

Supplementary Materials: Experimental and Kinetic Study on the Production of Furfural and HMF from Glucose

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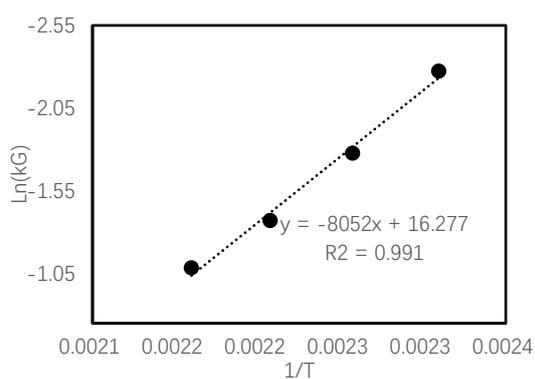
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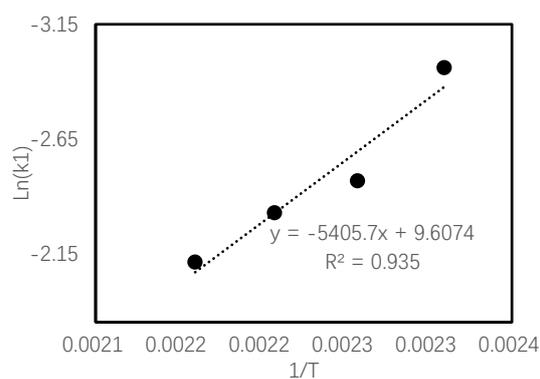
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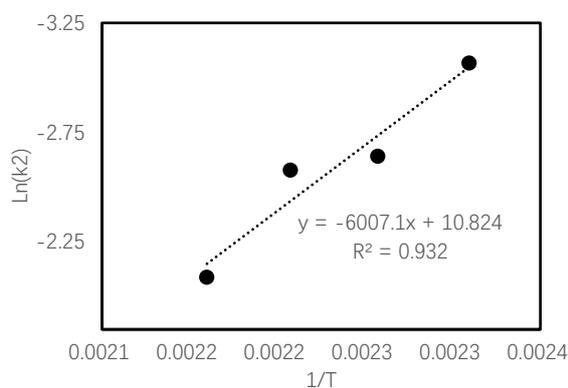
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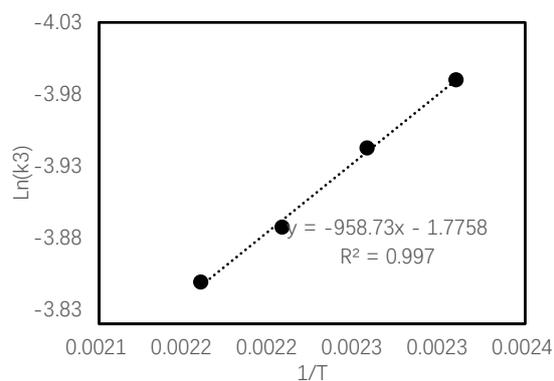
(a)



(b)



(c)



(d)

