

# Supporting Information

## **Lewis acid catalyzed conversion of 5-hydroxymethylfurfural to 1,2,4-benzenetriol, a potential renewable aromatic platform chemical**

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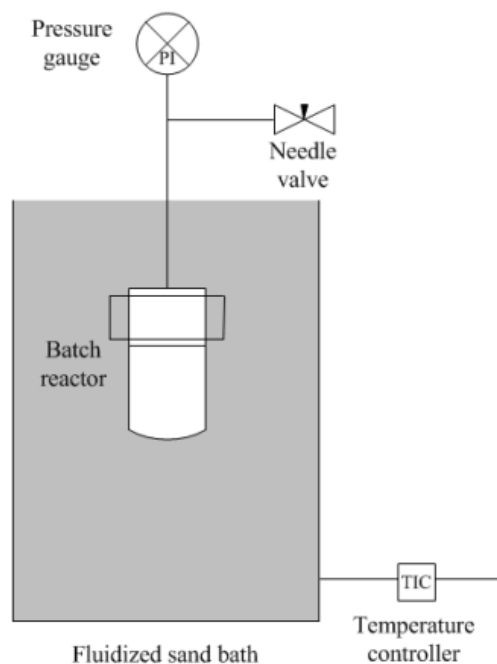
## S1. Materials and Methods

All materials were used without further purification. HMF with a  $\geq 99\%$  purity was purchased from Sigma-Aldrich. Milli-Q water was used for all experiments and analysis. The chemicals which were used as the analysis standards are: 1,2,4-benzenetriol with 99% purity (Sigma-Aldrich), formic acid with  $\geq 95\%$  purity (Sigma-Aldrich), acetic acid with 100% purity (Merck), levulinic acid with 98% purity (Sigma-Aldrich), glycerol with  $\geq 99.5\%$  purity (Sigma-Aldrich), acetone with 99.8% purity (Boom), 1,4-benzenediol with  $\geq 99\%$  purity (Fluka), 5-methyl furfural 99% purity (Sigma-Aldrich), furan with  $\geq 99\%$  purity (Sigma-Aldrich), furfural with 77% purity (Sigma-Aldrich), 2-butanone with  $\geq 99\%$  purity (Sigma-Aldrich), 2-cyclopenten-1-one with 98% purity (Sigma-Aldrich). Dimethyl sulfoxide which was used as the internal standard has a purity  $\geq 99.9\%$  (J.T.Baker). All the catalysts which were used in this experiment are commercial catalysts, both the metal catalysts and the salt catalysts. The metal catalysts are Ru/TiO<sub>2</sub> (2 wt%) homemade, Ru/C (5 wt%) from Kaida, Ru/C (5 wt%) from Sigma-Aldrich, Pt/C (5 wt%) from Sigma-Aldrich, Cu/Zn alloy (np < 150 nm) from Sigma-Aldrich, and Ni/SiO<sub>2</sub>.Al<sub>2</sub>O<sub>3</sub> (65 wt%) from Sigma-Aldrich. The salt catalysts which were used are europium (II) chloride with 99% purity (Sigma-Aldrich), iron (II) chloride with 98% purity (Sigma-Aldrich), anhydrous magnesium (II) chloride with  $\geq 98\%$  purity (Sigma-Aldrich), zinc (II) chloride with  $\geq 98\%$  purity (Sigma-Aldrich), trifluoromethanesulfonic acid with  $\geq 99\%$  purity (Sigma-Aldrich), iron (II) trifluoromethanesulfonate with 98% purity (Strem), zinc (II) trifluoromethanesulfonate with 98% purity (Sigma-Aldrich), iron (III) trifluoromethanesulfonate with 90% purity (Sigma-Aldrich), lanthanum (III) trifluoromethanesulfonate hydrate (Sigma-Aldrich), scandium (III) trifluoromethanesulfonate with  $>98\%$  purity (TCI), ytterbium (III) trifluoromethanesulfonate (Sigma-Aldrich), cerium (IV) trifluoromethanesulfonate hydrate (Sigma-Aldrich), hafnium (IV) trifluoromethanesulfonate with 98% purity (Alfa Aesar).

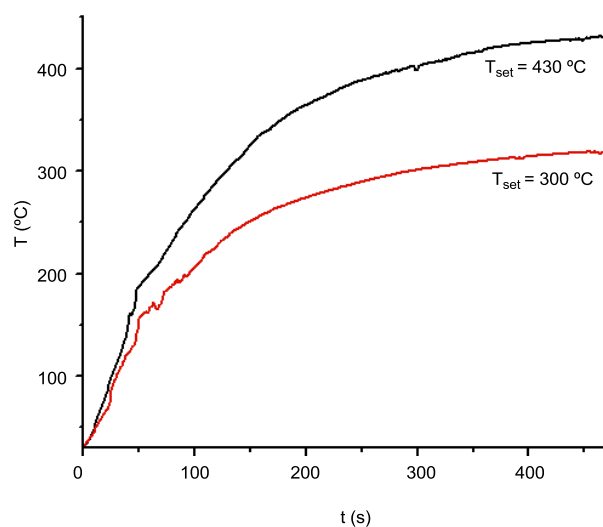
## S2. Experimental Procedure HMF to BTO

A batch reactor (**Figure S1**) made in-house from SS 316 material and with a volume capacity of 14.2 mL was used for the conversion of HMF to BTO. The maximum pressure of the reactor is 300 bar. The feed volume, the setting temperature, and later the initial pressure of  $N_2$  which was filled in to the reactor will determine the final pressure. The reactor was loaded with 2.5–10 mL of an aqueous feed solution of 0.01–0.25 M HMF, with a catalyst intake of 0.14–10 mM. The reactor was closed and was flushed 3x times using 120 bar of  $N_2$ . After no leakage was detected, the reactor was pressurized with  $N_2$  from 40-120 bar depend on some circumstances (the reaction temperature: 300–450 °C and the feed volume 2.5–10 mL). Then the reactor was submerged in a temperature controlled fluidized sand bath. A thermocouple was placed next to the reactor to monitor the temperature. To provide an indication of the heating rates two runs (300 °C and 430 °C) with only water were performed with a thermocouple inside the solution (**Figure S2**). The temperature reaches 300 °C in about 6 minutes while 430 °C is reached at 7-8 minutes.

The moment the reactor was submerged was used as  $t_0$ . The reaction was performed for 3–120 minutes. The reactor was taken out from the hot fluidized sand bath. For cooling, the reactor was submerged in a cool fluidized sand bath at room temperature for about 20 minutes. The pressure was released by opening the valve carefully (to prevent the liquid loss) then the reactor was opened. For analysis, 0.1 g dimethyl sulfoxide (DMSO) was added as the internal standard to the reactor after reaction completion before any work-up. Then the solution was filtered (cellulose acetate membrane 0.2  $\mu\text{m}$  FP, Whatman,) to ensure the complete removal of solids before HPLC analysis. Part of the results are outlined in more detail in Table S2)



**Figure S1** Schematic drawing of the used batch reactor setup



**Figure S2.** Heating profiles for the liquid inside the batch reactor at different set temperatures for the fluidized sand bath.

