Supplementary Information

Iridium-catalysed primary alcohol oxidation and hydrogen shuttling for the depolymerisation of lignin

Christopher S. Lancefield,[a*] Lucas W. Teunissen,[a] Bert M. Weckhuysen[a] and Pieter C. A. Bruijnincx[ab*]

[a]*Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands.*

[b]*Organic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands.*

E-mail: c.s.lancefield@uu.nl; p.c.a.bruijnincx@uu.nl

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Experimental Details

Equipment and Methods

Routine 1D and 2D NMR spectra were recorded on an Agilent 400MR spectrometer (with OneNMR probe) or a Varian 400 MHz VNMRS system (with an Auto Switchable (ASW) probe, with tuning optimized for both ^{1}H and ^{19}F) using the standard NMR experiments, as present in the VNMRJ 4.2 software. The ^{1}H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances and reported in ppm relative to TMS (0 ppm). Multiplicities are described using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet and the *J* couplings are reported in Hz. NMR spectra were processed using MestReNova 10.

High-field NMR spectra were acquired on a Bruker Avance II 600 MHz spectrometer equipped with a 5 mm CPTCI ^{1}H-^{13}C/^{15}N-^{2}H cryogenic probe with z-gradients at 25 °C. ^{1}H-^{13}C Heteronuclear single quantum coherence spectroscopy (HSQC) spectra were recorded using the Bruker pulse sequence 'hsqcetgpsp.3' using the following parameters: acquired from 13 to -1 ppm in F2 (^{1}H) with 2048 data points, 160 to 0 ppm in F1 (^{13}C) with 256 increments with a 1 s interscan delay (D1); cnst2 was set to 145 Hz. Processing used Gaussian apodization (GB = 0.1, LB = 0.3 Hz) in F2 and squared cosine-bell and one level of linear prediction (32 coefficients) in F1. Volume integration of HSQC signals used Bruker's TopSpin 3.5 typically following manual phase correction and automatic baseline correction. HSQC-TOCSY spectra were recorded using the Bruker pulse sequence 'hsqcdietgpsisp.2' using the following parameters: acquired from 13 to -1 ppm in F2 (^{1}H) with 1024 data points, 160 to 0 ppm in F1 (^{13}C) with 256 increments with a 1.5 s interscan delay (D1) and a mixing time of 80 ms. Processing used one level of linear prediction (32 coefficients) in F1.

For lignin and lignin oil NMR analyses DMSO-d_6 was used as solvent and the central DMSO solvent peak was used as internal reference (δC 39.6, δH 2.49 ppm) except for analysis of the enzyme lignin (EL) which used DMSO-d_6/pyridine-d_5 (4:1) as the NMR solvent. The relative quantity of side chains and other units are expressed as a number per 100 aromatic units (100Ar) (based on comparison to the G aromatic integral as previously reported).[1] Integrals from symmetrical units or those corresponding to non-diastereotopic CH_2's (i.e. β-β, DHCA, CA) were halved to calculate the number of linkages/units per 100Ar.

Gel Permeation Chromatography (GPC) measurements were performed on a Polymer Labs GPC 50 system, equipped with a series of three PLGel Mixed-E columns and a guard column and using THF spiked with 0.1 vol% acetic acid as mobile phase. Detection was done with an external Knauer UV detector at 280 nm and molecular weight determinations were based on calibration with polystyrene

standards (M_n = 162, 570, 1060, 1400, 2240, 3690, 4760, 7130, 12800 and 19690). Samples were acetylated (pyridine/acetic anhydride overnight then dried under a stream of N_2) before analysis.

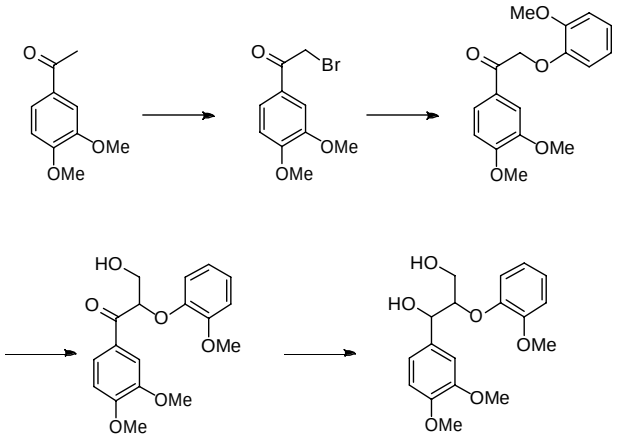
GC measurements were performed on a Varian GC equipped with a VF-5 ms capillary column and an FID detector. 1,3,5-trimethoxybenzene was used an internal standard; response factors were determined, after silylation, for all quantified products for which reference materials were available (commercial and synthesised). GC conditions for the analysis of all the samples: Injector temp.: 270 °C; Carrier gas: helium; Column flow: 2.0 mL/min; Oven temp.: 140 °C (hold 3 min.) to 300 °C at 10 °C/min, then 300°C (hold 20 min).

Chemicals and Materials

All chemicals were used as received from commercial suppliers (Sigma-Aldrich, Alfa Aesar, Acros, Strem). TLC analysis was performed on glass backed silica gel 60 plates (Merck) and visualized under a UV light (254 nm) or by staining with a cerium molybdate stain (Hanessian's stain). Silica gel column chromatography was performed with silica gel 60A (40-63μ) from Fluorochem, UK. NMR solvents were purchased from Cambridge Isotope Labs *via* BUCHEM (Netherlands) or from Euriso-top.

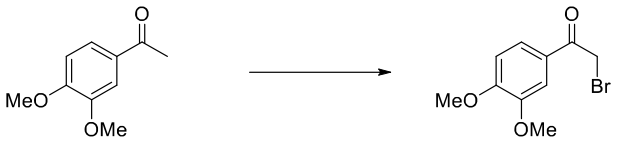
Synthetic Procedures

Synthesis of Model 1



Scheme S1 Steps in the optimized synthesis of **1**

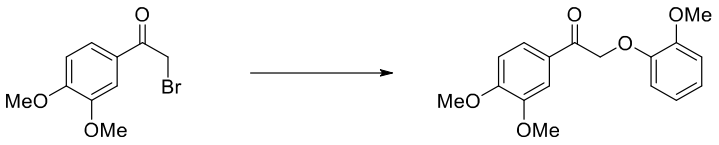
2-Bromo-1-(3,4-dimethoxyphenone)ethanone (S1)



Bromine (15.10 g, 94.6 mmol, 1.14 eq.) was added dropwise to a solution of 3,4-dimethoxyacetophenone (15.0 g, 83.2 mmol, 1 eq.) in ethanol (150 mL) at room temperature. After *ca.* 2 hours, the red colour of the bromine had faded and a white precipitate had spontaneously formed. The mixture was then stoppered and cooled on ice for *ca.* 3 hours. The precipitate was isolated by filtration, washed with cold ethanol and dried in air to yield the title compound **S1** as white crystals (12.6 g, 55%). Spectroscopic data was in accordance with previous reports.[2] **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.62 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.54 (d, *J* = 2.1 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 4.41 (s, 2H), 3.97 (s, 3H), 3.94 (s, 3H).

Note: Reaction at 125 g (~0.7 mol) scale gave 73% yield.

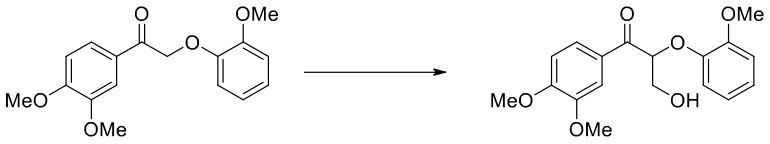
1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanone (S2)



To a solution of **S1** (6.02 g, 23.3 mmol, 1 eq.) in acetone (60 mL) was added guaiacol (2.88 g, 23.2 mmol, 1 eq.) followed by anhydrous K_2CO_3 (6.41 g, 46.4 mmol, 2 eq.). The mixture was then heated to reflux for 2 h, allowed to cool to room temperature, filtered and concentrated *in vacuo*. The resulting yellow solid was manually broken up with a spatula, suspended in ethanol and stirred for *ca.* 30 mins. The resulting solid was collected by filtration and allowed to air to give the title compound **S2** as a light yellow solid (4.15 g, 59%). Spectroscopic data was in accordance with previous reports.[3] **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.68 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.60 (d, *J* = 2.0 Hz, 1H), 7.00 – 6.75 (m, 5H), 5.29 (s, 2H), 3.95 (s, 3H), 3.93 (s, 3H), 3.88 (s, 3H).

Note: Reaction at 130 g (~0.5 mol) scale gave 85% yield.

1-(3,4-Dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propanone (S3)

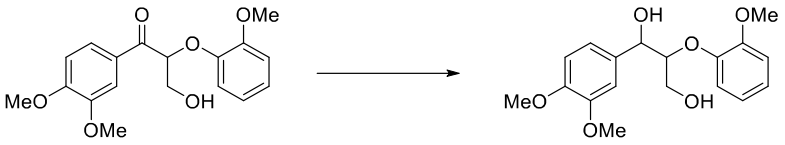


To a solution of **S2** (3.32 g, 10.9 mmol, 1 eq.) in 1,4-dioxane (30 mL) was added formaldehyde (37% in H_2O, 0.36 g, 12.1 mmol, 1.1 eq.) followed by K_2CO_3 (6.08 g, 44.0 mmol, 4 eq.). The mixture was stoppered and stirred vigorously overnight. After 20 hours, TLC indicated that unreacted starting material was present still, so a further portion of formaldehyde (0.18 g, 6.1 mmol) was added. After a further 3 hours, TLC indicated full consumption of starting material. The mixture was then filtered and concentrated *in vacuo*. The resulting oil was dissolved in methanol (30 mL) and left in the fridge overnight resulting in the formation of a white precipitate. The precipitate was collected by filtration, washed with methanol and air dried to give the title compound **S3** as a white solid (2.57 g, 71%). Spectroscopic data was in accordance with previous reports.[4] **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.75 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.61 (d, *J* = 2.0 Hz, 1H), 6.99 (ddd, *J* = 8.1, 7.2, 1.7 Hz, 1H), 6.94 – 6.85 (m, 3H), 6.81 (ddd, *J* = 7.9, 7.2, 1.6 Hz, 1H), 5.40 (t, *J* = 5.3 Hz, 1H), 4.07 (dd, *J* = 6.6, 5.2 Hz, 2H), 3.94 (s, 3H), 3.91 (s, 3H), 3.85 (s, 3H), 3.21 (t, *J* = 6.7 Hz, 1H). Hydroxyl protons were observed in this NMR.

Note 1: Seeding the product/methanol solution with previously isolated product results in immediate crystallisation/precipitation of the product without the need for refrigeration or standing overnight.

Note 2: Reaction at 70 g scale (230 mmol) gave 87% yield.

1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol (S4)

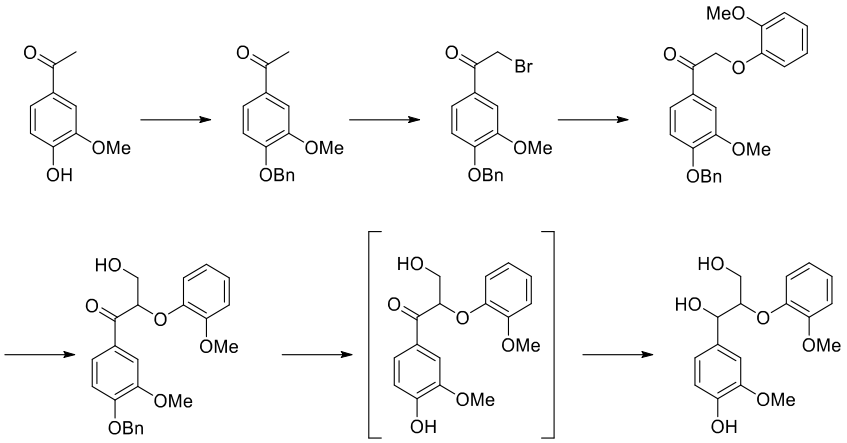


To a suspension of **S3** (1.98 g, 6.0 mmol, 1 eq.) in ethyl acetate:ethanol (4:1, 20 mL) $NaBH_4$ (0.11 g, 3.0 mmol, 0.5 eq.) was added portion-wise. The mixture was stirred for 1 hour forming a homogeneous solution. The reaction was quenched by addition of a saturated solution of NH_4Cl (20 mL) and vigorously stirred for 10 mins. The organic layer was separated, washed with water, brine, dried ($MgSO_4$) and concentrated *in vacuo* to give the title compound **S4** as a colourless, viscous oil (1.62 g, 81 %, 1:1 mixture if diastereoisomers). Spectroscopic data was in accordance with previous reports.[4] **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.15 – 6.72 (m, 7H), 5.04 – 4.89 (m, 1H), 4.15 (ddd, *J* = 6.0, 4.7, 3.4 Hz, 0.5H), 4.01 (dt, *J* = 8.0, 3.5 Hz, 0.5H), 3.96 – 3.79 (m, 9.5H), 3.71 – 3.56 (m, 1.5H), 3.54 – 3.42 (m, 1H), 2.78 – 2.62 (m, 1H). Hydroxyl protons were observed in this NMR.

Note: Reaction at 60 g scale gave ~100% yield.

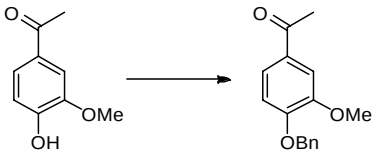
Synthesis of Model 18

Guaiacylglycerol-β-guaiacyl Ether (18) Synthesis



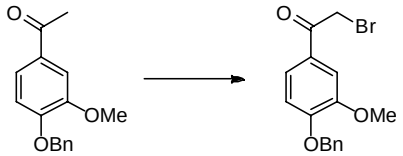
Scheme S2 Steps in the optimized synthesis of guaiacylglycerol-β-guaiacyl Ether (**18**)

1-(4-(Benzyloxy)-3-methoxyphenyl)ethan-1-one (S5)



To a solution of acetovanillone (25.0 g, 150 mmol, 1.0 eq.) in DMF (50 mL) was added benzyl chloride (20.0 g, 158 mmol, 1.05 eq.) and K_2CO_3 (41.5 g, 301 mmol, 2 eq.). The mixture was stirred at 70 °C for 2 h until complete conversion as indicated by TLC. The reaction mixture was cooled to room temperature, diluted with EtOH (100 mL) and poured slowly into rapidly stirring water (1 L). The white precipitate was vigorously stirred for 10 minutes, then filtered and washed with water (500 mL). The solid was dried overnight *in vacuo* over 4 Å molecule sieves to give the title compound **S5** as a white solid (38.4 g, 100%). Spectroscopic data was in accordance with previous reports.[5] **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.55 (d, *J* = 2.2 Hz, 1H), 7.50 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.48–7.29 (m, 5H), 6.89 (d, *J* = 8.2 Hz, 1H), 5.23 (s, 2H), 3.94 (s, 3H), 2.55 (s, 3H) ppm.

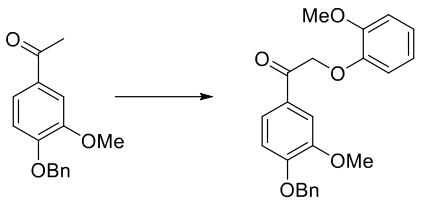
1-(4-(Benzyloxy)-3-methoxyphenyl)-2-bromoethan-1-one (S6)



A solution of Br_2 (24.0 g, 150 mmol, 1.1 eq.) in cyclohexane (80 mL) was added dropwise to a solution of **S5** (35 g, 137 mmol, 1.0 eq.) in a mixture of EtOH:DCM (9:1, 770 mL) at room temperature. During the addition, the reaction mixture was sparged with a slow stream of nitrogen delivered *via* a glass pipette. After the bromine

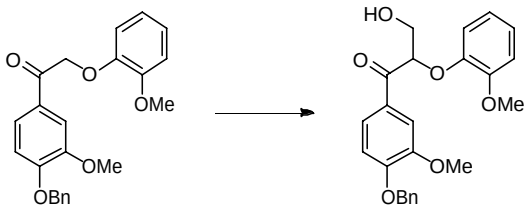
colour had dissipated the reaction mixture was cooled on ice and the resulting white precipitate was collected by filtration and washed with a small amount of cold EtOH to yield the title compound as a voluminous white solid (40.7 g, 89%). Spectroscopic data was in accordance with previous reports.[6] **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.56 (d, *J* = 2.1 Hz, 1H), 7.53 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.47 – 7.30 (m, 5H), 6.91 (d, *J* = 8.4 Hz, 1H), 5.25 (s, 2H), 4.39 (s, 2H), 3.95 (s, 3H) ppm.

1-(4-(Benzyloxy)-3-methoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-one (S7)



To a solution of **S6** (40.0 g, 119.33 mmol, 1.0 eq.) in acetone (200 mL) was added guaiacol (14.8 g, 119 mmol, 1.0 eq.) followed by K_2CO_3 (24.7 g, 1.5 eq.). The mixture was then heated to reflux for 2 h, allowed to cool to room temperature, filtered and concentrated *in vacuo*. The resulting oil was dissolved in MeOH (200 mL) and vigorously scratched with a spatula to induce crystallisation. The resulting solid was collected by filtration and washed with MeOH to yield the title compound as a white powder (41.0 g, 91%). TLC (Hexanes:EtOAc, 6:3 v/v): Rf = 0.38. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.67 – 7.55 (m, 2H), 7.48 – 7.28 (m, 5H), 7.00 – 6.77 (m, 5H), 5.27 (s, 2H), 5.23 (s, 2H), 3.94 (s, 3H), 3.87 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 193.3, 153.0, 149.8, 149.8, 147.7, 136.3, 128.8, 128.3, 128.2, 127.3, 122.6, 122.4, 120.9, 114.8, 112.3, 112.3, 111.0, 72.1, 70.9, 56.2, 56.0 ppm. **HR-MS (ESI)** $C_{23}H_{23}O_5$ $[M+H]^+$ m/z required 379.1540; found 379.1548.

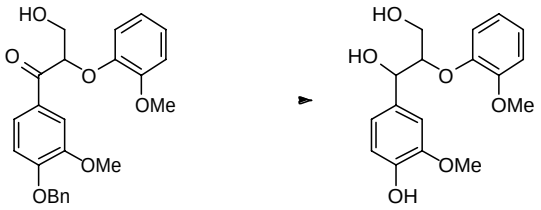
1-(4-(Benzyloxy)-3-methoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propan-1-one (S8)



To a solution of **S7** (30.0 g, 117 mmol, 1.0 eq.) in 1,4-dioxane (300 mL) formaldehyde (3.9 g, 129 mmol, 1.1 eq., 9.56 mL of a 37 wt% solution in water) and K_2CO_3 (16.2 g, 117 mmol, 1.0 eq.) were added. The mixture was then sealed and vigorously stirred overnight at room temperature, then filtered and concentrated *in vacuo*. The resulting oil was dissolved in MeOH (300 mL) and vigorously scratched with a spatula to induce crystallisation. The resulting white precipitate was collected by filtration and washed with methanol to yield the title compound as a white solid (26.7 g, 56%). TLC (Hexanes:EtOAc, 3:7 v/v): Rf = 0.66. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.66 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.63 (d, *J* = 1.8 Hz, 1H), 7.48 – 7.28 (m, 5H), 7.04 – 6.96 (m, 1H), 6.93 – 6.85 (m, 3H), 6.85 – 6.77 (m, 1H), 5.38 (t, *J* = 5.3 Hz, 1H), 5.22 (s, 2H), 4.05 (d, *J* = 5.3 Hz, 2H), 3.92 (s, 3H), 3.84 (s, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ** 195.1, 153.2, 150.5, 149.8, 147.1, 136.2, 128.9, 128.3, 128.3, 127.3, 123.7, 123.5, 121.3, 118.3,

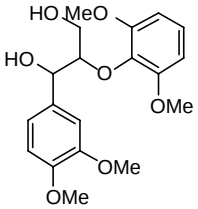
112.4, 112.3, 111.5, 84.5, 71.0, 63.9, 56.2, 55.9. **HR-MS (ESI)** $C_{24}H_{25}O_6$ $[M+H]^+$ m/z required 409.1646; found 409.1649.

