

SUPPORTING INFORMATION

Quantum Chemistry Analysis of Reaction Thermodynamics for Hydrogenation and Hydrogenolysis of Aromatic Biomass Model Compounds

Laurene Petitjean,^b Raphael Gagne,^a Evan Beach,^b Jason An, Paul Anastas,^{b,*} and Dequan Xiao^{a,*}

^a Laboratory for Integrative Materials Discovery
Department of Chemistry and Chemical Engineering
University of New Haven, 300 Boston Post Road, West Haven, CT 06516

^b Center for Green Chemistry and Green Engineering,
Yale University, 370 Prospect St., New Haven, CT 06520

*Corresponding authors: dxiao@newhaven.edu, paul.anastas@yale.edu

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1. Temperature dependence of the dielectric constant for methanol

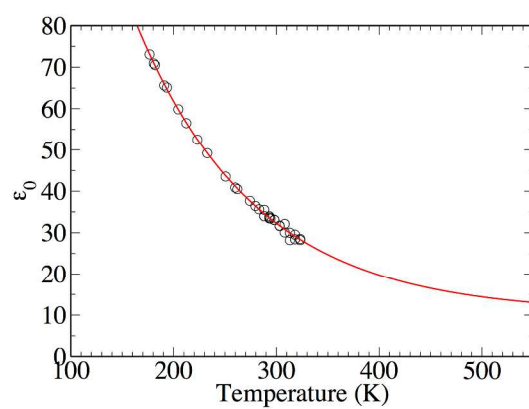
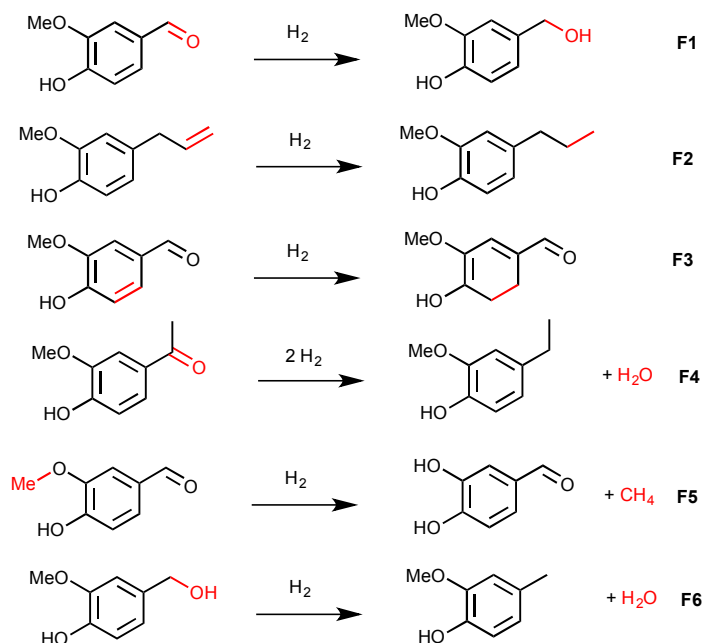


Figure S1. The variation of dielectric constants versus the change of temperature for methanol¹⁻⁶.

Table S1. Dielectric constants of methanol in different temperatures in the literature. Reproduced from http://www.ddbst.com/en/EED/PCP/DEC_C110.php.

T [K]	Dielectric Constant [-]	State	Reference
176.60	73.08000	Liquid	1
180.70	70.91000	Liquid	
182.00	70.52000	Liquid	
190.90	65.64000	Liquid	
193.50	65.10000	Liquid	
204.60	59.85000	Liquid	
212.30	56.51000	Liquid	
223.10	52.50000	Liquid	
232.70	49.19000	Liquid	
250.60	43.52000	Liquid	
260.00	40.85000	Liquid	
262.00	40.48000	Liquid	
274.20	37.68000	Liquid	
279.50	36.45000	Liquid	
283.15	35.65000	Liquid	2
288.00	34.00000	Liquid	3
288.15	34.00000	Liquid	4
288.15	35.53000	Liquid	5
293.15	33.45000	Liquid	6
293.15	33.71000	Liquid	2
293.15	33.95000	Liquid	5
294.20	33.42000	Liquid	1
298.00	33.10000	Liquid	3
298.15	33.05000	Liquid	5
298.15	33.10000	Liquid	4
303.15	31.62000	Liquid	5
303.15	31.71000	Liquid	2
308.00	32.12000	Liquid	3
308.15	30.08000	Liquid	5
308.15	32.12000	Liquid	4
313.15	28.20000	Liquid	6
313.15	29.98000	Liquid	2
318.00	28.44000	Liquid	3
318.15	28.44000	Liquid	4
318.15	29.54000	Liquid	5
323.15	28.24000	Liquid	2
323.15	28.53000	Liquid	5

2. Illustration of hydrogenation and hydrogenolysis reactions



Scheme S1. Hydrogenation and hydrogenolysis reactions of functional groups F1-F6 as shown in Scheme 1.

3. Reaction Gibbs Free Energy for Hydrogenation of the aldehyde group in Vanillin with varying basis sets

Table S2. Reaction Gibbs free energy for the hydrogenation of the aldehyde group in vanillin at 1 bar and 298°C (F1).

	6-31g*	6-311g*	cc-pvdz	cc-pvtz
ΔG (kcal/mol)	9.76	9.51	9.24	7.96

4. Solvation Free Energies for F1-F6 in Methanol at 303 K

Table S3. Solvation Free Energies for F1-F6 in Methanol at 303 K

	F1	F2	F3	F4	F5	F6
$\Delta G_{\text{solvation}}$ (kcal/mol)	-0.5954	0.4712	1.600	-4.109	-1.318	-3.763

5. Experimental Section

a. General Experimental

Chemicals and solvents were purchased from EMD Millipore, Sigma-Aldrich, Alfa-Aesar, JT Baker, Merck or TCI and used as received. All hydrogenation reactions were set-up in a 100 mL stainless-steel Parr reactor equipped with a mechanical stirrer. The reactions were then pressurized under Hydrogen Atmosphere (*Tech Air*, Ultra High Purity). The loaded reactor was placed on the bench-top Parr stand equipped with a Parr 4843 reactor controller.

X-Ray Powder Diffraction (XRPD) measurements were performed on a Bruker D8-focus X-Ray diffractometer equipped with a Cu line-focus sealed tube, a divergent beam goniometer and a NaI scintillation detector. Measurements were made with a 40 kV, 40 mA beam in the range 2θ from 3° to 80° locked couple scan type, a step size of 0.05° and a scan speed of 1 second/step.

