

Modification of Conjugated Microporous Poly-benzothiadiazole for Photosensitized Singlet Oxygen Generation in Water

Supplemental Information

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Supporting Information

General. Both ^1H NMR spectra and ^{13}C NMR were taken on DPX-400 MHz Bruker instruments. NMR chemical shifts were reported as δ values in ppm relative to deuterated solvent: D_2O (4.79). Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration and coupling constant(s) in Hz. Multiplets were reported over the range (in ppm) it appeared. ^{13}C {1H} CP-MAS measurements were carried out using a Bruker Avance 400 spectrometer operating at 100.6 MHz for ^{13}C using a Bruker 4 mm double resonance probe-head operating at a spinning rate of 10 kHz. Elemental analysis was performed for carbon, hydrogen and nitrogen using a Vario EL Elemental Analyzer. Fourier-transform infrared (FT-IR) spectroscopy was done at room temperature with a BioRad 6000 FT-IR spectrometer equipped with a Single Reflection Diamond ATR. UV/Vis absorption spectra were measured on a Perkin-Elmer spectrophotometer. The insoluble networks were first grounded and dispersed in DMF. The porous properties of the polymer

networks were investigated by nitrogen adsorption and desorption at 77.3 K using an Autosorb 1MP Instrument from Quantachrome Instruments. Data evaluation was performed using the QuadraWin Software from Quantachrome Instruments. Pore size distributions and pore volumes were derived from the adsorption isotherms using the Density Functional Theory method. Samples were degassed at 80 °C for 24 h under high vacuum before analysis. Photo-catalyzed reactions were carried out by using LED module emitting at 420 nm with 12 W light output (OSA Opto Lights, OLM-018 series, Berlin, Germany) at a distance of 2 – 5 cm. All chemicals and solvents were purchased from commercial sources and used without further purification. Air- and/or water-sensitive reactions were conducted under nitrogen using anhydrous solvents.

Typical synthetic procedure of unmodified CMPs. The conjugated networks were synthesized using palladium catalyzed Sonogashira-Hagihara cross coupling condensation reaction. In a general procedure, to silica nanoparticle dispersed DMF was added 4,7-dibromobenzo[c][1,2,5]thiadiazole (200 mg, 0.68 mmol), 1,3,5-triethynylbenzene (68 mg, 0.45 mmol), dichlorobis(triphenylphosphin)palladium(0) (16mg, 0.023 mmol), copper(I) iodide (4 mg, 0.023 mmol) and Et₃N (10 ml). The reaction mixture was degassed and heated under nitrogen at 80 °C overnight. The yellow solid precipitated was filtered off, washed with DCM, and methanol in the Soxhlet overnight. The product was dried under vacuum.

Typical conditions for thiol-yne addition of mercaptopropionic acid onto unmodified CMPs into water-dispersible WCMPs. To CMP (repeat unit ~ 348 g/mol, 60 mg, ~ 0.5 mmol of alkyne) suspended in DMF was added 3-mercaptopropionic acid

(5.2 mg, 0.05 mmol, 0.1 equiv.) and 2,2'-Azobis(2-methylpropionitrile) (8.5 mg, 0.05 mmol, 0.1 equiv.). The reaction mixture was put under vacuum and then refilled with nitrogen (x 3), then was heated to 90 °C for 20 h. The reaction mixture was then filtered and the solids were repeatedly washed with hot THF and with acetone. Functionalized WCMPs were then dried in vacuum oven at 80 °C overnight.

Typical conditions for heterogeneous photocatalytic reactions (Synthesis of 5-hydroxy-2(5H)-furanone). Furoic acid (224 mg, 2 mmol) and modified conjugated microporous polymer network (WCMPs) (2 mg) was suspended in 20 ml MilliQ water. Oxygen was bubbled into the reaction mixture at 15 mL / min. The reaction mixture was irradiated by a 12W blue LED at 420 nm at room temperature. After 22 hours, the reaction mixture was filtered through 0.22 µm CME syringe filter then was lyophilized. ¹H NMR (400 MHz, D₂O) δ 7.42 (d, *J* = 12.1 Hz, 1H), 6.25 (s, 1H), 6.24 (s, 1H) ¹³C NMR (100 MHz, D₂O) δ 173.92, 153.85, 123.63, 99.60.

