### Supporting Information

# Preparation of Sustainable Polar Aprotic Solvents from Biomass: One-Pot Two-Step Catalytic Reaction of Cellulose with N,N-Dimethylurea over Ru/C

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# I. Product Characterization for Compounds TMI and TMHI



**1,3,4-trimethylimidazolidin-2-one** (**TMI**); colorless liquid, <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.40 (d, 2H, J=8 Hz), 2.76 (m, 1H), 2.74 (s, 3H), 2.71 (s, 3H), 1.20 (d, 3H, J= 8 Hz); <sup>13</sup>C-NMR (100 MHz, CDCl3)  $\delta$  161.3, 52.6, 50.9, 30.9, 28.5, 17.8; MS (EI) m/z (rel. intensity): 128 (M<sup>+</sup>, 39), 113 (100), 98 (5), 85 (20), 72 (22), 58 (29), 42 (40)



**1,3,4-trimethyl-2,3-dihydroimidazol-2-one (TMHI);** Pale yellow solid, <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.9(q, 1H, J=1.3 Hz), 3.18 (s, 3H), 3.16 (s, 3H), 2.00 (d, 3H, J=1.3 Hz); <sup>13</sup>C-NMR (100 MHz, CDCl3)  $\delta$  153.6, 118.4, 106.9, 29.9, 27.1, 10.1; MS (EI) m/z (rel. intensity): 126 (M<sup>+</sup>, 100), 125 (26), 111 (16), 97 (18), 70 (6), 56 (92), 42 (40)

#### II. Instrumentation and Analysis

#### **HPLC** analysis

The selectivity and the yield of the target molecules in DMI, ethanol, Methanol, and water and the remaining amount of DMU were analyzed with Agilent 1260 Infinity Quaternary High-Performance Liquid Chromatography (HPLC) system, using Zorbax Eclipse XDB-C18 Column (250 x74.6mm) set at 25 °C. The chromatography apparatus is equipped with G1315D Diode Array Detector (DAD). All analysis was done at the wavenumber of 210 nm. A mixture of H<sub>2</sub>O (A) and acetonitrile (B) were used as the mobile phase at a flow rate of 0.5 mL/min. Nonlinear gradient was used (95% A and 5% B from beginning to 80% A and 20 % B at 30.0 minute and then back to the starting point over 10 minutes). A fixed amount (500µL) of internal standard benzyl alcohol (5.0 mM) was added into each sample for the quantification purposes. Standard curves for all the target products were made by comparison of the products to internal standard. All results were analyzed and quantified according to standard curves. Before analyzing by HPLC, the liquid samples were filtered through a 0.22µm cutoff syringe filter (25mm diameter).

All sugar and cellulose samples as well as the polyol products from their C-C bond cleavage were analyzed with Agilent 1260 Infinity Quaternary High-Performance Liquid Chromatography (HPLC) system, using Aminex HPX-87H column (300 x 7.8 mm) set at 70 °C. The chromatography apparatus is equipped with G1362A Refractive Index Detector (RID) calibrated with external standards. A 0.005 M sulfuric acid solution was employed as the mobile phase with flow of 0.6 mL/min. A fixed amount (500µL) of internal standard cis-1,5-cyclooctane diol (10 mM) was added into

each sample for quantification purposes. Before analyzing by HPLC, the aqueous solutions were filtered through a 0.22µm cutoff syringe filter (25 mm diameter).

Cellulose conversion =  $((m_i - m_d - m_{Ru/C}) / m_i)$ 

 $m_i$  = Initial mass of cellulose before the reaction

 $m_d$  = mass of dried solid residue (remaining cellulose + catalyst) at 60 °C overnight after the reaction

 $m_{Ru/C}$  = Initial mass of Ru/C before the reaction

Polyol selectivity % = (# mmoles of carbons in each compound / # mmoles of carbons converted in cellulose) \* 100

PAS selectivity % = (# mmoles of carbons in each compound / # mmoles of DMU converted) \* 100

# <sup>1</sup>H NMR Analysis

<sup>1</sup>H NMR analysis was performed on either a Varian Mercury-300 instrument equipped with a 5mm 4-nucleus/BB probe or a Bruker DRX-500 instrument equipped with a 5mm TXI Z-gradient cryoprobe.

