MATERIALS AND METHODS

General. Commercial chemicals were of reagent grade or better and were used without further purification. 1-Ethyl-3-methylimidazolium chloride (99.5%, [EMIM]Cl) was from Solvent-Innovation (Cologne, Germany). Glucose was from J. T. Baker (Phillipsburg, NJ). Cellulose (medium cotton linters, C6288), fructose, *N,N*-dimethylacetamide (DMA), and metal chlorides were from Sigma Chemical (St. Louis, MO). Magnesium chloride hexahydrate was from Fisher Scientific (Pittsburgh, PA). Boronic acids were from either Synthonix (Doylestown, PA) or Combi-Blocks (San Diego, CA). All reactions were performed in 4-mL glass vials heated in a temperature-controlled VWR Mini Shaker at 600 rpm.

The term "concentrated under reduced pressure" refers to the removal of solvents and other volatile materials with a rotary evaporator under reduced pressure provided by a Welch 2025 self-cleaning dry vacuum system while maintaining the water-bath temperature below 50 °C except where noted. The term "high vacuum" refers to a vacuum of <0.1 torr achieved by a Welch mechanical belt-drive oil pump. The term "speed vacuum" refers to spinning samples in a UVS400 Universal Vacuum System from Thermo Scientific (Waltham, MA) under reduced pressure provided by a Welch 2042 DryFast vacuum system.

NMR spectra were acquired with a Bruker DMX-400 Avance spectrometer (^{1}H, 400 MHz; ^{13}C, 100.6 MHz) at the National Magnetic Resonance Facility at Madison (NMRFAM). NMR spectra were obtained at ambient temperature unless indicated otherwise. Values of the coupling constant J are given in Hertz. Mass spectrometry was performed with a Micromass LCT (electrospray ionization, ESI) in the Mass Spectrometry Facility in the Department of Chemistry.

Analytical Methods. Reaction products were analyzed by HPLC and quantified by using calibration curves generated from commercially available standards. Product concentrations were calculated from HPLC-peak integrations, which were then used to calculate molar yields of HMF. During a reaction, an aliquot of the reaction mixture was removed, diluted with a known mass of deionized water, cooled to 4 °C, subjected to centrifugation at 12,000 rpm for 5 min to sediment insoluble products, and analyzed. HPLC was performed with an Agilent 1200 system equipped with refractive index and photodiode array detectors. HMF, glucose, and fructose were analyzed by ion-exclusion chromatography with a Bio-Rad Aminex HPX-87H column (300 × 7.8 mm) using a 5 mM H_2SO_4 mobile phase at a flow rate of 0.6 mL/min at 65 °C.

Representative Procedure for the Synthesis of HMF from Glucose. Glucose (51.6 mg, 286 μmol), 2-carboxyphenylboronic acid (47.3 mg, 285 μmol), and $MgCl_2 \cdot 6H_2O$ (145.5 mg, 716 μmol) were mixed in DMA (500 mg). The reaction mixture was heated at 120 °C for 4 h. At 1-h intervals, aliquots of the reaction mixture were removed for HPLC analysis. For reactions in [EMIM]Cl, ~500 mg of the ionic liquid was added to the vial in the place of DMA. Other boronic acids were used in a similar manner. Reactions were also performed by using anhydrous $MgCl_2$ and adding 1–12 equiv of H_2O, and in the presence of diaza-18-crown-6 at 1 equiv relative to Mg(II), which prevents Mg(II) from facilitating the conversion of glucose to HMF.

Representative Procedure for the Synthesis of HMF from Cellulose. Cellulose (21.6 mg, 133 μmol of glucose units in cellulose) and [EMIM]Cl (493.4 mg) were mixed and heated at 105 °C for 3 h. 2-Methoxycarbonylphenylboronic acid (48.4 mg, 269 μmol), $MgCl_2 \cdot 6H_2O$ (115 mg, 566 μmol), and concentrated HCl (3.4 μL, 109 μmol) were added, and the reaction mixture was heated for 4 h. At 1-h intervals, aliquots of the reaction mixture were removed for HPLC analysis. Other boronic acids and mineral acids were used in a similar manner.

