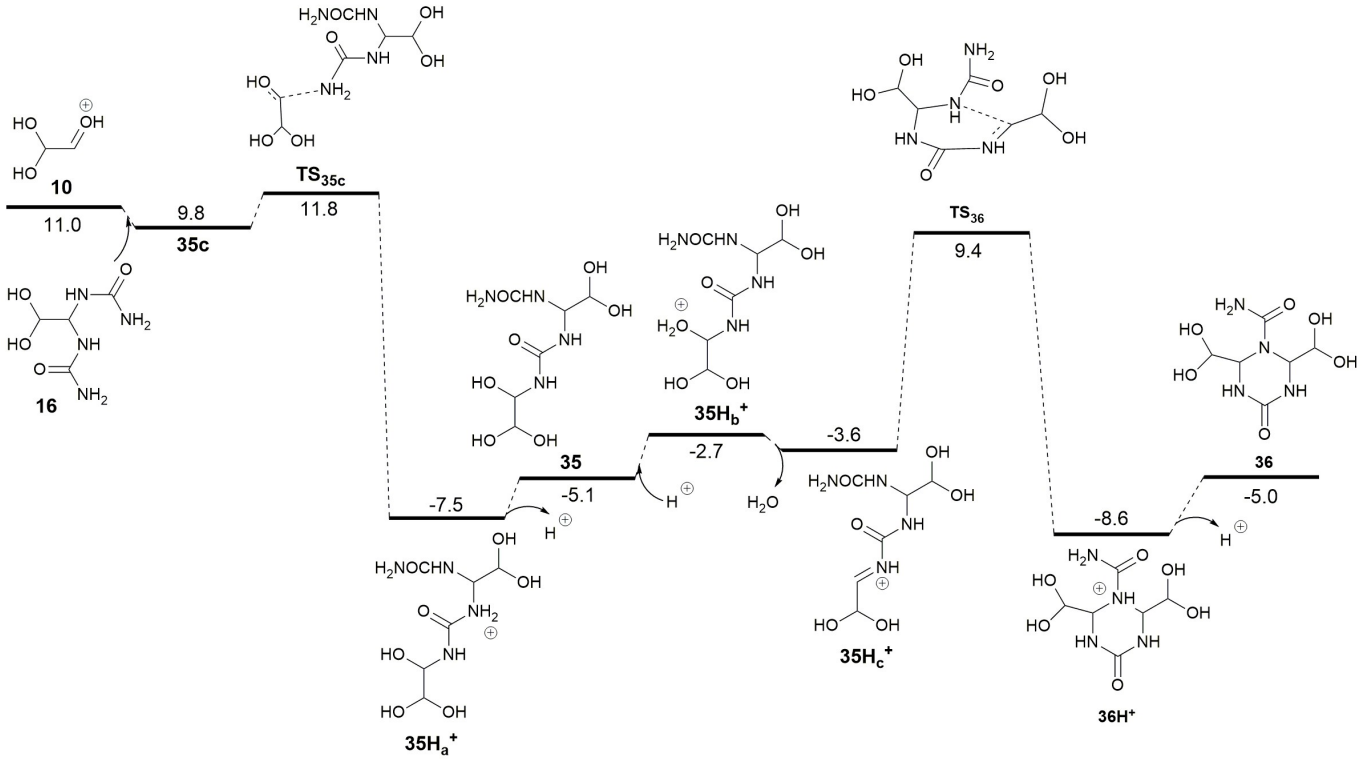


**Figure S9.2.** Energy landscape for the formation of saturated triazinone derivatives. The label "c" in numbering denotes the corresponding complexes (not shown) generated from their preceding reagents. Relative electronic energies are referred to **1** and **3** and given in kcal $mol^{-1}$.

## 10. CARTESIAN COORDINATES FOR ALL OPTIMIZED STRUCTURES AT THE M06-2X/6-311+G(d) LEVEL IN WATER (SMD)

**Cartesian coordinates for water, hydronium ion, and all stationary points involved in the formation of 11 at the M06-2X/6-311+G(d) level in water (SMD).**

Structure of **water**

```
Zero-point correction=                           0.021377 (Hartree/Particle)
 Thermal correction to Energy=                    0.024213
 Thermal correction to Enthalpy=                  0.025157
 Thermal correction to Gibbs Free Energy=         0.003736
 Sum of electronic and zero-point Energies=           -76.401771
 Sum of electronic and thermal Energies=              -76.398936
 Sum of electronic and thermal Enthalpies=            -76.397992
 Sum of electronic and thermal Free Energies=         -76.419413
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 8 | 0 | 0.000000 | 0.000000 | 0.115920 |
| 2 | 1 | 0 | 0.000000 | -0.769228 | -0.463680 |
| 3 | 1 | 0 | 0.000000 | 0.769228 | -0.463680 |

Structure of **hydronium ion**

```
Zero-point correction=                           0.035740 (Hartree/Particle)
 Thermal correction to Energy=                    0.038605
 Thermal correction to Enthalpy=                  0.039549
 Thermal correction to Gibbs Free Energy=         0.016627
 Sum of electronic and zero-point Energies=           -76.799633
 Sum of electronic and thermal Energies=              -76.796768
 Sum of electronic and thermal Enthalpies=            -76.795824
 Sum of electronic and thermal Free Energies=         -76.818746
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 8 | 0 | 0.000000 | 0.087211 | 0.000000 |
| 2 | 1 | 0 | -0.460670 | -0.233992 | 0.796791 |
| 3 | 1 | 0 | -0.460670 | -0.233992 | -0.796791 |
| 4 | 1 | 0 | 0.921340 | -0.229701 | 0.000000 |

Structure of **1**

```
Zero-point correction=                           0.062582 (Hartree/Particle)
 Thermal correction to Energy=                    0.067630
 Thermal correction to Enthalpy=                  0.068574
 Thermal correction to Gibbs Free Energy=         0.035499
 Sum of electronic and zero-point Energies=          -225.200751
 Sum of electronic and thermal Energies=             -225.195703
 Sum of electronic and thermal Enthalpies=           -225.194759
 Sum of electronic and thermal Free Energies=        -225.227834
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.000002 | 0.123566 | -0.002471 |
| 2 | 7 | 0 | -1.152769 | -0.592800 | -0.046956 |
| 3 | 1 | 0 | -1.145979 | -1.582651 | 0.149892 |

| | | | | | |
|---|---|---|---|---|---|
| 4 | 1 | 0 | -2.006644 | -0.091668 | 0.144674 |
| 5 | 7 | 0 | 1.152782 | -0.592785 | -0.046979 |
| 6 | 1 | 0 | 1.146010 | -1.582641 | 0.150048 |
| 7 | 1 | 0 | 2.006622 | -0.091621 | 0.144676 |
| 8 | 8 | 0 | -0.000011 | 1.363285 | 0.010385 |

## Structure of **3**

```
Zero-point correction=                           0.097383 (Hartree/Particle)
 Thermal correction to Energy=                    0.104227
 Thermal correction to Enthalpy=                  0.105172
 Thermal correction to Gibbs Free Energy=         0.067138
 Sum of electronic and zero-point Energies=           -380.601696
 Sum of electronic and thermal Energies=              -380.594852
 Sum of electronic and thermal Enthalpies=            -380.593908
 Sum of electronic and thermal Free Energies=         -380.631942
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.679593 | -0.049483 | 0.325167 |
| 2 | 1 | 0 | -0.578795 | -0.094582 | 1.412977 |
| 3 | 6 | 0 | 0.699592 | -0.025292 | -0.331609 |
| 4 | 1 | 0 | 0.585676 | -0.090263 | -1.419001 |
| 5 | 8 | 0 | 1.473243 | -1.123056 | 0.050954 |
| 6 | 8 | 0 | 1.393493 | 1.148520 | 0.032778 |
| 7 | 8 | 0 | -1.409500 | -1.189991 | -0.046483 |
| 8 | 8 | 0 | -1.318550 | 1.136242 | -0.078159 |
| 9 | 1 | 0 | 1.566237 | -1.126501 | 1.014454 |
| 10 | 1 | 0 | -1.508874 | -1.201141 | -1.009242 |
| 11 | 1 | 0 | -2.103207 | 1.279161 | 0.465681 |
| 12 | 1 | 0 | 0.809474 | 1.908258 | -0.098939 |

## Structure of **8**

```
Zero-point correction=                           0.062582 (Hartree/Particle)
 Thermal correction to Energy=                    0.067630
 Thermal correction to Enthalpy=                  0.068574
 Thermal correction to Gibbs Free Energy=         0.035499
 Sum of electronic and zero-point Energies=           -225.200751
 Sum of electronic and thermal Energies=              -225.195703
 Sum of electronic and thermal Enthalpies=            -225.194759
 Sum of electronic and thermal Free Energies=         -225.227834
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.000002 | 0.123566 | -0.002471 |
| 2 | 7 | 0 | -1.152769 | -0.592800 | -0.046956 |
| 3 | 1 | 0 | -1.145979 | -1.582651 | 0.149892 |
| 4 | 1 | 0 | -2.006644 | -0.091668 | 0.144674 |
| 5 | 7 | 0 | 1.152782 | -0.592785 | -0.046979 |
| 6 | 1 | 0 | 1.146010 | -1.582641 | 0.150048 |
| 7 | 1 | 0 | 2.006622 | -0.091621 | 0.144676 |
| 8 | 8 | 0 | -0.000011 | 1.363285 | 0.010385 |

## Structure of **9**

```
Zero-point correction=                           0.067674 (Hartree/Particle)
 Thermal correction to Energy=                    0.073268
 Thermal correction to Enthalpy=                  0.074212
 Thermal correction to Gibbs Free Energy=         0.038907
 Sum of electronic and zero-point Energies=           -304.184401
 Sum of electronic and thermal Energies=              -304.178807
 Sum of electronic and thermal Enthalpies=            -304.177862
```

```
 Sum of electronic and thermal Free Energies=         -304.213168
No imaginary frequencies.
```

```
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1          6           0       -0.501326    0.006680    0.419280
      2          1           0       -0.784954   -0.040128    1.471071
      3          8           0       -1.428547   -0.804001   -0.265720
      4          8           0       -0.541012    1.345151    0.023825
      5          1           0       -1.209766   -0.830720   -1.207795
      6          1           0        0.043617    1.477446   -0.737128
      7          6           0        0.890360   -0.590107    0.240528
      8          1           0        1.010136   -1.632500    0.571882
      9          8           0        1.795405    0.024659   -0.265215
 ---------------------------------------------------------------------
```

## Structure of **10**

```
Zero-point correction=                           0.080988 (Hartree/Particle)
 Thermal correction to Energy=                    0.086583
 Thermal correction to Enthalpy=                  0.087528
 Thermal correction to Gibbs Free Energy=         0.052306
 Sum of electronic and zero-point Energies=           -304.565714
 Sum of electronic and thermal Energies=              -304.560119
 Sum of electronic and thermal Enthalpies=            -304.559175
 Sum of electronic and thermal Free Energies=         -304.594397
No imaginary frequencies.
```

```
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1          6           0       -0.462436   -0.010804   -0.335230
      2          1           0       -0.303585   -0.041215   -1.412431
      3          6           0        0.848713   -0.097363    0.396150
      4          1           0        0.879694   -0.167227    1.484693
      5          8           0        1.901856   -0.041930   -0.261387
      6          8           0       -0.995982    1.245202   -0.022163
      7          8           0       -1.211732   -1.078412    0.145491
      8          1           0       -1.290976    1.254454    0.901620
      9          1           0       -1.879103   -1.331232   -0.506741
     10          1           0        2.723163   -0.064652    0.271809
 ---------------------------------------------------------------------
```

## Structure of **11**

```
Zero-point correction=                           0.136835 (Hartree/Particle)
 Thermal correction to Energy=                    0.147073
 Thermal correction to Enthalpy=                  0.148017
 Thermal correction to Gibbs Free Energy=         0.101347
 Sum of electronic and zero-point Energies=           -529.404289
 Sum of electronic and thermal Energies=              -529.394051
 Sum of electronic and thermal Enthalpies=            -529.393107
 Sum of electronic and thermal Free Energies=         -529.439777
No imaginary frequencies.
```

```
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1          6           0       -0.603032    0.674081   -0.517392
      2          8           0       -0.800611    1.835428    0.260609
      3          6           0       -1.328917   -0.451030    0.222326
      4          7           0        0.790353    0.417897   -0.789400
      5          1           0       -1.088960   -0.448021    1.285594
      6          1           0       -0.596001    2.609666   -0.277663
      7          8           0       -2.704703   -0.201748    0.046105
      8          1           0       -3.198353   -0.625142    0.758775
      9          8           0       -0.945767   -1.669077   -0.365352
     10          1           0       -1.260005   -2.395564    0.186914
```

| | | | | | |
|---|---|---|---|---|---|
| 11 | 1 | 0 | -1.080312 | 0.783239 | -1.494324 |
| 12 | 6 | 0 | 1.664405 | -0.014316 | 0.165258 |
| 13 | 1 | 0 | 1.069809 | 0.370045 | -1.759077 |
| 14 | 8 | 0 | 1.365392 | -0.055294 | 1.363750 |
| 15 | 7 | 0 | 2.906227 | -0.342273 | -0.279608 |
| 16 | 1 | 0 | 3.506464 | -0.815225 | 0.379243 |
| 17 | 1 | 0 | 3.062076 | -0.535243 | -1.258452 |

Structure of **8c**

```
Zero-point correction=                           0.157561 (Hartree/Particle)
 Thermal correction to Energy=                    0.172175
 Thermal correction to Enthalpy=                  0.173119
 Thermal correction to Gibbs Free Energy=         0.116159
 Sum of electronic and zero-point Energies=           -605.794714
 Sum of electronic and thermal Energies=              -605.780100
 Sum of electronic and thermal Enthalpies=            -605.779156
 Sum of electronic and thermal Free Energies=         -605.836116
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.694150 | -0.092471 | -0.081715 |
| 2 | 6 | 0 | -0.712096 | -1.219444 | 0.208245 |
| 3 | 1 | 0 | -0.523642 | -1.450221 | 1.268283 |
| 4 | 8 | 0 | -0.191652 | -1.844301 | -0.683332 |
| 5 | 7 | 0 | 1.383334 | 0.638649 | 0.920179 |
| 6 | 1 | 0 | 0.986629 | 0.950911 | 1.793958 |
| 7 | 6 | 0 | 1.194342 | 1.326434 | -0.225326 |
| 8 | 1 | 0 | -1.301545 | 0.545779 | -0.880101 |
| 9 | 1 | 0 | 1.861895 | -0.257725 | 0.874107 |
| 10 | 8 | 0 | -1.854556 | 0.630006 | 1.108076 |
| 11 | 1 | 0 | -2.196589 | 1.510983 | 0.909058 |
| 12 | 8 | 0 | -2.882346 | -0.717603 | -0.501173 |
| 13 | 1 | 0 | -3.420958 | -0.083703 | -0.991506 |
| 14 | 8 | 0 | 1.609733 | 0.908514 | -1.317914 |
| 15 | 7 | 0 | 0.560556 | 2.532559 | -0.115649 |
| 16 | 1 | 0 | -0.010076 | 2.702711 | 0.701558 |
| 17 | 1 | 0 | 0.193000 | 2.901939 | -0.981370 |
| 18 | 8 | 0 | 2.514466 | -1.990485 | 0.322869 |
| 19 | 1 | 0 | 2.813089 | -2.683094 | 0.922150 |
| 20 | 1 | 0 | 1.697218 | -2.312206 | -0.083282 |

Structure of **9c**

```
Zero-point correction=                           0.174167 (Hartree/Particle)
 Thermal correction to Energy=                    0.187430
 Thermal correction to Enthalpy=                  0.188374
 Thermal correction to Gibbs Free Energy=         0.133724
 Sum of electronic and zero-point Energies=           -606.209540
 Sum of electronic and thermal Energies=              -606.196277
 Sum of electronic and thermal Enthalpies=            -606.195333
 Sum of electronic and thermal Free Energies=         -606.249983
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.969365 | -0.072048 | 0.069591 |
| 2 | 6 | 0 | -2.820237 | 0.076923 | -0.058278 |
| 3 | 1 | 0 | 0.308065 | 0.516205 | 0.704865 |
| 4 | 8 | 0 | 0.403236 | -0.552418 | -1.053788 |
| 5 | 6 | 0 | 2.291830 | 0.612719 | -0.216794 |
| 6 | 1 | 0 | 2.123921 | 1.386984 | -0.968330 |
| 7 | 8 | 0 | 3.150628 | -0.383971 | -0.705754 |
| 8 | 8 | 0 | 2.746666 | 1.169111 | 0.985891 |
| 9 | 1 | 0 | 3.428918 | 1.824862 | 0.793615 |
| 10 | 1 | 0 | -4.366072 | -1.024166 | 0.640217 |

| | | | | | |
|---|---|---|---|---|---|
| 11 | 7 | 0 | -4.009879 | -0.084072 | 0.556568 |
| 12 | 7 | 0 | -2.467029 | 1.334782 | -0.401973 |
| 13 | 1 | 0 | -1.507167 | 1.493048 | -0.672380 |
| 14 | 8 | 0 | -2.084960 | -0.905088 | -0.301522 |
| 15 | 8 | 0 | 1.350128 | -1.226460 | 0.994203 |
| 16 | 1 | 0 | 0.569558 | -1.726391 | 1.299027 |
| 17 | 1 | 0 | 3.863629 | 0.009997 | -1.223381 |
| 18 | 1 | 0 | -2.987007 | 2.125301 | -0.050017 |
| 19 | 1 | 0 | -0.565823 | -0.710312 | -0.885109 |
| 20 | 1 | 0 | -4.673603 | 0.675009 | 0.604416 |
| 21 | 1 | 0 | 1.972600 | -1.840462 | 0.555548 |

## Structure of **10c**

```
Zero-point correction=                           0.146921 (Hartree/Particle)
 Thermal correction to Energy=                    0.157753
 Thermal correction to Enthalpy=                  0.158697
 Thermal correction to Gibbs Free Energy=         0.110330
 Sum of electronic and zero-point Energies=           -529.780440
 Sum of electronic and thermal Energies=              -529.769609
 Sum of electronic and thermal Enthalpies=            -529.768665
 Sum of electronic and thermal Free Energies=         -529.817031
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.496128 | -0.531783 | -0.314722 |
| 2 | 6 | 0 | -2.119894 | 0.828122 | -0.541065 |
| 3 | 6 | 0 | 2.217247 | -0.035041 | 0.043389 |
| 4 | 1 | 0 | -2.698603 | 1.081281 | -1.426345 |
| 5 | 1 | 0 | 0.791765 | 1.399656 | 0.202951 |
| 6 | 1 | 0 | -0.700738 | -0.637849 | -1.063219 |
| 7 | 8 | 0 | -2.436364 | -1.532331 | -0.565419 |
| 8 | 1 | 0 | -3.134550 | -1.503973 | 0.105623 |
| 9 | 8 | 0 | -0.999026 | -0.531179 | 0.980964 |
| 10 | 1 | 0 | -0.023312 | -0.721489 | 0.960270 |
| 11 | 7 | 0 | 3.409042 | -0.297781 | -0.527910 |
| 12 | 1 | 0 | 3.994882 | 0.445248 | -0.878465 |
| 13 | 1 | 0 | 3.839411 | -1.187847 | -0.328894 |
| 14 | 8 | 0 | 1.578597 | -0.929172 | 0.641042 |
| 15 | 1 | 0 | 2.187963 | 1.888390 | -0.683923 |
| 16 | 7 | 0 | 1.754938 | 1.231998 | -0.050612 |
| 17 | 1 | 0 | -1.440246 | 1.355082 | 1.079672 |
| 18 | 8 | 0 | -1.964680 | 1.714456 | 0.312960 |

## Structure of $I_{8c}$

```
Zero-point correction=                           0.160453 (Hartree/Particle)
 Thermal correction to Energy=                    0.173457
 Thermal correction to Enthalpy=                  0.174402
 Thermal correction to Gibbs Free Energy=         0.120878
 Sum of electronic and zero-point Energies=           -605.779166
 Sum of electronic and thermal Energies=              -605.766161
 Sum of electronic and thermal Enthalpies=            -605.765217
 Sum of electronic and thermal Free Energies=         -605.818741
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.655316 | -0.196949 | -0.214528 |
| 2 | 6 | 0 | -0.321083 | -0.885682 | 0.090564 |
| 3 | 1 | 0 | -0.443778 | -1.534047 | 0.975727 |
| 4 | 8 | 0 | 0.300450 | -1.386779 | -0.932720 |
| 5 | 7 | 0 | 0.617867 | 0.296366 | 0.817826 |
| 6 | 1 | 0 | 0.122222 | 0.647606 | 1.639781 |
| 7 | 6 | 0 | 1.011205 | 1.351716 | -0.103655 |
| 8 | 1 | 0 | -1.577672 | 0.412095 | -1.120241 |

| | | | | | |
|---|---|---|---|---|---|
| 9 | 1 | 0 | 1.463814 | -0.217846 | 1.095809 |
| 10 | 8 | 0 | -2.017863 | 0.600837 | 0.889350 |
| 11 | 1 | 0 | -2.805332 | 1.116923 | 0.670993 |
| 12 | 8 | 0 | -2.566377 | -1.248327 | -0.417142 |
| 13 | 1 | 0 | -3.300473 | -0.940682 | -0.962412 |
| 14 | 8 | 0 | 2.022786 | 1.209333 | -0.760694 |
| 15 | 7 | 0 | 0.171866 | 2.382807 | -0.137247 |
| 16 | 1 | 0 | -0.689668 | 2.380642 | 0.393690 |
| 17 | 1 | 0 | 0.351777 | 3.132600 | -0.790500 |
| 18 | 8 | 0 | 2.592081 | -1.785435 | 0.463765 |
| 19 | 1 | 0 | 2.644490 | -2.624638 | 0.933112 |
| 20 | 1 | 0 | 1.849032 | -1.858414 | -0.174781 |

## Structure of **11H⁺**

Zero-point correction= 0.150271 (Hartree/Particle)
Thermal correction to Energy= 0.160344
Thermal correction to Enthalpy= 0.161288
Thermal correction to Gibbs Free Energy= 0.115038
Sum of electronic and zero-point Energies= -529.813070
Sum of electronic and thermal Energies= -529.802996
Sum of electronic and thermal Enthalpies= -529.802052
Sum of electronic and thermal Free Energies= -529.848303
No imaginary frequencies.

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.497430 | 0.714383 | 0.462203 |
| 2 | 8 | 0 | 0.067774 | 1.681933 | -0.421727 |
| 3 | 6 | 0 | 1.459333 | -0.232856 | -0.246966 |
| 4 | 7 | 0 | -0.710748 | -0.069341 | 0.976112 |
| 5 | 1 | 0 | 1.081787 | -0.508523 | -1.232620 |
| 6 | 1 | 0 | -0.169320 | 2.493268 | 0.047028 |
| 7 | 8 | 0 | 2.657720 | 0.485408 | -0.362587 |
| 8 | 1 | 0 | 3.159385 | 0.152393 | -1.116916 |
| 9 | 8 | 0 | 1.588209 | -1.362142 | 0.576627 |
| 10 | 1 | 0 | 1.917844 | -2.109331 | 0.062208 |
| 11 | 1 | 0 | 0.968463 | 1.122190 | 1.357509 |
| 12 | 6 | 0 | -1.667137 | -0.407538 | -0.126847 |
| 13 | 1 | 0 | -0.362859 | -0.953340 | 1.374327 |
| 14 | 8 | 0 | -1.296226 | -1.188251 | -0.966805 |
| 15 | 7 | 0 | -2.825286 | 0.218095 | -0.024783 |
| 16 | 1 | 0 | -3.527938 | 0.047960 | -0.733394 |
| 17 | 1 | 0 | -3.034869 | 0.869023 | 0.720120 |
| 18 | 1 | 0 | -1.157837 | 0.465560 | 1.728036 |

## Structure **TS1$_{8c}$**

Zero-point correction= 0.159953 (Hartree/Particle)
Thermal correction to Energy= 0.172429
Thermal correction to Enthalpy= 0.173373
Thermal correction to Gibbs Free Energy= 0.121393
Sum of electronic and zero-point Energies= -605.779621
Sum of electronic and thermal Energies= -605.767145
Sum of electronic and thermal Enthalpies= -605.766201
Sum of electronic and thermal Free Energies= -605.818181
One imaginary frequency ($cm^{-1}$): 66.5677i

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.635378 | -0.220813 | -0.197893 |
| 2 | 6 | 0 | -0.316558 | -0.925259 | 0.129843 |
| 3 | 1 | 0 | -0.424328 | -1.519650 | 1.053290 |
| 4 | 8 | 0 | 0.305783 | -1.460261 | -0.862767 |
| 5 | 7 | 0 | 0.640618 | 0.325815 | 0.823422 |
| 6 | 1 | 0 | 0.162794 | 0.673055 | 1.656002 |
| 7 | 6 | 0 | 0.963541 | 1.363483 | -0.130948 |

| | | | | | |
|---|---|---|---|---|---|
| 8 | 1 | 0 | -1.519273 | 0.426262 | -1.072961 |
| 9 | 1 | 0 | 1.503559 | -0.174790 | 1.073082 |
| 10 | 8 | 0 | -2.035757 | 0.528933 | 0.924633 |
| 11 | 1 | 0 | -2.769893 | 1.108212 | 0.682107 |
| 12 | 8 | 0 | -2.542821 | -1.256751 | -0.483221 |
| 13 | 1 | 0 | -3.258397 | -0.918297 | -1.035285 |
| 14 | 8 | 0 | 1.905114 | 1.201278 | -0.883827 |
| 15 | 7 | 0 | 0.143658 | 2.412812 | -0.101203 |
| 16 | 1 | 0 | -0.665655 | 2.438008 | 0.504537 |
| 17 | 1 | 0 | 0.268338 | 3.143218 | -0.788316 |
| 18 | 8 | 0 | 2.670318 | -1.678505 | 0.460330 |
| 19 | 1 | 0 | 2.812190 | -2.487779 | 0.962851 |
| 20 | 1 | 0 | 1.910003 | -1.840650 | -0.138026 |

Structure **$TS2_{8c}$**

Zero-point correction= 0.157167 (Hartree/Particle)
Thermal correction to Energy= 0.168602
Thermal correction to Enthalpy= 0.169546
Thermal correction to Gibbs Free Energy= 0.120332
Sum of electronic and zero-point Energies= -605.769471
Sum of electronic and thermal Energies= -605.758037
Sum of electronic and thermal Enthalpies= -605.757093
Sum of electronic and thermal Free Energies= -605.806306
One imaginary frequency ($cm^{-1}$): 717.8665i

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.319298 | -0.836072 | -0.282318 |
| 2 | 8 | 0 | -0.284296 | -1.589872 | 0.678652 |
| 3 | 6 | 0 | 1.574988 | -0.144340 | 0.220138 |
| 4 | 7 | 0 | -0.687781 | 0.230247 | -0.784876 |
| 5 | 1 | 0 | -1.572456 | -0.366096 | -0.910019 |
| 6 | 1 | 0 | 1.364942 | 0.437286 | 1.124074 |
| 7 | 8 | 0 | -2.416124 | -1.712534 | -0.447199 |
| 8 | 1 | 0 | -1.295736 | -1.825023 | 0.243162 |
| 9 | 1 | 0 | -2.457007 | -2.388370 | -1.131575 |
| 10 | 8 | 0 | 2.493634 | -1.165388 | 0.506870 |
| 11 | 1 | 0 | 3.151060 | -0.841710 | 1.135679 |
| 12 | 8 | 0 | 2.016511 | 0.694617 | -0.818249 |
| 13 | 1 | 0 | 2.637068 | 1.346279 | -0.467722 |
| 14 | 1 | 0 | 0.550987 | -1.390928 | -1.200723 |
| 15 | 6 | 0 | -0.998509 | 1.289255 | 0.192597 |
| 16 | 1 | 0 | -0.364229 | 0.608687 | -1.678362 |
| 17 | 8 | 0 | -1.765560 | 1.037356 | 1.095418 |
| 18 | 7 | 0 | -0.384505 | 2.441210 | -0.047593 |
| 19 | 1 | 0 | -0.544802 | 3.214873 | 0.583635 |
| 20 | 1 | 0 | 0.308201 | 2.538323 | -0.777295 |

Structure **$TS_{9c}$**

Zero-point correction= 0.170929 (Hartree/Particle)
Thermal correction to Energy= 0.184676
Thermal correction to Enthalpy= 0.185620
Thermal correction to Gibbs Free Energy= 0.130745
Sum of electronic and zero-point Energies= -606.186232
Sum of electronic and thermal Energies= -606.172484
Sum of electronic and thermal Enthalpies= -606.171540
Sum of electronic and thermal Free Energies= -606.226415
One imaginary frequency ($cm^{-1}$): 235.1991i

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.574122 | 0.532599 | 0.195679 |
| 2 | 6 | 0 | 2.369088 | 0.036682 | 0.151721 |
| 3 | 1 | 0 | -0.654041 | 0.950716 | 1.188224 |
| 4 | 8 | 0 | -0.132757 | 1.217655 | -0.771869 |

| | | | | | |
|---|---|---|---|---|---|
| 5 | 6 | 0 | -1.091641 | -0.850370 | -0.153079 |
| 6 | 1 | 0 | -0.247065 | -1.474561 | -0.454464 |
| 7 | 8 | 0 | -1.978427 | -0.725530 | -1.229903 |
| 8 | 8 | 0 | -1.694891 | -1.333817 | 1.008501 |
| 9 | 1 | 0 | -1.791478 | -2.292781 | 0.943174 |
| 10 | 1 | 0 | 3.231612 | -0.721119 | -1.522653 |
| 11 | 7 | 0 | 2.638116 | -0.934400 | -0.735039 |
| 12 | 7 | 0 | 1.441564 | -0.286174 | 1.138474 |
| 13 | 1 | 0 | 1.535449 | 0.293058 | 1.965898 |
| 14 | 8 | 0 | 2.835457 | 1.173776 | 0.081372 |
| 15 | 8 | 0 | -2.810333 | 1.406659 | 0.260842 |
| 16 | 1 | 0 | -3.200923 | 1.218888 | 1.122633 |
| 17 | 1 | 0 | -1.860925 | -1.472465 | -1.829325 |
| 18 | 1 | 0 | 1.335600 | -1.271203 | 1.361629 |
| 19 | 1 | 0 | 0.157030 | 2.113485 | -0.519958 |
| 20 | 1 | 0 | 2.225730 | -1.853268 | -0.667861 |
| 21 | 1 | 0 | -3.261094 | 0.829864 | -0.368818 |

Structure **$TS_{10c}$**

```
Zero-point correction=                           0.145795 (Hartree/Particle)
 Thermal correction to Energy=                    0.156258
 Thermal correction to Enthalpy=                  0.157202
 Thermal correction to Gibbs Free Energy=         0.109392
 Sum of electronic and zero-point Energies=           -529.780334
 Sum of electronic and thermal Energies=              -529.769870
 Sum of electronic and thermal Enthalpies=            -529.768926
 Sum of electronic and thermal Free Energies=         -529.816737
One imaginary frequency (cm-1): 78.6805i
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.302277 | -0.568341 | -0.275845 |
| 2 | 6 | 0 | -1.745759 | 0.840032 | -0.598974 |
| 3 | 6 | 0 | 2.022853 | -0.008917 | 0.086264 |
| 4 | 1 | 0 | -2.060124 | 1.153843 | -1.591432 |
| 5 | 1 | 0 | 0.915824 | 1.548979 | 0.718898 |
| 6 | 1 | 0 | -0.405257 | -0.775564 | -0.872225 |
| 7 | 8 | 0 | -2.371072 | -1.381867 | -0.649897 |
| 8 | 1 | 0 | -2.039647 | -2.263996 | -0.863516 |
| 9 | 8 | 0 | -1.036544 | -0.614162 | 1.089395 |
| 10 | 1 | 0 | -0.071118 | -0.764343 | 1.225211 |
| 11 | 7 | 0 | 3.029628 | -0.308003 | -0.747642 |
| 12 | 1 | 0 | 3.366489 | 0.345285 | -1.438626 |
| 13 | 1 | 0 | 3.457005 | -1.219269 | -0.686230 |
| 14 | 8 | 0 | 1.633372 | -0.810674 | 0.960627 |
| 15 | 1 | 0 | 1.852105 | 1.890209 | -0.667042 |
| 16 | 7 | 0 | 1.397954 | 1.190443 | -0.095301 |
| 17 | 1 | 0 | -1.475772 | 1.279604 | 1.164017 |
| 18 | 8 | 0 | -1.773442 | 1.688143 | 0.305236 |