Proton nuclear magnetic resonance (^1H NMR) spectra were acquired using Agilent DD2 400 MHz, Agilent DD2 500 MHz, Agilent DD2 600 MHz or Varian Inova 500 MHz spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) and are calibrated to the residual solvent peak. Coupling constants (J) are reported in Hz. Multiplicities are reported using the following abbreviations: s = singlet; d = doublet; t = triplet; m = multiplet (range of multiplet is given).

Analytical thin layer chromatography was performed on pre-coated 250 μm layer thickness silica gel 60 F₂₅₄ Plates (EMD Chemicals Inc.). Visualization was performed by ultraviolet light and/or by staining with potassium permanganate, vanillin or iodine. Purifications by column chromatography were performed using SilicaFlash F60 silica gel (40-63 μm , 230-400 mesh, Silicycle).

b. Synthesis of the Cu-PMO Catalyst

A solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (18.8 g, 0.05 mol, 1 equiv.), $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (30.76 g, 0.12 mol, 2.4 equiv.) and $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (7.0g, 0.03 mol, 0.6 equiv.) in 300 mL distilled (DI) water was added dropwise over four hours to a stirring solution of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ (6.2 g, 0.05 mol, 1 equiv.) in 375 mL distilled water. The pH was kept constant at pH \sim 10 by adding aliquots of 1 M NaOH aqueous solution. Upon completion of the addition, the mixture is allowed to stir vigorously at room temperature for three days. The blue precipitate is collected by vacuum filtration and washed with 1.5 L distilled water. The filter cake is then suspended in a solution of Na_2CO_3 solution (62 g, 0.5 mol, 10 equiv.) in DI H_2O (250 mL, 2M) and allowed to stir at room temperature overnight. Upon completion, the precipitate is collected by vacuum filtration and washed with DI H_2O (2.5 L). The filter is left to dry overnight in a 378.15 K oven to obtain copper doped hydrotalcite. The solid is ground by mortar and pestle and subjected to calcination at 733.15 K in air for 24 h to obtain Cu-PMO (9.21 g) as a green powder. The Cu-PMO was analyzed by XRPD (Figure S2).

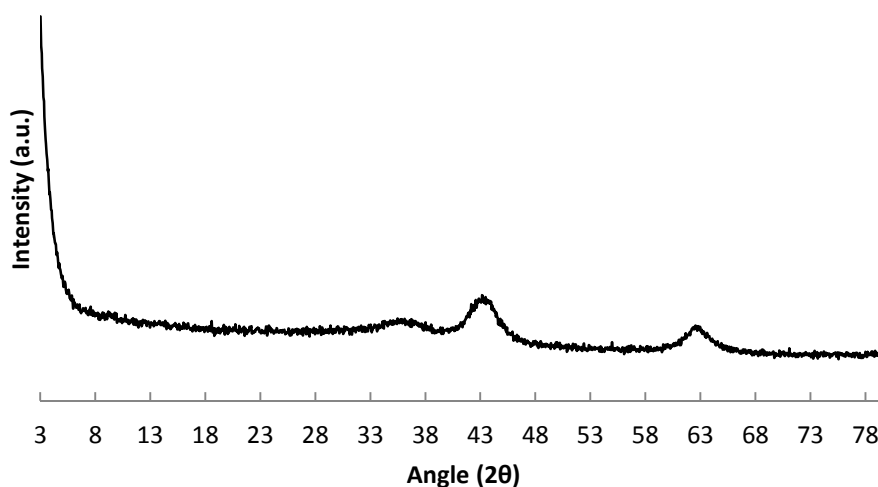
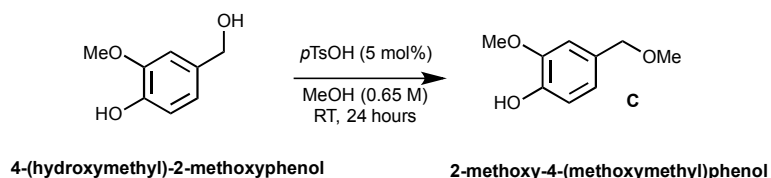


Figure S2: XPRD of Cu-PMO catalyst

c. Synthesis of 2-methoxy-4-(methoxymethyl)phenol



4-(hydroxymethyl)-2-methoxyphenol (5 g, 32.43 mmol, 1 equiv.) was added to a 250 mL round bottom flask equipped with a Teflon-coated stir bar. Methanol (50 mL, 0.65 M) was added by syringe. *P*-TsOH (308.5 mg, 1.62 mmol, 5 mol%) was added to the solution. The mixture was allowed to stir at room temperature for 24 hours. Upon completion, NaHCO_3 (160 mg, 1.9 mmol, 0.058 equiv.) was added. The reaction was allowed to stir at room temperature for 15 minutes then concentrated *in vacuo*. The residue was dissolved in EtOAc and eluted through a pad of silica gel. The combined organic fractions were evaporated *in vacuo* to afford pure **C** in 99% yield (5.453 g).

$R_f = 0.51$ (silica gel, 1:1 Hexanes:EtOAc);

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 6.89 – 6.82 (m, 2H), 6.80 (dd, $J = 8.0, 1.8$ Hz, 1H), 5.65 (s, 1H), 4.36 (s, 2H), 3.88 (s, 3H), 3.35 (s, 3H).

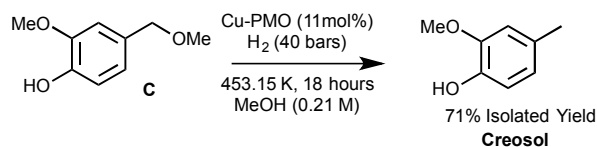
Analytical data is identical to that reported in the literature.⁷

d. General Procedures for Reduction of Lignin Model Compounds

Lignin model compound (1 equiv.), Cu-PMO (11 mol%, if applicable) and dodecane (if applicable, internal standard) were added to a 100 mL Parr reactor. Methanol (0.21 M)

was added by syringe. The reaction vessel was sealed and pressurized to the appropriate pressure of hydrogen. The sealed reactor was placed on the Parr stand and connected to the Parr controller. The heating mantle was lifted to the Parr reactor and heating was turned on. The reaction was allowed to stir vigorously for the appropriate amount of time at a set temperature. Pressure and temperature time points were recorded. Upon completion, the heating mantle was lowered and the Parr reactor was cooled with a slow stream of water until it reached 313.15 K internal temperature. At this point, the Parr reactor was lifted from its stand and placed in a tap water bath until internal temperature reached 292.15 K. The internal pressure was released and the Parr reactor was opened. The mixture was filtered (over filter paper) and concentrated *in vacuo* to afford a residue which was analyzed directly by ^1H NMR (after addition of 0.15 equiv. Dimethylformamide (DMF) as an internal standard).

