Supporting information:

Efficient C−C Coupling of Bio-based Furanics and Carbonyl Compounds to Liquid Hydrocarbon Precursors over Lignosulfonate Derived Acidic Carbocatalysts

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Estimation of kinetic dimeter

The kinetic diameter (σ) of product molecule are estimated from the properties of the fluid at the critical point (c), according to the equations suggested by Bird et al. [1]:

$$\sigma = 0.841 \times \sqrt[3]{V_c} \qquad (1)$$

or

$$\sigma = 2.44 \times \sqrt[3]{T_c / P_c} \qquad (2)$$

where V_c is the critical volume in $cm^3\ mol^{-1}$, T_c is the critical temperature in Kelvins and P_c is the critical pressure in atmospheres. Whenever available critical point data were obtained from the literature (CRC Handbook or NIST) otherwise the values were computed using Chem 3D ultra.

Table S1. Kinetic diameter of reactants and products

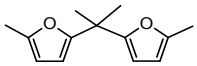
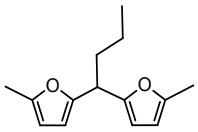
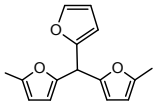
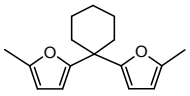
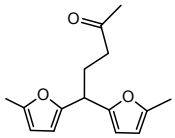
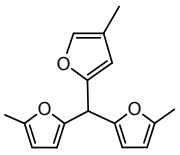
Molecule	Kinetic diameter, **σ** (nm)	Ref.
acetone	0.46	2
butanal	0.31	3
furfural	0.55	4
2-methylfuran	0.53	5
cyclohexanone	0.57[1], 0.603[2]	This work
levulinic acid	0.59[1], 0.622[2]	This work
α-angelica lactone	0.553[1], 0.616[2]	This work
 5,5'-(propane-2,2-diyl)bis(2-methylfuran)	0.718[1], 0.754[2]	This work
 5,5'-(butane-1,1-diyl)bis(2-methylfuran)	0.741[1], 0.784[2]	This work
 5,5'-(furan-2-ylmethylene)bis(2-methylfuran)	0.737[1], 0.760[2]	This work
 5,5'-(cyclohexane-1,1-diyl)bis(2-methylfuran)	0.758[1], 0.789[2]	This work
 5,5-bis(5-methylfuran-2-yl)pentan-2-one	0.762[1], 0.803[2]	This work
 tris(5-methylfuran-2-yl)methane	0.757[1], 0.790[2]	This work

Table S2. Composition of spent catalyst

Catalyst	XPS, at %			§EDS, at %		
	C	O	S	C	O	S
60LS40PS350H$^+$ (fresh)	84.1	13.2	2.03	83.5	15.3	1.3
60LS40PS350H$^+$ (spent*)	82	15.6	2.04	-	-	-
60LS40PS350H$^+$ (spent$^{\#}$)	82	15.7	1.97	80.8	18.1	1.1

*3rd cycle of furfural HAA, $^{\#}$5th cycle of butanal HAA,

§ Over a sample area of 50 μm × 50 μm, includes background signal from carbon tape

