Mechanochemical Cleavage of Lignin Models and Lignin via Oxidation and Subsequent Base-Catalyzed Strategy

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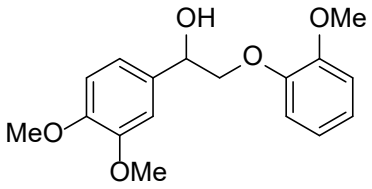
1. General experimental

All the reagents were purchased from commercial sources without further purification, unless otherwise indicated. The reactions were conducted in a Mixer Mill (MM 400 RetschGmbh, Hann, Germany) with 50 mL stainless steel vial and milled with two stainless steel grinding balls (14 mm diameter). Thin-layer chromatography (TLC) analysis were performed using precoated glass plates. ^{1}H and ^{13}C NMR spectrum were recorded with a Bruker instrument (400 MHz) using tetramethylsilane (TMS) as the internal standard. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and the *J* coupling constants were reported in Hertz unit (Hz). Mass spectra were measured with Thermo Finnigan LCQ-Advantage. HPLC measurements were conducted on Shimadzu apparatus using an Athena C18-WP (4.6 mm x 250 mm, 5 µm) column. H_2O (pH~3.5)/MeCN (60:40) eluent and a flow rate of 0.6 mL/min were used for the measurements of resulting products, and acetophenone was used as internal standard. Gel permeation chromatography (GPC) measurements were performed on a Shimadzu instrument equipped with a refractive index (RI) detector on a series of Waters Styragel 5E columns, and using THF as the mobile phase, with narrowly distributed polymethyl methacrylate (PMMA) as the standard samples. The flow rate was 0.3 mL/min, and the analyses were conducted at 40 °C. Lignin acetylation was conducted using acetic anhydride (1 mL) and pyridine (1 mL) for 10 mg of lignin at room temperature for 2 days. After removing acetic anhydride and pyridine under reduced pressure in a vacuum oven at 40 °C for 24 h, the acetylated lignin was dissolved to THF and then subjected to GPC analysis. GC-MS measurements using an Agilent 7890B/5977B instrument equipped with HP-5 MS capillary column. Analysis condition: injector temperature, 260 °C; carrier gas, helium; column flow, 1mL/min; temperature program, 60 °C hold 5 min, then was heated at a rate of 10 °C/min to 260 °C, followed by maintaining 260 °C for 5 min. GC measurements were performed on GC 9720 system equipped with SH-Rtx-1 capillary column and flame ionization detector detector (FID). Mesitylene was used as the internal standard. The temperature ramping program for the GC-FID was the same as the GC-MS method.

2. Synthesis and characterization of lignin *β*-O-4 model compounds

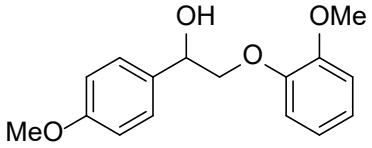
The lignin model compounds **1a**-**i** were synthesized according to the procedure described in literature.[1,2]

1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanol (1a)[1]



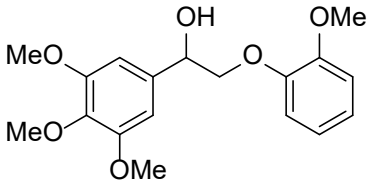
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.03-6.85 (m, 7H), 5.06 (dd, *J* = 9.2, 2.8 Hz, 1H), 4.17 (dd, *J* = 10.0, 3.2 Hz, 1H), 3.98 (t, *J* = 9.6 Hz, 1H), 3.90 (s, 3H), 3.89 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 150.3, 149.3, 148.9, 148.2, 132.4, 122.7, 121.3, 118.8, 116.2, 112.2, 111.2, 109.6, 76.5, 72.3, 56.1, 56.1, 56.0. **MS (ESI):** *m/z* 327.2 $[M + Na]^+$.

1-(4-Methoxyphenyl)-2-(2-methoxyphenoxy)ethanol (1b)[1]



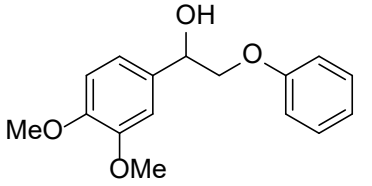
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 (d, *J* = 8.4 Hz, 2H), 7.02-6.89 (m, 6H), 5.08 (dd, *J* = 9.2, 2.8 Hz, 1H), 4.15 (dd, *J* = 10.0, 3.2 Hz, 1H), 4.00 (t, *J* = 9.6 Hz, 1H), 3.87 (s, 3H), 3.82 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 159.5, 150.2, 148.2, 132.0, 127.7, 122.5, 121.2, 115.8, 114.0, 112.1, 76.2, 72.1, 56.0, 55.4. **MS (ESI):** *m/z* 297.1 $[M + Na]^+$.

1-(3,4,5-Trimethoxyphenyl)-2-(2-methoxyphenoxy)ethanol (1c)[2]



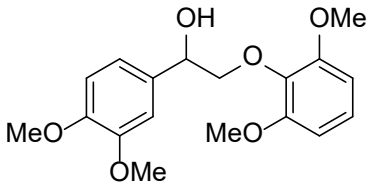
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.03-6.89 (m, 4H), 6.67 (s, 2H), 5.04 (dd, *J* = 9.2, 2.8 Hz, 1H), 4.18 (dd, *J* = 10, 2.8 Hz, 1H), 3.98 (t, *J* = 9.2 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 6H), 3.84 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 153.5, 150.3, 148.2, 137.8, 135.5, 122.8, 121.3, 116.3, 112.2, 103.4, 76.5, 72.6, 61.0, 56.3, 56.0. **MS (ESI):** *m/z* 357.1 $[M + Na]^+$.

1-(3,4-Dimethoxyphenyl)-2-phenoxyethanol (1d)[1]



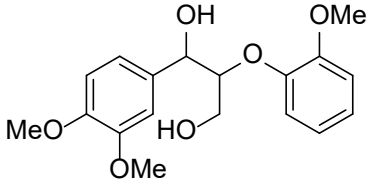
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32-7.28 (m, 2H), 7.03-6.88 (m, 6H), 5.08 (dd, *J* = 8.8, 3.2 Hz, 1H), 4.10 (dd, *J* = 9.6, 3.2 Hz, 1H), 4.02 (t, *J* = 8.8 Hz, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 2.81 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 158.6, 149.3, 149.1, 132.4, 129.8, 121.5, 118.8, 114.8, 111.3, 109.5, 73.5, 72.6, 56.2, 56.1. **MS (ESI):** *m/z* 297.3 $[M + Na]^+$.

1-(3,4-Dimethoxyphenyl)-2-(2,6-dimethoxyphenoxy)ethanol (1e)[1]



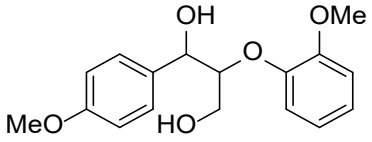
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.05 (t, *J* = 8.4 Hz, 1H), 6.97 (d, *J* = 2.0 Hz, 1H), 6.90 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 2H), 4.92 (dd, *J* = 10.4, 2.8 Hz, 1H), 4.55 (s, 1H), 4.40 (dd, *J* = 10.8, 2.4 Hz, 1H), 3.89 (s, 6H), 3.89 (s, 3H), 3.87 (s, 3H), 3.71 (dd, *J* = 11.2, 10.0 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 153.4, 149.2, 148.7, 137.0, 132.2, 124.3, 118.9, 111.1, 109.6, 105.3, 80.3, 72.4, 56.3, 56.1, 56.1. **MS (ESI):** *m/z* 357.4 $[M + Na]^+$.

1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (1f)[2]



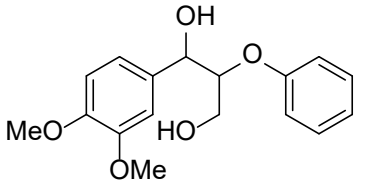
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30-7.22 (m, 1H), 7.01-6.93 (m, 4H), 6.89-6.81 (m, 2H), 5.01-4.98 (m, 1H), 4.42-4.37 (m, 1H), 4.14-4.09 (m, 1H), 3.97-3.56 (m, 9H), 3.60-3.56 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 151.7, 149.2, 148.9, 147.4, 132.5, 124.4, 121.8, 121.2, 118.8, 118.6, 112.3, 109.7, 88.5, 73.5, 61.1, 56.1, 56.1, 56.1. **MS (ESI):** *m/z* 357.4 $[M + Na]^+$.

1-(4-Methoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (1g)[2]



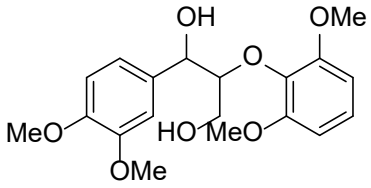
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 (d, *J* = 8.4 Hz, 0.6H), 7.32 (d, *J* = 8.4, 1.4H), 7.14 (dd, *J* = 7.7, 1.4H, 0.3H), 7.10-7.04 (m, 1H), 6.98-6.87 (m, 4.7H), 5.0 (d, *J* = 4.8 Hz, 1H), 4.18-4.14 (m, 0.7H), 4.06-4.02 (m, 0.4H), 3.94-3.88 (m, 3.7H), 3.81 (s, 3H), 3.68-3.60 (m, 1H), 3.46 (dd, *J* = 12.4, 4.0 Hz, 0.4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 159.5, 151.6, 147.4, 132.1, 128.0, 124.4, 121.8, 121.3, 114.1, 112.4, 88.7, 73.4, 61.1, 56.1, 55.5. **MS (ESI):** *m/z* 327.1 $[M + Na]^+$.

1-(3,4-Dimethoxyphenyl)-2-phenoxy-1,3- propanediol (1h)[1]



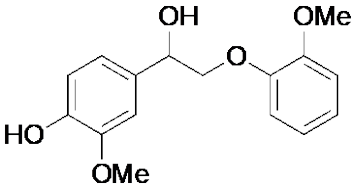
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30-7.22 (m, 2H), 7.01-6.81 (m, 6H), 5.00 (t, *J* = 8Hz, 1H), 4.42-4.37 (m, 1H), 3.97-3.93 (m, 0.5H), 3.89-3.79 (m, 7H), 3.58 (dd, *J* = 12, 4 Hz, 0.5H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 157.9, 149.0, 148.8, 132.7, 129.7, 121.9, 119.0, 116.6, 111.0, 109.7, 82.5, 73.8, 61.3, 55.9, 55.9. **MS (ESI):** *m/z* 327.1 $[M + Na]^+$.

1-(3,4-Dimethoxyphenyl)-2-(2,6-dimethoxyphenoxy)-1,3-propanediol (1i)[1]



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.10-7.03 (m, 1.4H), 7.02 (s, 1H), 6.96 (s, 0.3H), 6.86-6.83 (m, 1.3H), 6.66-6.63 (m, 2H), 5.06 (d, *J* = 8.8 Hz, 0.7H), 5.03 (d, *J* = 3.4 Hz, 0.3H), 4.37 (s, 0.5H), 4.18-4.15 (m, 0.5H), 3.94-3.85 (m, 13H), 3.60-3.48 (m, 1H), 3.33-3.29 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 153.6, 149.1, 148.7, 135.3, 132.5, 124.7, 120.0, 118.3, 111.2, 110.4, 109.2, 105.5, 88.2, 73.4, 60.7, 56.3, 56.3, 56.1, 56.1. **MS (ESI):** *m/z* 387.1 $[M + Na]^+$.

1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)ethanol (1j)[2]



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.02-6.87 (m, 7H), 5.68 (s, 1H), 5.04 (dd, *J* = 9.2, 2.4 Hz, 1H), 4.16(dd, *J* = 10, 2.8 Hz, 1H), 3.97 (t, *J* = 9.6 Hz, 1H), 3.91 (s, 3H), 3.89 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 150.3, 148.2, 146.9, 145.6, 131.7, 122.7, 121.3, 119.6, 116.2, 114.4, 112.2, 109.0, 76.6, 72.4, 56.1, 56.1. **MS (ESI):** *m/z* 313.4 $[M + Na]^+$.

3. General Procedure for the Mechanochemical Oxidation of Lignin Model Compounds.

A mixture of model compounds (**1a-1j**) (0.2 mmol, 1.0 equiv.), DDQ (0,03 mmol, 0.15 equiv.), $NaNO_2$ (0.1 mmol, 0.5 equiv.), and Na_2SO_4 (250 mg) was placed in a 50 mL stainless steel vessel with two stainless steel balls (d = 1.4 cm) for 90 min under ball milling at 25 Hz. After milling, the reaction mixture was extracted with EtOAc, and the products were purified by column chromatography on silica gel to yield **2a**-**2j**.

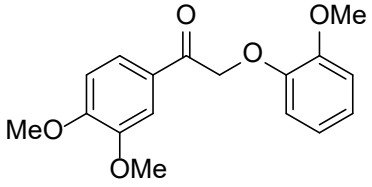
4. General Procedure for the Mechanochemical NaOH-Catalyzed of the Oxidized Lignin Model Compounds.

A mixture of model compounds (**2a-2i**) (0.2 mmol, 1.0 equiv.) and NaOH (1 mmol, 5 equiv.) was placed in a 50 mL stainless steel vessel with two stainless steel balls (d = 1.4 cm) for 120 min under ball milling at 25 Hz. After milling, the mixture was dissolved in water, neutralized with aqueous acetic acid (1 M), and then extracted with EtOAc (3 × 10 mL). The combined organic phase was washed with brine, dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residual samples were analyzed by HPLC using acetophenone as the internal standard.

A mixture of model compound (**2j**) (0.2 mmol, 1.0 equiv.) and NaOH (1.6 mmol, 8 equiv.) was placed in a 50 mL stainless steel vessel with two stainless steel balls (d = 1.4 cm) for 120 min under ball milling at 30 Hz. After milling, the mixture was dissolved in water, neutralized with aqueous acetic acid (1 M), and then extracted with EtOAc (3 × 10 mL). The combined organic phase was washed with brine, dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residual samples were analyzed by HPLC using acetophenone as the internal standard.

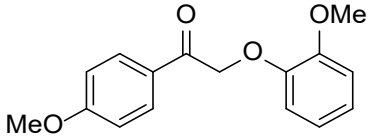
5. Spectroscopic data of the isolated products in step 1

1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)ethenone (2a) [1]



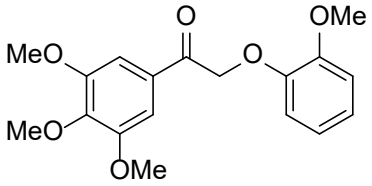
^{1}H NMR(400 MHz, $CDCl_3$) δ = 7.68 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.61 (d, *J* = 1.9 Hz, 1H), 6.97-6.85 (m, 5H), 5.30(s, 2H), 3.96 (s, 3H), 3.94 (s, 3H), 3.89 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 193.5, 154.0, 149.9, 149.4, 147.8, 128.0, 123.0, 122.5, 121.0, 114.9, 112.3, 110.6, 110.3, 72.2, 56.3, 56.2, 56.1. **MS (ESI):** *m/z* 325.2 $[M + Na]^+$.

1-(4-Methoxyphenyl)-2-(2-methoxyphenoxy)ethenone (2b) [1]



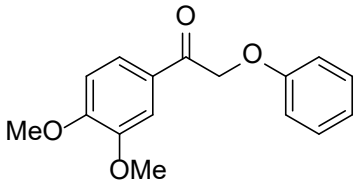
^{1}H NMR(400 MHz, $CDCl_3$) δ = 8.02 (d, *J* = 8.8 Hz, 2H), 6.99-6.91 (m, 4H), 6.86 (d, *J* = 3.8 Hz, 2H), 5.29 (s, 2H), 3.89 (s, 3H), 3.88 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 193.3, 164.2, 150.0, 147.8, 130.7, 127.9, 122.5, 121.0, 114.9, 114.1, 112.4, 72.2, 56.1, 55.7. **MS (ESI):** *m/z* 271.3 $[M - H]^-$.

1-(3,4,5-Trimethoxyphenyl)- 2-(2-methoxyphenoxy)ethenone (2c)[2]



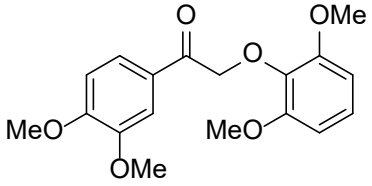
^{1}H NMR(400 MHz, $CDCl_3$) δ = 7.34 (s, 2H), 7.00-6.91 (m, 2H), 6.87 (d, *J* = 4 Hz, 2H), 5.27 (s, 2H), 3.93 (s, 3H), 3.92 (s, 6H), 3.89 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 194.0, 153.4, 149.9, 147.6, 143.4, 130.0, 122.7, 121.1, 114.9, 112.3, 106.1, 72.7, 61.2, 56.5, 56.0. **MS (ESI):** *m/z* 355.1 $[M + Na]^+$.

1-(3,4-Dimethoxyphenyl)-2-phenoxyethanone (2d) [1]



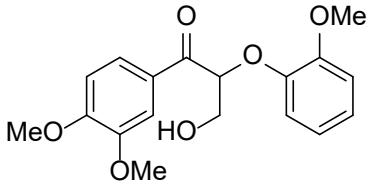
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.56 (d, *J* = 1.9 Hz, 1H), 7.33-7.28 (m, 2H), 7.02-6.92 (m, 4H), 5.25 (s, 2H), 3.98 (s, 3H), 3.96 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 193.4, 158.3, 154.1, 149.5, 129.8, 128.0, 123.0, 121.8, 115.0, 110.6, 110.3, 70.9, 56.3, 56.2. **MS (ESI):** *m/z* 273.1 $[M + H]^+$.

1-(3,4-Dimethoxyphenyl)-2-(2,6-dimethoxyphenoxy)ethenone (2e) [1]



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.73 (dd, *J* = 8.4 Hz, 2.0, 1H), 7.65 (d, *J* = 1.9 Hz, 1H), 7.02 (t, *J* = 8.4 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 2H), 5.16 (s, 2H), 3.95 (s, 3H), 3.95 (s, 3H), 3.82 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 193.7, 153.4, 153.3, 149.0, 136.7, 128.4, 124.1, 123.1, 110.7, 110.0, 105.3, 75.3, 56.1, 56.1, 56.1. **MS (ESI):** *m/z* 333.2 $[M + H]^+$.

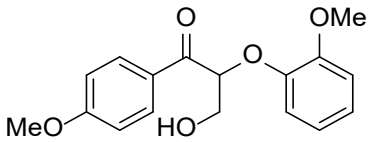
1-(3,4-Dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propanone (2f)[2]



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.00 (m, 1H), 6.93-6.88 (m, 3H), 6.81 (dt, *J* = 7.5, 1.5 Hz, 1H), 5.41 (t, *J* = 5.2 Hz, 1H), 4.07 (d, J = 5.3 Hz, 2H), 3.95 (s,

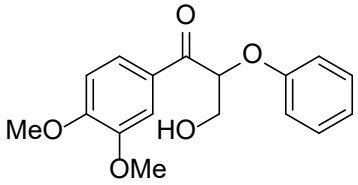
3H), 3.92 (s, 3H), 3.86 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 195.2, 154.1, 150.6, 149.4, 147.1, 128.2, 123.8, 123.8, 121.4, 118.6, 112.5, 111.1, 110.3, 84.7, 63.9, 56.3, 56.2, 56.0. **MS (ESI):** *m/z* 355.2 [M + Na]$^+$.

1-(4-Methoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propanone (2g)[2]



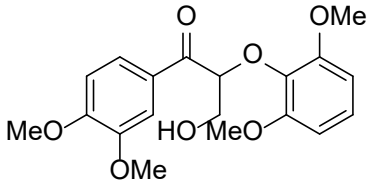
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.10-8.06 (m, 2H), 7.02-6.80 (m, 6H), 5.39 (t, *J* = 5.2 Hz, 1H), 4.07 (d, *J* = 5.6 Hz, 2H), 3.87 (s, 3H), 3.85 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 195.2, 164.2, 150.7, 147.2, 131.5, 128.2, 123.8, 121.3, 118.8, 114.2, 112.5, 84.9, 63.8, 56.0, 55.7. **MS (ESI):** *m/z* 325.1 [M + Na]$^+$.

1-(3,4-Dimethoxyphenyl)-3-hydroxy-2-phenoxypropanone (2h) [1]



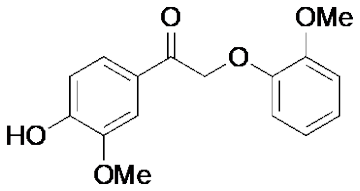
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.57 (d, *J* = 2.0 Hz, 1H), 7.25 (t, *J* = 8.3 Hz, 2H), 6.97 (t, *J* = 7.3 Hz, 1H), 6.91-6.89 (m, 3H), 5.54 (dd, *J* = 6.2, 4.2 Hz, 1H), 4.19-4.10 (m, 2H), 3.96 (s, 3H), 3.90 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 195.0, 157.3, 154.2, 149.3, 129.7, 127.8, 123.5, 121.9, 115.2, 110.9, 110.2, 80.9, 63.6, 56.2, 56.0. **MS (ESI):** *m/z* 325.2 [M + Na]$^+$.

1-(3,4-Dimethoxyphenyl)-3-hydroxy-2-(2,6-dimethoxyphenoxy)propanone (2i)[1]



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.65 (d, *J* = 2.0 Hz, 1H), 7.00 (t, *J* = 8.4 Hz, 1H), 6.87 (t, *J* = 8.5 Hz, 1H), 6.56 (d, *J* = 8.4, 2 H), 5.09 (dd, *J* = 7.7, 3.0 Hz, 1H), 3.99 (dd, *J* = 12.0, 7.7 Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 3.81 (dd, *J* = 12.0, 3.0 Hz, 1 H), 3.71 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 195.0, 153.5, 152.7, 149.1, 136.7, 128.6, 124.3, 123.4, 110.9, 110.0, 105.2, 87.5, 63.6, 56.1, 56.0, 55.9. **MS (ESI):** *m/z* 385.3 [M + Na]$^+$.

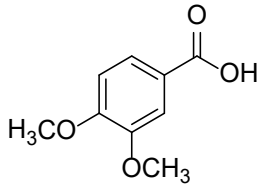
1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)ethenone (2j)[2]



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62(m, 2H), 6.96-6.85(m, 5H), 6.14(s, 1H), 5.30 (s, 2H), 3.96(s, 3H), 3.90(s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 193.3, 151.2, 149.9, 147.8, 147.0, 127.7, 123.5, 122.5, 121.0, 114.8, 114.2, 112.3, 110.4, 72.1, 56.3, 56.1. **MS (ESI):** *m/z* 301.2 $[M + Na]^+$.

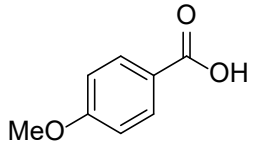
6. Spectroscopic data of the products in step 2

3,4-Dimethoxybenzoic acid3



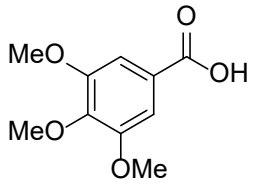
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.80 (dd, *J* = 8.4, 2 Hz, 1H), 7.61 (d, *J* = 2 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 3.97 (s, 3H), 3.96 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 172.2, 154.0, 148.9, 124.8, 121.9, 112.5, 110.5, 56.3, 56.2.

4-Methoxybenzoic acid[3]



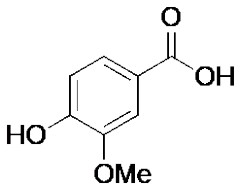
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.09 (t, *J* = 2 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 3.89 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 171.8, 164.3, 132.6, 121.9, 114.0, 55.7.