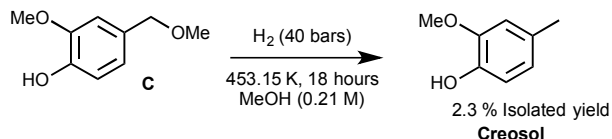
e. Model Compound Reductions Reactions



This reaction was performed using **C** (1105.4 mg, 6.572 mmol, 1 equiv.) and Cu-PMO (239 mg, 0.723 mmol, 11 mol%) in methanol (31.3 mL) according to the representative procedure outlined above. The reaction was allowed to stir for 18 hours at 453.15 K under 40 bars of H_2 . The product was isolated by column chromatography (5% EtOAc in Hexanes to 10% EtOAc in Hexanes) to obtain pure product in 71 % yield.

R_f = 0.39 (silica gel, 3:1 Hexanes:EtOAc); ^1H NMR (400 MHz, Chloroform-*d*) δ 6.81 (d, J = 7.8 Hz, 1H), 6.66 (d, J = 8.8 Hz, 2H), 5.44 (s, 1H), 3.87 (s, 3H), 2.29 (s, 3H).

Analytical data is identical to that reported in the literature.⁸



This reaction was performed using **C** (1105.4 mg, 6.572 mmol, 1 equiv.) in methanol (31.3 mL) according to the representative procedure outlined above. The reaction was allowed to stir for 18 hours at 453.15 K under 40 bars of H_2 . The product was isolated by column chromatography (5% EtOAc in Hexanes to 10% EtOAc in Hexanes) to obtain pure product in 2.3 % yield.

R_f = 0.39 (silica gel, 3:1 Hexanes:EtOAc); ^1H NMR (400 MHz, Chloroform-*d*) δ 6.81 (d, J = 7.8 Hz, 1H), 6.66 (d, J = 8.8 Hz, 2H), 5.44 (s, 1H), 3.87 (s, 3H), 2.29 (s, 3H).

Analytical data is identical to that reported in the literature.⁸

f. Crude ^1H NMR of Reaction Mixtures (c.f. manuscript Scheme 2)

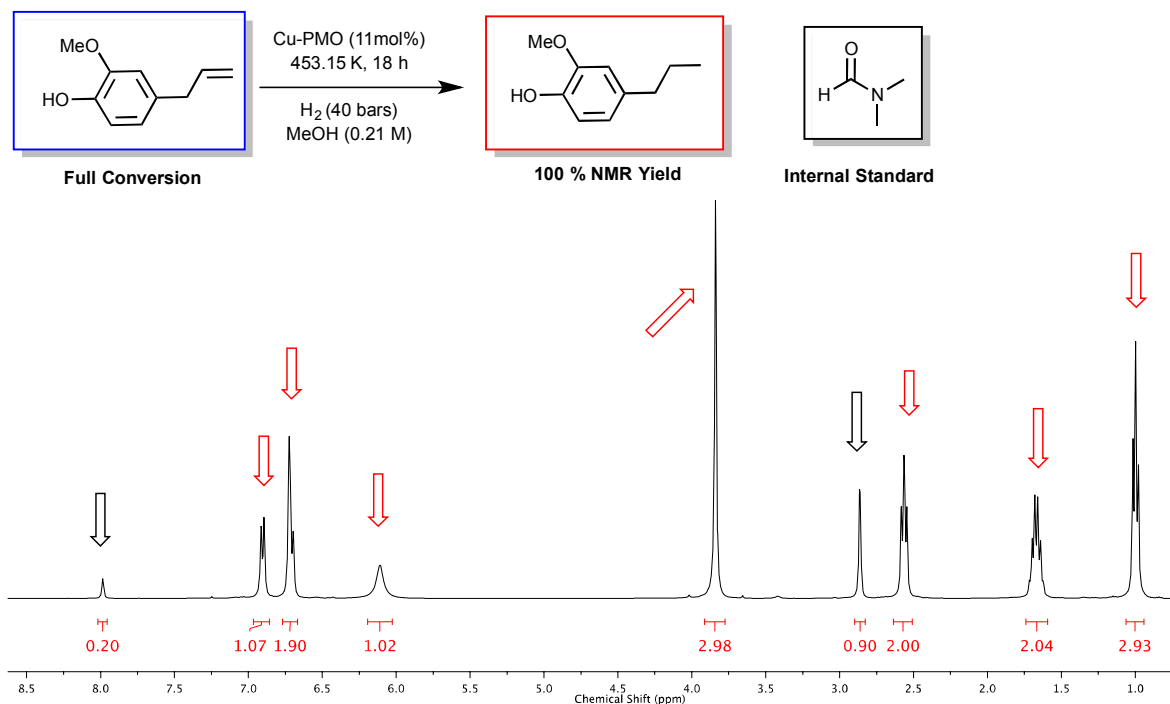


Figure S3: Crude NMR of a reaction showing complete conversion to dehydroeugenol. Conditions: Eugenol (6.456 mmol), Cu-PMO (11 mol%), MeOH (0.21 M), H_2 (40 bars), 453.15 K, 18 h, DMF (as internal standard, 0.15 equiv.).

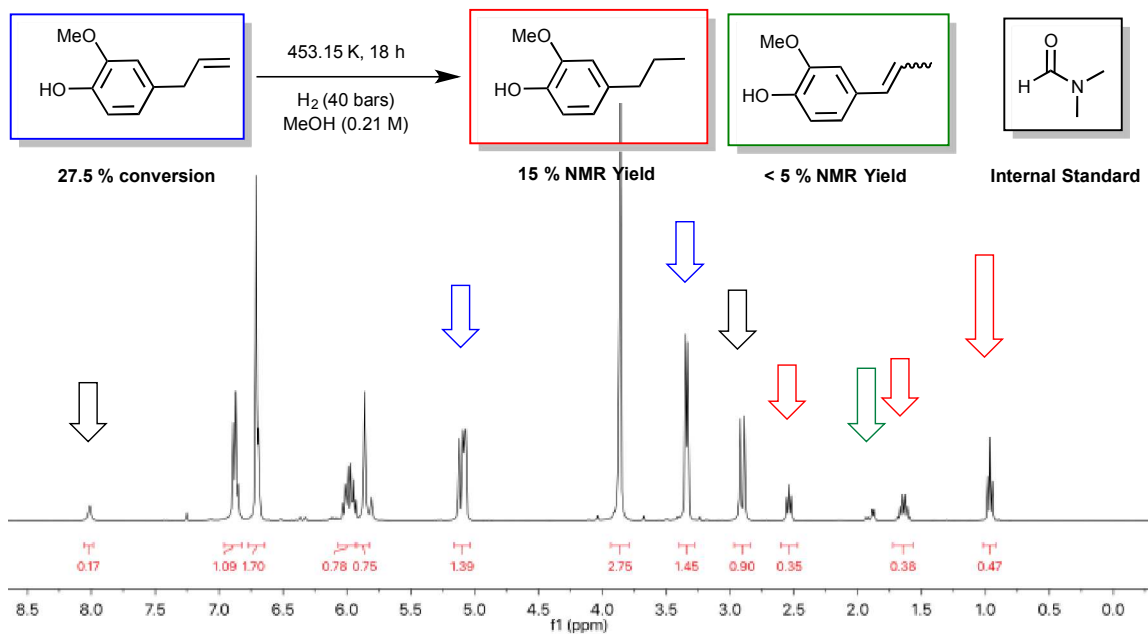


Figure S4: Crude NMR of a reaction showing eugenol (27.5% conversion) and dehydroeugenol (15% NMR yield). Conditions: Eugenol (6.456 mmol), MeOH (0.21 M), H₂ (40 bars), 453.15 K, 18 h, DMF (as internal standard, 0.15 equiv.).

