Electronic Supplementary Material (ESI) for Green Chemistry.

SUPPORTING INFORMATION

Highly Selective Hydrogenation and Hydrogenolysis using a Copper-doped Porous Metal Oxide Catalyst

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1. Experimental Section

a. General Experimental

Chemicals and solvents were purchased from Sigma-Aldrich, Alfa-Aesar, JT Baker 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 controller.

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). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were acquired using Agilent DD2 600 MHz spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) and are calibrated to the residual solvent peak. Fourier-transform infrared (FT-IR) spectra were recorded on a Thermo Nicolet 6700 spectrometer. 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 geometer 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. Analytical thin layer chromatography was performed on pre-coated 250 μm layer thickness silica gel 60 F_{254} 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). Scanning Electron Microscopy (SEM) was performed on a Hitachi SU-70 SEM with an in0lens arrangement at 10 kV working voltage and about 11 mm lens to detector distance, with a tilt angle of 35°. Transmission Electron Microscopy (TEM) was performed on a FEI Tecnai Osiris TEM with the field operation gun operated at 200 kV. Images were acquired digitally. Elemental analyses were performed using inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Perkin Elmer Optima 3000 equiped with a Scott nebulizer. The Sc standard was measured at 361.384 nm, Cu at 324.754 nm, Mg at 279.079 nm and Al at 308.215 nm. Samples were prepared for ICP-OES by dissolving a known solid amount in 2 mL of 6 M nitric acid and diluting to 50 mL with DI H_2O. Elemental components were quantified by comparison with purchased calibration standards. XPS analysis was performed using a ThermoScientific ESCALAB 250 instrument at the University of Oregon. Spectra were collected using a monochromatic Al X-ray source. A low energy electron flood and top-side contact were used for charge neutralization. Survey spectra were collected using a pass energy of 150 eV. Multiplex composition scans were acquired with 20 eV pass energy. Spectra were referenced by setting the C 1s hydrocarbon peak to 284.8 eV.

b. Synthesis of the Cu-PMO Catalyst

A solution of $Al(NO_3)_3.9H_2O$ (18.8 g, 0.05 mol, 1 equiv.), $Mg(NO_3)_2.6H_2O$ (30.76 g, 0.12 mol, 2.4 equiv.) and $Cu(NO_3)_2.2.5H_2O$ (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 $Na_2CO_3.H_2O$ (6.2 g, 0.05 mol, 1 equiv.) in 375 mL distilled water. The pH was kept constant at pH ~ 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 105°C oven to obtain copper doped hydrotalcite. The solid is ground by mortar and pestle and subjected to calcination at 460°C in air for 24 h to obtain Cu-PMO (9.21 g) as a green powder. The Cu-PMO was analyzed by XRPD (Figure S1), SEM (Figure S2) and TEM (Figure S3). Elemental analysis of Cu-PMO was performed by ICP-OES (Table S1). XPS measurements of Cu-PMO were also performed to determine metal speciation (Figure S4).

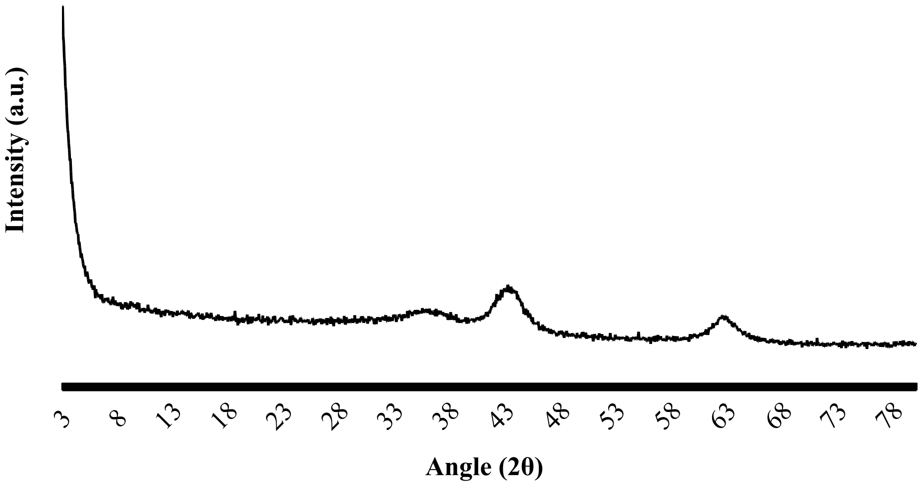


Figure S1: XPRD of Cu-PMO catalyst

Table S1: Metal Ion Composition of Cu-PMO determined by ICP-OES

	Cu	**Mg**	**Al**
Concentration (mg/L)	26.09	39.37	19.36
Mass in solution (mg)	1.305	1.969	0.968
Amount in solution (mmol)	0.0205	0.0806	0.0359
Normalized Ratio of Metals	0.57	2.25	1.00

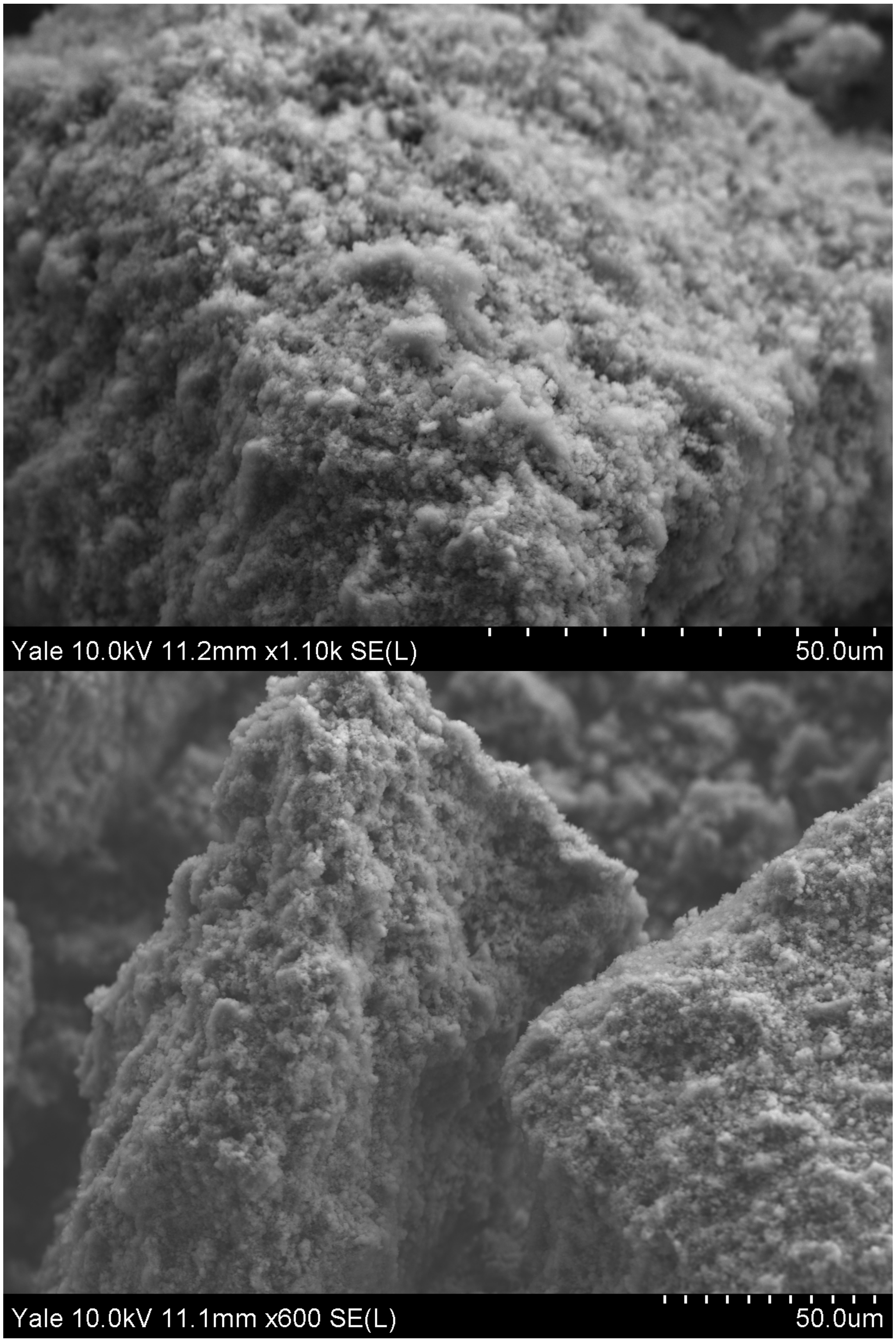


Figure S2: SEM images of Cu-PMO

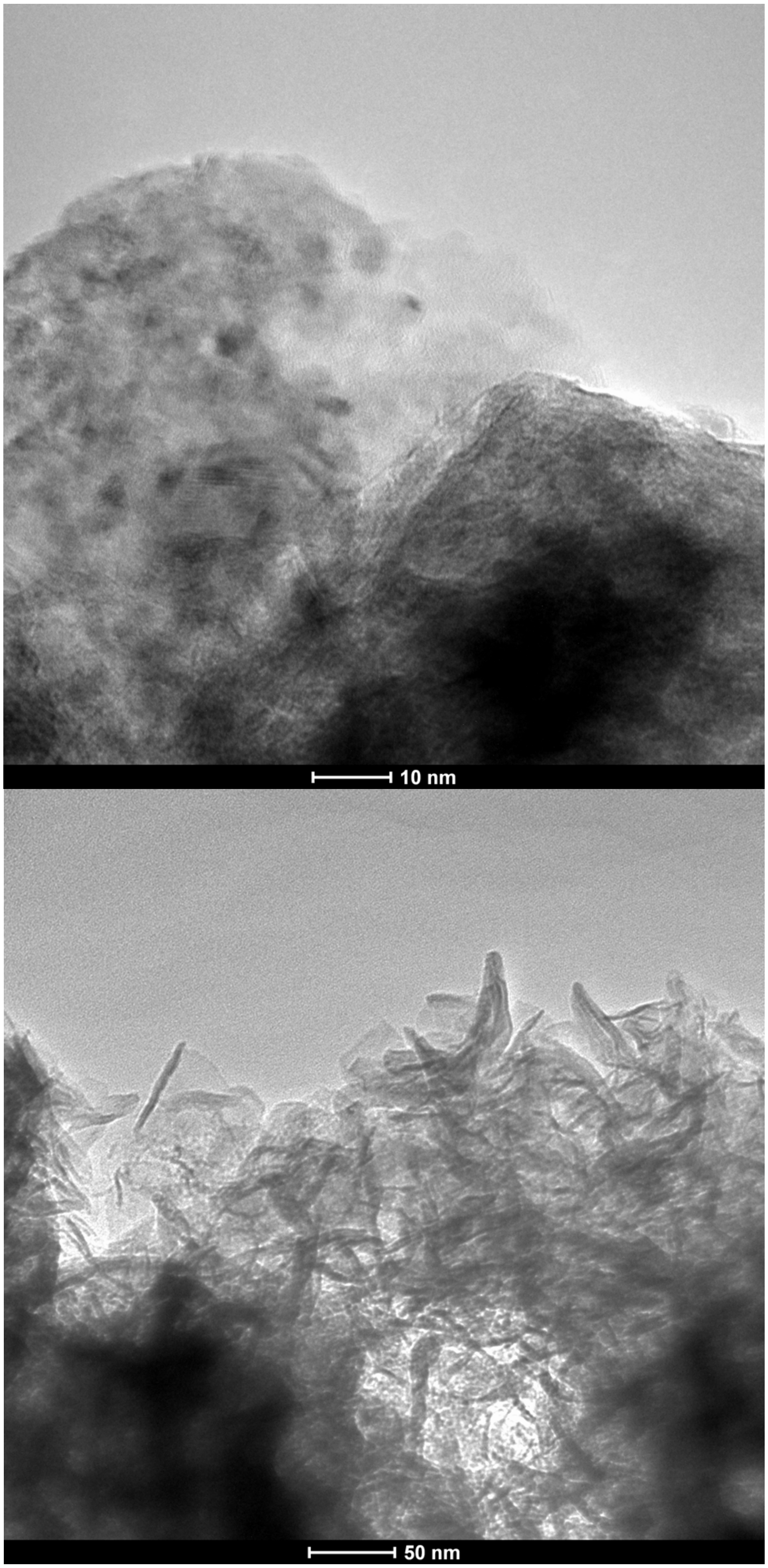


Figure S3: TEM Images of Cu-PMO

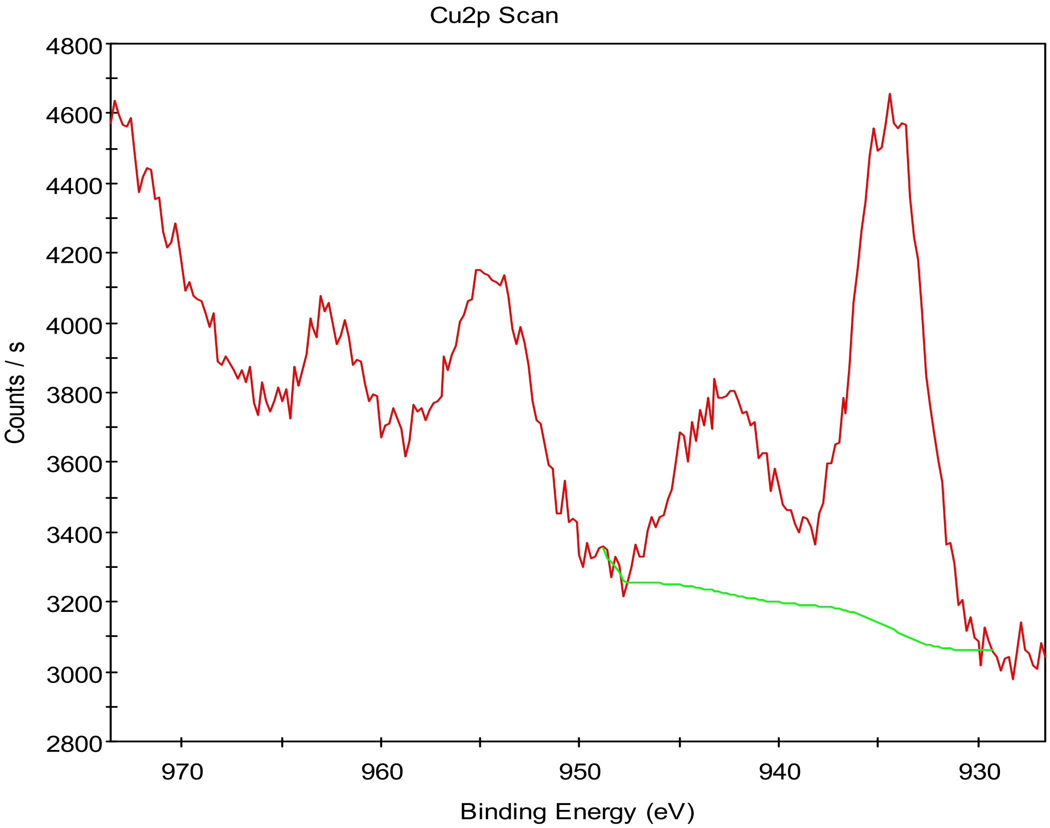


Figure S4: Cu 2p3 XPS of fresh Cu-PMO catalyst *c. Synthesis of the PMO control*

A solution of $Al(NO_3)_3.9H_2O$ (18.8 g, 0.05 mol, 1 equiv.), $Mg(NO_3)_2.6H_2O$ (38.46 g, 0.15 mol, 3 equiv.) in 300 mL distilled (DI) water was added dropwise over four hours to a stirring solution of $Na_2CO_3.H_2O$ (6.2 g, 0.05 mol, 1 equiv.) in 375 mL distilled water. The pH was kept constant at pH ~ 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 white 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 105°C oven to obtain hydrotalcite. The solid is ground by mortar and pestle and subjected to calcination at 460°C in air for 24 h to obtain PMO (8.56 g) as a white powder. The PMO was analyzed by XRPD (Figure S5).

