Supplementary Information

Direct biomass valorisation to γ-valerolactone by Ru-PNP catalysed hydrogenation in acid

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1. Experimental section

1.1. Material and Methods

Most chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Ru-MACHO-BH, 85 w/w% H_3PO_4 are commercially available and used without further purification. Beechwood sawdust was obtained from a local wood processing company. Peels of potato and banana were sourced from local supermarkets in Copenhagen. Grass and wheat straw were among the feedstock that was collected directly from the surrounding land. Toilet paper, coffee grounds, pistachio shells, potato flour, bamboo, and rice grains were purchased from local supermarkets in the Copenhagen municipality. Used coffee grounds were used as for the reaction. Chitin was commercially obtained from Merck. All the lignocellulosic biomass materials were grinded into powders using ball milling process and dried in vacuum oven before use.

H_2 gas (H_2O ≤ 3 ppm; O_2 ≤ 2 ppm) was purchased from Air Liquide. All reactions dealing with air or moisture-sensitive compounds were performed using standard Schlenk techniques or in an argon-filled glovebox. GC-FID were recorded on an Agilent 19091J-413 HP-5 5% Phenyl methyl siloxane capillary column using 1,4-dioxane as the internal standard. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance III 400 MHz spectrometer. The batches for gas analysis, the gas phase was carefully collected in a gas bag and analysed by MicroGC. TGA was fulfilled under N_2 atmosphere (30 mL min^{-1}) using a METTLER TOLEDO thermal analyser in the temperature interval 25-300 °C with a constant heating rate of 10 °C min^{-1}.

1.2. General procedure for catalysis

For a typical hydrogenation experiment, in a glove box, biomass (91 mg) and Ru-MACHO-BH (1.8 wt%, 1.6 mg) were weighed in a glass vial equipped with a magnetic stir bar and sealed with a Teflon-lined cap. Upon bringing the glass vial outside the glove box, 1 mL of solvent (H_2O) followed by addition of 85 w/w% aqueous phosphoric acid. Subsequently, the vial was placed in a seven-well reactor with a needle placed through the rubber stopper of the vials for the gas flow. The high-pressure reactor was sealed tightly and flushed with argon/hydrogen (three times) and finally required hydrogen pressure (30 bar) was loaded into the high-pressure reactor and desired temperature of 140 °C was also applied. The reactor was cooled to room temperature before the hydrogen was released and the sample was prepared for GC analysis. The liquid sample was prepared for GC analysis by adding 100 µl of 1,4-dioxane (internal standard) followed by dilution of the mixture with 3.75 mL of dichloromethane (DCM). The yield of GVL in the mixture is calculated by using calibration curve. To generate a calibration curve, standard GVL samples of various known concentrations along with 1,4-dioxane (100 µl) with total volume made up to 10 mL with DCM and are injected into the GC.

2. Theoretical yield calculation

For sawdust

Lignocellulosic content	wt%	M per unit
Hemicellulose	37	132 g mol^{-1}
Cellulose	42	162 g mol^{-1}
Lignin	19	-

Maximum theoretical yield is calculated assuming both hemicellulose and cellulose are completely converted into GVL. Also calculated with respect to dry biomass.

For e.g. beech wood sawdust (91 mg, corresponding to 0.26 mmol hemicellulose and 0.28 mmol cellulose.

Molecular weight of GVL=100.1 g mol^{-1}

Max theoretical amount yield $= 0.091\ g\left[\frac{0.42}{162\ g\ mol^{-1}} + \frac{0.37}{132\ g\ mol^{-1}}\right]$

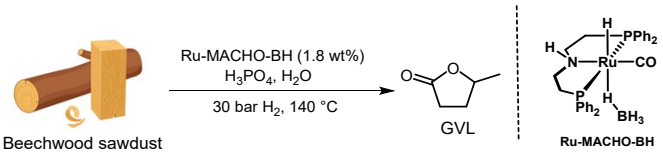
Max theoretical amount yield = 0.491 * 10^{-3} mol

Max theoretical weight yield = 0.491 * 10^{-3} mol * 100.1 g mol^{-1} = 49.1 mg

∴ Yield based on theoretical yield for 26 wt%: $\frac{0{,}26 * 91}{49.1} \times 100\% = 48\%$

3. Catalytic studies

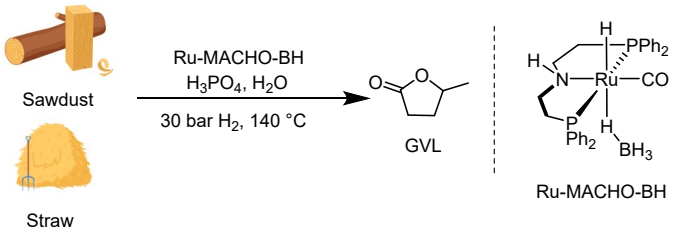
Table S1. Optimization of the direct conversion of beechwood sawdust to GVL.



Beechwood sawdust content		Entry	c(H_3PO_4) [M]	t [h]	GVL yield[a] [wt% (mol%)]
Lignocellulosic content	wt%	1	7.5	96	15 (28)
Hemicellulose	37	2	9.3	24	22 (41)
Cellulose	42	3	9.3	96	23 (43)
Lignin	19	4	9.3	168	20 (37)
		5	10.1	24	25 (46)
		6	10.1	38	21 (39)
		7	10.1	96	19 (35)
		8	10.9	18	21 (39)
		9	10.9	24	26 (48)
		10	10.9	96	18 (33)
		11[b]	10.9	24	14 (26)
		12[c]	10.9	48	-

Standard reaction conditions: Beech wood (91 mg, corresponding to 0.26 mmol hemicellulose and 0.28 mmol cellulose [34], Ru-MACHO-BH (1.65 mg, 0.0028 mmol), H_2O at 140 °C and 30 bar H_2, [a] Determined by GC-FID. Yields are calculated with respect to dry biomass. [b] 1:1 V/V EtOH/H_2O (1 mL). [c] no addition of H_2.

Table S2: Optimization of direct conversion of sawdust and straw to GVL.



Biomass		Entry	H_3PO_4 [M]	Time [h]	GVL yield[a] [wt% (mol%)]
Beechwood sawdust					
Lignocellulosic content	wt%	1[b]	10.9	48	8 (15)
Hemicellulose	37				
Cellulose	42				
Lignin	19				
Wheat straw					
Lignocellulosic content	wt%	2	9.3	24	12 (31)
Hemicellulose	25	3	10.9	24	12 (31)
Cellulose	33	4	11.8	96	17 (43)
Lignin	17	5[c]	10.9	24	11 (28)
		6[d]	10.9	48	3 (8)

Standard reaction conditions: Beech wood (1g) and wheat straw (91 mg), Ru-MACHO-BH (1.65 mg, 0.0028 mmol), H_2O (1 mL) at 140 °C and 30 bar H_2, [a] Determined by GC-FID using 1,4-dioxane as the internal standard. Yields are calculated with respect to dry biomass. [b] Beechwood (1g), Ru-MACHO-BH (20 mg), H_2O (15 mL).[c] 1:1 v/v EtOH/H_2O (1 mL). [d] Wheat straw (1g), Ru-MACHO-BH (20 mg), H_2O (15 mL).

4. Calibration curve, GC-FID and NMR

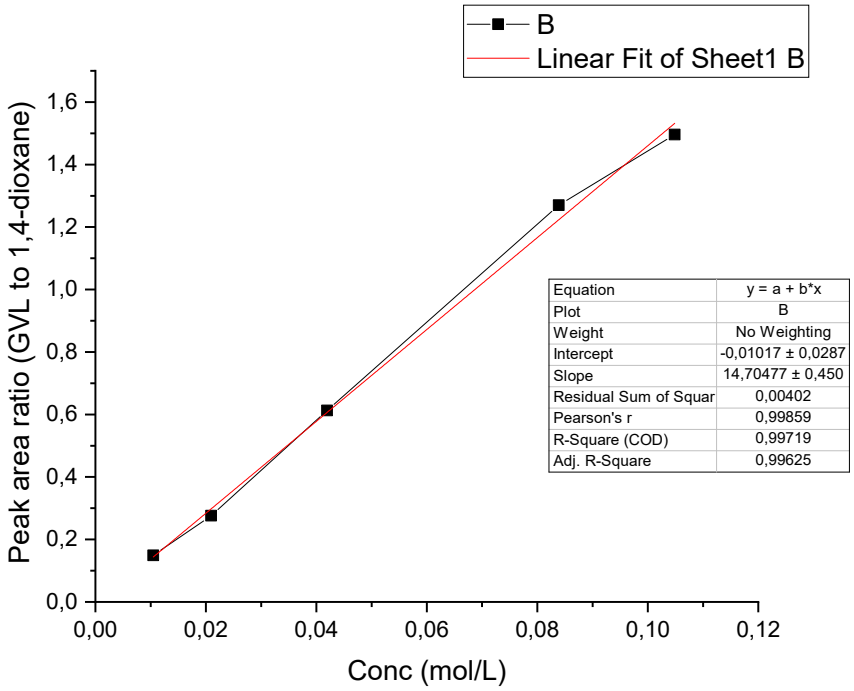
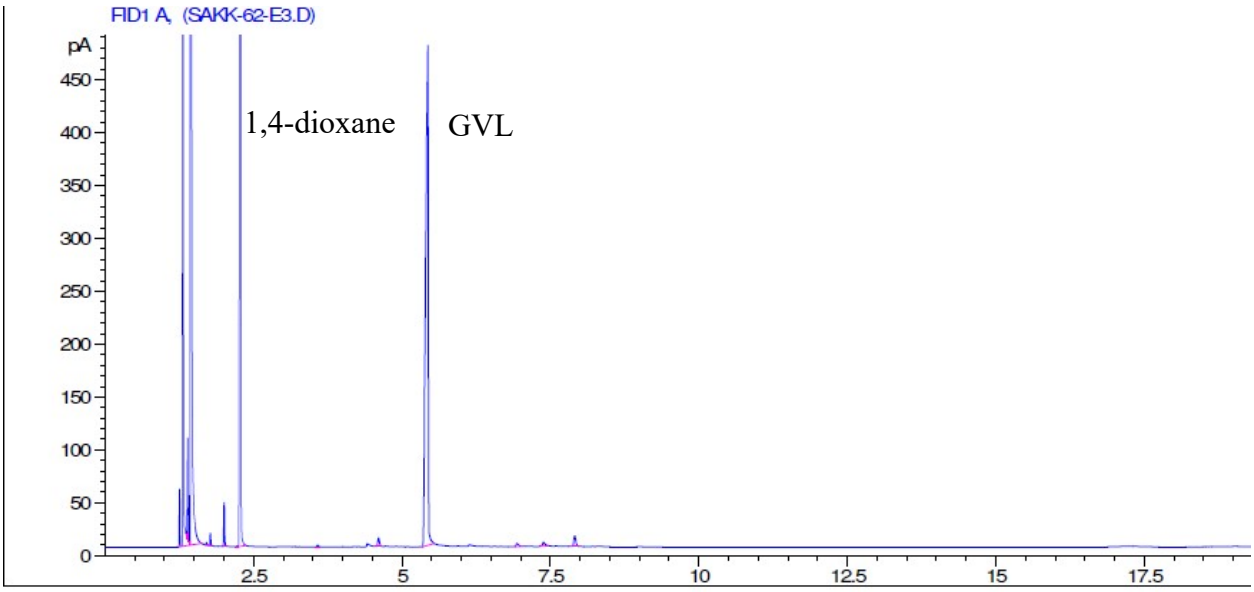


Figure S1. Calibration curve for GVL using 1,4-dioxane as the internal standard.



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3	1.370	BV X	7.47e-3	2.32947	0.00301	?
4	1.393	VV X	0.0141	83.79234	0.10836	?
5	1.414	VV X	8.36e-3	24.28563	0.03141	?
6	1.435	VB S	0.0102	6.77674e4	87.63684	?
7	1.709	BB	0.0143	2.55260	0.00330	?
8	1.776	BB	0.0117	9.05608	0.01171	?
9	2.007	BB	0.0139	37.99453	0.04913	?
10	2.221	BV	0.0151	6.83144e-1	0.00088	?
11	2.281	VB	0.0177	2557.00781	3.30672	?
12	2.993		0.0000	0.00000	0.00000	C14
13	3.466		0.0000	0.00000	0.00000	C15
14	3.577	BB	0.0277	3.27026	0.00423	?
15	3.926		0.0000	0.00000	0.00000	C16
16	4.604	BB	0.0311	16.18981	0.02094	?
17	5.433	BB	0.0399	1439.08240	1.86102	?
18	6.936	BB	0.0363	8.08529	0.01046	?

Figure S2. GC-FID of the crude mixture of the reaction of xylose (0.6 M) with Ru-MACHO-BH (0.5 mol%) using 5.7 M H_3PO_4(aq) and under 30 bar H_2 at 125 ºC in 1:1 v/v EtOH/H_2O after 48 hours.

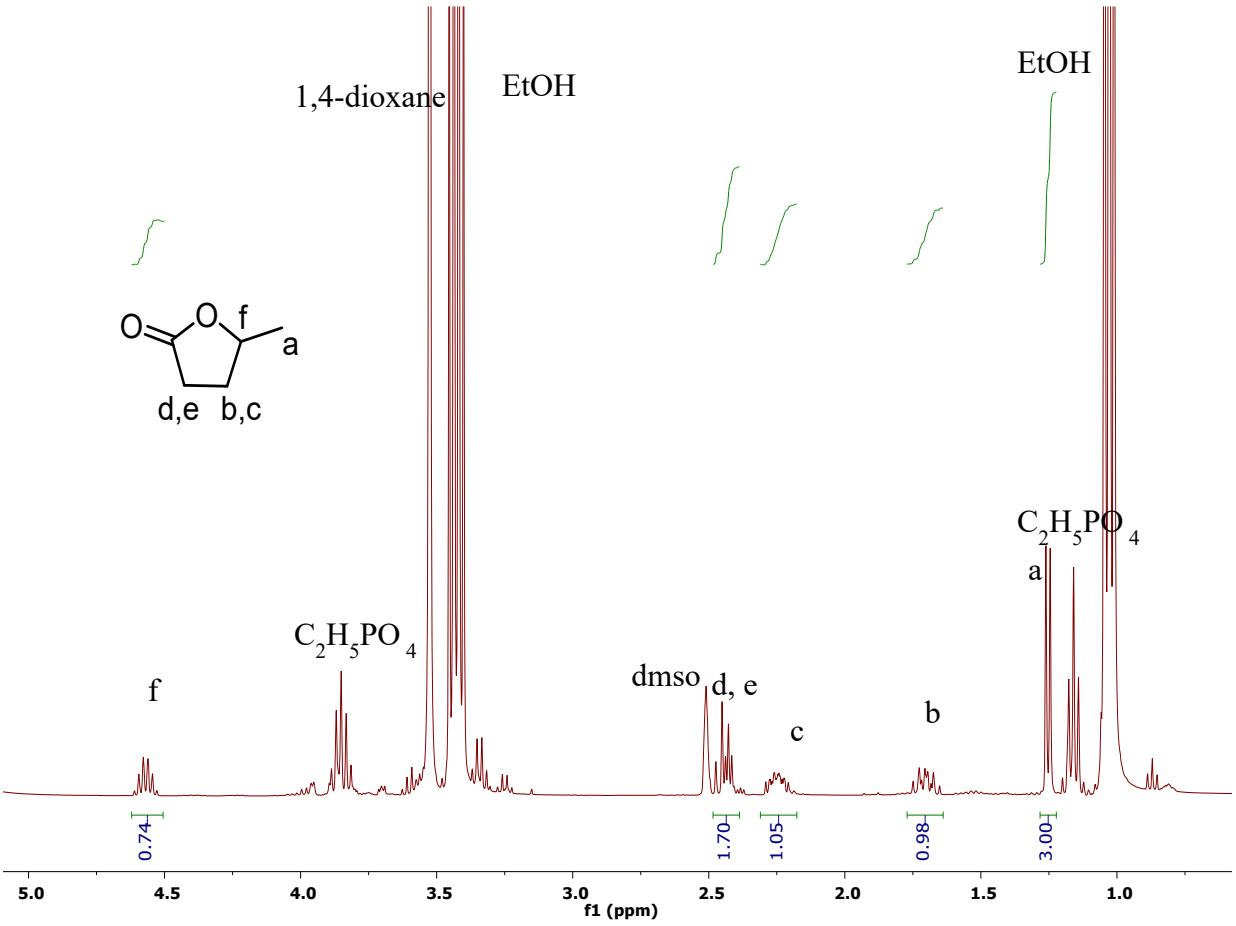
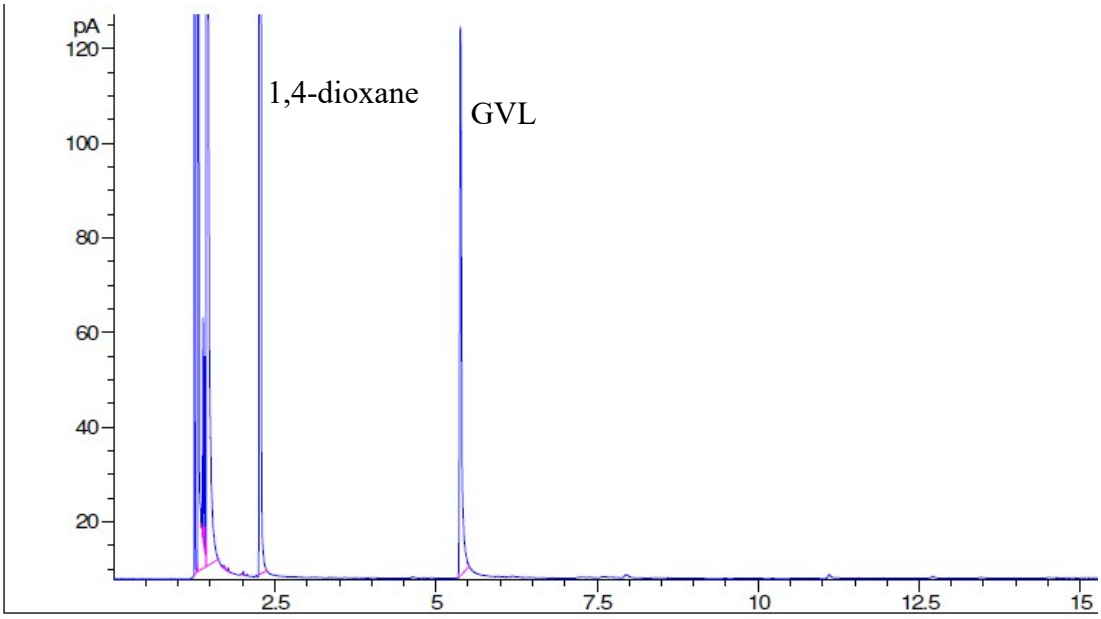


Figure S3. ^{1}H NMR (dmso-d_6, 400 MHz) of the crude reaction of 0.6 mmol xylose (0.6 M) and Ru-MACHO-BH (0.5 mol%) using 5.7 M H_3PO_4(aq) under 30 bar H_2 at 125 ^{o}C in 1:1 v/v EtOH/H_2O mixture after 48 hours.