Solid State NMR

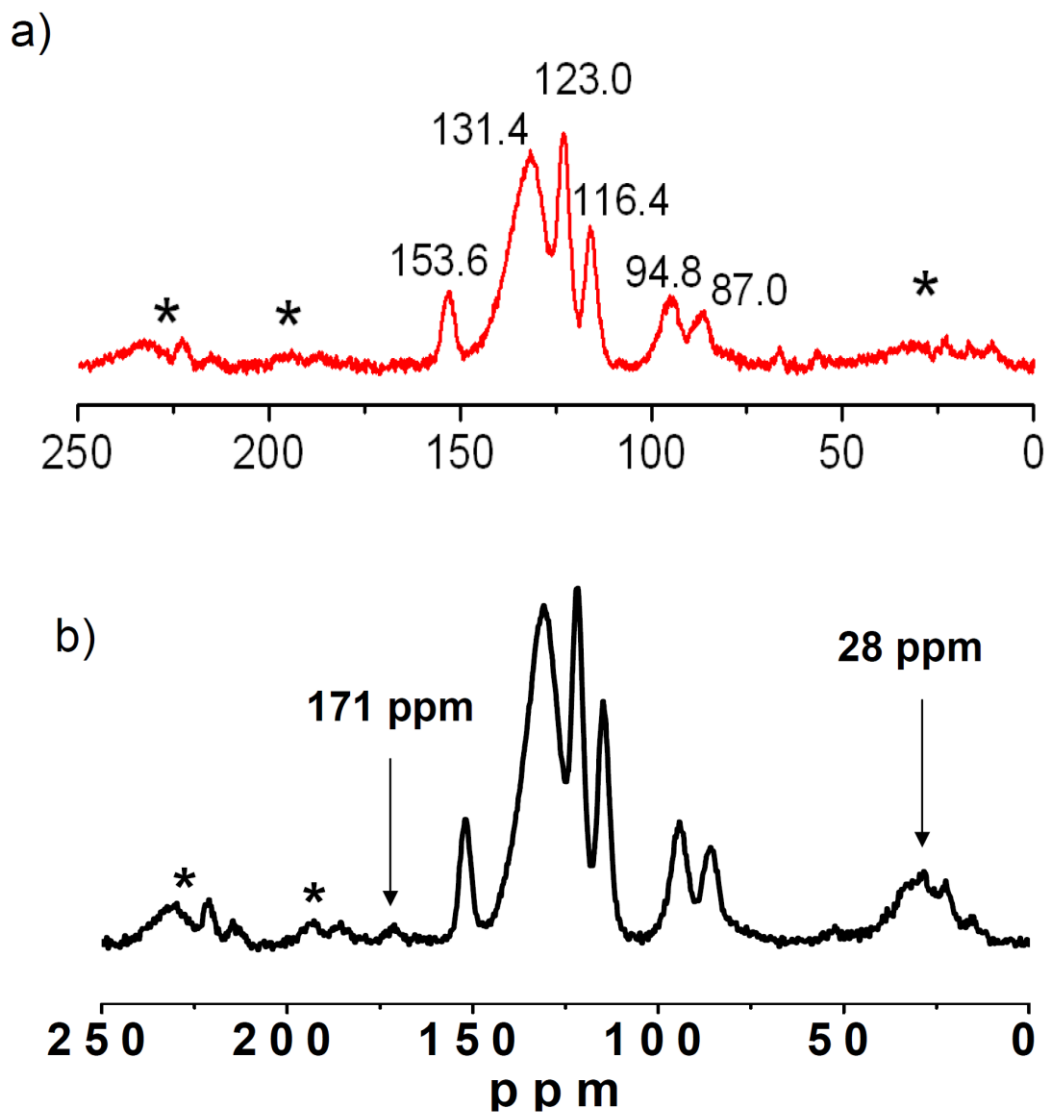


Figure S1. a) Solid state NMR spectra of unmodified **CMP** (ref) b) solid state NMR of MPA functionalized **WCMP**. The peak at ~ 30 ppm is attributed to the alkyl peaks from the MPA. The small peak at 171 ppm maybe due to the carbonyl group from the MPA as well. Peaks with asterisks are assigned as spinning side bands.