3,4,5-Trimethoxybenzoic acid[3]



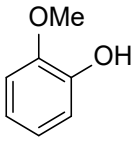
^{1}H NMR (400 MHz, CDCl3) δ = 7.39 (s, 2H), 3.94 (s, 3H), 3.94 (s, 6H). **^{13}C NMR (101 MHz, CDCl3)** δ = 171.9, 153.2, 143.2, 124.3, 107.6, 61.2, 56.5.

vanillic acid



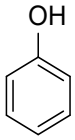
^{1}H NMR (400 MHz, d_6-DMSO) δ = 12.52 (s, 1H), 9.87 (s, 1H), 7.47 (s, 2H), 6.87 (d, 8.4 Hz, 1H), 3.84 (s, 3H). **^{13}C NMR (101 MHz, d_6-DMSO)** δ =167.7, 151.6, 147.7, 124.0, 122.1, 115.5, 113.2, 56.0.

Guaiacol [3]



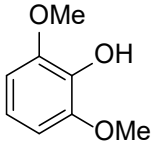
^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.96-6.86 (m, 4H), 5.63 (s, 1H), 3.90 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 146.8, 145.9, 121.7, 120.3, 114.7, 110.9, 56.1.

Phenol[3]



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29-7.24 (m, 2H), 6.95 (t, *J* = 7.2 Hz, 1H), 6.85 (d, *J* = 8 Hz, 2H), 4.85 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 155.7, 129.9, 121.0, 115.5.

2,6-Dimethoxyphenol[3]



^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.81 (t, *J* = 8.4 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 2H), 5.53 (s, 1H), 3.90 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 147.4, 135.1, 119.2, 105.1, 56.4.

7. The isolated and oxidation of birch lignin

Lignin isolated: The isolated birch lignin is prepared from birch powders according to the previous report.[4] To birch sawdust (100 g) was added 1,4-dioxane (720 mL) followed by 2N HCl (80 mL) and the mixture was heated to a gentle reflux under a N_2 atmosphere for 1 hour. The mixture was then allowed to cool and the lignin containing liquor was collected by filtration. The collected liquor was partially concentrated in vacuo to give a gummy residue which was taken up in acetone/water (9:1,

120 mL) and precipitated by addition to rapidly stirring water (1.25 L). The crude lignin was collected by filtration and dried under vacuum. The dried crude lignin was taken up in acetone/methanol (9:1) and precipitated by dropwise addition to rapidly stirring Et_2O (1 L). The precipitated lignin was collected by filtration and dried under vacuum to give an isolated birch lignin (15.8 g). This lignin was used in subsequent experiments without further processing.

Lignin oxidation:[5] The isolated birch lignin (500 mg) in dioxane (20 mL) was added DDQ (500 mg). The mixture was stirred at 80 ^oC for 3.5 h. The reaction was then cooled, filtered and the residual solid washed with dioxane (20 mL). The filtrate was then added dropwise to diethyl ether (200 mL) which resulted in precipitation. The precipitate was filtered, collected and dried under reduced pressure to give the oxidized birch lignin.

8. General Procedure for the Two-step Depolymerization of Birch Lignin.

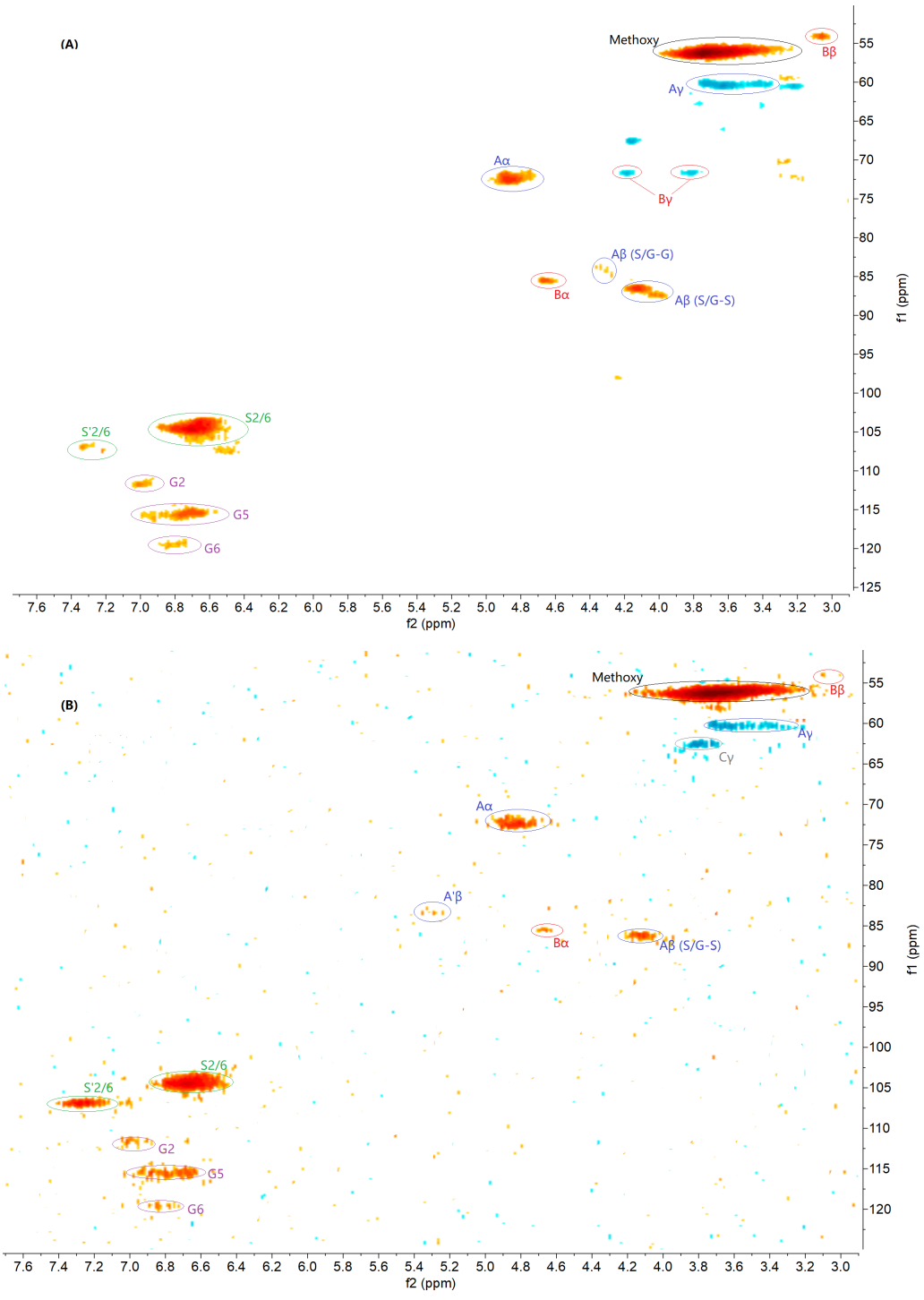
Step 1: In the preoxidation of birch lignin, a mixture of birch lignin (100 mg), DDQ (11 mg, 0.15 equiv.), and $NaNO_2$ (11 mg, 0.5 equiv.) was placed in a 50 mL stainless steel vessel with two stainless steel balls (d = 1.4 cm) for 90 min under ball milling at 25 Hz. The loading of DDQ and $NaNO_2$ was calculated by dividing the mass of the birch lignin sample by the molar mass of **1f**. After milling, the preoxidized birch lignin was collected and washed with water to remove the inorganic salts and then dried at 60 °C under vacuum for HSQC and GPC analysis.

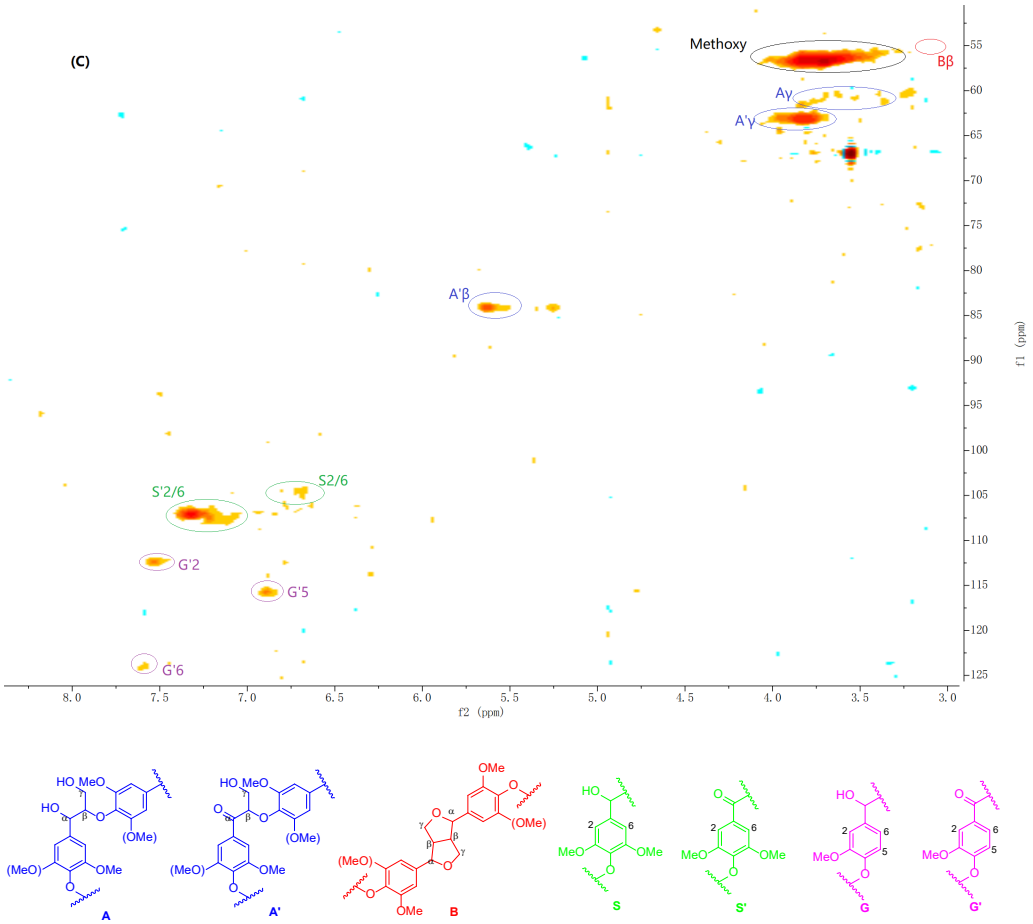
Step 2: In the NaOH-catalyzed depolymerization process, the preoxidized birch lignin (100 mg) and NaOH (100mg) were placed in a 50 mL stainless steel vessel with two stainless steel balls (d = 1.4 cm) for 8 h under ball milling at 20 Hz. This process was stopped for 5 min after every 30 min of milling to avoid overheating during the long milling time. After milling, the mixture was dissolved in water and neutralized with aqueous acetic acid (1 M). The water-insoluble residue was separated by centrifugation and then washed with EtOAc (3 × 10 mL). The residue was dried under vacuum and acetylated for GPC analysis. Meanwhile, the organic phases were combined, dried over anhydrous $MgSO_4$, filtered, and analyzed by GC-MS and GC-FID using mesitylene as the internal standard.

9. 2D-HSQC NMR spectra of the lignin samples

2D-HSQC NMR spectra were measured on a Bruker instrument with 400 MHz spectrometer at 300 K in d_6-DMSO. The 1H, 13C-HSQC experiment was acquired using standard Bruker pluses sequence 'hsqcedetgpsisp2.3'). Number of scans = 4. Pulse width = 10, acquisition time = 0.2 s, Relaxation Delay = 1.5 s.

Figure S1: 2D-HSQC NMR spectra of dioxasolv birch lignin in d_6-DMSO


(A)
Methoxy
Bβ
Aγ
Aα
Bγ
Aβ (S/G-G)
Bα
Aβ (S/G-S)
S2/6
S'2/6
G2
G5
G6
f1 (ppm)
f2 (ppm)
(B)
Methoxy
Bβ
Aγ
Cγ
Aα
A'β
Bα
Aβ (S/G-S)
S2/6
S'2/6
G2
G5
G6
f1 (ppm)
f2 (ppm)



Reaction conditions: (A)Untreated birch lignin. (B) Birch lignin milled for 90 min at 25 Hz in the presence of DDQ/$NaNO_2$. (C) the oxidised of birch lignin

10. GPC chromatograph of the lignin samples

Figure S2: GPC measurements for raw dioxasolv lignin (black), lignin milled for 90 min in the presence of DDQ/$NaNO_2$ (red), residual oxidized lignin milled for 8 h under NaOH depolymerization (green).

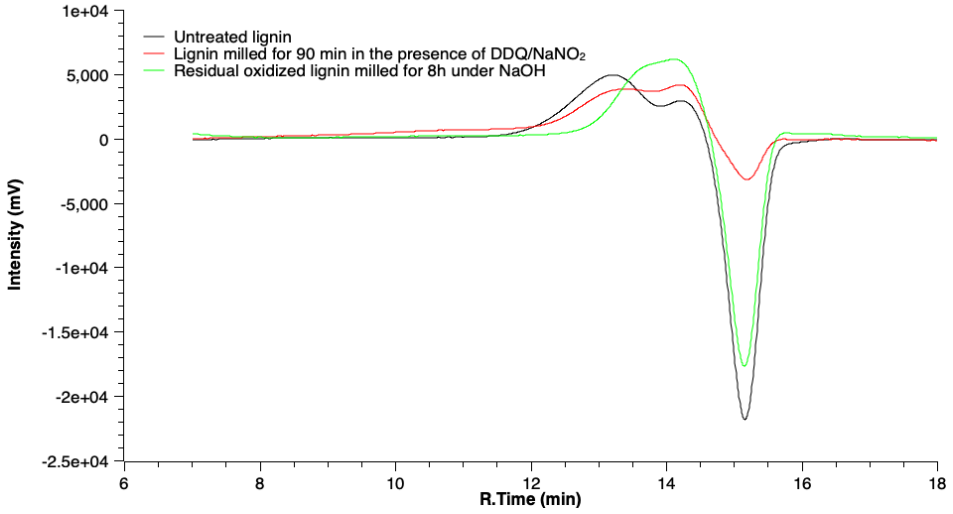


Table S1: Weight-Average (Mw), Number-Average (Mn) molecular weight and polydispersity (Mw/Mn) of the lignin samples

Entry	Mw [Da]	Mn [Da]	polydispersity
Raw lignin	9305	4166	2.234
Milled without catalysis	9766	3946	2.475
Milled with NaOH	2342	1043	2.245

11. GC-FID chromatograph of the organic-soluble products of birch lignin

Figure S3: GC-FID analysis of the ethyl acetate soluble aromatics from the depolymerization of birch lignin

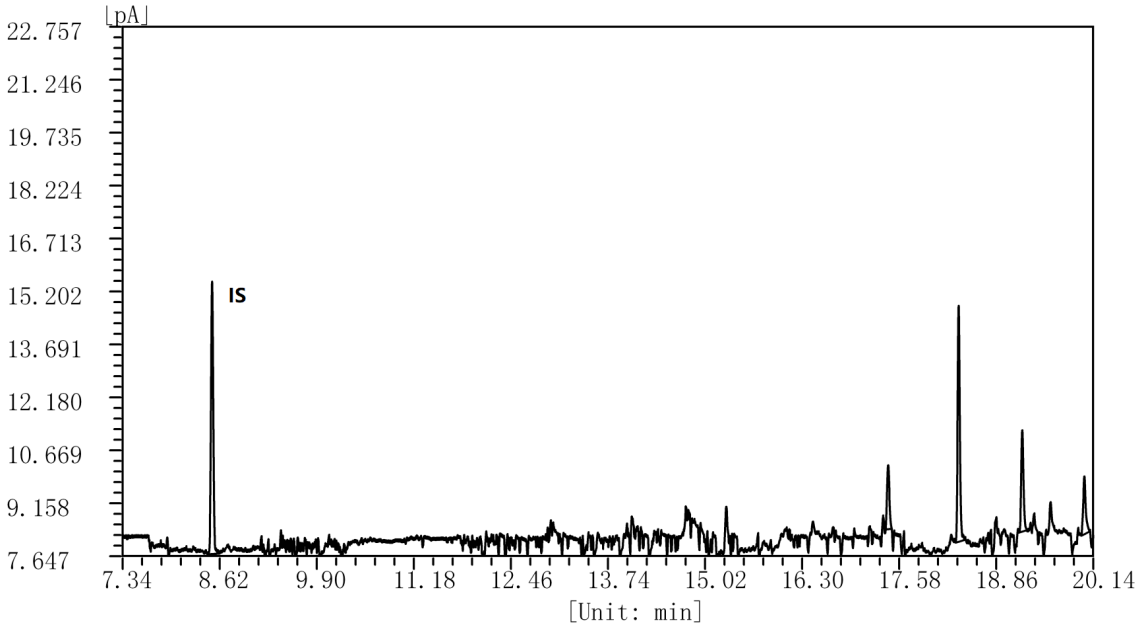


Figure S4: GC-FID analysis of the ethyl acetate soluble aromatics from the two-step depolymerization of birch lignin

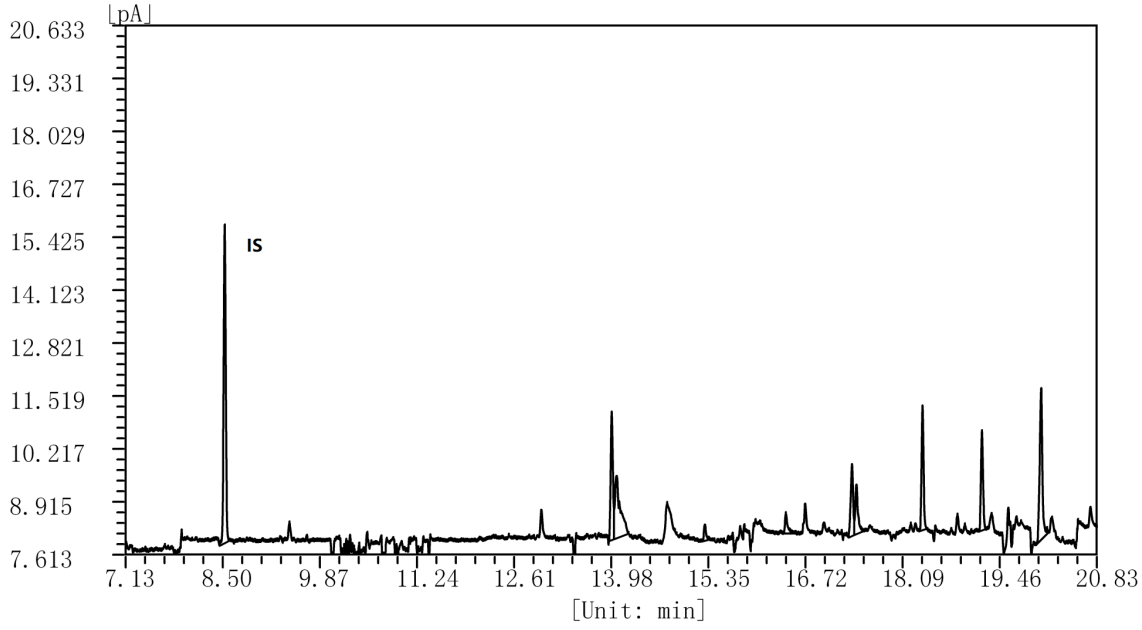


Figure S5: GC-FID analysis of the ethyl acetate soluble aromatics from the two-step depolymerization of oxidized birch lignin

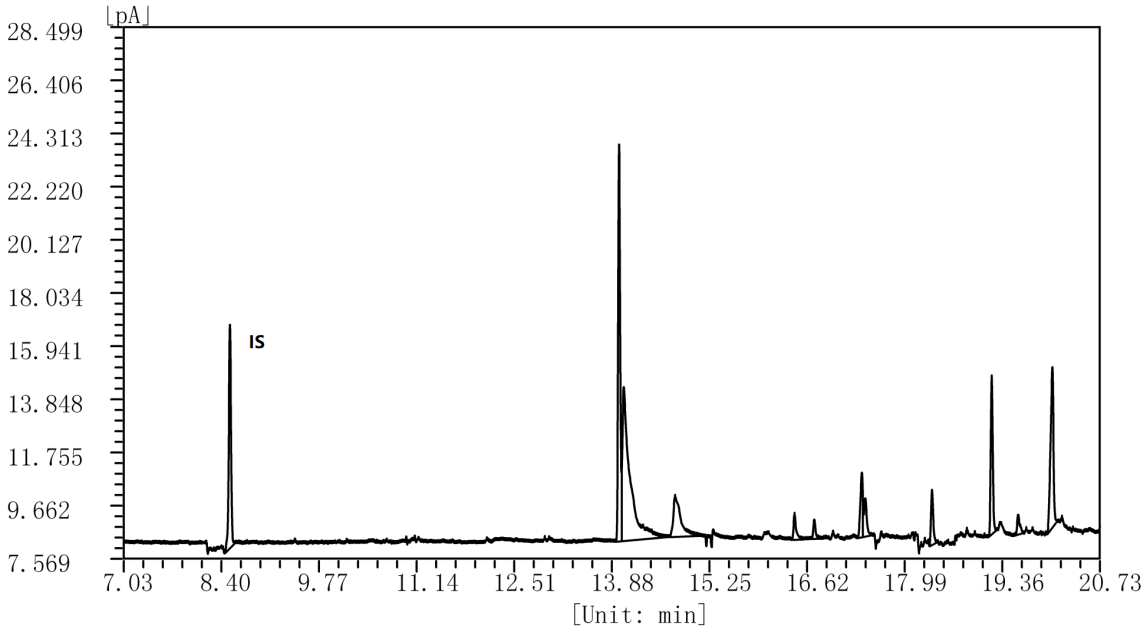
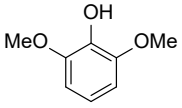
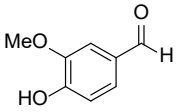
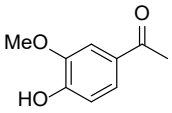
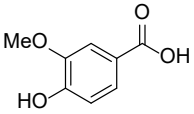
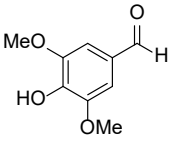
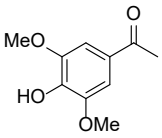
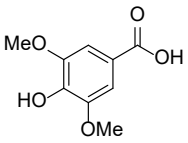


Table S2: Identified aromatic monomers obtained after milling different birch lignin samples

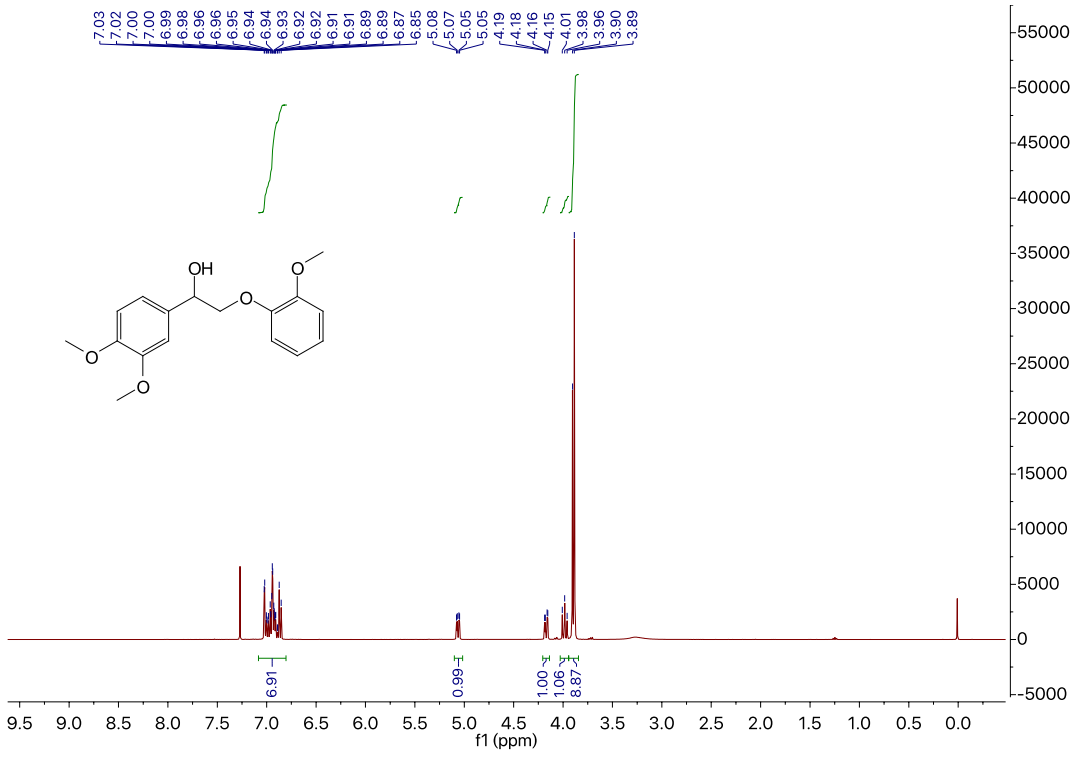
Entry	Retention time (min)	Monomers	Yield (wt%)		
			Lignin[a]	Lignin[b]	Lignin[c]
1	14.0		0.02	1.7	4.3
2	15.3		0.2	0.08	0.03
3	16.4		0.02	0.2	0.4
4	17.4		0.6	0.8	1.1
5	18.4		1.5	0.7	0.5
6	19.2		0.3	0.8	1.7