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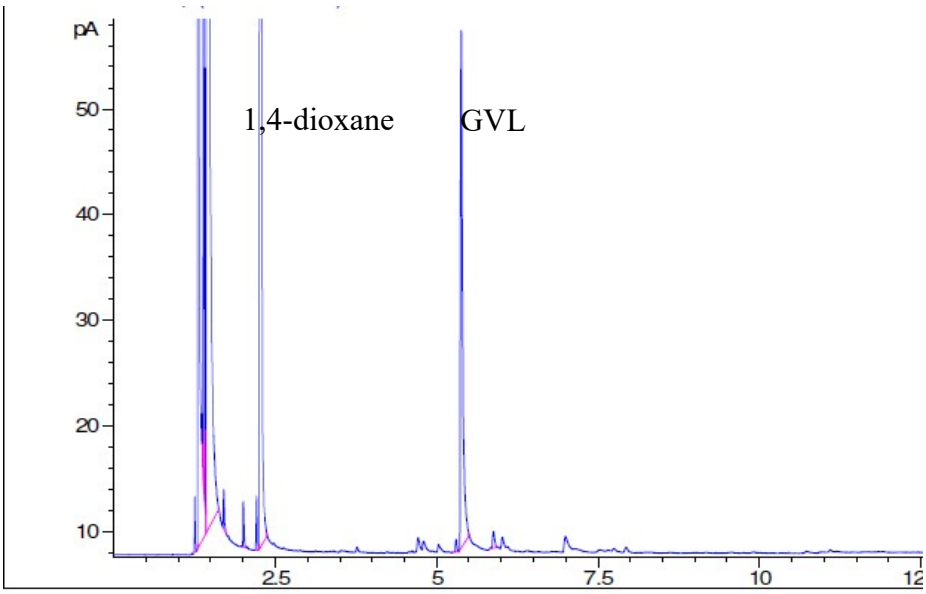
3	1.370	BV X	7.75e-3	2.13731	0.00301	?
4	1.392	VV X	0.0138	39.80243	0.05603	?
5	1.413	VV X	7.92e-3	20.70781	0.02915	?
6	1.435	VB S	0.0105	6.34078e4	89.25874	?
7	1.708	BB	0.0177	6.89576e-1	0.00097	?
8	1.777	BB	0.0108	4.93933e-1	0.00070	?
9	2.013	BB	0.0157	8.32473e-1	0.00117	?
10	2.280	BB	0.0180	2475.71704	3.48505	?
11	2.993		0.0000	0.00000	0.00000	C14
12	3.466		0.0000	0.00000	0.00000	C15
13	3.926		0.0000	0.00000	0.00000	C16
14	5.380	BB	0.0315	241.17174	0.33950	?

Figure S4. GC-FID of the reaction mixture of the reaction of xylose (0.1 M) and Ru-MACHO-BH (0.5 mol%) using 5.7 M H_3PO_4(aq) under 30 bar H_2 at 125 ^oC in 1:1 v/v EtOH/H_2O mixture after 48 hours.



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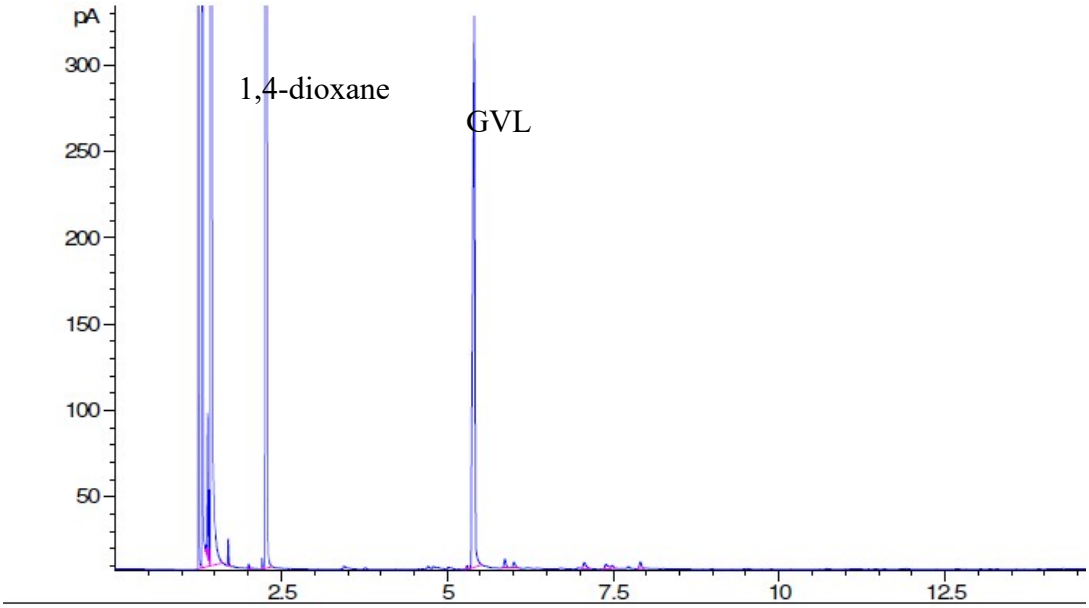
3	1.370	BV X	7.31e-3	2.04384	0.00274	?
4	1.393	VV X	0.0141	61.48492	0.08232	?
5	1.414	VV X	8.05e-3	21.36893	0.02861	?
6	1.436	VB S	0.0105	6.61445e4	88.56311	?
7	1.707	BB	0.0137	3.35637	0.00449	?
8	2.011	BB	0.0145	3.99035	0.00534	?
9	2.216	BB	0.0156	5.09153	0.00682	?
10	2.284	BB	0.0184	3242.40674	4.34137	?
11	2.993		0.0000	0.00000	0.00000	C14
12	3.466		0.0000	0.00000	0.00000	C15
13	3.926		0.0000	0.00000	0.00000	C16
14	5.301	BB	0.0248	1.83525	0.00246	?
15	5.378	BB	0.0338	113.39149	0.15182	?
16	5.880	BB	0.0340	3.44956	0.00462	?

Figure S5. GC-FID of the reaction mixture of glucose (0.1 M) and Ru-MACHO-BH (0.5 mol%) using 5.7 M H_3PO_4(aq) under 30 bar H_2 at 125 °C in 1:1 v/v EtOH/H_2O mixture after 48 hours.



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2	1.314	VV S	7.67e-3	4462.77783	6.12679	?
3	1.370	BV X	8.24e-3	2.49964	0.00343	?
4	1.392	VV X	0.0133	69.36193	0.09522	?
5	1.413	VV X	8.36e-3	20.82538	0.02859	?
6	1.435	VB S	9.95e-3	6.39320e4	87.76988	?
7	1.705	BB	0.0121	12.34311	0.01695	?
8	2.011	BB	0.0144	2.31383	0.00318	?
9	2.215	BB	0.0155	6.15900	0.00846	?
10	2.281	BB	0.0175	2825.18774	3.87860	?
11	2.993		0.0000	0.00000	0.00000	C14
12	3.466		0.0000	0.00000	0.00000	C15
13	3.926		0.0000	0.00000	0.00000	C16
14	5.297	BB	0.0249	3.10943	0.00427	?
15	5.407	BB	0.0344	754.19977	1.03541	?
16	5.866	BB	0.0317	10.75708	0.01477	?
17	6.004	BB	0.0338	8.02883	0.01102	?

Figure S6. GC-FID of the crude reaction mixture of fructose (0.1 M) and Ru-MACHO-BH (0.5 mol%) using 5.7 M H_3PO_4(aq) under 30 bar H_2 at 125 °C in 1:1 v/v EtOH/H_2O mixture after 48 hours.

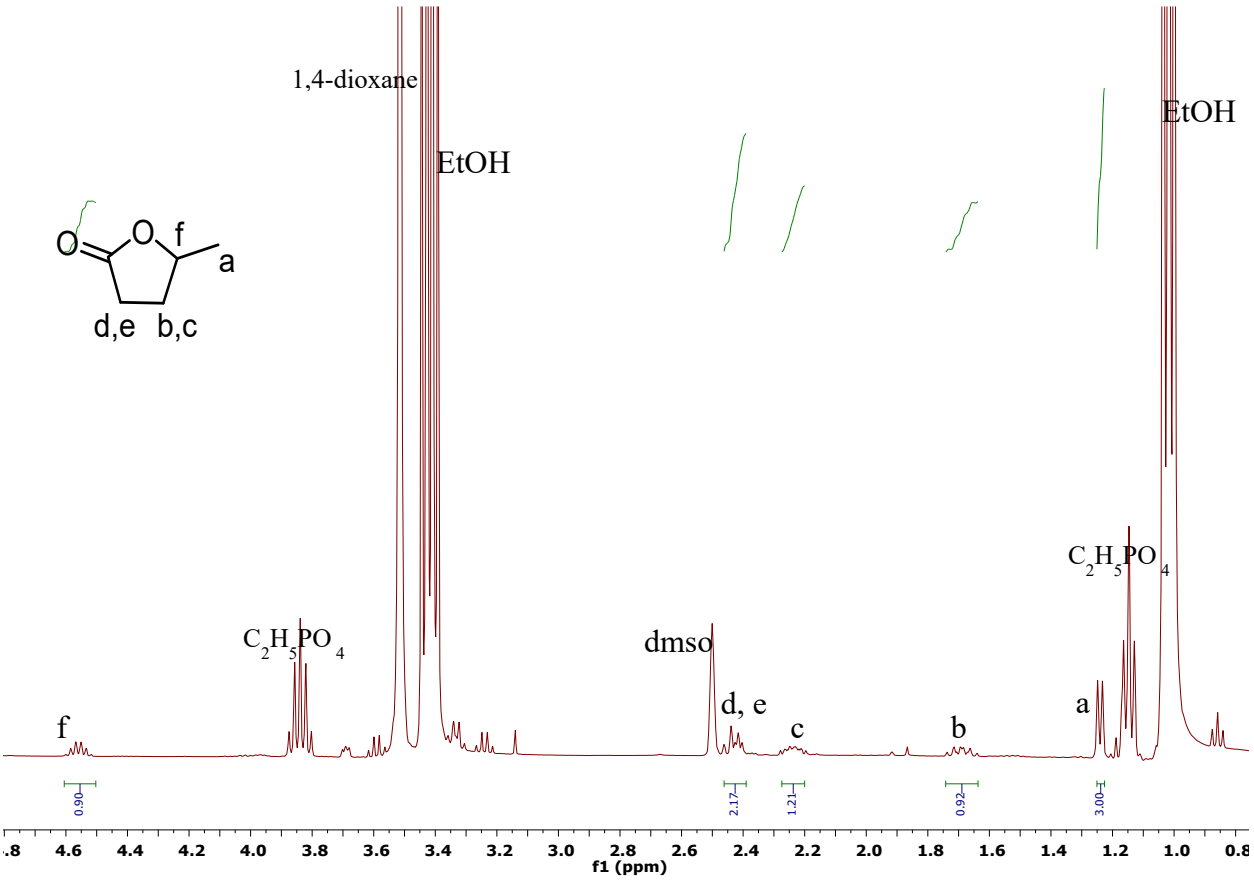
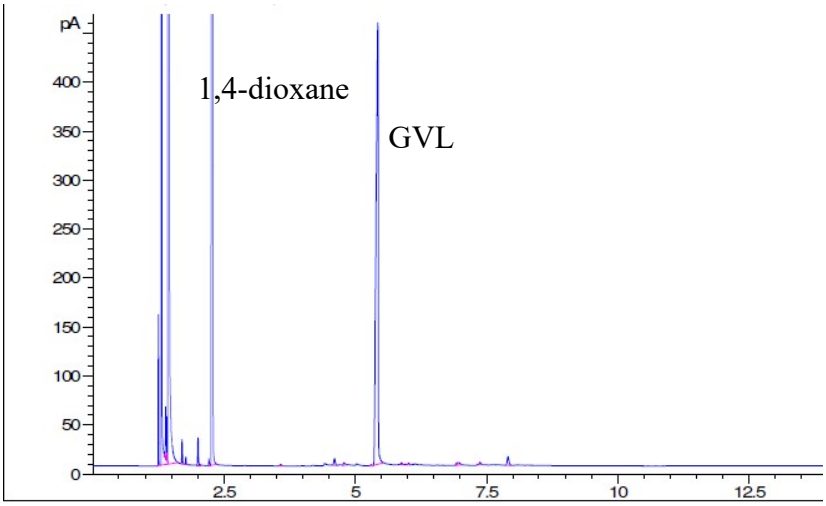


Figure S7. ^{1}H NMR (dmso-d_6, 400 MHz) of the crude reaction of fructose (0.1 M) and Ru-MACHO-BH (0.5 mol%) using 5.7 M H_3PO_4(aq) under 30 bar H_2 at 125 °C in 1:1 v/v EtOH/H_2O mixture after 48 hours.



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3	1.371	BV X	7.34e-3	2.04072	0.00250	?
4	1.393	VV X	0.0144	46.74556	0.05735	?
5	1.414	VV X	8.01e-3	22.86432	0.02805	?
6	1.435	VB S	0.0110	7.19634e4	88.29481	?
7	1.705	BB	0.0120	19.52512	0.02396	?
8	1.776	BB	0.0122	6.01460	0.00738	?
9	2.008	BB	0.0143	25.60098	0.03141	?
10	2.216	BB	0.0155	6.97473	0.00856	?
11	2.282	BB	0.0180	2797.69287	3.43260	?
12	2.993		0.0000	0.00000	0.00000	C14
13	3.466		0.0000	0.00000	0.00000	C15
14	3.578	BB	0.0269	2.47971	0.00304	?
15	3.926		0.0000	0.00000	0.00000	C16
16	4.604	BB	0.0300	12.75125	0.01565	?
17	4.782	BB	0.0295	5.19553	0.00637	?
18	5.305	BB	0.0224	1.40013	0.00172	?
19	5.428	BB	0.0377	1286.33301	1.57825	?
20	5.879	BB	0.0289	3.58793	0.00440	?
21	6.014	BB	0.0273	2.80556	0.00344	?
22	6.932	BV	0.0275	4.75725	0.00584	?
23	6.968	VB	0.0383	7.73025	0.00948	?
24	7.372	BB	0.0338	6.22408	0.00764	?
25	7.910	BB	0.0343	20.13674	0.02471	?

Figure S8. GC-FID of the reaction mixture of xylan from corn core (0.6 M) with 5.7 M of H_3PO_4 and Ru-MACHO-BH (0.5 mol%) under 30 bar H_2 and 125 ºC in 1:1 v/v EtOH/H_2O mixture for 48 hours.

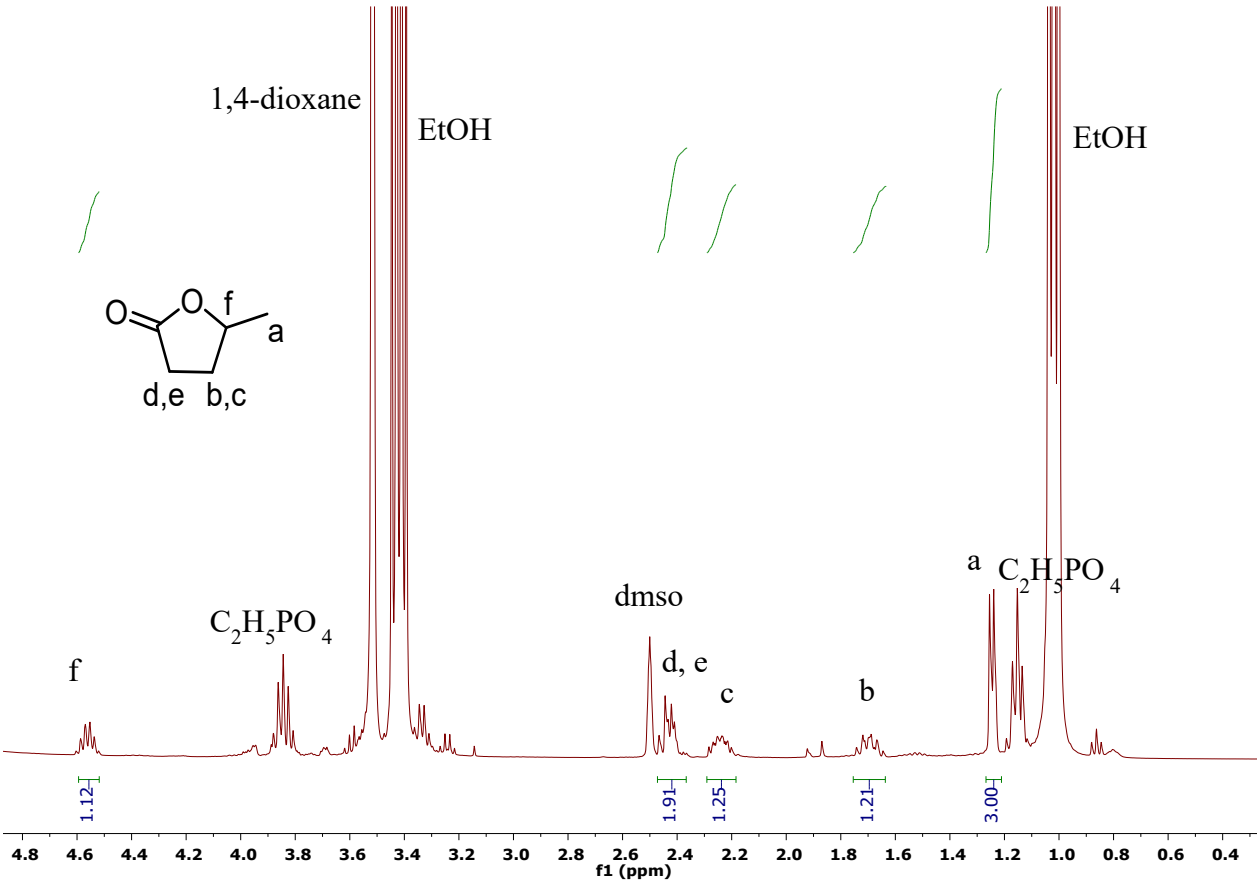
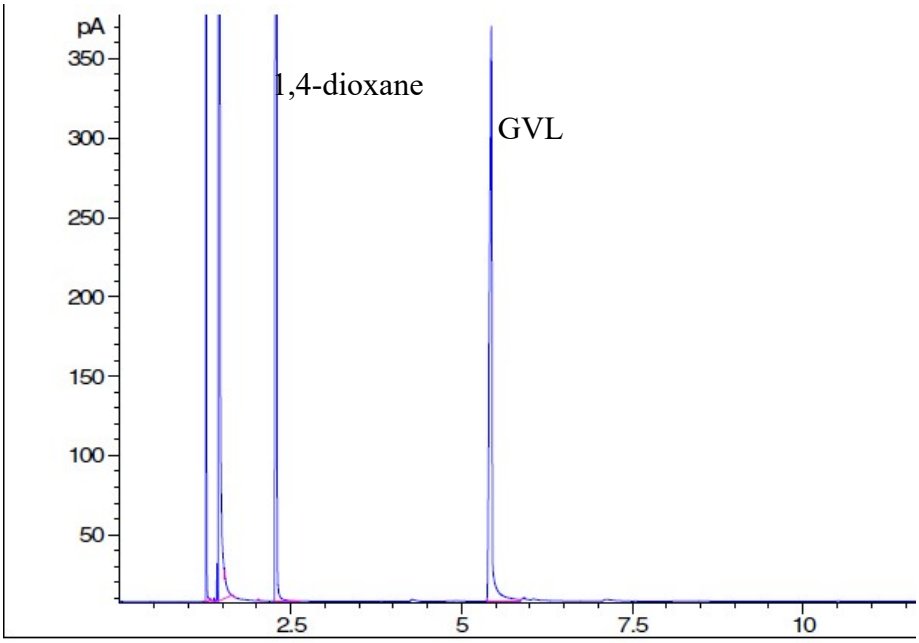


Figure S9. ^{1}H NMR (dmso-d_6, 400 MHz) of the crude reaction of 0.6 mmol Xylan from corn core (0.6 mmol) with 5.7 M of H_3PO_4 and Ru-MACHO-BH (0.5 mol%) under 30 bar H_2 and 125 ^{o}C in 1:1 v/v EtOH/H_2O mixture for 48 hours.



