Electronic Supplementary Material (ESI) for Green Chemistry.


# SUPPORTING INFORMATION

## Oxidative cleavage of C–C double bond in cinnamic acids with hydrogen peroxide catalysed by vanadium(V) oxide

**Monika Horvat, Jernej Iskra***

*Faculty of Chemistry and Chemical Technology, University of Ljubljana*

*Večna pot 113, 1000 Ljubljana*

*Slovenia*

**corresponding author: Jernej.iskra@fkkt.uni-lj.si*

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## 1. GENERAL INFORMATION

All chemicals and reagents were obtained from commercial suppliers (Sigma-Aldrich, Fluorochem) and used as received without further purification. The TLC was performed on Merck-60-F254 plates using mixtures of EtOAc/heptane (2/1). The crude products were purified by column chromatography on silica gel (63-200 µm, 70-230 mesh ASTM; Fluka). The products were characterized by $^{1}H$ and $^{13}C$ NMR spectra, IR spectroscopy and HRMS. $^{1}H$ and $^{13}C$ spectra were recorded on Bruker Avance III 500 instruments using TMS as the internal standard. IR spectra were measured on a Perkin Elmer 2000 Fourier transform infrared spectroscope. HRMS data were recorded with Agilent 6224 Accurate Mass TOF LC/MS System. FTIR: The spectra were recorded with ReactIR$^{TM}$ 45 instrument with a resolution of 4 $cm^{-1}$, averaging 128 scans. An EasyMax 102 controller was used to control reaction conditions during reaction. The instruments were controlled by iControl EasyMax 4.2 and iC IR 4.2 software.

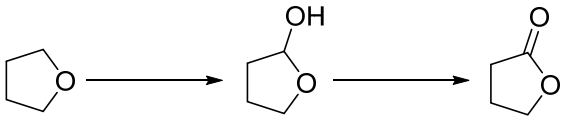
**Caution.** Although we have encountered no difficulties in working with hydrogen peroxide, routine precautions (shields, fume hoods, avoidance of transition metal salts) should be followed whenever possible, as hydrogen peroxide is a potentially hazardous compound. After the reaction is complete, the excess amount of $H_2O_2$ is removed by adding manganese dioxide to catalyze the decomposition.

## 2. EXPERIMENTAL

### 2.1. Effect of storage of hydrogen peroxide on conversion

During the research work, we found that conversion depends on the condition of storage of hydrogen peroxide. At one point, $H_2O_2$ from the same bottle failed to produce the same results. Using freshly bought $H_2O_2$ gave comparable results again. We found that purging used hydrogen peroxide with argon gave the same results and chemical conversions regardless of the type of package used. we anticipated that build-up of concentration of oxygen due to the decomposition of $H_2O_2$ acts inhibitory on the reaction conversion.

## 2.2. Oxidation of solvent tetrahydrofuran during the conversion of ferulic acid to vanillin




***Scheme S2.1.*** *Oxidation of tetrahydrofuran.*

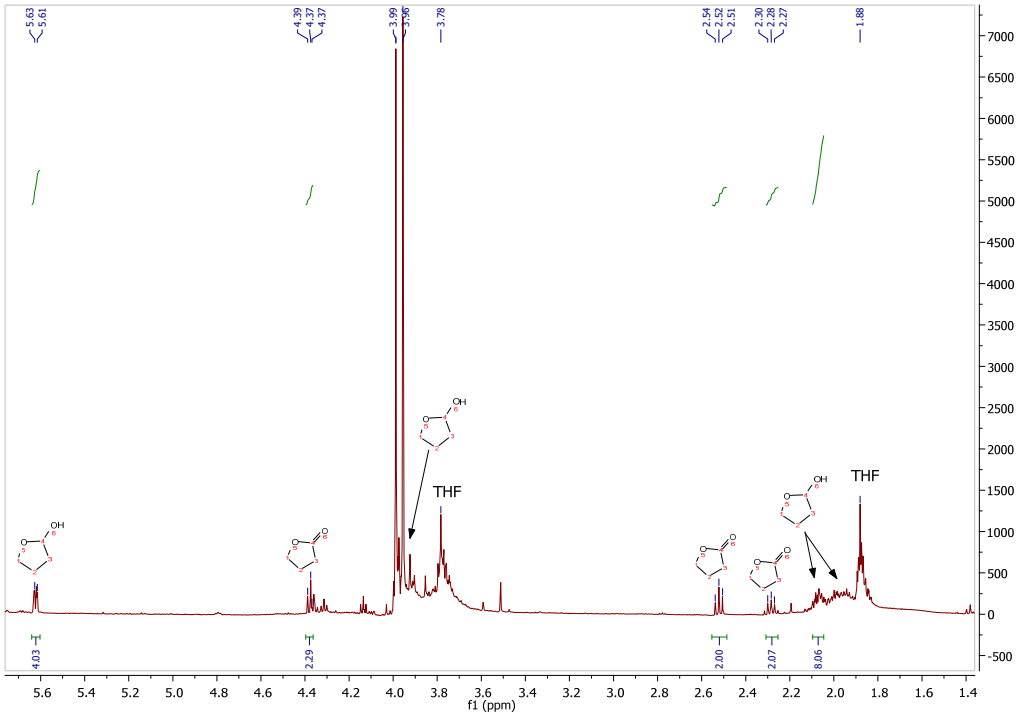



***Figure S2.1.*** *Oxidation of tetrahydrofuran to 2-hydroxytetrahydrofuran and γ-butyrolactone during reaction of* ***1a*** *(Table 2, entry 12).*