### S3. Analysis Method for 1,2,4-benzenetriol (BTO)

The composition of the liquid phase was determined using Agilent 1200 HPLC. Agilent 1200 HPLC consists of a Hewlett Packard 1200 pump, a Bio-Rad organic acid column Aminex HPX-87H, an RID and a UV detector. The mobile phase consists of aqueous sulphuric acid (5 mM) which was set at a flow rate of 0.55 cm<sup>3</sup> per minute. The column was operated at 60 °C. The analysis for a sample was complete in 80 min. The concentrations of each compound in the product mixture were determined using calibration curves obtained by analyzing standard solutions and internal standard of known concentrations.

The conversion of the HMF and the yield of BTO (and others products) were calculated using equation S1–S3.

$$\text{Conversion of HMF} = \frac{\text{mmol HMF}_o - \text{mmol HMF}}{\text{mmol HMF}_o} \times 100\% \quad \dots\dots\dots(S1)$$

$$\text{Yield of products} = \frac{\text{mmol products}}{\text{mmol HMF}_o} \times 100\% \quad \dots\dots\dots(S2)$$

$$\text{Yield correction for BTO} = \frac{\text{mmol BTO} + (2 \times \text{mmol BTO Dimer})}{\text{mmol HMF}_o} \times 100\% \quad \dots\dots\dots(S3)$$

The C balance numbers were calculated using equation S4-S6.

$$\text{Mmol Carbon in the feed} = (\text{mmol HMF}_o \times 6) \quad \dots\dots\dots(S4)$$

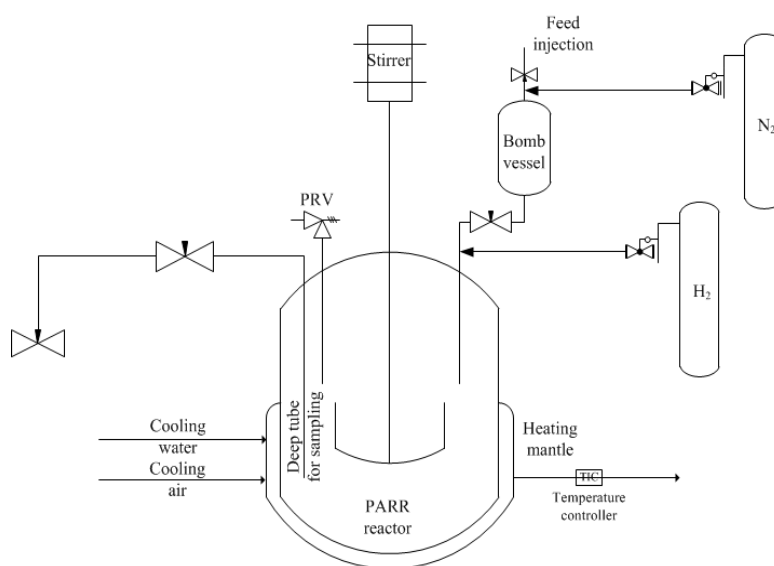
Where mmol HMF<sub>o</sub> is initial mmol of HMF

$$\text{Mmol Carbon in the products} = (\text{mmol HMF} \times 6) + (\text{mmol BTO} \times 6) + (\text{mmol Dimer} \times 12) + (\text{mmol FA} \times 1) + (\text{mmol Glycerol} \times 3) + (\text{mmol AA} \times 2) + (\text{mmol LA} \times 5) + (\text{mmol MEK} \times 4) + (\text{mmol 2CP} \times 5) + (\text{mmol 14 BDO} \times 6) + (\text{mmol Furan} \times 4) + (\text{mmol Furfural} \times 5) + (\text{mmol MF} \times 6) \quad \dots\dots\dots(S5)$$

$$\text{C balance} = \frac{\text{mmol C in the products}}{\text{mmol C in the feed}} \times 100\% \quad \dots\dots\dots(S6)$$

#### S4 Experimental procedure hydrodeoxygenation of BTO

A PARR reactor made from SS 316 material (batch autoclave) and with a volume capacity of 100 mL was used for this experiment (**Figure S3**). The maximum pressure of the reactor is 340 bar and the maximum temperature of the reactor is 350 °C. The autoclave was covered by a heating mantle (metal block) containing electrical heater (including the temperature controller) and the cooling system (air and water). A mechanical stirrer was used in the autoclave and was set to 600 rpm. A PRV (Pressure Release Valve) was installed for safety. This autoclave was attributed with a sampling tube. To control the sampling pressure and flow (also for safety issue), 2 needle valves were installed. A bomb vessel was installed for feed injection. A pipe containing N<sub>2</sub> gas was installed before the entrance of bomb vessel. Another gas line was installed for the pressurization with H<sub>2</sub> gas.



**Figure S3.** Schematic drawing of the reactor setup used for BTO hydrodeoxygenation reactions.

The reactor was loaded with 25 mL of mQ water containing 2.5 mmol BTO (degassed for 1 h to prevent dimer formation), 0.1 g Pd/Al<sub>2</sub>O<sub>3</sub> and 0.1g AlCl<sub>3</sub> or Al(OTf)<sub>3</sub>. The reactor was closed and was flushed 3x times using 90 bar of N<sub>2</sub>. After no leakage was detected, the reactor was filled in with 50 bar of H<sub>2</sub>. Then, the reactor was set to the desired temperature ( $t_0$ ).

The reaction was run for 0–5 hours and samples were taken through the sampling tube. For cooling, the temperature setting in the heater controller was turned down to 0. The pressure inside the reactor was released by opening the gas valve carefully (to prevent the liquid loss). Additionally, to compensate for solvent loss during the reaction workup, 500 µL of 0.1 g/10 mL dimethyl sulfoxide (DMSO) was used as the internal standard for analysis which was added after reaction completion before any work-up. Then, the solution was filtered (cellulose acetate membrane 0.2 µm FP, Whatman,) to ensure the complete removal of solids before HPLC analysis (see section S3).

## S5. Supplementary Data BTO Dimerization/Oligomerization

### 5,5'-BTO dimer isolation and characterization

When an aqueous solution of 1,2,4-benzenetriol (BTO), which has the appearance of a grey/beige powder (**Figure S4** left), was left in time exposed to air the solution slowly darkened (**Figure S4** middle), resulting in a very dark solution with a precipitate which can be isolated as a black powder after washing with water, to remove unreacted BTO, and drying (**Figure S4** right).