Elemental Analysis

Table S1. Elemental analysis found for unmodified **CMP** and **WCMP** modified with MPA.

sample	%C	%H	%N	%S
unmodified	66.4	2.0	10.4	11.0
WCMP_0.1	65.3	2.5	10.6	11.9
WCMP_0.4	65.0	2.6	10.5	12.0

UV / Vis

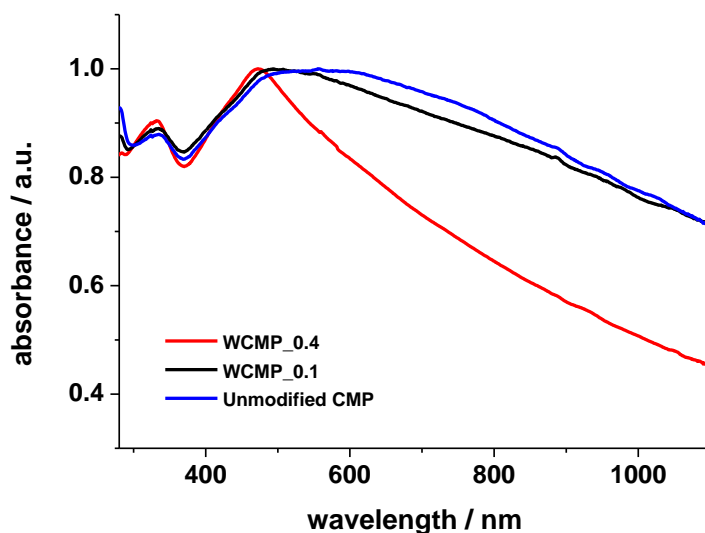


Figure S2. UV / Vis spectrum of unmodified **CMP** (blue line) and the modified **WCMPs** (red line <0.4 eq. of MPA and AIBN> and black line <0.1 eq. of MPA and AIBN>) dispersed in DMF.