Guaiacylglycerol-β-guaiacyl ether (18)



In a 250 mL flask a solution of **S8** (3.0 g, 7.34 mmol, 1.0 eq.) in EtOAc:ethanol (1:2, 75 mL) was degassed for 5 min under vacuum. 5% Pd/C (150 mg) was added under nitrogen and the flask evacuated again. A hydrogen balloon was attached and after the mixture vigorously stirred overnight. The reaction mixture was then filtered through a 0.45 μm nylon filter and concentrated *in vacuo* to yield the title compound **18** as a mixture of diastereomers (~2:1, major:minor, colourless oil, 2.2 g, 94%). Spectroscopic data was in accordance with previous reports.[7] **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.19 – 6.72 (m, 7H), 5.05 – 4.88 (m, 1H), 4.19 – 4.12 (m, 0.64H), 4.04 – 3.99 (m, 0.36H), 3.94 – 3.85 (m, 6.64H), 3.70 – 3.59 (m, 1H), 3.48 (dd, *J* = 12.5, 3.8 Hz, 0.36H) ppm.

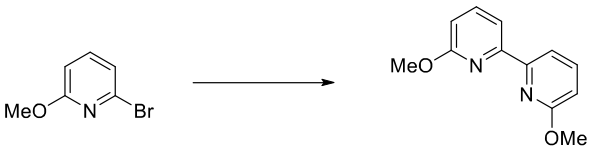
Synthesis of Model 19



Model **18** was synthesised according to previously reported methods without modification.[4]

Synthesis of Ligands and Iridium Complexes

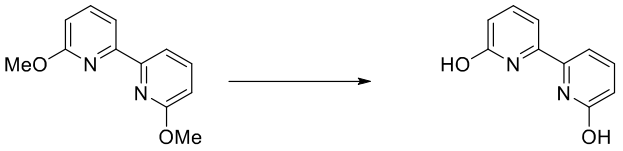
6,6'-Dimethoxy-2,2'-bipyridine (S9)



A catalytic amount of $NiCl_2.6H_2O$ (0.25 g, 1.1 mmol) and 2,2'-bipyridine (0.15 g, 1.0 mmol) was added to DMF (40 mL), and heated to 40 °C while stirring. At 40 °C, 2-bromo-5-methoxypyridine (3.75 g, 20.0 mmol, 1.0 eq.), zinc dust (1.44 g, 24.0 mmol, 1.2 eq.) and anhydrous LiCl (0.85 g, 20.0 mmol, 1.0 eq.) were added to the solution

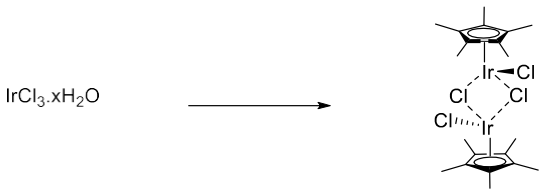
and the temperature was increased to 50 °C. A small iodine crystal and four drops of acetic acid were then added, causing the mixture to turn from blue to black. The reaction temperature was increased to 60 °C and stirred for 2 hours. The reaction was then cooled to room temperature and quenched by adding 25 mL 1 M HCl. The mixture was then basified by adding ammonia-solution (25% in water) and extracted with DCM. The organic phase was dried ($MgSO_4$) and concentrated *in vacuo* to give the title compound **S9** as a light tan coloured solid (1.61 g, 75%). Spectroscopic data was in accordance with previous reports.[8] **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.01 (2 H, d, *J* 7.4), 7.69 (2 H, dd, *J* 8.2, 7.4), 6.75 (2 H, d, *J* 8.2), 4.04 (7 H, s).

6,6'-Dihydroxy-2,2'-bipyridine (16)



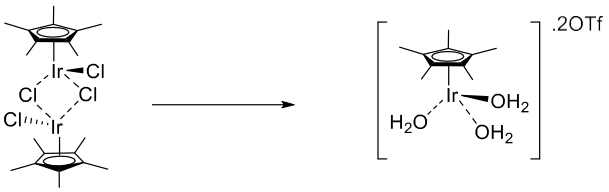
To **S9** (1.08 g, 5.05 mmol) was added a solution of 33wt% HBr in AcOH (20 mL) and the mixture was refluxed for 24 hours. The mixture was concentrated *in vacuo* and the resulting solid washed with acetone before being dispersed in boiling water. The pH was neutralized (pH ~7) with 1 M NaOH solution, after which the solid product was collected by filtration and dried *in vacuo* to give the title compound **16** as a gray/white solid (1.09 g, 86%). Spectroscopic data was in accordance with previous reports.[9] **^{1}H NMR (400 MHz, DMSO-d_6) δ** 11.04 (s, 2H), 7.66 (dd, *J* = 8.7, 7.2 Hz, 1H), 7.25 (d, *J* = 7.0 Hz, 1H), 6.57 (d, *J* = 8.7 Hz, 1H).

[(η^5-C_5Me_5)$IrCl_2$]$_2$ (17)



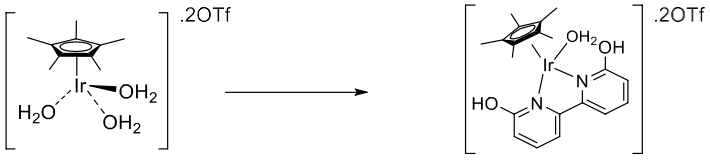
To a solution of $IrCl_3.xH_2O$ (1.02 g) in methanol (30 mL), pentamethylcyclopentadienyl (0.47 g, 3.45 mmol) was added and the mixture was refluxed for 48 hours. The mixture was cooled to room temperature and then on ice. The resulting precipitate was collected by filtration, washed with a small volume of methanol and air dried to give the title compound **17** as an orange solid (0.85 g). Spectroscopic data was in accordance with previous reports.[10] **^{1}H NMR (400 MHz, $CDCl_3$) δ** 1.59 (15 H, s).

[(η^5-C_5Me_5)Ir(H_2O)$_3$]OTf$_2$ (S10)[11,12]



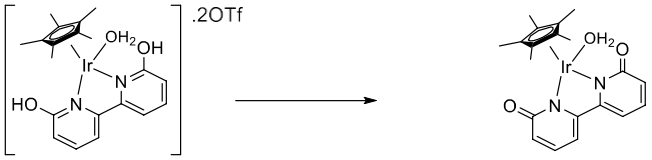
17 (0.3 g, 0.37 mmol, 1.0 eq.) was stirred at room temperature in water (2.5 mL) for 12 hours, in the presence of $AgCF_3SO_3$ (0.39 g, 1.51 mmol, 4.0 eq.). The precipitated AgCl was removed by filtration and the filtrate was concentrated *in vacuo* to give the title compound **S10** (0.46 g, 90%). **^{1}H NMR (400 MHz, DMSO-d6) δ** 1.64 (s, 15H).

[(η^5-C_5Me_5)Ir(6,6'-dihydroxy-2,2'-bipyridine)(H_2O)]OTf$_2$ (S11)



To a solution of compound **S10** (0.4426 g, 0.65 mmol, 1 eq.) in water (12 mL) 6,6'-dihydroxy-2,2'-bipyridine (**16**) (0.123 g, 0.65 mmol, 1.0 eq.) was added and the mixture was stirred at room temperature for 4 hours. The mixture was then filtered and the filtrate concentrated *in vacuo* to give the title compound **S11** as a yellow solid (0.51 g, 94%). Spectroscopic data was in accordance with previous reports. **^{1}H NMR (400 MHz, DMSO-d6) δ** 7.83 – 7.78 (m, 2H), 7.63 – 7.58 (m, 2H), 6.81 – 6.76 (m, 2H), 1.54 (s, 15H).

[(η^5-C_5Me_5)IrCl_2]$_2$Ir(BpyO)(H_2O)] (14)



To a solution of **S11** (0.469 g, 0.56 mmol, 1.0 eq.) in water (12 mL) was added NaO^{t}Bu (0.115 g, 1.2 mmol, 2.0 eq.). The mixture was stirred at room temperature for one hour. The resulting suspension was filtered and the resulting solid was washed with diethyl ether to give a portion of the product. A further portion of product was isolated by extraction of the aqueous filtrate with DCM and concentration of the organic extract *in vacuo*. Combination of both products gave the title compound **14** as an orange powder (0.216 g, 81%). Spectroscopic data was in accordance with previous reports.[13] **^{1}H NMR (400 MHz, Methanol-d4) δ** 7.42 (t, J = 7.9 Hz, 2H), 6.92 (d, J = 7.2 Hz, 2H), 6.43 (d, J = 8.5 Hz, 2H), 1.58 (s, 15H).

General Procedures for Iridium Catalyzed Reactions

Notes: All model and lignin reactions were run in 8 mL screw top vials and heated using an aluminium heating block which was maintained at the stated temperature. An analytical balance (precision = 0.01 mg) was used for weighing all the components. All reactions were run under air.

General procedure for model reactions

To a mixture of catalyst (separate components (**17**+**16**; 1:2.2 = 1:1.1 Ir:ligand) or preformed **14**) and base in water (0.25 mL) was added a stock solution of model compound in 1,4-dioxane (0.15 mmol, 0.25 mL). The mixture was then heated at 130 °C in a sealed vial for 1 h. The reaction was allowed to cool to room temperature and acidified (pH <1) by the dropwise addition of 1 M HCl. A stock solution of 1,3,5-trimethoxybenzene (0.015 mmol) in 1,4-dioxane was then added. The reaction mixture was extracted with DCM (2 x ~3 mL) and concentrated *in vacuo*. The yields of the individual products were calculated based on quantitative ^{1}H NMR analysis (D1 = 25 seconds) of the crude reaction mixtures.

General procedure for lignin reactions

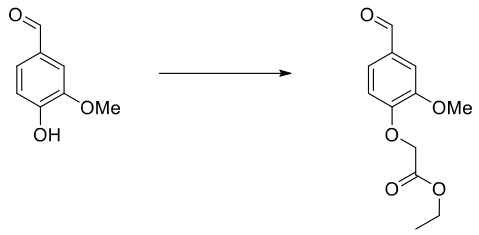
To a mixture of $[Cp^*IrCl_2]_2$ **17** (1.5 or 5wt%, 1.0 eq.), 6,6'-dihyroxy-2,2'-bipyridine **16** (2.2 eq.) and sodium carbonate (100 mg) in water (1 mL) was added lignin (100 mg) followed by the co-solvent (1 mL). The mixture was then heated at 130 °C in a sealed vial for 1-2 h. The reaction mixture was then allowed to cool to room temperature and acidified (pH <1) by the dropwise addition of 1 M HCl (caution bubbling). 1 mg of 1,3,5-trimethoxybenzene (100 μL of a 10 mg/mL stock solution) was then added and the aqueous layer was saturated with NaCl. The organic products were extracted with a mixture of EtOAc/MeCN (1:1) (2 x ~3 mL). The organic extracts were dried ($MgSO_4$), concentrated in vacuo, suspended in a mixture of toluene/pyridine (19:1, 1 mL) and silylated using a commercially available BSTFA + 1% TMSC mixture (150 μL) at 80 °C for 30 mins before GC-FID analysis. During the silylation procedure the crude reaction products became completely soluble.

Where samples for GPC or NMR analysis were required, these were removed before the silylation step.

Identification and quantification of the lignin depolymerisation products was achieved based on the synthesis of authentic compounds to be used as standards and for response factor calculations.

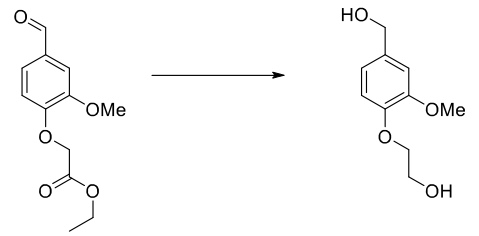
Synthesis of Standards for Quantification

Ethyl 2-(4-formyl-2-methoxyphenoxy)acetate (S12)



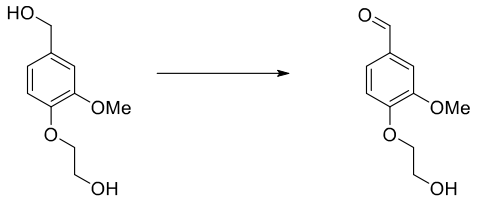
To a solution of vanillin (5.00 g, 32.9 mmol, 1.0 eq.) in acetone (50 mL) was added ethyl bromoacetate (5.60 g, 33.5 mmol, 1.02 eq.) and K_2CO_3 (6.81 g, 49.3 mmol, 1.5 eq.). The mixture was heated at reflux for 14 hours, allowed to cool to room temperature, filtered and the filtrate concentrated *in vacuo* to give the title compound **S12** as a white, crystalline solid (5.40 g, 69%). Spectroscopic data was in accordance with previous reports.[4] ^{1}**H NMR (400 MHz, $CDCl_3$)** δ 9.87 (1 H, s), 7.56 – 7.34 (2 H, m), 6.88 (1 H, d, *J* 8.1), 4.78 (2 H, s), 4.28 (2 H, q, *J* 7.1), 3.96 (3 H, s), 1.29 (3 H, t, *J* 7.1).

2-(4-(Hydroxymethyl)-2-methoxyphenoxy)ethanol (L1)



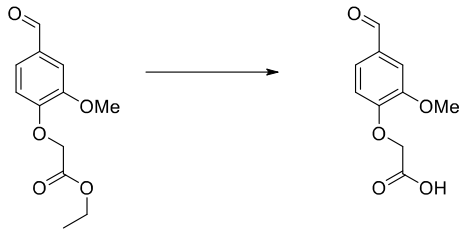
To a solution of **S12** (1.50 g, 6.30 mmol) in EtOH (20 mL) was added $NaBH_4$ (0.81 g, 21.9 mmol, 3.5 eq.). The mixture was heated to 50 °C and, while stirring, MeOH (~2.5 mL) was added dropwise over 5 min. After a further 1 h the mixture was allowed to cool to room temperature and quenched with 1 M HCl (pH <2). The mixture was then diluted with water (20 mL) and extracted with DCM (30 mL). The organic extracts were dried ($MgSO_4$) and concentrated *in vacuo* to give the title compound **L1** as a colourless oil (0.715 g, 57%). Spectroscopic data was in accordance with previous reports.[14] ^{1}**H NMR (400 MHz, $CDCl_3$)** δ 7.03 – 6.83 (3 H, m), 4.64 (2 H, s), 4.29 – 4.07 (2 H, m), 3.97 – 3.88 (2 H, m), 3.87 (3 H, s). ^{1}**H NMR (400 MHz, DMSO-d_6)** δ 6.98 – 6.86 (2 H, m), 6.80 (1 H, dd, *J* 8.2, 1.9), 5.07 (1 H, t, *J* 5.7), 4.82 (1 H, t, *J* 5.5), 4.41 (2 H, d, *J* 5.7), 3.93 (2 H, t, *J* 5.2), 3.75 (3 H, s), 3.70 (2 H, q, *J* 5.3). ^{13}**C NMR (101 MHz, DMSO-d_6)** δ 148.8, 147.0, 135.3, 118.6, 113.0, 110.8, 70.3, 62.8, 59.7, 55.4.

4-(2-Hydroxyethoxy)-3-methoxybenzaldehyde (L2)



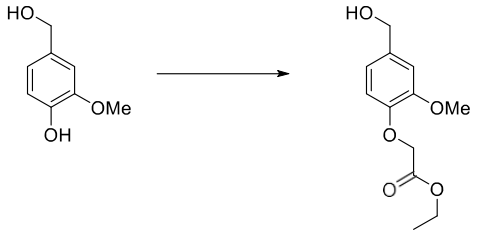
To a solution of **L1** (0.376 g, 1.9 mmol, 1.0 eq.) in DCM (20 mL) was added DDQ (0.430 g, 1.9 mmol, 1.0 eq.). TLC analysis indicated complete consumption of starting material after 15 minutes, at which point the reaction mixture was centrifuged and the liquid phase was isolated by decantation. The liquid was washed with a saturated $NaHCO_3$ solution (3 x 20 mL) and concentrated *in vacuo* to give the title compound **L2** as a light orange solid (0.240 g, 64%). Spectroscopic data was in accordance with previous reports.[15] **^{1}H NMR (400 MHz, $CDCl_3$) δ** 9.87 (1 H, s), 7.56 – 7.39 (2 H, m), 7.01 (1 H, d, *J* 8.0), 4.29 – 4.13 (2 H, m), 4.11 – 3.98 (2 H, m), 3.93 (3 H, s). **^{1}H NMR (400 MHz, DMSO-d_6) δ** 9.83 (1 H, s), 7.53 (1 H, dd, *J* 8.2, 1.8), 7.39 (1 H, d, *J* 1.8), 7.18 (1 H, d, *J* 8.3), 4.10 (2 H, t, *J* 5.0), 3.75 (2 H, t, *J* 4.9). **^{13}C NMR (101 MHz, DMSO-d_6) δ** 191.4, 153.7, 149.2, 129.6, 126.1, 112.1, 109.6, 70.4, 59.3, 55.5.

(4-Formyl-2-methoxyphenoxy)acetic acid (L3)



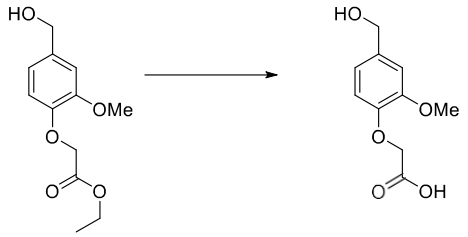
S12 (200 mg, 0.84 mmol) was dissolved in 1 M NaOH (4 mL) and left to stir at room temperature for 2 h. The solution was then acidified with 1 M HCl (pH < 1) and the resulting precipitate was collected by filtration, washed with water and dried in vacuo to give the title compound **L3** as a yellow solid (112 mg, 63%). Spectroscopic data was in accordance with previous reports.[16] **^{1}H NMR (400 MHz, DMSO-d_6) δ** 13.09 (1 H, s), 9.84 (1 H, s), 7.51 (1 H, dd, *J* 8.3, 1.9), 7.42 (1 H, d, *J* 1.9), 7.06 (1 H, d, *J* 8.3), 4.83 (2 H, s), 3.85 (3 H, s). **^{13}C NMR (101 MHz, DMSO-d_6) δ** 191.4, 169.6, 152.6, 149.2, 130.1, 125.6, 112.3, 110.1, 64.8, 55.6.

Ethyl 2-(4-(hydroxymethyl)-2-methoxyphenoxy)acetate (S13)



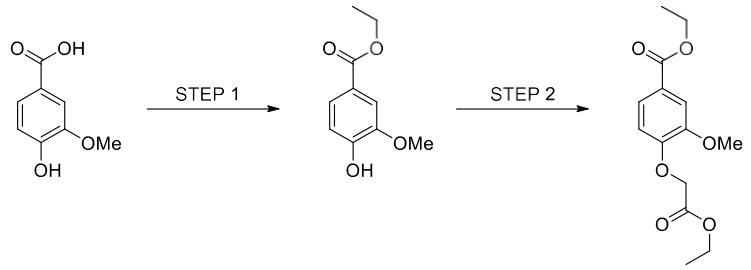
To a solution of 4-hydroxy-3-methoxy-benzyl alcohol (2.0 g, 13.0 mmol, 1.0 eq.) in acetonitrile (20 mL) was added ethyl bromoacetate (2.17 g, 13.0 mmol, 1.0 eq.) and potassium carbonate (2.69 g, 19.5 mmol, 1.5 eq.). The mixture was then refluxed for 6 hours, allowed to cool to room temperature, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography eluting with EtOAc/Hexanes (30-40%) to give the title compound **S13** as a colourless oil (1.59 g, 51%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 6.95 (d, *J* = 1.9 Hz, 1H), 6.89–6.70 (m, 2H), 4.67 (s, 2H), 4.62 (d, *J* = 2.9 Hz, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 169.1, 149.9, 146.9, 135.4, 119.3, 114.4, 111.2, 66.8, 65.3, 61.4, 56.0, 14.3. **HR-MS (ESI)** $C_{12}H_{16}O_5Na$ $[M+Na]^+$ m/z required 263.0890; found 263.0895.