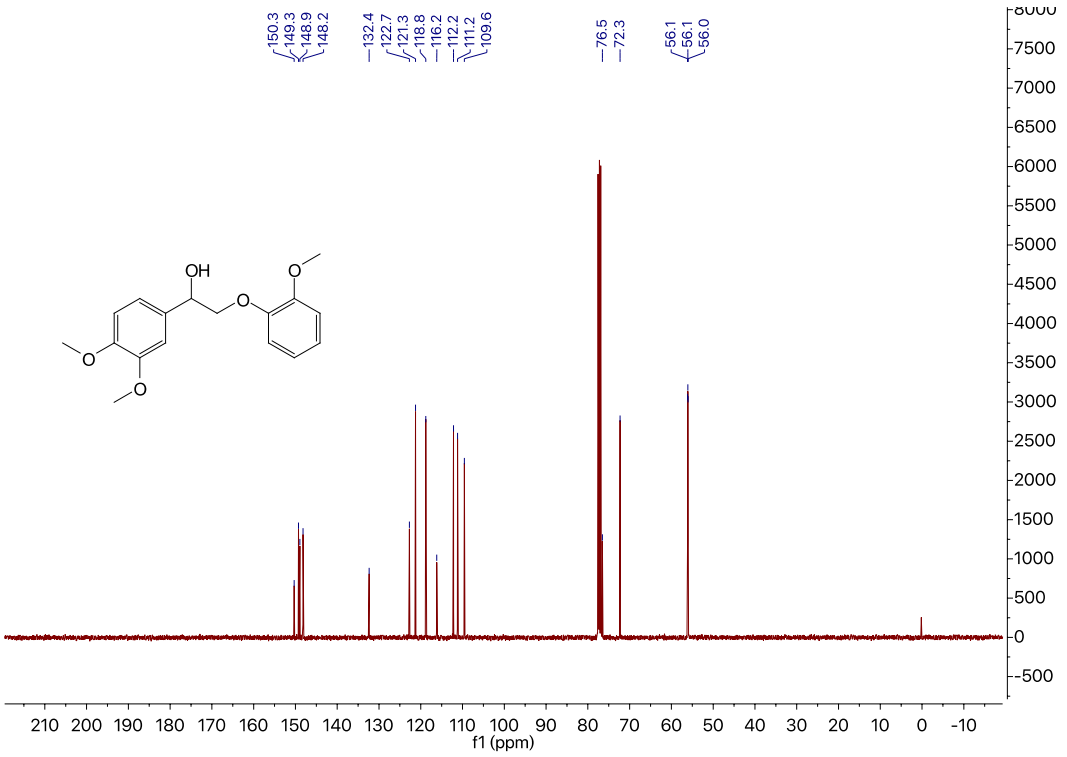
7	20.0		0.9	4.8	7.5
	Total monomers quantified		3.5	9.1	15.5

Reaction conditions: 100 mg lignin samples, 100 mg NaOH were placed in a 50 mL stainless steel vessel with two stainless steel balls (d = 1.4 cm) for 8 h under ball milling at 20 Hz. Yields were determined by GC-FID. Mesitylene was used as the internal standard. [a]Untreated birch lignin. [b]Birch lignin milled for 90 min at 25 Hz in the presence of DDQ/$NaNO_2$. [c]the oxidised of birch lignin.

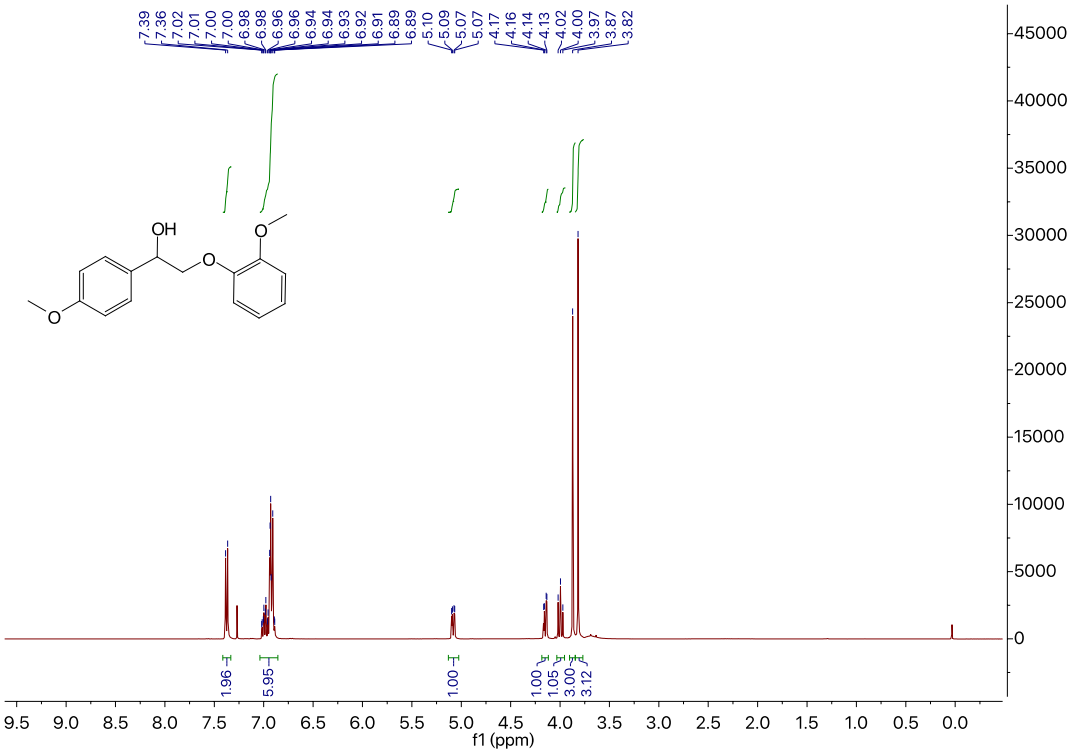
12. Copies of ^{1}H and ^{13}C NMR spectrum

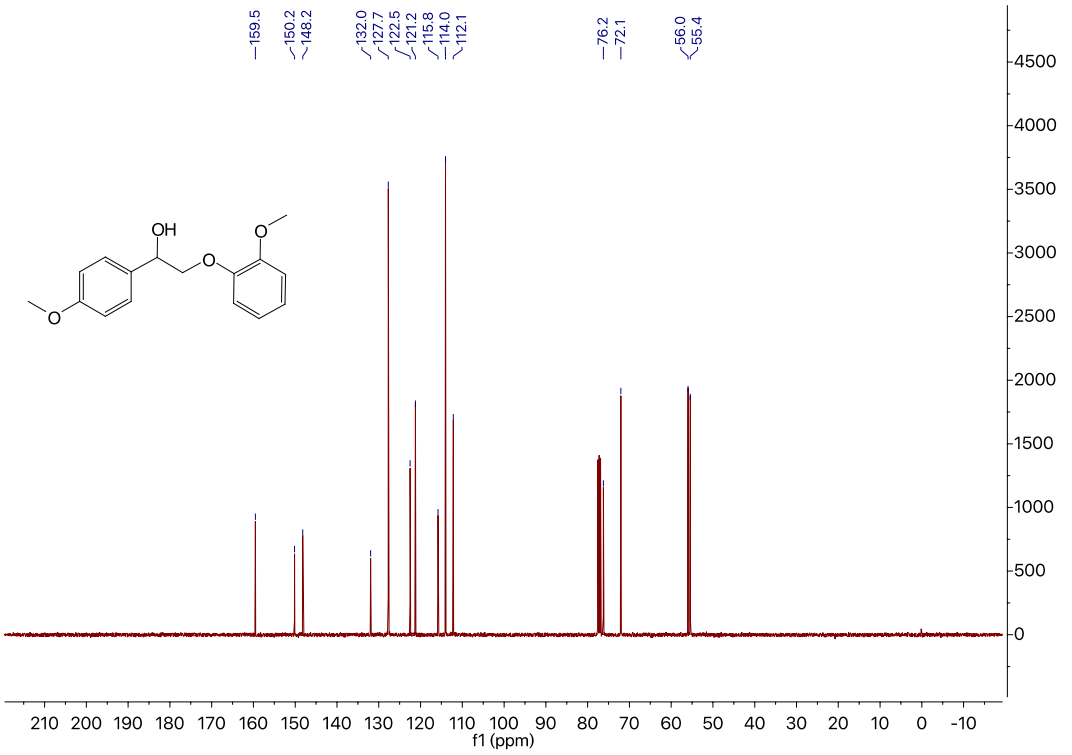
1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanol (1a)



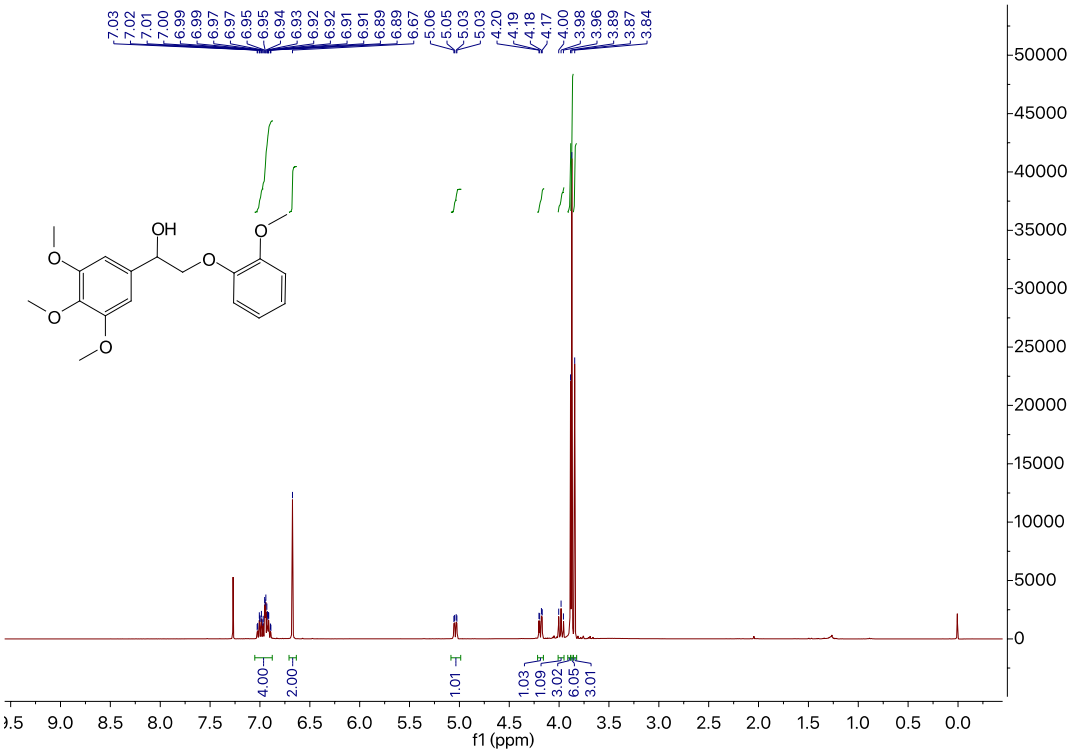


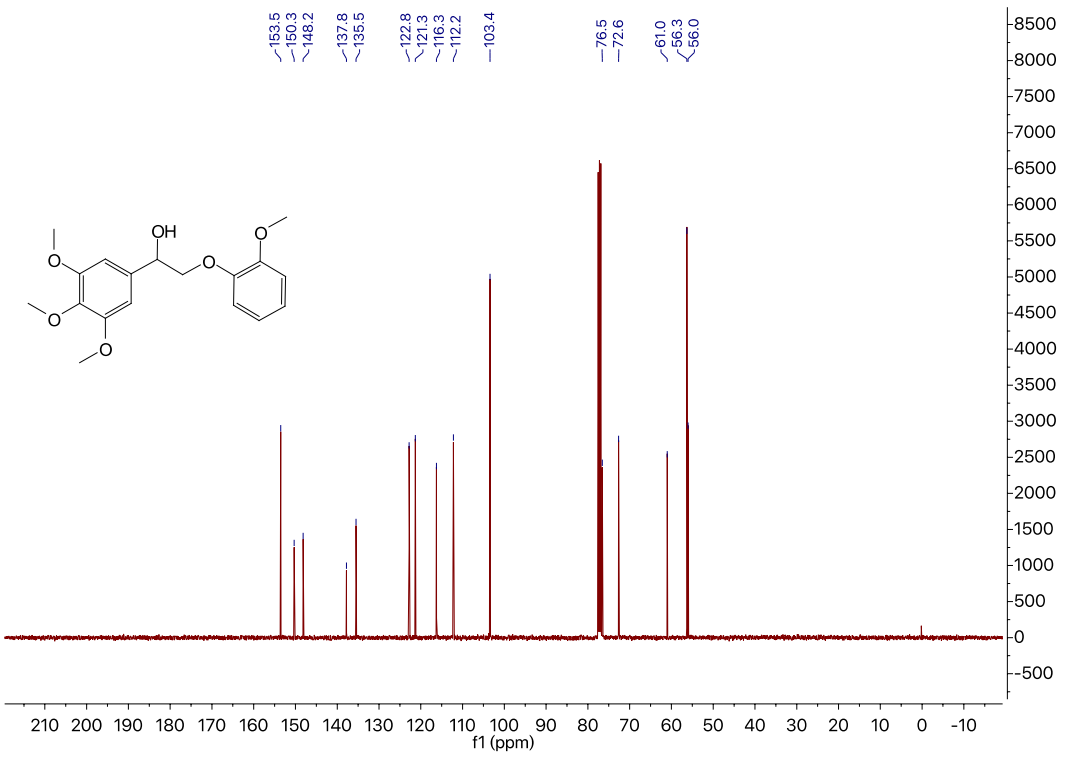
1-(4-Methoxyphenyl)-2-(2-methoxyphenoxy)ethanol (1b)



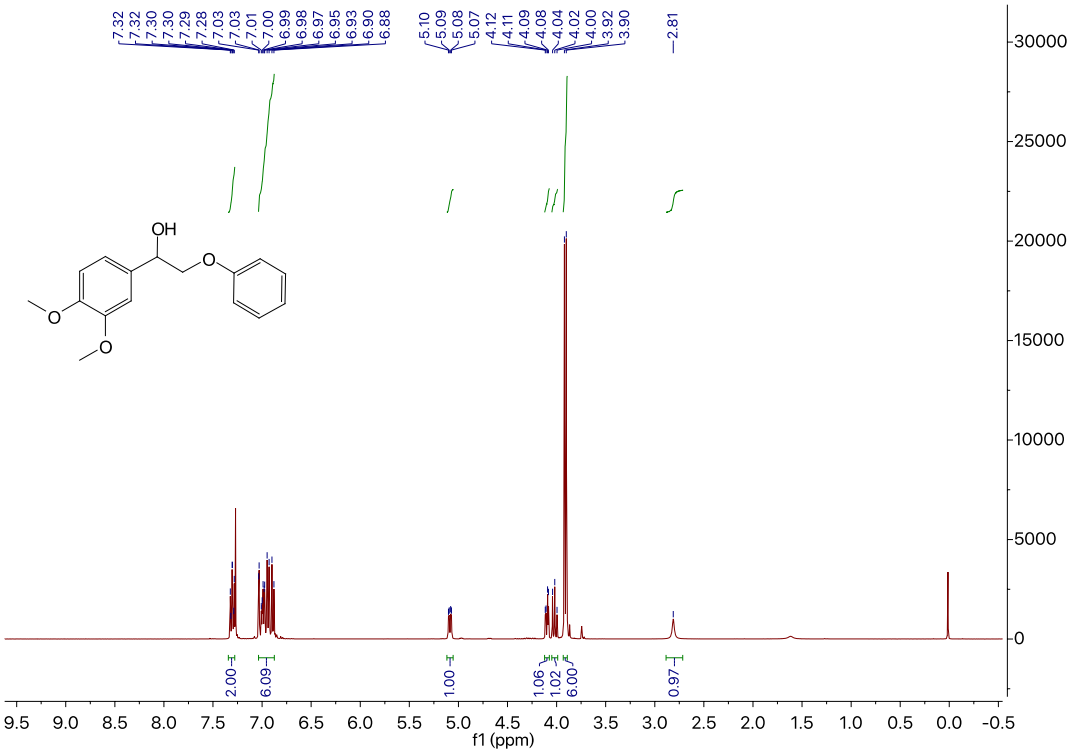


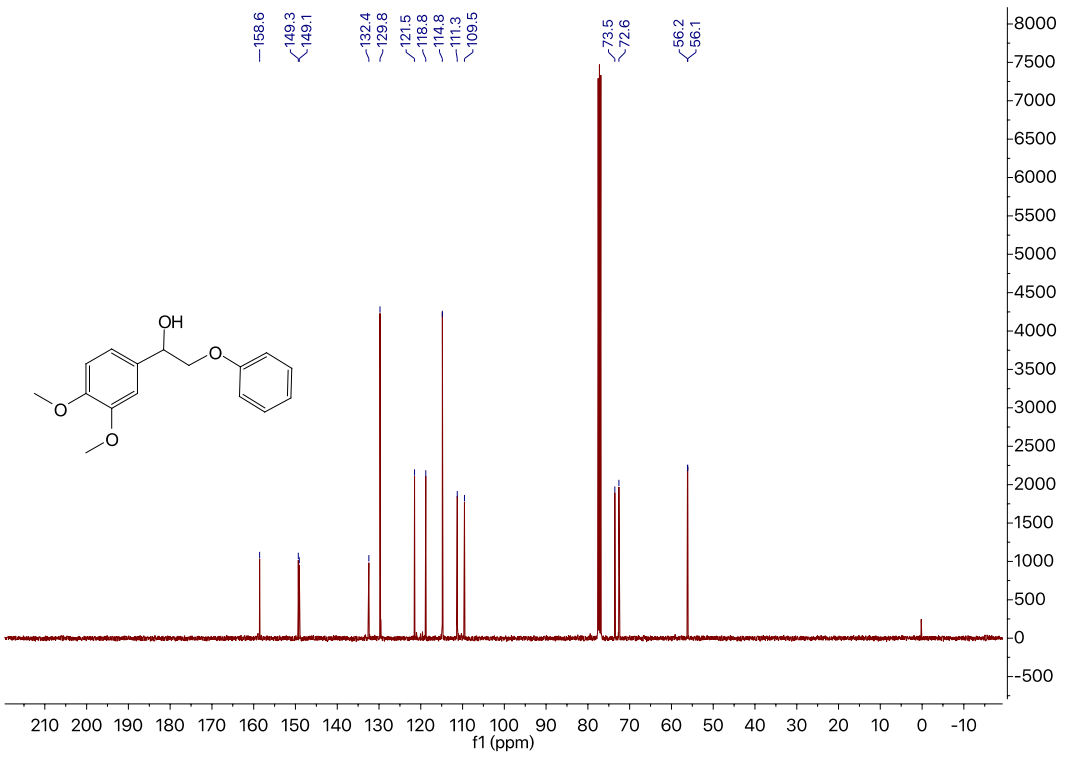
1-(3,4,5-Trimethoxyphenyl)-2-(2-methoxyphenoxy)ethanol (1c)



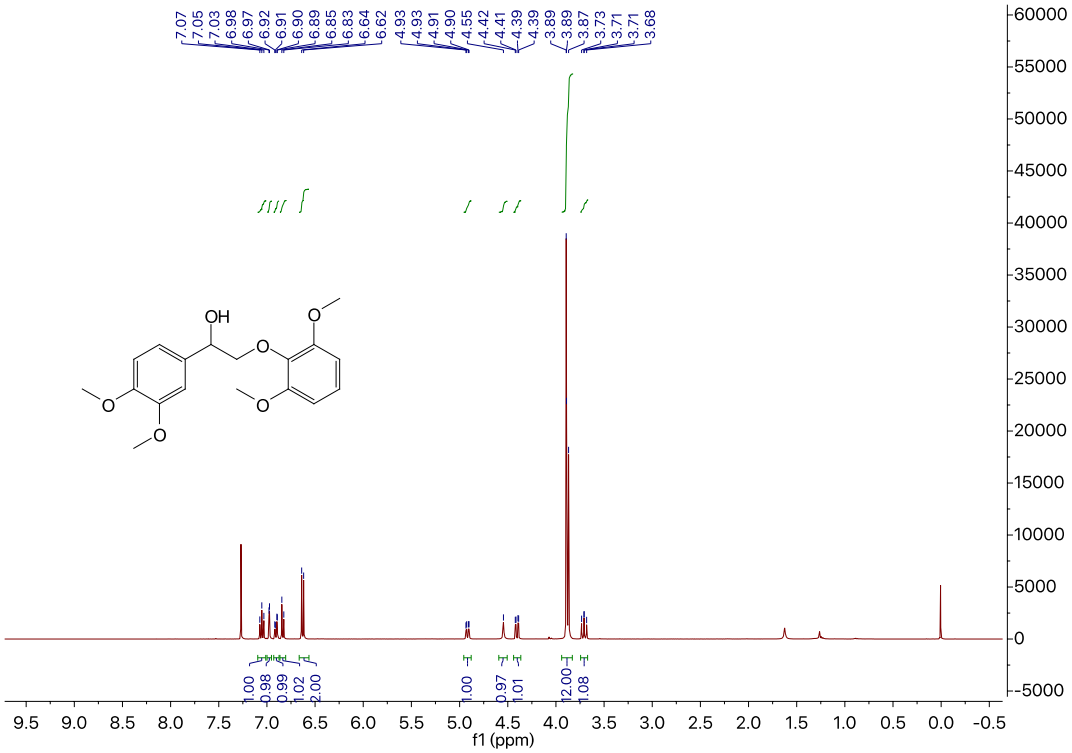


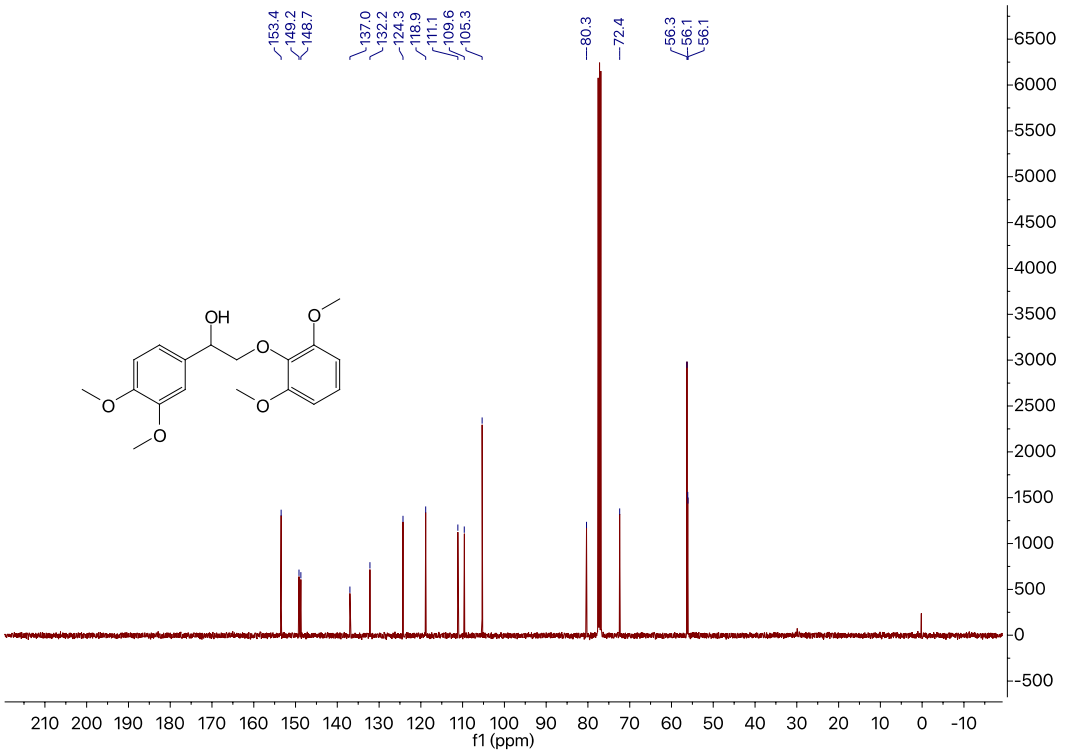
1-(3,4-Dimethoxyphenyl)-2-phenoxyethanol (1d)