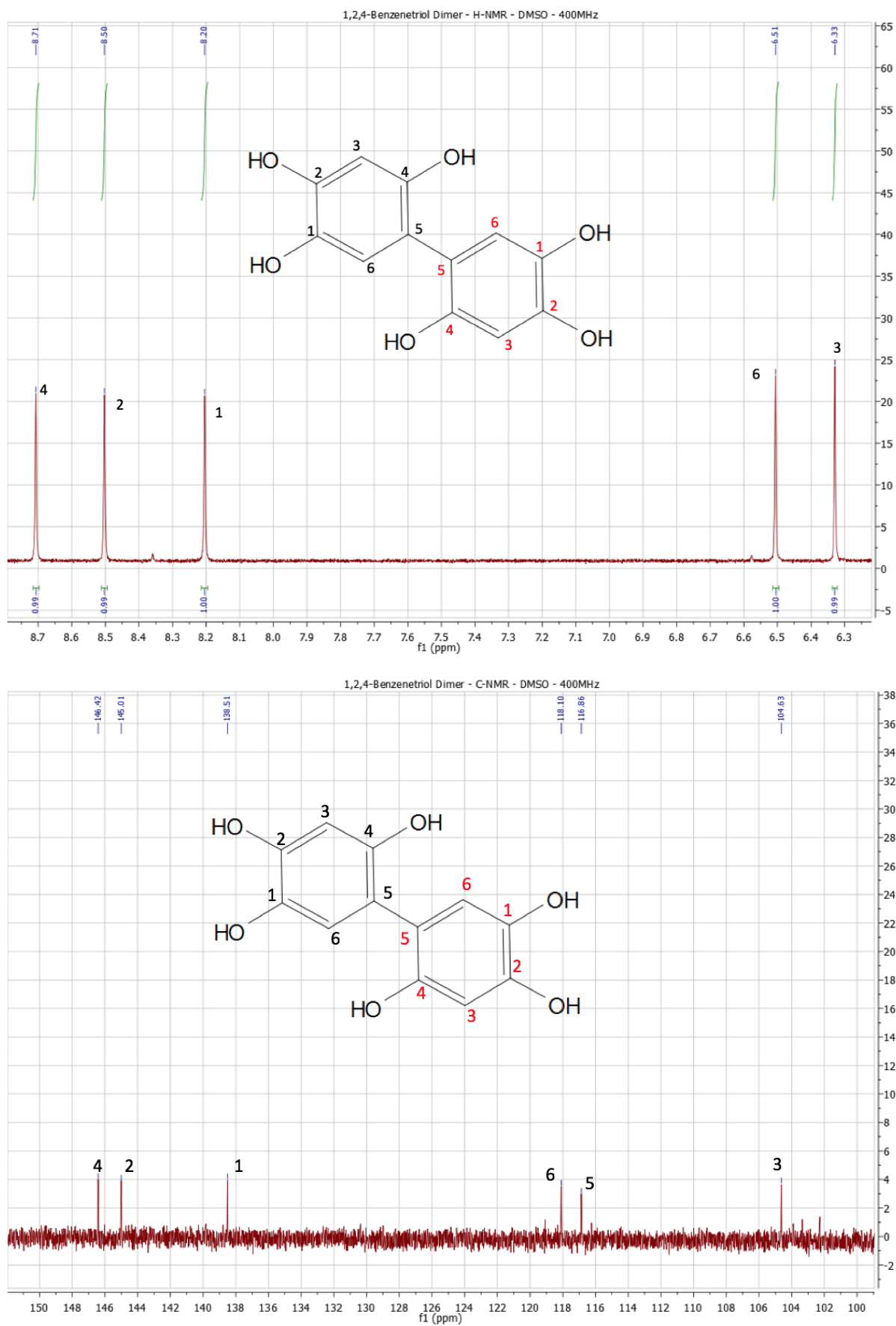
**Figure S4.** Left: BTO powder; middle: BTO solution exposed to air; right: 5,5'-BTO dimer

This black powder was confirmed to be the BTO dimer 2,2',4,4',5,5'-Hexahydroxybiphenyl (5,5'-BTO dimer) by NMR (**Figure S6**) and X-ray diffraction of a recrystallized fraction from water yielding very brittle black needles (**Figure S5**).



**Figure S5** 5,5'-BTO dimer needles suitable for X-ray diffraction.

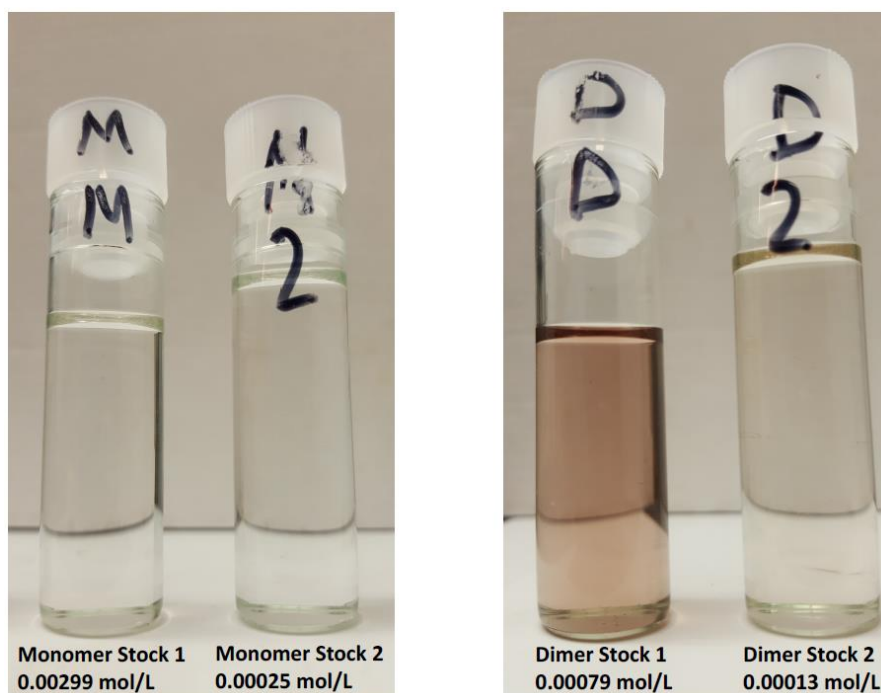
$^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of 5,5'-BTO dimer in  $d_6$ -DMSO (400 MHz/100 MHz respectively) are shown below (assignment also using a APT and gHSQC experiment).



