**Supplementary Information**

# Oxidative depolymerization of kraft lignin to high-value aromatics using a homogeneous vanadium–copper catalyst

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**Table S1** Summary of all reactions carried out, including reaction conditions and respective yields. Fixed reaction conditions: 25 g/L lignin concentration, 2 M NaOH aqueous solution. Yields are calculated on weight basis relative to initial lignin.

| **Catalyst** | **Catalyst amount** | **Catalyst ratio** | **Temper-ature** | **$O_2$ pressure** | **Reaction time** | **Bio-oil yield** | **Vanillin** | **Vanillic acid** | **Aceto-vanillone** | **4-Hydroxy-benzoic acid** | **4-Hydroxy-benzaldehyde** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | [mol] | [mmol:mmol] | [°C] | [bar] | [min] | [wt%] | [wt%] | [wt%] | [wt%] | [wt%] | [wt%] |
| Feed | | | - | - | - | 2.74 | 0.11 | 0.05 | 0.02 | 0.00 | 0.00 |
| Control (no catalyst) | | | 150 | 5 | 10 | 41.6 | 2.70 | 1.20 | 0.69 | 0.08 | 0.06 |
| Control (no catalyst) | | | 150 | 5 | 10 | 51.0 | 2.97 | 2.10 | 0.50 | 0.08 | 0.07 |
| Control (no catalyst) | | | 150 | 5 | 10 | 51.0 | 3.29 | 2.11 | 0.51 | 0.08 | 0.08 |
| $Mn(OAc)_2$ | 0.0017 | | 150 | 5 | 10 | 42.5 | 2.32 | 1.39 | 0.65 | 0.06 | 0.05 |
| $Cu(OAc)_2$ | 0.0017 | | 150 | 5 | 10 | 45.2 | 3.50 | 2.29 | 0.53 | 0.09 | 0.07 |
| $Cu(OAc)_2$ + $Mn(OAc)_2$ | 0.0017 | Cu:Mn 0.8:0.9 | 150 | 5 | 10 | 46.0 | 2.82 | 2.32 | 0.32 | 0.08 | 0.07 |
| $VO(acac)_2$ | 0.0011 | | 150 | 5 | 10 | 34.5 | 1.52 | 1.76 | 1.06 | 0.08 | 0.02 |
| $VO(acac)_2$ + $Cu(OAc)_2$ | 0.0014 | V:Cu 0.6:0.8 | 150 | 5 | 10 | 49.2 | 3.95 | 2.69 | 0.60 | 0.11 | 0.08 |
| $VO(acac)_2$ + $Cu(OAc)_2$ | 0.0014 | V:Cu 0.6:0.8 | 150 | 5 | 10 | 54.0 | 3.07 | 2.91 | 0.43 | 0.11 | 0.09 |
| Recycling of $VO(acac)_2$ + $Cu(OAc)_2$ | | | 150 | 5 | 10 | 38.7 | 1.91 | 2.17 | 0.54 | 0.12 | 0.05 |
| $VO(acac)_2$ + $Cu(OAc)_2$ | 0.0014 | V:Cu 0.2:1.2 | 150 | 5 | 10 | 47.7 | 3.82 | 2.39 | 0.38 | 0.10 | 0.09 |
| $VO(acac)_2$ + $Cu(OAc)_2$ | 0.0014 | V:Cu 0.2:1.2 | 150 | 5 | 10 | 49.7 | 3.33 | 2.32 | 0.42 | 0.08 | 0.07 |
| $VO(acac)_2$ + $Cu(OAc)_2$ | 0.0014 | V:Cu 1.2:0.2 | 150 | 5 | 10 | 36.2 | 2.58 | 2.58 | 0.65 | 0.08 | 0.05 |
| $VO(acac)_2$ + $Cu(OAc)_2$ | 0.0007 | V:Cu 0.6:0.8 | 150 | 5 | 10 | 49.3 | 3.56 | 2.89 | 0.48 | 0.09 | 0.08 |
| $VO(acac)_2$ + $Cu(OAc)_2$ | 0.0002 | V:Cu 0.6:0.8 | 150 | 5 | 10 | 51.7 | 3.49 | 2.58 | 0.46 | 0.09 | 0.08 |
| $VO(acac)_2$ + $Cu(OAc)_2$ | 0.0002 | V:Cu 0.6:0.8 | 150 | 5 | 10 | 54.2 | 3.35 | 2.62 | 0.44 | 0.08 | 0.09 |
| $VO(acac)_2$ + $Cu(OAc)_2$ | 0.0014 | V:Cu 0.6:0.8 | 130 | 5 | 10 | 35.6 | 2.68 | 1.88 | 0.52 | 0.08 | 0.06 |
| $VO(acac)_2$ + $Cu(OAc)_2$ | 0.0014 | V:Cu 0.6:0.8 | 170 | 5 | 10 | 44.4 | 3.60 | 3.05 | 0.87 | 0.11 | 0.09 |
| $VO(acac)_2$ + $Cu(OAc)_2$ | 0.0014 | V:Cu 0.6:0.8 | 150 | 3 | 10 | 33.5 | 2.05 | 1.57 | 0.71 | 0.09 | 0.05 |
| $VO(acac)_2$ + $Cu(OAc)_2$ | 0.0014 | V:Cu 0.6:0.8 | 150 | 7 | 10 | 55.7 | 2.70 | 0.96 | 0.22 | 0.15 | 0.08 |
| $VO(acac)_2$ + $Cu(OAc)_2$ | 0.0014 | V:Cu 0.6:0.8 | 150 | 5 | 60 | 61.3 | 3.31 | 2.92 | 0.36 | 0.13 | 0.09 |
| $VO(acac)_2$ + $Cu(OAc)_2$ | 0.0014 | V:Cu 0.6:0.8 | 150 | 5 | 180 | 58.7 | 2.94 | 3.31 | 0.48 | 0.16 | 0.08 |