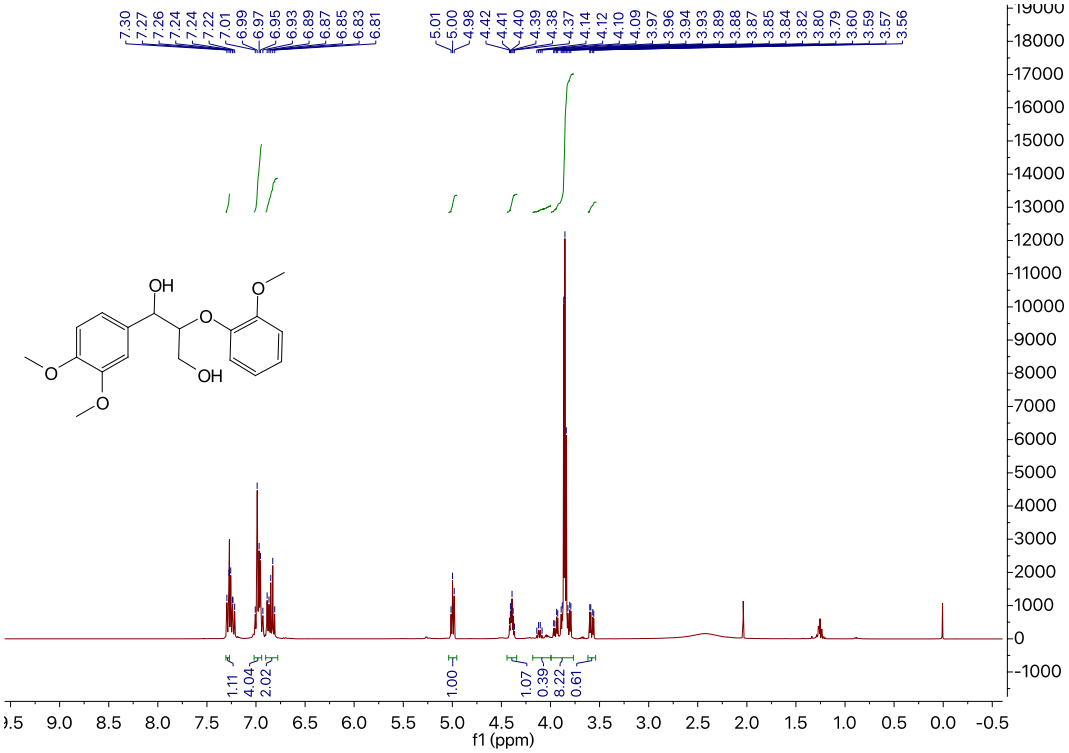


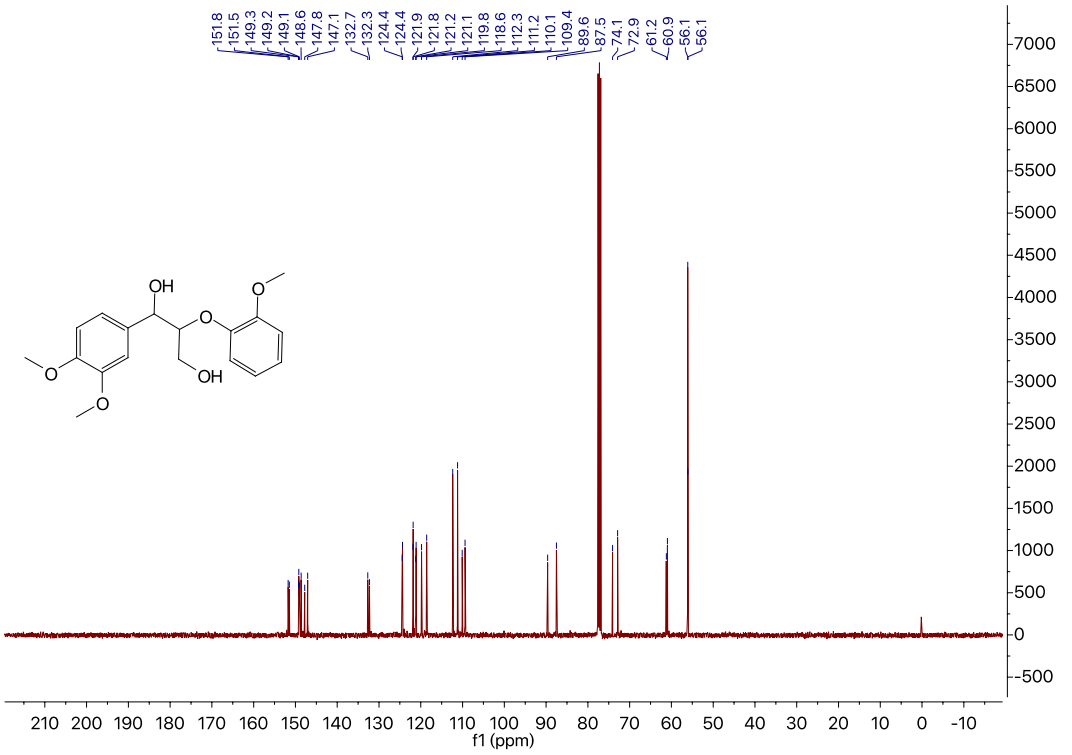
1-(3,4-Dimethoxyphenyl)-2-(2,6-dimethoxyphenoxy)ethanol (1e)



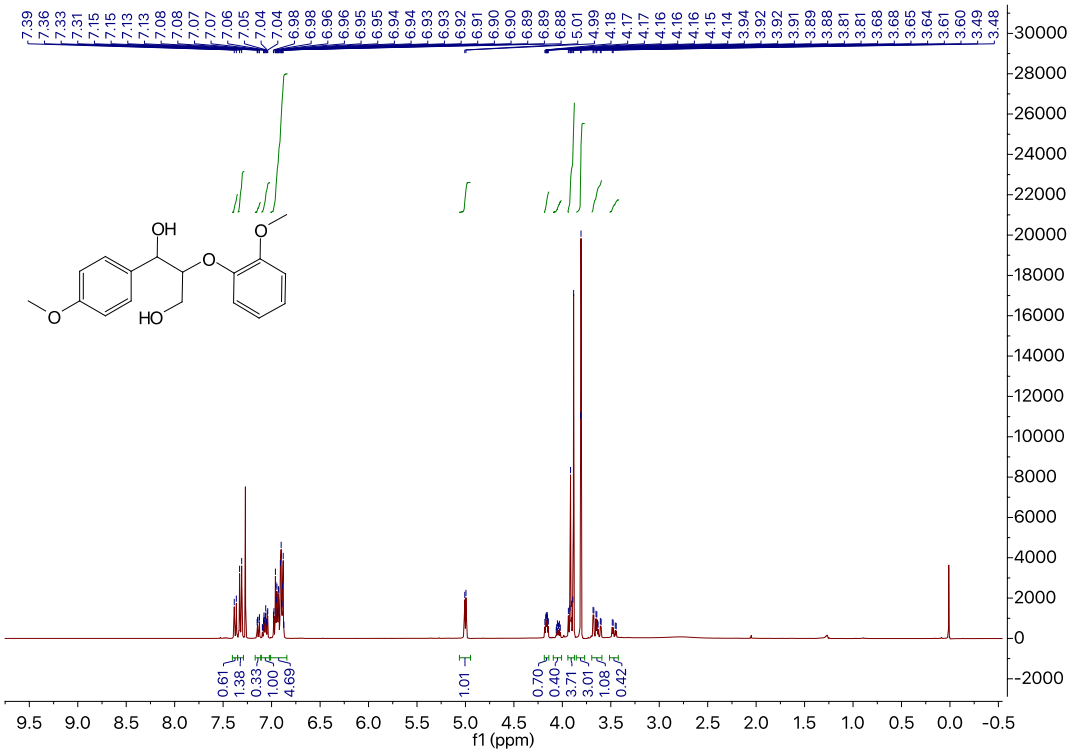


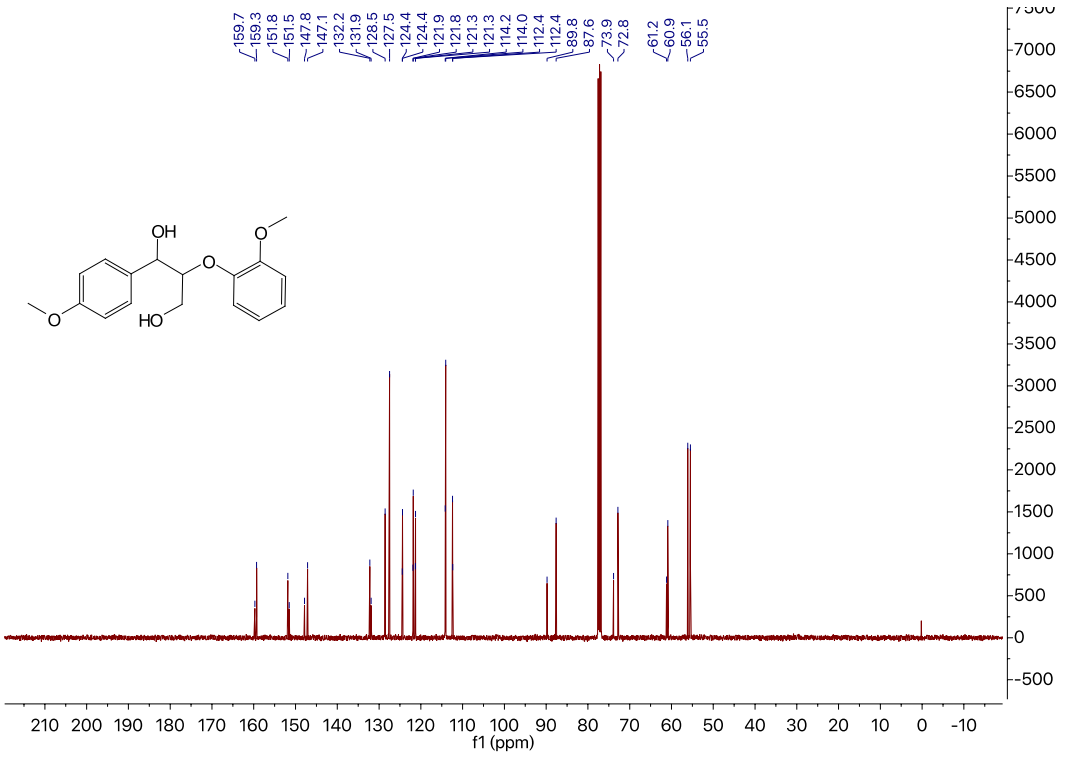
1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (1f)





1-(4-Methoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (1g)





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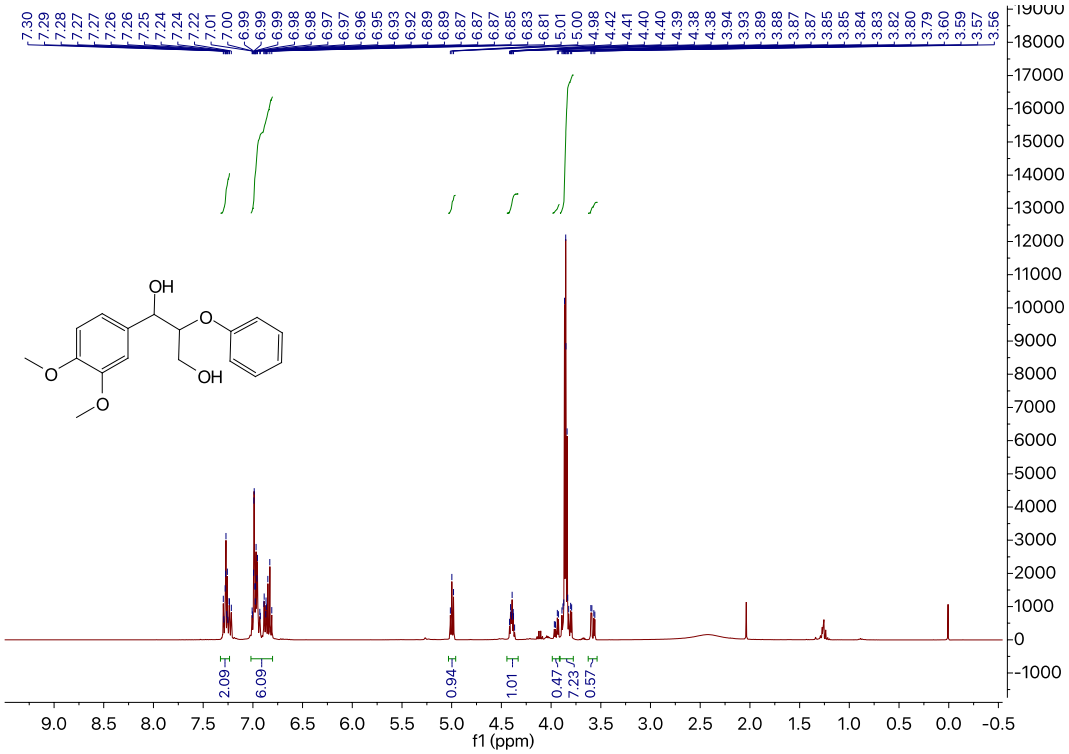
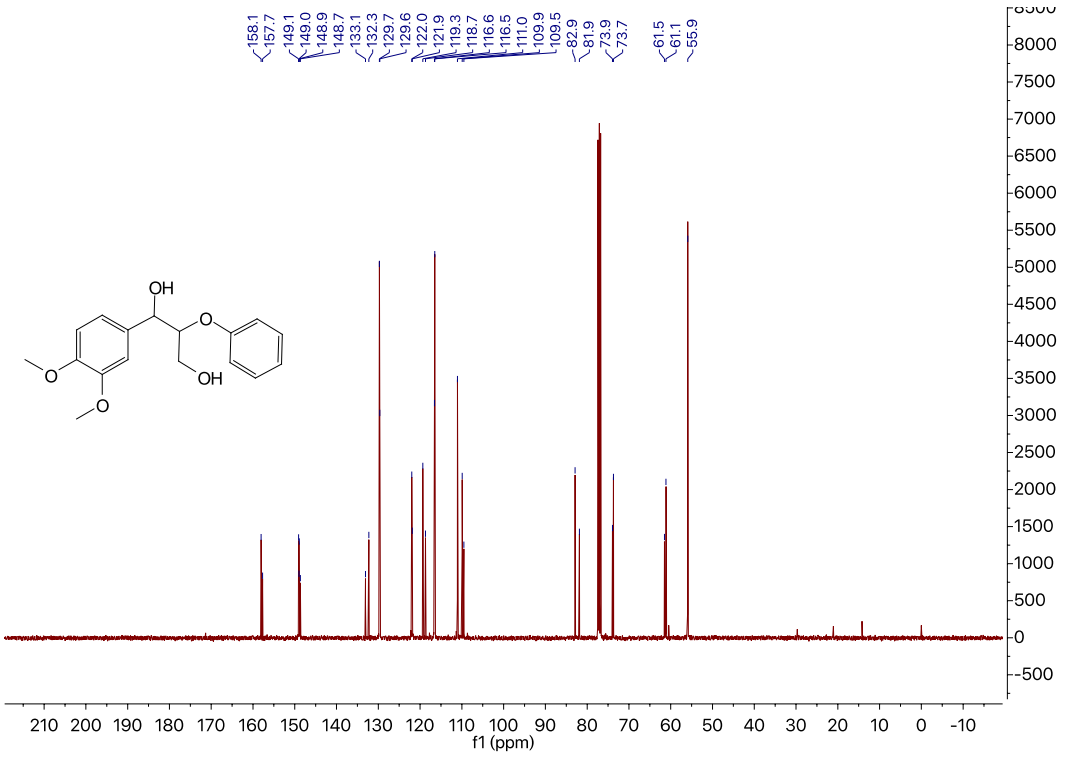
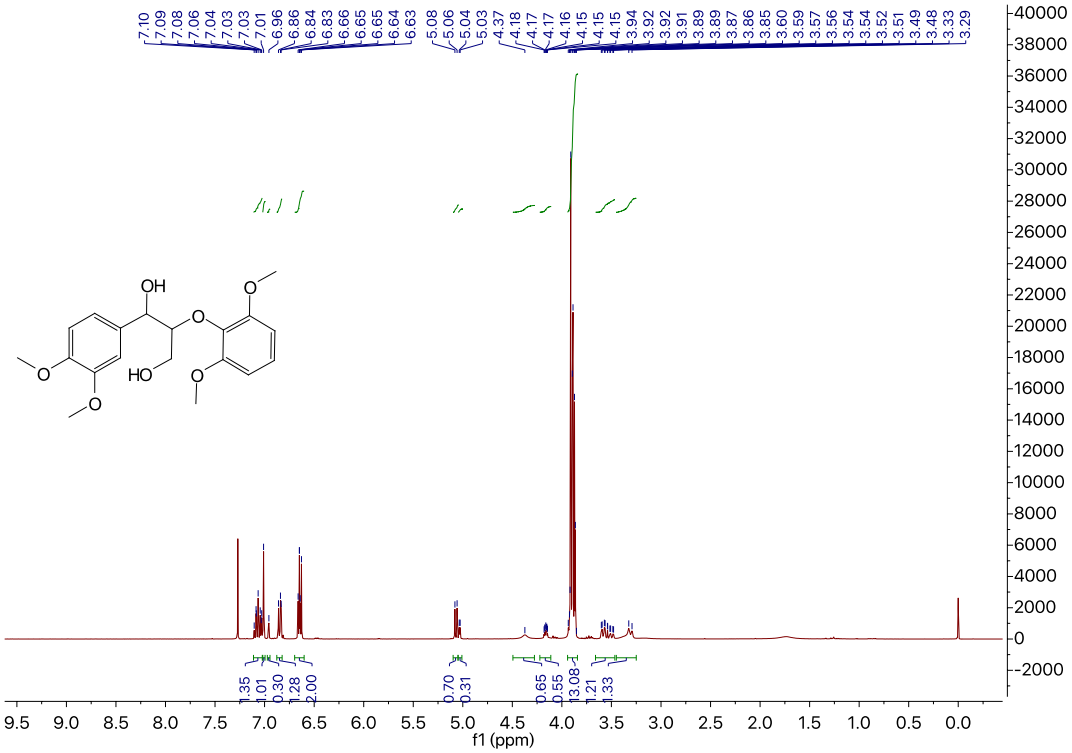
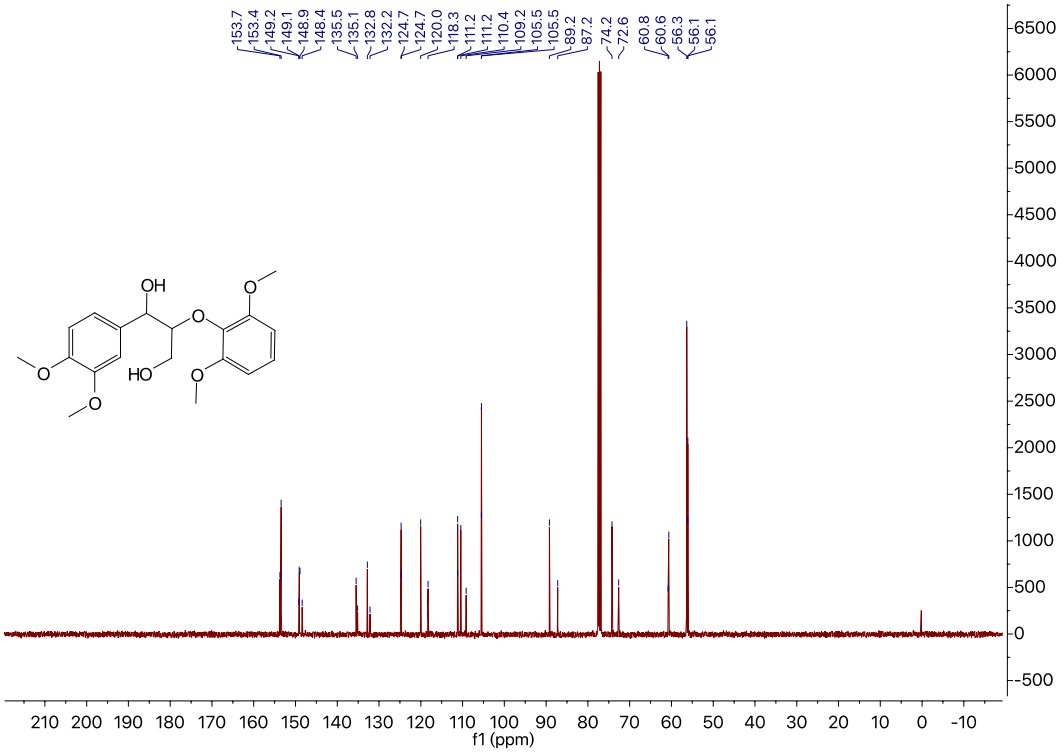


