Electronic Supplemental Information for:

Gold-Catalyzed Conversion of Lignin to Low Molecular Weight Aromatics

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Materials and Methods

Commercially available reagents were used as received. 4'-Methoxyacetophenone, malonic acid, $NaBH_4$, and vanillin were purchased from Acros Organics. 2-Bromo-4'-methoxyacetophenone, 3'-methoxyacetophenone, 3',4'-dimethoxyacetophenone, 4'-methylacetophenone, 4'-bromoacetophenone, benzaldehyde, chloroform-d, diphenyl ether, *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA), *n*-dodecane, KBH_4, $LiOH{\cdot}H_2O$, methane sulfonic anhydride, and NH_4OH (28-30.0 wt.%) were purchased from Alfa Aesar. $Al_2(CO_3)_3$ was purchased from Amresco Chemical. All organic solvents, formaldehyde (37 wt.%), and hydrochloric acid (36.5-38.0 wt.%) were purchased from BDH VWR Chemicals. 4-Hydroxy-3-methoxy-α-methylbenzyl alcohol and *p*-anisaldehyde were purchased from Chem Implex International. K_2CO_3 and pyridine were purchased from Fisher Scientific. 4-Methyoxyphenyl methyl carbinol was purchased from Oakwood Chemical. 1-Phenylethanol, acetophenone, benzophenone, benzyl alcohol, guiacol, $HAuCl_4$ (99.9999% trace metal basis), oxalyl chloride, *p*-toluenesulfonyl chloride, triethylamine, and vanillic acid were purchased from Sigma Aldrich. *p*-Anisic acid, and cyclopropyl phenyl ketone were purchased from TCI America.

^1H and ^{13}C NMR spectra were obtained using a Varian 400 MHz spectrometer with $CDCl_3$ solvent or tetramethylsilane used as the internal reference. Heteronuclear Single-quantum Coherence (HSQC) NMR spectra were acquired as prescribed[1,2] at the DOE Great Lakes Bioenergy Research Center (University of Wisconsin, Madison, WI, USA) on a Bruker Biospin (Billerica, MA) Avance 700 MHz spectrometer equipped with a 5-mm quadruple-resonance $^1H/^{31}P/^{13}C/^{15}N$ QCI gradient cryoprobe with inverse geometry (proton coils closest to the sample). Lignin samples were placed directly in NMR tubes (□15-30 mg for each sample) and dissolved using DMSO-d6/pyridine-d5 (4:1). The central DMSO solvent peak was used as an internal reference (δ_C 39.5 ppm, δ_H 2.5 ppm). The $^1H–^{13}C$ correlation experiment was an adiabatic HSQC experiment (Bruker standard pulse sequence 'hsqcetgpsisp2.2'; phase-sensitive gradient-edited-2D HSQC using adiabatic pulses for inversion and refocusing).[3] Experiments were carried out using the following parameters: acquired from 11.5 to -0.5 ppm in F2 (1H) with 3366 data points (acquisition time 200 ms), 215 to -5 ppm in F1 (13C) with 620 increments (F1 acquisition time 8 ms) of 32 scans with a 1 s interscan delay; the d24 delay was set to 0.86 ms (1/8J, J = 145 Hz). The total acquisition time for a sample was 6 h. In all cases, processing used typical matched Gaussian apodization (GB = 0.001, LB = -0.1) in F2 and squared cosine-bell and one level of linear prediction (32 coefficients) in F2. Volume integration of contours in HSQC plots used Bruker's TopSpin 3.5pl5 (Mac version) software.

Flash chromatography purification of lignin model compounds was carried out using SiliaFlash® P60 (Silicycle, particle size 40-63 μm, 230-400 mesh), employing a gravity eluted column equipped with a PTFE stopcock and a coarse (40-60 μm) glass fritted disc.

Gas chromatography-mass spectrometry (GC-MS) was performed using an Agilent 7890 GC with a tandem Agilent 5975C MS detector. The column used in the GC was a DB-1701 (60 m × 0.25 mm × 0.25 μm or 15 m × 0.25 mm × 0.25 μm as appropriate). Helium was used as carrier gas with the flow rate set to 1 mL/min for the 60 m column and 0.5 mL/min for the 15 m column. The inlet temperature for the 60 m column was maintained at 300 °C, with a method set to 45 °C for 3 min, ramp to 280 °C at 4 °C/min, and hold for 10 min. The inlet temperature for the 15 m column was maintained at 280 °C with a temperature ramp of 60 °C to 80 °C at 2 °C/min, then to 110 °C at 3 °C/min, followed by a 20 °C/min ramp to 190 °C, and finally at 2 °C/min reaching 230 °C. All analyses were quantified using a single point GC-MS internal standard method by obtaining internal response factors of all starting materials and products using *n*-dodecane as standard. All aliquots of β-O-4 lignin model dimers, lignin monomers, lignin oxidation products, and respective calibration samples were derivatized using BSTFA prior to GC-MS analysis.

Brunauer-Emmett-Teller (BET) surface area and pore volume measurements were conducted *via* nitrogen physisorption at −196 °C using a Micromeritics Tri-Star 3000 system. Catalyst samples were outgassed overnight at 160 °C under vacuum prior to measurements.

Pulsed CO_2 chemisorption was performed on a Micromeritics AutoChem II analyzer using 120 mg of sample. The catalyst sample was first dried at 120 °C under argon for 4 h and was then cooled to 50 °C under flowing Ar. The sample was then pulsed with CO_2 (100%) at 50 °C until saturated as indicated by a thermal conductivity detector (TCD). CO_2 was assumed to titrate base sites on a 1:1 molar ratio.

Elemental compositions were determined at the European Bioenergy Research Institute (EBRI) (Aston University, Birmingham, UK) by inductively coupled plasma optical emission spectroscopy (ICP-OES, Thermo Scientific iCAP 7200 analyzer) after digestion of the samples in 1 mL HNO_3 (Romil SPA grade 70%), 3 mL HCl (Romil SPA grade 37%) and 1 mL deionized water followed by aqueous dilution.

Powder X-ray diffraction (XRD) measurements were performed on a Phillips X'Pert diffractomer using Cu Kα radiation (λ=1.5406 Å) and a step size of 0.02º.

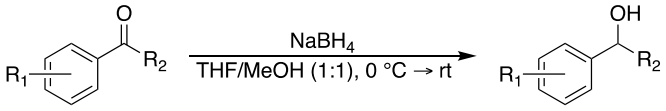
Transmission Electron Microscopy (TEM) studies were conducted at the University of Birmingham (Birmingham, UK) using a field emission JEOL 2010F operated at 200 kV equipped with a URP pole piece, GATAN 200 GIF, GATAN DigiScan II, Fischione HAADF STEM detector, Oxford energy-dispersive X-ray detector and EmiSpec EsVision software. Samples were dispersed in methanol and deposited on 300-mesh carbon-supported copper grids purchased from Electron Microscopy Science and dried under ambient conditions. Particle sizes were analyzed using ImageJ (version 1.51m9) for Mac OS X bundled with Java applet (version 1.8.0_101).

X-ray photoelectron spectroscopy was also performed at EBRI on a Kratos AXIS HSi spectrometer equipped with a charge neutralizer and non-monochromated Mg K_a excitation source (1253.6 eV), with energies referenced to adventitious carbon at 284.6 eV. Note that while the assumption that the binding energy of adventitious carbon is a constant across all materials has been debunked,[4,5] it does provide a common reference for calibrating binding energies within a family of electronically similar materials, as in the present work for our series of non-metallic oxides. High resolution spectra were acquired with a pass energy of 40 eV. Spectral fitting was performed using CasaXPS version 2.3.14, utilizing a common Gaussian-Lorentzian line shape and FWHM for each element, and the relevant instrument response factors for quantification.

Gel permeation chromatography (GPC) was carried out on an Agilent 1260 Infinity Quaternary LC system equipped with a G1311A Quaternary pump, G1329B Autosampler, G1364C Fraction Collector, G1316A Column Compartment, G1315C Diode-Array Detector (DAD), and a Corona® CAD detector (ESA Magellan Biosciences). Samples were analyzed using SUPREMA analytical linear S 10μm (50 x 8 mm) and SUPREMA analytical linear S 10μm (300 x 8 mm) GPC columns (Polymer Standards Services) connected in series, and eluted using inhibitor free THF/DMSO (v/v=1:1, 0.4 mL/min) with a column oven temperature of 25 °C.

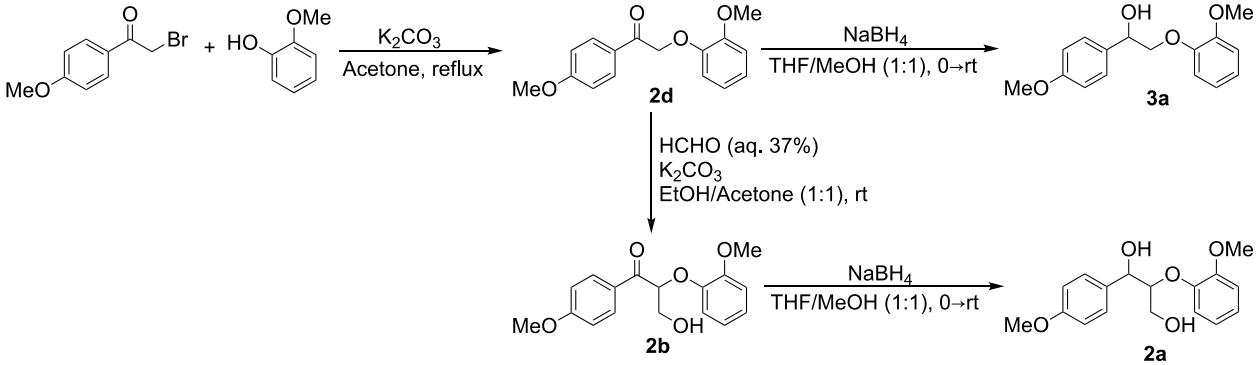
Synthesis of Lignin Model Compounds

General synthetic procedure for simple alcohols



Compounds **4a**, **6a**, **7a**, **8a**, **9a**, **10a**, and **11a** were prepared *via* reduction of the corresponding ketones. The appropriate ketone (0.2 mmol) was dissolved in THF:MeOH (v/v=1:1, 15 mL), and sodium borohydride (0.35 mmol) was added in portions to the reaction mixture under stirring at 0 °C. The mixture was left stirring overnight at room temperature. The reaction mixture was concentrated *in vacuo* and diluted with deionized water (20 mL). The mixture was extracted with dichloromethane (2×15 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Resulting products were analyzed by means of GC-MS. Yields were in all cases ≥ 95%.

Synthesis of β-O-4 linkage lignin model compounds



Synthesis of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)-ethanone (2d)

Compound **2d** was prepared from guaiacol and 4'-methoxy-2-bromoacetophenone according to a literature procedure.[6] 2-Bromo-4'-methoxyacetophenone (22 g, 0.11 mol) was added to a stirred solution of K_2CO_3 (20 g, 0.14 mol) and guaiacol (16 g, 0.13 mol) in acetone (100 mL). The reaction mixture was stirred at reflux temperature overnight. The reaction mixture was then filtered, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The crude product was recrystallized from EtOAc/hexanes giving **2d**. Yield: 28.5 g (96%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-8.01 (dd, *J*= 8.8, 1.4 Hz, 2H), 6.97-6.84 (m, 6H), 5.29 (s, 2H), 3.89 (s, 3H), 3.88 (s, 3H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 193.1, 163.9, 155.8, 149.7, 147.6, 130.5, 127.7, 122.3, 120.8, 114.7, 113.9, 112.1, 71.9, 55.9, 55.5.

Synthesis of 4-methoxy-α-[(2-methoxyphenoxy)methyl]-benzenemethanol (3a)

Compound **2d** (5 g, 18 mmol) was dissolved in THF:MeOH (v/v=2:1, 50 mL), and sodium borohydride (1.5 g, 39 mmol) was added in portions to the reaction mixture under stirring at 0 °C. The mixture was left to stir overnight at room temperature. The mixture was then concentrated *in vacuo*, diluted with 50 mL deionized water, and extracted with dichloromethane (3×30 mL). The combined organic extracts were dried over

anhydrous $MgSO_4$ and concentrated *in vacuo*. The crude product was recrystallized from ethanol to afford the pure alcohol **3a**. Yield: 4.7 g (93%).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.38-7.36 (dd, *J*= 8.7, 1.4 Hz, 2H), 6.93-6.81 (m, 6H), 5.05-5.03 (dd, *J*= 9.3, 2.5 Hz, 1H), 4.04-4.01 (dd, *J*= 7.1, 2.9 Hz, 1H), 3.97-3.92 (t, *J*= 9.8 Hz, 2H), 3.82 (s, 3H), 3.77 (s, 3H).

^{13}C NMR (400 MHz, $CDCl_3$) δ162.9, 159.4, 150.1, 148.0, 132.0, 131.7, 127.6, 122.4, 121.1, 115.9, 113.9, 112.0, 71.9, 55.8, 55.3.

Synthesis of 3-hydroxy-2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)-1-propanone (2b)

Compound **2b** was prepared according to a literature procedure.[7] To a stirred suspension of K_2CO_3 (2.8 g, 20 mmol) and previously synthesized compound **2d** (5 g, 18 mmol) in a 1:1 mixture of ethanol/acetone (100 mL) solution, aqueous formaldehyde solution (37 wt.%) (0.82 mL, 11 mmol) was added. The mixture was stirred overnight and concentrated *in vacuo* to give a yellow oil. The crude product was subjected to column chromatography on silica gel (DCM:ethyl acetate, v/v=6:1) to give a yellow-colored oil, which was crystallized from ethanol to give a pale yellow solid. Yield: 4.5 g (81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ8.08-8.05 (dd, *J*= 9.4, 2.0 Hz, 2H), 6.97-6.80 (m, 6H), 5.39-5.37 (t, *J*= 5.2 Hz, 1H), 4.06 -4.05 (d, *J*= 5.4 Hz, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 3.17 (s, 1H).

^{13}C NMR (400 MHz, $CDCl_3$) δ199.9, 188.9, 162.9, 131.2, 127.9, 123.4, 121.2, 118.1, 113.9, 112.3, 84.5, 63.6, 55.8, 55.5.

