Supporting Information

Microwave Assisted Conversion of Carbohydrates and Biopolymers to 5-Hydroxymethylfurfural with Aluminum Chloride Catalyst in Water

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Table S1 Optimization of reaction time for dehydration of 30 wt% of fructose catalyzed by AlCl₃ in biphasic water-MIBK (1/4 volume ratio).

<table>
<thead>
<tr>
<th>Entry</th>
<th>t (min)</th>
<th>HMF Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>27.7</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>32.8</td>
</tr>
<tr>
<td>3</td>
<td>75</td>
<td>33.3</td>
</tr>
<tr>
<td>4</td>
<td>90</td>
<td>33.9</td>
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Table S2 Results of fructose dehydration to HMF catalyzed by AlCl₃ in different reaction time.

<table>
<thead>
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<th>Entry</th>
<th>Fructose (wt%)</th>
<th>AlCl₃ (mol%)</th>
<th>t (min)</th>
<th>HMF Yield (%)</th>
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</thead>
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<td>52.3</td>
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<tr>
<td>3</td>
<td>5</td>
<td>50</td>
<td>5</td>
<td>53.9</td>
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<td>50</td>
<td>20</td>
<td>55.7</td>
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Solvent = water (2 mL), T = 120 °C, MW
Figure S1 Representative $^1$H NMR spectrum of HMF product obtained from dehydration reaction of fructose with AlCl$_3$ in water. This spectrum recorded in CDCl$_3$ at room temperature for determining HMF yield using mesitylene as an internal standard.
**Figure S2** Representative UV-Vis spectrum of HMF product solution obtained from dehydration reaction of fructose with AlCl₃ in water.
**Figure S3** Representative $^1$H NMR (in CDCl$_3$) spectrum of the reaction product collected from MIBK phase of fructose (30 wt%) dehydration reaction with 50 mol% AlCl$_3$ catalyst in biphasic water-MIBK solvent under microwave heating at $T = 120$ °C for 5 min.
Figure S4 Representative $^1$H NMR (DMSO-$d_6$) spectrum of the insoluble brown material obtained in fructose (30 wt%) dehydration with AlCl$_3$ in water under microwave heating at 120 °C for 5 min.
Figure S5 Representative $^1$H NMR spectrum for a mixture of glucose and AlCl$_3$ in DMSO-$d_6$ at room temperature to 100 °C; (a) $^1$H NMR spectrum of glucose (25 mg) at room temperature in DMSO-$d_6$. (b) $^1$H NMR spectrum of glucose (25 mg) + AlCl$_3$ (9.3 mg) (2:1 molar ratio) at room temperature displaying broad H$_{\text{O-H}}$ signals of glucose due to the interaction of Cl of AlCl$_3$ with OH of glucose in DMSO-$d_6$. (c) $^1$H NMR spectrum of glucose at 100 °C heated for 40 min. (d) $^1$H NMR spectrum of glucose + AlCl$_3$ (2:1 molar ratio) at 100 °C heated for 40 min. Data presented for $\delta$ 4 to 5 ppm with full spectrums ($\delta$ 1 to 10 ppm) as inset.
Figure S6 Representative $^1$H NMR spectrum for a mixture of glucose and SnCl$_4$ in DMSO-$d_6$ at room temperature to 120 °C; (a) $^1$H NMR spectrum of glucose (25 mg) at room temperature in DMSO-$d_6$. (b) $^1$H NMR spectrum of glucose (25 mg) + SnCl$_4$ (9 mg) (4:1 molar ratio) at room temperature displaying disappearance of $H_{O-H}$ signals of glucose due to the interaction of SnCl$_4$ with OH of glucose in DMSO-$d_6$. (c) $^1$H NMR spectrum of glucose + SnCl$_4$ (2:1 molar ratio) at 80 °C heated for 40 min. (d) $^1$H NMR spectrum of glucose + SnCl$_4$ (2:1 molar ratio) at 120 °C heated for 30 min. Full spectrums (δ0 to 11 ppm) for each steps presented as inset.
Figure S7 Representative $^1$H NMR spectrum for a mixture of glucose and Yb(OTf)$_3$ in DMSO-$d_6$ at room temperature to $120 \, ^\circ$C; (a) $^1$H NMR spectrum of glucose (25 mg) at room temperature in DMSO-$d_6$, (b) $^1$H NMR spectrum of glucose (25 mg) + Yb(OTf)$_3$ (9.3 mg) (2:1 molar ratio) at $120 \, ^\circ$C heated for 40 min in DMSO-$d_6$. Full spectrums ($\delta$ 0 to 11 ppm) for each steps presented as inset.