**Cartesian coordinates of all stationary points involved in the formation of 15 at the M06-2X/6-311+G(d) level in water (SMD).**

Structure of **12**

```
Zero-point correction=                           0.108106 (Hartree/Particle)
 Thermal correction to Energy=                    0.116778
 Thermal correction to Enthalpy=                  0.117722
 Thermal correction to Gibbs Free Energy=         0.074165
 Sum of electronic and zero-point Energies=           -452.973705
 Sum of electronic and thermal Energies=              -452.965033
 Sum of electronic and thermal Enthalpies=            -452.964089
 Sum of electronic and thermal Free Energies=         -453.007645
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.363645 | 0.109648 | 0.162928 |
| 2 | 1 | 0 | -0.263885 | 0.671752 | 1.095696 |
| 3 | 6 | 0 | -1.768780 | -0.198386 | -0.269100 |
| 4 | 7 | 0 | 0.632262 | -0.267833 | -0.528160 |
| 5 | 1 | 0 | -1.787734 | -0.741332 | -1.215685 |
| 6 | 8 | 0 | -2.329752 | -0.976457 | 0.760550 |
| 7 | 1 | 0 | -3.117286 | -1.427099 | 0.429794 |
| 8 | 8 | 0 | -2.408169 | 1.048769 | -0.397427 |
| 9 | 1 | 0 | -3.212640 | 0.947761 | -0.922270 |
| 10 | 6 | 0 | 1.906953 | 0.120180 | -0.008995 |
| 11 | 8 | 0 | 2.106898 | 1.193453 | 0.549054 |
| 12 | 7 | 0 | 2.847652 | -0.799801 | -0.236194 |
| 13 | 1 | 0 | 2.632172 | -1.652956 | -0.728761 |
| 14 | 1 | 0 | 3.790977 | -0.639466 | 0.085293 |

## Structure of **13**

```
Zero-point correction=                           0.149122 (Hartree/Particle)
 Thermal correction to Energy=                    0.159598
 Thermal correction to Enthalpy=                  0.160542
 Thermal correction to Gibbs Free Energy=         0.113585
 Sum of electronic and zero-point Energies=           -529.800949
 Sum of electronic and thermal Energies=              -529.790474
 Sum of electronic and thermal Enthalpies=            -529.789530
 Sum of electronic and thermal Free Energies=         -529.836487
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.496741 | 0.440483 | -0.645873 |
| 2 | 8 | 0 | -0.645407 | 1.783563 | 0.059738 |
| 3 | 6 | 0 | -1.335975 | -0.502197 | 0.216905 |
| 4 | 7 | 0 | 0.852429 | 0.150937 | -0.831684 |
| 5 | 1 | 0 | -0.904320 | -0.660675 | 1.202449 |
| 6 | 1 | 0 | -1.582378 | 1.915637 | 0.322461 |
| 7 | 8 | 0 | -2.583691 | 0.143174 | 0.326575 |
| 8 | 1 | 0 | -3.040893 | -0.162273 | 1.119895 |
| 9 | 8 | 0 | -1.411411 | -1.696532 | -0.504776 |
| 10 | 1 | 0 | -1.581059 | -2.427811 | 0.102029 |
| 11 | 1 | 0 | -0.978413 | 0.566973 | -1.613014 |
| 12 | 6 | 0 | 1.735782 | -0.106043 | 0.209867 |
| 13 | 1 | 0 | 1.232950 | 0.341618 | -1.749600 |
| 14 | 8 | 0 | 1.360673 | -0.158082 | 1.378327 |
| 15 | 7 | 0 | 3.009964 | -0.281759 | -0.174741 |
| 16 | 1 | 0 | 3.700399 | -0.489193 | 0.530679 |
| 17 | 1 | 0 | 3.289762 | -0.273640 | -1.144497 |
| 18 | 1 | 0 | -0.352491 | 2.534681 | -0.489725 |

## Structure of **14**

```
Zero-point correction=                           0.121253 (Hartree/Particle)
 Thermal correction to Energy=                    0.129800
 Thermal correction to Enthalpy=                  0.130744
 Thermal correction to Gibbs Free Energy=         0.087925
 Sum of electronic and zero-point Energies=           -453.391851
 Sum of electronic and thermal Energies=              -453.383304
 Sum of electronic and thermal Enthalpies=            -453.382359
 Sum of electronic and thermal Free Energies=         -453.425179
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.854737 | -0.039850 | 0.327038 |

| | | | | | |
|---|---|---|---|---|---|
| 2 | 6 | 0 | -0.438569 | -0.518630 | 0.221927 |
| 3 | 1 | 0 | -0.210990 | -1.577671 | 0.297615 |
| 4 | 7 | 0 | 0.518296 | 0.309851 | 0.068689 |
| 5 | 6 | 0 | 1.917694 | -0.141195 | -0.010720 |
| 6 | 1 | 0 | -2.156263 | -0.178711 | 1.372761 |
| 7 | 7 | 0 | 2.754092 | 0.864914 | -0.199409 |
| 8 | 1 | 0 | 2.449773 | 1.827305 | -0.271135 |
| 9 | 1 | 0 | 3.742483 | 0.660299 | -0.269413 |
| 10 | 8 | 0 | 2.156805 | -1.318096 | 0.095993 |
| 11 | 8 | 0 | -2.605324 | -0.858406 | -0.523538 |
| 12 | 1 | 0 | -3.519328 | -0.888263 | -0.212170 |
| 13 | 8 | 0 | -1.881323 | 1.309877 | -0.028001 |
| 14 | 1 | 0 | -2.610309 | 1.757484 | 0.420198 |
| 15 | 1 | 0 | 0.290328 | 1.307257 | -0.007914 |

## Structure of **15**

```
Zero-point correction=                           0.176629 (Hartree/Particle)
 Thermal correction to Energy=                    0.189856
 Thermal correction to Enthalpy=                  0.190801
 Thermal correction to Gibbs Free Energy=         0.137119
 Sum of electronic and zero-point Energies=           -678.212614
 Sum of electronic and thermal Energies=              -678.199386
 Sum of electronic and thermal Enthalpies=            -678.198442
 Sum of electronic and thermal Free Energies=         -678.252124
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 1.742236 | -1.206417 | 0.145777 |
| 2 | 6 | 0 | 0.483476 | -0.362900 | 0.291396 |
| 3 | 6 | 0 | -1.847107 | -1.092294 | 0.045432 |
| 4 | 1 | 0 | 0.177588 | -0.381942 | 1.334932 |
| 5 | 7 | 0 | 0.786885 | 0.998781 | -0.100591 |
| 6 | 6 | 0 | -0.137924 | 1.985004 | 0.089524 |
| 7 | 1 | 0 | 1.516170 | -2.242812 | 0.404863 |
| 8 | 7 | 0 | 0.110893 | 3.159861 | -0.551216 |
| 9 | 1 | 0 | 1.043074 | 3.349773 | -0.891738 |
| 10 | 1 | 0 | -0.415820 | 3.958000 | -0.227079 |
| 11 | 8 | 0 | -1.146070 | 1.810332 | 0.781371 |
| 12 | 8 | 0 | 2.716764 | -0.688841 | 1.017210 |
| 13 | 1 | 0 | 3.427761 | -1.334823 | 1.115342 |
| 14 | 8 | 0 | 2.150860 | -1.122881 | -1.200149 |
| 15 | 1 | 0 | 2.771143 | -1.836346 | -1.395272 |
| 16 | 7 | 0 | -2.861373 | -1.155812 | -0.854159 |
| 17 | 1 | 0 | -2.670113 | -1.241414 | -1.841694 |
| 18 | 1 | 0 | -3.741994 | -1.520409 | -0.522429 |
| 19 | 8 | 0 | -2.045547 | -1.178241 | 1.261747 |
| 20 | 1 | 0 | -0.532756 | -0.779815 | -1.487001 |
| 21 | 7 | 0 | -0.593307 | -0.944712 | -0.489260 |
| 22 | 1 | 0 | 1.471115 | 1.119657 | -0.837552 |

## Structure of **12c**

```
Zero-point correction=                           0.199515 (Hartree/Particle)
 Thermal correction to Energy=                    0.216223
 Thermal correction to Enthalpy=                  0.217167
 Thermal correction to Gibbs Free Energy=         0.155279
 Sum of electronic and zero-point Energies=           -754.594451
 Sum of electronic and thermal Energies=              -754.577744
 Sum of electronic and thermal Enthalpies=            -754.576800
 Sum of electronic and thermal Free Energies=         -754.638687
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -2.015372 | 0.702304 | -0.952474 |

| | | | | | |
|---|---|---|---|---|---|
| 2 | 6 | 0 | -0.518225 | 0.872008 | -0.943161 |
| 3 | 6 | 0 | 0.877020 | -1.885698 | 0.076156 |
| 4 | 1 | 0 | 0.009225 | 0.356750 | -1.749607 |
| 5 | 7 | 0 | 0.082891 | 1.563799 | -0.064820 |
| 6 | 6 | 0 | 1.515476 | 1.576892 | -0.187370 |
| 7 | 1 | 0 | 0.378282 | -0.809950 | 1.710954 |
| 8 | 8 | 0 | -1.475166 | -0.492315 | 2.274253 |
| 9 | 1 | 0 | -1.866057 | 0.127671 | 1.633368 |
| 10 | 1 | 0 | -1.784409 | -1.366934 | 2.010444 |
| 11 | 1 | 0 | -2.431807 | 1.278924 | -1.784014 |
| 12 | 7 | 0 | 2.081952 | 2.207227 | 0.843598 |
| 13 | 1 | 0 | 1.516737 | 2.587543 | 1.587132 |
| 14 | 1 | 0 | 3.087594 | 2.279595 | 0.896827 |
| 15 | 8 | 0 | 2.140249 | 1.080048 | -1.117679 |
| 16 | 8 | 0 | -2.541993 | 1.164565 | 0.266675 |
| 17 | 1 | 0 | -3.506109 | 1.174211 | 0.203997 |
| 18 | 8 | 0 | -2.349279 | -0.639314 | -1.197625 |
| 19 | 1 | 0 | -1.743309 | -1.224568 | -0.701396 |
| 20 | 7 | 0 | 1.921851 | -2.281026 | -0.696117 |
| 21 | 1 | 0 | 2.814923 | -1.820266 | -0.590965 |
| 22 | 1 | 0 | 1.689203 | -2.598264 | -1.625754 |
| 23 | 8 | 0 | -0.295492 | -2.194491 | -0.221191 |
| 24 | 1 | 0 | 2.089767 | -0.837569 | 1.358945 |
| 25 | 7 | 0 | 1.165592 | -1.216877 | 1.211012 |

## Structure of **13c**

```
Zero-point correction=                           0.214650 (Hartree/Particle)
 Thermal correction to Energy=                    0.231026
 Thermal correction to Enthalpy=                  0.231970
 Thermal correction to Gibbs Free Energy=         0.171576
 Sum of electronic and zero-point Energies=           -755.011621
 Sum of electronic and thermal Energies=              -754.995245
 Sum of electronic and thermal Enthalpies=            -754.994301
 Sum of electronic and thermal Free Energies=         -755.054694
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 1.100375 | 0.348292 | -0.345044 |
| 2 | 6 | 0 | -2.035242 | -1.362460 | -0.144895 |
| 3 | 1 | 0 | 0.711963 | 0.191156 | -1.345004 |
| 4 | 6 | 0 | 1.787025 | -0.883582 | 0.213539 |
| 5 | 1 | 0 | 1.060489 | -1.700756 | 0.243193 |
| 6 | 8 | 0 | 2.238477 | -0.568302 | 1.502339 |
| 7 | 8 | 0 | 2.836417 | -1.166463 | -0.671964 |
| 8 | 1 | 0 | 3.200171 | -2.040565 | -0.481093 |
| 9 | 1 | 0 | -2.172142 | -2.631136 | 1.426702 |
| 10 | 7 | 0 | -1.626933 | -2.419200 | 0.604320 |
| 11 | 7 | 0 | -1.527616 | -1.284612 | -1.408101 |
| 12 | 1 | 0 | -1.571040 | -0.367056 | -1.833104 |
| 13 | 8 | 0 | -2.833147 | -0.521377 | 0.288931 |
| 14 | 8 | 0 | 2.215065 | 1.389374 | -0.630415 |
| 15 | 1 | 0 | 2.951327 | 0.994617 | -1.140392 |
| 16 | 1 | 0 | 2.358213 | -1.377708 | 2.014397 |
| 17 | 1 | 0 | -0.710632 | -1.834882 | -1.638563 |
| 18 | 1 | 0 | -1.134858 | -3.187123 | 0.170559 |
| 19 | 1 | 0 | 2.579915 | 1.782049 | 0.184911 |
| 20 | 7 | 0 | 0.178594 | 0.906228 | 0.518107 |
| 21 | 6 | 0 | -0.830488 | 1.741019 | 0.042875 |
| 22 | 7 | 0 | -1.504028 | 2.406327 | 0.996280 |
| 23 | 1 | 0 | -2.345403 | 2.889420 | 0.717197 |
| 24 | 1 | 0 | -1.403167 | 2.164473 | 1.971901 |
| 25 | 8 | 0 | -1.040906 | 1.858599 | -1.160867 |
| 26 | 1 | 0 | 0.377776 | 0.862045 | 1.512003 |

## Structure of **14c**

```
Zero-point correction=                           0.186324 (Hartree/Particle)
 Thermal correction to Energy=                    0.200892
```

```
 Thermal correction to Enthalpy=                  0.201836
 Thermal correction to Gibbs Free Energy=         0.143183
 Sum of electronic and zero-point Energies=           -678.602444
 Sum of electronic and thermal Energies=              -678.587876
 Sum of electronic and thermal Enthalpies=            -678.586932
 Sum of electronic and thermal Free Energies=         -678.645584
No imaginary frequencies.

                        Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1          6           0        0.048423    1.443518   -0.159898
      2          6           0        1.373297    0.824675   -0.502174
      3          6           0       -3.124514   -0.694074   -0.034074
      4          1           0        1.942638    1.156441   -1.365143
      5          7           0        1.831013   -0.120861    0.220635
      6          6           0        3.113221   -0.774091   -0.076956
      7          1           0       -1.195122   -1.291460   -0.243756
      8          1           0       -0.658884    1.122883   -0.938422
      9          7           0        3.411201   -1.711206    0.807522
     10          1           0        2.819901   -1.931024    1.598411
     11          1           0        4.280205   -2.217215    0.696430
     12          8           0        3.740533   -0.417155   -1.043556
     13          8           0        0.259278    2.828325   -0.213725
     14          1           0       -0.596070    3.273307   -0.281478
     15          8           0       -0.359139    0.993660    1.088972
     16          1           0       -1.309255    0.721224    1.037316
     17          7           0       -4.376256   -0.945651   -0.468941
     18          1           0       -4.602199   -1.818130   -0.922916
     19          1           0       -5.129970   -0.420347   -0.052734
     20          8           0       -2.882117    0.294172    0.691646
     21          1           0       -2.331541   -2.252756   -1.121877
     22          7           0       -2.154925   -1.554708   -0.414431
     23          1           0        1.272061   -0.408121    1.032591
 ---------------------------------------------------------------------
```

## Structure of $I_{12c}$

```
Zero-point correction=                           0.201890 (Hartree/Particle)
 Thermal correction to Energy=                    0.217556
 Thermal correction to Enthalpy=                  0.218500
 Thermal correction to Gibbs Free Energy=         0.159189
 Sum of electronic and zero-point Energies=           -754.571399
 Sum of electronic and thermal Energies=              -754.555733
 Sum of electronic and thermal Enthalpies=            -754.554789
 Sum of electronic and thermal Free Energies=         -754.614099
No imaginary frequencies.

                        Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1          6           0       -0.824204    1.353146   -0.779986
      2          6           0        0.058958    0.118303   -0.652720
      3          6           0       -2.013559   -1.125315    0.282117
      4          1           0       -0.031762   -0.468404   -1.571834
      5          7           0        1.384706    0.409319   -0.274238
      6          6           0        2.175938   -0.669066   -0.292639
      7          1           0       -0.438185   -0.356313    1.353780
      8          8           0        0.819968    0.863965    2.494071
      9          1           0        1.239335    0.882775    1.609431
     10          1           0        0.135623    1.542847    2.446570
     11          1           0       -1.844633    1.066313   -1.054705
     12          7           0        3.491393   -0.458877    0.070107
     13          1           0        3.838391    0.482731   -0.043237
     14          1           0        4.131620   -1.182364   -0.224450
     15          8           0        1.800843   -1.851476   -0.543691
     16          8           0       -0.270483    2.131893   -1.809502
     17          1           0       -0.939940    2.750734   -2.126930
     18          8           0       -0.840239    2.027462    0.452737
     19          1           0       -1.594521    2.629983    0.477149
     20          7           0       -2.257232   -1.960667   -0.717733
     21          1           0       -1.518007   -2.350070   -1.288154
```

| | | | | | |
|---|---|---|---|---|---|
| 22 | 1 | 0 | -3.215369 | -2.216445 | -0.916808 |
| 23 | 8 | 0 | -2.811131 | -0.606641 | 1.031195 |
| 24 | 1 | 0 | 0.009078 | -1.652281 | 0.392394 |
| 25 | 7 | 0 | -0.582594 | -0.805997 | 0.437247 |

Structure of **15H$^+$**

```
Zero-point correction=                           0.190804 (Hartree/Particle)
 Thermal correction to Energy=                    0.203878
 Thermal correction to Enthalpy=                  0.204822
 Thermal correction to Gibbs Free Energy=         0.151671
 Sum of electronic and zero-point Energies=           -678.621123
 Sum of electronic and thermal Energies=              -678.608049
 Sum of electronic and thermal Enthalpies=            -678.607105
 Sum of electronic and thermal Free Energies=         -678.660256
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.278679 | -0.656136 | 0.408656 |
| 2 | 6 | 0 | 0.322496 | 1.839091 | -0.074830 |
| 3 | 1 | 0 | 0.184839 | -1.272422 | 1.302160 |
| 4 | 6 | 0 | 1.578323 | -1.006637 | -0.313374 |
| 5 | 1 | 0 | 1.613595 | -0.560281 | -1.312020 |
| 6 | 8 | 0 | 1.598604 | -2.402356 | -0.401996 |
| 7 | 8 | 0 | 2.614886 | -0.498179 | 0.485031 |
| 8 | 1 | 0 | 3.442929 | -0.499827 | -0.012934 |
| 9 | 1 | 0 | 1.579766 | 2.904695 | -1.230109 |
| 10 | 7 | 0 | 1.519325 | 2.199411 | -0.506993 |
| 11 | 7 | 0 | 0.371428 | 0.771568 | 0.969797 |
| 12 | 1 | 0 | -0.455236 | 0.896201 | 1.569843 |
| 13 | 8 | 0 | -0.764669 | 2.229262 | -0.423087 |
| 14 | 1 | 0 | 2.150433 | -2.671221 | -1.147433 |
| 15 | 1 | 0 | 1.217048 | 0.834559 | 1.549553 |
| 16 | 1 | 0 | 2.370351 | 1.783309 | -0.148213 |
| 17 | 7 | 0 | -0.845682 | -0.809252 | -0.440502 |
| 18 | 6 | 0 | -2.101959 | -0.568819 | 0.091922 |
| 19 | 7 | 0 | -3.115828 | -0.566250 | -0.784240 |
| 20 | 1 | 0 | -4.052295 | -0.433923 | -0.433389 |
| 21 | 1 | 0 | -2.987021 | -0.801803 | -1.757051 |
| 22 | 8 | 0 | -2.239530 | -0.375726 | 1.303384 |
| 23 | 1 | 0 | -0.708676 | -0.616624 | -1.427742 |

Structure **TS1$_{12c}$**

```
Zero-point correction=                           0.199181 (Hartree/Particle)
 Thermal correction to Energy=                    0.215239
 Thermal correction to Enthalpy=                  0.216183
 Thermal correction to Gibbs Free Energy=         0.155636
 Sum of electronic and zero-point Energies=           -754.568349
 Sum of electronic and thermal Energies=              -754.552291
 Sum of electronic and thermal Enthalpies=            -754.551347
 Sum of electronic and thermal Free Energies=         -754.611894
One imaginary frequency (cm-1): 325.9818i
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.734622 | 1.413141 | -0.719207 |
| 2 | 6 | 0 | 0.228033 | 0.232483 | -0.722392 |
| 3 | 6 | 0 | -2.120514 | -1.055786 | 0.147649 |
| 4 | 1 | 0 | 0.157890 | -0.364090 | -1.633855 |
| 5 | 7 | 0 | 1.419683 | 0.416758 | -0.148228 |
| 6 | 6 | 0 | 2.305773 | -0.615358 | -0.348375 |
| 7 | 1 | 0 | -0.485274 | -0.653826 | 1.291806 |
| 8 | 8 | 0 | 0.709903 | 0.278786 | 2.603445 |
| 9 | 1 | 0 | 1.109163 | 0.582370 | 1.763907 |
| 10 | 1 | 0 | 0.176863 | 1.014462 | 2.925532 |

| | | | | | |
|---|---|---|---|---|---|
| 11 | 1 | 0 | -1.693478 | 1.111715 | -1.151184 |
| 12 | 7 | 0 | 3.565465 | -0.357953 | 0.073524 |
| 13 | 1 | 0 | 3.775166 | 0.500553 | 0.557050 |
| 14 | 1 | 0 | 4.251060 | -1.096518 | 0.065703 |
| 15 | 8 | 0 | 2.015296 | -1.718555 | -0.855530 |
| 16 | 8 | 0 | -0.130124 | 2.388152 | -1.522392 |
| 17 | 1 | 0 | -0.793056 | 3.049160 | -1.761207 |
| 18 | 8 | 0 | -0.942030 | 1.941648 | 0.570003 |
| 19 | 1 | 0 | -1.712360 | 1.504722 | 0.964343 |
| 20 | 7 | 0 | -2.516904 | -1.919474 | -0.784865 |
| 21 | 1 | 0 | -1.868216 | -2.530538 | -1.260632 |
| 22 | 1 | 0 | -3.500889 | -1.984956 | -1.004535 |
| 23 | 8 | 0 | -2.852731 | -0.301542 | 0.778571 |
| 24 | 1 | 0 | -0.197944 | -1.832626 | 0.128515 |
| 25 | 7 | 0 | -0.710168 | -0.975792 | 0.341816 |

## Structure **$TS2_{12c}$**

```
Zero-point correction=                           0.197045 (Hartree/Particle)
 Thermal correction to Energy=                    0.211362
 Thermal correction to Enthalpy=                  0.212307
 Thermal correction to Gibbs Free Energy=         0.156038
 Sum of electronic and zero-point Energies=           -754.563253
 Sum of electronic and thermal Energies=              -754.548937
 Sum of electronic and thermal Enthalpies=            -754.547992
 Sum of electronic and thermal Free Energies=         -754.604261
One imaginary frequency (cm-1): 1226.2561i
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.102649 | 0.271833 | 0.421241 |
| 2 | 6 | 0 | 0.262726 | 1.571096 | -0.303614 |
| 3 | 7 | 0 | 1.141020 | -0.537716 | 0.715991 |
| 4 | 1 | 0 | 0.717728 | -1.773838 | 0.724181 |
| 5 | 1 | 0 | 0.666884 | 1.386494 | -1.299864 |
| 6 | 8 | 0 | 0.043860 | -2.723134 | 0.409280 |
| 7 | 1 | 0 | -0.670436 | -2.089155 | 0.008707 |
| 8 | 1 | 0 | -0.319328 | -3.160193 | 1.191676 |
| 9 | 8 | 0 | -0.873601 | 2.382444 | -0.464527 |
| 10 | 1 | 0 | -1.595630 | 2.066770 | 0.114731 |
| 11 | 8 | 0 | 1.237602 | 2.201564 | 0.498831 |
| 12 | 1 | 0 | 1.636031 | 2.926023 | 0.000193 |
| 13 | 1 | 0 | -0.455618 | 0.565664 | 1.416427 |
| 14 | 6 | 0 | 2.183153 | -0.536249 | -0.283782 |
| 15 | 1 | 0 | 1.498963 | -0.264530 | 1.629312 |
| 16 | 8 | 0 | 1.899828 | -0.726180 | -1.453897 |
| 17 | 7 | 0 | 3.418434 | -0.391377 | 0.197398 |
| 18 | 1 | 0 | 4.196457 | -0.454892 | -0.443772 |
| 19 | 1 | 0 | 3.603261 | -0.185428 | 1.168433 |
| 20 | 7 | 0 | -1.070797 | -0.543138 | -0.267764 |
| 21 | 6 | 0 | -2.340744 | -0.230398 | -0.013103 |
| 22 | 8 | 0 | -2.745401 | 0.759935 | 0.665717 |
| 23 | 7 | 0 | -3.290037 | -1.048048 | -0.598345 |
| 24 | 1 | 0 | -2.982579 | -1.977574 | -0.848858 |
| 25 | 1 | 0 | -4.199291 | -1.012108 | -0.159803 |

## Structure **$TS_{13c}$**

```
Zero-point correction=                           0.211476 (Hartree/Particle)
 Thermal correction to Energy=                    0.228216
 Thermal correction to Enthalpy=                  0.229160
 Thermal correction to Gibbs Free Energy=         0.166931
 Sum of electronic and zero-point Energies=           -755.004403
 Sum of electronic and thermal Energies=              -754.987663
 Sum of electronic and thermal Enthalpies=            -754.986718
 Sum of electronic and thermal Free Energies=         -755.048948
One imaginary frequency (cm-1): 154.0667i
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.641493 | -0.021075 | -0.234641 |
| 2 | 6 | 0 | -2.060880 | -1.181661 | -0.199189 |
| 3 | 1 | 0 | 0.777175 | 0.253798 | -1.270580 |
| 4 | 6 | 0 | 1.402819 | -1.183671 | 0.363503 |
| 5 | 1 | 0 | 0.709788 | -1.873154 | 0.852819 |
| 6 | 8 | 0 | 2.275727 | -0.633700 | 1.317310 |
| 7 | 8 | 0 | 2.066446 | -1.802241 | -0.697470 |
| 8 | 1 | 0 | 2.312446 | -2.700982 | -0.442231 |
| 9 | 1 | 0 | -2.877680 | -2.035936 | 1.450556 |
| 10 | 7 | 0 | -2.156236 | -2.127824 | 0.750770 |
| 11 | 7 | 0 | -1.056961 | -1.369250 | -1.137929 |
| 12 | 1 | 0 | -1.213185 | -0.856802 | -1.998921 |
| 13 | 8 | 0 | -2.731919 | -0.149003 | -0.202489 |
| 14 | 8 | 0 | 2.959760 | 1.403863 | -0.479909 |
| 15 | 1 | 0 | 3.348431 | 1.026194 | -1.276848 |
| 16 | 1 | 0 | 2.562740 | -1.324909 | 1.928517 |
| 17 | 1 | 0 | -0.714800 | -2.313801 | -1.280608 |
| 18 | 1 | 0 | -1.662266 | -3.005345 | 0.679213 |
| 19 | 1 | 0 | 3.188642 | 0.801176 | 0.241473 |
| 20 | 7 | 0 | 0.004849 | 0.794625 | 0.540295 |
| 21 | 6 | 0 | -0.655036 | 1.963322 | -0.004334 |
| 22 | 7 | 0 | -1.212185 | 2.723470 | 0.929422 |
| 23 | 1 | 0 | -1.709203 | 3.555324 | 0.642324 |
| 24 | 1 | 0 | -1.193849 | 2.479724 | 1.910561 |
| 25 | 8 | 0 | -0.630194 | 2.155497 | -1.200455 |
| 26 | 1 | 0 | -0.073448 | 0.590745 | 1.537900 |

## Structure **$TS_{14c}$**

```
Zero-point correction=                           0.186654 (Hartree/Particle)
 Thermal correction to Energy=                    0.200061
 Thermal correction to Enthalpy=                  0.201005
 Thermal correction to Gibbs Free Energy=         0.146359
 Sum of electronic and zero-point Energies=           -678.599554
 Sum of electronic and thermal Energies=              -678.586146
 Sum of electronic and thermal Enthalpies=            -678.585202
 Sum of electronic and thermal Free Energies=         -678.639849
One imaginary frequency (cm-1): 144.5275i
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.549498 | 1.490752 | -0.363724 |
| 2 | 6 | 0 | 0.463546 | 0.382231 | -0.570757 |
| 3 | 6 | 0 | -2.273708 | -0.990956 | 0.243062 |
| 4 | 1 | 0 | 0.461181 | -0.200652 | -1.483557 |
| 5 | 7 | 0 | 1.510710 | 0.332043 | 0.185346 |
| 6 | 6 | 0 | 2.547403 | -0.655456 | -0.045556 |
| 7 | 1 | 0 | -0.580694 | -1.190163 | 1.311589 |
| 8 | 1 | 0 | -1.493220 | 1.213092 | -0.837063 |
| 9 | 7 | 0 | 3.564057 | -0.548200 | 0.798619 |
| 10 | 1 | 0 | 3.611788 | 0.167622 | 1.510714 |
| 11 | 1 | 0 | 4.329274 | -1.203578 | 0.716184 |
| 12 | 8 | 0 | 2.405407 | -1.466028 | -0.935035 |
| 13 | 8 | 0 | 0.037211 | 2.584699 | -1.006780 |
| 14 | 1 | 0 | -0.650815 | 3.222004 | -1.241702 |
| 15 | 8 | 0 | -0.722343 | 1.765043 | 0.996664 |
| 16 | 1 | 0 | -1.495355 | 1.264866 | 1.316303 |
| 17 | 7 | 0 | -2.914212 | -1.583806 | -0.769684 |
| 18 | 1 | 0 | -2.467124 | -2.275314 | -1.353751 |
| 19 | 1 | 0 | -3.886627 | -1.364337 | -0.927065 |
| 20 | 8 | 0 | -2.802792 | -0.178444 | 1.009988 |
| 21 | 1 | 0 | -0.575738 | -2.103246 | -0.109618 |
| 22 | 7 | 0 | -0.913407 | -1.265460 | 0.354975 |
| 23 | 1 | 0 | 1.550970 | 0.926069 | 1.016322 |

**Cartesian coordinates of all stationary points involved in the formation of 16 at the M06-2X/6-311+G(d) level in water (SMD).**

Structure of **16a**

```
Zero-point correction=                           0.149082 (Hartree/Particle)
 Thermal correction to Energy=                    0.159568
 Thermal correction to Enthalpy=                  0.160512
 Thermal correction to Gibbs Free Energy=         0.113628
 Sum of electronic and zero-point Energies=           -529.800251
 Sum of electronic and thermal Energies=              -529.789765
 Sum of electronic and thermal Enthalpies=            -529.788821
 Sum of electronic and thermal Free Energies=         -529.835705
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.498686 | 0.722813 | -0.444041 |
| 2 | 8 | 0 | -0.589708 | 1.779461 | 0.484704 |
| 3 | 6 | 0 | -1.264234 | -0.437351 | 0.189133 |
| 4 | 7 | 0 | 0.843999 | 0.361105 | -0.797912 |
| 5 | 1 | 0 | -1.121317 | -0.525161 | 1.261510 |
| 6 | 1 | 0 | -0.420589 | 2.614270 | 0.030232 |
| 7 | 8 | 0 | -2.714750 | 0.013175 | 0.106840 |
| 8 | 1 | 0 | -3.295954 | -0.456994 | 0.733707 |
| 9 | 8 | 0 | -1.106757 | -1.584429 | -0.511868 |
| 10 | 1 | 0 | -1.351196 | -2.350928 | 0.025214 |
| 11 | 1 | 0 | -1.000700 | 0.988052 | -1.378583 |
| 12 | 6 | 0 | 1.718036 | -0.137975 | 0.134708 |
| 13 | 1 | 0 | 1.221152 | 0.802591 | -1.626174 |
| 14 | 8 | 0 | 1.328987 | -0.532117 | 1.238307 |
| 15 | 7 | 0 | 3.017427 | -0.166487 | -0.236066 |
| 16 | 1 | 0 | 3.658732 | -0.679206 | 0.350084 |
| 17 | 1 | 0 | 3.295038 | 0.020678 | -1.188266 |
| 18 | 1 | 0 | -3.088018 | -0.069272 | -0.792548 |

