Synthesis of Furfural from Xylose and Xylan

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Rising fossil energy prices and environmental preservation call for alternative sources of energy, such as renewable fuels based on biomass.[1] Biofuels could reduce carbon dioxide emissions and decrease fuel prices, particularly if derived from nonfood biomass resources such as agricultural, forest, and landfill wastes. Hemicellulose, a mixture of polysaccharides containing xylose, arabinose, glucose, galactose, mannose, and other sugars, is typically the second-most-abundant component of biomass, after cellulose.[2] In grasses and hardwoods, xylan, a polymer of xylose, is often the primary hemicellulose. As a result, xylan conversion is critical for utilization of important biomass feedstocks such as bagasse, corn stover, *Miscanthus*, switchgrass, and poplar.

Both xylan and xylose can be dehydrated into furfural, a biofuel precursor and industrial chemical (Figure 1).[3] Indeed, furfural is perhaps the most common industrial chemical derived from lignocellulosic biomass, with an annual production volume of more than 200 000 t.[4] The commercial utility of furfural was first discovered at the Quaker Oats Company in 1921.[5] The company had produced vast quantities of oat hulls

from the manufacture of oatmeal (at one point, Quaker Oats had amassed so much of this byproduct that the leftover oat hulls were stored in a circus tent). Though they could be used as livestock feed, the hulls were only partially digestible. Quaker Oats tested a variety of processes to valorize the hulls and found that treating them with dilute sulfuric acid yielded useful amounts of furfural.

Since this initial discovery, many others have examined the conversion of pentoses into furfural.[6] The process used by Quaker Oats employs a dilute sulfuric acid catalyst and steam pressure, achieving 50% molar yields of furfural from xylan.[3a] Most industrial processes achieve similar yields, likely limited by side reactions such as homopolymerization and condensation with unreacted xylose. Moreau and co-workers have converted xylose into furfural in about 50% yield by using acidic dealuminated zeolites in water along with toluene as an extracting solvent.[6b] Sulfated zirconia has also been used as a catalyst for xylose dehydration, producing yields of around 50%.[6d] In all of these cases, Brønsted acid catalysts were used in aqueous solution at temperatures greater than 150°C. Although questions remain about the mechanism for furfural formation from xylose under these conditions, recent computational work by Nimlos and co-workers[7] supports a mechanism proposed by Antal and co-workers (Figure 1).[8] In this mechanism, the C-2 hydroxyl group is displaced to form a xylose-2,5-anhydride. Subsequent dehydration steps produce furfural. Other evidence supports alternative mechanisms involving acyclic intermediates, and different mechanisms might operate under different conditions of temperature and pH.[9]

Recently, we and others reported on the conversion of sugars[10] and biomass[11] into 5-hydroxymethylfurfural (HMF) in ionic liquids and *N,N*-dimethylacetamide containing lithium chloride (DMA-LiCl). In these initial studies, we found that the pentosans in biomass were converted into furfural in moderate yields by using a combination of chromium(II) or chromium(III) salts and HCl. Unlike Cr^VI, which is highly toxic, Cr^III is essential for the normal metablism of carbohydrates, lipids, and fats in humans, and is thus an essential dietary element.[12] Cr^II oxidizes in air to Cr^III. Our reaction conditions—Cr^II or Cr^III as a catalyst in a nonaqueous solvent—contrast markedly with the aqueous Brønsted acid catalysis typical for furfural production. We chose to investigate the reactions of xylose and xylan in DMA-LiCl and related solvents, and report our findings herein. Others have reported on the acid-catalyzed production of furfural from xylose in ionic liquids.[13]

We began by investigating the reactivity of xylose in DMA with acid and chromium catalysts and halide additives at 100°C (Table 1). Only low yields of furfural and moderate conversions of xylose were observed in DMA, both alone and with HCl. For example, 12 mol% HCl in DMA accomplished 47% conversion of xylose with only a 6% yield of furfural. Although
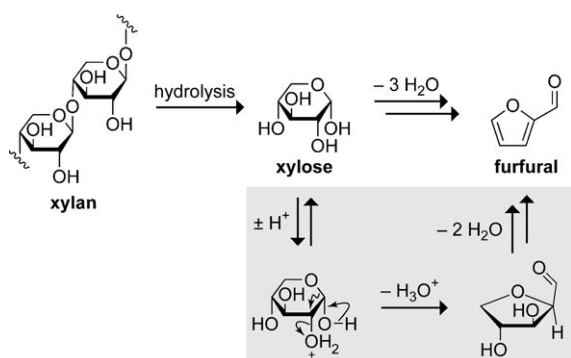