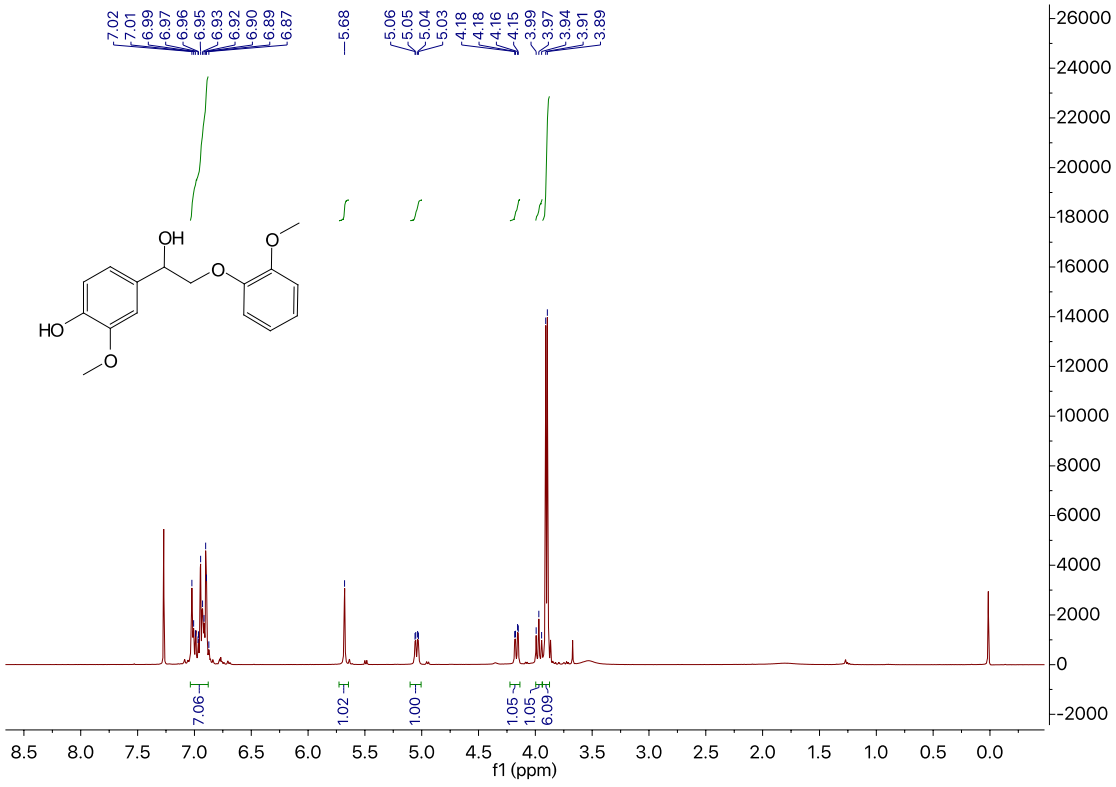


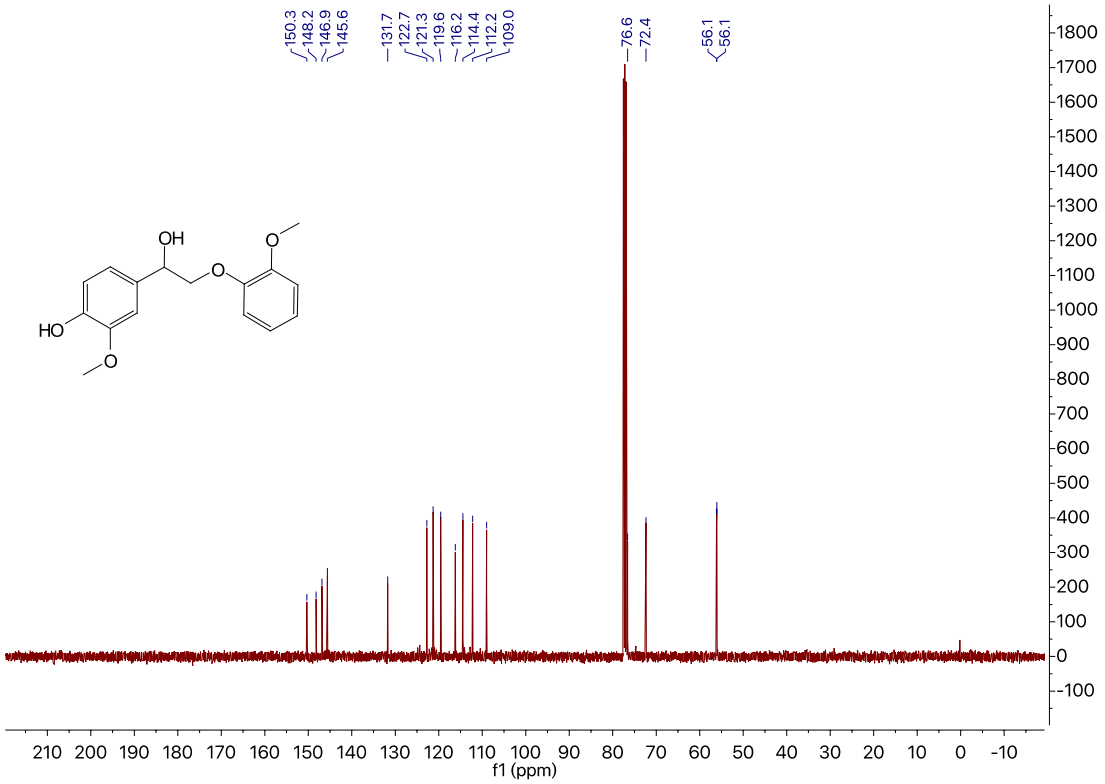
1-(3,4-Dimethoxyphenyl)-2-(2,6-dimethoxyphenoxy)-1,3-propanediol (1i)



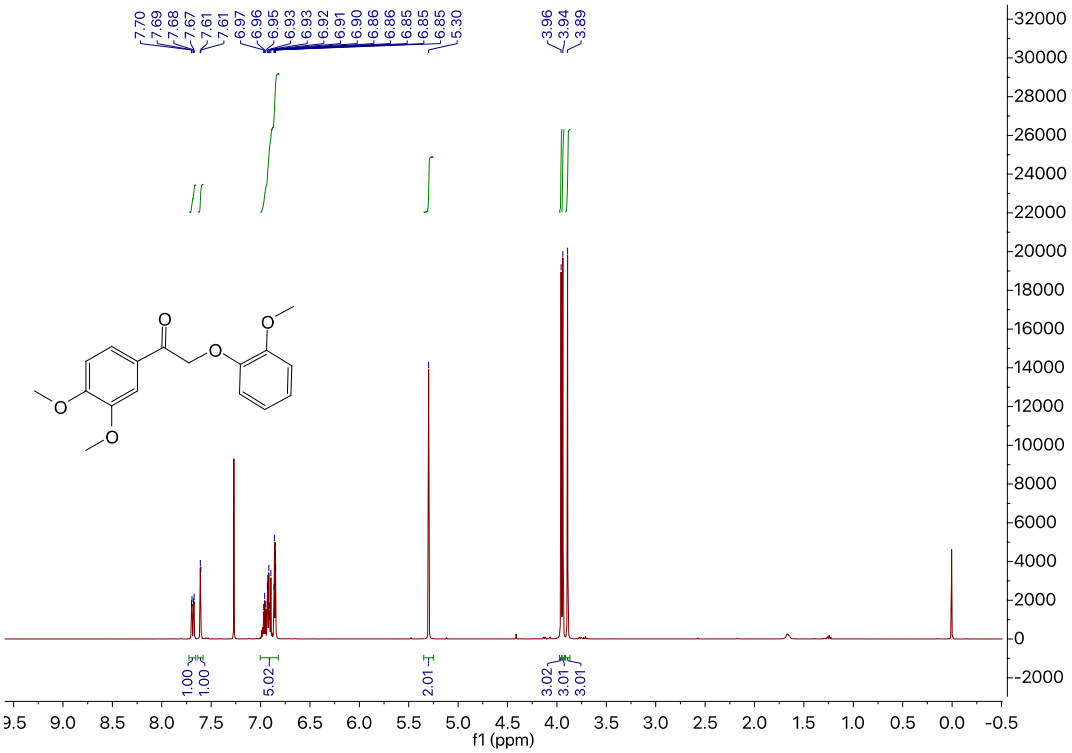


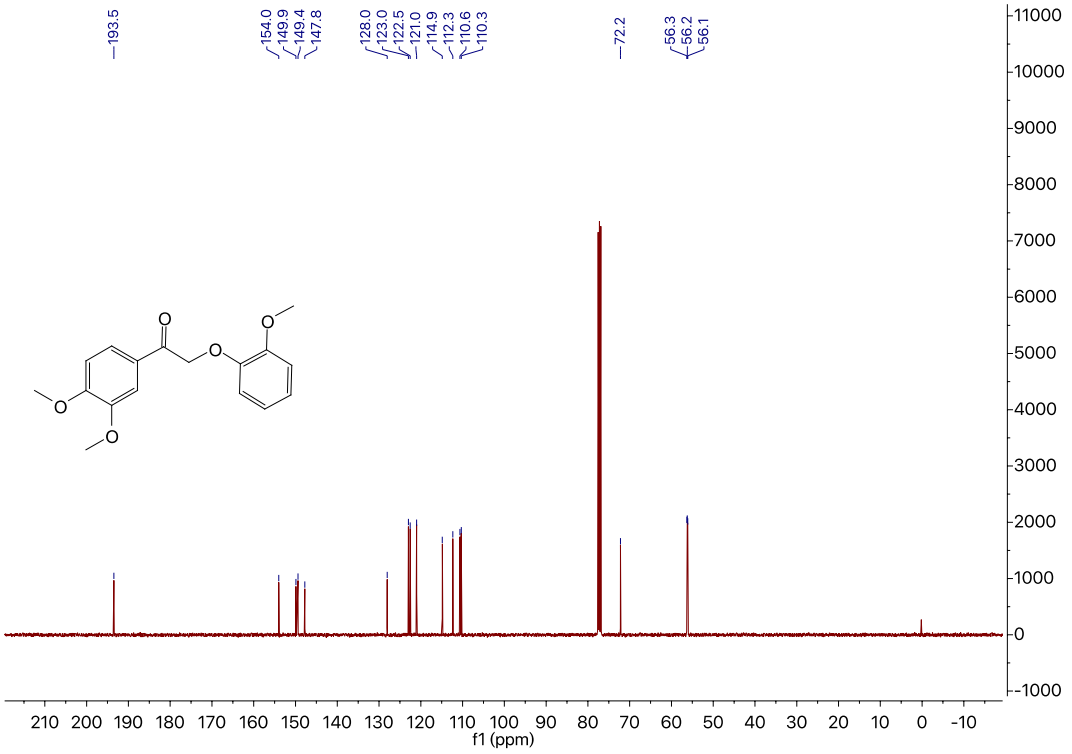
1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)ethanol (1j)



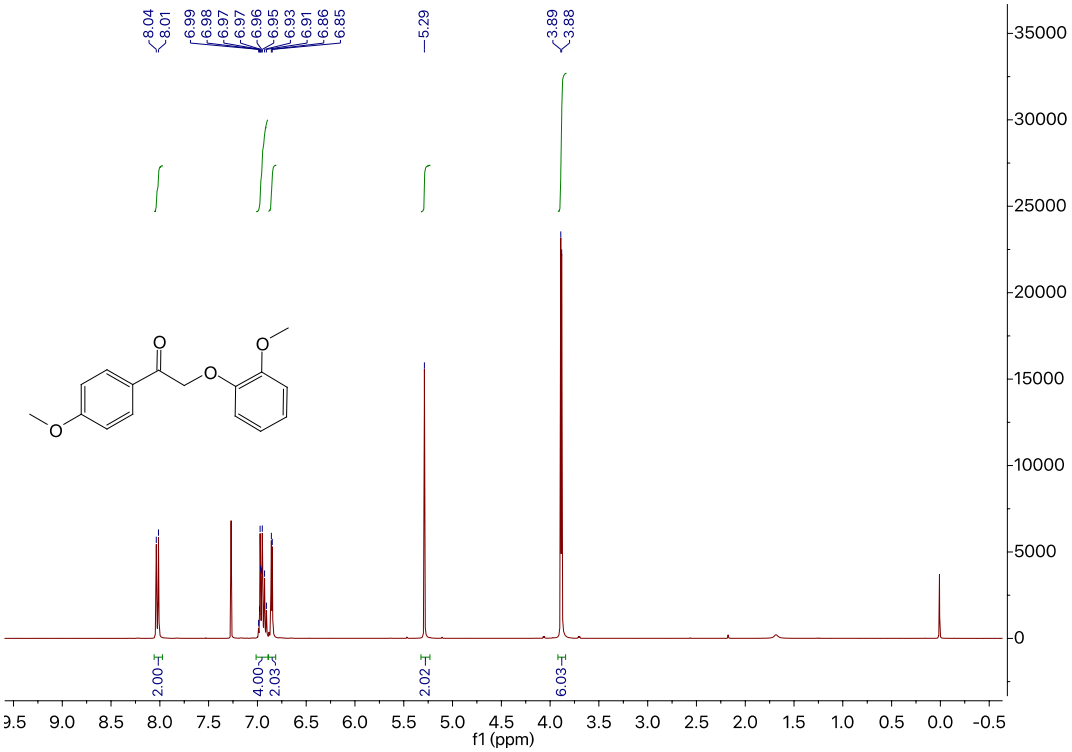


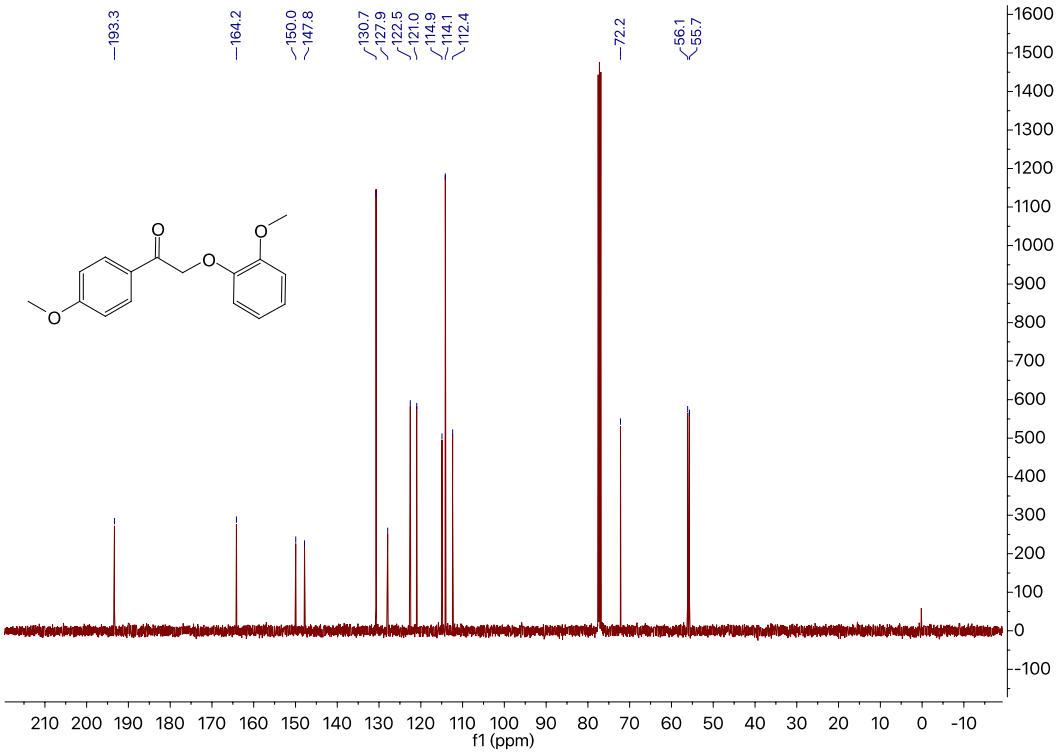
1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)ethenone (2a)



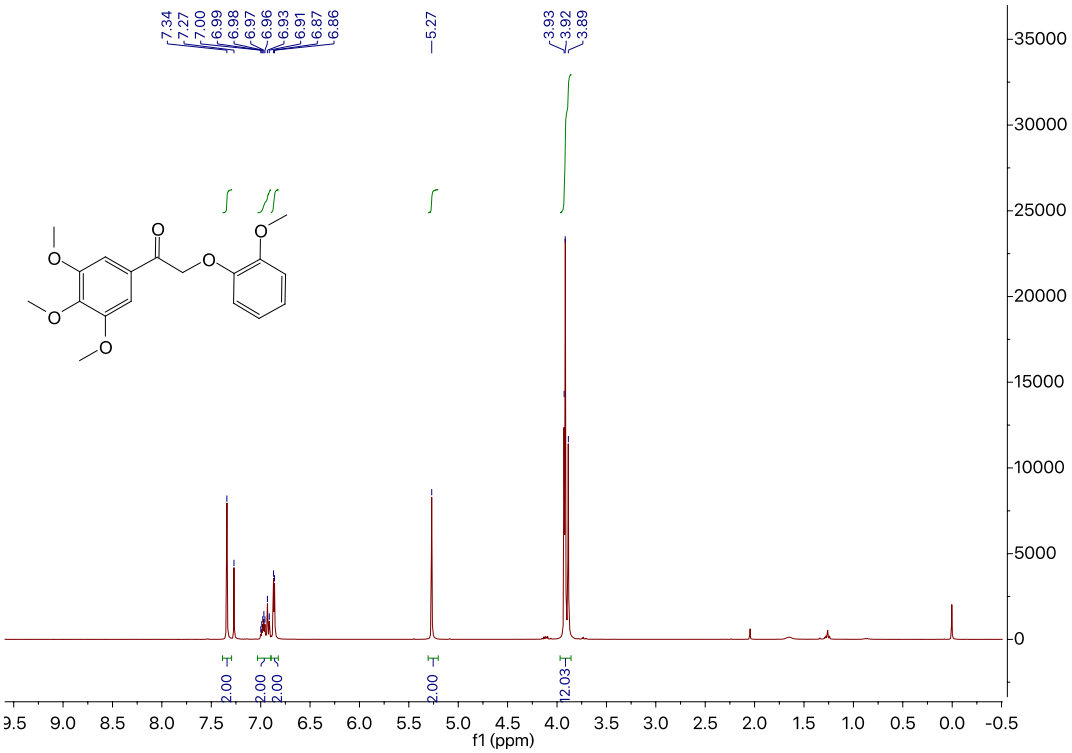


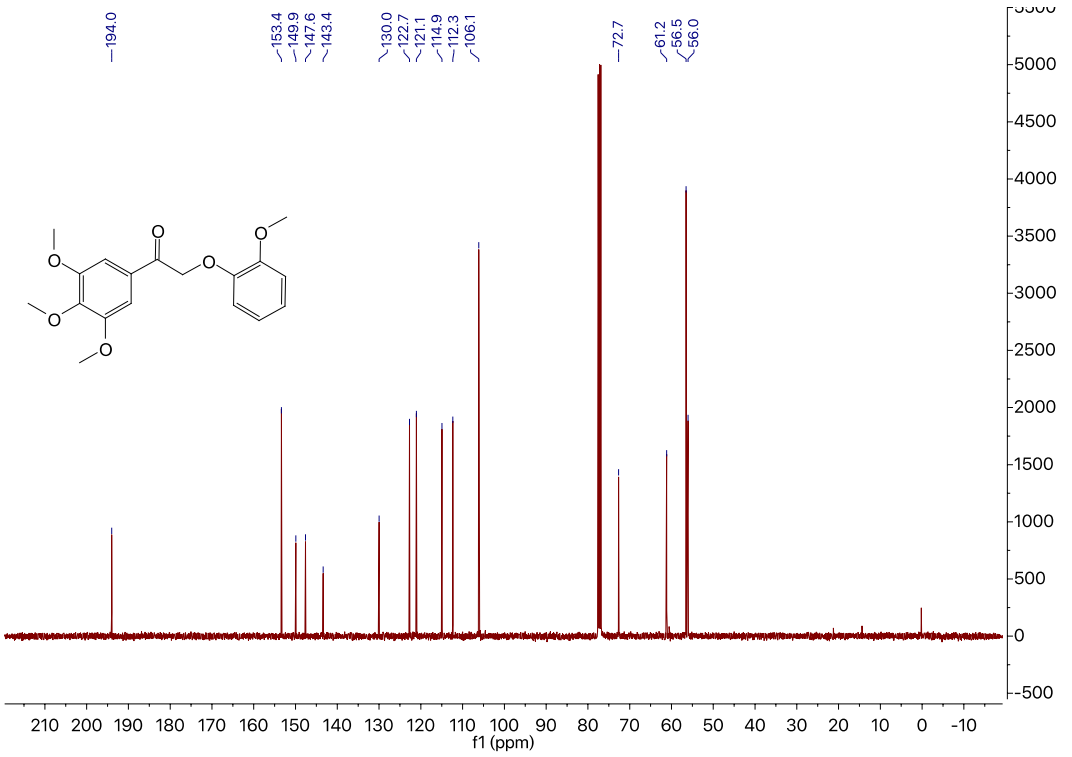
1-(4-Methoxyphenyl)-2-(2-methoxyphenoxy)ethenone (2b)



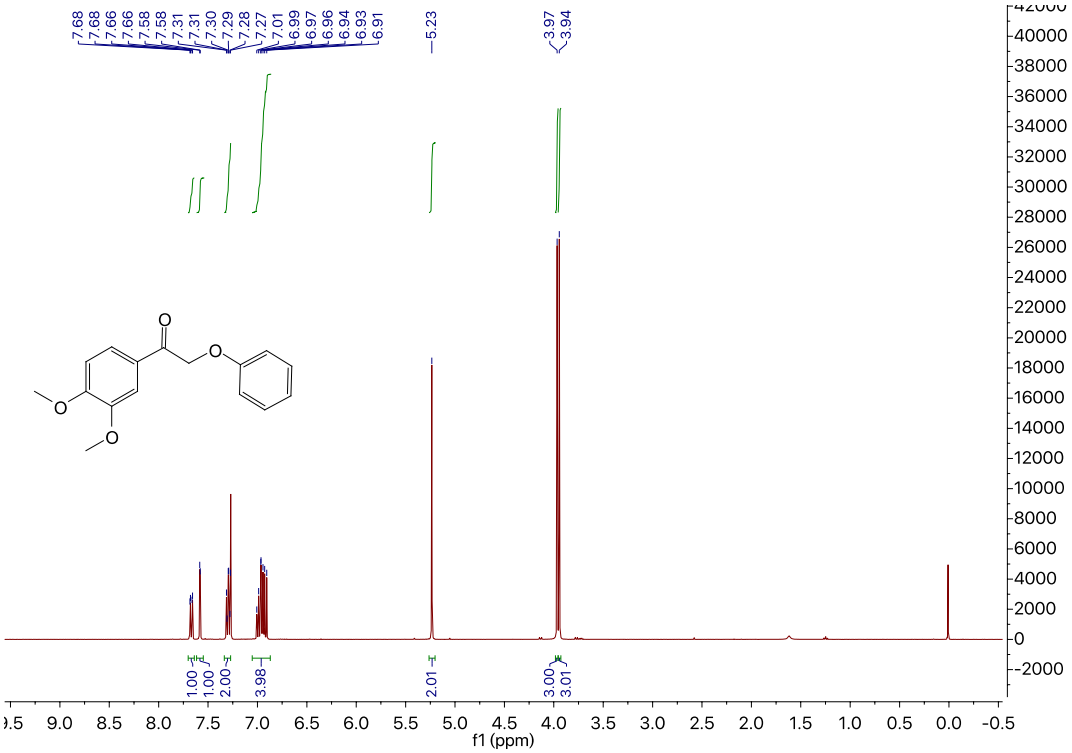


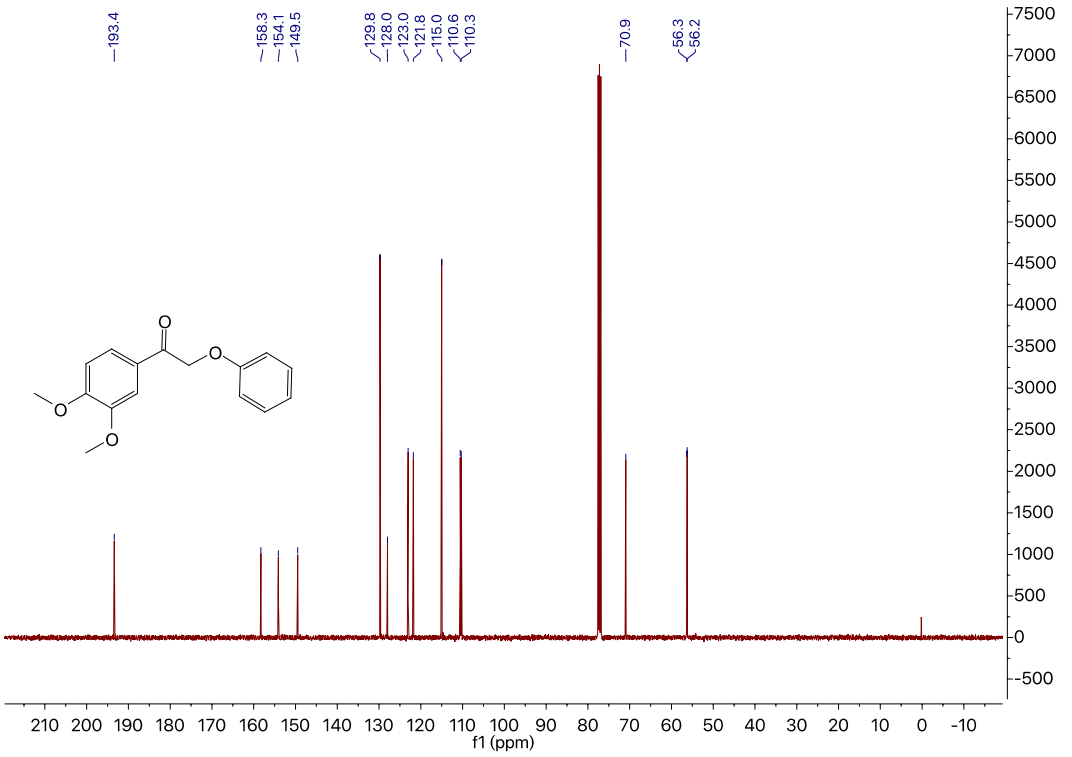
1-(3,4,5-Trimethoxyphenyl)- 2-(2-methoxyphenoxy)etenone (2c)