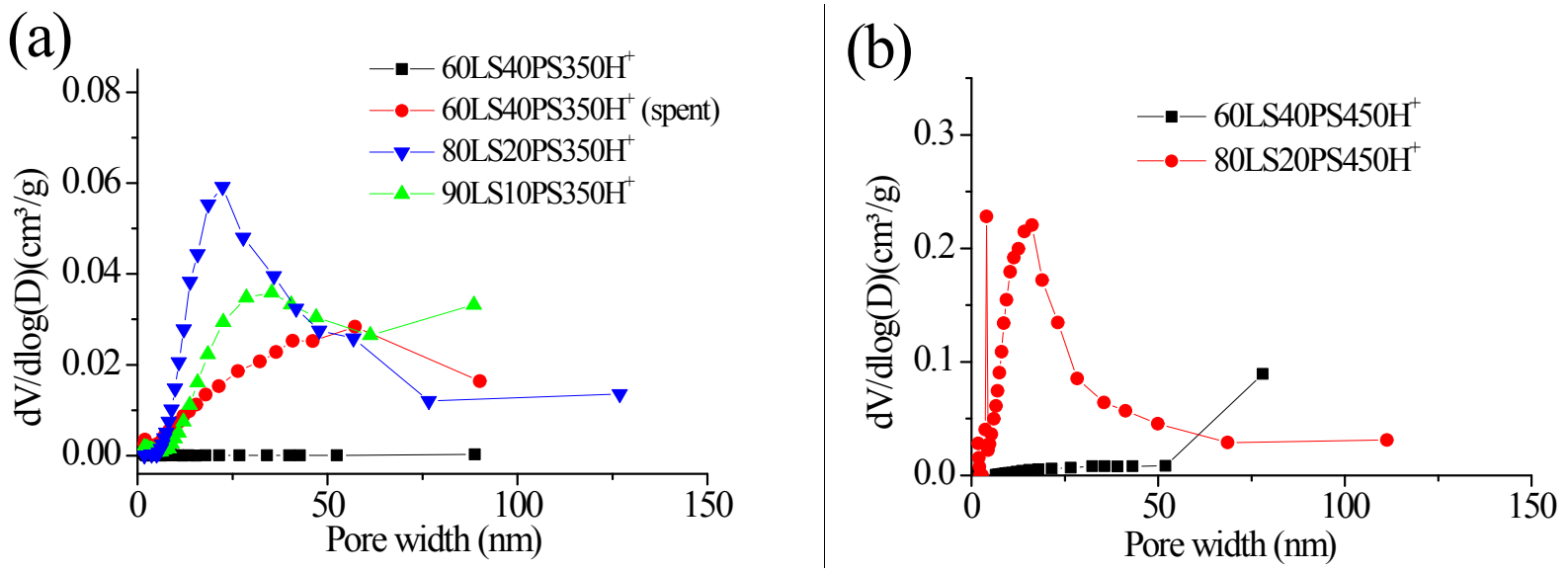


Figure S1. Differential (BJH desorption) pore width distribution curves of carbocatalysts obtained at (a) 350 °C and (b) 450 °C

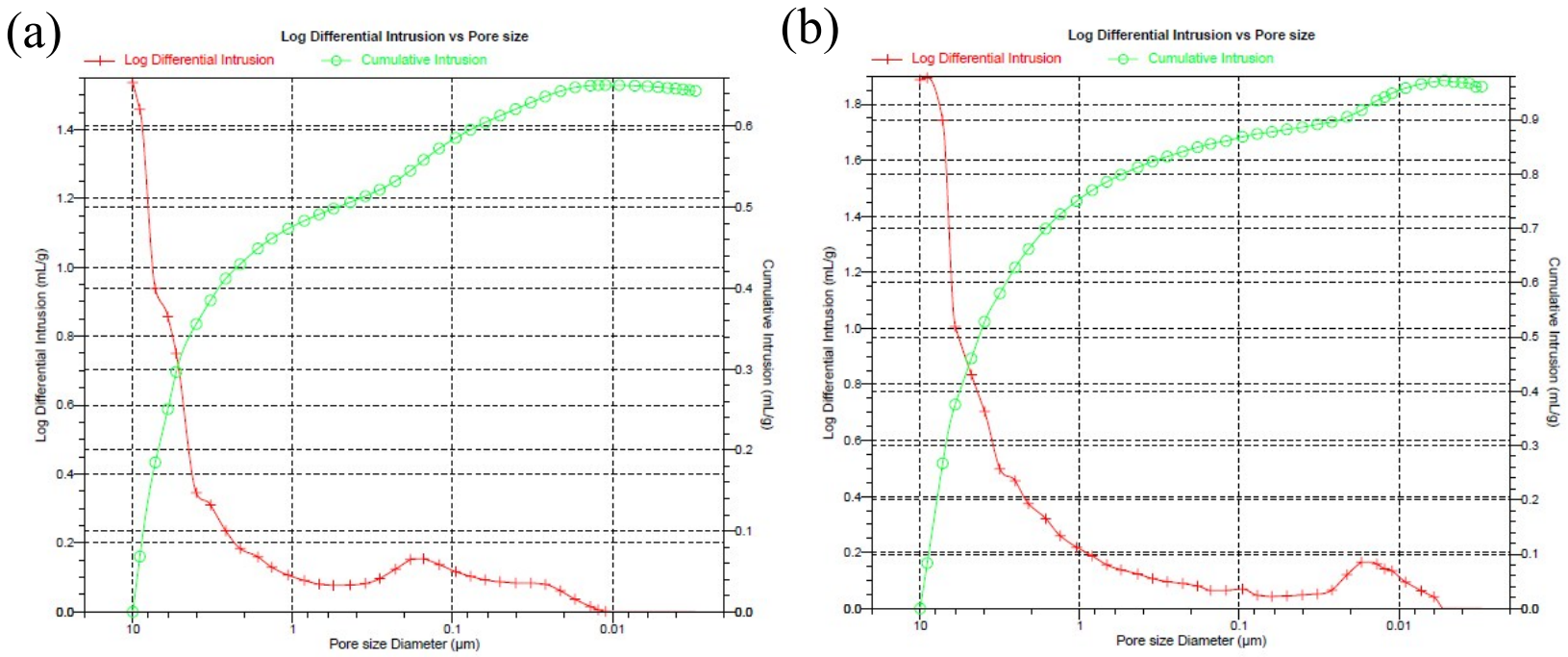


Figure S2. Pore width distribution curves of the selected carbocatalysts (a) 80LS20PS450H$^+$ and (b) 80LS20PS350H$^+$ obtained from Mercury Intrusion Porosimetry. It should be noted that pores larger than 2 µm represents contribution from pores between particles (inter particle space) as very fine powders (particle size less than 100 µm) were used for the measurements. Therefore, the average pore widths were not estimated from the Hg-intrusion data.