Structure of **16b**

```
Zero-point correction=                           0.120072 (Hartree/Particle)
 Thermal correction to Energy=                    0.128827
 Thermal correction to Enthalpy=                  0.129771
 Thermal correction to Gibbs Free Energy=         0.086315
 Sum of electronic and zero-point Energies=           -453.377069
 Sum of electronic and thermal Energies=              -453.368314
 Sum of electronic and thermal Enthalpies=            -453.367370
 Sum of electronic and thermal Free Energies=         -453.410825
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.685794 | 0.186054 | 0.184424 |
| 2 | 8 | 0 | 1.094718 | 1.095978 | -0.804520 |
| 3 | 6 | 0 | 1.855467 | -0.695122 | 0.466218 |
| 4 | 7 | 0 | -0.462837 | -0.598793 | -0.116886 |
| 5 | 1 | 0 | 1.780046 | -1.593916 | 1.073163 |
| 6 | 1 | 0 | 0.770914 | 1.981610 | -0.596412 |
| 7 | 1 | 0 | 0.503958 | 0.701016 | 1.139718 |
| 8 | 6 | 0 | -1.703254 | -0.019470 | 0.111542 |
| 9 | 1 | 0 | -0.384458 | -1.270239 | -0.873303 |
| 10 | 8 | 0 | -1.810793 | 1.017652 | 0.764821 |
| 11 | 7 | 0 | -2.746221 | -0.675575 | -0.423410 |
| 12 | 1 | 0 | -3.675655 | -0.358886 | -0.191319 |
| 13 | 1 | 0 | -2.639805 | -1.584421 | -0.849585 |
| 14 | 8 | 0 | 2.982191 | -0.391754 | 0.039950 |
| 15 | 1 | 0 | 2.951443 | 0.441640 | -0.495299 |

## Structure of **16ca**

```
Zero-point correction=                           0.213869 (Hartree/Particle)
 Thermal correction to Energy=                    0.230609
 Thermal correction to Enthalpy=                  0.231553
 Thermal correction to Gibbs Free Energy=         0.168967
 Sum of electronic and zero-point Energies=           -755.009773
 Sum of electronic and thermal Energies=              -754.993033
 Sum of electronic and thermal Enthalpies=            -754.992089
 Sum of electronic and thermal Free Energies=         -755.054675
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.002902 | 1.635078 | -0.428762 |
| 2 | 6 | 0 | -2.407185 | -0.882628 | -0.131345 |
| 3 | 1 | 0 | -0.219161 | 1.223754 | -1.409450 |
| 4 | 8 | 0 | -1.075146 | 2.166574 | 0.213915 |
| 5 | 6 | 0 | 0.747764 | 0.680824 | 0.489182 |
| 6 | 1 | 0 | 0.009572 | 0.021994 | 0.941337 |
| 7 | 8 | 0 | 1.359466 | 1.503285 | 1.459112 |
| 8 | 1 | 0 | -2.623013 | -1.185061 | 1.855822 |
| 9 | 7 | 0 | -2.116675 | -1.502554 | 1.042565 |
| 10 | 7 | 0 | -1.509658 | -1.067318 | -1.135793 |
| 11 | 1 | 0 | -1.812679 | -0.825556 | -2.067528 |
| 12 | 8 | 0 | -3.425330 | -0.191240 | -0.282006 |
| 13 | 8 | 0 | 1.002902 | 2.725832 | -0.732738 |
| 14 | 1 | 0 | 0.649482 | 3.417558 | -1.323550 |
| 15 | 1 | 0 | 1.649239 | 0.969508 | 2.210033 |
| 16 | 1 | 0 | -0.790941 | -1.773244 | -1.044936 |
| 17 | 1 | 0 | -1.750439 | 2.446123 | -0.419521 |
| 18 | 1 | 0 | -1.182024 | -1.866910 | 1.187720 |
| 19 | 1 | 0 | 1.335789 | 3.135538 | 0.092609 |
| 20 | 7 | 0 | 1.684448 | -0.128299 | -0.229861 |
| 21 | 6 | 0 | 1.728442 | -1.488091 | -0.056579 |
| 22 | 7 | 0 | 2.800051 | -2.107452 | -0.594556 |
| 23 | 1 | 0 | 3.430508 | -1.618181 | -1.213072 |
| 24 | 1 | 0 | 2.776346 | -3.114711 | -0.645258 |
| 25 | 8 | 0 | 0.843447 | -2.104571 | 0.550846 |
| 26 | 1 | 0 | 2.480741 | 0.338412 | -0.648706 |

## Structure of **16cb**

```
Zero-point correction=                           0.185519 (Hartree/Particle)
 Thermal correction to Energy=                    0.199948
 Thermal correction to Enthalpy=                  0.200892
 Thermal correction to Gibbs Free Energy=         0.143131
 Sum of electronic and zero-point Energies=           -678.589182
 Sum of electronic and thermal Energies=              -678.574753
 Sum of electronic and thermal Enthalpies=            -678.573809
 Sum of electronic and thermal Free Energies=         -678.631570
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.806126 | 0.767508 | -0.071540 |
| 2 | 6 | 0 | -0.725110 | 2.154768 | -0.619087 |
| 3 | 6 | 0 | 2.664851 | -0.679369 | 0.079705 |
| 4 | 1 | 0 | -1.221159 | 2.470494 | -1.534009 |
| 5 | 1 | 0 | 2.159418 | 1.268013 | -0.212553 |
| 6 | 1 | 0 | -0.216125 | 0.167408 | -0.783966 |
| 7 | 8 | 0 | -0.196898 | 0.784410 | 1.187896 |
| 8 | 1 | 0 | 0.558295 | 0.137304 | 1.186524 |
| 9 | 7 | 0 | 3.479215 | -1.651753 | -0.375845 |
| 10 | 1 | 0 | 4.286458 | -1.435243 | -0.941357 |
| 11 | 1 | 0 | 3.449867 | -2.545915 | 0.089705 |
| 12 | 8 | 0 | 1.778754 | -0.926947 | 0.926717 |

| | | | | | |
|---|---|---|---|---|---|
| 13 | 1 | 0 | 3.462252 | 0.717431 | -1.204336 |
| 14 | 7 | 0 | 2.857616 | 0.565213 | -0.410436 |
| 15 | 1 | 0 | 0.359312 | 2.583745 | 0.796460 |
| 16 | 8 | 0 | -0.022015 | 2.991957 | -0.028681 |
| 17 | 7 | 0 | -2.149745 | 0.295602 | -0.117742 |
| 18 | 6 | 0 | -2.336963 | -1.077916 | -0.189519 |
| 19 | 8 | 0 | -1.406574 | -1.834122 | -0.465539 |
| 20 | 7 | 0 | -3.591935 | -1.495570 | 0.051243 |
| 21 | 1 | 0 | -4.356301 | -0.843642 | 0.147908 |
| 22 | 1 | 0 | -3.807785 | -2.467176 | -0.114192 |
| 23 | 1 | 0 | -2.846337 | 0.840790 | 0.378784 |

## Structure of **16**

```
Zero-point correction=                           0.176206 (Hartree/Particle)
 Thermal correction to Energy=                    0.189585
 Thermal correction to Enthalpy=                  0.190530
 Thermal correction to Gibbs Free Energy=         0.136672
 Sum of electronic and zero-point Energies=           -678.209121
 Sum of electronic and thermal Energies=              -678.195742
 Sum of electronic and thermal Enthalpies=            -678.194798
 Sum of electronic and thermal Free Energies=         -678.248655
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.438898 | 0.060976 | -0.659248 |
| 2 | 6 | 0 | 0.020780 | -1.801687 | 0.083028 |
| 3 | 1 | 0 | -1.616034 | 0.532185 | -1.630591 |
| 4 | 8 | 0 | -2.654283 | -0.351536 | -0.084632 |
| 5 | 6 | 0 | -0.817328 | 1.114942 | 0.264699 |
| 6 | 1 | 0 | -0.642819 | 0.695818 | 1.254112 |
| 7 | 8 | 0 | -1.732348 | 2.185155 | 0.319585 |
| 8 | 1 | 0 | 1.417049 | -3.244427 | 0.368027 |
| 9 | 7 | 0 | 1.105380 | -2.531921 | -0.274482 |
| 10 | 7 | 0 | -0.538610 | -1.048424 | -0.921702 |
| 11 | 1 | 0 | -0.015244 | -0.976786 | -1.785009 |
| 12 | 8 | 0 | -0.439522 | -1.827015 | 1.228397 |
| 13 | 1 | 0 | -1.480321 | 2.777192 | 1.039369 |
| 14 | 1 | 0 | -3.169732 | -0.825907 | -0.748686 |
| 15 | 1 | 0 | 1.390297 | -2.611971 | -1.239208 |
| 16 | 7 | 0 | 0.452860 | 1.557440 | -0.271694 |
| 17 | 6 | 0 | 1.630145 | 0.996492 | 0.166751 |
| 18 | 7 | 0 | 2.667157 | 1.063781 | -0.702908 |
| 19 | 1 | 0 | 2.607080 | 1.616027 | -1.545679 |
| 20 | 1 | 0 | 3.588037 | 0.879252 | -0.333799 |
| 21 | 8 | 0 | 1.741433 | 0.472703 | 1.279061 |
| 22 | 1 | 0 | 0.423754 | 1.813702 | -1.253717 |

## Structure of **16H$^+$**

```
Zero-point correction=                           0.190019 (Hartree/Particle)
 Thermal correction to Energy=                    0.203101
 Thermal correction to Enthalpy=                  0.204045
 Thermal correction to Gibbs Free Energy=         0.150322
 Sum of electronic and zero-point Energies=           -678.617008
 Sum of electronic and thermal Energies=              -678.603925
 Sum of electronic and thermal Enthalpies=            -678.602981
 Sum of electronic and thermal Free Energies=         -678.656704
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.725586 | 1.132390 | -0.511168 |
| 2 | 6 | 0 | -2.021210 | -1.010409 | -0.065418 |
| 3 | 1 | 0 | -0.570249 | 1.698098 | -1.430381 |
| 4 | 8 | 0 | -1.771841 | 1.600296 | 0.251581 |

| | | | | | |
|---|---|---|---|---|---|
| 5 | 6 | 0 | 0.546502 | 1.128194 | 0.336825 |
| 6 | 1 | 0 | 0.365894 | 0.578116 | 1.263565 |
| 7 | 8 | 0 | 0.820132 | 2.478100 | 0.589127 |
| 8 | 1 | 0 | -2.024354 | -2.094876 | 1.620776 |
| 9 | 7 | 0 | -1.437420 | -1.609101 | 0.954828 |
| 10 | 7 | 0 | -1.043348 | -0.306476 | -0.970689 |
| 11 | 1 | 0 | -1.497243 | -0.257226 | -1.889073 |
| 12 | 8 | 0 | -3.188683 | -0.942842 | -0.357764 |
| 13 | 1 | 0 | 1.342169 | 2.552712 | 1.398369 |
| 14 | 1 | 0 | -0.179613 | -0.852834 | -1.090667 |
| 15 | 1 | 0 | -2.469351 | 1.970128 | -0.305818 |
| 16 | 1 | 0 | -0.421599 | -1.646384 | 1.046951 |
| 17 | 7 | 0 | 1.651181 | 0.516214 | -0.376063 |
| 18 | 6 | 0 | 2.126130 | -0.718056 | -0.023297 |
| 19 | 7 | 0 | 3.377370 | -1.014056 | -0.407798 |
| 20 | 1 | 0 | 3.947831 | -0.358742 | -0.921224 |
| 21 | 1 | 0 | 3.702812 | -1.962418 | -0.299701 |
| 22 | 8 | 0 | 1.408511 | -1.521647 | 0.596402 |
| 23 | 1 | 0 | 2.269248 | 1.163386 | -0.851158 |

## Structure $TS_{16ca}$

```
Zero-point correction=                           0.211792 (Hartree/Particle)
 Thermal correction to Energy=                    0.228361
 Thermal correction to Enthalpy=                  0.229305
 Thermal correction to Gibbs Free Energy=         0.168217
 Sum of electronic and zero-point Energies=          -754.993609
 Sum of electronic and thermal Energies=             -754.977040
 Sum of electronic and thermal Enthalpies=           -754.976096
 Sum of electronic and thermal Free Energies=        -755.037184
One imaginary frequency (cm-1): 176.7329i
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.123336 | 1.375366 | -0.380326 |
| 2 | 6 | 0 | -2.506494 | -0.554260 | -0.188634 |
| 3 | 1 | 0 | 0.081811 | 1.394008 | -1.439951 |
| 4 | 8 | 0 | -0.952288 | 2.181168 | 0.131851 |
| 5 | 6 | 0 | 0.629215 | 0.489581 | 0.592217 |
| 6 | 1 | 0 | -0.098936 | -0.187943 | 1.040401 |
| 7 | 8 | 0 | 1.176105 | 1.322289 | 1.584825 |
| 8 | 1 | 0 | -2.919988 | -1.583690 | 1.508474 |
| 9 | 7 | 0 | -2.277150 | -1.501236 | 0.735375 |
| 10 | 7 | 0 | -1.499040 | -0.397909 | -1.138999 |
| 11 | 1 | 0 | -1.837062 | 0.034087 | -1.992731 |
| 12 | 8 | 0 | -3.494540 | 0.180581 | -0.195397 |
| 13 | 8 | 0 | 1.838438 | 2.763920 | -0.614399 |
| 14 | 1 | 0 | 2.469830 | 2.456690 | -1.275832 |
| 15 | 1 | 0 | 1.232018 | 0.826672 | 2.411924 |
| 16 | 1 | 0 | -0.920595 | -1.214489 | -1.315113 |
| 17 | 1 | 0 | -1.398930 | 2.752236 | -0.519632 |
| 18 | 1 | 0 | -1.400936 | -2.011729 | 0.755122 |
| 19 | 1 | 0 | 2.281430 | 2.693518 | 0.240535 |
| 20 | 7 | 0 | 1.602376 | -0.297251 | -0.099572 |
| 21 | 6 | 0 | 1.567526 | -1.668380 | -0.065022 |
| 22 | 7 | 0 | 2.660554 | -2.292123 | -0.542017 |
| 23 | 1 | 0 | 3.419672 | -1.784677 | -0.971988 |
| 24 | 1 | 0 | 2.615940 | -3.291588 | -0.670299 |
| 25 | 8 | 0 | 0.586396 | -2.285112 | 0.371176 |
| 26 | 1 | 0 | 2.434213 | 0.179916 | -0.428276 |

## Structure $TS_{16cb}$

```
Zero-point correction=                           0.185465 (Hartree/Particle)
 Thermal correction to Energy=                    0.199259
 Thermal correction to Enthalpy=                  0.200203
 Thermal correction to Gibbs Free Energy=         0.144203
 Sum of electronic and zero-point Energies=          -678.588151
 Sum of electronic and thermal Energies=             -678.574357
```

```
 Sum of electronic and thermal Enthalpies=            -678.573413
 Sum of electronic and thermal Free Energies=         -678.629413
One imaginary frequency (cm-1): 82.6682i
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.505944 | 0.548363 | 0.012768 |
| 2 | 6 | 0 | 0.044028 | 1.716355 | -0.756735 |
| 3 | 6 | 0 | 2.478298 | -0.804680 | 0.094038 |
| 4 | 1 | 0 | -0.011187 | 1.785239 | -1.840138 |
| 5 | 1 | 0 | 2.683809 | 1.180733 | 0.313343 |
| 6 | 1 | 0 | -0.063818 | -0.357821 | -0.411450 |
| 7 | 8 | 0 | -0.176340 | 0.718968 | 1.364440 |
| 8 | 1 | 0 | 0.582449 | 0.130296 | 1.570033 |
| 9 | 7 | 0 | 2.895301 | -1.810274 | -0.688071 |
| 10 | 1 | 0 | 3.373410 | -1.647622 | -1.561569 |
| 11 | 1 | 0 | 2.740528 | -2.759336 | -0.383669 |
| 12 | 8 | 0 | 1.934939 | -1.002623 | 1.196884 |
| 13 | 1 | 0 | 3.227666 | 0.606806 | -1.190624 |
| 14 | 7 | 0 | 2.606512 | 0.468333 | -0.402948 |
| 15 | 1 | 0 | 0.542734 | 2.515959 | 0.827453 |
| 16 | 8 | 0 | 0.533662 | 2.686173 | -0.150068 |
| 17 | 7 | 0 | -1.909482 | 0.504316 | -0.242171 |
| 18 | 6 | 0 | -2.534983 | -0.737116 | -0.168692 |
| 19 | 8 | 0 | -1.889094 | -1.782199 | -0.197469 |
| 20 | 7 | 0 | -3.874499 | -0.689263 | -0.078637 |
| 21 | 1 | 0 | -2.444814 | 1.311576 | 0.061010 |
| 22 | 1 | 0 | -4.382978 | 0.178934 | -0.159570 |
| 23 | 1 | 0 | -4.386357 | -1.556628 | -0.140607 |

**Cartesian coordinates of all stationary points involved in the formation of 17 and 18 at the M06-2X/6-311+G(d) level in water (SMD).**

Structure of **17**

```
Zero-point correction=                           0.110805 (Hartree/Particle)
 Thermal correction to Energy=                    0.117905
 Thermal correction to Enthalpy=                  0.118850
 Thermal correction to Gibbs Free Energy=         0.079590
 Sum of electronic and zero-point Energies=           -453.005007
 Sum of electronic and thermal Energies=              -452.997906
 Sum of electronic and thermal Enthalpies=            -452.996962
 Sum of electronic and thermal Free Energies=         -453.036222
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.655426 | 0.819421 | 0.490264 |
| 2 | 6 | 0 | 0.768789 | -0.724608 | 0.499136 |
| 3 | 6 | 0 | -1.396230 | -0.108108 | -0.046467 |
| 4 | 1 | 0 | 1.122566 | 1.274331 | 1.360593 |
| 5 | 1 | 0 | 0.805540 | -1.111015 | 1.517383 |
| 6 | 7 | 0 | -0.467107 | -1.108305 | -0.167787 |
| 7 | 7 | 0 | -0.771539 | 0.996863 | 0.478725 |
| 8 | 1 | 0 | -0.799027 | -2.062544 | -0.107377 |
| 9 | 1 | 0 | -1.169386 | 1.910690 | 0.301254 |
| 10 | 8 | 0 | -2.584309 | -0.185494 | -0.337671 |
| 11 | 8 | 0 | 1.918371 | -1.187342 | -0.148403 |
| 12 | 1 | 0 | 2.024310 | -0.682803 | -0.969024 |
| 13 | 8 | 0 | 1.223379 | 1.342105 | -0.694949 |
| 14 | 1 | 0 | 2.059085 | 1.777054 | -0.488814 |

Structure of **18**

```
Zero-point correction=                           0.110241 (Hartree/Particle)
```

```
 Thermal correction to Energy=                    0.117732
 Thermal correction to Enthalpy=                  0.118676
 Thermal correction to Gibbs Free Energy=         0.078438
 Sum of electronic and zero-point Energies=           -453.004869
 Sum of electronic and thermal Energies=              -452.997378
 Sum of electronic and thermal Enthalpies=            -452.996434
 Sum of electronic and thermal Free Energies=         -453.036672
No imaginary frequencies.

                        Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1          6           0        0.891835    0.682353    0.348277
      2          6           0        0.891774   -0.682425   -0.348263
      3          6           0       -1.293017    0.000053   -0.000003
      4          1           0        1.580247    0.706571    1.191407
      5          7           0       -0.484027   -0.776845   -0.789366
      6          7           0       -0.483973    0.776929    0.789299
      7          1           0       -0.852120   -1.635865   -1.177256
      8          1           0       -0.851994    1.635898    1.177363
      9          8           0       -2.519098    0.000090    0.000001
     10          8           0        1.239973    1.659660   -0.607764
     11          1           0        1.345713    2.511669   -0.165767
     12          1           0        1.580233   -0.706719   -1.191351
     13          8           0        1.239737   -1.659780    0.607791
     14          1           0        1.345472   -2.511783    0.165782
 ---------------------------------------------------------------------
```

Structure of **17H⁺**

```
Zero-point correction=                           0.123929 (Hartree/Particle)
 Thermal correction to Energy=                    0.131263
 Thermal correction to Enthalpy=                  0.132207
 Thermal correction to Gibbs Free Energy=         0.092368
 Sum of electronic and zero-point Energies=           -453.408725
 Sum of electronic and thermal Energies=              -453.401392
 Sum of electronic and thermal Enthalpies=            -453.400447
 Sum of electronic and thermal Free Energies=         -453.440286
No imaginary frequencies.

                        Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1          6           0       -0.650766    0.884039    0.442399
      2          6           0       -0.836535   -0.635919    0.492668
      3          6           0        1.447993   -0.072085   -0.020468
      4          1           0       -1.071851    1.367533    1.320753
      5          7           0        0.389716   -1.113198   -0.273709
      6          7           0        0.800074    0.987836    0.458663
      7          1           0        0.184664   -1.147751   -1.282179
      8          1           0        1.292095    1.854869    0.641781
      9          8           0        2.606513   -0.288399   -0.228406
     10          8           0       -1.210247    1.376155   -0.740062
     11          1           0       -1.393517    2.319247   -0.644788
     12          8           0       -2.001713   -1.041261   -0.104715
     13          1           0        0.722082   -2.037423    0.021068
     14          1           0       -0.714627   -1.001175    1.511026
     15          1           0       -2.267964   -1.905929    0.235533
 ---------------------------------------------------------------------
```

Structure of **18H⁺**

```
Zero-point correction=                           0.124103 (Hartree/Particle)
 Thermal correction to Energy=                    0.131420
 Thermal correction to Enthalpy=                  0.132364
 Thermal correction to Gibbs Free Energy=         0.092443
 Sum of electronic and zero-point Energies=           -453.408971
 Sum of electronic and thermal Energies=              -453.401654
 Sum of electronic and thermal Enthalpies=            -453.400710
 Sum of electronic and thermal Free Energies=         -453.440631
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.974401 | -0.622379 | -0.365410 |
| 2 | 6 | 0 | 0.887883 | 0.757025 | 0.290172 |
| 3 | 6 | 0 | -1.314960 | -0.180268 | -0.047129 |
| 4 | 1 | 0 | 1.602243 | -0.595955 | -1.253127 |
| 5 | 7 | 0 | -0.522705 | 0.745108 | 0.845820 |
| 6 | 7 | 0 | -0.409126 | -0.867962 | -0.736746 |
| 7 | 1 | 0 | -0.943068 | 1.681795 | 0.845287 |
| 8 | 1 | 0 | -0.693007 | -1.597024 | -1.381248 |
| 9 | 8 | 0 | -2.511294 | -0.185036 | -0.040639 |
| 10 | 8 | 0 | 1.449342 | -1.530058 | 0.589148 |
| 11 | 1 | 0 | 1.700977 | -2.356982 | 0.157101 |
| 12 | 8 | 0 | 0.976571 | 1.735500 | -0.678611 |
| 13 | 1 | 0 | -0.549126 | 0.377406 | 1.806181 |
| 14 | 1 | 0 | 1.586165 | 0.880127 | 1.114122 |
| 15 | 1 | 0 | 1.217736 | 2.581094 | -0.276816 |

## Structure $TS_{17}$

```
Zero-point correction=                           0.120774 (Hartree/Particle)
 Thermal correction to Energy=                    0.128590
 Thermal correction to Enthalpy=                  0.129535
 Thermal correction to Gibbs Free Energy=         0.088603
 Sum of electronic and zero-point Energies=           -453.362050
 Sum of electronic and thermal Energies=              -453.354234
 Sum of electronic and thermal Enthalpies=            -453.353289
 Sum of electronic and thermal Free Energies=         -453.394221
One imaginary frequency (cm-1): 109.2539i
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.955686 | -0.499540 | 0.490588 |
| 2 | 6 | 0 | 1.042231 | 1.007437 | 0.283619 |
| 3 | 6 | 0 | -1.401665 | -0.304344 | -0.024174 |
| 4 | 1 | 0 | 0.980887 | -0.701661 | 1.560930 |
| 5 | 7 | 0 | -1.392922 | 0.582745 | 1.034967 |
| 6 | 7 | 0 | -0.243404 | -1.035302 | -0.126657 |
| 7 | 1 | 0 | -2.264583 | 1.087828 | 1.142578 |
| 8 | 1 | 0 | -0.091212 | -1.461127 | -1.035325 |
| 9 | 8 | 0 | -2.314901 | -0.383165 | -0.832244 |
| 10 | 8 | 0 | 2.089938 | -0.999630 | -0.153434 |
| 11 | 1 | 0 | 2.553188 | -1.614752 | 0.429529 |
| 12 | 8 | 0 | 0.894151 | 1.423367 | -0.883204 |
| 13 | 1 | 0 | -1.035524 | 0.235650 | 1.920452 |
| 14 | 1 | 0 | 1.345137 | 1.690999 | 1.074977 |
| 15 | 1 | 0 | 1.035368 | 2.385065 | -1.000459 |

## Structure $TS_{18}$

```
Zero-point correction=                           0.120432 (Hartree/Particle)
 Thermal correction to Energy=                    0.128036
 Thermal correction to Enthalpy=                  0.128980
 Thermal correction to Gibbs Free Energy=         0.088426
 Sum of electronic and zero-point Energies=           -453.370473
 Sum of electronic and thermal Energies=              -453.362869
 Sum of electronic and thermal Enthalpies=            -453.361925
 Sum of electronic and thermal Free Energies=         -453.402479
One imaginary frequency (cm-1): 111.4226i
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|

| | | | | | |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 1.018102 | -0.472007 | -0.514822 |
| 2 | 6 | 0 | 1.258080 | 0.789920 | 0.278688 |
| 3 | 6 | 0 | -1.334530 | -0.163340 | -0.023707 |
| 4 | 1 | 0 | 1.627764 | -0.391634 | -1.420813 |
| 5 | 7 | 0 | -0.874804 | -0.094380 | 1.278549 |
| 6 | 7 | 0 | -0.361532 | -0.556469 | -0.907918 |
| 7 | 1 | 0 | -1.578468 | 0.207535 | 1.941444 |
| 8 | 1 | 0 | -0.590975 | -0.513810 | -1.892007 |
| 9 | 8 | 0 | -2.459927 | 0.158149 | -0.370621 |
| 10 | 8 | 0 | 1.452411 | -1.515811 | 0.313384 |
| 11 | 1 | 0 | 1.562316 | -2.318301 | -0.213838 |
| 12 | 8 | 0 | 0.928266 | 1.867798 | -0.259526 |
| 13 | 1 | 0 | -0.330525 | -0.888532 | 1.603338 |
| 14 | 1 | 0 | 1.802671 | 0.784755 | 1.221104 |
| 15 | 1 | 0 | 1.145654 | 2.667401 | 0.259509 |

**Cartesian coordinates of all stationary points involved in the formation of 20 and 21 at the M06-2X/6-311+G(d) level in water (SMD).**

Structure of **19c**

```
Zero-point correction=                           0.219935 (Hartree/Particle)
 Thermal correction to Energy=                    0.236223
 Thermal correction to Enthalpy=                  0.237167
 Thermal correction to Gibbs Free Energy=         0.176678
 Sum of electronic and zero-point Energies=           -833.992804
 Sum of electronic and thermal Energies=              -833.976516
 Sum of electronic and thermal Enthalpies=            -833.975572
 Sum of electronic and thermal Free Energies=         -834.036061
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -2.104508 | -0.578932 | 0.328355 |
| 2 | 6 | 0 | -1.102670 | -1.707904 | 0.507246 |
| 3 | 6 | 0 | -0.262899 | 2.143817 | -0.253270 |
| 4 | 1 | 0 | -0.916587 | -2.165226 | 1.473225 |
| 5 | 1 | 0 | 0.391681 | 0.594796 | -1.332304 |
| 6 | 1 | 0 | -1.803546 | 0.281008 | 0.925791 |
| 7 | 8 | 0 | -3.319636 | -1.037917 | 0.853785 |
| 8 | 1 | 0 | -3.686599 | -1.732306 | 0.285858 |
| 9 | 8 | 0 | -2.175305 | -0.307684 | -1.032784 |
| 10 | 1 | 0 | -1.986829 | 0.641678 | -1.195718 |
| 11 | 7 | 0 | -0.057970 | 2.916945 | 0.822610 |
| 12 | 1 | 0 | 0.826604 | 2.957021 | 1.306108 |
| 13 | 1 | 0 | -0.722473 | 3.657642 | 0.992412 |
| 14 | 8 | 0 | -1.275549 | 2.262443 | -0.966882 |
| 15 | 7 | 0 | 0.688519 | 1.200322 | -0.572497 |
| 16 | 1 | 0 | -0.907785 | -1.814670 | -1.325559 |
| 17 | 8 | 0 | -0.646985 | -2.291249 | -0.498208 |
| 18 | 6 | 0 | 1.491325 | 0.538039 | 0.408889 |
| 19 | 1 | 0 | 1.974971 | 1.256770 | 1.071383 |
| 20 | 6 | 0 | 2.585692 | -0.258122 | -0.289784 |
| 21 | 1 | 0 | 3.274414 | 0.424585 | -0.793546 |
| 22 | 8 | 0 | 0.651484 | -0.319672 | 1.181677 |
| 23 | 1 | 0 | 1.188739 | -0.800960 | 1.828506 |
| 24 | 8 | 0 | 3.246238 | -0.971172 | 0.725636 |
| 25 | 1 | 0 | 4.059559 | -1.354393 | 0.373893 |
| 26 | 8 | 0 | 1.975118 | -1.113959 | -1.221010 |
| 27 | 1 | 0 | 2.609444 | -1.354511 | -1.907163 |

Structure of **19H$_a$$^+$**

```
Zero-point correction=                           0.222438 (Hartree/Particle)
 Thermal correction to Energy=                    0.238132
 Thermal correction to Enthalpy=                  0.239076
 Thermal correction to Gibbs Free Energy=         0.180232
 Sum of electronic and zero-point Energies=           -834.016001
```

```
 Sum of electronic and thermal Energies=             -834.000306
 Sum of electronic and thermal Enthalpies=           -833.999362
 Sum of electronic and thermal Free Energies=        -834.058207
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.227212 | -0.815220 | 0.174823 |
| 2 | 6 | 0 | -0.069423 | 1.371441 | 0.709544 |
| 3 | 1 | 0 | -1.066711 | -1.676337 | -0.473444 |
| 4 | 8 | 0 | -1.343099 | -1.145916 | 1.504250 |
| 5 | 6 | 0 | -2.462048 | -0.048966 | -0.284131 |
| 6 | 1 | 0 | -2.702987 | 0.764566 | 0.407096 |
| 7 | 8 | 0 | -3.499609 | -0.987758 | -0.306689 |
| 8 | 8 | 0 | -2.157884 | 0.449944 | -1.561254 |
| 9 | 1 | 0 | -2.800024 | 1.128186 | -1.807883 |
| 10 | 1 | 0 | -0.514636 | 3.302092 | 0.379709 |
| 11 | 7 | 0 | -0.420392 | 2.392379 | -0.054759 |
| 12 | 7 | 0 | 0.012639 | 0.068118 | -0.047161 |
| 13 | 8 | 0 | 0.199835 | 1.365843 | 1.883709 |
| 14 | 1 | 0 | -4.344879 | -0.538833 | -0.180096 |
| 15 | 1 | 0 | 0.056740 | 0.250451 | -1.060667 |
| 16 | 1 | 0 | -0.899647 | -1.985118 | 1.687320 |
| 17 | 1 | 0 | -0.699316 | 2.280060 | -1.020789 |
| 18 | 6 | 0 | 1.299602 | -0.669234 | 0.330781 |
| 19 | 1 | 0 | 1.306906 | -0.749094 | 1.414198 |
| 20 | 6 | 0 | 2.467193 | 0.171946 | -0.180623 |
| 21 | 1 | 0 | 2.449224 | 1.181902 | 0.238908 |
| 22 | 8 | 0 | 1.273795 | -1.938371 | -0.210433 |
| 23 | 1 | 0 | 1.489020 | -1.912311 | -1.155988 |
| 24 | 8 | 0 | 2.312207 | 0.216075 | -1.576889 |
| 25 | 1 | 0 | 2.850778 | 0.924070 | -1.952440 |
| 26 | 8 | 0 | 3.627179 | -0.503488 | 0.214685 |
| 27 | 1 | 0 | 4.381722 | 0.096458 | 0.156106 |

## Structure of **19H$_b^+$**