2-hydroxytetrahydrofuran: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 5.63–5.61 (m, 1H), 3.80–3.76 (m, 2H), 2.10–1.91 (m, 4H).[1]

*γ*-butyrolactone: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 4.39–4.36 (m, 1H), 2.54–2.51 (m, 1H), 2.30–2.27 (m, 1H).[2]

## 2.3. ATR-IR spectra from the oxidative degradation of C-C double bond of 1a in DME

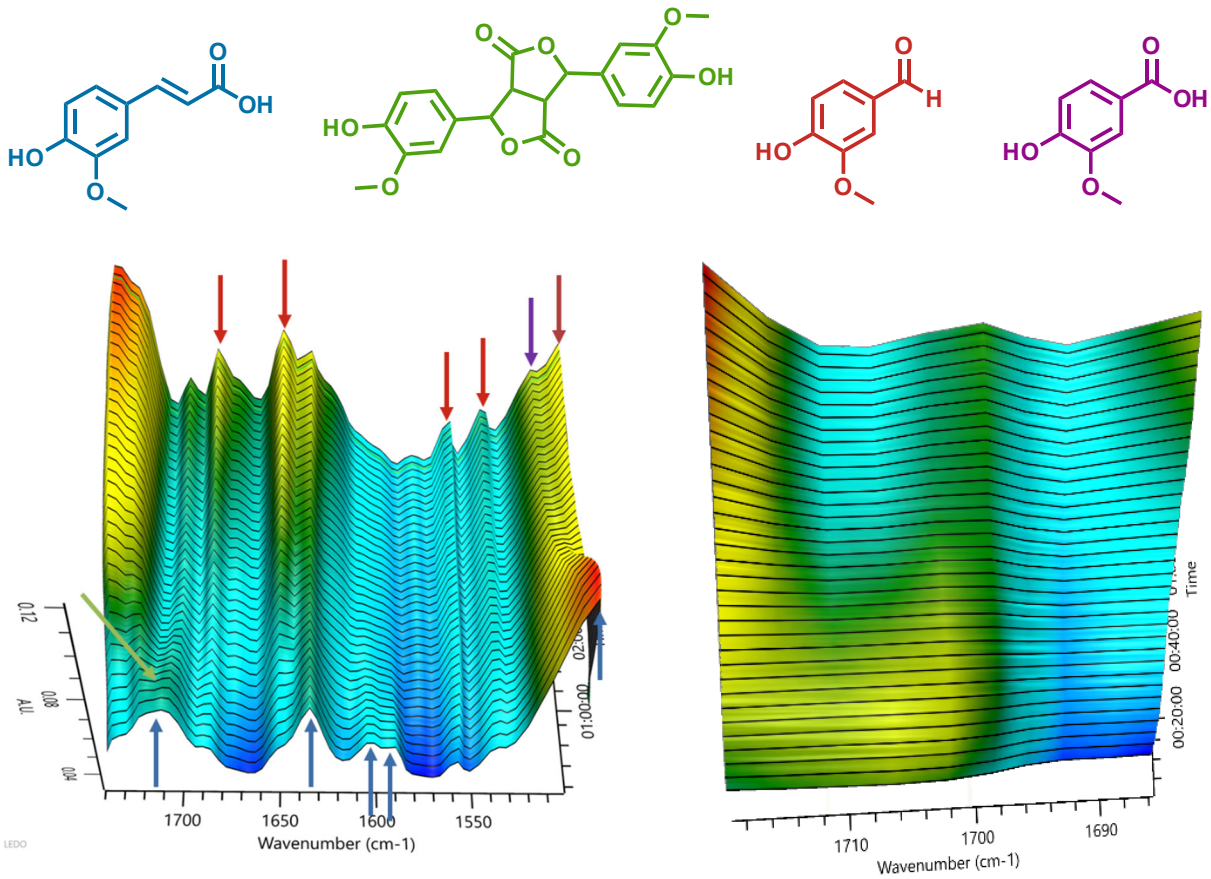



***Figure S2.2.*** *ATR-IR of the reaction of ferulic acid **1a** in DME as solvent. Reaction conditions: **1a** (6.2 mmol), 100% $H_2O_2$ (30.0 mmol), $V_2O_5$ (0.3 mmol), DME (25 mL), rt. **1a** – 1717 $cm^{-1}$, 1638 $cm^{-1}$, 1607 $cm^{-1}$, 1592 $cm^{-1}$, 1518 $cm^{-1}$; **1a´** – 1704 $cm^{-1}$; **2a** – 1693 $cm^{-1}$, 1652 $cm^{-1}$, 1559 $cm^{-1}$, 1540 $cm^{-1}$, 1514 $cm^{-1}$; **3a** – 1521 $cm^{-1}$.*