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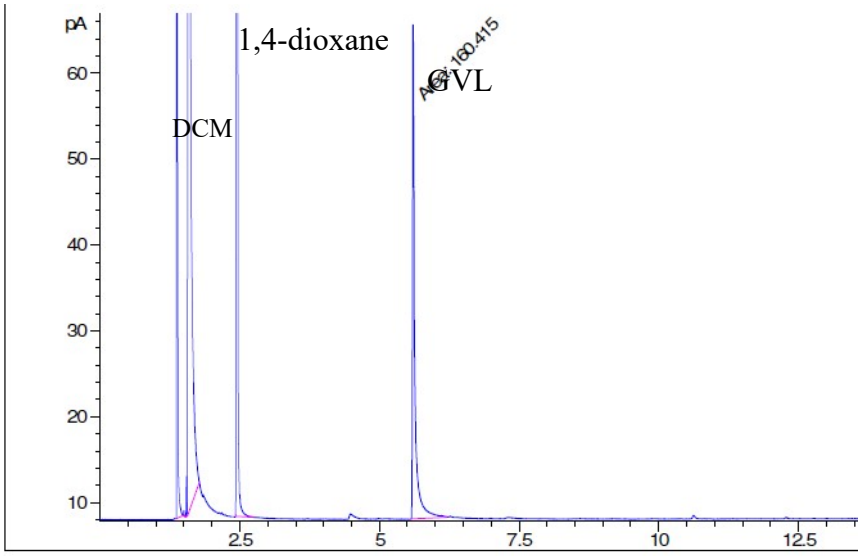
3	1.381	BV	9.55e-3	1.14271	0.00203	?
4	1.424	VV	8.18e-3	12.44108	0.02214	?
5	1.446	VB S	0.0111	5.24361e4	93.31871	?
6	1.533	BB X	9.33e-3	1.75392	0.00312	?
7	1.649	BB	0.0130	4.90495e-1	0.00087	?
8	2.030	BB	0.0176	1.26432	0.00225	?
9	2.292	BH	0.0170	2263.52075	4.02831	?
10	2.993		0.0000	0.00000	0.00000	C14
11	3.466		0.0000	0.00000	0.00000	C15
12	3.926		0.0000	0.00000	0.00000	C16
13	5.435	HH	0.0397	983.90466	1.75102	?

Figure S10: GC-FID of the reaction mixture of cellulose (0.6) with 7.5 M of H_3PO_4(aq) and Ru-MACHO-BH (0.5 mol%) under 30 bar H_2 and 140 °C in water for 96 hours.



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2	1.502	BB	9.87e-3	3.96411e-1	0.00276	?
3	1.549	BV	9.28e-3	2.71882	0.01893	?
4	1.577	VB S	0.0103	1.34929e4	93.95897	?
5	2.450	HB	0.0176	502.00952	3.49578	?
6	2.993		0.0000	0.00000	0.00000	C14
7	3.466		0.0000	0.00000	0.00000	C15
8	3.926		0.0000	0.00000	0.00000	C16
9	5.602	MM	0.0464	160.41508	1.11706	?

Figure S11. GC-FID of the reaction mixture of beechwood sawdust (91 mg) with 10.9 M of H_3PO_4(aq) and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 24 hours (Table 4 in manuscript).

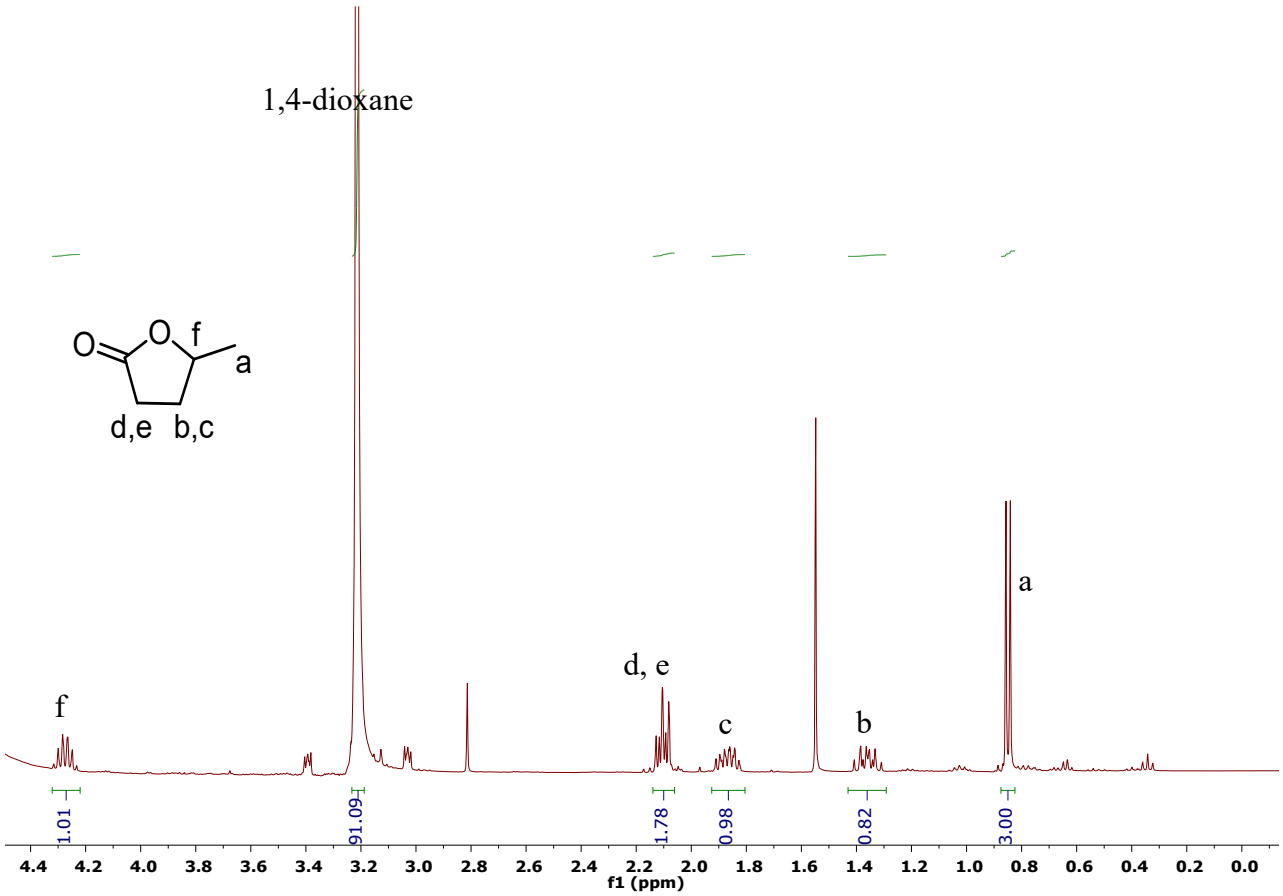
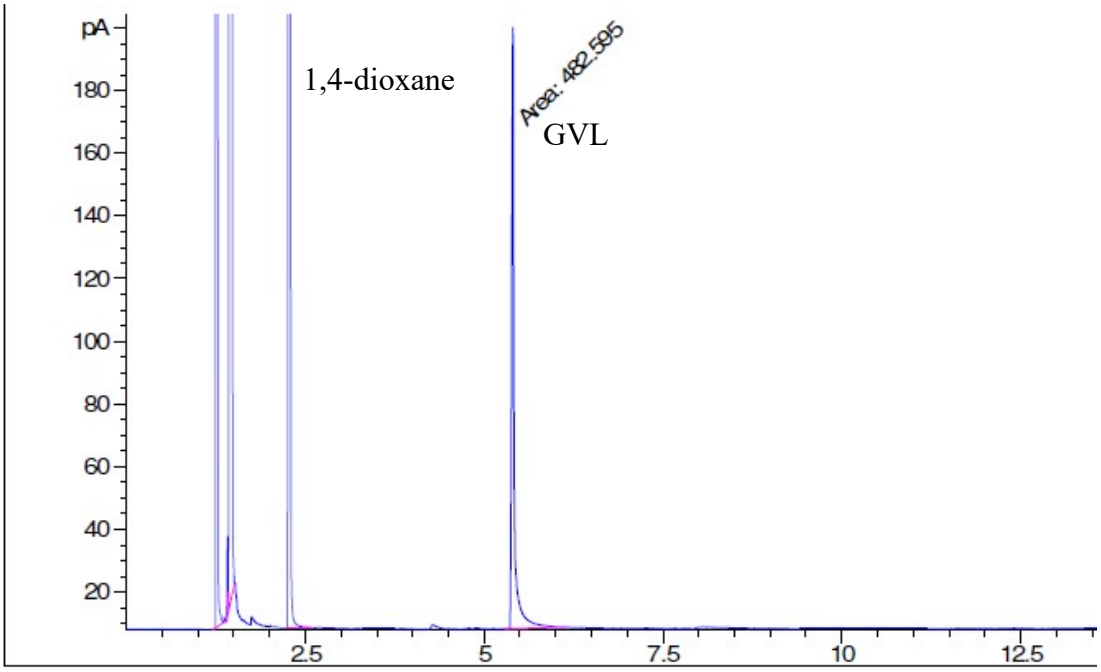


Figure S12. ^{1}H NMR (D_2O, 400 MHz) of the crude reaction of beechwood sawdust (91 mg) with 10.9 M of H_3PO_4(aq) and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 24 hours (Table 4 in manuscript).



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Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %	Name
1	1.257	BB S	0.0122	2293.85376	1.90489	?
2	1.370	BV	0.0120	1.65894	0.00138	?
3	1.414	BV	0.0117	20.32687	0.01688	?
4	1.435	VB S	0.0261	1.15164e5	95.63568	?
5	2.286	BH	0.0252	2457.04810	2.04041	?
6	2.993		0.0000	0.00000	0.00000	C14
7	3.466		0.0000	0.00000	0.00000	C15
8	3.926		0.0000	0.00000	0.00000	C16
9	5.400	MM	0.0419	482.59518	0.40076	?

Figure S13. GC-FID of the reaction mixture of wheat straw (91 mg) with 10.9 M of H_3PO_4(aq) and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 48 hours (Table 4 in manuscript).

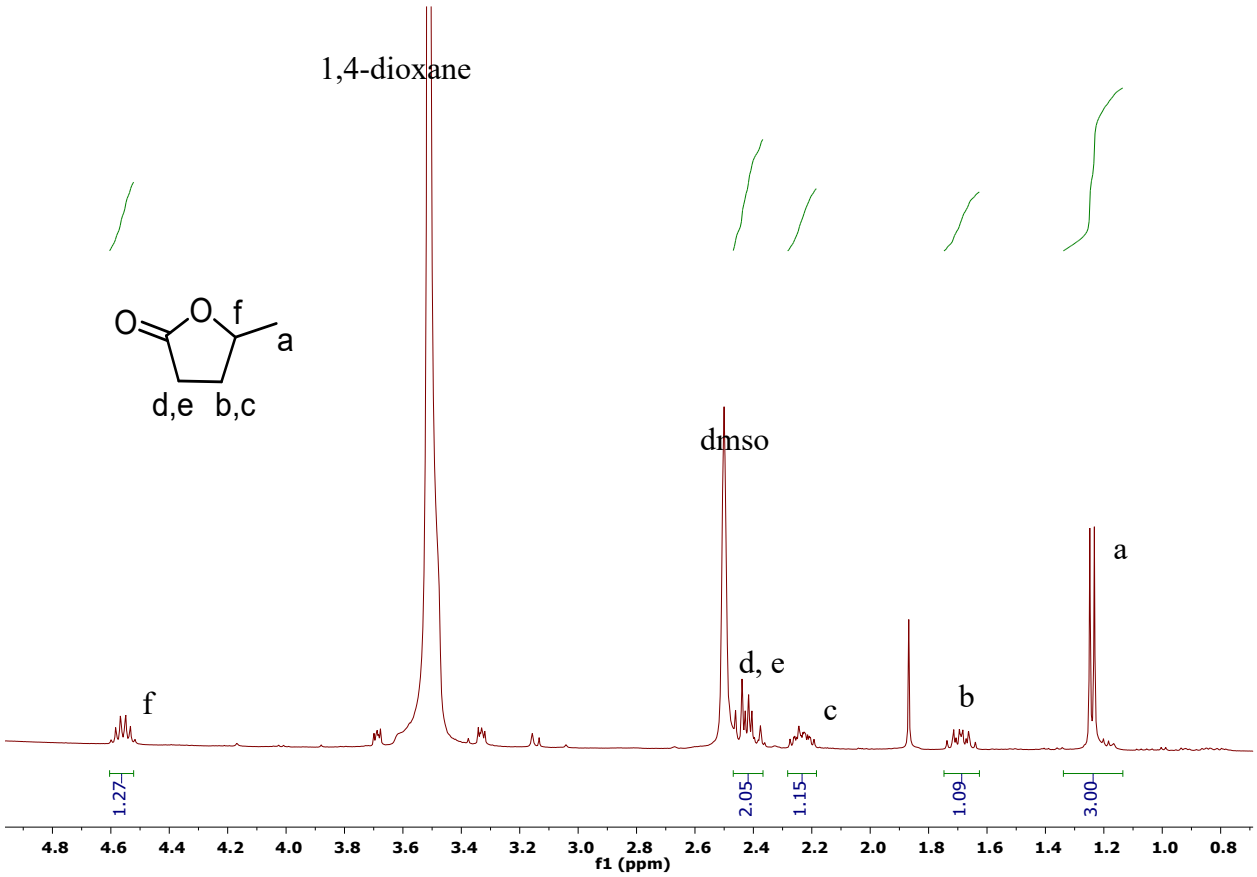
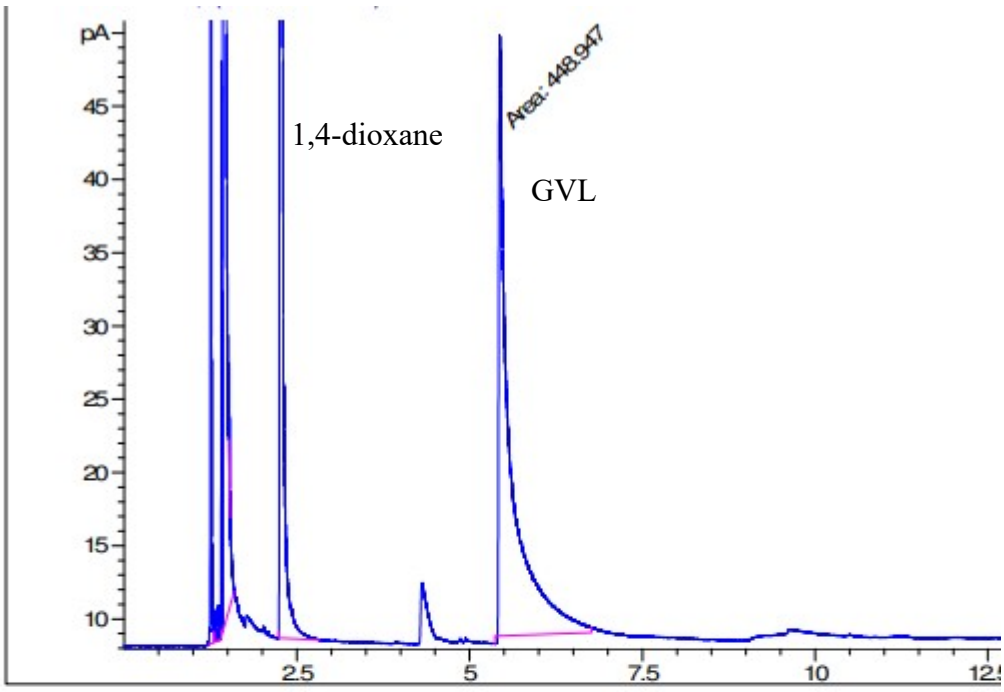


Figure S14. ^{1}H NMR (DMSO-d_6, 400 MHz) of the crude reaction of wheat straw (91 mg) with 10.9 M of H_3PO_4(aq) and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 48 hours (Table 4 in manuscript).



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Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %	Name
1	1.256	BV	8.01e-3	114.89941	0.10618	?
2	1.316	VV	0.0156	2.42280	0.00224	?
3	1.370	VV	8.06e-3	1.22932	0.00114	?
4	1.413	BV	8.33e-3	21.09981	0.01950	?
5	1.433	VB S	0.0145	1.04980e5	97.01040	?
6	1.523	BB X	9.18e-3	4.56623	0.00422	?
7	2.276	HB	0.0176	2642.05371	2.44147	?
8	2.993		0.0000	0.00000	0.00000	C14
9	3.466		0.0000	0.00000	0.00000	C15
10	3.926		0.0000	0.00000	0.00000	C16
11	5.434	MM	0.1824	448.94739	0.41486	?