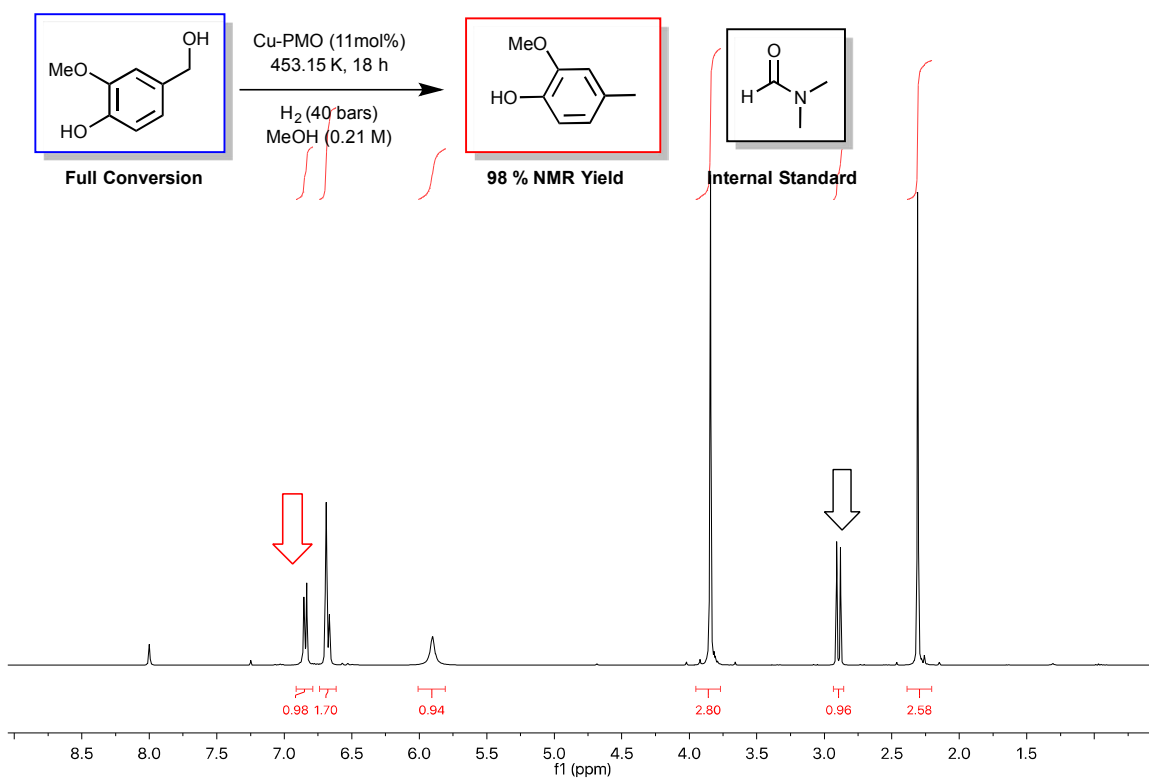


Figure S5: Crude NMR of a reaction showing vanillyl alcohol (100% conversion) and creosol (98% NMR yield). Conditions: Vanillyl alcohol (6.572 mmol), MeOH (0.21 M), H₂ (40 bars), 453.15 K, 18 h, DMF (as internal standard, 0.16 equiv.).

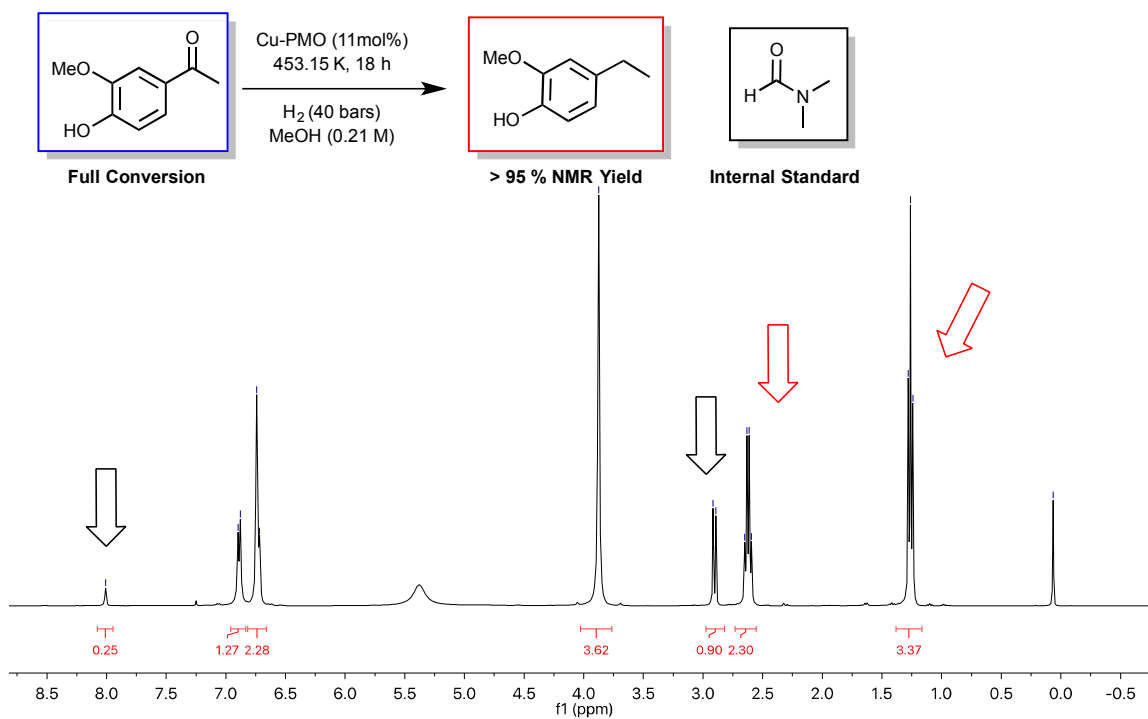


Figure S6: Crude NMR of a reaction showing acetovanillone (100% conversion) and 4-ethyl-2-methoxyphenol (> 95% NMR yield). Conditions: Acetovanillone (6.456 mmol), Cu-PMO (11 mol%), MeOH (0.21 M), H₂ (40 bars), 453.15 K, 18 h, DMF (as internal standard, 0.15 equiv.).

