Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Green synthesis of furfural from xylose and corn cob biomass

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EXPERIMENTAL PROCEDURES

Synthesis of $CX4SO_3H$

The $CX4SO_3H$ will be synthesized from the methodology described by Gustche et al. Initially, the *p*-tert-butylcalix[4]arene (CX4PTB) will be obtained from the condensation of *p*-tert-butylphenol and formaldehyde, in basic medium and under heating[1] (**Fig. S1** (a)). Then, the synthesis of calix[4]arene (CX4) will be carried out CX4PTB, using phenol and anhydrous aluminum chloride in toluene[2] (**Fig. S1** (b)). Finally, to obtain $CX4SO_3H$ from CX4, it will be placed in the presence of concentrated sulfuric acid and heated for four hours[3] (**Fig. S1** (c)).

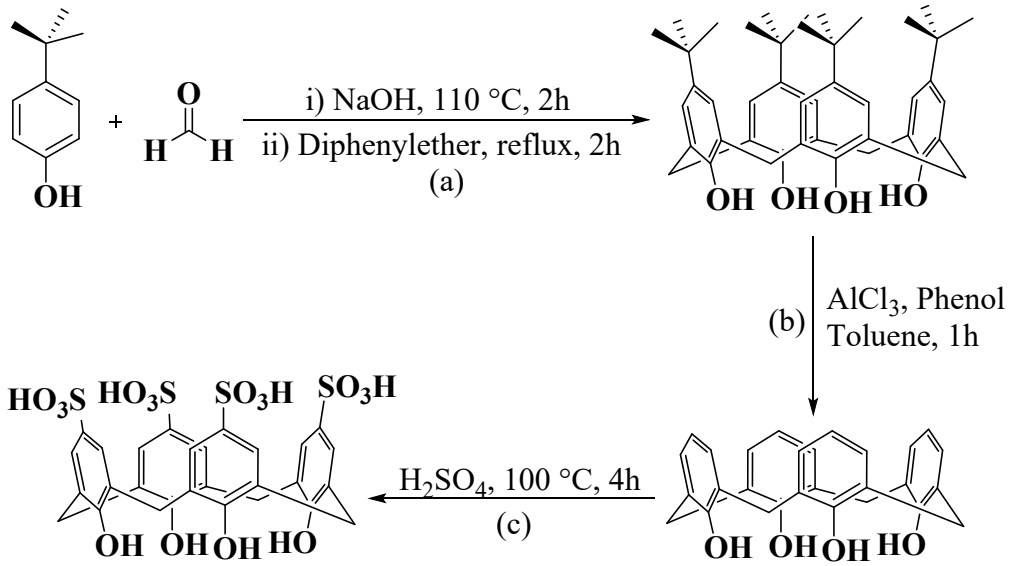

Fig. S1. Synthetic route to obtain $CX4SO_3H$.

CX4PTB: **^{1}H NMR** (300 MHz, $CDCl_3$): 1.21 (s, 36H, H-6), 3.48 (d, 4H, *J* 12.4, CH_2-Ha), 4.28 (d, 4H, *J* 12.4, CH_2-Hb), 7.05 (s, 8H, H-3), 10.34 (s, 4H, OH). **^{13}C NMR** (75 MHz, $CDCl_3$): 31.4 (C-6), 32.7 (CH_2), 34.0 (C-5), 125.9 (C-3), 127.6 (C-2), 144.3 (C-4), 146.7 (C-1). **IR** (ATR, cm^{-1}): 3150, 3057, 3024, 2952, 1737, 1605, 1480, 1456, 1391, 1362, 1231, 1200, 871, 814, 780.