**Table S2** SEC analysis of feed, control and catalyzed LB samples.

| **Sample** | **$M_w$** [a] | **$M_n$** [b] | **PDI** [c] |
|---|---|---|---|
| Feed | 5980 | 1668 | 3.58 |
| Control | 1239 | 861 | 1.44 |
| $Cu(OAc)_2$ | 1094 | 765 | 1.43 |
| $VO(acac)_2$-$Cu(OAc)_2$ | 1135 | 790 | 1.44 |

[a] $M_w$: Weight-average molecular weight. [b] $M_n$: Number-average molecular weight. [c] PDI: Polydispersity index.

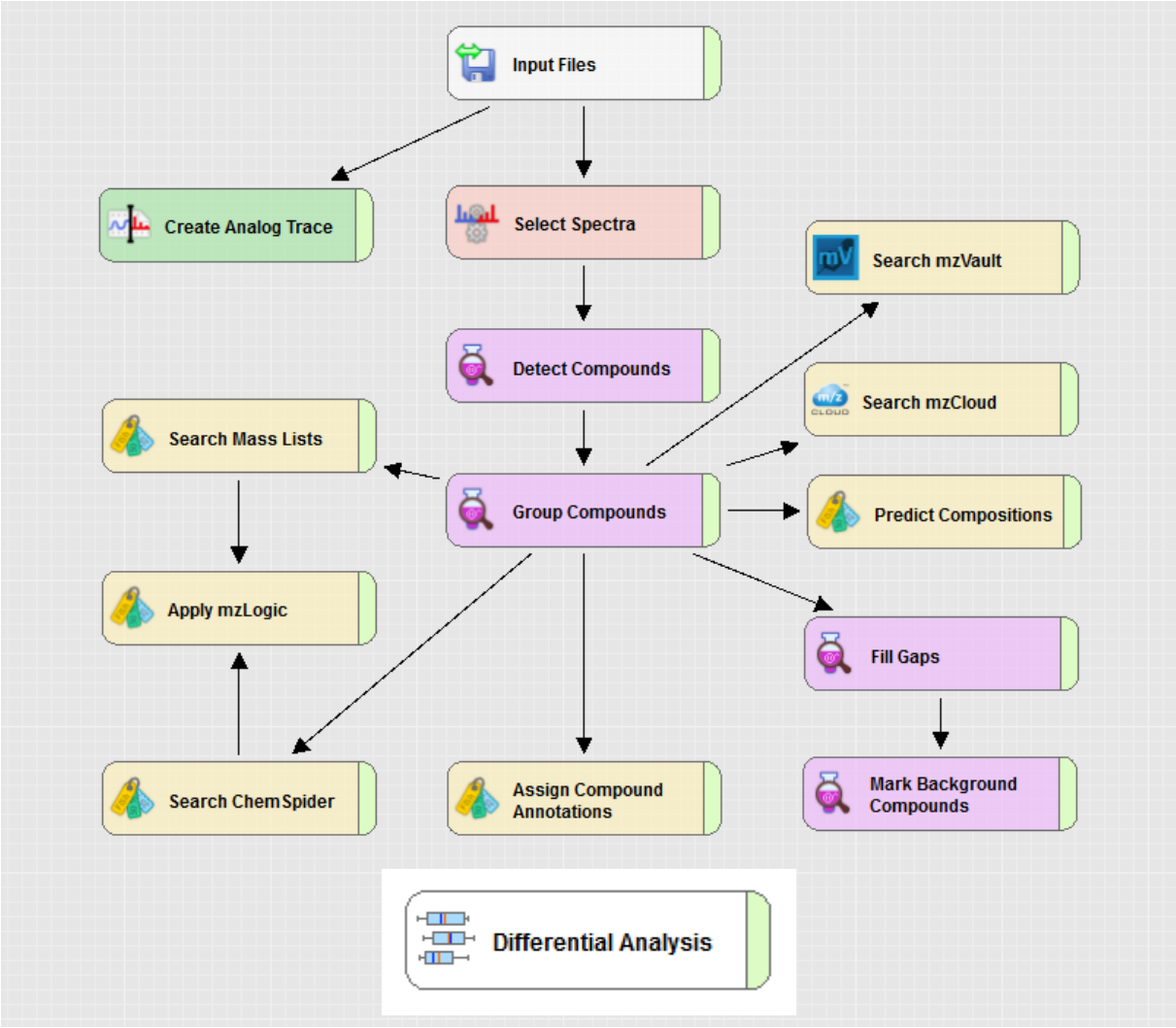


**Fig. S1** Compound Discoverer untargeted workflow used for deconvolution and processing of the obtained high-resolution mass spectrometry data.