2-(4-(Hydroxymethyl)-2-methoxyphenoxy)acetic acid (L4)



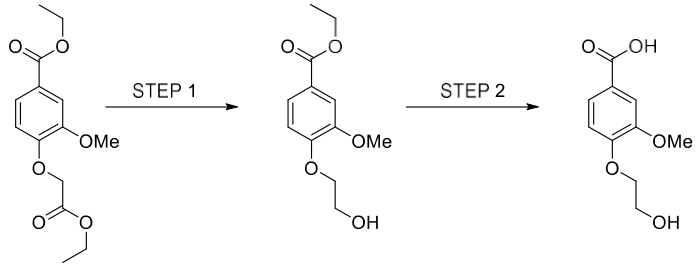
S13 (200 mg, 0.83 mmol) was suspended in water/acetone (2:1, 2 mL) and Na_2CO_3 was added (176 mg, 1.66 mmol, 2.0 eq). The solution was then stirred at 40 °C for 5 hours before being acidified with 2 M H_2SO_4 (pH <1) and extracted with DCM (4 mL). The organic extract was dried ($MgSO_4$) and concentrated *in vacuo* to give the title compound **L4** as a colourless oil which solidified on standing (153 mg, 87%). **^{1}H NMR (400 MHz, DMSO-d_6) δ** 6.99 – 6.89 (1 H, m), 6.84 – 6.66 (2 H, m), 4.61 (2 H, s), 4.41 (2 H, s), 3.76 (3 H, s). **^{13}C NMR (101 MHz, DMSO-d_6) δ** 170.3, 148.7, 146.0, 135.9, 118.4, 113.1, 111.0, 65.2, 62.7, 55.5. **HR-MS (ESI)** $C_{12}H_{12}O_5Na$ $[M+Na]^+$ m/z required 235.0577; found 235.0582.

Ethyl 4-(2-ethoxy-2-oxoethoxy)-3-methoxybenzoate (S14)



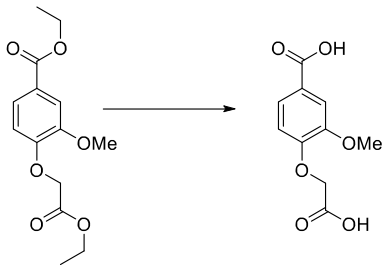
Step 1: Acetyl chloride (1.0 mL) was added dropwise, with stirring to absolute ethanol (20 mL) at room temperature. Vanillic acid (2.00 g, 11.9 mmol, 1.0 eq.) was then added and the solution heated at reflux for 6 hours. **Step 2:** After cooling to room temperature, K_2CO_3 (4.0 g, 28.9 mmol, 2.4 eq.) and ethyl bromoacetate (1.99 g, 11.9 mmol, 1.0 eq.) were added and the mixture heated at reflux for a further 1 h. The crude reaction mixture was then concentrated *in vacuo* and re-suspended in acetone (40 mL). After stirring for 5 minutes the mixture was filtered and the filtrate concentrated *in vacuo* to give the title compound **S14** as a white crystalline solid (1.85 g, 55% over 2 steps). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.63 (1 H, dd, *J* 8.4, 2.0), 7.58 (1 H, d, *J* 2.0), 6.79 (1 H, d, *J* 8.4), 4.74 (2 H, s), 4.35 (2 H, q, *J* 7.1), 4.26 (2 H, q, *J* 7.1), 3.94 (3 H, s), 1.38 (3 H, t, *J* 7.1), 1.28 (3 H, t, *J* 7.1). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 168.4, 166.3, 151.1, 149.1, 124.5, 123.2, 112.9, 112.5, 66.1, 61.6, 61.0, 56.2, 14.5, 14.3. **HR-MS (ESI)** $C_{14}H_{18}O_6Na$ $[M+Na]^+$ m/z required 305.0996; found 305.1001.

4-(2-Hydroxyethoxy)-3-methoxybenzoic acid (L5)



Step 1: To a solution of **S14** (200 mg, 0.71 mmol, 1 eq.) in ethanol (4.0 mL) was added $NaBH_4$ (27 mg, 0.71 mmol, 1.0 eq.). The mixture was stirred at room temperature for 16 h before being concentrated *in vacuo*. **Step 2:** The crude product was dissolved in 1 M NaOH (4 mL), stirred for 1 h at room temperature and then acidified with 1 M HCl. The resulting white precipitated was collected by filtration, washed with water and dried *in vacuo* to give the title compound **L5** as a white solid (135 mg, 90%). Spectroscopic data was in accordance with previous reports.[17] **^{1}H NMR (400 MHz, DMSO-d_6) δ** 12.65 (1 H, s), 7.54 (1 H, dd, *J* 8.4, 2.0), 7.44 (1 H, d, *J* 2.0), 7.04 (1 H, d, *J* 8.4), 4.89 (1 H, s), 4.12 – 3.99 (2 H, m), 3.80 (3 H, s), 3.78 – 3.69 (2 H, m). **^{13}C NMR (101 MHz, DMSO-d_6) δ** 167.1, 152.1, 148.4, 123.2, 122.9, 112.1, 112.0, 111.9, 70.2, 59.4, 55.4.

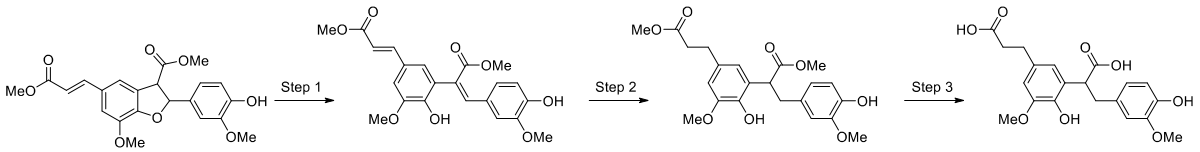
4-(Carboxymethoxy)-3-methoxybenzoic acid (L6)



S13 (107 mg) was dissolved in 1 M NaOH (2 mL) and left to stir at room temperature for 2 h. The solution was then acidified with 1 M HCl (pH <1) and the resulting white precipitate was collected by filtration, washed with water and dried in vacuo to give the title compound **L6** as a white solid (79 mg, 92%). **^{1}H NMR (400 MHz, DMSO-d_6) δ** 12.87 (2 H, s), 7.52 (1 H, dd, *J* 8.4, 1.9), 7.46 (1 H, d, *J* 2.0), 6.93 (1 H, d, *J* 8.5), 4.76 (2 H, s), 3.82 (3 H, s). **^{13}C NMR (101 MHz, DMSO-d_6) δ** 169.8, 167.1, 151.0, 148.4, 123.6, 122.9, 112.4, 112.1, 64.8, 55.6. **HR-MS (ESI)** $C_{10}H_{10}O_6Na$ $[M+Na]^+$ m/z required 249.0370; found 249.0375.

Synthesis of Compounds for Lignin Assignments

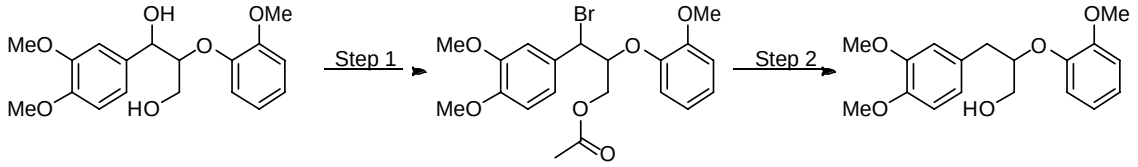
B' Phenylcoumaran Derivative: 2-(5-(2-carboxyethyl)-2-hydroxy-3-methoxyphenyl)-3-(4-hydroxy-3-methoxyphenyl)propanoic acid (S17)



Step 1: S15 was prepared from dimethyl dehydrodiferulate (**S14**)[18] according to literature procedures without modification.[19] **Step 2:** To a solution of **S15** (500 mg, 1.20 mmol) in methanol (10 mL) was added 5% Pd/C (25 mg) under nitrogen. The flask was then evacuated and a H_2 balloon was attached. The mixture was then vigorously stirred at 40 °C for 6 hours after which time NMR analysis indicated complete conversion of the starting material to **S16**. The mixture was then filtered through a 45 μm nylon filter and concentrated in vacuo to give **S16** as a light yellow oil (488 mg, 98%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 6.76 (d, *J* = 8.0 Hz, 1H), 6.72 – 6.56 (m, 4H), 5.86 (s, 1H), 5.49 (s, 1H), 4.22 (dd, *J* = 8.6, 6.7 Hz, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 3.67 (s, 3H), 3.61 (s, 3H), 3.27 (dd, *J* = 13.8, 8.6 Hz, 1H), 2.94 (dd, *J* = 13.8, 6.7 Hz, 1H), 2.85 (t, *J* = 7.8 Hz, 2H), 2.56 (t, *J* = 7.8 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 174.4, 173.5, 146.6, 146.2, 144.1, 141.8, 132.1, 131.5, 124.6, 121.8, 120.1, 114.2, 111.8, 109.9, 56.1, 55.9, 52.1, 51.7, 46.8, 38.2, 36.3, 30.9. **HR-MS (ESI)** $C_{22}H_{26}O_8Na$ $[M+Na]^+$ m/z required 441.1512; found 441.1525. **Step 3: S16** (65 mg, 0.16 mmol) was dissolved in 1 M NaOH (2 mL) and stirred at room temperature for 2 hours. The mixture was then acidified with 1 M HCl (pH <1) and extracted with DCM (2 x 2 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo* to give the title compound

S17 as a yellow oil (29 mg, 48%). **^{1}H NMR (400 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ HR-MS (ESI)** $C_{20}H_{22}O_8Na$ $[M+Na]^+$ m/z required 413.1207; found 413.1212.

Ar (Reduced) β-O-4 model: 3-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)propan-1-ol (S19)



1 **S18** **S19**

Step 1: 1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol (**1**) (300 mg, 0.90 mmol, 1.0 eq.) was dissolved in acetic acid:acetyl bromide (4:1, 5 mL) and stirred, protected from light, at room temperature for 16 hours. The reaction mixture was then concentrated *in vacuo* and residual acetic acid removed by azeotropic distillation with hexanes (5 x 20 mL) to give intermediate benzyl bromide **S18** which was used immediately in the next step.[20] **Step 2:** The remaining oil was dissolved in THF (6 mL) and a solution of $LiAlH_4$ in THF (2.4 M, 5 eq.) was added dropwise at -78 °C. The mixture was allowed to warm to room temperature and stirred for 2 hours. The reaction was quenched by the slow addition of EtOAc (5 mL) at 0 °C, acidified with 1 M HCl and partitioned between water (20 mL) and EtOAc (20 mL). The organic layer was washed with brine, dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography eluting with 20-40% EtOAc/hexanes to yield the title compound **S19** as a colourless oil (168 mg, 59%). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.00 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H), 6.90 (dd, *J* = 8.2, 1.6 Hz, 1H), 6.85 (ddd, *J* = 7.7, 7.7, 1.6 Hz, 1H), 6.82 – 6.75 (m, 4H), 4.25 (dddd, *J* = 6.8, 6.8, 5.3, 3.1 Hz, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.85 (s, 3H), 3.73 – 3.58 (m, 2H), 3.08 (dd, *J* = 13.9, 6.8 Hz, 1H), 2.92 (dd, *J* = 13.9, 6.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 151.3, 149.0, 147.8, 147.6, 130.5, 123.6, 121.6, 121.5, 120.2, 112.9, 112.2, 111.4, 85.2, 63.6, 56.0, 56.0, 55.9, 37.4. **HR-MS (ESI)** $C_{18}H_{22}O_5Na$ $[M+Na]^+$ m/z required 341.1359; found 341.1365.

Lignin Isolation

Enzyme lignin (EL) was isolated based on previously reported methods from commercially available softwood sawdust pellets intended for animal bedding.[21] Briefly, 20 g of sawdust pellets were ball milled in a 125 mL agate jar containing agate balls (6 x 20 mm, 20 x 10 mm) for 48 hours using a Fritsch 'Pulverisette 7' planetary ball mill at speed setting 7. The ball milled wood was then digested with Celluclast 1.5L (Sigma) (1 mL/g) in acetate buffer (pH 5.2, 50 mM, 2 wt% loading) at 50 °C for 96 h with stirring. The mixture was filtered using a nylon membrane (45 μm) and the collected solid washed with water and dried. The collected solid (~7.1g, enzyme lignin) was then ball milled in 50 mL agate jars (1 g per jar) containing agate balls (1 x 20 mm, 1 x 15 mm, 6 x 10 mm) for 2 h at speed setting 7 to produce a fine powder of enzyme lignin which was used for all further experiments without further processing.

Dioxasolv lignin was isolated based on previously reported methods.[4] Briefly, 30 g of softwood sawdust was extracted with 1,4-dioxane/water (8:2, 200 mL) containing 0.1 M HCl at reflux for 1 h. The mixture was then cooled, filtered and concentrated *in vacuo*. The resulting oil was dissolved in acetone/water (8:2) and precipitated in water (10 vols). The resulting powder was collected by filtration and air dried. The crude lignin was then dissolved in acetone/methanol (9:1) and precipitated in diethyl ether (10 vols). The purified lignin was collected by filtration and air dried to give the softwood dioxasolv lignin (1.1 g).

Supplementary Tables

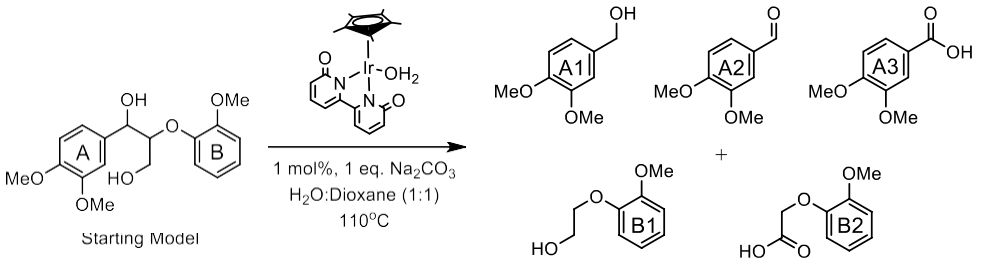


Table S1 Base Screening. Conditions: Model **1**, 2 mol% **14**, 1 eq. base, 130 °C, 1 h, dioxane/water (1:1)

	Base	Conversion (%)	A1 (%)	A2 (%)	A3 (%)	B1 (%)	B2 (%)
1	Na_2CO_3	100	28	31	26	70	25
2	K_2CO_3	100	42	18	32	62	36
3	Cs_2CO_3	100	23	32	24	59	24
4	Li_2CO_3	40	9	15	6	30	8
5	NaOH	100	25	38	24	67	28
6	NEt_3	21	0	0	0	0	0

Table S2 Base Equivalents Screening. Base = Na_2CO_3. Conditions: Model **1**, 2 mol% **14**, 130 °C, 1 h, dioxane/water (1:1)

	Base equivalent	Conversion (%)	A1 (%)	A2 (%)	A3 (%)	B1 (%)	B2 (%)
1	0	5	0	0	0	0	0
2	0.2	58	12	28	13	41	15
3	0.5	96	25	38	24	67	28
4	1	100	28	31	26	70	25

Table S3 Catalyst Screening. Conditions: Model **1**, 2 mol% (Ir), 1 eq. Na_2CO_3, 130 °C, 1 h, dioxane/water (1:1)

	Catalyst	Conversion (%)	A1 (%)	A2 (%)	A3 (%)	B1 (%)	B2 (%)
1	Preformed (**14**)	100	28	31	26	70	25
2	In Situ (**16**+**17**)	100	13	33	33	46	42
3	$[Cp^*IrCl_2]_2$ (**17**), no ligand	21	0	2	0	0	0

Table S4 Solvent Composition Screening. Conditions: Model **1**, 1 mol% **14**, 1 eq. Na_2CO_3, 130 °C, 1 h.

	Solvent (Dioxane:Water)	Conversion (%)	A1 (%)	A2 (%)	A3 (%)	B1 (%)	B2 (%)
1	1:1	84	23	43	12	56	20
2	1:0	34	4	5	6	7	0
3	0:1	79	14	11	23	37	12
4	3:1	56	9	27	7	42	8
5	1:3	82	15	22	19	53	17

Table S5 Reaction Time. Conditions: Model **1**, 1 mol% **7**, 1 eq. Na_2CO_3, 130 °C, 1 h, dioxane/water (1:1).

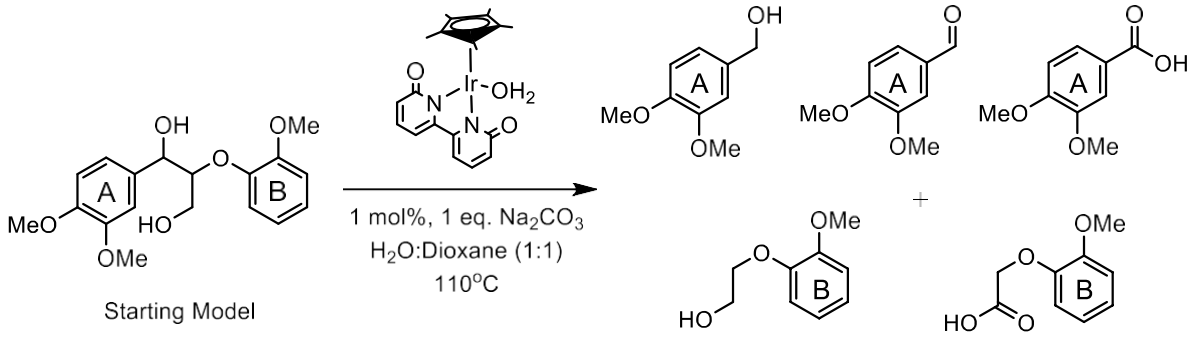
	Reaction Time (min)	Conversion (%)	A1 (%)	A2 (%)	A3 (%)	B1 (%)	B2 (%)
1	60	84	23	43	12	56	20
2	1440	100	23	9	38	41	36

Table S6 Atmosphere. Conditions: Model **1**, 2 mol% **16+17**, 1 eq. Na_2CO_3, 130 °C, 1 h, dioxane/water (1:1).

	Atm.	Conversion (%)	A1 (%)	A2 (%)	A3 (%)	A1:A2:A3	B1 (%)	B2 (%)	B1:B2
1	Air	97	36	17	21	2.2:1.0:1.3	57	24	1.1:1.0
2	O_2	97	15	33	23	1.0:2.2:1.5	46	29	1.1:1.0
3	N_2	96	50	11	18	4.6:1.0:1.6	69	19	1.1:1.0

Supplementary Figures

Reaction Time Course



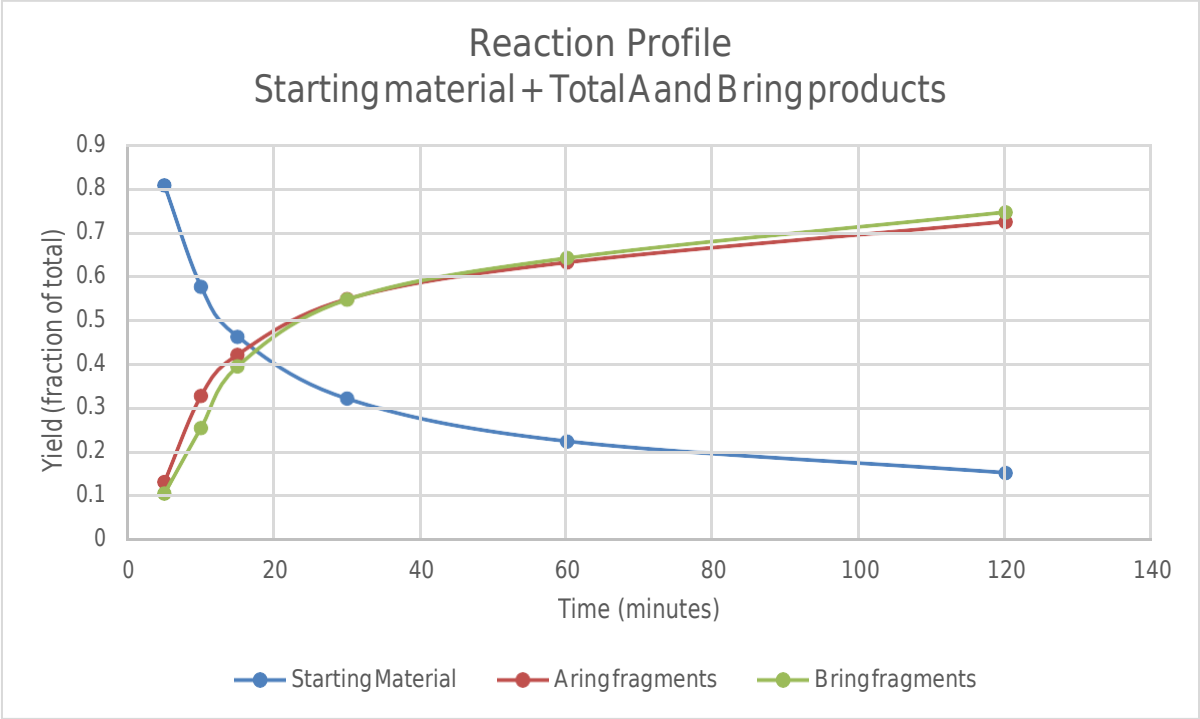


Figure S1 Reaction profile of starting material and total A and B ring products during the Ir catalyzed cleavage of model **1**. Conditions: 1 mol% **Ir cat.** (in situ **16+17**), 1 eq. Na_2CO_3, 110 °C, dioxane/water (1:1). Yields were calculated by quantitative ^{1}H NMR analysis using the total aromatic integral as an internal standard. The lower temperature of 110 °C (*c.f.* 130 °C) was used for the time course reaction to allow for easier sampling of the reaction mixture using a septum vial and syringe.