```
Zero-point correction=                           0.223167 (Hartree/Particle)
 Thermal correction to Energy=                    0.238405
 Thermal correction to Enthalpy=                  0.239350
 Thermal correction to Gibbs Free Energy=         0.181749
 Sum of electronic and zero-point Energies=           -833.998053
 Sum of electronic and thermal Energies=              -833.982815
 Sum of electronic and thermal Enthalpies=            -833.981871
 Sum of electronic and thermal Free Energies=         -834.039472
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.214980 | -0.265267 | 0.736269 |
| 2 | 6 | 0 | -0.021008 | 1.621658 | -0.161804 |
| 3 | 1 | 0 | -0.990662 | -1.282099 | 1.060235 |
| 4 | 8 | 0 | -1.677790 | 0.414238 | 1.869351 |
| 5 | 6 | 0 | -2.320221 | -0.347686 | -0.325063 |
| 6 | 1 | 0 | -2.896507 | 0.565538 | -0.446629 |
| 7 | 8 | 0 | -3.340927 | -1.280783 | 0.305279 |
| 8 | 8 | 0 | -1.849087 | -0.888495 | -1.473327 |
| 9 | 1 | 0 | -2.436773 | -0.693927 | -2.217094 |
| 10 | 1 | 0 | 1.078612 | 3.198772 | -0.703075 |
| 11 | 7 | 0 | 1.138020 | 2.201377 | -0.551816 |
| 12 | 7 | 0 | 0.021140 | 0.289129 | 0.200640 |
| 13 | 8 | 0 | -1.093628 | 2.238157 | -0.128933 |
| 14 | 1 | 0 | -4.215289 | -1.230974 | -0.123615 |
| 15 | 1 | 0 | -1.886187 | 1.325676 | 1.612165 |
| 16 | 1 | 0 | 2.009897 | 1.848565 | -0.167680 |
| 17 | 6 | 0 | 1.015395 | -0.679300 | -0.298285 |
| 18 | 1 | 0 | 0.519781 | -1.648051 | -0.294832 |
| 19 | 6 | 0 | 2.214857 | -0.805843 | 0.640678 |
| 20 | 1 | 0 | 1.858122 | -0.967295 | 1.661307 |

| | | | | | |
|---|---|---|---|---|---|
| 21 | 8 | 0 | 1.385282 | -0.459888 | -1.632870 |
| 22 | 1 | 0 | 1.940201 | 0.327375 | -1.716955 |
| 23 | 8 | 0 | 2.975441 | 0.376625 | 0.575991 |
| 24 | 1 | 0 | 3.502658 | 0.477716 | 1.378017 |
| 25 | 8 | 0 | 2.952521 | -1.915058 | 0.194129 |
| 26 | 1 | 0 | 3.596989 | -2.159100 | 0.870371 |
| 27 | 1 | 0 | -3.053702 | -2.215470 | 0.318284 |

Structure of **19H$_c^+$**

```
Zero-point correction=                           0.192741 (Hartree/Particle)
 Thermal correction to Energy=                    0.207032
 Thermal correction to Enthalpy=                  0.207976
 Thermal correction to Gibbs Free Energy=         0.151851
 Sum of electronic and zero-point Energies=           -757.571005
 Sum of electronic and thermal Energies=              -757.556714
 Sum of electronic and thermal Enthalpies=            -757.555770
 Sum of electronic and thermal Free Energies=         -757.611894
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 1.715698 | 0.146877 | -0.191107 |
| 2 | 6 | 0 | 0.074427 | 1.867764 | -0.262868 |
| 3 | 1 | 0 | 2.200763 | 0.812173 | -0.919746 |
| 4 | 8 | 0 | 2.421228 | 0.292809 | 1.003967 |
| 5 | 6 | 0 | 1.890656 | -1.194909 | -0.816368 |
| 6 | 1 | 0 | 1.411746 | -1.433459 | -1.766770 |
| 7 | 8 | 0 | 2.636923 | -2.022973 | -0.263392 |
| 8 | 1 | 0 | 2.743557 | -2.867050 | -0.748943 |
| 9 | 1 | 0 | -1.363393 | 3.254664 | -0.384116 |
| 10 | 7 | 0 | -1.207426 | 2.266770 | -0.243597 |
| 11 | 7 | 0 | 0.313137 | 0.483432 | -0.171324 |
| 12 | 8 | 0 | 1.018294 | 2.651052 | -0.350554 |
| 13 | 1 | 0 | 2.076834 | -0.294711 | 1.692315 |
| 14 | 1 | 0 | -1.957193 | 1.624703 | -0.477379 |
| 15 | 6 | 0 | -0.587019 | -0.466112 | 0.525957 |
| 16 | 1 | 0 | 0.044749 | -1.288544 | 0.873953 |
| 17 | 6 | 0 | -1.621532 | -1.091628 | -0.412146 |
| 18 | 1 | 0 | -1.136140 | -1.412254 | -1.337614 |
| 19 | 8 | 0 | -1.165951 | 0.072522 | 1.681754 |
| 20 | 1 | 0 | -1.996377 | 0.523940 | 1.476105 |
| 21 | 8 | 0 | -2.610438 | -0.130767 | -0.687606 |
| 22 | 1 | 0 | -3.089338 | -0.362944 | -1.493444 |
| 23 | 8 | 0 | -2.155983 | -2.193079 | 0.274904 |
| 24 | 1 | 0 | -2.661149 | -2.736393 | -0.343310 |

Structure of **19H$_d^+$**

```
Zero-point correction=                           0.193069 (Hartree/Particle)
 Thermal correction to Energy=                    0.206125
 Thermal correction to Enthalpy=                  0.207069
 Thermal correction to Gibbs Free Energy=         0.154672
 Sum of electronic and zero-point Energies=           -757.591029
 Sum of electronic and thermal Energies=              -757.577973
 Sum of electronic and thermal Enthalpies=            -757.577029
 Sum of electronic and thermal Free Energies=         -757.629426
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 1.933351 | -0.601904 | 0.305552 |
| 2 | 6 | 0 | -1.541333 | -1.674663 | -0.519243 |
| 3 | 6 | 0 | -1.638680 | -0.186136 | -0.232840 |
| 4 | 6 | 0 | 0.593639 | -0.202804 | 0.958505 |
| 5 | 1 | 0 | 2.364886 | -1.453894 | 0.824071 |
| 6 | 1 | 0 | -2.025433 | 0.216574 | -1.175553 |

| | | | | | |
|---|---|---|---|---|---|
| 7 | 1 | 0 | 0.837632 | 0.515888 | 1.742270 |
| 8 | 8 | 0 | 2.851126 | 0.399706 | 0.222560 |
| 9 | 8 | 0 | 0.003331 | -1.352722 | 1.492569 |
| 10 | 8 | 0 | 1.642763 | -1.056407 | -1.087972 |
| 11 | 1 | 0 | 2.381133 | 1.241029 | 0.035037 |
| 12 | 1 | 0 | -0.338103 | -1.166997 | 2.376218 |
| 13 | 1 | 0 | -2.420522 | -2.261828 | -0.225377 |
| 14 | 8 | 0 | -0.630673 | -2.193064 | -1.129864 |
| 15 | 1 | 0 | 0.737676 | -1.524215 | -1.209146 |
| 16 | 8 | 0 | -2.625242 | 0.093544 | 0.728434 |
| 17 | 1 | 0 | -2.398999 | -0.303828 | 1.581390 |
| 18 | 7 | 0 | -0.353341 | 0.428927 | 0.008126 |
| 19 | 6 | 0 | -0.164876 | 1.781873 | -0.215640 |
| 20 | 8 | 0 | 0.955687 | 2.282500 | -0.044642 |
| 21 | 7 | 0 | -1.211914 | 2.506278 | -0.645807 |
| 22 | 1 | 0 | -1.043613 | 3.493163 | -0.780605 |
| 23 | 1 | 0 | -2.167637 | 2.220725 | -0.489326 |
| 24 | 1 | 0 | 2.361225 | -1.609712 | -1.441898 |

## Structure of **19**

Zero-point correction= 0.209543 (Hartree/Particle)
Thermal correction to Energy= 0.225273
Thermal correction to Enthalpy= 0.226217
Thermal correction to Gibbs Free Energy= 0.167114
Sum of electronic and zero-point Energies= -833.595406
Sum of electronic and thermal Energies= -833.579676
Sum of electronic and thermal Enthalpies= -833.578732
Sum of electronic and thermal Free Energies= -833.637835
No imaginary frequencies.

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.225801 | -0.567282 | 0.470233 |
| 2 | 6 | 0 | 0.098788 | 1.460094 | 0.332817 |
| 3 | 1 | 0 | -1.084641 | -1.634138 | 0.301242 |
| 4 | 8 | 0 | -1.519470 | -0.315562 | 1.831173 |
| 5 | 6 | 0 | -2.483273 | -0.155181 | -0.295357 |
| 6 | 1 | 0 | -2.880082 | 0.790442 | 0.081654 |
| 7 | 8 | 0 | -3.419168 | -1.179870 | -0.060859 |
| 8 | 8 | 0 | -2.167440 | -0.046013 | -1.660972 |
| 9 | 1 | 0 | -2.948556 | 0.268586 | -2.134833 |
| 10 | 1 | 0 | -0.775271 | 3.214141 | -0.191831 |
| 11 | 7 | 0 | -0.747003 | 2.222362 | -0.375994 |
| 12 | 7 | 0 | 0.015715 | 0.079061 | 0.040335 |
| 13 | 8 | 0 | 0.876204 | 1.917448 | 1.167487 |
| 14 | 1 | 0 | -4.311418 | -0.829775 | -0.171939 |
| 15 | 1 | 0 | -0.963706 | -0.872656 | 2.390450 |
| 16 | 1 | 0 | -1.234924 | 1.845132 | -1.176518 |
| 17 | 6 | 0 | 1.199346 | -0.706847 | 0.387354 |
| 18 | 1 | 0 | 1.251997 | -0.918500 | 1.463630 |
| 19 | 6 | 0 | 2.521336 | -0.032689 | -0.014017 |
| 20 | 1 | 0 | 2.818952 | 0.721992 | 0.710348 |
| 21 | 8 | 0 | 1.054056 | -1.919115 | -0.324753 |
| 22 | 1 | 0 | 1.768001 | -2.509733 | -0.051334 |
| 23 | 8 | 0 | 2.367571 | 0.541702 | -1.287527 |
| 24 | 1 | 0 | 3.124103 | 1.114119 | -1.466553 |
| 25 | 8 | 0 | 3.476151 | -1.071566 | -0.021088 |
| 26 | 1 | 0 | 4.348962 | -0.704331 | 0.161421 |

## Structure of **20H$^+$**

Zero-point correction= 0.195549 (Hartree/Particle)
Thermal correction to Energy= 0.208426
Thermal correction to Enthalpy= 0.209370
Thermal correction to Gibbs Free Energy= 0.157327
Sum of electronic and zero-point Energies= -757.592432
Sum of electronic and thermal Energies= -757.579555
Sum of electronic and thermal Enthalpies= -757.578611
Sum of electronic and thermal Free Energies= -757.630654

No imaginary frequencies.

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.439602 | 1.255007 | -0.137398 |
| 2 | 6 | 0 | -1.374008 | -1.321332 | 0.230633 |
| 3 | 6 | 0 | 0.111188 | -1.181231 | 0.495243 |
| 4 | 6 | 0 | 0.073494 | 1.266551 | 0.022096 |
| 5 | 1 | 0 | 0.450348 | 1.941337 | -0.745387 |
| 6 | 8 | 0 | -1.778860 | 1.229948 | -1.449780 |
| 7 | 8 | 0 | 0.347774 | 1.778465 | 1.303901 |
| 8 | 8 | 0 | -2.022998 | 0.017066 | 0.514565 |
| 9 | 1 | 0 | -2.706805 | 1.476971 | -1.567218 |
| 10 | 1 | 0 | 1.295667 | 1.965205 | 1.352869 |
| 11 | 1 | 0 | -1.905730 | 2.054266 | 0.435586 |
| 12 | 7 | 0 | 0.654916 | -0.044985 | -0.234818 |
| 13 | 6 | 0 | 2.031774 | -0.000484 | -0.506513 |
| 14 | 8 | 0 | 2.640126 | 1.065470 | -0.463823 |
| 15 | 7 | 0 | 2.630196 | -1.173922 | -0.798286 |
| 16 | 1 | 0 | 3.596434 | -1.109878 | -1.086437 |
| 17 | 1 | 0 | 2.103326 | -1.950777 | -1.170183 |
| 18 | 1 | 0 | 0.574814 | -2.097960 | 0.134778 |
| 19 | 8 | 0 | 0.237916 | -1.073364 | 1.891933 |
| 20 | 1 | 0 | 1.174244 | -1.036681 | 2.129091 |
| 21 | 8 | 0 | -1.602590 | -1.644183 | -1.062399 |
| 22 | 1 | 0 | -2.502693 | -1.979925 | -1.176446 |
| 23 | 1 | 0 | -1.858062 | -1.969827 | 0.958691 |
| 24 | 1 | 0 | -2.205347 | 0.141334 | 1.466858 |

## Structure of **21H**$^{+}$

```
Zero-point correction=                           0.195917 (Hartree/Particle)
 Thermal correction to Energy=                    0.208809
 Thermal correction to Enthalpy=                  0.209753
 Thermal correction to Gibbs Free Energy=         0.157416
 Sum of electronic and zero-point Energies=           -757.589257
 Sum of electronic and thermal Energies=              -757.576366
 Sum of electronic and thermal Enthalpies=            -757.575422
 Sum of electronic and thermal Free Energies=         -757.627758
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.674497 | 0.024352 | -0.568821 |
| 2 | 6 | 0 | 1.423614 | -0.894443 | 0.235814 |
| 3 | 6 | 0 | 0.437906 | -2.048882 | 0.112626 |
| 4 | 1 | 0 | -0.724050 | 0.542485 | -1.526415 |
| 5 | 1 | 0 | 1.924147 | -0.939547 | 1.201652 |
| 6 | 1 | 0 | 0.796756 | -2.908236 | -0.448904 |
| 7 | 8 | 0 | -0.603898 | -1.407180 | -0.848238 |
| 8 | 8 | 0 | 2.425522 | -0.945183 | -0.742223 |
| 9 | 1 | 0 | 2.044255 | -0.899646 | -1.631242 |
| 10 | 7 | 0 | 0.566546 | 0.281944 | 0.144295 |
| 11 | 6 | 0 | 1.070027 | 1.574960 | 0.047284 |
| 12 | 8 | 0 | 0.336069 | 2.488611 | -0.338998 |
| 13 | 7 | 0 | 2.337830 | 1.764561 | 0.443486 |
| 14 | 1 | 0 | 2.713607 | 2.694302 | 0.323691 |
| 15 | 1 | 0 | 2.996280 | 1.003453 | 0.520136 |
| 16 | 8 | 0 | -0.177051 | -2.309201 | 1.273547 |
| 17 | 1 | 0 | -0.635824 | -3.161385 | 1.247358 |
| 18 | 6 | 0 | -1.951223 | 0.255596 | 0.244297 |
| 19 | 1 | 0 | -2.054788 | -0.510678 | 1.013951 |
| 20 | 8 | 0 | -2.987529 | 0.164026 | -0.698293 |
| 21 | 1 | 0 | -3.823872 | 0.019438 | -0.237600 |
| 22 | 8 | 0 | -1.926268 | 1.485518 | 0.908348 |
| 23 | 1 | 0 | -1.502020 | 2.160137 | 0.352788 |
| 24 | 1 | 0 | -0.434836 | -1.608088 | -1.790229 |

## Structure of **20**

```
Zero-point correction=                           0.184403 (Hartree/Particle)
 Thermal correction to Energy=                    0.197006
 Thermal correction to Enthalpy=                  0.197950
 Thermal correction to Gibbs Free Energy=         0.146299
 Sum of electronic and zero-point Energies=           -757.205229
 Sum of electronic and thermal Energies=              -757.192625
 Sum of electronic and thermal Enthalpies=            -757.191681
 Sum of electronic and thermal Free Energies=         -757.243332
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.479998 | 1.194670 | 0.032416 |
| 2 | 6 | 0 | -1.442476 | -1.203246 | 0.269104 |
| 3 | 6 | 0 | 0.078656 | -1.209785 | 0.351741 |
| 4 | 6 | 0 | 0.039926 | 1.264559 | 0.076143 |
| 5 | 1 | 0 | -1.885847 | 2.023099 | 0.614192 |
| 6 | 1 | 0 | 0.419293 | -2.096487 | -0.180581 |
| 7 | 1 | 0 | 0.361809 | 1.989197 | -0.669789 |
| 8 | 8 | 0 | -1.862864 | 1.294615 | -1.313510 |
| 9 | 8 | 0 | 0.402068 | 1.704184 | 1.368361 |
| 10 | 8 | 0 | -1.997267 | 0.036566 | 0.657548 |
| 11 | 1 | 0 | -2.827609 | 1.274237 | -1.364772 |
| 12 | 1 | 0 | 1.345071 | 1.918133 | 1.350067 |
| 13 | 1 | 0 | -1.834705 | -1.918344 | 0.992430 |
| 14 | 8 | 0 | -1.790730 | -1.571024 | -1.037539 |
| 15 | 1 | 0 | -2.752849 | -1.638798 | -1.095014 |
| 16 | 8 | 0 | 0.400520 | -1.307002 | 1.722754 |
| 17 | 1 | 0 | 1.340188 | -1.507685 | 1.821387 |
| 18 | 7 | 0 | 0.632717 | -0.019019 | -0.281677 |
| 19 | 6 | 0 | 2.002295 | 0.047801 | -0.535408 |
| 20 | 8 | 0 | 2.598542 | 1.124916 | -0.489465 |
| 21 | 7 | 0 | 2.638769 | -1.113012 | -0.809523 |
| 22 | 1 | 0 | 3.600753 | -1.021826 | -1.103286 |
| 23 | 1 | 0 | 2.140921 | -1.919341 | -1.155408 |

## Structure of **20a**

```
Zero-point correction=                           0.183550 (Hartree/Particle)
 Thermal correction to Energy=                    0.195933
 Thermal correction to Enthalpy=                  0.196877
 Thermal correction to Gibbs Free Energy=         0.145876
 Sum of electronic and zero-point Energies=           -757.201641
 Sum of electronic and thermal Energies=              -757.189258
 Sum of electronic and thermal Enthalpies=            -757.188314
 Sum of electronic and thermal Free Energies=         -757.239315
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.377021 | -1.723907 | -0.443548 |
| 2 | 6 | 0 | 1.445999 | 0.427970 | -0.517918 |
| 3 | 6 | 0 | 0.625909 | 0.855849 | 0.688749 |
| 4 | 6 | 0 | -0.513913 | -1.279674 | 0.717089 |
| 5 | 1 | 0 | 0.672248 | -2.766852 | -0.322925 |
| 6 | 1 | 0 | 1.130418 | 0.480182 | 1.580403 |
| 7 | 1 | 0 | -1.489692 | -1.747270 | 0.622759 |
| 8 | 8 | 0 | -0.369232 | -1.529374 | -1.615583 |
| 9 | 8 | 0 | 0.127866 | -1.664315 | 1.904974 |
| 10 | 8 | 0 | 1.586962 | -0.994568 | -0.474122 |
| 11 | 1 | 0 | 0.112493 | -1.910021 | -2.361433 |
| 12 | 1 | 0 | -0.505410 | -1.627752 | 2.632486 |
| 13 | 1 | 0 | 0.969636 | 0.725794 | -1.456767 |
| 14 | 8 | 0 | 2.721963 | 0.970899 | -0.398915 |
| 15 | 1 | 0 | 3.180789 | 0.904723 | -1.246323 |

| | | | | | |
|---|---|---|---|---|---|
| 16 | 8 | 0 | 0.540093 | 2.250593 | 0.731192 |
| 17 | 1 | 0 | 0.329890 | 2.534523 | 1.629875 |
| 18 | 7 | 0 | -0.691559 | 0.179817 | 0.653381 |
| 19 | 6 | 0 | -1.765685 | 0.608064 | -0.129770 |
| 20 | 8 | 0 | -2.771031 | -0.100253 | -0.256695 |
| 21 | 7 | 0 | -1.683213 | 1.816972 | -0.721719 |
| 22 | 1 | 0 | -2.534115 | 2.166801 | -1.136608 |
| 23 | 1 | 0 | -0.951801 | 2.468674 | -0.477513 |

## Structure of **20b**

Zero-point correction= 0.182514 (Hartree/Particle)
Thermal correction to Energy= 0.195180
Thermal correction to Enthalpy= 0.196124
Thermal correction to Gibbs Free Energy= 0.144554
Sum of electronic and zero-point Energies= -757.194612
Sum of electronic and thermal Energies= -757.181947
Sum of electronic and thermal Enthalpies= -757.181003
Sum of electronic and thermal Free Energies= -757.232573
No imaginary frequencies.

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.502272 | -0.631665 | -0.399554 |
| 2 | 6 | 0 | 0.818637 | -1.334213 | -0.425607 |
| 3 | 6 | 0 | 1.102273 | -0.421251 | 0.764924 |
| 4 | 6 | 0 | -1.173298 | 0.297466 | 0.767656 |
| 5 | 1 | 0 | -1.452363 | -0.114242 | -1.361018 |
| 6 | 1 | 0 | 0.787884 | -0.939447 | 1.672965 |
| 7 | 1 | 0 | -1.195830 | -0.312491 | 1.674425 |
| 8 | 8 | 0 | -2.759558 | -1.185462 | -0.181043 |
| 9 | 8 | 0 | -2.105643 | 1.332050 | 0.870197 |
| 10 | 8 | 0 | -0.556706 | -1.703286 | -0.382669 |
| 11 | 1 | 0 | -3.092777 | -1.564005 | -1.004329 |
| 12 | 1 | 0 | -2.179106 | 1.595488 | 1.795203 |
| 13 | 1 | 0 | 1.037250 | -0.822249 | -1.372248 |
| 14 | 8 | 0 | 1.566869 | -2.498509 | -0.292853 |
| 15 | 1 | 0 | 1.575663 | -2.971344 | -1.134765 |
| 16 | 8 | 0 | 2.465352 | -0.122301 | 0.826893 |
| 17 | 1 | 0 | 2.707475 | 0.087215 | 1.737997 |
| 18 | 7 | 0 | 0.222021 | 0.766291 | 0.627042 |
| 19 | 6 | 0 | 0.465376 | 1.665971 | -0.434516 |
| 20 | 8 | 0 | -0.443875 | 2.138656 | -1.116839 |
| 21 | 7 | 0 | 1.745472 | 2.050802 | -0.607731 |
| 22 | 1 | 0 | 1.941935 | 2.603249 | -1.428891 |
| 23 | 1 | 0 | 2.501611 | 1.571145 | -0.141416 |

## Structure of **21**

Zero-point correction= 0.183654 (Hartree/Particle)
Thermal correction to Energy= 0.196479
Thermal correction to Enthalpy= 0.197424
Thermal correction to Gibbs Free Energy= 0.145152
Sum of electronic and zero-point Energies= -757.207351
Sum of electronic and thermal Energies= -757.194526
Sum of electronic and thermal Enthalpies= -757.193581
Sum of electronic and thermal Free Energies= -757.245853
No imaginary frequencies.

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.675711 | 0.002977 | -0.591854 |
| 2 | 6 | 0 | -1.352060 | 0.968348 | 0.227938 |
| 3 | 6 | 0 | -0.265528 | 2.016833 | 0.000935 |
| 4 | 1 | 0 | 0.713122 | -0.559315 | -1.528303 |
| 5 | 1 | 0 | -1.823558 | 1.069605 | 1.206650 |
| 6 | 1 | 0 | -0.636606 | 2.913874 | -0.493164 |

| | | | | | |
|---|---|---|---|---|---|
| 7 | 8 | 0 | 0.626967 | 1.383035 | -0.897393 |
| 8 | 8 | 0 | -2.317330 | 0.999049 | -0.803084 |
| 9 | 1 | 0 | -2.969976 | 1.682618 | -0.601563 |
| 10 | 7 | 0 | -0.580714 | -0.251814 | 0.123646 |
| 11 | 6 | 0 | -1.142234 | -1.506990 | 0.050807 |
| 12 | 8 | 0 | -0.462488 | -2.479102 | -0.306541 |
| 13 | 7 | 0 | -2.424838 | -1.629108 | 0.451488 |
| 14 | 1 | 0 | -2.846403 | -2.535841 | 0.308364 |
| 15 | 1 | 0 | -3.045012 | -0.832421 | 0.435900 |
| 16 | 8 | 0 | 0.327802 | 2.307736 | 1.234450 |
| 17 | 1 | 0 | 0.981624 | 3.009311 | 1.115620 |
| 18 | 6 | 0 | 1.929859 | -0.314970 | 0.229813 |
| 19 | 1 | 0 | 2.053659 | 0.407198 | 1.037759 |
| 20 | 8 | 0 | 2.992389 | -0.206914 | -0.689043 |
| 21 | 1 | 0 | 3.825087 | -0.152567 | -0.203491 |
| 22 | 8 | 0 | 1.881844 | -1.585643 | 0.823437 |
| 23 | 1 | 0 | 1.318962 | -2.178480 | 0.295848 |

## Structure of **21a**

```
Zero-point correction=                           0.183646 (Hartree/Particle)
 Thermal correction to Energy=                    0.196512
 Thermal correction to Enthalpy=                  0.197456
 Thermal correction to Gibbs Free Energy=         0.144772
 Sum of electronic and zero-point Energies=           -757.206020
 Sum of electronic and thermal Energies=              -757.193153
 Sum of electronic and thermal Enthalpies=            -757.192209
 Sum of electronic and thermal Free Energies=         -757.244894
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.725608 | -0.210543 | -0.424711 |
| 2 | 6 | 0 | -1.324760 | -0.649720 | 0.690430 |
| 3 | 6 | 0 | -0.936538 | -1.789528 | -0.240154 |
| 4 | 1 | 0 | 0.849386 | 0.170432 | -1.440729 |
| 5 | 1 | 0 | -2.369024 | -0.367919 | 0.570667 |
| 6 | 1 | 0 | -1.082067 | -2.782766 | 0.181540 |
| 7 | 8 | 0 | 0.449505 | -1.603872 | -0.429331 |
| 8 | 8 | 0 | -1.041258 | -1.050255 | 2.007951 |
| 9 | 1 | 0 | -1.330991 | -0.362270 | 2.620678 |
| 10 | 7 | 0 | -0.438743 | 0.406362 | 0.211915 |
| 11 | 6 | 0 | -0.903783 | 1.609466 | -0.292563 |
| 12 | 8 | 0 | -0.274324 | 2.238564 | -1.142738 |
| 13 | 7 | 0 | -2.085491 | 2.052339 | 0.203954 |
| 14 | 1 | 0 | -2.326692 | 3.003904 | -0.033466 |
| 15 | 1 | 0 | -2.440837 | 1.709970 | 1.084788 |
| 16 | 8 | 0 | -1.650828 | -1.609583 | -1.432850 |
| 17 | 1 | 0 | -1.464757 | -2.347569 | -2.027515 |
| 18 | 6 | 0 | 2.005745 | 0.003351 | 0.367076 |
| 19 | 1 | 0 | 1.902474 | -0.414849 | 1.372632 |
| 20 | 8 | 0 | 2.229903 | 1.388555 | 0.432180 |
| 21 | 1 | 0 | 2.852737 | 1.576624 | 1.145092 |
| 22 | 8 | 0 | 3.024531 | -0.660757 | -0.338889 |
| 23 | 1 | 0 | 3.781539 | -0.795835 | 0.244167 |

## Structure $TS_{19c}$

```
Zero-point correction=                           0.219132 (Hartree/Particle)
 Thermal correction to Energy=                    0.235245
 Thermal correction to Enthalpy=                  0.236189
 Thermal correction to Gibbs Free Energy=         0.175298
 Sum of electronic and zero-point Energies=           -833.982965
 Sum of electronic and thermal Energies=              -833.966852
 Sum of electronic and thermal Enthalpies=            -833.965908
 Sum of electronic and thermal Free Energies=         -834.026799
One imaginary frequency (cm-1): 81.4259i
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 2.609677 | -0.119679 | -0.323254 |
| 2 | 6 | 0 | 1.724907 | -1.350407 | -0.317721 |
| 3 | 6 | 0 | -0.009863 | 1.721545 | 0.068789 |
| 4 | 1 | 0 | 1.331832 | -1.799673 | -1.224593 |
| 5 | 1 | 0 | -0.288940 | 0.042847 | 1.115596 |
| 6 | 1 | 0 | 2.159269 | 0.659814 | -0.942440 |
| 7 | 8 | 0 | 3.797104 | -0.603956 | -0.876529 |
| 8 | 1 | 0 | 4.202876 | 0.075951 | -1.430297 |
| 9 | 8 | 0 | 2.799384 | 0.289252 | 0.995186 |
| 10 | 1 | 0 | 2.189848 | 1.035247 | 1.181502 |
| 11 | 7 | 0 | -0.481983 | 2.463351 | -0.944011 |
| 12 | 1 | 0 | -1.278522 | 2.203236 | -1.504585 |
| 13 | 1 | 0 | -0.175071 | 3.424227 | -0.985583 |
| 14 | 8 | 0 | 0.820961 | 2.173916 | 0.876691 |
| 15 | 7 | 0 | -0.392197 | 0.402062 | 0.169426 |
| 16 | 1 | 0 | 1.920527 | -1.457330 | 1.514939 |
| 17 | 8 | 0 | 1.527083 | -1.954184 | 0.752069 |
| 18 | 6 | 0 | -1.470949 | -0.211150 | -0.570870 |
| 19 | 1 | 0 | -1.515449 | 0.213337 | -1.576192 |
| 20 | 6 | 0 | -2.819495 | 0.001233 | 0.113417 |
| 21 | 1 | 0 | -3.055330 | 1.069108 | 0.153827 |
| 22 | 8 | 0 | -1.151005 | -1.583135 | -0.639482 |
| 23 | 1 | 0 | -1.898132 | -2.056115 | -1.032370 |
| 24 | 8 | 0 | -2.734329 | -0.529652 | 1.411405 |
| 25 | 1 | 0 | -3.412933 | -0.130826 | 1.969385 |
| 26 | 8 | 0 | -3.760845 | -0.685094 | -0.674829 |
| 27 | 1 | 0 | -4.653199 | -0.444139 | -0.395347 |

## Structure **$TS_{20}$**

Zero-point correction= 0.194144 (Hartree/Particle)
Thermal correction to Energy= 0.207018
Thermal correction to Enthalpy= 0.207962
Thermal correction to Gibbs Free Energy= 0.155838
Sum of electronic and zero-point Energies= -757.570738
Sum of electronic and thermal Energies= -757.557864
Sum of electronic and thermal Enthalpies= -757.556920
Sum of electronic and thermal Free Energies= -757.609044
One imaginary frequency ($cm^{-1}$): 81.4429i

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 1.929677 | -0.736090 | 0.261099 |
| 2 | 6 | 0 | -1.393947 | -1.606535 | -0.372416 |
| 3 | 6 | 0 | -1.515516 | -0.122243 | -0.089511 |
| 4 | 6 | 0 | 0.758347 | -0.060106 | 0.980203 |
| 5 | 1 | 0 | 2.502212 | -1.316521 | 0.989243 |
| 6 | 1 | 0 | -2.002212 | 0.291806 | -0.976925 |
| 7 | 1 | 0 | 1.141397 | 0.738454 | 1.618197 |
| 8 | 8 | 0 | 2.812570 | 0.198847 | -0.299320 |
| 9 | 8 | 0 | 0.022081 | -1.003240 | 1.721494 |
| 10 | 8 | 0 | 1.367568 | -1.588732 | -0.702148 |
| 11 | 1 | 0 | 2.329162 | 1.012396 | -0.534766 |
| 12 | 1 | 0 | 0.593413 | -1.466404 | 2.348014 |
| 13 | 1 | 0 | -1.586759 | -2.343073 | 0.402001 |
| 14 | 8 | 0 | -1.232180 | -2.065826 | -1.518509 |
| 15 | 1 | 0 | -1.061790 | -1.403270 | -2.221370 |
| 16 | 8 | 0 | -2.409992 | 0.051077 | 0.974061 |
| 17 | 1 | 0 | -1.981838 | -0.235627 | 1.796318 |
| 18 | 7 | 0 | -0.230880 | 0.515936 | 0.051806 |
| 19 | 6 | 0 | -0.078802 | 1.863687 | -0.263804 |
| 20 | 8 | 0 | 1.053224 | 2.354536 | -0.281134 |
| 21 | 7 | 0 | -1.182777 | 2.563547 | -0.574195 |
| 22 | 1 | 0 | -1.045842 | 3.537827 | -0.803629 |
| 23 | 1 | 0 | -2.103673 | 2.291153 | -0.261004 |
| 24 | 1 | 0 | 2.006806 | -2.268696 | -0.948337 |

Structure **$TS_{21}$**