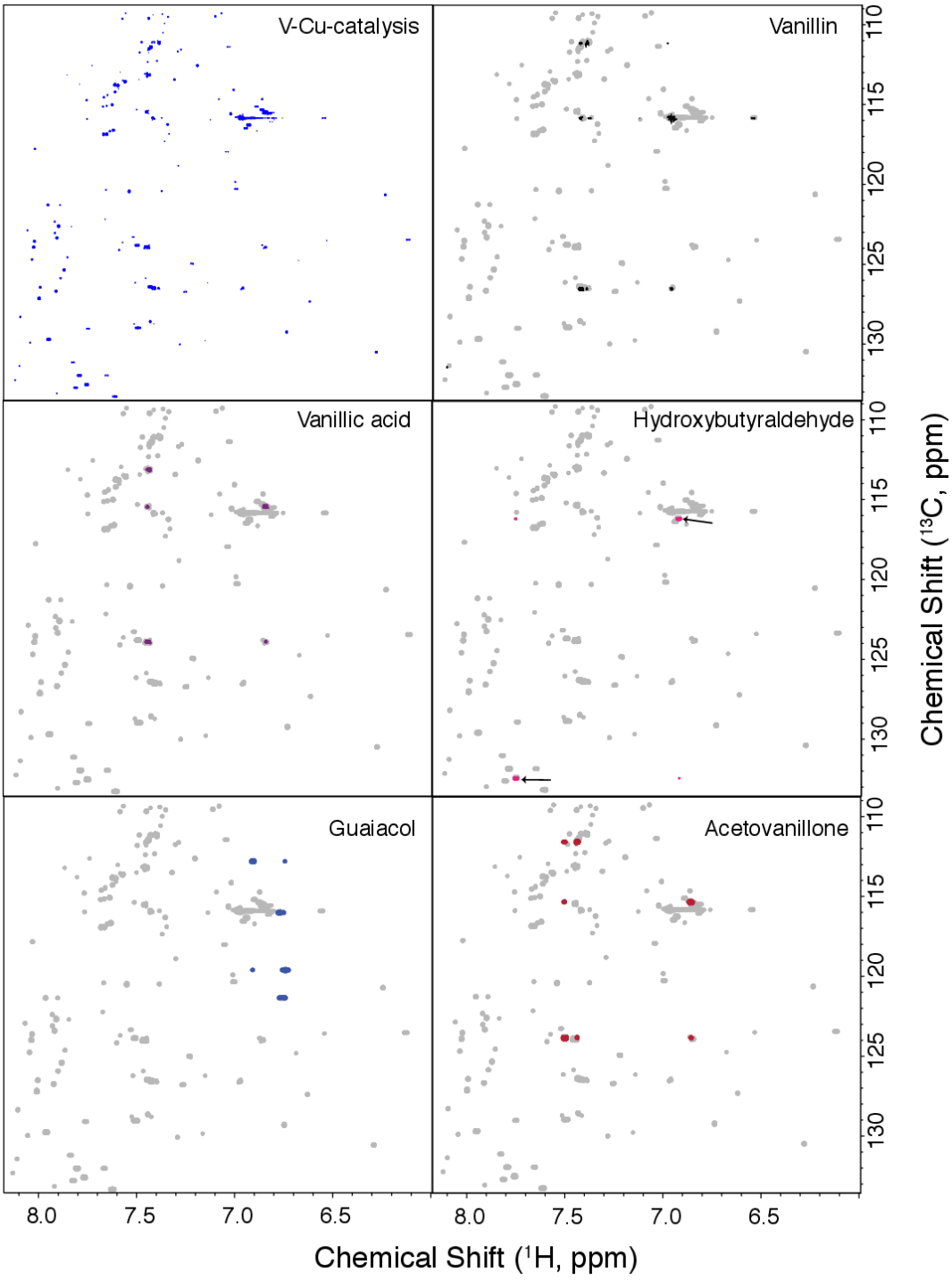


**Fig. S2** $^{1}H–^{13}C$ HSQC NMR spectra of the bio-oil obtained upon V-Cu catalysis and the spectra of selected compounds which were used for identification and quantification. Reaction conditions: 150 °C, 10 min, 5 bar initial $O_2$, 60 mL of 25 g/L lignin in 2 M NaOH, 1.4 mmol $VO(acac)_2$-$Cu(OAc)_2$ (V:Cu ratio = 0.75).