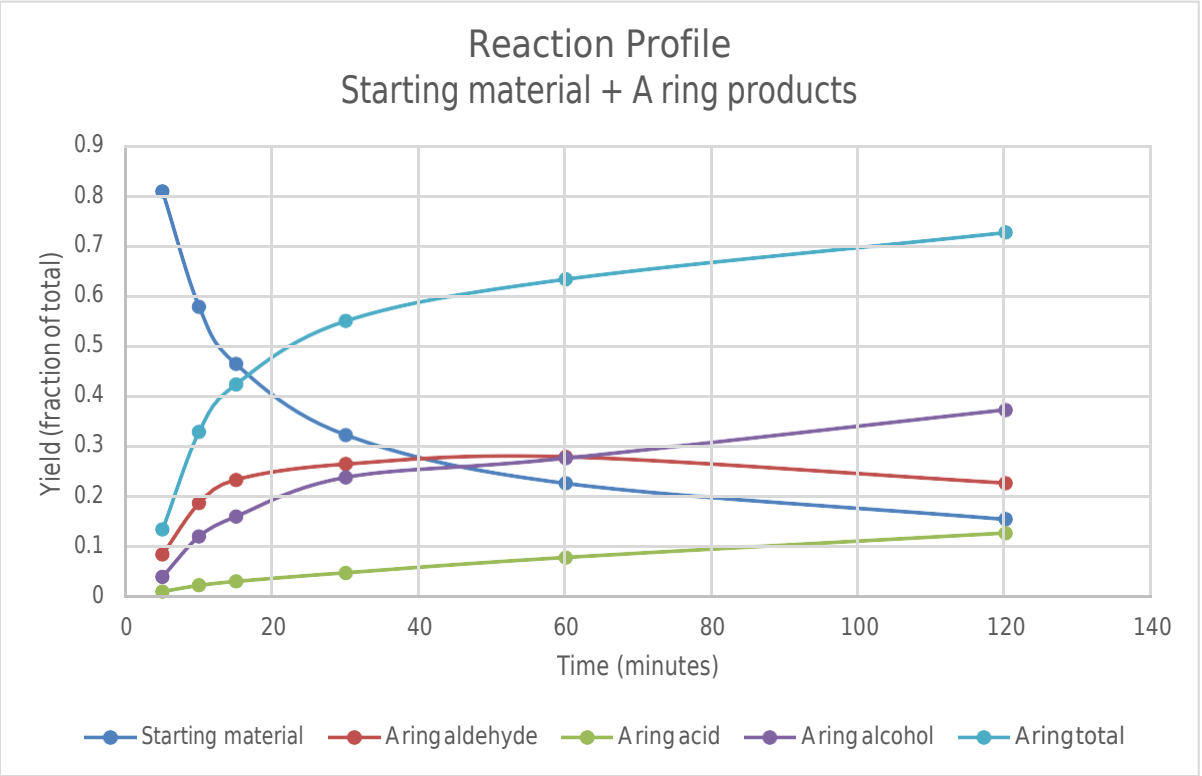


Figure S2 Reaction profile of starting material and A ring products during the Ir catalyzed cleavage of model **1**. Conditions: 1 mol% **Ir cat.** (in situ **16+17**), 1 eq. Na_2CO_3, 110 °C, dioxane/water (1:1). Yields were calculated by quantitative ^1H NMR analysis using the total aromatic integral as an internal standard.

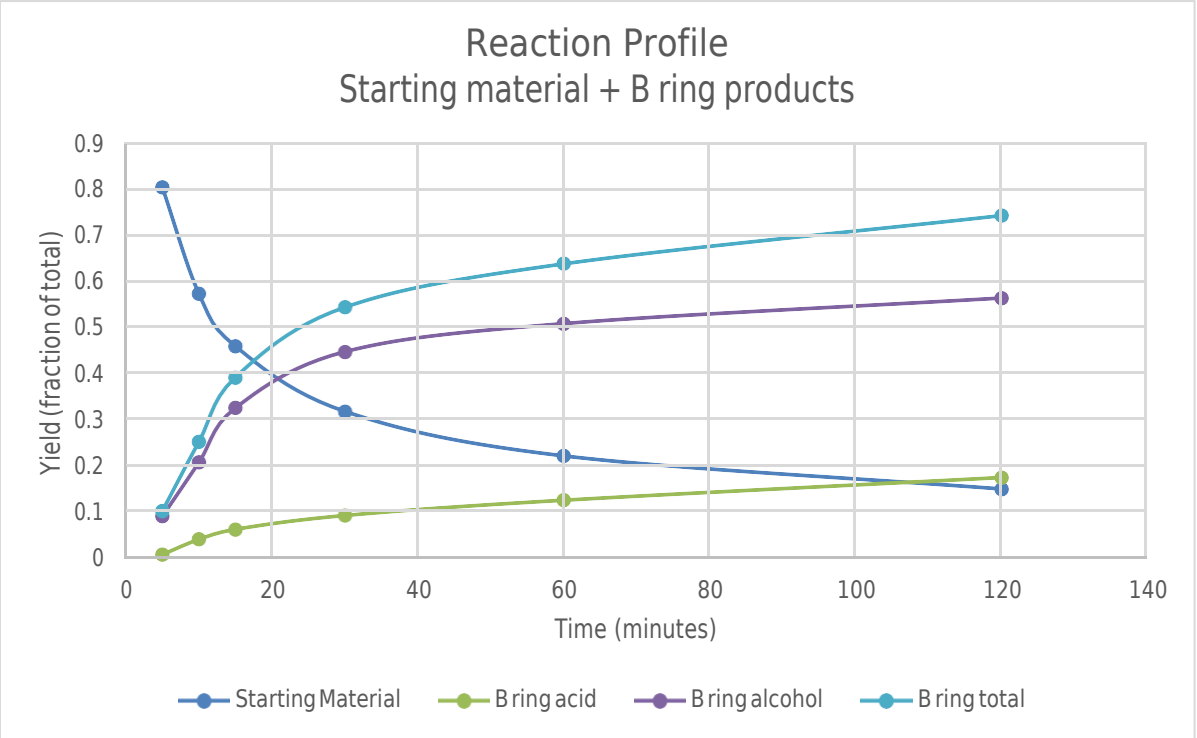


Figure S3 Reaction profile of starting material and B ring products during the Ir catalyzed cleavage of model **1**. Conditions: 1 mol% **Ir cat.** (in situ **16+17**), 1 eq. Na_2CO_3, 110 °C, dioxane/water (1:1). Yields were calculated by quantitative ^1H NMR analysis using the total aromatic integral as an internal standard.

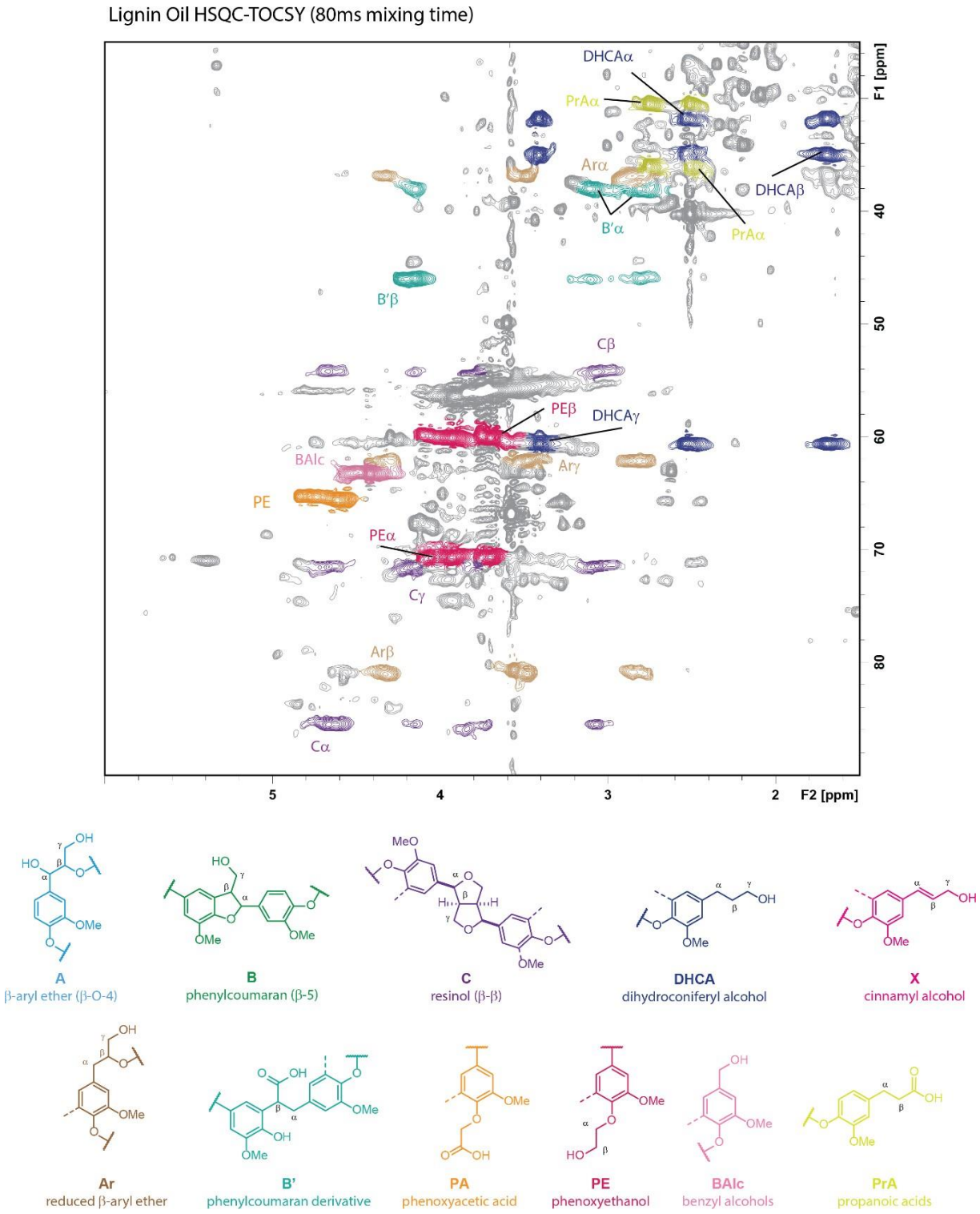


Figure S4 HSQC-TOCSY NMR analysis of the depolymerized lignin oil corresponding to Table 2, Entry 1 in the manuscript.

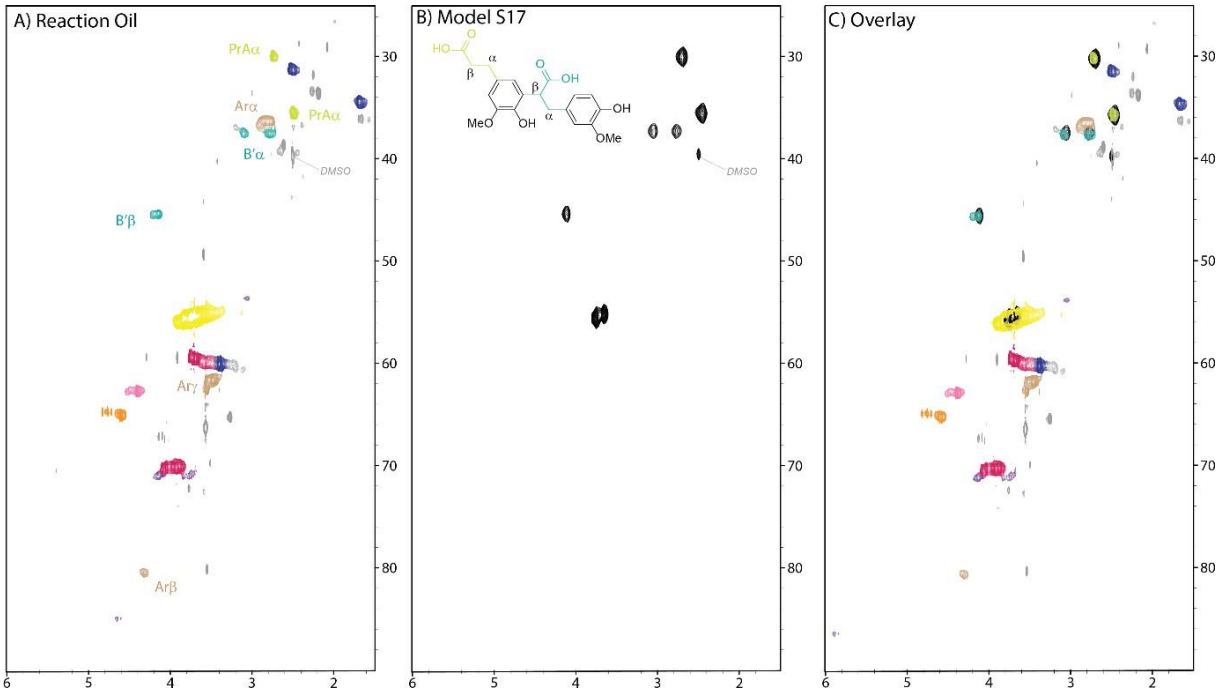


Figure S5 Comparison of the HSQC NMR spectra obtained from the depolymerized lignin oil corresponding to Table 2, Entry 1 in the manuscript and B' model **S17**.

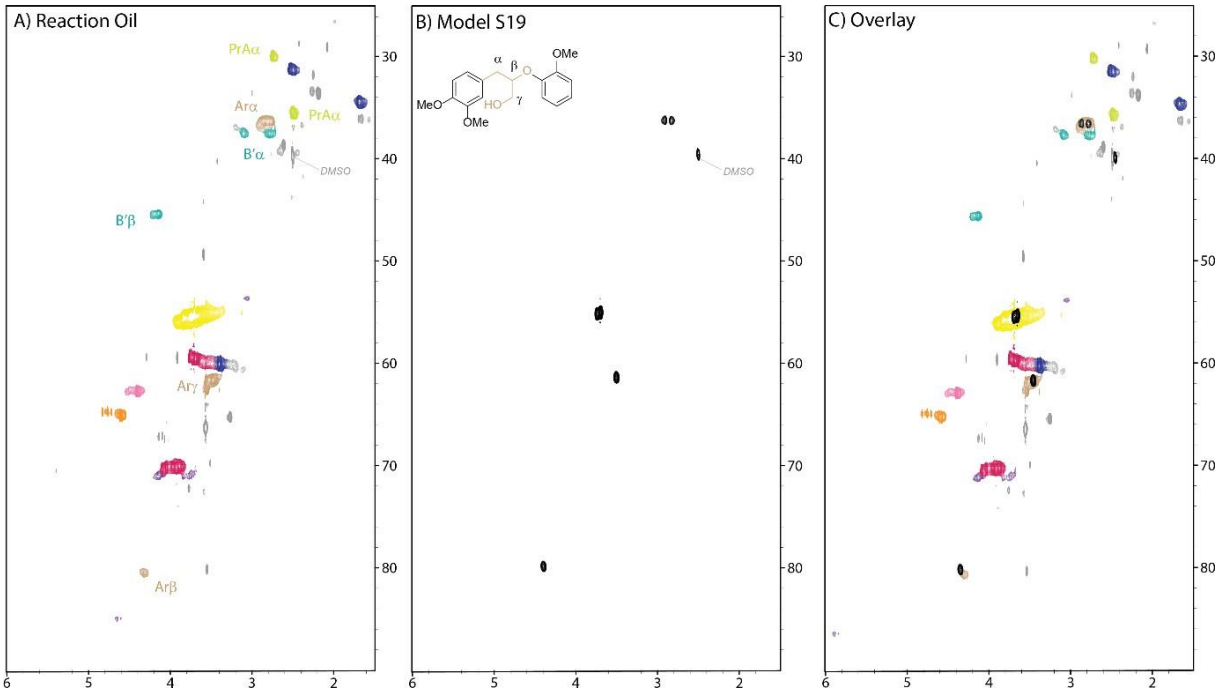


Figure S6 Comparison of the HSQC NMR spectra obtained from the depolymerized lignin oil corresponding to Table 2, Entry 1 in the manuscript and benzylic reduced β-O-4 model (Ar) **S19**.

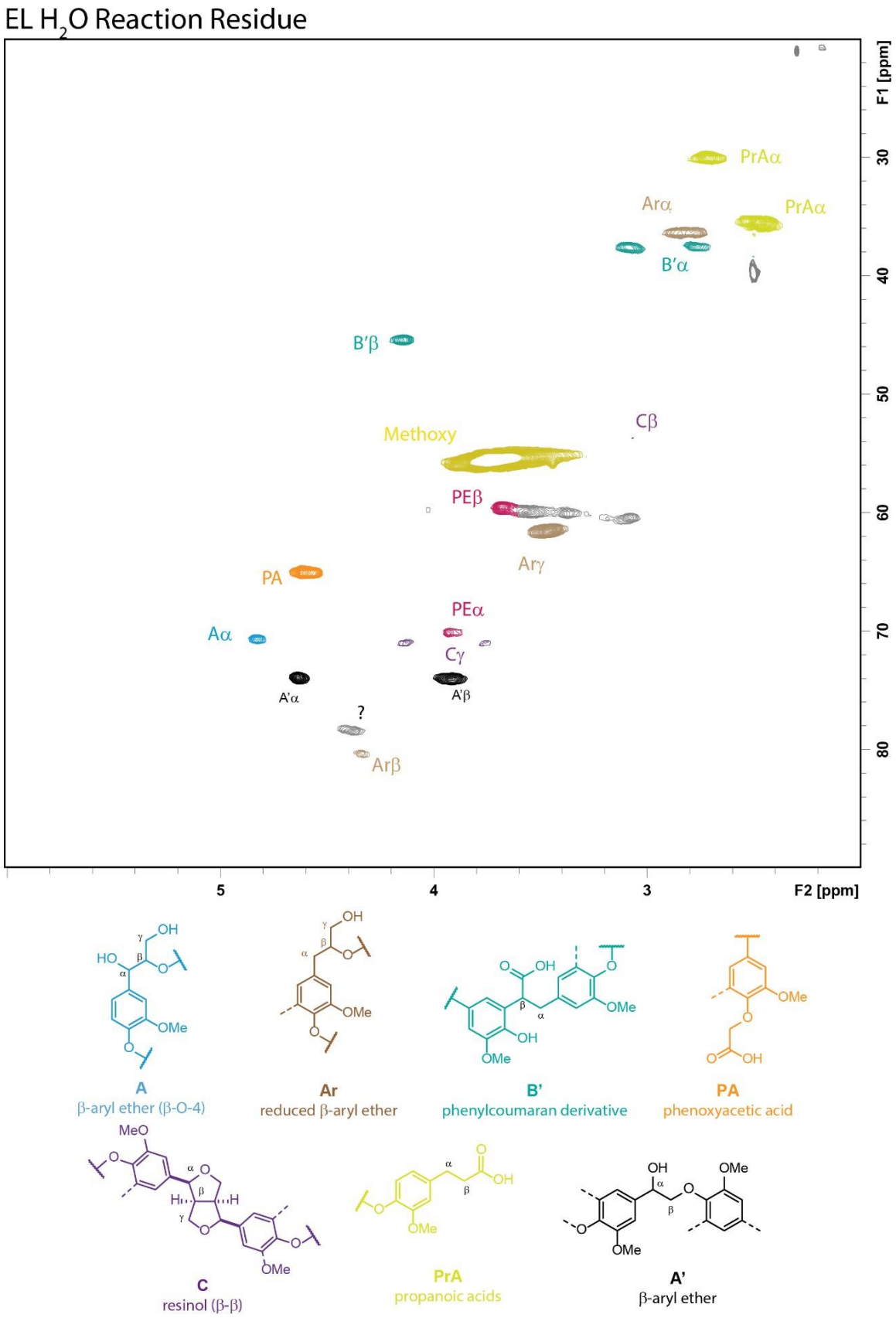


Figure S7 HSQC NMR spectrum obtained of the insoluble lignin residue from the attempted water only lignin depolymerization reaction corresponding to Table 2, Entry 5 in the manuscript. This demonstrates a much larger preference for dehydrogenation to acids and a secondary alcohol oxidation/retro-aldol/hydrogenation pathway to give A' units in water.