BET

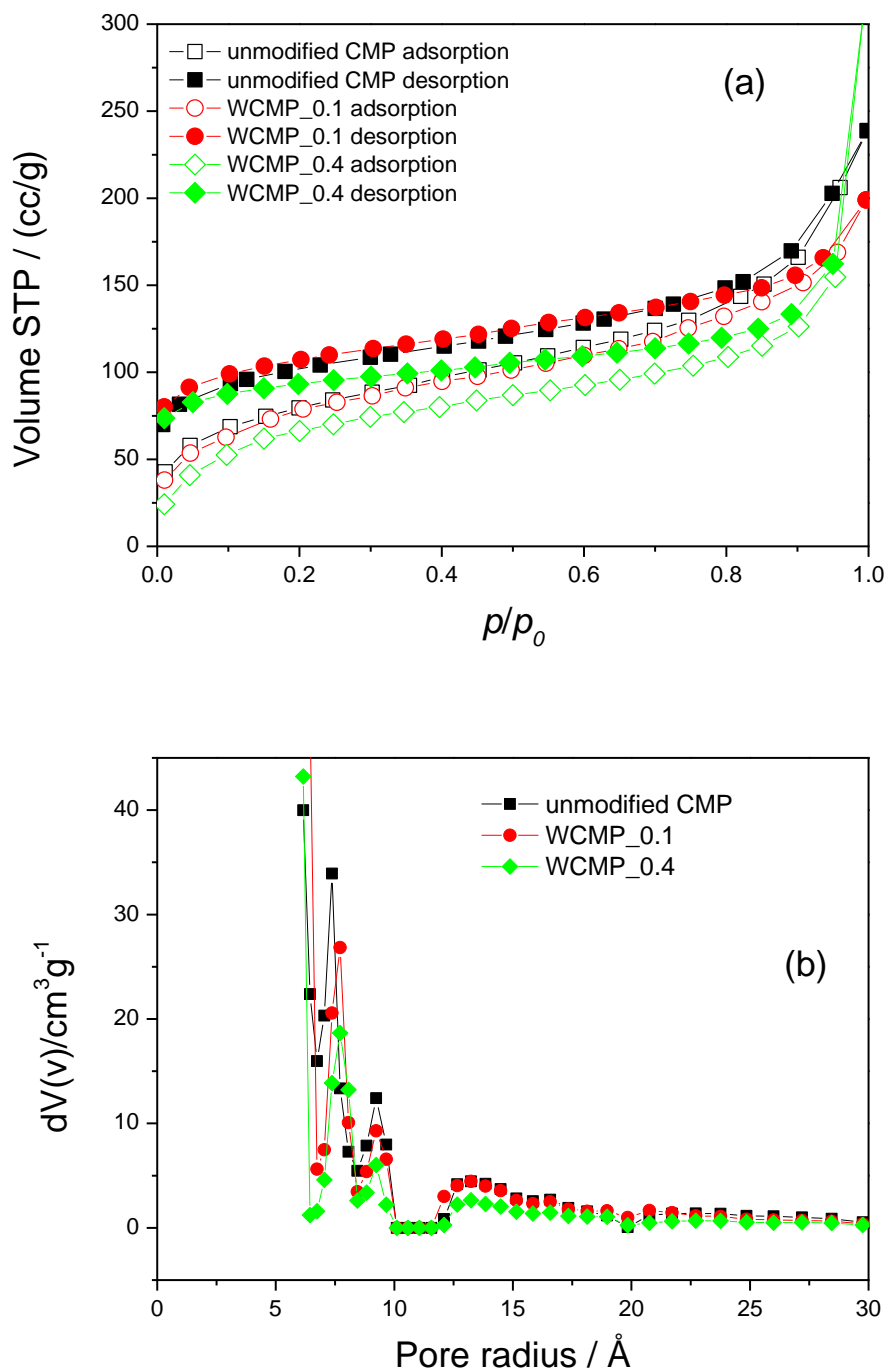


Figure S3. (a) BET isotherms of unmodified CMP (black line) and the modified WCMPs (green: 0.4 eq. of MPA and AIBN; and red: 0.1 eq. of MPA and AIBN), full symbols refer to the adsorption isotherm, hollow symbols refer to the desorption isotherms. (b) Pore size distributions of the unmodified CMP and modified WCMPs.

^1H NMR of the reaction mixture (5-hydroxy-2(5H)-furanone)