Figure S15. GC-FID of the reaction mixture of bamboo stem (91 mg) with 10.9 M of H_3PO_4(aq) and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 48 hours (Table 4 in manuscript).

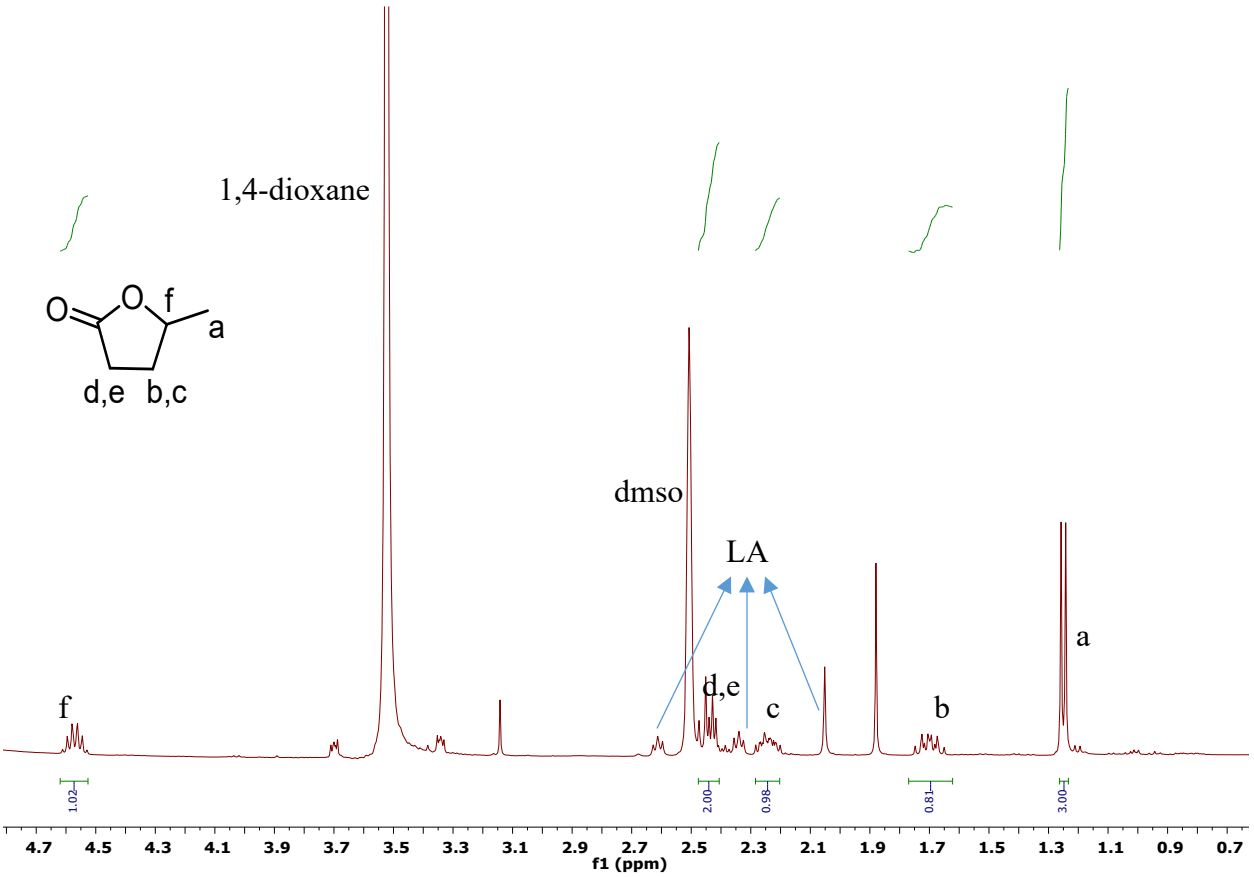


Figure S16. ^{1}H NMR (DMSO-d_6, 400 MHz) of the crude reaction of bamboo stem (91 mg) with 10.9 M of H_3PO_4(aq) and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 48 hours (Table 4 in manuscript).

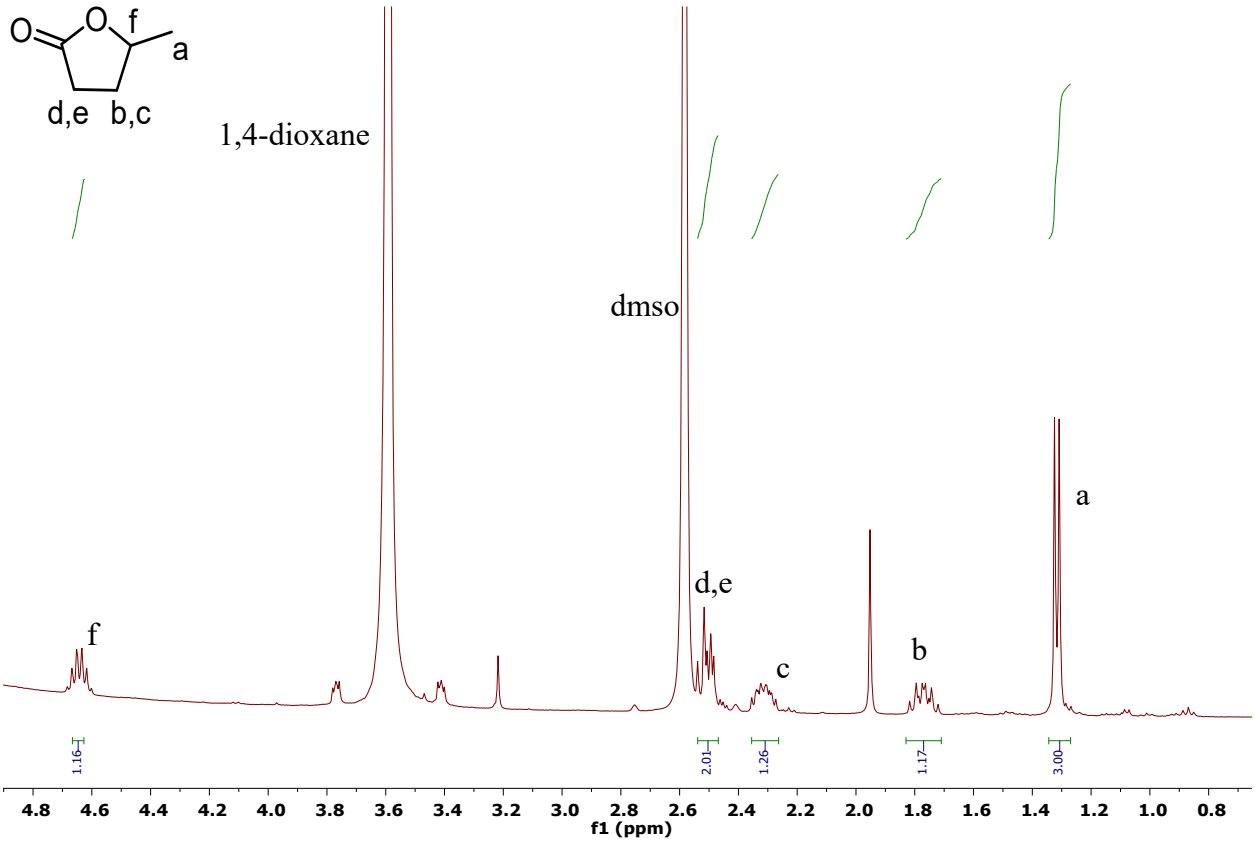
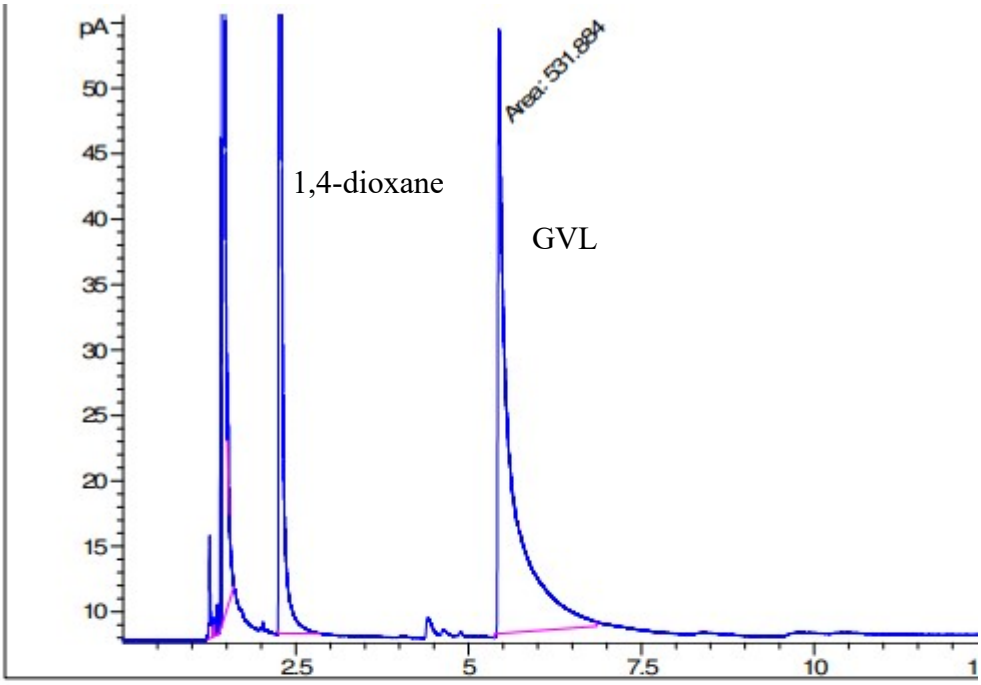


Figure S17. ^{1}H NMR (DMSO-d_6, 400 MHz) of the crude reaction of bamboo stem (91 mg) with 10.9 M of H_3PO_4(aq) and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 96 hours (Table 4 in manuscript).



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Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %	Name
1	1.257	BV	0.0142	8.14015	0.00760	?
2	1.307	VV	8.56e-3	7.91185e-1	0.00074	?
3	1.319	VB	0.0133	1.29824	0.00121	?
4	1.369	BB	7.58e-3	1.06093	0.00099	?
5	1.412	BV	8.60e-3	19.80924	0.01850	?
6	1.433	VB S	0.0143	1.04414e5	97.52235	?
7	1.523	BB X	9.46e-3	4.80699	0.00449	?
8	2.273	HB	0.0175	2084.95435	1.94734	?
9	2.993		0.0000	0.00000	0.00000	C14
10	3.466		0.0000	0.00000	0.00000	C15
11	3.926		0.0000	0.00000	0.00000	C16
12	5.435	MM	0.1920	531.88446	0.49678	?

Figure S18. GC-FID of the reaction mixture of paper (91 mg) with 10.9 M of H_3PO_4(aq) and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 48 hours (Table 4 in manuscript).

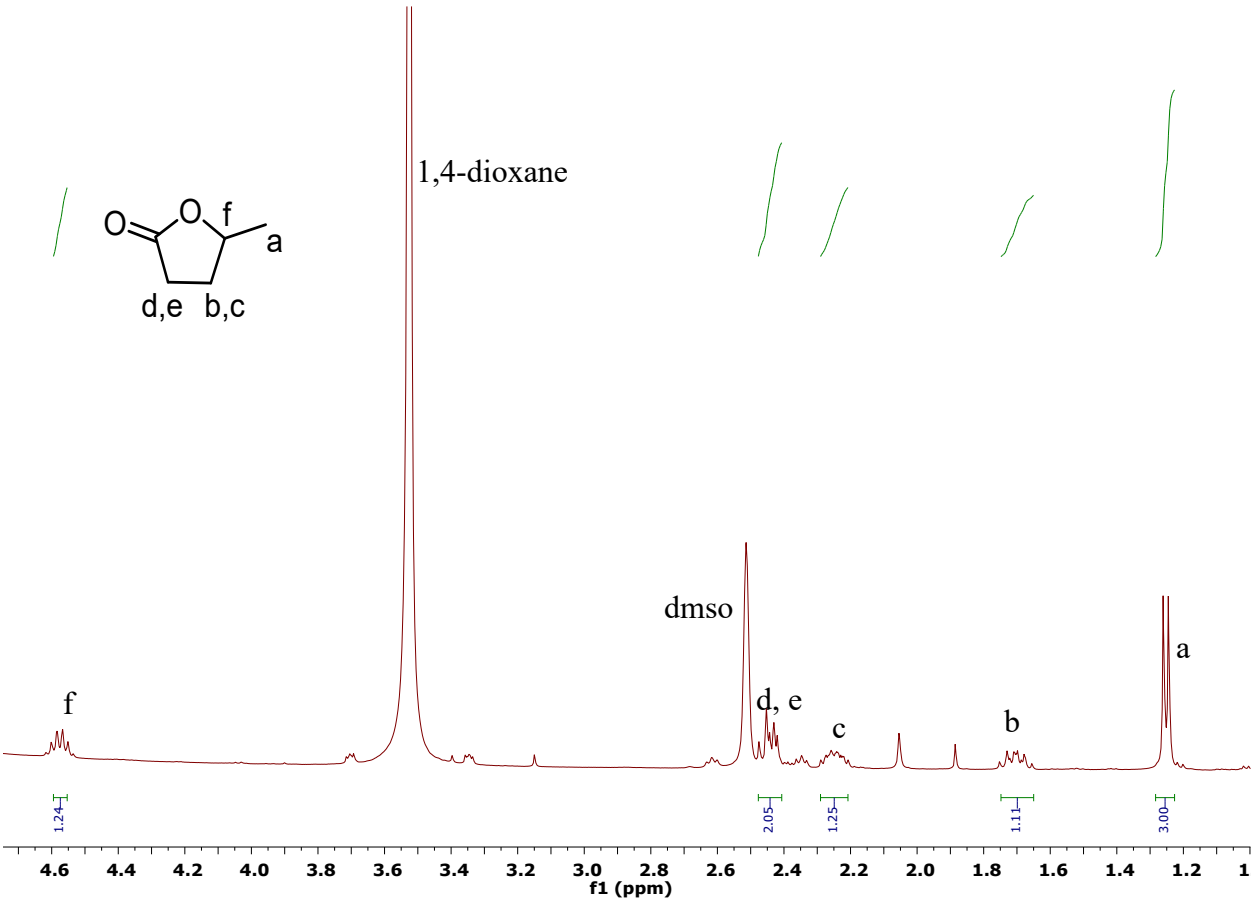
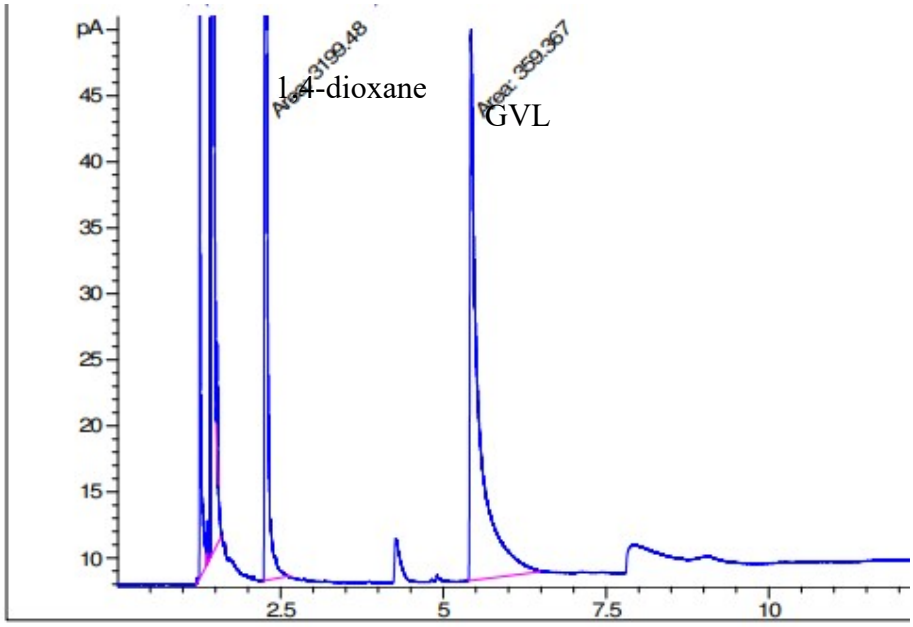


Figure S19. ^{1}H NMR (DMSO-d_6, 400 MHz) of the crude reaction of paper (91 mg) with 10.9 M of H_3PO_4(aq) and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 48 hours (Table 4 in manuscript).



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Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %	Name
1	1.208	BB	8.69e-3	2.49820e-1	0.00022	?
2	1.256	BV	0.0101	73.56629	0.06408	?
3	1.369	VV	0.0104	2.37678	0.00207	?
4	1.413	VV	8.48e-3	22.61652	0.01970	?
5	1.433	VB S	0.0148	1.11096e5	96.76491	?
6	1.524	BB X	9.56e-3	5.10735	0.00445	?
7	2.280	MM	0.0202	3199.48071	2.78677	?
8	2.993		0.0000	0.00000	0.00000	C14
9	3.466		0.0000	0.00000	0.00000	C15
10	3.926		0.0000	0.00000	0.00000	C16
11	5.427	MM	0.1435	359.36694	0.31301	?
12	19.115	BB	0.0783	51.43044	0.04480	?

Figure S20. GC-FID of the reaction mixture of miscanthus grass (91 mg) with 10.9 M of H_3PO_4(aq) and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 48 hours (Table 4 in manuscript).