## 2.4. Reaction profile for vanillin formation in DME with 100% $H_2O_2$

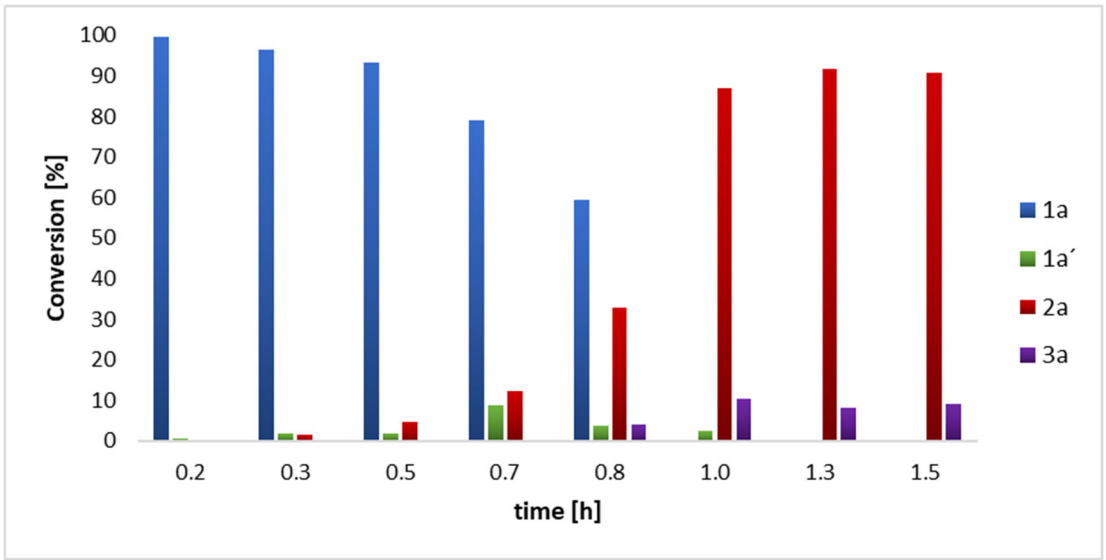



***Figure S2.3.*** *Reaction profile of conversion of ferulic acid **1a** to vanillin **2a** in DME with 100% $H_2O_2$ and $V_2O_5$ catalyst. Reaction conditions: **1a** (6.2 mmol), 100% $H_2O_2$ (30.0 mmol), $V_2O_5$ (0.3 mmol), DME (25 mL), rt.*

## 2.5. ATR-IR spectra from the oxidative degradation of C-C double bond of ferulic acid in TFE

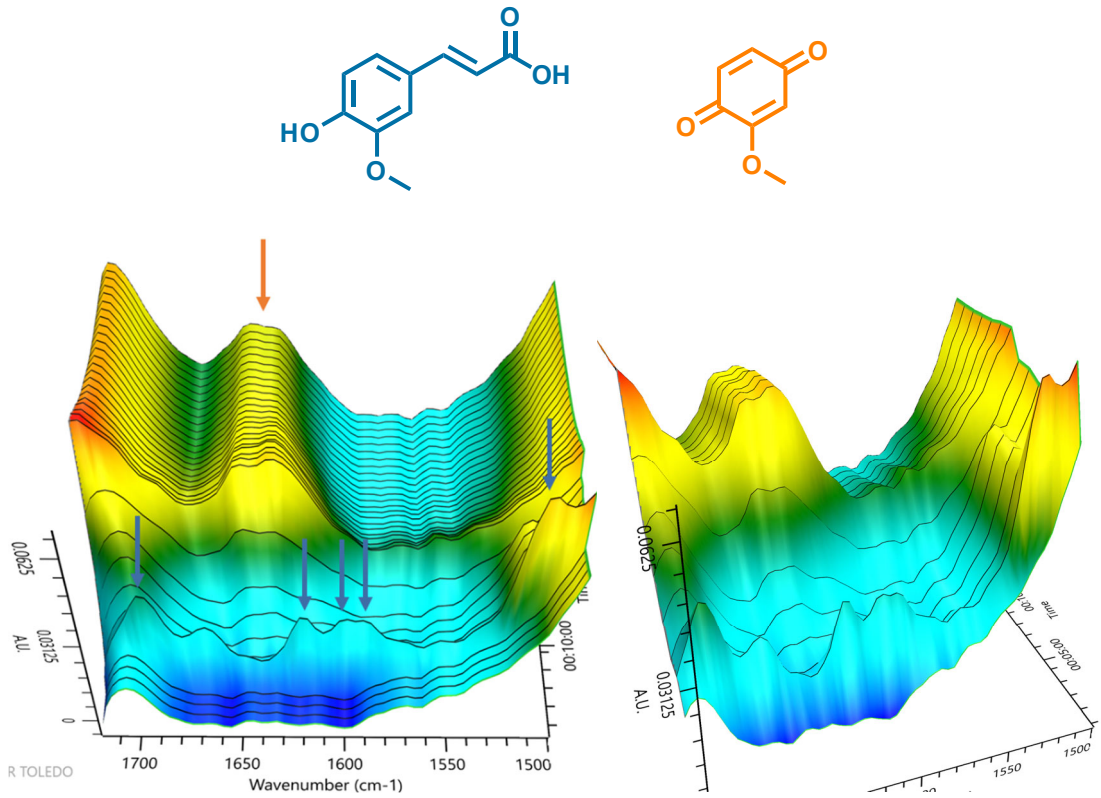



***Figure S2.4.*** *ATR-IR spectra of ferulic acid* ***1a*** *to in TFE as solvent.* ***1a*** *– 1717 cm$^{-1}$, 1638 cm$^{-1}$, 1607 cm$^{-1}$, 1592 cm$^{-1}$, 1518 cm$^{-1}$;* ***4a*** *– 1645 cm$^{-1}$.*

## 2.6. Presentation of green chemistry metric by pentagram

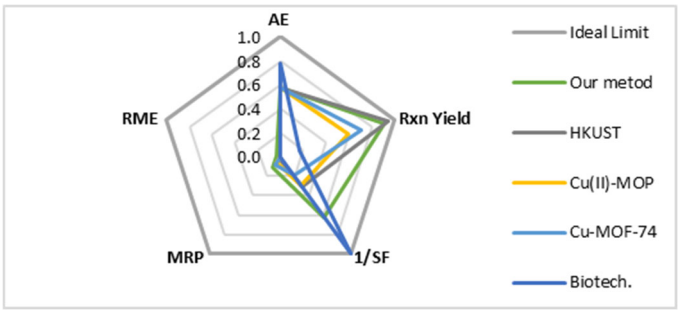



**Figure S2.5.** *Pentagram representation of the green metrics for 1a to 2a conversion (AE (atom economy), SF (stoichiometric factor), MRP (materials recovery parameter), RME (reaction mass efficiency)).*