Catalyst Recovery and Recycling. Cellulose (248.2 mg, 1.531 mmol of glucose units in cellulose) and [EMIM]Cl (2.5173 g) were mixed and heated at 105 °C for 3 h.

2-Ethoxycarbonylphenylboronic acid (488.7 mg, 2.519 mmol), $MgCl_2 \cdot 6H_2O$ (973.0 mg, 4.786 mmol), and concentrated H_2SO_4 (12.0 μL, 0.225 mmol) were added, and the reaction mixture was heated for 1 h. The reaction mixture was then cooled to 4 °C and dissolved *via* sonication in basic H_2O prepared from an NH_4OH solution (15 mL). Vacuum filtration was done to remove insoluble humins and unreacted cellulose. Five extractions were done with ethyl acetate (7.5 mL) to remove HMF from the aqueous phase. The extracts were combined and concentrated under reduced pressure to yield HMF (50.1 mg, 26.0% recovered HMF yield). The reaction mixture was subjected to speed vacuum overnight, and then to high vacuum overnight. Cellulose (233.2 mg) was added to the reaction mixture, which was heated at 80 °C for 4 h. The temperature was then increased to 105 °C. Concentrated H_2SO_4 (11.0 μL, 0.206 mmol) was added, and the reaction mixture was heated for 1 h. Work-up of the reaction mixture and isolation of HMF were done as described above. The reaction mixture was recycled for a total of four reactions with a final recovered HMF yield of 18% (*i.e.*, 201.9 mg of cellulose yielded 28.0 mg of HMF).

Isotopic Labeling Experiments. 2-Deuteroglucose (48.5 mg, 268 μmol), 2-ethoxycarbonylphenylboronic acid (54.1 mg, 279 μmol), and $MgCl_2 \cdot 6H_2O$ (126.2 mg, 621 μmol) were dissolved in DMA (532 μL). The reaction mixture was heated at 105 °C for 4 h, placed under high vacuum overnight to remove DMA, extracted with ethyl acetate, concentrated under reduced pressure, and analyzed by ^1H NMR spectroscopy. The aldehyde peak of HMF (9.56 ppm) showed <5% deuterium retention, indicating that the isomerization mechanism from glucose to fructose is not a 1,2-hydride shift.

Glucose (100.5 mg, 558 μmol) and 2-ethoxycarbonylphenylboronic acid (120.0 mg, 619 μmol) were dissolved in DMA (1064 μL), and D_2O (500 μL) was added to exchange any labile protons with deuterons. This mixture was then concentrated under reduced pressure to remove D_2O and H_2O. The D_2O exchange was repeated. Anhydrous $MgCl_2$ (123.2 mg, 1.29 mmol) and D_2O (150.8 mg, 7.53 mmol) were then added, and the reaction mixture was heated at 105 °C for 4 h, placed under high vacuum overnight to remove DMA, extracted with ethyl acetate, concentrated under reduced pressure, and analzyed by ^1H NMR spectroscopy. The aldehyde peak of HMF (9.56 ppm) showed 35% deuterium incorporation relative to other HMF peaks (Fig. 1S), consistent with the isomerization of glucose to fructose proceeding by an enolization mechanism.

Table S1 Screen of metal halides for the conversion of glucose to HMF in DMA

metal halide	*T* (°C)	time (h)	HMF yield (%)
$CaCl_2 \cdot 2H_2O$	120	6	13
LiCl	120	6	5
LiBr	120	6	1
NaCl	120	6	0
KCl	120	6	0
CuCl	120	6	12
$CuCl_2$	120	6	9
CsCl	120	6	0
$FeCl_2$	120	4.5	7
$FeCl_3$	120	4.5	4
$MoCl_3$	120	1.5	12
VCl_3	120	1.5	16
RbCl	120	6	0
$BaCl_2 \cdot 2H_2O$	120	6	0
$CoCl_2 \cdot 6H_2O$	120	3	11
$PdCl_2$	120	6	4
$MnCl_2 \cdot 4H_2O$	120	6	10

Metal halides were at 3 equiv relative to glucose. Glucose was at 10 wt% relative to DMA. HMF yield is relative to glucose.