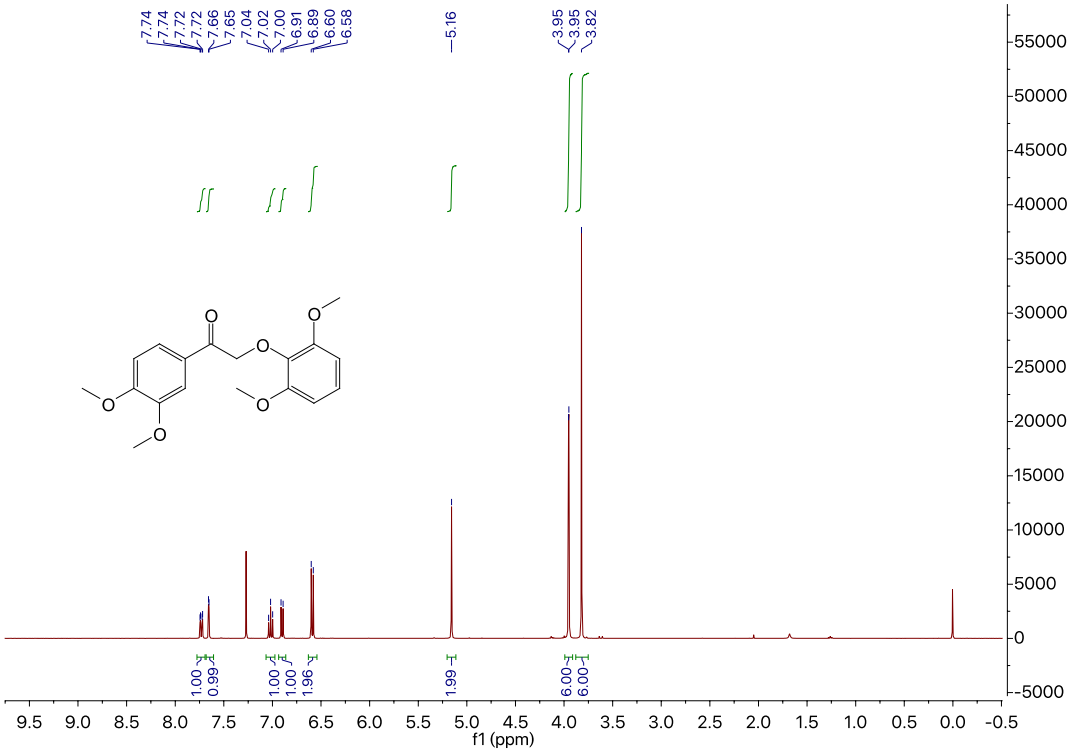


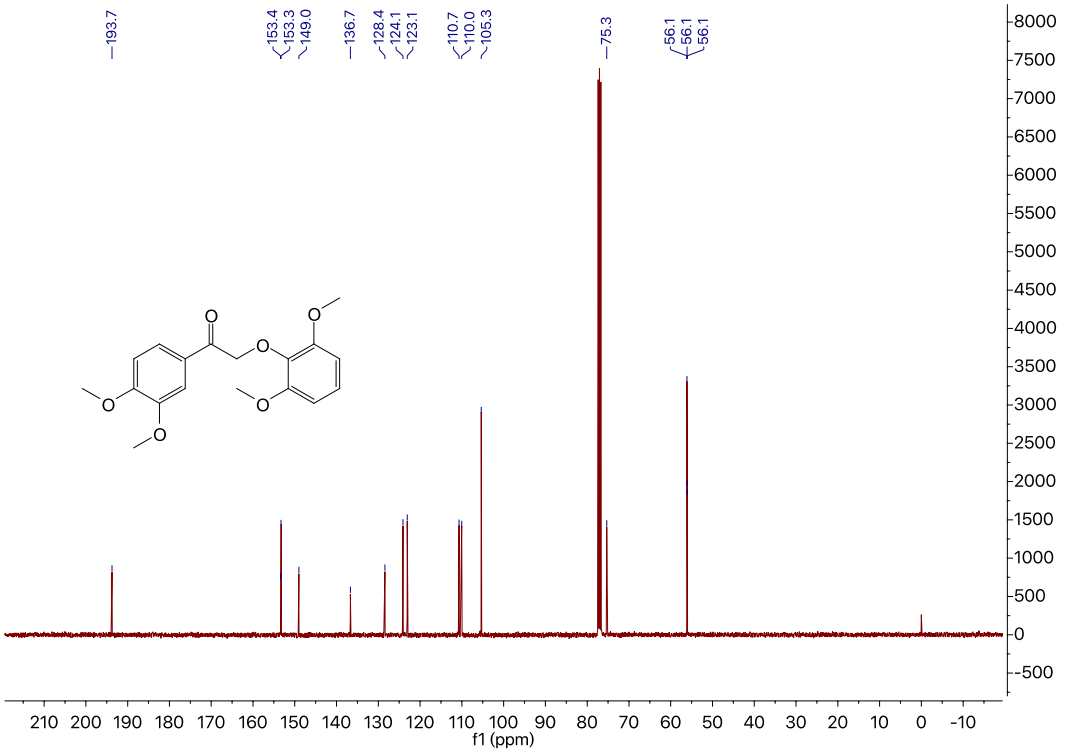
1-(3,4-Dimethoxyphenyl)-2-phenoxyethanone (2d)



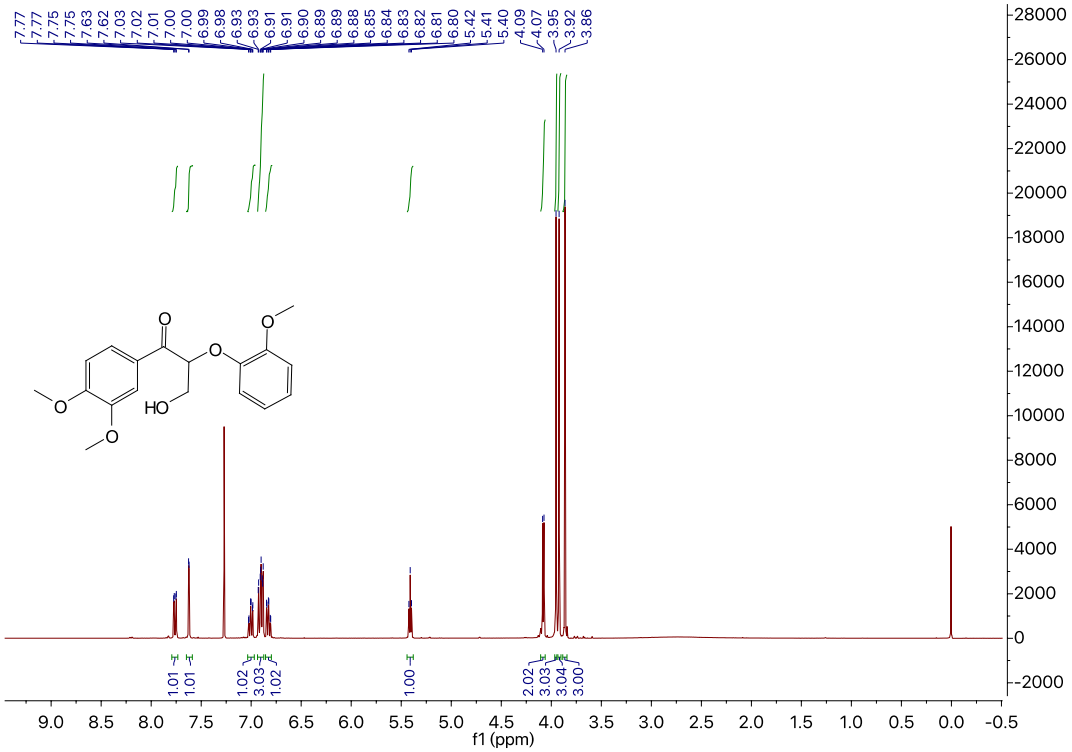


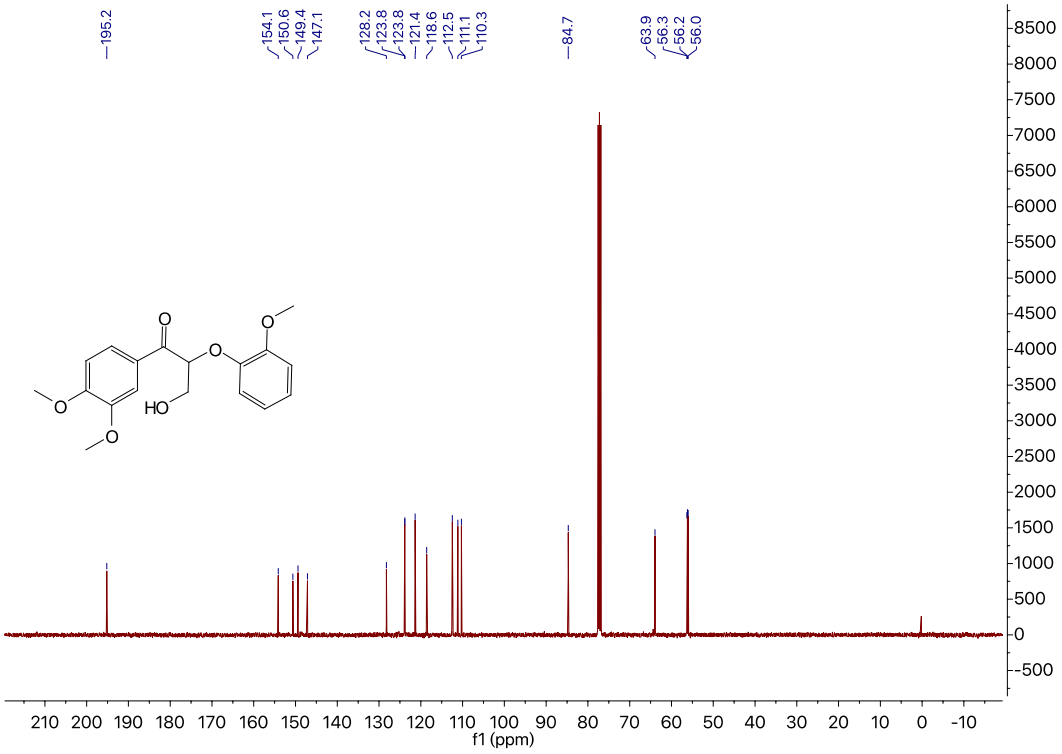
1-(3,4-Dimethoxyphenyl)-2-(2,6-dimethoxyphenoxy)ethenone (2e)



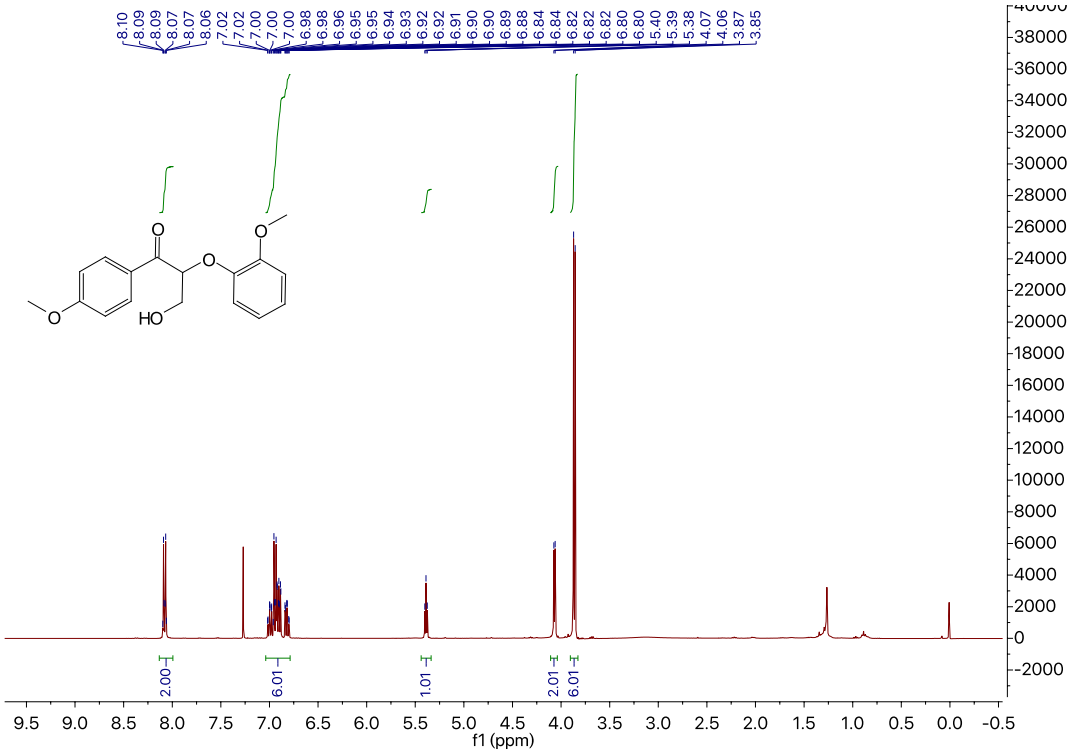


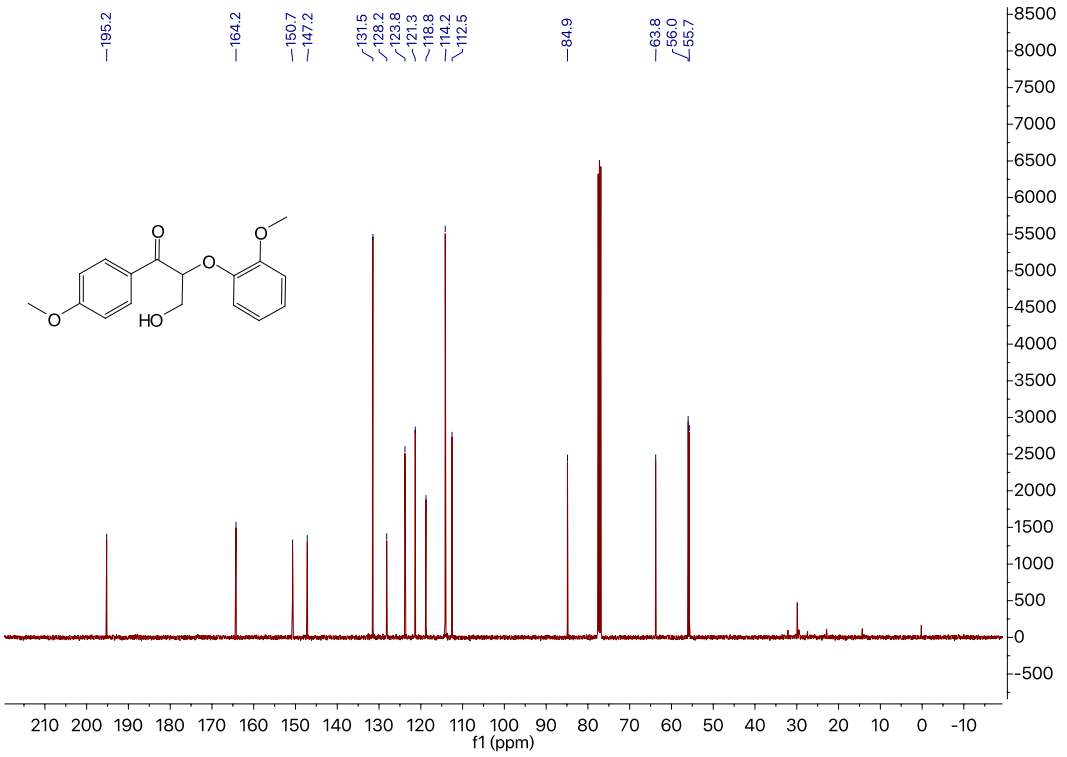
1-(3,4-Dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propanone (2f)



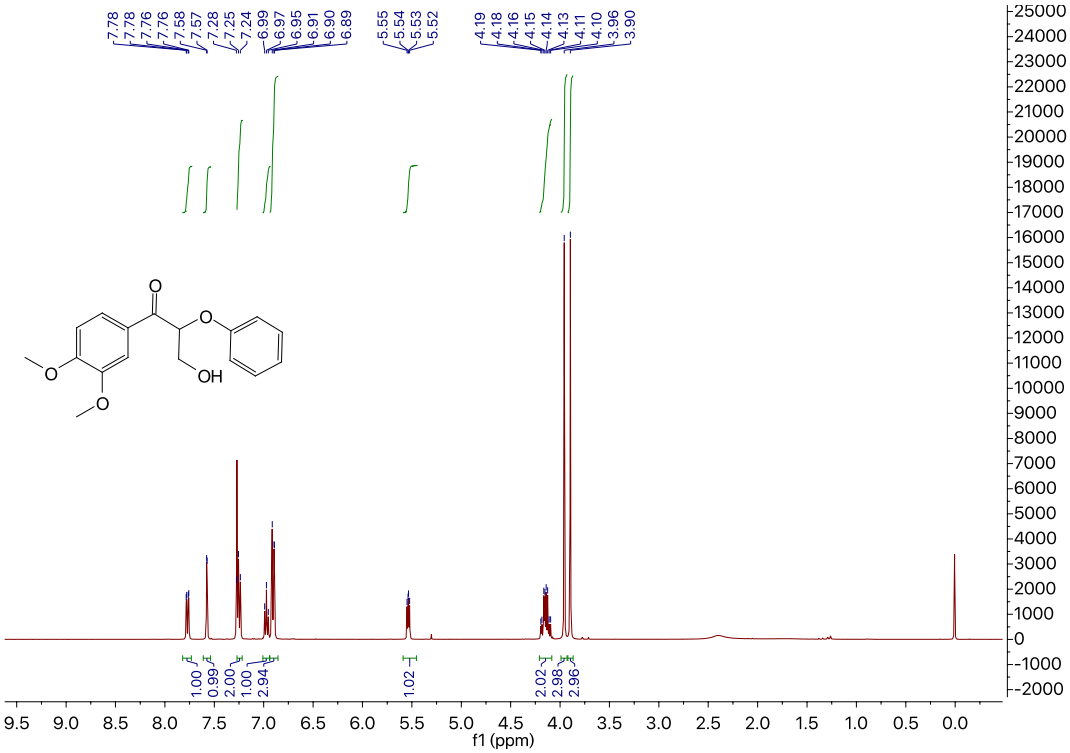


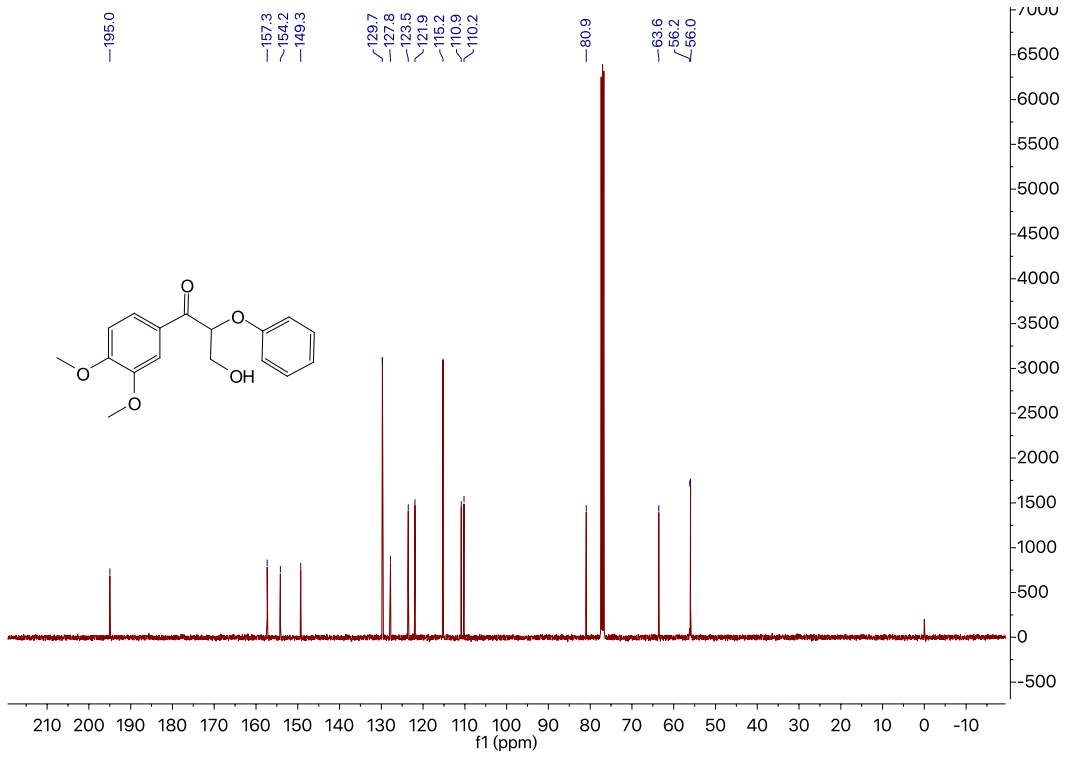
1-(4-Methoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propanone (2g)