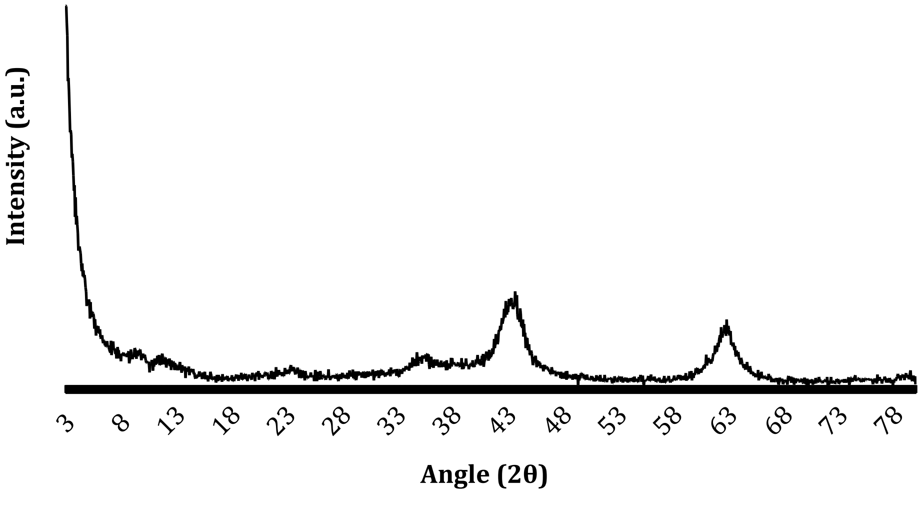


Figure S5: XPRD of PMO

d. General Procedures for Hydrogenation and Hydrogenolysis

Amounts used for each reagent are summarized in Table S2-S5.

Representative Procedure A: Substrate (1 equiv.), Cu-PMO (11 mol%) and dodecane (if applicable, used as internal standard, 0.15 equiv.) 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. 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 40^{o}C internal temperature. At this point, the Parr reactor was lifted from its stand and placed in a tap water bath until internal temperature reached 19^{o}C. The internal pressure was released and the Parr reactor was opened. The mixture was filtered over a pad of celite and concentrated *in vacuo* to afford a residue, which was analyzed directly by ^{1}H NMR (if applicable, after addition of 0.15 equiv. dimethylformamide (DMF) as an internal standard).

Representative Procedure B: Substrate (1 equiv.), PMO and dodecane (if applicable, used as internal standard, 0.15 equiv.) 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. 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 40^{o}C internal temperature. At this point, the Parr reactor was lifted from its stand and placed in a tap water bath until internal temperature reached 19^{o}C. The internal pressure was released and the Parr reactor was opened. The mixture was filtered over a pad of celite and concentrated *in vacuo* to afford a residue, which was analyzed directly by ^{1}H NMR (if applicable, after addition of 0.15 equiv. dimethylformamide (DMF) as an internal standard).

Representative Procedure C: Substrate (1 equiv.) and dodecane (if applicable, used as internal standard, 0.15 equiv.) 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. 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 40^{o}C internal temperature. At this point, the Parr reactor was lifted from its stand and placed in a tap water bath until internal temperature reached 19^{o}C. The internal pressure was released and the Parr reactor was opened. The mixture was filtered over a pad of celite and concentrated *in vacuo* to afford a residue, which was analyzed directly by ^{1}H NMR (if applicable, after addition of 0.15 equiv. dimethylformamide (DMF) as an internal standard).

Representative Procedure D: Substrate (1 equiv.) and $Cu(OAc)_2.H_2O$ 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. 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 40^{o}C internal temperature. At this point, the Parr reactor was lifted from its stand and placed in a tap water bath until internal temperature reached 19^{o}C. The internal pressure was released and the Parr reactor was opened. The mixture was filtered over a pad of celite and concentrated *in vacuo* to afford a residue, which was analyzed directly by ^{1}H NMR (after addition of 0.15 equiv. dimethylformamide (DMF) as an internal standard).

Table S2: Amounts and reagents used for Eugenol Reduction (Table 1)

Entry	Eugenol	Catalyst	Solvent	Internal Standard	Temp.	Time	Hydrogen Pressure
1[‡]	1.00 mL, 1.06 g, 6.456 mmol	Cu-PMO 250 mg 0.75 mmol	MeOH 30 mL 0.21 M	DMF 74.6 µL 0.968 mmol	180°C	18 h	4 MPa
2[‡]	1.00 mL, 1.06 g, 6.456 mmol	Cu-PMO 250 mg 0.75 mmol	MeOH 30 mL 0.21 M	Dodecane 0.21 mL 0.968 mmol	100°C	18 h	4 MPa
3[‡]	1.00 mL, 1.06 g, 6.456 mmol	Cu-PMO 250 mg 0.75 mmol	MeOH 30 mL 0.21 M	Dodecane 0.21 mL 0.968 mmol	60°C	18 h	4 MPa
4[‡]	1.00 mL, 1.06 g, 6.456 mmol	Cu-PMO 250 mg 0.75 mmol	MeOH 30 mL 0.21 M	Dodecane 0.21 mL 0.968 mmol	22°C	18 h	4 MPa
5[‡]	1.00 mL, 1.06 g, 6.456 mmol	Cu-PMO 250 mg 0.75 mmol	MeOH 30 mL 0.21 M	Dodecane 0.21 mL 0.968 mmol	100°C	3 h	4 MPa
6[‡]	1.00 mL, 1.06 g, 6.456 mmol	Cu-PMO 250 mg 0.75 mmol	MeOH 30 mL 0.21 M	Dodecane 0.21 mL 0.968 mmol	70°C	3 h	4 MPa
7[‡]	1.00 mL, 1.06 g, 6.456 mmol	Cu-PMO 250 mg 0.75 mmol	MeOH 30 mL 0.21 M	DMF 74.6 µL 0.968 mmol	100°C	3 h	1 MPa
8[‡]	1.00 mL, 1.06 g, 6.456 mmol	Cu-PMO 250 mg 0.75 mmol	MeOH 30 mL 0.21 M	DMF 74.6 µL 0.968 mmol	100°C	4 h	1 MPa
9[§]	1.00 mL, 1.06 g, 6.456 mmol	PMO 250 mg	MeOH 30 mL 0.21 M	DMF 74.6 µL 0.968 mmol	180°C	18 h	4 MPa
10[♯]	1.00 mL, 1.06 g, 6.456 mmol	-	MeOH 30 mL 0.21 M	DMF 74.6 µL 0.968 mmol	180°C	21 h	4 MPa

Table S2 contn.: Amounts and reagents used for Eugenol Reduction (Table 1)

11[ϕ]	1.00 mL, 1.06 g, 6.456 mmol	$Cu(OAc)_2.H_2O$ 4.5 mg 0.0225 mmol	MeOH 30 mL 0.21 M	DMF 74.6 µL 0.968 mmol	180°C	18 h	4 MPa
12[§]	1.00 mL, 1.06 g, 6.456 mmol	PMO 250 mg	MeOH 30 mL 0.21 M	DMF 74.6 µL 0.968 mmol	100°C	4 h	1 MPa
13[♯]	1.00 mL, 1.06 g, 6.456 mmol	-	MeOH 30 mL 0.21 M	DMF 74.6 µL 0.968 mmol	100°C	4 h	1 MPa
14[ϕ]	1.00 mL, 1.06 g, 6.456 mmol	$Cu(OAc)_2.H_2O$ 4.5 mg 0.0225 mmol	MeOH 30 mL 0.21 M	DMF 74.6 µL 0.968 mmol	100°C	4 h	1 MPa

[‡]Reactions were performed according to representative Procedure A; [§]Reactions were performed according to representative Procedure B; [♯]Reactions were performed according to representative Procedure C; [ϕ]Reactions were performed according to representative Procedure D.

Table S3: Amounts and reagents used for Vanillin Reduction (Table 2)

Entry	**Vanillin**	**Catalyst**	**Solvent**	**Internal Standard**	**Temp.**	**Time**	**Hydrogen Pressure**
1[‡]	1.00 g, 6.572 mmol	Cu-PMO 239.4 mg 0.75 mmol	MeOH 31.3 mL 0.21 M	Dodecane 0.22 mL 0.986 mmol	180°C	18 h	4 MPa
2[§]	1.00 g, 6.572 mmol	PMO 239.4 mg	MeOH 31.3 mL 0.21 M	DMF 76 µL 0.986 mmol	180°C	18 h	4 MPa
3[♯]	1.00 g, 6.572 mmol	-	MeOH 31.3 mL 0.21 M	DMF 76 µL 0.986 mmol	180°C	18 h	4 MPa
4[ϕ]	1.00 g, 6.572 mmol	$Cu(OAc)_2.H_2O$ 4.6 mg 0.023 mmol	MeOH 31.3 mL 0.21 M	DMF 76 µL 0.986 mmol	180°C	18 h	4 MPa
5[‡]	1.00 g, 6.572 mmol	Cu-PMO 239.4 mg 0.75 mmol	MeOH 31.3 mL 0.21 M	Dodecane 0.22 mL 0.986 mmol	100°C	4 h	1 MPa
6[§]	1.00 g, 6.572 mmol	PMO 239.4 mg	MeOH 31.3 mL 0.21 M	DMF 76 µL 0.986 mmol	100°C	4 h	1 MPa
7[♯]	1.00 g, 6.572 mmol	-	MeOH 31.3 mL 0.21 M	DMF 76 µL 0.986 mmol	100°C	4 h	1 MPa
8[ϕ]	1.00 g, 6.572 mmol	$Cu(OAc)_2.H_2O$ 4.6 mg 0.026 mmol	MeOH 31.3 mL 0.21 M	DMF 76 µL 0.986 mmol	100°C	4 h	1 MPa

[‡]Reactions were performed according to representative Procedure A; [§]Reactions were performed according to representative Procedure B; [♯]Reactions were performed according to representative Procedure C; [ϕ]Reactions were performed according to representative Procedure D.

Table S4: Amounts and reagents used for Acetovanillone Reduction (Table 3)

Entry	**Aceto-Vanillone**	**Catalyst**	**Solvent**	**Internal Standard**	**Temp.**	**Time**	**Hydrogen Pressure**
1[‡]	1.072 g, 6.456 mmol	Cu-PMO 250 mg 0.75 mmol	MeOH 30 mL 0.21 M	DMF 74.6 µL 0.968 mmol	180°C	18 h	4 MPa
2[§]	1.072 g, 6.456 mmol	PMO 250 mg	MeOH 30 mL 0.21 M	-	180°C	18 h	4 MPa
3[♯]	1.072 g, 6.456 mmol	-	MeOH 30 mL 0.21 M	DMF 76 µL 0.986 mmol	180°C	18 h	4 MPa
4 [ϕ]	1.072 g, 6.456 mmol	$Cu(OAc)_2.H_2O$ 4.5 mg 0.0225 mmol	MeOH 30 mL 0.21 M	DMF 74.6 µL 0.968 mmol	180°C	18 h	4 MPa
5[‡]	1.072 g, 6.456 mmol	Cu-PMO 250 mg 0.75 mmol	MeOH 30 mL 0.21 M	DMF 74.6 µL 0.968 mmol	100°C	4 h	1 MPa

[‡]Reactions were performed according to representative Procedure A; [§]Reactions were performed according to representative Procedure B; [♯]Reactions were performed according to representative Procedure C; [ϕ]Reactions were performed according to representative Procedure D.

Table S5: Amounts and reagents used for substrate scope investigation (Table 4)

Entry	Substrate	Catalyst	Solvent	Internal Standard	Temp.	Time	Hydrogen Pressure
1[‡]	2-acetonaphthone 1098.9 mg 6.456 mmol	Cu-PMO 250 mg 0.75 mmol	MeOH 30 mL 0.21 M	DMF 74.6 µL 0.968 mmol	180°C	18 h	4 MPa
2[♯]	2-acetonaphthone 1098.9 mg 6.456 mmol	-	MeOH 30 mL 0.21 M	DMF 74.6 µL 0.968 mmol	180°C	18 h	4 MPa
3[‡]	Benzophenone 1176 mg 6.456 mmol	Cu-PMO 250 mg 0.75 mmol	MeOH 30 mL 0.21 M	DMF 74.6 µL 0.968 mmol	180°C	18 h	4 MPa
4[♯]	Benzophenone 1176 mg 6.456 mmol	-	MeOH 30 mL 0.21 M	DMF 74.6 µL 0.968 mmol	180°C	18 h	4 MPa

[‡]Reactions were performed according to representative Procedure A; [♯]Reactions were performed according to representative Procedure C.