Table S2 Screen of boronic acids for the conversion of glucose to HMF in DMA

boronic acid	metal halide	*T* (°C)	time (h)	HMF yield (%)
phenylboronic acid	—	105	4	0
phenylboronic acid	$MgCl_2{\cdot}6H_2O$	105	4	4
2-(hydroxymethyl)phenyl	—	100	6	0
2-(hydroxymethyl)phenyl	$MgCl_2{\cdot}6H_2O$	100	6	6
2-formylphenyl	—	105	4	0
2-formylphenyl	$MgCl_2{\cdot}6H_2O$	105	4	4
2-acetylphenyl	—	105	4	0
2-acetylphenyl	$MgCl_2{\cdot}6H_2O$	105	4	2
2-aminocarbonylphenyl	—	105	4	0
2-aminocarbonylphenyl	$MgCl_2{\cdot}6H_2O$	105	4	8
2-nitrophenyl	—	105	4	0
2-nitrophenyl	$MgCl_2{\cdot}6H_2O$	105	4	7
2-(*N,N*-dimethylaminomethyl)phenyl	—	120	6	0
2-(*N,N*-dimethylaminomethyl)phenyl	$MgCl_2{\cdot}6H_2O$	120	6	2
2-methoxyphenyl	—	120	6	6
2-methoxyphenyl	$MgCl_2{\cdot}6H_2O$	120	5	33
2,4-bis(trifluoromethyl)phenyl	—	100	9	ND
2,4-bis(trifluoromethyl)phenyl	$MgCl_2{\cdot}6H_2O$	100	9	ND
5-amino-2-hydroxymethylphenyl	—	120	1	6
5-amino-2-hydroxymethylphenyl	$MgCl_2{\cdot}6H_2O$	120	1	3
2,6-dimethoxyphenyl	—	120	6	0
2,6-dimethoxyphenyl	$MgCl_2{\cdot}6H_2O$	120	6	28
2,6-dimethylphenyl	—	120	6	8
2,6-dimethylphenyl	$MgCl_2{\cdot}6H_2O$	120	6	27
3-carboxyphenyl	—	100	7.5	24
3-carboxyphenyl	$MgCl_2{\cdot}6H_2O$	100	7.5	25
3-carboxy-5-nitrophenyl	—	100	4.5	5
3-carboxy-5-nitrophenyl	$MgCl_2{\cdot}6H_2O$	100	9	36
3,5-bis(trifluoromethyl)phenyl	—	100	6	18
3,5-bis(trifluoromethyl)phenyl	$MgCl_2{\cdot}6H_2O$	100	9	25
4-carboxyphenyl	—	100	6	1
4-carboxyphenyl	$MgCl_2{\cdot}6H_2O$	100	9	28
4-methylphenyl	—	120	6	0
4-methylphenyl	$MgCl_2{\cdot}6H_2O$	120	9	23
Benzoic acid	$MgCl_2{\cdot}6H_2O$	100	9	22
Phthalic acid	$MgCl_2{\cdot}6H_2O$	100	9	18

Boronic acids were at 1 equiv, and $MgCl_2{\cdot}6H_2O$ was at 2 equiv relative to glucose. Glucose was at 10 wt% relative to DMA. Mol% and HMF yield are relative to glucose. ND = not determined (because HMF and the boronic acid have the same retention time during HPLC).

Table S3 Screen of catalyst concentrations for the conversion of glucose to HMF in DMA

boronic acid, mol%	metal halide, mol %	*T* (°C)	time (h)	HMF yield (%)
2-carboxyphenyl, 100	$MgCl_2 \cdot 6H_2O$, 200	120	4	54
2-carboxyphenyl, 50	$MgCl_2 \cdot 6H_2O$, 200	120	6	48
2-carboxyphenyl, 25	$MgCl_2 \cdot 6H_2O$, 200	120	6	46
2-carboxyphenyl, 10	$MgCl_2 \cdot 6H_2O$, 200	120	6	31
2-carboxyphenyl, 100	$MgCl_2 \cdot 6H_2O$, 250	110	6	55
2-carboxyphenyl, 100	$MgCl_2 \cdot 6H_2O$, 200	110	5	51
2-carboxyphenyl, 100	$MgCl_2 \cdot 6H_2O$, 150	110	5	48
2-carboxyphenyl, 100	$MgCl_2 \cdot 6H_2O$, 100	110	5	43

Glucose was at 10 wt% relative to DMA. Mol% and HMF yield are relative to glucose. Entries highlighted in gray is also listed in the main text.

