SUPPORTING INFORMATION
Decomposition of Lignin Models Enabled by Copper-Based Photocatalysis Under Biphasic Conditions

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GENERAL :

All reactions that were carried out under anhydrous conditions were performed under an inert argon or nitrogen atmosphere in glassware that had previously been dried overnight at 120 °C or had been flame dried and cooled under a stream of argon or nitrogen. All chemical products were obtained from Sigma-Aldrich Chemical Company, Oakwood Chemical or Alfa Aesar and were reagent quality. Technical solvents were obtained from VWR International Co. Anhydrous solvents (CH_2Cl_2, Et_2O, THF, DMF, toluene, and *n*-hexane) were dried and deoxygenated using a GlassContour system (Irvine, CA). Isolated yields reflect the mass obtained following flash column silica gel chromatography. Organic compounds were purified using silica gel obtained from Silicycle Chemical division (40-63 nm; 230-240 mesh). Analytical thin-layer chromatography (TLC) was performed on glass-backed silica gel 60 coated with a fluorescence indicator (Silicycle Chemical division, 0.25 mm, F254.). Visualization of TLC plate was performed by UV (254 nm), $KMnO_4$ or *p*-anisaldehyde stains. All mixed solvent eluents are reported

as v/v solutions. Concentration refers to removal of volatiles at low pressure on a rotary evaporator. All reported compounds were homogeneous by thin layer chromatography (TLC) and by ^{1}H NMR. NMR spectra were taken in deuterated $CDCl_3$ using Bruker AV-300 and AV-400 instruments unless otherwise noted. Signals due to the solvent served as the internal standard ($CHCl_3$: δ 7.27 for 1H, δ 77.0 for 13C). The acquisition parameters are shown on all spectra. The ^{1}H NMR chemical shifts and coupling constants were determined assuming first-order behavior. Multiplicity is indicated by one or more of the following: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad); the list of couplings constants (*J*) corresponds to the order of the multiplicity assignment. High resolution mass spectroscopy (HRMS) was done by the Centre régional de spectrométrie de masse at the Département de Chimie, Université de Montréal from an Agilent LC-MSD TOF system using ESI mode of ionization unless otherwise noted.

SYNTHESIS OF LIGANDS AND CATALYSTS

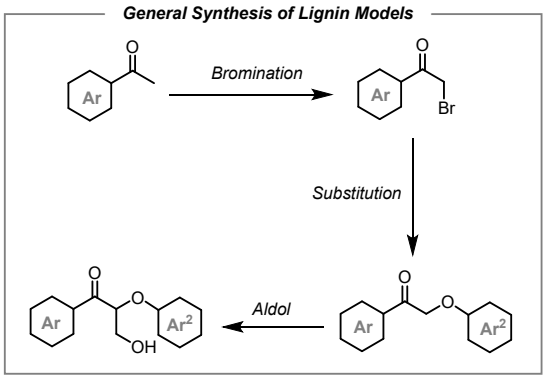
General Comments/Procedures for Ligands:

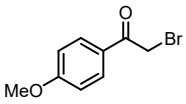
Commercially available diimines include: 1,10-phenanthroline (**phen**), 2,9-dimethyl-1,10-phenanthroline (**dmp**), 3,4,7,8-tetramethyl-1,10-phenanthroline (**tmp**), 4-4′-dimethoxy-2-2′-bipyridine (**dmbp**), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (**dtbbp**), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (**batho**), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (**bathocup)** 2,2′-biquinoline (**dq**). Previously synthesized diimines[1-4] include: 2-(1-(p-tolyl)-1H-1,2,3-triazol-4-yl)pyridine (**pytri**), 2-(1-(p-tolyl)-1H-1,2,3-triazol-4-yl)quinoline (**quintri**), 1-(1-(p-tolyl)-1H-1,2,3-triazol-4-yl)isoquinoline (**iquintri**), 3,6-dimethyl-dipyrido[3,2-f:2′,3′-h]-quinoxaline (**ddpq**), 3,6-dimethyldipyrido[3,2-a:2',3'-c]phenazine (**ddppz**), 3,6-dimethylbenzo[i]dipyrido[3,2-a:2',3'-c]phenazine (**dbdppz**), di(pyridin-3-yl)amine **(dpa)**, 2,9-dibutyl-1,10-phenanthroline **(bphen)** and 1,10-phenanthroline-5,6-dione **(dmop).**

The optimized catalyst Cu(**batho**)(**XantPhos**)BF_4 was prepared using a reported procedure.[4] The photophysical properties have been investigated by several groups. A summary is provided below:

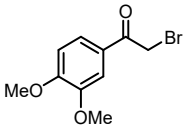
Abs max (nm) (CH_2Cl_2)[4]	Em max (nm) (CH_2Cl_2)[4]	Lifetime (μs) (DME:H_2O)	ET (eV) (CH_2Cl_2)[4]	E*red vs SCE (MeCN)[5]	E* ox vs SCE (MeCN)[5]
397	441	2.6	2.66	-1,37 V	+1,05 V

SUBSTRATE SYNTHESIS

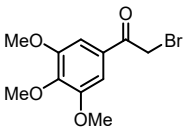




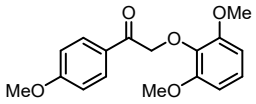
2-Bromo-1-(4-methoxyphenyl)ethan-1-one (2aS): To a solution of 1-(4-methoxyphenyl)ethan-1-one (1.50 g, 9.99 mmol) in EtOAc (30 mL, 333 mM) is added $CuBr_2$ (3.35 g, 15.0 mmol). The reaction mixture was stirred overnight at 90°C. The reaction was then allowed to cool to room temperature and filtered through a filter paper. The filtrate was added to a separatory funnel along with water (30 mL). It was then extracted three times with EtOAc (3 X 30 mL) and the combined organic phases were dried with Na_2SO_4 (2 g) and concentrated *in vacuo*. The product was then purified by column chromatography with Hexanes/EtOAc (8 : 2) to give a pink solid (1.48 g, 65%). Spectral data were in accordance with previous report.[6] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.00 (dt, 2H), 6.98 (dt, 2H), 4.43 (s, 2H), 3.91 (s, 3H).



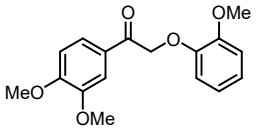
2-Bromo-1-(3,4-dimethoxyphenyl)ethan-1-one (1aS): To a solution of 1-(3,4-dimethoxyphenyl)ethan-1-one (1.80 g, 9.99 mmol) in EtOAc (30 mL, 333 mM) is added $CuBr_2$ (3.35 g, 15.0 mmol). The reaction mixture was stirred overnight at 90°C. The reaction was then allowed to cool to room temperature and filtered through a filter paper. The filtrate was added to a separatory funnel along with water (30 mL). It was then extracted three times with EtOAc (3 X 30 mL) and the combined organic phases were dried with Na_2SO_4 (2 g) and concentrated *in vacuo*. The product was then purified by flash chromatography (Hexanes : EtOAc ; 8 : 2) to give a slightly yellow solid (1.33 g, 51%). Spectral data were in accordance with previous report.[6] **H NMR (400 MHz, $CDCl_3$)**: δ 7.65 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.58 (d, *J* = 2.1 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 4.44 (s, 2H), 4.00 (s, 3H), 3.98 (s, 3H).



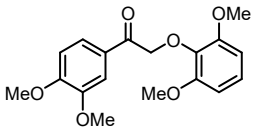
2-Bromo-1-(3,4,5-trimethoxyphenyl)ethan-1-one (10aS): To a solution of 1-(3,4,5-trimethoxyphenyl)ethan-1-one (2.10 g, 9.99 mmol) in EtOAc (30 mL, 333 mM) is added $CuBr_2$ (3.35 g, 15.0 mmol). The reaction mixture was stirred overnight at 90°C. The reaction was then allowed to cool to room temperature and filtered through a filter paper. The filtrate was added to a separatory funnel along with water (30 mL). It was then extracted three times with EtOAc (3 X 30 mL) and the combined organic phase was dried with Na_2SO_4 (2 g) and concentrated *in vacuo*. The product was then purified by flash chromatograph (Hexanes : EtOAc ; 8 : 2) to give a yellow solid (2.17 g, 75%). Spectral data were in accordance with previous report.[6] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.00 (m, 2H), 6.98 (m, 2H), 4.43 (s, 2H), 3.91 (s, 3H).



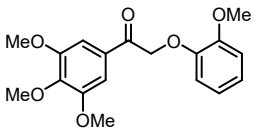
2-(2,6-Dimethoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (2): To a solution of 2,6-dimethoxyphenol (443 mg, 2.87 mmol) in acetone (6.31 mL, 446 mM) is added cesium carbonate (917 mg, 2.82 mmol). The solution was stirred for 15 minutes before 2-bromo-1-(4-methoxyphenyl)ethan-1-one (6.45 g, 2.82 mmol) was added. The solution was then stirred overnight at room temperature. The solvent was evaporated under vacuum. The reaction vessel was then washed with water (30 mL) and EtOAc (30 mL), both of which were added to a separatory funnel. The aqueous phase was extracted three times with EtOAc (3 X 30 mL) and the combined organic phase was dried with Na_2SO_4 (2 g) and concentrated *in vacuo*. The product was then purified by flash chromatography (Hexanes : EtOAc ; 7 : 3) to give a white solid (800 mg, 94%). Spectral data were in accordance with previous report.[7] **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.10 – 8.04 (m, 2H), 7.04 – 6.94 (m, 1H), 6.98 – 6.91 (m, 2H), 6.58 (d, *J* = 8.4 Hz, 2H), 5.13 (s, 2H), 3.87 (s, 3H), 3.81 (s, 6H).



1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-one (1): To a solution of 2-methoxyphenol (605 uL, 5.39 mmol) in acetone (11.5 mL, 446 mM) is added cesium carbonate (1.67 g, 5.13 mmol). The solution was stirred for 15 minutes before 2-bromo-1-(3,4-dimethoxyphenyl)ethan-1-one (1.33 g, 5.13 mmol) was added. The solution was then stirred overnight at room temperature. The solvent was evaporated under vacuum. The reaction vessel was then washed with water (30 mL) and EtOAc (30 mL), both of which were added to a separatory funnel. The aqueous phase was extracted three times with EtOAc (3 X 30 mL) and the combined organic phase was dried with Na_2SO_4 (2 g) and concentrated *in vacuo*. The product was then purified by flash chromatograph (Hexanes : EtOAc ; 7 : 3) to give a slightly pink powder (1.27 g, 82%). Spectral data were in accordance with previous report.[7] **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.63 (d, *J* = 2.0 Hz, 1H), 7.04 – 6.94 (m, 1H), 6.98 – 6.90 (m, 2H), 6.93 – 6.84 (m, 2H), 5.32 (s, 2H), 3.98 (s, 3H), 3.97 (s, 3H), 3.92 (s, 3H).

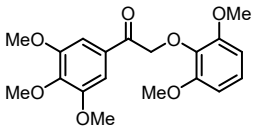


2-(2,6-Dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethan-1-one (6): To a solution of 2,6-dimethoxyphenol (315 mg, 2.05 mmol) in acetone (10 mL, 193 mM) is added cesium carbonate (673 mg, 2.06 mmol). The solution was stirred for 15 minutes before 2-bromo-1-(3,4-dimethoxyphenyl)ethan-1-one (500 mg, 1.93 mmol) was added. The solution was then stirred for 6h at room temperature. The solvent was evaporated under vacuum. The reaction vessel was then washed with water (30 mL) and EtOAc (30 mL), both of which were added to a separatory funnel. The aqueous phase was extracted three times with EtOAc (3 X 30 mL) and the combined organic phase was dried with Na_2SO_4 and concentrated *in vacuo*. The product was then purified by flash chromatography (Hexanes : EtOAc ; 7 : 3) to give a white solid (601 mg, 94%). Spectral data were in accordance with previous report.[7] **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.73 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.65 (d, *J* = 2.0 Hz, 1H), 7.01 (dd, *J* = 8.4 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 2H), 5.15 (s, 2H), 3.95 (s, 4H), 3.95 (s, 3H), 3.82 (s, 6H).

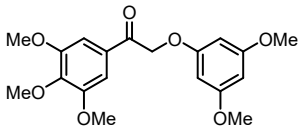


2-(2-methoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)ethan-1-one (10): To a solution of 2-methoxyphenol (323 uL, 2.94 mmol) in acetone (6.30 mL, 445 mM) is added cesium carbonate (913 mg, 2.80 mmol). The solution was stirred for 15 minutes before 2-bromo-1-(3,4,5-trimethoxyphenyl)ethan-1-one (810 mg, 2.80 mmol) was added. The solution was then stirred overnight at room temperature. The solvent was evaporated under vacuum. The reaction vessel was then washed with water (30 mL) and EtOAc (30 mL), both of which were added to a separatory funnel. The aqueous phase was

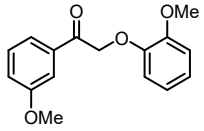
extracted three times with EtOAc (3 X 30 mL) and the combined organic phase was dried with Na_2SO_4 (2 g) and concentrated *in vacuo*. The product was then purified by flash chromatograph (Hexanes : EtOAc ; 7 : 3) to give a white powder (570 mg, 61%). Spectral data were in accordance with previous report.[8] **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 (s, 2H), 7.05 – 6.86 (m, 4H), 5.29 (s, 2H), 3.95 (s, 3H), 3.94 (s, 6H), 3.91 (s, 3H).



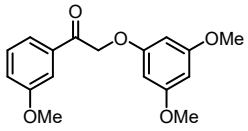
2-(2,6-Dimethoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)ethan-1-one (9): To a solution of 2,6-dimethoxyphenol (560 mg, 3.63 mmol) in acetone (7.76 mL, 446 mM) is added cesium carbonate (1.13 g, 3.46 mmol). The solution was stirred for 15 minutes before 2-bromo-1-(3,4,5-trimethoxyphenyl)ethan-1-one (1.00 g, 3.46 mmol) was added. The solution was then stirred overnight at room temperature. The solvent was evaporated under vacuum. The reaction vessel was then washed with water (30 mL) and EtOAc (30 mL), both of which were added to a separatory funnel. The aqueous phase was extracted three times with EtOAc (3 X 30 mL) and the combined organic phase was dried with Na_2SO_4 (2 g) and concentrated *in vacuo*. The product was then purified by flash chromatograph (Hexanes : EtOAc ; 7 : 3) to give a white fluffy solid (1.07 g, 85%). Spectral data were in accordance with previous report.[8] **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 (s, 2H), 7.06 (dd, *J* = 8.4 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 2H), 5.16 (s, 2H), 3.95 (bs, 9H) 3.85 (s, 6H).



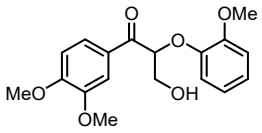
2-(3,5-Dimethoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)ethan-1-one (12S): To a solution of 3,5-dimethoxyphenol (544 mg, 3.46 mmol) in acetone (7.76 mL, 446 mM) is added cesium carbonate (1.13 g, 3.46 mmol). The solution was stirred for 15 minutes before 2-bromo-1-(3,4,5-trimethoxyphenyl)ethan-1-one (1.00 g, 3.46 mmol) was added. The solution was then stirred overnight at room temperature. The solvent was evaporated under vacuum. The reaction vessel was then washed with water (30 mL) and EtOAc (30 mL), both of which were added to a separatory funnel. The aqueous phase was extracted three times with EtOAc (3 X 30 mL) and the combined organic phase was dried with Na_2SO_4 (2 g) and concentrated *in vacuo*. The product was then purified by flash chromatography (Hexanes : EtOAc ; 7 : 3) to give a slightly yellow solid (756 mg, 60%). Spectral data were in accordance with previous report.[9] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.29 (s, 2H), 6.18 – 6.12 (m, 3H), 5.20 (s, 2H), 3.96 (s, 3H), 3.94 (s, 6H), 3.78 (s, 6H).



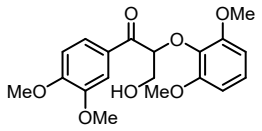
2-(2-Methoxyphenoxy)-1-(3-methoxyphenyl)ethan-1-one (4S): To a solution of 2-methoxyphenol (509 µL, 4.63 mmol) in acetone (9.70 mL, 446 mM) is added cesium carbonate (1.52 g, 4.67 mmol). The solution was stirred for 15 minutes before 2-bromo-1-(3-methoxyphenyl)ethan-1-one (1.00 g, 4.37 mmol) was added. The solution was then stirred for 3 h at room temperature. The solvent was evaporated under vacuum. The reaction vessel was then washed with water (30 mL) and EtOAc (30 mL), both of which were added to a separatory funnel. The aqueuous phase was extracted three times with EtOAc (3 X 30 mL) and the combined organic phase was dried with Na_2SO_4 and concentrated *in vacuo*. The product was then purified by flash chromatography (Hexanes : EtOAc ; 7 : 3) to give a white solid (951 mg, 80%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 – 7.55 (m, 2H), 7.42 (dd, *J* = 8.0 Hz, 1H), 7.18 (ddd, *J* = 8.3, 2.7, 1.0 Hz, 1H), 7.04 – 6.93 (m, 2H), 6.90 – 6.85 (m, 2H), 5.36 (s, 2H), 3.92 (s, 3H), 3.89 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 194.35, 159.97, 149.83, 147.54, 135.93, 129.79, 122.51, 120.81, 120.54, 120.37, 114.95, 112.33, 112.23, 77.36, 77.04, 76.72, 72.18, 55.92, 55.50. **HRMS (ESI)** m/z calculated for $C_{16}H_{16}O_4$ $[M+H]^+$ 273.1121; found 273.1128.



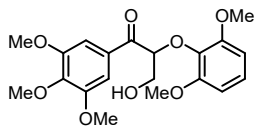
2-(3,5-Dimethoxyphenoxy)-1-(3-methoxyphenyl)ethan-1-one (5): To a solution of 3,5-dimethoxyphenol (808 mg, 5.24 mmol) in acetone (25 mL, 173 mM) is added cesium carbonate (1.85 g, 5.68 mmol). The solution was stirred for 15 minutes before 2-bromo-1-(3-methoxyphenyl)ethan-1-one (1 g, 4.37 mmol) was added. The solution was then stirred for 6h at room temperature. The solvent was evaporated under vacuum. The reaction vessel was then washed with water and EtOAc , both of which were added to a separatory funnel. The aqueous phase was extracted three times with EtOAc and the combined organic phases was dried with Na_2SO_4 and concentrated *in vacuo*. The product was then purified by flash chromatography (Hexanes : EtOAc ; 7 : 3) to give a off-white solid (1.10 g, 83%). Spectral data were in accordance with previous report.[10] **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.56 (ddd, *J* = 7.6, 1.6, 0.9 Hz, 1H), 7.52 (dd, *J* = 2.7, 1.5 Hz, 1H), 7.40 (dd, *J* = 7.9 Hz, 1H), 7.16 (ddd, *J* = 8.3, 2.7, 0.9 Hz, 1H), 6.15 – 6.09 (m, 3H), 5.22 (s, 2H), 3.87 (s, 3H), 3.76 (s, 6H).



1-(3,4-Dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propan-1-one (7): To a solution of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-one (509 mg, 1.68 mmol) in EtOH : acetone (1 : 1, 8.42 mL, 200 mM) was added potassium carbonate (249 mg, 1.80 mmol). The solution was stirred for 15 minutes after which an aqueous formaldehyde solution was added (241 uL of a 37% w.t. aqueous formaldehyde solution, 3.06 mmol). The resulting mixture was stirred at room temperature for 4 h. The solvents were evaporated under vacuum. The reaction vessel was washed with water (30 mL) and EtOAc (30 mL) both of which were added to a separatory funnel. The aqueous phase was extracted three times with EtOAc (3 X 30 mL) and the combined organic phase was dried with Na_2SO_4 (2 g) and concentrated *in vacuo*. The product was then purified by flash chromatograph (Hexanes : EtOAc ; 5 : 5) to give a transparent oil (406 mg, 73%). Spectral data were in accordance with previous report.[7] **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.64 (d, *J* = 2.0 Hz, 1H), 7.07 – 6.99 (m, 1H), 6.99 – 6.85 (m, 4H), 6.89 – 6.79 (m, 1H), 5.43 (t, *J* = 5.3 Hz, 1H), 4.10 (d, *J* = 5.3 Hz, 2H), 3.98 (s, 3H), 3.95 (s, 3H), 3.89 (s, 3H).

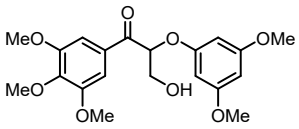


2-(2,6-Dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)-3-hydroxypropan-1-one (8): To a solution of 2-(2,6-dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethan-1-one (550 mg, 1.65 mmol) in EtOH : acetone (1 : 1, 16.5 mL, 100 mM) was added potassium carbonate (228 mg, 1.65 mmol). The solution was stirred for 15 minutes after which an aqueous formaldehyde solution was added (201 uL of a 37% w.t. aqueous formaldehyde solution, 2.48 mmol). The resulting mixture was stirred at room temperature for 2 h. The solvents were evaporated under vacuum. The reaction vessel was washed with water (30 mL) and EtOAc (30 mL) both of which were added to a separatory funnel. The aqueous phase was extracted three times with EtOAc (3 X 30 mL) and the combined organic phase was dried with Na_2SO_4 (2 g) and concentrated *in vacuo*. The product was then purified by flash chromatograph (Hexanes : EtOAc ; 5 : 5) to give a transparent oil (322 mg, 54%). Spectral data were in accordance with previous report.[11] **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.73 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.65 (d, *J* = 2.0 Hz, 1H), 7.01 (dd, *J* = 8.4 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 2H), 5.15 (s, 2H), 3.95 (s, 3H), 3.95 (s, 3H), 3.82 (s, 6H).

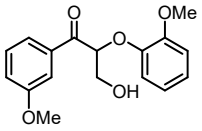


2-(2,6-Dimethoxyphenoxy)-3-hydroxy-1-(3,4,5-trimethoxyphenyl)propan-1-one (11): To a solution of 2-(2,6-dimethoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)ethan-1-one (500 mg, 1.38 mmol) in EtOH : acetone (1 : 1, 6.90 mL, 200 mM) was added potassium carbonate (200 mg, 1.45 mmol). The solution was stirred for 15 minutes after which an aqueous formaldehyde solution was added (196 uL of a 37% w.t. aqueous formaldehyde solution, 2.48 mmol). The resulting mixture was stirred at room temperature for 2 h. The solvents were evaporated under vacuum. The reaction vessel was washed with water (30 mL) and EtOAc (30 mL) both of which were added to a separatory funnel. The aqueous phase was extracted three times with EtOAc (3 X 30 mL) and the combined organic phase was dried with Na_2SO_4 (2 g)

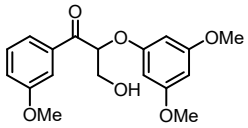
and concentrated *in vacuo*. The product was then purified by flash chromatograph (Hexanes : EtOAc ; 5 : 5) to give a transparent oil (361 mg, 67%). Spectral data were in accordance with previous report.[11] **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 (s, 2H), 7.07 (dd, *J* = 8.4 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 2H), 5.13 (dd, *J* = 7.3, 3.1 Hz, 1H), 4.05 (dd, *J* = 12.1, 7.3 Hz, 1H), 3.95 (s, 3H), 3.92 (s, 6H), 3.86 (dd, 1H), 3.78 (s, 6H).



2-(3,5-Dimethoxyphenoxy)-3-hydroxy-1-(3,4,5-trimethoxyphenyl)propan-1-one (12): To a solution of 2-(3,5-dimethoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)ethan-1-one (500 mg, 1.38 mmol) in EtOH : acetone (1 : 1, 6.90 mL, 200 mM) was added potassium carbonate (200 mg, 1.45 mmol). The solution was stirred for 15 minutes after which an aqueous formaldehyde solution was added (196 uL of a 37% w.t. aqueous formaldehyde solution, 2.48 mmol). The resulting mixture was stirred at room temperature for 2 h. The solvents were evaporated under vacuum. The reaction vessel was washed with water (30 mL) and EtOAc (30 mL) both of which were added to a separatory funnel. The aqueous phase was extracted three times with EtOAc (3 X 30 mL) and the combined organic phase was dried with Na_2SO_4 (2 g) and concentrated *in vacuo*. The product was then purified by flash chromatograph (Hexanes : EtOAc ; 5 : 5) to give a transparent oil (361 mg, 67%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.34 (s, 2H), 6.12 (s, 3H), 5.47 (dd, *J* = 6.1, 4.3 Hz, 1H), 4.23 – 4.08 (m, 2H), 3.95 (s, 3H), 3.89 (s, 6H), 3.75 (s, 6H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 195.34, 161.83, 159.24, 153.28, 143.61, 129.76, 106.53, 94.30, 94.13, 81.02, 63.42, 61.11, 56.41, 55.50. **HRMS (ESI)** m/z calculated for $C_{20}H_{24}O_8$ $[M+Na]^+$ 415.1363; found 415.1369.

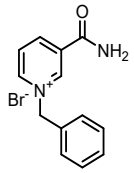


3-Hydroxy-2-(2-methoxyphenoxy)-1-(3-methoxyphenyl)propan-1-one (4): To a solution of 2-(2-methoxyphenoxy)-1-(3-methoxyphenyl)ethan-1-one (450 mg, 1.65 mmol) in EtOH : acetone (1 : 1, 16.5 mL, 100 mM) was added potassium carbonate (228 mg, 1.65 mmol). The solution was stirred for 15 minutes after which an aqueous formaldehyde solution was added (201 uL of a 37% w.t. aqueous formaldehyde solution, 2.48 mmol). The resulting mixture was stirred at room temperature for 2 h. The solvents were evaporated under vacuum. The reaction vessel was washed with water (30 mL) and EtOAc (30 mL) both of which were added to a separatory funnel. The aqueous phase was extracted three times with EtOAc (3 X 30 mL) and the combined organic phase was dried with Na_2SO_4 (2 g) and concentrated *in vacuo*. The product was then purified by flash chromatograph (Hexanes : EtOAc ; 5 : 5) to give a transparent oil (213 mg, 43%). Spectral data were in accordance with previous report.[12] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.63 (ddd, *J* = 7.7, 1.6, 0.9 Hz, 1H), 7.57 (dd, *J* = 2.7, 1.6 Hz, 1H), 7.38 (dd, *J* = 8.0 Hz, 1H), 7.14 (ddd, *J* = 8.3, 2.7, 0.9 Hz, 1H), 7.02 (ddd, *J* = 8.1, 7.3, 1.6 Hz, 1H), 6.92 (ddd, *J* = 8.2, 3.8, 1.6 Hz, 2H), 6.84 (ddd, *J* = 8.0, 7.4, 1.5 Hz, 1H), 5.43 (dd, *J* = 6.3, 4.0 Hz, 1H), 4.09 – 4.02 (m, 2H), 3.85 (s, 3H), 3.85 (s, 3H).