Table S5 cont.: Amounts and reagents used for substrate scope investigation (Table 4)

Entry	**Substrate**	**Catalyst**	**Solvent**	**Internal Standard**	**Temp.**	**Time**	**Hydrogen Pressure**
5[‡]	Benzylacetone 956.8 mg 0.97 mL 6.456 mmol	Cu-PMO 250 mg 0.75 mmol	MeOH 30 mL 0.21 M	DMF 74.6 μL 0.968 mmol	180°C	18 h	4 MPa
6[♯]	Benzylacetone 956.8 mg 0.97 mL 6.456 mmol	-	MeOH 30 mL 0.21 M	DMF 74.6 μL 0.968 mmol	180°C	18 h	4 MPa
7[‡]	4'-hydroxy acetophenone 879.0 mg 6.456 mmol	Cu-PMO 250 mg 0.75 mmol	MeOH 30 mL 0.21 M	DMF 74.6 μL 0.968 mmol	180°C	18 h	4 MPa
8[♯]	4'-hydroxy acetophenone 879.0 mg 6.456 mmol		MeOH 30 mL 0.21 M	DMF 74.6 μL 0.968 mmol	180°C	18 h	4 MPa

[‡]Reactions were performed according to representative Procedure A; [♯]Reactions were performed according to representative Procedure C.

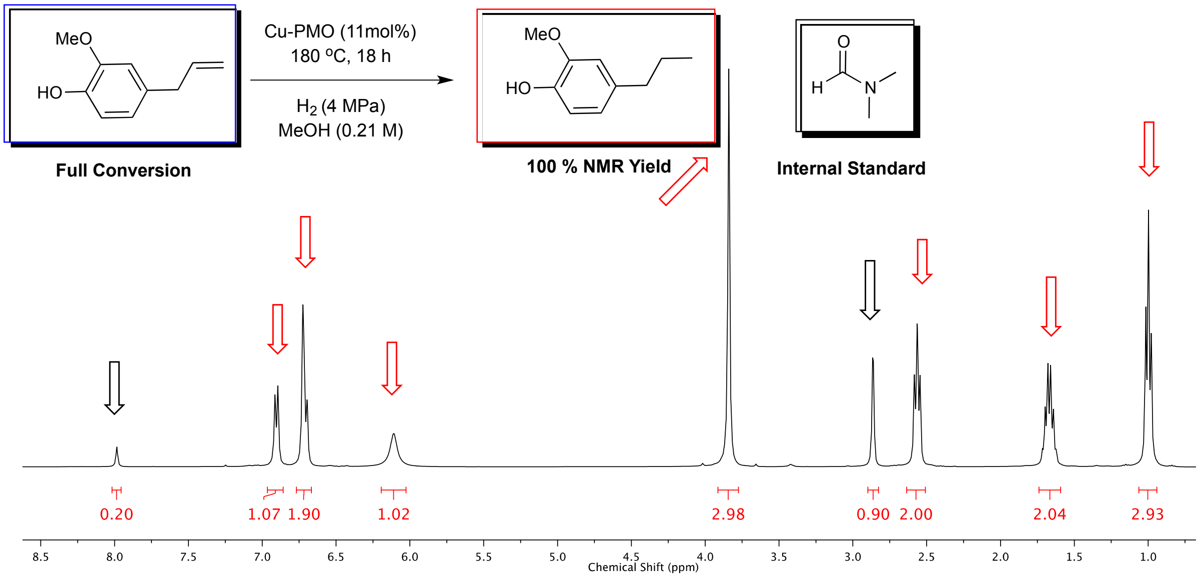


Figure S6: Crude NMR of a representative reaction showing complete conversion to **S1**. Conditions: Eugenol (6.456 mmol), Cu-PMO (11 mol%), MeOH (0.21 M), H_2 (40 bars), 180^{o}C, 18 h, DMF (as internal standard, 0.15 equiv.).

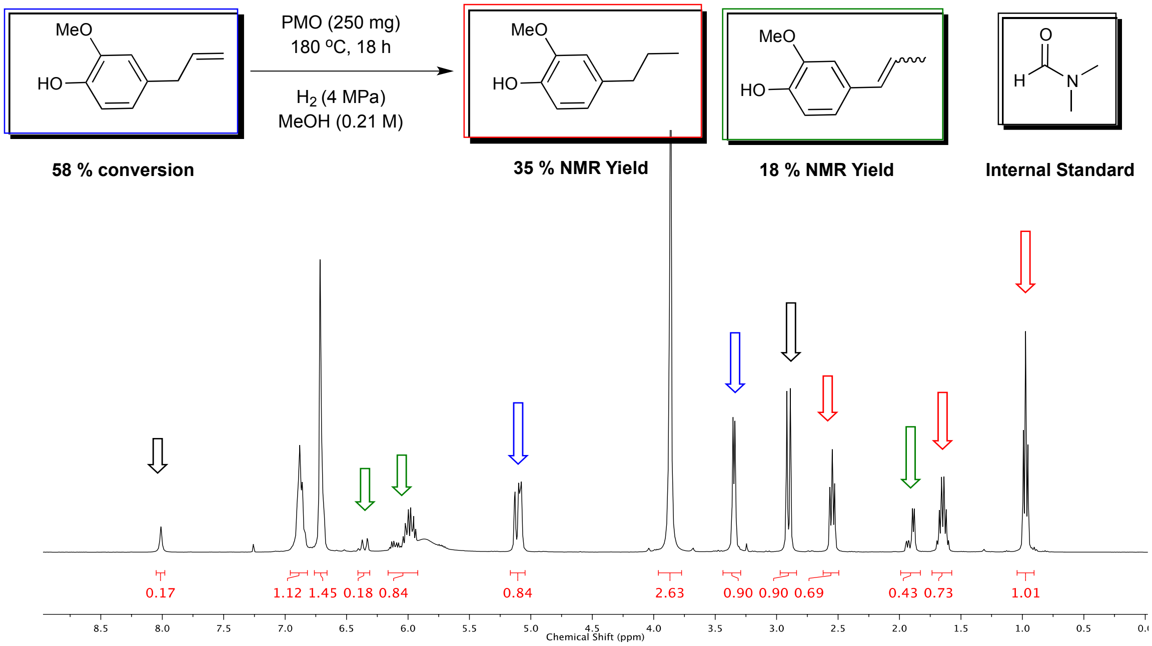
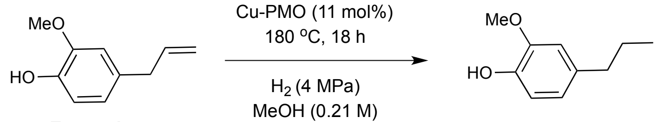


Figure S7: Crude NMR of a representative reaction showing eugenol (58% conversion), **S1** (35% NMR yield) and **IsoE** (18% NMR yield). Conditions: Eugenol (6.456 mmol), PMO (250 mg), MeOH (0.21 M), H_2 (40 bars), 180^{o}C, 18 h, DMF (as internal standard, 0.15 equiv.).

e. Product Isolation and Characterization



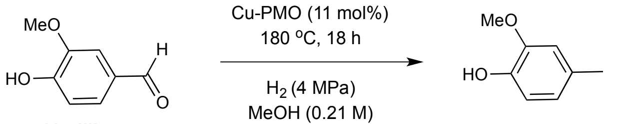
Eugenol
Chemical Formula: $C_{10}H_{12}O_2$
Exact Mass: 164.08

S1
Chemical Formula: $C_{10}H_{14}O_2$
Exact Mass: 166.10

This reaction was performed following General Procedure A (Table S1, Entry 1). The crude reaction mixture was subjected to column chromatography (1% Ethyl Acetate in Hexanes) to afford pure **S1** (1029 mg, 96 % isolated yield) as a clear pale yellow oil.

R_f = 0.14 (silica gel, 95:5 Hexanes:EtOAc); **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 6.83 (dd, *J* = 7.7, 0.6 Hz, 1H), 6.70 - 6.65 (m, 2H), 5.44 (s, 1H), 3.88 (s, 3H), 2.56 - 2.49 (m, 2H), 1.68 - 1.56 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.21, 143.46, 134.67, 120.92, 114.00, 110.95, 55.81, 37.74, 24.86, 13.80. **IR** (neat) v = 3444.8, 2957.9, 2931.3, 2670.6, 1607.1, 1512.5, 1285.8, 1232.0, 1150.3 cm^{-1}.

Analytical data is identical to that reported in the literature.[1]



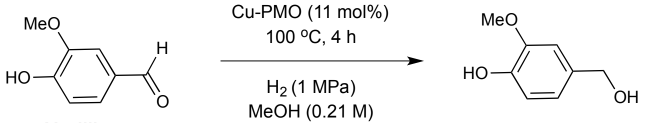
Vanillin
Chemical Formula: $C_8H_8O_3$
Exact Mass: 152.05

S2
Chemical Formula: $C_8H_{10}O_2$
Exact Mass: 138.07

This reaction was performed following General Procedure A (Table S2, Entry 1). The crude reaction mixture was subjected to column chromatography (5% Ethyl Acetate in Hexanes) to afford pure **S2** (544.4 mg, 60 % isolated yield) as a clear oil.

R_f = 0.39 (silica gel, 3:1 Hexanes:EtOAc); **^{1}H 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); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.22, 143.28, 129.58, 121.47, 114.07, 111.62, 55.80, 21.05; **IR** (neat) v = 3444.8, 2938.7, 1606.9, 1512.0, 1463.7, 1423.3, 1363.2, 1268.4, 1231.3, 1203.0, 1148.6, 1120.5, 1032.0 cm^{-1}.

Analytical data is identical to that reported in the literature.[2]

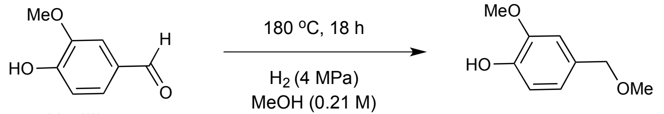


Vanillin
Chemical Formula: $C_8H_8O_3$
Exact Mass: 152.05

S3
Chemical Formula: $C_8H_{10}O_3$
Exact Mass: 154.06

This reaction was performed following General Procedure A (Table S2, Entry 4). The crude reaction mixture was subjected to column chromatography (5% Ethyl Acetate in Hexanes to 50% Ethyl Acetate in Hexanes) to afford pure **S3** (364.5 mg, 36 % isolated yield) as a white solid.

R_f = 0.11 (silica gel, 3:1 Hexanes:EtOAc); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.94 – 6.85 (m, 7H), 6.84 (dd, *J* = 8.0, 1.8 Hz, 3H), 5.60 (s, 3H), 4.60 (d, *J* = 5.8 Hz, 7H), 3.90 (s, 10H), 1.56 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.62, 145.23, 132.91, 120.20, 114.22, 109.89, 65.46, 55.89; **IR** (neat) ν = 3437.8, 3152.3, 2965.5, 2889.2, 1602.9, 1511.4, 1430.8, 1372.2, 1233.8, 1152.4, 1123.0 cm^{-1}.



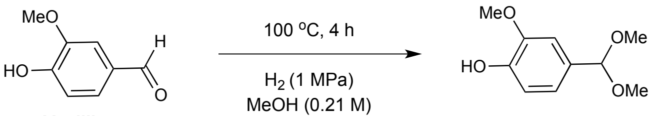
Vanillin
Chemical Formula: $C_8H_8O_3$
Exact Mass: 152.05

S4
Chemical Formula: $C_9H_{12}O_3$
Exact Mass: 168.08

This reaction was performed following General Procedure C (Table S2, Entry 3). The crude reaction mixture was subjected to column chromatography (5% Ethyl Acetate in Hexanes to 25% Ethyl Acetate in Hexanes) to afford pure **S4** (209.9 mg, 19 % isolated yield) as a clear oil.

R_f = 0.29 (silica gel, 3:1 Hexanes:EtOAc); **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 6.89 – 6.85 (m, 2H), 6.81 (dd, *J* = 8.0, 1.8 Hz, 1H), 5.61 (s, 1H), 4.37 (s, 2H), 3.89 (s, 3H), 3.36 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.55, 145.22, 130.07, 121.10, 114.01, 110.41, 74.72, 57.81, 55.86; **IR** (neat) ν = 3370.8, 2935.1, 1605.0, 1514.0, 1463.1, 1429.1, 1363.5, 1271.0, 1238.5, 1185.4, 1152.4, 1079.7 cm^{-1}.

Analytical data is identical to that reported in the literature.[3]

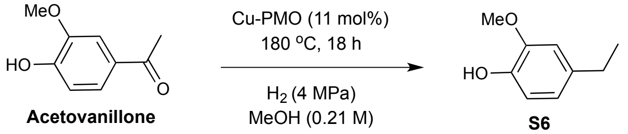


Vanillin
Chemical Formula: $C_8H_8O_3$
Exact Mass: 152.05

S5
Chemical Formula: $C_{10}H_{14}O_4$
Exact Mass: 198.09

This reaction was performed following General Procedure C (Table S2, Entry 6). The crude reaction mixture was subjected to column chromatography (5% Ethyl Acetate in Hexanes) to afford pure **S5** (130.2 mg, 10 % isolated yield) as a clear oil.

R_f = 0.33 (silica gel, 3:1 Hexanes:EtOAc); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.03 – 6.85 (m, 12H), 5.64 (d, *J* = 0.8 Hz, 3H), 5.29 (s, 3H), 3.96 (s, 1H), 3.90 (s, 11H), 3.51 – 3.45 (m, 1H), 3.32 (s, 19H), 3.31 (s, 1H), 1.29 – 1.19 (m, 2H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.46, 145.75, 130.15, 119.91, 113.89, 108.86, 103.28, 55.89, 52.75; **IR** (neat) ν = 3393.9, 2938.8, 2830.3, 1608.2, 1513.8, 1464.0, 1426.4, 1348.2, 1267.7, 1155.3, 1096.5, 1031.6, 985.5 cm^{-1}.