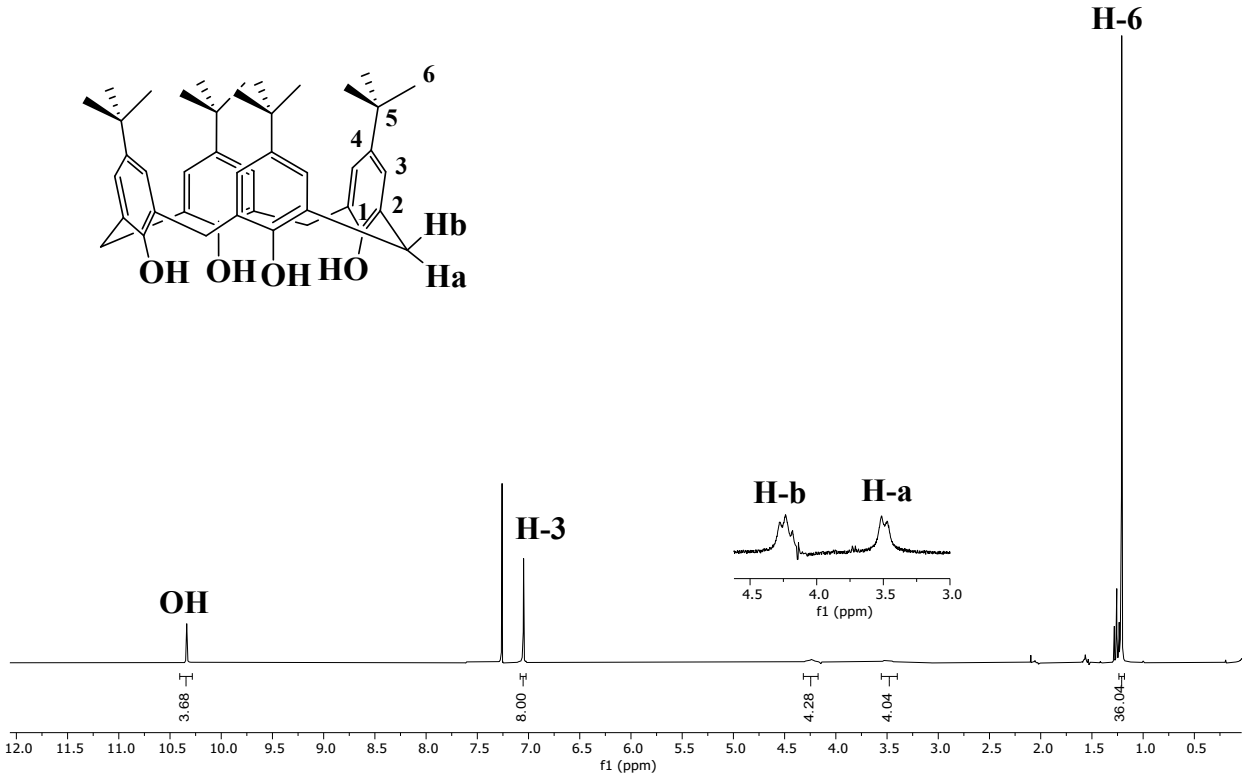

Fig. S2. ^{1}H NMR spectrum (300 MHz; $CDCl_3$) of the CX4PTB.

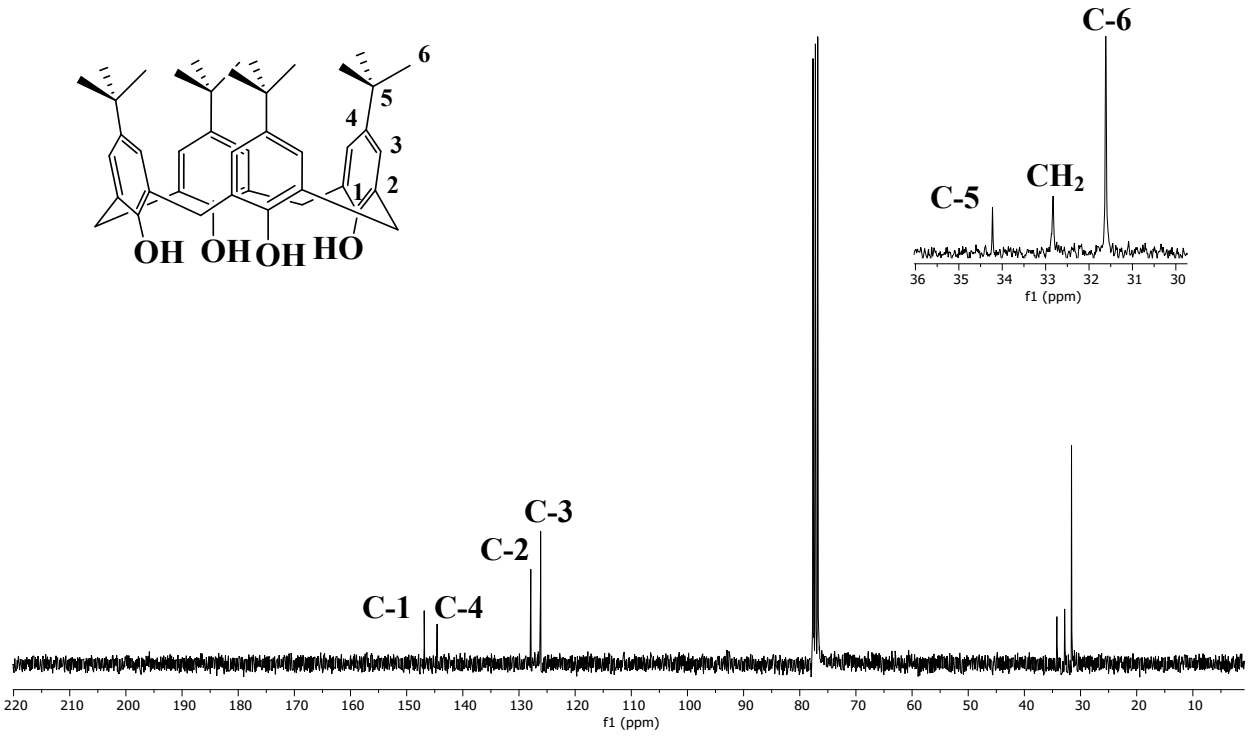

Fig. S3. ^{13}C NMR spectrum (75 MHz; $CDCl_3$) of the CX4PTB.

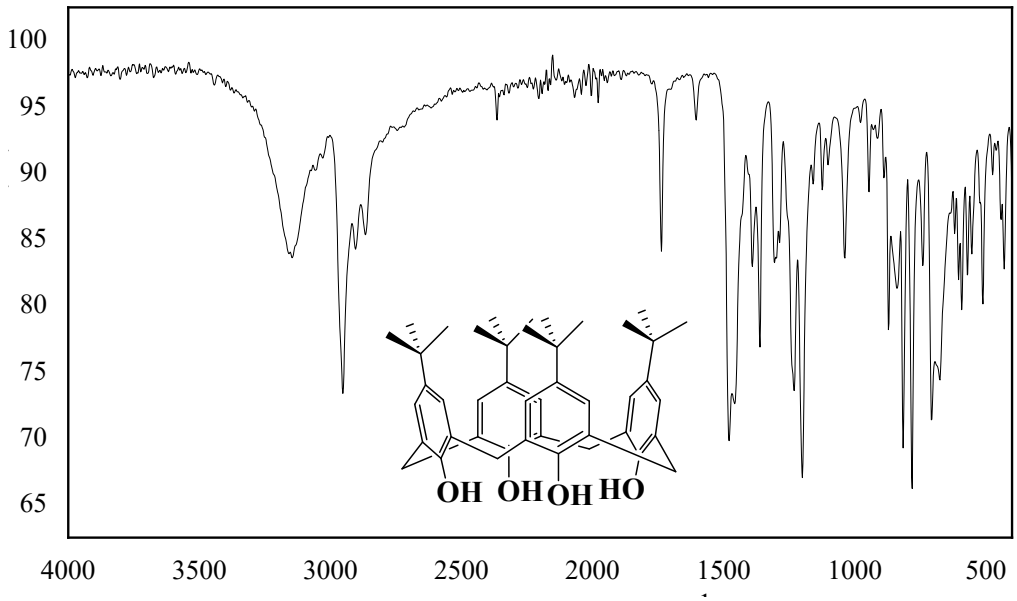

Fig. S4. FTIR Spectrum of CX4PTB.