Figure 1. Route for the synthesis of furfural from xylan. Gray box: Putative mechanism for the acid-catalyzed dehydration of xylose, in which displacement of the protonated C-2 hydroxyl group leads to a 2,5-anhydride intermediate that dehydrates to furfural.[8, 7]

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Table 1. Synthesis of furfural from xylose at 100 °C.[a]

Solvent	Catalyst	Amount [mol %]	Additive	Amount [wt %]	Time [h]	Yield [%]
DMA	–	–	–	–	2	< 5
DMA	$CrCl_3$	6	–	–	2	37
DMA	$CrCl_3$	6	–	–	4	38
DMA	$CrCl_3$	6	–	–	6	37
DMA	HCl	3	–	–	2	3
DMA	HCl	6	–	–	2	1
DMA	HCl	12	–	–	2	6
DMA	HCl	24	–	–	2	8
DMA	HCl	3	[EMIM]Cl	5	2	1
DMA	HCl	6	[EMIM]Cl	5	2	2
DMA	HCl	12	[EMIM]Cl	5	2	3
DMA	$CrCl_3$	6	[EMIM]Cl	5	2	37
DMA	$CrCl_3$	6	[EMIM]Cl	5	4	37
DMA	$CrCl_3$	6	[EMIM]Cl	5	6	34
DMA	$CrCl_3$	6	[EMIM]Cl	10	2	37
DMA	$CrCl_3$	6	[EMIM]Cl	10	4	37
DMA	$CrCl_3$	6	[EMIM]Cl	10	6	38
DMA	$CrCl_3$	6	[EMIM]Cl	20	2	40
DMA	$CrCl_2$	6	[EMIM]Cl	5	2	45
DMA	$CrCl_2$	6	[EMIM]Cl	10	2	38
DMA	$CrCl_2$	6	[EMIM]Cl	20	2	41
DMA-LiCl (10 %)	$CrCl_3$	6	[EMIM]Cl	5	2	40
DMA-LiCl (10 %)	$CrCl_3$	6	[EMIM]Cl	10	2	30
DMA-LiCl (10 %)	$CrCl_3$	6	[EMIM]Cl	20	2	37
DMA-LiCl (10 %)	$CrCl_2$	6	[EMIM]Cl	5	2	24
DMA-LiCl (10 %)	$CrCl_2$	6	[EMIM]Cl	10	2	33
DMA-LiCl (10 %)	$CrCl_2$	6	[EMIM]Cl	20	2	36
DMA	$CrCl_3$	6	LiBr	10	4	47
DMA	$CrBr_3$	6	LiBr	10	4	50
DMA	$CrCl_2$	6	NaBr	10	4	54
DMA	$CrCl_2$	6	[BMIM]Br	20	4	55
DMA	$CrCl_2$	6	LiBr	10	4	56

[a] Xylose was reacted at a concentration of 10 wt % relative to the total mass of the reaction mixture. The solvent composition is indicated by the wt % of LiCl relative to DMA with additive concentrations relative to the total mass of the reaction mixture. Catalyst loading is relative to xylose. Yields are based on HPLC analysis.

Figure 2. Log–log plots of initial rates of furfural formation vs. the concentration of xylose and $CrCl_2$. a) Xylose; linear regression analysis gives slope = 1.0, which is consistent with a first-order dependence of the rate of furfural formation on [xylose]. b) $CrCl_2$; linear regression analysis gives slope = 0.4, which is consistent with a complex dependence of the rate of furfural formation on [$CrCl_2$].

Brønsted acids such as HCl are typically used to produce furfural, these reactions are commonly carried out at temperatures > 150 °C. Under our more mild reaction conditions, acids alone were less effective for rapid xylose conversion.

Conversely, xylose was converted into furfural in 30–40 % yield in DMA using $CrCl_2$ and $CrCl_3$ (Table 1). With these catalysts, we observed no consistent effect of 1-ethyl-3-methylimidazolium ([EMIM]) chloride or LiCl additives on the furfural yield. Bromide additives such as 1-butyl-3-methylimidazolium ([BMIM]) bromide and LiBr improved furfural yields up to 56 %. Yields in these reactions are probably reduced by the reaction of furfural with itself and with xylose to form oligomeric species.[3a] The contrast between furfural yields using acid and chromium catalysts suggests that an alternative mechanism of xylose dehydration might be occurring in the presence of chromium salts.