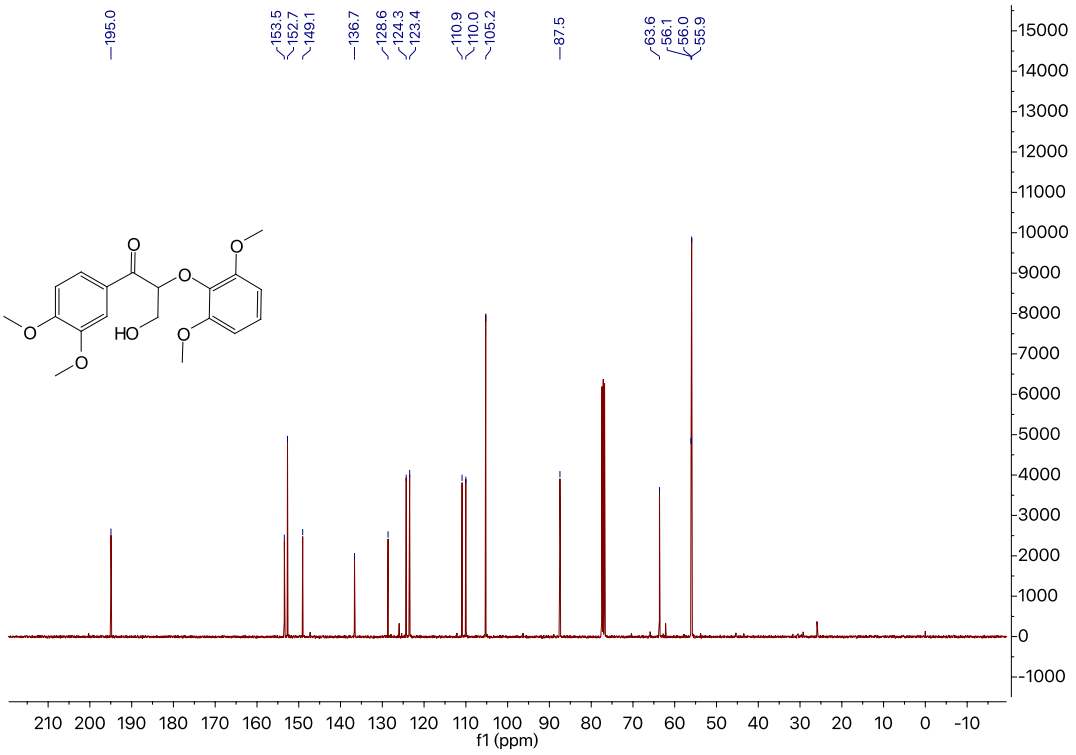


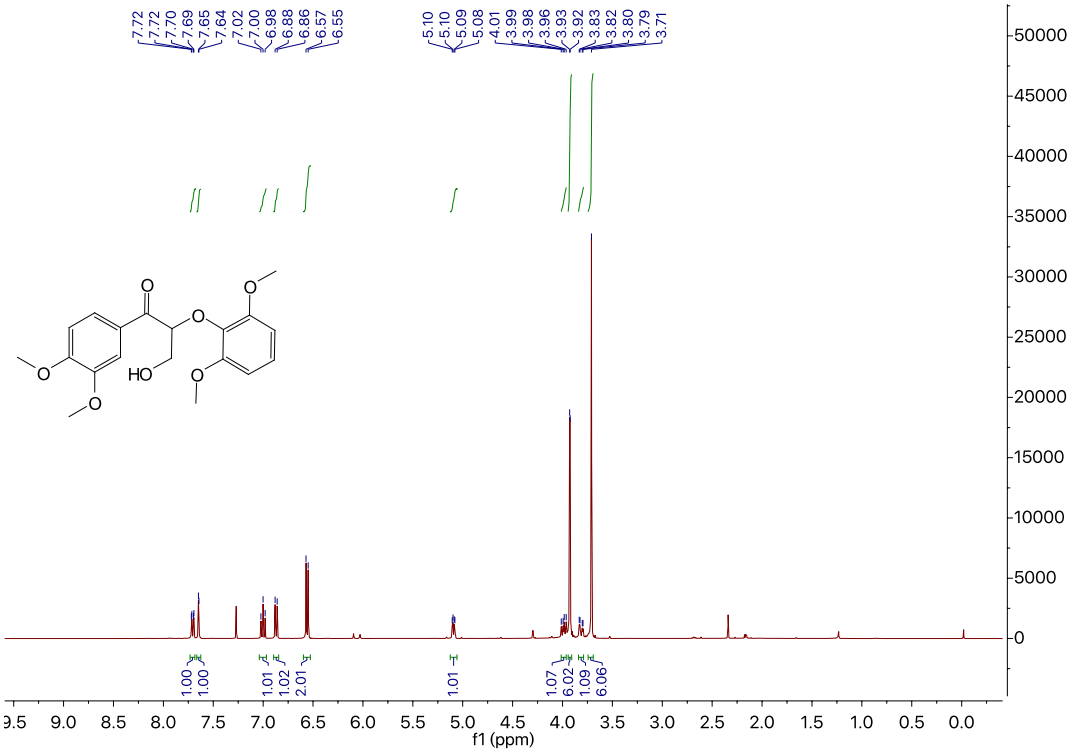
1-(3,4-Dimethoxyphenyl)-3-hydroxy-2-phenoxypropanone (2h)



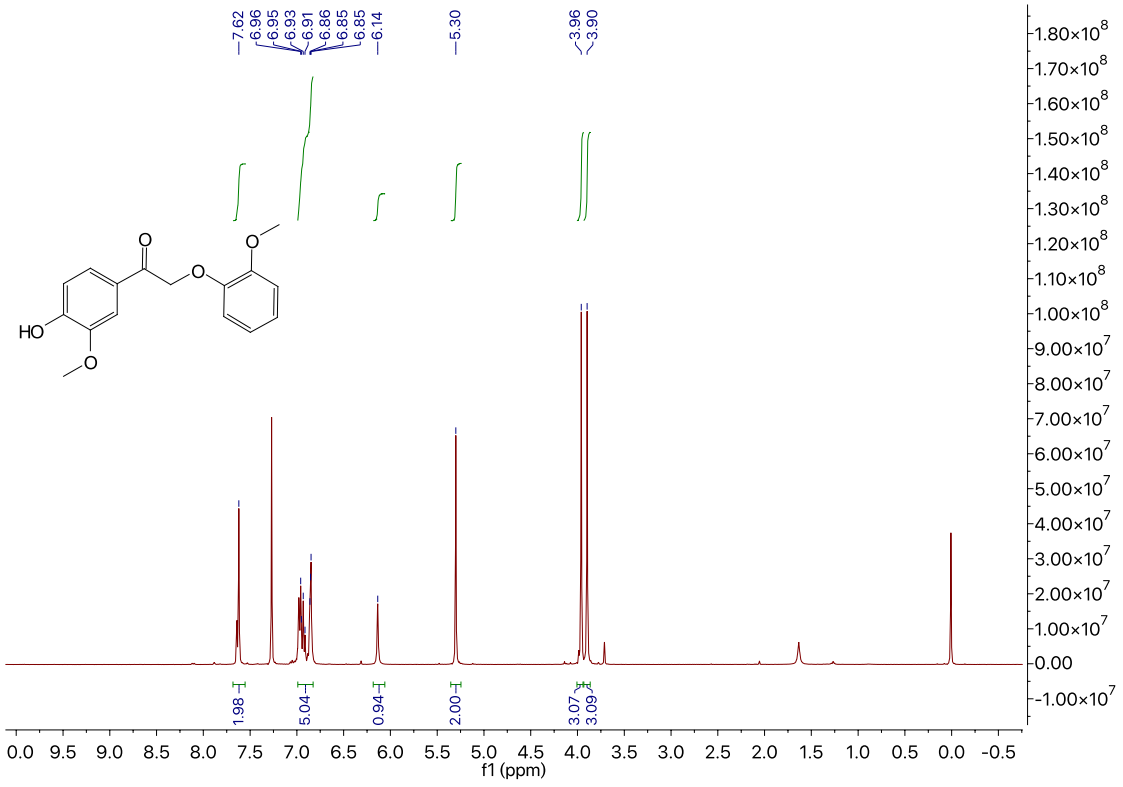


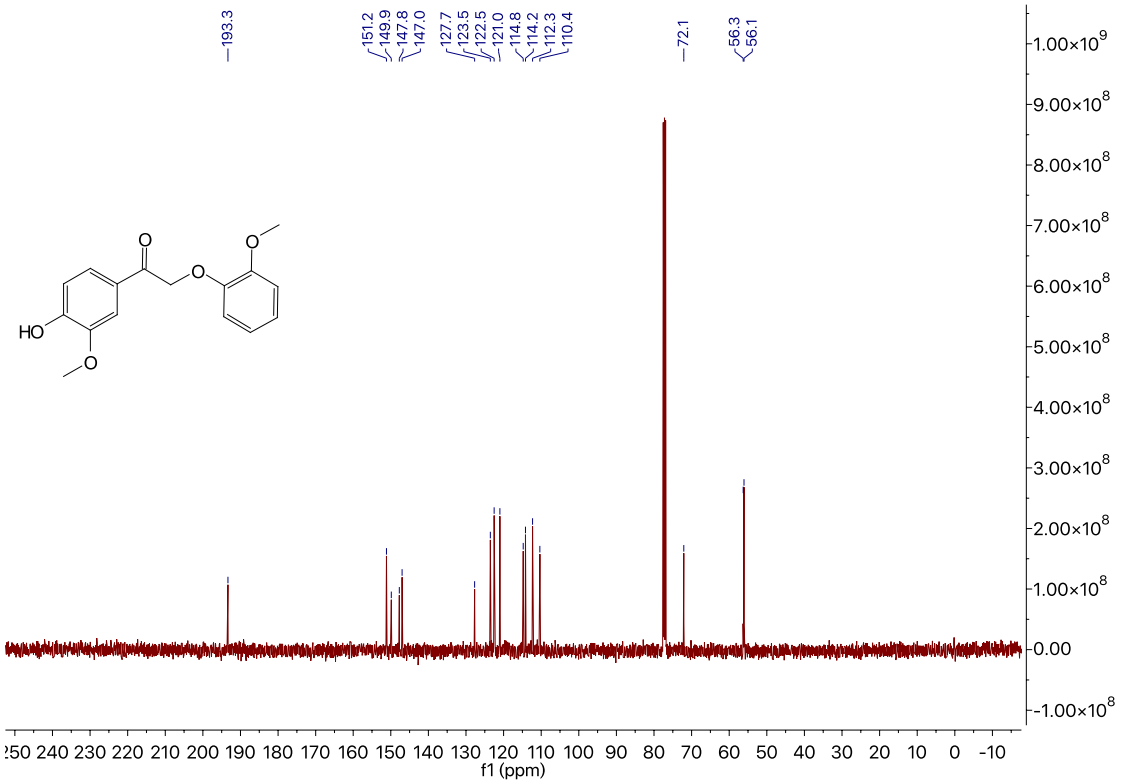
1-(3,4-Dimethoxyphenyl)-3-hydroxy-2-(2,6-dimethoxyphenoxy)propanone (2i)



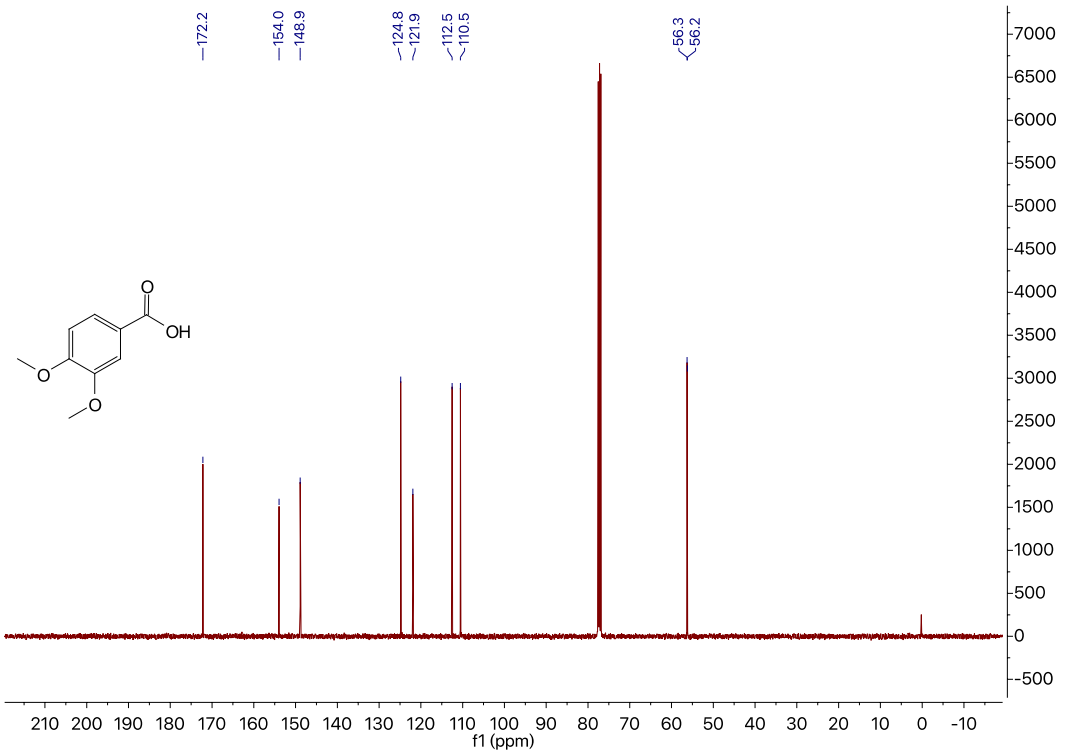


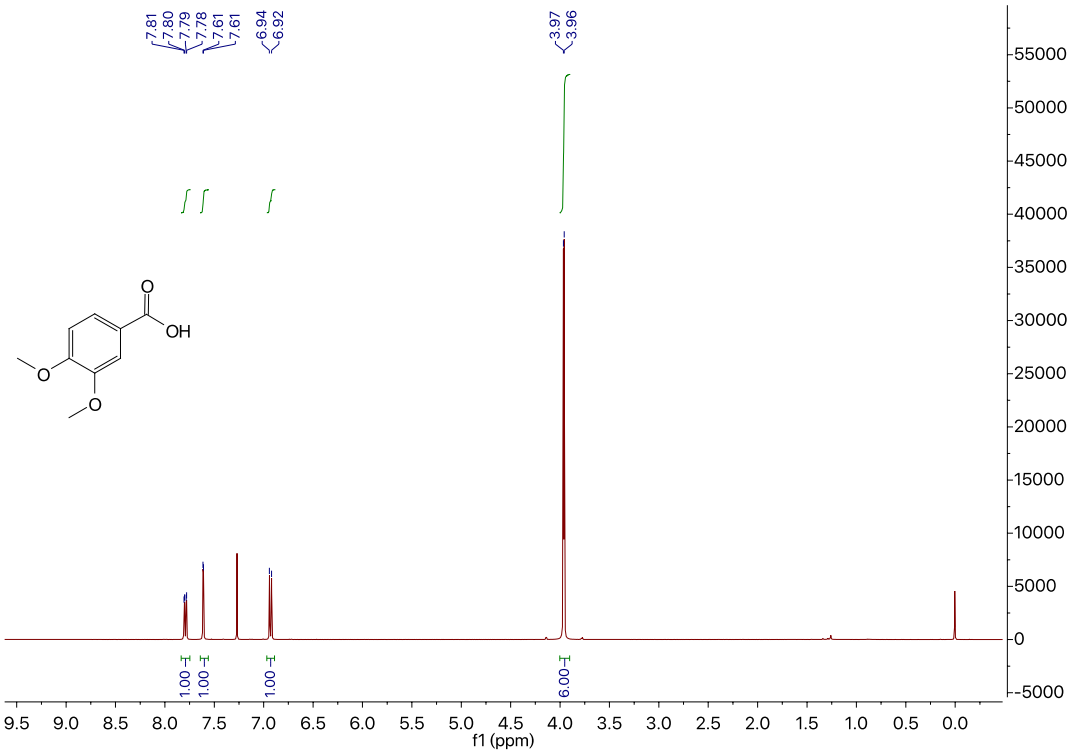
1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)ethenone (2j)