Table S4 Screen of boronic acids and metal halides for the conversion of glucose to HMF in DMA

boronic acid	metal halide, mol%	*T* (°C)	time (h)	HMF yield (%)
2-carboxyphenyl	$CrCl_2$, 25	100	6	37
2-carboxyphenyl	$CrCl_2$ + $6H_2O$, 25	100	6	48
2-methoxycarbonylphenyl	$CrCl_2$, 25	100	1.5	39
2-methoxycarbonylphenyl	$CrCl_2$ + $6H_2O$, 25	100	1.5	28
2-ethoxycarbonylphenyl	$CrCl_2$, 25	100	3	33
2-ethoxycarbonylphenyl	$CrCl_2$ + $6H_2O$, 25	100	1.5	26
2-carboxyphenyl	$MgCl_2$, 200	120	1	19
2-carboxyphenyl	$MgCl_2 \cdot 6H_2O$, 200	120	4	54
2-methoxycarbonylphenyl	$MgCl_2$, 200	120	1	19
2-methoxycarbonylphenyl	$MgCl_2 \cdot 6H_2O$, 200	120	4	57
2-ethoxycarbonylphenyl	$MgCl_2$, 200	120	1	18
2-ethoxycarbonylphenyl	$MgCl_2 \cdot 6H_2O$, 200	120	4	52
2-carboxyphenyl	$CaCl_2 \cdot 2H_2O$, 300	120	3	38
2-carboxyphenyl	LiCl + $6H_2O$, 300	105	4	16
2-carboxyphenyl	LiBr + $6H_2O$, 300	105	4	4
2-carboxyphenyl	NaCl + $6H_2O$, 300	105	4	2
2-carboxyphenyl	KCl + $6H_2O$, 300	105	4	2
2-carboxyphenyl	CuCl + $6H_2O$, 300	105	4	0
2-carboxyphenyl	$CuCl_2$ + $6H_2O$, 300	105	4	4
2-carboxyphenyl	CsCl + $6H_2O$, 300	105	4	7
2-carboxyphenyl	$FeCl_2$ + $6H_2O$, 300	105	4	10
2-carboxyphenyl	$FeCl_3$ + $6H_2O$, 300	105	4	4
2-carboxyphenyl	$MoCl_3$ + $6H_2O$, 300	105	1	15
2-carboxyphenyl	VCl_3 + $6H_2O$, 300	105	4	29
2-carboxyphenyl	RbCl + $6H_2O$, 300	105	4	2
2-carboxyphenyl	$BaCl_2 \cdot 2H_2O$, 300	105	4	1
2-carboxyphenyl	$CoCl_2 \cdot 6H_2O$, 300	105	4	17
2-carboxyphenyl	$PdCl_2$ + $6H_2O$, 300	105	4	3
2-carboxyphenyl	$MnCl_2 \cdot 4H_2O$, 300	105	4	5

Boronic acids were at 1 equiv relative to glucose. Glucose was at 10 wt% relative to DMA. Mol% and HMF yield are relative to the glucose. Added water is relative to the metal halide. Entries highlighted in gray are also listed in the main text.