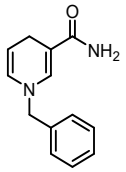


2-(3,5-Dimethoxyphenoxy)-3-hydroxy-1-(3-methoxyphenyl)propan-1-one (5): To a solution of 2-(3,5-dimethoxyphenoxy)-1-(3-methoxyphenyl)ethan-1-one (500 mg, 1.65 mmol) in EtOH : acetone (1 : 1, 16.5 mL, 100 mM) was added potassium carbonate (228 mg, 1.65 mmol). The solution was stirred for 15 minutes after which an aqueous formaldehyde solution was added (201 uL of a 37% w.t. aqueous formaldehyde solution, 2.48 mmol). The resulting mixture was stirred at room temperature for 2 h. The solvents were evaporated under vacuum. The reaction vessel was washed with water (30 mL) and EtOAc (30 mL) both of which were added to a separatory funnel. The aqueous phase was extracted three times with EtOAc (3 X 30 mL) and the combined organic phase was dried with Na_2SO_4 (2 g) and concentrated *in vacuo*. The product was then purified by flash chromatograph (Hexanes : EtOAc ; 5 : 5) to give a transparent oil (315 mg, 57%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.62 (ddd, *J* = 7.7, 1.6, 0.9 Hz, 1H), 7.53 (dd, *J* = 2.7, 1.6 Hz, 1H), 7.38 (dd, *J* = 8.0 Hz, 1H), 7.15 (ddd, *J* = 8.2, 2.7, 0.9 Hz, 1H), 6.11 – 6.05 (m, 3H), 5.54 (dd, *J* = 6.1, 3.9 Hz, 1H), 4.15 (dd, *J* = 12.1, 3.9 Hz, 1H), 4.07 (dd, *J* = 12.1, 6.1 Hz, 1H), 3.83 (s, 3H), 3.71 (s, 6H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 196.2,

161.7, 160.1, 159.2, 136.0, 130.0, 121.2, 120.9, 112.9, 94.3, 94.2, 80.9, 63.4, 55.6, 55.5; **HRMS (ESI)** m/z calculated for $C_{18}H_{20}O_6$ $[M+Na]^+$ 355.1152; found 355.1146.



1-Benzyl-3-carbamoylpyridin-1-ium bromide (NABn): To a solution of nicotinamide (2.00 g, 16.4 mmol) in acetonitrile (49.6 mL, 0.33 M) was added benzyl chloride (3.20 mL, 16.4 mmol). The solution was then refluxed for 4 h and allowed to cool to room temperature Diethyl ether (50 mL) was added to further precipitate the final product. The precipitate was recovered by filtration and washed with diethyl ether (3 × 10 mL) to afford a white powder (4.56 g, 95%). Spectral data were in accordance with previous report.[13] **^{1}H NMR (400 MHz, D_2O):** δ 9.29 (s, 1H), 9.00 (dt, *J* = 6.2, 1.4 Hz, 1H), 8.84 (dt, *J* = 8.1, 1.5 Hz, 1H), 8.12 (dd, *J* = 8.2, 6.2 Hz, 1H), 7.49 – 7.40 (m, 5H), 5.83 (s, 2H).



1-Benzyl-1,4-dihydropyridine-3-carboxamide (NaBnH): To a solution of 1-benzyl-3-carbamoylpyridin-1-ium bromide (2.93 g, 10 mmol) in water (60 mL) was added sodium bicarbonate (4.20 g, 50 mmol) and sodium hydrosulfite (8.71 g, 50 mmol). The reaction mixture was stirred at room temperature for 3 h in the dark. The precipitate was filtered, washed with cold water (3 × 10 mL) and dried under vacuum to afford a bright yellow powder (1.65, 77%).[13] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.45 – 7.16 (m, 6H), 5.77 (dq, *J* = 8.1, 1.7 Hz, 1H), 5.21 (s, 2H), 4.78 (dt, *J* = 8.1, 3.4 Hz, 1H), 4.32 (s, 2H), 3.20 (dd, *J* = 3.5, 1.7 Hz, 2H).

General procedure for the photochemical decomposition of lignin models

Photochemistry: All the photochemical reactions were performed in 1-dram vials that were placed in the center of an aluminum cylinder the interior of which was lined with a light-emitting diode (LED) strip connected to a power source. The reactions media were thoroughly purged under a nitrogen stream prior to irradiation. LED strips were purchased from Creative Lightings (https://www.creativelightings.com/).

Representative Procedure of the *in-situ* optimization: To a 4 mL vial equipped with a cross-shaped stir bar was added $[Cu(MeCN)_4]BF_4$ (5 mol%) and a diphosphine (5 mol%). The vial was closed and N_2 degassed dichloromethane (1.60 mL, 50 mM) was added. The solution was allowed to stir for 1h before a diimine (5 mol%) was added. The solution was allowed to stir again for 1 h at which point 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-one (24.2 mg, 80.0 µmol), Hantzsch Ester (30.4 mg, 120 µmol) and diphenyl phosphoric acid (1.00 mg, 5 mol%) were added. The solution was then degassed using N_2 for 5 minutes. Additional N_2 degassed dichloromethane was added to compensate for evaporated solvent during degassing. The vial was then stirred under blue LED irradiation for 24 h. The solution was filtered through celite into a 10 mL volumetric flask containing 15.0 mg of 1,3,5-trimethoxybenzene (internal standard) and the volume was completed using EtOAc. The resulting solution was analysed by an Agilent 6890N-5973N GC-MS. Using the calibration curve below, the 1-(3,4-dimethoxyphenyl)ethan-1-one yield was determined.

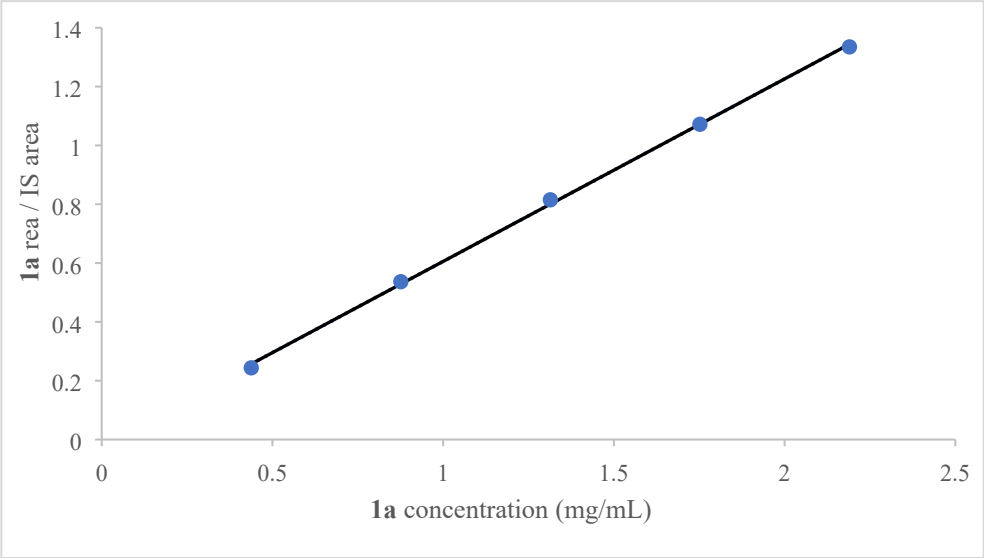


Figure S1. Calibration curve of 1-(3,4-dimethoxyphenyl)ethan-1-one.

Table S1. Data used to build the 1-(3,4-dimethoxyphenyl)ethan-1-one calibration curve.

	IS added (mg)	1-(3,4-dimethoxyphenyl)ethan-1-one concentration (mg/mL)	1-(3,4-dimethoxyphenyl)ethan-1-one area/IS area
Standard Solution 1	15.0	0.438	0.2438062
Standard Solution 2		0.876	0.53662017
Standard Solution 3		1.314	0.81504239
Standard Solution 4		1.752	1.071823
Standard Solution 5		2.19	1.33494341

Representative Procedure for isolated yield reactions (scope): To a 4 mL vial equipped with a cross-shaped stir bar was added Cu(**bathocup**)(**Xantphos**)BF_4 (1.70 mg, 1.65 µmol), NaBnH (7.1 mg, 33 µmol), 1-(3,4-dimethoxyphenyl)ethan-1-one (50 mg, 165 µmol), $NaHCO_3$ (16.6 mg, 198 µmol), and $Na_2S_2O_4$ (40.6 mg, 198 µmol). The vial was closed and N_2 degassed water (830 µL) and THF (2.48 mL) were added. The resulting solution was further degassed with N_2 for 5 minutes. The vial was then stirred under blue LED irradiation for 24 h. The solution was transferred to a separatory funnel and the vial was washed with EtOAc (3 x 2 mL). Water (30 mL) was added and extracted with EtOAc (3 x 30 mL). The combined organic phase was dried with Na_2SO_4 (2 g) and concentrated *in vacuo*. The desired products were purified by flash chromatography.

Tabular Data from Screening:

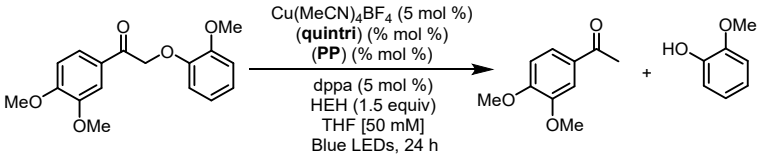


Table S2. Evaluation of Cu(quintri)(**PP**)BF_4-Based Photocatalysts in a Model Lignin Decomposition Process.

	PP	τ (ns)	E_T (eV)	% **XX**[a]
1	NXantPhos	19	2.49	90
2	PhanePhos	1948	2.25	97
3	XantPhos	1133	2.21	99
4	DPEPhos	14300	2.17	0
5	dppf	1.5	2.17	0
6	dppn	1.43	2.15	0
7	BINAP	2188	1.94	65
8	SEGPhos	340	1.92	12
9	none	90	1.65	0

[a] Yield of the acetophenone by GC-MS analysis

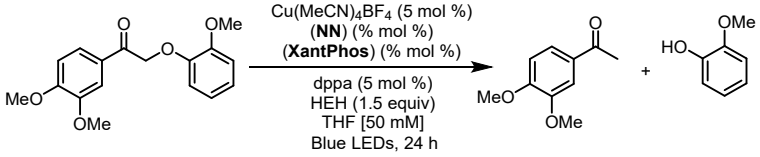


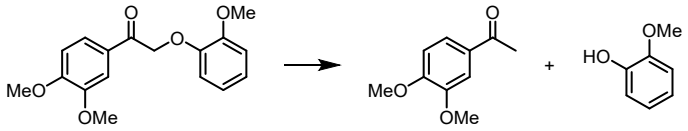
Table S3. Evaluation of Cu(**NN**)(XantPhos)BF_4-Based Photocatalysts in a Model Lignin Decomposition Process; INSITU ONLY 5 mol %

	NN	τ (ns)	E_T (eV)	In situ% **XX**[a]
1	phen	391	2.27	0
2	dmp	1133	2.21	99
3	tmp	1119	2.07	78
4	bphen	1798	2.61	99
5	dmbp	72	1.95	0
6	dtbbp	143	1.99	77
7	batho	3.2	2.50	0
8	bathocup	4	2.66	99
9	dq	393	1.89	0
10	pytri	752	2.26	0
11	quintri	3.6	2.59	99
12	iquintri	3.8	2.69	14
13	dpq	3	2.21	48
14	dppz	71	1.95	50
15	bdppz	75	2.19	45
16	dpa	3	2.88	0
17	dmop	4	2.55	22

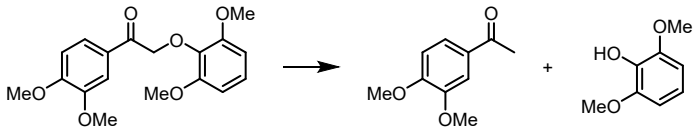
[a] Yield of the acetophenone by GC-MS analysis

Decomposition of Lignin Models

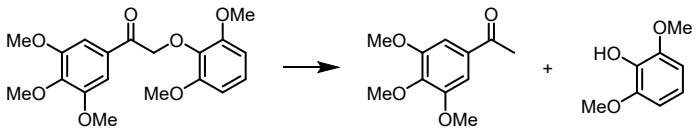
2-(2,6-Dimethoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one: According to the general procedure, 1-(4-methoxyphenyl)ethan-1-one (150 mg, 495 µmol) was converted to 1-(4-methoxyphenyl)ethan-1-one (52.4 mg 69%) and 2,6-dimethoxyphenol (51.4 mg, 69%). Spectral data were in accordance with previous report[14]; **1-(4-methoxyphenyl)ethan-1-one : ^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.96 (m, 2H), 6.96 (m, 2H), 3.89 (s, 3H), 2.58 (s, 3H); **2,6-dimethoxyphenol : ^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.83 (dd, *J* = 8.7, 7.9 Hz, 1H), 6.62 (d, *J* = 8.3 Hz, 2H), 5.54 (s, 1H), 3.92 (s, 6H).



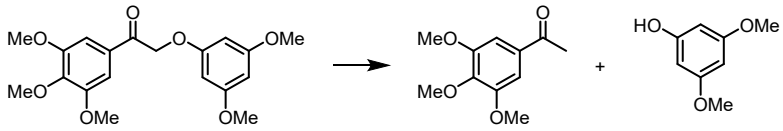
1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-one: According to the general procedure, 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-one (150 mg, 495 µmol) was converted to 1-(3,4-dimethoxyphenyl)ethan-1-one (66.0 mg 74%) and 2-methoxyphenol (41.4 mg, 67%). Spectral data were in accordance with previous report[14]; **3-Methoxyacetophenone : ^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.58 (dd, *J* = 8.4, 2.0, 1H), 7.53 (d, *J* = 2.0 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 3.95 (s, 3H), 3.94 (s, 3H), 2.57 (s, 3H); **2-Methoxyphenol : ^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.09 – 7.01 (m, 1H), 7.01 – 6.90 (m, 3H), 5.80 (s, 1H), 3.92 (s, 3H).



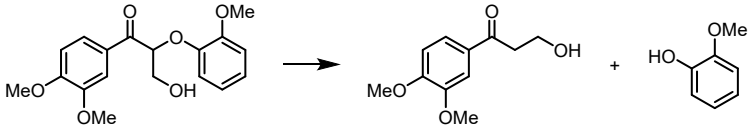
2-(2,6-dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethan-1-one: According to the general procedure, 1-(3,4-dimethoxyphenyl)ethan-1-one (164.4 mg, 495 µmol) was converted to 1-(3,4-dimethoxyphenyl)ethan-1-one (66.9 mg 75%) and 2,6-dimethoxyphenol (54.9 mg, 72%). Spectral data were in accordance with previous report[14]; **1-(3,4-Dimethoxyphenyl)ethan-1-one : ^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.58 (dd, *J* = 8.4, 2.0, 1H), 7.53 (d, *J* = 2.0 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 3.95 (s, 3H), 3.94 (s, 3H), 2.57 (s, 3H); **2,6-Dimethoxyphenol : ^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.83 (dd, *J* = 8.7, 7.9 Hz, 1H), 6.62 (d, *J* = 8.3 Hz, 2H), 5.54 (s, 1H), 3.92 (s, 6H).



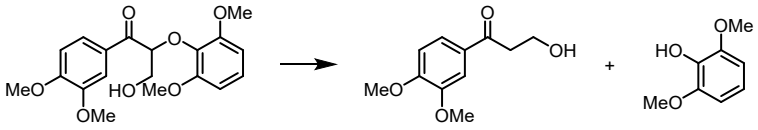
2-(2,6-dimethoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)ethan-1-one: According to the general procedure, 2-(2,6-dimethoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)ethan-1-one (179.4 mg, 495 µmol) was converted to 1-(3,4,5-trimethoxyphenyl)ethan-1-one (91.6 mg 88%) and 2,6-dimethoxyphenol (52.7 mg, 69%). Spectral data were in accordance with previous report[14]; **2-(2,6-Dimethoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)ethan-1-one : ^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.23 (s, 2H), 3.93 (s, 6H), 3.93 (s, 3H), 2.60 (s, 3H), 2.18 (s, 1H); **2,6-dimethoxyphenol: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.83 (dd, *J* = 8.7, 7.9 Hz, 1H), 6.62 (d, *J* = 8.3 Hz, 2H), 5.54 (s, 1H), 3.92 (s, 6H).



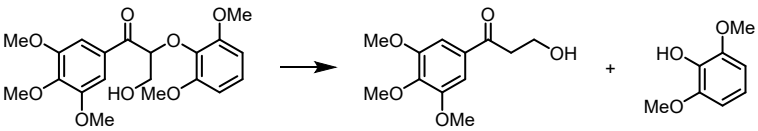
2-(3,5-dimethoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)ethan-1-one: According to the general procedure, 2-(3,5-dimethoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)ethan-1-one (179.4 mg, 495 µmol) was converted to 1-(3,4,5-trimethoxyphenyl)ethan-1-one (59.3 mg 57%) and 3,5-dimethoxyphenol (56.5 mg, 74%). Spectral data were in accordance with previous report[14]; **2-(2,6-Dimethoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)ethan-1-one : ^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.23 (s, 2H), 3.93 (s, 6H), 3.93 (s, 3H), 2.60 (s, 3H), 2.18 (s, 1H); **3,5-Dimethoxyphenol : ^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.14 – 6.04 (m, 3H), 4.94 (s, 1H), 3.78 (s, 6H).



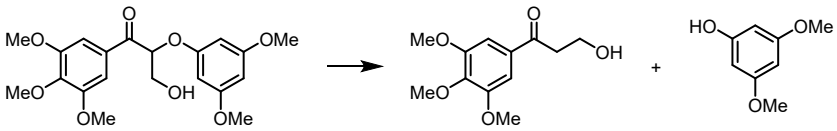
1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propan-1-one: According to the general procedure, 1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propan-1-one (164.4 mg, 495 µmol) was converted to 1-(3,4-dimethoxyphenyl)-3-hydroxypropan-1-one (55.2 mg 53%) and 2-methoxyphenol (36.9 mg, 60%). Spectral data were in accordance with previous report[14]; **1-(3,4-dimethoxyphenyl)-3-hydroxypropan-1-one : ^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.59 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.53 (d, *J* = 2.0 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 4.03 (t, *J* = 5.4 Hz, 2H), 3.95 (s, 3H), 3.94 (s, 3H), 3.20 (t, *J* = 5.4 Hz, 2H), 2.76 (s, 1H); **2-Methoxyphenol : ^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.09 – 7.01 (m, 1H), 7.01 – 6.90 (m, 3H), 5.80 (s, 1H), 3.92 (s, 3H).



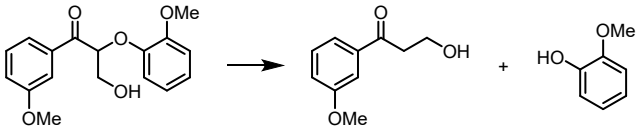
2-(2,6-Dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)-3-hydroxypropan-1-one: According to the general procedure, 2-(2,6-dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)-3-hydroxypropan-1-one (179.4 mg, 495 µmol) was converted to 1-(3,4-dimethoxyphenyl)-3-hydroxypropan-1-one (83.2 mg 80%) and 2,6-dimethoxyphenol (65.6 mg, 86%). Spectral data were in accordance with previous report[14]; **1-(3,4-Dimethoxyphenyl)-3-hydroxypropan-1-one : ^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.59 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.53 (d, *J* = 2.0 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 4.03 (t, *J* = 5.4 Hz, 2H), 3.95 (s, 3H), 3.94 (s, 3H), 3.20 (t, *J* = 5.4 Hz, 2H), 2.76 (s, 1H); **2,6-Dimethoxyphenol : ^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.83 (dd, *J* = 8.7, 7.9 Hz, 1H), 6.62 (d, *J* = 8.3 Hz, 2H), 5.54 (s, 1H), 3.92 (s, 6H).



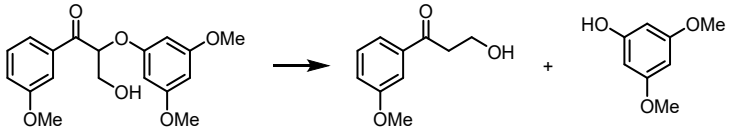
2-(2,6-Dimethoxyphenoxy)-3-hydroxy-1-(3,4,5-trimethoxyphenyl)propan-1-one: According to the general procedure, 2-(2,6-dimethoxyphenoxy)-3-hydroxy-1-(3,4,5-trimethoxyphenyl)propan-1-one (194.1 mg, 495 µmol) was converted to 3-hydroxy-1-(3,4,5-trimethoxyphenyl)propan-1-one (64.2 mg 53%) and 2,6-dimethoxyphenol (52.7 mg, 69%). Spectral data were in accordance with previous report[14]; **3-Hydroxy-1-(3,4,5-trimethoxyphenyl)propan-1-one : ^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.22 (s, 2H), 4.02 (t, *J* = 5.4 Hz, 2H), 3.92 (s, 3H), 3.91 (s, 6H), 3.20 (t, *J* = 5.5 Hz, 2H), 2.78 (s, 1H); **2,6-Dimethoxyphenol: ^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.83 (dd, *J* = 8.7, 7.9 Hz, 1H), 6.62 (d, *J* = 8.3 Hz, 2H), 5.54 (s, 1H), 3.92 (s, 6H).



2-(3,5-Dimethoxyphenoxy)-3-hydroxy-1-(3,4,5-trimethoxyphenyl)propan-1-one: According to the general procedure, 2-(3,5-dimethoxyphenoxy)-3-hydroxy-1-(3,4,5-trimethoxyphenyl)propan-1-one (194.1 mg, 495 µmol) was converted to 3-hydroxy-1-(3,4,5-trimethoxyphenyl)propan-1-one (63.0 mg 53%) and 3,5-dimethoxyphenol (57.2 mg, 75%). Spectral data were in accordance with previous report[14]; **3-Hydroxy-1-(3,4,5-trimethoxyphenyl)propan-1-one : ^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.22 (s, 2H), 4.02 (t, *J* = 5.4 Hz, 2H), 3.92 (s, 3H), 3.91 (s, 6H), 3.20 (t, *J* = 5.5 Hz, 2H), 2.78 (s, 1H); **3,5-Dimethoxyphenol : ^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.14 – 6.04 (m, 3H), 4.94 (s, 1H), 3.78 (s, 6H).



3-Hydroxy-2-(2-methoxyphenoxy)-1-(3-methoxyphenyl)propan-1-one: According to the general procedure, 3-hydroxy-2-(2-methoxyphenoxy)-1-(3-methoxyphenyl)propan-1-one (150 mg, 495 µmol) was converted to 3-hydroxy-1-(3-methoxyphenyl)propan-1-one (66.0 mg 74%) and 2-methoxyphenol (yield not determined). Spectral data were in accordance with previous report[15]; **3-Hydroxy-1-(3-methoxyphenyl)propan-1-one : ^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.54 (ddd, *J* = 7.7, 1.3 Hz, 1H), 7.49 (dd, *J* = 2.7, 1.5 Hz, 1H), 7.38 (dd, *J* = 7.9 Hz, 1H), 7.13 (ddd, *J* = 8.2, 2.7, 1.0 Hz, 1H), 4.03 (t, *J* = 5.3 Hz, 2H), 3.86 (s, 3H), 3.22 (t, *J* = 5.3 Hz, 2H); **2-Methoxyphenol : ^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.09 – 7.01 (m, 1H), 7.01 – 6.90 (m, 3H), 5.80 (s, 1H), 3.92 (s, 3H).



2-(3,5-Dimethoxyphenoxy)-3-hydroxy-1-(3-methoxyphenyl)propan-1-one: According to the general procedure, 2-(3,5-dimethoxyphenoxy)-3-hydroxy-1-(3-methoxyphenyl)propan-1-one (164.4 mg, 495 µmol) was converted to 3-hydroxy-1-(3-methoxyphenyl)propan-1-one (59.8 mg 67%) and 3,5-dimethoxyphenol (47.3 mg, 62%). Spectral data were in accordance with previous report[15]; **3-Hydroxy-1-(3-methoxyphenyl)propan-1-one : ^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.95 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.5 Hz, 2H), 4.08 – 4.02 (m, 2H), 3.88 (s, 3H), 3.19 (t, *J* = 5.3 Hz, 2H), 2.79 (s, 1H); **3,5-Dimethoxyphenol : ^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.14 – 6.04 (m, 3H), 4.94 (s, 1H), 3.78 (s, 6H).

Reaction Scale-up using Flow Chemistry

Representative procedure for the degradation of 1 using the continuous flow setup:

1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-one (1.0 g, 3.31 mmol, 1 eq.), Cu(**bathocup**)(**Xantphos**)BF_4 (34 mg, 33.1 µmol, 1 mol %), and NABnH (142 mg, 0.62 mmol, 20 mol %) were dissolved in dimethoxyethane [66 mL, 25 mM]. $NaHCO_3$ (333 mg, 3,97 mmol, 1.2 eq.), and $Na_2S_2O_4$ (691 mg, 3.97 mmol, 1.2 eq.) were dissolved in H_2O [66 mL, 25 mM]. Both solutions were sparged with N_2 for 15 minutes. With an Asia Syringe Pump, the solutions were mixed by a T-mixer, and pumped through a 13.6 mL PFA-coiled reactor. The coil was irradiated with 450 nm LED and two 450 nm Kessil Lamps, and the flow rate was calculated for a 3-hour irradiation. The reaction mixture was then transferred to a separatory funnel. Water was added and extracted with EtOAc three times. The combined organic phase was dried with Na_2SO_4 and concentrated *in vacuo*. The desired products were purified by flash chromatography to give 2-methoxyphenol (270 mg, 71%) and 1-(3,4-dimethoxyphenyl)ethan-1-one (417 mg, 70%) as pure products. **3-Methoxyacetophenone : ^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.58 (dd, *J* = 8.4, 2.0, 1H), 7.53 (d, *J* = 2.0 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 3.95 (s, 3H), 3.94 (s, 3H), 2.57 (s, 3H);**1-(3,4-Dimethoxyphenyl)ethan-1-one : ^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.58 (dd, *J* = 8.4, 2.0, 1H), 7.53 (d, *J* = 2.0 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 3.95 (s, 3H), 3.94 (s, 3H), 2.57 (s, 3H);

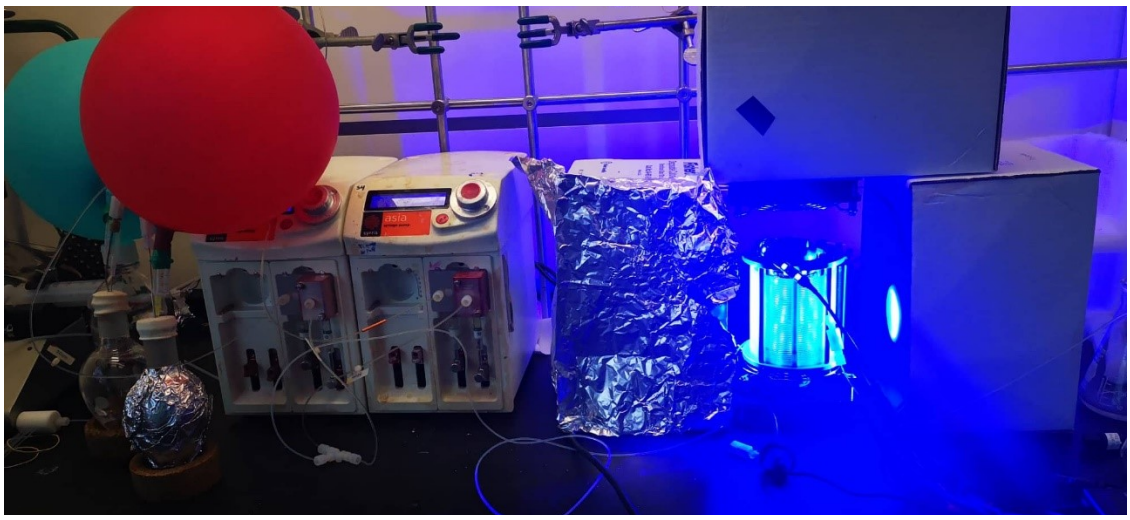
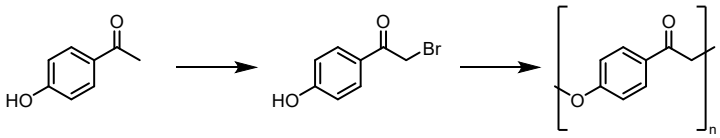
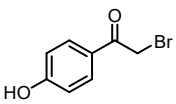


Figure S2 : Continuous flow reactor set-up used for the scale-up reactions.