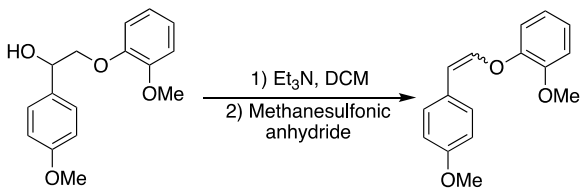
Synthesis of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)-1,3-propanediol (2a)

Compound **2b** (1.5 g, 5 mmol) was dissolved in THF:MeOH (v/v=2:1, 30 mL), and sodium borohydride (0.4 g, 10 mmol) was added in portions to the reaction mixture under stirring at 0 °C. The mixture was left to stir overnight at room temperature. The reaction mixture was concentrated *in vacuo* and diluted with 20 mL deionized water. The mixture was extracted with dichloromethane (3×15 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The crude product was subjected to column chromatography on silica gel (DCM:ethyl acetate, v/v=4:1) to give a yellow oil. Yield: 1.35 g (90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.36-7.24 (ddd, *J*= 13.5, 8.5, 1.7 Hz, 2H), 7.11-7.01 (m, 2H), 6.91-6.86 (m, 4H), 4.97 (s, 1H), 4.13 -4.01 (m, 1H), 3.88 (s, 3H), 3.77 (s, 3H), 3.5 (m, 1H).

^{13}C NMR (400 MHz, $CDCl_3$) δ162.9, 151.7, 147.8, 147.1, 128.5, 127.5, 124.5, 121.8, 121.1, 114.1, 113.9, 112.3, 87.5, 72.6, 60.8, 56.0, 55.4.

Synthesis of [2-(2-methoxyphenoxy)-ethenyl]-4-methoxybenzene (3b)



3a **3b**

A DCM (50 mL) solution of compound **3a** (3.0 g, 0.011 mol) and Et_3N (6.2 mL, 0.048 mol) was stirred at room temperature for 10 minutes. The reaction mixture was cooled to 0 °C prior to the addition of

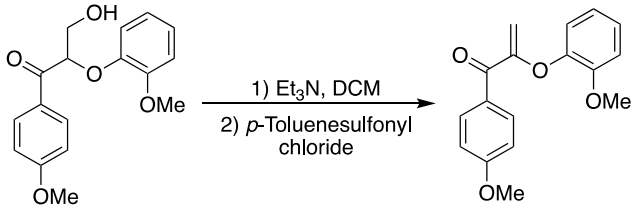
methanesulfonic anhydride (4.0 g, 0.023 mol). The reaction mixture was stirred overnight and diluted with additional DCM (30 mL) followed by washing with deionized water (2×50 mL). The organic layer was washed sequentially with 1 M HCl (2×20 mL) and saturated NaCl solution (20 mL), dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The crude product was purified *via* column chromatography (hexane:ethyl acetate, v/v= 5:1) giving a yellow oil. Yield: 0.8 g (28%).

^{1}H NMR (400MHz, $CDCl_3$) δ7.68-7.66 (dd, *J*= 8.7, 2.0 Hz, 2H), 7.25-7.05 (m, 3H), 6.98-6.92 (m, 2H), 6.88-6.86 (dd, *J*= 8.8, 1.8 Hz, 1H), 6.47-6.45 (d, *J*= 6.80 Hz, 1H), 5.56-5.54 (d, *J*= 6.80 Hz, 1H), 3.89 (s, 3H), 3.80 (s, 3H).

^{13}C NMR (400 MHz, $CDCl_3$) δ162.9, 158.2, 150.2, 146.8, 142.9, 141.3, 129.9, 127.9, 126.8, 123.9, 120.9, 117.7, 113.7, 112.8, 109.6, 56.2, 55.2.

HRMS (**EI**) calculated for $C_{16}H_{17}O_3$ $[M + H]^+$ 257.3030, found 257.1172.

Synthesis of 1-(4-methoxyphenyl)-2-(2-methoxyphenoxy)-2-propen-1-one (2c)



2b **2c**

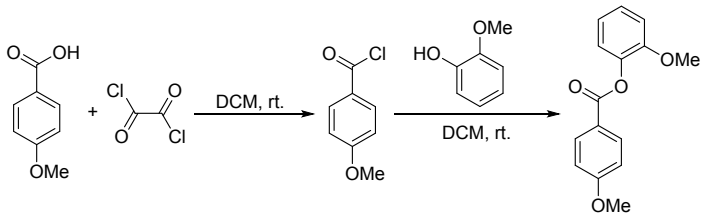
Compound **2c** was prepared according to the literature.[8] A DCM (30 mL) solution of previously synthesized compound **2b** (1.5 g, 5 mmol) and Et_3N (2.0 mL, 14 mmol) was stirred at 30 °C for 10 minutes prior to the addition of *p*-toluenesulfonyl chloride (1.43 g, 7.5 mmol). The mixture was stirred overnight, diluted with additional DCM (20 mL), washed with deionized water (2×20 mL), dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The crude product was purified *via* column chromatography (DCM:ethyl acetate, v/v= 1:1) giving a yellow oil. Yield: 0.89 g (78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ8.31-8.29 (dd, *J*= 8.5, 2.7 Hz, 2H), 8.11-8.03 (m 2H), 7.96-7.93 (dd, 8.2, 2.2 Hz, 1H), 7.56-7.54 (dd, *J*= 8.3, 2.2 Hz, 2H), 6.96-6.87(m, 2H), 5.19-5.18 (d, *J*= 2.20 Hz, 1H), 4.72-4.71 (d, *J*= 2.13 Hz, 1H), 3.90 (s, 3H), 3.85 (s, 3H).

^{13}C NMR (400 MHz, $CDCl_3$) δ169.3, 163.1, 162.6, 151.3, 151.1, 142.9, 132.9, 132.4, 122.3, 113.7, 113.2, 112.2, 101.8, 55.5, 55.1.

HRMS (EI) calculated for $C_{17}H_{17}O_6$ $[M + H]^+$ 285.1162, found 285.1122.

Synthesis of (2-methoxyphenyl)-4-methoxybenzoate (2g)



2g

p-Anisic acid (4.9 g, 0.032 mol) was slowly added to a stirred solution of oxalyl chloride (4.35 g, 0.035 mol) in DCM (100 mL). The reaction mixture was left stirring overnight at room temperature. The mixture was concentrated *in vacuo* to give a pale yellow colored oil. DCM (50 mL) was added to redissolve the mixture to which guaiacol (4.003 g, mmol) was added. The solution was left stirring for 4 h at room temperature. The reaction mixture was washed with deionized water (2×20 mL) and the organic extract was dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give a clear colored oil. The crude product was recrystallized from ethanol giving a white crystalline solid. Yield: 7.45 g (90%). Spectral data are consistent with those reported in the literature.[9]

^{1}H NMR (400 MHz, $CDCl_3$) δ8.2-8.16 (dd, *J*= 8.8, 1.8 Hz, 2H), 7.25-7.20 (t, *J*= 6.5 Hz, 1H), 7.15-7.13 (dd, *J*= 6.6, 1.6 Hz, 1H), 7.02-6.96 (m, 4H), 3.88 (s, 1H), 3.81 (s, 1H).

^{13}C NMR (400 MHz, $CDCl_3$) δ164.5, 163.8, 163.0, 151.5, 140.1, 132.4, 132.1, 126.8, 123.1, 121.8, 120.8, 113.8, 112.5, 55.9, 55.5.

Catalyst Preparation

Synthesis of layered double hydroxides (LDHs)

Li-Al (1:2) LDH was prepared according to a literature protocol.[10] An aqueous solution of $Al_2(CO_3)_3$ (400 mL, 0.5 M) was added dropwise to an aqueous solution of $LiOH{\cdot}H_2O$ (50 mL, 4.8 M) at room temperature. The addition was continued until the mixture attained a pH of 10 while maintaining vigorous stirring using an overhead stirrer. The mixture was left to age under continuous stirring at 75 °C overnight. A series of centrifuging/decanting/washing steps was applied to the resulting slurry until the washings attained a pH of 7. The solid was then dried at 60 °C in a vacuum oven for 24 h.

Mg-Al (3:1) LDH[11] and Ni-Al (2:1) LDH[12] were also synthesized according to published protocols.

Synthesis of Li-Al LDH supported Au nanoparticles

The synthesis of Li-Al LDH-supported Au nanoparticle catalysts was adapted from a literature method.[13] Li-Al LDH (3 g) was added to aqueous $HAuCl_4$ (150 mL, 2×10^{-3} M). After stirring the mixture for 2 min, aqueous NH_3 (10 wt.%, 2.9 M) was added dropwise until the slurry reached a pH of 9. The mixture was stirred at room temperature for 12 h after which the resulting slurry was filtered, washed, and dried *in vacuo* at 30 °C. The resulting solid was chemically reduced in a stirred solution of KBH_4 (0.2 mol, 1.0 g) in THF:methanol (v/v=1:1, 10 mL) at room temperature for 1 h. A series of centrifuging/decanting/washing steps was applied to the resulting slurry using deionized water until the pH of the washings was 7. The solid was dried at 40 °C in a vacuum oven for 24 h to produce Li-Al LDH-supported Au^0 NPs as a purple solid.

Catalyst Characterization

Table S1. Physical data for Au/Li-Al LDH catalyst and support

	ICP [wt.%]			Li:Al Molar Ratio	BET Surface Area [$m^2 g^{-1}$]	Pore volume [$cm^3 g^{-1}$]
	Li	Al	Au			
Li-Al LDH	4.4	37.33	-	1: 2.20	84	0.43
Au/Li-Al LDH	4.53	34.79	0.85	1: 1.99	86	0.45

Fig. S1. High resolution X-ray photoelectron spectra of Li-Al LDH and associated fitted chemical states

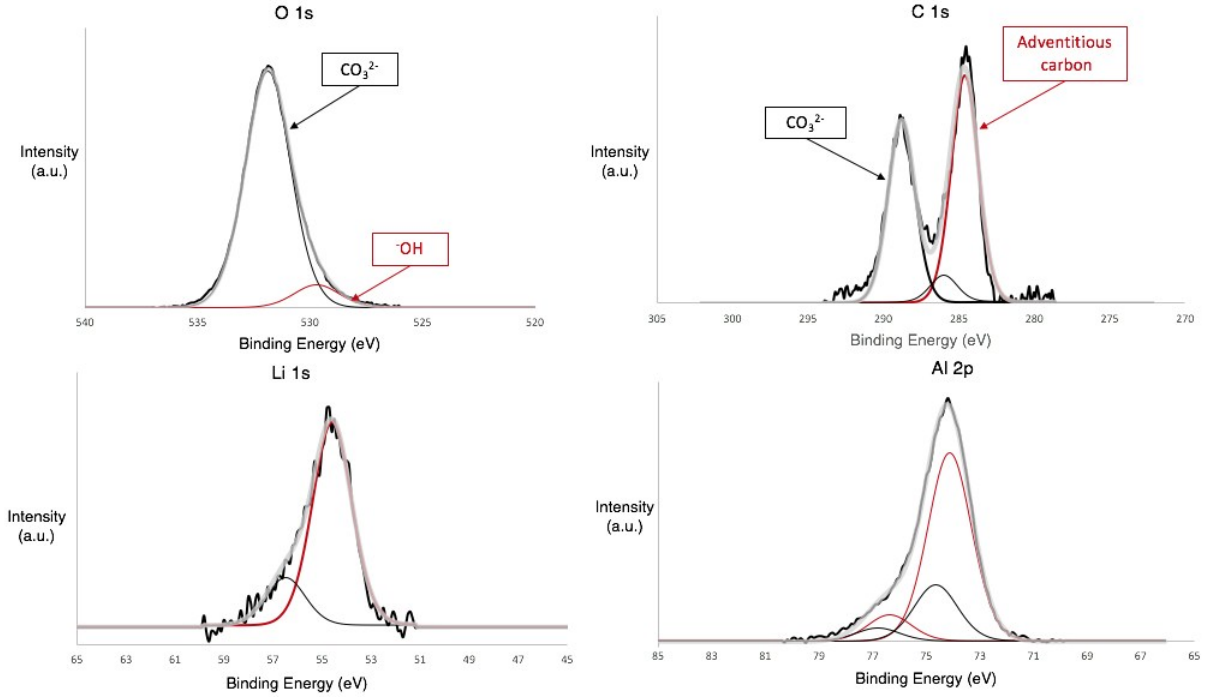


Fig. S2. High resolution XP spectra of (a) Au/γ-Alumina, (b) Au/Mg-Al LDH, (c) Au/Ni-Al LDH, (d) Au/Li-Al LDH. Labeled peaks represent the Au 4f $_{7/2}$ region.

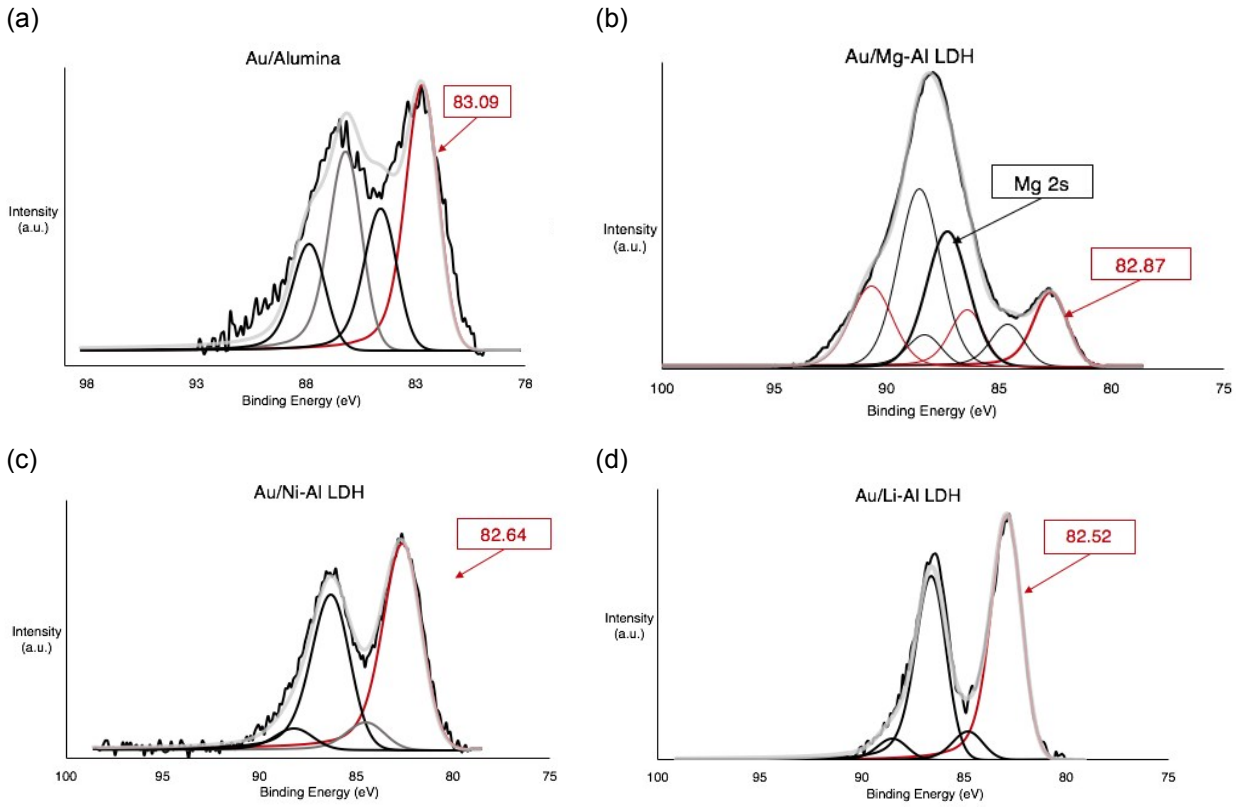
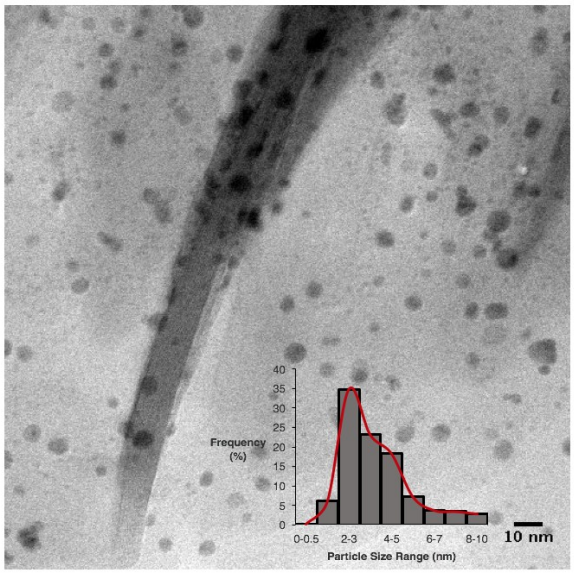