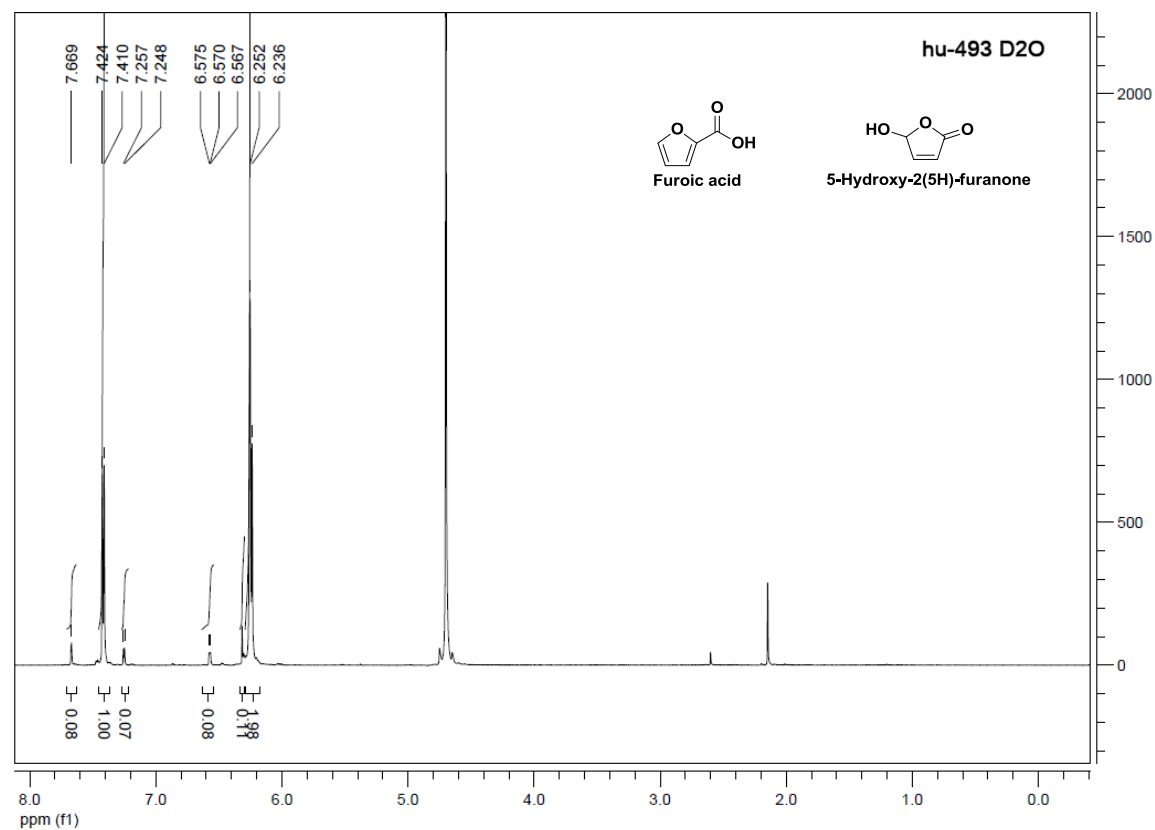


Figure S4. ^1H NMR of the mixture of furoic acid and 5-hydroxy-2(5H)-furanone (NMR conversion: ~ 93%) in D_2O . Peaks at 7.67, 7.25, 6.57 ppm attributed to furoic acid, 7.42, 6.25 ppm attributed to the furanone. Small peak at ~ 6.3 ppm, most likely attributed to maleic acid.

^{13}C NMR of the reaction mixture (5-hydroxy-2(5H)-furanone)