Table S5 Screen of water concentrations for the conversion of glucose to HMF in DMA

metal halide	added water (equiv)	total water (equiv)	*T* (°C)	Time (h)	HMF yield (%)
$MgCl_2$	0	0	100	3	22
$MgCl_2$	1	1	100	3	24
$MgCl_2$	2	2	100	4.5	28
$MgCl_2$	3	3	100	6	30
$MgCl_2$	4	4	100	6	33
$MgCl_2$	5	5	100	6	36
$MgCl_2$	6	6	100	6	40
$MgCl_2$	7	7	100	6	43
$MgCl_2$	8	8	100	6	43
$MgCl_2$	9	9	100	6	46
$MgCl_2$	10	10	100	6	46
$MgCl_2$	11	11	100	6	56
$MgCl_2$	12	12	100	6	54
$MgCl_2 \cdot 6H_2O$	1	13	100	3	54
$MgCl_2 \cdot 6H_2O$	2	14	100	4.5	56
$MgCl_2 \cdot 6H_2O$	3	15	100	6	57
$MgCl_2 \cdot 6H_2O$	4	16	100	4.5	57
$MgCl_2 \cdot 6H_2O$	5	17	100	4.5	58

Glucose was at 10 wt% to DMA. Mol%, HMF yield, and water equiv are relative to glucose (not $MgCl_2$). 2-Carboxyphenylboronic acid was at 1 equiv, and $MgCl_2$ and $MgCl_2 \cdot 6H_2O$ were at 2 equiv relative to glucose.

Table S6 Initial screens of catalysts for the conversion of cellulose to HMF in [EMIM]Cl

acid, wt%	boronic acid	additive	*T* (°C)	time (h)	HMF yield (%)
—	2-carboxyphenyl	—	120	4.5	0
—	2-methoxycarbonylphenyl	—	120	4.5	0
—	2-ethoxycarbonylphenyl	—	120	3.8	12
HCl, 0.88	—	—	105	2	10
HCl, 0.88	—	$MgCl_2·6H_2O$	105	3	16
HCl, 0.88	2-methoxycarbonylphenyl	—	105	2	16
HCl, 0.88	2-methoxycarbonylphenyl	$MgCl_2·6H_2O$	105	1	26
HCl, 0.88	2-ethoxycarbonylphenyl	—	105	1	22
HCl, 0.88	2-ethoxycarbonylphenyl	$MgCl_2·6H_2O$	105	1	29
HCl, 0.88	2-methoxycarbonylphenyl	—	120	2	12
HCl, 0.88	2-methoxycarbonylphenyl	$MgCl_2·6H_2O$	120	2	28
HCl, 0.88	2-ethoxycarbonylphenyl	—	120	1	21
HCl, 0.88	2-ethoxycarbonylphenyl	$MgCl_2·6H_2O$	120	1	30
HCl, 0.8	2-ethoxycarbonylphenyl	$MgCl_2·6H_2O$	105	1	27
H_2SO_4, 0.8	2-ethoxycarbonylphenyl	$MgCl_2·6H_2O$	105	1	32
H_3PO_4, 0.8	2-ethoxycarbonylphenyl	$MgCl_2·6H_2O$	105	2	31
AcOH, 0.8	2-ethoxycarbonylphenyl	$MgCl_2·6H_2O$	105	3	29

Boronic acids were at 2 equiv, and $MgCl_2·6H_2O$ was at 4 equiv relative to glucose monomers within the cellulose. Wt% is relative to the [EMIM]Cl. Cellulose was at 5 wt% to [EMIM]Cl. HMF yield is relative to the glucose monomers within cellulose.

Table S7 Screen of catalyst concentration for the conversion of cellulose to HMF in [EMIM]Cl

