Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting information

Hydrodeoxygenation by deuterium gas -- a powerful way to provide insight into the reaction mechanisms

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1. Materials and Methods

All reagents used in this study were purchased from VWR International or Sigma-Aldrich (St. Louis, MO) and used as received. Wood chips used in this study were acquired from a 15-year old Loblolly pine tree from the southeastern U.S.A. The wood chips were refined with a Wiley mill through a 0.13 cm screen and dried under high vacuum at 50 °C for 48 h. Pine wood samples were stored at ~ 0 °C prior to use. Deuterium gas was purchased from Airgas.

1.1 Lignin separation and purification

The milled pine wood was ethanol-organosolv-pretreated as previously described in the literatures. [1-4] Briefly, a 100.0 g (dry weight) sample of the milled pine wood was treated with 65% ethanol/water solution with 1.2 w/w % sulfuric acid as a catalyst at 170 °C for 60 min. The solid to liquid ratio used was 1:8. The pretreatments were carried out in a Parr reactor equipped with a temperature controller (Parr Instrument Company, Moline, IL). The pre-treated pine wood was washed with warm (60 °C) ethanol/water (8:1, 3×50.0 mL). The washes were combined and 3 volumes of water were added to precipitate the Ethanol Organosolv Lignin (EOL), which was collected by centrifugation and air dried. The EOL was purified by Soxhlet extraction with pentane and stored at ~ 0 °C prior to use.

1.2 Equipment and process of pyrolysis [5,6]

Pyrolysis experiments were conducted in a quartz pyrolysis tube heated with a split-tube furnace. Typically, a sample of lignin powder (3.00 g) was placed in a quartz sample boat that was then positioned in the center of a pyrolysis tube. A K-type thermal couple was immersed in the sample powder during the pyrolysis to measure the heating rate. The pyrolysis tube was flushed with nitrogen gas and the flow rate was adjusted to a value of 500 mL/min and then inserted in the pre-heated furnace. The outflow from pyrolysis was passed through two sequentially connected condensers, which were immersed in liquid N_2. Upon completion of pyrolysis the reaction tube was removed from the furnace and allowed to cool to room temperature under constant N_2 flow. The condensers were then removed from liquid nitrogen. The pyrolysis char and pyrolysis oils were collected for subsequent chemical analysis. In general, the liquid products contained two immiscible phases which were referred to as a heavy oil (containing water insoluble components) and a light oil (containing water soluble components and ~80 wt% of water). The light oil was acquired by decantation and the heavy oil was recovered by washing the reactor with acetone followed by evaporation under reduced pressure. Char yields were determined gravimetrically and gas formation was calculated by mass difference.

1.3 Hydrogenation process

Hydrogenation of EOL heavy oil was examined in two steps which were carried out in a 75mL Parr 4590 Micro Stirred Reactor. In the first step, 150.0 mg heavy oil and 20.00 mL DI water (for deuterium system used D_2O) were loaded in a glass liner with 15.0 mg 5 wt% Ru/activated carbon catalyst (Alfa Aesar, Product No. 7440-18-8). The reactor was then purged 5 times with nitrogen gas to remove the air present in the reaction vessel. Then the reactor was purged 5 times with hydrogen (for deuterium system used deuterium gas) to replace nitrogen. The initial hydrogen (for deuterium system used deuterium gas) pressure was set to 1.0 Mpa and the stirring rate was 200 rpm. The reactor temperature stayed at 300 °C for 4 hours and the reactor pressure was stable at ~1.2 Mpa. After the first step hydrogenation, the EOL heavy oil has been upgraded to water soluble components and the water solution of the products was filtered through a 0.45 μm syringe filter.