<sup>1</sup>H NMR yields were determined by integration of the produce versus a known quantity of internal standard (naphthalene). The amount of product was calculated by the following equation:

 $mol_{prod} = mol_{std} * (Integral_{prod} / Integral_{std}) * (N_{std} / N_{prod})$ 

Where *N* is the number of nuclei for the corresponding signal. The yield is then determined by the following formula:

$$Yield_{prod} \% = (mol_{prod} / mol_{l.r.}) * 100$$

Where mol<sub>*l.r.*</sub> is the moles of limiting reactant in the reaction. The selectivity is then defined as:

Selectivity % =  $(mol_{prod} / (mol_{i (reactant)} - mol_{f(reactant)})) * 100$ 

Table S1. The effect of catalyst loading on cellulose conversion and PAS selectivit	y.a
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	% Cellulose conversion (% PAS				
Catalyst (g)	selectivity)				
	H2O	MeOH	DMI		
0.4	46 (7)	37 (15)	23 (35)		
0.2	32 (5)	21 (12)	13 (31)		
0.1	19 (1)	14 (5)	8 (11)		

<sup>a</sup>Sigmacell cellulose (2.0 g), DMU (0.2 g, 2.23 mmol), Ru/C (0.4, 0.2, 0.1 g), and solvent (20 ml) were heated in a 75 ml stainless steel autoclave at 200 °C in two steps: first, under N<sub>2</sub> inert atmosphere (35 bar) for 6 hours, then H<sub>2</sub> (30 bar) for 6 hours. Ru/C has 5 wt% Ru content.

Α	mmoles (% DMU conversion or % PAS Selectivity)							
							Total	
entry	Solvent	DMU⁵	DMHI	DMI	ТМНІ	TMI	(PAS)	
1	H <sub>2</sub> O	1.2 (51)	0.09 (8)	0.18 (16)	0.05 (4)	0.16 (14)	0.48 (41)	
2	MeOH	1.1 (49)	0.11 (10)	0.23 (20)	0.09 (8)	0.32 (29)	0.75 (67)	
3	EtOH	1.3 (58)	0.16 (12)	0.27 (21)	0.11 (9)	0.30 (22)	0.84 (64)	
4	DMI	1.4 (60)	0.07 (5)	0.45 (33)	0.09 (7)	0.54 (40)	1.16 (85)	
5	DMI/ H <sub>2</sub> O	1.5 (63)	0.05 (3)	0.18 (13)	0.14 (10)	0.32 (22)	0.68 (48)	
В			mmoles of	of carbons i	n PAS fron	n cellulose		
entry	Solvent		DMHI	DMI	ТМНІ	TMI	total	
1	H <sub>2</sub> O		0.18	0.36	0.14	0.48	1.16 (5)	
2	MeOH		0.23	0.45	0.27	0.95	1.91 (12)	
3	EtOH		0.32	0.54	0.34	0.89	2.09 (15)	
4	DMI		0.14	0.91	0.27	1.63	2.95 (31)	
5	DMI/ H <sub>2</sub> O		0.09	0.36	0.41	0.95	1.82 (11)	
С	mmo	les of carb	ons (% Cell	ulose Conv	ersion or %	6 PAS Selec	ctvity)	
entry	Solvent		Cellulose <sup>c</sup>	Sorbitol	Glycerol	PG	EG	
1	H <sub>2</sub> O		23.7 (32)	7.3 (31)	3.3 (14)	3.6 (15)	5.2 (22)	
2	MeOH		15.6 (21)	3.9 (25)	1.4 (9)	3.7 (24)	2.3 (15)	
3	EtOH		14.1 (19)	5.5 (23)	0.7 (5)	2.7 (19)	1.8 (13)	
4	DMI		9.6 (13)	2.5 (26)	0.96 (10)	1.1 (11)	1.3 (13)	
5	DMI/ H <sub>2</sub> O		16.3 (22)	5.2 (32)	2.1 (13)	2.0 (12)	2.4 (15)	
aSigmo	$\frac{1}{2}$							