To illuminate further the mechanism of this reaction, we examined the initial rates of furfural appearance in DMA-LiCl containing $CrCl_2$ (Figure 2). These analyses revealed that the rate of furfural formation ha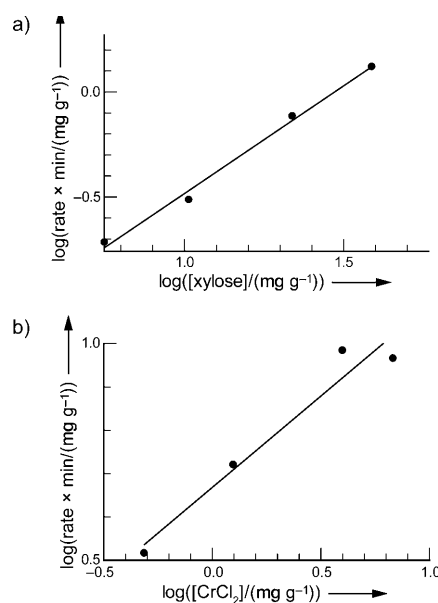s a first-order dependence on xylose concentration and a half-order dependence on Cr^{II} concentration. These results indicate that chromium is directly involved in the mechanism of conversion prior to the rate-determining step, perhaps in a complex manner.

Based on the kinetic analyses (Figure 2) and on the different efficacies of chromium and HCl as catalysts (Table 1), we propose a mechanism by which chromium could effect the transformation of xylose into furfural when the acid-catalyzed mechanism is sluggish. In this mechanism (Figure 3), which is analogous to that of the chromium-catalyzed conversion of glucose into HMF,[14] chromium catalyzes xylose isomerization through a 1,2-hydride shift. Acting as a Lewis acid, chromium then converts the resulting xylulose into an oxocarbenium ion. Deprotonation of this species produces an enol, which loses two molecules of water to form furfural. This mechanism is consistent with our observations of carbohydrate reactivity. Aldohexoses likely form HMF through this isomerization mechanism, implying that xylose might do so under similar conditions.[14] In addition, xylulose is far more predisposed to form furfural than is xylose at 100 °C,[9b] suggesting that transformation of xylose into xylulose would facilitate efficient furfural formation.

To test the validity of our hydride-shift mechanism, we performed two deuterium-labeling experiments.[14] In the first, unlabeled xylose was dehydrated in the presence of D_2O;[15] < 5 % deuterium incorporation was observed in the furfural product by ^{1}H NMR spectroscopy. This result is compatible with the proposed hydride-shift mechanism (as well as the 2,5-anhydride mechanism proposed for acid catalysis; Figure 1), but inconsistent with a mechanism that avails an enediol intermediate (Figure 3). In the second experiment, xylose-2-*d* was con-
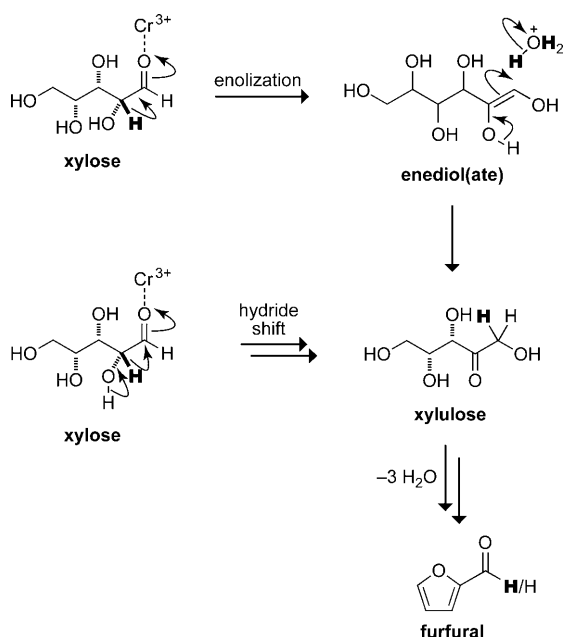
Figure 3. Putative mechanisms for the chromium(III)-catalyzed conversion of xylose into furfural. Hydrogens replaced with deuteriums in isotopic labeling studies are depicted in boldface type.

verted into furfural in the presence of H_2O;[16] 48% deuterium incorporation was observed at C-1 of furfural by ^1H NMR spectroscopy. This transfer of the deuterium label from C-2 to C-1 is consistent only with the hydride-shift mechanism (Figure 3).