1.4 Characterization of heavy oil by GPC

The average molecular weight were determined by GPC analysis following literature methods.[5,6] Prior to GPC analysis, the heavy oil and tar were dissolved in THF (1 mg/mL) and filtered through a 0.45 μm syringe filter. The samples were injected into a Polymer Standards Service (PSS) Security 1200 system featuring Agilent HPLC vacuum degasser, isocratic pump, refractive index (RI) detector and UV detector (270 nm). Separation was achieved with four Waters Styragel columns (HR0.5, HR2, HR4, HR6) using THF as the mobile phase (1.0 mL/min) with injection volumes of 30 μL. Data collection and processing were performed using PSS WinGPC Unity software. Molecular weights (M_n and M_w) were calibrated against a polystyrene calibration curve. The calibration curve was created by fitting a third order polynomial equation to the retention volumes obtained from a series of narrow molecular weight distribution polystyrene standards (i.e., 3.90×10^6, 3.64×10^6, 2.22×10^6, 1.36×10^6, 9.96×10^5,

6.68×10^5, 5.38×10^5, 1.97×10^5, 5.51×10^4, 3.14×10^4, 1.39×10^4, 7.21×10^3, 4.43×10^3, 1.39×10^3, 5.80×10^2 Da), phenol and acetone. The curve fit had an R^2 value of 0.9984. The weight average molecular weight for EOL pyrolysis oil is 265g/mol.

1.5 Characterization of heavy oil, hydrogenation products and tar by NMR

1.5.1 Preparation of NMR samples

1.5.1.1 Pyrolysis oil

EOL heavy oil (70.0 mg) dissolved in 450 μL DMSO-*d*$_6$.

1.5.1.2 Hydrogenation products

The water solution of 1st step hydrogenation products (20.00 mL) was extracted by 1.00 mL $CDCl_3$. The $CDCl_3$ phase was dried by $MgSO_4$ and filtered through a 0.45 μm syringe filter. The relaxation reagent Chromium (III) acetylacetonate (0.01 M)[7] was added to the $CDCl_3$ filtrate to provide complete relaxation of all nuclei and the $CDCl_3$ solution was used as the NMR sample for the 1st step hydrogenation product.

1.5.1.3 EOL

EOL (100 mg) dissolved in 450 μL DMSO-*d*$_6$.

1.5.2 Quantitative ^{13}C NMR

All NMR spectral data reported in this study were recorded with a Bruker Avance/DMX 400 MHz NMR spectrometer. Quantitative ^{13}C NMR employs an inverse gated decoupling pulse sequence, 90° pulse angle, a pulse delay of 5 s for heavy oils, 12 s for lignin and 10 s for hydrogenation products (Note: the longest T1 for pyrolysis oil was determined to be 0.8 s, and for the hydrogenation products after adding the relaxation reagent the T1 reduced from 6s to 2s. The T1 was measured using Inversion-Recovery method and calculated with Bruker's TopSpin software 2.1.) and 6000 scans. [5,6]

1.5.3 HSQC-NMR

HSQC-NMR were employing a standard Bruker pulse sequence "hsqcetgpsi.2" with a 90° pulse, 0.11 s acquisition time, a 1.5 s pulse delay, a $^1J_{C\text{–}H}$ of 145 Hz, 48 scans and acquisition of 1024 data points (for ^{1}H) and 256 increments (for ^{13}C). The ^{1}H and ^{13}C pulse widths are p1=11.30 μs and p3=10.00 μs, respectively. The ^{1}H and ^{13}C spectral widths are 13.02 ppm and 220.00 ppm, respectively. HSQC data processing and plots were carried out using MestReNova v7.1.0 software's default processing template and automatic phase and baseline correction.[8]

1.5.4 ^{2}D-NMR

Deuterium NMR was carried out with Bruker's pulse program "zg2h" by using the lock channel in a Bruker's BBO probe. A 90° C pulse, 4.5 s acquisition time and 800 scans were employed for acquiring the ^{2}D-NMR spectra.

1.5.5 Quantitative ^{1}H-NMR

Quantitative ^{1}H-NMR was acquired with 16 transients and 1s pulse delay. (Note: the longest T1 was determined to be 0.16 s)

1.6 Elemental analysis of EOL and EOL heavy oil and carbon content of hydrogenation products

Elemental analysis data of EOL and EOL heavy oil was obtained by Atlantic Microlab. Inc. (Norcross, GA) utilizing combustion to determine carbon, hydrogen and sulfur contents and the oxygen content was calculated by mass difference. The error is 0.3%.

The carbon contents of the 1st and 2nd step hydrogenation products were determined by Total Organic Carbon (TOC) analyzer (Ionics Inc 1555B).