6. Optimized geometries

The following are the optimized geometry by NWChem using the DFT/6-31g* method.

Compound 1 (Vanillin)

19

C	1.77535	0.18931	-0.09650
C	1.04216	-0.99381	-0.26255
C	1.12633	1.41095	0.01923
C	-0.36890	-0.95105	-0.29415
C	-0.27356	1.46657	-0.02738
C	-1.00539	0.27956	-0.17896
O	-1.12181	-2.07598	-0.51119
O	1.63883	-2.21042	-0.40673
H	2.60190	-2.09352	-0.38393
C	-1.09365	-3.06435	0.52407
H	-1.78823	-3.84582	0.20876
H	-1.43395	-2.63874	1.47729
H	-0.09349	-3.49025	0.64716
H	-2.09168	0.29844	-0.21910
H	2.86290	0.13920	-0.07047
H	1.68339	2.33416	0.14195
C	-0.97576	2.75819	0.08879
O	-0.42944	3.83677	0.23480
H	-2.08538	2.68752	0.03298

Compound 2 (Vanillyl Alcohol)

21

C	1.85630	0.06692	-0.20577
C	1.09403	-1.09311	-0.35381
C	1.24464	1.31423	-0.07807
C	-0.31086	-0.99883	-0.34685
C	-0.14778	1.42080	-0.08500
C	-0.90809	0.25268	-0.20914
O	-1.11610	-2.09718	-0.53133
O	1.65384	-2.33523	-0.51061
H	2.61887	-2.23941	-0.50028
H	-1.99456	0.28961	-0.20649
H	2.94308	-0.00884	-0.20082
H	1.84799	2.20758	0.03986
C	-0.82830	2.76729	-0.00266
O	-0.03333	3.65585	0.77799
H	-0.39652	4.54713	0.66682
H	-1.83334	2.64462	0.43227
H	-0.96862	3.17350	-1.01933
C	-1.07261	-3.08547	0.50072
H	-1.80583	-3.84518	0.21967
H	-1.35472	-2.65061	1.46920
H	-0.08188	-3.54303	0.57950

Compound 3 (Eugenol)

24

C	1.89881	-0.32637	-0.08478
C	1.24494	0.90232	-0.21549
C	-0.14779	0.96066	-0.24668
C	-0.87292	-0.23741	-0.13749
C	-0.23149	-1.46968	-0.00676
C	1.17966	-1.51309	0.01938
O	1.76615	-2.74202	0.15172
H	2.98713	-0.36397	-0.06105
H	-1.95693	-0.19690	-0.15785
O	-0.85945	-2.67596	0.10474
H	1.82718	1.81646	-0.28705
C	-0.87516	2.28758	-0.41590
C	-2.27541	-2.69237	0.08408
H	-2.56301	-3.74077	0.18344
H	-2.67224	-2.29571	-0.86049
H	-2.70041	-2.11943	0.91963
H	2.72796	-2.61839	0.15577
C	-0.40125	3.35949	0.53269
H	-1.95065	2.11898	-0.26254
H	-0.76612	2.64976	-1.44793
C	0.09404	4.54191	0.16469
H	-0.47453	3.11597	1.59331
H	0.18974	4.81999	-0.88333
H	0.41778	5.27973	0.89405

Compound 4 (Acetovanillone)

22

C	-1.51980	-0.92534	0.00000
C	-1.89227	0.40870	0.00000
C	-0.94085	1.43840	0.00000
C	0.43192	1.11038	0.00000
C	0.78969	-0.24180	0.00000
C	-0.15908	-1.27130	0.00000
C	0.18796	-2.72521	0.00000
O	-0.69669	-3.57119	0.00000
H	-2.94749	0.68025	0.00000
O	-1.32786	2.75364	0.00000
O	1.49234	1.97037	0.00000
H	1.85395	-0.44630	0.00000
C	1.64067	-3.18635	0.00000
H	-2.26014	-1.71707	0.00000
H	2.38408	-2.38858	0.00000
H	1.80016	-3.81840	-0.88015
H	1.80016	-3.81840	0.88015
H	-2.29730	2.78520	0.00000
C	1.33754	3.38904	0.00000
H	2.35783	3.77926	0.00000
H	0.81067	3.74038	0.89168
H	0.81067	3.74038	-0.89168

Product for the hydrogenation of F3 on Compound 1

21

C	-0.07923	-1.10422	0.05424
C	-1.53865	-0.95742	-0.13413
C	-2.08565	0.26274	-0.24959
C	-1.21558	1.49604	-0.26191
C	0.06295	1.30552	0.56835
C	0.70374	-0.05435	0.35578
H	-3.15328	0.35476	-0.42378
H	1.77090	-0.16220	0.52132
O	0.31472	-2.40554	-0.10695
C	1.68909	-2.71032	0.08588
H	2.31269	-2.16958	-0.63669
H	1.78898	-3.78492	-0.07380
H	2.00789	-2.45429	1.10412
O	-2.27755	-2.10418	-0.19093
C	1.07799	2.41099	0.33027
O	0.88872	3.39738	-0.34349
H	-1.65417	-2.84916	-0.14285
H	-0.19058	1.38855	1.64547
H	-1.76467	2.36351	0.11811
H	-0.93470	1.75541	-1.29531
H	2.05330	2.25811	0.85034

Product for the hydrogenolysis of F5 on compound 1

16

C	1.57718	-0.42478	-0.00033
C	0.61039	-1.43107	0.00089
C	1.18549	0.91013	-0.00249
C	-0.76143	-1.11354	-0.00006
C	-0.17745	1.23670	-0.00348
C	-1.14611	0.22079	-0.00228
O	-1.70000	-2.10069	0.00119
O	0.88972	-2.77419	0.00297
H	1.84908	-2.91258	0.00461
H	-2.20618	0.46042	-0.00299
H	2.63201	-0.69346	0.00041
H	1.91651	1.71161	-0.00345
C	-0.60310	2.65039	-0.00581
O	0.15290	3.60469	-0.00692
H	-1.70604	2.80095	-0.00652
H	-1.23292	-2.95368	0.00290

Product for the hydrogenolysis of F6 on Compound 2

20

C	1.78229	0.49301	-0.01904
C	1.04368	-0.66808	-0.24003
C	1.14495	1.72943	0.11388
C	-0.36162	-0.58434	-0.30979
C	-0.24516	1.83403	0.03139