CX4: ^{1}**H NMR** (300 MHz, $CDCl_3$): 3.56 (d, 4H, *J* 12.6, H-a), 4.27 (d, 4H, *J* 12.6, H-b), 6.79 (t, 4H, *J* 7.5, H-4), 7.08 (d, 8H, *J* 7.5 Hz, H-3), 10.23 (s, 4H, OH). ^{13}**C NMR** (75 MHz; $CDCl_3$): 31.9 (CH_2), 122.5 (C-4), 128.5 (C-2), 129.2 (C-3), 149.0 (C-1). **IR** (ATR, cm^{-1}): 3152, 3092, 2935, 1593, 1466, 1447, 1410, 1369, 1238, 774, 749.

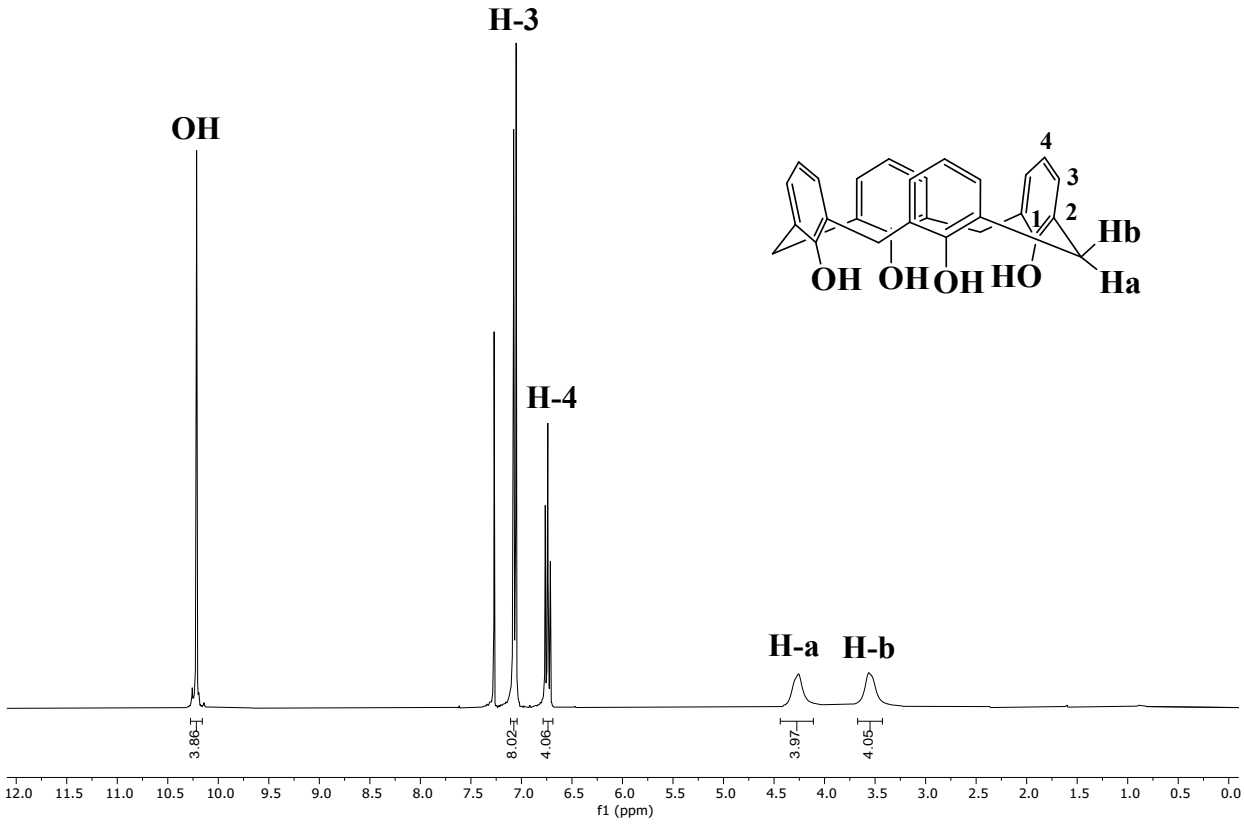

Fig. S5. ^{1}H NMR spectrum (300 MHz; $CDCl_3$) of the CX4.