### 2.7. The influence of the reaction conditions on the oxidation of ferulic acid

In a 5 mL volumetric flask, ferulic acid **1a** (0.1 mmol, 19.4 mg) and catalyst (0.05 – 0.1 equiv.) were added to a 1 mL solution of the solvent. The 30%$_{aq}$ $H_2O_2$ (2 – 10 equiv.) was first purged with argon and added to a reaction mixture. The mixture was stirred for 15 min to 24 h at room or reflux temperature. When the reaction was complete, the reaction mixture was extracted with EtOAC (2×3 mL). The organic layer was dried over anhydrous $Na_2SO_4$ and evaporated in vacuo. The product was analysed by NMR spectroscopy. The results are shown in *Tables 1, 2, 3, 4 and Figure 1.*

### 2.8. The influence of the reaction conditions on the oxidation cinnamic acid

In a 5 mL volumetric flask, cinnamic acid **1g** (0.1 mmol, 14.8 mg) and catalyst (0.005-0.3 equiv.) were added in a 1 mL solution of the MeCN. The 30%$_{aq}$ $H_2O_2$ (5 – 30 equiv.) was first purged with argon and slowly added to a reaction mixture. The mixture was stirred for 24 h at room temperature. When the reaction was complete, the reaction mixture was extracted with EtOAC (2×3 mL). The organic layer was dried over anhydrous $Na_2SO_4$ and evaporated in vacuo. The product was analysed by $^1$H NMR spectroscopy. The results are presented in *Figure 3.*

### 2.9. In situ ATR-IR

Preparation of 100% $H_2O_2$: The 100% hydrogen peroxide was prepared by azeotropic evaporation of water from a solution of 30% aqueous solution of $H_2O_2$ (30 mmol) and acetonitrile (2×75 mL).[3] To the concentrated $H_2O_2$, 25 mL of the solvent DME or TFE was immediately added because 100% $H_2O_2$ is a hazardous chemical.

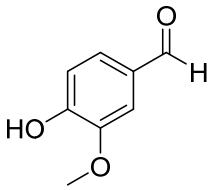
In DME: In a 100 mL glass reactor, previously prepared 100% $H_2O_2$ (30.0 mmol) in DME (25 mL) and $V_2O_5$ (0.3 mmol, 54 mg) were added. Ferulic acid **1a** (6.2 mmol, 1.2 g) was slowly added to the reaction mixture at 22 °C. The reaction was followed by in situ ATR-IR spectroscopy. The results are shown in *Figure 2*, *SI Figure S2.2* and *SI Figure S2.3.*

In TFE: In a 100 mL glass reactor, previously prepared 100% $H_2O_2$ (30.0 mmol) in TFE (25 mL) and $V_2O_5$ (0.3 mmol, 54 mg) were added. Ferulic acid **1a** (6.2 mmol, 1.2 g) was slowly added to the reaction mixture at 22 °C. The reaction was followed by in situ ATR-IR spectroscopy. The results are shown in *SI Figure S2.4.*

### 2.10. General procedure for aldehyde synthesis

In a 10 mL volumetric flask, substrate **1** (0.5 mmol) and $V_2O_5$ catalyst (0.05 equiv.) were added in a 5 mL solution of solvent DME. The 30%$_{aq}$ hydrogen peroxide (7 equiv.) was first purged with argon and slowly added to a reaction mixture in three portions. The mixture was stirred at room temperature and monitored with TLC. After completion of the reaction the reaction mixture was extracted with EtOAc (2×5 mL). The organic layer was evaporated under vacuum. The crude reaction was subjected to column chromatography with mobile phase EtOAc/heptane (2/1). The solvent was evaporated in vacuo to provide the product.

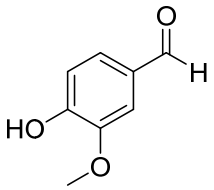
**4-hydroxy-3-methoxybenzaldehyde/vanillin**[4] (**2a**)




Prepared according to *general procedure for aldehyde synthesis*, using ferulic acid **1a** (0.5 mmol, 97.1 mg), $V_2O_5$ (0.05 equiv., 4.5 mg), DME (5 mL), 30%$_{aq}$ $H_2O_2$ (7 equiv., 360 µL), reaction time 3 h. The product **2a** (71.5 mg, 94%) was obtained as a white solid after purification by column chromatography (EtOAc/heptane (2/1)).

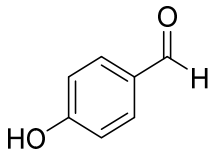
**$^1$H NMR** (500 MHz, $CDCl_3$): $\delta$ = 9.83 (s, 1H), 7.44 – 7.42 (m, 2H), 7.05 (d, $J$ = 8.5 Hz, 1H), 6.19 (s, 1H, OH) 3.97 (s, 3H) ppm. **$^{13}$C NMR** (126 MHz, $CDCl_3$): $\delta$ = 191.0, 151.8, 147.3, 130.0, 127.7, 114.5, 108.9, 56.3 ppm. **IR** (cm$^{-1}$): 3184, 2945, 2857, 1664, 1587, 1509, 1464, 1430. **HRMS** (EI): *m/z* $(M+H)^+$ calcd. for $C_8H_8O_3$ 153.0546, found 153.0546.