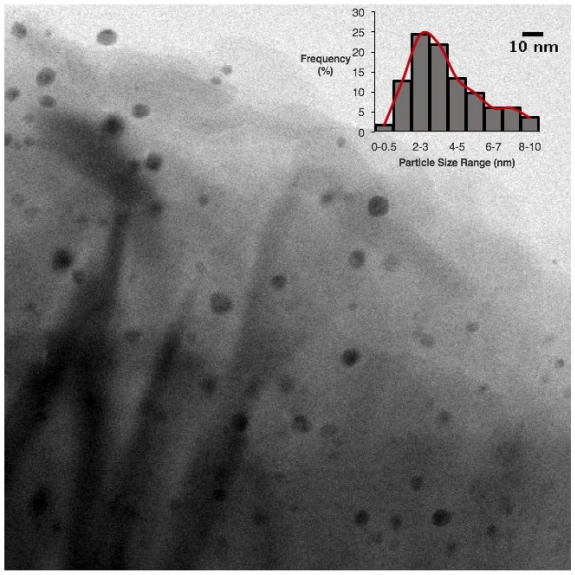
Fig. S3. TEM images of Au/Li-Al LDH catalyst showing nanosheets and Au nanoparticle size range (a), (b); near-parallel lattice planes of Li-Al LDH and Au nanoparticle, indicating epitaxial

growth of Au nanoparticle (c).

(a)



(b)



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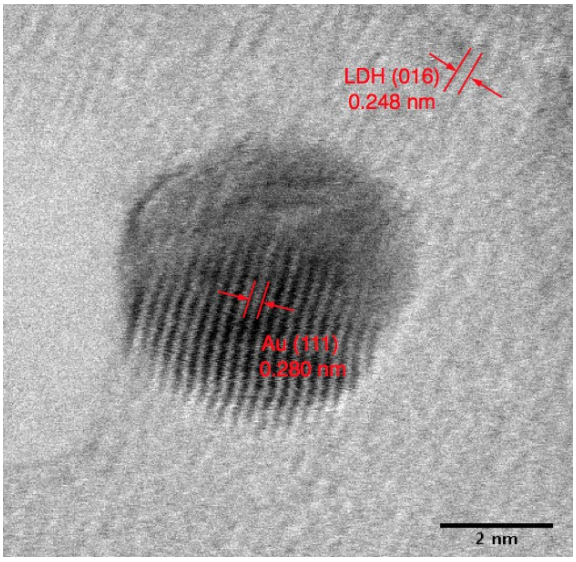


Fig. S4. X-ray diffractogram of Au/Li-Al LDH catalyst

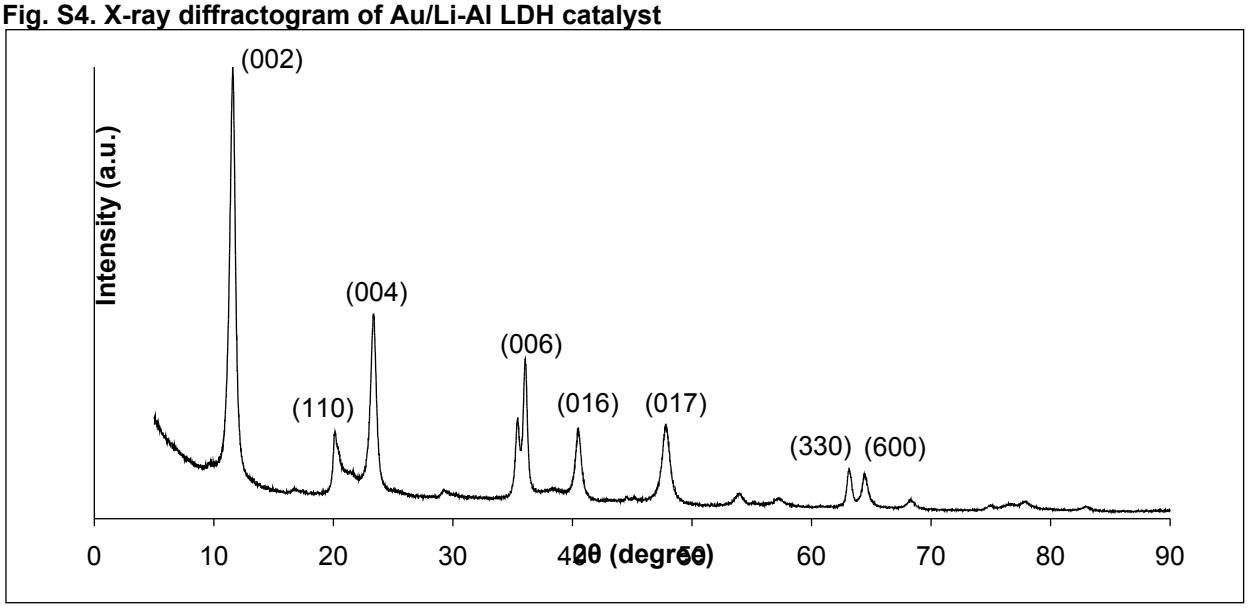
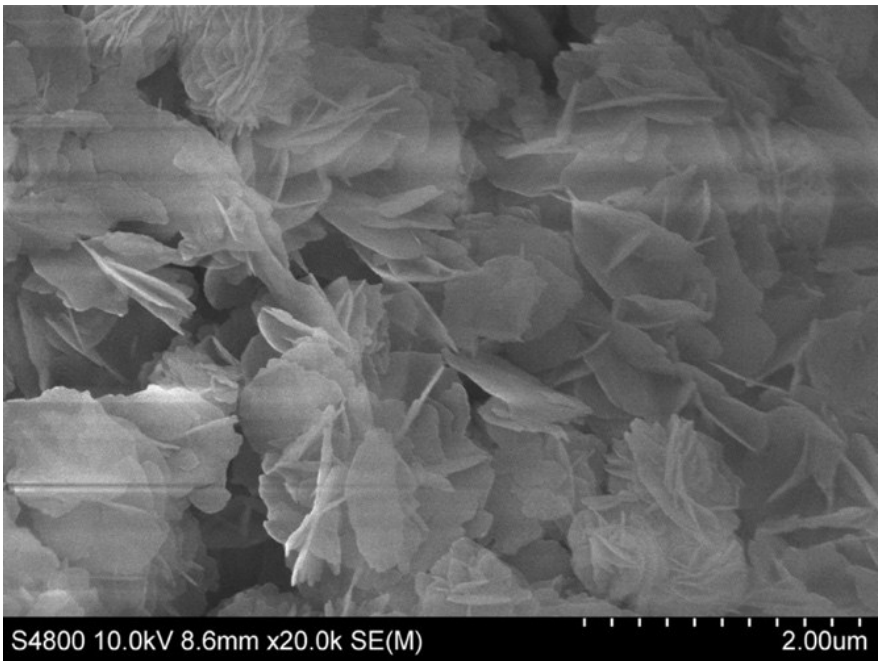


Fig. S5. Scanning electron micrograph of parent Li-Al LDH showing characteristic sand rose morphology

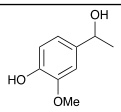
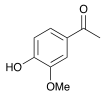
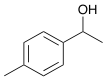
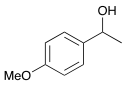
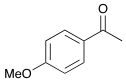
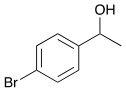
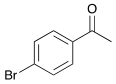
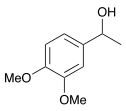
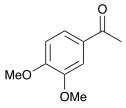
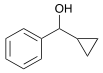
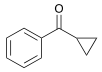
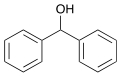
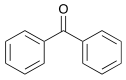
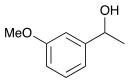
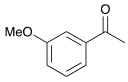


Catalytic Aerobic Oxidation of Lignin Model Compounds

General procedure for aerobic oxidation of simple alcohols

Oxidation of alcohols (**1**-**11**) was conducted in a 25 mL 3-neck round-bottom flask, employing alcohol (1 mmol), Au/Li-Al LDH (50 mg), and dodecane (1 mmol) in 10 mL of diphenyl ether under flowing O_2 (10 mL• min^{-1}) at appropriate temperatures and 500 rpm stirring (sufficient to eliminate mass transport effects).

Table S2. Aerobic oxidation of simple benzylic alcohols using Au/Li-Al LDH

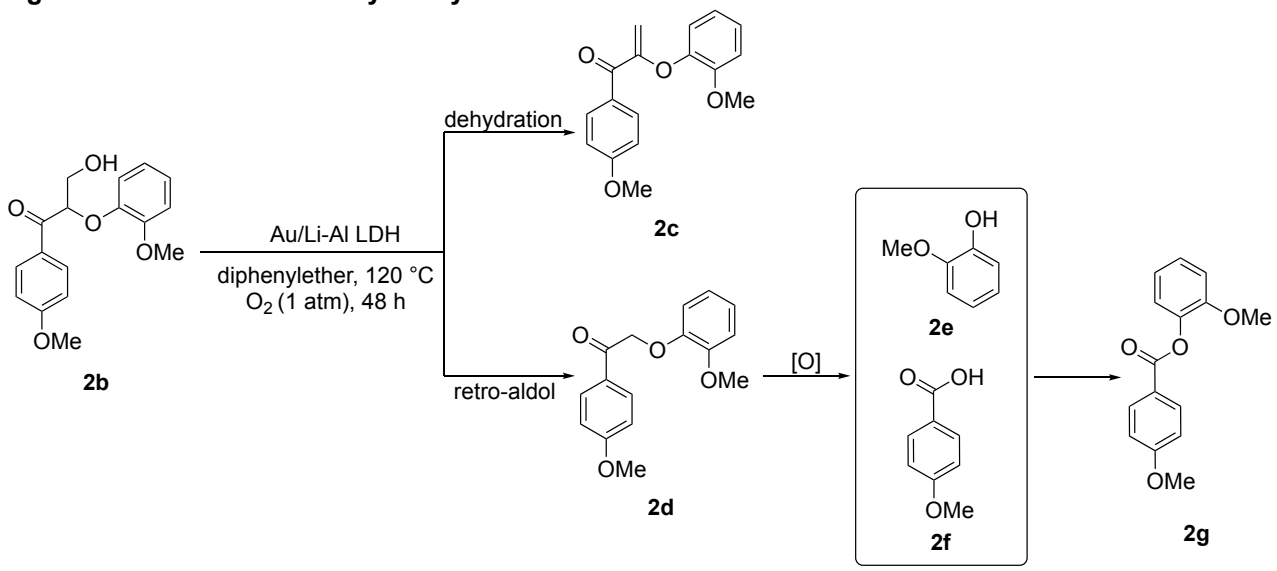
Entry	Substrate	*T* (°C)	t [h]	Conversion [%]	Product	Selectivity [%]
1		80	4	80		78
2		80	2	98		98
3		80	0.5	> 99		> 99
4		80	2	67		> 99
5		80	4	80		> 99
6		100	2	> 99		> 99
7		80	0.5	> 99		> 99
8		80	4	> 99		> 99
9		80	2	72		> 99
10		80	4	50		50
11		80	2	99		> 99

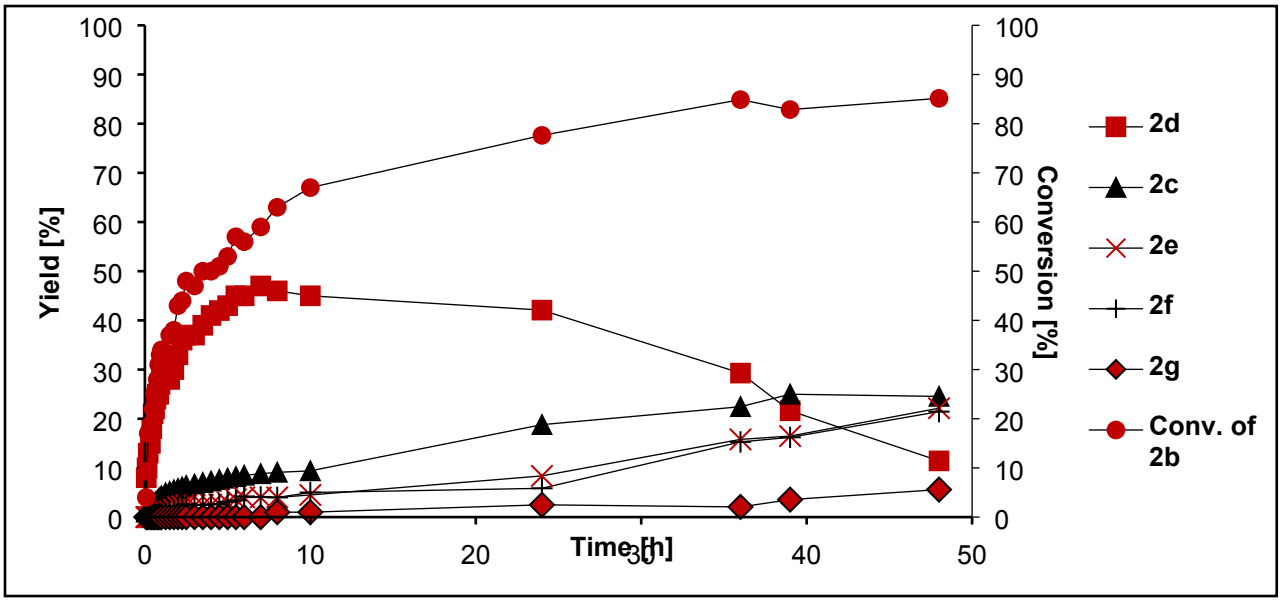
General procedure for aerobic oxidation of lignin model compounds

Oxidation of lignin model compounds (**2a**-**2d**, **3a**, and **3b**) was conducted in a 100 mL 3-neck round-bottom flask using a Radleys Starfish reactor, employing the substrate (1 mmol), Au/Li-Al LDH (100 mg), and dodecane (1 mmol) in 10 mL of diphenylether under flowing O_2 (10 mL• min^{-1}) at 120 °C and 500 rpm stirring. Aliquots were taken periodically and analyzed by means of GC-MS using dodecane as internal standard.