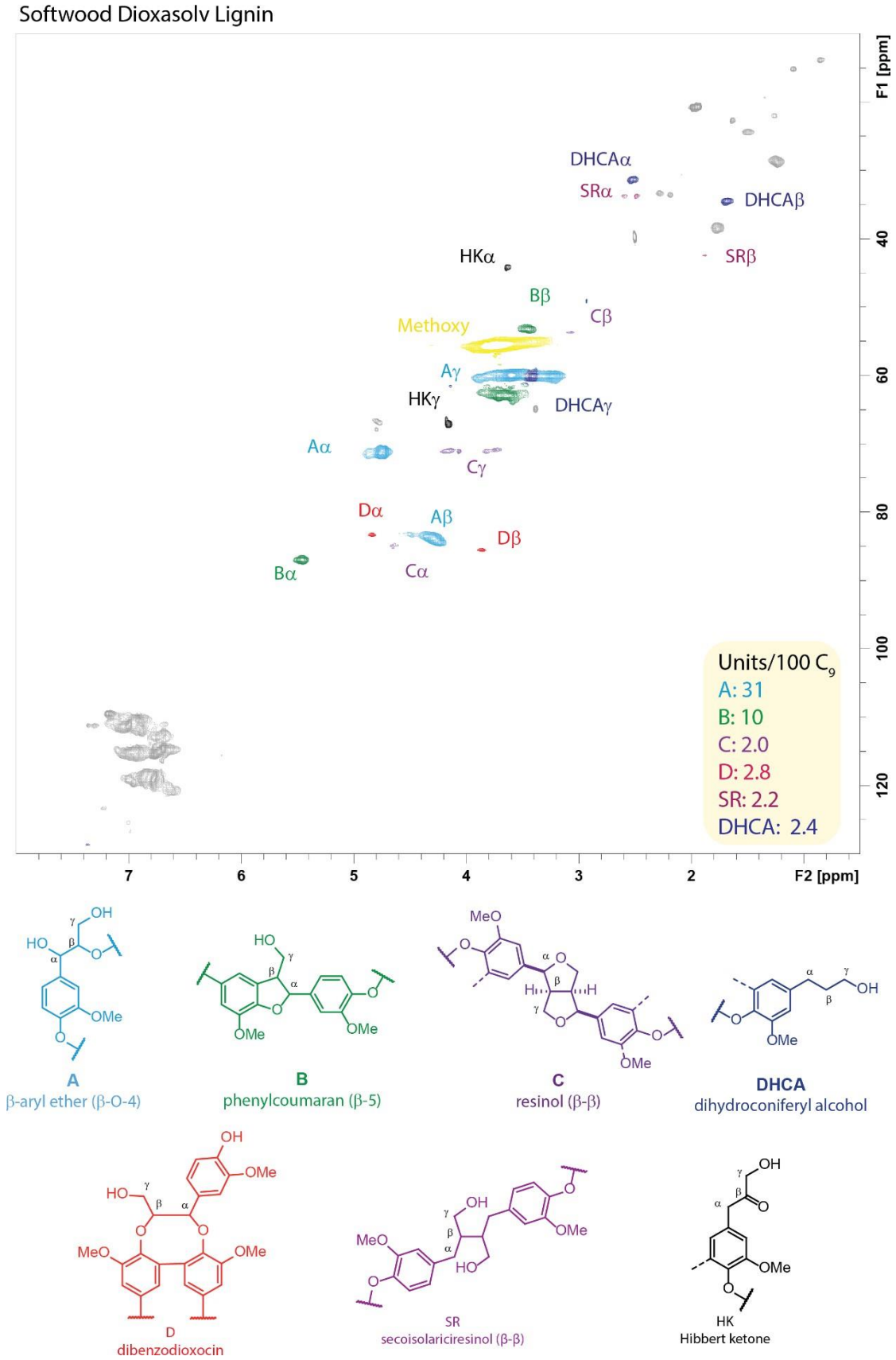


Figure S8 HSQC NMR spectrum of softwood dioxasolv lignin.

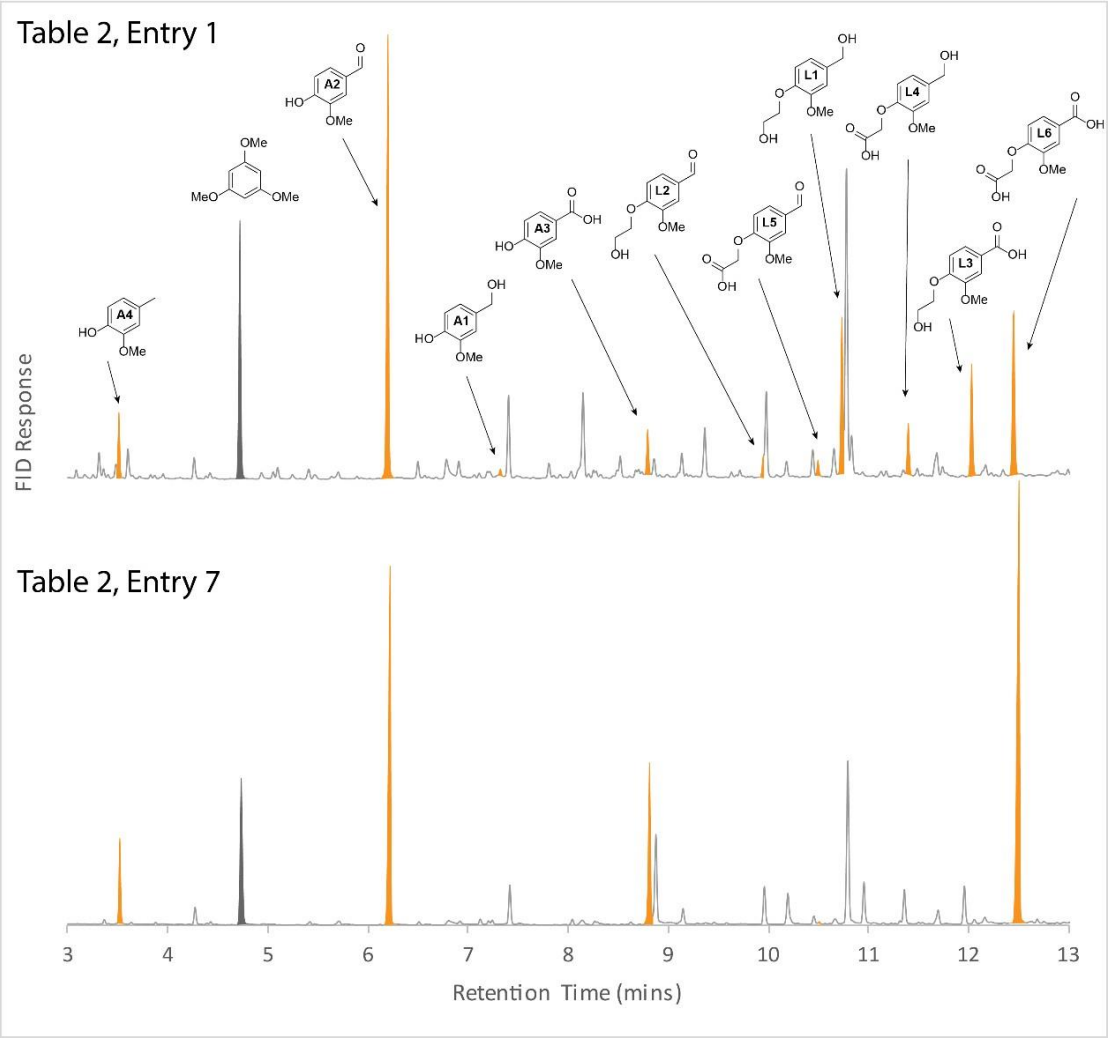


Figure S9 Examples of the GC-FID chromatograms obtained after lignin depolymerization reactions showing the identified monomeric products.

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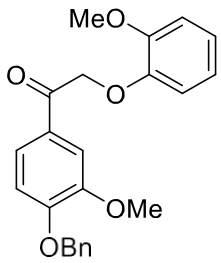
NMR Spectra



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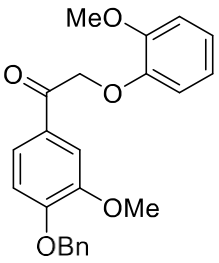

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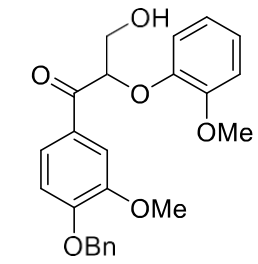

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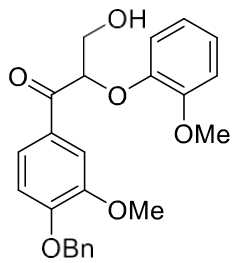