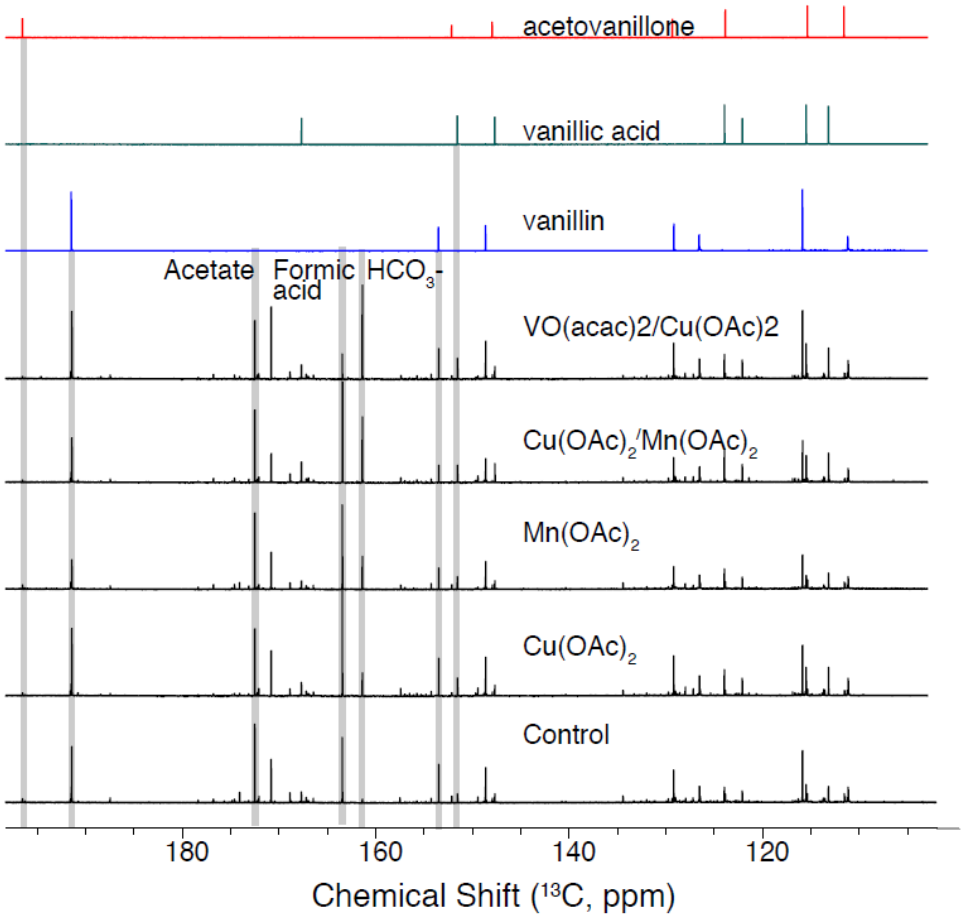


**Fig. S3** $^{13}C$ NMR spectra of the prepared standards for vanillin, vanillic acid, acetovanillone compared to the bio-oil obtained by various catalyzed and control experiments.

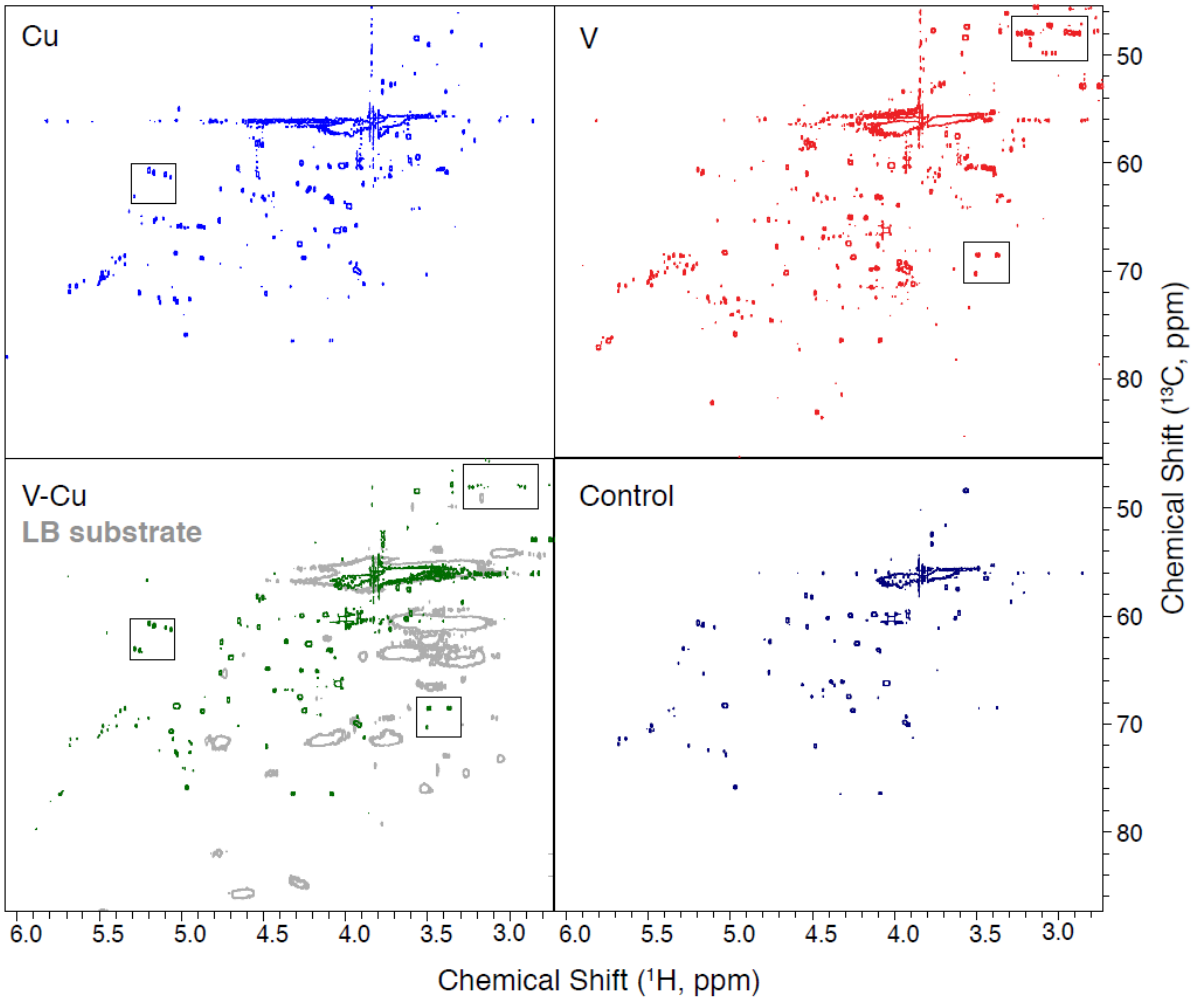


**Fig. S4** Comparison of $^{1}H–^{13}C$ HSQC NMR spectra of the LB substrate and the bio-oils obtained upon Cu, V and V-Cu catalysis in comparison to the bio-oil obtained in the control reaction. Reaction conditions: 150 °C, 10 min, 5 bar initial $O_2$, 60 mL of 25 g/L lignin in 2 M NaOH. Amounts and ratios of the respective catalysts are given in Table S1 (ESI). The figure is an enlarged version of Fig. 7.