C	-0.97879	0.65637	-0.17528
O	-1.14177	-1.68363	-0.57751
O	1.62264	-1.90108	-0.40375
H	2.58520	-1.79721	-0.34737
C	-1.14908	-2.70464	0.42273
H	-1.85361	-3.46273	0.07251
H	-1.49633	-2.30516	1.38535
H	-0.15930	-3.15381	0.54831
H	-2.06325	0.68282	-0.24527
H	2.86826	0.43135	0.03944
H	1.74554	2.62026	0.27979
C	-0.94721	3.16644	0.15912
H	-0.23952	3.96704	0.39738
H	-1.70775	3.14817	0.94953
H	-1.45904	3.44298	-0.77162

Product for the hydrogenation of F2 on Compound 3

26

C	1.93746	-0.63733	-0.00537
C	1.39372	0.65478	-0.00136
C	0.01435	0.84265	-0.00269
C	-0.81125	-0.29911	-0.00826
C	-0.28405	-1.58744	-0.01223
C	1.11985	-1.75915	-0.01075
O	1.59331	-3.04324	-0.01486
H	3.01858	-0.76988	-0.00433
H	-1.88798	-0.16166	-0.00951
O	-1.01565	-2.73938	-0.01772
H	2.06822	1.50424	0.00271
C	-0.64504	2.21312	0.00215
C	-2.42732	-2.62861	-0.01941
H	-2.80711	-3.65211	-0.02375
H	-2.79215	-2.10272	-0.91241
H	-2.79482	-2.10932	0.87634
H	2.56235	-3.00633	-0.01385
C	0.29307	3.42534	-0.00115
H	-1.30576	2.28482	0.87964
H	-1.31432	2.28657	-0.86862
H	0.95311	3.38257	0.87556
C	-0.46986	4.75401	0.00170
H	0.94689	3.38241	-0.88251
H	-1.10893	4.84340	0.88884
H	-1.11521	4.84359	-0.88086
H	0.21746	5.60743	-0.00064

Product for the hydrogenolysis of F4 on compound 4

23

C	-1.47122	-1.07961	-0.05197
C	-1.79902	0.20993	-0.47495
C	-0.82162	1.20177	-0.55888
C	0.50281	0.89319	-0.19198

C	0.81077	-0.39945	0.22704
C	-0.15899	-1.40917	0.29947
C	0.21630	-2.81704	0.71329
H	-2.82562	0.44922	-0.74979
O	-1.08916	2.47626	-0.99039
O	1.51915	1.81234	-0.29700
H	1.84438	-0.60284	0.49553
C	0.72185	-3.67545	-0.46006
H	-2.25179	-1.83482	0.00236
H	1.60939	-3.22693	-0.92041
H	-0.04466	-3.76574	-1.23804
H	0.98648	-4.68469	-0.12314
H	-2.03017	2.53127	-1.21830
C	1.43202	2.94440	0.57127
H	2.33772	3.52914	0.39371
H	1.40587	2.62820	1.62300
H	0.55166	3.55556	0.35067
H	-0.65295	-3.30747	1.16976
H	0.99199	-2.77799	1.48898

Product for the hydrogenation of F1, i.e., Compound 2

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C	1.85630	0.06692	-0.20577
C	1.09403	-1.09311	-0.35381
C	1.24464	1.31423	-0.07807
C	-0.31086	-0.99883	-0.34685
C	-0.14778	1.42080	-0.08500
C	-0.90809	0.25268	-0.20914
O	-1.11610	-2.09718	-0.53133
O	1.65384	-2.33523	-0.51061
H	2.61887	-2.23941	-0.50028
H	-1.99456	0.28961	-0.20649
H	2.94308	-0.00884	-0.20082
H	1.84799	2.20758	0.03986
C	-0.82830	2.76729	-0.00266
O	-0.03333	3.65585	0.77799
H	-0.39652	4.54713	0.66682
H	-1.83334	2.64462	0.43227
H	-0.96862	3.17350	-1.01933
C	-1.07261	-3.08547	0.50072
H	-1.80583	-3.84518	0.21967
H	-1.35472	-2.65061	1.46920
H	-0.08188	-3.54303	0.57950

7. ^1H and ^{13}C NMR of isolated products

Figure S7: 2-methoxy-4-(methoxymethyl)phenol **C** (^1H NMR in CDCl_3)