Synthesis and degradation of the model polymer

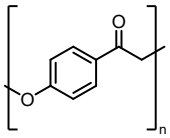


Scheme S1 : Synthesis of the model polymer

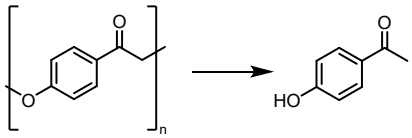


2-B -1-(4-hydroxyphenyl)ethan-1-one (13S): To a solution of 1-(4-hydroxyphenyl)ethan-1-one (1 g, 7.34 mmol) in EtOAc (40 mL, 134 mM) and $CHCl_3$ (15 mL, 134 mM) is added $CuBr_2$ (3.28 g, 14.7 mmol). The reaction mixture was stirred 2h30 at 80°C. The reaction was then allowed to cool to room temperature and filtered through a filter paper. The filtrate was

added to a separatory funnel along with water (30 mL). It was then extracted three times with EtOAc (3 X 30 mL) and the combined organic phases were dried with Na_2SO_4 (2 g) and concentrated *in vacuo*. The product was then purified by flash chromatography (Hexanes : EtOAc ; 8 : 2) to give a white solid (1.58 g, 82%). Spectral data were in accordance with previous report[16]. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.98 – 7.91 (m, 2H), 6.94 – 6.86 (m, 2H), 4.39 (s, 2H).



Model polymer (13): To a solution of 2-bromo-1-(4-hydroxyphenyl)ethan-1-one (400 mg, 1.86 mmol) in DMF (5 mL, 372 mM) is added Cs_2CO_3 (1.21 g, 3.72 mmol). The reaction mixture was stirred for 24h at room temperature and 20 mL of H_2O was added. The orange precipitate was then filtered and washed with 5 mL of DMF and 5 mL of H_2O. The solid was then lyophilized to remove traces of solvent to give the pure polymer as an orange solid (345 mg, 69%). Characterisation of the polymer was done by HSQC.



Procedure for the degradation of the model polymer: To a 20 mL vial equipped with a cross-shaped stir bar was added Cu(**bathocup**)(Xantphos)BF_4 (1.9 mg, 1.84 μmol), NABnH (7.9 mg, 37 μmol), the polymer (25 mg), $NaHCO_3$ (18.5 mg, 220 μmol), and $Na_2S_2O_4$ (38.8 mg, 220 μmol). The vial was closed and N_2 degassed water (4 mL) and DME (4 mL) were added. The resulting solution was further degassed with N_2 for 5 minutes. The vial was then stirred under blue KESSIL® Lamp irradiation for 72 h. The solution was transferred to a separatory funnel and the vial was washed with EtOAc (3 x 2 mL). Water (30 mL) was added and extracted with EtOAc (3 x 30 mL). The combined organic phase was dried with Na_2SO_4 (2 g) and concentrated *in vacuo*. Purification by flash chromatography (80:20 Hexanes:EtOAc) gave the pure product **13a** as a white solid (15.1 mg, 60%). Spectral data were in accordance with previous report[17]. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.95 – 7.88 (m, 2H), 6.96 – 6.89 (m, 2H), 2.58 (s, 3H), 2.20 (s, 1H).

Stern-Volmer Experiments

Quenching experiments were performed by examining the effect on the excited state lifetime of the copper complexes through the addition of each component of the reaction. Lifetime measurements were done with an Edinburgh Instruments FLS-920 fluorimeter with an EPL 405 laser (exciting at 405 nm). To ensure complete solubility and homogeneous conditions, a 1:1 mix of DME:H_2O was used. Solutions were purged with N_2 for 5 min prior to measurement.

Table S4: Excited State Lifetime Quenching with NABnH

[NABnH] (mM)	Excited State Lifetime (ns)
0	2551
0.1	2144
0.3	1850
0.6	1234
0.9	1086
1.2	614

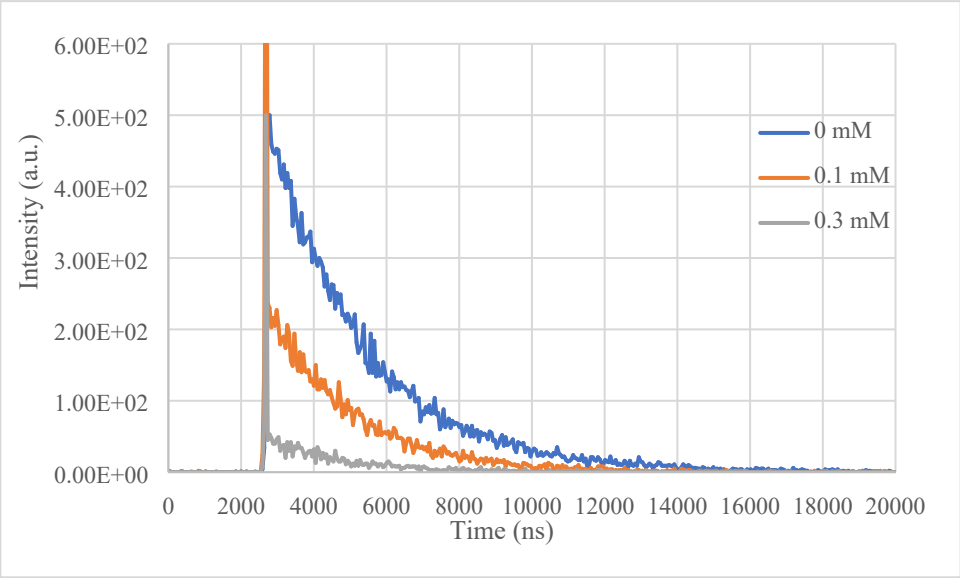


Figure S3: Life-time spectra of Cu(**bathocup**)(**Xantphos**)BF_4 with various concentrations of NABnH, excited at 405 nm, recorded at ambient temperature in 1:1 DME:H_2O (1.10^{-4}M).

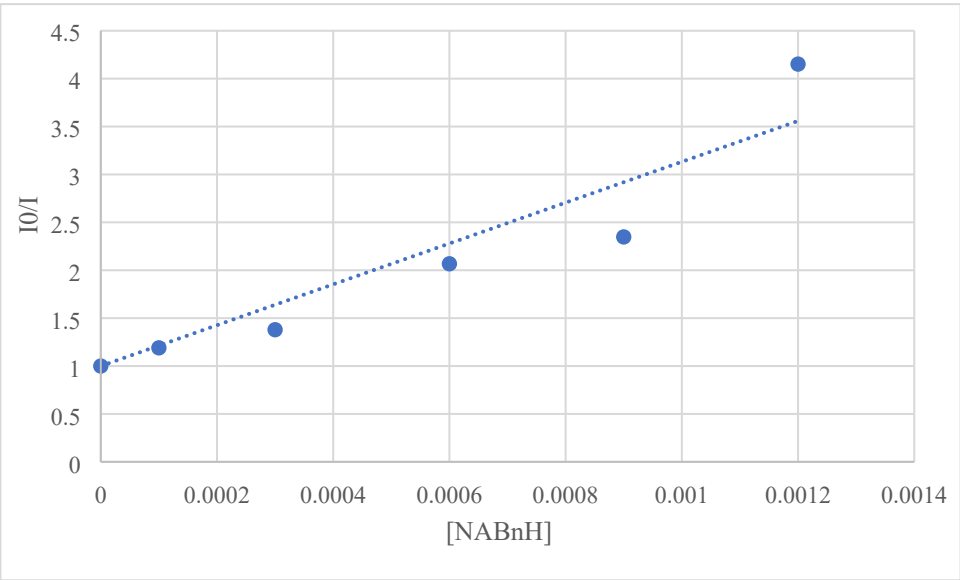


Figure S4: Stern-Volmer plot of Cu(**bathocup**)(**Xantphos**)BF_4 with NABnH

Table S5: Excited State Lifetime Quenching with 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-one (1)

[1] (mM)	Excited State Lifetime (ns)
0	2551
0,3	2475
0,6	2478
1,2	2524
2,4	2486
4,8	2501

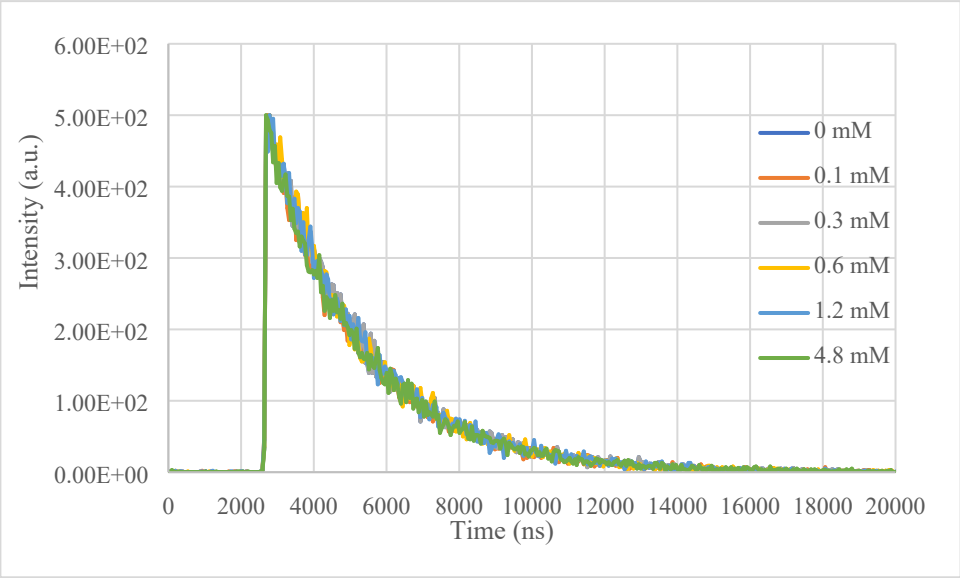


Figure S5: Life-time spectra of Cu(**bathocup**)(**Xantphos**)BF_4 with various concentrations of 1, excited at 405 nm, recorded at ambient temperature in 1:1 DME:H_2O (1.10^{-4}M).

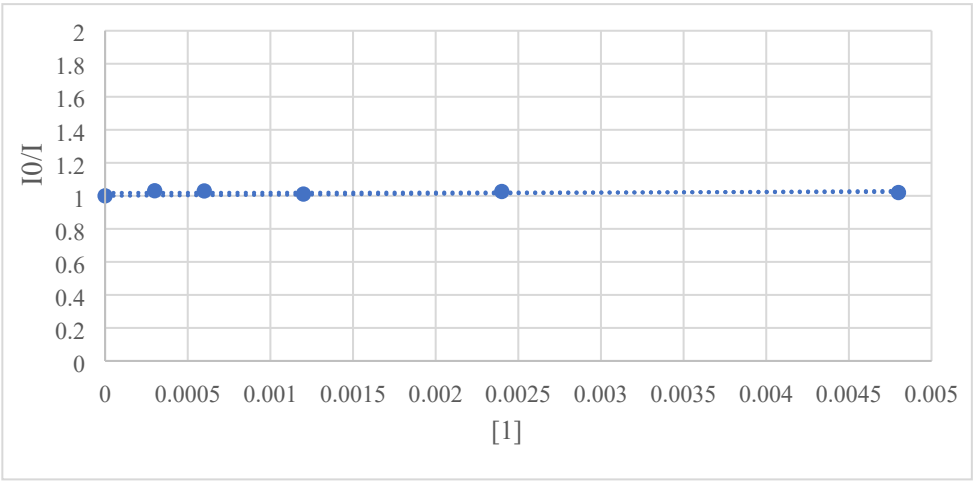


Figure S6: Stern-Volmer plot of Cu(Bathocup)(Xantphos)BF_4 with 1

Table S6: Excited State Lifetime Quenching with $NaHCO_3$ and $Na_2S_2O_4$

[$NaHCO_3$]/ [$Na_2S_2O_4$] (mM)	**Excited State Lifetime (ns)**
0	2551
0,6	2431,93
1,2	2411,69
12	2442,23

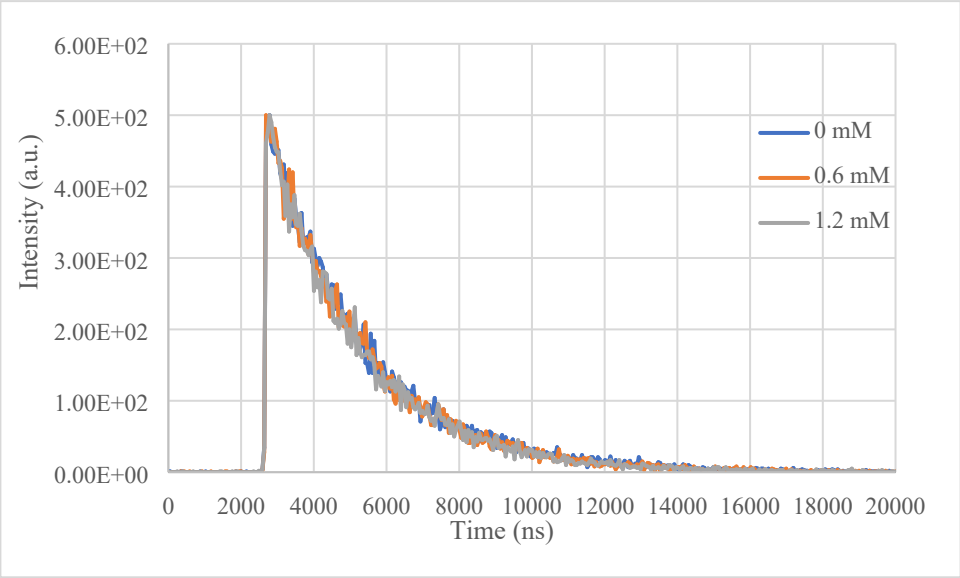


Figure S7: Life-time spectra of Cu(**bathocup**)(**Xantphos**)BF_4 with various concentrations of $NaHCO_3$ and $Na_2S_2O_4$, excited at 405 nm, recorded at ambient temperature in 1:1 DME:H_2O (1.10^{-4}M).

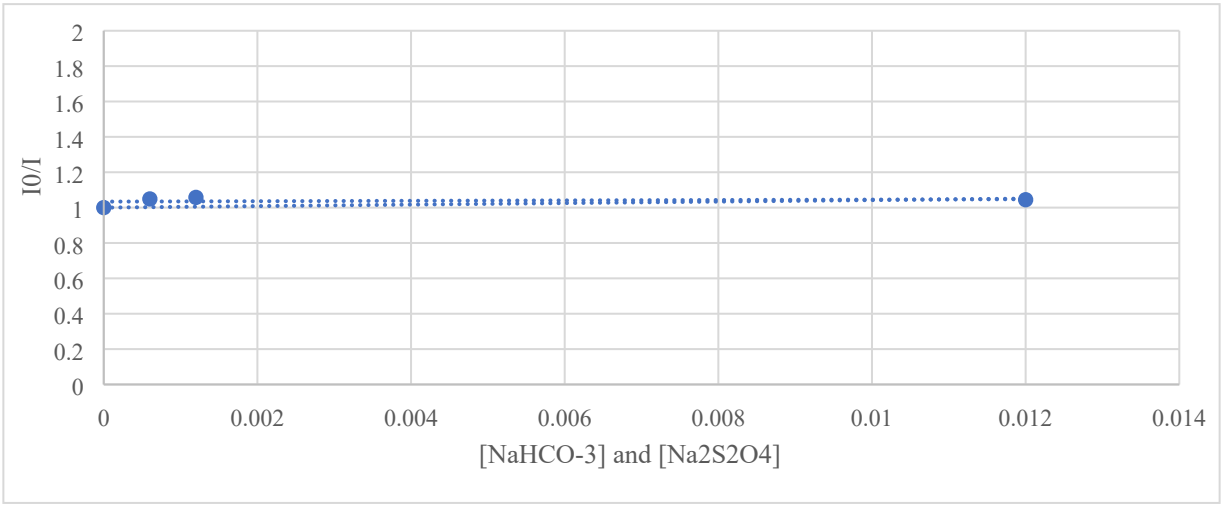


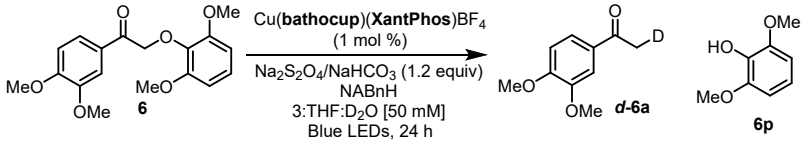
Figure S8: Stern-Volmer plot of Cu(**bathocup**)(**Xantphos**)BF_4 with $NaHCO_3$ and $Na_2S_2O_4$.

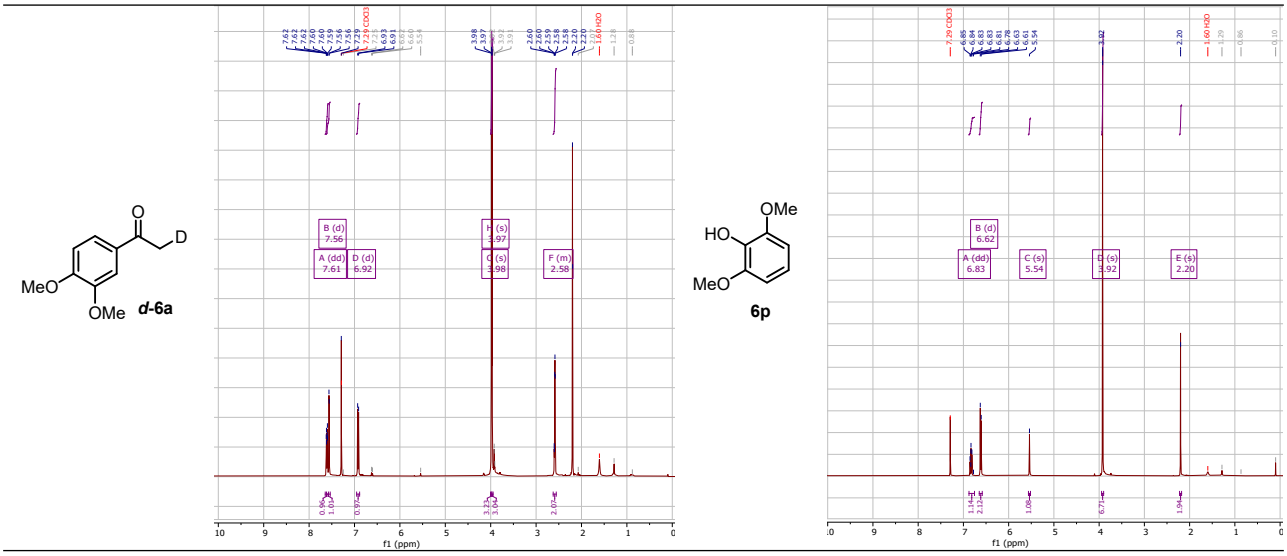
Table S7: Bimolecular quenching constant k_q

Quench	k_q ($M^{-1} . s^{-1}$)
NABnH	8,34E+09
1	2,54E+06
$NaHCO_3$ and $Na_2S_2O_4$	1,70E+06

Deuteration Experiment

Deuteration experiment was carried out in a solvent mixture of 3:1 THF:D_2O.

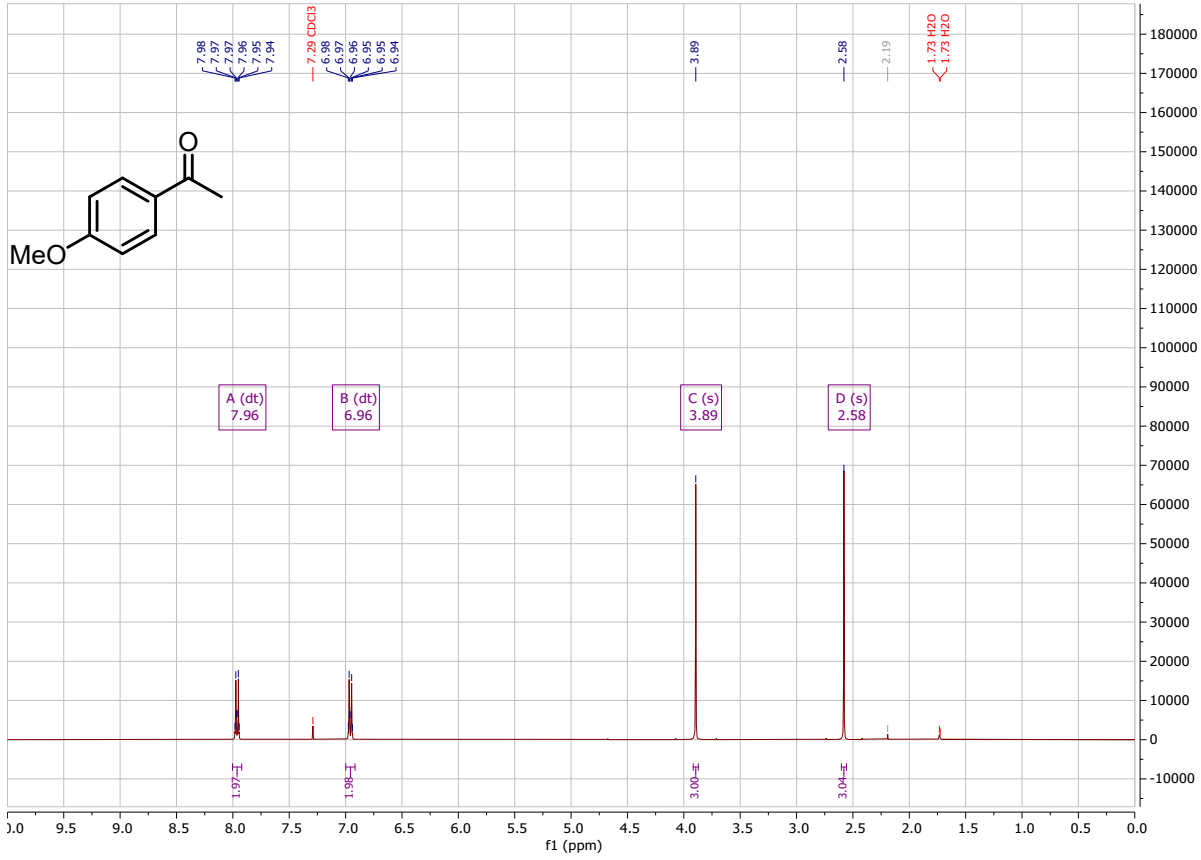


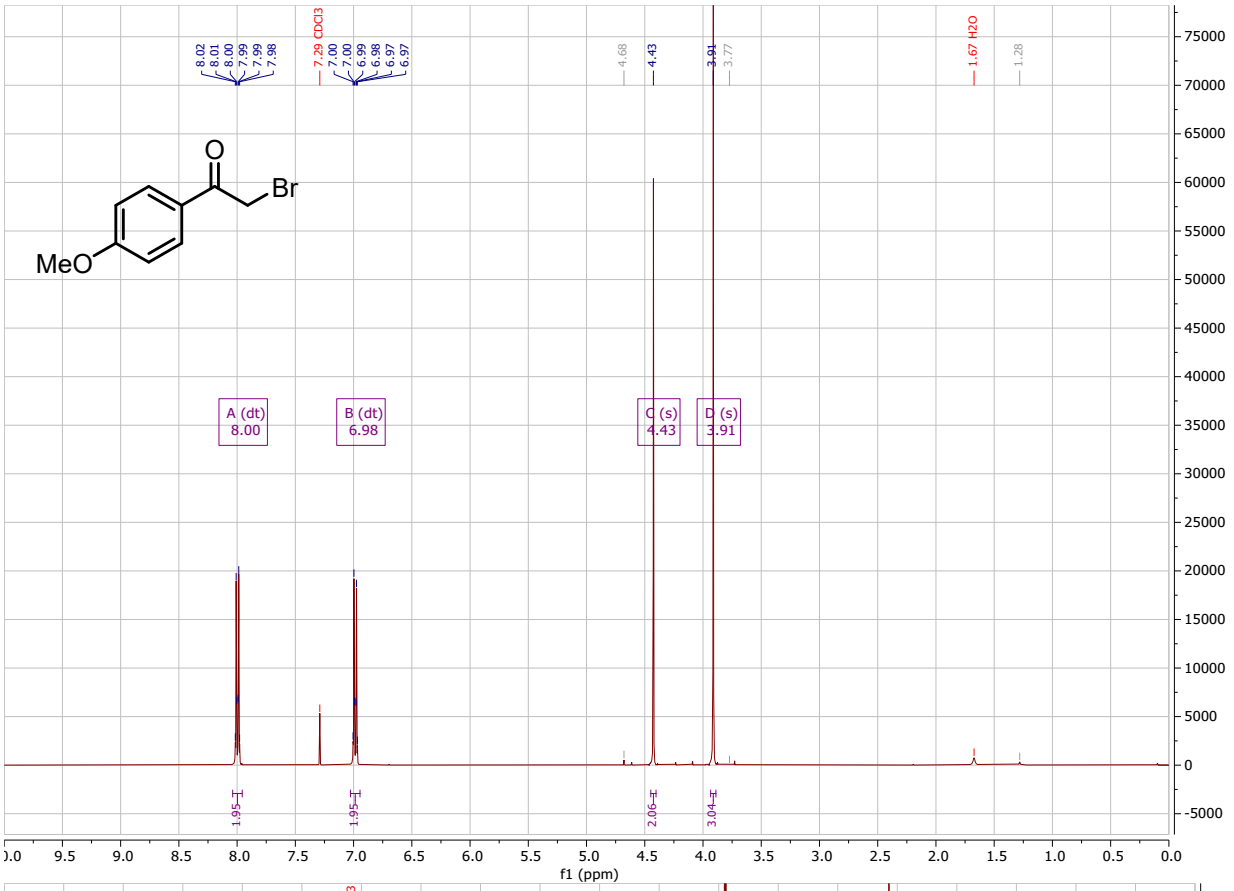


NMR Spectra

Lignin Models

For previously reported compounds only the ^{1}H NMR is shown. For new compounds both the ^{1}H and ^{13}C NMR spectra are provided:

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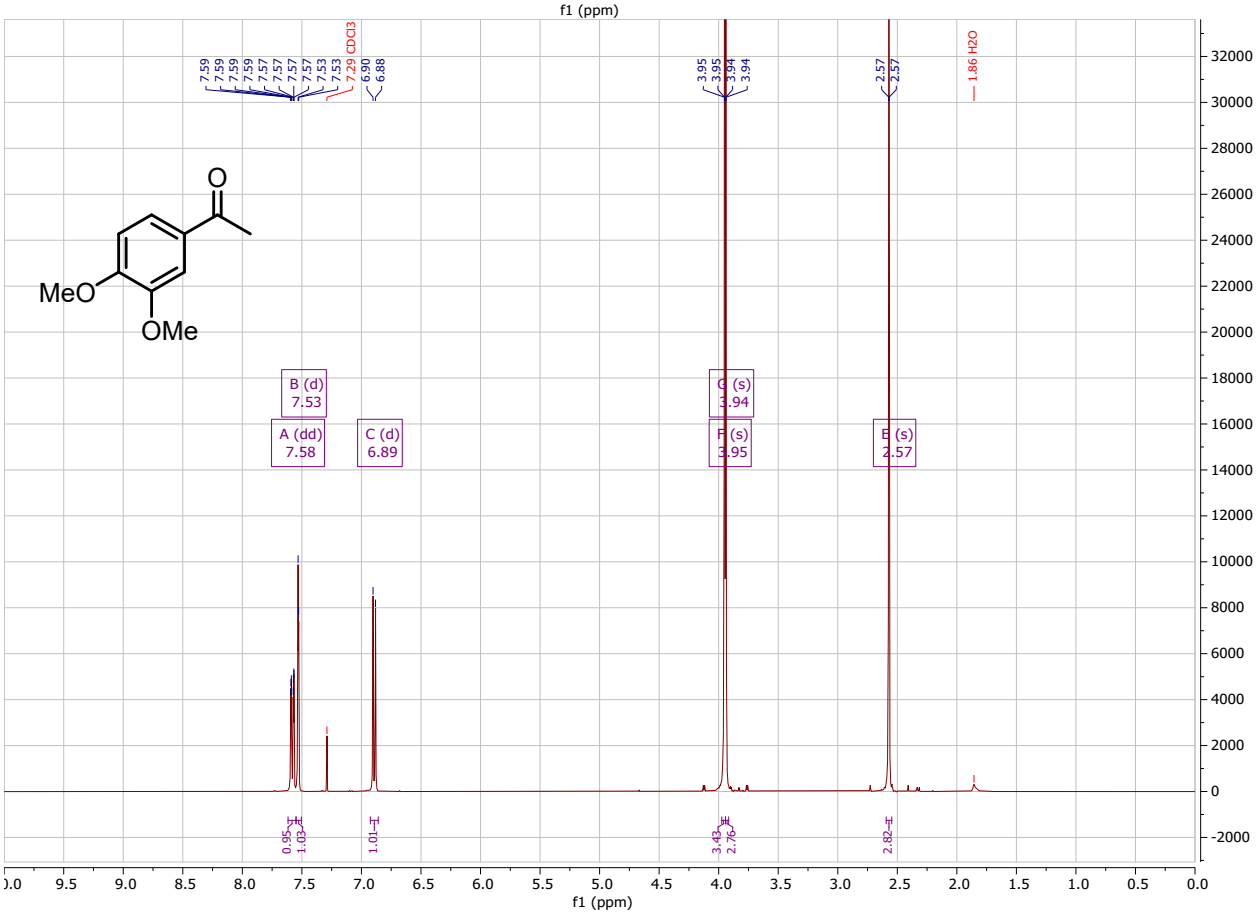
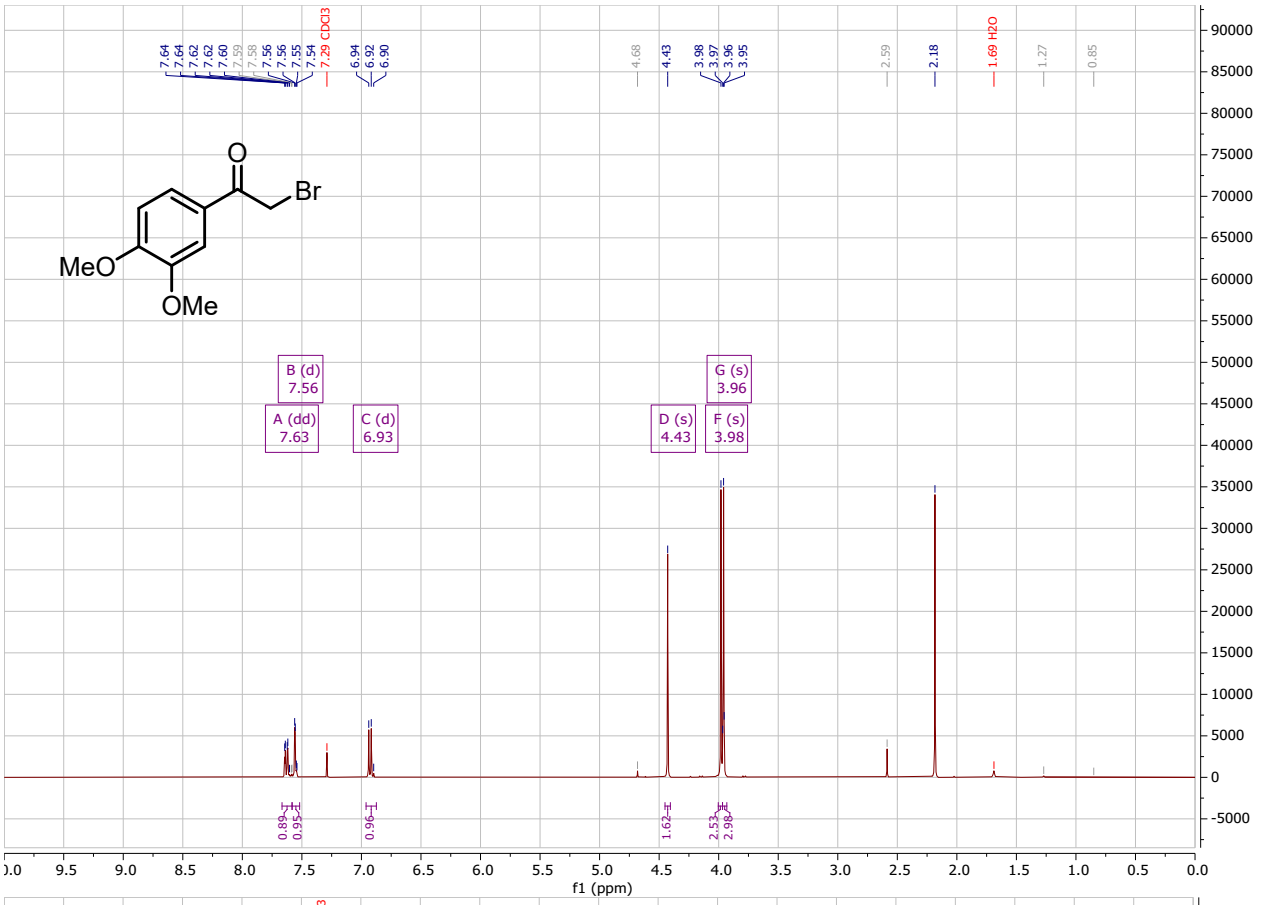
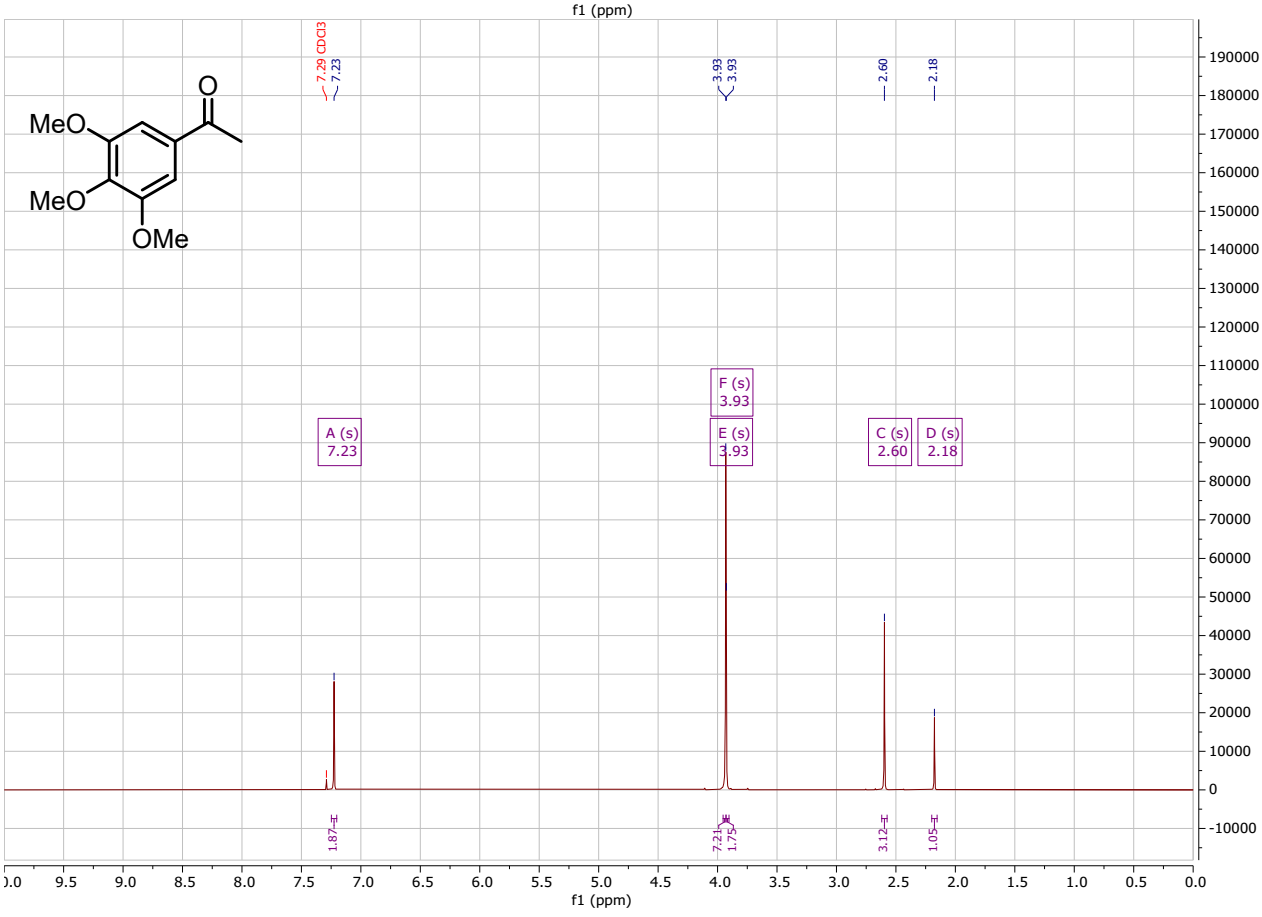
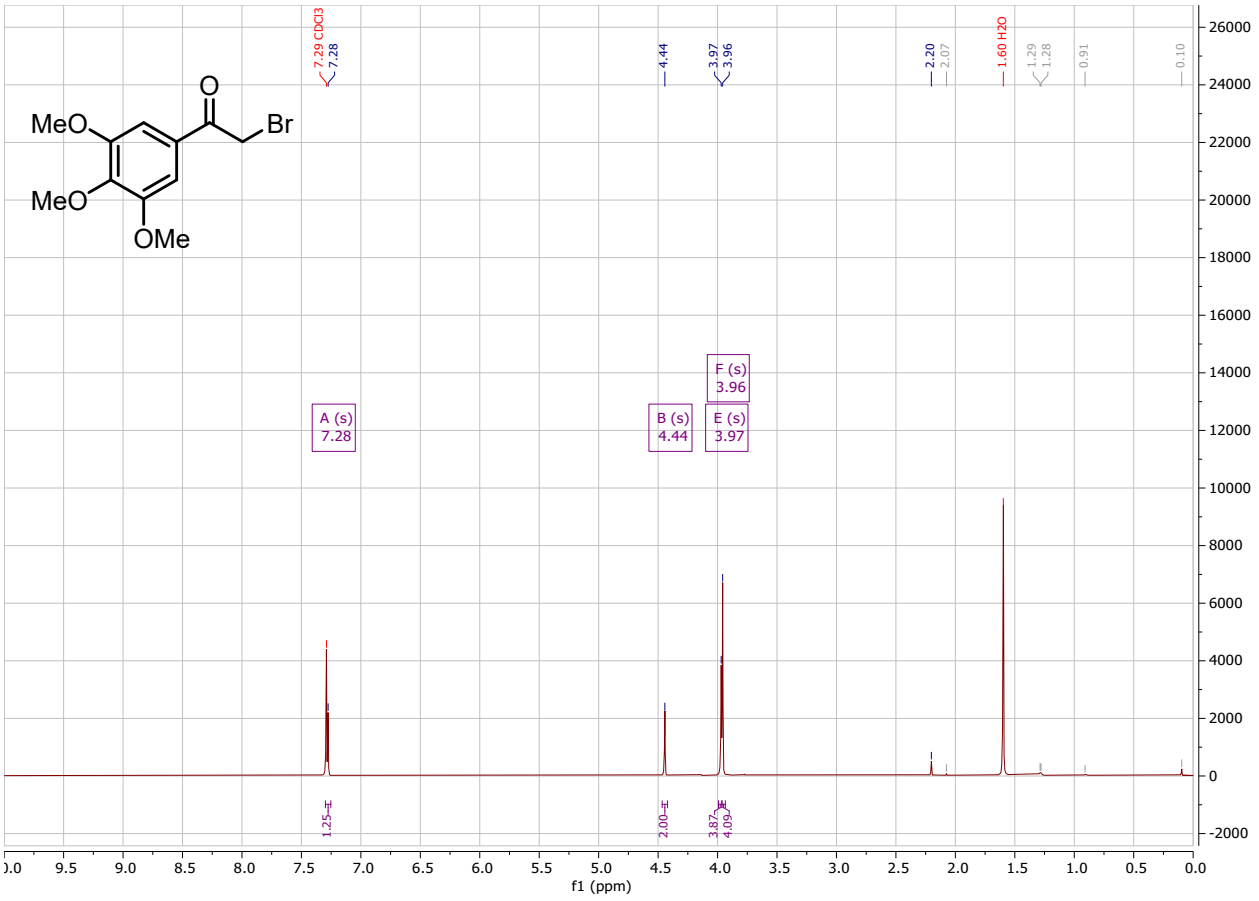
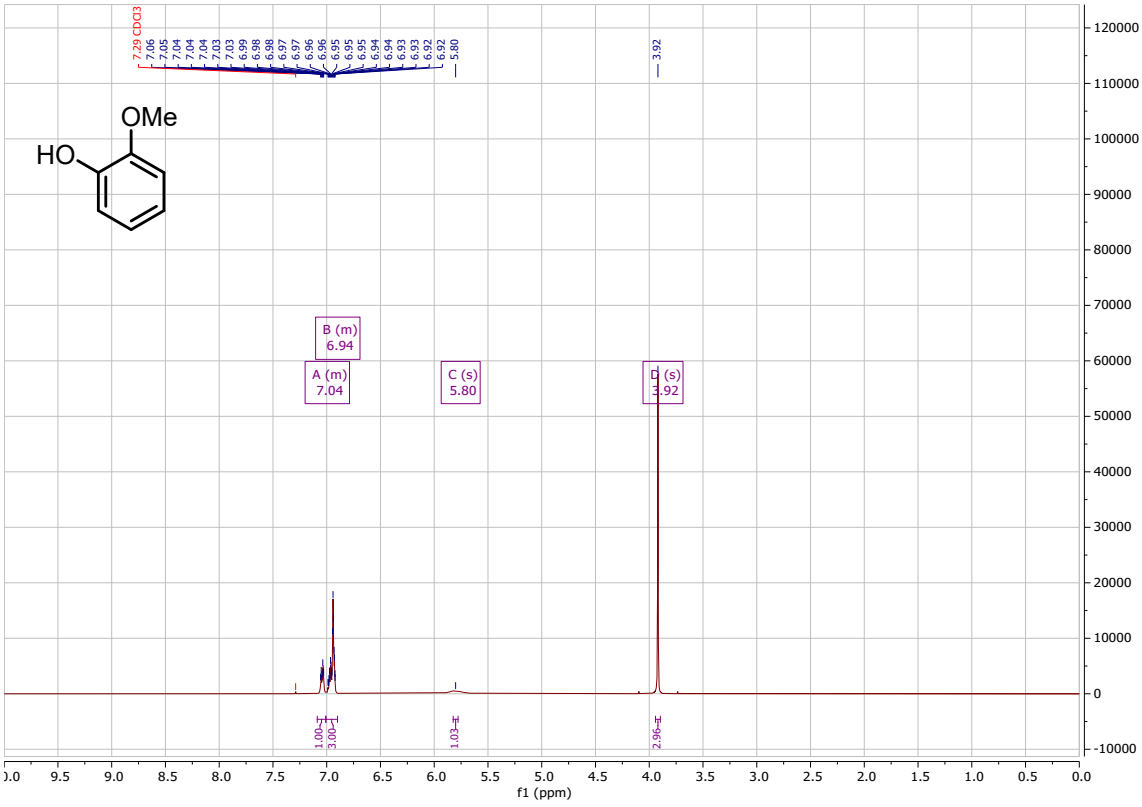
8.01
8.00
7.99
7.99
7.98
7.29 CDCl3
7.00
7.00
6.99
6.98
6.97
6.97
4.68
4.43
3.91
3.77
1.67 H2O
1.28
O
Br
MeO
A (dt)
8.00
B (dt)
6.98
C (s)
4.43
D (s)
3.91
1.95
1.95
2.06
3.04
f1 (ppm)

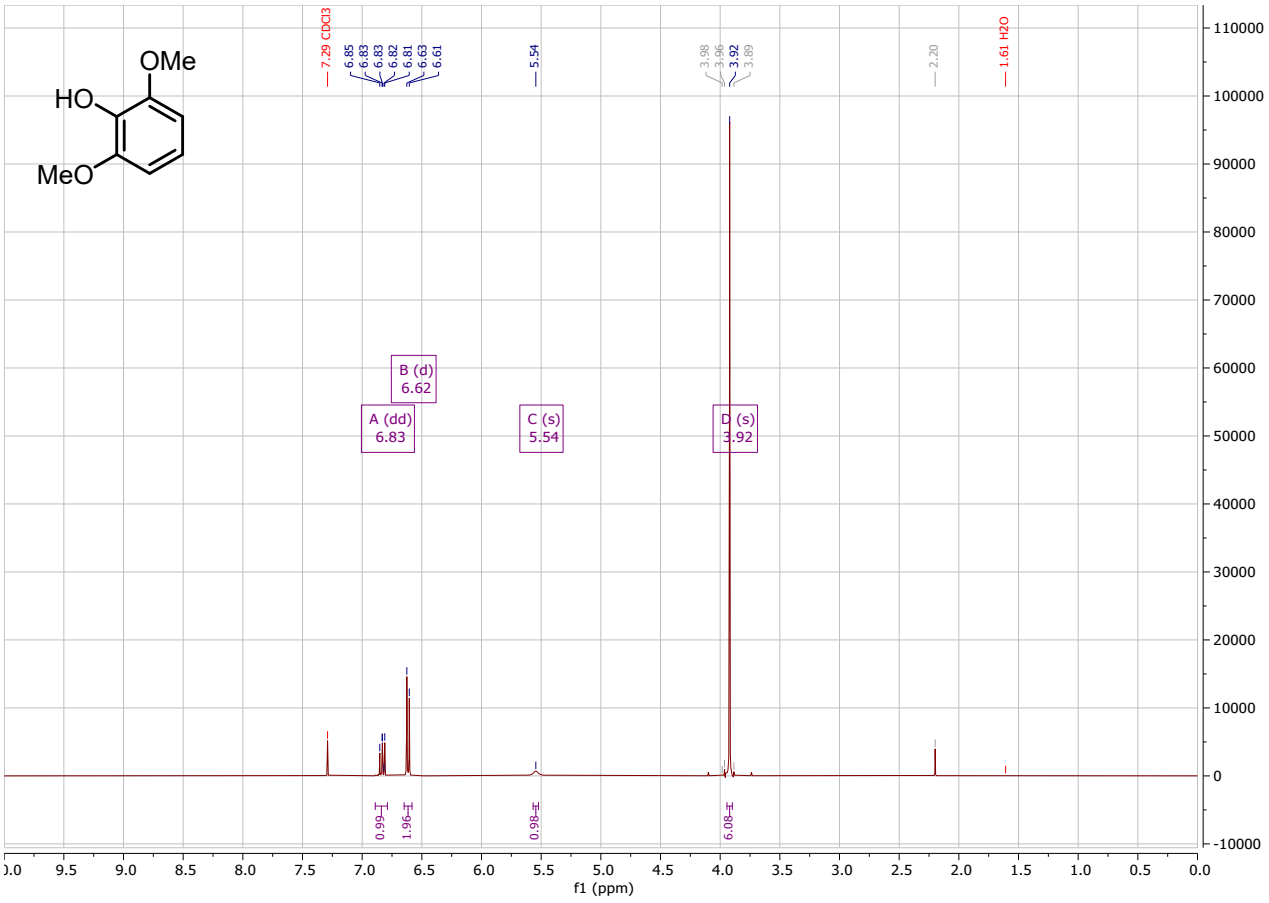

7.59
7.59
7.59
7.59
7.57
7.57
7.57
7.57
7.53
7.53
7.29 CDCl3
6.90
6.88
3.95
3.95
3.94
3.94
2.57
2.57
1.86 H2O
O
MeO
OMe
B (d)
7.53
A (dd)
7.58
C (d)
6.89
C (s)
3.94
F (s)
3.95
E (s)
2.57
0.95
1.03
1.01
3.43
2.76
2.82
f1 (ppm)

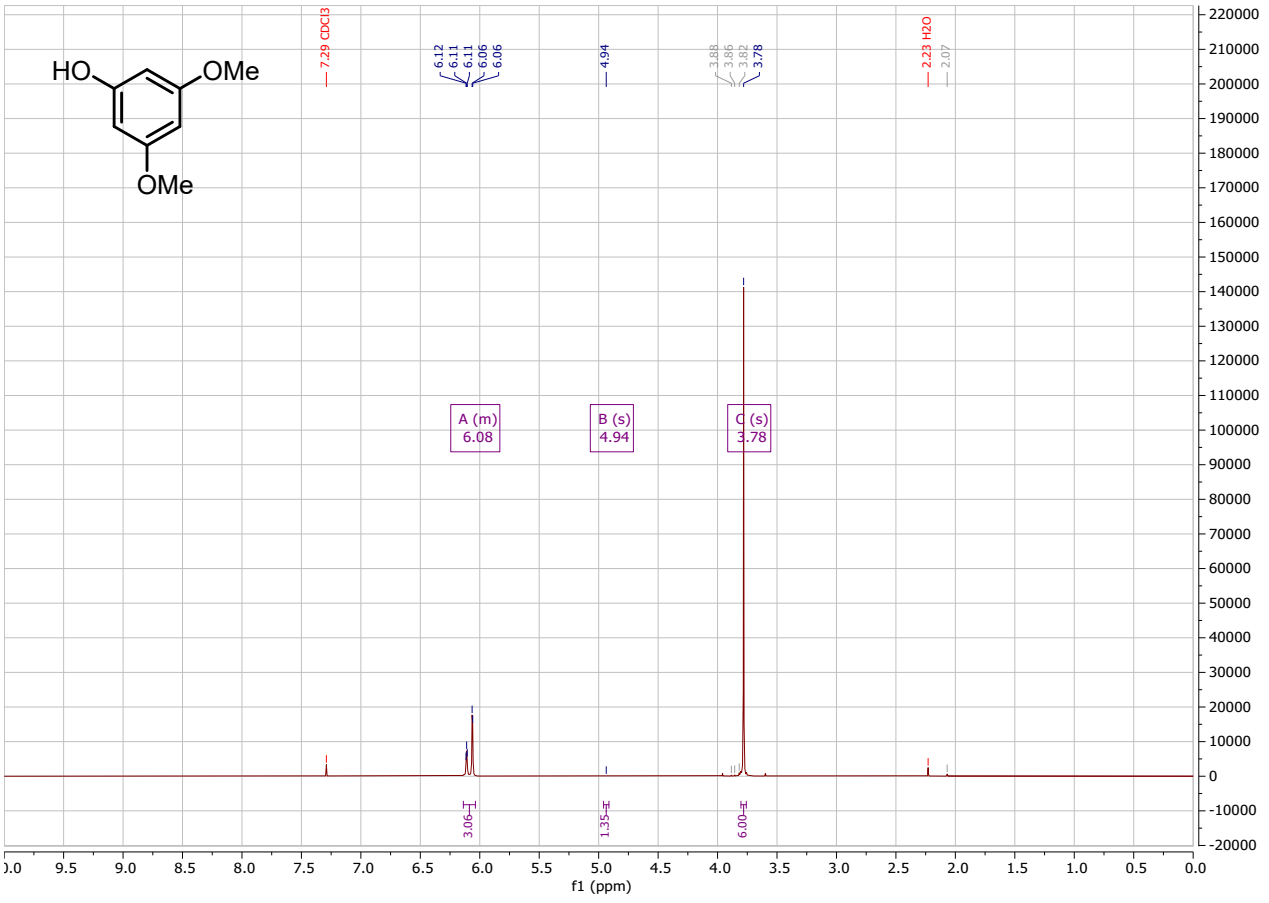

7.64
7.64
7.62
7.62
7.60
7.59
7.58
7.56
7.56
7.55
7.54
7.29 CDCl3
6.94
6.92
6.90
4.68
4.43
3.98
3.97
3.96
3.95
2.59
2.18
1.69 H2O
1.27
0.85
O
Br
MeO
OMe
B (d)
7.56
A (dd)
7.63
C (d)
6.93
G (s)
3.96
D (s)
4.43
F (s)
3.98
0.89
0.95
0.96
1.62
2.53
2.98
f1 (ppm)

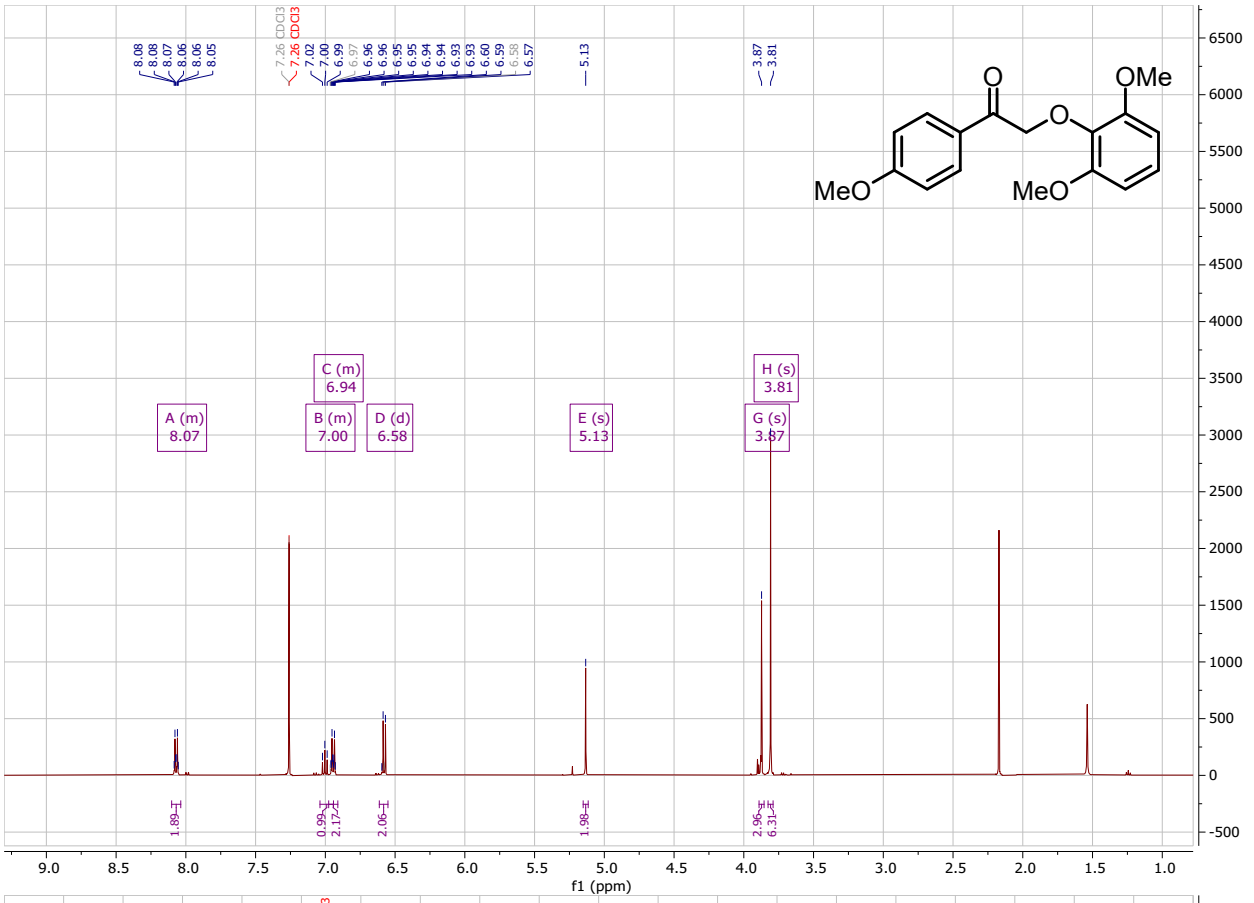

7.29 CDCl3
7.23
3.93
3.93
2.60
2.18
O
MeO
MeO
OMe
F (s)
3.93
A (s)
7.23
E (s)
3.93
C (s)
2.60
D (s)
2.18
1.87
7.21
1.75
3.12
1.05
f1 (ppm)