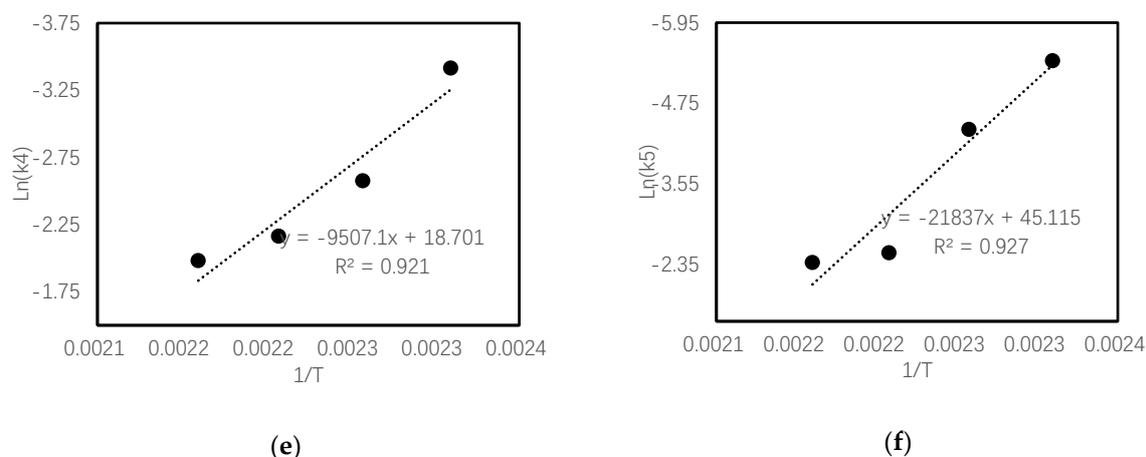


Figure S1. (a) Arrhenius plots of $\ln(k_1)$ versus $1/T$; (b) Arrhenius plots of $\ln(k_2)$ versus $1/T$; (c) Arrhenius plots of $\ln(k_3)$ versus $1/T$; (d) Arrhenius plots of $\ln(k_4)$ versus $1/T$; (e) Arrhenius plots of $\ln(k_5)$ versus $1/T$; (f) Arrhenius plots of $\ln(k_6)$ versus $1/T$.

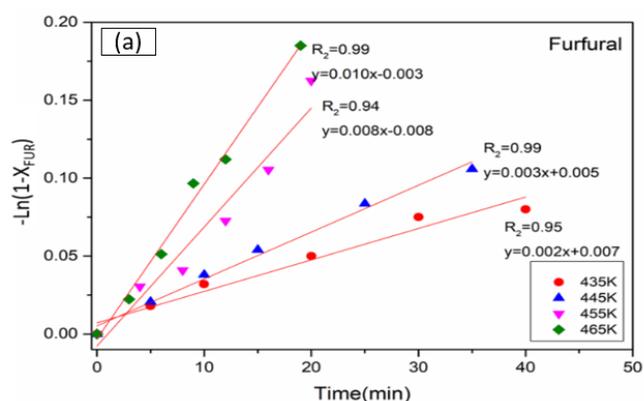
Another method to obtain k_3 and k_4 from experimental data of furfural and HMF degradation.

$$\text{HMF degradation } (X_{\text{HMF}} \%) = \frac{\text{moles of converted HMF}}{\text{moles of starting HMF}} \times 100\% \quad (1)$$

$$\text{Furfural degradation } (X_{\text{FUR}} \%) = \frac{\text{moles of converted furfural}}{\text{moles of starting furfural}} \times 100\% \quad (2)$$

Reaction conditions: 0.0555 mol/L furfural or HMF; 1.6 mL GVL; 0.4 mL water; 0.1 wt% H_2SO_4 ; and 0.014 mol/L SnSO_4

As a comparison, another reported method was also employed to calculate the above parameters from experimental data. The conversion rate constants for glucose (k_c) over different temperatures were obtained using a nonlinear curve fitting, as Equation (10) in manuscript, where the data are from Figure 1a. Figure S2 gave the formation rate constants of furfural (k_1) and HMF (k_2) over different temperatures based on experimental data, while the degradation rate constants of furfural (k_3) and HMF (k_4) over different temperatures were obtained using a nonlinear curve fitting. The results presented in Table S1.



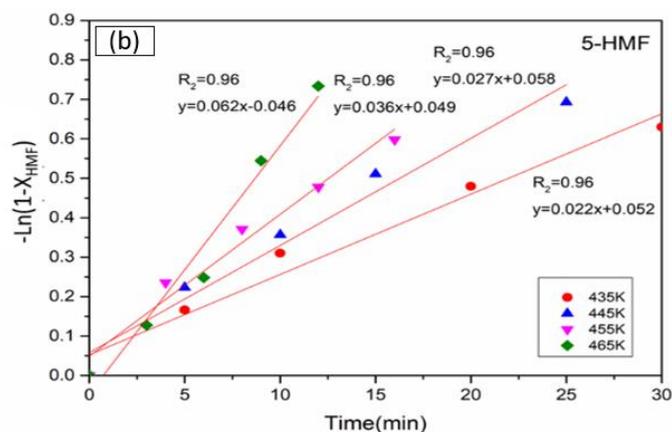
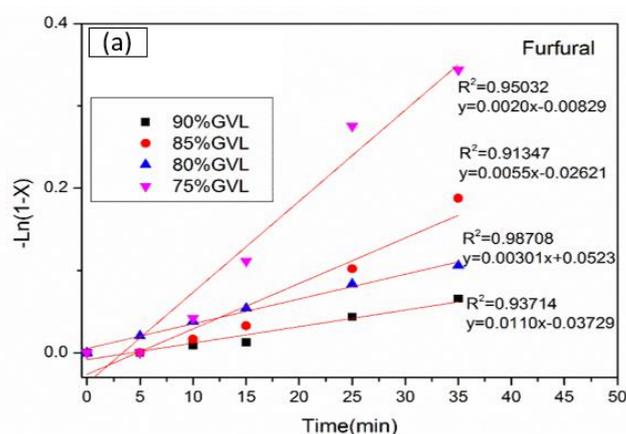