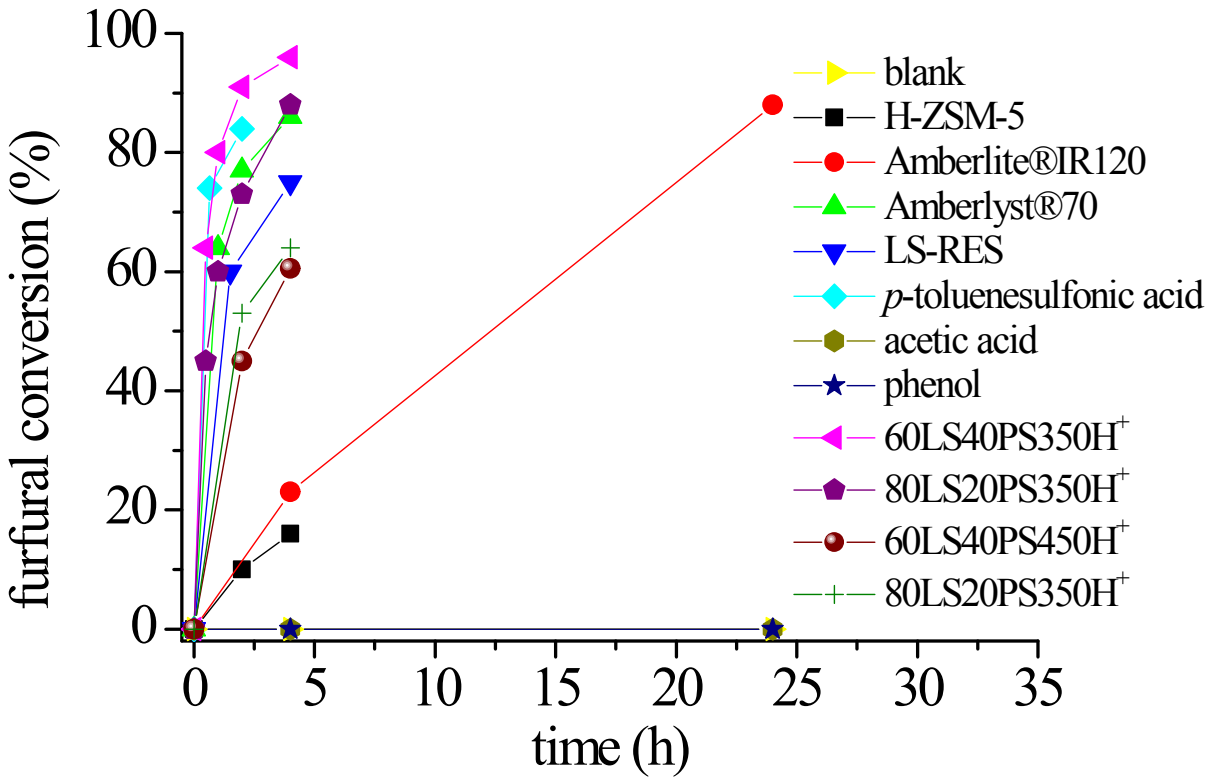


Figure S3. Furfural conversion as a function of time over different catalysts (conditions: 37 mg catalyst, 10.5 mmol 2-methylfuran, 5.25 mmol furfural, 300 rpm stirring rate)