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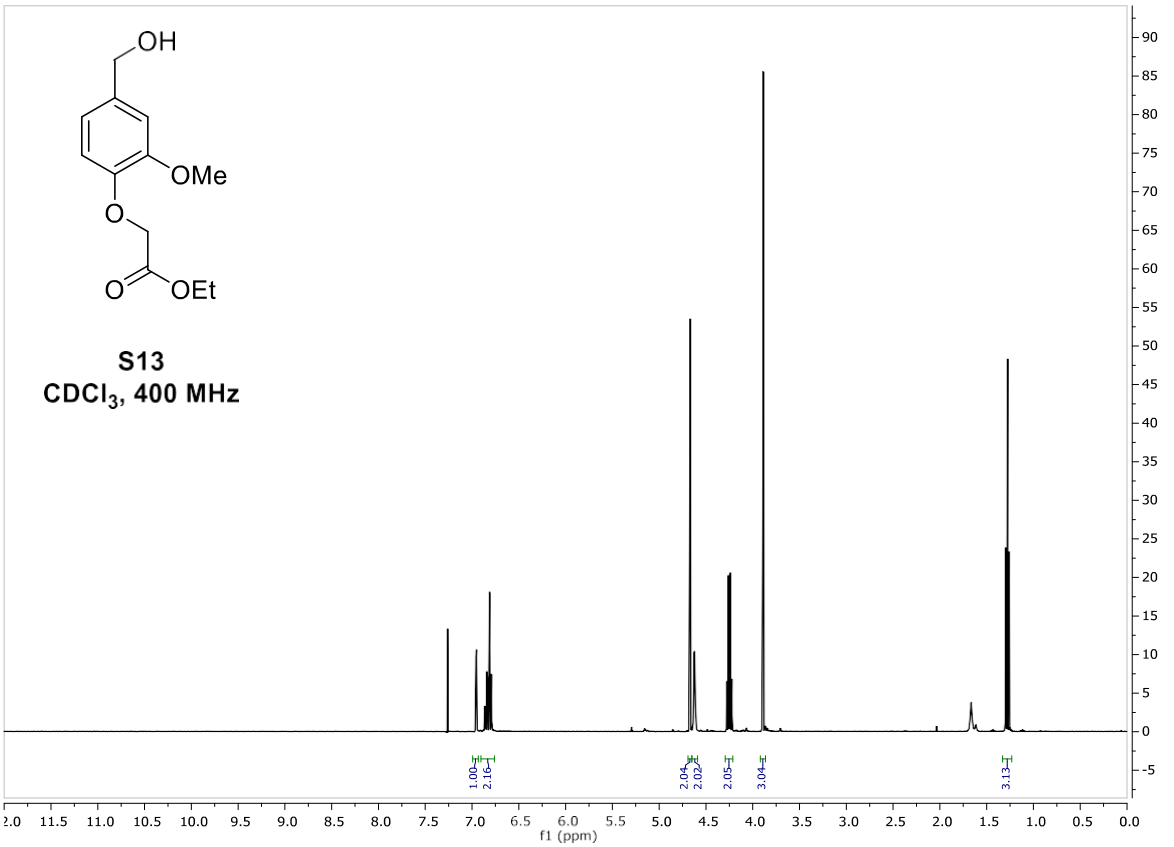
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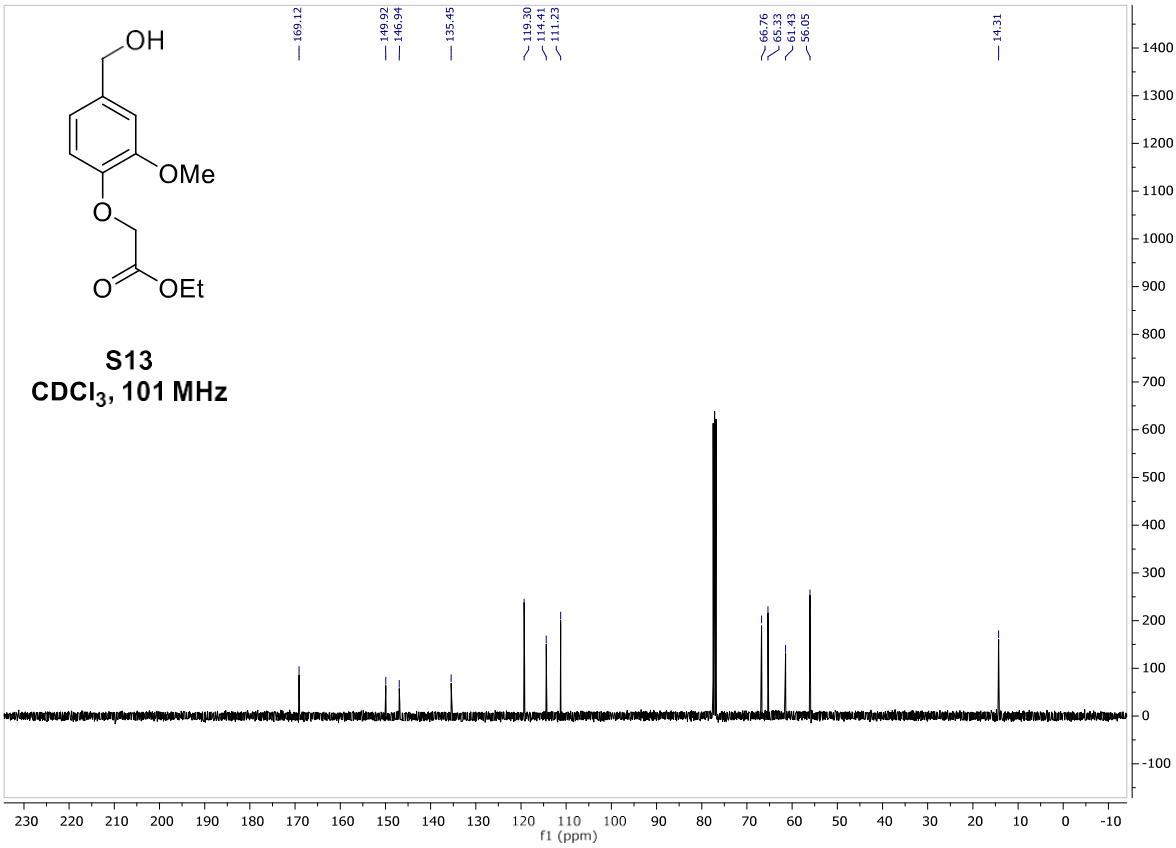
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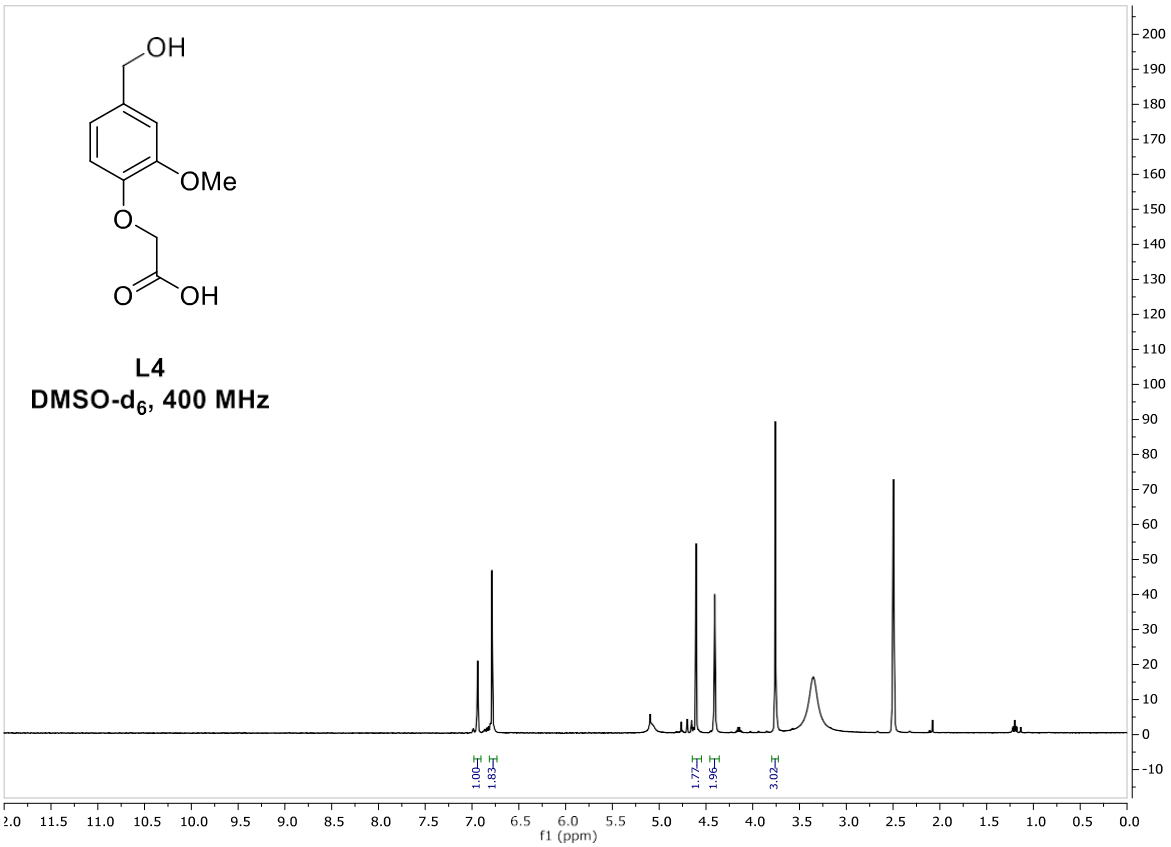
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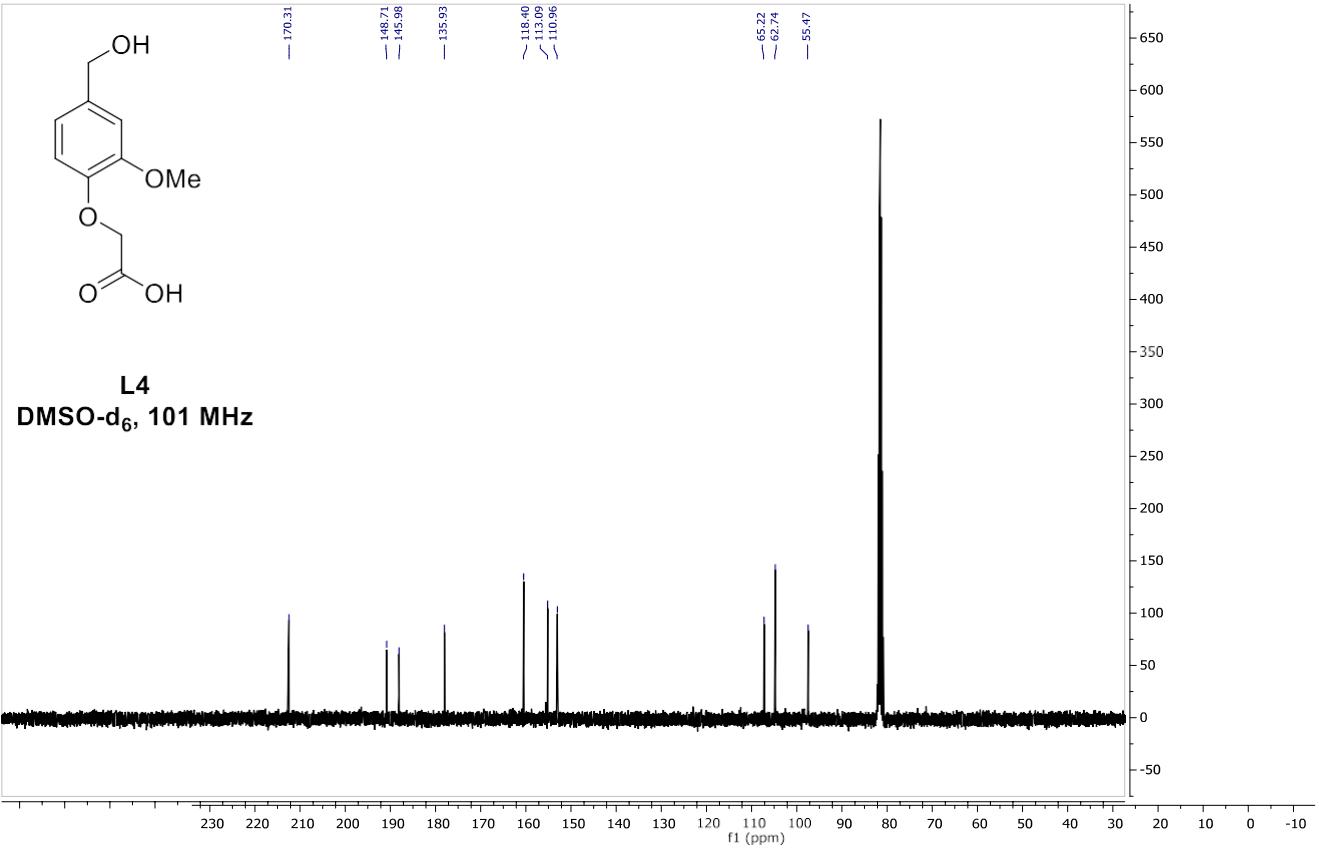
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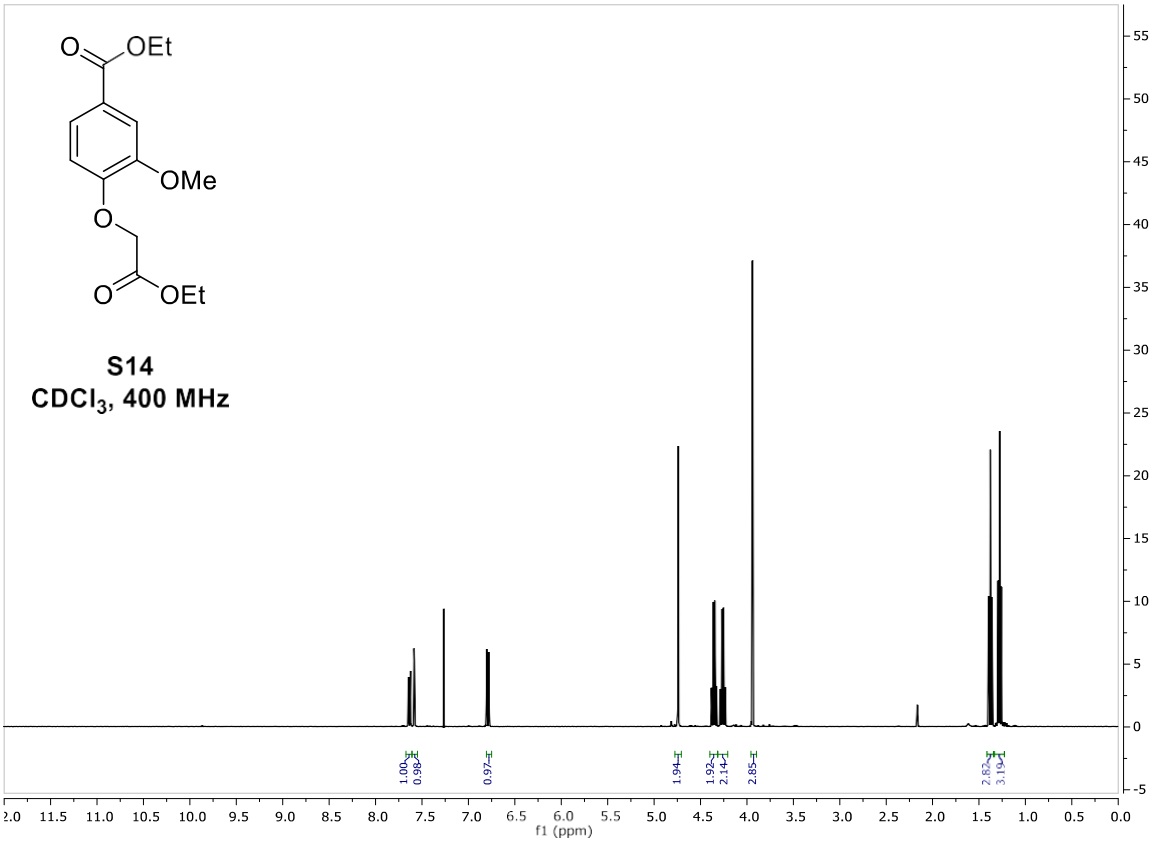
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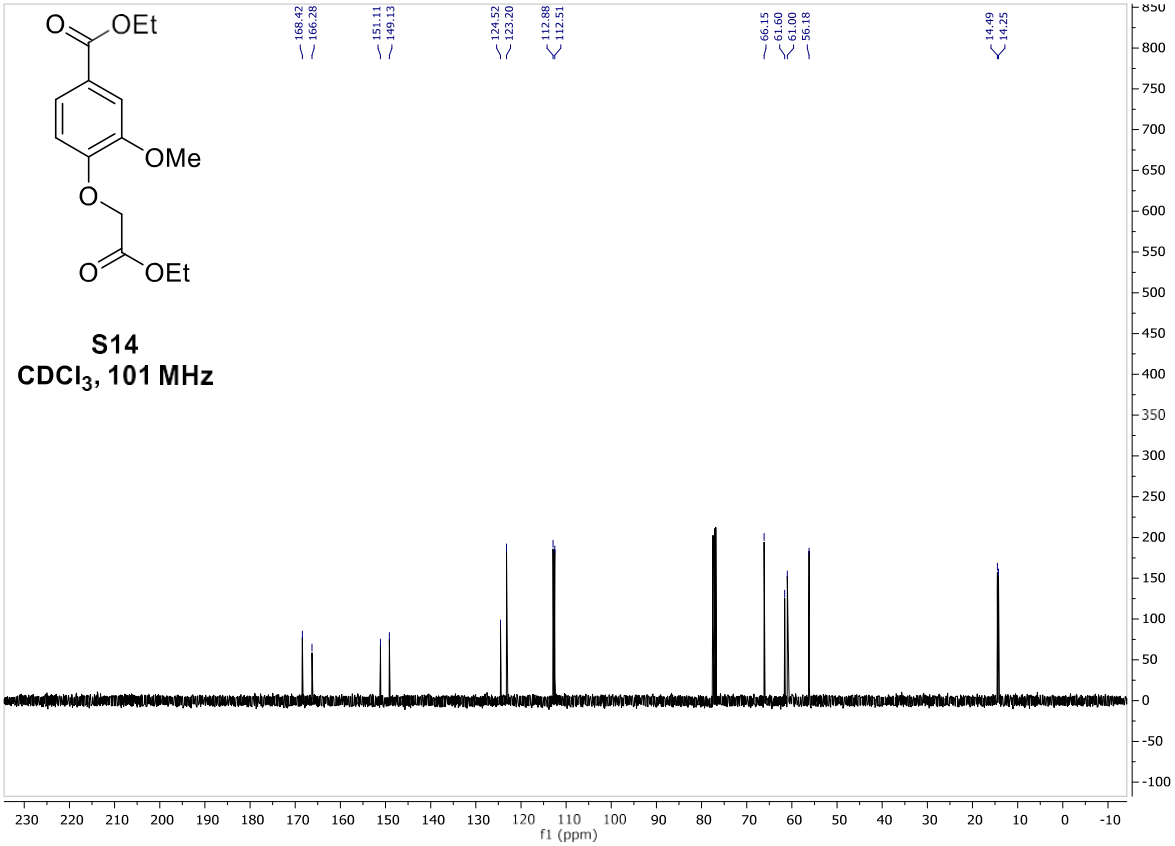
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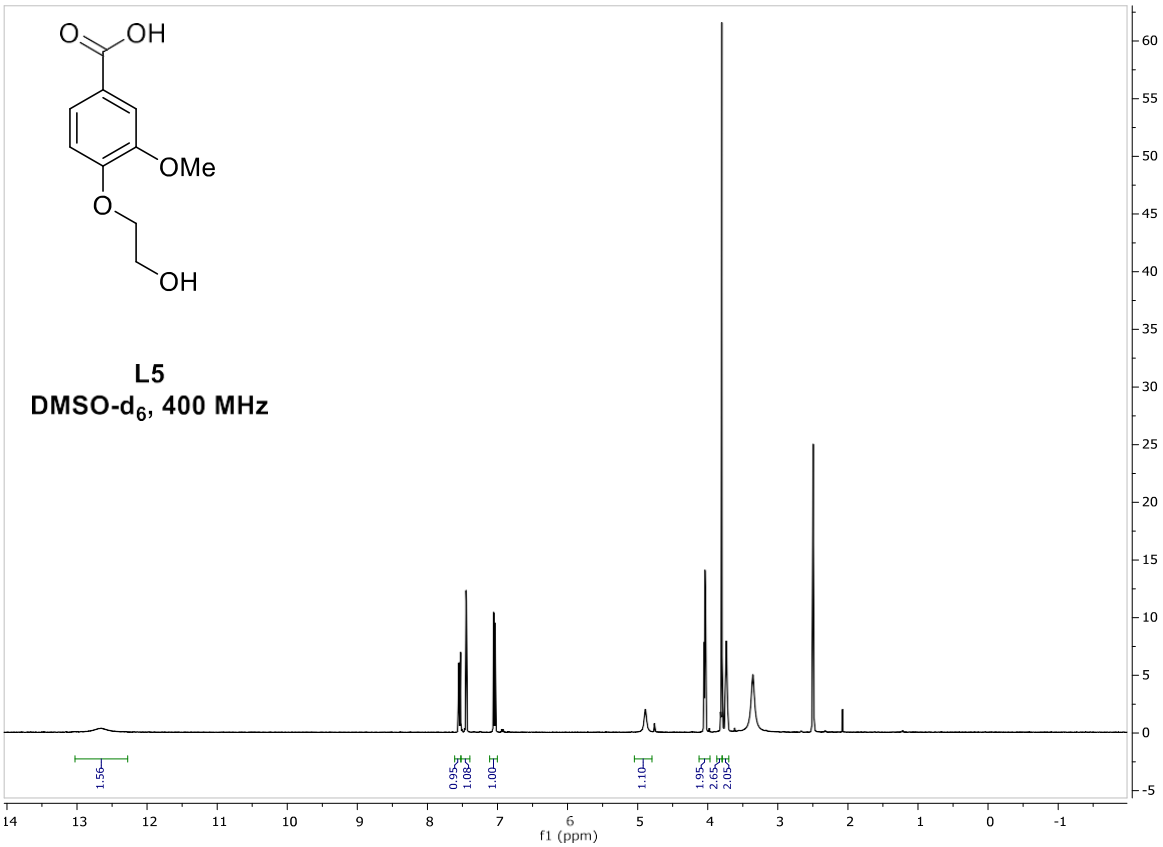
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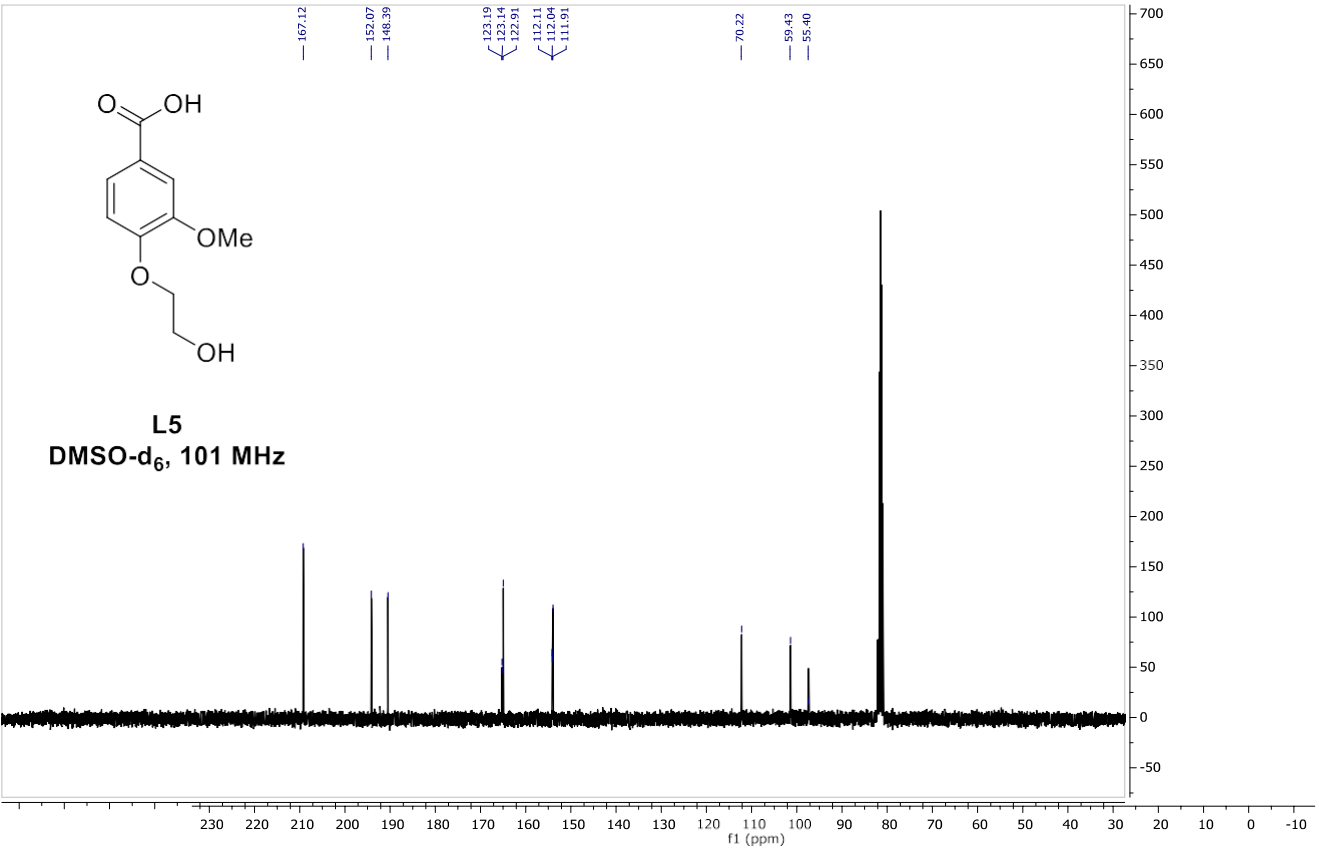