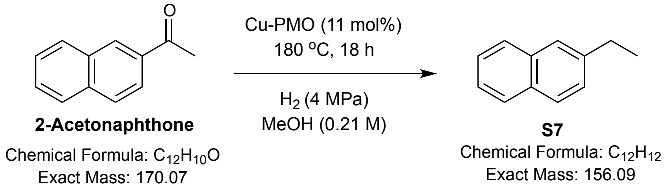


Acetovanillone
Chemical Formula: $C_9H_{10}O_3$
Exact Mass: 166.06

S6
Chemical Formula: $C_9H_{12}O_2$
Exact Mass: 152.08

This reaction was performed following General Procedure A (Table S3, Entry 1). The crude reaction mixture was subjected to a silica plug (eluted with Ethyl Acetate) to afford pure **S6** (569.5 mg, 58 % isolated yield) as a yellow oil.

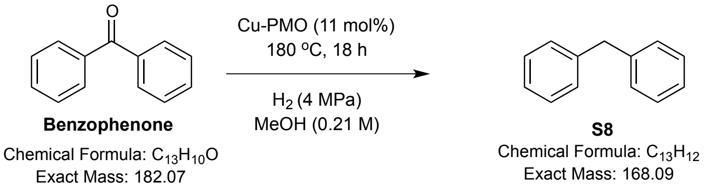
R_f = 0.44 (silica gel, 3:1 Hexanes:EtOAc); **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 6.84 (d, *J* = 7.7 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 2H), 5.47 (d, *J* = 0.9 Hz, 1H), 3.88 (d, *J* = 0.9 Hz, 4H), 2.58 (q, *J* = 7.6 Hz, 2H), 1.22 (td, *J* = 7.6, 0.9 Hz, 4H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.29, 143.46, 136.25, 120.23, 114.13, 110.45, 55.81, 28.55, 15.94; **IR** (neat) ν = 3442.9, 2962.7, 1611.5, 1512.5, 1452.8, 1429.6, 1230.5, 1149.5, 1121.8 cm^{-1}.
Analytical data is identical to that reported in the literature.[4]



This reaction was performed following General Procedure A (Table S4, Entry 1). The crude reaction mixture was subjected to a silica plug (eluted with 7:1 Hexanes:Ethyl Acetate) to afford pure **S7** (920.4 mg, 91 % isolated yield) as a clear oil.

R_f = 0.81 (silica gel, 7:1 Hexanes:EtOAc); **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.87 (m, 3H), 7.71 (s, 1H), 7.51 (m, 2H), 7.43 (d, *J* = 12 Hz, 1H), 2.89 (q, *J* = 6 Hz, 2H), 1.42 (t, *J* = 6 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 141.77, 133.70, 131.93, 127.81, 127.61, 127.42, 127.10, 125.84, 125.54, 125.02, 29.07, 15.57; **IR** (neat) ν = 3052.2, 2964.1, 2930.0, 2871.9, 1632.0, 1601.0, 1508.4, 1452.5, 1374.2, 1319.4, 1269.4, 1124.5, 1054.6, 1018.3 cm^{-1}.

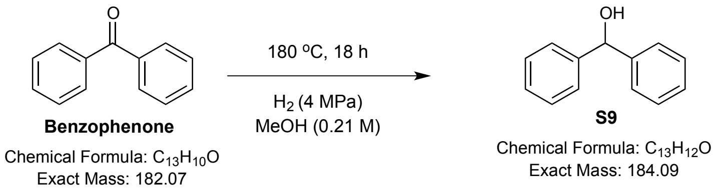
Analytical data is identical to that reported in the literature[5].



This reaction was performed following General Procedure A (Table S4, Entry 3). The crude reaction mixture was subjected to a silica plug (eluted with 5:1 Hexanes:Ethyl Acetate) to afford pure **S8** (1041 mg, 96 % isolated yield) as a clear oil.

R_f = 0.48 (silica gel, 5:1 Hexanes:EtOAc); **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.31 (dd, *J* = 8.5, 6.9 Hz, 4H), 7.26 - 7.20 (m, 6H), 4.02 (s, 2H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 141.11, 128.94, 128.46, 126.06, 41.95; **IR** (neat) ν = 3062.2, 3026.5, 1599.4, 1493.4, 1450.6, 1075.7, 1029.4 cm^{-1}.

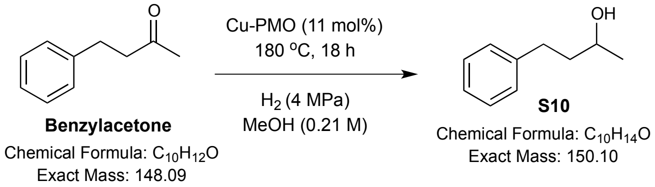
Analytical data is identical to that reported in the literature[6].



This reaction was performed following General Procedure C (Table S4, Entry 4). The crude reaction mixture was subjected to column chromatography (eluted with 6:1 Hexanes:Ethyl Acetate) to afford pure **S9** (125.8 mg, 10.5 % isolated yield) as a white solid.

R_f = 0.30 (silica gel, 6:1 Hexanes:EtOAc); **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 6 Hz, 4H), 7.34 (t, *J* = 6 Hz, 4 H), 7.27 (t, J = 6 Hz, 2H), 5.84 (s, 1H), 2.23 (br s, 1H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 143.76, 128.49, 127.56, 126.51, 77.22, 77.01, 76.79, 76.26; **IR** (neat) v = 3270.9, 1596.7, 1492.5, 1453.8, 1445.9, 1344.0, 1315.5, 1196.8, 1174.8, 1084.0, 1031.3, 1015.6 cm^{-1}.

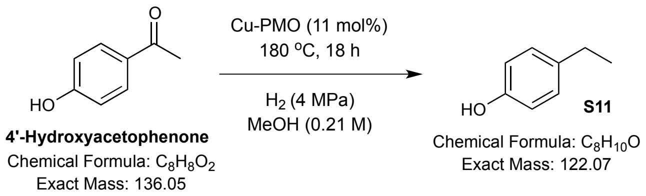
Analytical data is identical to that reported in the literature[7].



This reaction was performed following General Procedure A (Table S4, Entry 4). The crude reaction mixture was subjected to column chromatography (eluted with 5:1 Hexanes:Ethyl Acetate) to afford pure **S10** (822 mg, 95 % isolated yield) as a clear oil.

R_f = 0.19 (silica gel, 5:1 Hexanes:EtOAc); **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.23 - 7.16 (m, 3H), 3.87 - 3.79 (m, 1H), 2.76 (ddd, *J* = 13.7, 9.5, 6.1 Hz, 1H), 2.67 (ddd, *J* = 13.8, 9.3, 6.8 Hz, 1H), 1.84 - 1.73 (m, 2H), 1.47 (d, *J* = 2.4 Hz, 1H), 1.28 - 1.21 (m, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 142.04, 128.38, 125.80, 67.50, 40.84, 32.13, 23.63; **IR** (neat) v = 3345.1, 2926.3, 1495.1, 1453.5, 1373.5, 1127.1, 1053.4 cm^{-1}.

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

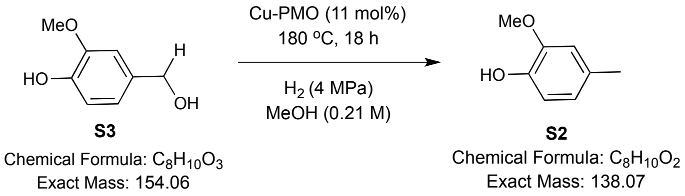


This reaction was performed following General Procedure A (Table S4, Entry 5). The crude reaction mixture was subjected to a silica plug (eluted with Ethyl Acetate) to afford pure **S11** (748.8 mg, 95 % isolated yield) as a white solid.

R_f = 0.54 (silica gel, 5:1 Hexanes:EtOAc); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.08 (d, *J* = 8 Hz, 2H), 6.84 (d, *J* = 8 Hz, 2H), 2.61 (q, *J* = 8 Hz, 2H), 1.25 (t, *J* = 4 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 153.34, 128.88, 115.06, 27.96, 15.88; **IR** (neat) v = 3232.6, 3022.0, 2962.2, 2929.7, 2869.7, 1612.8, 1598.3, 1511.0, 1449.3, 1369.1, 1215.9, 1173.2, 1110.8, 1063.5, 1014.8 cm^{-1}.

Analytical data is identical to that reported in the literature[9].

f. Reduction of S3 with Cu-PMO



This reaction was performed following General Procedure A using **S3** (1013.1 mg, 6.572 mmol, 1 equiv.) and Cu-PMO (239 mg, 0.723 mmol, 0.11 equiv.). The crude reaction mixture was analyzed directly by ^{1}H NMR after addition of DMF (0.15 equiv., 76 μL) as an internal standard. Analysis revealed complete conversion of **S3** to creosol.

g. Recycling studies with Cu-PMO

General Procedure for recycling studies: Eugenol (1.00 mL, 1060 mg, 6.456 mmol, 1 equiv.) and Cu-PMO (250 mg, 0.750 mmol, 11 mol%) were added to a 100 mL Parr reactor. Methanol (0.21 M) was added by syringe. The reaction vessel was sealed and pressurized to 4 MPa H_2 at room temperature. 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 to 180°C. The reaction was allowed to stir vigorously for the appropriate amount of time at 180°C. 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 40°C internal temperature. At this point, the Parr reactor was lifted from its stand and placed in a tap water bath until internal temperature reached 19°C. The internal pressure was released and the Parr reactor was opened. The mixture was filtered over a borosilicate glass filter, using 30 mL MeOH for transfer. The resulting filtrate was concentrated *in vacuo* to afford a residue that was analyzed directly by ^{1}H NMR after addition of dimethylformamide (DMF, 0.0746 mL, 0.968 mmol, 0.15 equiv.) as an internal standard. The isolated purple solid was washed twice with 5 mL MeOH, collected and placed in a dessicator until utilized in the next hydrogenation cycle.

Table S6: Results of Recycling Experiments with Cu-PMO

	Eugenol Conversion (%)	**Yield S1[a] (%)**
Cycle 1	100	98
Cycle 2	100	100
Cycle 3	100	100
Cycle 4	100	99.5
Cycle 5	100	96
Cycle 6	100	95
Cycle 7	100	100
Cycle 8	100	100
Cycle 9	100	94
Cycle 10	100	95.5
Cycle 11	100	100
Cycle 12	92	92
Cycle 13	40	40
Cycle 14	27	15

[a] NMR Yield as determined using DMF as internal standard

h. *Analysis of Cu-PMO After Reaction*

Cu-PMO was recovered after reaction with Eugenol (General Procedure A) by filtration over a borosilicate glass filter, using 30 mL MeOH to transfer the heterogeneous reaction mixture to the filter. The isolated purple solid was washed twice with 5 mL MeOH and placed in a dessicator until analysis by XRPD (Figure S8), SEM (Figure S9) and TEM (Figure S10). Elemental analysis of the recovered Cu-PMO was performed by ICP-OES (Table S7). XPS measurements of the recovered Cu-PMO were performed to determine metal speciation (Figure S11).

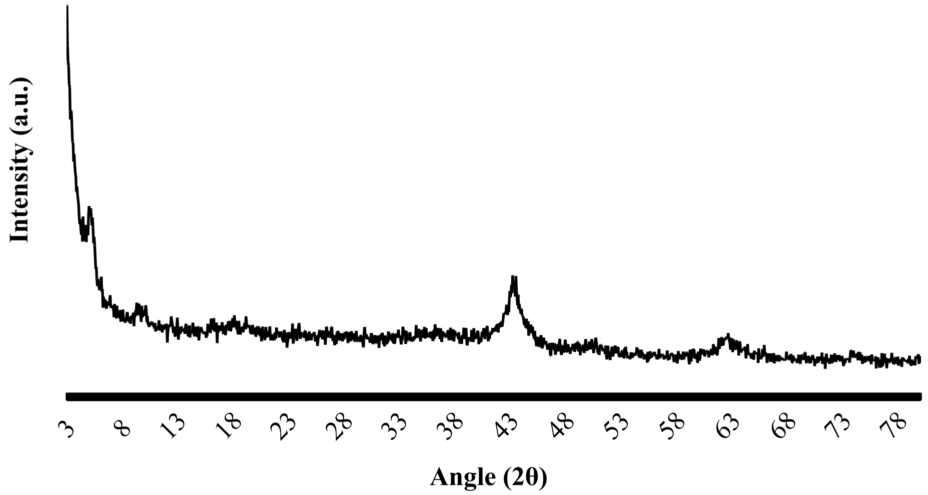


Figure S8: XRPD of Cu-PMO after reaction with Eugenol

Table S7: Metal Ion Composition of recovored Cu-PMO determined by ICP-OES

	Cu	**Mg**	**Al**
Concentration (mg/L)	37.17	56.94	28.46
Mass in solution (mg)	1.859	2.847	1.423
Amount in solution (mmol)	0.0293	0.117	0.0527
Normalized Ratio of Metals	0.55	2.22	1.00