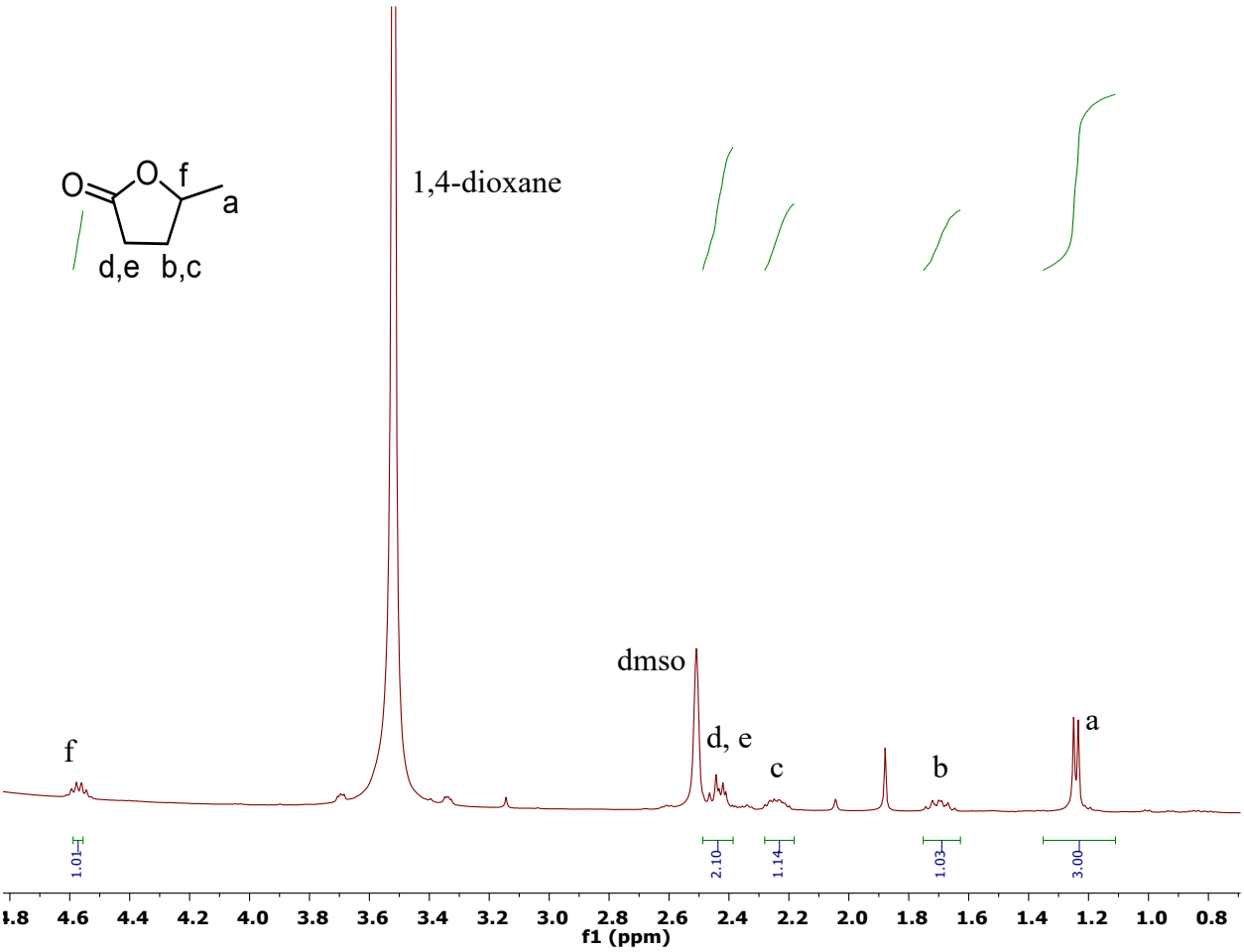
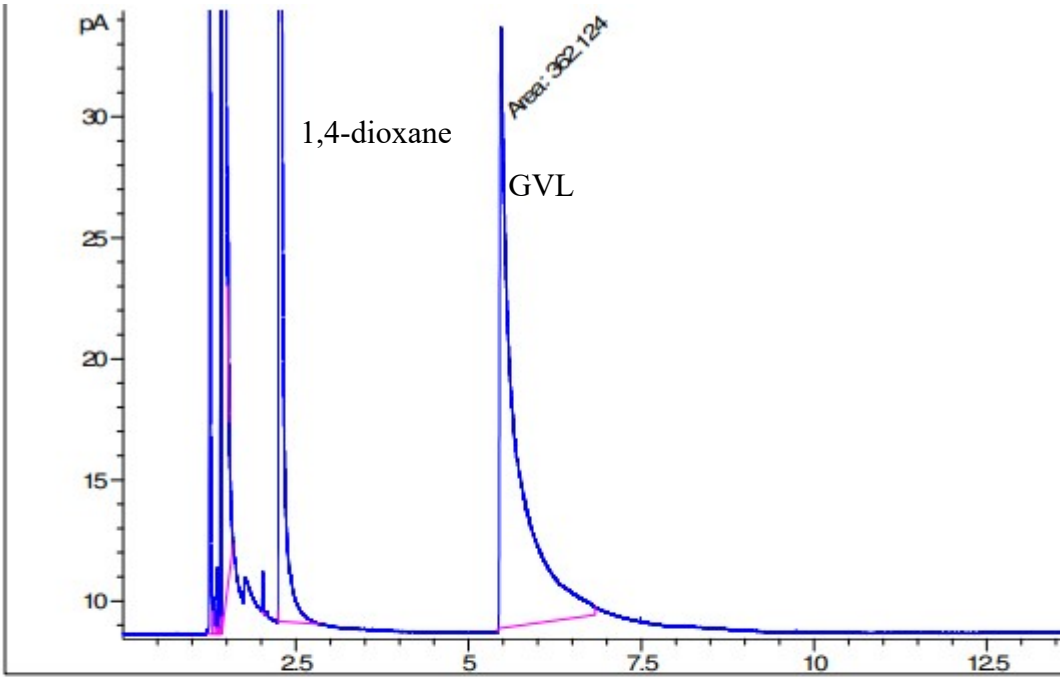


Figure S21. ^{1}H NMR (DMSO-d_6, 400 MHz) of the crude reaction of miscanthus grass (91 mg) with 10.9 M of H_3PO_4(aq) and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 48 hours (Table 4 in manuscript).



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Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %	Name
1	1.256	BV	7.32e-3	203.24084	0.18245	?
2	1.308	VV	0.0216	2.64006	0.00237	?
3	1.370	VV	9.60e-3	1.78459	0.00160	?
4	1.413	VV	8.53e-3	22.59807	0.02029	?
5	1.433	VB S	0.0144	1.08294e5	97.21673	?
6	1.524	BB X	9.42e-3	4.62379	0.00415	?
7	2.023	BB	0.0164	1.80526	0.00162	?
8	2.275	HB	0.0180	2501.60205	2.24571	?
9	2.993		0.0000	0.00000	0.00000	C14
10	3.466		0.0000	0.00000	0.00000	C15
11	3.926		0.0000	0.00000	0.00000	C16
12	5.468	MM	0.2432	362.12445	0.32508	?

Figure S22. GC-FID of the reaction mixture of pistachio shells (91 mg) with 10.9 M of H_3PO_4(aq) and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water after 72 hours (Table 4 in manuscript).

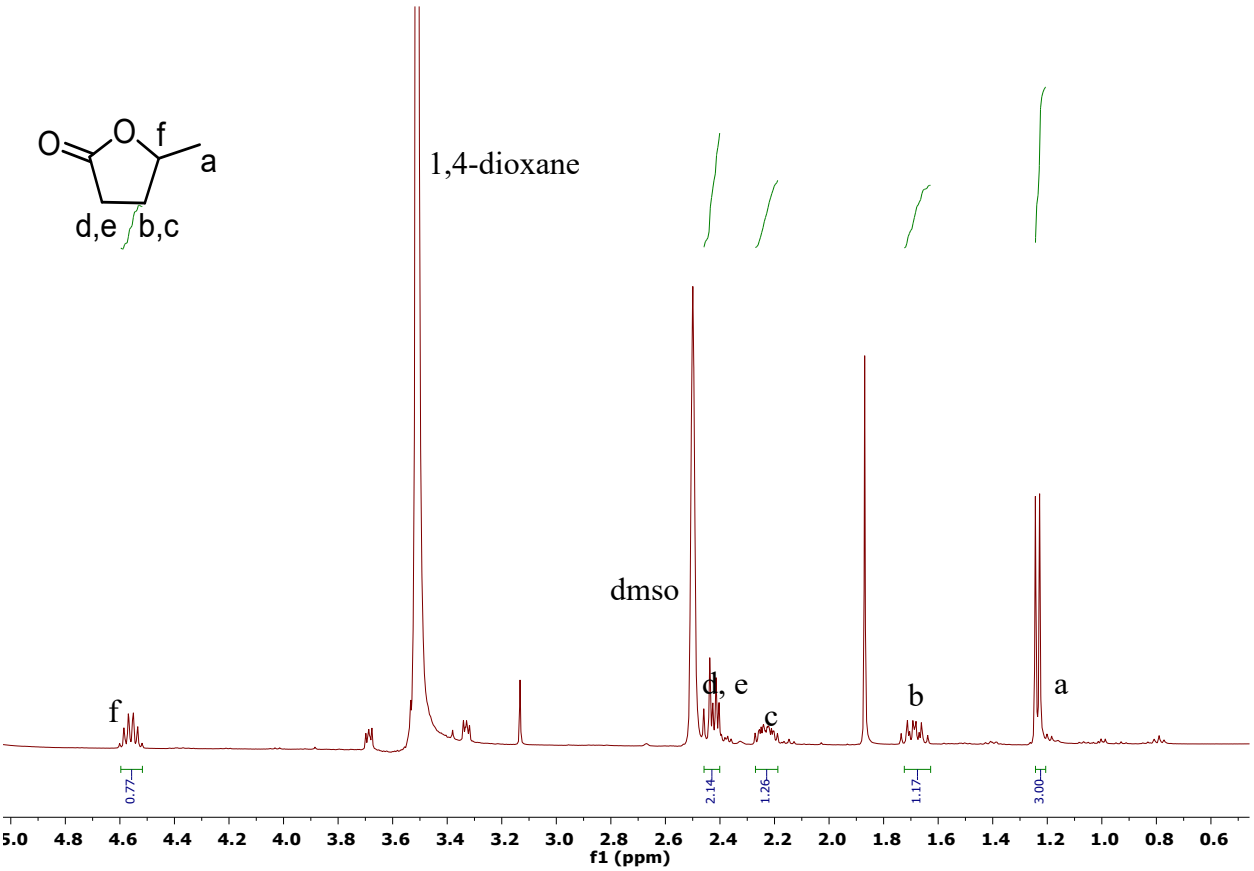
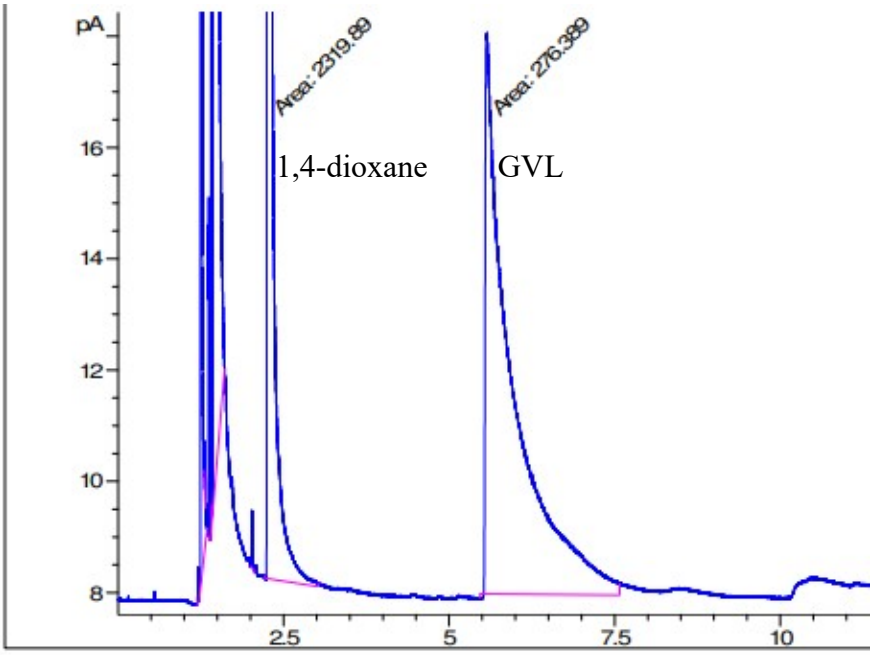


Figure S23. ^{1}H NMR (DMSO-d_6, 400 MHz) of the crude reaction of pistachio shells (91 mg) with 10.9 M of H_3PO_4(aq) and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 72 hours (Table 4 in manuscript).



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Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %	Name
1	1.208	BB	8.37e-3	3.49768e-1	0.00030	?
2	1.255	BB S	7.53e-3	356.68106	0.30155	?
3	1.307	BB X	0.0106	5.12615e-1	0.00043	?
4	1.371	BB	8.28e-3	3.26983	0.00276	?
5	1.412	BV	8.37e-3	22.13661	0.01871	?
6	1.432	VB S	0.0150	1.15298e5	97.47626	?
7	1.523	BB X	9.43e-3	4.75673	0.00402	?
8	2.026	BB	0.0171	1.16840	0.00099	?
9	2.277	MM	0.0194	2319.88721	1.96131	?
10	2.993		0.0000	0.00000	0.00000	C14
11	3.466		0.0000	0.00000	0.00000	C15
12	3.926		0.0000	0.00000	0.00000	C16
13	5.572	MM	0.4569	276.38931	0.23367	?

Totals : 1.18283e5

Figure S24. GC-FID of the reaction mixture of banana peel (91 mg) with 10.9 M of H_3PO_4(aq) and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water after 96 hours (Table 4 in manuscript).

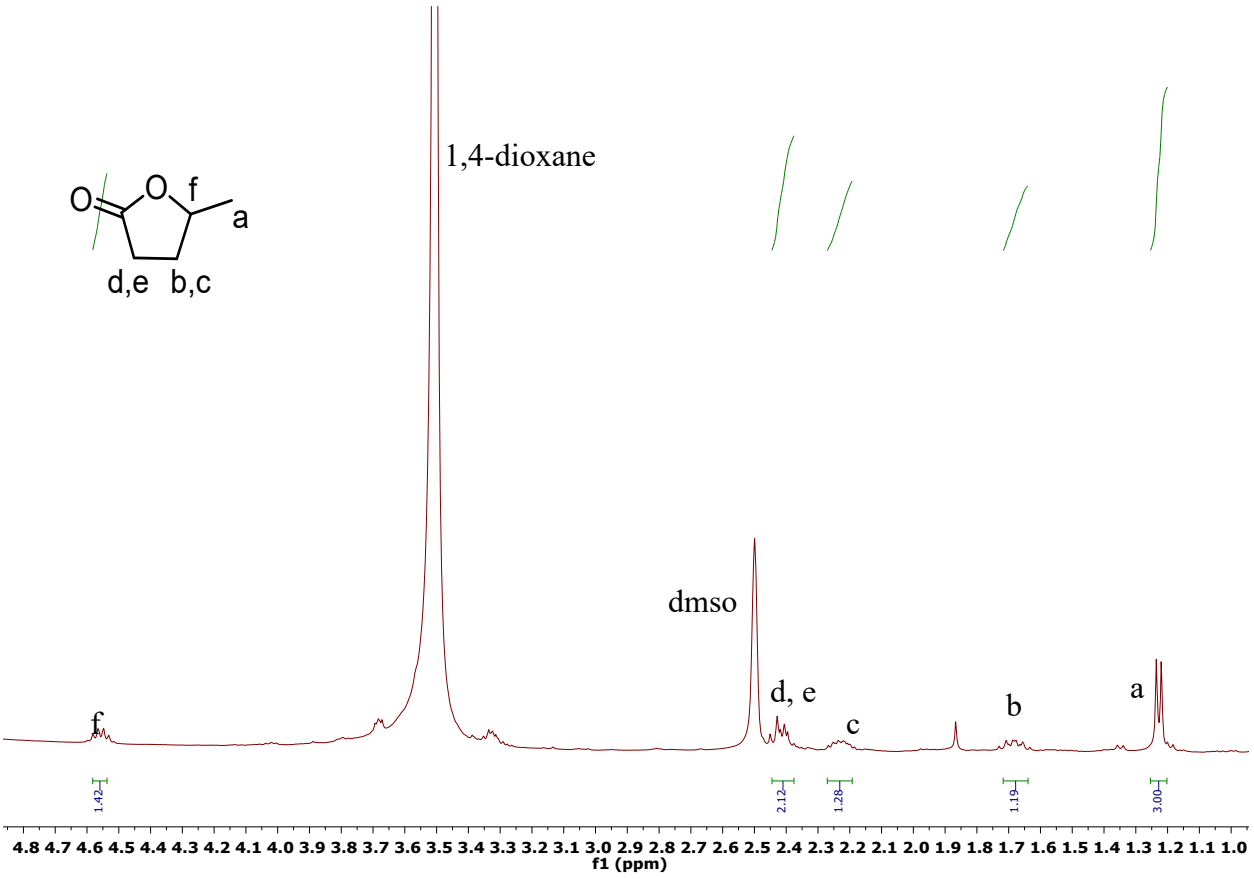
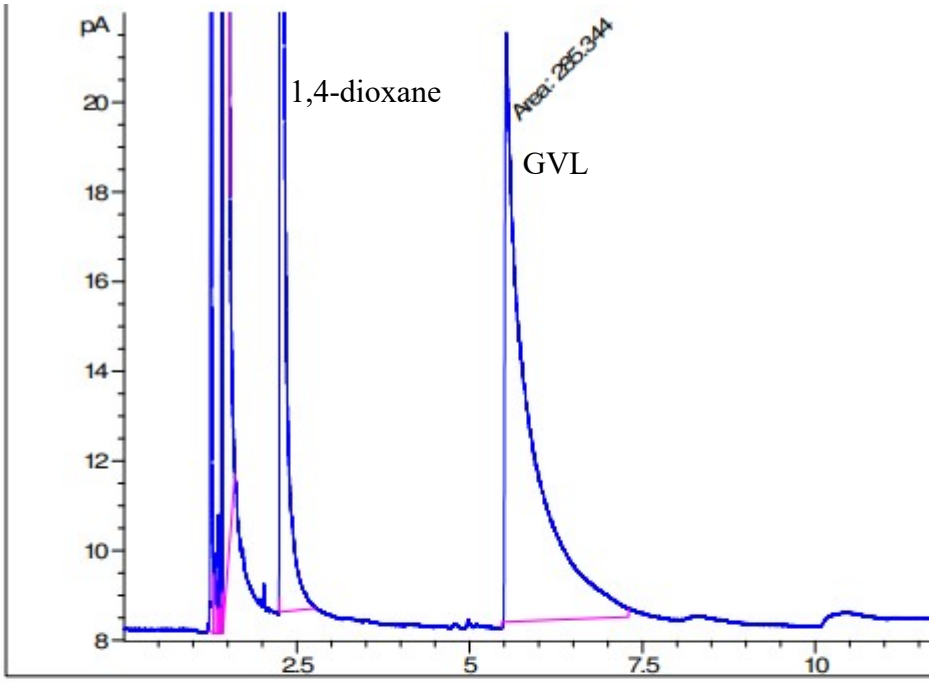


Figure S25. ^{1}H NMR (DMSO-d_6, 400 MHz) of the crude reaction of banana peel (91 mg) with 10.9 M of H_3PO_4(aq) and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 96 hours (Table 4 in manuscript).