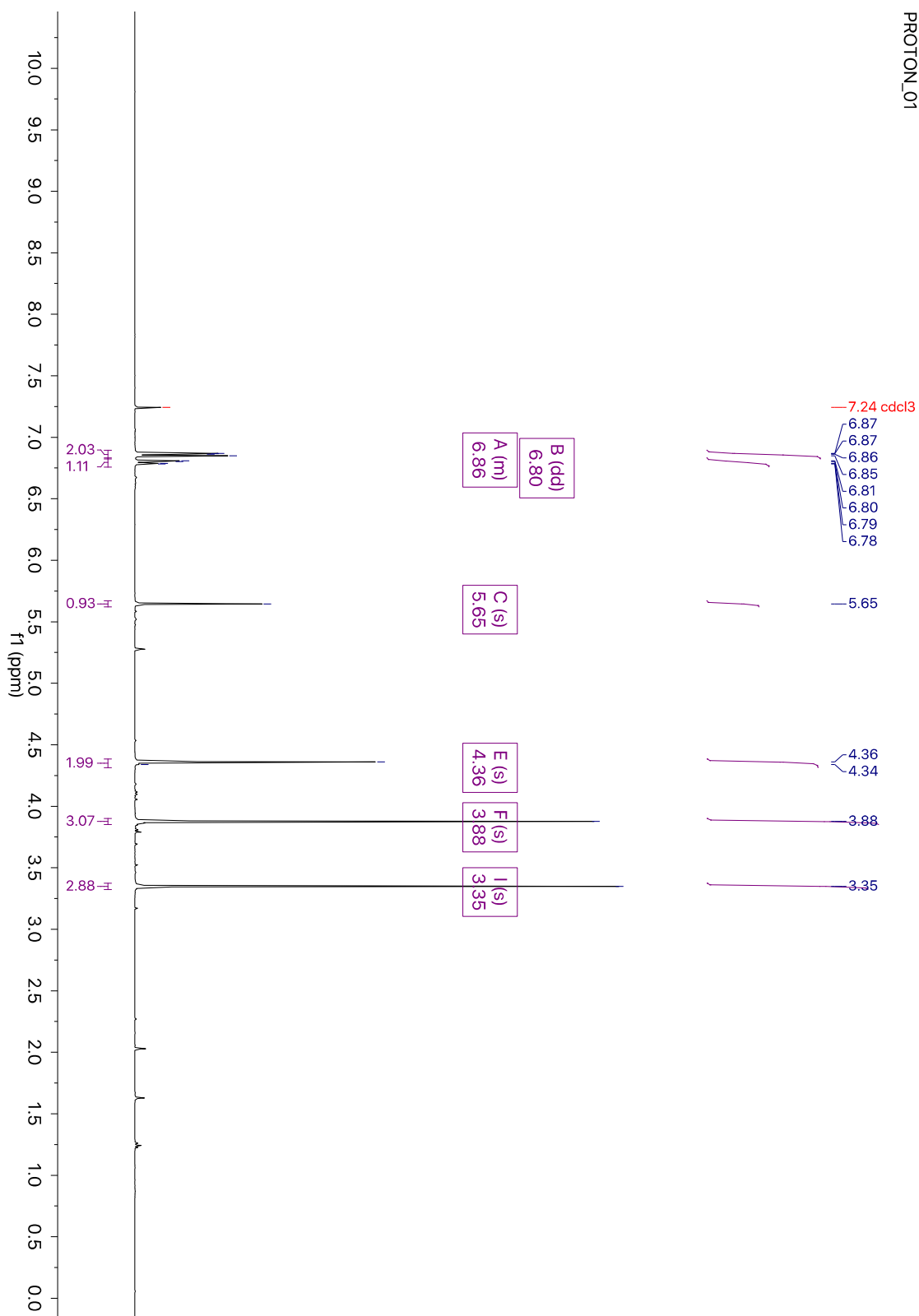


Figure S8: 2-methoxy-4-(methoxymethyl)phenol **C** (^{13}C NMR in CDCl_3)

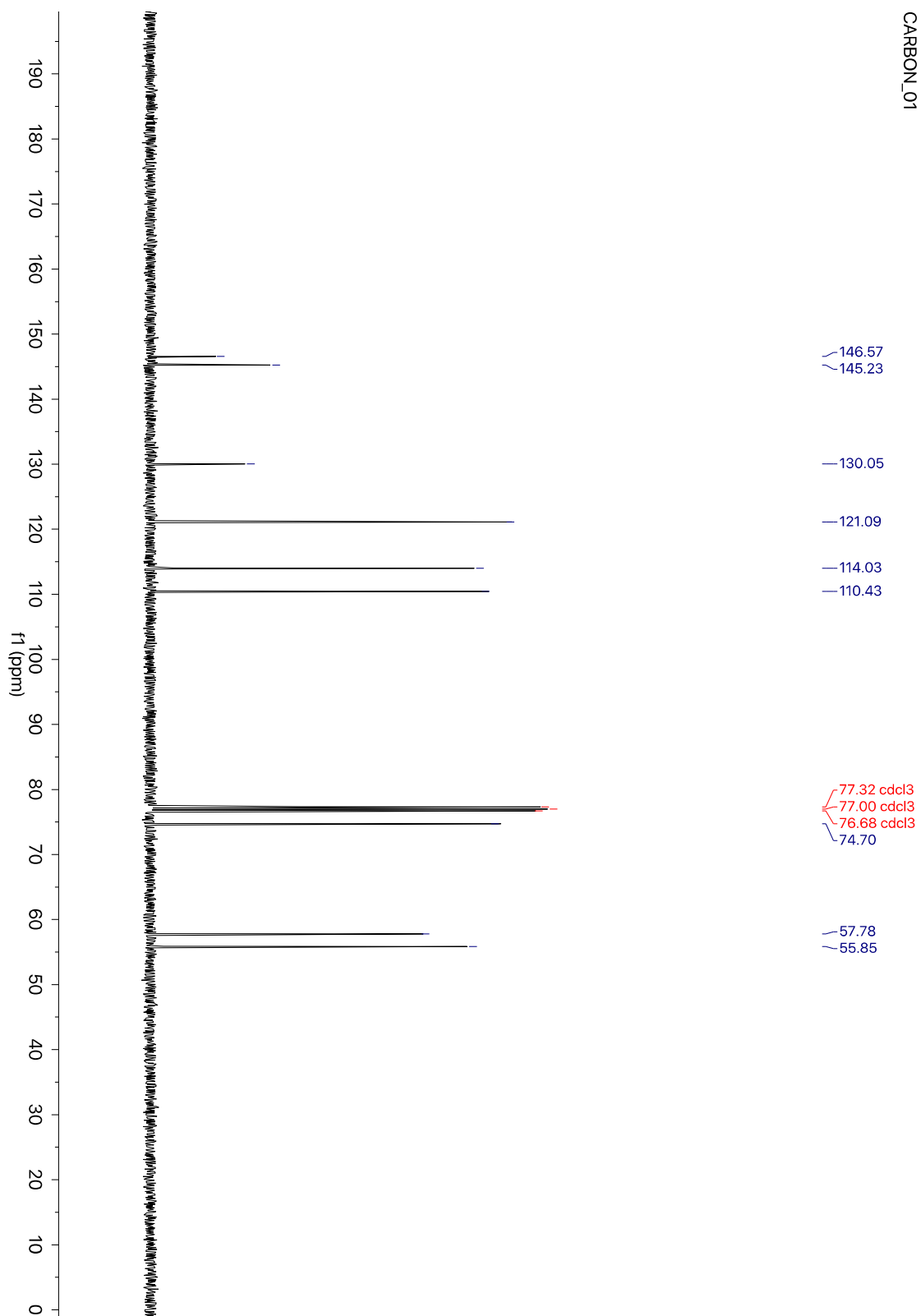


Figure S9: *Creosol* (^1H NMR in CDCl_3)