**4-hydroxy-3-methoxybenzaldehyde/vanillin**[4] (**2a**) from **1b**




Prepared according to *general procedure for aldehyde synthesis*, using ethyl ferulate **1b** (0.5 mmol, 111.1 mg), $V_2O_5$ (0.05 equiv., 4.5 mg), DME (5 mL), 30%$_{aq}$ $H_2O_2$ (7 equiv., 360 µL), reaction time 4 h. The product **2a** (69.2 mg, 91%) was obtained as a white solid after purification by column chromatography (EtOAc/heptane (2/1)).

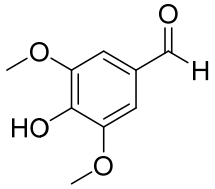
**4-hydroxybenzaldehyde**[4] (**2c**)



Prepared according to *general procedure for aldehyde synthesis*, using *p*-coumaric acid **1c** (0.5 mmol, 82.1 mg), $V_2O_5$ (0.05 equiv., 4.5 mg), DME (5 mL), 30%$_{aq}$ $H_2O_2$ (7 equiv., 360 µL), reaction time 24 h. The product **2c** (56.1 mg, 92%) was obtained as a white solid after purification by column chromatography (EtOAc/heptane (2/1)).

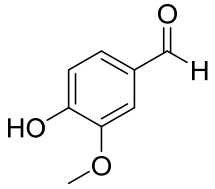
**$^1$H NMR** (500 MHz, $CDCl_3$): $\delta$ = 9.88 (s, 1H), 7.81 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H) ppm. **$^{13}$C NMR** (126 MHz, $CDCl_3$): $\delta$ = 191.0, 161.3, 132.5, 130.3, 116.1 ppm. **IR** (cm$^{-1}$): 3168, 1669, 1600, 1518, 1454, 1386. **HRMS** (EI): *m/z* $(M+H)^+$ calcd. for $C_7H_6O_2$ 123.0441, found 123.0442.

**4-hydroxy-3,5-dimethoxybenzaldehyde** (2d)



Prepared according to *general procedure for aldehyde synthesis*, using sinapic acid **1d** (0.5 mmol, 112.1 mg), $V_2O_5$ (0.05 equiv., 4.5 mg), DME (5 mL), 30%$_{aq}$ $H_2O_2$ (7 equiv., 360 µL), reaction time 24 h. The percentage yield of product **2d** (15%) was determined by $^1$H NMR spectroscopy, using 1,3,5-trimethoxybenzene as an internal standard. $^1$H NMR data is in agreement with literature[5].

**4-hydroxy-3-methoxybenzaldehyde/vanillin**[4] (**2a**) from **1e**

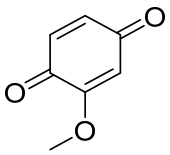


Prepared according to *general procedure for aldehyde synthesis*, using 2-Methoxy-4-vinylphenol **1e** (0.5 mmol, 75.1 mg), $V_2O_5$ (0.05 equiv., 4.5 mg), DME (5 mL), 30%$_{aq}$ $H_2O_2$ (30%, 7 equiv., 360 µL), reaction time 2 h. The product **2a** (64.7 mg, 85%) was obtained as a white solid after purification by column chromatography (EtOAc/heptane (2/1)).

### 2.11. General procedure for benzoquinone synthesis

In a 5 mL volumetric flask, substrate **1** (0.2 mmol) and $V_2O_5$ catalyst (0.05 equiv.) were added in a 2 mL solution of solvent TFE (2,2,2-trifluoroethanol). The 30%$_{aq}$ $H_2O_2$ (7 equiv.) was first purged with argon and slowly added to a reaction mixture. The mixture was stirred at room temperature for 2 h. After completion of the reaction the reaction mixture was extracted with EtOAc (2×3 mL). The organic layer was evaporated under vacuum. The crude reaction was subjected to column chromatography with mobile phase EtOAc/heptane (2/1). The solvent was evaporated in vacuo to provide the product.

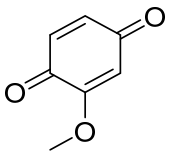
**2-methoxy-1,4-benzoquinone**[6] (**4a**)



Prepared according to *general procedure for benzoquinone synthesis*, using ferulic acid **1a** (0.2 mmol, 38.8 mg), $V_2O_5$ (0.05 equiv., 2 mg), TFE (2 mL), 30%$_{aq}$ $H_2O_2$ (7 equiv., 144 µL), reaction time 2 h. The product **4a** (23.3 mg, 84%) was obtained as a white solid after purification by column chromatography (EtOAc/heptane (2/1)).

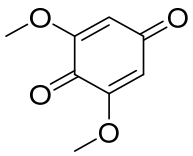
**$^1$H NMR** (500 MHz, $CDCl_3$): $\delta$ = 6.72 (s, 2H), 5.95 (s, 1H), 3.84 (s, 3H) ppm. **$^{13}$C NMR** (126 MHz, $CDCl_3$): $\delta$ = 187.6, 181.9, 158.8, 137.4, 134.6, 107.9, 56.4 ppm. **IR** ($cm^{-1}$): 2970, 2924, 1739, 1699, 1588, 1554, 1476, 1417. **HRMS** (EI): *m/z* $(M+H)^+$ calcd. for $C_7H_6O_3$ 139.0390, found 139.0393.