Results for aerobic oxidation of lignin model dimers

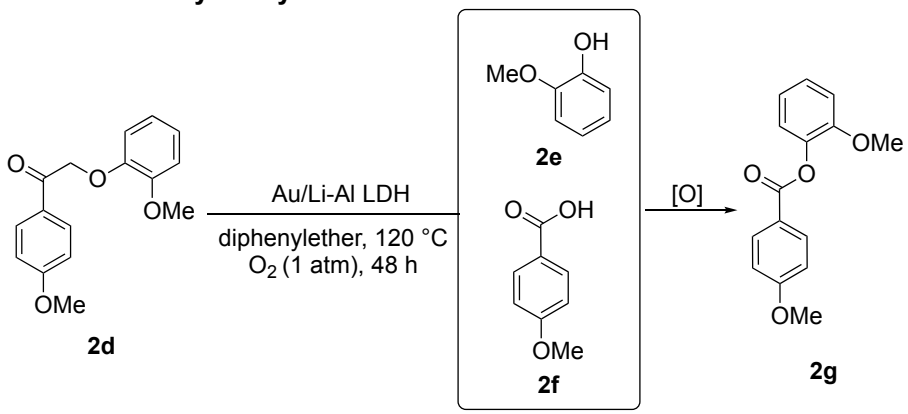
Fig. S6. Oxidation of 2b catalyzed by Au/Li-Al LDH

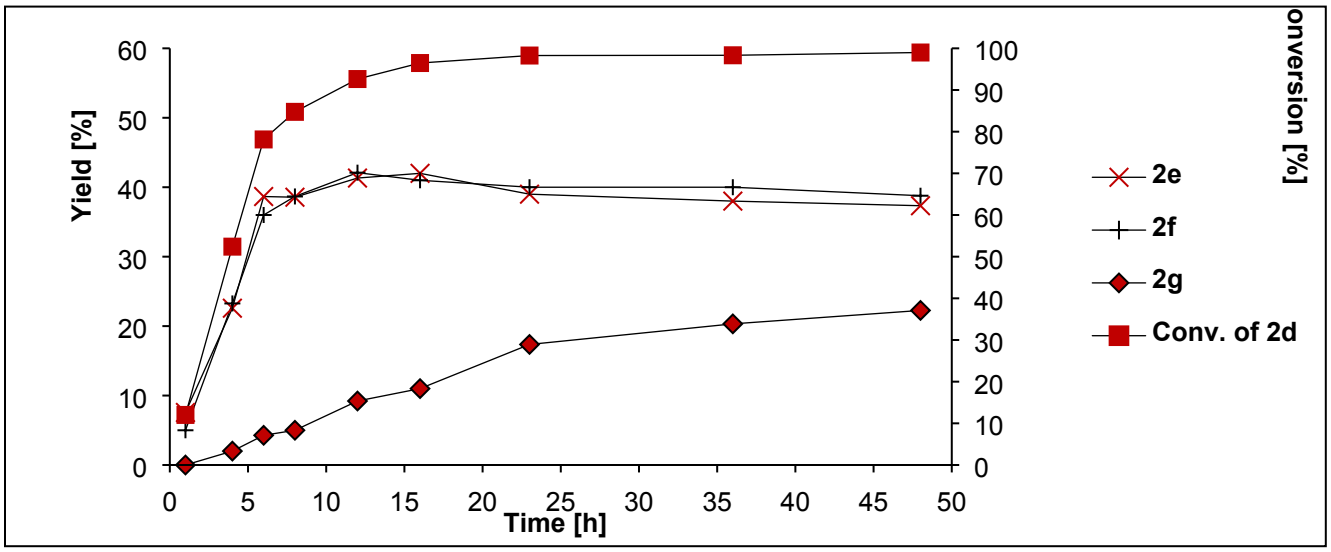




Substrate	Conversion [%]	t [h]	Product	Selectivity [%]	Yield [%]
			2c	13	11
			2d	30	25
2b	85	48	**2e**	25	21
			2f	26	22
			2g	7	6

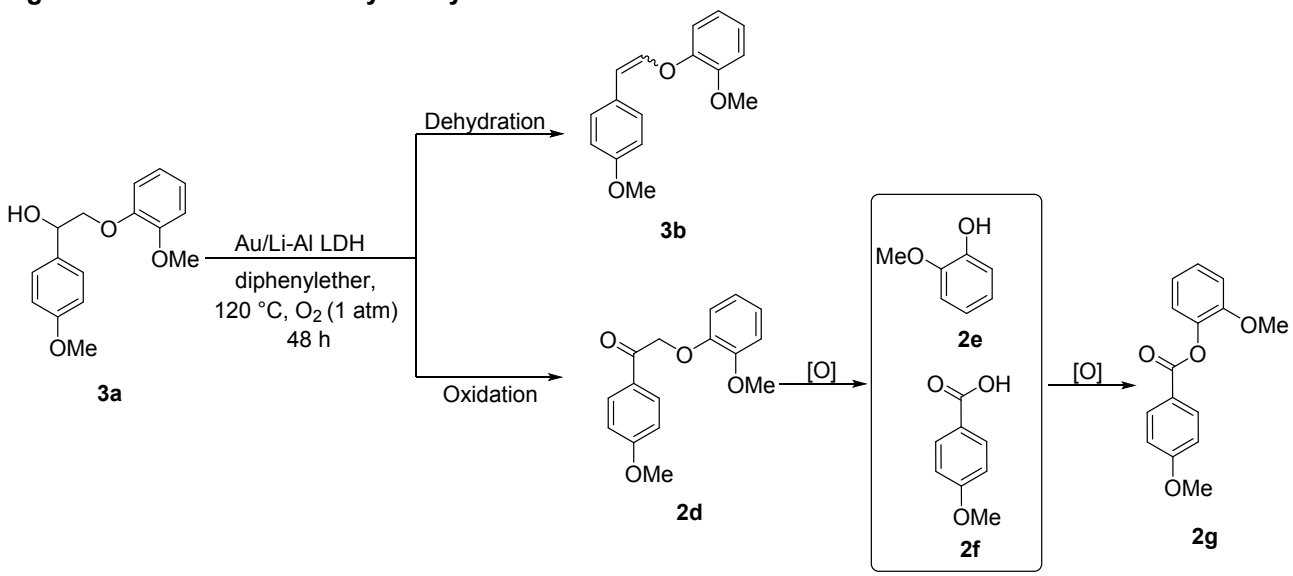
Fig. S7. Oxidation of 2d catalyzed by Au/Li-Al LDH

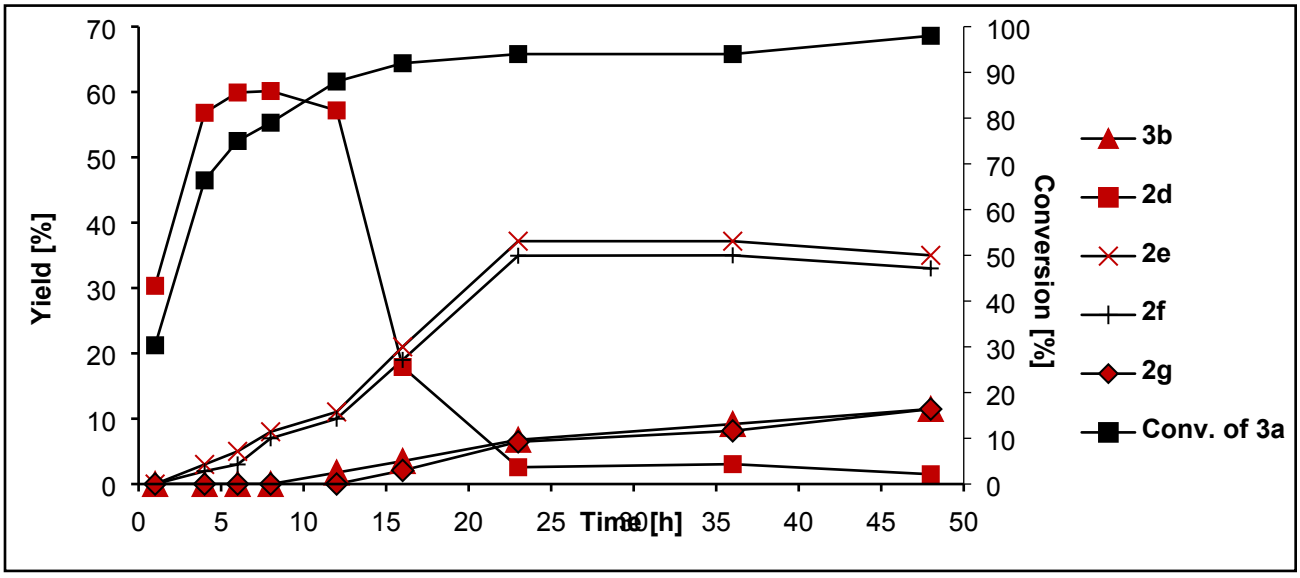




Substrate	Conversion [%]	t [h]	Product	Selectivity [%]	Yield [%]
			2e	39	39
2d	99	48	**2f**	37	37
			2g	22	22

Fig. S8. Oxidation of 3a catalyzed by Au/Li-Al LDH





Substrate	Conversion [%]	t [h]	Product	Selectivity [%]	Yield [%]
3a	96	48	**3b**	11	11
			2d	1	1
			2e	38	36
			2f	35	34
			2g	11	11

Procedure and results for Au/Li-Al LDH reusability study

Catalyst reusability tests were conducted using model compound **3a,** employing conditions previously described. After appropriate reaction times, Au/Li-Al LDH was recovered from the reaction mixture *via* filtration using a PTFE membrane (0.2 μm). The recovered catalyst was washed with excess THF and dried *in vacuo* for 24 h prior to reuse. Before performing the fourth recycle experiment for 16 h (**Table S4**), the filtered catalyst was stirred in deionized H_2O for 1 h, filtered *via* centrifugation, washed with excess THF: pentane (v/v = 1:1) and dried *in vacuo* for 4 h.

Table S3. Catalyst reusability study using model compound 3a after 4 h

Substrate		Conversion [%]	Product	Selectivity [%]	Yield [%]
3a	First Run	58	3b	0	0
			2d	92	53
			2e	5	3
			2f	2	1
			2g	0	0
	Second Run	60	3b	0	0
			2d	92	55
			2e	3	2
			2f	3	2
			2g	0	0
	Third Run	57	3b	0	0
			2d	90	54
			2e	2	1
			2f	2	1
			2g	0	0

Table S4. Catalyst reusability study using model compound 3a after 16 h

Substrate		Conversion [%]	Product	Selectivity [%]	Yield [%]
3a	**First Run**	98	**3b**	3	3
			2d	20	20
			2e	32	31
			2f	33	32
			2g	4	4
	Second Run	97	**3b**	4	4
			2d	50	48
			2e	19	18
			2f	20	19
			2g	1	1
	Third Run	95	**3b**	4	4
			2d	79	75
			2e	6	6
			2f	4	4
			2g	0	0
	Fourth Run	97	**3b**	2	2
			2d	53	52
			2e	20	19
			2f	21	20
			2g	2	2

Catalytic Aerobic Oxidation of Indulin AT Kraft Lignin and γ-Valerolactone (GVL) Lignin

General procedure for aerobic oxidation of lignin

The oxidation of lignins was conducted in a 100 mL 3-neck round-bottom flask using a Radleys Starfish reactor, employing lignin sample (500 mg), Au/Li-Al LDH (200 mg), and dimethylformamide (10 mL) under flowing O_2 (10 mL• min^{-1}) at 120 °C and 500 rpm stirring for 24 h. The resulting mixture was filtered and washed with additional dimethylformamide (15 mL) and concentrated *in vacuo*. The samples were further dried in a vacuum oven at 50 °C for 46 h affording dark brown solids. Yield: kraft lignin 415 mg (83%), GVL lignin 453 mg (91%).

Control experiments followed the above procedure excluding the use of Au/Li-Al LDH catalyst.

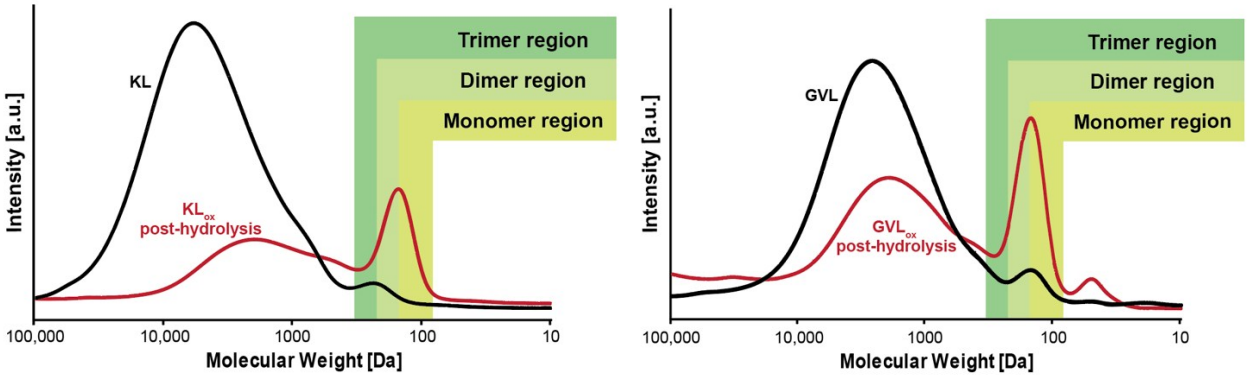
General procedure for hydrolysis of lignin

A mixture consisting of oxidized lignin (50 mg) and 1M NaOH (5 mL) was stirred at room temperature for 30 min. The mixture was then acidified to pH 2 by the addition of 1M HCl and stirred for an additional 30 min. Upon completion, the mixture was extracted with EtOAc (3 x 15 mL). The organic extracts were combined, washed with sat. $NaHCO_3$ followed by brine, dried over $MgSO_4$, and concentrated *in vacuo*. Yield: kraft lignin, 10 mg (20%); GVL lignin, 28 mg (56%).