```
Zero-point correction=                           0.191511 (Hartree/Particle)
 Thermal correction to Energy=                    0.204437
 Thermal correction to Enthalpy=                  0.205382
 Thermal correction to Gibbs Free Energy=         0.152387
 Sum of electronic and zero-point Energies=           -757.583864
 Sum of electronic and thermal Energies=              -757.570938
 Sum of electronic and thermal Enthalpies=            -757.569994
 Sum of electronic and thermal Free Energies=         -757.622989
One imaginary frequency (cm-1): 182.4868i
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.564765 | -0.378271 | 0.841309 |
| 2 | 6 | 0 | 1.149770 | 1.115949 | -0.169543 |
| 3 | 6 | 0 | -0.003975 | 2.074755 | -0.364747 |
| 4 | 1 | 0 | -0.389244 | -1.012609 | 1.709606 |
| 5 | 1 | 0 | 1.687423 | 1.146471 | -1.124207 |
| 6 | 1 | 0 | 0.087065 | 3.058793 | 0.092271 |
| 7 | 8 | 0 | -0.959461 | 0.914447 | 1.241598 |
| 8 | 8 | 0 | 2.038751 | 1.618904 | 0.792451 |
| 9 | 1 | 0 | 1.632935 | 1.599054 | 1.671920 |
| 10 | 7 | 0 | 0.682659 | -0.218270 | 0.076029 |
| 11 | 6 | 0 | 1.477816 | -1.333786 | -0.110996 |
| 12 | 8 | 0 | 1.025306 | -2.454065 | 0.122350 |
| 13 | 7 | 0 | 2.725824 | -1.127005 | -0.592411 |
| 14 | 1 | 0 | 3.312132 | -1.949211 | -0.628977 |
| 15 | 1 | 0 | 3.205507 | -0.249484 | -0.450762 |
| 16 | 8 | 0 | -0.912399 | 1.939787 | -1.211583 |
| 17 | 1 | 0 | -1.135892 | 0.959796 | -1.470373 |
| 18 | 6 | 0 | -1.670292 | -1.020193 | -0.009621 |
| 19 | 1 | 0 | -1.479934 | -2.088299 | -0.105993 |
| 20 | 8 | 0 | -2.887310 | -0.784348 | 0.628387 |
| 21 | 1 | 0 | -3.509699 | -1.486481 | 0.401296 |
| 22 | 8 | 0 | -1.629632 | -0.441008 | -1.307977 |
| 23 | 1 | 0 | -2.355834 | -0.764439 | -1.858489 |
| 24 | 1 | 0 | -0.647211 | 1.102873 | 2.138174 |

**Cartesian coordinates of all stationary points involved in the formation of 23 and 24 at the M06-2X/6-311+G(d) level in water (SMD).**

Structure of **22c**

```
Zero-point correction=                           0.221332 (Hartree/Particle)
 Thermal correction to Energy=                    0.237871
 Thermal correction to Enthalpy=                  0.238815
 Thermal correction to Gibbs Free Energy=         0.177041
 Sum of electronic and zero-point Energies=           -834.001773
 Sum of electronic and thermal Energies=              -833.985234
 Sum of electronic and thermal Enthalpies=            -833.984290
 Sum of electronic and thermal Free Energies=         -834.046063
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.574242 | -0.332746 | 0.249146 |
| 2 | 6 | 0 | 1.562130 | 0.192937 | -0.160289 |
| 3 | 1 | 0 | -1.156179 | -0.235498 | 1.245295 |
| 4 | 6 | 0 | -2.013192 | -1.680624 | -0.269133 |
| 5 | 1 | 0 | -1.728775 | -1.787941 | -1.318840 |
| 6 | 8 | 0 | -3.410098 | -1.686185 | -0.130674 |
| 7 | 8 | 0 | -1.379870 | -2.633062 | 0.530617 |
| 8 | 1 | 0 | -1.386285 | -3.487391 | 0.079580 |

| | | | | | |
|---|---|---|---|---|---|
| 9 | 1 | 0 | -3.791631 | -2.308225 | -0.764239 |
| 10 | 1 | 0 | 0.899752 | -1.625824 | 0.108334 |
| 11 | 7 | 0 | -1.847379 | 0.738255 | -0.404180 |
| 12 | 6 | 0 | -1.482024 | 2.050534 | 0.114627 |
| 13 | 7 | 0 | -1.904928 | 3.041845 | -0.650328 |
| 14 | 1 | 0 | -1.694546 | 3.990752 | -0.369441 |
| 15 | 1 | 0 | -2.451366 | 2.892681 | -1.488349 |
| 16 | 8 | 0 | -0.847512 | 2.120403 | 1.145849 |
| 17 | 1 | 0 | -2.294569 | 0.674386 | -1.322080 |
| 18 | 8 | 0 | 0.628745 | -0.839919 | -0.391671 |
| 19 | 1 | 0 | 1.240659 | 1.034744 | -0.778198 |
| 20 | 6 | 0 | 2.947027 | -0.268613 | -0.589166 |
| 21 | 1 | 0 | 2.925765 | -0.546329 | -1.645327 |
| 22 | 8 | 0 | 3.832764 | 0.801501 | -0.381131 |
| 23 | 1 | 0 | 4.643318 | 0.645026 | -0.881631 |
| 24 | 8 | 0 | 3.272002 | -1.389588 | 0.197757 |
| 25 | 1 | 0 | 3.904770 | -1.944120 | -0.273314 |
| 26 | 8 | 0 | 1.613327 | 0.547892 | 1.194257 |
| 27 | 1 | 0 | 0.842185 | 1.099787 | 1.398624 |

Structure of **22H$_a^+$**

```
Zero-point correction=                           0.221043 (Hartree/Particle)
 Thermal correction to Energy=                    0.236916
 Thermal correction to Enthalpy=                  0.237860
 Thermal correction to Gibbs Free Energy=         0.177845
 Sum of electronic and zero-point Energies=           -834.012287
 Sum of electronic and thermal Energies=              -833.996414
 Sum of electronic and thermal Enthalpies=            -833.995470
 Sum of electronic and thermal Free Energies=         -834.055485
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.994005 | 0.508115 | 0.079564 |
| 2 | 6 | 0 | -1.355258 | -0.550820 | -0.095917 |
| 3 | 1 | 0 | 0.930781 | 0.364256 | 1.156450 |
| 4 | 6 | 0 | 1.558334 | 1.883711 | -0.260157 |
| 5 | 1 | 0 | 1.696250 | 1.992204 | -1.339248 |
| 6 | 8 | 0 | 2.776634 | 1.971337 | 0.417245 |
| 7 | 8 | 0 | 0.609081 | 2.806737 | 0.210528 |
| 8 | 1 | 0 | 0.677606 | 3.634767 | -0.280956 |
| 9 | 1 | 0 | 3.339285 | 2.627913 | -0.012743 |
| 10 | 1 | 0 | -0.836807 | 1.445208 | -0.103200 |
| 11 | 7 | 0 | 1.653850 | -0.538938 | -0.555162 |
| 12 | 6 | 0 | 1.705167 | -1.806671 | 0.001108 |
| 13 | 7 | 0 | 2.460142 | -2.693536 | -0.654491 |
| 14 | 1 | 0 | 2.523712 | -3.631136 | -0.287433 |
| 15 | 1 | 0 | 3.011377 | -2.446376 | -1.463190 |
| 16 | 8 | 0 | 1.080632 | -2.078792 | 1.032484 |
| 17 | 1 | 0 | 2.096705 | -0.363106 | -1.450064 |
| 18 | 8 | 0 | -0.439430 | 0.592744 | -0.409114 |
| 19 | 1 | 0 | -0.984530 | -1.367551 | -0.713484 |
| 20 | 6 | 0 | -2.713536 | -0.041352 | -0.556501 |
| 21 | 1 | 0 | -2.699902 | 0.136292 | -1.633515 |
| 22 | 8 | 0 | -3.636268 | -1.035902 | -0.220997 |
| 23 | 1 | 0 | -4.433979 | -0.923876 | -0.753490 |
| 24 | 8 | 0 | -2.926306 | 1.164272 | 0.136585 |
| 25 | 1 | 0 | -3.557508 | 1.713514 | -0.344324 |
| 26 | 8 | 0 | -1.351486 | -0.810078 | 1.238486 |
| 27 | 1 | 0 | -0.596075 | -1.395239 | 1.442444 |

Structure of **22H$_b^+$**

```
Zero-point correction=                           0.222804 (Hartree/Particle)
 Thermal correction to Energy=                    0.238488
 Thermal correction to Enthalpy=                  0.239432
 Thermal correction to Gibbs Free Energy=         0.180260
 Sum of electronic and zero-point Energies=           -834.008715
 Sum of electronic and thermal Energies=              -833.993030
```

```
 Sum of electronic and thermal Enthalpies=            -833.992086
 Sum of electronic and thermal Free Energies=         -834.051258
No imaginary frequencies.

                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1          6           0       -0.913353   -0.447006    0.058299
      2          6           0        1.362746    0.258804   -0.037351
      3          1           0       -0.962515   -0.335108    1.144191
      4          6           0       -1.703915   -1.682595   -0.349452
      5          1           0       -1.802724   -1.794294   -1.428754
      6          8           0       -3.118270   -1.411108    0.086289
      7          8           0       -1.227441   -2.777926    0.292213
      8          1           0       -1.467449   -3.587458   -0.179672
      9          1           0       -3.767773   -1.990632   -0.355539
     10          7           0       -1.467740    0.721642   -0.549385
     11          6           0       -1.343153    1.954744    0.042101
     12          7           0       -1.808852    2.992299   -0.672463
     13          1           0       -1.769333    3.913525   -0.264462
     14          1           0       -2.285457    2.866947   -1.552940
     15          8           0       -0.832989    2.091219    1.164015
     16          1           0       -1.718426    0.675838   -1.530684
     17          8           0        0.408327   -0.740442   -0.351287
     18          1           0        1.111372    1.186249   -0.562130
     19          6           0        2.693426   -0.257437   -0.558712
     20          1           0        2.595453   -0.512020   -1.616969
     21          8           0        3.620577    0.786757   -0.391578
     22          1           0        4.403554    0.604075   -0.926039
     23          8           0        3.045980   -1.397423    0.184016
     24          1           0        3.690505   -1.914198   -0.314204
     25          8           0        1.452978    0.483218    1.338854
     26          1           0        0.778027    1.142771    1.577146
     27          1           0       -3.236879   -1.486701    1.053518
 ---------------------------------------------------------------------
```

Structure of **22H$_c^+$**

```
Zero-point correction=                           0.193407 (Hartree/Particle)
 Thermal correction to Energy=                    0.207369
 Thermal correction to Enthalpy=                  0.208313
 Thermal correction to Gibbs Free Energy=         0.152602
 Sum of electronic and zero-point Energies=           -757.581409
 Sum of electronic and thermal Energies=              -757.567447
 Sum of electronic and thermal Enthalpies=            -757.566503
 Sum of electronic and thermal Free Energies=         -757.622214
No imaginary frequencies.

                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1          6           0        0.502944    2.382404    0.452820
      2          6           0       -2.254746   -0.314641    0.166394
      3          6           0       -1.219742   -0.388522   -0.954849
      4          6           0        0.547259    0.934149    0.104186
      5          8           0       -0.391519    3.117603    0.002241
      6          8           0       -0.368861    0.762278   -0.953141
      7          8           0       -1.610841   -0.652216    1.370169
      8          1           0       -0.987401    2.623850   -0.617390
      9          1           0       -2.665997    0.697237    0.224433
     10          8           0       -3.258697   -1.239694   -0.164467
     11          1           0       -4.037860   -1.074521    0.381863
     12          1           0        1.217105    2.833443    1.137586
     13          1           0       -2.156027   -0.381789    2.120052
     14          8           0       -0.494555   -1.575930   -0.941871
     15          1           0       -0.142292   -1.760381   -0.053848
     16          7           0        1.882713    0.522573   -0.160800
     17          1           0        2.344609    0.942660   -0.960375
     18          6           0        2.276148   -0.747598    0.231376
     19          7           0        3.441549   -1.167129   -0.281033
     20          1           0        4.021677   -0.567838   -0.849925
     21          1           0        3.821416   -2.042653    0.046819
```

| | | | | | |
|---|---|---|---|---|---|
| 22 | 8 | 0 | 1.589723 | -1.419241 | 1.005958 |
| 23 | 1 | 0 | 0.212602 | 0.431240 | 1.025377 |
| 24 | 1 | 0 | -1.730846 | -0.326511 | -1.912432 |

Structure of **22**

```
Zero-point correction=                           0.210385 (Hartree/Particle)
 Thermal correction to Energy=                    0.225942
 Thermal correction to Enthalpy=                  0.226886
 Thermal correction to Gibbs Free Energy=         0.167698
 Sum of electronic and zero-point Energies=           -833.615931
 Sum of electronic and thermal Energies=              -833.600373
 Sum of electronic and thermal Enthalpies=            -833.599429
 Sum of electronic and thermal Free Energies=         -833.658617
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.909167 | -0.512633 | 0.066773 |
| 2 | 6 | 0 | 1.326411 | 0.313620 | -0.056962 |
| 3 | 1 | 0 | -0.944283 | -0.383241 | 1.150655 |
| 4 | 6 | 0 | -1.683686 | -1.773179 | -0.302106 |
| 5 | 1 | 0 | -1.670119 | -1.928994 | -1.385844 |
| 6 | 8 | 0 | -3.002396 | -1.592027 | 0.148402 |
| 7 | 8 | 0 | -1.056310 | -2.848357 | 0.348588 |
| 8 | 1 | 0 | -1.338405 | -3.676371 | -0.059484 |
| 9 | 1 | 0 | -3.572601 | -2.248206 | -0.270767 |
| 10 | 7 | 0 | -1.508323 | 0.633889 | -0.552866 |
| 11 | 6 | 0 | -1.501901 | 1.863736 | 0.037893 |
| 12 | 7 | 0 | -2.145420 | 2.843480 | -0.627386 |
| 13 | 1 | 0 | -2.226234 | 3.744091 | -0.181218 |
| 14 | 1 | 0 | -2.721523 | 2.648885 | -1.432583 |
| 15 | 8 | 0 | -0.920977 | 2.073305 | 1.116220 |
| 16 | 1 | 0 | -1.963036 | 0.516198 | -1.449785 |
| 17 | 8 | 0 | 0.427612 | -0.735734 | -0.352068 |
| 18 | 1 | 0 | 1.025304 | 1.220777 | -0.591557 |
| 19 | 6 | 0 | 2.683609 | -0.134706 | -0.571471 |
| 20 | 1 | 0 | 2.602122 | -0.404871 | -1.627219 |
| 21 | 8 | 0 | 3.555026 | 0.958587 | -0.413582 |
| 22 | 1 | 0 | 4.358233 | 0.799434 | -0.925136 |
| 23 | 8 | 0 | 3.099090 | -1.247445 | 0.181252 |
| 24 | 1 | 0 | 3.755048 | -1.744534 | -0.321932 |
| 25 | 8 | 0 | 1.409622 | 0.566091 | 1.317365 |
| 26 | 1 | 0 | 0.686764 | 1.178861 | 1.542448 |

Structure of **23H$^+$**

```
Zero-point correction=                           0.194268 (Hartree/Particle)
 Thermal correction to Energy=                    0.207556
 Thermal correction to Enthalpy=                  0.208500
 Thermal correction to Gibbs Free Energy=         0.154448
 Sum of electronic and zero-point Energies=           -757.596762
 Sum of electronic and thermal Energies=              -757.583475
 Sum of electronic and thermal Enthalpies=            -757.582531
 Sum of electronic and thermal Free Energies=         -757.636583
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 2.373512 | -0.073772 | -0.296270 |
| 2 | 6 | 0 | 0.296885 | 1.515481 | -0.350324 |
| 3 | 6 | 0 | -0.505676 | 0.301323 | 0.092649 |
| 4 | 6 | 0 | 1.386569 | -1.151485 | 0.132689 |
| 5 | 1 | 0 | 2.467653 | 0.001382 | -1.377249 |
| 6 | 1 | 0 | -0.518102 | 0.254484 | 1.185247 |
| 7 | 1 | 0 | 1.303176 | -1.179266 | 1.227328 |
| 8 | 8 | 0 | 3.592005 | -0.111731 | 0.287971 |

| | | | | | |
|---|---|---|---|---|---|
| 9 | 8 | 0 | 1.854983 | -2.342845 | -0.392039 |
| 10 | 8 | 0 | 0.123496 | -0.863810 | -0.439135 |
| 11 | 8 | 0 | 1.727841 | 1.250531 | 0.086266 |
| 12 | 1 | 0 | 3.535357 | -0.404067 | 1.211323 |
| 13 | 1 | 0 | 1.456020 | -3.085655 | 0.079326 |
| 14 | 7 | 0 | -1.830963 | 0.400413 | -0.400510 |
| 15 | 1 | 0 | -1.928285 | 0.605550 | -1.389455 |
| 16 | 1 | 0 | 0.389187 | 1.603903 | -1.432826 |
| 17 | 8 | 0 | -0.102734 | 2.637076 | 0.289356 |
| 18 | 1 | 0 | 0.181673 | 3.427335 | -0.191457 |
| 19 | 6 | 0 | -2.820589 | -0.368497 | 0.188437 |
| 20 | 7 | 0 | -3.960979 | -0.465658 | -0.518910 |
| 21 | 8 | 0 | -2.658532 | -0.903092 | 1.286173 |
| 22 | 1 | 0 | -4.102034 | 0.041380 | -1.379817 |
| 23 | 1 | 0 | -4.753142 | -0.919159 | -0.089674 |
| 24 | 1 | 0 | 1.831414 | 1.443496 | 1.041374 |

Structure of **24H⁺**

```
Zero-point correction=                           0.194518 (Hartree/Particle)
 Thermal correction to Energy=                    0.208217
 Thermal correction to Enthalpy=                  0.209161
 Thermal correction to Gibbs Free Energy=         0.153743
 Sum of electronic and zero-point Energies=           -757.588831
 Sum of electronic and thermal Energies=              -757.575132
 Sum of electronic and thermal Enthalpies=            -757.574188
 Sum of electronic and thermal Free Energies=         -757.629606
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.299168 | -0.428683 | 0.184388 |
| 2 | 6 | 0 | 0.425249 | 1.322938 | 0.264251 |
| 3 | 6 | 0 | 0.734112 | 0.162896 | -0.687488 |
| 4 | 1 | 0 | -1.103020 | -1.306576 | 0.803512 |
| 5 | 1 | 0 | 1.124918 | 1.482026 | 1.081784 |
| 6 | 1 | 0 | 1.150270 | 0.547945 | -1.613513 |
| 7 | 6 | 0 | -2.770932 | -0.245001 | -0.122995 |
| 8 | 1 | 0 | -2.922668 | 0.686180 | -0.674744 |
| 9 | 8 | 0 | -3.133170 | -1.356823 | -0.893418 |
| 10 | 8 | 0 | -3.417999 | -0.209475 | 1.119053 |
| 11 | 1 | 0 | -3.906244 | -1.141849 | -1.430744 |
| 12 | 1 | 0 | -4.250510 | 0.272495 | 1.039220 |
| 13 | 8 | 0 | -0.540094 | -0.375872 | -0.975358 |
| 14 | 8 | 0 | -0.828712 | 0.751757 | 0.947132 |
| 15 | 8 | 0 | 0.062676 | 2.425002 | -0.419211 |
| 16 | 7 | 0 | 1.605890 | -0.841220 | -0.133569 |
| 17 | 1 | 0 | 0.047556 | 3.202648 | 0.157023 |
| 18 | 1 | 0 | 1.209273 | -1.487536 | 0.540465 |
| 19 | 6 | 0 | 2.932952 | -0.499226 | 0.016009 |
| 20 | 7 | 0 | 3.685379 | -1.360727 | 0.730244 |
| 21 | 1 | 0 | 4.683615 | -1.213485 | 0.730495 |
| 22 | 1 | 0 | 3.342529 | -2.279684 | 0.969621 |
| 23 | 8 | 0 | 3.379364 | 0.539334 | -0.479190 |
| 24 | 1 | 0 | -0.724407 | 0.582547 | 1.903104 |

Structure of **23**

```
Zero-point correction=                           0.183198 (Hartree/Particle)
 Thermal correction to Energy=                    0.196158
 Thermal correction to Enthalpy=                  0.197102
 Thermal correction to Gibbs Free Energy=         0.143643
 Sum of electronic and zero-point Energies=           -757.210453
 Sum of electronic and thermal Energies=              -757.197493
 Sum of electronic and thermal Enthalpies=            -757.196549
 Sum of electronic and thermal Free Energies=         -757.250008
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -2.431172 | -0.228841 | 0.171414 |
| 2 | 6 | 0 | -0.645662 | 1.327528 | -0.144845 |
| 3 | 6 | 0 | 0.350292 | 0.178297 | -0.190791 |
| 4 | 6 | 0 | -1.426082 | -1.373926 | 0.183916 |
| 5 | 1 | 0 | -3.347557 | -0.528530 | -0.337751 |
| 6 | 1 | 0 | 0.476536 | -0.147967 | -1.223572 |
| 7 | 1 | 0 | -1.715018 | -2.129209 | 0.915383 |
| 8 | 8 | 0 | -2.674729 | 0.122692 | 1.506922 |
| 9 | 8 | 0 | -1.387843 | -1.901168 | -1.114598 |
| 10 | 8 | 0 | -0.159006 | -0.907704 | 0.598640 |
| 11 | 8 | 0 | -1.922571 | 0.857748 | -0.574675 |
| 12 | 1 | 0 | -3.411173 | 0.747176 | 1.537947 |
| 13 | 1 | 0 | -0.869630 | -2.716240 | -1.107375 |
| 14 | 7 | 0 | 1.610408 | 0.572422 | 0.339960 |
| 15 | 1 | 0 | 1.587008 | 1.056216 | 1.230902 |
| 16 | 1 | 0 | -0.729550 | 1.730591 | 0.869482 |
| 17 | 8 | 0 | -0.239929 | 2.302215 | -1.051324 |
| 18 | 1 | 0 | -0.700720 | 3.129088 | -0.860778 |
| 19 | 6 | 0 | 2.728139 | -0.185170 | 0.062024 |
| 20 | 7 | 0 | 3.807477 | 0.080428 | 0.824282 |
| 21 | 8 | 0 | 2.740558 | -1.027490 | -0.840560 |
| 22 | 1 | 0 | 3.808469 | 0.806594 | 1.524244 |
| 23 | 1 | 0 | 4.671509 | -0.395346 | 0.616264 |

## Structure of **23a**

```
Zero-point correction=                           0.182027 (Hartree/Particle)
 Thermal correction to Energy=                    0.194979
 Thermal correction to Enthalpy=                  0.195923
 Thermal correction to Gibbs Free Energy=         0.142285
 Sum of electronic and zero-point Energies=           -757.209642
 Sum of electronic and thermal Energies=              -757.196690
 Sum of electronic and thermal Enthalpies=            -757.195746
 Sum of electronic and thermal Free Energies=         -757.249384
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 2.310699 | 0.043430 | -0.288303 |
| 2 | 6 | 0 | 0.388616 | 1.447430 | -0.292011 |
| 3 | 6 | 0 | -0.479423 | 0.274613 | 0.150103 |
| 4 | 6 | 0 | 1.444627 | -1.125900 | 0.163055 |
| 5 | 1 | 0 | 2.378360 | 0.058030 | -1.380809 |
| 6 | 1 | 0 | -0.526819 | 0.251732 | 1.242399 |
| 7 | 1 | 0 | 1.421958 | -1.177786 | 1.260100 |
| 8 | 8 | 0 | 3.608182 | -0.016760 | 0.208722 |
| 9 | 8 | 0 | 1.947762 | -2.292848 | -0.399936 |
| 10 | 8 | 0 | 0.127024 | -0.928654 | -0.330052 |
| 11 | 8 | 0 | 1.711047 | 1.240213 | 0.186846 |
| 12 | 1 | 0 | 3.581992 | -0.105046 | 1.172294 |
| 13 | 1 | 0 | 1.568245 | -3.057336 | 0.051576 |
| 14 | 7 | 0 | -1.791638 | 0.381349 | -0.386848 |
| 15 | 1 | 0 | -1.863308 | 0.645524 | -1.362816 |
| 16 | 1 | 0 | 0.409777 | 1.515924 | -1.387381 |
| 17 | 8 | 0 | -0.096609 | 2.611904 | 0.289787 |
| 18 | 1 | 0 | 0.290476 | 3.377001 | -0.154401 |
| 19 | 6 | 0 | -2.818845 | -0.355592 | 0.155186 |
| 20 | 7 | 0 | -3.948687 | -0.400397 | -0.587891 |
| 21 | 8 | 0 | -2.709630 | -0.932076 | 1.239877 |
| 22 | 1 | 0 | -4.076635 | 0.228996 | -1.367046 |
| 23 | 1 | 0 | -4.778023 | -0.761816 | -0.140872 |

## Structure of **24**

```
Zero-point correction=                           0.183316 (Hartree/Particle)
 Thermal correction to Energy=                    0.196546
 Thermal correction to Enthalpy=                  0.197490
```

```
 Thermal correction to Gibbs Free Energy=         0.142876
 Sum of electronic and zero-point Energies=           -757.205673
 Sum of electronic and thermal Energies=              -757.192443
 Sum of electronic and thermal Enthalpies=            -757.191498
 Sum of electronic and thermal Free Energies=         -757.246113
No imaginary frequencies.

                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1          6           0       -1.318043   -0.548370    0.363951
      2          6           0        0.225286    1.138671    0.316628
      3          6           0        0.699565    0.014451   -0.600943
      4          1           0       -1.390861   -1.446246    0.983605
      5          1           0        0.995252    1.544809    0.971604
      6          1           0        1.007159    0.381629   -1.575569
      7          6           0       -2.697858   -0.152494   -0.140909
      8          1           0       -2.639960    0.745459   -0.761021
      9          8           0       -3.172141   -1.242381   -0.892108
     10          8           0       -3.483985    0.080005    1.000656
     11          1           0       -3.871920   -0.945326   -1.486639
     12          1           0       -4.275293    0.572723    0.749983
     13          8           0       -0.462892   -0.774385   -0.746307
     14          8           0       -0.721742    0.476320    1.133393
     15          8           0       -0.359239    2.130822   -0.479636
     16          7           0        1.761948   -0.787550   -0.030378
     17          1           0       -0.627219    2.872166    0.078973
     18          1           0        1.498892   -1.342477    0.777932
     19          6           0        3.038740   -0.280469   -0.050825
     20          7           0        3.929266   -0.890833    0.763841
     21          1           0        4.903422   -0.661760    0.635836
     22          1           0        3.709924   -1.768665    1.210943
     23          8           0        3.345745    0.675325   -0.771911
 ---------------------------------------------------------------------
```

## Structure of **24a**

```
Zero-point correction=                           0.183200 (Hartree/Particle)
 Thermal correction to Energy=                    0.196330
 Thermal correction to Enthalpy=                  0.197274
 Thermal correction to Gibbs Free Energy=         0.143295
 Sum of electronic and zero-point Energies=           -757.206095
 Sum of electronic and thermal Energies=              -757.192966
 Sum of electronic and thermal Enthalpies=            -757.192022
 Sum of electronic and thermal Free Energies=         -757.246001
No imaginary frequencies.