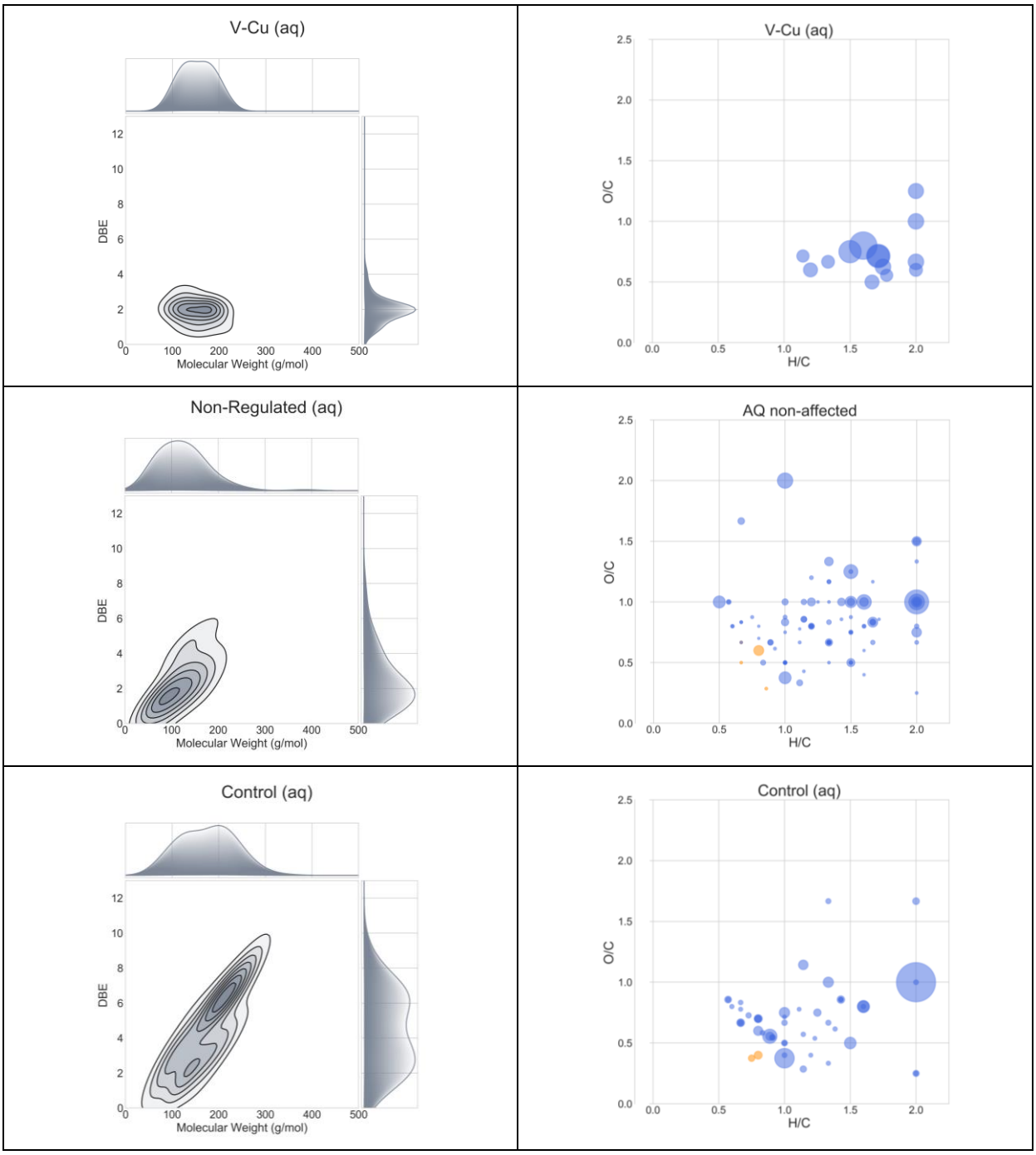


**Fig. S5** Kernel density (left) and van Krevelen plots (right) of the selected aqueous samples.

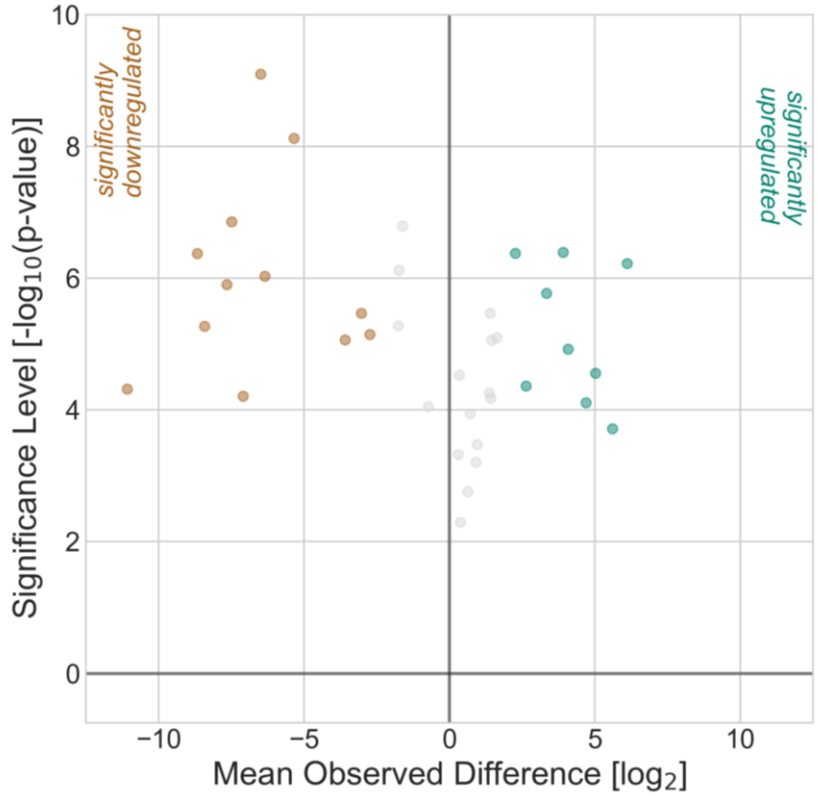


**Fig. S6** Volcano plot of control organic vs. LB sample.

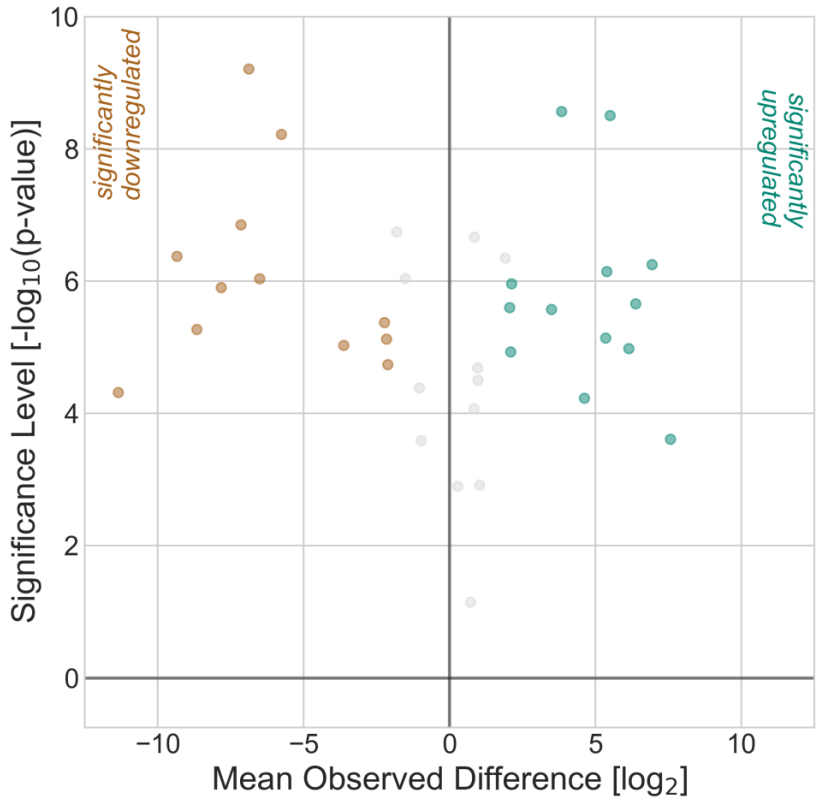