**Figure S6**  $^1\text{H}$  (top) and  $^{13}\text{C}$  NMR of the 5,5'-BTO dimer.

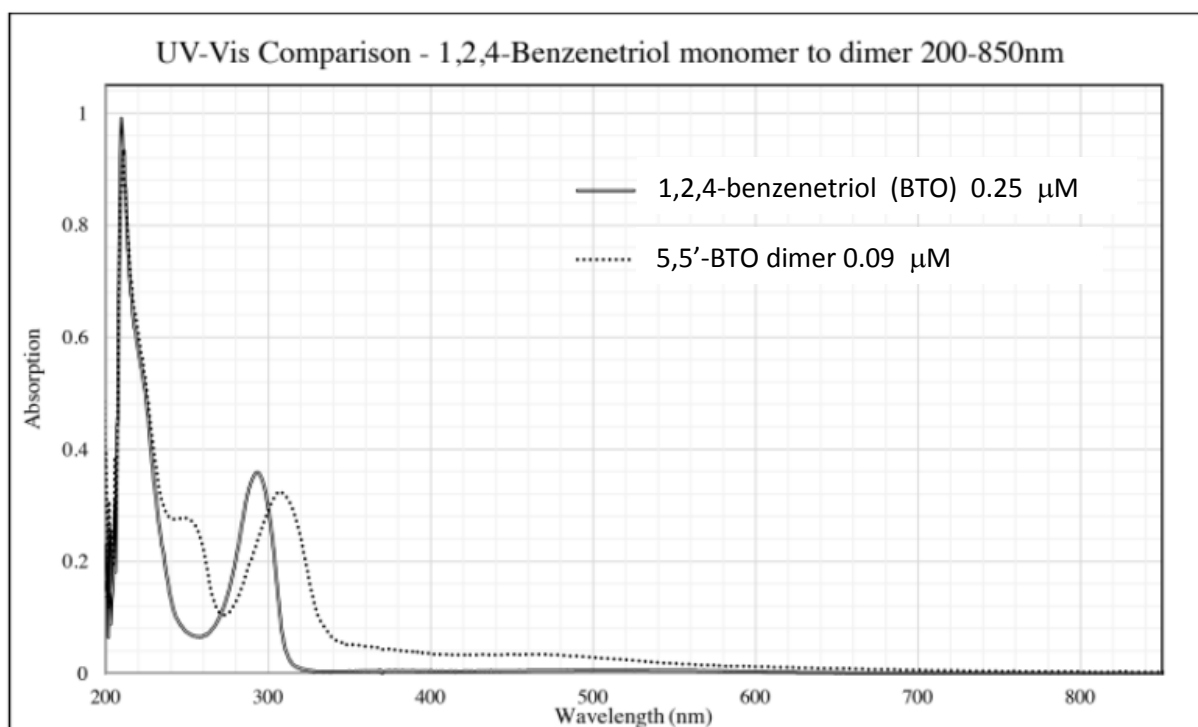


UV-Vis of the BTO monomer and Dimer



**Figure S7**  
Photographs showing the colours of BTO (left) and 5,5'-BTO dimer (right) solutions in THF.

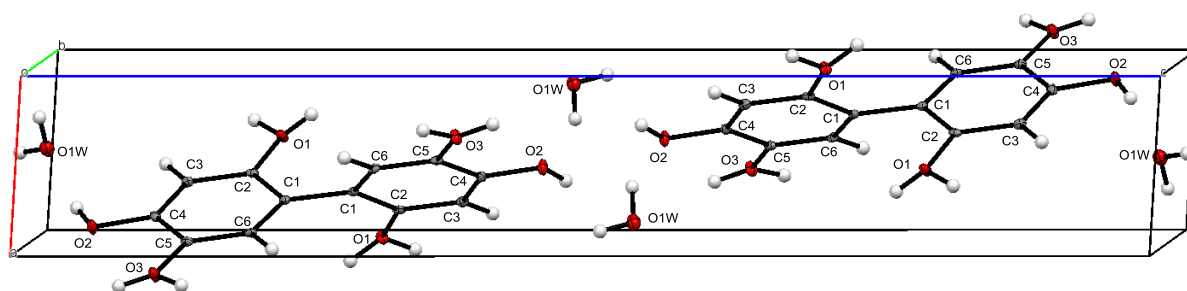
To illustrate the colour change that occurs to the solution when comparing BTO (**Figure S7** left) and the dimer (**Figure S7** right) UV-Vis spectra were recorded of the BTO and BTO dimer (**Figure S8**) which clearly shows a shift to the visible light region. The absorption maxima are 293 nm for BTO and 307 nm/460nm for the dimer.



**Figure S8** UV-Vis spectra of BTO and 5,5'-BTO dimer solutions in THF.

## X-ray crystallography

A single crystal of 2,2',4,4',5,5'-hexahydroxybiphenyl was mounted on top of a cryoloop and transferred into the cold nitrogen stream (100 K) of a Bruker-AXS D8 Venture diffractometer. Data collection and reduction was done using the Bruker software suite APEX3.<sup>i</sup> The final unit cell was obtained from the xyz centroids of 5785 reflections after integration. A multiscan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (*SADABS*). The structures were solved by direct methods using *SHELXT*<sup>ii</sup> and refinement of the structure was performed using *SHELXL*.<sup>iii</sup> The carbon-bound hydrogen atoms were generated by geometrical considerations, constrained to idealized geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. The oxygen-bound hydrogen atoms were tentatively located in a difference Fourier map, which indicated that those on O1 and O3 were likely disordered over two positions (in line with the expected hydrogen-bonding network). The hydrogen atom on O2 were generated by geometrical considerations, constrained to an idealized geometry and allowed to ride on O2 with an isotropic displacement parameter related to the equivalent displacement parameter of O2. The hydrogen atoms on O1 and O3 (each oxygen having a 50/50 ratio of two O-H orientations) were obtained from a difference Fourier synthesis and constrained to O-H distances of 0.84 Å, with isotropic displacement parameters related to the equivalent displacement parameters of their carrier atoms. The hydrogen atoms on the water molecule (O1W) were constrained to have O-H distances of 0.86 Å, with a H-H distance of 1.47 Å. Crystal data and details on data collection and refinement are presented in Table S1.