GPC analysis of KL, GVL, and EtOAc soluble products obtained from KL_{OX} and GVL_{OX} post-hydrolysis

Approximately 2 mg of each sample was acetylated in 2mL of acetic anhydride/pyridine (v/v=1:1) at 40 °C for 4 h. Volatiles were removed *in vacuo* after addition of ethanol followed by toluene, and each addition/distillation procedure was repeated twice. Finally, the samples were dried overnight in a vacuum oven at 30 °C. For GPC analyses, the samples were dissolved in 1 mL THF/DMSO (v/v=1:1) and filtered through a 0.2 µm syringe filter prior to injection.

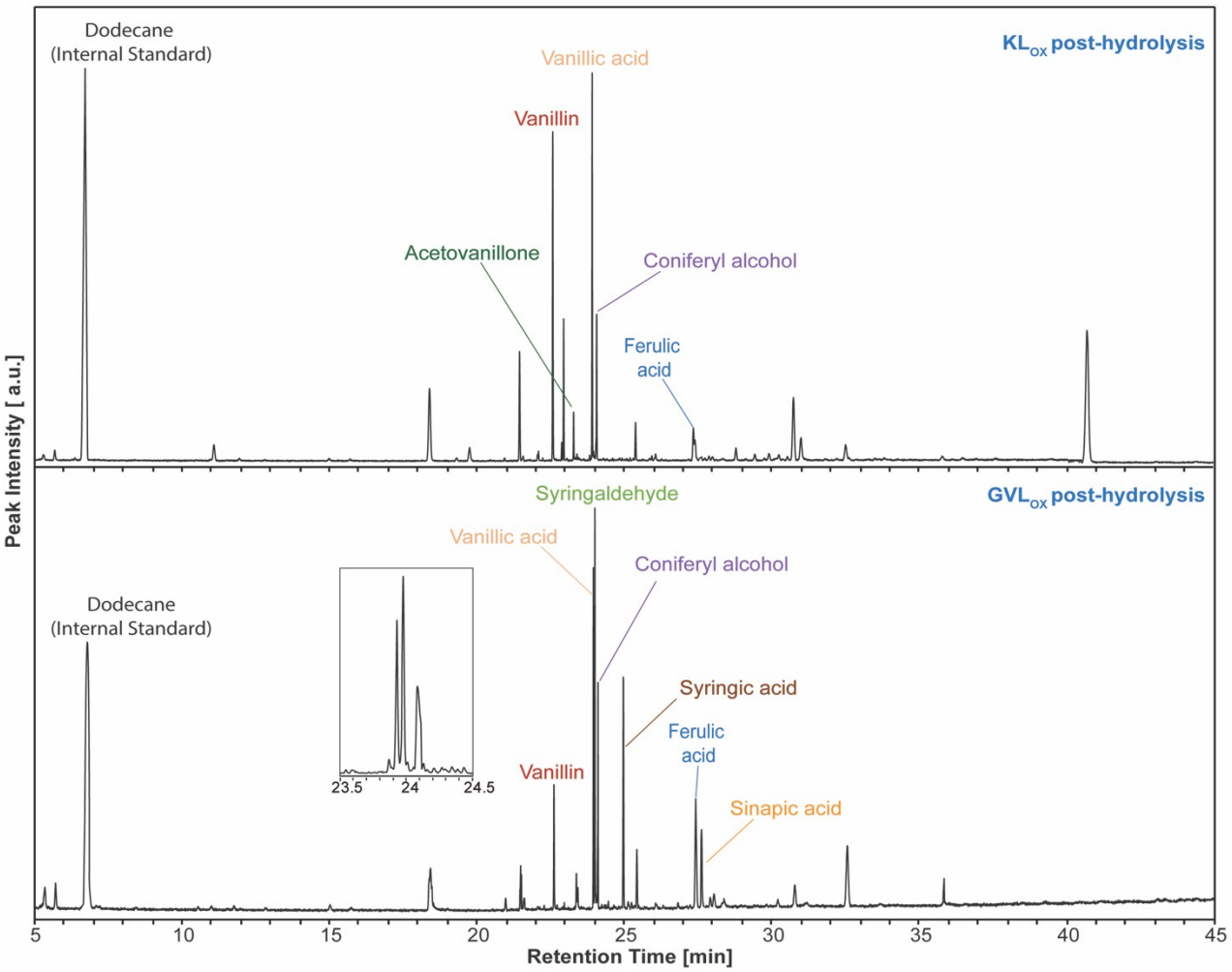
Fig. S9. GP chromatograms of KL and KL_{ox} post-hydrolysis; GVL and GVL_{ox} post-hydrolysis



Complete results of identified EtOAc soluble products obtained from lignin oxidation experiments

			Vanillin	Vanillic acid	Coniferyl alcohol	Ferulic acid	Aceto-vanillone	Syring-aldehyde	Syringic acid	Sinapic acid	Total
Catalyst free	KLox	Pre-hydrolysis		1.5%							1.5%
		Post-hydrolysis	1.2%	0.7%	0.2%	0.2%	0.1%				2.4%
	GVLox	Pre-hydrolysis		1.8%				1.9%			3.7%
		Post-hydrolysis	1.2%	1.8%		2.9%		3.1%	2.1%		11.1%
With Au/ Li-Al LDH	KLox	Pre-hydrolysis		2.3%	1.0%						3.3%
		Post-hydrolysis	3.4%	3.4 %	1.2%	1.1%	0.4%				9.5%
	GVLox	Pre-hydrolysis	0.3%	3.8%	1.1%	2.1%		2.1%			9.4%
		Post-hydrolysis	2.8%	7.8%	2.8%	7.8%		11.2%	5.0%	2.8%	40.2%

GC-MS analysis of EtOAc soluble products obtained from KL_{OX} and GVL_{OX} post-hydrolysis



References

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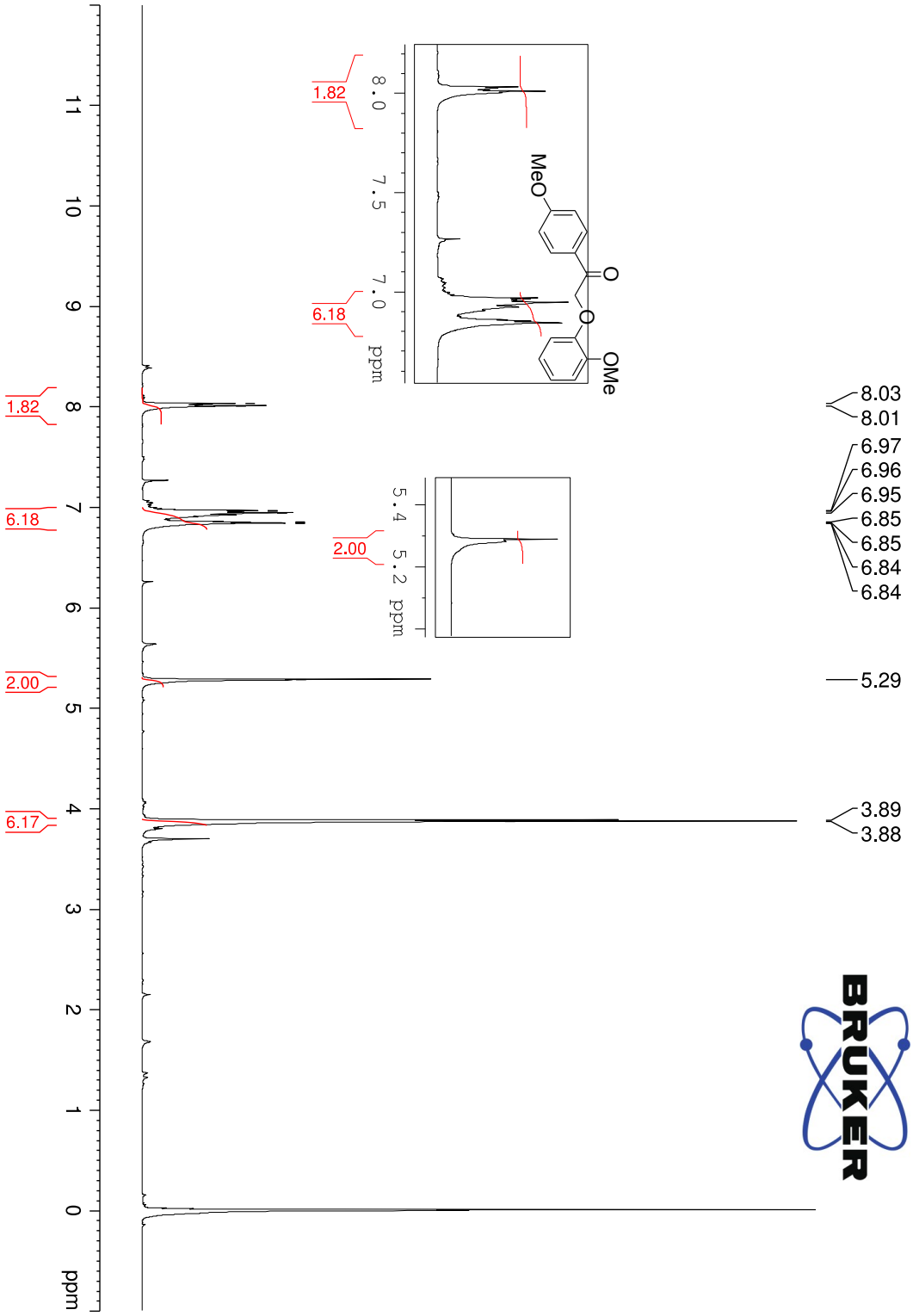
NMR Spectra of Synthesized Lignin Model Compounds