The conversion of xylan into furfural was significantly more challenging than was the dehydration of xylose. Birch xylan, the typical material used in these studies, was not readily soluble in DMA. Instead, it was solubilized by heating and stirring in DMA with LiCl or LiBr at 80–120 °C for several hours. Xylan dissolved in DMA-LiCl precipitated by addition of water, indicating that it was not fully depolymerized into xylose under these conditions. Initially, we attempted the conversion of xylan at 100 °C using conditions similar to those used successfully with xylose (Table 2). With xylan, however, only trace yields of furfural were obtained. Slightly higher yields were possible from reactions performed at 120 °C (Table 3), suggesting that these conditions were too mild to accomplish the depolymerization of xylan into xylose. By increasing the reaction temperature to 140 °C, 7–8% yields of furfural were obtained when using $CrCl_2$, although $CrCl_3$ was less effective (Table 4). In similar studies that emphasize the role of temperature in the conversion of xylan to furfural, Zhao and co-workers obtained a furfural yield of up to 63% in ionic liquids heated to ~200 °C by microwave irradiation.[17] Adding HCl to the reaction mix-

Table 2. Synthesis of furfural from xylan at 100 °C.[a]

Solvent	Catalyst	Amount [mol%]	Additive	Amount [wt%]	Yield [%]
DMA-LiCl (10%)	HCl	3	–	–	0
DMA-LiCl (10%)	HCl	6	–	–	1
DMA-LiCl (10%)	HCl	12	–	–	0
DMA-LiCl (10%)	$CrCl_2$	6	[EMIM]Cl	5	0
DMA-LiCl (10%)	$CrCl_2$	6	[EMIM]Cl	10	0
DMA-LiCl (10%)	$CrCl_2$	6	[EMIM]Cl	20	0
DMA-LiCl (10%)	$CrCl_3$	6	[EMIM]Cl	5	0
DMA-LiCl (10%)	$CrCl_3$	6	[EMIM]Cl	10	1
DMA-LiCl (10%)	$CrCl_3$	6	[EMIM]Cl	20	0
DMA-LiCl (10%)	HCl	3	[EMIM]Cl	10	0
DMA-LiCl (10%)	HCl	6	[EMIM]Cl	10	0
DMA-LiCl (10%)	HCl	12	[EMIM]Cl	10	1

[a] Birch xylan was reacted for 4 h at a concentration of 5 wt% relative to the total mass of the reaction mixture. The solvent composition is indicated by the wt% of LiCl relative to DMA with additive concentrations relative to the mass of the reaction mixture. Catalyst loading and yield are relative to moles of xylose monomers contained in xylan. Yields are based on HPLC analysis.

Table 3. Synthesis of furfural from xylan at 120 °C.[a]

Solvent	Catalyst	Amount [mol%]	Additive	Amount [wt%]	Yield [%]
DMA-LiCl (10%)	$CrCl_2$	6	–	–	0
DMA-LiCl (10%)	$CrCl_3$	6	–	–	4
DMA-LiCl (10%)	HCl	6	–	–	3
DMA-LiCl (10%)	$CrCl_2$	6	[EMIM]Cl	10	0
DMA-LiCl (10%)	$CrCl_2$	6	[EMIM]Cl	20	3
DMA-LiCl (10%)	$CrCl_3$	6	[EMIM]Cl	10	3
DMA-LiCl (10%)	$CrCl_3$	6	[EMIM]Cl	20	0

[a] Birch xylan was reacted for 4 h at a concentration of 5 wt% relative to the total mass of the reaction mixture. The solvent composition is indicated by the wt% of LiCl relative to DMA with additive concentrations relative to the mass of the reaction mixture. Catalyst loading and yield are relative to moles of xylose monomers contained in xylan. Yields are based on HPLC analysis.