**2-methoxy-1,4-benzoquinone**[6] (**4a**) from **1b**



Prepared according to *general procedure for benzoquinone synthesis*, using ethyl ferulate **1b** (0.2 mmol, 44.4 mg), $V_2O_5$ (0.05 equiv., 2 mg), TFE (2 mL), 30%$_{aq}$ $H_2O_2$ (7 equiv., 144 µL), reaction time 2 h. The product **4a** (24.2 mg, 88%) was obtained as a white solid after purification by column chromatography (EtOAc/heptane (2/1)).

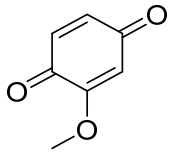
**2,6-dimethoxy-1,4-benzoquinone**[6] (**4d**)



Prepared according to *general procedure for benzoquinone synthesis*, using sinapic acid **1d** (0.2 mmol, 44.8 mg), $V_2O_5$ (0.05 equiv., 2 mg), TFE (2 mL), 30%$_{aq}$ $H_2O_2$ (7 equiv., 144 µL), reaction time 2 h. The product **4d** (30.6 mg, 91%) was obtained as a white solid after purification by column chromatography (EtOAc/heptane (2/1)).

**$^1$H NMR** (500 MHz, $CDCl_3$): $\delta$ = 5.86 (s, 2H), 3.82 (s, 6H) ppm. **$^{13}$C NMR** (126 MHz, $CDCl_3$): $\delta$ = 186.8, 176.5, 157.6, 107.2, 56.6 ppm. **IR** ($cm^{-1}$): 2844, 1716, 1665, 1644, 1597.

**2-methoxy-1,4-benzoquinone**[6] (**4a**) from **1e**



Prepared according to *general procedure for benzoquinone synthesis*, using 2-Methoxy-4-vinylphenol **1e** (0.2 mmol, 30.0 mg), $V_2O_5$ (0.05 equiv., 2 mg), TFE (2 mL), 30%$_{aq}$ $H_2O_2$ (7 equiv., 144 µL), reaction time 2 h. The product **4a** (21.7 mg, 79%) was obtained as a white solid after purification by column chromatography (EtOAc/heptane (2/1)).

## 2.12. General procedure for aromatic benzoic acid synthesis

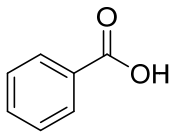
**Conditions A**

In a 10 mL volumetric flask, substrate **1** (0.5 mmol) and $V_2O_5$ catalyst (0.01 equiv.) were added in a 5 mL solution of solvent MeCN. The 30%$_{aq}$ $H_2O_2$ (28 equiv.) was first purged with argon and slowly added to a reaction mixture in three portions. The mixture was stirred for 24 h at room temperature. After completion of the reaction, the reaction mixture was extracted with EtOAc (2×5 mL). The organic layer was dried over anhydrous $Na_2SO_4$ and evaporated under vacuum. The crude reaction was subjected to column chromatography with mobile phase EtOAc/heptane (2/1). The solvent was evaporated in vacuo to provide the product.

**Conditions B**

In a 10 mL volumetric flask, substrate **1** (0.5 mmol) and $V_2O_5$ catalyst (0.01 equiv.) were added in a 5 mL solution of solvent mixture of MeCN/TFA (1/1). The 30%$_{aq}$ $H_2O_2$ (40 equiv.) was first purged with argon and slowly added to a reaction mixture in three portions. The mixture was stirred for 24 h at room temperature. After completion of the reaction, the reaction mixture was extracted with EtOAc (2×5 mL). The organic layer was dried over anhydrous $Na_2SO_4$ and evaporated under vacuum. The crude reaction was subjected to column chromatography with mobile phase EtOAc/heptane (2/1). The solvent was evaporated in vacuo to provide the product.

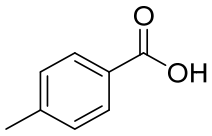
**Benzoic acid**[7] (**3f**)




Prepared according to *General procedure for aromatic benzoic acid synthesis (conditions **A**)*, using cinnamic acid **1f** (0.5 mmol, 74 mg), $V_2O_5$ (0.01 equiv., 1 mg), MeCN (5 mL), 30%$_{aq}$ $H_2O_2$ (28 equiv., 1.4 mL), reaction time 24 h. The product **3f** (57.4 mg, 94%) was obtained as a colorless solid after purification by column chromatography (EtOAc/heptane (2/1)).

**$^1$H NMR** (500 MHz, $CDCl_3$): $\delta$ = 8.13 – 8.12 (m, 2H), 7.64 – 7.61 (m, 1H), 7.50 – 7.47 (m, 2H) ppm. **$^{13}$C NMR** (126 MHz, $CDCl_3$): $\delta$ = 172.3, 134.0, 130.4, 129.5, 128.6 ppm. **IR** ($cm^{-1}$): 3081, 2829, 2668, 2552, 1680, 1790. **HRMS** (EI): *m/z* $(M+H)^+$ calcd. for $C_7H_6O_2$ 123.0441, found 123.0441.

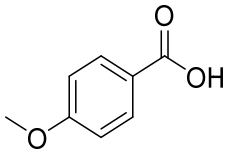
**4-methylbenzoic acid**[7] (**3g**)



Prepared according to *General procedure for aromatic benzoic acid synthesis (conditions **A**)*, using 4-methylcinnamic acid **1g** (0.5 mmol, 81 mg), $V_2O_5$ (0.01 equiv., 1 mg), MeCN (5 mL), 30%$_{aq}$ $H_2O_2$ (28 equiv., 1.4 mL), reaction time 24 h. The product **3g** (59.9 mg, 88%) was obtained as a white solid after purification by column chromatography (EtOAc/heptane (2/1)).