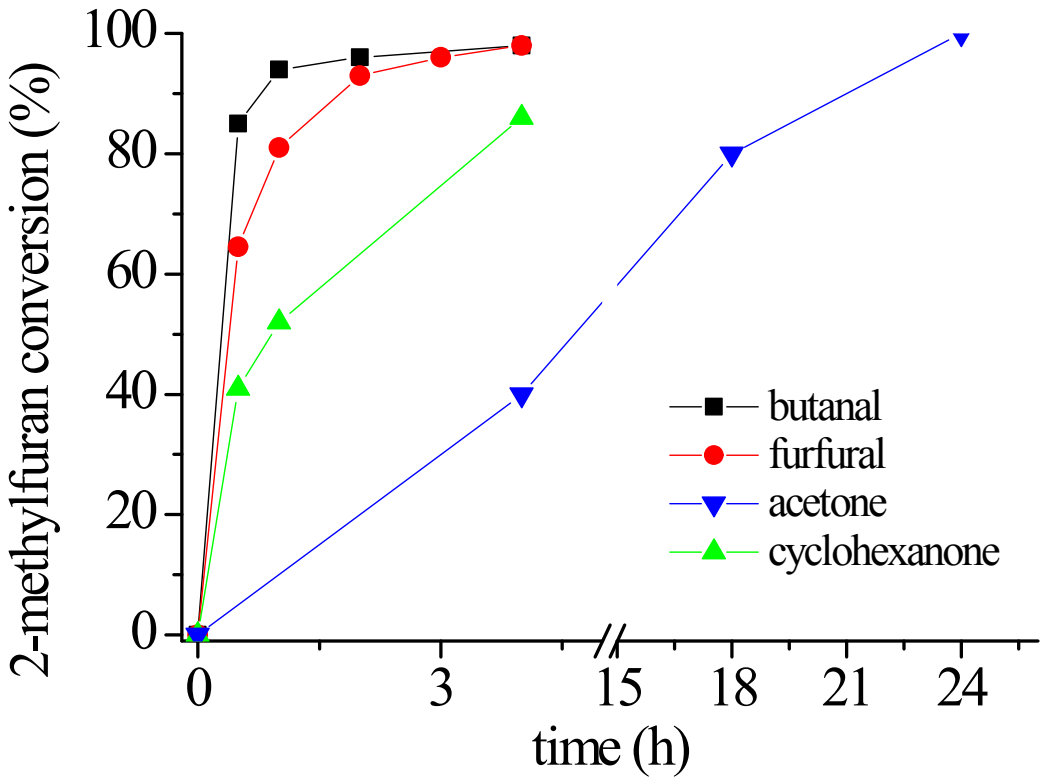


Figure S4. 2-methylfuran conversion as a function on time for different carbonyl compounds (conditions: 37 mg 60LS40PS350H$^+$, 10.5 mmol 2-methylfuran, 5.25 mmol carbonyl compound, 300 rpm stirring rate)

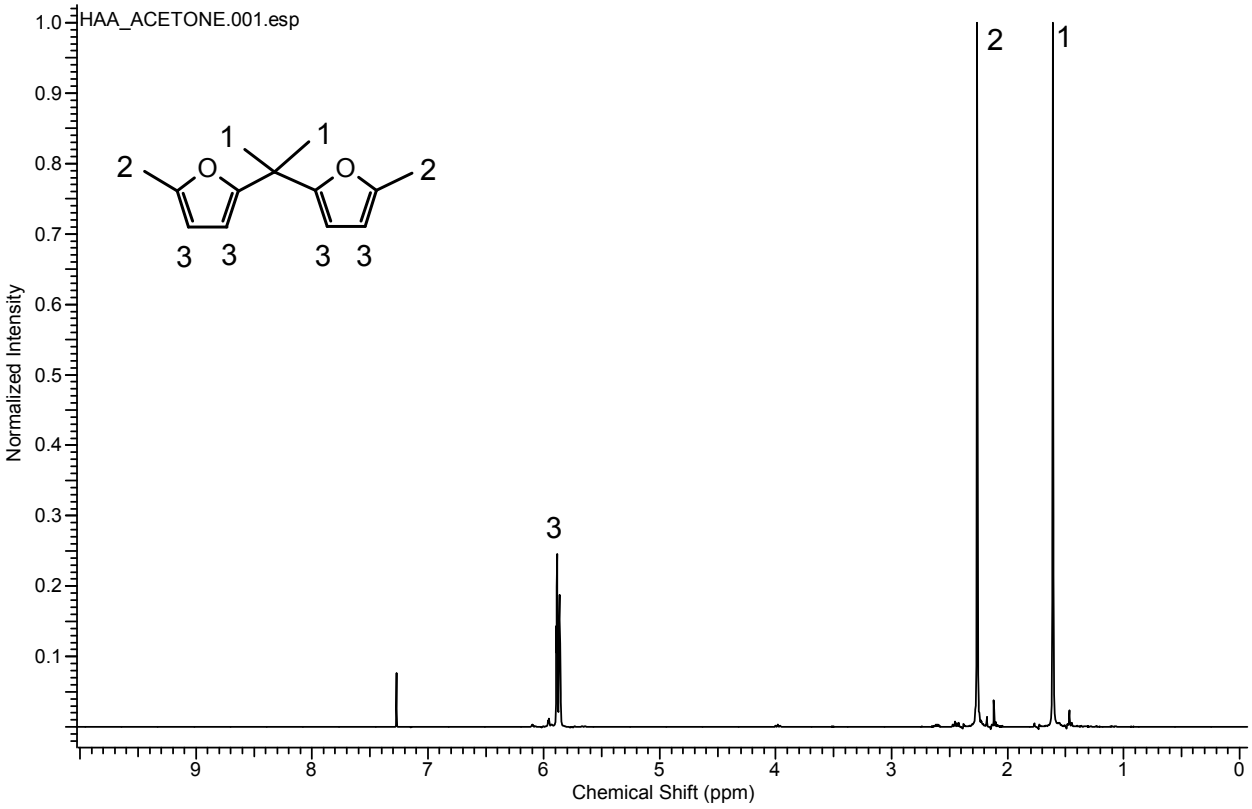


Figure S5. [1]H-NMR spectra of 5,5'-(propane-2,2-diyl)bis(2-methylfuran)