1.7 Computational Methodology and Approach

Structures were constructed using the Avogadro program to build the structures and perform initial exploration of the configuration space using the UFF force field. These structures were then minimized using the global hybrid density functional PBE0 and the 6-311+G(d,p) triple- ζ Pople-style basis set with diffuse function on the heavy atoms and polarization functions on all atoms, overall model chemistry PBE0/6-311+G(d,p). Minima were verified by exact second derivatives calculations. Free energies were calculated at STP. All quantum calculations were completed using the Gaussian 09

Revision D.01 suite of programs. Reaction energies were computed as the difference between the products and the reactants with a negative indicating an exothermic reaction.

1.8 Prediction of HSQC NMR

All the predicted HSQC NMR spectrums in this study were conducted by MestReNova 8.1.2-11880 version and used default method.

2. Experimental data

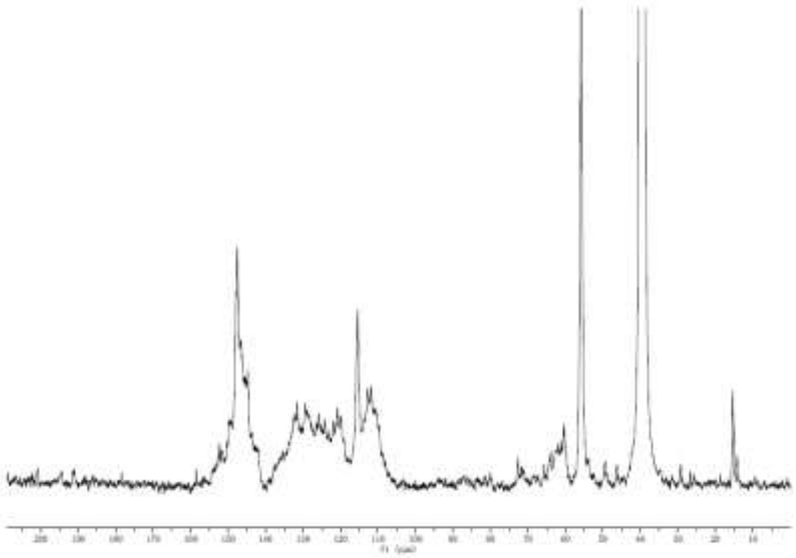
2.1 Elemental analysis of EOL and EOL heavy oil. The results are shown in weight percentage.

	C	H	O	S
EOL	66.89	5.64	27.47	0.00
EOL heavy oil	69.28	6.25	24.47	0.00

2.2 Yields of light oil, heavy oil, char, and gas for the pyrolysis of EOL at 600 °C for 30 min. The results are shown in weight percentage of EOL.