Table 4. Synthesis of furfural from xylan at 140 °C.[a]

Biomass	Solvent	Catalyst	Amount [mol%]	Additive	Amount [wt%]	Yield [%]
xylan	DMA-LiCl (10%)	$CrCl_2$	6	[EMIM]Cl	5	8
xylan	DMA-LiCl (10%)	$CrCl_2$	6	[EMIM]Cl	10	7
xylan	DMA-LiCl (10%)	$CrCl_3$	6	[EMIM]Cl	20	1
xylan	DMA-LiCl (10%)	HCl	6	–	–	1
xylan	[EMIM]Cl	HCl	6	–	–	2
xylan	[EMIM]Cl	$CrCl_2$, HCl	10, 10	–	–	18
xylan (oat)	[EMIM]Cl	$CrCl_2$, HCl	10, 10	–	–	25
xylan (beech)	[EMIM]Cl	$CrCl_2$, HCl	10, 10	–	–	11
corn stover	[EMIM]Cl	$CrCl_2$, HCl	10, 10	–	–	22

[a] Xylan was reacted for 2 h at a concentration of 5 wt% relative to the total mass of the reaction mixture. Birch xylan was used except where noted. The solvent composition is indicated by the wt% of LiCl relative to DMA with additive concentrations relative to the mass of the reaction mixture. Catalyst loading and yield are relative to moles of xylose monomers contained in xylan. Yield from corn stover is based on a xylan content of 22.8%. Yields are based on HPLC analysis.

ture as a co-catalyst for xylan saccharification and using [EMIM]Cl as the solvent improved the yield of furfural to 18%. Disparate yields under these conditions were obtained with each xylan source, suggesting that xylan recalcitrance depends on its origin. These results imply that depolymerization is a major barrier for chromium-catalyzed furfural production from xylan.

We attempted to address this problem by using acid for xylan saccharification prior to furfural synthesis. To do so, we treated xylan with HCl at 140 °C prior to addition of the chromium catalyst and reaction at 120 °C (Table 5). This process en-

by using high temperatures and strong acid catalysts, we have found that chromium halide catalysts enable furfural synthesis from xylose in *N,N*-dimethylacetamide and ionic liquids at moderate temperatures. Mechanistic investigations suggest that these catalysts isomerize xylose into xylulose, a reactive ketose intermediate that dehydrates readily into furfural. We have also demonstrated the transformation of xylan into furfural under similar conditions. Our chromium-based process offers an advantageous route from pentoses and pentosans to renewable furfural-derived fuels and chemicals.

Table 5. Synthesis of furfural from xylan at 120 °C after treatment with HCl at 140 °C.[a]					
Solvent	Catalyst	Amount [mol%]	Additive	Amount [wt%]	Yield [%]
DMA	HCl	25	–	–	7
DMA	CrCl$_3$	6	–	–	0
DMA	CrCl$_3$, HCl	6, 25	–	–	11
DMA	HCl	25	[EMIM]Cl	5	10
DMA	CrCl$_3$	6	[EMIM]Cl	10	3
DMA	CrCl$_3$, HCl	6, 25	[EMIM]Cl	20	15
DMA-LiCl (10%)	CrCl$_2$, HCl	6, 25	–	–	7
DMA-LiCl (10%)	CrCl$_3$, HCl	6, 25	–	–	4
DMA-LiCl (10%)	CrCl$_2$, HCl	6, 25	–	–	6
DMA-LiCl (10%)	CrCl$_3$, HCl	6, 25	–	–	6
DMA-LiCl (5%)	CrCl$_2$, HCl	6, 25	–	–	6
DMA-LiCl (5%)	CrCl$_3$, HCl	6, 25	–	–	6
DMA-LiCl (5%)	CrCl$_2$, HCl	6, 25	[EMIM]Cl	5	8
DMA-LiCl (5%)	CrCl$_2$, HCl	6, 25	[EMIM]Cl	10	4
DMA-LiCl (5%)	CrCl$_3$, HCl	6, 25	[EMIM]Cl	5	0
DMA-LiCl (5%)	CrCl$_3$, HCl	6, 25	[EMIM]Cl	10	8
DMA	CrCl$_2$, HCl	6, 25	[BMIM]Br	20	6
DMA	CrCl$_2$, HCl	6, 25	LiBr	10	11

[a] Birch xylan was reacted for 2 h at a concentration of 5 wt% relative to the total mass of the reaction mixture. The solvent composition is indicated by the wt% of LiCl relative to DMA with additive concentrations relative to the mass of the reaction mixture. Catalyst loading and yield are relative to moles of xylose monomers contained in xylan. Yields are based on HPLC analysis.