**Fig. S7** Volcano plot of V-Cu catalyzed organic vs. LB sample.

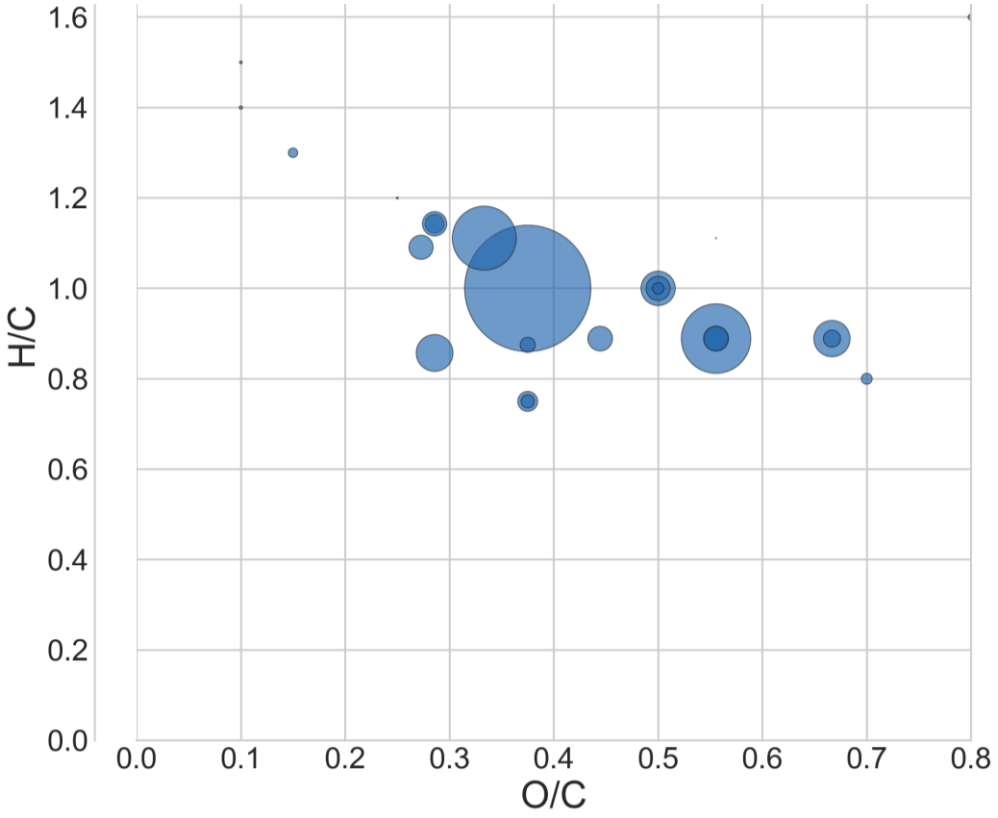


**Fig. S8** Van Krevelen analysis of the statistically indistinguishable species obtained from volcano plot of V-Cu catalyzed vs. control organic sample.