acid, wt%	boronic acid, mol%	additive, mol%	*T* (°C)	time (h)	HMF yield (%)
HCl, 0.33	2-ethoxycarbonylphenyl, 200	$MgCl_2 \cdot 6H_2O$, 400	105	2	26
HCl, 0.61	2-ethoxycarbonylphenyl, 200	$MgCl_2 \cdot 6H_2O$, 400	105	1	30
HCl, 0.88	2-ethoxycarbonylphenyl, 200	$MgCl_2 \cdot 6H_2O$, 400	105	1	30
H_2SO_4, 0.33	2-ethoxycarbonylphenyl, 200	$MgCl_2 \cdot 6H_2O$, 400	105	1	27
H_2SO_4, 0.61	2-ethoxycarbonylphenyl, 200	$MgCl_2 \cdot 6H_2O$, 400	105	1	30
H_2SO_4, 0.88	2-ethoxycarbonylphenyl, 200	$MgCl_2 \cdot 6H_2O$, 400	105	1	32
H_3PO_4, 0.33	2-ethoxycarbonylphenyl, 200	$MgCl_2 \cdot 6H_2O$, 400	105	2	32
H_3PO_4, 0.61	2-ethoxycarbonylphenyl, 200	$MgCl_2 \cdot 6H_2O$, 400	105	2	28
H_3PO_4, 0.88	2-ethoxycarbonylphenyl, 200	$MgCl_2 \cdot 6H_2O$, 400	105	1	26
H_2SO_4, 0.88	2-methoxycarbonylphenyl, 200	$MgCl_2 \cdot 6H_2O$, 940	105	1	32
H_2SO_4, 0.88	2-methoxycarbonylphenyl, 200	$MgCl_2 \cdot 6H_2O$, 720	105	1	32
H_2SO_4, 0.88	2-methoxycarbonylphenyl, 200	$MgCl_2 \cdot 6H_2O$, 500	105	1	33
H_2SO_4, 0.88	2-methoxycarbonylphenyl, 200	$MgCl_2 \cdot 6H_2O$, 260	105	1	29
H_2SO_4, 0.88	2-methoxycarbonylphenyl, 400	$MgCl_2 \cdot 6H_2O$, 400	105	1	29
H_2SO_4, 0.88	2-methoxycarbonylphenyl, 340	$MgCl_2 \cdot 6H_2O$, 400	105	1	35
H_2SO_4, 0.88	2-methoxycarbonylphenyl, 260	$MgCl_2 \cdot 6H_2O$, 400	105	1	33
H_2SO_4, 0.88	2-methoxycarbonylphenyl, 160	$MgCl_2 \cdot 6H_2O$, 400	105	1	36
H_2SO_4, 0.88	2-methoxycarbonylphenyl, 120	$MgCl_2 \cdot 6H_2O$, 400	105	0.5	39
H_2SO_4, 0.88	2-methoxycarbonylphenyl, 80	$MgCl_2 \cdot 6H_2O$, 400	105	2	29
H_2SO_4, 0.88	2-methoxycarbonylphenyl, 40	$MgCl_2 \cdot 6H_2O$, 400	105	2	22
H_2SO_4, 0.88	2-ethoxycarbonylphenyl, 200	$MgCl_2 \cdot 6H_2O$, 940	105	1	32
H_2SO_4, 0.88	2-ethoxycarbonylphenyl, 200	$MgCl_2 \cdot 6H_2O$, 720	105	1	32
H_2SO_4, 0.88	2-ethoxycarbonylphenyl, 200	$MgCl_2 \cdot 6H_2O$, 500	105	1	33
H_2SO_4, 0.88	2-ethoxycarbonylphenyl, 200	$MgCl_2 \cdot 6H_2O$, 260	105	1	29
H_2SO_4, 0.88	2-ethoxycarbonylphenyl, 400	$MgCl_2 \cdot 6H_2O$, 400	105	1	26
H_2SO_4, 0.88	2-ethoxycarbonylphenyl, 340	$MgCl_2 \cdot 6H_2O$, 400	105	1	25
H_2SO_4, 0.88	2-ethoxycarbonylphenyl, 260	$MgCl_2 \cdot 6H_2O$, 400	105	1	26
H_2SO_4, 0.88	2-ethoxycarbonylphenyl, 160	$MgCl_2 \cdot 6H_2O$, 400	105	1	30

Wt% is relative to [EMIM]Cl. Cellulose was at 5 wt% relative to [EMIM]Cl. Mol% and HMF yield are relative to glucose monomers within the cellulose.

Table S8 Screen of catalysts for the conversion of fructose to HMF in DMA

boronic acid, mol%	additive, mol%	*T* (°C)	time (h)	HMF yield (%)
2-carboxyphenyl, 100	—	105	4	13
2-carboxyphenyl, 100	$MgCl_2 \cdot 6H_2O$, 200	105	2	61
2-methoxycarbonylphenyl, 100	—	105	4	40
2-methoxycarbonylphenyl, 100	$MgCl_2 \cdot 6H_2O$, 200	105	4	52
2-ethoxycarbonylphenyl, 100	—	105	3	84
2-ethoxycarbonylphenyl, 100	$MgCl_2 \cdot 6H_2O$, 200	105	4	59

Boronic acids were at 1 equiv and $MgCl_2 \cdot 6H_2O$ was at 2 equiv relative to fructose. Fructose was at 10 wt% to the DMA. HMF yield is relative to fructose.