Sample	Light oil	Heavy oil	Total oil	Char	Gas
EOL	13.31	32.37	45.68	41.37	12.95

2.3 ^{13}C-NMR spectrum for EOL



2.4 Predicted HSQC NMR

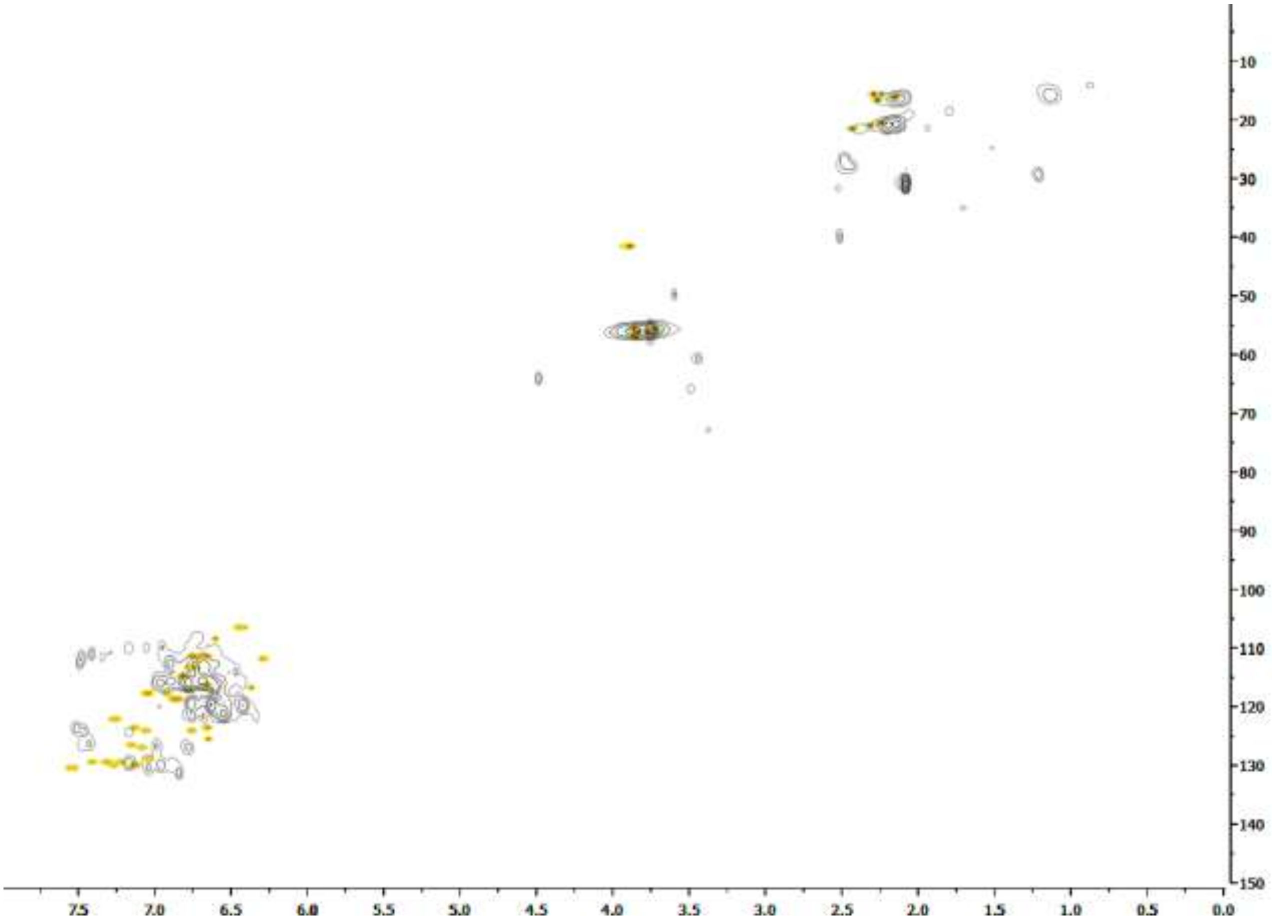


Fig. S1. Comparison of predicted HSQC NMR (shown in color) of proposed composite structures (1-5 shown in Fig. 6) and real HSQC NMR for EOL pyrolysis oil (shown in black).