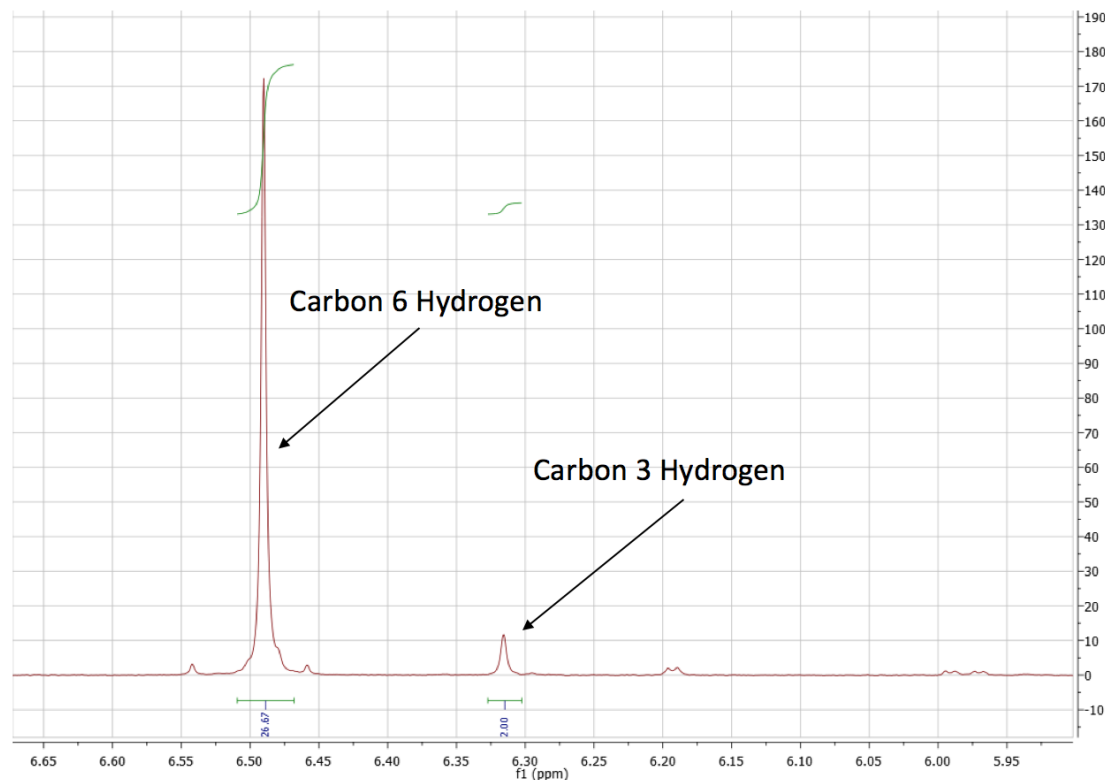
**Figure S9.** Molecular structure of 2,2',4,4',5,5'-hexahydroxybiphenyl (5,5'-BTO dimer), showing 50% probability ellipsoids. The two hydrogens shown at O1 and O3 have a relative 50/50 probability ratio as described in the text above.

**Table S1.** Crystallographic data for 2,2',4,4',5,5'-hexahydroxybiphenyl

Chem. formula	286.23
$M_r$	286.23
cryst syst	monoclinic
color, habit	dark brown, needle
size (mm)	0.71 x 0.14 x 0.03
space group	<i>P2/n</i>
a (Å)	3.8541(4)
b (Å)	6.0625(5)
c (Å)	24.554(2)
$\alpha$ , deg	90
$\beta$ , deg	94.163(4)
$\gamma$ , deg	90
V (Å <sup>3</sup> )	572.21(9)
Z	2
$\rho_{\text{calc}}$ , g.cm <sup>-3</sup>	1.661
$\mu(\text{Mo K}\alpha)$ , cm <sup>-1</sup>	0.142
F(000)	300
temp (K)	100(2)
$\theta$ range (deg)	3.328 – 26.372
data collected (h,k,l)	-4:4, -7:7, -30:30
no. of rflns collected	9007
no. of indepndt rflns	1168
observed rflns	1076 ( $F_o \geq 2 \sigma(F_o)$ )
R(F) (%)	6.68
wR(F <sup>2</sup> ) (%)	17.29
GooF	1.039
Weighting a,b	0.0640, 2.9567
params refined	110
restraints	7
min, max resid dens	-0.666, 0.529

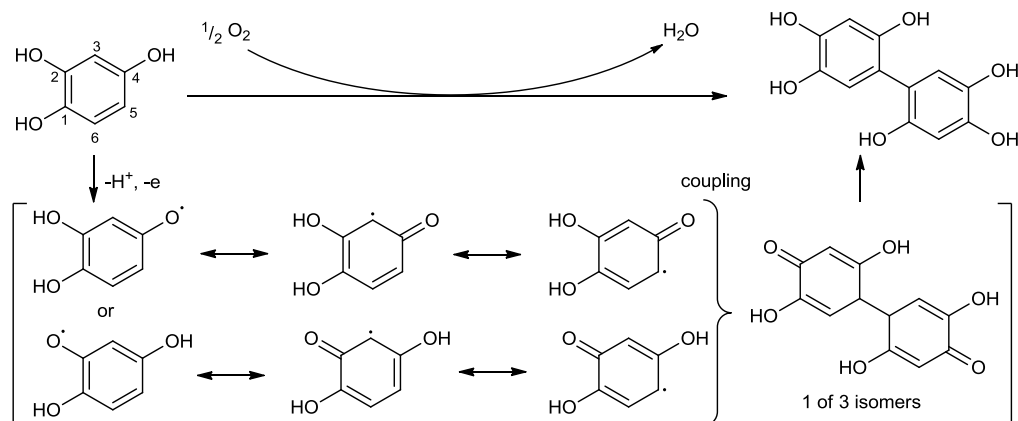
### Mechanism for BTO dimer and oligomer formation

When the aqueous solutions of BTO were exposed to base or heated to 60 °C the reaction became more complex showing the formation of trimers and higher oligomers of BTO by LCMS (ES<sup>-</sup>). These were shown by <sup>1</sup>H-NMR to be mainly coupled through the 3 and 5 positions of BTO as relatively only the hydrogen on the 6 position can be observed in the final product (**Figure S10**).



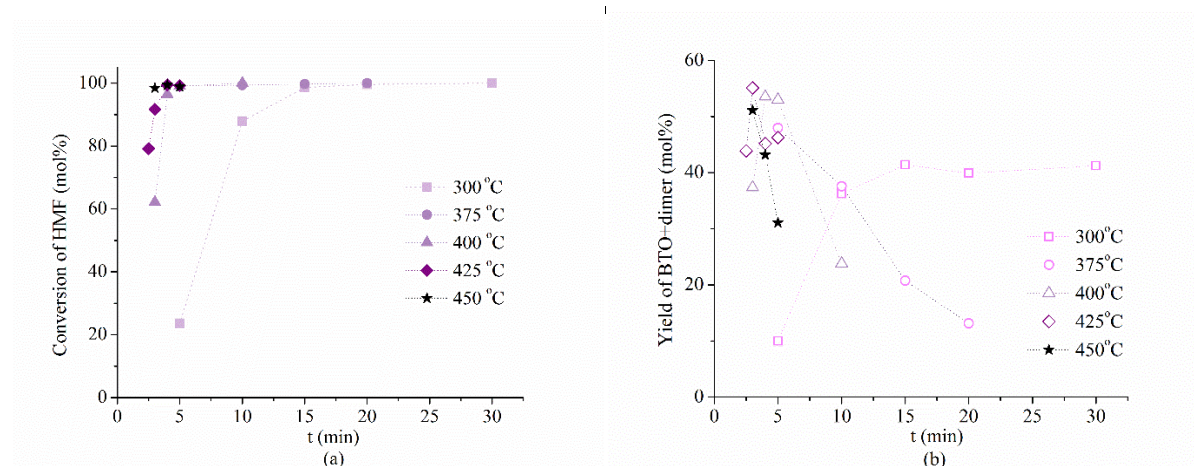
**Figure S10.** <sup>1</sup>H-NMR (d<sub>6</sub>-dmsol) of the oligomeric material.