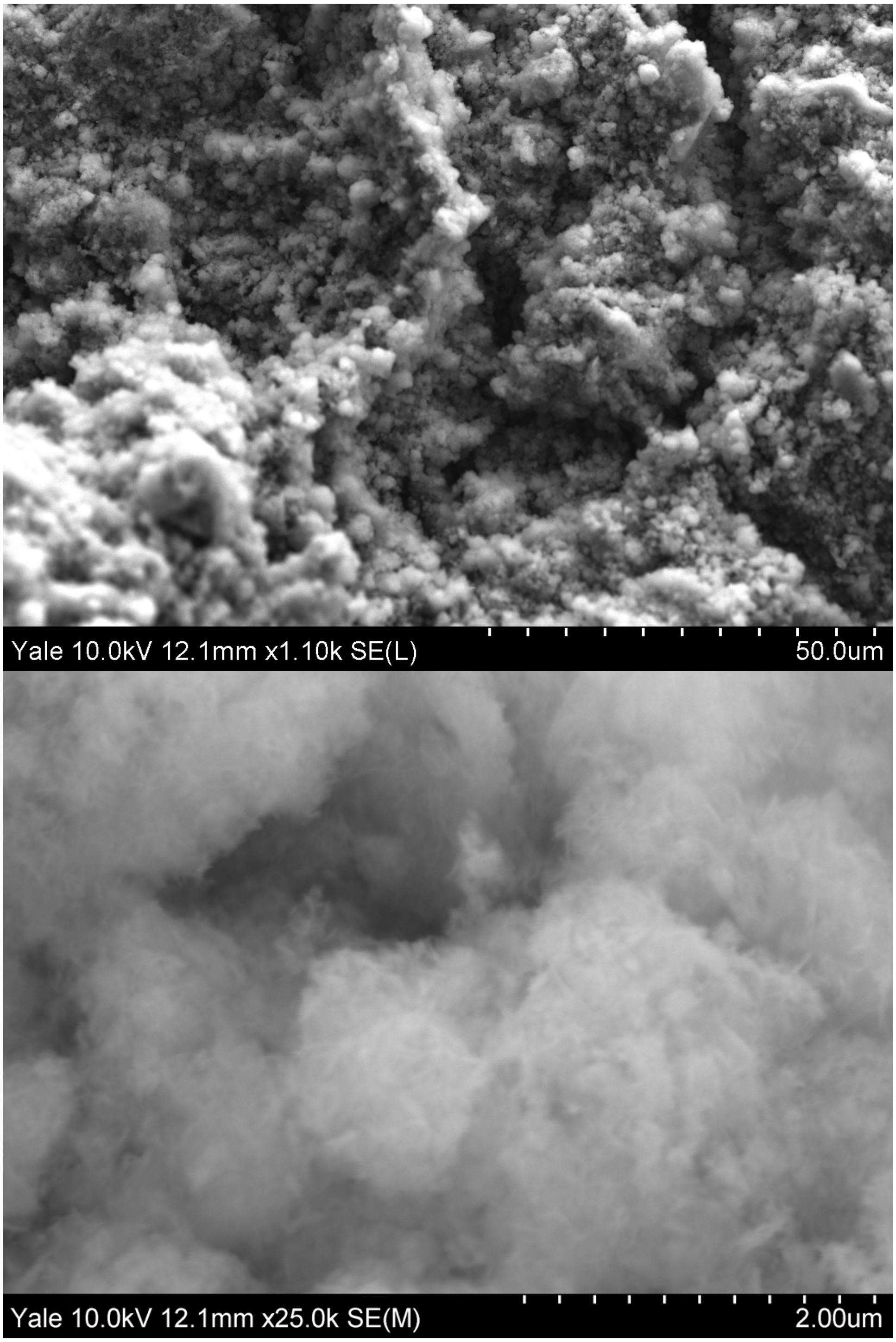


Figure S9: SEM Images of Cu-PMO as recovered after hydrogenation of Eugenol

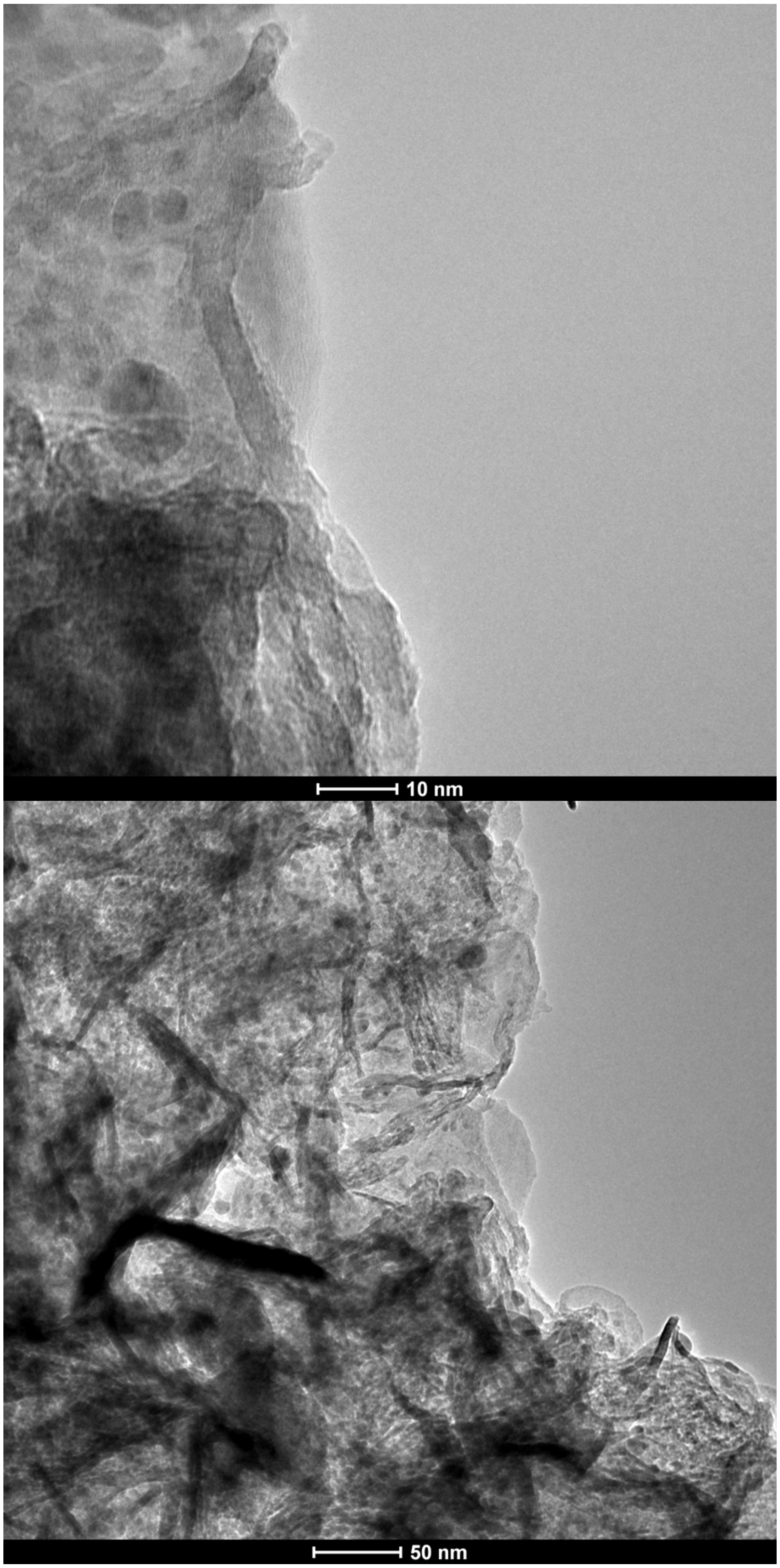


Figure S10: TEM Images of Cu-PMO as recovered after hydrogenation of Eugenol

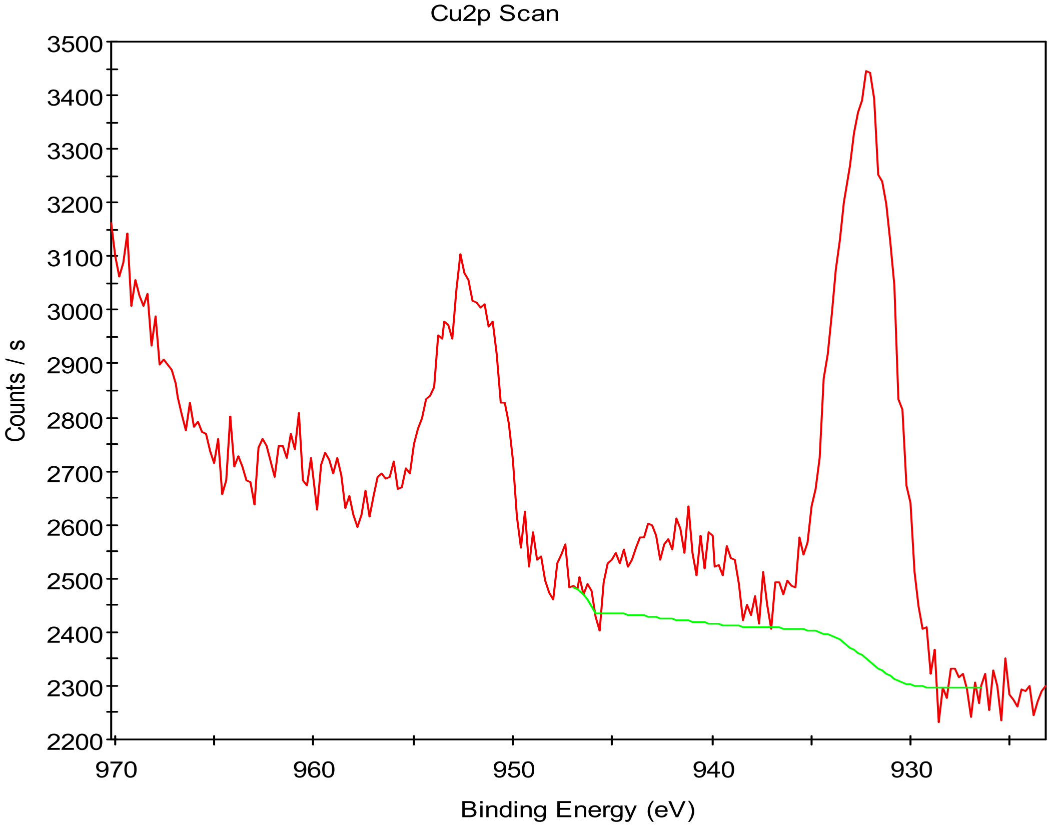


Figure S11: Cu 2p3 XPS of recovered Cu-PMO from reaction with eugenol

i. *Born-Haber Cycle used for calculating Gibbs Free Energy of Reactions in Solution*

$$\Delta G_g$$

$$R(g)+H_2(g)\rightarrow RH_2(g)$$

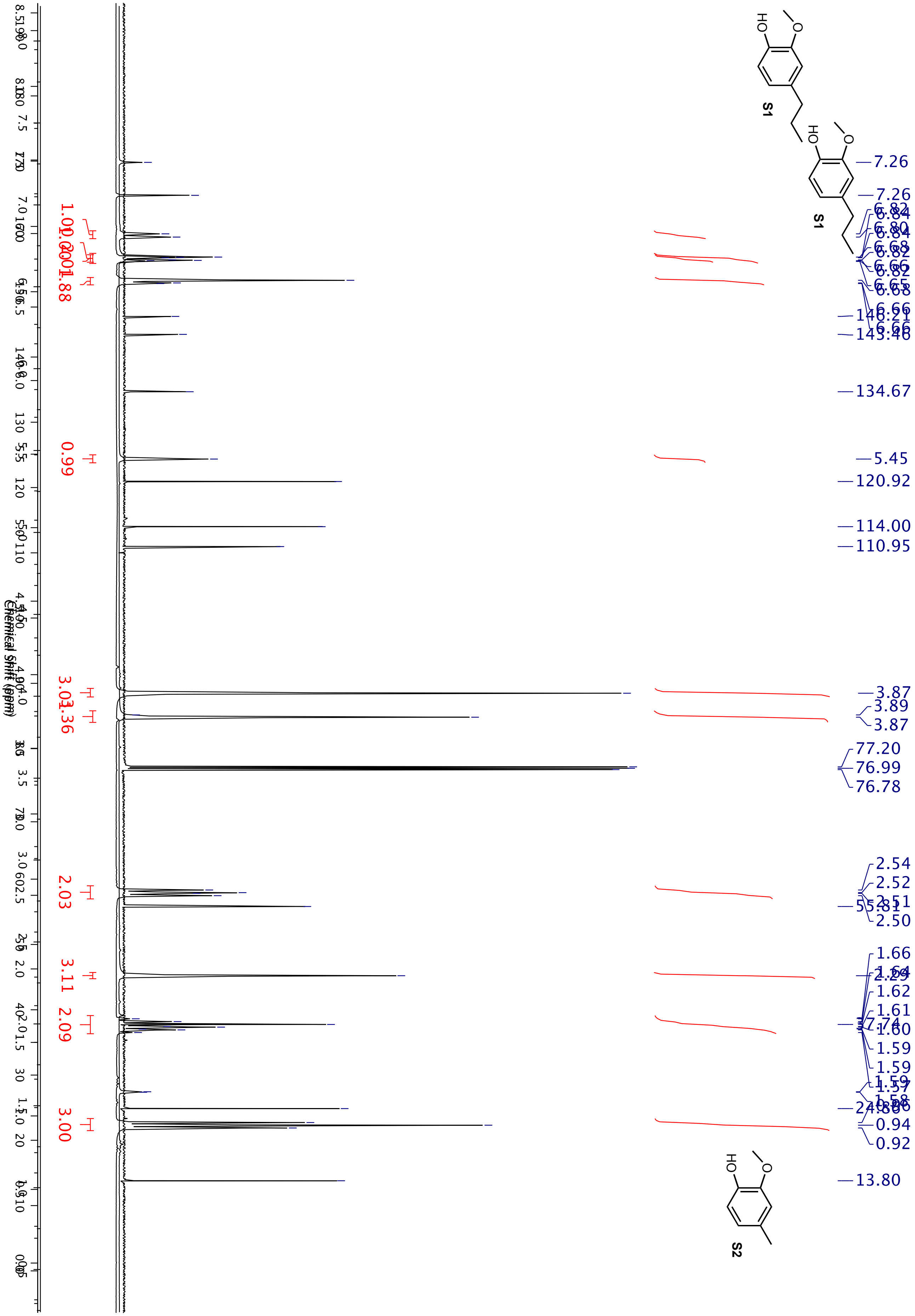
$$\Delta G_{s,R} \qquad \Delta G_{s,H_2} \qquad \Delta G_{s,RH_2}$$