Figure S2. $-\ln(1-X)$ versus reaction time for (a) furfural degradation and (b) HMF degradation over different temperatures.

Table S1. Kinetic parameters for the conversion of glucose into HMF and furfural at different temperatures.

Temp.	435 K	445 K	455 K	465 K
k_3	1.09×10^{-3}	2.10×10^{-3}	3.01×10^{-3}	9.92×10^{-3}
k_4	2.19×10^{-2}	2.72×10^{-2}	3.60×10^{-2}	6.24×10^{-2}

The conversion rate constants for glucose (k_C) over over different ratios of GVL to water were obtained using a nonlinear curve fitting, as Equation (10) in manuscript, where the data are from Figure 1a. Figure S3 gave the formation rate constants of furfural (k_1) and HMF (k_2) over different ratios of GVL to water based on experimental data, while the degradation rate constants of furfural (k_3) and HMF (k_4) over different ratios of GVL to water were obtained using a nonlinear curve fitting. The results presented in Table S2.



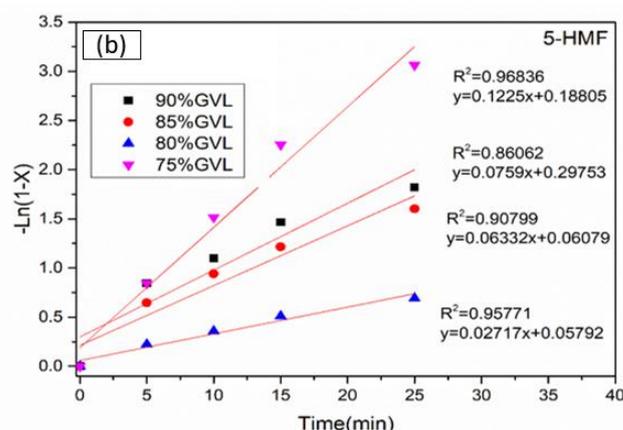


Figure S3. $-\ln(1-X)$ versus reaction time for (a) furfural conversion and (b) 5-HMF conversion based on the mixed catalyzed system over different ratios of GVL to water.

Table S2. Kinetic parameters for the conversion of glucose to furfural at a different water content.

GVL/Water ratio	90%	85%	80%	75%
k_3	2.00×10^{-3}	5.50×10^{-3}	3.01×10^{-3}	1.10×10^{-3}
k_4	7.59×10^{-2}	6.33×10^{-2}	2.72×10^{-2}	1.23×10^{-2}

Table S3. Glucose conversions into furfural and 5-HMF using single and mixed catalysts.

Entry	Substrate	Brønsted acid (mol/L)	Lewis acid (mol/L)	Furfural yield (%)	5-HMF yield (%)
1	Fructose	H ₂ SO ₄ (0.018)	SnSO ₄ (0.014)	9	49

Reaction conditions: 0.0555 mol/L glucose; 1.8 mL GVL; 0.2 mL water; temperature, 445 K; reaction time, 10 min.

Table S4. Glucose conversions into furfural and 5-HMF using single and mixed catalysts.

Entry	Substrate	Brønsted acid (mol/L)	Lewis acid (mol/L)	Furfural yield (%)
1	5-HMF	H ₂ SO ₄ (0.018)	SnSO ₄ (0.014)	0 ± 0.0

Reaction conditions: 0.0555 mol/L glucose; 1.8 mL GVL; 0.2 mL water; temperature, 445 K; reaction time, 25 min.