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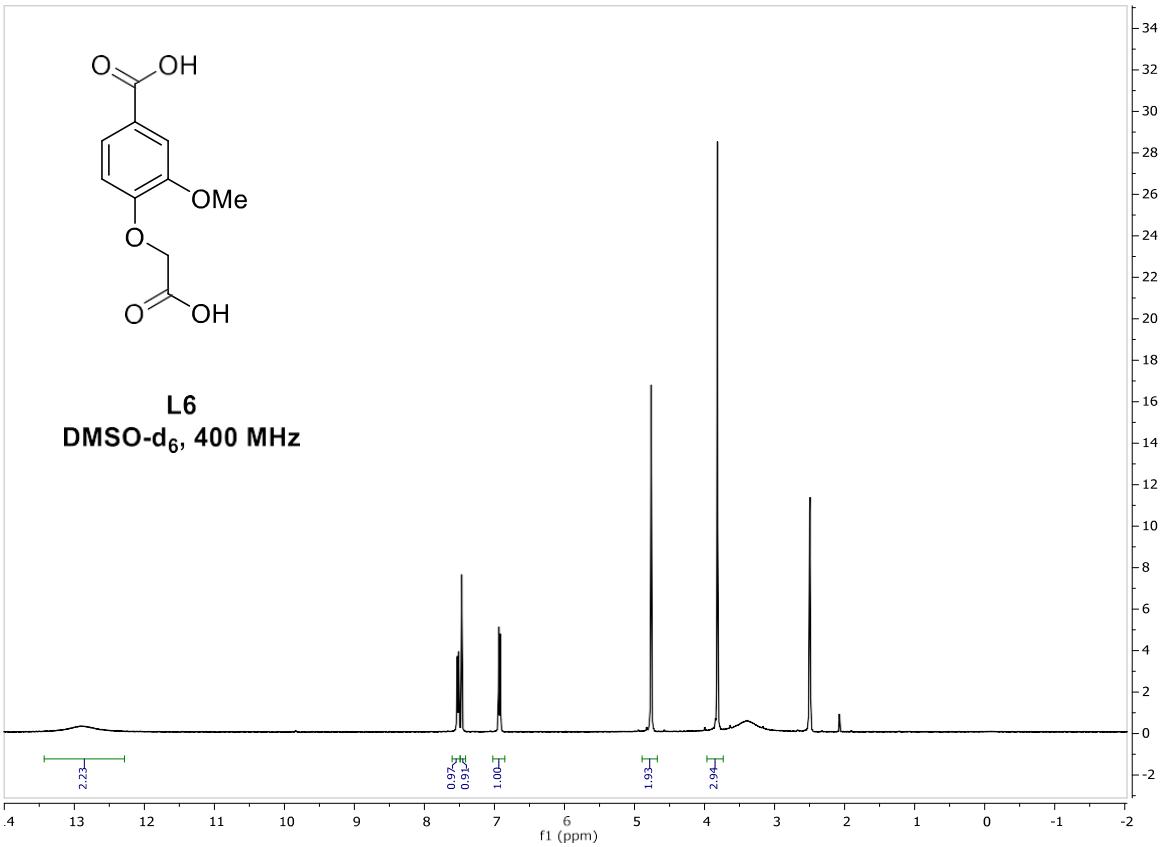
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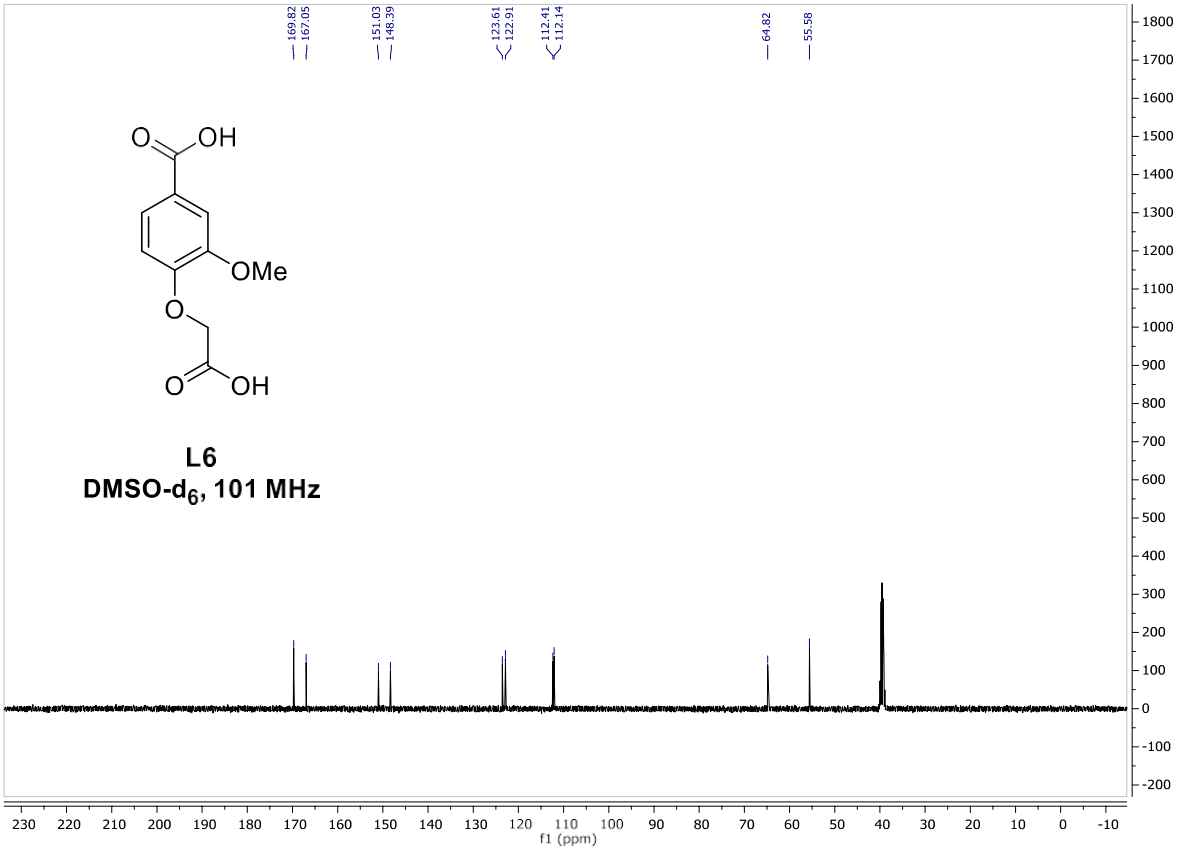
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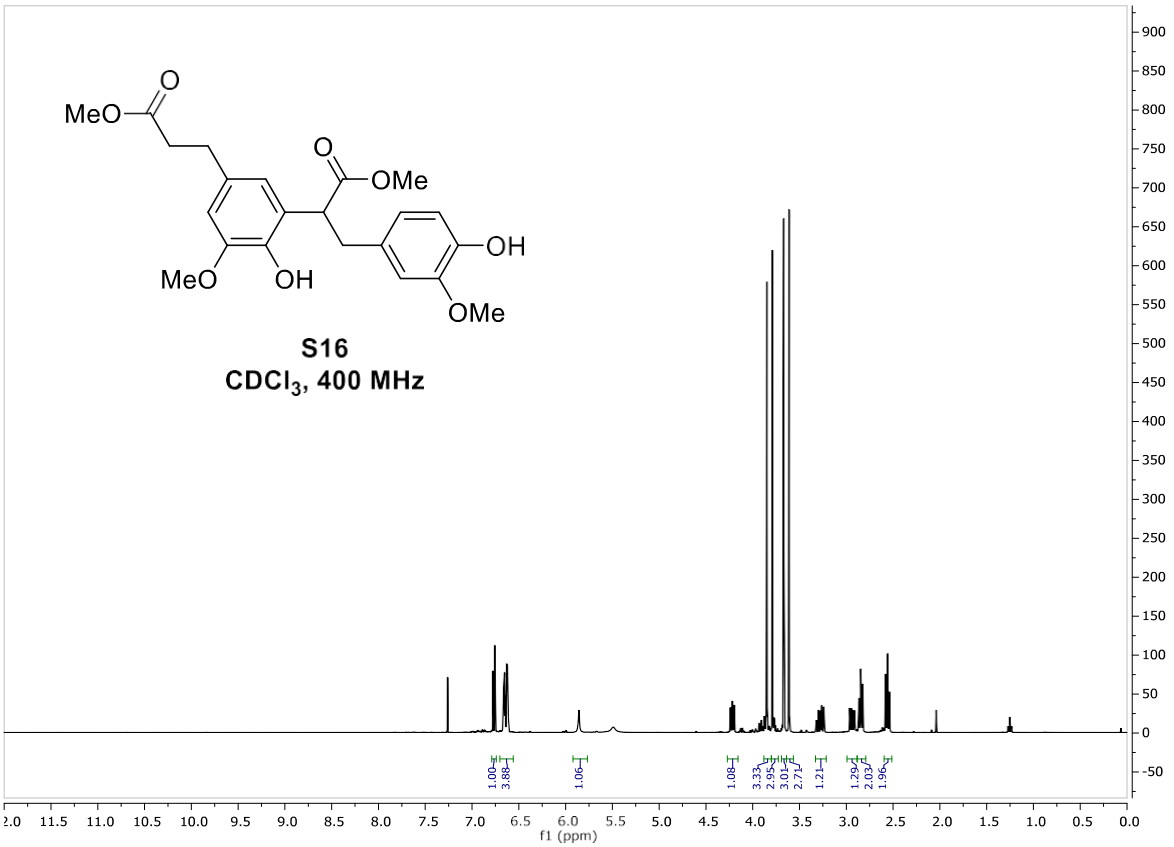
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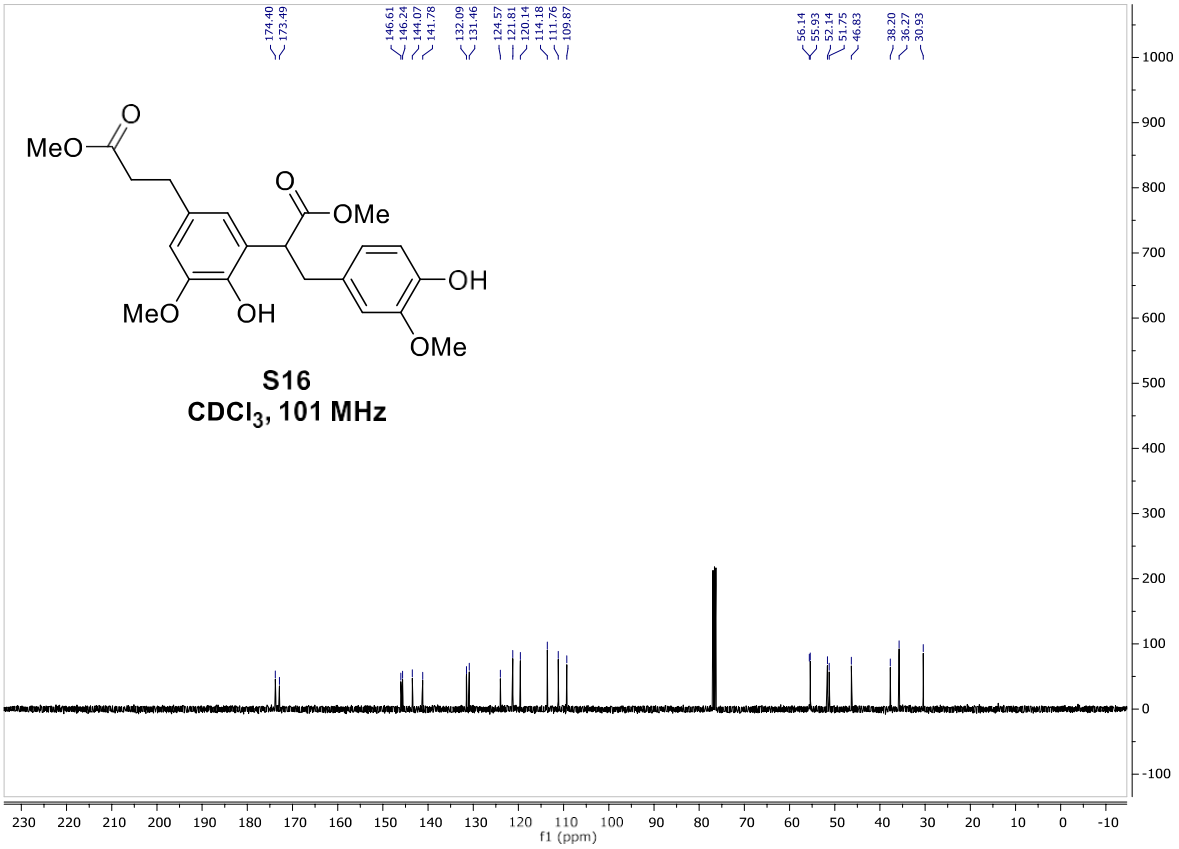
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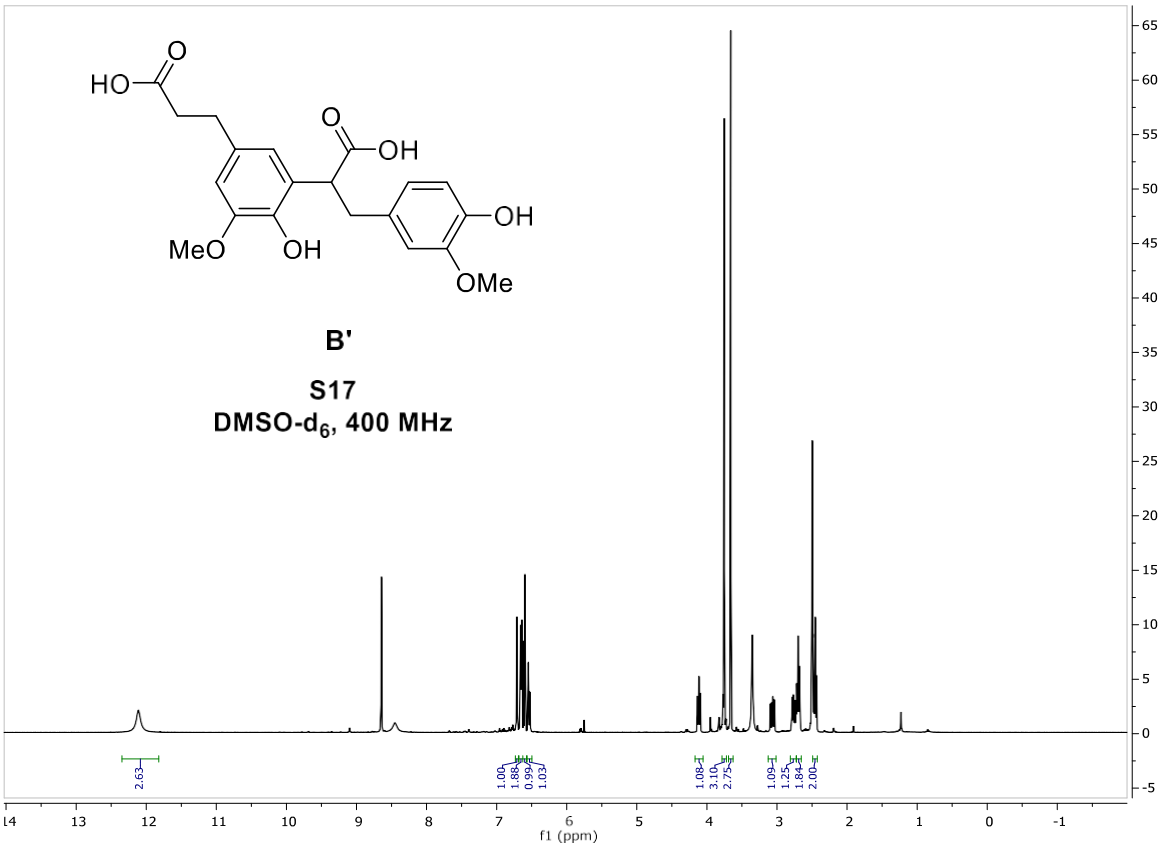
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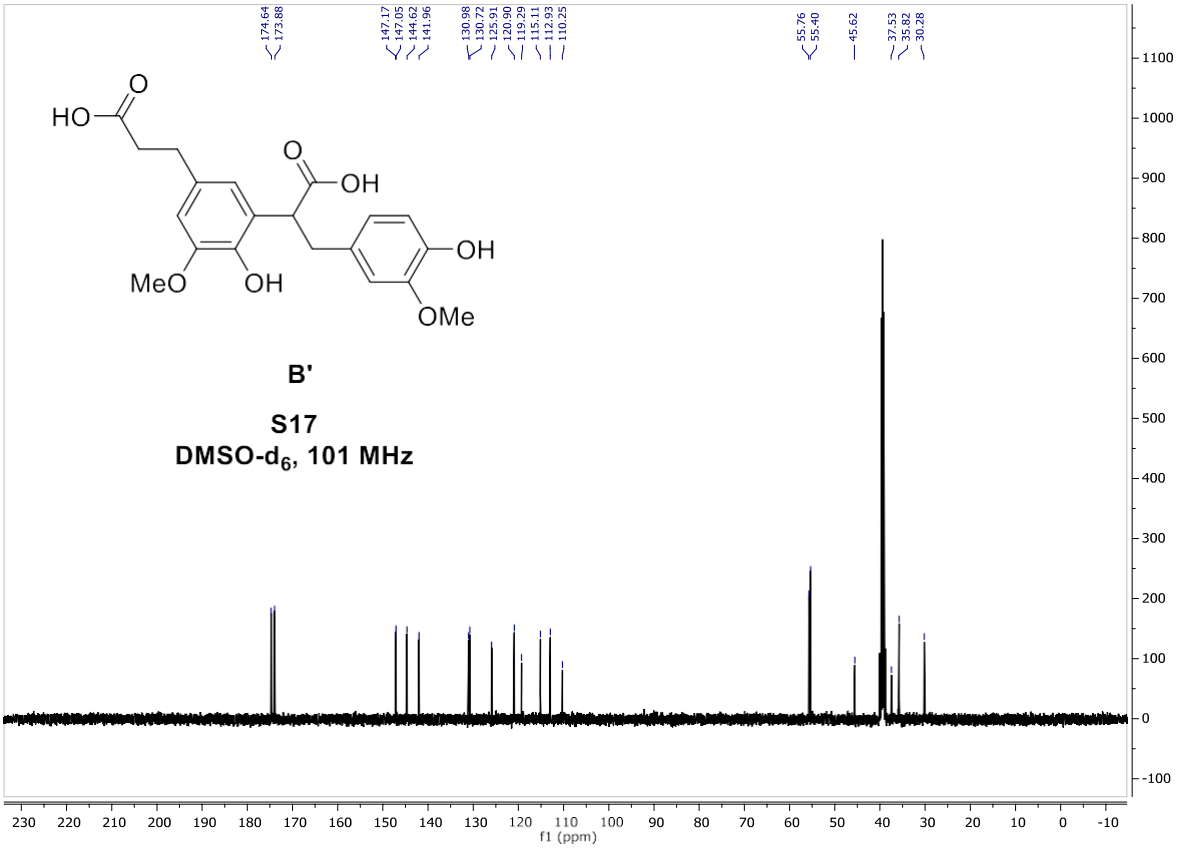
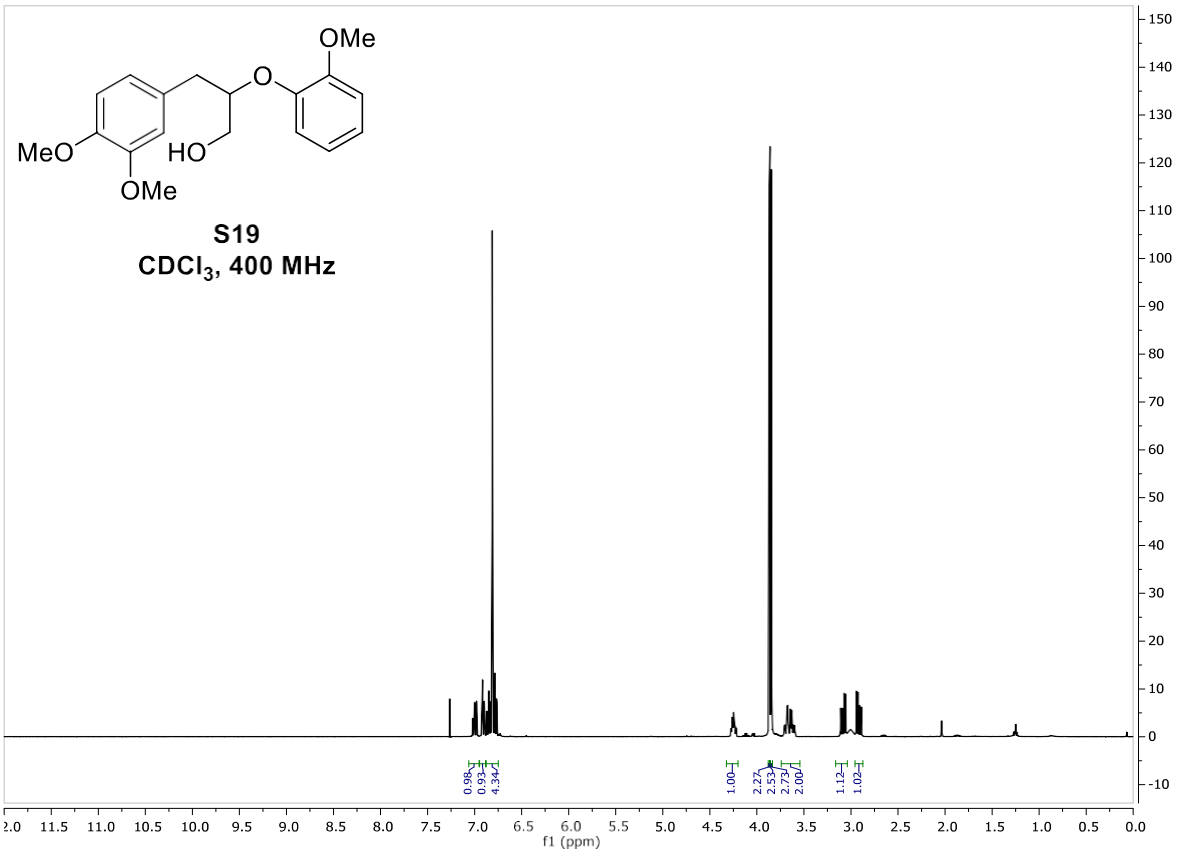
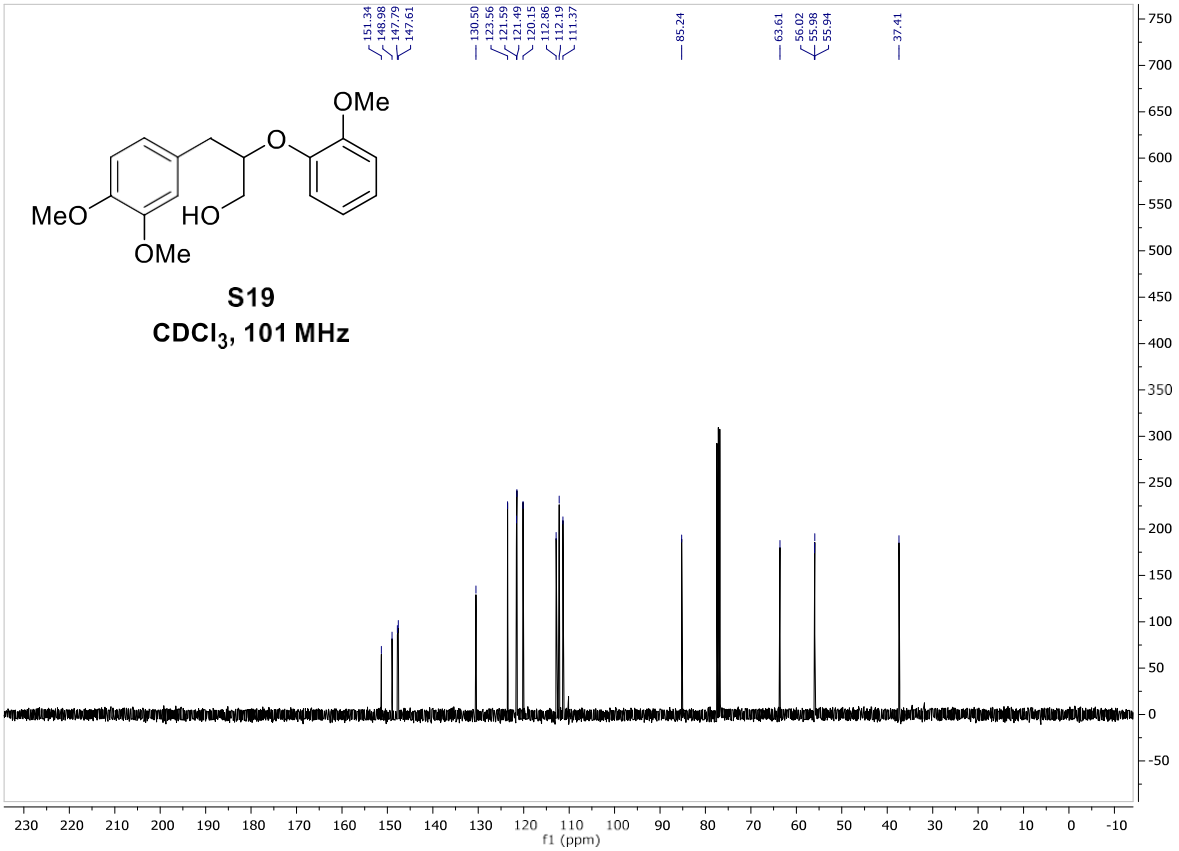
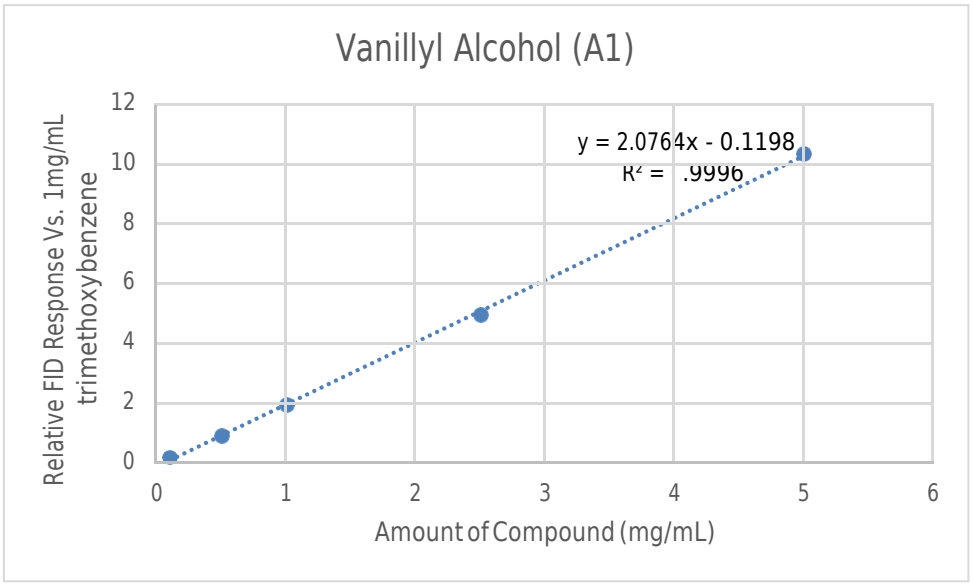
DMSO-d6, 400 MHz
f1 (ppm)