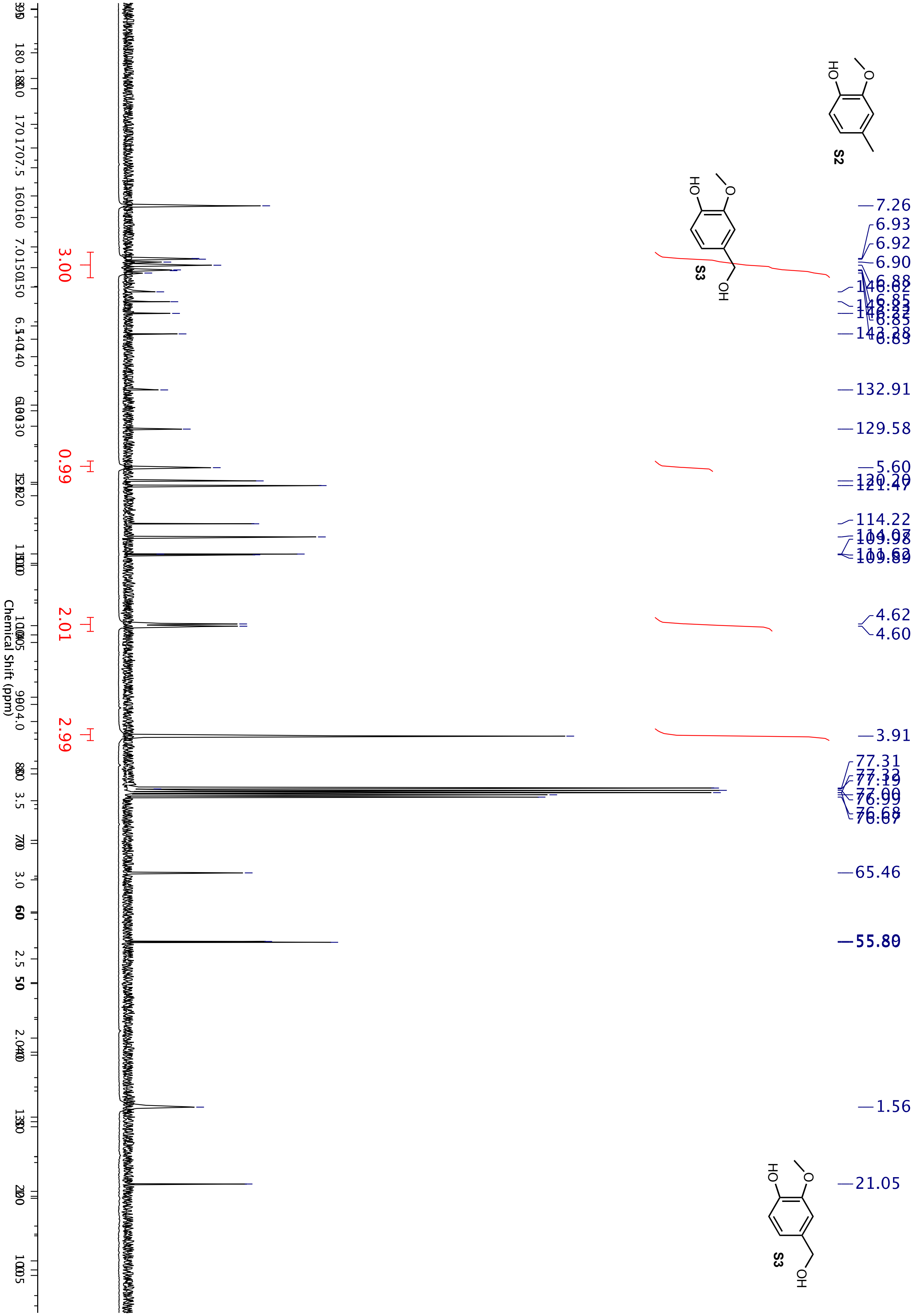
$$R(solu)+H_2(solu)\rightarrow RH_2(solu)$$

$$\Delta G_{solu}$$

Scheme S1: Born-Haber Cycle for Gibbs Free Energy of Solutions

2. Analytical Data


S1
S1
S2
HO
O
7.26
7.26
6.84
6.84
6.82
6.82
6.80
6.68
6.68
6.66
6.66
6.65
146.21
143.46
134.67
5.45
120.92
114.00
110.95
3.87
3.89
3.87
77.20
76.99
76.78
2.54
2.52
2.51
2.50
55.81
1.66
1.64
2.29
1.62
1.61
1.60
1.59
1.59
1.59
1.58
1.57
37.74
24.86
0.94
0.92
13.80
1.01
2.00
1.88
0.99
3.01
3.36
2.03
3.11
2.09
3.00
Chemical Shift (ppm)


S2
S3
S3
HO
O
OH
3.00
0.99
2.01
2.99
7.26
6.93
6.92
6.90
6.88
6.85
6.85
6.83
146.62
143.38
132.91
129.58
5.60
120.20
121.47
114.22
114.07
109.98
111.63
109.89
4.62
4.60
3.91
77.31
77.32
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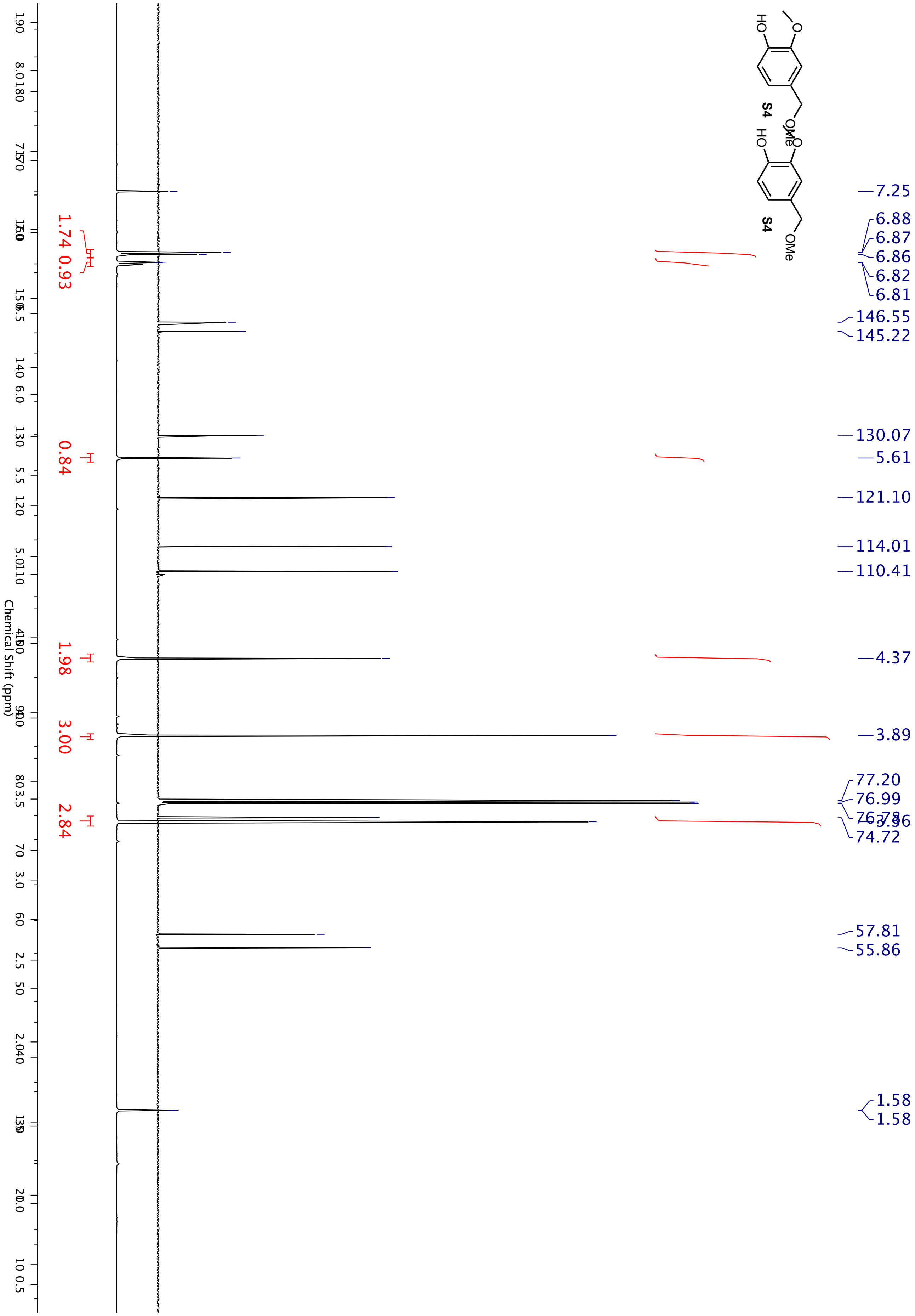
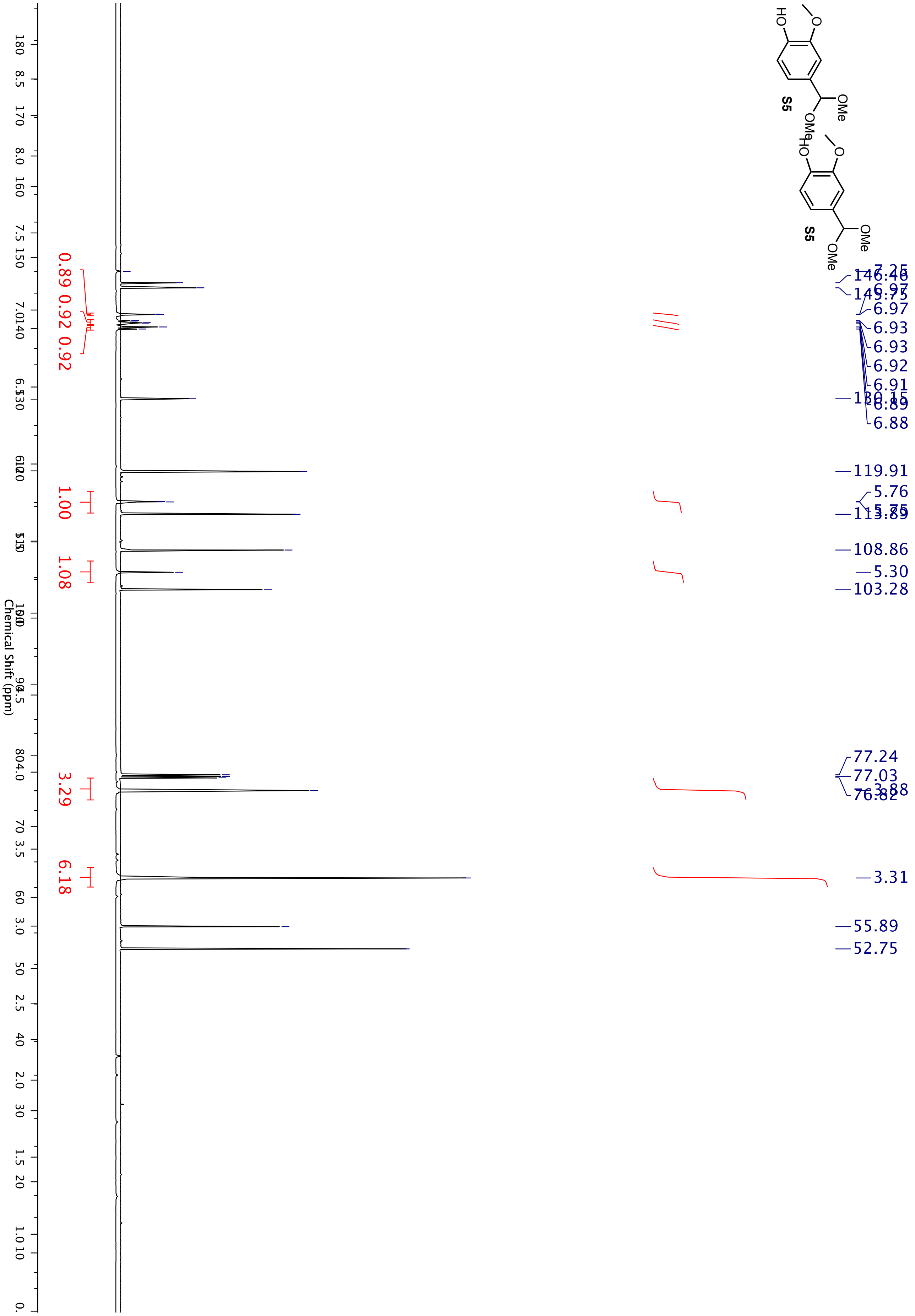
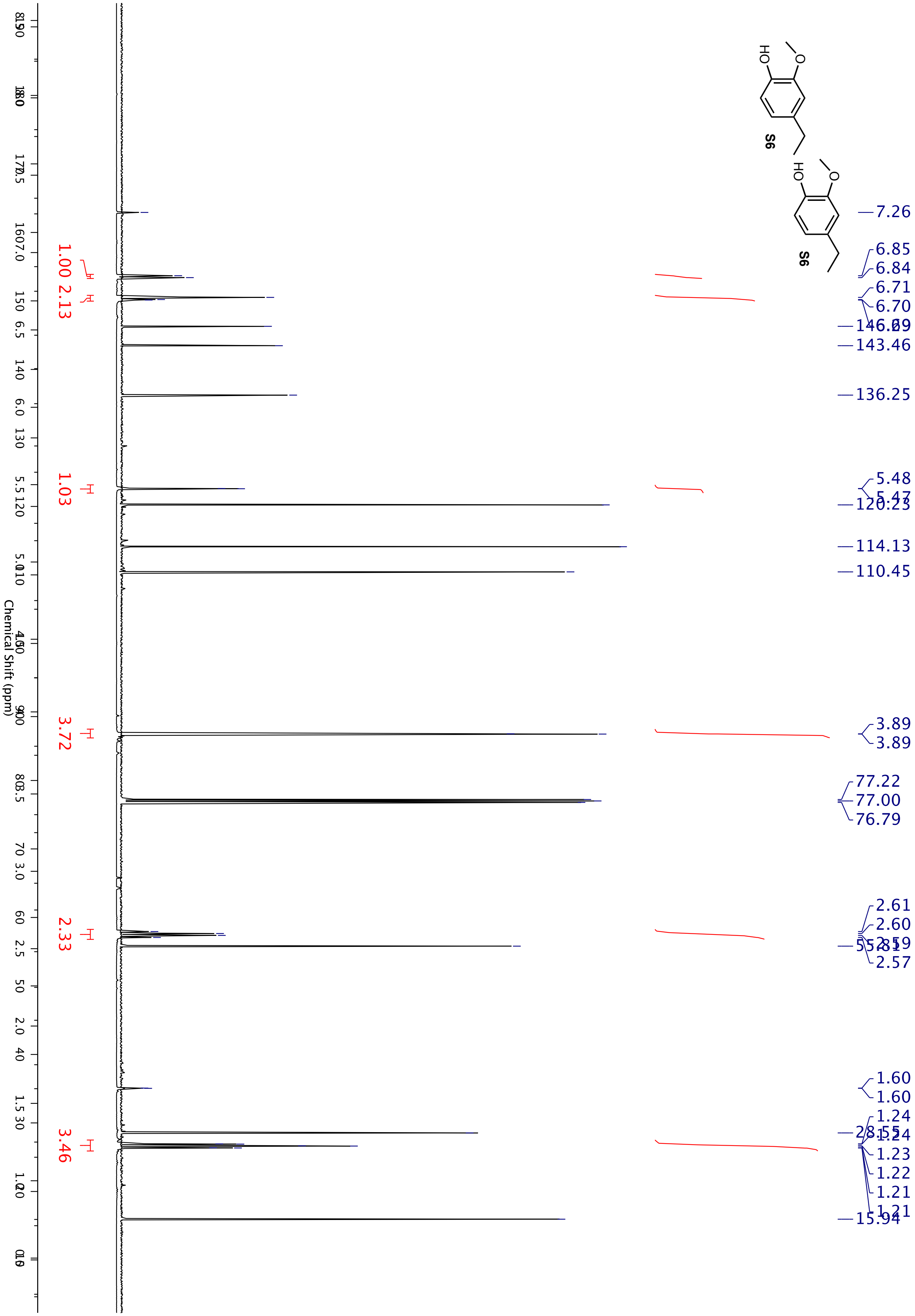
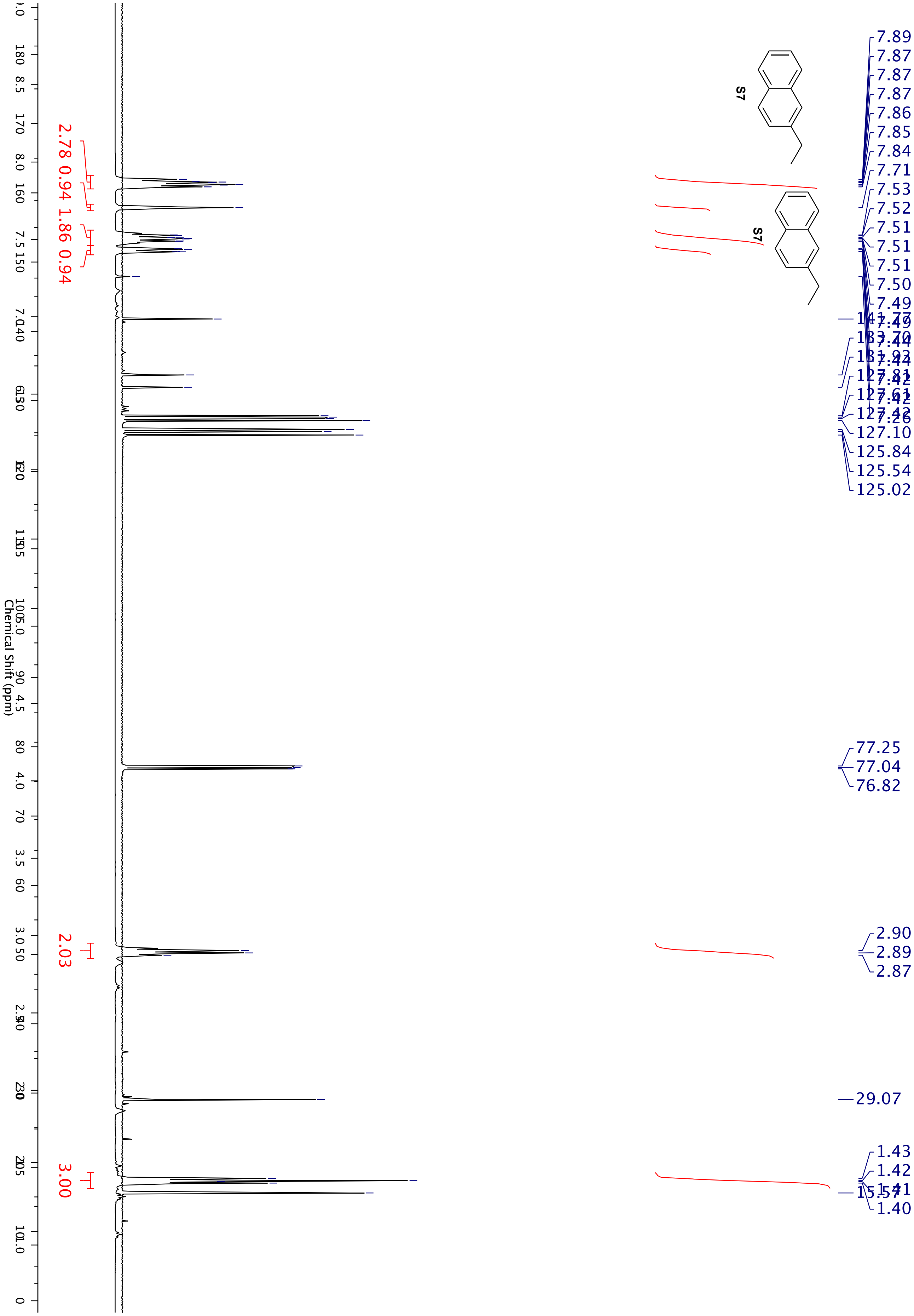
77.00
76.99
76.68
76.67
65.46
55.80
1.56
21.05
Chemical Shift (ppm)