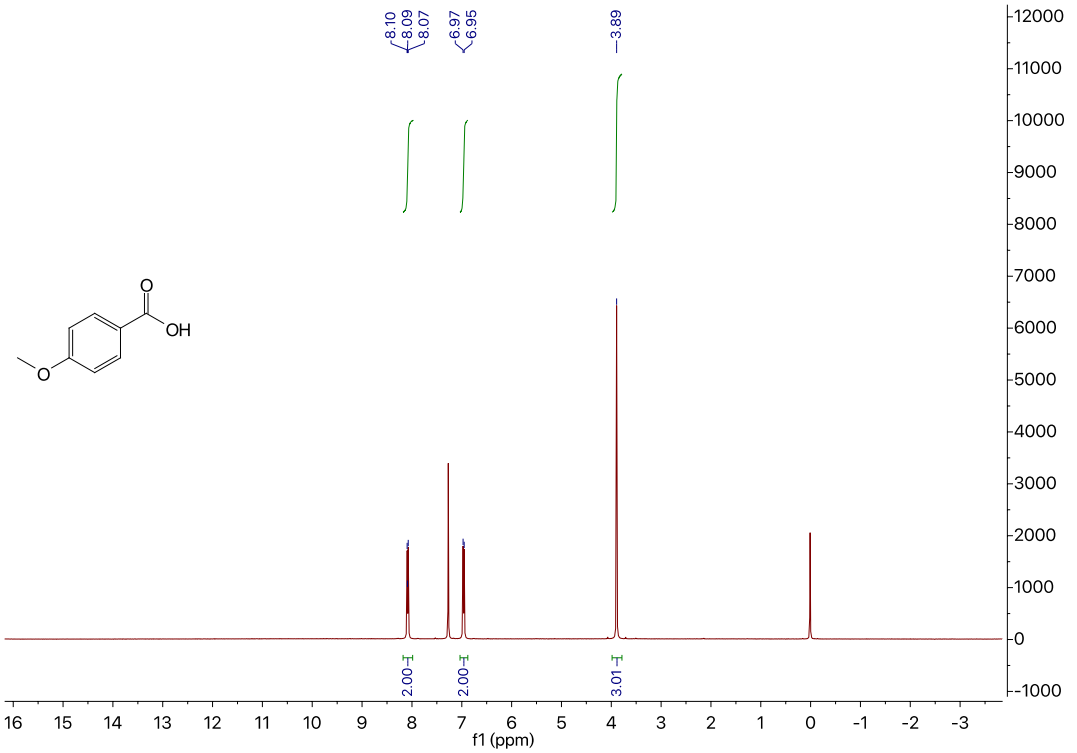


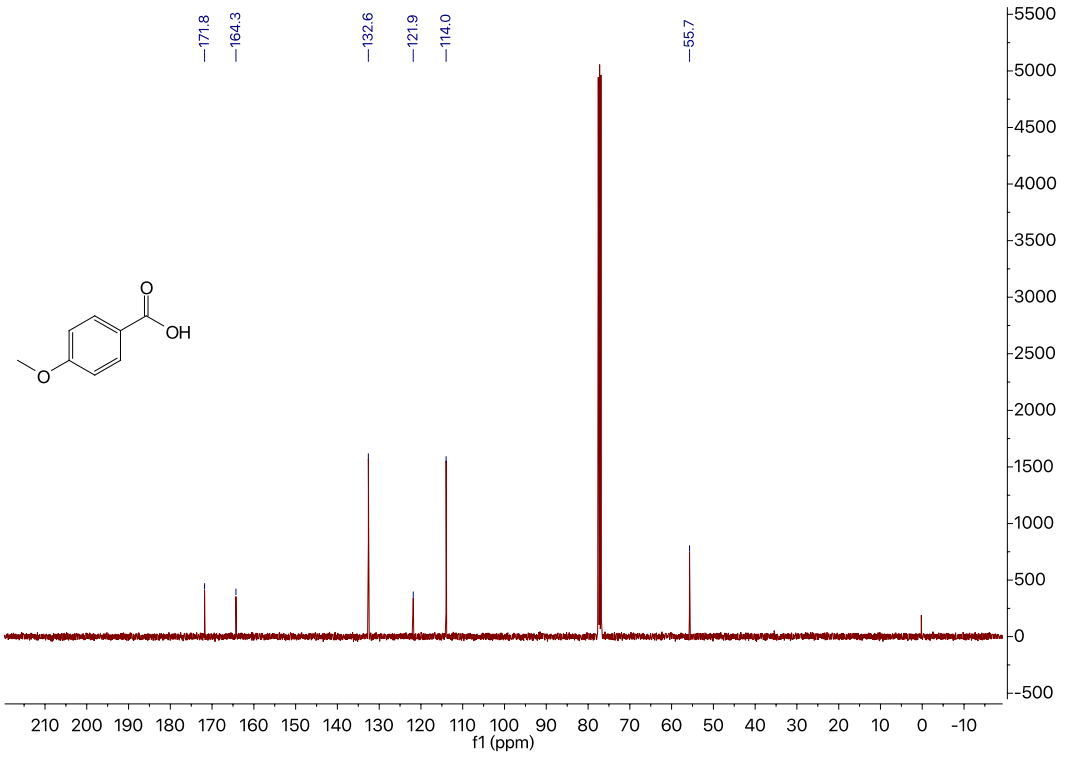
3,4-Dimethoxybenzoic acid



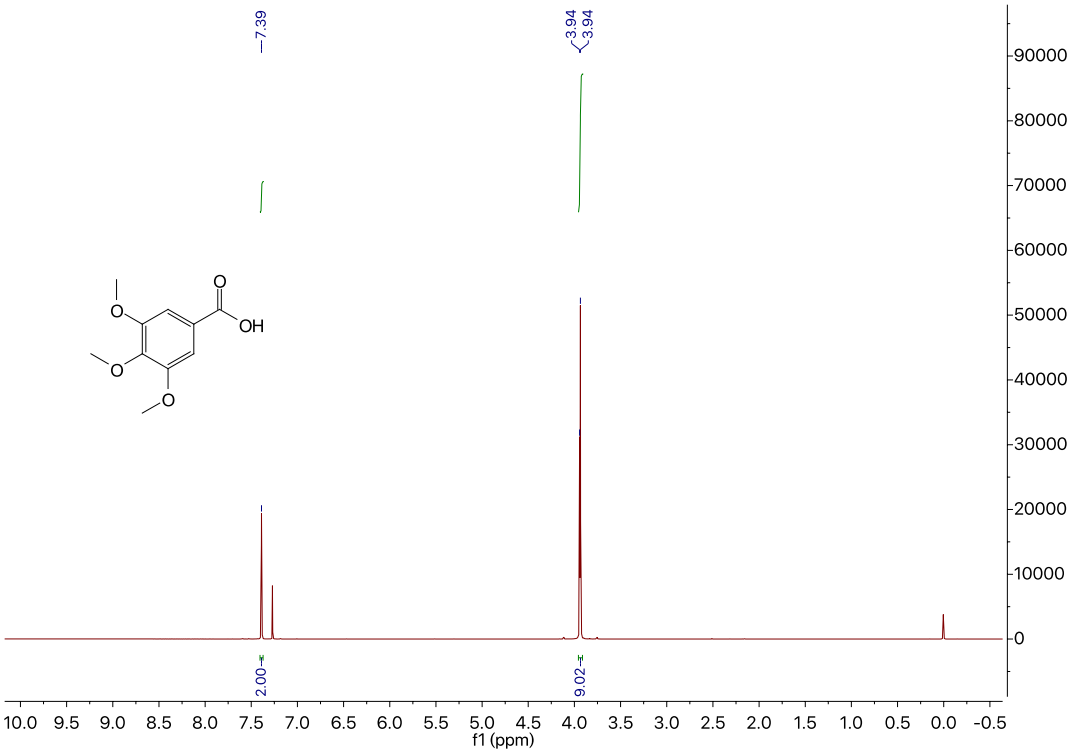


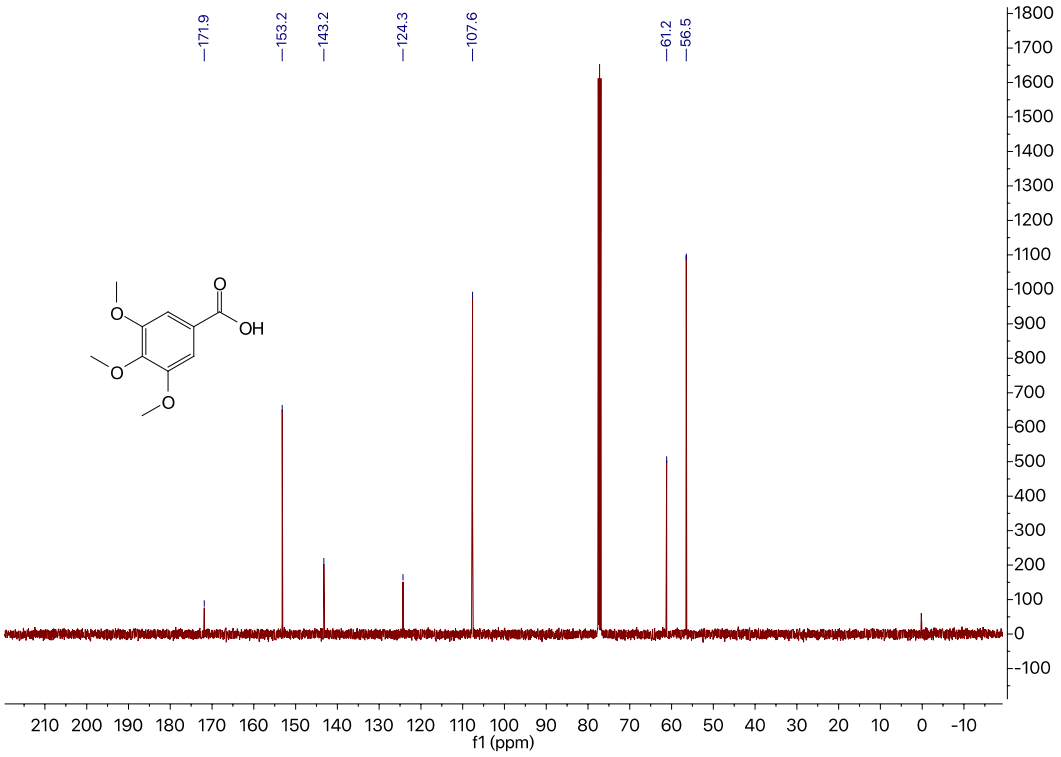
4-Methoxybenzoic acid



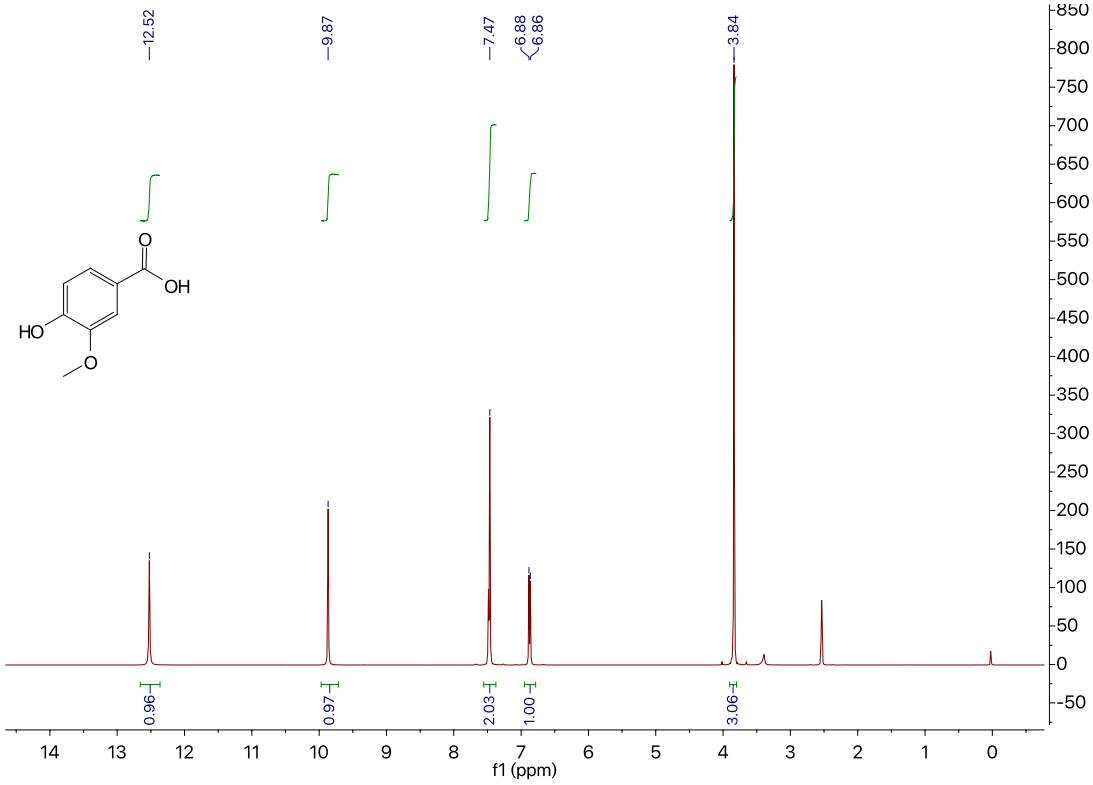


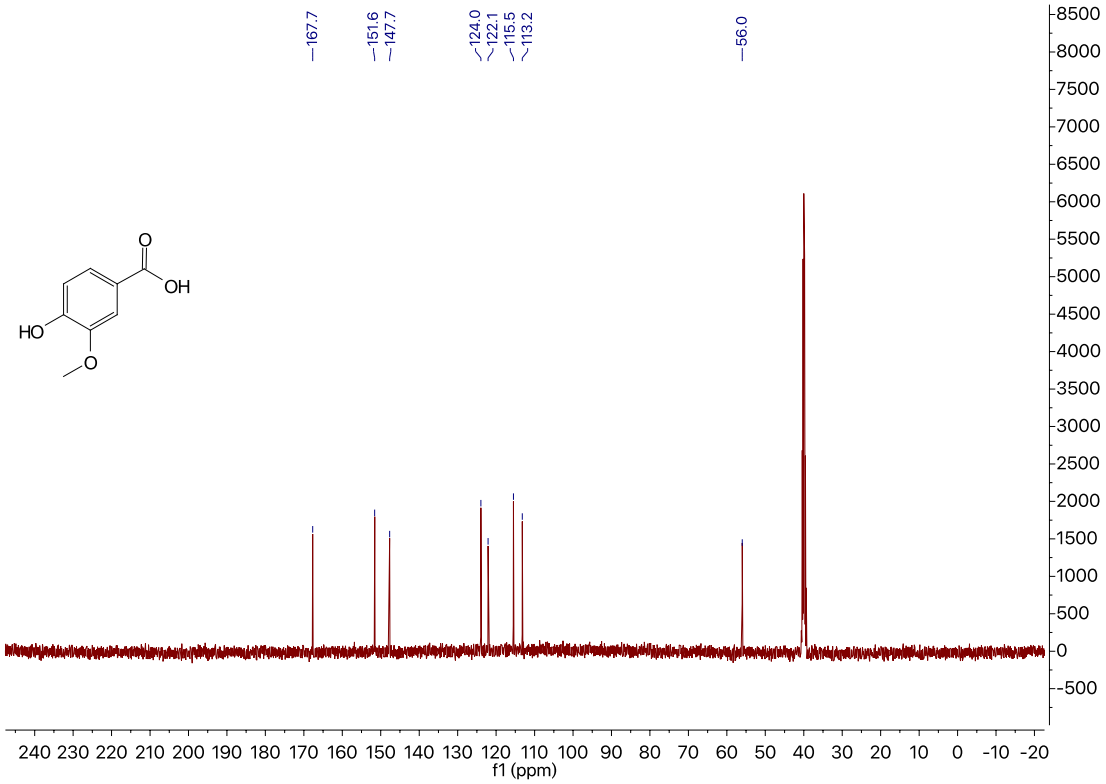
3,4,5-Trimethoxybenzoic acid



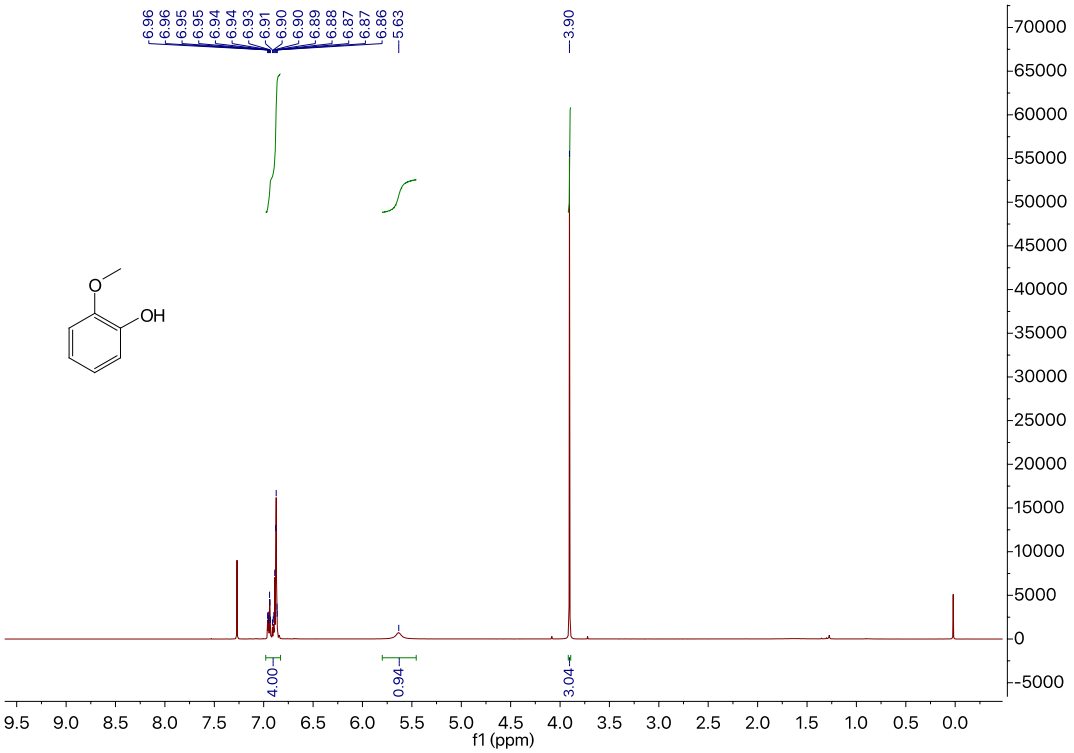


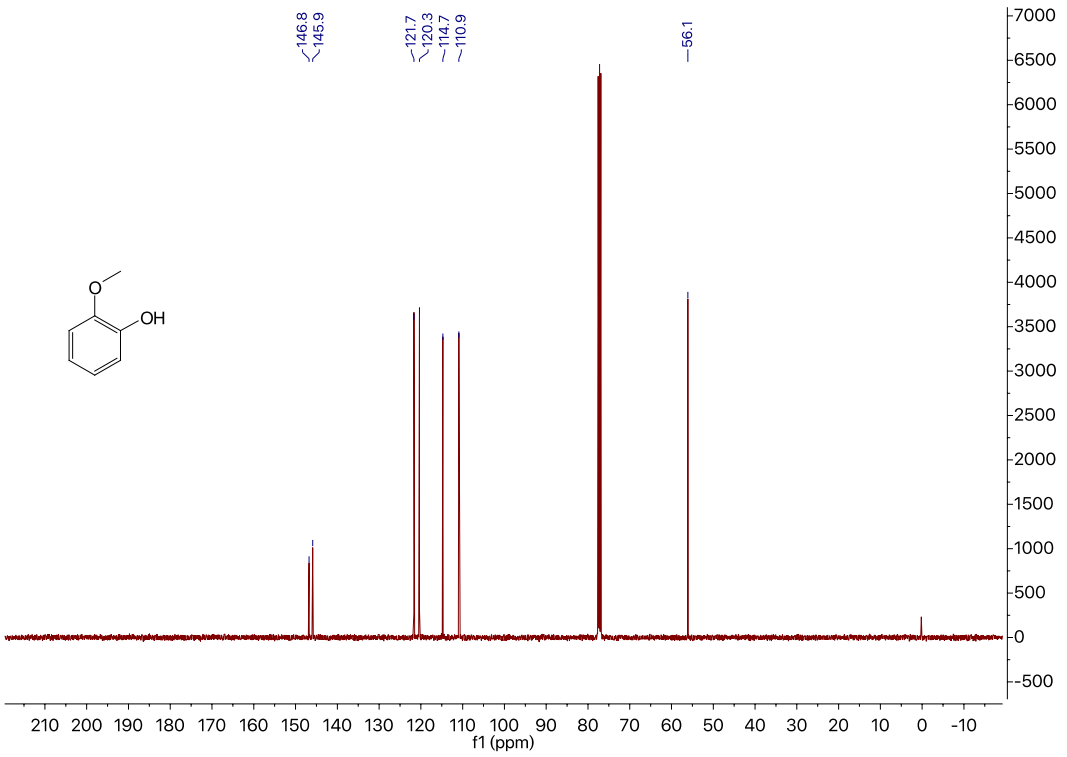
Vanillic acid



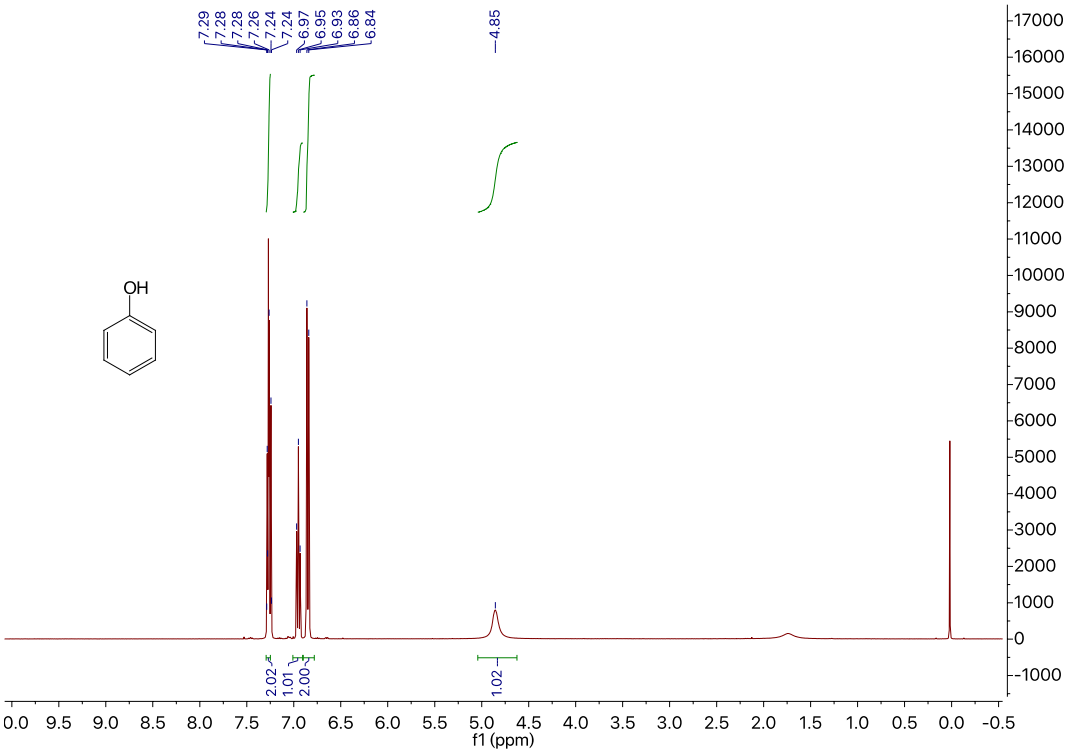

167.7
151.6
147.7
124.0
122.1
115.5
113.2
56.0
O
OH
HO
O
f1 (ppm)

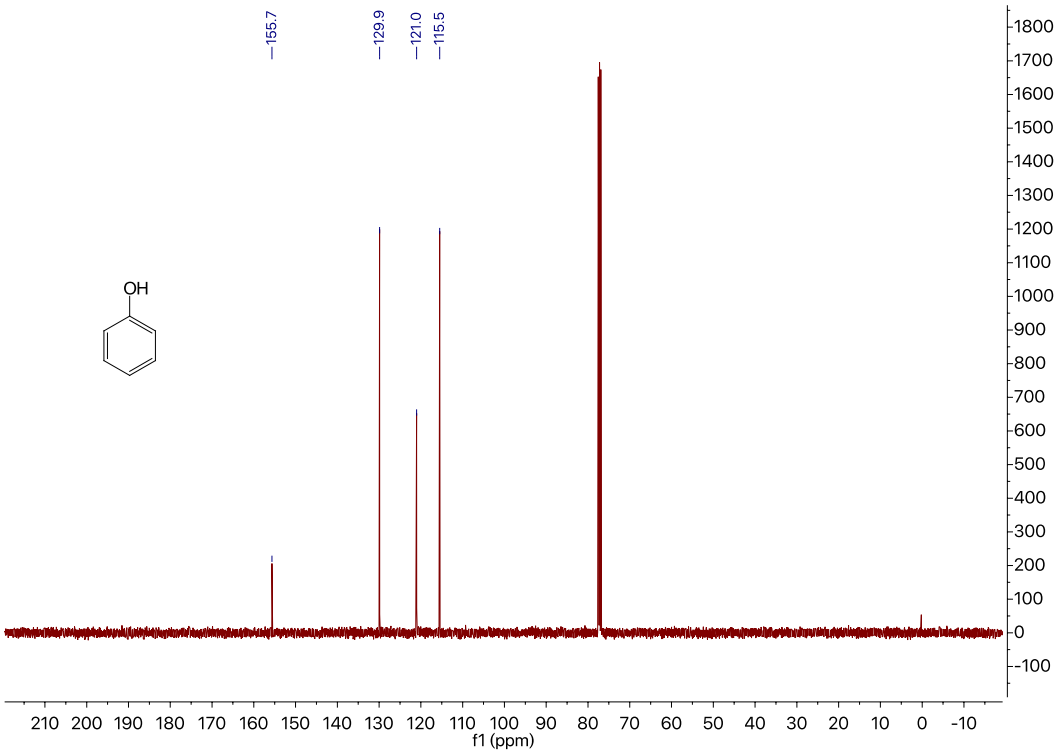
Guaiacol


6.96
6.96
6.95
6.95
6.94
6.94
6.93
6.91
6.90
6.90
6.89
6.88
6.87
6.87
6.86
5.63
3.90
O
OH
4.00
0.94
3.04
f1 (ppm)

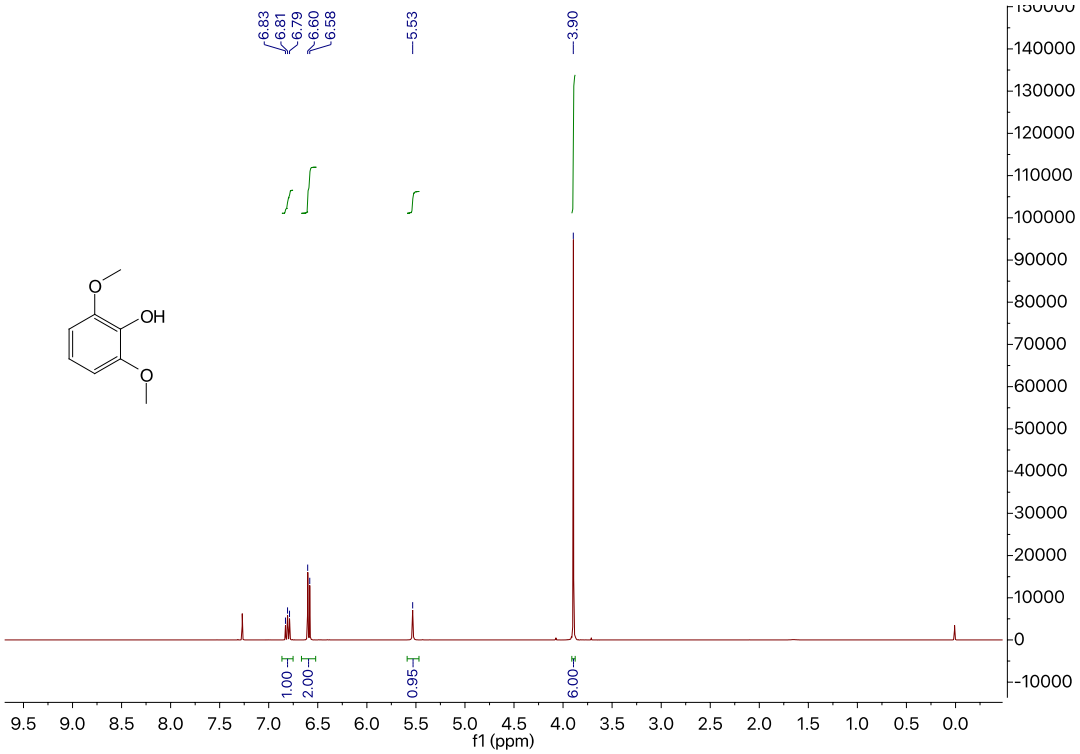

146.8
145.9
121.7
120.3
114.7
110.9
56.1
O
OH
f1 (ppm)

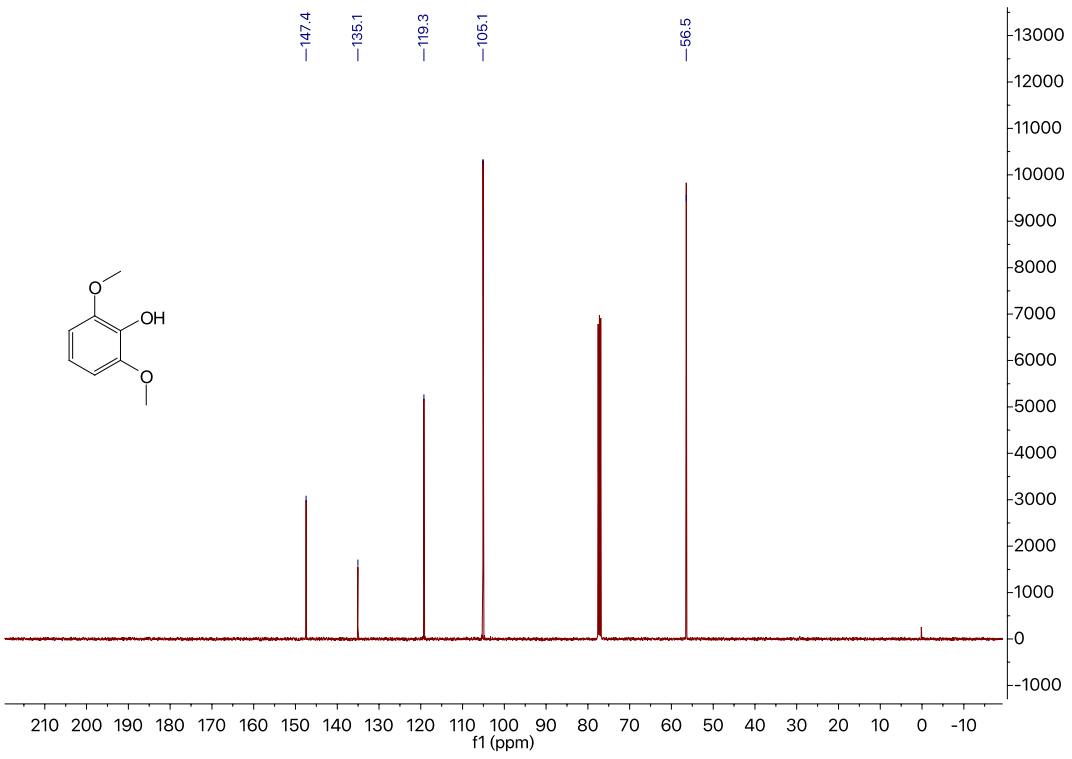
Phenol


7.29
7.28
7.28
7.26
7.24
7.24
6.97
6.95
6.93
6.86
6.84
4.85
OH
2.02
1.01
2.00
1.02
f1 (ppm)



2,6-Dimethoxyphenol





13. References

(1) Zhang, C.; Li, H.; Lu, J.; Zhang, X.; MacArthur, K. E.; Heggen, M.; Wang, F. Promoting Lignin Depolymerization and Restraining the Condensation via an Oxidation-Hydrogenation Strategy. *ACS Catal.* 2017, **7**, 3419-3429.

(2) Luo, J.; Zhang, X.; Lu, J.; Zhang, J. Fine Tuning the Redox Potentials of Carbazolic Porous Organic Frameworks for Visible-Light Photoredox Catalytic Degradation of Lignin *β*-O-4 Models. *ACS Catal.* 2017, **7**, 5062-5070.

(3) Luo, H.; Wang, L.; Li, G.; Shang, S.; Lv, Y.; Niu, J. Nitrogen-Doped Carbon-Modified Cobalt-Nanoparticle-Catalyzed Oxidative Cleavage of Lignin *β*-O-4 Model Compounds under Mild Conditions. *ACS Sustainable Chem. Eng.* 2018, **6**, 14188-14196.

(4) Lancefield, C. S.; Ojo, O. S.; Tran, F.; Westwood, N. J. Isolation of Functionalized Phenolic Monomers through Selective Oxidation and C-O Bond Cleavage of the *β*-O-4 Linkages in Lignin. *Angew. Chem., Int. Ed.* 2015, **54**, 258-262.

(5) H. Guo, D. M. Miles-Barrett, A. R. Neal, T. Zhang, C. Li and N. J. Westwood, *Chem. Sci.*, 2018, **9**, 702-711.