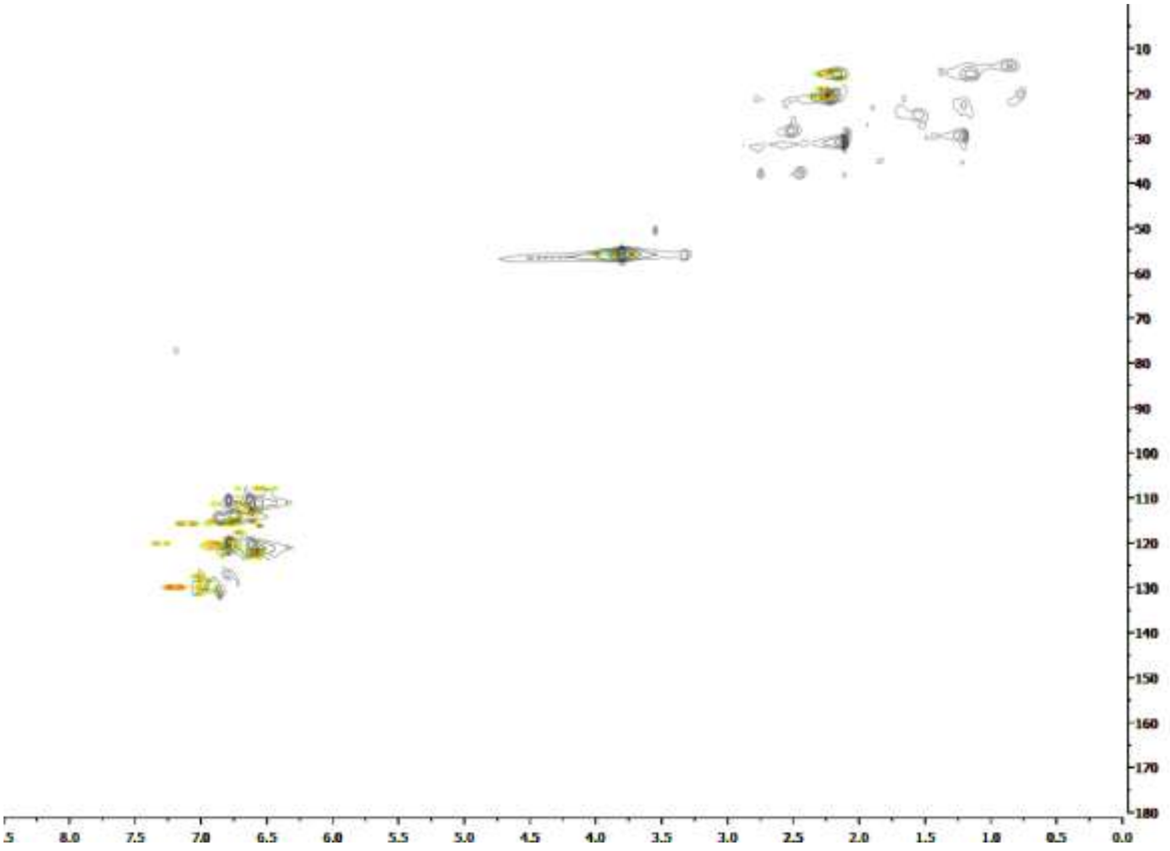


Fig. S2. Comparison of predicted HSQC NMR (shown in color) of proposed HDO products (products from 1-5 shown in Fig. 6) and real HSQC NMR for upgraded EOL pyrolysis oil (shown in black).

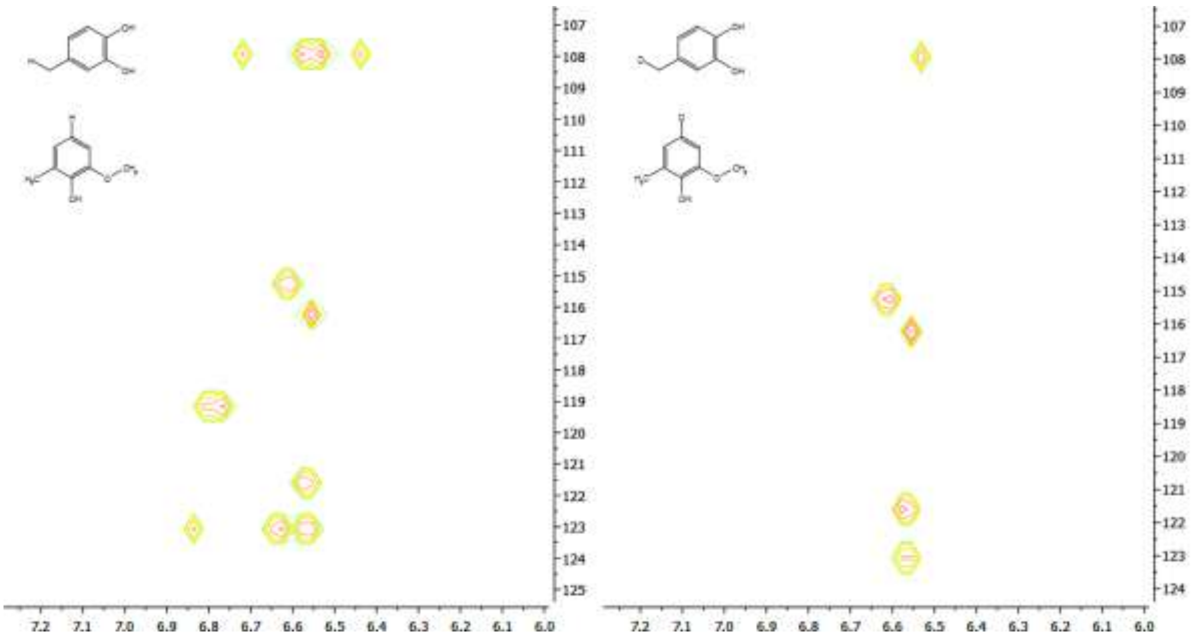


Fig. S3. Predicted HSQC NMR for simulated HDO process for reaction 1 shown in Fig. 6 in H and D systems.