Table S2. Mass balance, cellulose and DMU conversion, and PAS product selectivity for the reactions of cellulose with  $DMU.^a$ 

<sup>a</sup>Sigmacell cellulose (2.0 g), DMU (0.2 g, 2.23 mmol), Ru/C (0.2 g), and solvent (20 ml) were heated in a 75 ml stainless steel autoclave at 200 °C in two steps: first, under N<sub>2</sub> inert atmosphere (35 bar) for 6 hours, then H<sub>2</sub> (30 bar) for 6 hours. **A**) DMU conversion and PAS selectivities are calculated. Selectivity is measured by HPLC/UV with benzyl alcohol solution (5.0 mM) as an internal standard. **B**) mmoles of carbons recovered in PAS from cellulose. **C**) Cellulose conversion and carbon recovered (mmoles) in polyols. Polyol selectivity were measured by HPLC/RID calibrated with cis-1,5-cyclooctane diol (10 mM) as an internal standard. <sup>b, c</sup>DMU and cellulose converted. Selectivity is reported in parentheses.

Α	mmoles (% DMU conversion or % PAS selectivity)						
entry	Sugar	Solvent	DMU <sup>b</sup>	DMHI	DMI	TMHI	TMI
1	Fructos	Water	1.8 (74)	0.045 (3)	0.16 (10)	0.14 (8)	0.43 (26)
2	Glucose	water	1.7 (75)	0.068 (4)	0.48 (28)	0.09 (5)	0.18 (11)
3	Fructos	MeOH	1.6 (72)	0.14 (8)	0.27 (17)	0.11 (7)	0.52 (32)
4	Glucose	MeOH	1.7 (76)	0.09 (5)	0.64 (37)	0.05 (3)	0.34 (20)
5	Fructos	EtOH	1.75 (77)	0.07 (4)	0.43 (25)	0.20 (12)	0.57 (33)
6	Glucose	EtOH	1.7 (75)	0.20 (12)	0.70 (41)	0.16 (9)	0.25 (15)
7	Fructos	DMI	1.97 (87)	0.11 (6)	0.36 (18)	0.05 (2)	1.2 (61)
8	Glucose	DMI	1.84 (81)	0.27 (15)	0.66 (36)	0.09 (5)	0.48 (26)
9	Fructos	DMI/ H <sub>2</sub> O	1.8 (79)	0.09 (5)	0.18 (10)	0.20 (11)	0.41 (23)
10	Glucose	DMI/ H <sub>2</sub> O	1.93 (85)	0.20 (11)	0.48 (25)	0.05 (2)	0.25 (13)
В		m	moles of carl	oons in PA	AS from glu	ican	
				DMHI	DMI	ТМНІ	TMI
1	Fructos	Water		0.09	0.32	0.41	1.3
2	Glucose	water		0.14	0.95	0.27	0.54
3	Fructos	MeOH		0.27	0.54	0.34	1.57
4	Glucose	MeOH		0.18	1.27	0.14	1.02
5	Fructos	EtOH		0.14	0.86	0.61	1.70
6	Glucose	EtOH		0.41	1.41	0.48	0.75
7	Fructos	DMI		0.23	0.73	0.14	3.61
8	Glucose	DMI		0.54	1.32	0.27	1.43
9	Fructos	DMI/ H <sub>2</sub> O		0.18	0.36	0.61	1.23
10	Glucose	DMI/ H <sub>2</sub> O		0.41	0.95	0.14	0.75
С	mmoles of carbons (% sugar conversion or % polyol selectivity)					y)	
entry		Solvent	Glucan <sup>c</sup>	Sorbitol	Glycerol	PG	EG
1	Fructos	Water	33.3 (100)	10.7 (32)	1.3 (4)	7.3 (22)	5.3 (16)
2	Glucose	water	33.3 (100)	10.3 (31)	2.0 (6)	4.3 (13)	10.0 (30)
3	Fructos	MeOH	33.3 (100)	9.3 (28)	1.0 (3)	7.7 (23)	5.3 (16)
4	Glucose	MeOH	33.3 (100)	8.0 (24)	2.3 (7)	5.7 (17)	9.7 (29)
5	Fructos	EtOH	33.3 (100)	6.3 (19)	5.0 (14)	8.3 (25)	6.0 (18)
6	Glucose	EtOH	33.3 (100)	7.0 (21)	3.0 (9)	4.0 (12)	11.3 (34)
7	Fructos	DMI	33.3 (100)	8.3 (25)	1.7 (5)	10.7 (32)	3.7 (11)
8	Glucose	DMI	33.3 (100)	8.0 (24)	2.7 (8)	5.3 (16)	9.0 (27)
9	Fructos	DMI/ H <sub>2</sub> O	33.3 (100)	9.0 (27)	1.7 (5)	7.7 (23)	5.7 (17)
10	Glucose	DMI/ H <sub>2</sub> O	33.3 (100)	8.3 (25)	3.0 (9)	6.0 (18)	8.7 (26)