Addition of a small amount of hydrogen peroxide caused complete conversion of BTO in less than a minute (but unselective coupling). These observations, combined with the observing that the reaction was suppressed upon oxygen removal by degassing the solution and running it under an argon atmosphere, led us to believe the reaction goes through a oxygen induced radical dimerization and oligomerization. The regioselectivity is believed the result of preferred localization of the radical on the 3 and 5 position due to resonance and preference reactivity on the 5 position due to steric hinderance of the 3 position (**Scheme S1**).

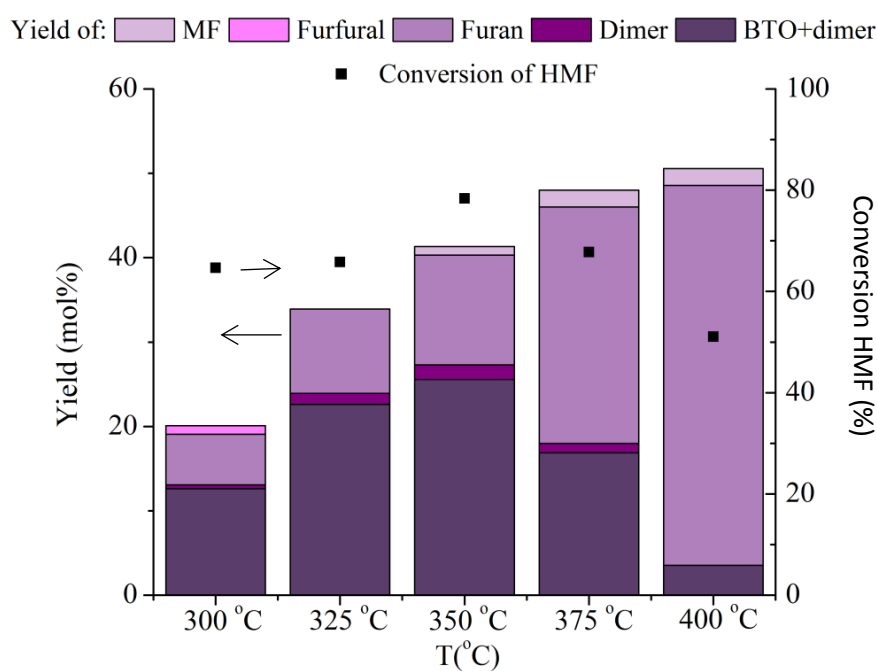


**Scheme S1** Proposed O<sub>2</sub> radical pathway to 5,5'-BTO dimer

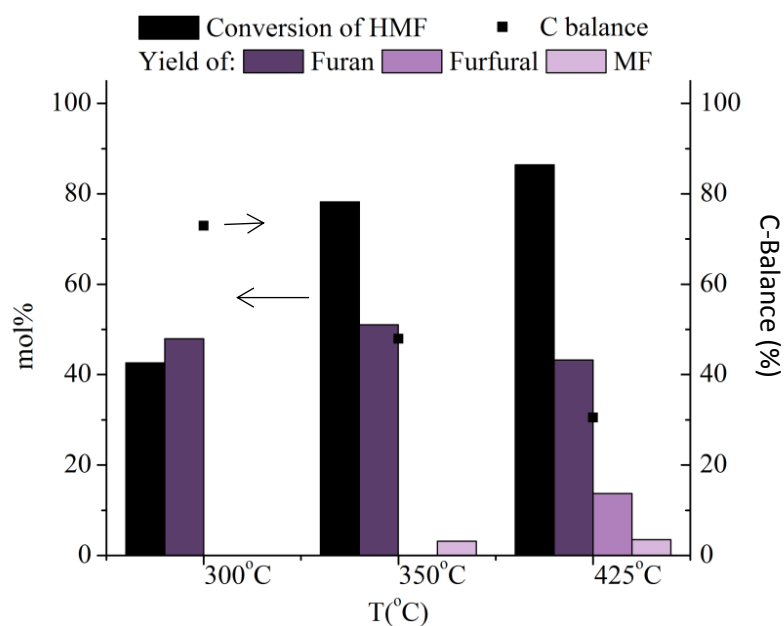
## S6. Supplementary Data HMF to BTO reactions



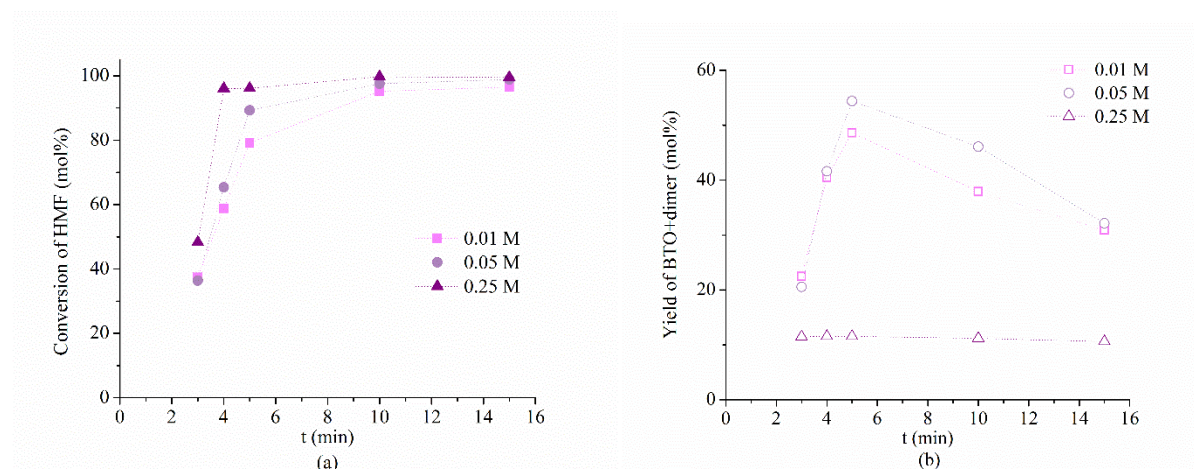
**Figure S11.** a) Conversion of HMF and b) BTO yield using  $\text{Zn}(\text{OTf})_2$  as catalyst at different sand bath temperatures and reaction times (Conditions; 5 mL 0.05 M aqueous HMF and 1.2 mM  $\text{Zn}(\text{OTf})_2$ ,  $P_o = 80\text{--}120$  bar  $\text{N}_2$  depending on the final temperature, analysis by HPLC using dimethylsulfoxide as internal standard)