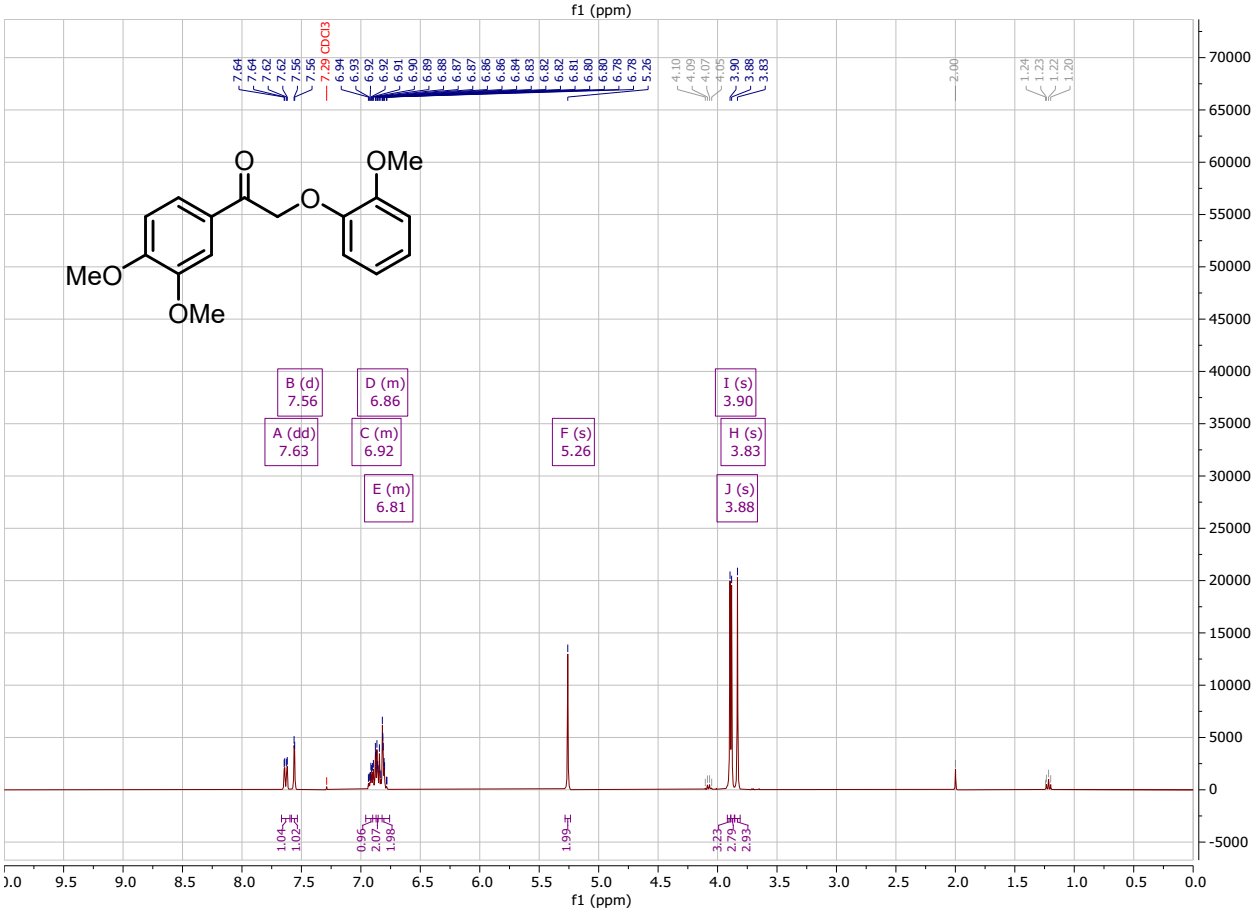

MeO
MeO
OMe
O
Br
7.29 CDCl3
7.28
4.44
3.97
3.96
2.20
2.07
1.60 H2O
1.29
1.28
0.91
0.10
A (s)
7.28
B (s)
4.44
E (s)
3.97
F (s)
3.96
1.25
2.00
3.87
4.09
f1 (ppm)

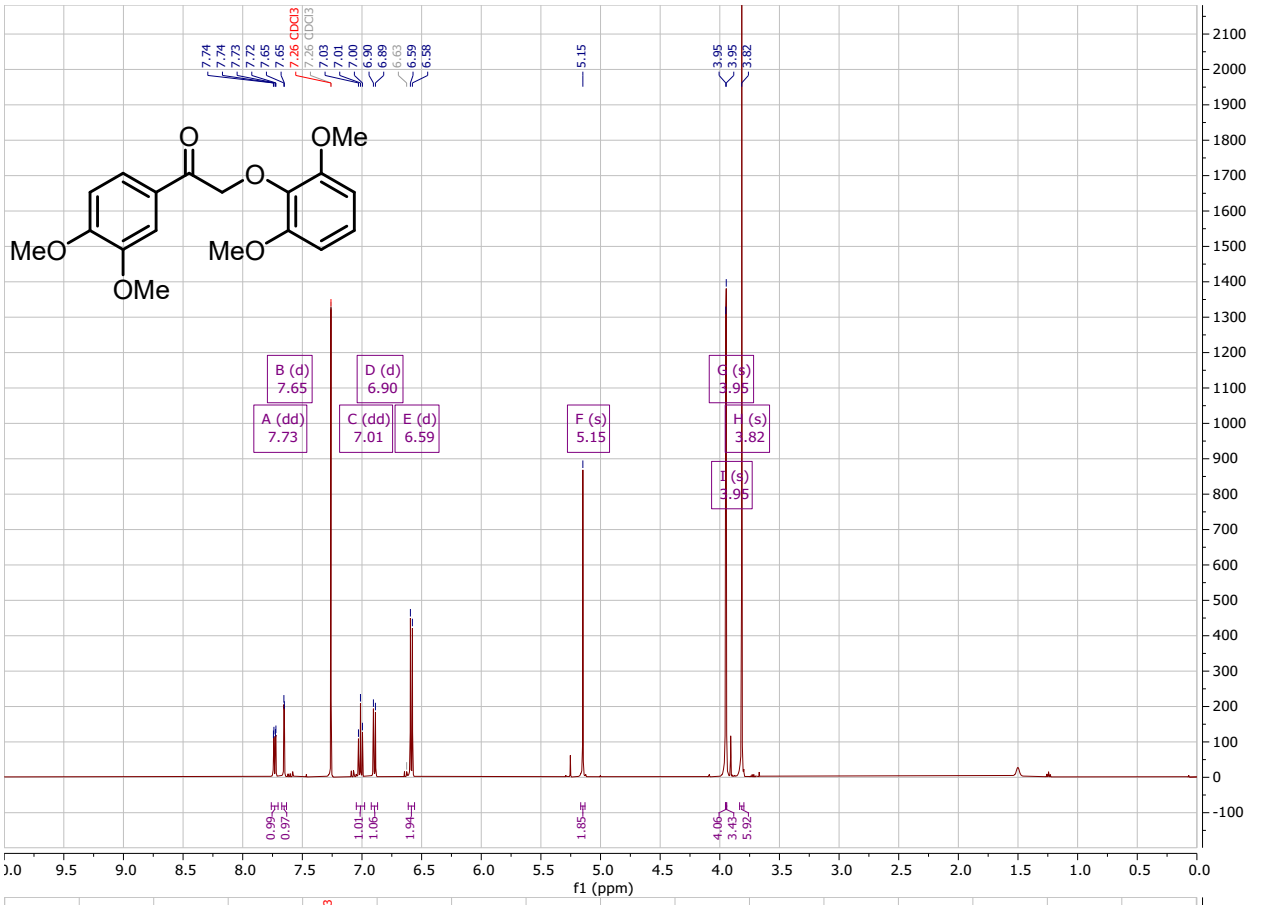

OMe
HO
7.29 CDCl3
7.06
7.05
7.04
7.04
7.04
7.03
7.03
6.99
6.98
6.98
6.97
6.97
6.96
6.96
6.95
6.95
6.95
6.94
6.94
6.93
6.93
6.92
6.92
5.80
3.92
B (m)
6.94
A (m)
7.04
C (s)
5.80
D (s)
3.92
1.00
3.00
1.03
2.96
f1 (ppm)

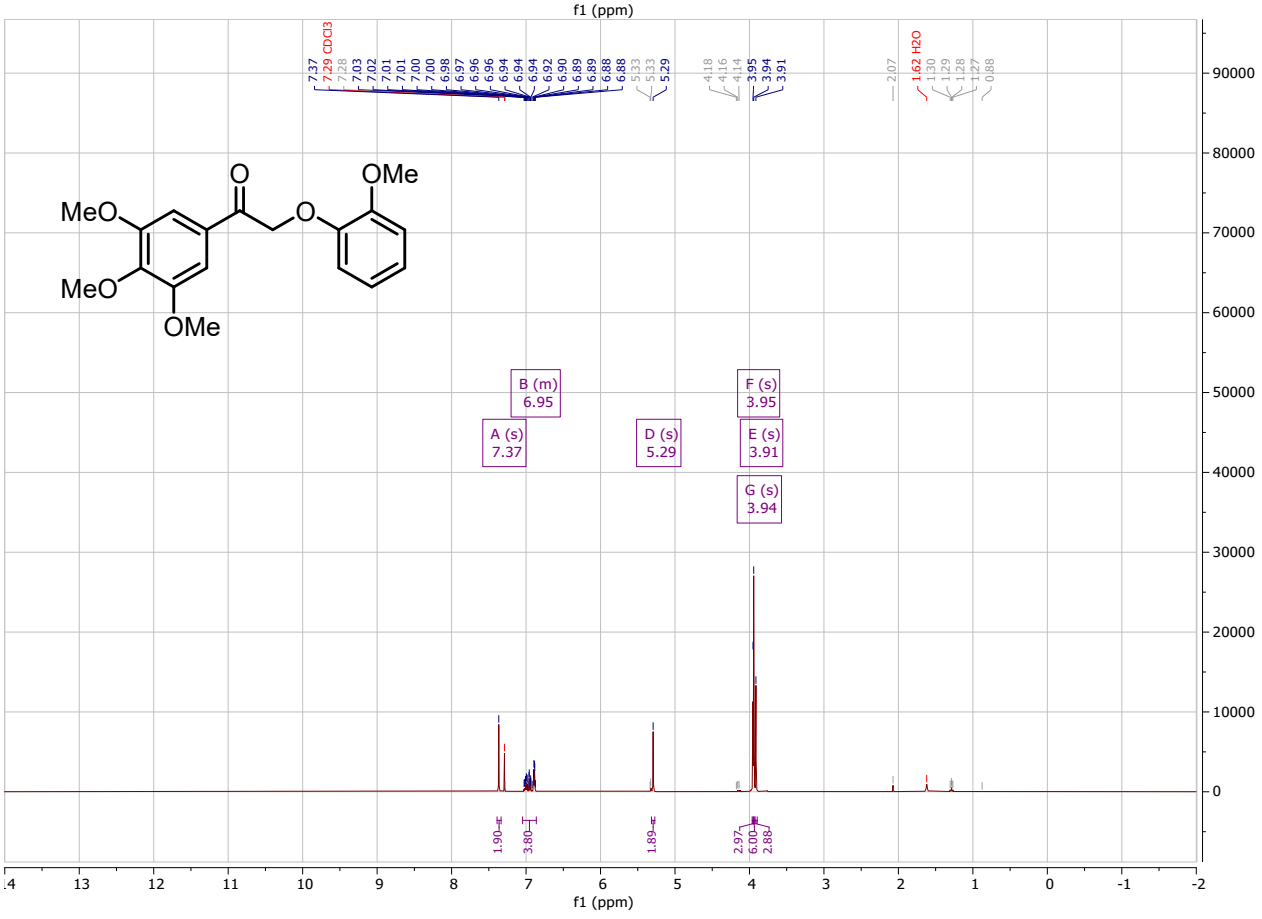

OMe
HO
MeO
7.29 CDCl3
6.85
6.83
6.83
6.82
6.81
6.63
6.61
5.54
3.98
3.96
3.92
3.89
2.20
1.61 H2O
B (d)
6.62
A (dd)
6.83
C (s)
5.54
D (s)
3.92
0.99
1.96
0.98
6.08
f1 (ppm)

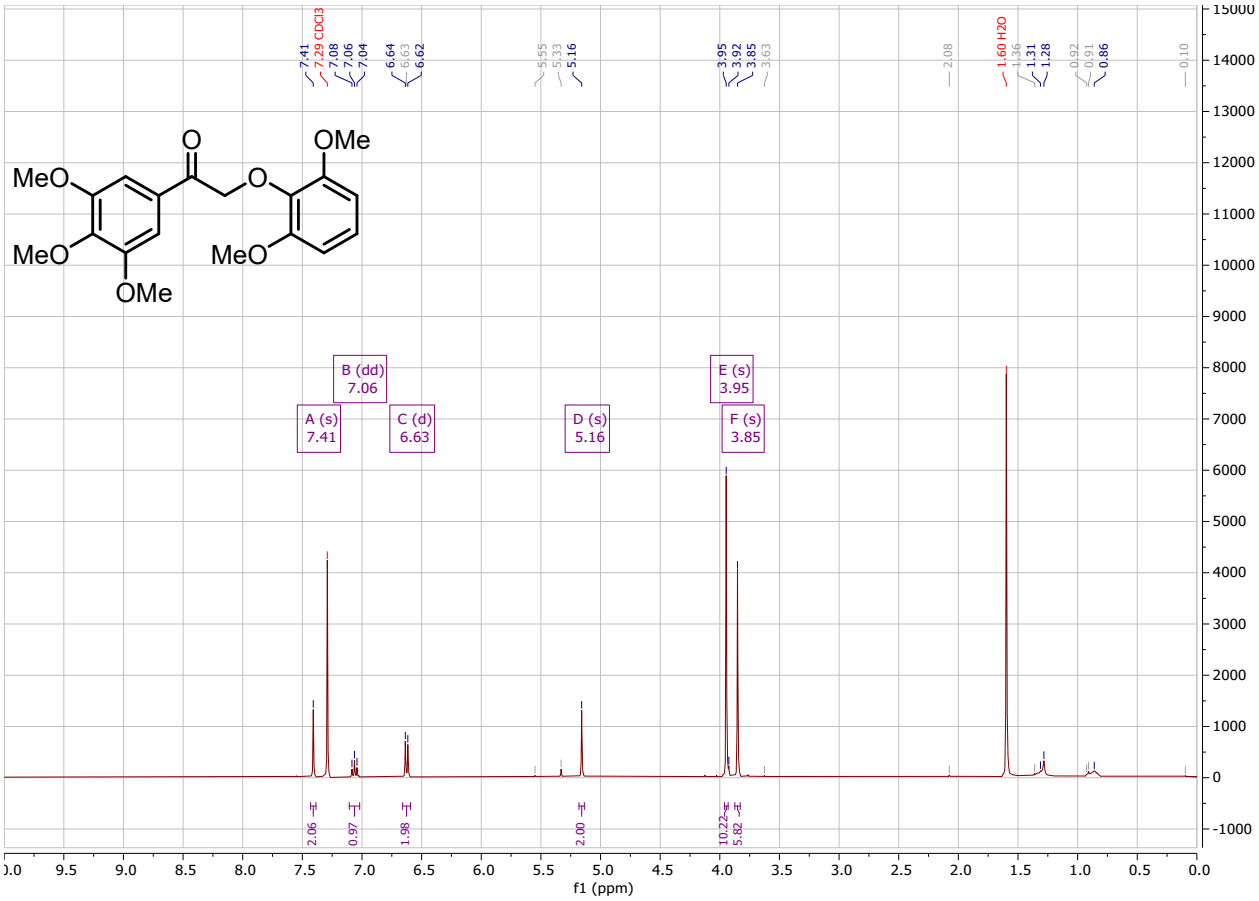

HO
OMe
OMe
7.29 CDCl3
6.12
6.11
6.11
6.06
6.06
4.94
3.88
3.86
3.82
3.78
2.23 H2O
2.07
A (m)
6.08
B (s)
4.94
C (s)
3.78
3.06
1.35
6.00
f1 (ppm)

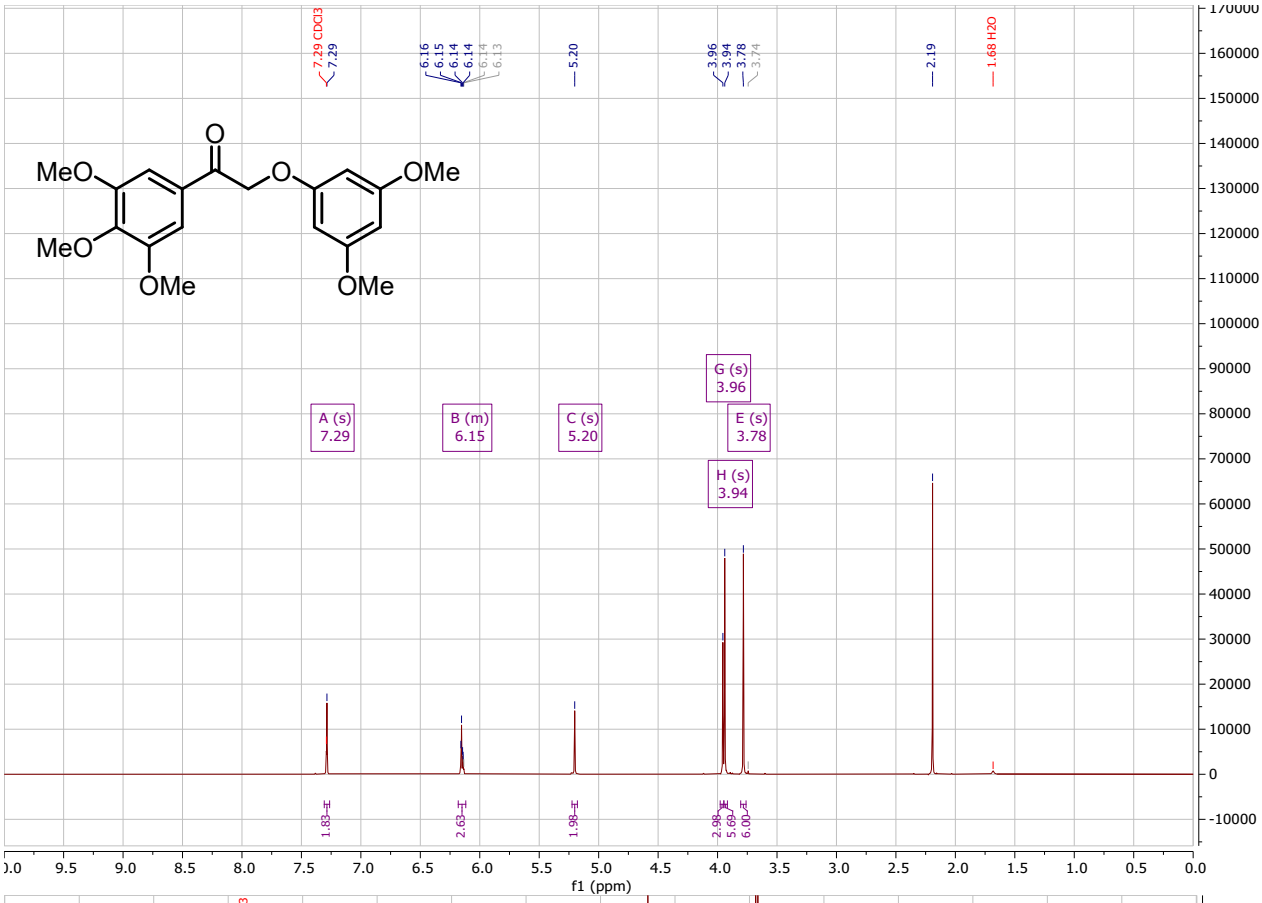

A (m) 8.07
B (m) 7.00
C (m) 6.94
D (d) 6.58
E (s) 5.13
G (s) 3.87
H (s) 3.81
MeO
OMe
f1 (ppm)

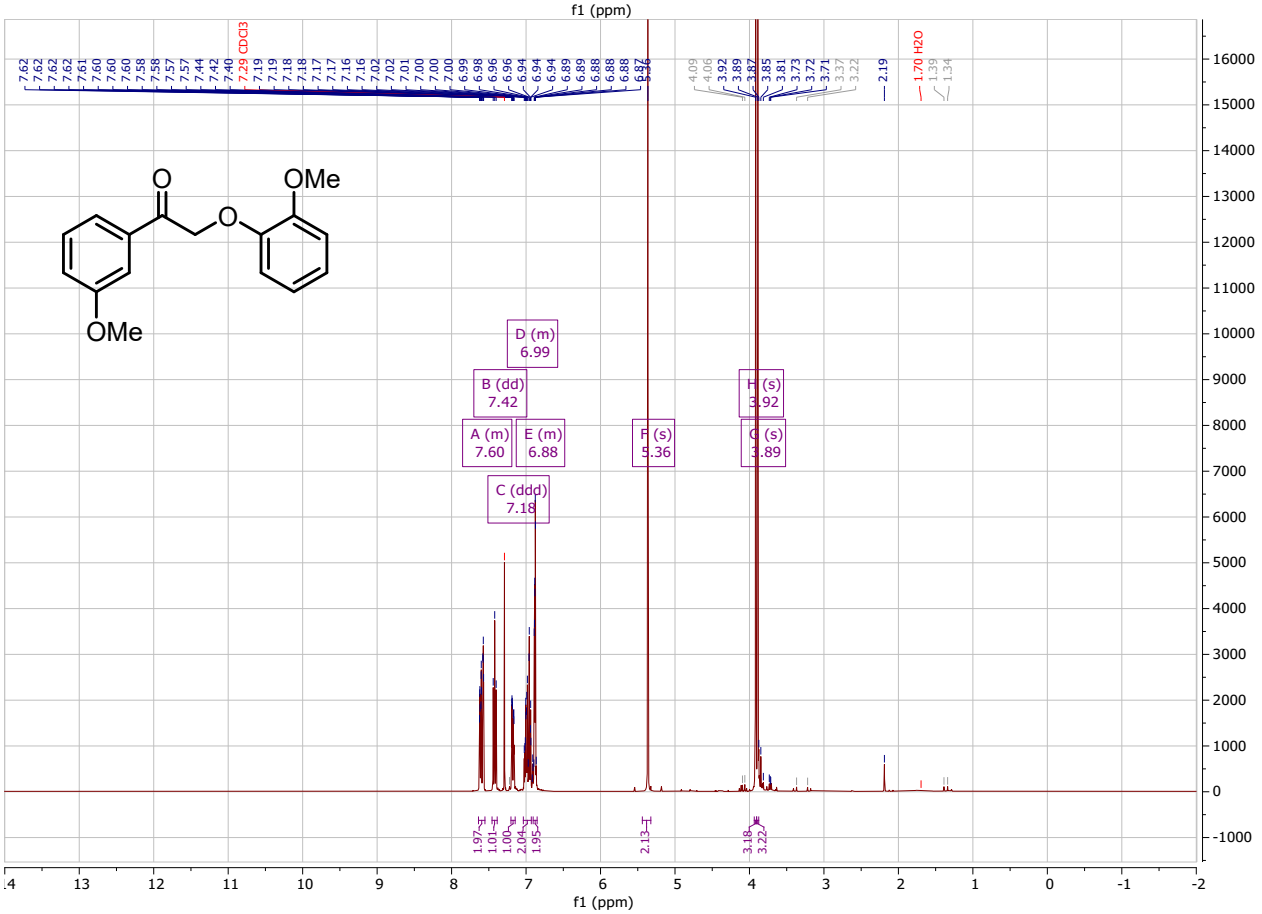

A (dd) 7.63
B (d) 7.56
C (m) 6.92
D (m) 6.86
E (m) 6.81
F (s) 5.26
H (s) 3.83
I (s) 3.90
J (s) 3.88
MeO
OMe
f1 (ppm)