Comparison with previous kinetic models:

Table S5 summarizes kinetic studies from literature involving HMF production from glucose (Entry 1) and furfural production from xylose (Entry 2) using Brønsted and/or Lewis acid catalysts. The results from these studies were then compared with the results of this study. Because of insufficient studies for furfural production from glucose, we selected the kinetic study for furfural production from xylose for the substitute.

Regarding the HMF production pathway, its activation energies for the production and degradation in this study ($E_{a2} = 49.9$ and $E_{a4} = 79.0$ kJ mol⁻¹) are both lower than that from 1 ($E_{a1} = 65.4$ and $E_{a3} = 82.1$ kJ mol⁻¹). The possible reason should be that weak Brønsted acid of H₃PO₄ was employed for glucose decomposition to HMF in water for Entry 1, while the utilization of stronger Brønsted acid of H₂SO₄ and solvent of GVL in this study contributed to smaller E_a values.

Comparing the furfural production pathway with Entry 2, E_a for furfural degradation in this study ($E_{a3} = 8.0$ kJ mol⁻¹) is significantly smaller compared to that in Entry 2 ($E_{a3} =$

98.8 kJ mol⁻¹). This indicates that the furfural decomposition is not sensitive to the temperature and furfural is much more thermally stable and in our reaction system. Promising furfural production was obtained in this study, possibly owing to that GVL inhibited furfural side reaction effectively.

Table S5. Comparison with previous kinetic models.

Entry	Model	Solvent	Reaction conditions	E _a (kJ mol ⁻¹)	Refs.
1	$\begin{array}{ccc} \text{Glucose} & \xrightarrow{k_1} & \text{HMF} \\ & \downarrow k_2 & \downarrow k_3 \\ & \text{Humin} & \text{Humin} \end{array}$	Water	H ₃ PO ₄ -CrCl ₃ 423–452 K	E _{a1} = 65.4 E _{a2} = 85.6 E _{a3} = 82.1	[1]
2	$\begin{array}{ccc} \text{Xylose} & \xrightarrow{k_1} & \text{Furfural} \\ & \downarrow k_2 & \downarrow k_3 \\ \text{Condensation} & & \text{Resignification} \\ \text{products} & & \text{products} \end{array}$	Water	AlCl ₃ -Formic acid 373–443 K	E _{a1} = 67.2 E _{a2} = 99.5 E _{a3} = 98.8	[2]
3	$\begin{array}{l} \text{Glucose} \begin{cases} \xrightarrow{k_1} \text{Furfural} \xrightarrow{k_3} \text{Degradation Products} \\ \xrightarrow{k_2} \text{5-HMF} \xrightarrow{k_4} \text{Degradation products} \\ \xrightarrow{k_5} \text{Degradation Products} \end{cases} \end{array}$	GVL	SnSO ₄ -H ₂ SO ₄ 435–465 K	E _{a1} = 44.9 E _{a2} = 49.9 E _{a3} = 8.0 E _{a4} = 79.0 E _{a5} = 181.5	Our work

3-deoxy-glucosone(3-DG) was determined using a published method for [3]. Dicarbonyl compounds such as 3-deoxy-glucosone can be analyzed as 2,3-diaminonaphthalene (DAN)- 3-deoxy-glucosone (Figure S4). DAN-3-DG was determined on Thermo Fisher Scientific™ LC-MS/MS using an Agilent Zorbax Eclipse Plus C18 column (2.1 × 150 mm, 1.8 μm, Agilent Technologies, USA). The DAN-3-DG mixture was prepared under an optimal reaction condition (2 min; 445K; 0.0555 mol L⁻¹ glucose; 1.6 mL GVL; 0.4 mL water; 0.1 wt% H₂SO₄; and 0.014 mol L⁻¹ SnSO₄). The 0.1 mL of the mixture was combined with 0.9 mL (2 mM DAN) and incubated at 50 °C for 1 h. LC-MS/MS test condition is presented as follows.

The mobile phase of the eluent was 0.1% formic acid in water (A) and methanol (B), and the flow rate was 0.4 mL/min. The optimum gradient elution program was set as follows: 0–4 min, 10–100% B; 4–6 min, 100% B; 6–9 min, 100–10%. The injection volume was 1 μL. Samples were analyzed in the positive ionization using H-ESI ion source type, vaporizer temperature and ion transfer tube temperature are 350°C and 325°C, respectively. Data were collected in full-scan (at m/z 50–500) and MSⁿ mode simultaneously, an initial HCD collision energy of 10 eV, and a collision energy ramp from 10 eV to 40 eV. Data acquisition and analysis were carried out using Xcalibur™ software.