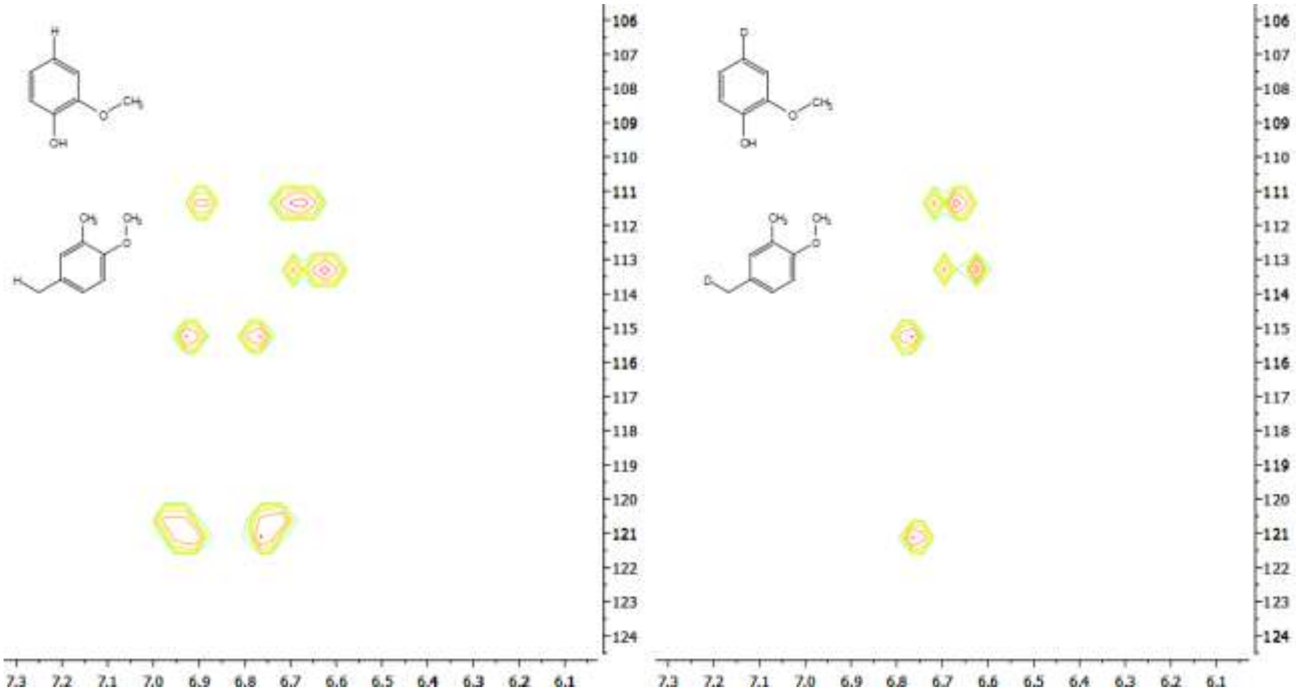


Fig. S4. Predicted HSQC NMR for simulated HDO process for reaction 2 shown in Fig. 6 in H and D systems.