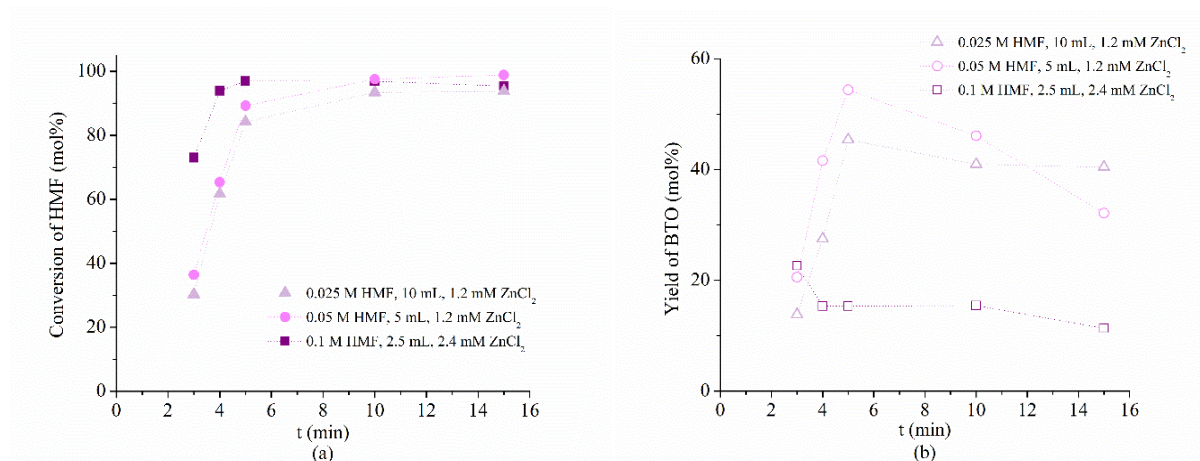
**Figure S12.** Blank reactions (no catalyst) at different sand bath temperatures. Conversion of HMF and product yields (Conditions; 5 mL 0.05 M aqueous HMF,  $P_o = 40\text{--}120$  bar  $\text{N}_2$  depending on the final temperature,  $t = 15$  minutes)



**Figure S13.** Thermal conversion of HMF without solvent or catalyst. (Feed = 0.0631 g HMF,  $T_{\text{bath}} = 300\text{--}425^\circ\text{C}$ ,  $P_o = 110$  bar  $\text{N}_2$  depending on the final temperature,  $t = 5$  minutes)



**Figure S14.** a) Conversion of HMF and b) BTO yield using different feed concentrations and reaction times (Conditions; 5 mL 0.01–0.25 M aqueous HMF and 1.2 mM  $\text{ZnCl}_2$ ,  $T_{\text{bath}} = 400^\circ\text{C}$ ,  $P_o = 70\text{--}120$  bar  $\text{N}_2$ , analysis by HPLC using dimethylsulfoxide as internal standard)



**Figure S15.** a) Conversion of HMF and b) BTO yield using different feed concentrations, total volume and reaction times (Conditions; 2.5–10 mL 0.025–0.1 M aqueous HMF and 1.2–2.4 mM ZnCl<sub>2</sub>, T<sub>bath</sub> = 400 °C, P<sub>o</sub> = 40–120 bar N<sub>2</sub> depending on the final temperature, analysis by HPLC using dimethylsulfoxide as internal standard)

**Table S2.** Overview of data BTO production

Catalysts	T <sub>bath</sub> (°C)	t (min)	C HMF (M)	V feed (mL)	P <sub>0</sub> N <sub>2</sub> (bar)	P <sub>final</sub> N <sub>2</sub> (bar)	Conversion of HMF (%)	BTO corr. <sup>(a)</sup>	BTO-Dimer	FA	Glycerol	Yield (mol%)								C balance (mol%)
												AA	LA	MEK	2CP	14BDO	Furan	Furfural	MF	
-	300	5	0.05	5	120	285	37	1	0	0	2	0	0	0	0	0	3	0	0	68
		10				285	44	6	0	0	3	0	0	0	0	8	0	0	70	
		15				300	65	13	0	0	4	0	1	0	0	5	0	0	55	
		20				300	82	14	1	0	4	0	2	0	0	4	0	1	39	
		30				300	95	17	1	1	2	0	2	0	0	0	1	1	31	
		45				300	99	17	1	0	4	1	2	0	1	0	0	1	1	24
		60				300	99	16	1	0	3	1	2	0	1	0	2	1	0	27
		90				300	100	15	1	0	3	1	2	0	2	0	0	3	0	23
1.2 mM ZnCl <sub>2</sub>	300	5	0.05	5	120	260	23	9	0	3	0	0	1	0	0	0	8	0	0	92
		10				280	73	33	3	2	0	0	3	4	0	7	0	0	71	
		15				280	85	40	4	1	0	4	4	3	1	0	1	0	1	65
		20				280	99	41	3	0	4	1	4	2	1	0	0	0	1	41
		30				280	100	35	3	0	0	0	4	3	1	0	0	0	1	42
		45				280	100	38	4	1	0	1	4	3	2	0	0	0	0	45
		60				280	100	35	3	1	0	2	1	3	2	0	0	0	0	41
		90				280	100	29	2	1	0	1	3	2	2	0	0	0	0	35
1.2 mM ZnCl <sub>2</sub>	325	5	0.05	5	120	260	29	14	0	0	3	0	2	0	0	0	6	0	0	91
		10				290	86	43	4	5	1	0	4	0	0	5	0	1	63	
		15				300	99	43	5	5	1	1	4	5	2	0	0	0	54	
		20				300	100	42	4	3	1	2	4	0	3	0	0	0	0	49
		30				300	100	32	2	0	0	0	3	0	4	0	0	0	0	36
		45				300	100	32	3	0	0	0	3	0	6	0	0	0	0	39
		60				300	100	30	3	0	0	0	3	0	6	0	0	0	0	37
		90				300	100	25	2	0	0	0	3	0	7	0	0	0	0	33
1.2 mM ZnCl <sub>2</sub>	350	5	0.05	5	120	285	56	23	2	0	0	0	2	0	1	0	14	0	0	79
		10			120	300	98	34	4	0	5	0	4	0	3	0	6	0	0	48
		15			100	295	99	47	5	0	1	2	4	0	3	0	0	0	2	57
		20			100	285	99	43	5	0	1	2	3	0	5	0	0	0	0	52
		30			100	300	100	35	4	0	0	2	4	0	7	0	6	0	0	49
		45			100	290	100	29	3	0	0	2	3	0	10	0	6	0	0	45