See below.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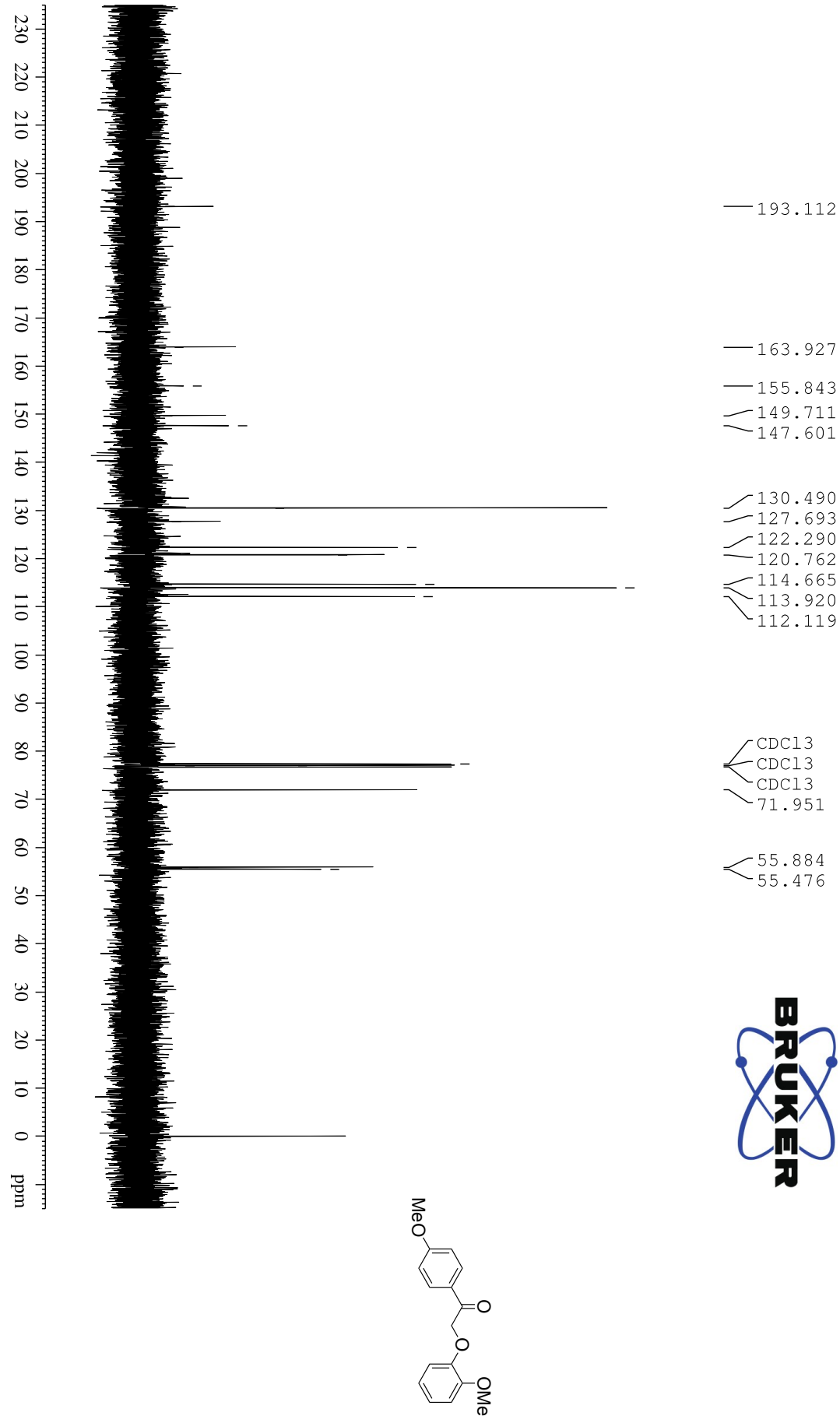
2.00
6.17
ppm
1.82
6.18
MeO
OMe
2.00
8.03
8.01
6.97
6.96
6.95
6.85
6.85
6.84
6.84
5.29
3.89
3.88
BRUKER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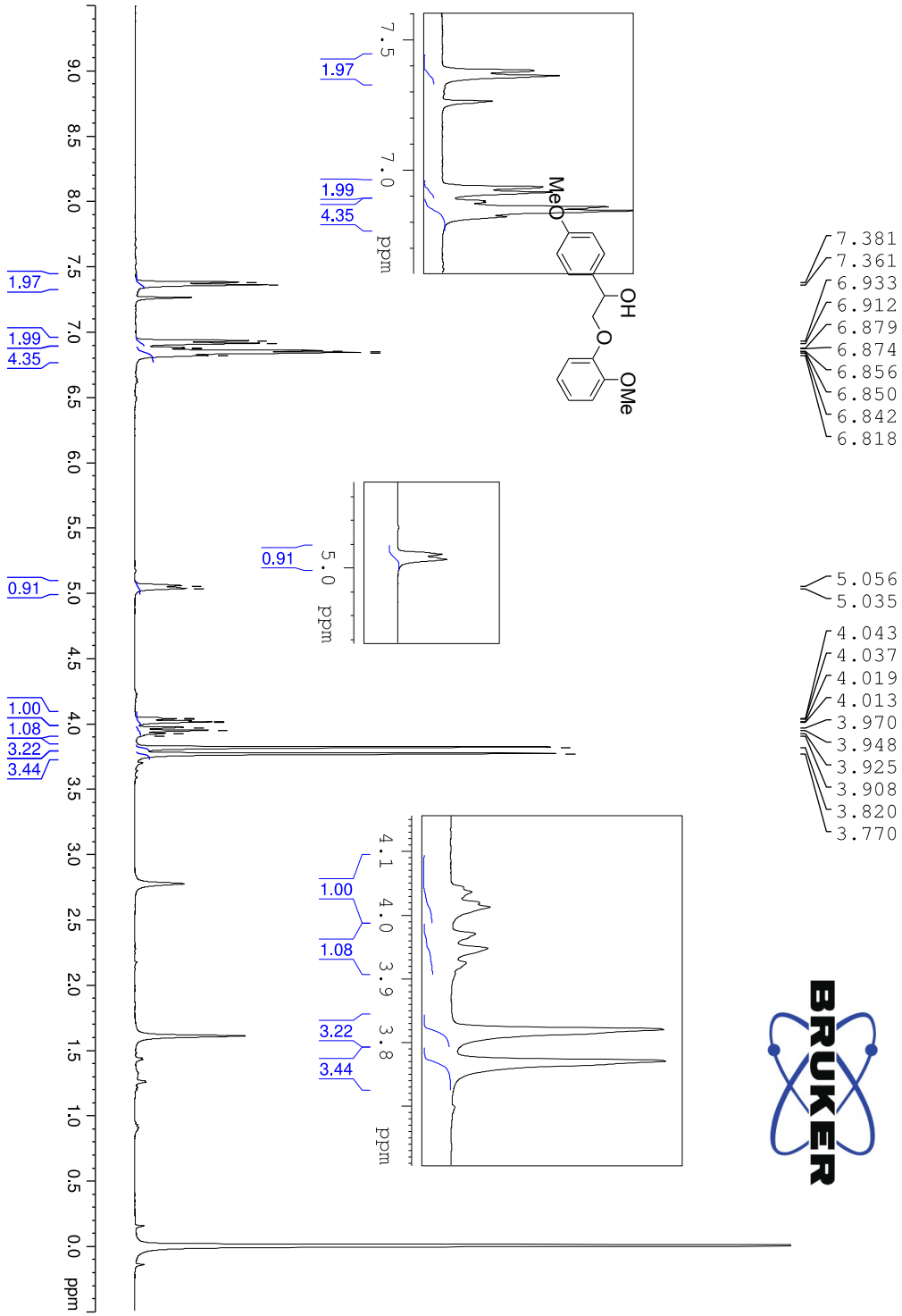
163.927
155.843
149.711
147.601
130.490
127.693
122.290
120.762
114.665
113.920
112.119
CDCl3
CDCl3
CDCl3
71.951
55.884
55.476
BRUKER
MeO
O
O
OMe
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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1.99
4.35
0.91
1.00
1.08
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3.44
MeO
OH
O
OMe
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6.933
6.912
6.879
6.874
6.856
6.850
6.842
6.818
5.056
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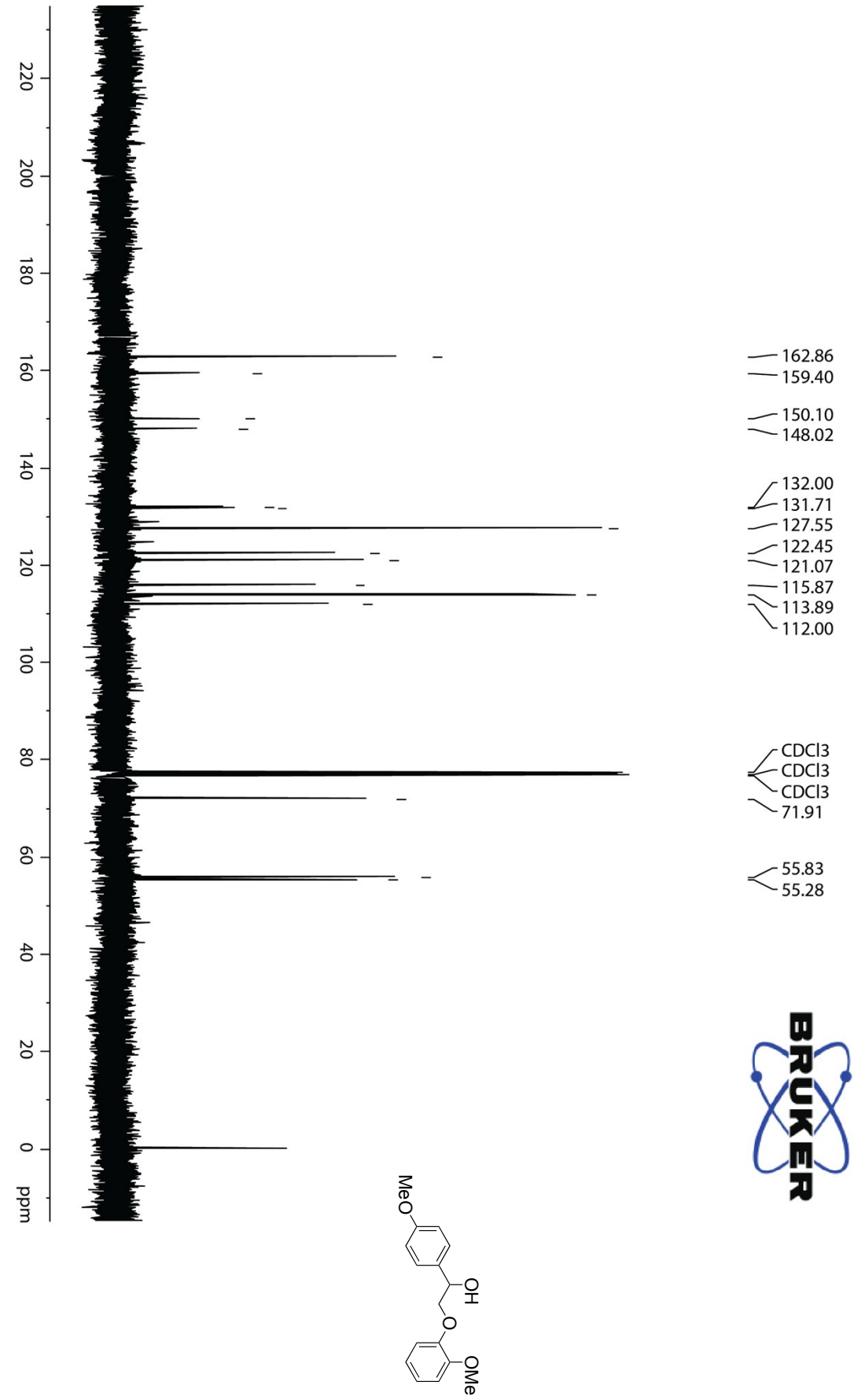
3.925
3.908
3.820
3.770
ppm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200
180
160
140
120
100
80
60
40
20
0
ppm
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159.40
150.10
148.02
132.00
131.71
127.55
122.45
121.07
115.87
113.89
112.00
CDCl3
CDCl3
CDCl3
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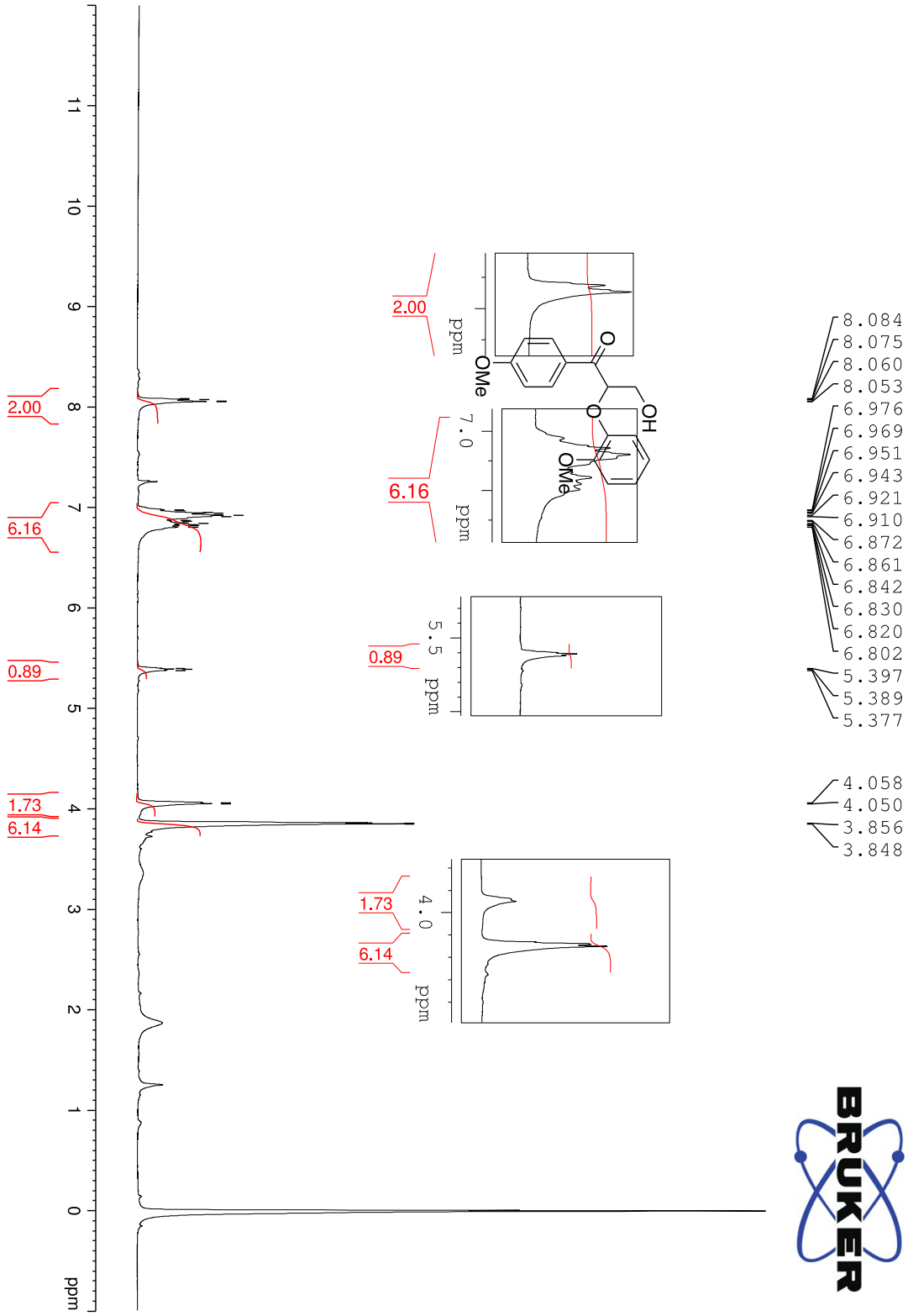
55.83
55.28
MeO
OH
O
OMe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8.075
8.060
8.053
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6.969
6.951
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6.842
6.830
6.820
6.802
5.397
5.389
5.377
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3.856
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2.00
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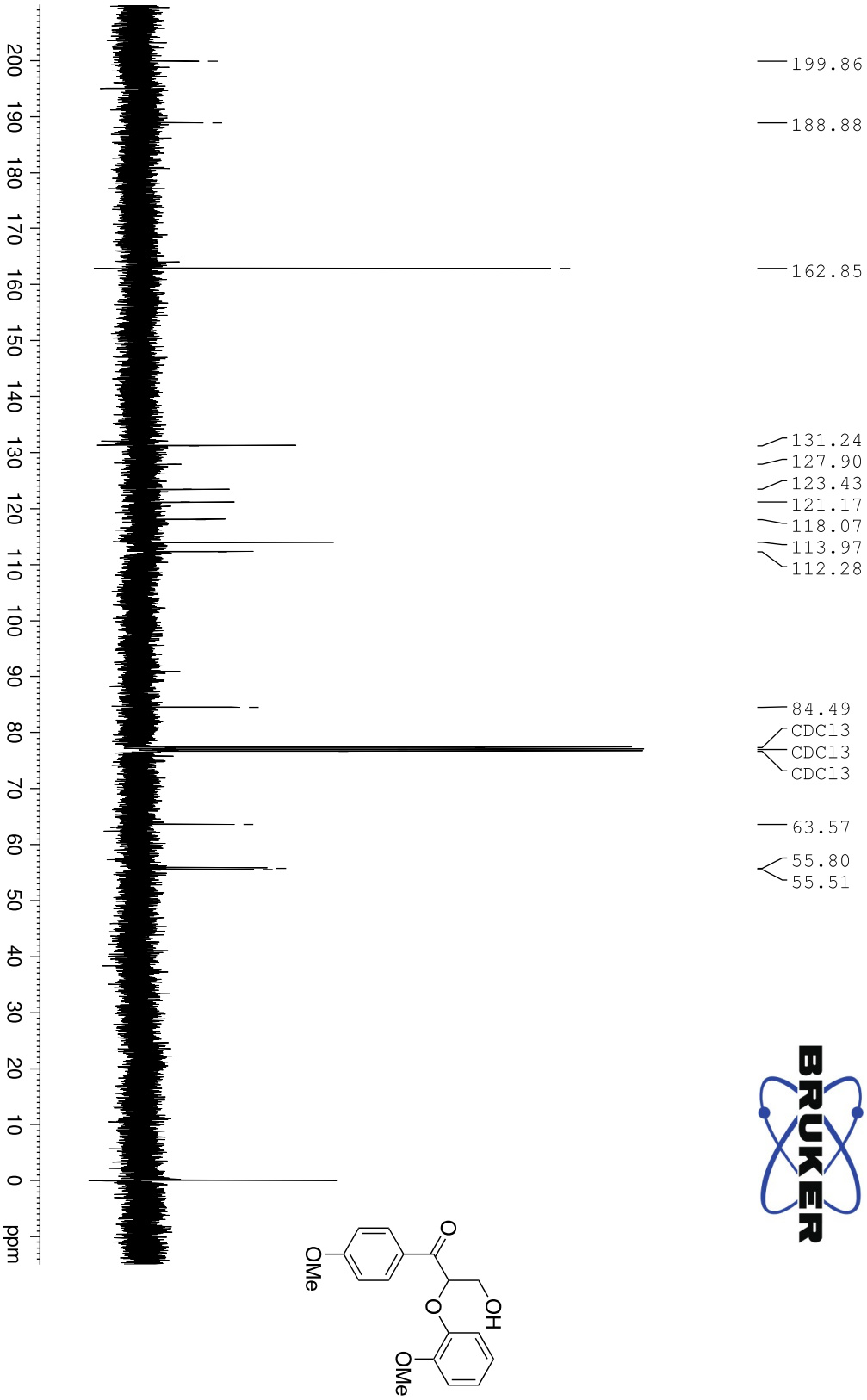
0.89
1.73
6.14
OMe
OH
O
ppm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188.88
162.85
131.24
127.90
123.43
121.17
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113.97
112.28
84.49
CDCl3
CDCl3
CDCl3
63.57
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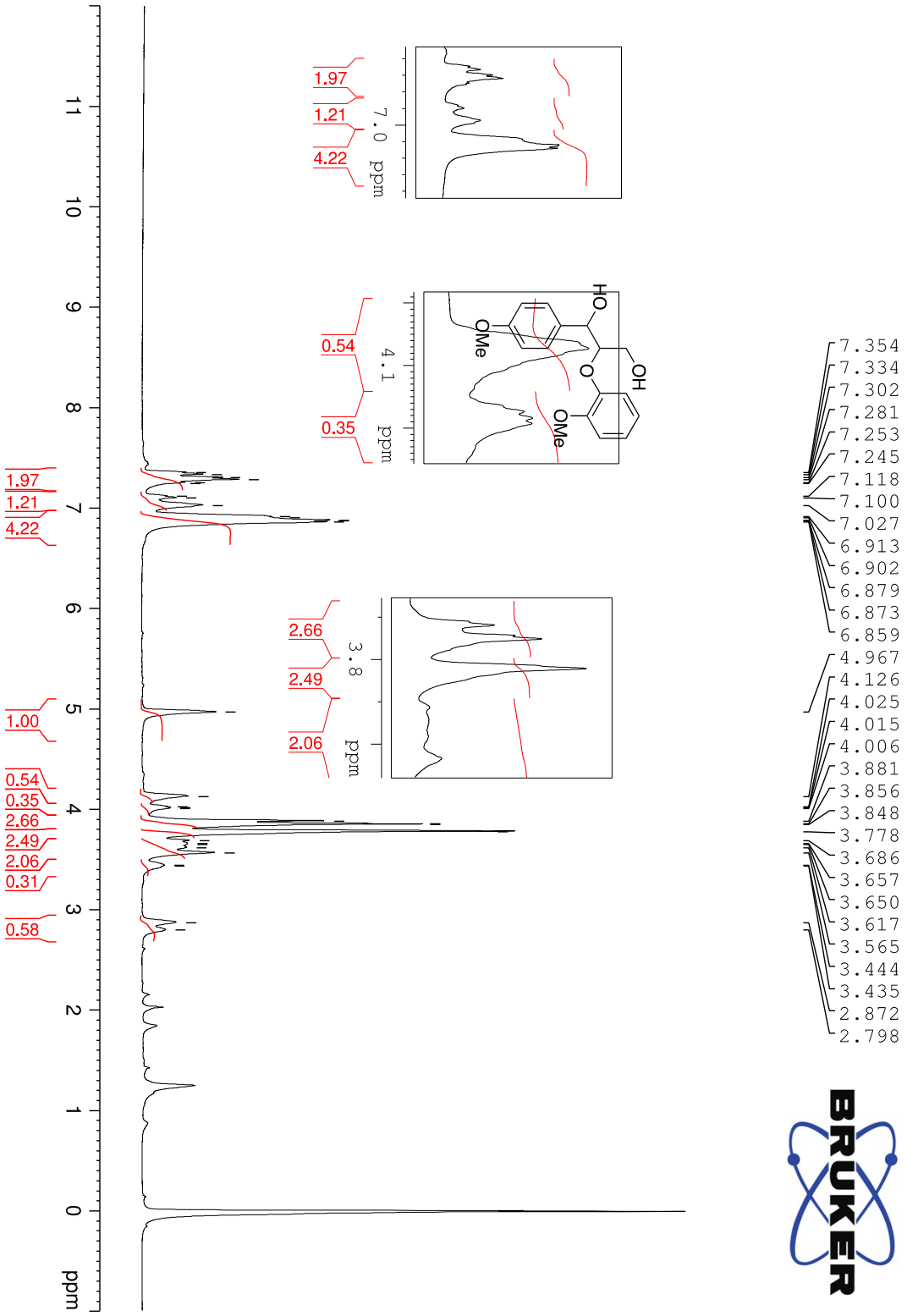
55.51
OMe
O
O
OH
OMe
BRUKER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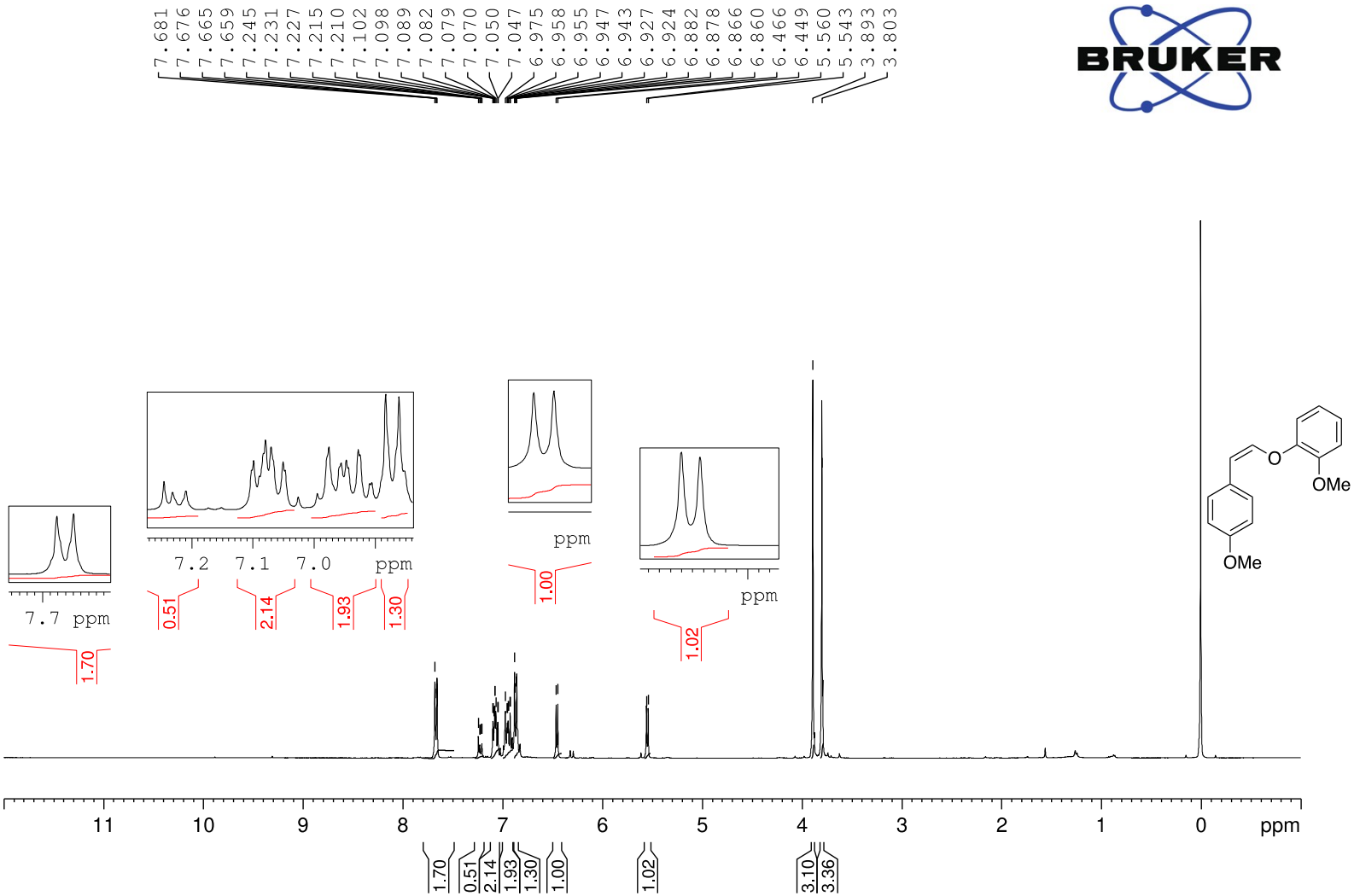
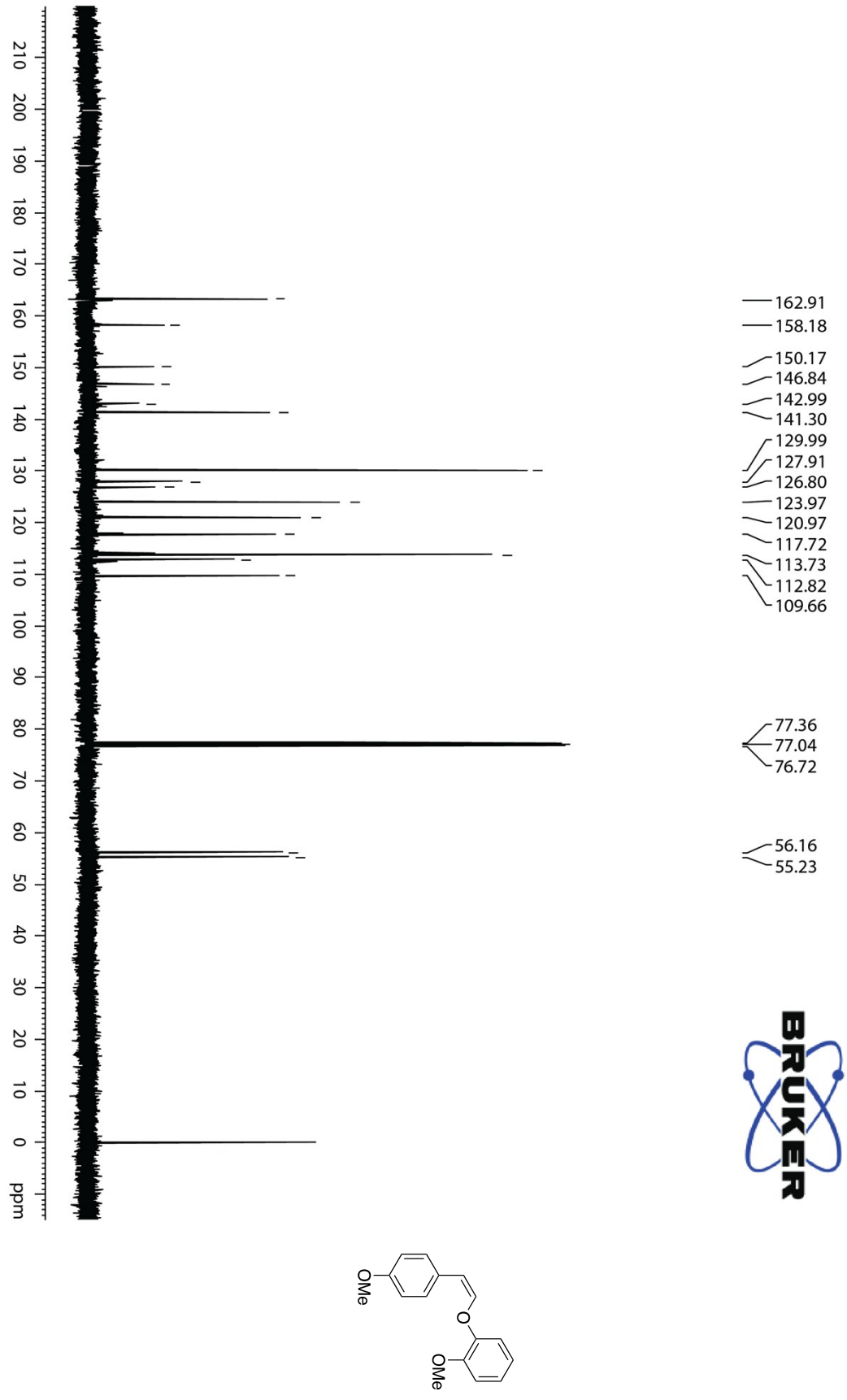
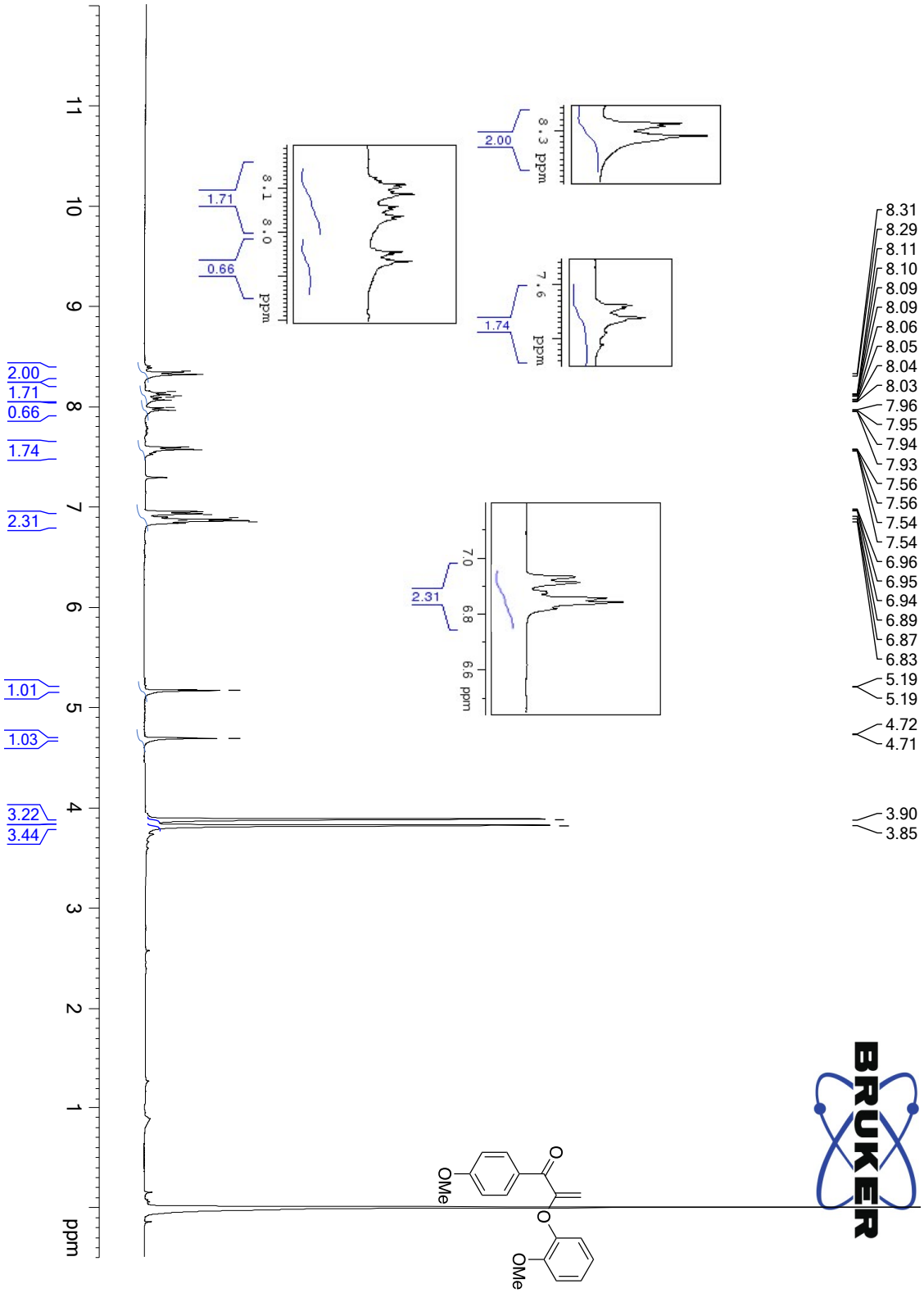
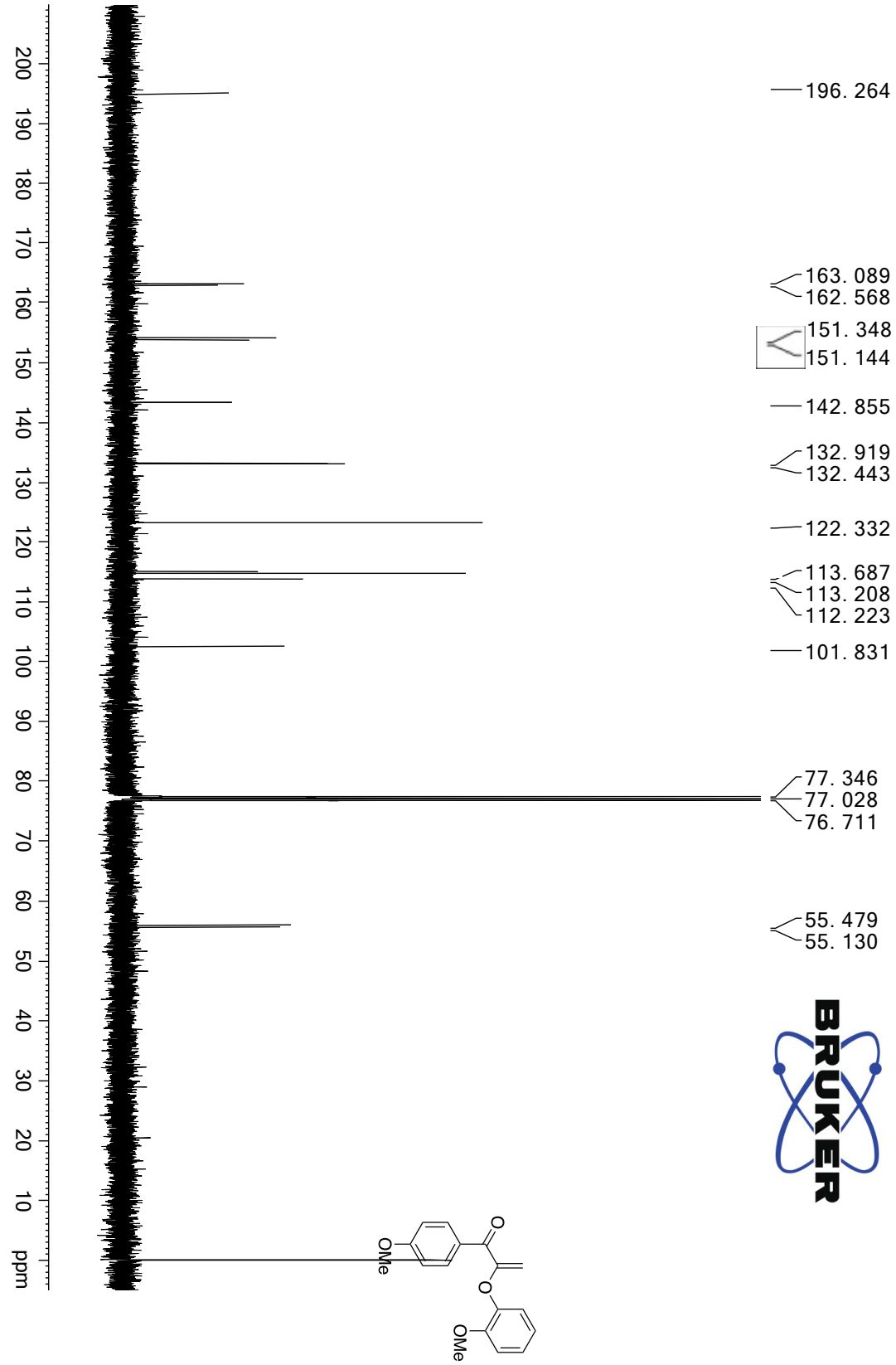
4.22
7.0 ppm
0.54
0.35
4.1 ppm
HO
OMe
O
OH
OMe
2.66
2.49
2.06
3.8 ppm
1.97
1.21
4.22
1.00
0.54
0.35
2.66
2.49
2.06
0.31
0.58
11 10 9 8 7 6 5 4 3 2 1 0 ppm
7.354
7.334
7.302
7.281
7.253
7.245
7.118
7.100
7.027
6.913
6.902
6.879
6.873
6.859
4.967
4.126
4.025
4.015
4.006
3.881
3.856
3.848
3.778
3.686
3.657
3.650
3.617
3.565
3.444
3.435
2.872
2.798
BRUKER