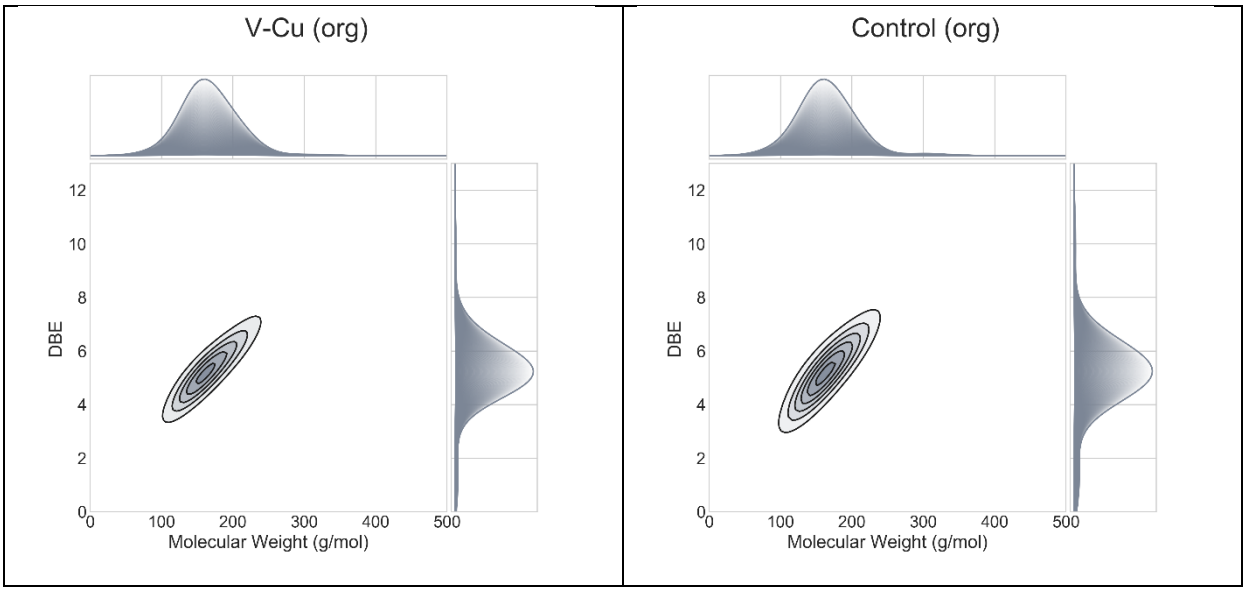


**Fig. S9** 2D kernel density plots of organic fraction of V-Cu and control sample.

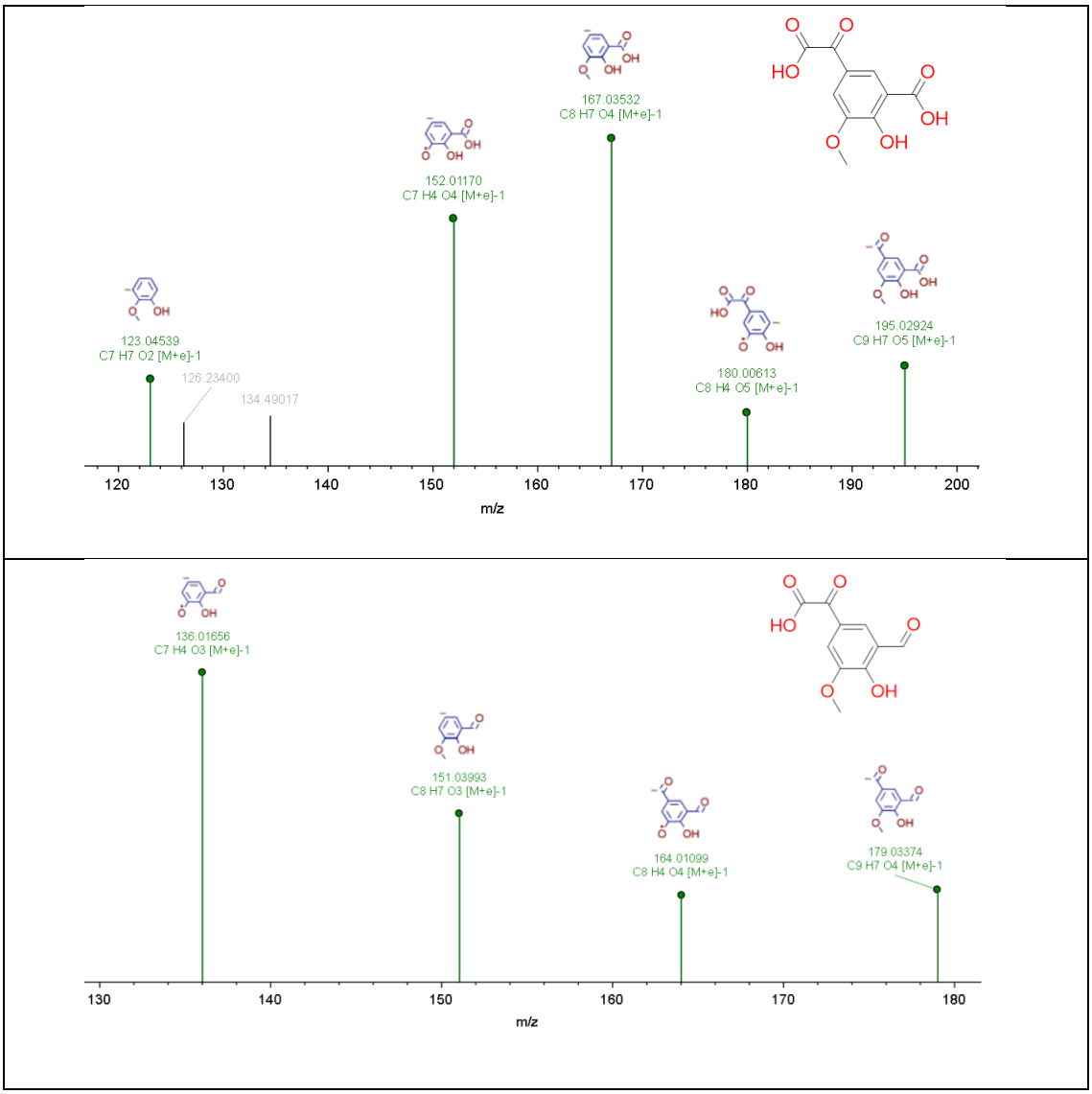


**Fig. S10** Fragmentation patters of collision-induced dissociation by HRMS of tentative structures, explained using the FiSH algorithm.

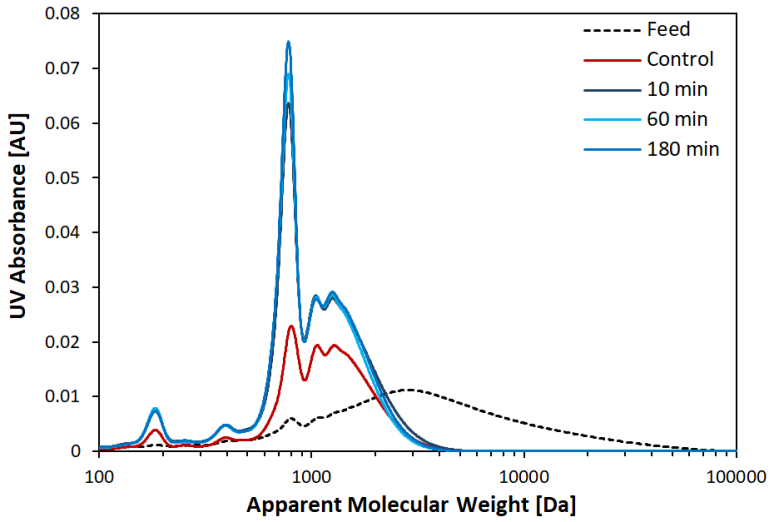