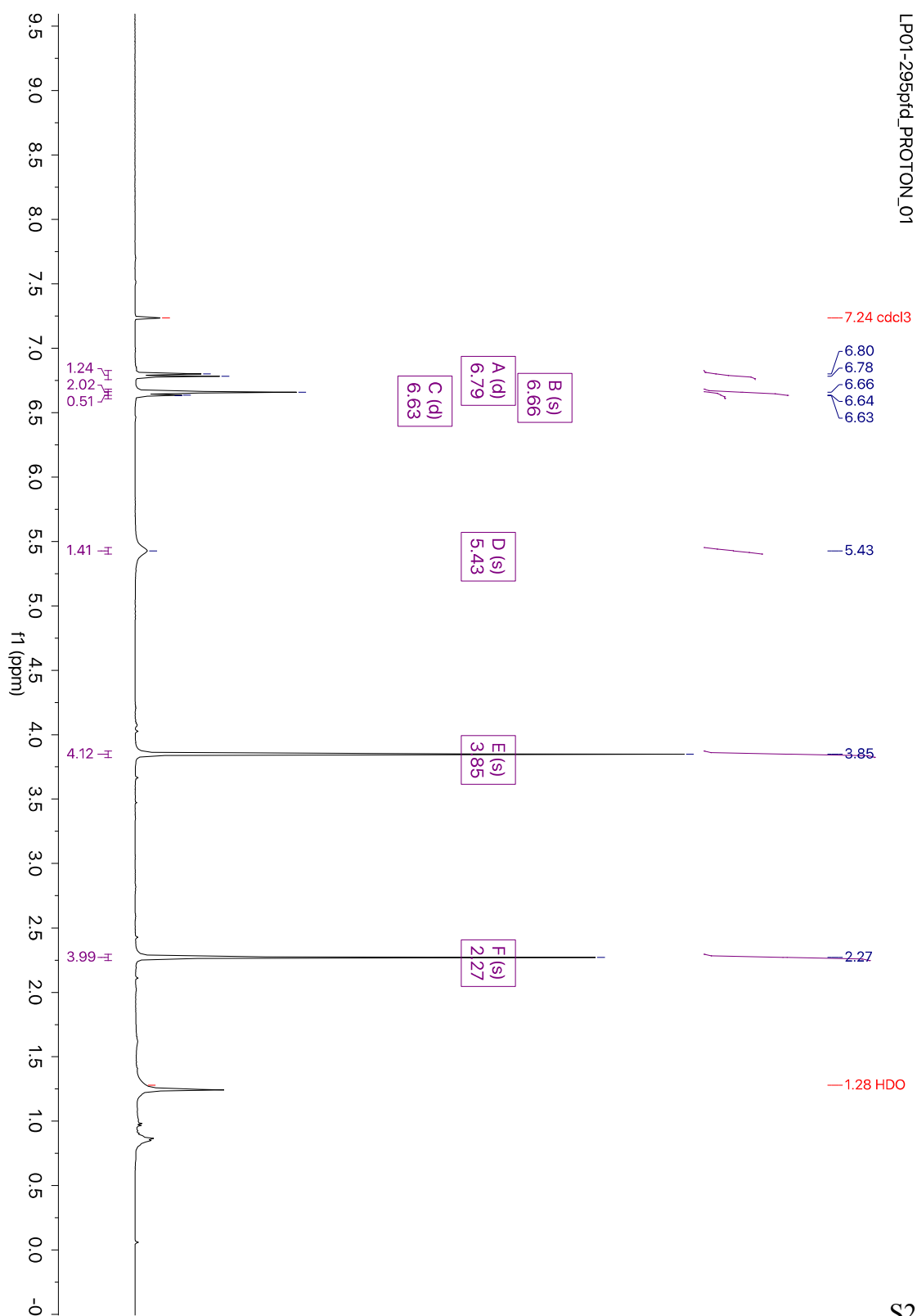
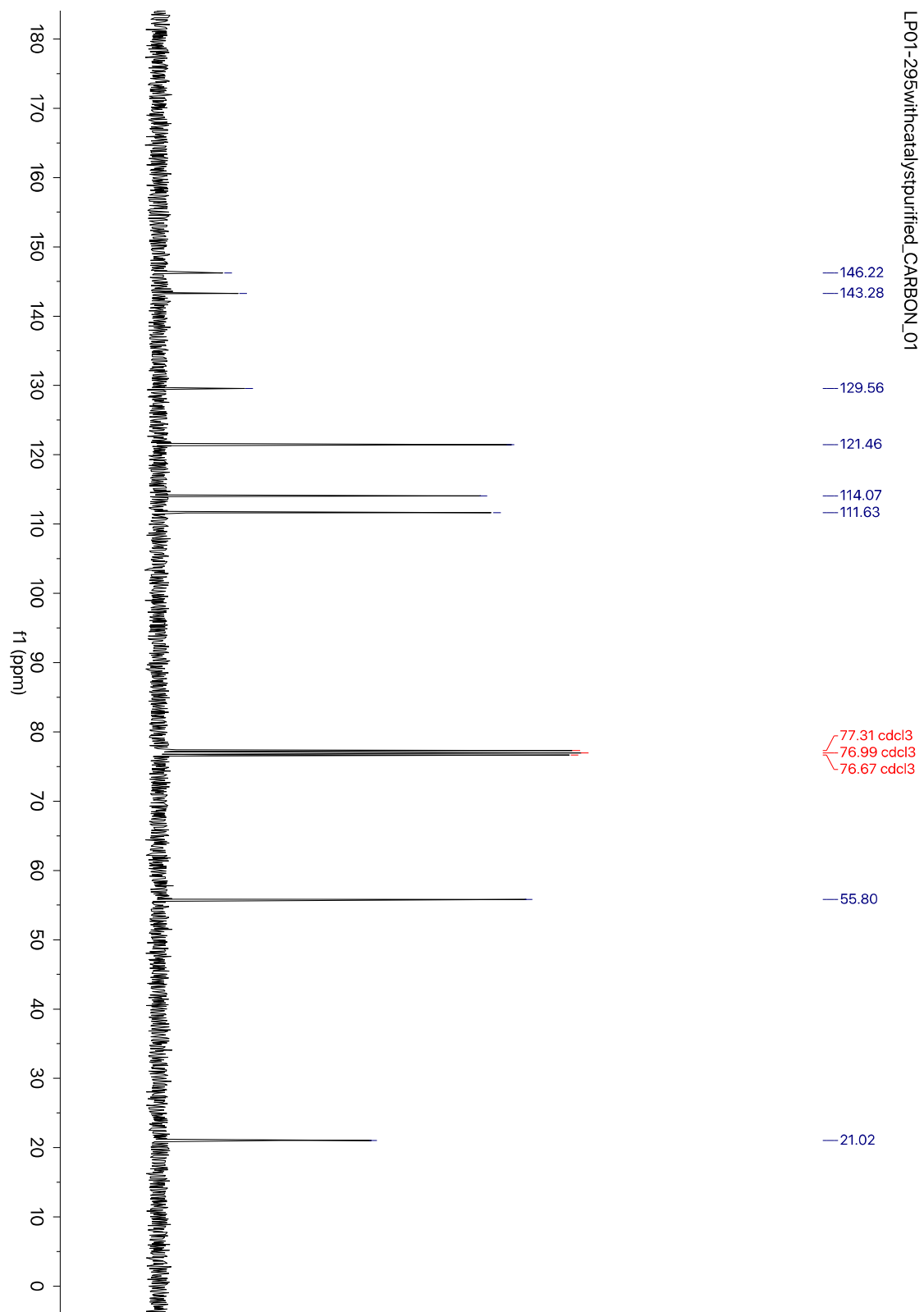


Figure S10: *Creosol* (^1H NMR in CDCl_3)



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