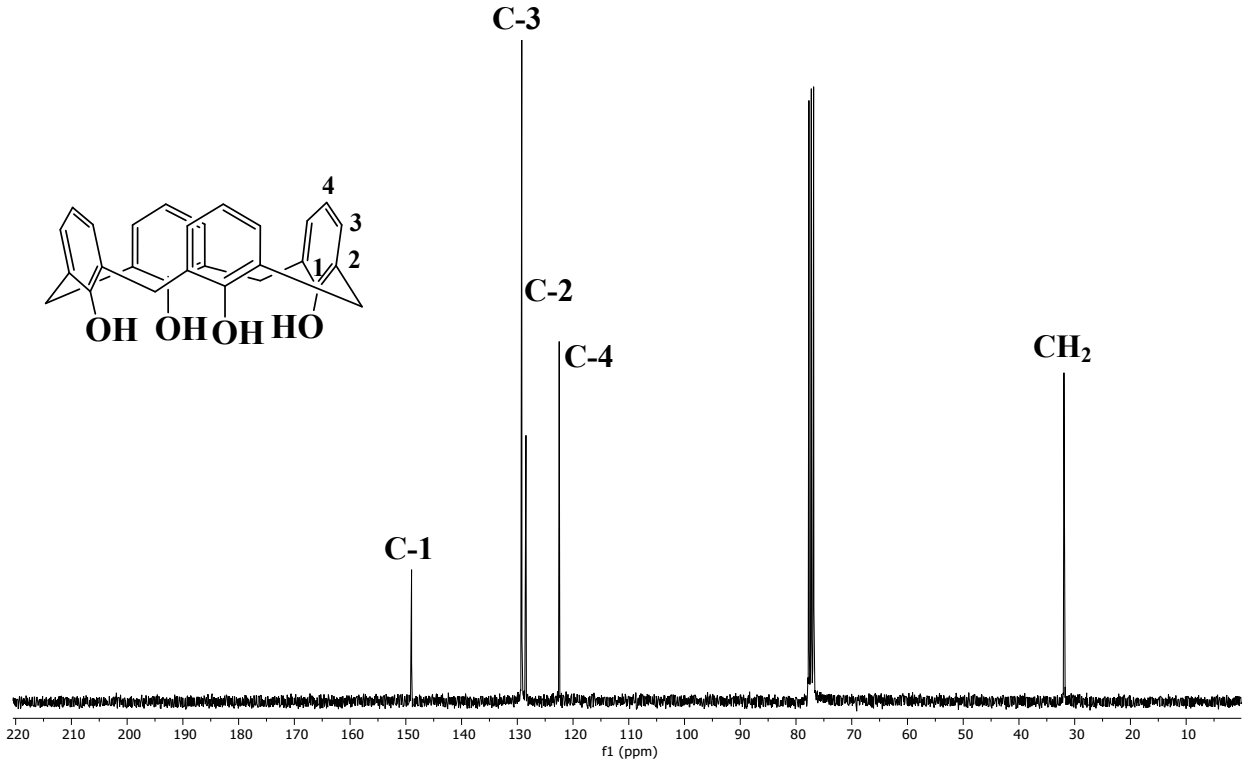

Fig. S6. ^{13}C NMR spectrum (75 MHz; $CDCl_3$) of the CX4.

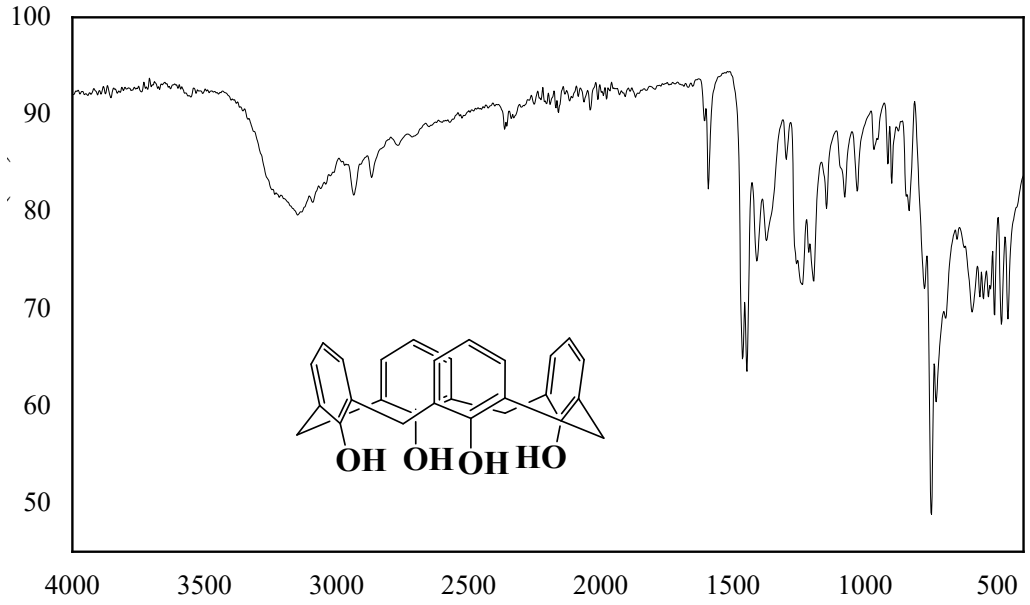

Fig. S7. FTIR Spectrum of the CX4.

CX4SO$_3$H: ^{1}**H NMR** (300 MHz, D_2O): 3.84 (s, 8H, CH_2), 7.39 (s, 8H, H-3). ^{13}**C NMR** (75 MHz, D_2O): 30.7 (CH_2), 126.6 (C-3), 128.2 (C-2), 135.8 (C-4), 151.9 (C-1). **IR** (ATR, cm^{-1}): 3182, 1705, 1636, 1599, 1455, 1147, 1117, 623.