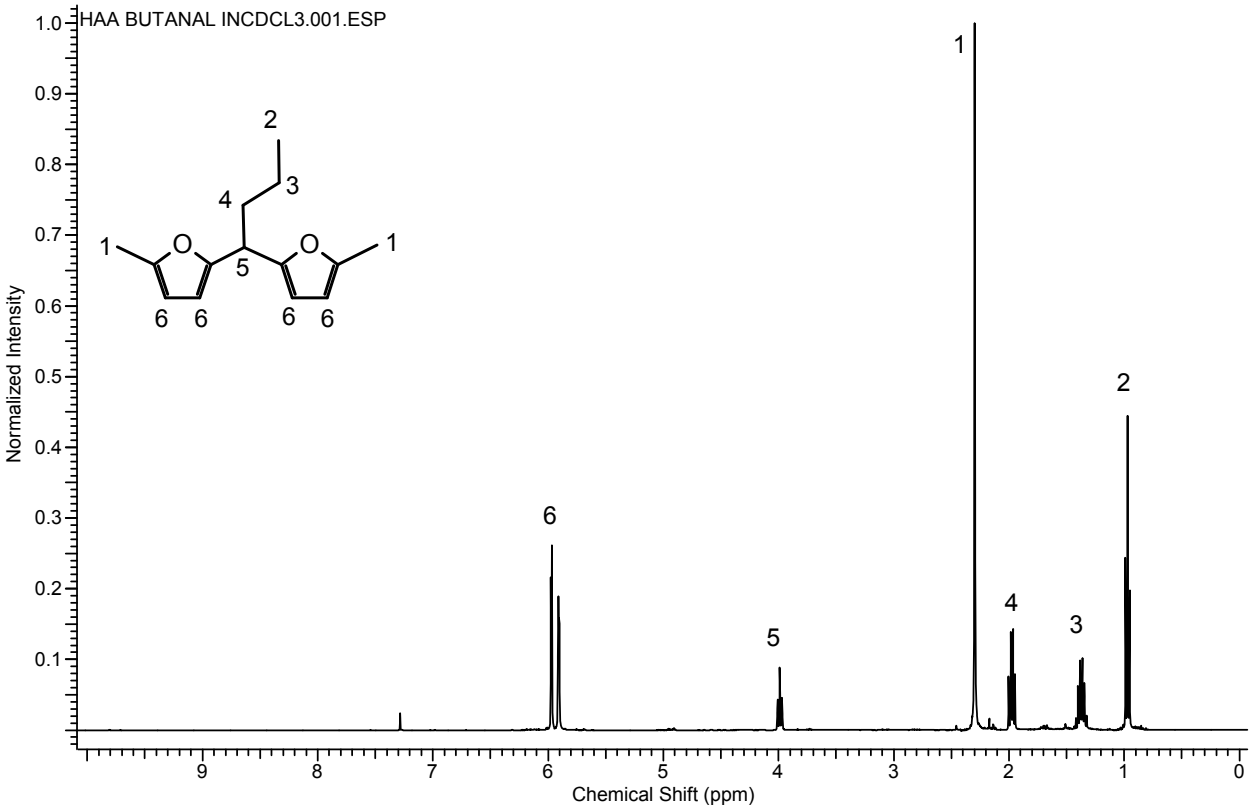


Figure S6. [1]H-NMR spectra of 5,5'-(butane-1,1-diyl)bis(2-methylfuran)