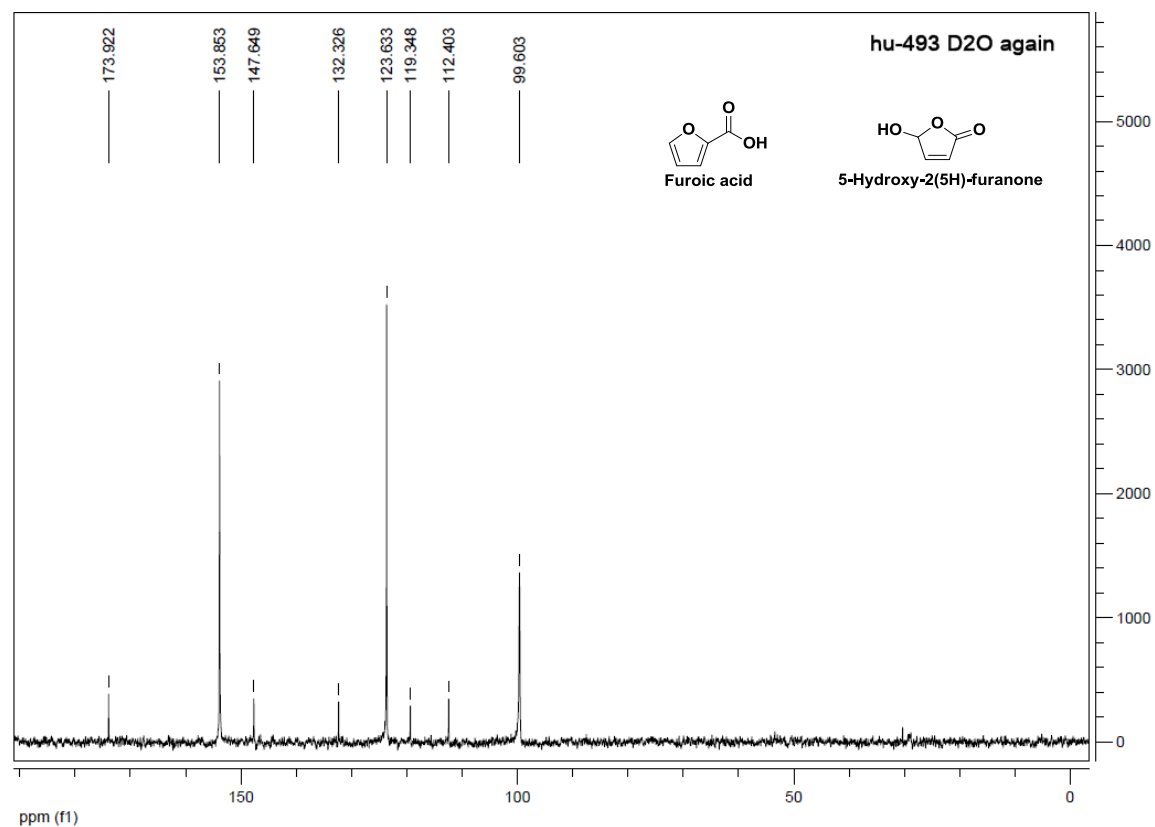


Figure S5. ^{13}C NMR of the mixture of furoic acid and 5-hydroxy-2(5H)-furanone in D_2O . Peaks at 147.65, 119.35, 112.40 ppm attributed to furoic acid, 173.92, 153.85, 123.63, 99.60 ppm attributed to the furanone. Peak at 132 ppm, most likely attributed to maleic acid.

^1H NMR and ^{13}C NMR of furoic acid (starting material to 5-hydroxy-2(5H)-furanone)

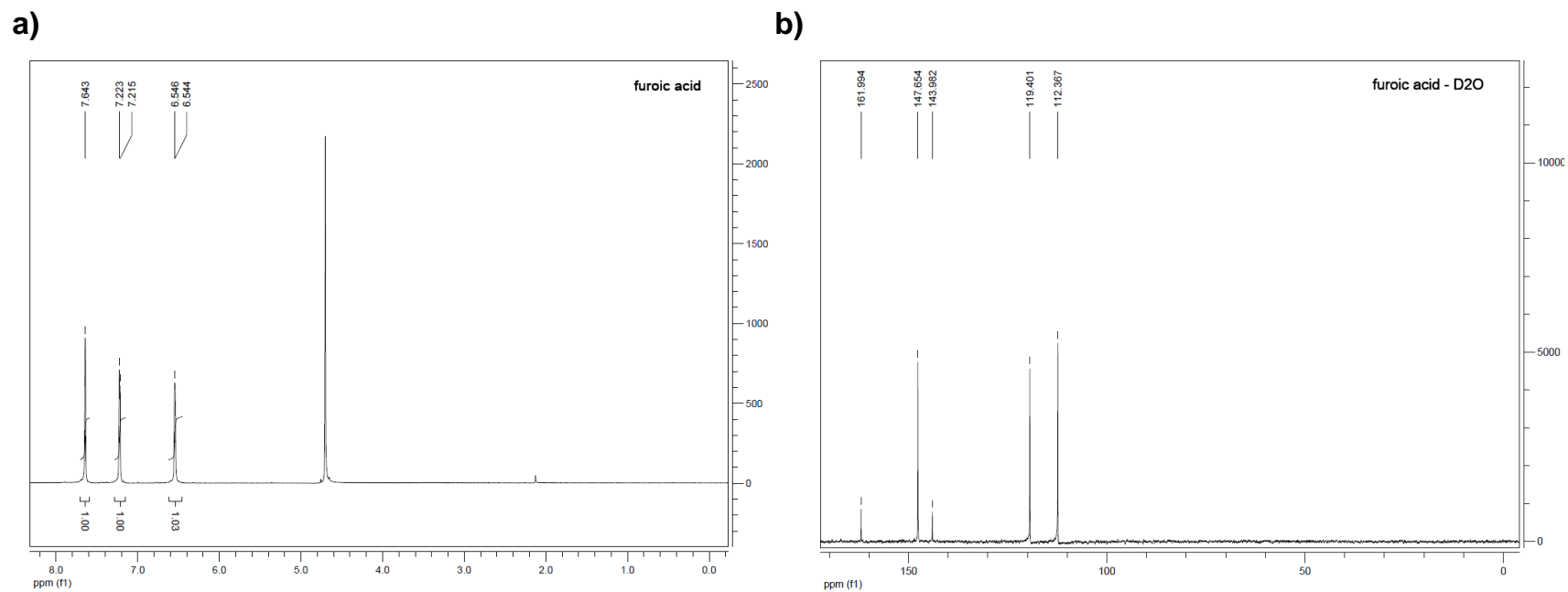


Figure S6. a) ^1H NMR and b) ^{13}C NMR of furoic acid