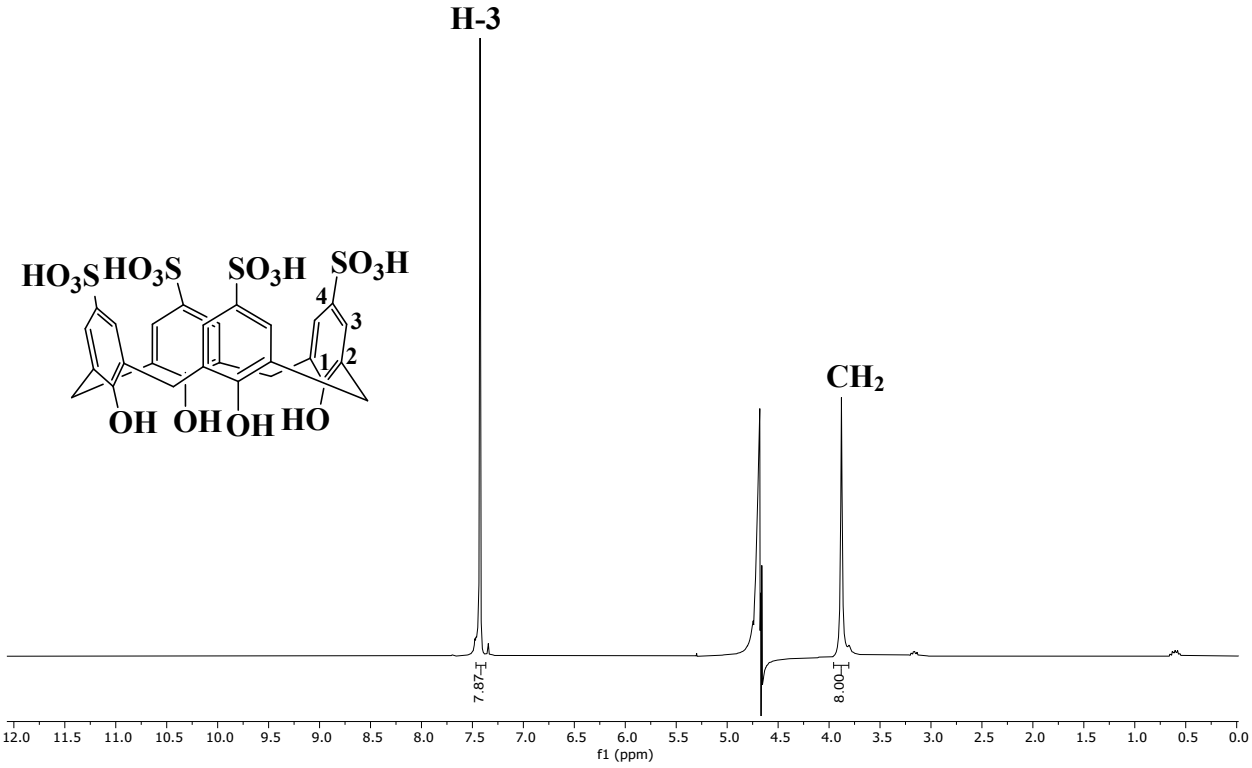

Fig. S8. ^{1}H NMR spectrum (300 MHz; D_2O) of CX4SO$_3$H.

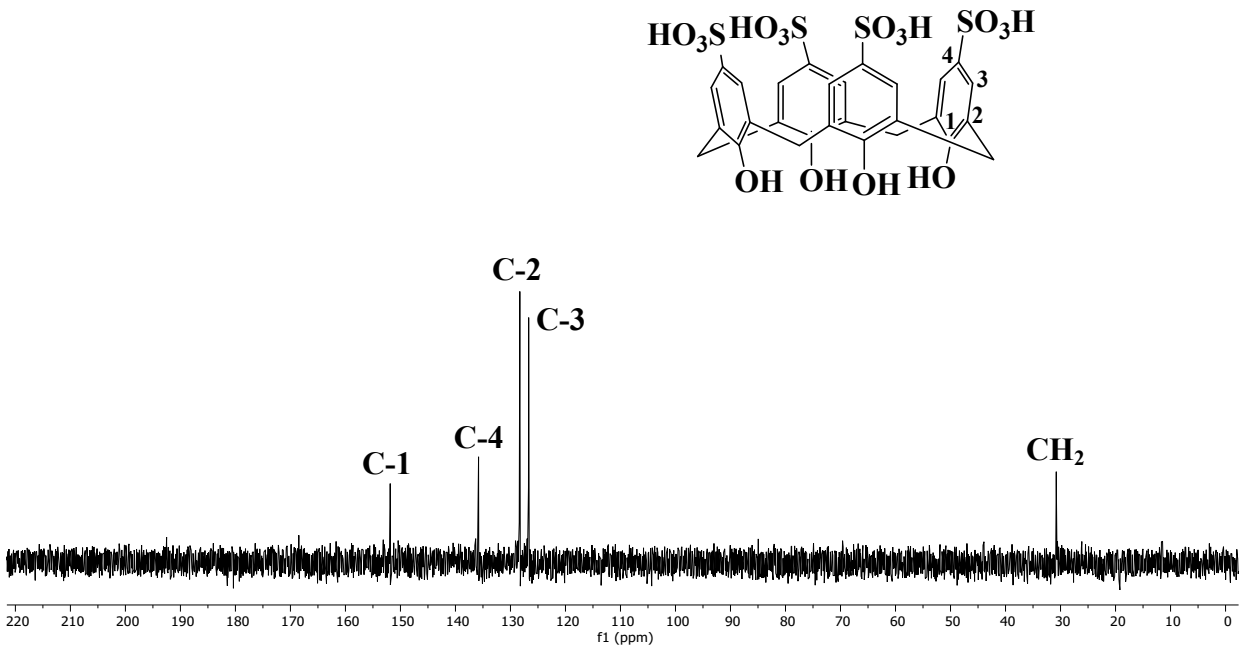

Fig. S9. ^{13}C NMR spectrum (75 MHz; D_2O) of $CX4SO_3H$.