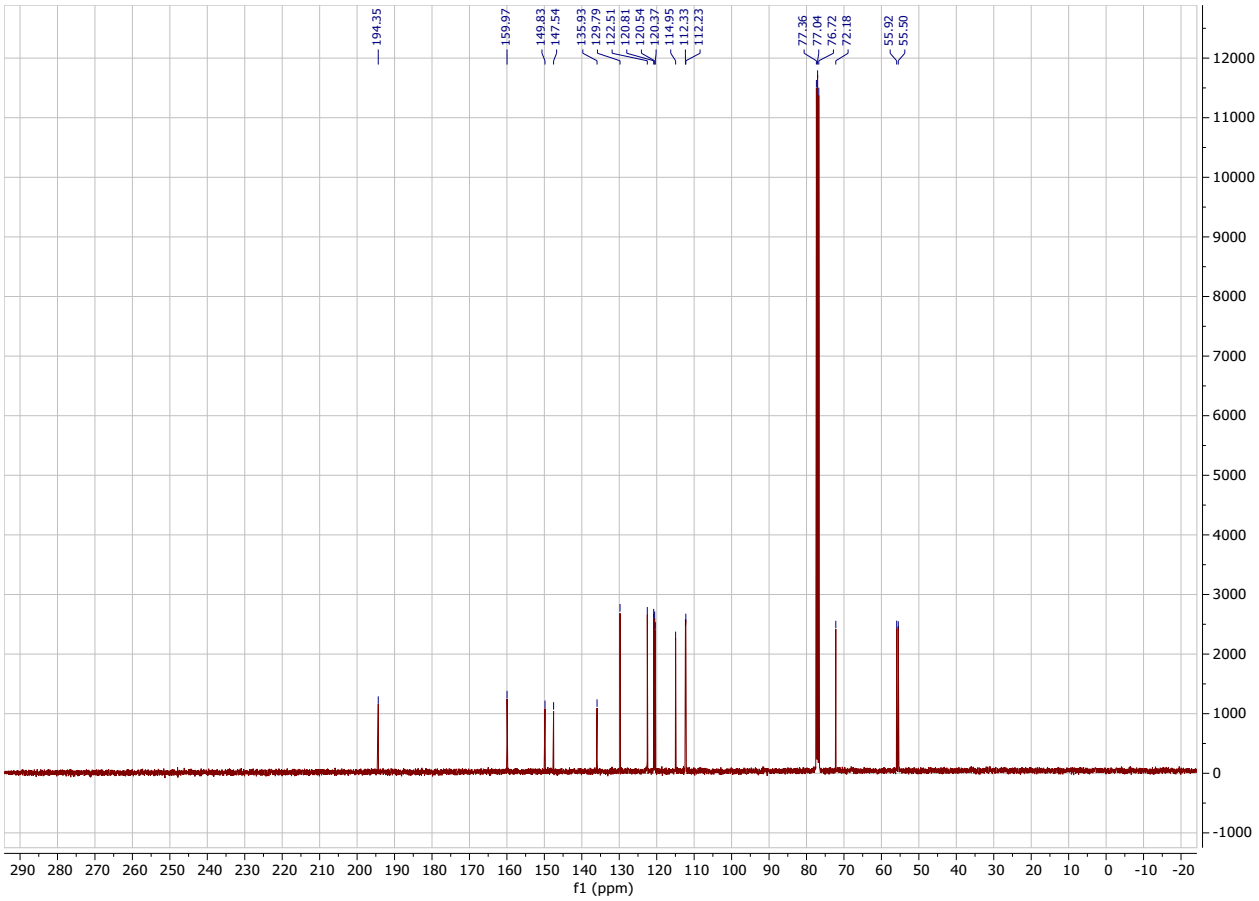

O
OMe
O
MeO
MeO
OMe
B (d) 7.65
D (d) 6.90
G (s) 3.95
A (dd) 7.73
C (dd) 7.01
E (d) 6.59
F (s) 5.15
H (s) 3.82
I (s) 3.95
f1 (ppm)

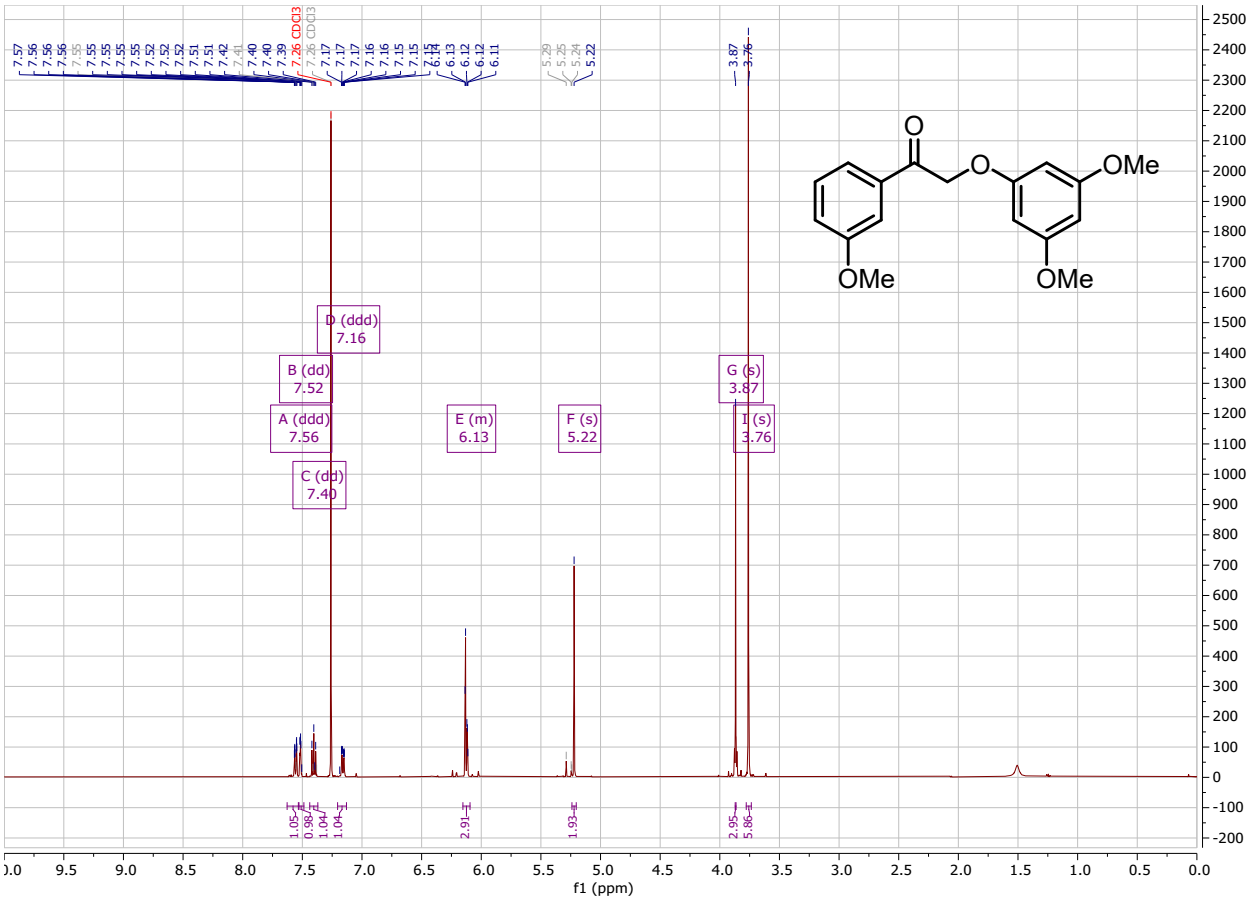

O
OMe
MeO
O
MeO
OMe
B (m) 6.95
F (s) 3.95
A (s) 7.37
D (s) 5.29
E (s) 3.91
G (s) 3.94
f1 (ppm)

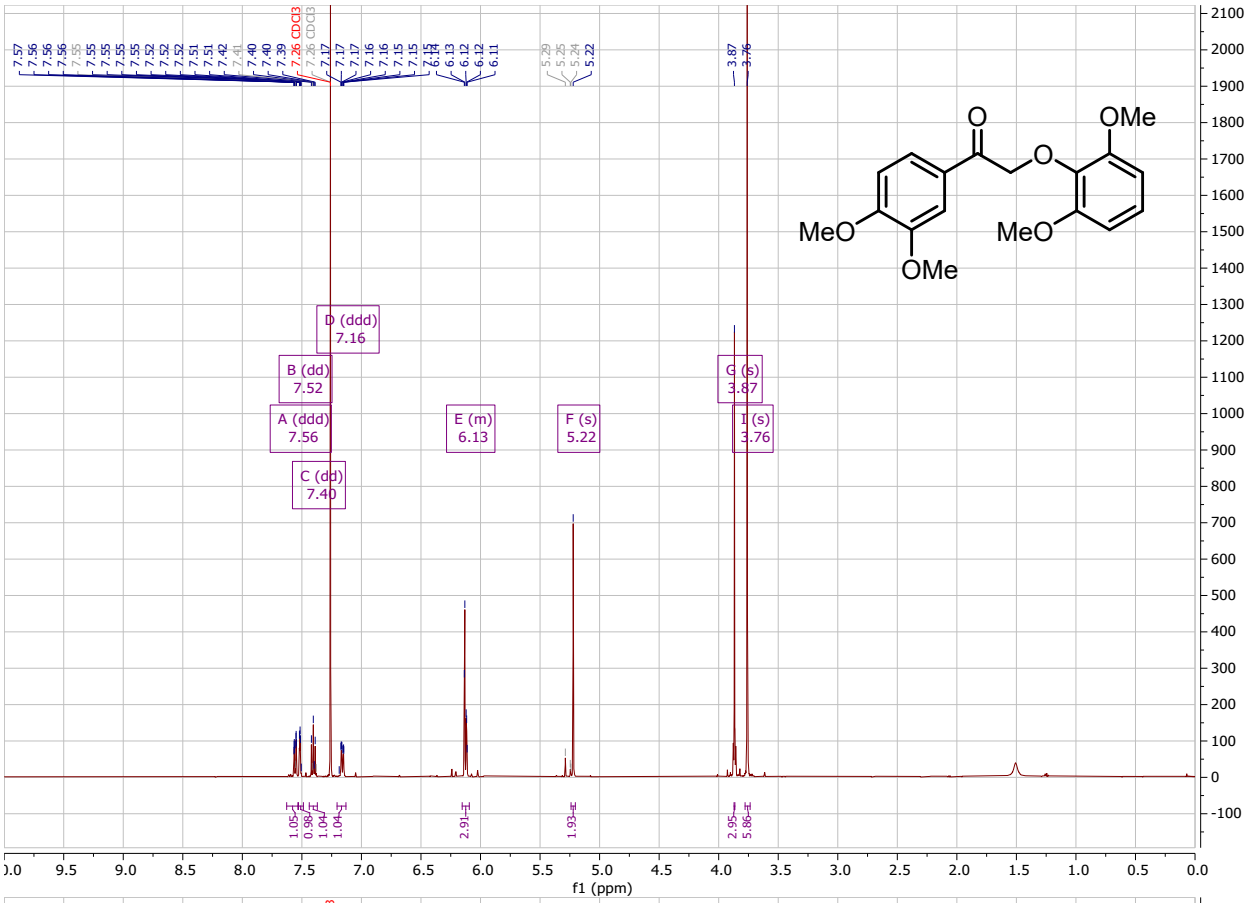

MeO
MeO
OMe
O
O
OMe
MeO
OMe
B (dd)
7.06
A (s)
7.41
C (d)
6.63
D (s)
5.16
E (s)
3.95
F (s)
3.85
f1 (ppm)

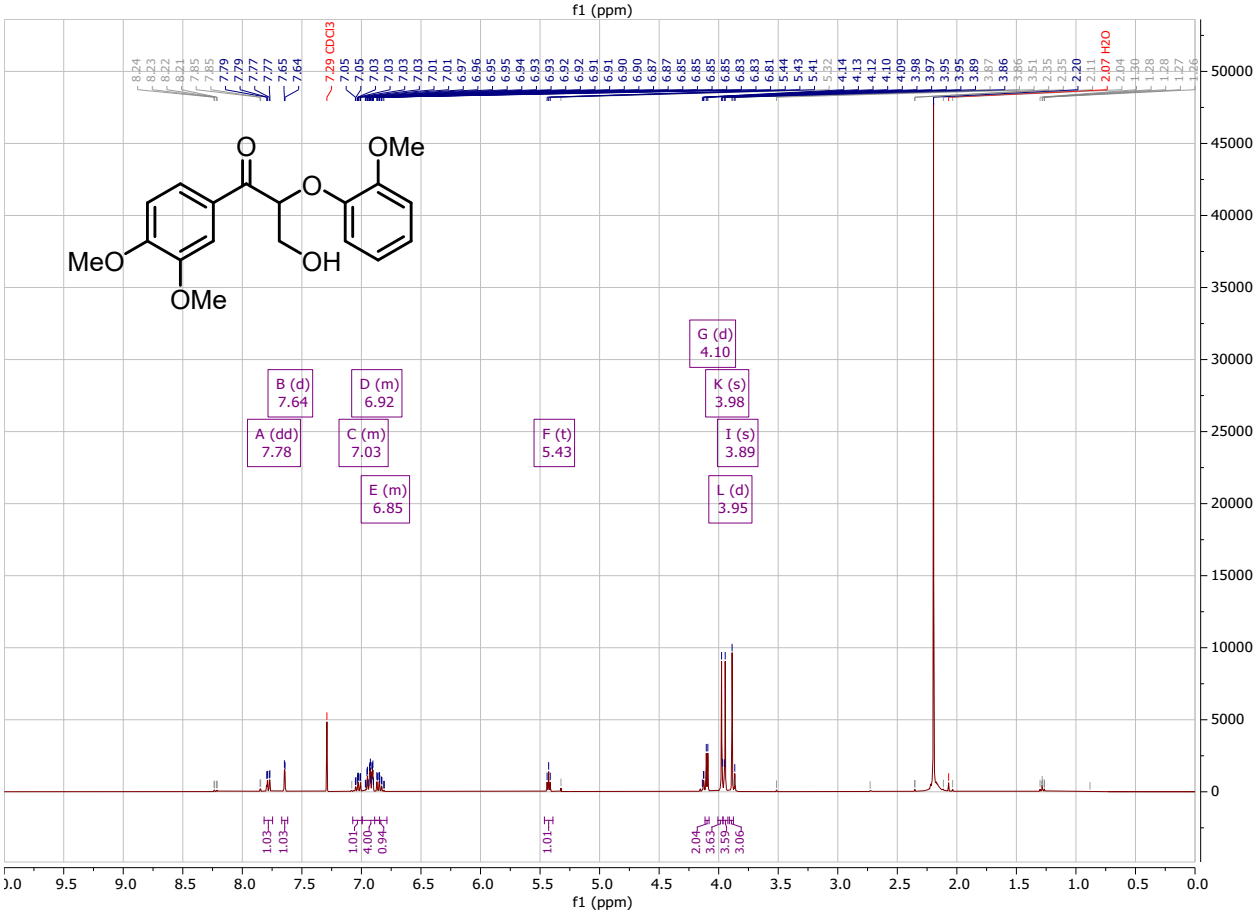

MeO
MeO
OMe
OMe
OMe
O
O
A (s)
7.29
B (m)
6.15
C (s)
5.20
G (s)
3.96
E (s)
3.78
H (s)
3.94
f1 (ppm)

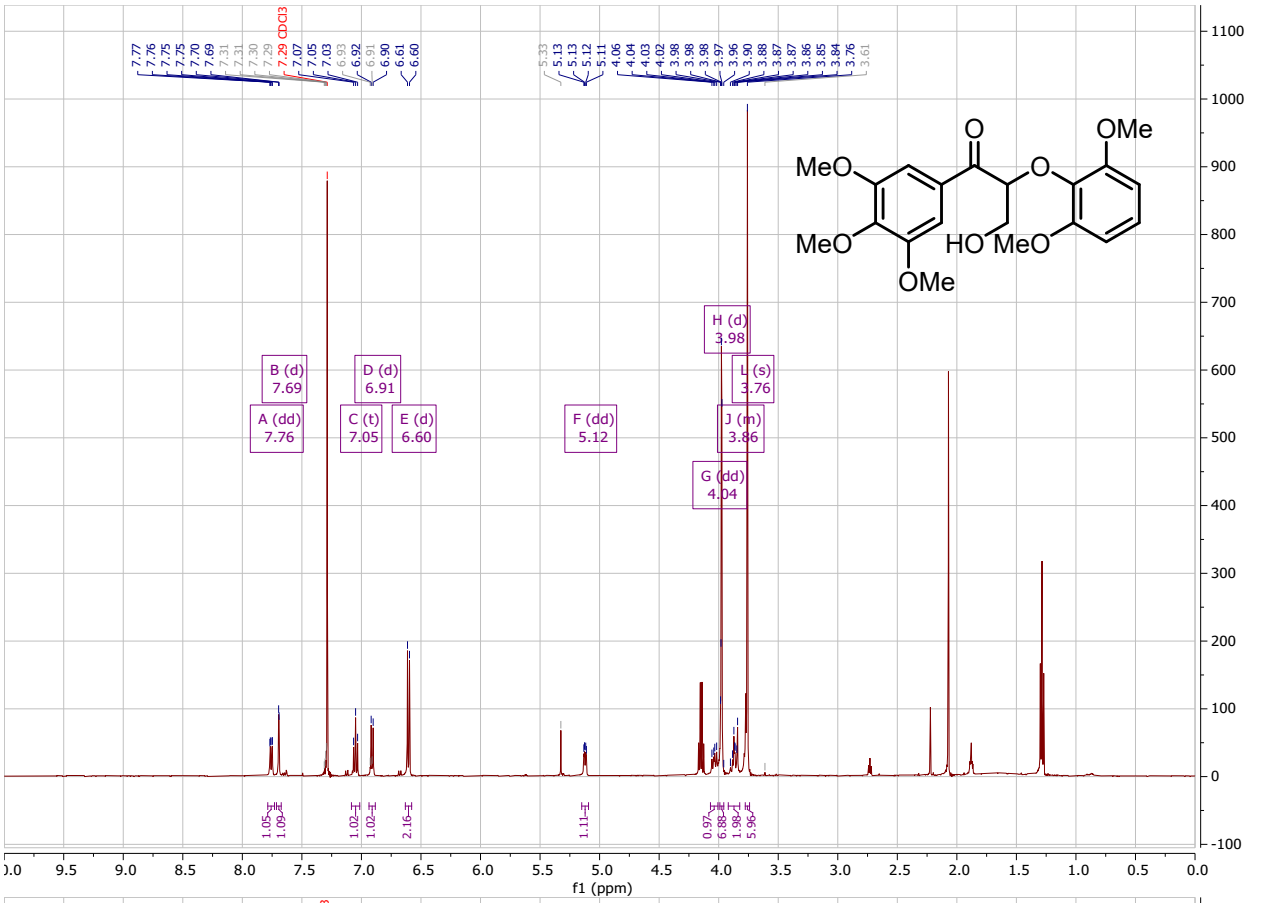

OMe
OMe
O
O
D (m)
6.99
B (dd)
7.42
A (m)
7.60
E (m)
6.88
C (ddd)
7.18
H (s)
3.92
f1 (ppm)

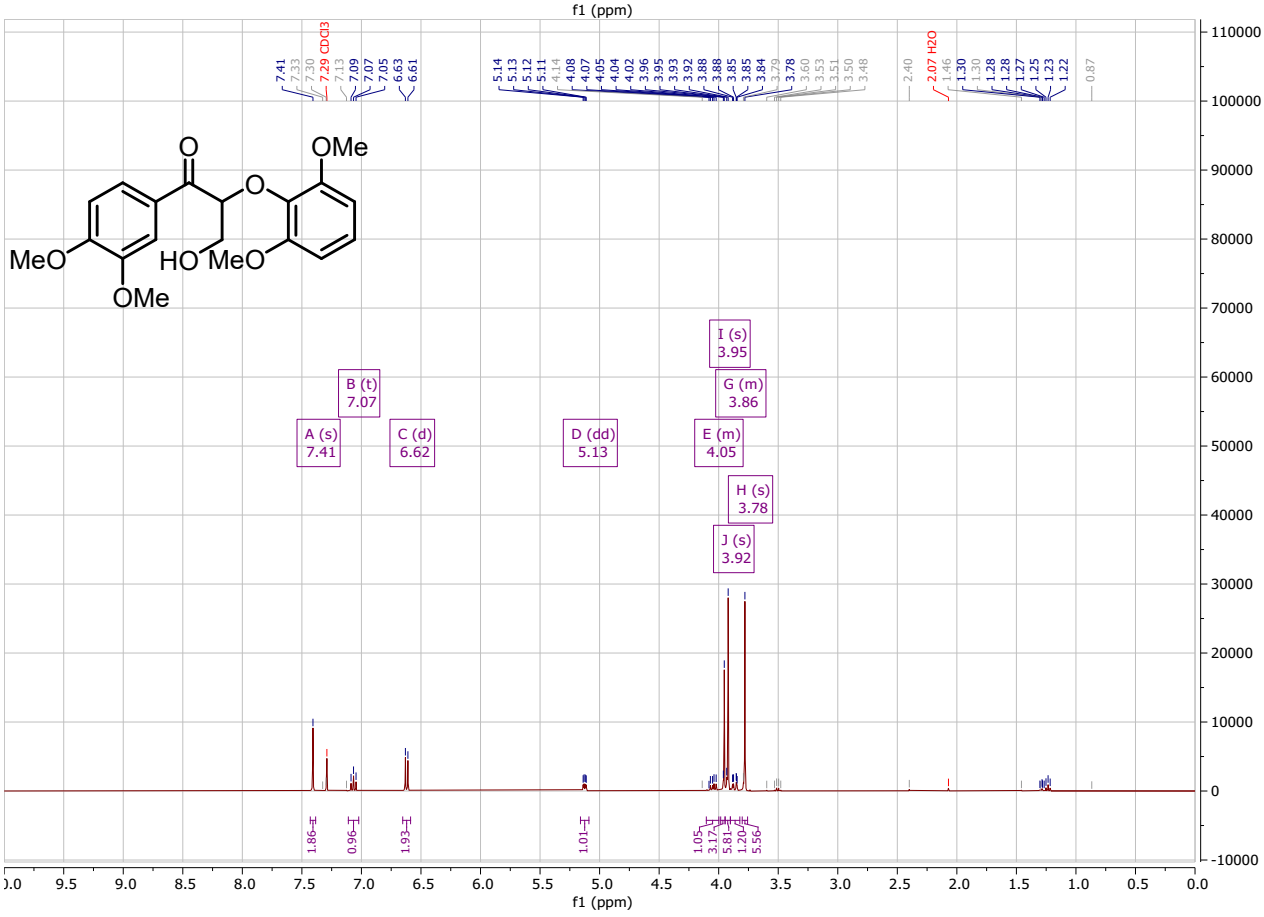

194.35
159.97
149.83
147.54
135.93
129.79
122.51
120.81
120.54
120.37
114.95
112.33
112.23
77.36
77.04
76.72
72.18
55.92
55.50
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
290 280 270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

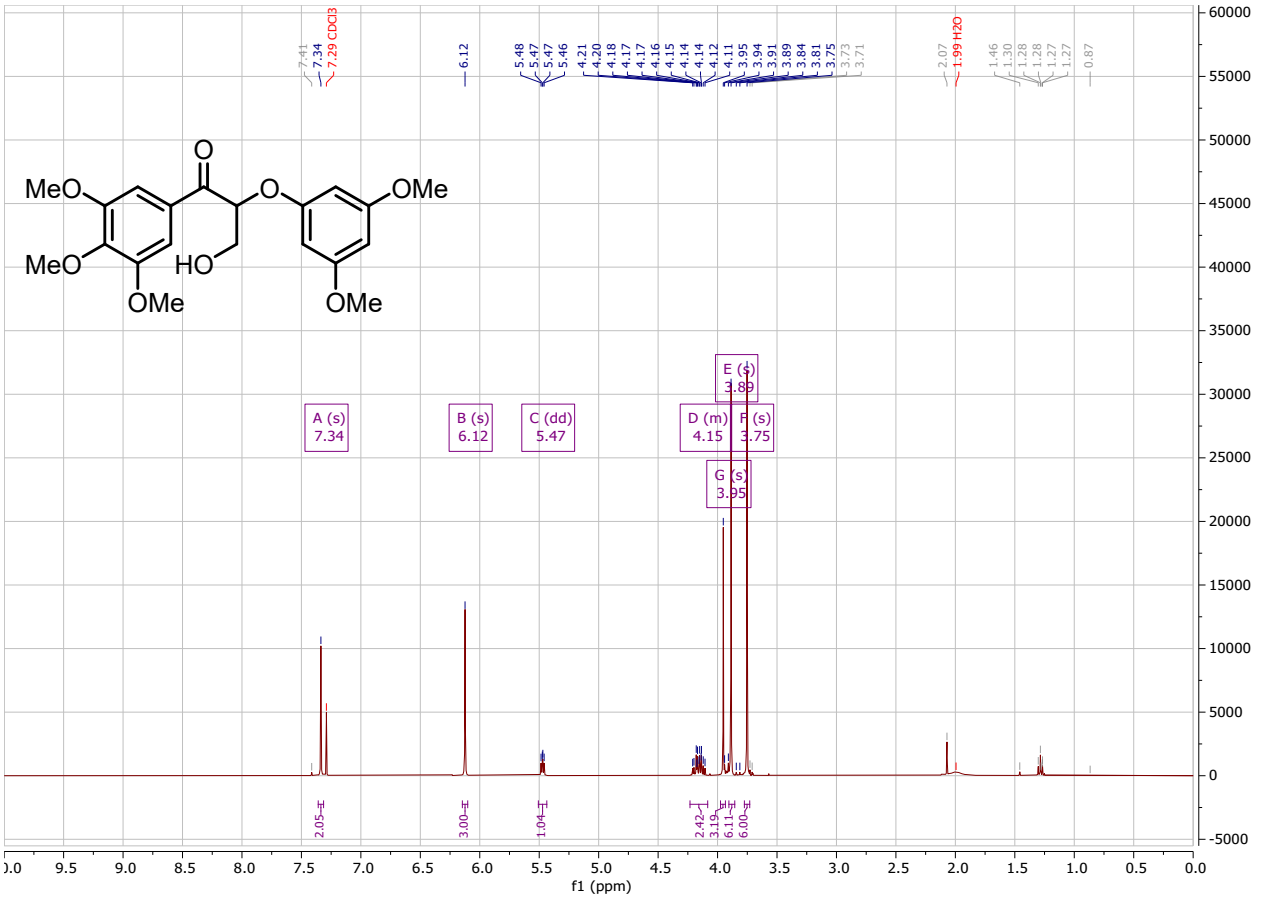

D (ddd)
7.16
B (dd)
7.52
A (ddd)
7.56
C (dd)
7.40
E (m)
6.13
F (s)
5.22
G (s)
3.87
I (s)
3.76
OMe
OMe
OMe
f1 (ppm)

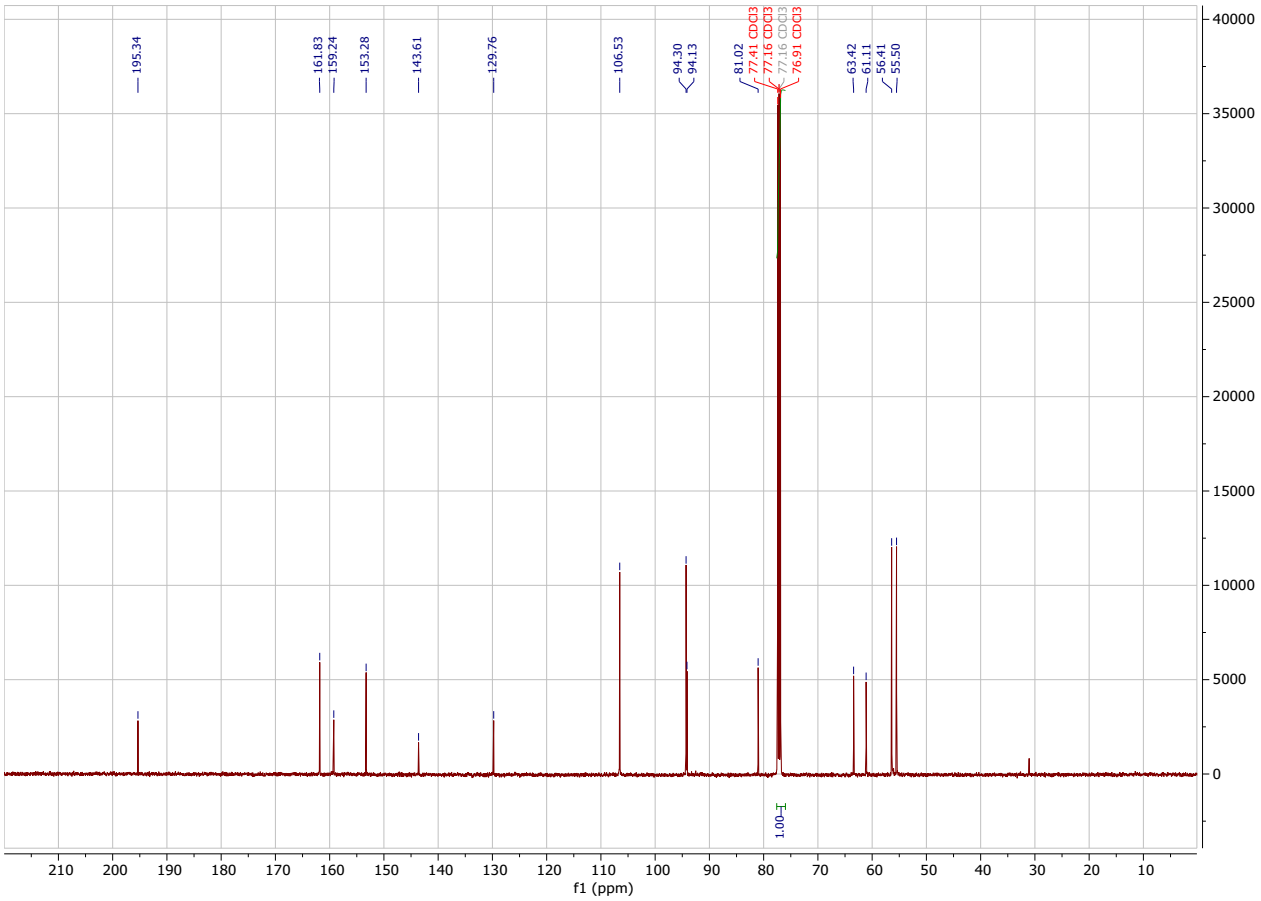

O
OMe
O
MeO
MeO
OMe
D (ddd) 7.16
B (dd) 7.52
A (ddd) 7.56
C (dd) 7.40
E (m) 6.13
F (s) 5.22
G (s) 3.87
I (s) 3.76
f1 (ppm)