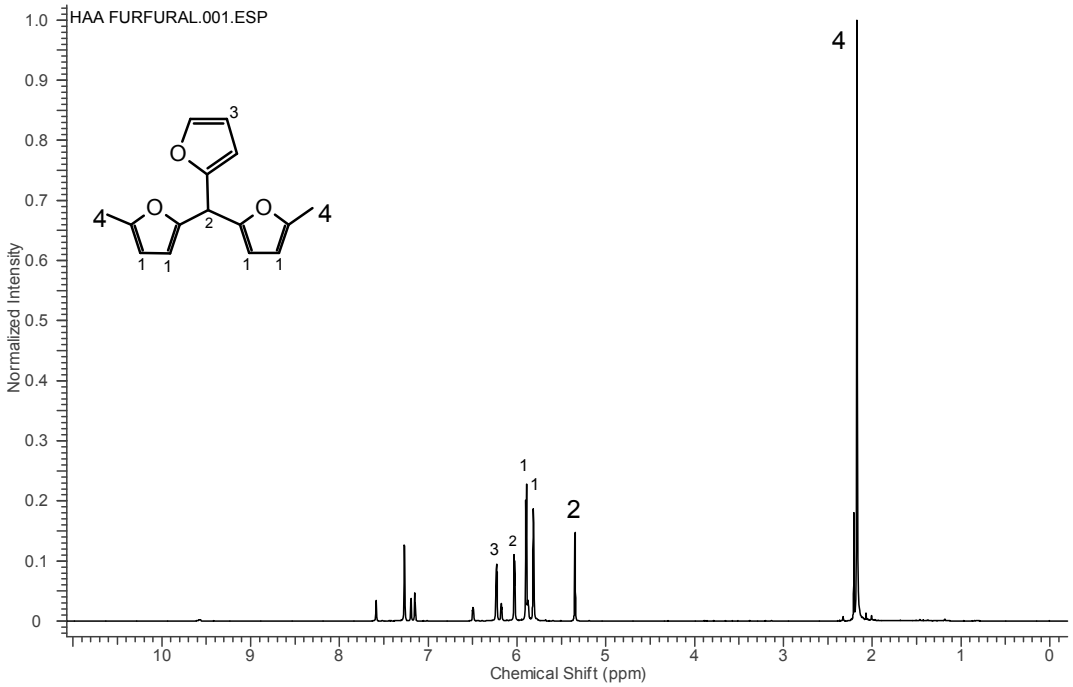


Figure S7. [1]H-NMR spectra of 5,5'-(furan-2-ylmethylene)bis(2-methylfuran)

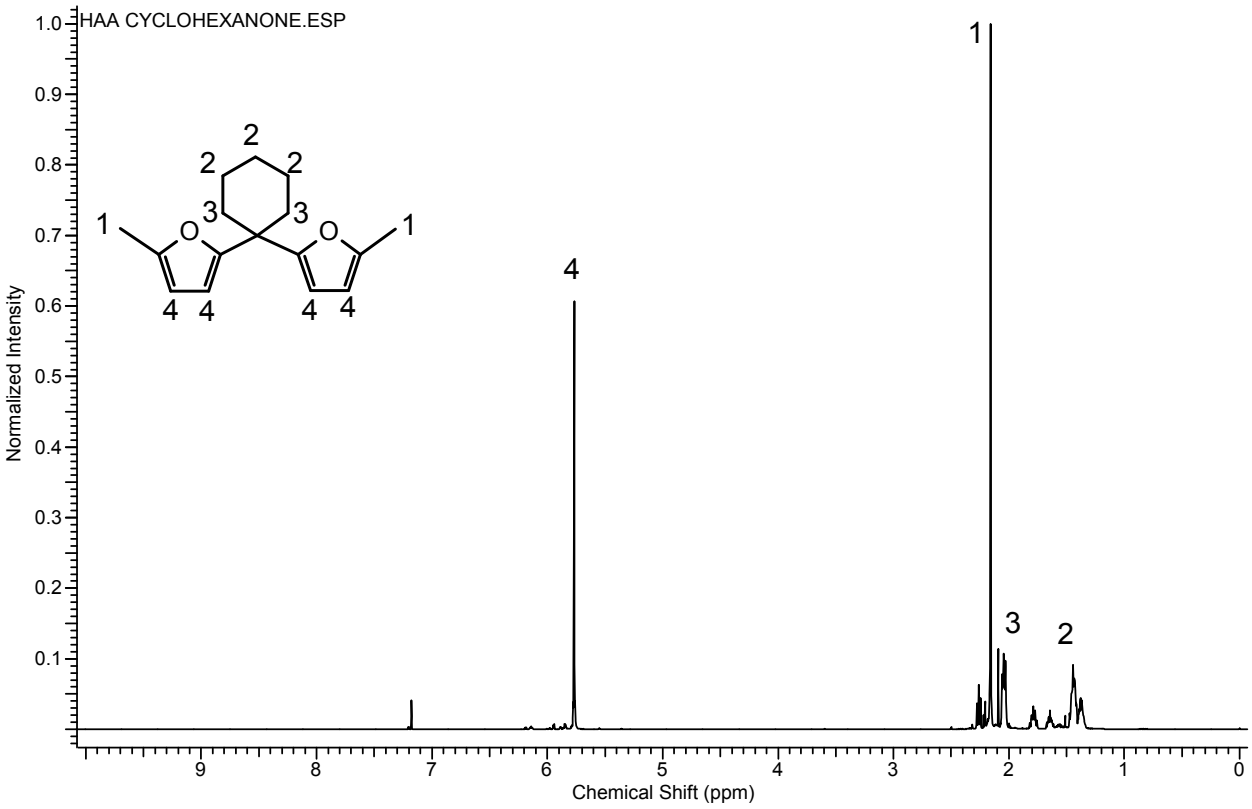


Figure S8. ^{1}H-NMR spectra of 5,5'-(cyclohexane-1,1-diyl)bis(2-methylfuran)