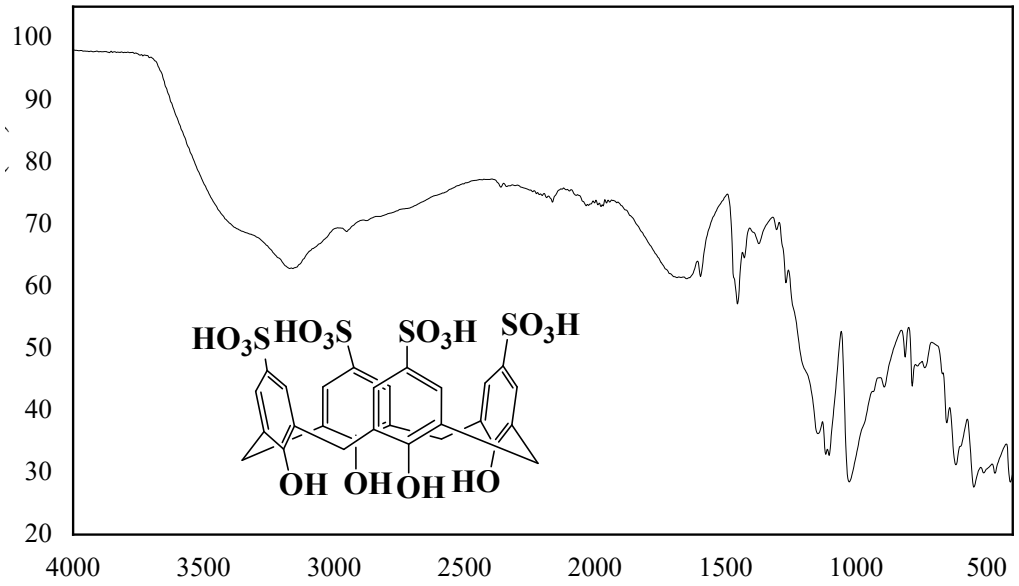

Fig. S10. FTIR Spectrum of $CX4SO_3H$.

Spectroscopic Data for furfural

Furfural: Yellow liquid. **GC-MS** (*m/z*) (abundance %): 96 (100, M+), 95 (98), 67 (15), 51 (3). **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 9.63 (s, 1H), 7.67–7.66 (m, 1H), 7.23 (dd, J = 3.6 Hz, 1H), 6.68 (dd, J = 3.6 Hz, 1H). **IR** (ATR, cm^{-1}) $\bar{\nu}_{max}$: 3134, 2849, 1671, 1567, 1468, 1397, 1278, 1019, 930, 748.

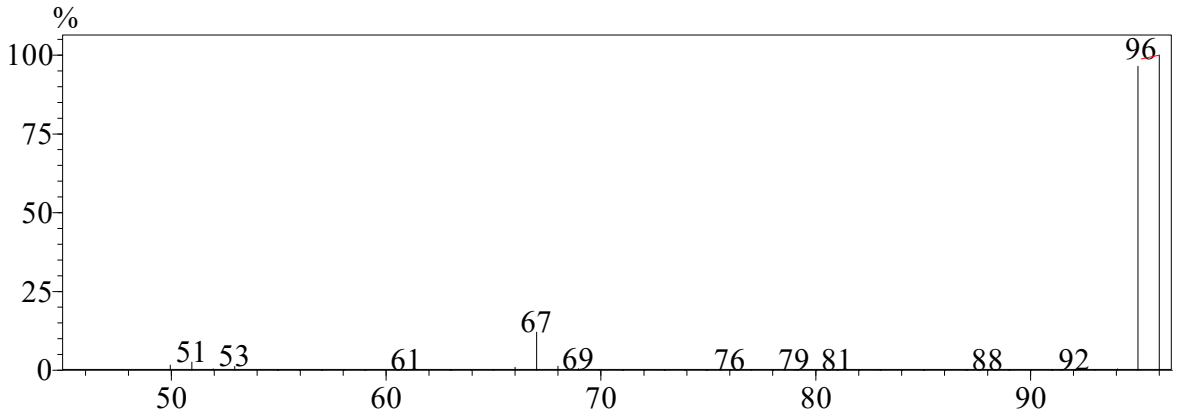

Fig. S11. Mass spectrum of furfural.