                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1          6           0        1.536766    0.422695    0.206700
      2          6           0       -0.404615    1.388452   -0.451090
      3          6           0       -0.714317    0.455472    0.717947
      4          1           0        2.211635    1.201213    0.575539
      5          1           0       -1.122203    1.346248   -1.269810
      6          1           0       -1.292661    0.945724    1.496470
      7          6           0        2.311059   -0.832338   -0.149003
      8          1           0        1.623527   -1.614616   -0.486101
      9          8           0        3.203878   -0.479201   -1.174740
     10          8           0        2.980218   -1.230115    1.020599
     11          1           0        3.494336   -1.275392   -1.636563
     12          1           0        3.231511   -2.159088    0.947491
     13          8           0        0.570920    0.141411    1.212730
     14          8           0        0.818355    0.861118   -0.925804
     15          8           0       -0.253889    2.684483    0.056000
     16          7           0       -1.375544   -0.766856    0.310582
     17          1           0       -0.084657    3.294474   -0.674015
     18          1           0       -0.787243   -1.453294   -0.149286
     19          6           0       -2.700864   -0.717351   -0.029261
     20          7           0       -3.189542   -1.807222   -0.669233
     21          1           0       -4.193599   -1.881921   -0.738597
     22          1           0       -2.662524   -2.668589   -0.688010
```

| | | | | | |
|---|---|---|---|---|---|
| 23 | 8 | 0 | -3.398320 | 0.270079 | 0.231426 |

Structure **$TS_{22c}$**

```
Zero-point correction=                           0.221129 (Hartree/Particle)
 Thermal correction to Energy=                    0.236711
 Thermal correction to Enthalpy=                  0.237656
 Thermal correction to Gibbs Free Energy=         0.177907
 Sum of electronic and zero-point Energies=           -834.001541
 Sum of electronic and thermal Energies=              -833.985959
 Sum of electronic and thermal Enthalpies=            -833.985014
 Sum of electronic and thermal Free Energies=         -834.044763
One imaginary frequency (cm-1): 110.1977i
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.429188 | -0.393885 | 0.214647 |
| 2 | 6 | 0 | 1.511949 | 0.284722 | -0.148400 |
| 3 | 1 | 0 | -1.084001 | -0.272535 | 1.235485 |
| 4 | 6 | 0 | -1.858115 | -1.758277 | -0.273810 |
| 5 | 1 | 0 | -1.658542 | -1.859316 | -1.343328 |
| 6 | 8 | 0 | -3.237186 | -1.810644 | -0.018310 |
| 7 | 8 | 0 | -1.134116 | -2.692660 | 0.470350 |
| 8 | 1 | 0 | -1.165415 | -3.550330 | 0.026835 |
| 9 | 1 | 0 | -3.655918 | -2.418904 | -0.641545 |
| 10 | 1 | 0 | 0.870122 | -1.553113 | 0.138239 |
| 11 | 7 | 0 | -1.805068 | 0.662815 | -0.435065 |
| 12 | 6 | 0 | -1.579592 | 1.991013 | 0.090228 |
| 13 | 7 | 0 | -2.148890 | 2.943200 | -0.632582 |
| 14 | 1 | 0 | -2.043607 | 3.903396 | -0.333608 |
| 15 | 1 | 0 | -2.717744 | 2.745518 | -1.445155 |
| 16 | 8 | 0 | -0.917594 | 2.130788 | 1.100791 |
| 17 | 1 | 0 | -2.241282 | 0.558541 | -1.352175 |
| 18 | 8 | 0 | 0.587902 | -0.769475 | -0.363000 |
| 19 | 1 | 0 | 1.177958 | 1.111575 | -0.778793 |
| 20 | 6 | 0 | 2.891503 | -0.184506 | -0.586772 |
| 21 | 1 | 0 | 2.859266 | -0.474458 | -1.639189 |
| 22 | 8 | 0 | 3.776418 | 0.888678 | -0.397911 |
| 23 | 1 | 0 | 4.581404 | 0.730336 | -0.906970 |
| 24 | 8 | 0 | 3.220751 | -1.295843 | 0.211245 |
| 25 | 1 | 0 | 3.844137 | -1.860802 | -0.260150 |
| 26 | 8 | 0 | 1.564665 | 0.653741 | 1.197708 |
| 27 | 1 | 0 | 0.805275 | 1.226908 | 1.391543 |

Structure **$TS_{23}$**

```
Zero-point correction=                           0.193273 (Hartree/Particle)
 Thermal correction to Energy=                    0.206535
 Thermal correction to Enthalpy=                  0.207479
 Thermal correction to Gibbs Free Energy=         0.153592
 Sum of electronic and zero-point Energies=           -757.580221
 Sum of electronic and thermal Energies=              -757.566960
 Sum of electronic and thermal Enthalpies=            -757.566015
 Sum of electronic and thermal Free Energies=         -757.619902
One imaginary frequency (cm-1): 42.8591i
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.270119 | 2.215628 | 0.423695 |
| 2 | 6 | 0 | -2.402457 | -0.280372 | -0.041340 |
| 3 | 6 | 0 | -1.188963 | -0.658356 | -0.882923 |
| 4 | 6 | 0 | 0.542927 | 0.783968 | 0.083178 |
| 5 | 8 | 0 | -0.631954 | 2.847351 | -0.151127 |
| 6 | 8 | 0 | -0.297450 | 0.459425 | -0.998922 |
| 7 | 8 | 0 | -1.943442 | -0.075716 | 1.271721 |
| 8 | 1 | 0 | -1.074475 | 2.291967 | -0.843063 |

| | | | | | |
|---|---|---|---|---|---|
| 9 | 1 | 0 | -2.853197 | 0.634634 | -0.436249 |
| 10 | 8 | 0 | -3.303748 | -1.352679 | -0.127167 |
| 11 | 1 | 0 | -4.180417 | -1.056468 | 0.148674 |
| 12 | 1 | 0 | 0.833279 | 2.742324 | 1.190482 |
| 13 | 1 | 0 | -2.638761 | 0.332266 | 1.803474 |
| 14 | 8 | 0 | -0.535559 | -1.792687 | -0.414711 |
| 15 | 1 | 0 | -0.585266 | -1.852580 | 0.550565 |
| 16 | 7 | 0 | 1.930711 | 0.617578 | -0.191400 |
| 17 | 1 | 0 | 2.260977 | 1.041313 | -1.052896 |
| 18 | 6 | 0 | 2.555094 | -0.549162 | 0.240321 |
| 19 | 7 | 0 | 3.701524 | -0.845766 | -0.393571 |
| 20 | 1 | 0 | 4.093367 | -0.248291 | -1.105906 |
| 21 | 1 | 0 | 4.257197 | -1.611096 | -0.043297 |
| 22 | 8 | 0 | 2.085899 | -1.227027 | 1.151686 |
| 23 | 1 | 0 | 0.311913 | 0.231211 | 1.001219 |
| 24 | 1 | 0 | -1.500543 | -0.847532 | -1.907635 |

Structure **$TS_{24}$**

```
Zero-point correction=                           0.193020 (Hartree/Particle)
 Thermal correction to Energy=                    0.206600
 Thermal correction to Enthalpy=                  0.207544
 Thermal correction to Gibbs Free Energy=         0.151661
 Sum of electronic and zero-point Energies=           -757.581427
 Sum of electronic and thermal Energies=              -757.567846
 Sum of electronic and thermal Enthalpies=            -757.566902
 Sum of electronic and thermal Free Energies=         -757.622785
One imaginary frequency (cm-1): 117.4293i
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.982972 | -0.319114 | 0.291247 |
| 2 | 6 | 0 | 0.371773 | 2.219002 | 0.125926 |
| 3 | 6 | 0 | 0.865257 | 0.915663 | -0.435954 |
| 4 | 1 | 0 | -0.460303 | -1.177979 | 0.718094 |
| 5 | 1 | 0 | 1.402335 | 1.166624 | -1.356787 |
| 6 | 6 | 0 | -2.364487 | -0.715441 | -0.200529 |
| 7 | 1 | 0 | -2.848080 | 0.140392 | -0.683807 |
| 8 | 8 | 0 | -2.181426 | -1.761396 | -1.115848 |
| 9 | 8 | 0 | -3.089942 | -1.113633 | 0.932913 |
| 10 | 1 | 0 | -2.980013 | -1.863245 | -1.649190 |
| 11 | 1 | 0 | -4.034847 | -1.066946 | 0.741126 |
| 12 | 8 | 0 | -0.259316 | 0.162333 | -0.837514 |
| 13 | 8 | 0 | -1.020791 | 0.684211 | 1.274521 |
| 14 | 8 | 0 | -0.536751 | 2.863999 | -0.443401 |
| 15 | 7 | 0 | 1.754067 | 0.290183 | 0.480837 |
| 16 | 1 | 0 | -0.955760 | 2.387587 | -1.194357 |
| 17 | 1 | 0 | 1.450872 | 0.219157 | 1.446967 |
| 18 | 6 | 0 | 2.576326 | -0.715871 | -0.008059 |
| 19 | 7 | 0 | 3.164017 | -1.479274 | 0.927348 |
| 20 | 1 | 0 | 3.833430 | -2.171582 | 0.627305 |
| 21 | 1 | 0 | 3.057979 | -1.300502 | 1.914978 |
| 22 | 8 | 0 | 2.751290 | -0.863737 | -1.217240 |
| 23 | 1 | 0 | 0.854693 | 2.720049 | 0.961435 |
| 24 | 1 | 0 | -1.846796 | 1.190433 | 1.233715 |

**Cartesian coordinates of all stationary points involved in the formation of 25 at the M06-2X/6-311+G(d) level in water (SMD).**

Structure of **26c**

```
Zero-point correction=                           0.220814 (Hartree/Particle)
 Thermal correction to Energy=                    0.237043
 Thermal correction to Enthalpy=                  0.237988
 Thermal correction to Gibbs Free Energy=         0.176820
 Sum of electronic and zero-point Energies=           -833.987662
 Sum of electronic and thermal Energies=              -833.971433
```

```
 Sum of electronic and thermal Enthalpies=            -833.970489
 Sum of electronic and thermal Free Energies=         -834.031657
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -3.127622 | 0.813759 | -0.272312 |
| 2 | 6 | 0 | -3.986231 | -0.235844 | -0.927458 |
| 3 | 6 | 0 | 0.139993 | -0.745503 | 0.338288 |
| 4 | 1 | 0 | -4.386956 | -0.136230 | -1.933216 |
| 5 | 1 | 0 | -1.568788 | -1.831102 | 0.245056 |
| 6 | 1 | 0 | -2.174091 | 0.812075 | -0.821647 |
| 7 | 8 | 0 | -3.810853 | 2.019646 | -0.420115 |
| 8 | 1 | 0 | -3.182193 | 2.750821 | -0.359183 |
| 9 | 8 | 0 | -2.943311 | 0.430279 | 1.051462 |
| 10 | 1 | 0 | -1.976333 | 0.331741 | 1.228342 |
| 11 | 7 | 0 | 1.383869 | -0.658375 | -0.208730 |
| 12 | 1 | 0 | 1.763059 | -1.471732 | -0.679444 |
| 13 | 8 | 0 | -0.294845 | 0.133109 | 1.105796 |
| 14 | 1 | 0 | -0.290777 | -2.440456 | -0.745181 |
| 15 | 7 | 0 | -0.586080 | -1.835898 | 0.007829 |
| 16 | 1 | 0 | -3.841072 | -1.251536 | 0.598776 |
| 17 | 8 | 0 | -4.238288 | -1.283065 | -0.313268 |
| 18 | 6 | 0 | 2.331499 | 0.312884 | 0.274752 |
| 19 | 1 | 0 | 1.832743 | 1.272332 | 0.389173 |
| 20 | 6 | 0 | 3.442760 | 0.450369 | -0.759002 |
| 21 | 1 | 0 | 3.029518 | 0.770545 | -1.718330 |
| 22 | 8 | 0 | 4.346240 | 1.410516 | -0.274295 |
| 23 | 1 | 0 | 4.916613 | 1.700652 | -0.996962 |
| 24 | 8 | 0 | 4.041676 | -0.818294 | -0.887631 |
| 25 | 1 | 0 | 4.534687 | -0.866514 | -1.715801 |
| 26 | 8 | 0 | 2.848856 | -0.008203 | 1.550282 |
| 27 | 1 | 0 | 3.360876 | -0.826570 | 1.491257 |

## Structure of **26H$_a^+$**

```
Zero-point correction=                           0.224047 (Hartree/Particle)
 Thermal correction to Energy=                    0.239835
 Thermal correction to Enthalpy=                  0.240779
 Thermal correction to Gibbs Free Energy=         0.180722
 Sum of electronic and zero-point Energies=           -834.016562
 Sum of electronic and thermal Energies=              -834.000775
 Sum of electronic and thermal Enthalpies=            -833.999830
 Sum of electronic and thermal Free Energies=         -834.059887
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 2.481851 | -0.590824 | -0.543977 |
| 2 | 8 | 0 | 3.133927 | -1.579563 | 0.206043 |
| 3 | 6 | 0 | 2.803972 | 0.748788 | 0.120156 |
| 4 | 7 | 0 | 1.047718 | -0.850513 | -0.644730 |
| 5 | 1 | 0 | 2.711677 | 0.679298 | 1.205350 |
| 6 | 1 | 0 | 3.239896 | -2.374780 | -0.330811 |
| 7 | 8 | 0 | 4.138439 | 1.023325 | -0.229914 |
| 8 | 1 | 0 | 4.532384 | 1.603240 | 0.433128 |
| 9 | 8 | 0 | 1.917125 | 1.708147 | -0.391318 |
| 10 | 1 | 0 | 2.000275 | 2.519885 | 0.124650 |
| 11 | 1 | 0 | 2.843496 | -0.561652 | -1.572791 |
| 12 | 6 | 0 | 0.254019 | -0.794946 | 0.415515 |
| 13 | 1 | 0 | 0.661869 | -1.024649 | -1.564569 |
| 14 | 8 | 0 | 0.534808 | -0.562727 | 1.562839 |
| 15 | 7 | 0 | -1.189695 | -1.051026 | 0.100597 |
| 16 | 1 | 0 | -1.488699 | -1.871131 | 0.645483 |
| 17 | 6 | 0 | -2.035639 | 0.150831 | 0.495669 |
| 18 | 1 | 0 | -1.943858 | 0.258854 | 1.574803 |
| 19 | 6 | 0 | -3.470293 | -0.170844 | 0.100284 |
| 20 | 1 | 0 | -3.822715 | -1.039569 | 0.663374 |

| | | | | | |
|---|---|---|---|---|---|
| 21 | 8 | 0 | -1.566519 | 1.246605 | -0.204492 |
| 22 | 1 | 0 | -0.960524 | 1.765573 | 0.341428 |
| 23 | 8 | 0 | -4.223336 | 0.965407 | 0.417271 |
| 24 | 1 | 0 | -5.154135 | 0.719790 | 0.492171 |
| 25 | 8 | 0 | -3.461725 | -0.451714 | -1.276367 |
| 26 | 1 | 0 | -4.244278 | -0.967140 | -1.508927 |
| 27 | 1 | 0 | -1.366772 | -1.250828 | -0.892737 |

Structure of **26H$_b^+$**

```
Zero-point correction=                           0.222408 (Hartree/Particle)
 Thermal correction to Energy=                    0.238580
 Thermal correction to Enthalpy=                  0.239524
 Thermal correction to Gibbs Free Energy=         0.178670
 Sum of electronic and zero-point Energies=           -834.009546
 Sum of electronic and thermal Energies=              -833.993374
 Sum of electronic and thermal Enthalpies=            -833.992430
 Sum of electronic and thermal Free Energies=         -834.053284
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -2.582913 | -0.797216 | 0.309831 |
| 2 | 8 | 0 | -2.910506 | -1.630915 | -0.779271 |
| 3 | 6 | 0 | -3.113805 | 0.590876 | -0.049676 |
| 4 | 7 | 0 | -1.171664 | -0.827577 | 0.627078 |
| 5 | 1 | 0 | -2.843377 | 0.864450 | -1.070025 |
| 6 | 1 | 0 | -2.859917 | -2.553363 | -0.499494 |
| 7 | 8 | 0 | -4.515201 | 0.500852 | 0.061614 |
| 8 | 1 | 0 | -4.922633 | 1.184535 | -0.483749 |
| 9 | 8 | 0 | -2.579386 | 1.511563 | 0.866571 |
| 10 | 1 | 0 | -2.760303 | 2.406042 | 0.552292 |
| 11 | 1 | 0 | -3.096432 | -1.125294 | 1.216173 |
| 12 | 6 | 0 | -0.225199 | -0.321565 | -0.192060 |
| 13 | 1 | 0 | -0.894516 | -1.261212 | 1.497384 |
| 14 | 8 | 0 | -0.454385 | 0.192540 | -1.279439 |
| 15 | 7 | 0 | 1.074203 | -0.439195 | 0.290869 |
| 16 | 1 | 0 | 1.245179 | -0.737708 | 1.244791 |
| 17 | 6 | 0 | 2.137942 | 0.058965 | -0.437528 |
| 18 | 1 | 0 | 1.972081 | 0.023563 | -1.509148 |
| 19 | 6 | 0 | 3.473939 | -0.543745 | -0.043317 |
| 20 | 1 | 0 | 3.493745 | -1.584126 | -0.376441 |
| 21 | 8 | 0 | 2.230193 | 1.584361 | -0.207009 |
| 22 | 1 | 0 | 2.973022 | 1.982599 | -0.702617 |
| 23 | 8 | 0 | 4.448446 | 0.216317 | -0.704229 |
| 24 | 1 | 0 | 5.291153 | -0.255165 | -0.701563 |
| 25 | 8 | 0 | 3.580354 | -0.463777 | 1.351787 |
| 26 | 1 | 0 | 4.222505 | -1.111686 | 1.668115 |
| 27 | 1 | 0 | 2.325814 | 1.823348 | 0.734981 |

Structure of **26H$_c^+$**

```
Zero-point correction=                           0.194118 (Hartree/Particle)
 Thermal correction to Energy=                    0.208714
 Thermal correction to Enthalpy=                  0.209658
 Thermal correction to Gibbs Free Energy=         0.151926
 Sum of electronic and zero-point Energies=           -757.595830
 Sum of electronic and thermal Energies=              -757.581234
 Sum of electronic and thermal Enthalpies=            -757.580289
 Sum of electronic and thermal Free Energies=         -757.638021
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 2.323649 | 0.735620 | 0.337444 |

| | | | | | |
|---|---|---|---|---|---|
| 2 | 8 | 0 | 2.703026 | 1.591471 | -0.708023 |
| 3 | 6 | 0 | 2.865139 | -0.650194 | -0.015008 |
| 4 | 7 | 0 | 0.880765 | 0.752026 | 0.557067 |
| 5 | 1 | 0 | 2.693437 | -0.881507 | -1.067502 |
| 6 | 1 | 0 | 2.693937 | 2.504992 | -0.395354 |
| 7 | 8 | 0 | 4.247198 | -0.580573 | 0.238805 |
| 8 | 1 | 0 | 4.706884 | -1.231951 | -0.304193 |
| 9 | 8 | 0 | 2.225933 | -1.588433 | 0.809885 |
| 10 | 1 | 0 | 2.428853 | -2.476590 | 0.490597 |
| 11 | 1 | 0 | 2.764279 | 1.045439 | 1.286258 |
| 12 | 6 | 0 | 0.027572 | 0.239563 | -0.322881 |
| 13 | 1 | 0 | 0.537909 | 1.179552 | 1.409534 |
| 14 | 8 | 0 | 0.255458 | -0.288000 | -1.380720 |
| 15 | 7 | 0 | -1.368521 | 0.366801 | 0.125666 |
| 16 | 1 | 0 | -1.585445 | 0.773979 | 1.042115 |
| 17 | 6 | 0 | -2.338996 | -0.032513 | -0.598574 |
| 18 | 1 | 0 | -2.127998 | -0.471943 | -1.568983 |
| 19 | 6 | 0 | -3.753123 | 0.130335 | -0.128755 |
| 20 | 1 | 0 | -4.195498 | 0.933619 | -0.731087 |
| 21 | 8 | 0 | -4.386119 | -1.091435 | -0.379264 |
| 22 | 1 | 0 | -5.339774 | -0.948679 | -0.440855 |
| 23 | 8 | 0 | -3.723754 | 0.478059 | 1.222839 |
| 24 | 1 | 0 | -4.481688 | 1.035715 | 1.438797 |

Structure of **22H$_d^+$**

```
Zero-point correction=                           0.220578 (Hartree/Particle)
 Thermal correction to Energy=                    0.236243
 Thermal correction to Enthalpy=                  0.237187
 Thermal correction to Gibbs Free Energy=         0.177291
 Sum of electronic and zero-point Energies=           -834.017199
 Sum of electronic and thermal Energies=              -834.001533
 Sum of electronic and thermal Enthalpies=            -834.000589
 Sum of electronic and thermal Free Energies=         -834.060485
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.967135 | 0.450750 | -0.145126 |
| 2 | 6 | 0 | 1.379114 | 0.012555 | -0.375256 |
| 3 | 1 | 0 | -0.889354 | 0.410831 | -1.233811 |
| 4 | 6 | 0 | -1.207083 | 1.893125 | 0.291296 |
| 5 | 1 | 0 | -1.260603 | 1.973100 | 1.379773 |
| 6 | 8 | 0 | -2.385807 | 2.325544 | -0.311353 |
| 7 | 8 | 0 | -0.096162 | 2.650748 | -0.180147 |
| 8 | 1 | 0 | -0.070581 | 3.515174 | 0.253145 |
| 9 | 1 | 0 | -2.731370 | 3.094050 | 0.160833 |
| 10 | 7 | 0 | -2.027129 | -0.379923 | 0.299693 |
| 11 | 6 | 0 | -2.069217 | -1.682187 | -0.145706 |
| 12 | 7 | 0 | -2.925253 | -2.494187 | 0.511663 |
| 13 | 1 | 0 | -3.106196 | -3.398673 | 0.102744 |
| 14 | 1 | 0 | -3.619891 | -2.117614 | 1.140126 |
| 15 | 8 | 0 | -1.358129 | -2.066452 | -1.077032 |
| 16 | 1 | 0 | -2.458826 | -0.157863 | 1.188977 |
| 17 | 8 | 0 | 0.269544 | -0.020831 | 0.427120 |
| 18 | 1 | 0 | 1.151211 | -0.068506 | -1.437179 |
| 19 | 6 | 0 | 2.388342 | -1.024057 | 0.082058 |
| 20 | 1 | 0 | 1.894174 | -1.996832 | 0.130552 |
| 21 | 8 | 0 | 3.425653 | -1.025447 | -0.859457 |
| 22 | 1 | 0 | 3.951905 | -1.828012 | -0.752218 |
| 23 | 8 | 0 | 2.818209 | -0.609268 | 1.352382 |
| 24 | 1 | 0 | 3.230691 | -1.343964 | 1.824174 |
| 25 | 8 | 0 | 2.032991 | 1.335721 | -0.235869 |
| 26 | 1 | 0 | 2.517171 | 1.382993 | 0.614027 |
| 27 | 1 | 0 | 1.263823 | 2.032848 | -0.219387 |

Structure of **22H$_e^+$**

```
Zero-point correction=                           0.192072 (Hartree/Particle)
 Thermal correction to Energy=                    0.206690
 Thermal correction to Enthalpy=                  0.207634
 Thermal correction to Gibbs Free Energy=         0.150056
 Sum of electronic and zero-point Energies=           -757.572149
 Sum of electronic and thermal Energies=              -757.557532
 Sum of electronic and thermal Enthalpies=            -757.556587
 Sum of electronic and thermal Free Energies=         -757.614165
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.555864 | -0.460292 | 0.035953 |
| 2 | 6 | 0 | 2.636609 | 0.875128 | -0.036833 |
| 3 | 6 | 0 | -1.377264 | 0.803451 | 0.930771 |
| 4 | 1 | 0 | 0.249884 | -0.030397 | -0.914735 |
| 5 | 8 | 0 | 3.845298 | 0.878792 | 0.179717 |
| 6 | 7 | 0 | 1.885271 | -0.232199 | 0.335792 |
| 7 | 7 | 0 | 1.990009 | 1.884464 | -0.651692 |
| 8 | 1 | 0 | 2.386474 | -0.923800 | 0.881601 |
| 9 | 1 | 0 | 0.990133 | 2.017060 | -0.596292 |
| 10 | 8 | 0 | -0.283807 | 0.254089 | 1.121495 |
| 11 | 6 | 0 | 0.154334 | -1.929628 | 0.138289 |
| 12 | 1 | 0 | 0.428492 | -2.333271 | 1.116494 |
| 13 | 6 | 0 | -2.219533 | 0.809988 | -0.326233 |
| 14 | 1 | 0 | -1.711900 | 0.449172 | -1.218864 |
| 15 | 8 | 0 | -1.232923 | -1.978018 | -0.046401 |
| 16 | 1 | 0 | -1.592462 | -2.771792 | 0.370025 |
| 17 | 8 | 0 | 0.853817 | -2.570376 | -0.888368 |
| 18 | 1 | 0 | 0.956904 | -3.506019 | -0.672956 |
| 19 | 8 | 0 | -3.306939 | -0.013982 | 0.012172 |
| 20 | 1 | 0 | -3.074219 | -0.929559 | -0.207231 |
| 21 | 8 | 0 | -2.635290 | 2.126825 | -0.451184 |
| 22 | 1 | 0 | -2.916316 | 2.293741 | -1.361186 |
| 23 | 1 | 0 | -1.806999 | 1.294736 | 1.806158 |
| 24 | 1 | 0 | 2.541744 | 2.703756 | -0.862835 |

## Structure of **26**

```
Zero-point correction=                           0.210038 (Hartree/Particle)
 Thermal correction to Energy=                    0.225926
 Thermal correction to Enthalpy=                  0.226870
 Thermal correction to Gibbs Free Energy=         0.166573
 Sum of electronic and zero-point Energies=           -833.612083
 Sum of electronic and thermal Energies=              -833.596194
 Sum of electronic and thermal Enthalpies=            -833.595250
 Sum of electronic and thermal Free Energies=         -833.655548
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -2.525210 | -0.789334 | 0.317447 |
| 2 | 8 | 0 | -2.808553 | -1.653957 | -0.763939 |
| 3 | 6 | 0 | -3.130988 | 0.561769 | -0.064449 |
| 4 | 7 | 0 | -1.120560 | -0.748320 | 0.646171 |
| 5 | 1 | 0 | -2.870307 | 0.836931 | -1.086492 |
| 6 | 1 | 0 | -2.713486 | -2.568158 | -0.469929 |
| 7 | 8 | 0 | -4.527051 | 0.392469 | 0.038219 |
| 8 | 1 | 0 | -4.968029 | 1.046409 | -0.517211 |
| 9 | 8 | 0 | -2.663460 | 1.527781 | 0.841216 |
| 10 | 1 | 0 | -2.897966 | 2.403490 | 0.510415 |
| 11 | 1 | 0 | -3.032167 | -1.131618 | 1.222664 |
| 12 | 6 | 0 | -0.175017 | -0.269430 | -0.207952 |
| 13 | 1 | 0 | -0.822018 | -1.306590 | 1.434451 |
| 14 | 8 | 0 | -0.453841 | 0.341099 | -1.238842 |
| 15 | 7 | 0 | 1.124178 | -0.544801 | 0.155021 |
| 16 | 1 | 0 | 1.287276 | -0.856033 | 1.106026 |
| 17 | 6 | 0 | 2.178595 | 0.239352 | -0.410394 |

| | | | | | |
|---|---|---|---|---|---|
| 18 | 1 | 0 | 2.029380 | 0.316125 | -1.488069 |
| 19 | 6 | 0 | 3.513609 | -0.448174 | -0.157109 |
| 20 | 1 | 0 | 3.552787 | -1.401336 | -0.690080 |
| 21 | 8 | 0 | 2.156240 | 1.532462 | 0.176927 |
| 22 | 1 | 0 | 2.819274 | 2.083697 | -0.260073 |
| 23 | 8 | 0 | 4.502700 | 0.425919 | -0.644517 |
| 24 | 1 | 0 | 5.340761 | -0.046686 | -0.722907 |
| 25 | 8 | 0 | 3.640635 | -0.659977 | 1.228033 |
| 26 | 1 | 0 | 4.309865 | -1.335859 | 1.390818 |

Structure of **25H$_a^+$**

```
Zero-point correction=                           0.197599 (Hartree/Particle)
 Thermal correction to Energy=                    0.210755
 Thermal correction to Enthalpy=                  0.211700
 Thermal correction to Gibbs Free Energy=         0.157714
 Sum of electronic and zero-point Energies=           -757.604344
 Sum of electronic and thermal Energies=              -757.591188
 Sum of electronic and thermal Enthalpies=            -757.590243
 Sum of electronic and thermal Free Energies=         -757.644229
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 1.002046 | -0.130800 | -0.166908 |
| 2 | 6 | 0 | 0.141173 | 2.118557 | 0.051270 |
| 3 | 6 | 0 | -1.240708 | -0.002851 | 0.543312 |
| 4 | 1 | 0 | 0.686053 | -0.426496 | -1.172480 |
| 5 | 1 | 0 | -1.732781 | 0.152979 | 1.502010 |
| 6 | 8 | 0 | 0.088058 | 3.298565 | 0.260271 |
| 7 | 7 | 0 | 1.184245 | 1.312494 | -0.091757 |
| 8 | 7 | 0 | -1.151101 | 1.359551 | -0.135341 |
| 9 | 1 | 0 | 2.116057 | 1.703082 | 0.011041 |
| 10 | 1 | 0 | -1.292668 | 1.249222 | -1.150927 |
| 11 | 8 | 0 | 0.038282 | -0.494153 | 0.796634 |
| 12 | 6 | 0 | 2.300044 | -0.835577 | 0.190097 |
| 13 | 1 | 0 | 2.560048 | -0.639918 | 1.234205 |
| 14 | 6 | 0 | -2.082128 | -0.922589 | -0.334759 |
| 15 | 1 | 0 | -1.586258 | -1.125661 | -1.289310 |
| 16 | 8 | 0 | 2.067279 | -2.200416 | -0.019069 |
| 17 | 1 | 0 | 2.693274 | -2.718722 | 0.501512 |
| 18 | 8 | 0 | 3.276610 | -0.312978 | -0.670715 |
| 19 | 1 | 0 | 4.152751 | -0.456459 | -0.291766 |
| 20 | 8 | 0 | -2.243736 | -2.100495 | 0.400956 |
| 21 | 1 | 0 | -2.408943 | -2.837713 | -0.199911 |
| 22 | 8 | 0 | -3.286218 | -0.231558 | -0.536489 |
| 23 | 1 | 0 | -3.749528 | -0.597248 | -1.300107 |
| 24 | 1 | 0 | -1.914777 | 1.960470 | 0.194637 |

Structure of **25H$_b^+$**

```
Zero-point correction=                           0.195259 (Hartree/Particle)
 Thermal correction to Energy=                    0.208562
 Thermal correction to Enthalpy=                  0.209506
 Thermal correction to Gibbs Free Energy=         0.155595
 Sum of electronic and zero-point Energies=           -757.586291
 Sum of electronic and thermal Energies=              -757.572987
 Sum of electronic and thermal Enthalpies=            -757.572043
 Sum of electronic and thermal Free Energies=         -757.625954
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 1.315036 | 0.068336 | -0.506811 |
| 2 | 6 | 0 | 0.040743 | 2.155471 | -0.027155 |

| | | | | | |
|---|---|---|---|---|---|
| 3 | 6 | 0 | -1.064620 | 0.045141 | 0.189193 |
| 4 | 1 | 0 | 1.807590 | 0.100592 | -1.479102 |
| 5 | 1 | 0 | -0.695364 | -0.249283 | 1.172337 |
| 6 | 8 | 0 | 0.065291 | 3.372386 | -0.101130 |
| 7 | 7 | 0 | 1.175574 | 1.386055 | 0.074399 |
| 8 | 7 | 0 | -1.132231 | 1.434389 | 0.016126 |
| 9 | 1 | 0 | 2.032817 | 1.926609 | 0.016220 |
| 10 | 1 | 0 | -1.927400 | 1.833672 | -0.471731 |
| 11 | 8 | 0 | -0.020952 | -0.445034 | -0.787442 |
| 12 | 6 | 0 | 2.033831 | -0.916490 | 0.409001 |
| 13 | 1 | 0 | 1.602690 | -0.917051 | 1.412730 |
| 14 | 6 | 0 | -2.336566 | -0.705568 | -0.164759 |
| 15 | 1 | 0 | -2.734053 | -0.371438 | -1.126187 |
| 16 | 8 | 0 | 1.857937 | -2.167218 | -0.206548 |
| 17 | 1 | 0 | 1.891762 | -2.872669 | 0.451814 |
| 18 | 8 | 0 | 3.362616 | -0.488090 | 0.425764 |
| 19 | 1 | 0 | 3.794177 | -0.792981 | 1.233579 |
| 20 | 8 | 0 | -1.951855 | -2.053640 | -0.227253 |
| 21 | 1 | 0 | -2.550478 | -2.543258 | -0.805384 |
| 22 | 8 | 0 | -3.227720 | -0.436170 | 0.876208 |
| 23 | 1 | 0 | -4.134168 | -0.561453 | 0.567562 |
| 24 | 1 | 0 | -0.004056 | -1.435055 | -0.839122 |

## Structure of **25**

```
Zero-point correction=                           0.183832 (Hartree/Particle)
 Thermal correction to Energy=                    0.196972
 Thermal correction to Enthalpy=                  0.197916
 Thermal correction to Gibbs Free Energy=         0.143912
 Sum of electronic and zero-point Energies=           -757.206255
 Sum of electronic and thermal Energies=              -757.193116
 Sum of electronic and thermal Enthalpies=            -757.192171
 Sum of electronic and thermal Free Energies=         -757.246176
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.964695 | -0.058430 | -0.107396 |
| 2 | 6 | 0 | -0.452086 | 1.949900 | 0.030094 |
| 3 | 6 | 0 | -1.202977 | -0.268707 | 0.767517 |
| 4 | 1 | 0 | 0.725871 | -0.545791 | -1.060186 |
| 5 | 1 | 0 | -1.703158 | -0.636803 | 1.663615 |
| 6 | 8 | 0 | -0.690721 | 3.121632 | -0.278598 |
| 7 | 7 | 0 | 0.768020 | 1.379652 | -0.184715 |
| 8 | 7 | 0 | -1.360842 | 1.175413 | 0.693722 |
| 9 | 1 | 0 | 1.389524 | 1.894039 | -0.795627 |
| 10 | 1 | 0 | -2.308935 | 1.529184 | 0.685929 |
| 11 | 8 | 0 | 0.160624 | -0.574025 | 0.925745 |
| 12 | 6 | 0 | 2.411700 | -0.371623 | 0.230086 |
| 13 | 1 | 0 | 2.674413 | 0.022200 | 1.215448 |
| 14 | 6 | 0 | -1.835500 | -0.962182 | -0.441288 |
| 15 | 1 | 0 | -1.460155 | -0.562164 | -1.387791 |
| 16 | 8 | 0 | 2.534848 | -1.769858 | 0.207230 |
| 17 | 1 | 0 | 3.330213 | -2.030177 | 0.688440 |
| 18 | 8 | 0 | 3.183282 | 0.243316 | -0.771414 |
| 19 | 1 | 0 | 4.085379 | 0.371515 | -0.454213 |
| 20 | 8 | 0 | -1.541944 | -2.329695 | -0.330344 |
| 21 | 1 | 0 | -1.725720 | -2.768144 | -1.170768 |
| 22 | 8 | 0 | -3.213166 | -0.700560 | -0.331487 |
| 23 | 1 | 0 | -3.636060 | -0.819550 | -1.191025 |