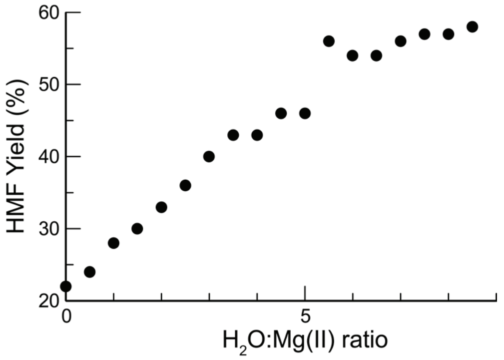

Fig. S1 Dependence of HMF yield on H_2O:Mg(II) ratio. Data are from Table S5.

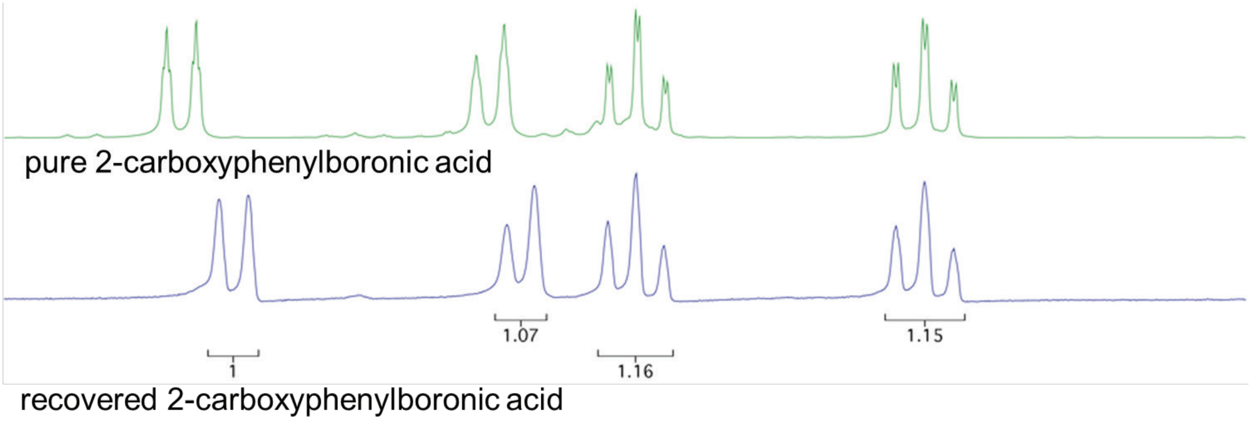

Fig. S2 Comparison of ^1H NMR spectra of pure 2-carboxyphenylboronic acid with that after use in a glucose-conversion reaction. Slight differences in chemical shifts are a result of NH_4HCO_3 being added to the sample during recovery from the reaction mixture. Recovered material has HRMS (ESI) *m*/*z* 192.0701 [calculated for $C_9H_{10}BO_4$ $(M - H)^-$ 192.0703].