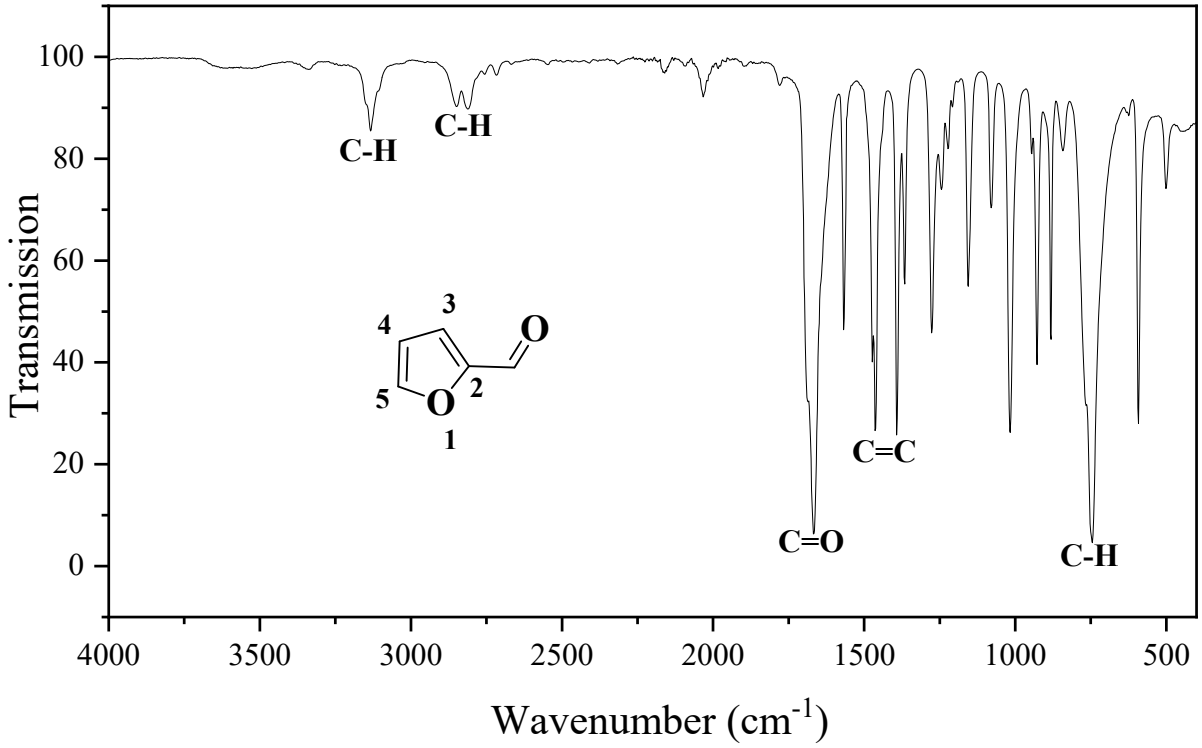

Fig. S12. FTIR Spectrum of furfural.

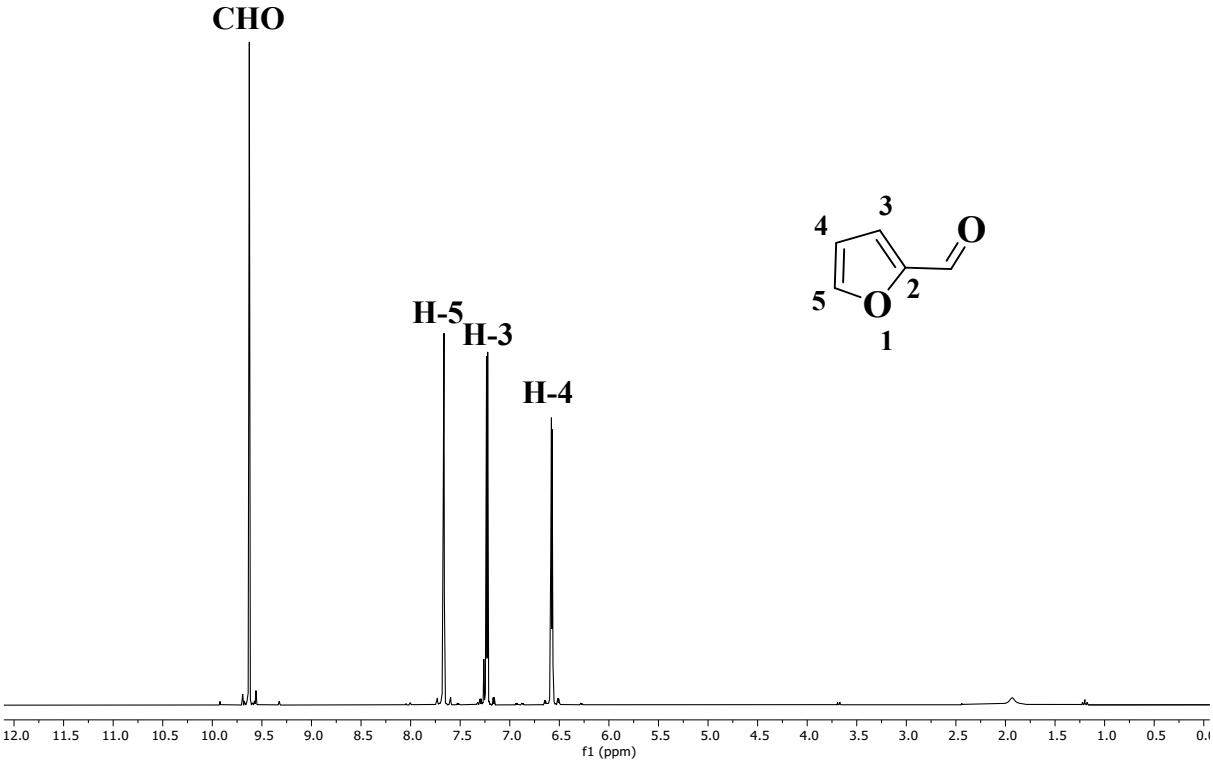

Fig. S13. ^{1}H NMR spectrum (300 MHz; $CDCl_3$) of furfural.

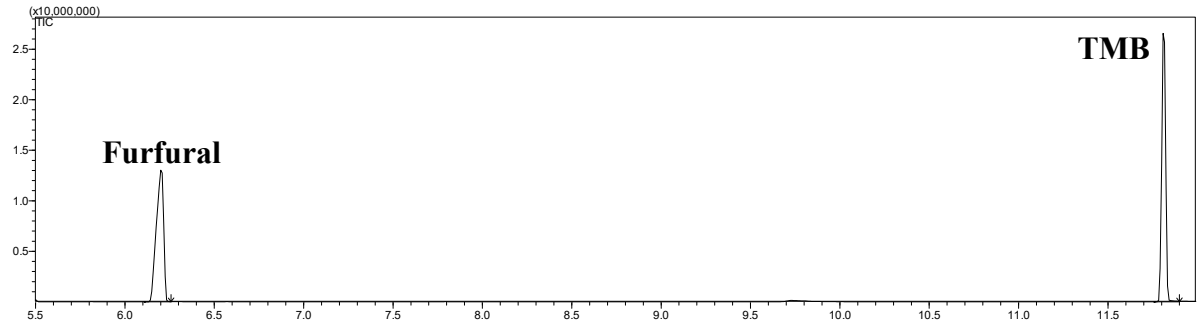

Fig. S14. Typical chromatogram of GC-MS analysis of furfural using TMB as internal standard.