Table S3. Mass balance, sugar and DMU conversion, and PAS product selectivity for the reactions of sugars with DMU.<sup>a</sup>

<sup>a</sup>Sugars (1.0 g), DMU (0.2 g, 2.23 mmol), 0.1 g Ru/C (5wt%), and 20 ml solvent were heated in a 75 ml stainless steel autoclave at 200 °C in two steps: first, under N<sub>2</sub> inert atmosphere (35 bar) for 6 hours, then H<sub>2</sub> (30 bar) for 6 hours. **A**) DMU conversion and PAS selectivities are calculated. Selectivities are reported in parentheses and analyzed by HPLC/UV with benzyl alcohol solution (5.0 mM) as an internal standard. **B**) mmoles of carbons recovered in PAS from sugars. **C**) Sugar conversions and mmoles of carbons recovered in polyols. Polyol selectivities were analyzed by HPLC/RID calibrated with cis-1,5-cyclooctane diol (10 mM) as an internal standard. <sup>b, c</sup>Converted DMU and glucan.

	Time	Temp	TMHI %
1	24	80	0
2	12	120	10
3	12	150	32
4	12	180	79
5	12	200	81

Table S4. Results of coupling reactions of 1,2-PG and DMU at various temperature.<sup>a</sup>

<sup>a</sup>1,2-PG (0.15 g, 14 mmol), DMU (0.088 g, 7 mmol), 0.2 g Ru/C (5 wt%), and 20 ml 2-MeTHF were heated in a 75 ml stainless steel autoclave under inert atmosphere (N<sub>2</sub>, 35 bar) at 200 °C. Yields were analyzed by <sup>1</sup>H-NMR with naphthalene as an internal standard.



Table S5. Results of *in situ* formation of homohgeneous Ru catalysts with varying phosphine ligands.<sup>a</sup>

Entry	Ligand	♭TMHI %	°Diol %	°DMU %
1	$P\left(\left\langle \right\rangle \right)_3$	38	19	44
2	P	44	30	60
3		61	56	82
5	P	23	23	56

<sup>a</sup>RuCl<sub>3</sub>·3H<sub>2</sub>O (0.02 mmol), phosphine ligands (0.04 mmol), 1,2-PG (0.15 g, 2 mmol), DMU (0.088 g, 1 mmol), and 2-MeTHF (1.5 ml) were heated in a 10 ml microwave vial under  $N_2$ inert atmosphere at 200°C for 2 hours. bYields and cselectivity was analyzed by 1H-NMR with naphthalene as an internal standard.

III. Figure S1. <sup>1</sup>H NMR of the oxidation reaction of 1,2-propylene glycol into hydroxyacetone