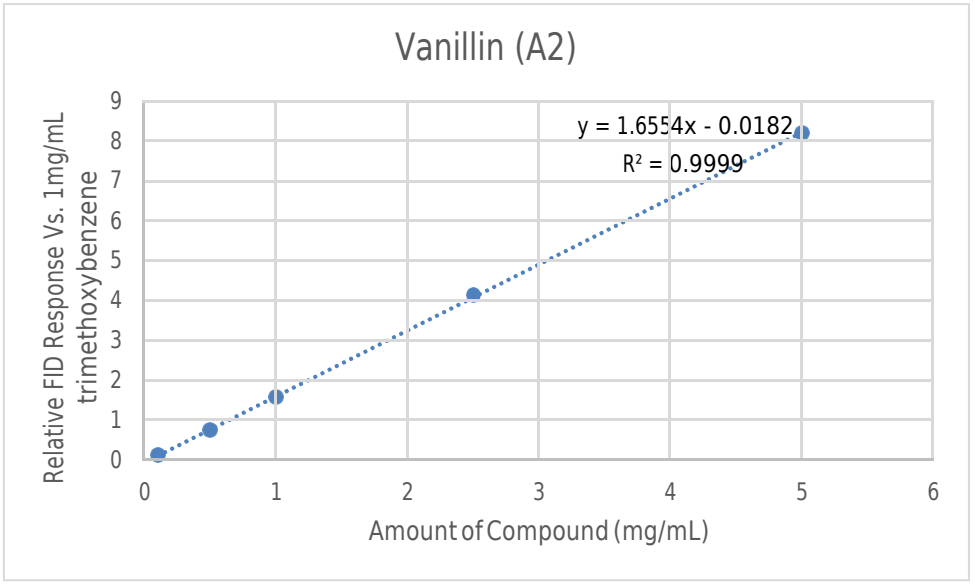

174.64
173.88
147.17
147.05
144.62
141.96
130.98
130.72
125.91
120.90
119.29
115.11
112.93
110.25
55.76
55.40
45.62
37.53
35.82
30.28
HO
O
O
OH
OH
MeO
OH
OMe
B'
S17
DMSO-d6, 101 MHz
f1 (ppm)

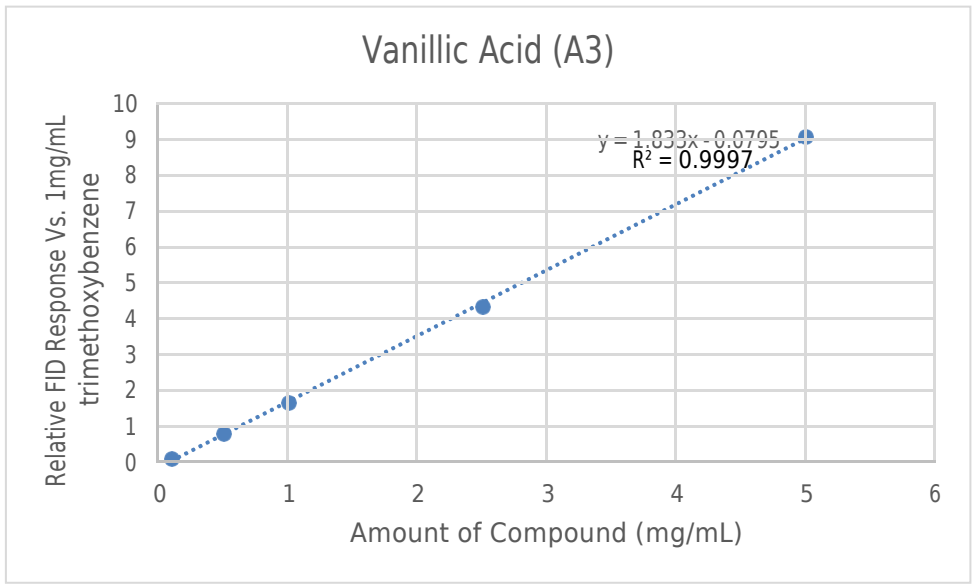

OMe
O
MeO
HO
OMe
S19
CDCl3, 400 MHz
f1 (ppm)

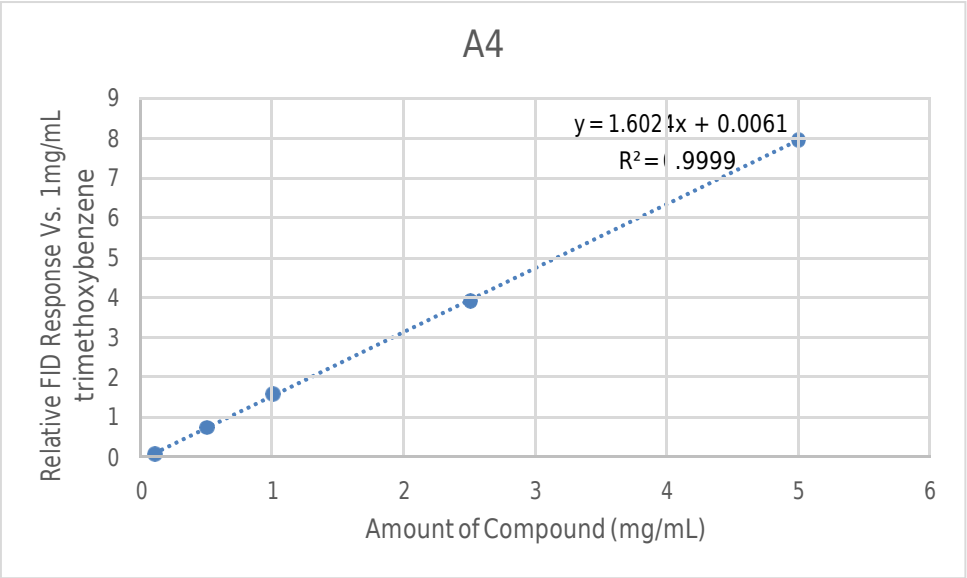

151.34
148.98
147.79
147.61
130.50
123.56
121.59
121.49
120.15
112.86
112.19
111.37
85.24
63.61
56.02
55.98
55.94
37.41
OMe
O
MeO
HO
OMe
S19
CDCl3, 101 MHz
f1 (ppm)

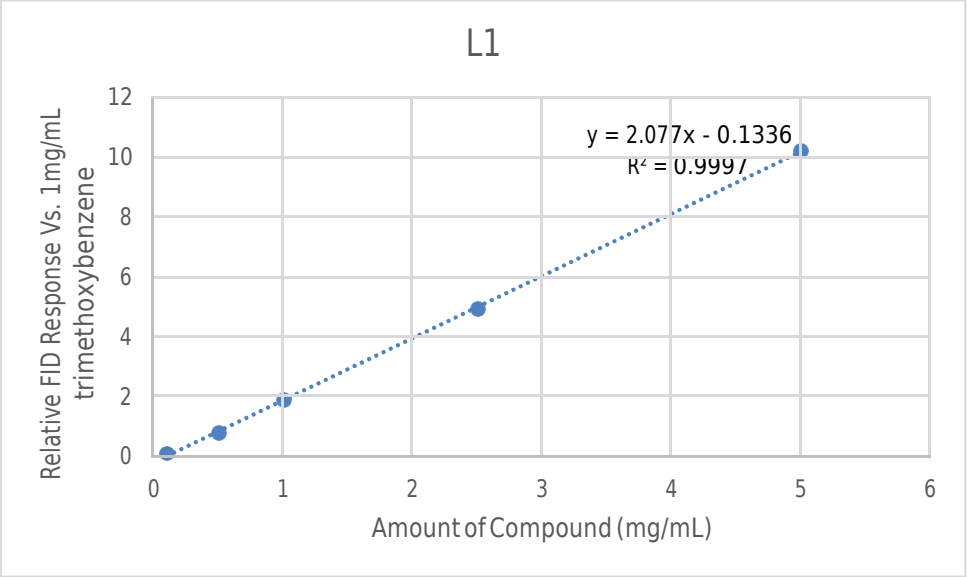
GC Calibration Curves

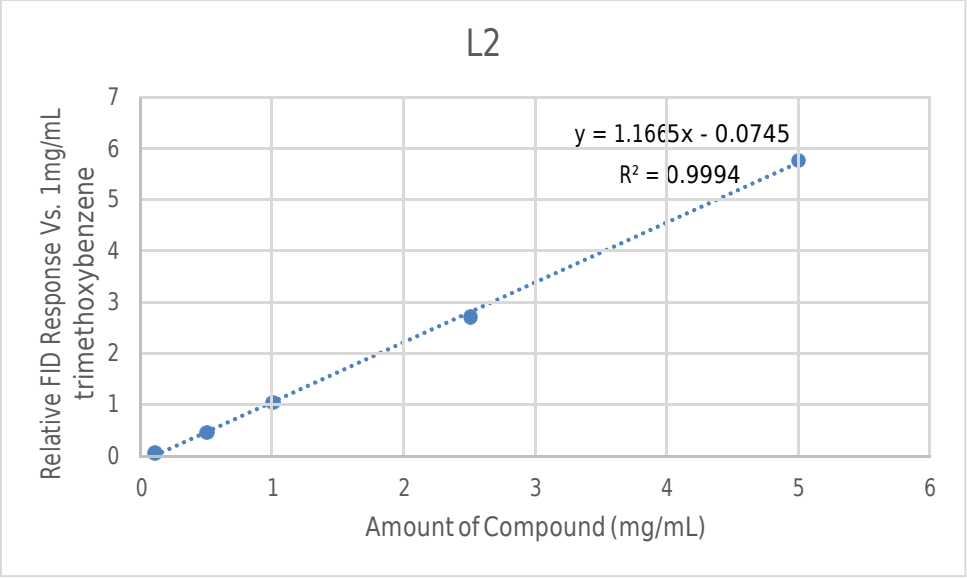


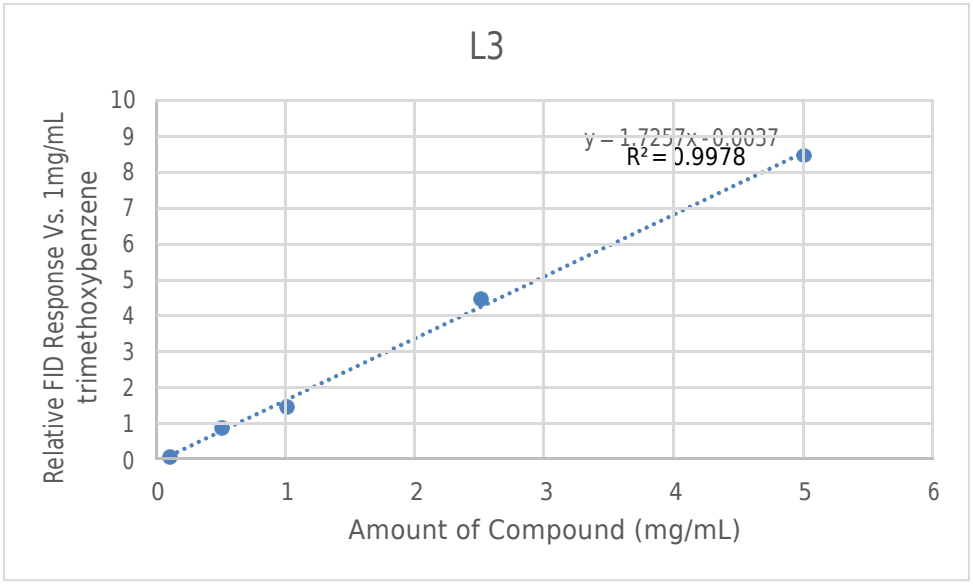


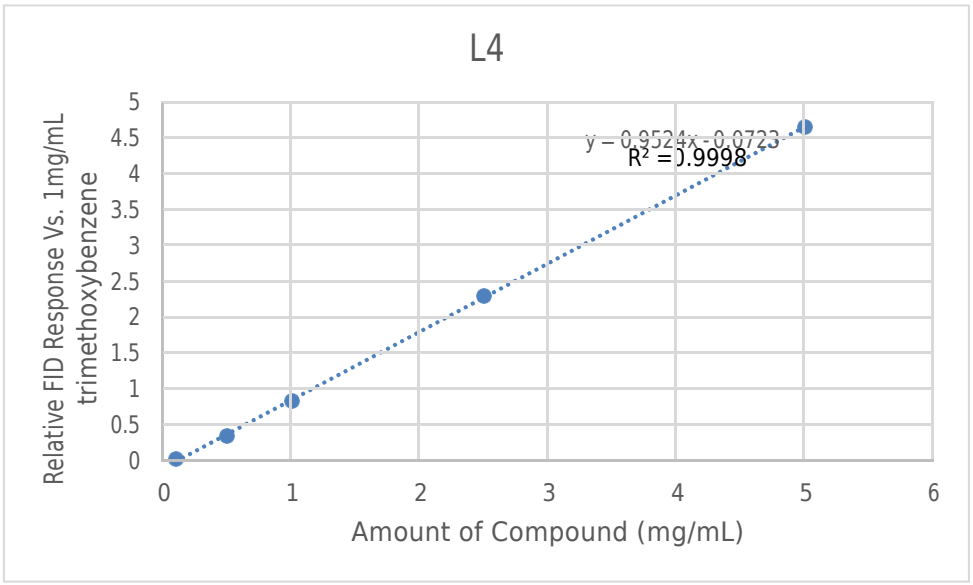


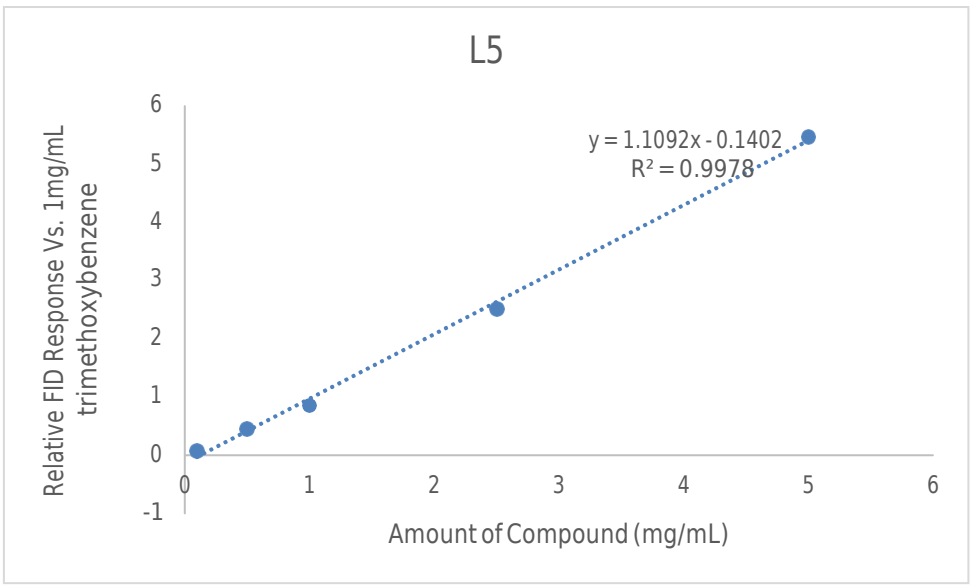

A4
y = 1.6021x + 0.0061
R² = 0.9999
Relative FID Response Vs. 1mg/mL trimethoxybenzene
Amount of Compound (mg/mL)
0
1
2
3
4
5
6
7
8
9

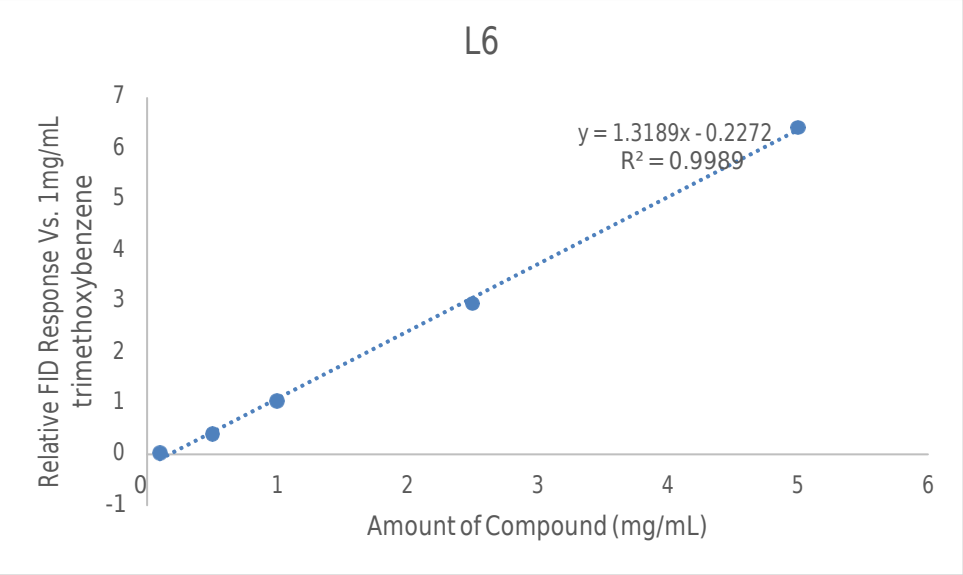

L1
y = 2.077x - 0.1336
R² = 0.9997
Relative FID Response Vs. 1mg/mL trimethoxybenzene
Amount of Compound (mg/mL)
0
2
4
6
8
10
12


L2
y = 1.1665x - 0.0745
R² = 0.9994
Relative FID Response Vs. 1mg/mL trimethoxybenzene
Amount of Compound (mg/mL)
0
1
2
3
4
5
6
7


L3
Relative FID Response Vs. 1mg/mL trimethoxybenzene
y = 1.7257x - 0.0037
R² = 0.9978
Amount of Compound (mg/mL)


L4
Relative FID Response Vs. 1mg/mL trimethoxybenzene
y = 0.9524x - 0.0723
R² = 0.9998
Amount of Compound (mg/mL)


L5
Relative FID Response Vs. 1mg/mL trimethoxybenzene
y = 1.1092x - 0.1402
R² = 0.9978
Amount of Compound (mg/mL)


L6
y = 1.3189x - 0.2272
R² = 0.9989
Relative FID Response Vs. 1mg/mL trimethoxybenzene
Amount of Compound (mg/mL)
7
6
5
4
3
2
1
0
-1
0
1
2
3
4
5
6