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Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %	Name
1	1.256	BV	7.21e-3	196.77211	0.17131	?
2	1.308	VV	0.0249	3.56810	0.00311	?
3	1.370	VV	0.0120	2.26136	0.00197	?
4	1.413	VV	8.61e-3	20.91136	0.01821	?
5	1.432	VB S	0.0150	1.12096e5	97.58983	?
6	1.524	BB X	9.12e-3	4.52648	0.00394	?
7	2.276	HB	0.0174	2255.04639	1.96323	?
8	2.993		0.0000	0.00000	0.00000	C14
9	3.466		0.0000	0.00000	0.00000	C15
10	3.926		0.0000	0.00000	0.00000	C16
11	5.529	MM	0.3617	285.34384	0.24842	?

Figure S26. GC-FID of the reaction mixture of potato peel (91 mg) with 10.9 M of H_3PO_4(aq) and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water after 72 hours (Table 4 in manuscript).

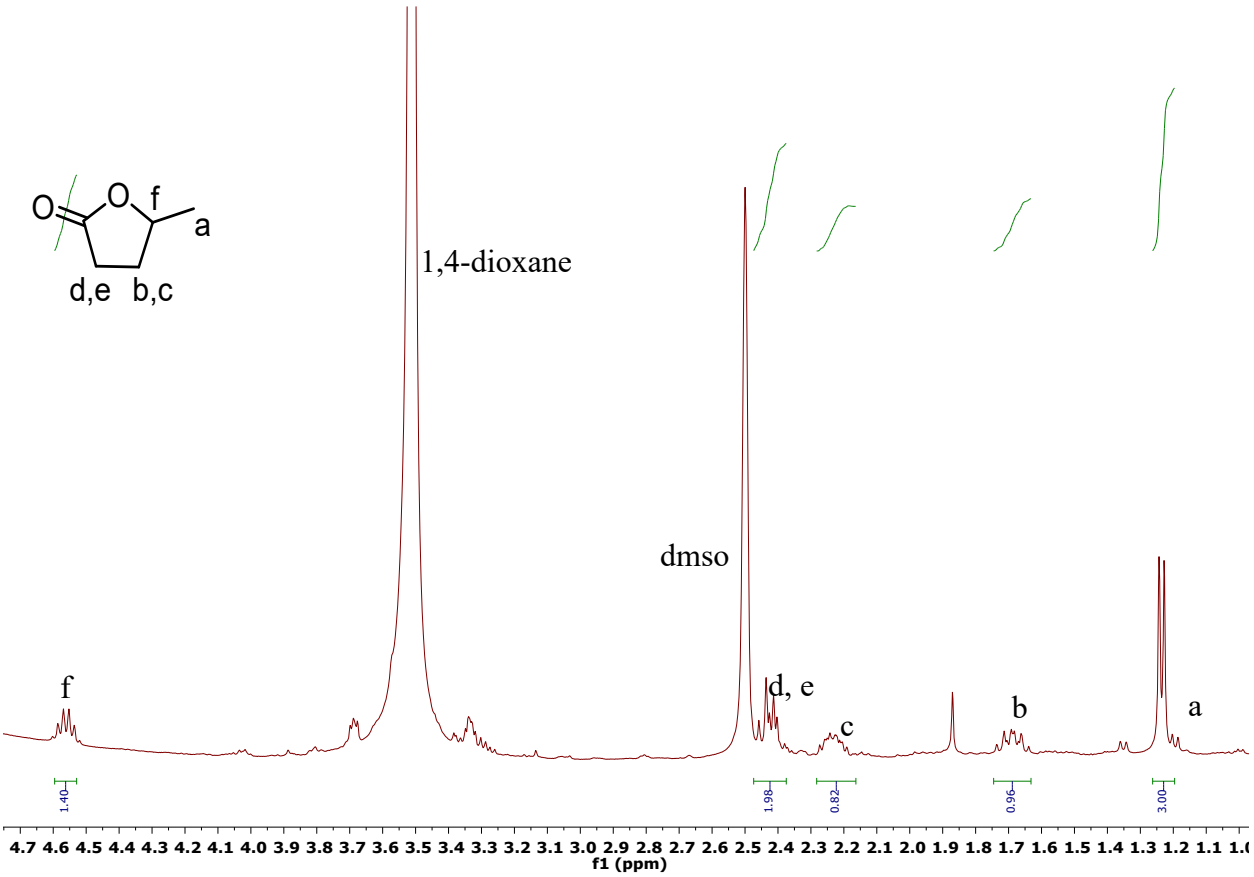
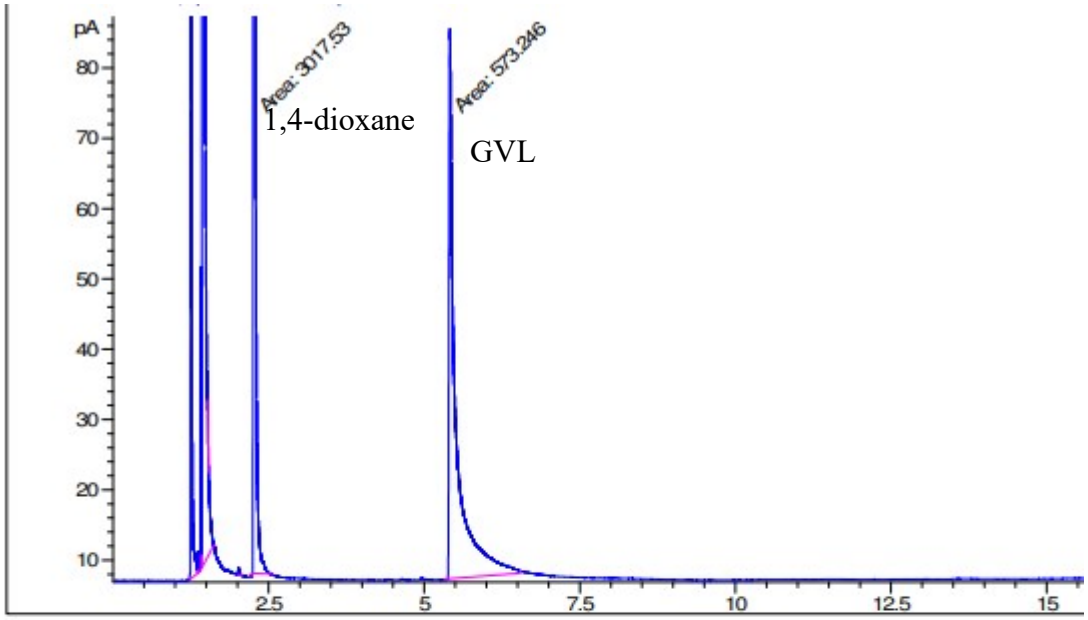


Figure S27. ^{1}H NMR (DMSO-d_6, 400 MHz) of the crude reaction of potato peel (91 mg) with 10.9 M of H_3PO_4(aq) and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 72 hours (Table 4 in manuscript).



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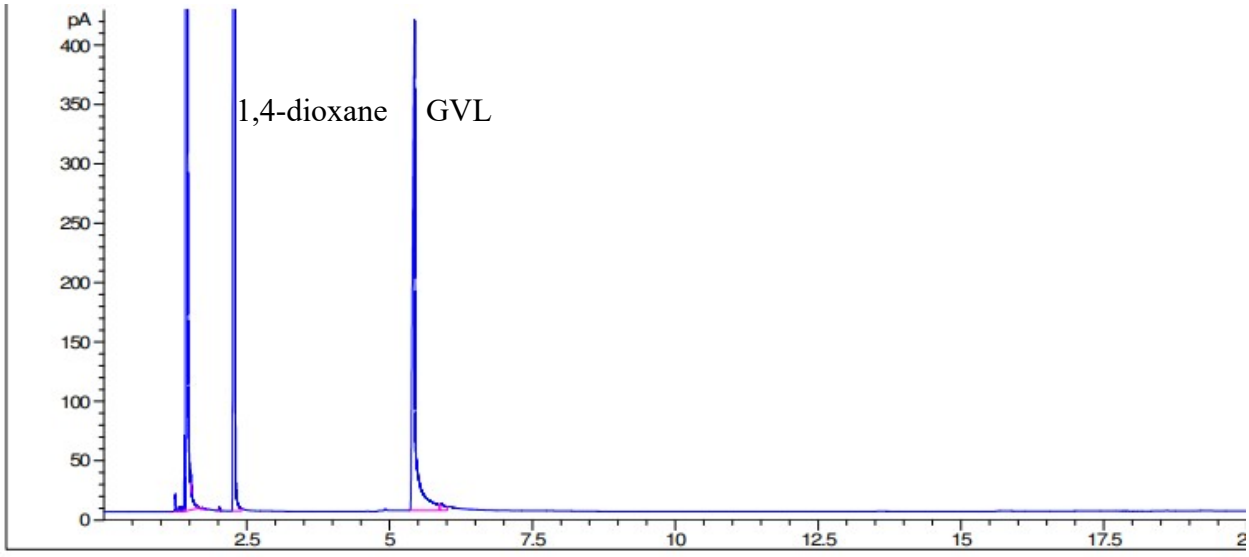
Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %	Name
1	1.255	BV	9.37e-3	296.92310	0.22451	?
2	1.369	VB	9.51e-3	1.89549	0.00143	?
3	1.412	BV	9.39e-3	25.52670	0.01930	?
4	1.432	VB S	0.0161	1.28332e5	97.03557	?
5	1.522	BB X	0.0108	4.24467	0.00321	?
6	2.023	BB	0.0176	1.17273	0.00089	?
7	2.280	MM	0.0209	3017.52808	2.28164	?
8	2.993		0.0000	0.00000	0.00000	C14
9	3.466		0.0000	0.00000	0.00000	C15
10	3.926		0.0000	0.00000	0.00000	C16
11	5.411	MM	0.1221	573.24591	0.43345	?
Totals :				1.32253e5		

Figure S28. GC-FID of the reaction mixture of rice grains (91 mg) with 10.9 M of H_3PO_4 and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 72 hours (Table 5 in manuscript).



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Dilution : 1.0000
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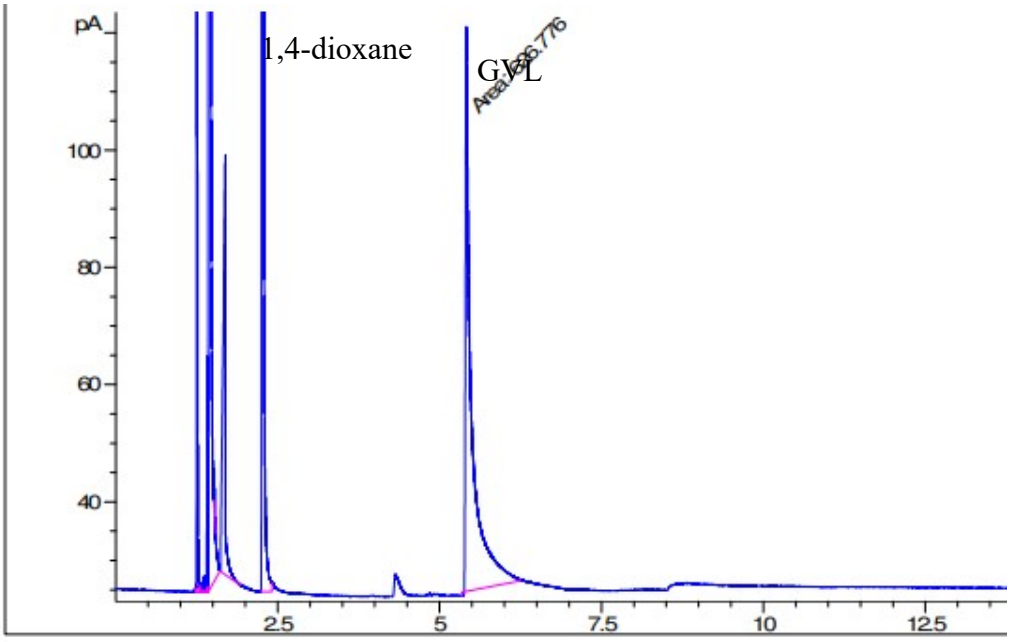
Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %	Name
1	1.255	BB	0.0100	10.00459	0.00536	?
2	1.316	BB	0.0147	3.70818	0.00199	?
3	1.368	BB	7.96e-3	2.03438	0.00109	?
4	1.411	BV	8.68e-3	36.07652	0.01932	?
5	1.432	VB S	0.0190	1.79040e5	95.89713	?
6	1.526	BB X	9.07e-3	7.12259	0.00381	?
7	1.630	BB X	9.42e-3	2.87165e-1	0.00015	?
8	1.724	BB	0.0369	3.21941	0.00172	?
9	2.021	BB	0.0176	3.45120	0.00185	?
10	2.294	HH	0.0217	6137.80908	3.28753	?
11	2.993		0.0000	0.00000	0.00000	C14
12	3.466		0.0000	0.00000	0.00000	C15
13	3.926		0.0000	0.00000	0.00000	C16
14	5.434	HH	0.0439	1424.71912	0.76311	?
15	5.900	HH	0.0656	31.61740	0.01693	?

Totals : 1.86700e5

Figure S29. GC-FID of the reaction mixture of potato flour (91 mg) with 10.9 M of H_3PO_4 and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 72 hours (Table 5 in manuscript).



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Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %	Name
1	1.238	BV	7.60e-3	6.41491e-1	0.00053	?
2	1.256	VV	7.59e-3	183.67702	0.15249	?
3	1.308	VV	0.0215	2.76684	0.00230	?
4	1.370	VV	0.0101	1.84508	0.00153	?
5	1.413	VV	8.82e-3	23.41998	0.01944	?
6	1.433	VB S	0.0149	1.16551e5	96.76067	?
7	1.524	BB X	9.67e-3	5.00796	0.00416	?
8	1.694	BB	0.0328	188.25348	0.15629	?
9	2.280	HH	0.0182	2869.48584	2.38224	?
10	2.993		0.0000	0.00000	0.00000	C14
11	3.466		0.0000	0.00000	0.00000	C15
12	3.926		0.0000	0.00000	0.00000	C16
13	5.413	MM	0.1085	626.77557	0.52035	?

Figure S30. GC-FID of the reaction mixture of chitin (0.6 mmol) with 10.9 M of H_3PO_4(aq) and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 96 hours (Table 4 in manuscript).

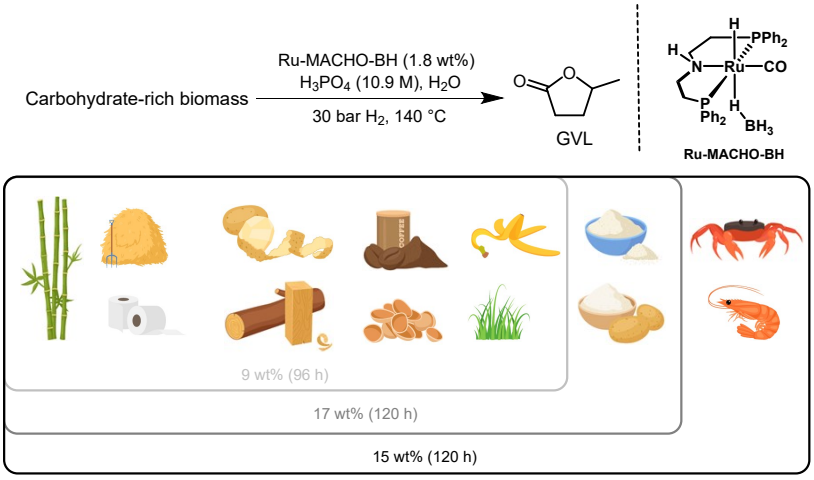
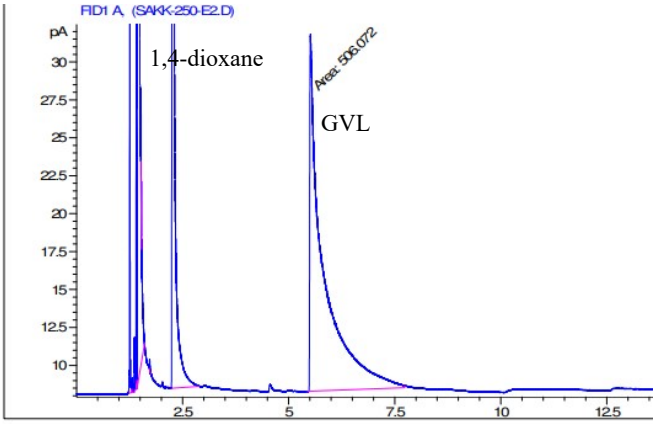


Figure S31. Conversion of carbohydrate-rich biomass to GVL by the Ru-MACHO-BH/ H_3PO_4(aq)/H_2 system. Yields are calculated corresponding to the moles of cellulose and hemicellulose.



Area Percent Report

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Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

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1	1.257	BV	8.58e-3	16.93864	0.01707	?
2	1.320	VB	0.0129	9.07395e-1	0.00091	?
3	1.370	BB	7.34e-3	1.59424	0.00161	?
4	1.412	BV	8.02e-3	21.42163	0.02158	?
5	1.430	VB S	0.0136	9.61023e4	96.83200	?
6	1.522	BB X	9.02e-3	3.43370	0.00346	?
7	1.724	BB	0.0133	6.12539e-1	0.00062	?
8	2.273	BB	0.0179	2593.14722	2.61284	?
9	2.993		0.0000	0.00000	0.00000	C14
10	3.466		0.0000	0.00000	0.00000	C15
11	3.926		0.0000	0.00000	0.00000	C16
12	5.511	MM	0.3587	506.07217	0.50991	?

Figure S32. GC-FID of the crude reaction of mixing all eleven substrates (lignocellulosic biomass along with starchy biomass) with 10.9 M of H_3PO_4(aq) and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 120 hours (Fig. 2 in manuscript).