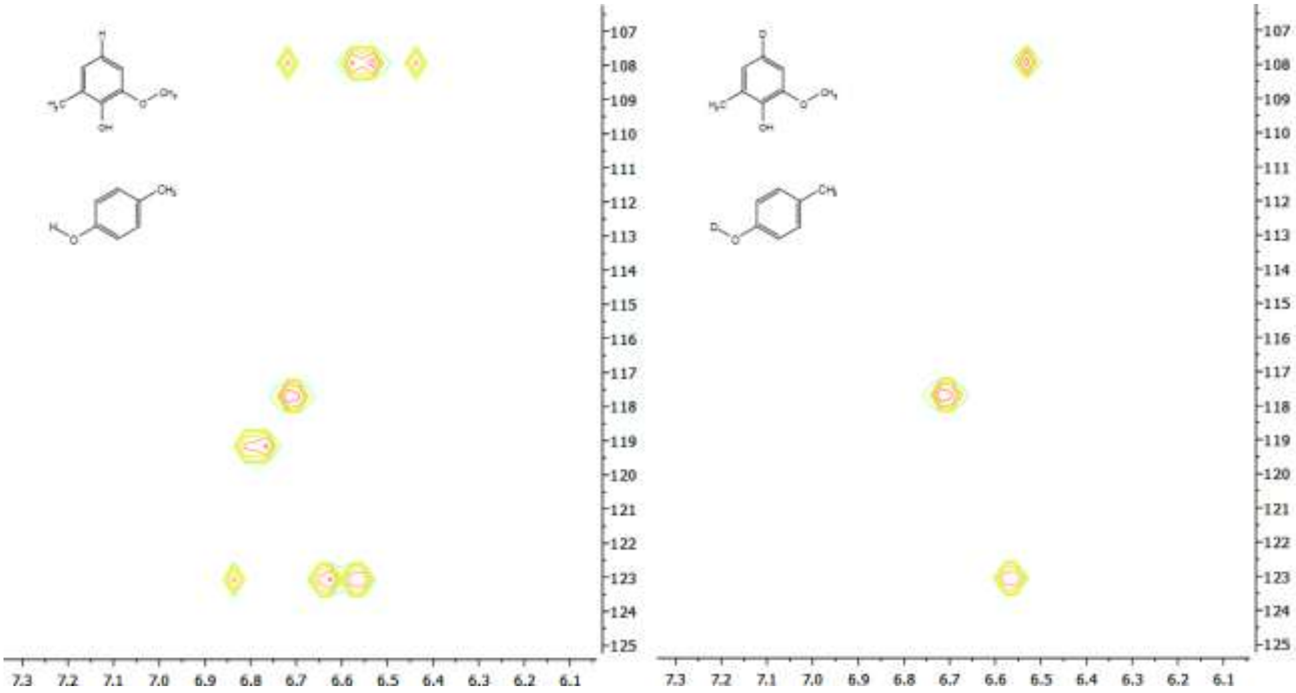


Fig. S5. Predicted HSQC NMR for simulated HDO process for reaction 3 shown in Fig. 6 in H and D systems.