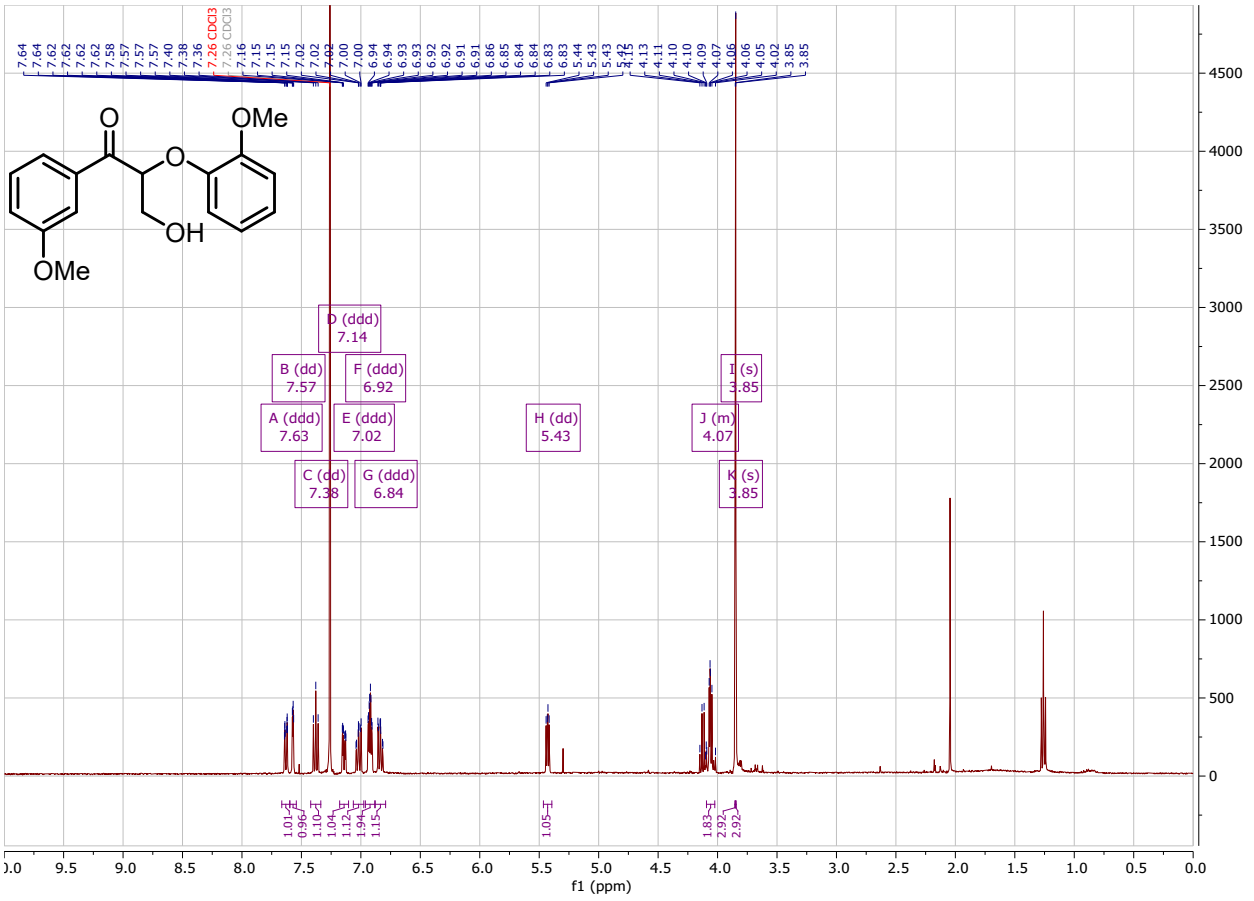

O
OMe
O
MeO
OH
OMe
G (d) 4.10
B (d) 7.64
D (m) 6.92
K (s) 3.98
A (dd) 7.78
C (m) 7.03
F (t) 5.43
I (s) 3.89
E (m) 6.85
L (d) 3.95
f1 (ppm)

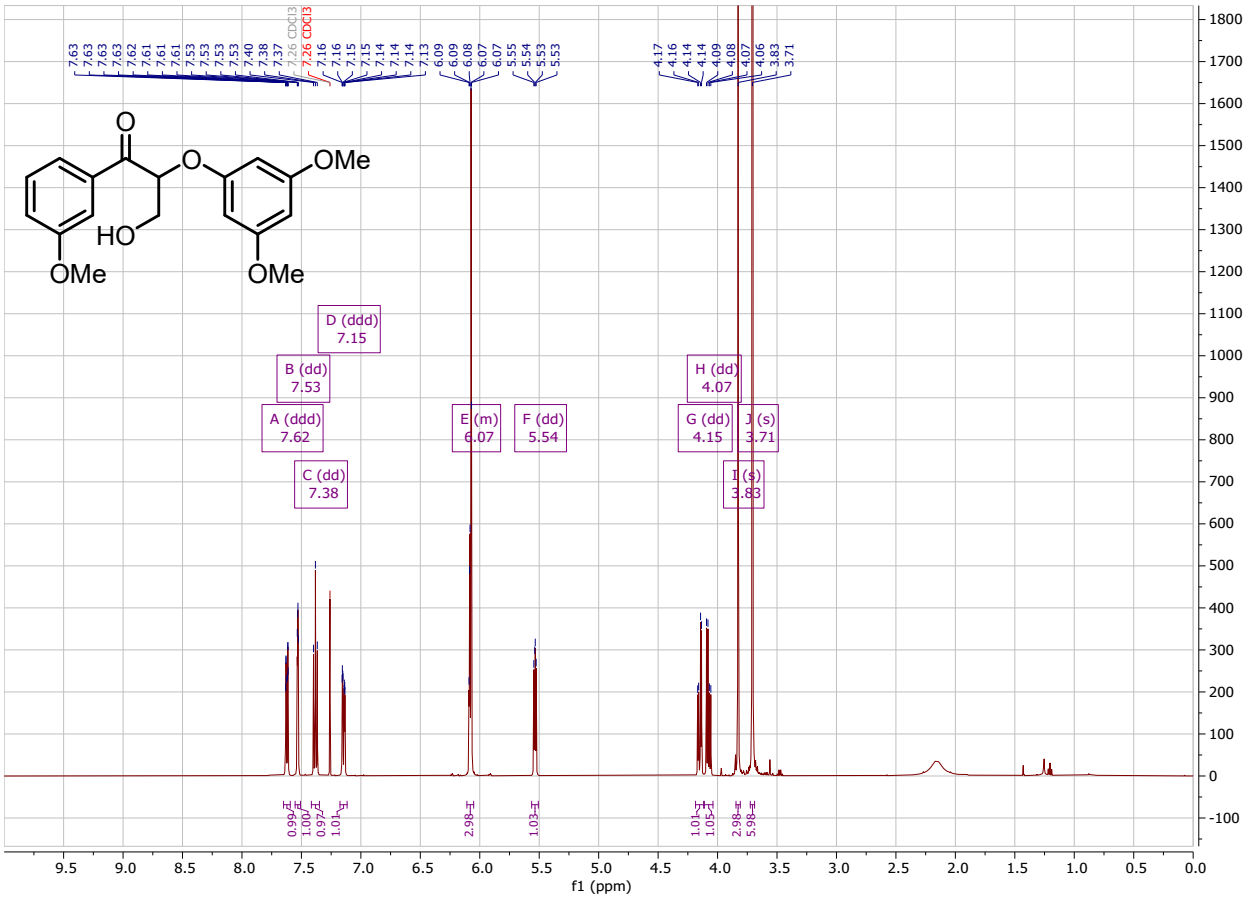

MeO
MeO
OMe
O
O
OMe
HO
MeO
OMe
B (d) 7.69
A (dd) 7.76
D (d) 6.91
C (t) 7.05
E (d) 6.60
F (dd) 5.12
H (d) 3.98
L (s) 3.76
J (m) 3.86
G (dd) 4.04
f1 (ppm)

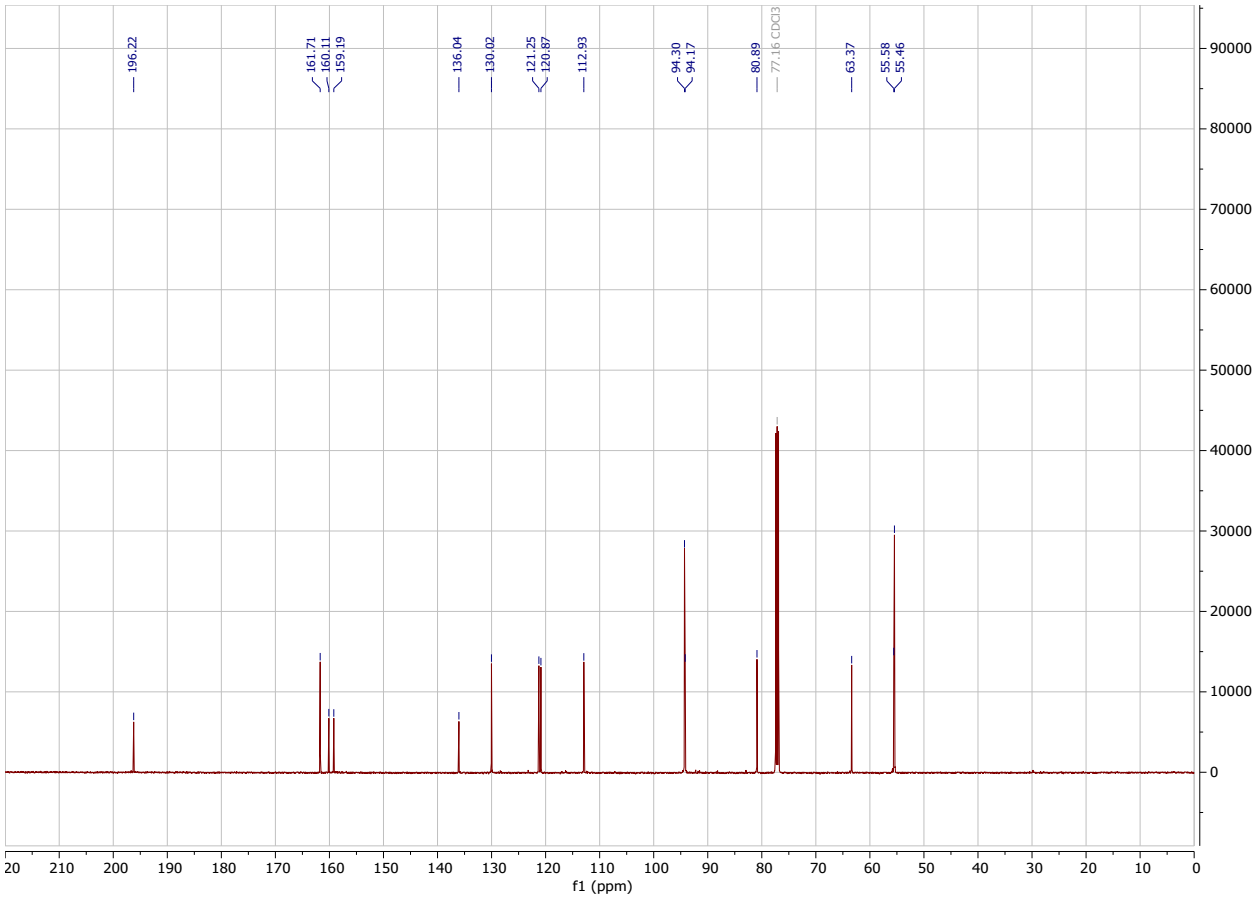

MeO
HO
MeO
OMe
O
O
OMe
I (s) 3.95
G (m) 3.86
B (t) 7.07
A (s) 7.41
C (d) 6.62
D (dd) 5.13
E (m) 4.05
H (s) 3.78
J (s) 3.92
f1 (ppm)

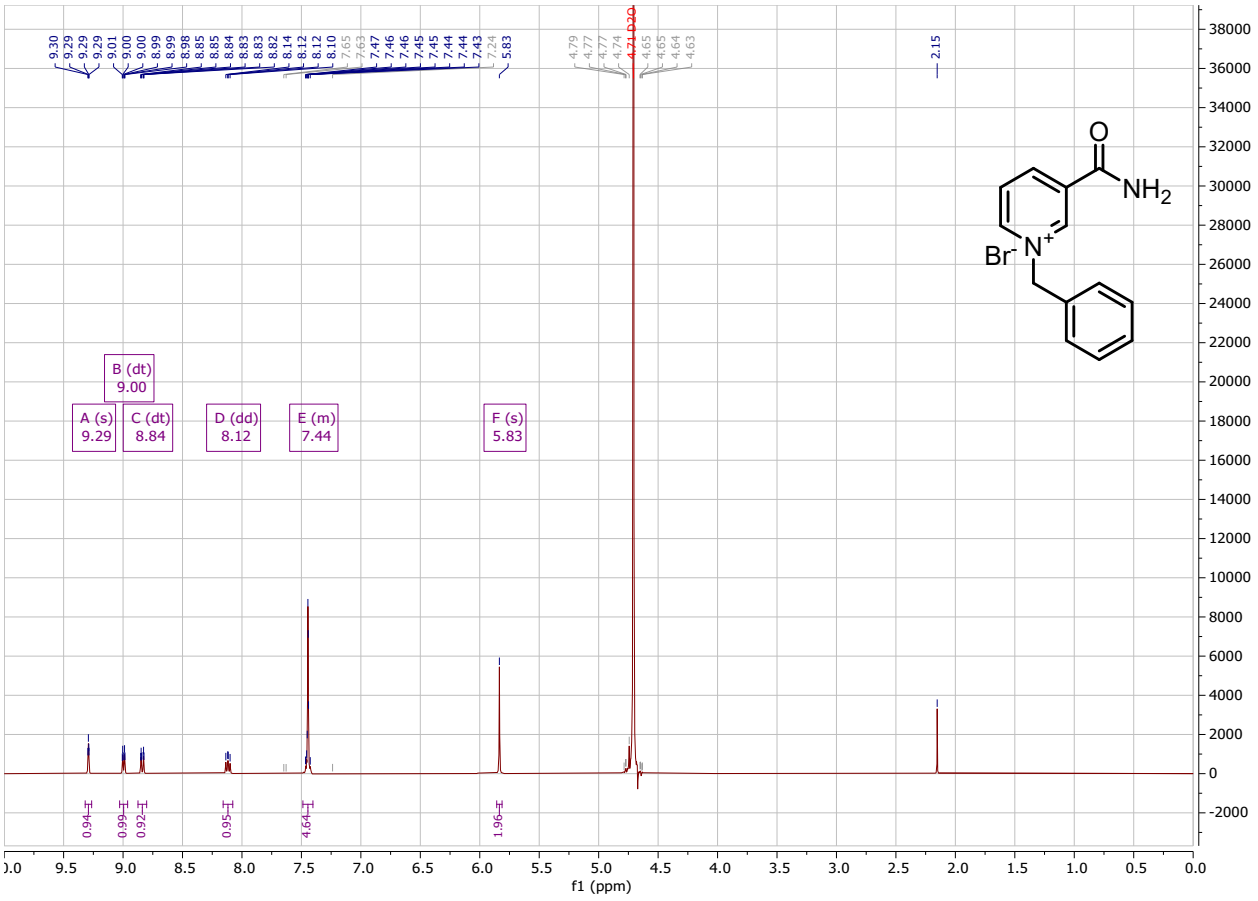

MeO
MeO
OMe
HO
O
O
OMe
OMe
A (s) 7.34
B (s) 6.12
C (dd) 5.47
D (m) 4.15
E (s) 3.89
F (s) 3.75
G (s) 3.95
f1 (ppm)

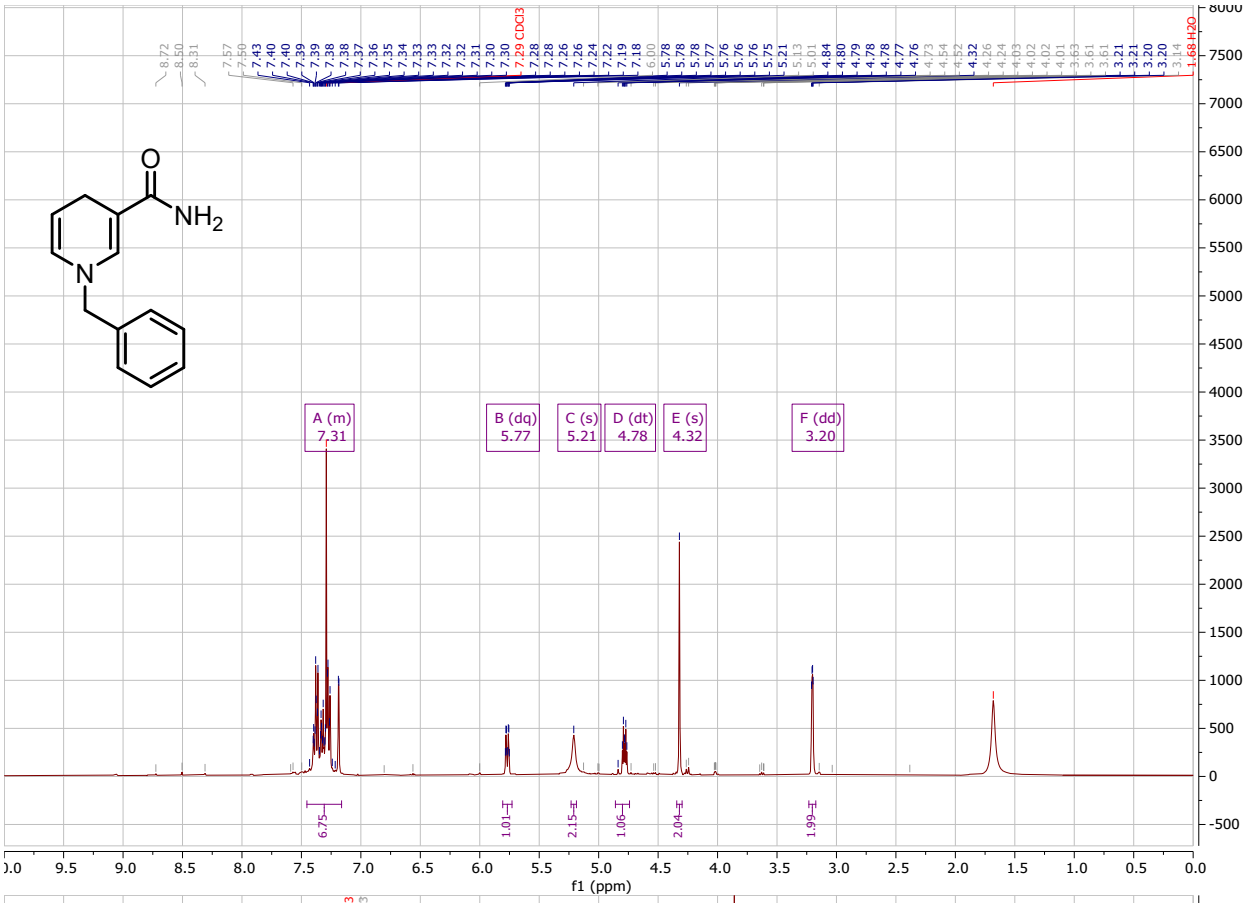

195.34
161.83
159.24
153.28
143.61
129.76
106.53
94.30
94.13
81.02
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
63.42
61.11
56.41
55.50
f1 (ppm)

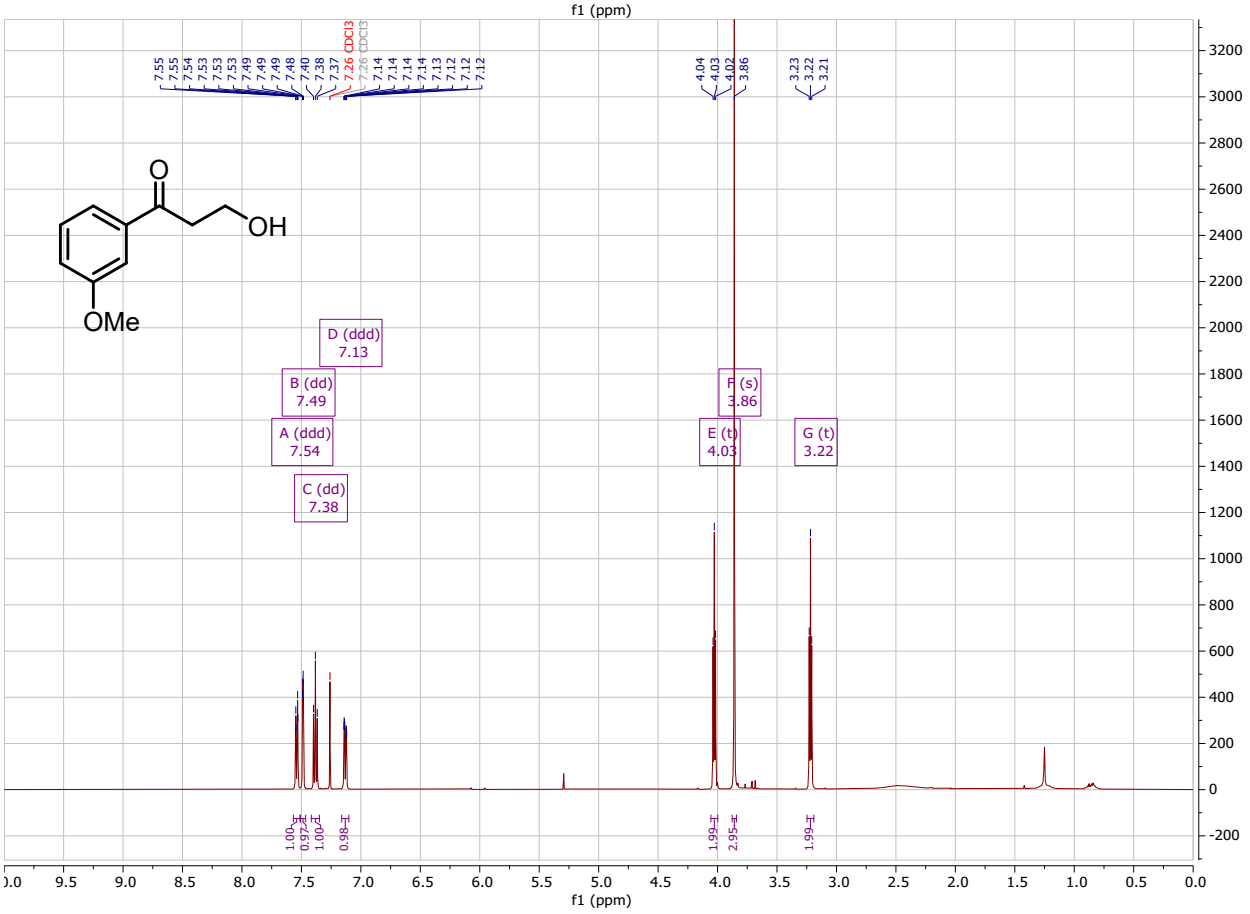

O
OMe
O
OH
OMe
D (ddd) 7.14
B (dd) 7.57
F (ddd) 6.92
I (s) 3.85
A (ddd) 7.63
E (ddd) 7.02
H (dd) 5.43
J (m) 4.07
C (dd) 7.38
G (ddd) 6.84
K (s) 3.85
f1 (ppm)

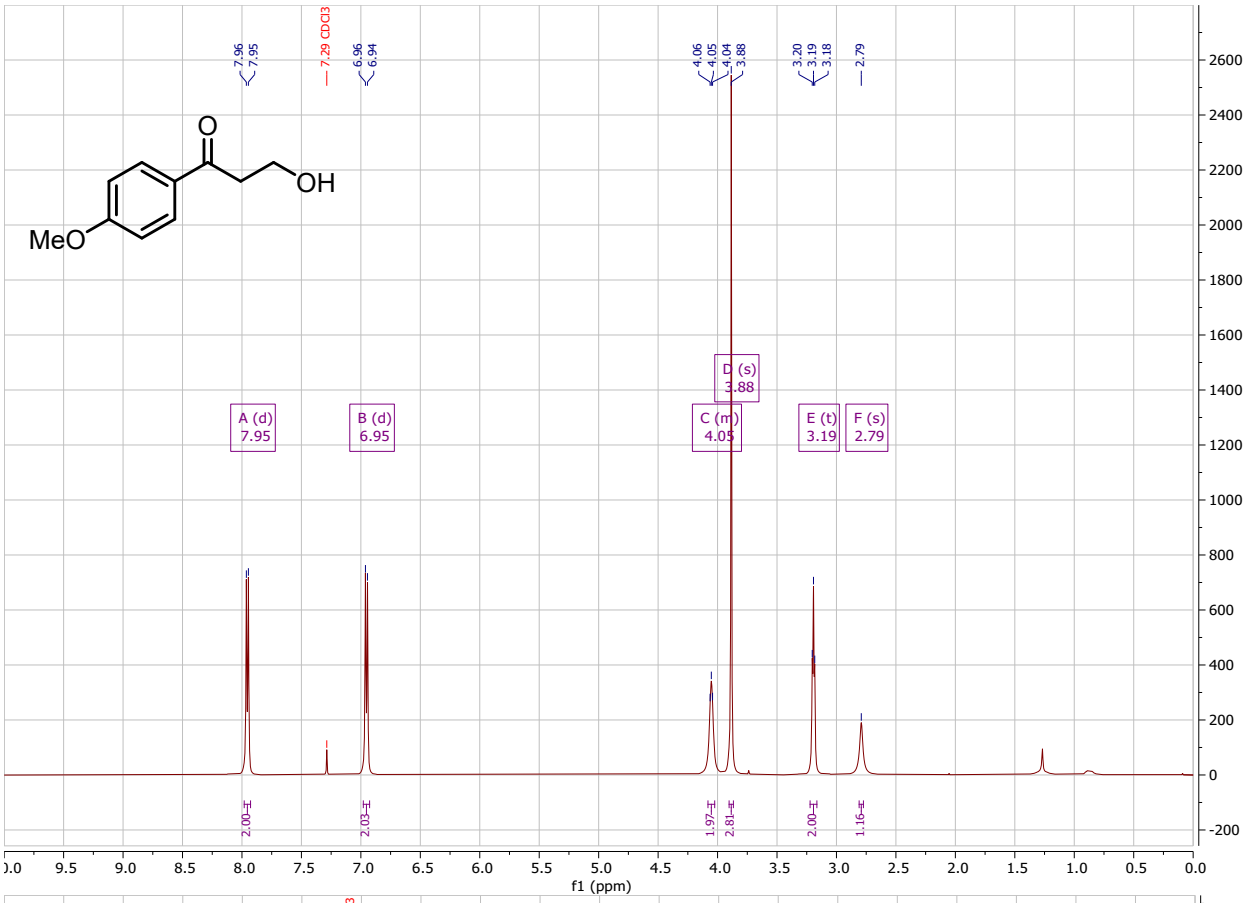

O
O
OMe
HO
OMe
OMe
D (ddd) 7.15
B (dd) 7.53
H (dd) 4.07
A (ddd) 7.62
E (m) 6.07
F (dd) 5.54
G (dd) 4.15
J (s) 3.71
C (dd) 7.38
I (s) 3.83
f1 (ppm)