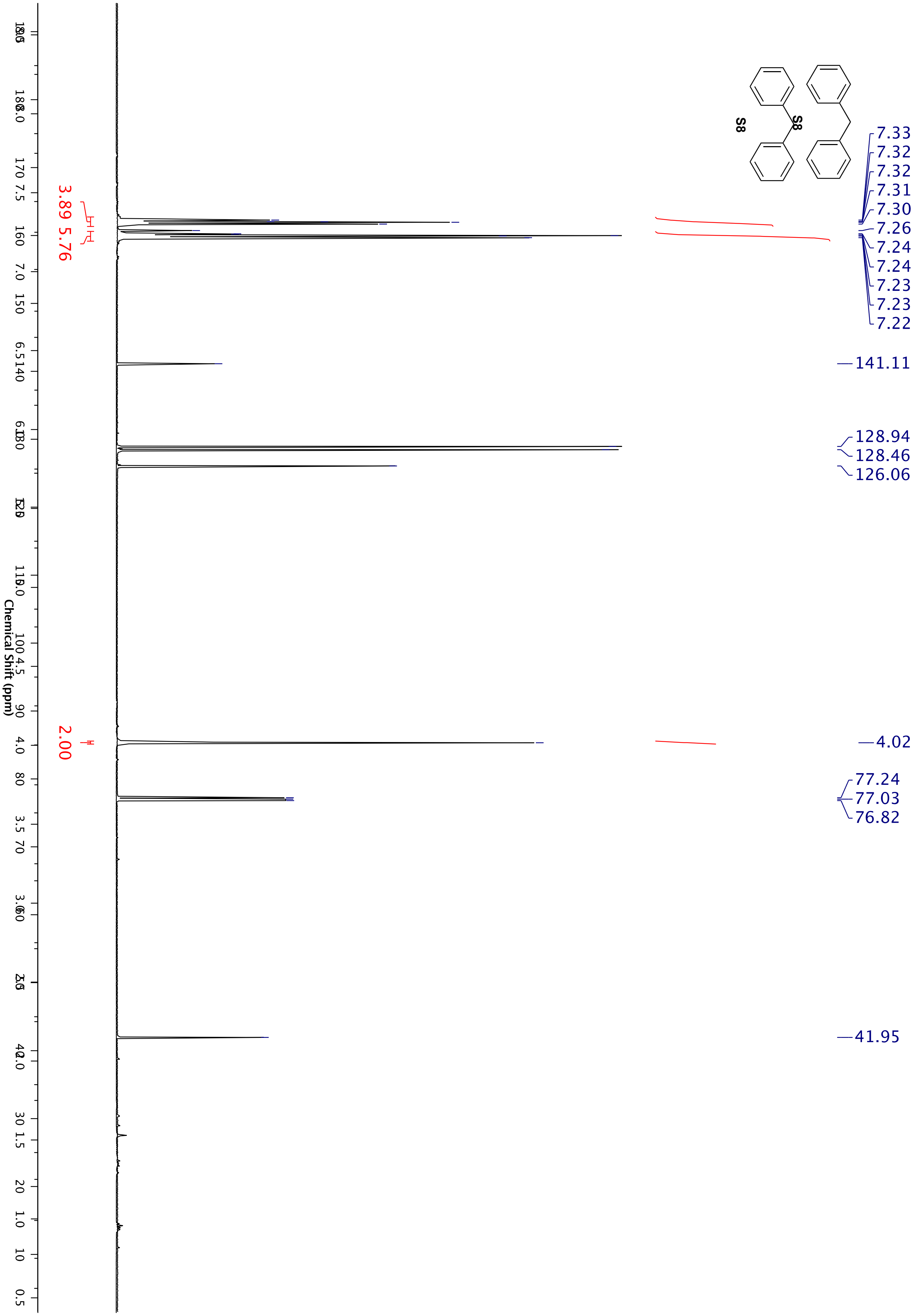


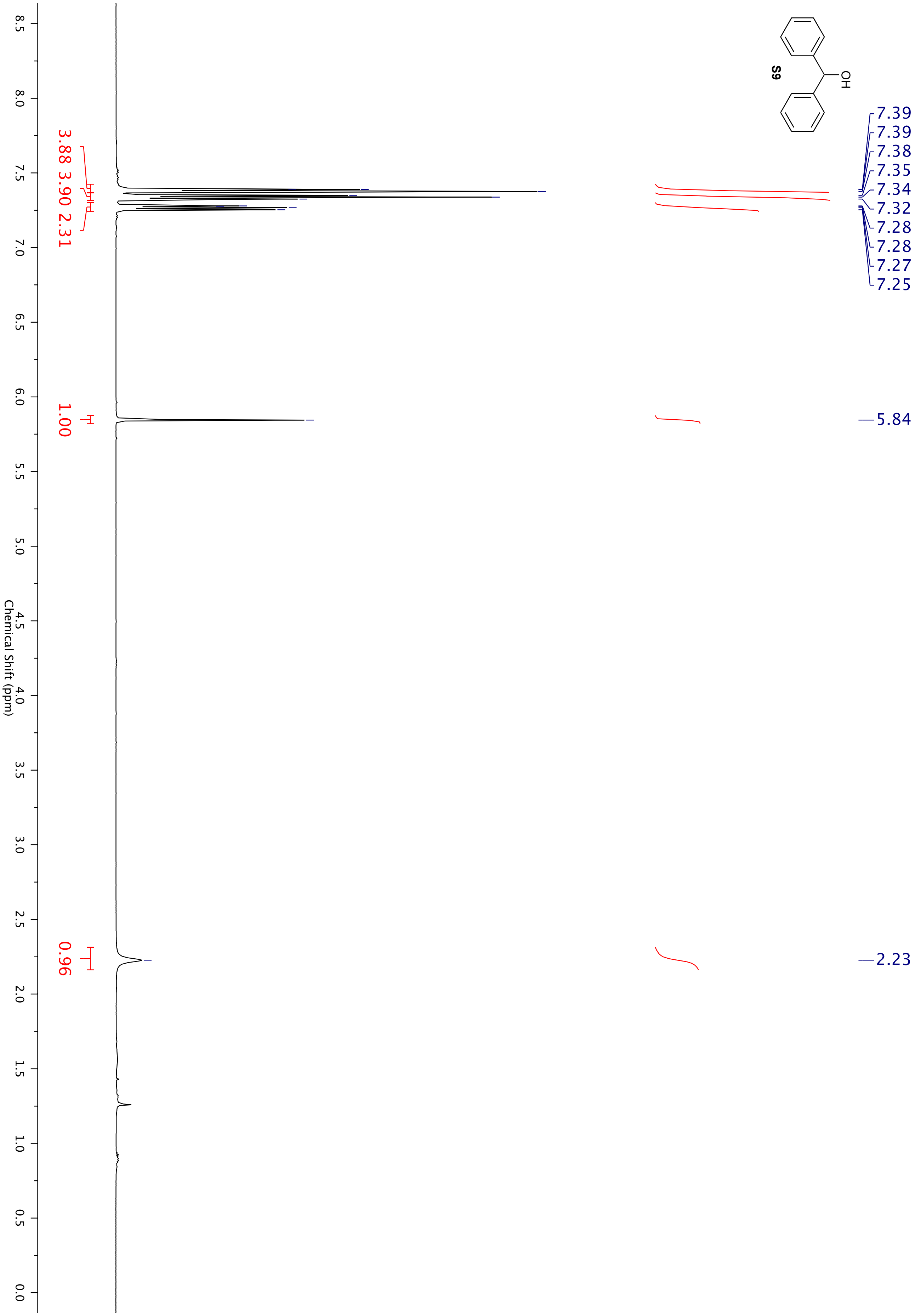
HO
O
OMe
S4
HO
O
OMe
S4
7.25
6.88
6.87
6.86
6.82
6.81
146.55
145.22
130.07
5.61
121.10
114.01
110.41
4.37
3.89
77.20
76.99
76.78
3.86
74.72
57.81
55.86
1.58
1.58
1.74
0.93
0.84
1.98
3.00
2.84
190
8.0
180
7.5
170
7.0
160
150
6.5
140
6.0
130
5.5
120
5.0
110
4.5
100
4.0
90
80
3.5
70
3.0
60
2.5
50
2.0
40
1.5
30
20
1.0
10
0.5
Chemical Shift (ppm)

