## Efficient metal-free conversion of glucose to 5-hydroxymethylfurfural using a boronic acid

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## Graham & Raines

Table S1 Screen			version of glucose to I		
D · · · 1	HMF Yield (%)	HMF Yield (%)	D 1 1	HMF Yield (%)	HMF Yield (%)
Boronic acid	(anhydrous)	(aqueous)	Boronic acid HO <sub>B</sub> OH	(anhydrous)	(aqueous)
HO、 <sub>B</sub> _OH OH	20.3	0.3		7.0	0.1
HO_B_OH	6.9	0	HO <sub>B</sub> OH	24.5	18.5
HO <sub>B</sub> -OH	0.4	19.6	HO <sub>B</sub> OH	3.4	4.5
HO <sub>`B</sub> OH O N <sup>*</sup> O	15.1	0.2	HO <sub>B</sub> OH	9.5	0.1
HO <sub>B</sub> OH NH <sub>2</sub>	0.4	2.2	HO <sub>B</sub> OH	6.6	0.1
HO_B_OH	24.1	44.1	HO, B, OH	8.2	0.6
HO <sub>B</sub> OH H	23.9	0.5	HO <sub>B</sub> OH	10.0	0.2
HO <sub>B</sub> OH	4.1	0.0	HO <sub>B</sub> OH	16.3	0.3
HO <sub>B</sub> OH	10.6	0.7	HO. <sub>B</sub> .CH	1.6	0.1
HO <sub>B</sub> OH	12.8	0.3	HO <sub>B</sub> OH	8.2	0.4
HO <sub>B</sub> OH	0	0	None	0.15	0

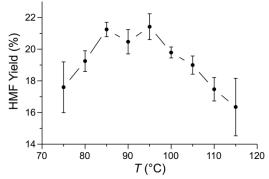
Table S1	Screen of h	oronic acids	for the meta	l-free conversion	n of glucose t	o HMF in	[BMIM]Cl a
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<sup>a</sup> Reaction conditions: [BMIM]Cl (1.0 g), glucose (10% w/v), and boronic acid (1 equiv), shaken (650 rpm) at 105 °C for 2 h. Two reactions were performed with each boronic acid: one with no added water (anhydrous) and one with added water (60 µL, 12 equiv) to mimic water from the MgCl<sub>2</sub>·6H<sub>2</sub>O (2 equiv) in Caes et al. (2013).

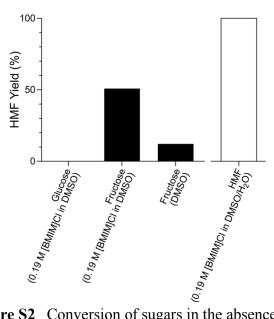
glucose to HMF in DMF. <sup>a</sup>						
Boronic Acid	HMF Yield (%)	Boronic Acid	HMF Yield (%)			
HO <sub>B</sub> OH	0.0	HO.B.OH	0.0			
HO_B_OH	3.3	HO. B.OH	0.0			
HO B OF	0.0	HO <sub>B</sub> OH	0.0			
HO <sub>B</sub> OH NH <sub>2</sub>	0.0	HO <sub>B</sub> OH	0.0			
HO <sub>B</sub> OH OH	58.2	HO	0.0			
HO <sub>B</sub> OH	0.0	HO <sup>B</sup> ,OH	0.0			
HO <sub>B</sub> OH	0.0	HO,B,OH	0.0			
HO <sub>B</sub> OH	0.0	HO.B-O	0.0			
HO.B.OH	0.0	HO, B, OH	16.3			

**Table S2**Screen of boronic acids for the metal-free conversion of<br/>glucose to HMF in DMF.<sup>a</sup>

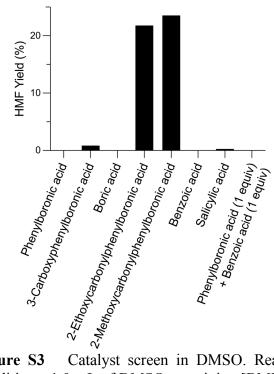
<sup>a</sup> Reaction conditions: A 0.5-mL solution of DMF containing [BMIM]Cl (0.19 M), glucose (10% w/v), and catalyst (1 equiv); shaken (650 rpm) at 95 °C for 1 h.



**Figure S1** Temperature-dependence of the conversion of glucose to HMF in [BMIM]Cl. Reaction conditions: [BMIM]Cl (1.0 g), glucose (10% w/v), and 2-CPBA (1 equiv), shaken (650 rpm) at the specified temperature for 2 h. n = 4 at each temperature.



**Figure S2** Conversion of sugars in the absence of a boronic acid. Reaction conditions: 1.0 mL of solvent containing sugar (10% w/v), shaken (650 rpm) at 95 °C for 2 h. The solution containing HMF had 0.2 mL of added water to allow for HMF hydrolysis.



**Figure S3** Catalyst screen in DMSO. Reaction conditions: 1.0 mL of DMSO containing [BMIM]Cl (0.19 M), glucose (10% w/v), and catalyst (1 equiv); 95 °C, 1 h, shaking at 650 rpm.