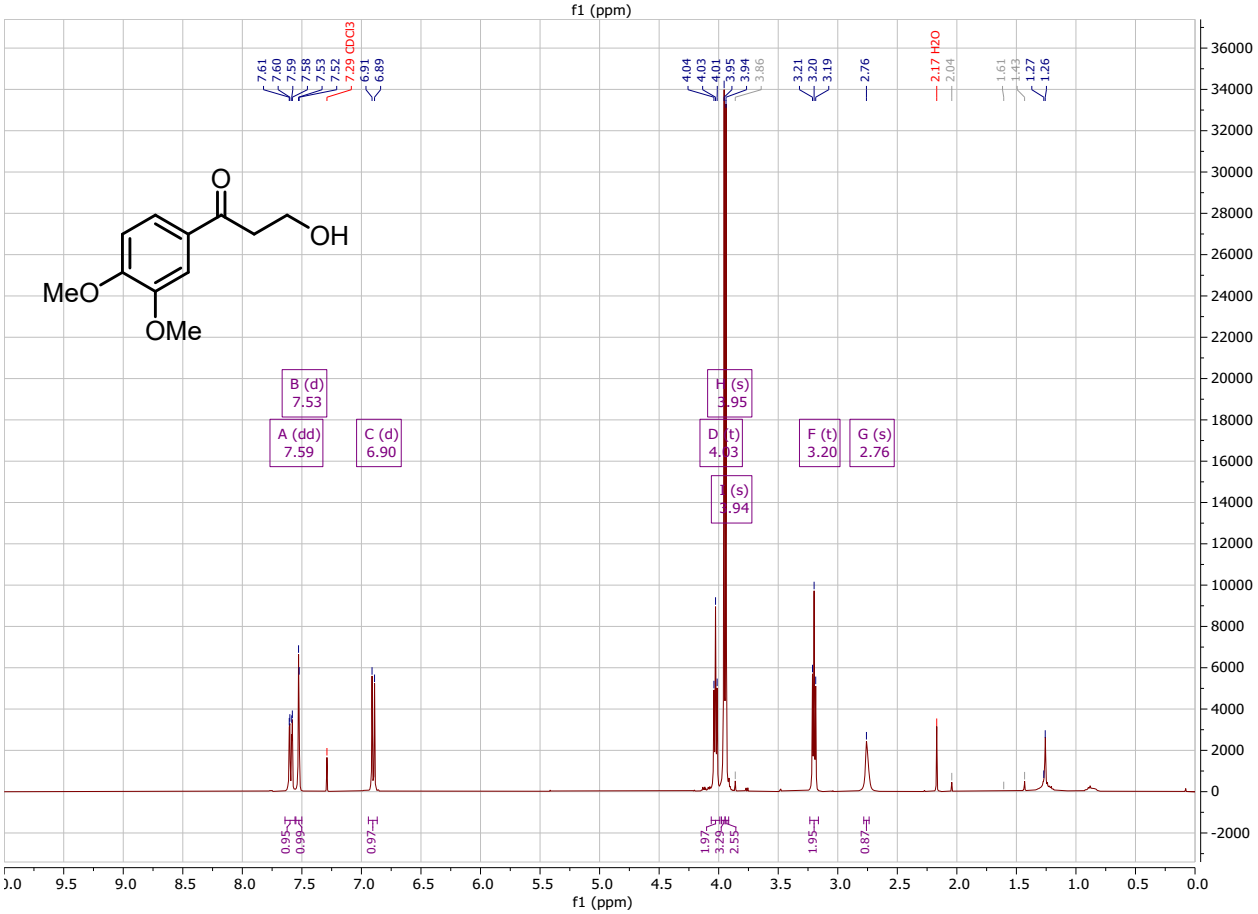

196.22
161.71
160.11
159.19
136.04
130.02
121.25
120.87
112.93
94.30
94.17
80.89
77.16 CDCl3
63.37
55.58
55.46
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

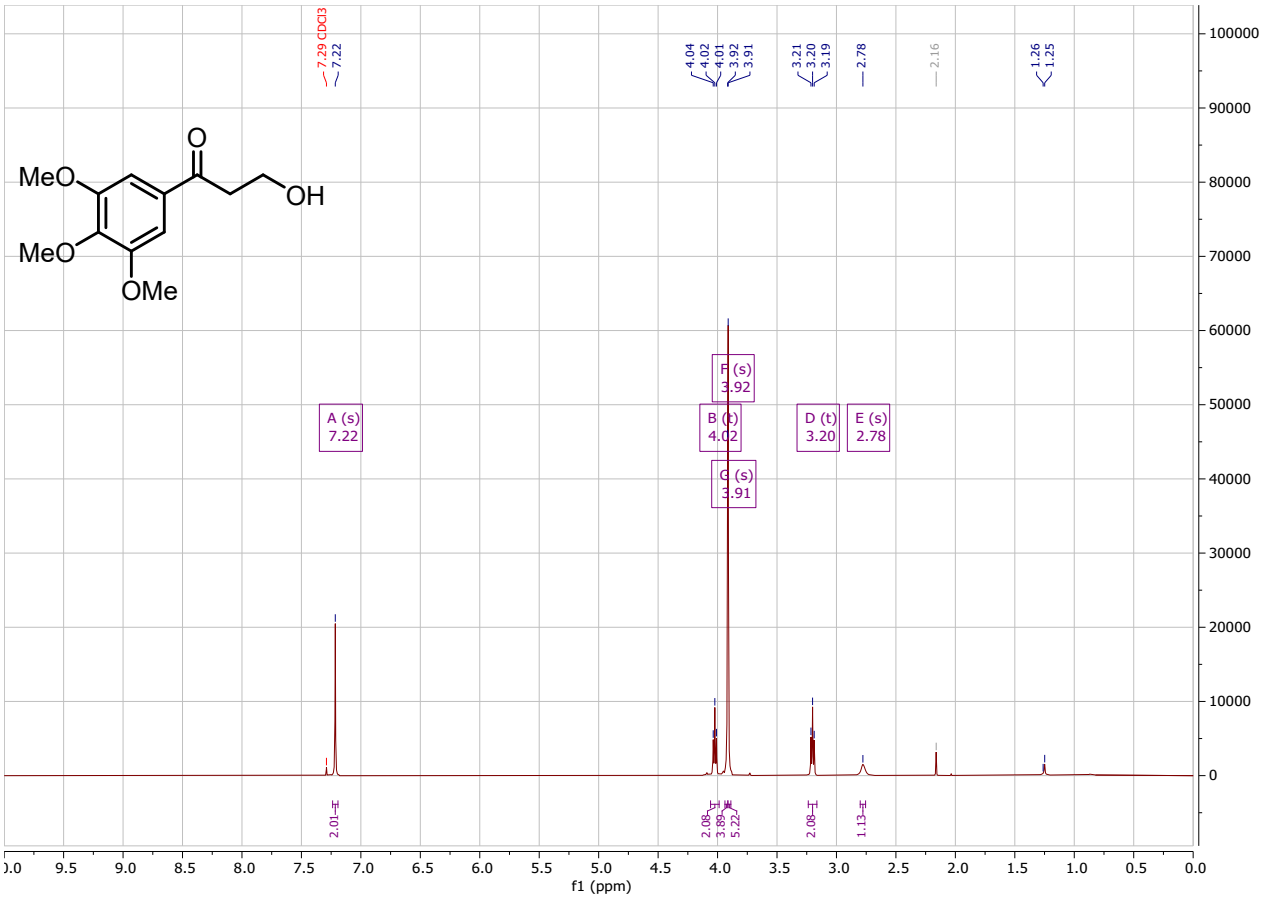

B (dt)
9.00
A (s)
9.29
C (dt)
8.84
D (dd)
8.12
E (m)
7.44
F (s)
5.83
O
NH2
Br-
N+
f1 (ppm)

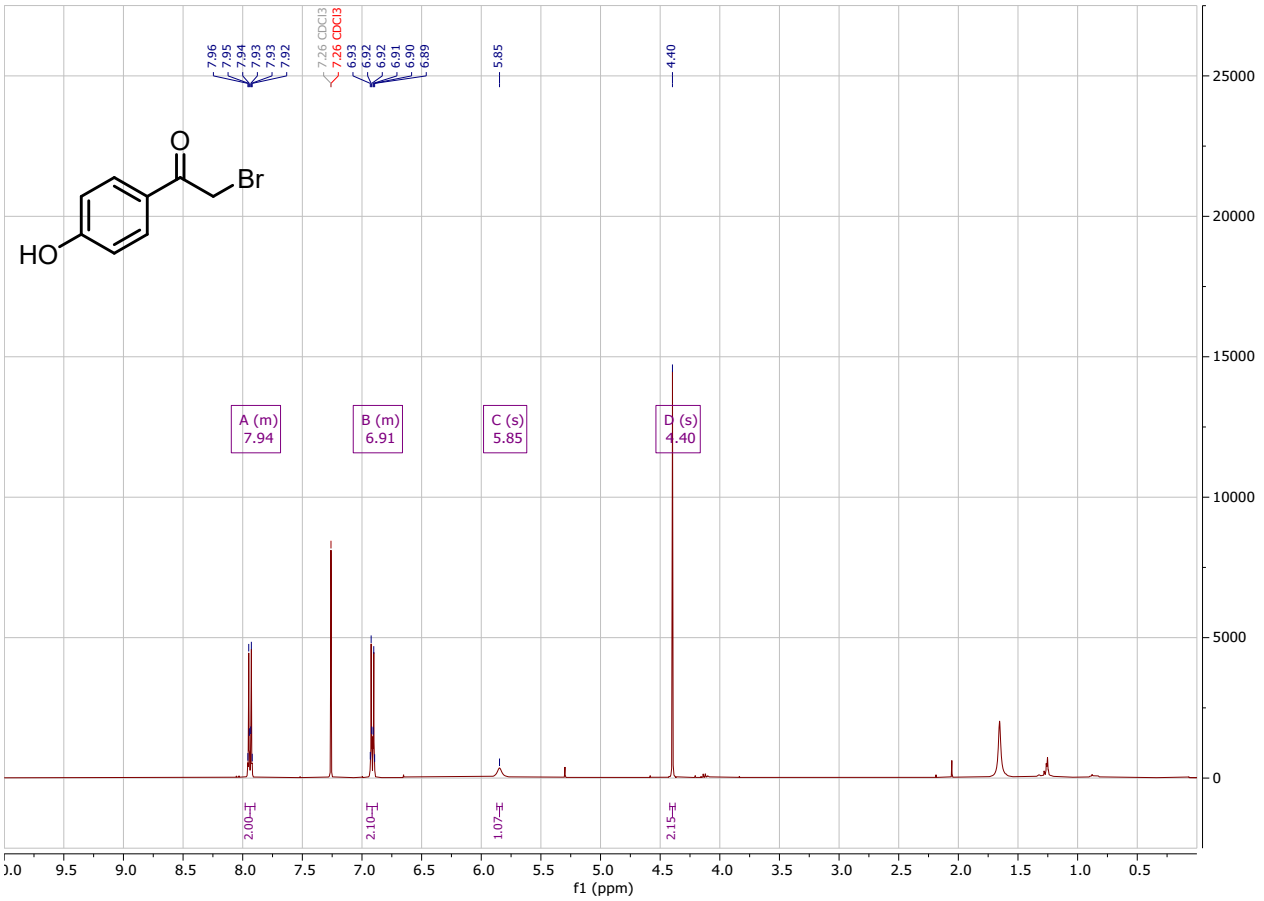

O
NH2
N
A (m)
7.31
B (dq)
5.77
C (s)
5.21
D (dt)
4.78
E (s)
4.32
F (dd)
3.20
f1 (ppm)

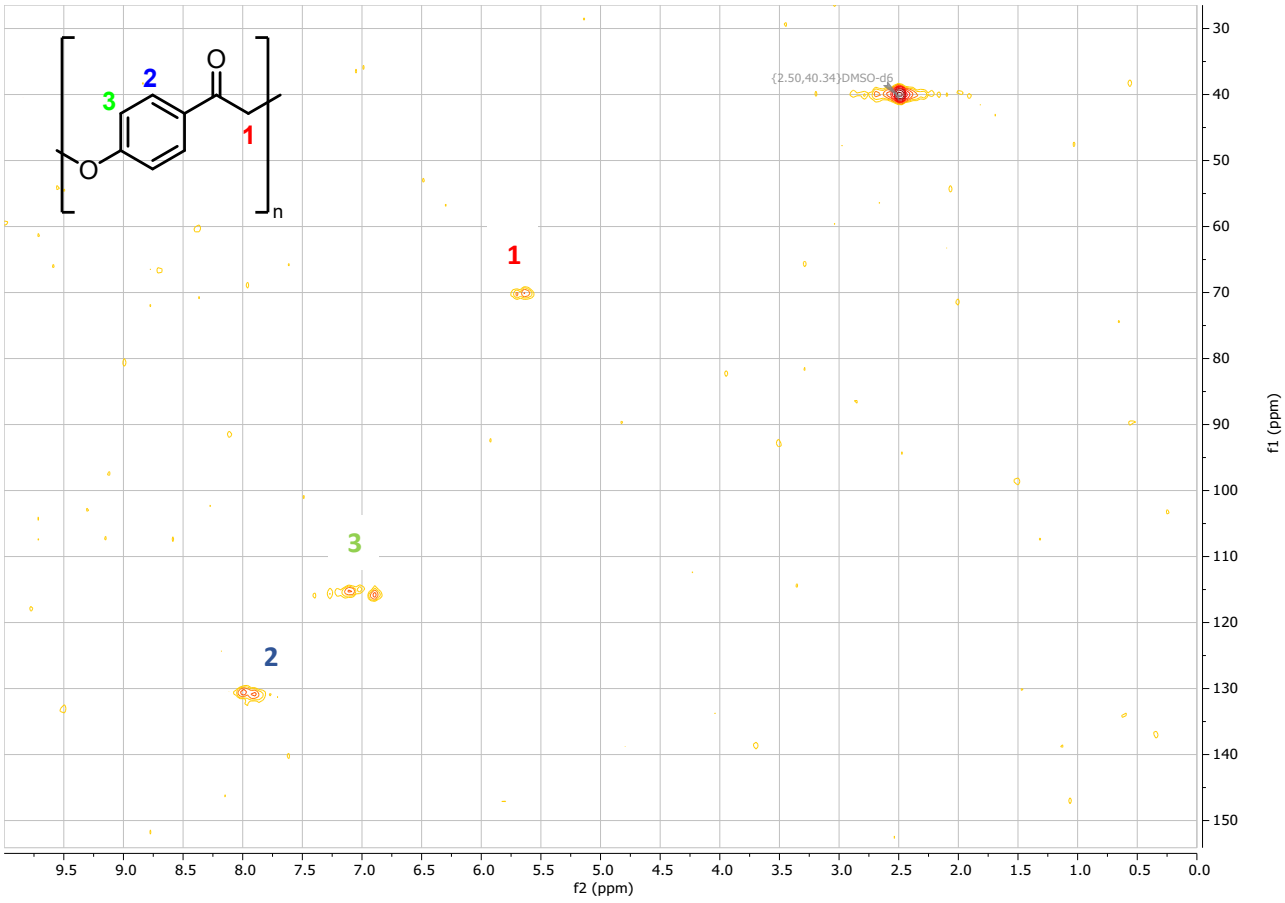

O
OH
OMe
D (ddd)
7.13
B (dd)
7.49
A (ddd)
7.54
C (dd)
7.38
F (s)
3.86
E (t)
4.03
G (t)
3.22
f1 (ppm)

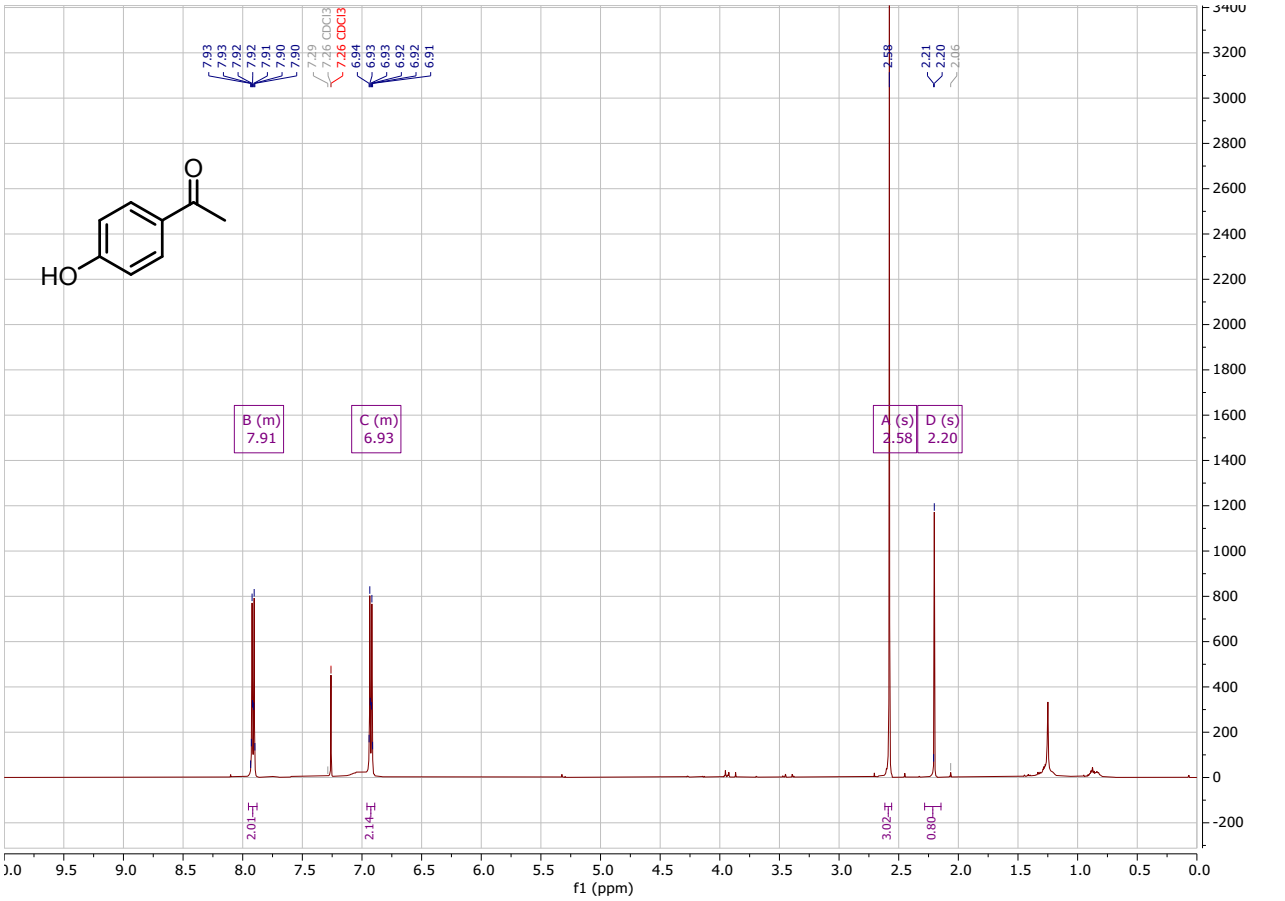

7.96
7.95
7.29 CDCl3
6.96
6.94
4.06
4.05
4.04
3.88
3.20
3.19
3.18
2.79
O
OH
MeO
A (d)
7.95
B (d)
6.95
D (s)
3.88
C (m)
4.05
E (t)
3.19
F (s)
2.79
2.00
2.03
1.97
2.81
2.00
1.16
f1 (ppm)


7.61
7.60
7.59
7.58
7.53
7.52
7.29 CDCl3
6.91
6.89
4.04
4.03
4.01
3.95
3.94
3.86
3.21
3.20
3.19
2.76
2.17 H2O
2.04
1.61
1.43
1.27
1.26
O
OH
MeO
OMe
B (d)
7.53
A (dd)
7.59
C (d)
6.90
D (t)
4.03
F (t)
3.20
G (s)
2.76
0.95
0.99
0.97
1.97
3.29
2.55
1.95
0.87
f1 (ppm)


MeO
MeO
OMe
O
OH
7.29 CDCl3
7.22
4.04
4.02
4.01
3.92
3.91
3.21
3.20
3.19
2.78
2.16
1.26
1.25
A (s) 7.22
F (s) 3.92
B (t) 4.02
G (s) 3.91
D (t) 3.20
E (s) 2.78
2.01
2.08
3.89
5.22
2.08
1.13
f1 (ppm)


HO
O
Br
7.96
7.95
7.94
7.93
7.93
7.92
7.26 CDCl3
7.26 CDCl3
6.93
6.92
6.92
6.91
6.90
6.89
5.85
4.40
A (m) 7.94
B (m) 6.91
C (s) 5.85
D (s) 4.40
2.00
2.10
1.07
2.15
f1 (ppm)


3
2
O
1
O
n
{2.50,40.34}DMSO-d6
1
3
2
f2 (ppm)
f1 (ppm)


7.93
7.93
7.92
7.92
7.91
7.90
7.90
7.29
7.26 CDCl3
7.26 CDCl3
6.94
6.93
6.93
6.92
6.92
6.91
2.58
2.21
2.20
2.06
HO
O
B (m)
7.91
C (m)
6.93
A (s)
2.58
D (s)
2.20
2.01
2.14
3.02
0.80
f1 (ppm)

References

1. Minozzi, C.; Caron, A.; Grenier-Petel, J.-C.; Santandrea, J.; Collins, S. K., Heteroleptic Copper(I)-Based Complexes for Photocatalysis: Combinatorial Assembly, Discovery, and Optimization. *Angew. Chem., Int. Ed.* **2018,** *57* (19), 5477-5481.
2. Sosoe, J.; Cruché, C.; Morin, É.; Collins, S. K., Evaluating heteroleptic copper(I)-based complexes bearing π-extended diimines in different photocatalytic processes. *Can. J. Chem.* **2020,** *98* (9), 461-465.
3. Caron, A.; Morin, É.; Collins, S. K., Bifunctional Copper-Based Photocatalyst for Reductive Pinacol-Type Couplings. *ACS Catal.* **2019,** *9* (10), 9458-9464.
4. Cruché, C.; Neiderer, W.; Collins, S. K., Heteroleptic Copper-Based Complexes for Energy-Transfer Processes: E → Z Isomerization and Tandem Photocatalytic Sequences. *ACS Catalysis* **2021,** *11* (14), 8829-8836.
5. Zheng, L.; Jiang, Q.; Bao, H.; Zhou, B.; Luo, S.-P.; Jin, H.; Wu, H.; Liu, Y., Tertiary Amines Acting as Alkyl Radical Equivalents Enabled by a P/N Heteroleptic Cu(I) Photosensitizer. *Org. Lett.* **2020,** *22* (22), 8888-8893.
6. Zuleta, E. C.; Bozell, J. J., Alkylation of monomeric, dimeric, and polymeric lignin models through carbon-hydrogen activation using Ru-catalyzed Murai reaction. *Tetrahedron* **2021,** *100*, 132475.
7. Guo, T.; Liu, T.; He, J.; Zhang, Y., One-Pot Transformation of Lignin and Lignin Model Compounds into Benzimidazoles. *European Journal of Organic Chemistry* **2022,** *2022* (2), e202101152.
8. Biannic, B.; Bozell, J. J., Efficient Cobalt-Catalyzed Oxidative Conversion of Lignin Models to Benzoquinones. *Organic Letters* **2013,** *15* (11), 2730-2733.
9. Arias, L.; Vara, Y.; Cossío, F. P., Regioselective Preparation of Benzo[b]furans from Phenols and α-Bromoketones. *The Journal of Organic Chemistry* **2012,** *77* (1), 266-275.
10. Lee, J. H.; Kim, M.; Kim, I., Palladium-Catalyzed α-Arylation of Aryloxyketones for the Synthesis of 2,3-Disubstituted Benzofurans. *J. Org. Chem.* **2014,** *79* (13), 6153-6163.
11. Hofmann, L. E.; Hofmann, D.; Prusko, L.; Altmann, L.-M.; Heinrich, M. R., Sequential Cleavage of Lignin Systems by Nitrogen Monoxide and Hydrazine. *Advanced Synthesis & Catalysis* **2020,** *362* (7), 1485-1489.
12. Dias, K. d. A.; Pereira Junior, M. V. P.; Andrade, L. H., Benzoic acid resin (BAR): a heterogeneous redox organocatalyst for continuous flow synthesis of benzoquinones from β-O-4 lignin models. *Green Chemistry* **2021,** *23* (6), 2308-2316.
13. Tan, Z.; Han, Y.; Fu, Y.; Zhang, X.; Xu, M.; Na, Q.; Zhuang, W.; Qu, X.; Ying, H.; Zhu, C., Investigating the Structure-Reactivity Relationships Between Nicotinamide Coenzyme Biomimetics and Pentaerythritol Tetranitrate Reductase. *Advanced Synthesis & Catalysis* **2022,** *364* (1), 103-113.
14. Bosque, I.; Magallanes, G.; Rigoulet, M.; Kärkäs, M. D.; Stephenson, C. R. J., Redox Catalysis Facilitates Lignin Depolymerization. *ACS Central Science* **2017,** *3* (6), 621-628.
15. Yun, J.-J.; Liu, X.-Y.; Deng, W.; Chu, X.-Q.; Shen, Z.-L.; Loh, T.-P., Chromium(III)-Catalyzed Addition of Water and Alcohol to α,β-Unsaturated Ketones for the Synthesis of β-Hydroxyl and β-Alkoxyl Ketones in Aqueous Media. *The Journal of Organic Chemistry* **2018,** *83* (18), 10898-10907.
16. Damodar, K.; Shin, S.; Jeon, S. H.; Lee, J. T., First synthesis of tabamides A–C and their derivatives: In vitro nitric oxide inhibitory activity. *Tetrahedron Letters* **2021,** *85*, 153482.
17. Zhu, C.; Wang, R.; Falck, J. R., Mild and Rapid Hydroxylation of Aryl/Heteroaryl Boronic Acids and Boronate Esters with N-Oxides. *Org. Lett.* **2012,** *14* (13), 3494-3497.