abled furfural yields similar to those obtained at 140 °C. Use of HCl during the solubilization step was essential for furfural production, though HCl alone did not result in yields as high as those obtained with both chromium and HCl. The effects of other additives such as LiCl, LiBr, and ionic liquids were modest. These data suggest that pretreatment of xylan to form xylose improves furfural yields. We anticipate that improved methods for xylan depolymerization under our reaction conditions would provide higher furfural yields at lower temperatures. Using HCl in water/ionic liquid mixtures, we have demonstrated that 77% of birch xylan can be hydrolyzed to xylose.[18] The major side products observed by HPLC analysis are furfural and species with retention times characteristic of carbohydrate oligomers. Both xylose and xylose oligomers are possible intermediates on the route from xylan to furfural. Combining this hydrolysis process with chromium catalysts could enable the efficient transformation of xylan into furfural.

In conclusion, renewable fuels and chemicals such as pentose-derived furfural can reduce the dependence of humanity on fossil resources. Although furfural is produced industrially

Experimental Section

General considerations: Commercial chemicals were of reagent grade or better, and were used without further purification. Reactions were performed in glass vessels heated in a temperature-controlled oil bath with magnetic stirring. [EMIM]Cl (99.5%) was from Solvent-Innovation (Cologne, Germany). Birchwood xylan (X0502, 98% xylose residues, ca. 95% dry solids) and beechwood xylan (X4252, 95% xylose residues, ca. 95% dry solids) were from Aldrich Chemical (Milwaukee, WI). Oat hull xylan (X0011, 70.2% xylose residues, ca. 95% dry solids) was from TCI (Tokyo, Japan). Milled and sieved corn stover (ca. 95% dry solids) was generously provided by B. E. Dale and co-workers (Michigan State University),[19] and was passed through a 40-mesh screen prior to use.

Analytical methods: All reaction products were analyzed by HPLC and quantified using calibration curves generated with commercially available standards. Following a typical reaction, the product mixture was diluted with a known mass of deionized water, centrifuged to sediment insoluble products, and analyzed. The concentrations of products were calculated from HPLC-peak integrations and used to calculate molar yields. HPLC was performed with an Agilent 1200 system equipped with refractive index and photodiode array detectors. Furfural was analyzed by ion-exclusion chromatography using a Bio-Rad Aminex HPX-87H column (300×7.8 mm; 5 mM H_2SO_4, 0.6 or 0.9 mL min^{-1}, 65 °C).

Representative procedure for synthesis of furfural from xylose: Xylose (25.5 mg, 170 µmol) was mixed with DMA (225 mg) and CrCl$_2$ (2.5 mg, 20 µmol), and the reaction mixture was stirred at 100 °C for 4 h. For reactions of xylose using [EMIM]Cl, chromium salts were mixed with a portion of the ionic liquid (25 mg) before addition to the reaction mixture.

Representative procedures for synthesis of furfural from xylan: Xylan (10.2 mg, 72 µmol) and concd HCl (1.6 µL, 19 µmol) were stirred in DMA (240 mg) at 140 °C for 2 h. Following addition of CrCl$_3$ (1 mg, 6 µmol), the reaction mixture was stirred at 120 °C for 2 h.

In another procedure, xylan (6.0 mg, 43.5 µmol) and [EMIM]Cl (266.9 mg) were stirred at 85 °C for 24 h. Following addition of HCl (0.33 µL, 4 µmol) and CrCl$_2$ (0.8 mg, 6.5 µmol), the reaction mixture was stirred at 140 °C for 2 h.

Kinetic analysis of furfural formation from xylose: Xylose (250.7 mg, 1.67 mmol) and LiCl (227.8 mg) were added to DMA (2.0427 g) and dissolved at 100 °C for 5 min. Five known weights of this stock solution (~0.4 g) were combined with CrCl$_2$ (five different weights from 0–15 mg g^{-1}). The solutions were heated at 100 °C for 10 min and cooled rapidly on ice prior to HPLC analysis.

Acknowledgements

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[15] Reaction conditions: DMA (825 mg), CrCl$_2$ (6 mol%), D$_2$O (100 mg), xylose (100 mg), LiCl (100 mg), 100 °C, 4 h.

[16] Reaction conditions: DMA (825 mg), CrCl$_2$ (6 mol%), H$_2$O (100 mg), xylose-2-*d* (100 mg; Omicron Biochemicals), LiCl (100 mg), 100 °C, 4 h.

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