**$^1$H NMR** (500 MHz, $CDCl_3$): $\delta$ = 8.00 (m, 2H), 7.28 (m, 2H), 2.43 (s, 3H) ppm. **$^{13}$C NMR** (126 MHz, $CDCl_3$): $\delta$ = 171.2, 144.7, 130.4, 129.4, 126.7, 21.9 ppm. **IR** (cm$^{-1}$): 2920, 2851, 1739, 1671, 1611, 1576, 1515, 1418. **HRMS** (EI): *m/z* $(M+H)^+$ calcd. for $C_8H_8O_2$ 137.0597, found 137.0596.

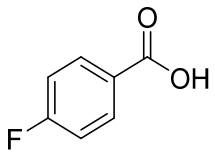
**4-methoxybenzoic acid**[8] (**3h**)



Prepared according to *General procedure for aromatic benzoic acid synthesis (conditions **A**)*, using 4-methoxycinnamic acid **1h** (0.5 mmol, 89 mg), $V_2O_5$ (0.01 equiv., 1 mg), MeCN (5 mL), 30%$_{aq}$ $H_2O_2$ (28 equiv., 1.4 mL), reaction time 24 h. The product **3h** (69.2 mg, 91%) was obtained as a white solid after purification by column chromatography (EtOAc/heptane (2/1)).

**$^1$H NMR** (500 MHz, $CDCl_3$): $\delta$ = 8.07 (d, $J$ = 9.0 Hz, 2H), 6.95 (d, $J$ = 9.0 Hz, 2H), 3.88 (s, 3H) ppm. **$^{13}$C NMR** (126 MHz, $CDCl_3$): $\delta$ = 171.4, 164.2, 132.5, 121.8, 113.9, 55.6 ppm. **IR** (cm$^{-1}$): 2970, 1739, 1681, 1603, 1577, 1515, 1427. **HRMS** (EI): *m/z* $(M+H)^+$ calcd. for $C_8H_8O_3$ 153.0546, found 153.0544.

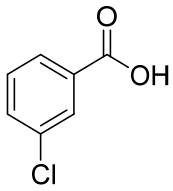
**4-fluorobenzoic acid**[7] (**3i**)




Prepared according to *General procedure for aromatic benzoic acid synthesis (conditions **A**)*, using 4-fluorocinnamic acid **1i** (0.5 mmol, 83.1 mg), $V_2O_5$ (0.01 equiv., 1 mg), MeCN (5 mL), 30%$_{aq}$ $H_2O_2$ (28 equiv., 1.4 mL), reaction time 24 h. The product **3i** (60.2 mg, 86%) was obtained after column chromatography purification (EtOAc/heptane (2/1)) as a white solid.

**$^1$H NMR** (500 MHz, $CDCl_3$): $\delta$ = 8.16 – 8.13 (m, 2H), 7.17 – 7.14 (m, 2H) ppm. **$^{13}$C NMR** (126 MHz, $CDCl_3$): $\delta$ = 171.0, 166.5 (d, $J$ = 255 Hz), 133.1 (d, $J$ = 9.5 Hz), 125.7 (d, $J$ = 2.9 Hz), 116.0 (d, $J$ = 22.1 Hz) ppm. **IR** (cm$^{-1}$): 2921, 2672, 1678, 1604, 1510, 1429. **HRMS** (EI): *m/z* $(M+H)^+$ calcd. for $C_7H_5FO_2$ 141.0346, found 141.0347.

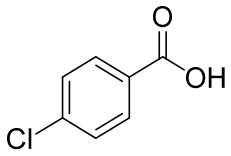
**3-chlorobenzoic acid**[9] (**3j**)




Prepared according to *General procedure for aromatic benzoic acid synthesis (conditions **A**)*, using 3-chlorocinnamic acid **1j** (0.5 mmol, 91.3 mg), $V_2O_5$ (0.01 equiv., 1 mg), MeCN (5 mL), 30%$_{aq}$ $H_2O_2$ (28 equiv., 1.4 mL), reaction time 24 h. The product **3j** (70.5 mg, 90%) was obtained as a white solid after purification by column chromatography (EtOAc/heptane (2/1)).

**$^1$H NMR** (500 MHz, $CDCl_3$): $\delta$ = 8.10 (t, $J$ = 1.8 Hz, 1H), 8.02 – 7.99 (m, 1H), 7.62 – 7.58 (m, 1H), 7.43 (t, $J$ = 7.9 Hz, 1H) ppm. **$^{13}$C NMR** (126 MHz, $CDCl_3$): $\delta$ = 170.8, 134.9, 134.1, 131.1, 130.4, 130.0, 128.5 ppm. **IR** (cm$^{-1}$): 2920, 2657, 2546, 1692, 1597, 1574, 1415. **HRMS** (EI): *m/z* $(M+H)^+$ calcd. for $C_7H_5ClO_2$ 157.0051, found 157.0050.

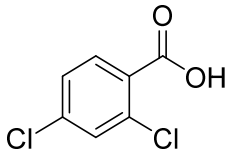
**4-chlorobenzoic acid**[7] (**3k**)



Prepared according to *General procedure for aromatic benzoic acid synthesis (conditions **B**)*, using 4-chlorocinnamic acid **1k** (0.5 mmol, 91.3 mg), $V_2O_5$ (0.01 equiv., 1 mg), MeCN/TFA 1/1 (5 mL), 30%$_{aq}$ $H_2O_2$ (40 equiv., 2 mL), reaction time 24 h. The product **3k** (68.1 mg, 87%) was obtained as a white solid after purification by column chromatography (EtOAc/heptane (2/1)).