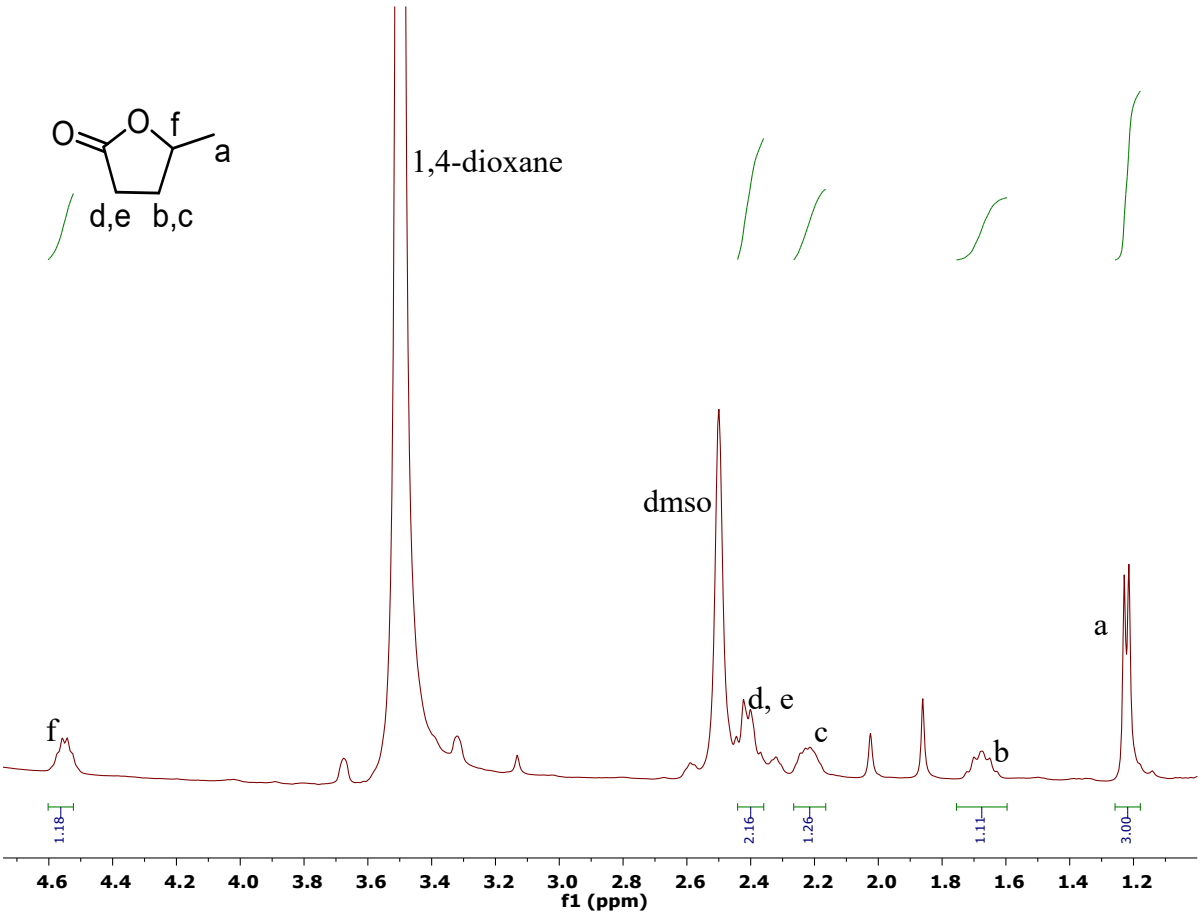
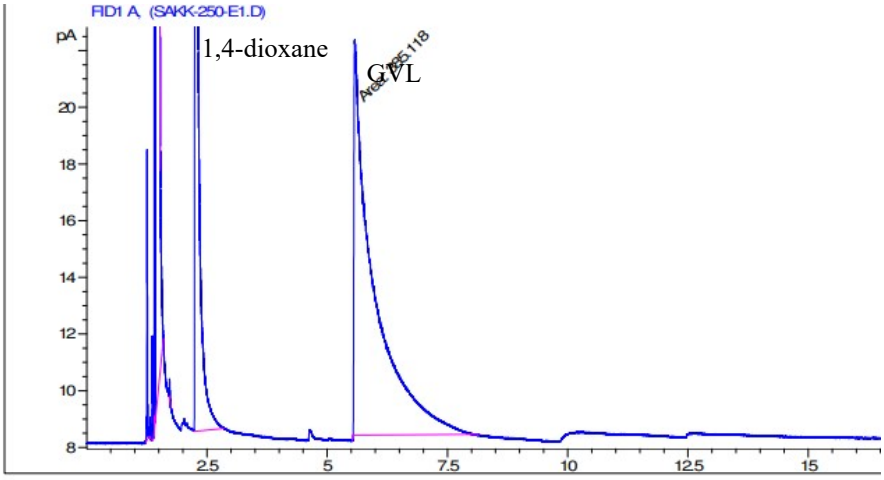


Figure S33. ^{1}H NMR (DMSO-d_6, 400 MHz) of the crude reaction of mixing all eleven substrates (lignocellulosic biomass along with starchy biomass) with 10.9 M of H_3PO_4(aq) and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 120 hours.



Area Percent Report

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Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %	Name
1	1.258	BB	9.57e-3	6.28510	0.00609	?
2	1.320	BB	7.94e-3	3.52435e-1	0.00034	?
3	1.370	BV	7.68e-3	1.77256	0.00172	?
4	1.411	BV	7.97e-3	21.84990	0.02118	?
5	1.430	VB S	0.0141	1.00568e5	97.46867	?
6	1.522	BB X	9.02e-3	3.63259	0.00352	?
7	1.725	BB	0.0134	6.24076e-1	0.00060	?
8	2.271	BB	0.0176	2192.19141	2.12463	?
9	2.993		0.0000	0.00000	0.00000	C14
10	3.466		0.0000	0.00000	0.00000	C15
11	3.926		0.0000	0.00000	0.00000	C16
12	5.569	MM	0.4607	385.11813	0.37325	?

Figure S34. GC-FID of the crude reaction of mixing all eleven substrates (lignocellulosic, starchy and chitin biomass) with 10.9 M of H_3PO_4(aq) and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 120 hours.

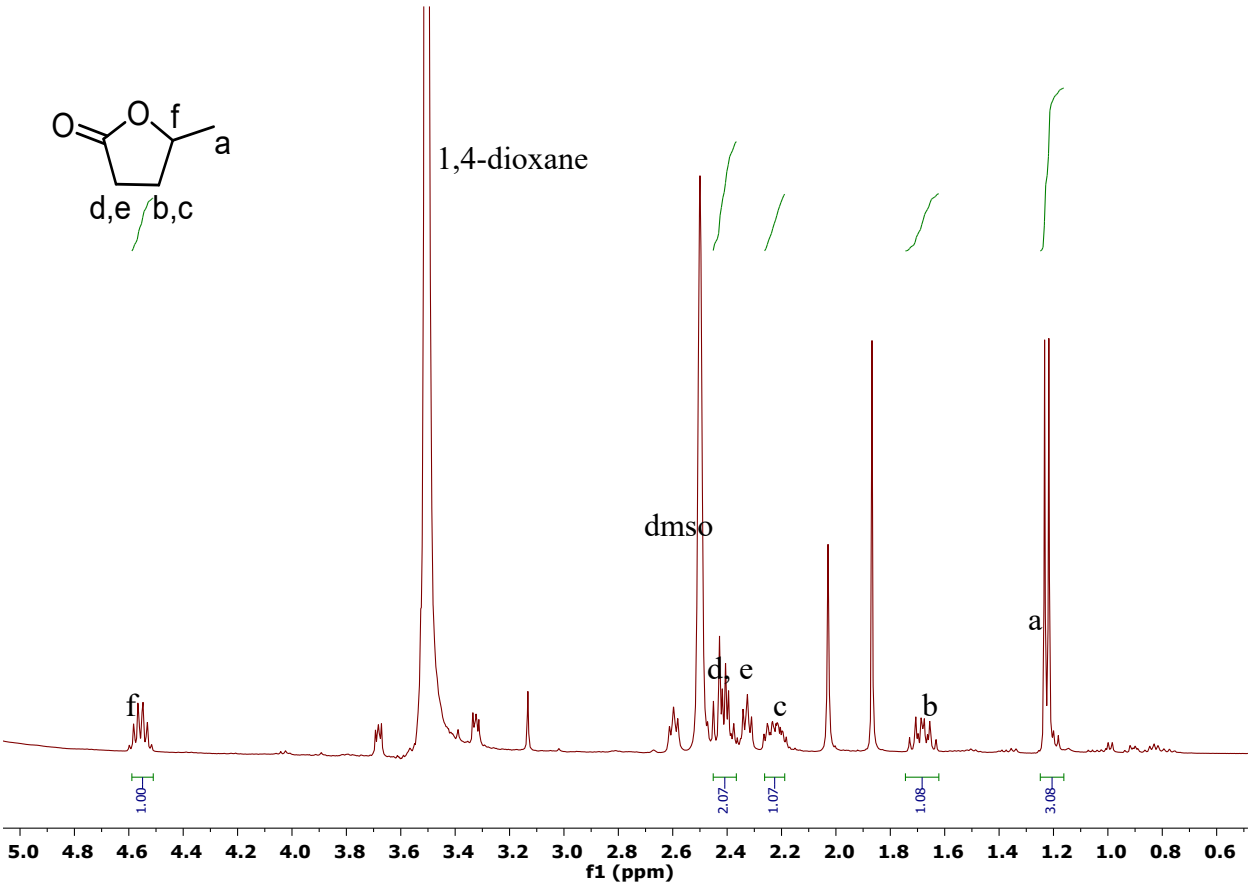

Figure S35. ^{1}H NMR (DMSO-d_6, 400 MHz) of the crude reaction of mixing all twelve substrates (lignocellulosic, starchy and chitin biomass) with 10.9 M of H_3PO_4(aq) and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 120 hours.

Gas phase analysis by MicroGC

External Standard Report

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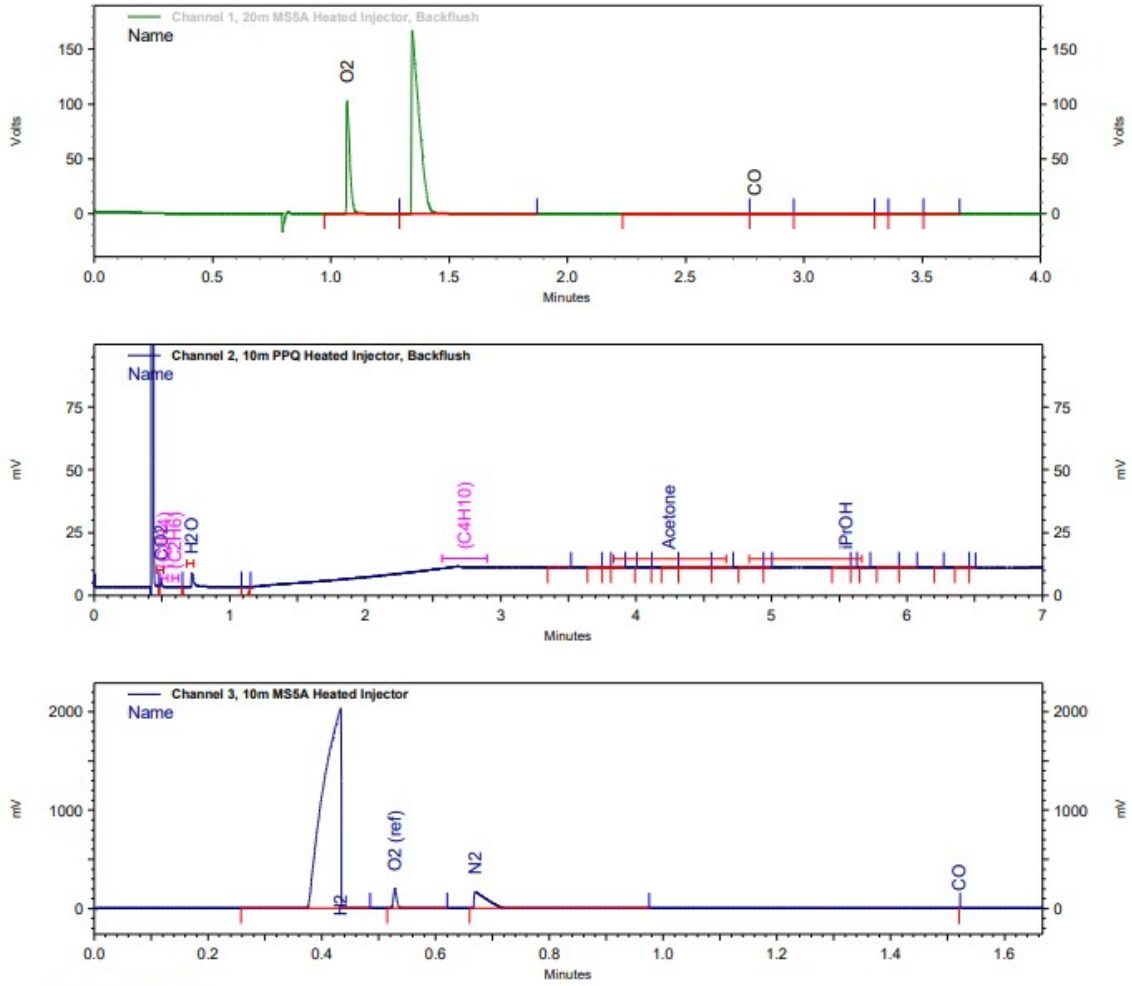

Channel 1, 20m MS5A Heated Injector, Backflush Results

Pk #	*Name*	*Retention Time*	*Area*	*Concentration*
1	O2	1.1	9718633	**9.0**
	N2			**0.0 BDL**
	CH4			**0.0 BDL**
4	CO	2.8	1256	**0.0**

External Standard Report

Method Name: C:\Users\Administrator\Agilent\Method\20190717_Luca_Final.met
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Totals			8750365	**8.1**

Channel 2, 10m PPQ Heated Injector, Backflush Results

Pk #	*Name*	*Retention Time*	*Area*	*Concentration*
2	CO2	0.5	160760958	**78.5**
	C2H4			**0.0 BDL**
	C2H6			**0.0 BDL**
3	H2O	0.7	186150748	**2729.0**
	C4H10			**0.0 BDL**
12	Acetone	4.3	624	**0.0**
20	iPrOH	5.3	222	**0.0**

Totals			346912552	**2807.6**

Channel 3, 10m MS5A Heated Injector Results

Pk #	*Name*	*Retention Time*	*Area*	*Concentration*
1	H2	0.4	454464004	**59.8**
2	O2 (ref)	0.5	7356593	**7.7**
3	N2	0.7	22241869	**30.9**
4	CO	1.5	15	**0.0**

Totals			484062481	**98.4**

Figure S36. MicroGC report of hydrogenation of beechwood sawdust (Table 4 in the manuscript)

External Standard Report

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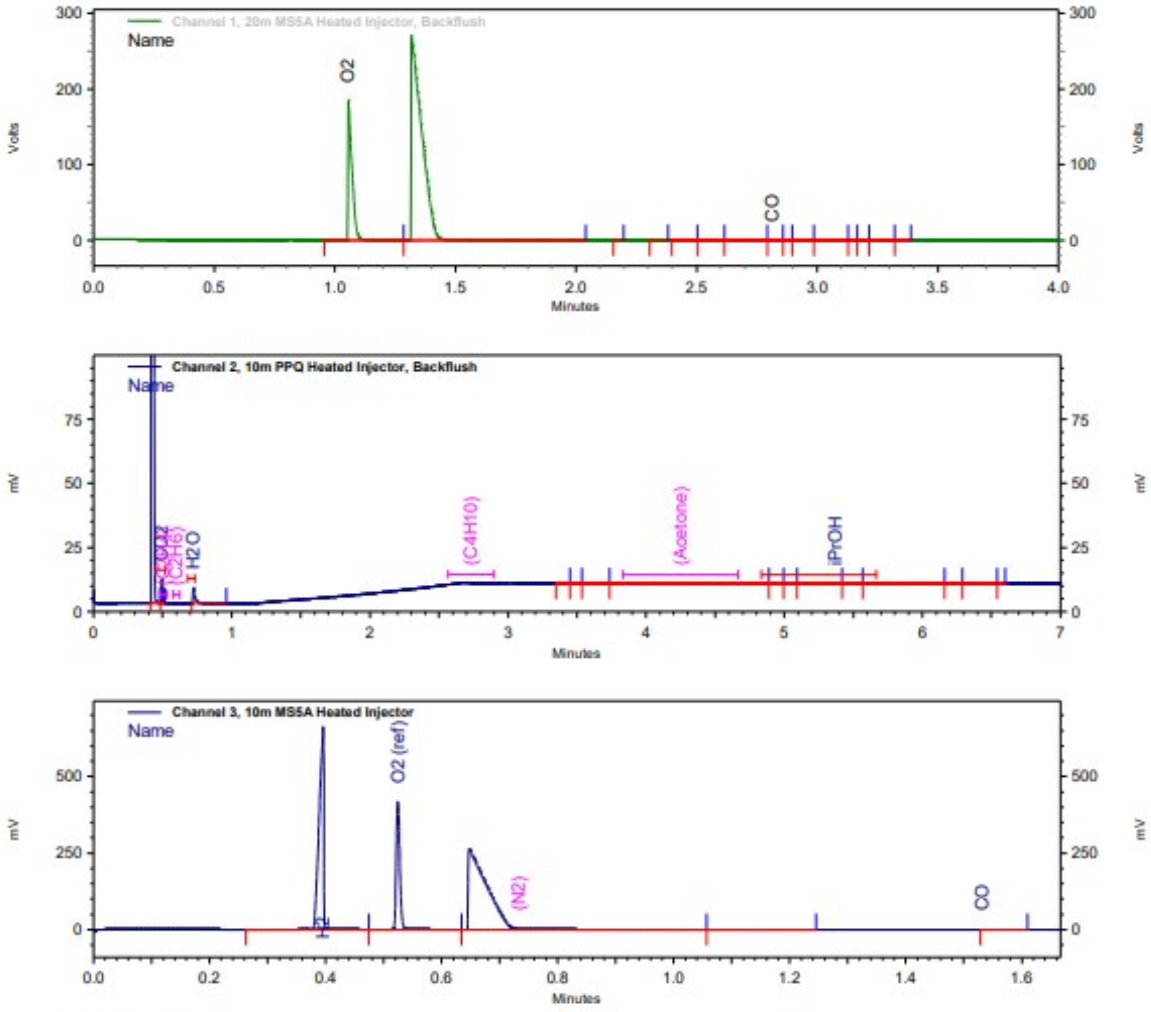

Channel 1, 20m MS5A Heated Injector, Backflush Results

Pk #	*Name*	*Retention Time*	*Area*	*Concentration*
1	O2	1.1	21417274	**19.9**
	N2			**0.0 BDL**
	CH4			**0.0 BDL**
8	CO	2.8	230	**0.0**

External Standard Report

Method Name: C:\Users\Administrator\Agilent\Method\20190717_Luca_Final.met
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Totals			21417504	**19.9**

Channel 2, 10m PPQ Heated Injector, Backflush Results

Pk #	*Name*	*Retention Time*	*Area*	*Concentration*
2	CO2	0.5	582417	**0.3**
	C2H4			**0.0 BDL**
	C2H6			**0.0 BDL**
3	H2O	0.7	670108	**9.8**
	C4H10			**0.0 BDL**
	Acetone			**0.0 BDL**
10	iPrOH	5.4	9466	**0.0**

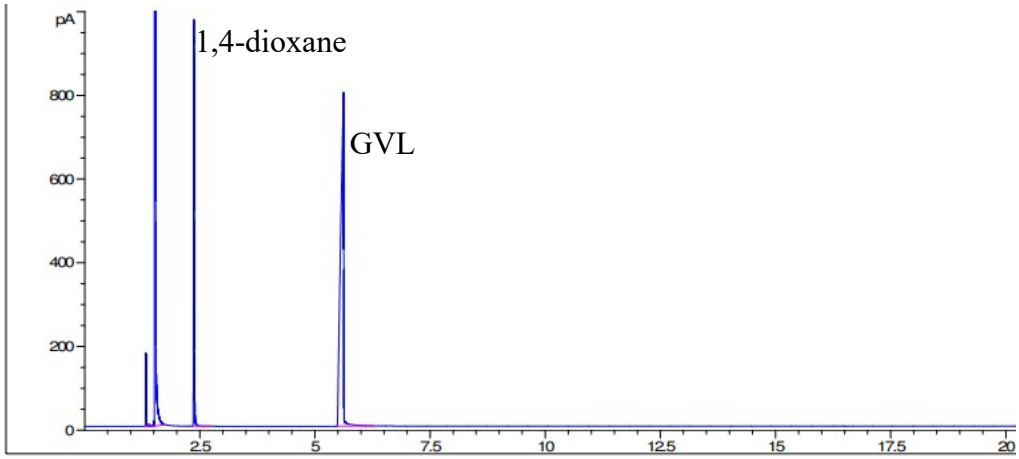
Totals			1261991	**10.1**

Channel 3, 10m MS5A Heated Injector Results

Pk #	*Name*	*Retention Time*	*Area*	*Concentration*
1	H2	0.4	36056238	**4.7**
2	O2 (ref)	0.5	18194089	**19.0**
	N2			**0.0 BDL**
5	CO	1.5	1399	**0.0**

Totals			54251726	**23.8**

Figure S37. MicroGC report of the blank reaction using GVL as the substrate with Ru-MACHO-BH and H_3PO_4(aq) under 30 bar H_2 at 140 °C in water after 72 hours.