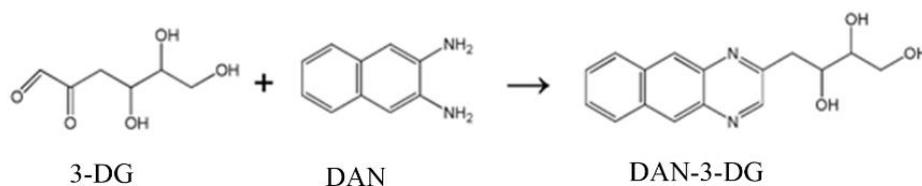


Figure S4. 3-DG determination mechanism.

LC-MS/MS allows us to infer the elemental composition of the fragments and the structural information of the compound through the molecular weight. The secondary mass spectrum in Figure S5 allows us to infer and confirm the formation of DAN-3-DG (2.32 min). In the positive ion mode, LC-MS spectra of m/z 285.12 (DAN-3-DG) and its

fracture process shown in Figure S6. In detail, m/z 285.12 corresponds to DAN-3-DG. Some fragments continuously lost from DAN-3-DG results in m/z 267.12, 249.05, 237.015, 221.13, 209.11; 197.10, 195.15, 182.11, 160.06. These m/z corresponding structures are presented in Figures S6 and S7.

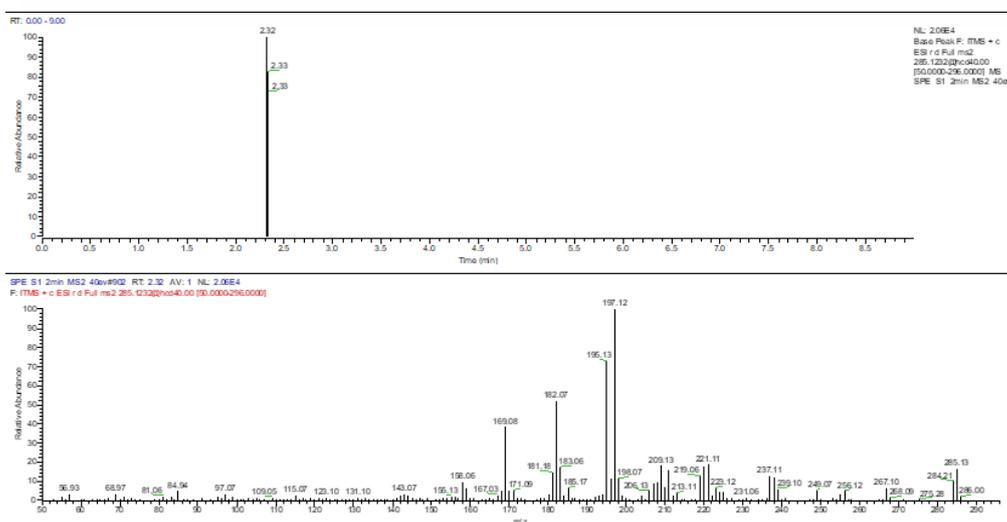


Figure S5. LC-MS spectra of m/z 285.12 (DAN-3-DG) and its fracture process.