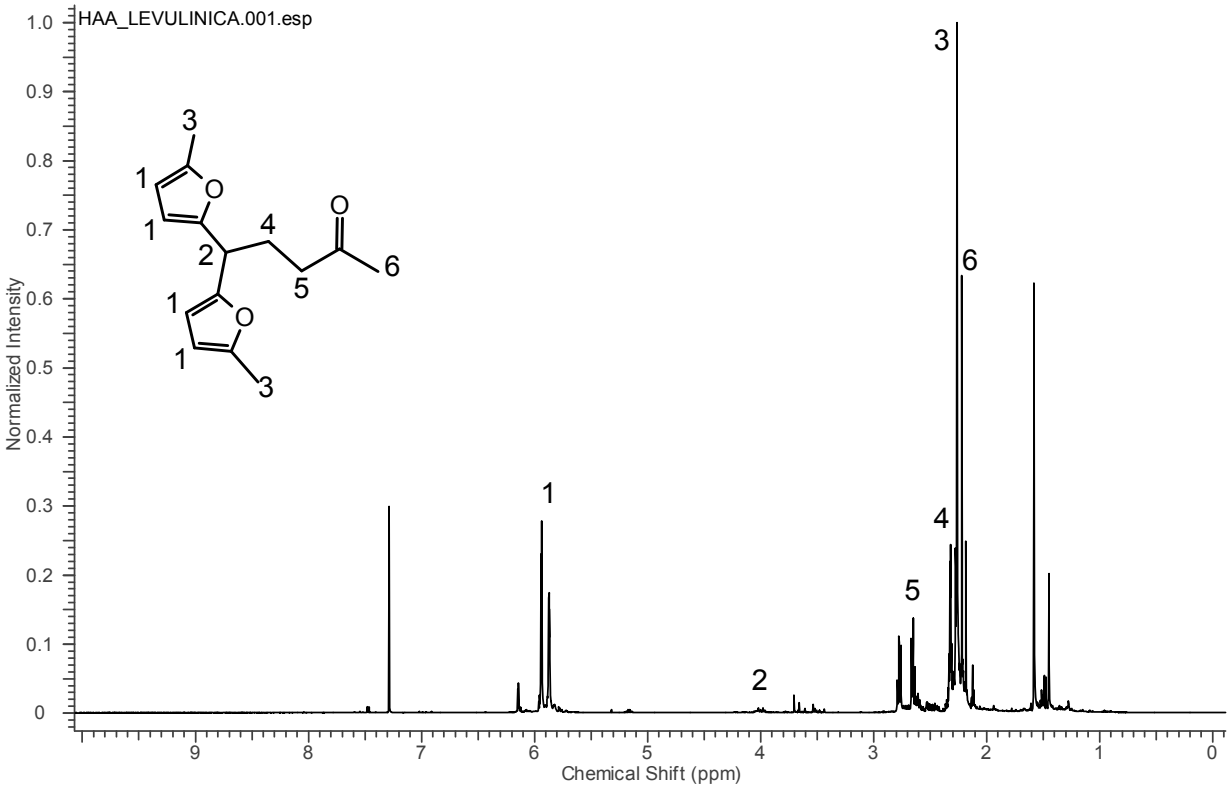


Figure S9. ^{1}H-NMR spectra of 5,5-bis(5-methylfuran-2-yl)pentan-2-one, levulinic acid HAA