Area Percent Report

Sorted By : Signal
Calib. Data Modified : 12/8/2006 12:33:15 PM
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %	Name
1	1.328	BB	7.80e-3	86.76977	0.25062	?
2	1.391	BB	9.28e-3	2.52223	0.00729	?
3	1.448	BB	8.89e-3	5.78413e-1	0.00167	?
4	1.493	BV	8.91e-3	7.27009	0.02100	?
5	1.517	VB S	9.25e-3	2.97472e4	85.92125	?
6	2.378	HB	0.0163	1024.79126	2.95999	?
7	2.993		0.0000	0.00000	0.00000	C14
8	3.466		0.0000	0.00000	0.00000	C15
9	3.926		0.0000	0.00000	0.00000	C16
10	5.623	HB	0.0572	3752.33105	10.83818	?

Totals : 3.46214e4

Figure S38. GC-FID of the reaction mixture of GVL with 10.9 M of H_3PO_4(aq) and Ru-MACHO-BH under 30 bar H_2 and 140 °C in water after 72 hours hours.

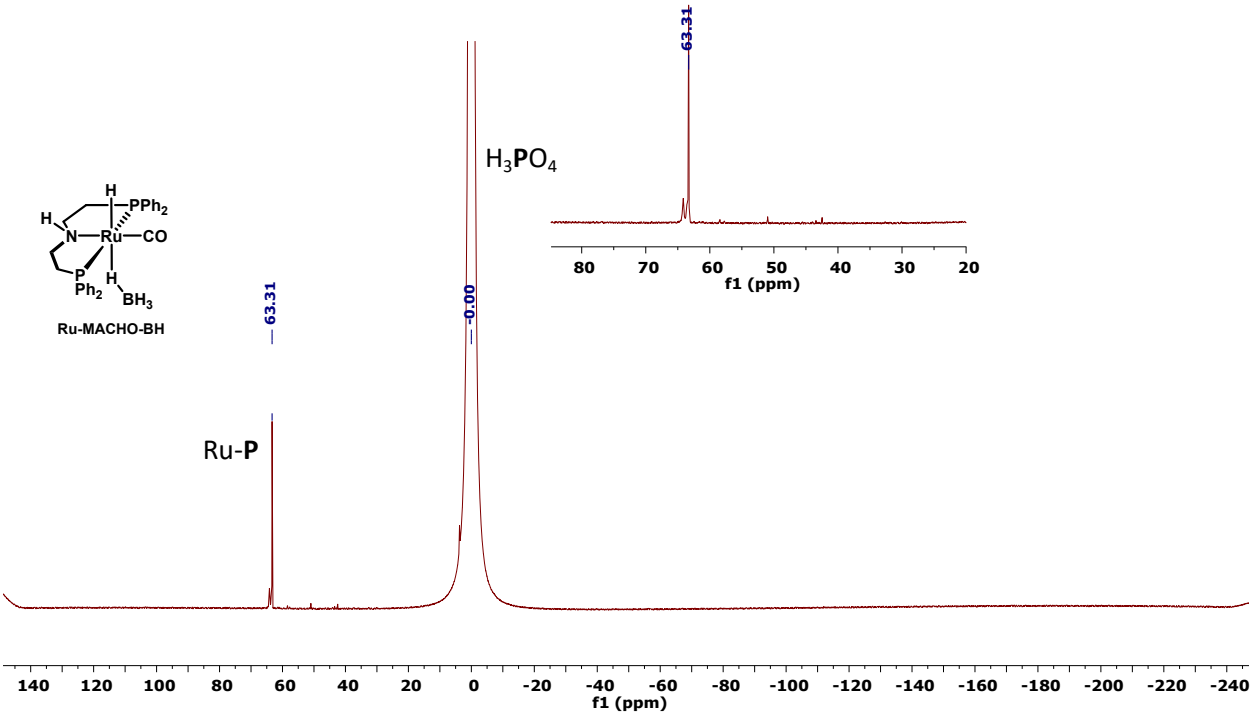
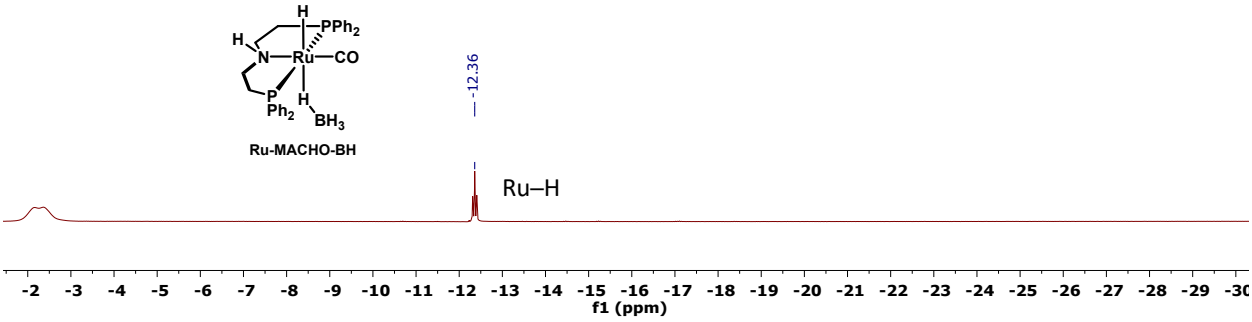
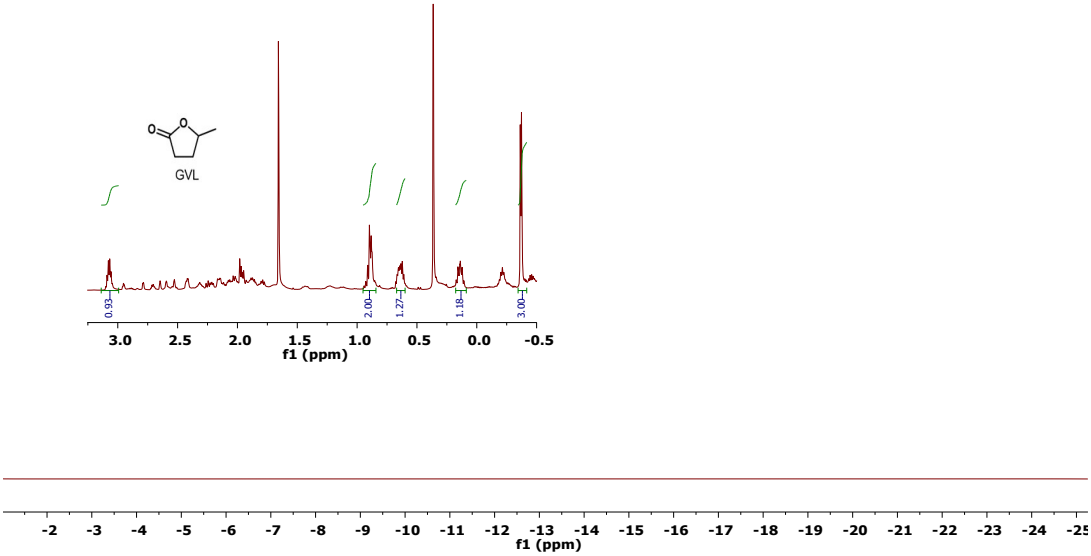


Figure S39. ^{31}P NMR of the of the crude reaction mixture of sawdust with Ru-MACHO-BH and H_3PO_4 in H_2O and H_2 source after 48 hours.



a. Standard ^{1}H NMR of Ru-MACHO-BH



b. ^{1}H NMR of the crude reaction mixture using beechwood sawdust as the substrate.

Figure S40. ^{1}H NMR without addition of a deuterated lock solvent of the ruthenium hydride species in the catalyst (a), reaction crude of sawdust with Ru-MACHO-BH and H_3PO_4 in H_2O and H_2 source at 140 °C after 48 hours (b). No hydride peak is detected.

Moisture determination by TGA analysis

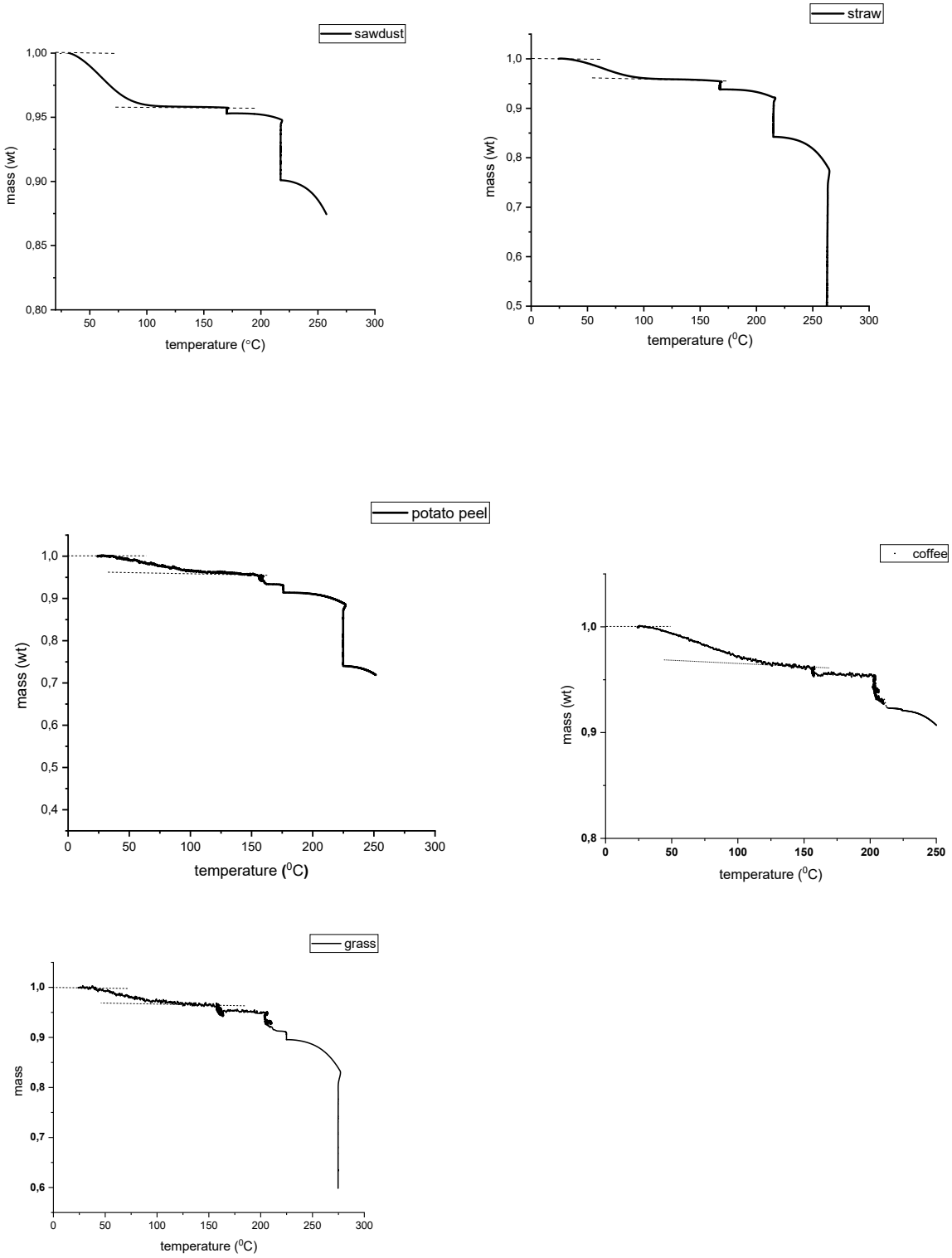


Figure S41. TGA profile for moisture content analysis based on thermal degradation of lignocellulosic biomass feedstock.

Comparison of reaction conditions and GVL yields to state-of-the-art

Table S3. Comparison table of state-of-the-art and this work for the direct production of GVL from monosaccharides, polysaccharides, and raw biomass.

	Catalysis type	Catalyst	Acid	H-donor	Conditions	Substrate	GVL yield	Manuscript reference
Raw biomass	Heterogeneous	Ru/ZrO_2	$Al_2(SO_4)_3$	*i*PrOH	180 °C 800 W microwave 60 min	Poplar Corncob Bamboo	12.2 wt% 8.9 wt% 10.6 wt%	8b
	Homogeneous	1.8 wt% Ru-MACHO-BH	10.9 M H_3PO_4	30 bar H_2	140 °C H_2O 24-120 h	Beechwood sawdust Wheat straw Bamboo Paper Grass Pistachio shells Used coffee grounds Banana peel Potato peel Rice grains Potato flour Chitin All combined	26 wt% 18 wt% 20 wt% 22 wt% 12 wt% 12 wt% 11 wt% 10 wt% 10 wt% 16 wt% 20 wt% 13 wt% 15 wt%	This work
Polysaccharides	Heterogeneous	Ru/C	TFA	94 bar H_2	180 °C H_2O 8 h	Cellulose	29%	8a
		Ru/TiO_2	$H_3PW_{12}O_{40}$	40 bar H_2	150 °C water–GBL 6 h	Cellulose Starch	40.5% 48%	8c
		Ru-Cu/zeolite Y		30 bar H_2	250 °C Methanol 5 h	Cellulose	49.8%	8d
		Chitosan-Ru/ZSM-5		formic acid	170 °C PPh_3 EtOH/H_2O 30 h	Hemicellulose	30%	9a
	Homogeneous	0.5 mol% Ru-MACHO-BH	7.5 M H_3PO_4	30 bar H_2	140 °C H_2O 48 h	Cellulose	50%	This work
		0.5 mol% Ru-MACHO-BH	7.5 M H_3PO_4	30 bar H_2	125 °C 1:1 EtOH/H_2O 48 h	Corn core hemicellulose Beechwood hemicellulose	57% 75%	
Monosaccharides	Heterogeneous	Ru/C	TFA	94 bar H_2	180 °C H_2O 8 h	Fructose	62%	8a
		Ru/TiO_2	$H_3PW_{12}O_{40}$	40 bar H_2	130-150 °C water–GBL 6 h	Fructose Glucose	68% 55%	8c
		Chitosan-supported ruthenium catalyst with ZSM		HCOOH	170 °C 30 h	Xylose	37%	9a
		Zr-Al-beta zeolite		*i*PrOH	190 °C 48 h	Xylose	35%	9c
	Homogeneous	Cat/substrate 1:270 mol/mol $RuCl_3$, TPPTS	TFA	94 bar H_2	180 °C H_2 NaI 8 h	Glucose	23%	8a
		0.5 mol% Ru-MACHO-BH	5.7 M H_3PO_4	30 bar H_2	125 °C 1:1 EtOH/H_2O 48 h	Glucose Fructose Xylose	31% 34% 73%	This work

Table S4. Solvent optimization for various biomass substrates.

Substrate	H_3PO_4 (M)	Solvent	GVL Yield [a]
Xylose	3.8	DMSO	-
Xylose	3.8	IPA	43
Xylose	3.8	MeOH	38
Xylose	3.8	MeOH/H_2O	40
Xylose	3.8	EtOH	44
Xylose	3.8	EtOH/H_2O (1:1)	45
Xylose	3.8	EtOH/H_2O (7:3)	45
Xylose	3.8	EtOH/H_2O (3:7)	27
Glucose	3.8	MeOH	6
Glucose	3.8	MeOH/H_2O (1:1)	17
Glucose	3.8	EtOH	8
Glucose	3.8	EtOH/H_2O (1:1)	21
Fructose	3.8	MeOH	20
Fructose	5.7	MeOH/H_2O (1:1)	28
Fructose[b]	3.8	EtOH	17
Fructose	3.8	EtOH/H_2O (1:1)	25
Hemicellulose (corn core)	3.8	MeOH	43
Hemicellulose (corn core)	3.8	EtOH	52
Hemicellulose (corn core)	5.7	EtOH/H_2O (1:1)	56
Hemicellulose (corn core)	7.5	H_2O	8
Cellulose (0.6)	5.7	EtOH/H_2O (1:1)	5
Cellulose (0.6)	5.7	H_2O	19

Standard reaction conditions: Substrate (0.6 M), Ru-MACHO-BH (0.5 mol%), Solvent (1 mL), at 125 °C and 30 bar H_2, [a] Determined by GC-FID using 1,4-dioxane as the internal standard, [b] 96 hours.