## Structure $TS_{26c}$

```
Zero-point correction=                           0.219346 (Hartree/Particle)
 Thermal correction to Energy=                    0.235368
 Thermal correction to Enthalpy=                  0.236312
 Thermal correction to Gibbs Free Energy=         0.175008
 Sum of electronic and zero-point Energies=           -833.987626
```

```
 Sum of electronic and thermal Energies=              -833.971603
 Sum of electronic and thermal Enthalpies=            -833.970659
 Sum of electronic and thermal Free Energies=         -834.031963
One imaginary frequency (cm-1): 20.0524i
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -2.841284 | 0.895490 | -0.160949 |
| 2 | 6 | 0 | -3.449673 | -0.210949 | -0.998273 |
| 3 | 6 | 0 | 0.021930 | -0.813600 | 0.315953 |
| 4 | 1 | 0 | -3.473567 | -0.195070 | -2.085170 |
| 5 | 1 | 0 | -1.557739 | -2.055007 | 0.241001 |
| 6 | 1 | 0 | -1.814651 | 1.071219 | -0.496838 |
| 7 | 8 | 0 | -3.668781 | 1.989558 | -0.412245 |
| 8 | 1 | 0 | -3.172121 | 2.808127 | -0.279177 |
| 9 | 8 | 0 | -2.895709 | 0.494699 | 1.172917 |
| 10 | 1 | 0 | -1.994063 | 0.227087 | 1.461691 |
| 11 | 7 | 0 | 1.220809 | -0.599378 | -0.279484 |
| 12 | 1 | 0 | 1.516663 | -1.211504 | -1.030560 |
| 13 | 8 | 0 | -0.294711 | -0.249216 | 1.375791 |
| 14 | 1 | 0 | -0.511225 | -2.203172 | -1.097373 |
| 15 | 7 | 0 | -0.858504 | -1.619256 | -0.347707 |
| 16 | 1 | 0 | -3.916980 | -1.065936 | 0.560501 |
| 17 | 8 | 0 | -4.006372 | -1.161618 | -0.426712 |
| 18 | 6 | 0 | 2.232289 | 0.189502 | 0.380705 |
| 19 | 1 | 0 | 1.766721 | 1.075310 | 0.806272 |
| 20 | 6 | 0 | 3.260814 | 0.614254 | -0.658851 |
| 21 | 1 | 0 | 2.776294 | 1.165785 | -1.468019 |
| 22 | 8 | 0 | 4.200361 | 1.428991 | -0.006364 |
| 23 | 1 | 0 | 4.714368 | 1.910108 | -0.666862 |
| 24 | 8 | 0 | 3.843893 | -0.566795 | -1.157934 |
| 25 | 1 | 0 | 4.295746 | -0.382966 | -1.990750 |
| 26 | 8 | 0 | 2.837698 | -0.489615 | 1.460158 |
| 27 | 1 | 0 | 3.358931 | -1.229759 | 1.119239 |

## Structure $TS_{25a}$

```
Zero-point correction=                           0.192791 (Hartree/Particle)
 Thermal correction to Energy=                    0.206291
 Thermal correction to Enthalpy=                  0.207236
 Thermal correction to Gibbs Free Energy=         0.152772
 Sum of electronic and zero-point Energies=           -757.564585
 Sum of electronic and thermal Energies=              -757.551085
 Sum of electronic and thermal Enthalpies=            -757.550140
 Sum of electronic and thermal Free Energies=         -757.604604
One imaginary frequency (cm-1): 206.2967i
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.925883 | -0.143508 | -0.139140 |
| 2 | 6 | 0 | 0.441873 | 2.242020 | -0.041613 |
| 3 | 6 | 0 | -1.272934 | -0.160131 | 0.803061 |
| 4 | 1 | 0 | 0.416155 | -0.424778 | -1.057067 |
| 5 | 8 | 0 | 0.734236 | 3.315907 | 0.451291 |
| 6 | 7 | 0 | 1.355148 | 1.206806 | -0.124854 |
| 7 | 7 | 0 | -0.833109 | 1.919591 | -0.478209 |
| 8 | 1 | 0 | 2.214109 | 1.394527 | 0.384247 |
| 9 | 1 | 0 | -0.876245 | 1.455942 | -1.383845 |
| 10 | 8 | 0 | -0.034899 | -0.264521 | 0.995232 |
| 11 | 6 | 0 | 2.039880 | -1.130855 | 0.160740 |
| 12 | 1 | 0 | 2.481235 | -0.923761 | 1.140011 |
| 13 | 6 | 0 | -2.071445 | -0.744678 | -0.343319 |
| 14 | 1 | 0 | -1.543816 | -0.829629 | -1.292342 |
| 15 | 8 | 0 | 1.432989 | -2.392250 | 0.144395 |
| 16 | 1 | 0 | 1.955544 | -3.010778 | 0.669663 |
| 17 | 8 | 0 | 2.982534 | -0.965221 | -0.860295 |
| 18 | 1 | 0 | 3.834791 | -1.316517 | -0.572309 |
| 19 | 8 | 0 | -2.357458 | -2.019553 | 0.185304 |

| | | | | | |
|---|---|---|---|---|---|
| 20 | 1 | 0 | -1.741886 | -2.671184 | -0.180266 |
| 21 | 8 | 0 | -3.225921 | 0.009528 | -0.433806 |
| 22 | 1 | 0 | -3.710708 | -0.239734 | -1.232755 |
| 23 | 1 | 0 | -1.846626 | 0.123196 | 1.686437 |
| 24 | 1 | 0 | -1.468213 | 2.709734 | -0.435688 |

Structure **$TS_{25b}$**

```
Zero-point correction=                           0.194551 (Hartree/Particle)
 Thermal correction to Energy=                    0.207588
 Thermal correction to Enthalpy=                  0.208532
 Thermal correction to Gibbs Free Energy=         0.154794
 Sum of electronic and zero-point Energies=           -757.577054
 Sum of electronic and thermal Energies=              -757.564017
 Sum of electronic and thermal Enthalpies=            -757.563073
 Sum of electronic and thermal Free Energies=         -757.616810
One imaginary frequency (cm-1): 155.4519i
```

Standard orientation:
Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.200861 | -0.170642 | 0.227026 |
| 2 | 6 | 0 | -0.041611 | 1.968364 | -0.051033 |
| 3 | 6 | 0 | 1.451247 | 0.133504 | -0.288093 |
| 4 | 1 | 0 | -1.186557 | -0.062115 | 1.311889 |
| 5 | 1 | 0 | 1.266884 | 0.124876 | -1.356056 |
| 6 | 8 | 0 | -0.040027 | 3.172940 | -0.067035 |
| 7 | 7 | 0 | -1.041588 | 1.135976 | -0.420953 |
| 8 | 7 | 0 | 1.107234 | 1.210327 | 0.379194 |
| 9 | 1 | 0 | -1.907501 | 1.590163 | -0.696783 |
| 10 | 1 | 0 | 1.466972 | 1.382631 | 1.317749 |
| 11 | 8 | 0 | -0.118700 | -1.039254 | -0.079479 |
| 12 | 6 | 0 | -2.526700 | -0.784041 | -0.206033 |
| 13 | 1 | 0 | -2.514454 | -1.000778 | -1.279499 |
| 14 | 6 | 0 | 2.528792 | -0.776647 | 0.251701 |
| 15 | 1 | 0 | 2.288511 | -1.076721 | 1.274660 |
| 16 | 8 | 0 | -2.669277 | -1.965380 | 0.532785 |
| 17 | 1 | 0 | -3.289643 | -2.553327 | 0.083490 |
| 18 | 8 | 0 | -3.515268 | 0.164236 | 0.093224 |
| 19 | 1 | 0 | -4.308038 | -0.018086 | -0.427296 |
| 20 | 8 | 0 | 2.561297 | -1.878984 | -0.606372 |
| 21 | 1 | 0 | 2.950975 | -2.634997 | -0.149460 |
| 22 | 8 | 0 | 3.707468 | -0.017416 | 0.216978 |
| 23 | 1 | 0 | 4.351400 | -0.402846 | 0.825948 |
| 24 | 1 | 0 | -0.247208 | -1.485284 | -0.934555 |

**Cartesian coordinates of all stationary points involved in the formation of 7 at the M06-2X/6-311+G(d) level in water (SMD).**

Structure of **$33H_a^+$**

```
Zero-point correction=                           0.188008 (Hartree/Particle)
 Thermal correction to Energy=                    0.202049
 Thermal correction to Enthalpy=                  0.202993
 Thermal correction to Gibbs Free Energy=         0.146586
 Sum of electronic and zero-point Energies=           -678.608249
 Sum of electronic and thermal Energies=              -678.594208
```

```
 Sum of electronic and thermal Enthalpies=            -678.593264
 Sum of electronic and thermal Free Energies=         -678.649671
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.861461 | 1.024570 | -0.648919 |
| 2 | 6 | 0 | -2.088009 | -0.917517 | 0.215271 |
| 3 | 1 | 0 | -0.635489 | 1.419252 | -1.642132 |
| 4 | 8 | 0 | -1.505822 | 2.012017 | 0.131300 |
| 5 | 6 | 0 | 0.457743 | 0.764138 | 0.073931 |
| 6 | 1 | 0 | 0.335123 | 0.478429 | 1.111408 |
| 7 | 8 | 0 | 1.064358 | 2.184306 | 0.152172 |
| 8 | 1 | 0 | -3.363173 | -2.437112 | 0.638115 |
| 9 | 7 | 0 | -3.077213 | -1.785283 | -0.076246 |
| 10 | 7 | 0 | -1.622151 | -0.173718 | -0.848786 |
| 11 | 1 | 0 | -2.153833 | -0.205650 | -1.709305 |
| 12 | 8 | 0 | -1.614053 | -0.799068 | 1.347729 |
| 13 | 1 | 0 | 1.806883 | 2.223220 | 0.784989 |
| 14 | 1 | 0 | -2.154988 | 2.479669 | -0.409758 |
| 15 | 1 | 0 | -3.406255 | -1.927452 | -1.019284 |
| 16 | 7 | 0 | 1.322419 | -0.066467 | -0.613339 |
| 17 | 6 | 0 | 2.355258 | -0.716384 | 0.051024 |
| 18 | 7 | 0 | 3.110357 | -1.510711 | -0.721249 |
| 19 | 1 | 0 | 2.921015 | -1.648274 | -1.703014 |
| 20 | 1 | 0 | 3.881350 | -2.004232 | -0.297465 |
| 21 | 8 | 0 | 2.535205 | -0.551896 | 1.255966 |
| 22 | 1 | 0 | 1.247667 | -0.130199 | -1.621913 |
| 23 | 1 | 0 | 0.369131 | 2.813877 | 0.440532 |

## Structure of **33H$_b^+$**

```
Zero-point correction=                           0.160759 (Hartree/Particle)
 Thermal correction to Energy=                    0.172952
 Thermal correction to Enthalpy=                  0.173896
 Thermal correction to Gibbs Free Energy=         0.121235
 Sum of electronic and zero-point Energies=           -602.193093
 Sum of electronic and thermal Energies=              -602.180899
 Sum of electronic and thermal Enthalpies=            -602.179955
 Sum of electronic and thermal Free Energies=         -602.232617
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.642590 | 0.733560 | -0.349081 |
| 2 | 6 | 0 | -2.671411 | -0.550104 | 0.017836 |
| 3 | 1 | 0 | -0.717879 | 0.306481 | -1.348555 |
| 4 | 8 | 0 | -0.876652 | 2.120619 | -0.360119 |
| 5 | 6 | 0 | 0.754694 | 0.589943 | 0.180073 |
| 6 | 1 | 0 | 1.049345 | 1.118681 | 1.084461 |
| 7 | 1 | 0 | -4.385646 | -1.438549 | 0.635769 |
| 8 | 7 | 0 | -3.558422 | -0.951106 | 0.945047 |
| 9 | 7 | 0 | -1.496563 | -0.012236 | 0.526289 |
| 10 | 1 | 0 | -1.505184 | 0.285818 | 1.496957 |
| 11 | 8 | 0 | -2.862589 | -0.656778 | -1.193351 |
| 12 | 1 | 0 | -1.545991 | 2.324793 | -1.027259 |
| 13 | 1 | 0 | -3.349581 | -0.925887 | 1.932068 |
| 14 | 7 | 0 | 1.624470 | -0.146190 | -0.395761 |
| 15 | 6 | 0 | 2.987675 | -0.284125 | 0.147970 |
| 16 | 7 | 0 | 3.732401 | -1.097991 | -0.580813 |
| 17 | 1 | 0 | 3.390305 | -1.565161 | -1.410547 |
| 18 | 1 | 0 | 4.691051 | -1.255031 | -0.297715 |
| 19 | 8 | 0 | 3.278690 | 0.325682 | 1.146177 |
| 20 | 1 | 0 | 1.374586 | -0.650317 | -1.250938 |

Structure of **33H$_c^+$**

```
Zero-point correction=                           0.163488 (Hartree/Particle)
 Thermal correction to Energy=                    0.174488
 Thermal correction to Enthalpy=                  0.175432
 Thermal correction to Gibbs Free Energy=         0.126034
 Sum of electronic and zero-point Energies=           -602.215397
 Sum of electronic and thermal Energies=              -602.204398
 Sum of electronic and thermal Enthalpies=            -602.203453
 Sum of electronic and thermal Free Energies=         -602.252852
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.196882 | -1.172139 | -0.415848 |
| 2 | 6 | 0 | 0.010887 | -0.611309 | 0.341105 |
| 3 | 6 | 0 | -1.633999 | 1.117850 | -0.090823 |
| 4 | 1 | 0 | -0.904523 | -1.752964 | -1.288506 |
| 5 | 7 | 0 | -0.561620 | 0.693800 | 0.882474 |
| 6 | 7 | 0 | -1.880861 | 0.041977 | -0.835307 |
| 7 | 1 | 0 | 0.147260 | 1.428699 | 0.984858 |
| 8 | 1 | 0 | -2.615623 | 0.051147 | -1.533552 |
| 9 | 8 | 0 | -2.078929 | 2.227954 | -0.093257 |
| 10 | 8 | 0 | -1.947866 | -1.931657 | 0.488560 |
| 11 | 1 | 0 | -2.637616 | -2.414247 | 0.013481 |
| 12 | 1 | 0 | -0.995813 | 0.550763 | 1.803915 |
| 13 | 7 | 0 | 1.107892 | -0.373757 | -0.518611 |
| 14 | 1 | 0 | 0.941508 | -0.274375 | -1.512900 |
| 15 | 6 | 0 | 2.327112 | -0.009610 | 0.016944 |
| 16 | 8 | 0 | 2.470699 | 0.092713 | 1.236852 |
| 17 | 7 | 0 | 3.302422 | 0.226045 | -0.876680 |
| 18 | 1 | 0 | 3.186000 | 0.026993 | -1.859183 |
| 19 | 1 | 0 | 4.226874 | 0.432429 | -0.530113 |
| 20 | 1 | 0 | 0.283163 | -1.225724 | 1.193356 |

Structure of **33H$_d^+$**

```
Zero-point correction=                           0.188800 (Hartree/Particle)
 Thermal correction to Energy=                    0.202378
 Thermal correction to Enthalpy=                  0.203322
 Thermal correction to Gibbs Free Energy=         0.148421
 Sum of electronic and zero-point Energies=           -678.608066
 Sum of electronic and thermal Energies=              -678.594487
 Sum of electronic and thermal Enthalpies=            -678.593543
 Sum of electronic and thermal Free Energies=         -678.648445
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.337344 | -1.562470 | -0.311773 |
| 2 | 6 | 0 | -0.246986 | -0.503919 | -0.335841 |
| 3 | 6 | 0 | 2.160987 | -0.433689 | -0.218666 |
| 4 | 1 | 0 | -0.205744 | -0.087883 | -1.339866 |
| 5 | 7 | 0 | -0.596609 | 0.574726 | 0.574266 |
| 6 | 6 | 0 | -0.570782 | 1.882740 | 0.122070 |
| 7 | 1 | 0 | -1.266511 | -2.281319 | -1.124533 |
| 8 | 7 | 0 | -0.404599 | 2.818087 | 1.078954 |
| 9 | 1 | 0 | -0.385633 | 2.574717 | 2.058381 |
| 10 | 1 | 0 | -0.562825 | 3.782934 | 0.830258 |
| 11 | 8 | 0 | -0.711480 | 2.159951 | -1.070064 |
| 12 | 8 | 0 | -2.580533 | -0.790308 | -0.637867 |
| 13 | 1 | 0 | -3.384191 | -1.342766 | -0.670123 |
| 14 | 8 | 0 | -1.443117 | -2.118578 | 0.926693 |
| 15 | 1 | 0 | -1.890418 | -2.975566 | 0.888164 |
| 16 | 7 | 0 | 3.262770 | -0.947525 | 0.364959 |
| 17 | 1 | 0 | 3.257967 | -1.864294 | 0.787165 |
| 18 | 1 | 0 | 4.153120 | -0.533013 | 0.135152 |

| | | | | | |
|---|---|---|---|---|---|
| 19 | 8 | 0 | 2.172617 | 0.604379 | -0.882896 |
| 20 | 1 | 0 | 0.980825 | -1.795749 | 0.757267 |
| 21 | 7 | 0 | 0.998702 | -1.156644 | -0.030418 |
| 22 | 1 | 0 | -0.343532 | 0.417601 | 1.543804 |
| 23 | 1 | 0 | -2.710059 | -0.054689 | -0.001665 |

Structure of **33H$_e^+$**

Zero-point correction= 0.159603 (Hartree/Particle)
Thermal correction to Energy= 0.171829
Thermal correction to Enthalpy= 0.172773
Thermal correction to Gibbs Free Energy= 0.120369
Sum of electronic and zero-point Energies= -602.179086
Sum of electronic and thermal Energies= -602.166861
Sum of electronic and thermal Enthalpies= -602.165917
Sum of electronic and thermal Free Energies= -602.218321
No imaginary frequencies.

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.490891 | 2.192163 | 0.259922 |
| 2 | 6 | 0 | -0.122814 | 0.760825 | 0.115131 |
| 3 | 6 | 0 | 2.090483 | -0.238132 | 0.066939 |
| 4 | 1 | 0 | -0.041416 | 0.428694 | 1.164322 |
| 5 | 7 | 0 | -1.141770 | -0.025272 | -0.511747 |
| 6 | 6 | 0 | -1.500586 | -1.239773 | 0.043001 |
| 7 | 1 | 0 | 0.248959 | 2.906555 | 0.618484 |
| 8 | 7 | 0 | -2.163392 | -2.071761 | -0.781392 |
| 9 | 1 | 0 | -2.424882 | -1.803311 | -1.718409 |
| 10 | 1 | 0 | -2.571650 | -2.905444 | -0.386656 |
| 11 | 8 | 0 | -1.240735 | -1.516858 | 1.214797 |
| 12 | 8 | 0 | -1.652148 | 2.574770 | 0.022495 |
| 13 | 1 | 0 | -1.809028 | 3.526601 | 0.198316 |
| 14 | 7 | 0 | 3.153979 | -0.504633 | -0.713619 |
| 15 | 1 | 0 | 3.336747 | 0.017600 | -1.557662 |
| 16 | 1 | 0 | 3.904104 | -1.051658 | -0.318890 |
| 17 | 8 | 0 | 1.910071 | -0.758188 | 1.167210 |
| 18 | 1 | 0 | 1.277987 | 0.919521 | -1.435100 |
| 19 | 7 | 0 | 1.199885 | 0.689554 | -0.450213 |
| 20 | 1 | 0 | -1.256385 | 0.097922 | -1.511586 |

Structure of **33H$_f^+$**

Zero-point correction= 0.163003 (Hartree/Particle)
Thermal correction to Energy= 0.173817
Thermal correction to Enthalpy= 0.174761
Thermal correction to Gibbs Free Energy= 0.125568
Sum of electronic and zero-point Energies= -602.213319
Sum of electronic and thermal Energies= -602.202505
Sum of electronic and thermal Enthalpies= -602.201561
Sum of electronic and thermal Free Energies= -602.250754
No imaginary frequencies.

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.505313 | 1.044091 | 0.404936 |
| 2 | 6 | 0 | 0.036474 | 0.060977 | -0.650627 |
| 3 | 6 | 0 | -2.097032 | -0.719587 | -0.030640 |
| 4 | 1 | 0 | 0.214976 | 1.299905 | 1.178898 |
| 5 | 7 | 0 | -1.127981 | -0.745547 | -0.942037 |
| 6 | 7 | 0 | -1.625014 | 0.237381 | 1.035607 |
| 7 | 1 | 0 | -2.402836 | 0.833931 | 1.340698 |
| 8 | 8 | 0 | -3.154155 | -1.274739 | 0.042744 |
| 9 | 8 | 0 | -1.051361 | 2.136021 | -0.238224 |
| 10 | 1 | 0 | -1.177691 | 2.864977 | 0.384682 |

| | | | | | |
|---|---|---|---|---|---|
| 11 | 7 | 0 | 1.121540 | -0.772951 | -0.194618 |
| 12 | 1 | 0 | 0.872652 | -1.548044 | 0.410831 |
| 13 | 6 | 0 | 2.357657 | -0.190228 | -0.028347 |
| 14 | 8 | 0 | 2.594214 | 0.939689 | -0.464033 |
| 15 | 7 | 0 | 3.267134 | -0.931254 | 0.640099 |
| 16 | 1 | 0 | 3.105334 | -1.911510 | 0.820815 |
| 17 | 1 | 0 | 4.223090 | -0.608032 | 0.630914 |
| 18 | 1 | 0 | 0.349443 | 0.623101 | -1.526470 |
| 19 | 1 | 0 | -1.298227 | -0.303149 | 1.847661 |
| 20 | 1 | 0 | -1.196800 | -1.343867 | -1.757215 |

## Structure of **33**

```
Zero-point correction=                           0.150140 (Hartree/Particle)
 Thermal correction to Energy=                    0.160741
 Thermal correction to Enthalpy=                  0.161685
 Thermal correction to Gibbs Free Energy=         0.113295
 Sum of electronic and zero-point Energies=           -601.809655
 Sum of electronic and thermal Energies=              -601.799054
 Sum of electronic and thermal Enthalpies=            -601.798110
 Sum of electronic and thermal Free Energies=         -601.846500
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.553655 | 1.025202 | -0.436592 |
| 2 | 6 | 0 | 0.009294 | 0.105463 | 0.673686 |
| 3 | 6 | 0 | 2.066597 | -0.682170 | -0.051614 |
| 4 | 1 | 0 | -0.198712 | 1.266669 | -1.186410 |
| 5 | 7 | 0 | 1.184142 | -0.669576 | 0.993694 |
| 6 | 7 | 0 | 1.606303 | 0.203648 | -0.996216 |
| 7 | 1 | 0 | 1.161570 | -1.439163 | 1.648635 |
| 8 | 1 | 0 | 2.265904 | 0.591331 | -1.658814 |
| 9 | 8 | 0 | 3.081644 | -1.365086 | -0.131531 |
| 10 | 8 | 0 | 1.032071 | 2.199868 | 0.181022 |
| 11 | 1 | 0 | 1.278218 | 2.838434 | -0.500013 |
| 12 | 7 | 0 | -1.075893 | -0.756860 | 0.239849 |
| 13 | 1 | 0 | -0.811479 | -1.558503 | -0.322021 |
| 14 | 6 | 0 | -2.308518 | -0.202186 | 0.017927 |
| 15 | 8 | 0 | -2.586844 | 0.937850 | 0.405912 |
| 16 | 7 | 0 | -3.190921 | -0.977992 | -0.660069 |
| 17 | 1 | 0 | -3.015969 | -1.967129 | -0.764842 |
| 18 | 1 | 0 | -4.156926 | -0.685405 | -0.638834 |
| 19 | 1 | 0 | -0.329158 | 0.700318 | 1.517844 |

## Structure of **34H$_a$$^+$**

```
Zero-point correction=                           0.161778 (Hartree/Particle)
 Thermal correction to Energy=                    0.173105
 Thermal correction to Enthalpy=                  0.174049
 Thermal correction to Gibbs Free Energy=         0.123577
 Sum of electronic and zero-point Energies=           -602.202858
 Sum of electronic and thermal Energies=              -602.191531
 Sum of electronic and thermal Enthalpies=            -602.190587
 Sum of electronic and thermal Free Energies=         -602.241059
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.558319 | 0.918534 | -0.498943 |
| 2 | 6 | 0 | -0.004782 | 0.026013 | 0.624208 |
| 3 | 6 | 0 | 2.098929 | -0.725518 | -0.021277 |
| 4 | 1 | 0 | -0.149740 | 1.191638 | -1.274123 |
| 5 | 7 | 0 | 1.158998 | -0.755493 | 0.966421 |
| 6 | 7 | 0 | 1.706264 | 0.255619 | -0.920313 |

| | | | | | |
|---|---|---|---|---|---|
| 7 | 1 | 0 | 1.118707 | -1.528192 | 1.617051 |
| 8 | 1 | 0 | 2.241652 | 0.482643 | -1.747152 |
| 9 | 8 | 0 | 3.100532 | -1.409915 | -0.114148 |
| 10 | 8 | 0 | 0.857973 | 2.276788 | 0.123559 |
| 11 | 1 | 0 | 1.029045 | 2.963801 | -0.547431 |
| 12 | 7 | 0 | -1.093057 | -0.808520 | 0.173361 |
| 13 | 1 | 0 | -0.842456 | -1.559939 | -0.461237 |
| 14 | 6 | 0 | -2.333795 | -0.228064 | 0.023665 |
| 15 | 8 | 0 | -2.578419 | 0.892737 | 0.478669 |
| 16 | 7 | 0 | -3.244756 | -0.963307 | -0.649304 |
| 17 | 1 | 0 | -3.079607 | -1.939273 | -0.848652 |
| 18 | 1 | 0 | -4.201994 | -0.644380 | -0.627505 |
| 19 | 1 | 0 | -0.349492 | 0.634577 | 1.455946 |
| 20 | 1 | 0 | 1.589025 | 2.278361 | 0.771401 |

Structure of **34H$_b^+$**

Zero-point correction= 0.133776 (Hartree/Particle)
Thermal correction to Energy= 0.142989
Thermal correction to Enthalpy= 0.143933
Thermal correction to Gibbs Free Energy= 0.098681
Sum of electronic and zero-point Energies= -525.793254
Sum of electronic and thermal Energies= -525.784041
Sum of electronic and thermal Enthalpies= -525.783097
Sum of electronic and thermal Free Energies= -525.828349
No imaginary frequencies.

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 1.063213 | 1.433785 | 0.291720 |
| 2 | 6 | 0 | 0.072397 | 0.323518 | 0.408029 |
| 3 | 6 | 0 | 2.183531 | -0.503532 | -0.140807 |
| 4 | 1 | 0 | 0.857327 | 2.488433 | 0.432010 |
| 5 | 7 | 0 | 0.896769 | -0.819614 | 0.033503 |
| 6 | 7 | 0 | 2.214992 | 0.962664 | 0.008816 |
| 7 | 1 | 0 | 0.580442 | -1.778827 | 0.110805 |
| 8 | 1 | 0 | 3.076187 | 1.500079 | -0.102625 |
| 9 | 8 | 0 | 3.165602 | -1.149409 | -0.371864 |
| 10 | 7 | 0 | -1.104212 | 0.544944 | -0.358150 |
| 11 | 1 | 0 | -0.978363 | 0.721519 | -1.349385 |
| 12 | 6 | 0 | -2.265794 | -0.102778 | 0.045705 |
| 13 | 8 | 0 | -2.348856 | -0.631898 | 1.153604 |
| 14 | 7 | 0 | -3.270210 | -0.076612 | -0.842874 |
| 15 | 1 | 0 | -3.190277 | 0.378122 | -1.740065 |
| 16 | 1 | 0 | -4.148766 | -0.500304 | -0.586332 |
| 17 | 1 | 0 | -0.211977 | 0.255809 | 1.464724 |

Structure of **34H$_c^+$**

Zero-point correction= 0.137164 (Hartree/Particle)
Thermal correction to Energy= 0.145230
Thermal correction to Enthalpy= 0.146174
Thermal correction to Gibbs Free Energy= 0.102468
Sum of electronic and zero-point Energies= -525.812541
Sum of electronic and thermal Energies= -525.804475
Sum of electronic and thermal Enthalpies= -525.803531
Sum of electronic and thermal Free Energies= -525.847238
No imaginary frequencies.

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.950181 | -0.114809 | -0.272619 |
| 2 | 6 | 0 | 0.046883 | -0.779113 | 0.821236 |
| 3 | 6 | 0 | 0.063300 | 0.775009 | 0.807129 |
| 4 | 6 | 0 | 1.947595 | -0.018066 | -0.285113 |

| | | | | | |
|---|---|---|---|---|---|
| 5 | 8 | 0 | -2.991228 | -0.073548 | -0.861504 |
| 6 | 8 | 0 | 3.059876 | -0.007315 | -0.776917 |
| 7 | 7 | 0 | -1.237247 | 1.152876 | 0.136601 |
| 8 | 1 | 0 | -1.088352 | 1.733680 | -0.697625 |
| 9 | 7 | 0 | -1.205775 | -1.118010 | 0.171298 |
| 10 | 1 | 0 | -1.511251 | -2.076778 | 0.046296 |
| 11 | 7 | 0 | 1.216246 | -1.121078 | 0.057971 |
| 12 | 1 | 0 | 1.685512 | -2.008241 | 0.180619 |
| 13 | 7 | 0 | 1.191147 | 1.106464 | 0.006042 |
| 14 | 1 | 0 | 1.685124 | 1.975642 | 0.164253 |
| 15 | 1 | 0 | 0.063934 | 1.226041 | 1.793924 |
| 16 | 1 | 0 | -1.854210 | 1.675681 | 0.770239 |
| 17 | 1 | 0 | 0.073881 | -1.199013 | 1.822482 |

## Structure of **7**

```
Zero-point correction=                           0.122916 (Hartree/Particle)
 Thermal correction to Energy=                    0.131174
 Thermal correction to Enthalpy=                  0.132119
 Thermal correction to Gibbs Free Energy=         0.088981
 Sum of electronic and zero-point Energies=           -525.409197
 Sum of electronic and thermal Energies=              -525.400939
 Sum of electronic and thermal Enthalpies=            -525.399995
 Sum of electronic and thermal Free Energies=         -525.443132
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.984218 | -0.000087 | -0.233549 |
| 2 | 6 | 0 | 0.000037 | -0.780456 | 0.709665 |
| 3 | 6 | 0 | -0.000031 | 0.780463 | 0.709659 |
| 4 | 6 | 0 | 1.984213 | 0.000089 | -0.233568 |
| 5 | 8 | 0 | -3.146538 | -0.000121 | -0.624549 |
| 6 | 8 | 0 | 3.146541 | 0.000118 | -0.624541 |
| 7 | 7 | 0 | -1.220575 | 1.110676 | 0.006724 |
| 8 | 7 | 0 | -1.220061 | -1.110752 | 0.005644 |
| 9 | 1 | 0 | -1.693404 | -1.988054 | 0.171507 |
| 10 | 7 | 0 | 1.220568 | -1.110688 | 0.006703 |
| 11 | 1 | 0 | 1.694122 | -1.987821 | 0.172792 |
| 12 | 7 | 0 | 1.220055 | 1.110749 | 0.005614 |
| 13 | 1 | 0 | 1.693395 | 1.988062 | 0.171432 |
| 14 | 1 | 0 | 0.000454 | 1.209595 | 1.709141 |
| 15 | 1 | 0 | -0.000427 | -1.209578 | 1.709151 |
| 16 | 1 | 0 | -1.694079 | 1.987864 | 0.172659 |

## Structure $\mathbf{TS_{33a}}$

```
Zero-point correction=                           0.160919 (Hartree/Particle)
 Thermal correction to Energy=                    0.171560
 Thermal correction to Enthalpy=                  0.172504
 Thermal correction to Gibbs Free Energy=         0.124072
 Sum of electronic and zero-point Energies=           -602.187546
 Sum of electronic and thermal Energies=              -602.176906
 Sum of electronic and thermal Enthalpies=            -602.175962
 Sum of electronic and thermal Free Energies=         -602.224393
One imaginary frequency (cm-1): 257.6673i
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.102349 | -1.130665 | -0.633733 |
| 2 | 6 | 0 | 0.210913 | -0.828792 | 0.060645 |
| 3 | 6 | 0 | -1.745270 | 1.067949 | 0.120176 |
| 4 | 1 | 0 | -0.894178 | -1.574646 | -1.610079 |
| 5 | 7 | 0 | -1.095128 | 0.584486 | 1.266935 |
| 6 | 7 | 0 | -1.807413 | 0.106957 | -0.838862 |

| | | | | | |
|---|---|---|---|---|---|
| 7 | 1 | 0 | -0.856362 | 1.324052 | 1.919694 |
| 8 | 1 | 0 | -2.282622 | 0.294055 | -1.711524 |
| 9 | 8 | 0 | -2.118378 | 2.217721 | -0.025598 |
| 10 | 8 | 0 | -1.761950 | -2.040163 | 0.209299 |
| 11 | 1 | 0 | -2.513306 | -2.424239 | -0.261960 |
| 12 | 1 | 0 | -1.588405 | -0.177068 | 1.729255 |
| 13 | 7 | 0 | 1.137933 | -0.167800 | -0.554587 |
| 14 | 1 | 0 | 0.936233 | 0.278135 | -1.450724 |
| 15 | 6 | 0 | 2.437385 | 0.035602 | 0.056420 |
| 16 | 8 | 0 | 2.646263 | -0.394392 | 1.168884 |
| 17 | 7 | 0 | 3.271568 | 0.707362 | -0.726025 |
| 18 | 1 | 0 | 3.024551 | 1.010298 | -1.658658 |
| 19 | 1 | 0 | 4.205681 | 0.893019 | -0.386874 |
| 20 | 1 | 0 | 0.488126 | -1.370533 | 0.956920 |