					60		100	280	100	27	2	0	0	2	4	0	13	0	10	0	0	49
					90		100	290	100	13	1	0	0	2	3	0	17	0	13	0	0	39
1.2 mM																						
ZnCl <sub>2</sub>	375	5	0.05	5	90	285	91	51	51	6	0	3	0	2	0	3	0	8	0	2	74	
		10			90	300	98	53	53	6	0	0	1	2	0	4	0	0	0	0	61	
		15			90	300	99	43	43	4	0	0	1	3	0	7	0	0	0	3	56	
		20			85	300	99	34	34	3	0	0	1	3	0	10	0	4	0	1	50	
1.2 mM																						
ZnCl <sub>2</sub>	400	3	0.05	5	80	230	36	21	21	1	4	0	0	1	0	0	0	8	0	0	91	
		4			80	260	65	42	42	4	5	0	0	3	0	0	0	12	0	0	87	
		5			80	280	89	54	54	6	3	0	0	2	0	2	0	10	0	2	78	
		10			80	300	98	46	46	5	1	0	1	2	0	6	0	0	0	3	59	
		15			80	300	99	32	32	3	0	0	1	3	0	12	0	0	0	2	48	
1.2 mM																						
ZnCl <sub>2</sub>	425	3	0.05	5	80	240	32	20	20	2	0	3	0	1	0	2	0	10	0	0	99	
		4			80	280	78	42	42	4	1	2	0	1	0	2	0	9	0	2	82	
		5			90	300	91	51	51	5	2	0	0	2	0	4	0	9	0	3	74	
1.2 mM																						
ZnCl <sub>2</sub>	450	3	0.05	10	80	300	79	45	45	4	19	0	0	4	0	2	0	14	0	2	86	
		4			80	300	88	43	43	4	8	0	0	3	0	2	0	12	0	2	71	
		5			80	300	83	27	27	2	2	0	1	2	0	6	0	22	0	3	69	
		10			80	300	88	24	24	1	2	0	2	2	0	5	0	21	0	4	70	
0.14 mM																						
ZnCl <sub>2</sub>	400	3	0.05	5	110	200	43	23	23	1	0	1	3	1	0	1	0	18	0	2	97	
		4			100	270	63	31	31	2	0	1	2	2	0	1	0	13	0	3	83	
		5			80	295	73	33	33	2	0	1	2	2	0	1	0	15	0	2	77	
		10			80	300	92	33	33	2	0	1	2	2	0	3	1	8	0	4	57	
		15			70	290	91	24	24	1	0	1	3	3	0	6	0	13	0	5	55	
0.6 mM																						
ZnCl <sub>2</sub>	400	3	0.05	5	80	210	30	10	10	0	5	0	1	3	0	0	0	8	0	0	89	
		4			80	250	64	33	33	2	5	0	1	3	0	0	0	11	0	0	80	
		5			80	270	89	45	45	4	7	0	1	3	0	2	0	11	0	2	71	
		10			80	300	98	45	45	5	4	0	3	4	0	6	0	9	0	3	66	
		15			80	300	98	28	28	2	3	0	3	3	0	10	0	8	0	3	50	
2.4 mM																						
ZnCl <sub>2</sub>	400	3	0.05	5	80	225	46	26	26	2	3	0	0	2	0	0	0	9	0	0	88	
		4			80	240	71	42	42	4	7	0	0	3	0	3	0	7	0	0	82	
		5			80	260	89	49	49	5	5	0	0	3	0	2	0	7	0	1	71	
		10			80	300	98	38	38	3	0	1	2	3	0	7	0	3	0	2	54	

		15			80	300	99	23	2	0	0	4	3	0	16	0	11	0	2	51
10 mM																				
ZnCl <sub>2</sub>	400	3	0.05	5	80	190	46	13	1	0	1	0	1	0	0	0	6	0	0	73
		4			80	220	88	46	4	0	1	0	4	0	0	0	6	0	0	65
		5			80	260	99	46	4	0	1	0	3	0	2	0	0	0	0	52
		10			80	300	100	36	3	0	0	1	3	0	8	0	5	0	0	49
		15			70	295	100	21	1	0	0	1	3	0	16	0	9	0	0	44

(a) yield BTO + BTO-dimer

\*Note: BTO: 1,2,4-benzenetriol; FA: Formic acid; LA: AA: Acetic acid; Levulinic acid; MEK: Methyl ethyl ketone/butanone; 2CP: 2-cyclopenten-1-one; 14 BDO: 1,4-benzenediol; MF: 5-methylfurfural;

## S7. Supplementary Data BTO hydrodeoxygenation

**Table S3.** Overview of data hydrogenation of BTO

Catalysts I	Catalysts II	T (°C)	t (min) <sup>(a)</sup>	BTO (mmol)	V mQ (mL)	Flushing with N <sub>2</sub> (bar)	P H <sub>2</sub> (bar)	Conversion of BTO (%)	Cyclohexanone	Cyclohexanol	AA	4HCH	Yield (mol%) <sup>(c)</sup>				
													t12CHD	14BDO	c12CHD	CPM	
Pd/Al <sub>2</sub> O <sub>3</sub> 30 wt%	AlCl <sub>3</sub> 30 wt%	250	30	0.25	25	3x80	50	97	45	0	0	1	0	0	0	0	
Pd/Al <sub>2</sub> O <sub>3</sub> 30 wt%	Al(OTf) <sub>3</sub> 30 wt%	250	30	0.25	25	3x80	50	94	36	0	0	0	1	0	0	0	
Pd/Al <sub>2</sub> O <sub>3</sub> 30 wt%	Al(OTf) <sub>3</sub> 30 wt%	250	30	0.25	25	3x80	50										
Pd/Al <sub>2</sub> O <sub>3</sub> 30 wt%	Al(OTf) <sub>3</sub> 30 wt%	20.8	0	0.25	25	3x80		<5	0	0	0	0	0	0	0	0	
		73.2	5					<5	0	0	0	1	0	0	0	0	
		In time	147.9	10					<5	0	0	0	1	0	0	0	0
			225.5	15					<5	0	0	0	4	0	0	0	0
			206.7	20					40	0	0	0	21	0	0	0	0
			245.7	25.5					62	0	3	0	45	2	0	2	0
			250	31 <sup>(b)</sup>					96	20	7	0	41	3	0	3	0
							100	33	4	0	6	0	0	0	0		
Pd/Al <sub>2</sub> O <sub>3</sub> 30 wt%	Al(OTf) <sub>3</sub> 30 wt%	250	0 h	0.25	25	3x80	60	57	8	0	4	26	1	0	5	0	
			245	½ h				60	84	22	2	5	25	1	0	5	0
		In time	242	1 h				60	96	24	4	0	12	1	0	2	0
			248	2 h				60	99	15	4	2	0	0	0	0	0
			241	3 h				60	97	6	0	2	0	0	0	0	0
					<sup>(b)</sup>			-	97	1	0	0	0	0	0	0	0

(a) t when the T<sub>set</sub> has been achieved (about 30 min); (b) Sample from the reactor after cooling the whole reaction mixture; (15 minutes before t = 0 which in this case was the time the reactor reached 250 °C. (c) Yield of identified products, several additional signals for unidentified products were observed

AA: acetic acid; LA: levulinic acid; 4-HCH: 4-hydroxy cyclohexanone; t12CHD: trans-1,2-cyclohexanediol; 14BDO: 1,4-benzenediol; c12CHD: cis-1,2-cyclohexanediol; CPM: cyclopentane methanol

## References:

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- <sup>i</sup> Bruker, (2016). *APEX3* (v2012.4-3), *SAINT* (Version 8.18C) and *SADABS* (Version 2012/1). Bruker AXS Inc., Madison, Wisconsin, USA.
- <sup>ii</sup> Sheldrick, G. M. (2015) *Acta Cryst.* **A71**, 3-8
- <sup>iii</sup> Sheldrick, G. M. (2008). *Acta Cryst.* A64, 112-122