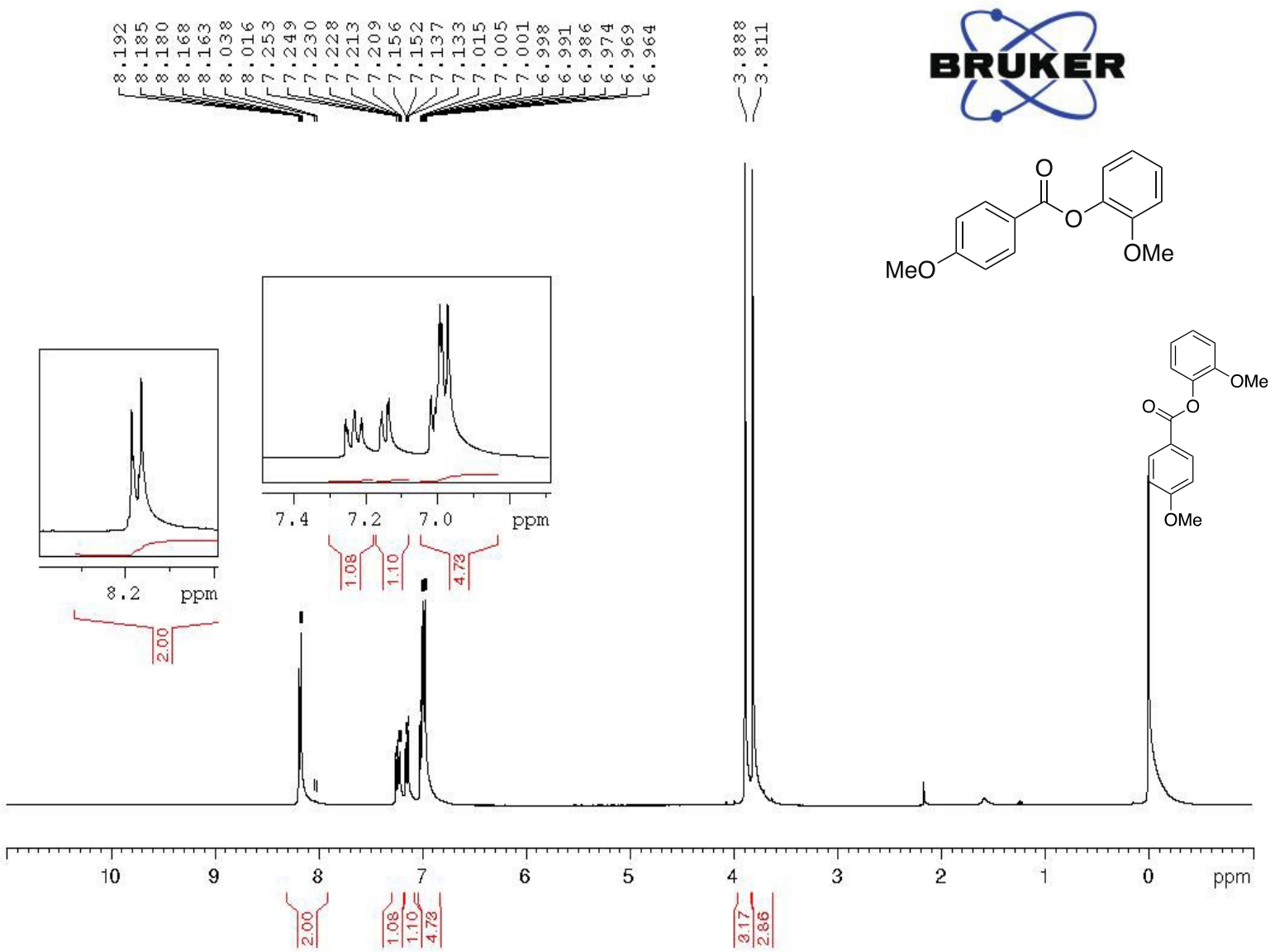
220
200
180
160
140
120
100
80
60
40
20
0
ppm
162.
151.
147.
147.
128.
127.
124.
121.
121.
114.
113.
112.
87.4
77.5
77.1
76.8
72.7
60.8
56.0
55.4
HO
OMe
O
OH
OMe
BRUKER