## Structure **$TS_{33b}$**

```
Zero-point correction=                           0.160245 (Hartree/Particle)
 Thermal correction to Energy=                    0.171084
 Thermal correction to Enthalpy=                  0.172029
 Thermal correction to Gibbs Free Energy=         0.123696
 Sum of electronic and zero-point Energies=           -602.173419
 Sum of electronic and thermal Energies=              -602.162580
 Sum of electronic and thermal Enthalpies=            -602.161636
 Sum of electronic and thermal Free Energies=         -602.209968
One imaginary frequency (cm-1): 93.4065i
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.022778 | 0.767783 | 0.804494 |
| 2 | 6 | 0 | 0.389932 | 1.534716 | -0.423292 |
| 3 | 6 | 0 | 1.705205 | -0.947849 | 0.151982 |
| 4 | 7 | 0 | 1.311154 | -0.887335 | -1.144824 |
| 5 | 7 | 0 | 0.862938 | -0.350290 | 1.074721 |
| 6 | 1 | 0 | 1.913362 | -1.371979 | -1.796110 |
| 7 | 1 | 0 | 1.258836 | -0.345620 | 2.006215 |
| 8 | 8 | 0 | 2.755728 | -1.466574 | 0.523197 |
| 9 | 8 | 0 | 1.524482 | 2.052925 | -0.408416 |
| 10 | 1 | 0 | 0.313448 | -0.899998 | -1.352453 |
| 11 | 1 | 0 | -0.288572 | 1.733774 | -1.251665 |
| 12 | 1 | 0 | 1.741672 | 2.585664 | -1.200624 |
| 13 | 7 | 0 | -1.440053 | 0.524453 | 0.812115 |
| 14 | 1 | 0 | -1.895775 | 0.647995 | 1.706918 |
| 15 | 6 | 0 | -2.058134 | -0.248967 | -0.137256 |
| 16 | 8 | 0 | -1.472346 | -0.551982 | -1.185837 |
| 17 | 7 | 0 | -3.318116 | -0.621899 | 0.130348 |
| 18 | 1 | 0 | -3.805774 | -0.311102 | 0.957703 |
| 19 | 1 | 0 | -3.839716 | -1.094631 | -0.592402 |
| 20 | 1 | 0 | 0.142794 | 1.492336 | 1.608775 |

## Structure **$TS_{34}$**

```
Zero-point correction=                           0.133806 (Hartree/Particle)
 Thermal correction to Energy=                    0.141834
 Thermal correction to Enthalpy=                  0.142778
 Thermal correction to Gibbs Free Energy=         0.100624
 Sum of electronic and zero-point Energies=           -525.786073
 Sum of electronic and thermal Energies=              -525.778044
 Sum of electronic and thermal Enthalpies=            -525.777100
 Sum of electronic and thermal Free Energies=         -525.819255
One imaginary frequency (cm-1): 250.7702i
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 2.040585 | -0.045173 | -0.258923 |

| | | | | | |
|---|---|---|---|---|---|
| 2 | 6 | 0 | -0.021097 | 0.824413 | 0.659455 |
| 3 | 6 | 0 | -0.302081 | -0.603109 | 1.058502 |
| 4 | 6 | 0 | -2.026144 | 0.072875 | -0.255553 |
| 5 | 8 | 0 | 3.253390 | -0.061323 | -0.333766 |
| 6 | 8 | 0 | -3.099781 | -0.027634 | -0.785771 |
| 7 | 7 | 0 | 1.205002 | -1.133716 | -0.555981 |
| 8 | 1 | 0 | 0.597966 | -0.964062 | -1.357006 |
| 9 | 7 | 0 | 1.317778 | 1.014508 | 0.201898 |
| 10 | 1 | 0 | 1.823960 | 1.833906 | 0.511818 |
| 11 | 7 | 0 | -1.084247 | 1.032736 | -0.317724 |
| 12 | 1 | 0 | -1.299149 | 1.946177 | -0.698308 |
| 13 | 7 | 0 | -1.482787 | -0.927243 | 0.640660 |
| 14 | 1 | 0 | -1.968294 | -1.799615 | 0.838280 |
| 15 | 1 | 0 | 0.239344 | -1.164022 | 1.807587 |
| 16 | 1 | 0 | 1.729423 | -1.993651 | -0.686735 |
| 17 | 1 | 0 | -0.189927 | 1.454896 | 1.537802 |

**Cartesian coordinates of all stationary points involved in the formation of 36 at the M06-2X/6-311+G(d) level in water (SMD).**

Structure of **35c**

```
Zero-point correction=                           0.258557 (Hartree/Particle)
 Thermal correction to Energy=                    0.278661
 Thermal correction to Enthalpy=                  0.279605
 Thermal correction to Gibbs Free Energy=         0.208443
 Sum of electronic and zero-point Energies=           -982.794946
 Sum of electronic and thermal Energies=              -982.774842
 Sum of electronic and thermal Enthalpies=            -982.773898
 Sum of electronic and thermal Free Energies=         -982.845060
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 3.709882 | 0.336053 | 0.759034 |
| 2 | 6 | 0 | 4.764503 | -0.607634 | 0.244848 |
| 3 | 6 | 0 | 0.387544 | -0.690177 | -0.623843 |
| 4 | 1 | 0 | 5.389963 | -1.218018 | 0.891166 |
| 5 | 1 | 0 | 2.132832 | -1.061131 | -1.598754 |
| 6 | 1 | 0 | 2.916971 | -0.294047 | 1.189487 |
| 7 | 8 | 0 | 4.334022 | 1.120220 | 1.729312 |
| 8 | 1 | 0 | 3.661769 | 1.506086 | 2.306874 |
| 9 | 8 | 0 | 3.238552 | 1.056418 | -0.331656 |
| 10 | 1 | 0 | 2.254844 | 0.941994 | -0.390706 |
| 11 | 7 | 0 | -0.779443 | -1.282216 | -0.244899 |
| 12 | 1 | 0 | -1.074398 | -2.109832 | -0.749972 |
| 13 | 8 | 0 | 0.673158 | 0.465726 | -0.255749 |
| 14 | 1 | 0 | 1.013801 | -2.385221 | -1.619979 |
| 15 | 7 | 0 | 1.207877 | -1.417841 | -1.406547 |
| 16 | 1 | 0 | 4.311822 | -0.094465 | -1.457136 |
| 17 | 8 | 0 | 4.921991 | -0.720525 | -0.979770 |
| 18 | 6 | 0 | -1.834177 | -0.472803 | 0.327796 |
| 19 | 1 | 0 | -1.412419 | 0.150899 | 1.110479 |
| 20 | 6 | 0 | -2.858383 | -1.405541 | 0.961276 |
| 21 | 1 | 0 | -2.383922 | -2.022791 | 1.727623 |
| 22 | 8 | 0 | -3.854245 | -0.598696 | 1.536409 |
| 23 | 1 | 0 | -4.362293 | -1.124190 | 2.167340 |
| 24 | 8 | 0 | -3.371006 | -2.219335 | -0.068591 |
| 25 | 1 | 0 | -3.823493 | -2.982733 | 0.311430 |
| 26 | 7 | 0 | -2.457969 | 0.406263 | -0.640141 |
| 27 | 1 | 0 | -3.078084 | -0.027361 | -1.313616 |
| 28 | 6 | 0 | -2.631761 | 1.736211 | -0.376889 |
| 29 | 8 | 0 | -2.069178 | 2.313105 | 0.559899 |
| 30 | 7 | 0 | -3.481380 | 2.387392 | -1.215933 |
| 31 | 1 | 0 | -3.749407 | 1.958141 | -2.089986 |
| 32 | 1 | 0 | -3.433587 | 3.395512 | -1.203780 |

## Structure of **35**

```
Zero-point correction=                           0.249252 (Hartree/Particle)
 Thermal correction to Energy=                    0.268496
 Thermal correction to Enthalpy=                  0.269440
 Thermal correction to Gibbs Free Energy=         0.200761
 Sum of electronic and zero-point Energies=           -982.421026
 Sum of electronic and thermal Energies=              -982.401783
 Sum of electronic and thermal Enthalpies=            -982.400839
 Sum of electronic and thermal Free Energies=         -982.469517
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -2.921548 | 0.278878 | -0.290663 |
| 2 | 6 | 0 | -0.547237 | -0.124963 | -0.481321 |
| 3 | 1 | 0 | -2.751753 | 1.265088 | 0.150926 |
| 4 | 8 | 0 | -3.208896 | 0.415313 | -1.665606 |
| 5 | 6 | 0 | -4.142217 | -0.355609 | 0.357946 |
| 6 | 1 | 0 | -4.381186 | -1.305881 | -0.130643 |
| 7 | 8 | 0 | -5.204307 | 0.549950 | 0.199011 |
| 8 | 8 | 0 | -3.835874 | -0.569000 | 1.713010 |
| 9 | 1 | 0 | -4.486880 | -1.170464 | 2.095805 |
| 10 | 7 | 0 | 0.494978 | -0.991804 | -0.287246 |
| 11 | 7 | 0 | -1.763413 | -0.550450 | -0.056305 |
| 12 | 8 | 0 | -0.403472 | 0.970667 | -1.035007 |
| 13 | 1 | 0 | -6.041776 | 0.080474 | 0.297823 |
| 14 | 1 | 0 | -1.878454 | -1.470267 | 0.348095 |
| 15 | 1 | 0 | -2.520269 | 0.969069 | -2.057437 |
| 16 | 1 | 0 | 0.364456 | -1.732089 | 0.393332 |
| 17 | 6 | 0 | 1.846045 | -0.487985 | -0.412748 |
| 18 | 1 | 0 | 1.942056 | 0.033967 | -1.360526 |
| 19 | 6 | 0 | 2.798701 | -1.676160 | -0.421415 |
| 20 | 1 | 0 | 2.545781 | -2.355903 | -1.238315 |
| 21 | 8 | 0 | 2.654944 | -2.332328 | 0.817502 |
| 22 | 1 | 0 | 2.996587 | -3.232423 | 0.752196 |
| 23 | 8 | 0 | 4.096593 | -1.166812 | -0.595346 |
| 24 | 1 | 0 | 4.684155 | -1.882211 | -0.869719 |
| 25 | 7 | 0 | 2.194029 | 0.445173 | 0.636508 |
| 26 | 1 | 0 | 2.246386 | 0.085480 | 1.581120 |
| 27 | 6 | 0 | 2.673500 | 1.692198 | 0.374032 |
| 28 | 7 | 0 | 2.994639 | 2.436675 | 1.469199 |
| 29 | 8 | 0 | 2.764315 | 2.149355 | -0.771645 |
| 30 | 1 | 0 | 3.139660 | 1.981725 | 2.359098 |
| 31 | 1 | 0 | 3.549727 | 3.260972 | 1.292790 |

## Structure of **35H$_a$$^+$**

```
Zero-point correction=                           0.263407 (Hartree/Particle)
 Thermal correction to Energy=                    0.282215
 Thermal correction to Enthalpy=                  0.283159
 Thermal correction to Gibbs Free Energy=         0.215640
 Sum of electronic and zero-point Energies=           -982.824806
 Sum of electronic and thermal Energies=              -982.805999
 Sum of electronic and thermal Enthalpies=            -982.805054
 Sum of electronic and thermal Free Energies=         -982.872573
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -3.058489 | -0.862650 | -0.010350 |
| 2 | 6 | 0 | -0.575214 | -1.291556 | -0.280155 |
| 3 | 1 | 0 | -3.976232 | -1.187009 | -0.503105 |
| 4 | 8 | 0 | -2.905395 | -1.366170 | 1.262093 |
| 5 | 6 | 0 | -3.005919 | 0.660837 | 0.058871 |

| | | | | | |
|---|---|---|---|---|---|
| 6 | 1 | 0 | -2.271095 | 0.987959 | 0.799693 |
| 7 | 8 | 0 | -4.291531 | 1.057416 | 0.442968 |
| 8 | 8 | 0 | -2.656657 | 1.118497 | -1.222951 |
| 9 | 1 | 0 | -2.494381 | 2.071197 | -1.194661 |
| 10 | 7 | 0 | -0.053712 | -0.076456 | -0.388022 |
| 11 | 7 | 0 | -1.933979 | -1.395131 | -0.904059 |
| 12 | 1 | 0 | -2.107118 | -2.393357 | -1.067431 |
| 13 | 8 | 0 | -0.118029 | -2.268287 | 0.253939 |
| 14 | 1 | 0 | -4.243566 | 1.900418 | 0.910692 |
| 15 | 1 | 0 | -1.973365 | -0.909247 | -1.810374 |
| 16 | 1 | 0 | -3.299204 | -2.246144 | 1.333363 |
| 17 | 1 | 0 | -0.529019 | 0.642870 | -0.927192 |
| 18 | 6 | 0 | 1.221158 | 0.240850 | 0.238782 |
| 19 | 1 | 0 | 1.300101 | -0.332028 | 1.159705 |
| 20 | 6 | 0 | 1.199757 | 1.726273 | 0.584283 |
| 21 | 1 | 0 | 0.391526 | 1.935144 | 1.290132 |
| 22 | 8 | 0 | 0.982703 | 2.424113 | -0.619454 |
| 23 | 1 | 0 | 0.681940 | 3.321310 | -0.428567 |
| 24 | 8 | 0 | 2.445920 | 2.024060 | 1.154296 |
| 25 | 1 | 0 | 2.388067 | 2.863396 | 1.627868 |
| 26 | 7 | 0 | 2.339510 | -0.106778 | -0.599664 |
| 27 | 1 | 0 | 2.527473 | 0.516714 | -1.376890 |
| 28 | 6 | 0 | 3.409048 | -0.788068 | -0.067749 |
| 29 | 7 | 0 | 4.519291 | -0.807114 | -0.839883 |
| 30 | 8 | 0 | 3.341485 | -1.389280 | 1.008318 |
| 31 | 1 | 0 | 4.621804 | -0.182448 | -1.625924 |
| 32 | 1 | 0 | 5.355312 | -1.207341 | -0.441681 |

Structure of **35H$_b^+$**

```
Zero-point correction=                           0.262753 (Hartree/Particle)
 Thermal correction to Energy=                    0.281615
 Thermal correction to Enthalpy=                  0.282559
 Thermal correction to Gibbs Free Energy=         0.215302
 Sum of electronic and zero-point Energies=           -982.817479
 Sum of electronic and thermal Energies=              -982.798617
 Sum of electronic and thermal Enthalpies=            -982.797673
 Sum of electronic and thermal Free Energies=         -982.864930
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -2.925768 | 0.203811 | -0.216160 |
| 2 | 6 | 0 | -0.546200 | -0.087062 | -0.380109 |
| 3 | 1 | 0 | -2.744070 | 1.266311 | -0.073582 |
| 4 | 8 | 0 | -3.368768 | 0.079281 | -1.673758 |
| 5 | 6 | 0 | -4.145645 | -0.273998 | 0.561859 |
| 6 | 1 | 0 | -4.274472 | -1.354823 | 0.456682 |
| 7 | 8 | 0 | -5.239750 | 0.405785 | -0.000920 |
| 8 | 8 | 0 | -3.913646 | 0.082156 | 1.891915 |
| 9 | 1 | 0 | -4.453001 | -0.470785 | 2.471924 |
| 10 | 7 | 0 | 0.482662 | -0.929158 | -0.134894 |
| 11 | 7 | 0 | -1.792169 | -0.565205 | 0.000500 |
| 12 | 8 | 0 | -0.422034 | 1.010963 | -0.911383 |
| 13 | 1 | 0 | -6.052918 | -0.094347 | 0.142679 |
| 14 | 1 | 0 | -1.903109 | -1.544365 | 0.239925 |
| 15 | 1 | 0 | -2.765467 | 0.541112 | -2.286176 |
| 16 | 1 | 0 | 0.341555 | -1.726811 | 0.473912 |
| 17 | 6 | 0 | 1.841842 | -0.485906 | -0.360428 |
| 18 | 1 | 0 | 1.900184 | -0.014729 | -1.337873 |
| 19 | 6 | 0 | 2.750234 | -1.709598 | -0.362140 |
| 20 | 1 | 0 | 2.438469 | -2.413072 | -1.137907 |
| 21 | 8 | 0 | 2.637688 | -2.307604 | 0.908431 |
| 22 | 1 | 0 | 2.961898 | -3.215793 | 0.873272 |
| 23 | 8 | 0 | 4.052230 | -1.247159 | -0.612511 |
| 24 | 1 | 0 | 4.605970 | -1.987905 | -0.889638 |
| 25 | 7 | 0 | 2.280081 | 0.485499 | 0.619422 |
| 26 | 1 | 0 | 2.492028 | 0.122927 | 1.541670 |
| 27 | 6 | 0 | 2.921264 | 1.630610 | 0.229891 |
| 28 | 7 | 0 | 3.584815 | 2.288466 | 1.216923 |
| 29 | 8 | 0 | 2.906178 | 2.041798 | -0.934776 |

| | | | | | |
|---|---|---|---|---|---|
| 30 | 1 | 0 | 3.406826 | 2.058538 | 2.184346 |
| 31 | 1 | 0 | 3.844821 | 3.243708 | 1.019697 |
| 32 | 1 | 0 | -4.275974 | 0.443921 | -1.766061 |

Structure of **35H$_c^+$**

```
Zero-point correction=                           0.234036 (Hartree/Particle)
 Thermal correction to Energy=                    0.251792
 Thermal correction to Enthalpy=                  0.252736
 Thermal correction to Gibbs Free Energy=         0.187481
 Sum of electronic and zero-point Energies=           -906.400494
 Sum of electronic and thermal Energies=              -906.382738
 Sum of electronic and thermal Enthalpies=            -906.381794
 Sum of electronic and thermal Free Energies=         -906.447049
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -3.084438 | 0.224365 | -0.161296 |
| 2 | 6 | 0 | -0.716435 | -0.023695 | -0.409264 |
| 3 | 1 | 0 | -2.963724 | 1.204449 | -0.617299 |
| 4 | 6 | 0 | -4.454765 | -0.225445 | 0.262577 |
| 5 | 1 | 0 | -4.440536 | -1.240692 | 0.662279 |
| 6 | 8 | 0 | -5.225410 | -0.142494 | -0.900989 |
| 7 | 8 | 0 | -4.833972 | 0.704847 | 1.236424 |
| 8 | 1 | 0 | -5.387357 | 0.277700 | 1.903327 |
| 9 | 7 | 0 | 0.246791 | -0.884680 | -0.101432 |
| 10 | 7 | 0 | -2.046115 | -0.499428 | 0.003442 |
| 11 | 8 | 0 | -0.618456 | 1.040147 | -0.964852 |
| 12 | 1 | 0 | -5.913401 | -0.821172 | -0.891412 |
| 13 | 1 | 0 | -2.130420 | -1.425018 | 0.433989 |
| 14 | 1 | 0 | 0.059707 | -1.700890 | 0.473281 |
| 15 | 6 | 0 | 1.636339 | -0.514224 | -0.352196 |
| 16 | 1 | 0 | 1.706363 | -0.114259 | -1.360815 |
| 17 | 6 | 0 | 2.484036 | -1.777099 | -0.266909 |
| 18 | 1 | 0 | 2.148781 | -2.509367 | -1.005408 |
| 19 | 8 | 0 | 2.322908 | -2.289077 | 1.033959 |
| 20 | 1 | 0 | 2.623467 | -3.205910 | 1.062890 |
| 21 | 8 | 0 | 3.805653 | -1.384802 | -0.524503 |
| 22 | 1 | 0 | 4.323050 | -2.157701 | -0.783187 |
| 23 | 7 | 0 | 2.091103 | 0.498412 | 0.563304 |
| 24 | 1 | 0 | 2.354434 | 0.185528 | 1.490764 |
| 25 | 6 | 0 | 2.664662 | 1.655604 | 0.096823 |
| 26 | 7 | 0 | 3.330684 | 2.381610 | 1.027092 |
| 27 | 8 | 0 | 2.584561 | 2.008514 | -1.082741 |
| 28 | 1 | 0 | 3.230361 | 2.172812 | 2.009889 |
| 29 | 1 | 0 | 3.573367 | 3.329001 | 0.778055 |

Structure of **36H$^+$**

```
Zero-point correction=                           0.236685 (Hartree/Particle)
 Thermal correction to Energy=                    0.253045
 Thermal correction to Enthalpy=                  0.253990
 Thermal correction to Gibbs Free Energy=         0.193542
 Sum of electronic and zero-point Energies=           -906.411795
 Sum of electronic and thermal Energies=              -906.395434
 Sum of electronic and thermal Enthalpies=            -906.394490
 Sum of electronic and thermal Free Energies=         -906.454938
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.738210 | 0.107486 | -0.772251 |
| 2 | 6 | 0 | -0.574119 | 2.072730 | 0.011341 |
| 3 | 6 | 0 | -1.420405 | -0.205164 | 0.400309 |

| | | | | | |
|---|---|---|---|---|---|
| 4 | 1 | 0 | 0.369917 | -0.363835 | -1.687831 |
| 5 | 1 | 0 | -1.848128 | -0.676344 | 1.286266 |
| 6 | 8 | 0 | -0.633862 | 3.281987 | 0.212806 |
| 7 | 7 | 0 | 0.425084 | 1.509258 | -0.719756 |
| 8 | 7 | 0 | -1.522510 | 1.214538 | 0.507963 |
| 9 | 1 | 0 | 1.161729 | 2.140597 | -1.012217 |
| 10 | 1 | 0 | -2.018482 | 1.573299 | 1.313822 |
| 11 | 6 | 0 | 2.243359 | -0.138539 | -0.707628 |
| 12 | 1 | 0 | 2.688923 | 0.292683 | 0.193149 |
| 13 | 6 | 0 | -2.135695 | -0.781754 | -0.830738 |
| 14 | 1 | 0 | -1.915535 | -0.209721 | -1.736079 |
| 15 | 8 | 0 | 2.387151 | -1.531994 | -0.722128 |
| 16 | 1 | 0 | 3.241900 | -1.779224 | -0.347141 |
| 17 | 8 | 0 | 2.757716 | 0.481273 | -1.852000 |
| 18 | 1 | 0 | 3.684247 | 0.712143 | -1.710315 |
| 19 | 8 | 0 | -1.687702 | -2.106447 | -0.950691 |
| 20 | 1 | 0 | -1.837950 | -2.431132 | -1.847081 |
| 21 | 8 | 0 | -3.497478 | -0.698325 | -0.523148 |
| 22 | 1 | 0 | -4.008978 | -0.654367 | -1.340711 |
| 23 | 7 | 0 | 0.041335 | -0.625417 | 0.342842 |
| 24 | 6 | 0 | 0.696440 | -0.475541 | 1.698642 |
| 25 | 7 | 0 | 0.959118 | -1.640881 | 2.263608 |
| 26 | 8 | 0 | 0.881572 | 0.635961 | 2.120247 |
| 27 | 1 | 0 | 1.380033 | -1.635944 | 3.184961 |
| 28 | 1 | 0 | 0.806478 | -2.530728 | 1.806966 |
| 29 | 1 | 0 | 0.028749 | -1.614856 | 0.054874 |

## Structure of **36**

```
Zero-point correction=                           0.223179 (Hartree/Particle)
 Thermal correction to Energy=                    0.239324
 Thermal correction to Enthalpy=                  0.240269
 Thermal correction to Gibbs Free Energy=         0.180468
 Sum of electronic and zero-point Energies=          -906.007187
 Sum of electronic and thermal Energies=             -905.991042
 Sum of electronic and thermal Enthalpies=           -905.990098
 Sum of electronic and thermal Free Energies=        -906.049898
No imaginary frequencies.
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 1.004060 | 0.313847 | -0.349536 |
| 2 | 6 | 0 | -0.012500 | 2.246156 | 0.609772 |
| 3 | 6 | 0 | -1.331704 | 0.128333 | 0.239504 |
| 4 | 1 | 0 | 0.641893 | 0.584019 | -1.349555 |
| 5 | 1 | 0 | -1.889007 | -0.214664 | 1.113353 |
| 6 | 8 | 0 | -0.006367 | 3.434275 | 0.947235 |
| 7 | 7 | 0 | 1.136393 | 1.512359 | 0.467936 |
| 8 | 7 | 0 | -1.165753 | 1.578378 | 0.338606 |
| 9 | 1 | 0 | 1.965973 | 2.075042 | 0.315354 |
| 10 | 1 | 0 | -2.015641 | 2.101133 | 0.504238 |
| 11 | 6 | 0 | 2.368980 | -0.324189 | -0.582952 |
| 12 | 1 | 0 | 2.916370 | -0.509720 | 0.337660 |
| 13 | 6 | 0 | -2.162445 | -0.232190 | -0.989961 |
| 14 | 1 | 0 | -1.622357 | -0.017880 | -1.916221 |
| 15 | 8 | 0 | 2.149586 | -1.519896 | -1.283872 |
| 16 | 1 | 0 | 2.946526 | -2.062274 | -1.238489 |
| 17 | 8 | 0 | 3.065223 | 0.621339 | -1.364756 |
| 18 | 1 | 0 | 4.014548 | 0.496682 | -1.245691 |
| 19 | 8 | 0 | -2.428402 | -1.609948 | -0.882660 |
| 20 | 1 | 0 | -2.569879 | -1.991098 | -1.757816 |
| 21 | 8 | 0 | -3.341173 | 0.528576 | -0.914139 |
| 22 | 1 | 0 | -3.769210 | 0.550248 | -1.778746 |
| 23 | 7 | 0 | -0.030113 | -0.523553 | 0.231584 |
| 24 | 6 | 0 | 0.264326 | -1.494035 | 1.181627 |
| 25 | 7 | 0 | -0.782268 | -2.278154 | 1.535431 |
| 26 | 8 | 0 | 1.387958 | -1.631871 | 1.661907 |
| 27 | 1 | 0 | -0.564591 | -3.054796 | 2.142687 |
| 28 | 1 | 0 | -1.561341 | -2.387242 | 0.897892 |

## Structure $TS_{35c}$

```
Zero-point correction=                           0.258993 (Hartree/Particle)
 Thermal correction to Energy=                    0.278114
 Thermal correction to Enthalpy=                  0.279058
 Thermal correction to Gibbs Free Energy=         0.210497
 Sum of electronic and zero-point Energies=           -982.793396
 Sum of electronic and thermal Energies=              -982.774276
 Sum of electronic and thermal Enthalpies=            -982.773332
 Sum of electronic and thermal Free Energies=         -982.841893
One imaginary frequency (cm-1): 13.9959i
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -3.442348 | 0.002088 | 0.840167 |
| 2 | 6 | 0 | -4.293318 | 0.672504 | -0.215324 |
| 3 | 6 | 0 | -0.534159 | 0.008832 | -0.810429 |
| 4 | 1 | 0 | -4.624859 | 1.705523 | -0.144535 |
| 5 | 1 | 0 | -2.070644 | -0.348382 | -2.069221 |
| 6 | 1 | 0 | -2.501213 | 0.559053 | 0.918727 |
| 7 | 8 | 0 | -4.196548 | 0.095600 | 2.009304 |
| 8 | 1 | 0 | -3.604829 | 0.065158 | 2.772761 |
| 9 | 8 | 0 | -3.237162 | -1.314248 | 0.434878 |
| 10 | 1 | 0 | -2.284500 | -1.447985 | 0.231836 |
| 11 | 7 | 0 | 0.464116 | 0.899986 | -0.578153 |
| 12 | 1 | 0 | 0.600251 | 1.647093 | -1.249510 |
| 13 | 8 | 0 | -0.610872 | -1.067792 | -0.193921 |
| 14 | 1 | 0 | -1.314184 | 1.173805 | -2.309804 |
| 15 | 7 | 0 | -1.494201 | 0.392979 | -1.693055 |
| 16 | 1 | 0 | -4.303183 | -0.905535 | -1.159041 |
| 17 | 8 | 0 | -4.665118 | 0.020774 | -1.202583 |
| 18 | 6 | 0 | 1.622550 | 0.491722 | 0.185022 |
| 19 | 1 | 0 | 1.290283 | -0.028214 | 1.079216 |
| 20 | 6 | 0 | 2.384932 | 1.741537 | 0.608037 |
| 21 | 1 | 0 | 1.750093 | 2.386100 | 1.220419 |
| 22 | 8 | 0 | 3.499405 | 1.308907 | 1.345148 |
| 23 | 1 | 0 | 3.870204 | 2.058706 | 1.827106 |
| 24 | 8 | 0 | 2.763353 | 2.413252 | -0.571164 |
| 25 | 1 | 0 | 3.011389 | 3.322657 | -0.363257 |
| 26 | 7 | 0 | 2.475609 | -0.414126 | -0.555575 |
| 27 | 1 | 0 | 3.003153 | -0.010893 | -1.320824 |
| 28 | 6 | 0 | 2.964196 | -1.554012 | 0.018893 |
| 29 | 8 | 0 | 2.523818 | -2.011825 | 1.078699 |
| 30 | 7 | 0 | 3.983603 | -2.151395 | -0.655607 |
| 31 | 1 | 0 | 4.164664 | -1.894402 | -1.615753 |
| 32 | 1 | 0 | 4.183362 | -3.108155 | -0.402462 |

## Structure $TS_{36}$

```
Zero-point correction=                           0.232878 (Hartree/Particle)
 Thermal correction to Energy=                    0.249696
 Thermal correction to Enthalpy=                  0.250640
 Thermal correction to Gibbs Free Energy=         0.188386
 Sum of electronic and zero-point Energies=           -906.381794
 Sum of electronic and thermal Energies=              -906.364977
 Sum of electronic and thermal Enthalpies=            -906.364033
 Sum of electronic and thermal Free Energies=         -906.426287
One imaginary frequency (cm-1): 239.7272i
```

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.829919 | -0.488400 | -0.499781 |
| 2 | 6 | 0 | 0.909535 | -1.212308 | 1.239277 |
| 3 | 6 | 0 | 1.698471 | 0.851141 | 0.179513 |
| 4 | 1 | 0 | -0.485701 | -0.805279 | -1.489880 |

| | | | | | |
|---|---|---|---|---|---|
| 5 | 1 | 0 | 1.865788 | 1.911636 | 0.343257 |
| 6 | 8 | 0 | 1.373468 | -2.044260 | 1.987193 |
| 7 | 7 | 0 | -0.197428 | -1.344511 | 0.507537 |
| 8 | 7 | 0 | 1.485036 | 0.125451 | 1.230117 |
| 9 | 1 | 0 | -0.619967 | -2.267224 | 0.559118 |
| 10 | 1 | 0 | 1.396723 | 0.600322 | 2.128931 |
| 11 | 6 | 0 | -2.340679 | -0.751170 | -0.444964 |
| 12 | 1 | 0 | -2.761396 | -0.474150 | 0.523996 |
| 13 | 6 | 0 | 2.178872 | 0.285770 | -1.144743 |
| 14 | 1 | 0 | 1.530430 | 0.602940 | -1.964150 |
| 15 | 8 | 0 | -2.901538 | 0.023402 | -1.470232 |
| 16 | 1 | 0 | -3.849564 | 0.121933 | -1.316157 |
| 17 | 8 | 0 | -2.497001 | -2.129461 | -0.667044 |
| 18 | 1 | 0 | -3.325476 | -2.432844 | -0.275804 |
| 19 | 8 | 0 | 3.453269 | 0.861622 | -1.265172 |
| 20 | 1 | 0 | 3.765218 | 0.740036 | -2.171936 |
| 21 | 8 | 0 | 2.243592 | -1.104507 | -1.056656 |
| 22 | 1 | 0 | 1.936939 | -1.507565 | -1.878767 |
| 23 | 7 | 0 | -0.509317 | 0.927584 | -0.402122 |
| 24 | 6 | 0 | -1.040386 | 1.682606 | 0.659338 |
| 25 | 7 | 0 | -1.253330 | 2.975489 | 0.383909 |
| 26 | 8 | 0 | -1.213884 | 1.167563 | 1.758551 |
| 27 | 1 | 0 | -1.550990 | 3.583983 | 1.132227 |
| 28 | 1 | 0 | -1.119924 | 3.365453 | -0.537935 |
| 29 | 1 | 0 | -0.575438 | 1.371971 | -1.313943 |