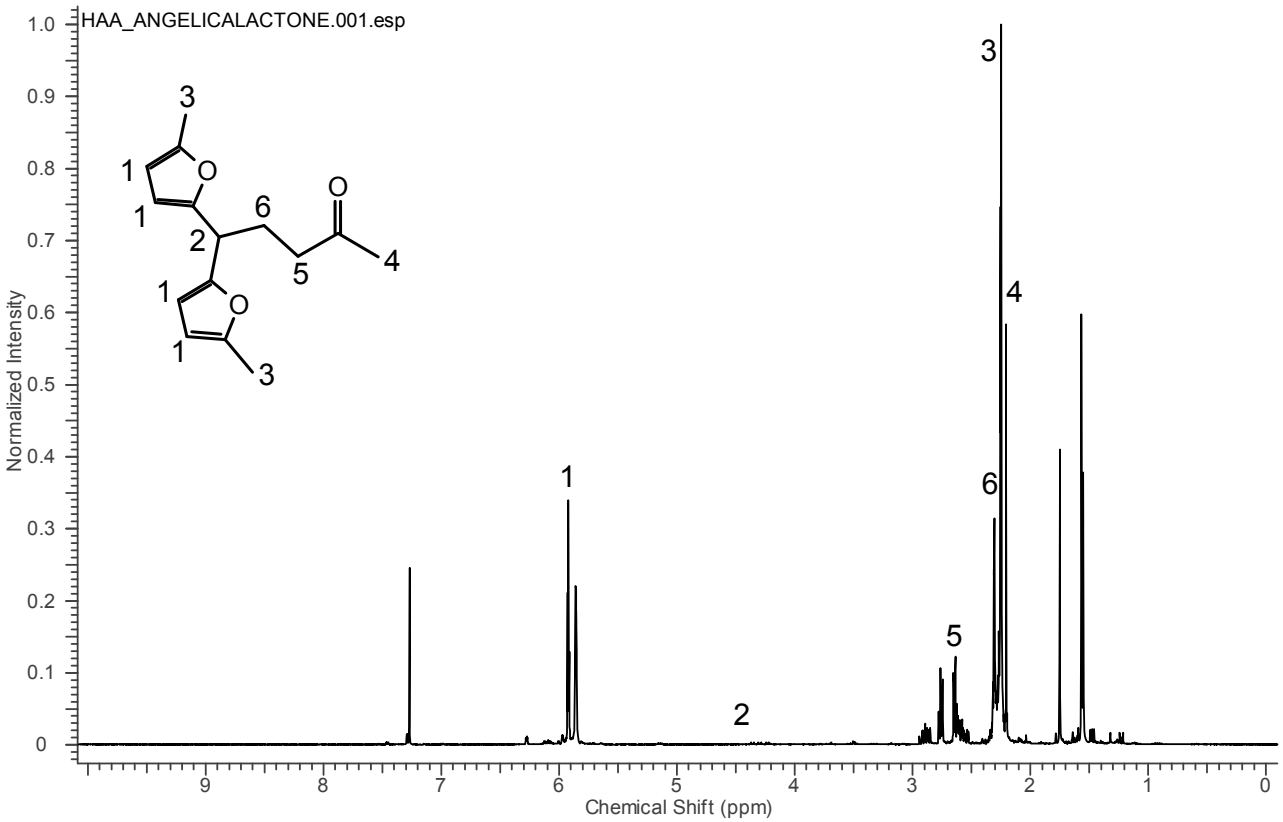


Figure S10. ^{1}H-NMR spectra of 5,5-bis(5-methylfuran-2-yl)pentan-2-one, angelica lactone HAA

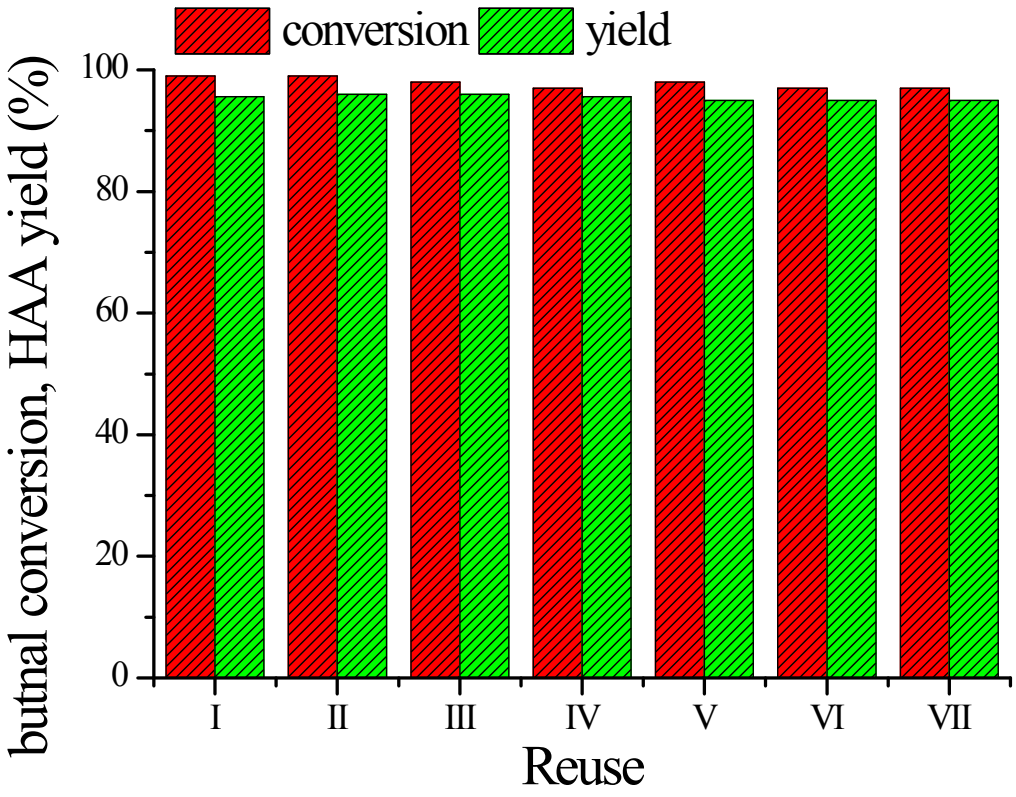


Figure S11. long term stability investigated upon butanal HAA (conditions: 37 mg, 10.5 mmol 2-methylfuran, 5.25 mmol carbonyl compound, 300 rpm stirring rate, 4h reaction)

References

1. R.B. Bird, W.E. Stewart, E.N. Lightfoot, Transport Phenomena, John Wiley & Sons, New York, 1960. p. 26.
2. L. Gales, A. Mendes, C. Costa, Carbon 2000, 38, 1083–1088.
3. T. C. Keller, S. Isabettini, D. Verboekend, E. G. Rodriguesa, J. Pérez-Ramírez, Chem. Sci., 2014,5, 677-684.
4. K. Wang, J. Zhang, B. H. Shanksc, R. C. Brown, Green Chem., 2015,17, 557-564.
5. J. Jae, G. A. Tompsett, A. J. Foster, K D. Hammond, S. M. Auerbach, R. F. Lobo, G. W. Huber, J. Catl., 2011, 279, 257–268.