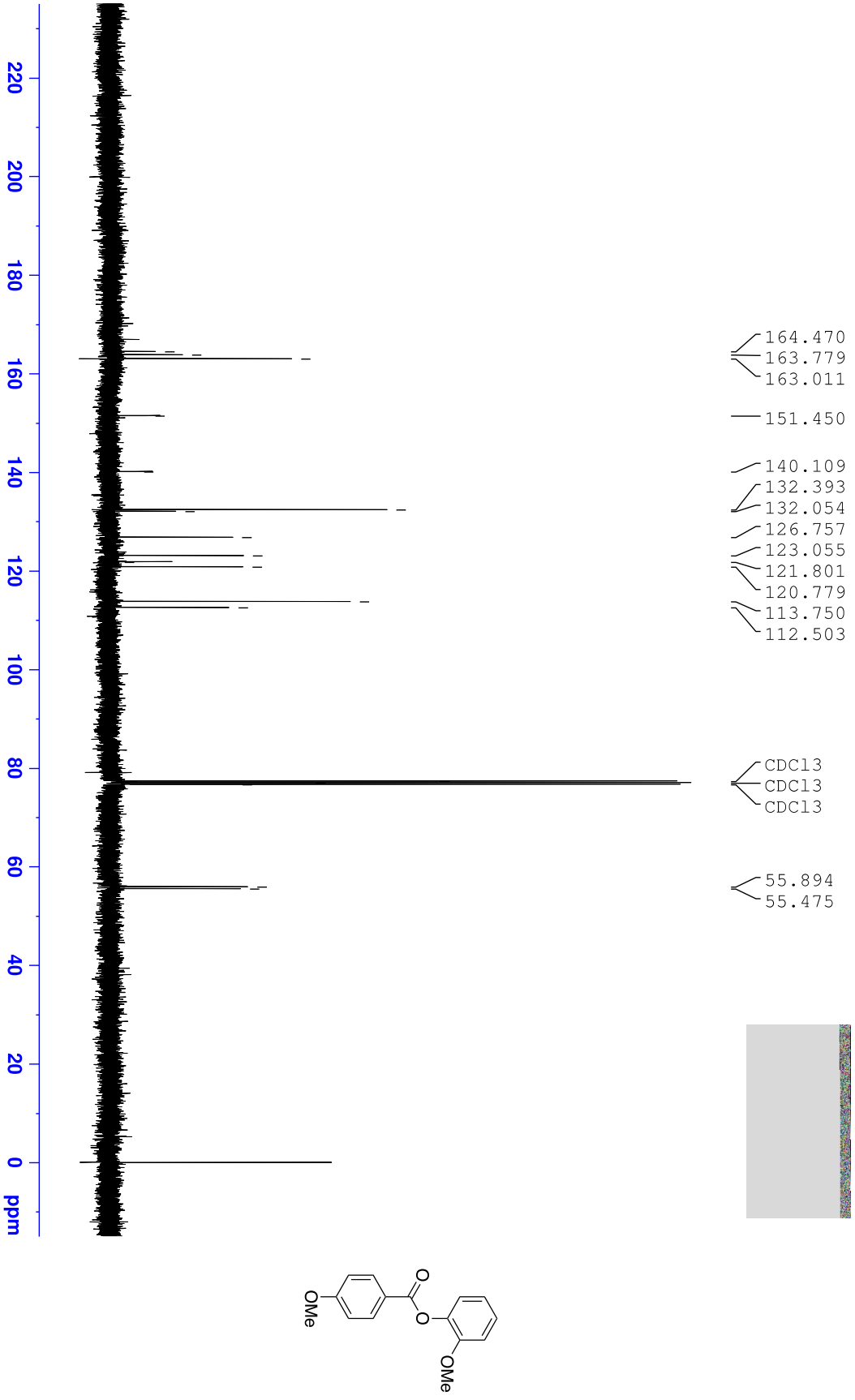

7.681
7.676
7.665
7.659
7.245
7.231
7.227
7.215
7.210
7.102
7.098
7.089
7.082
7.079
7.070
7.050
7.047
6.975
6.958
6.955
6.947
6.943
6.927
6.924
6.882
6.878
6.866
6.860
6.466
6.449
5.560
5.543
3.893
3.803
7.7 ppm
1.70
7.2
7.1
7.0
ppm
0.51
2.14
1.93
1.30
ppm
1.00
ppm
1.02
O
OMe
OMe
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.70
0.51
2.14
1.93
1.30
1.00
1.02
3.10
3.36


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
162.91
158.18
150.17
146.84
142.99
141.30
129.99
127.91
126.80
123.97
120.97
117.72
113.73
112.82
109.66
77.36
77.04
76.72
56.16
55.23
OMe
OMe
BRUKER


8.31
8.29
8.11
8.10
8.09
8.09
8.06
8.05
8.04
8.03
7.96
7.95
7.94
7.93
7.56
7.56
7.54
7.54
6.96
6.95
6.94
6.89
6.87
6.83
5.19
5.19
4.72
4.71
3.90
3.85
2.00
1.71
0.66
1.74
2.31
1.01
1.03
3.22
3.44
ppm
OMe
OMe
BRUKER


196.264
163.089
162.568
151.348
151.144
142.855
132.919
132.443
122.332
113.687
113.208
112.223
101.831
77.346
77.028
76.711
55.479
55.130
OMe
OMe
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.192
8.185
8.180
8.168
8.163
8.038
8.016
7.253
7.249
7.230
7.228
7.213
7.209
7.156
7.152
7.137
7.133
7.015
7.005
7.001
6.998
6.991
6.986
6.974
6.969
6.964
3.888
3.811
BRUKER
MeO
OMe
OMe
OMe
8.2
ppm
7.4
7.2
7.0
ppm
2.00
1.08
1.10
4.73
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.08
1.10
4.73
3.17
2.86


220
200
180
160
140
120
100
80
60
40
20
0
ppm
164.470
163.779
163.011
151.450
140.109
132.393
132.054
126.757
123.055
121.801
120.779
113.750
112.503
CDCl3
CDCl3
CDCl3
55.894
55.475
OMe
O
O
OMe