Calibration curves

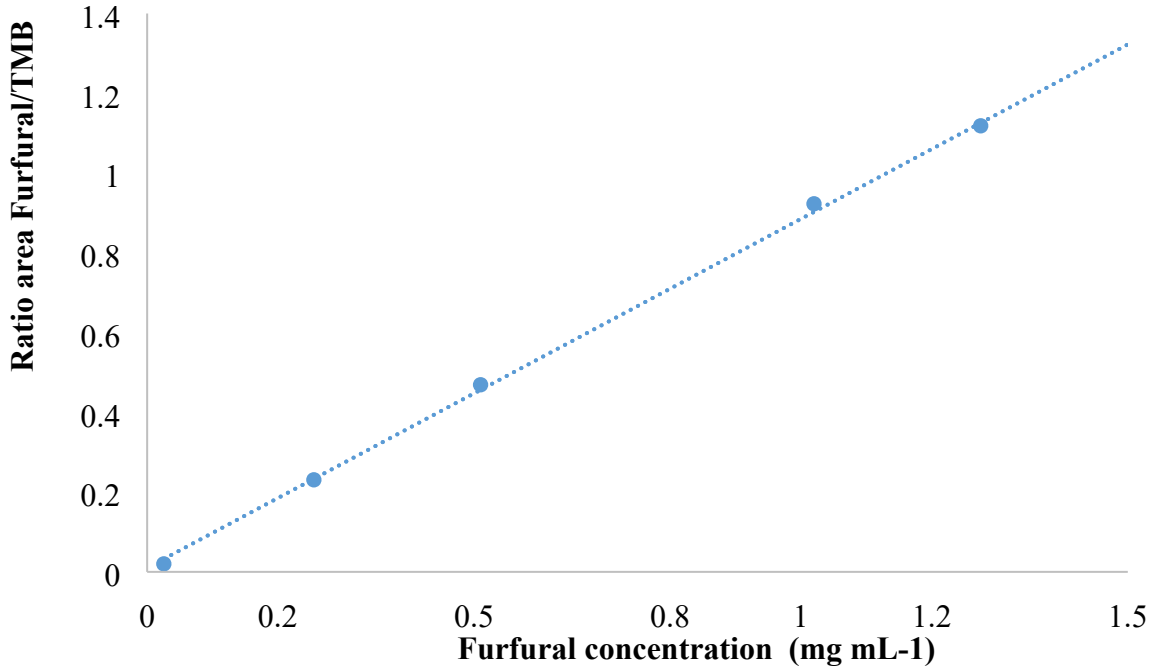

Fig. S15. Furfural calibration curve.

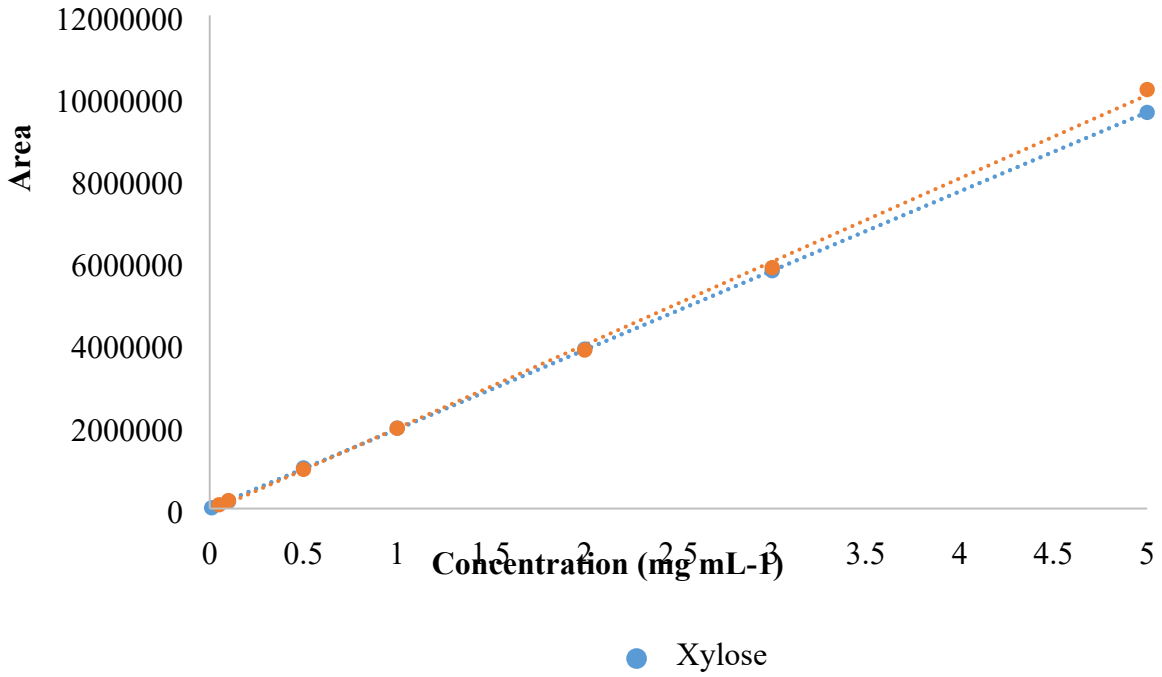

Fig. S16. Xylose and arabinose calibration curve.

References

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