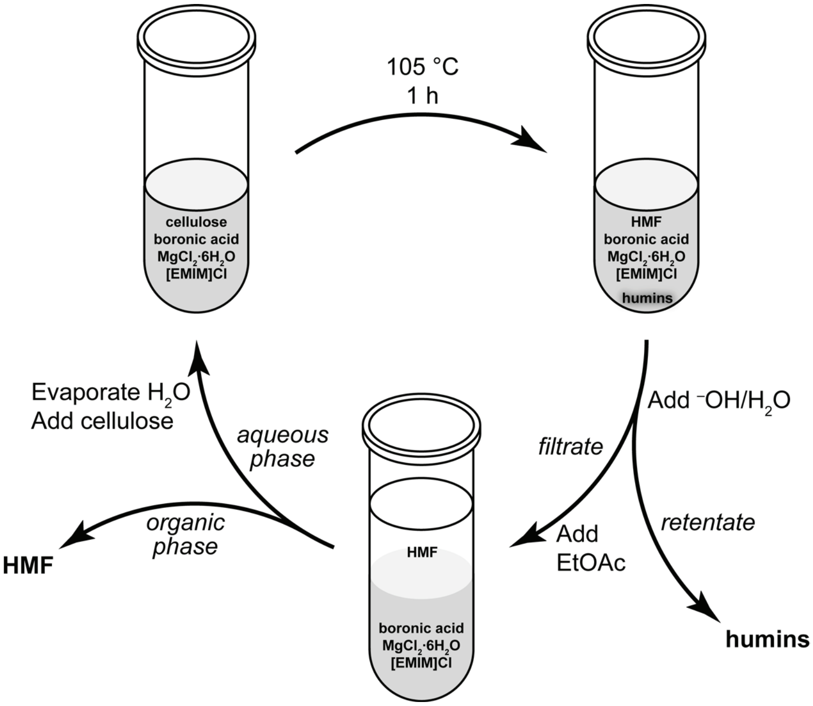

Fig. S3 Scheme for the recovery and recycling of catalysts for the conversion of cellulose to HMF.

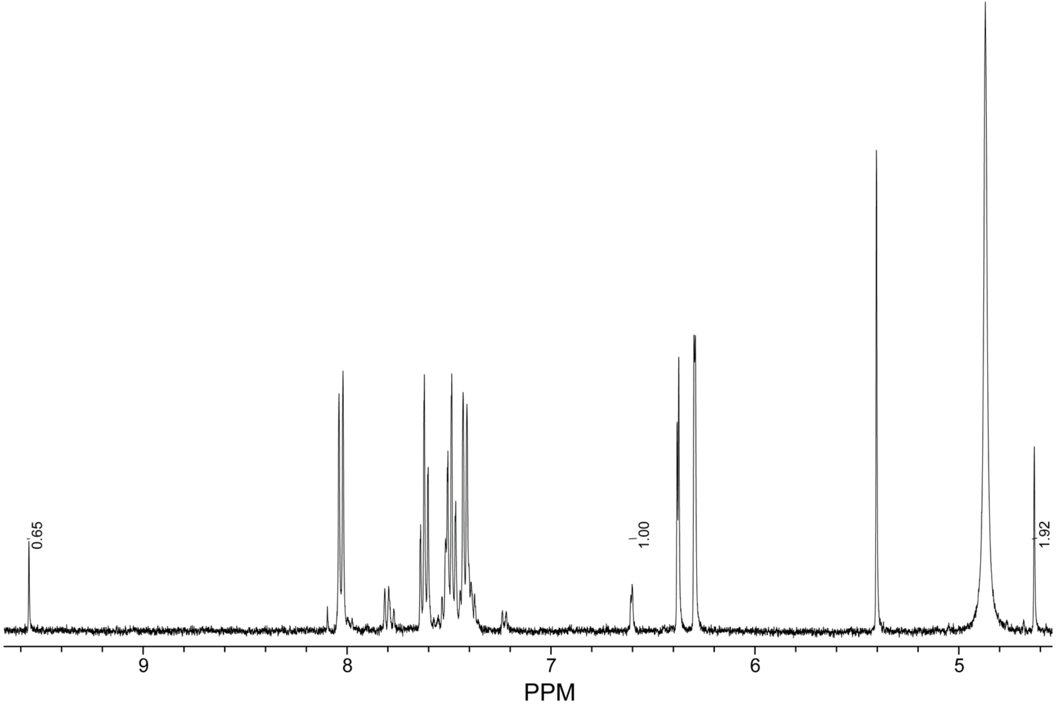

Fig. S4 ^{1}H NMR spectrum showing peak integrations of HMF after its conversion from glucose in DMA containing D_2O. The aldehyde peak at 9.56 ppm integrates to only $^2/_3$ that expected from the two diagnostic peaks. The incorporation of solvent deuterium is consistent with the isomerization of glucose to fructose occurring via an enolization mechanism.