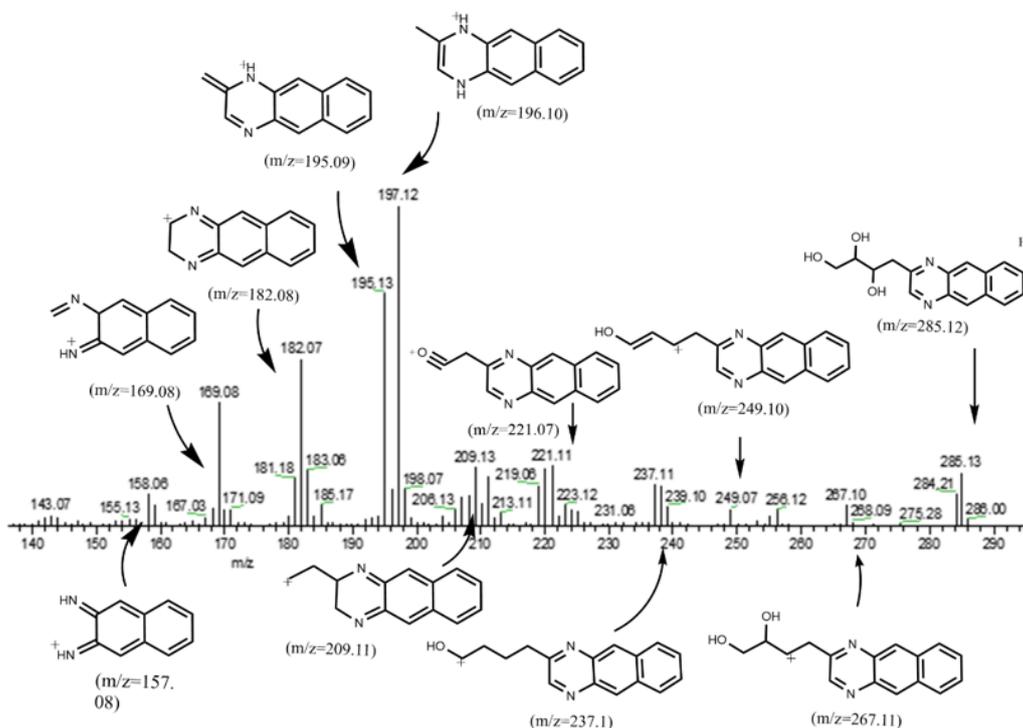


Figure S6. MS spectra of m/z 285.12 (DAN-3-DG) and corresponding structures.

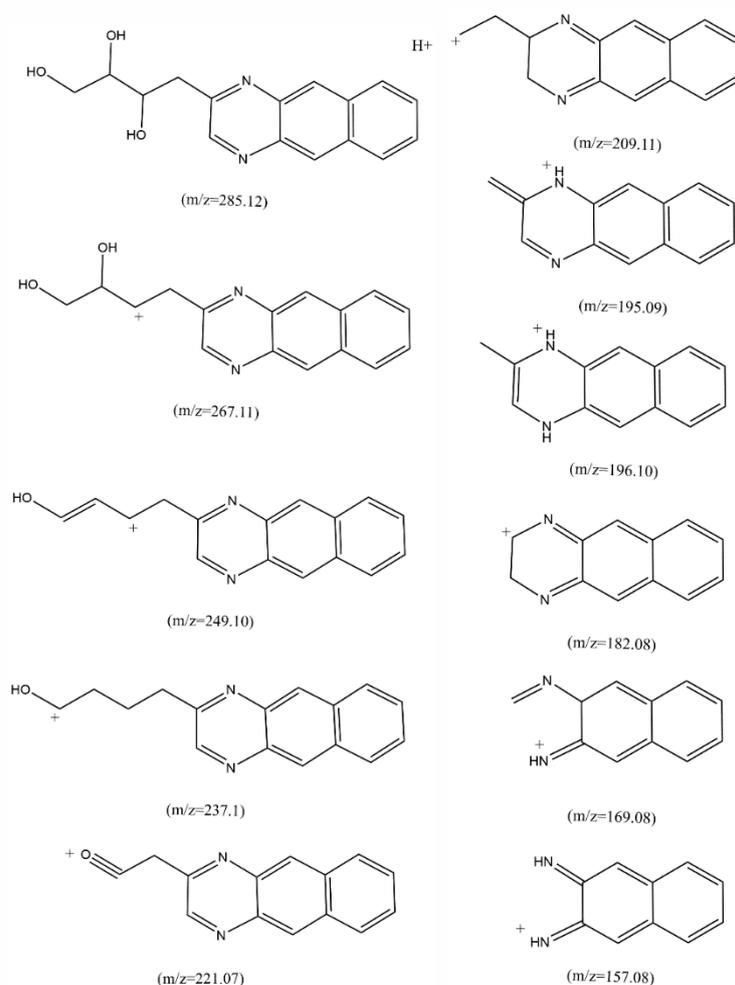


Figure S7. Fragments of DAN-3-DG.

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