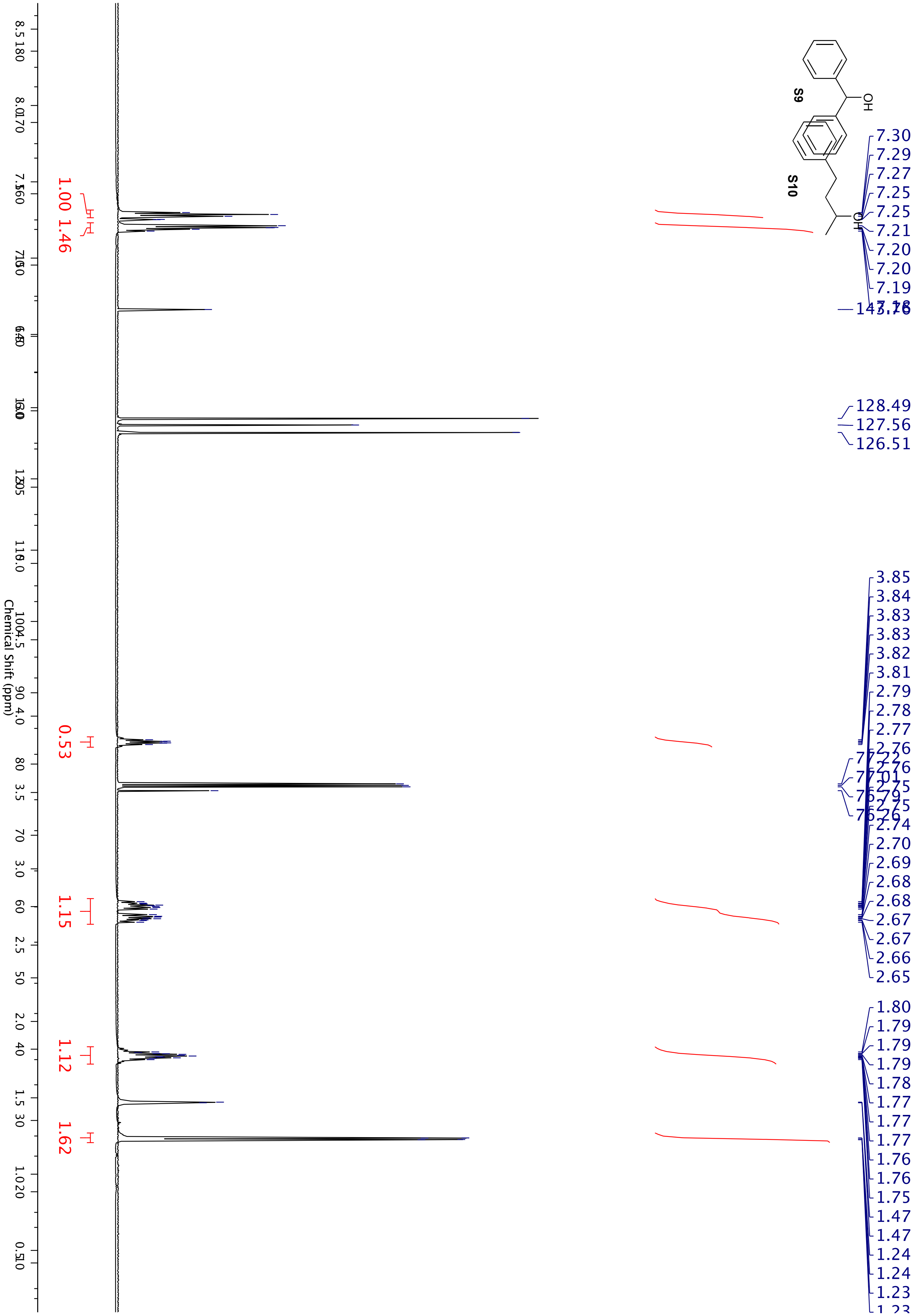

S5
S5
OMe
OMe
HO
O
7.25
6.97
6.97
6.93
6.93
6.92
6.91
6.89
6.88
5.76
5.75
5.30
3.88
3.31
146.40
145.75
130.15
119.91
113.89
108.86
103.28
77.24
77.03
76.82
55.89
52.75
0.89
0.92
0.92
1.00
1.08
3.29
6.18
Chemical Shift (ppm)

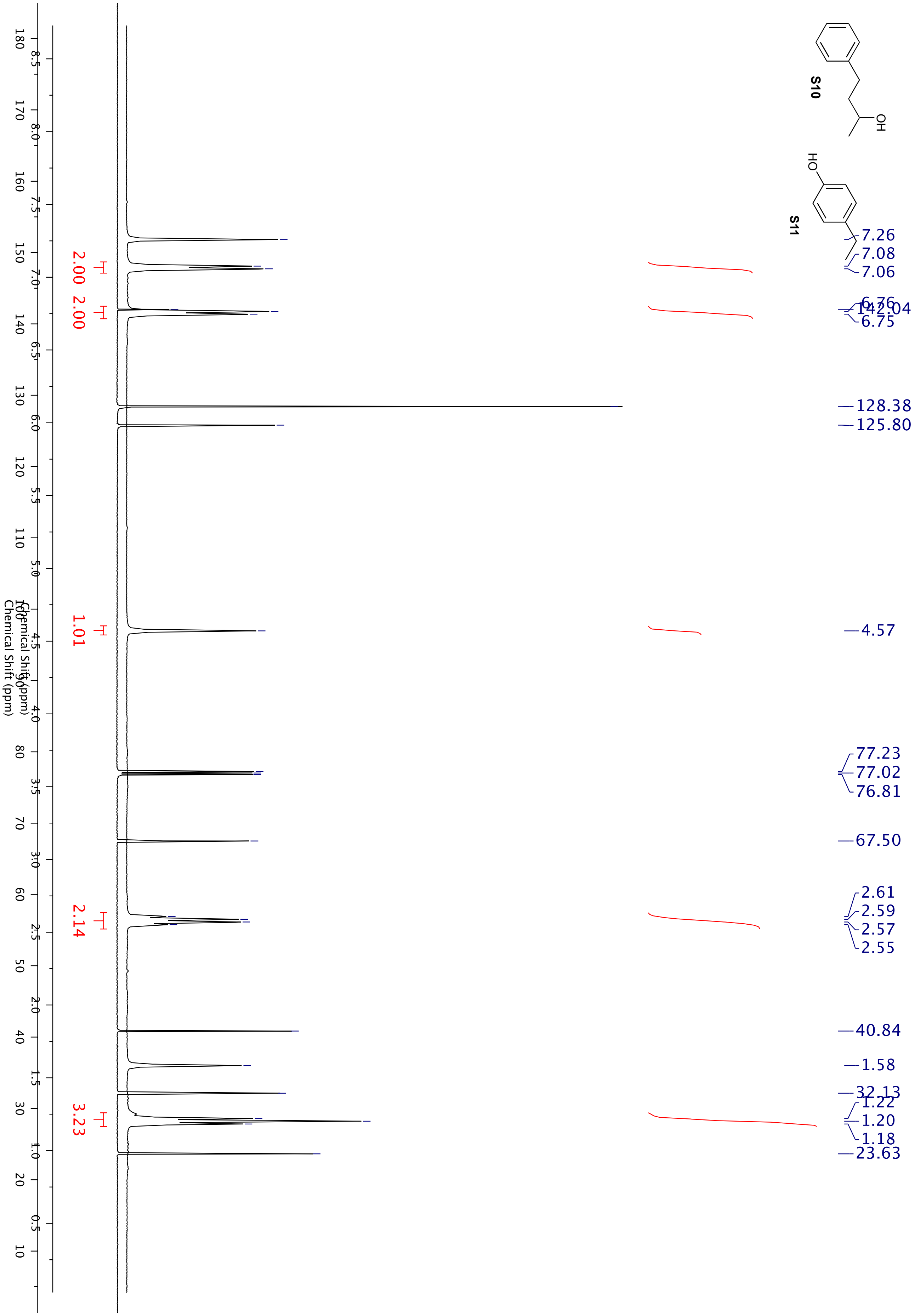

S6
S6
HO
O
7.26
6.85
6.84
6.71
6.70
146.09
143.46
136.25
5.48
5.47
120.23
114.13
110.45
3.89
3.89
77.22
77.00
76.79
2.61
2.60
2.59
2.57
55.81
1.60
1.60
1.24
1.24
1.23
1.22
1.21
1.21
28.55
15.94
1.00
2.13
1.03
3.72
2.33
3.46
Chemical Shift (ppm)

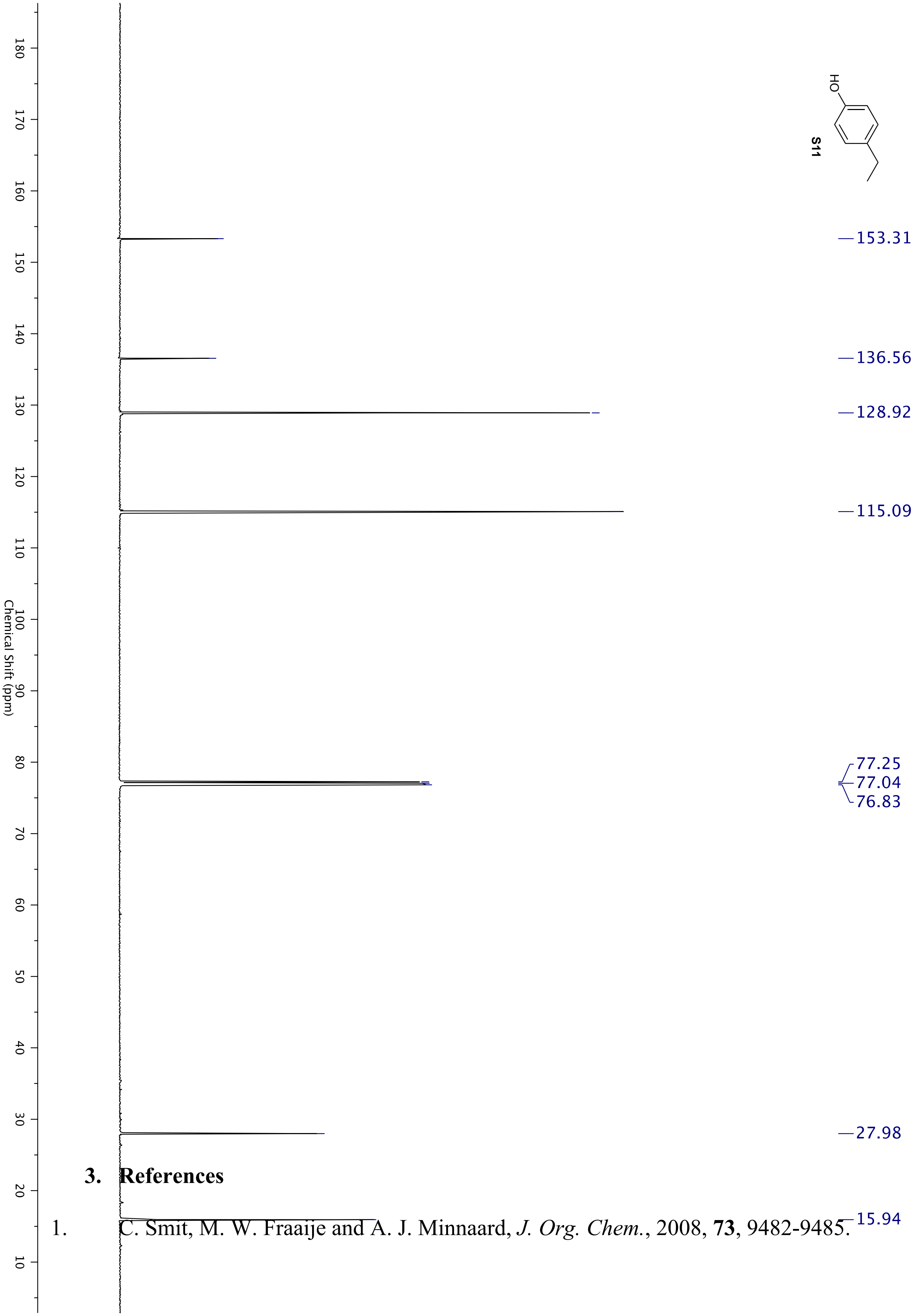

S7
S7
7.89
7.87
7.87
7.87
7.86
7.85
7.84
7.71
7.53
7.52
7.51
7.51
7.51
7.50
7.49
7.49
7.44
7.44
7.42
7.42
7.26
141.77
133.70
131.93
127.81
127.61
127.42
127.10
125.84
125.54
125.02
77.25
77.04
76.82
2.90
2.89
2.87
29.07
1.43
1.42
1.41
1.40
15.57
2.78
0.94
1.86
0.94
2.03
3.00
Chemical Shift (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
8.5
8.0
7.5
7.0
6.5
2.0
1.5
1.0
5.0
4.5
4.0
3.5
3.0
2.5


S8
S8
7.33
7.32
7.32
7.31
7.30
7.26
7.24
7.24
7.23
7.23
7.22
141.11
128.94
128.46
126.06
4.02
77.24
77.03
76.82
41.95
3.89
5.76
2.00
Chemical Shift (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


S9
OH
7.39
7.39
7.38
7.35
7.34
7.32
7.28
7.28
7.27
7.25
5.84
2.23
3.88
3.90
2.31
1.00
0.96
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)


OH
S9
OH
S10
7.30
7.29
7.27
7.25
7.25
7.21
7.20
7.20
7.19
7.18
143.76
128.49
127.56
126.51
3.85
3.84
3.83
3.83
3.82
3.81
2.79
2.78
2.77
2.76
2.76
2.75
2.75
2.74
2.70
2.69
2.68
2.68
2.67
2.67
2.66
2.65
77.22
77.01
76.79
76.26
1.80
1.79
1.79
1.79
1.78
1.77
1.77
1.77
1.76
1.76
1.75
1.47
1.47
1.24
1.24
1.23
1.00
1.46
0.53
1.15
1.12
1.62
8.5
180
8.0
170
7.5
160
7.0
150
6.5
140
6.0
130
5.5
120
5.0
110
4.5
100
4.0
90
80
3.5
70
3.0
60
2.5
50
2.0
40
1.5
30
1.0
20
0.5
10
Chemical Shift (ppm)


S10
OH
HO
S11
7.26
7.08
7.06
6.76
142.04
6.75
128.38
125.80
4.57
77.23
77.02
76.81
67.50
2.61
2.59
2.57
2.55
40.84
1.58
32.13
1.22
1.20
1.18
23.63
2.00
2.00
1.01
2.14
3.23
Chemical Shift (ppm)
Chemical Shift (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5



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