**Fig. S11** Molecular weight distributions of the feed, the control and the V-Cu-catalyzed samples (10, 60 and 180 min). Reaction conditions: 150 °C, 10 min, 5 bar initial $O_2$, 60 mL of 25 g/L lignin in 2 M NaOH, 1.4 mmol $VO(acac)_2$-$Cu(OAc)_2$ (V:Cu = 0.75).

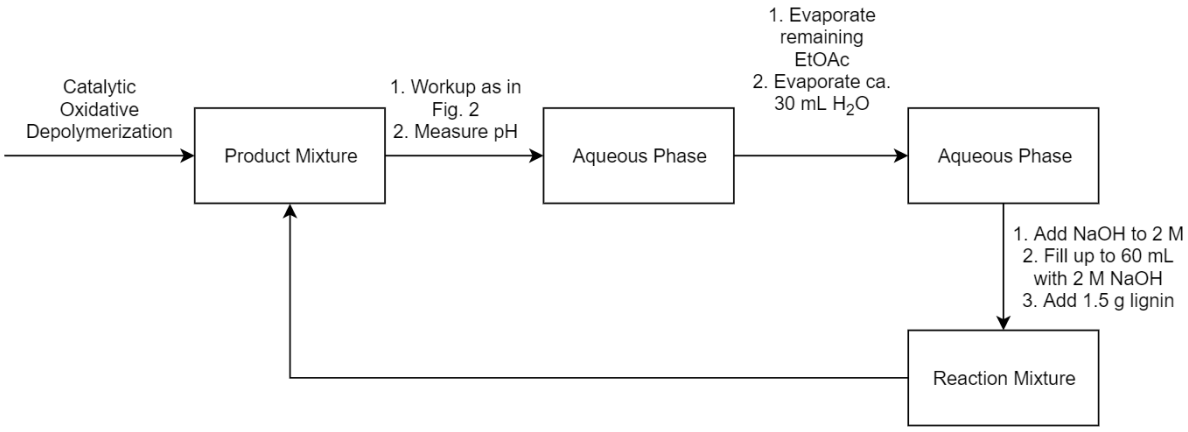


**Fig. S12** Workup procedure for the catalyst recycling experiment.