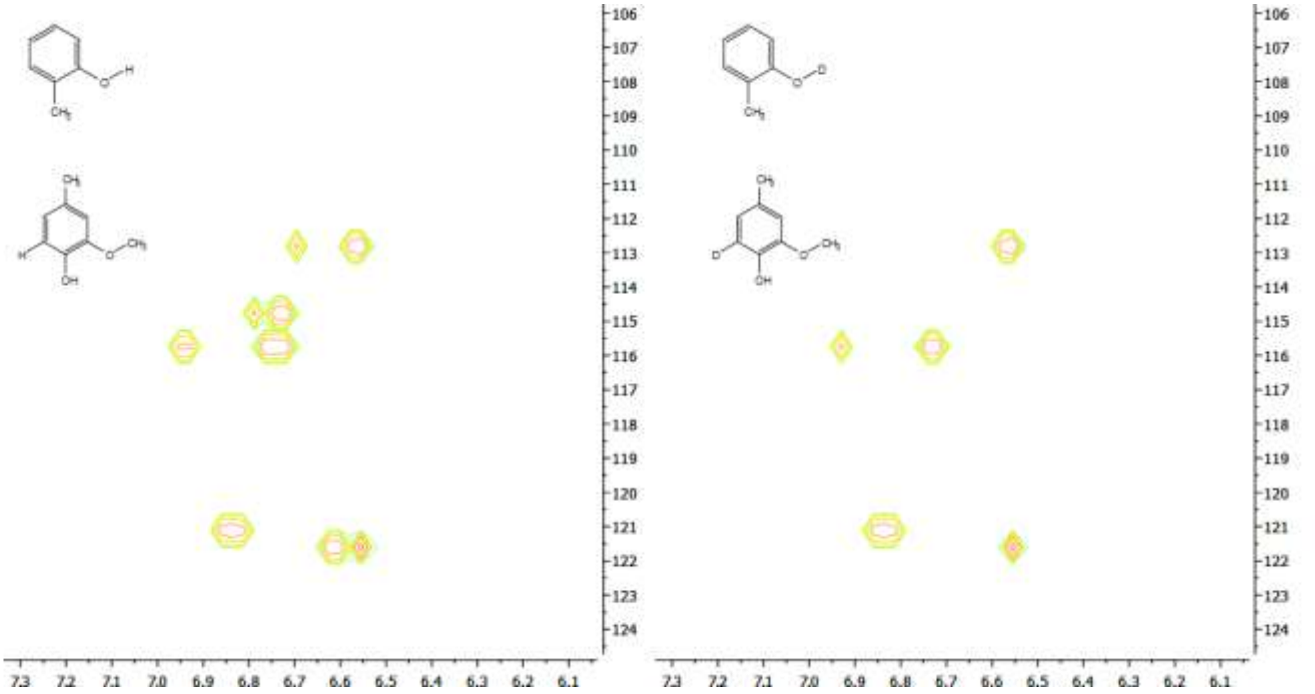


Fig. S6. Predicted HSQC NMR for simulated HDO process for reaction 4 shown in Fig. 6 in H and D systems.

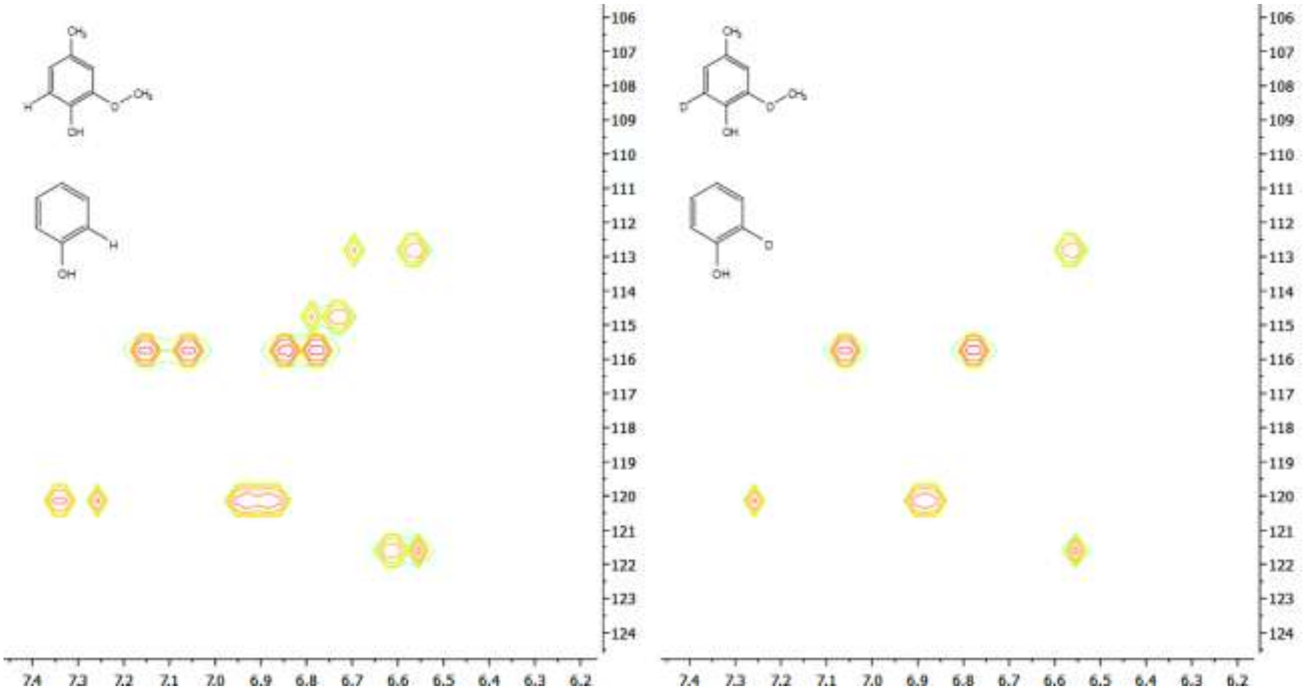


Fig. S7. Predicted HSQC NMR for simulated HDO process for reaction 5 shown in Fig. 6 in H and D systems.

3. Reference

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