**$^1$H NMR** (500 MHz, $CDCl_3$): $\delta$ = 8.08 – 8.00 (m, 2H), 7.50 – 7.43 (m, 2H) ppm. **$^{13}$C NMR** (126 MHz, $CDCl_3$): $\delta$ = 169.8, 140.5, 131.7, 129.1, 127.7 ppm. **IR** (cm$^{-1}$): 2970, 1739, 1686, 1593, 1427. **HRMS** (EI): *m/z* $(M+H)^+$ calcd. for $C_7H_5ClO_2$ 157.0051, found 157.0050.

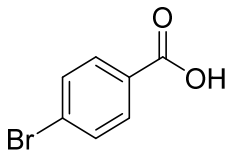
**2,4-dichlorobenzoic acid**[10] (**3l**)



Prepared according to *General procedure for aromatic benzoic acid synthesis (conditions **B**)*, using 2,4-dichlorocinnamic acid **1l** (0.5 mmol, 108.5 mg), $V_2O_5$ (0.01 equiv., 1 mg), MeCN/TFA 1/1 (5 mL), 30%$_{aq}$ $H_2O_2$ (30%, 40 equiv., 2 mL), reaction time 24 h. The product **3l** (88.8 mg, 93%) was obtained as a white solid after purification by column chromatography (EtOAc/heptane (2/1)).

**$^1$H NMR** (500 MHz, $CDCl_3$): $\delta$ = 7.98 (d, *J* = 8.5 Hz, 1H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.35 (dd, *J* = 8.5, 2.0 Hz, 1H) ppm. **$^{13}$C NMR** (126 MHz, $CDCl_3$): $\delta$ = 168.1, 139.6, 136.1, 133.6, 131.6, 127.3, 126.7 ppm. **IR** (cm$^{-1}$): 2970, 1739, 1699, 1587, 1554, 1476, 1415. **HRMS** (EI): *m/z* $(M+H)^+$ calcd. for $C_7H_4Cl_2O_2$ 190.9661, found 190.9662.

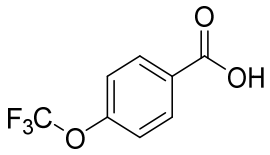
**4-bromobenzoic acid**[7] (**3m**)




Prepared according to *General procedure for aromatic benzoic acid synthesis (conditions **B**)*, using 4-bromocinnamic acid **1m** (0.5 mmol, 113.5 mg), $V_2O_5$ (0.01 equiv., 1 mg), MeCN/TFA 1/1 (5 mL), 30%$_{aq}$ $H_2O_2$ (40 equiv., 2 mL), reaction time 24 h. The product **3m** (85.4 mg, 85%) was obtained as a white solid after purification by column chromatography (EtOAc/heptane (2/1)).

**$^1$H NMR** (500 MHz, $CDCl_3$): $\delta$ = 7.94 – 7.89 (m, 2H), 7.64 – 7.50 (m, 2H) ppm. **$^{13}$C NMR** (126 MHz, $CDCl_3$): $\delta$ = 168.3, 131.7, 131.6, 129.7, 128.0 ppm. **IR** (cm$^{-1}$): 2970, 1739, 1679, 1586, 1427, 1366. **HRMS** (EI): *m/z* $(M+H)^+$ calcd. for $C_7H_6BrO_2$ 200.9546, found 200.9543.

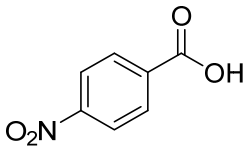
**4-(trifluoromethoxy)benzoic acid**[11] (**3n**)




Prepared according to *General procedure for aromatic benzoic acid synthesis (conditions **A**)*, using 3-(4-(Trifluoromethoxy)phenyl)acrylic acid **1n** (0.5 mmol, 116.1 mg), $V_2O_5$ (0.01 equiv., 1 mg), MeCN 1 (5 mL), 30%$_{aq}$ $H_2O_2$ (28 equiv., 1.4 mL), reaction time 24 h. The product **3n** (93.8 mg, 91%) was obtained as a white solid after purification by column chromatography (EtOAc/heptane (2/1).

**$^1$H NMR** (500 MHz, $CDCl_3$): $\delta$ = 8.18 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 2H) ppm. **$^{13}$C NMR** (126 MHz, $CDCl_3$): $\delta$ = 171.0, 153.6, 132.5, 127.7, 120.5, 120.4 (q, *J* = 225 Hz) ppm. **IR** (cm$^{-1}$): 2820, 1684, 1607, 1509, 1429. **HRMS** (EI): *m/z* $(M+H)^+$ calcd. for $C_8H_5F_3O_3$ 207.0264, found 207.0263.

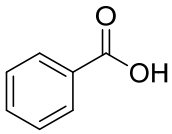
**4-nitrobenzoic acid**[7] (**3o**)



Prepared according to *General procedure for aromatic benzoic acid synthesis (conditions **B**)*, using 4-nitrocinnamic acid **1o** (0.5 mmol, 96.6 mg), $V_2O_5$ (0.01 equiv., 1 mg), MeCN/TFA 1/1 (5 mL), 30%$_{aq}$ $H_2O_2$ (40 equiv., 2 mL), reaction time 24 h. The product **3o** (70.2 mg, 84%) was obtained as a colorless solid after purification by column chromatography (EtOAc/heptane (2/1)).

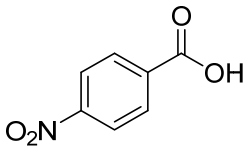
**$^1$H NMR** (500 MHz, $CDCl_3$): $\delta$ = 8.31 (d, *J* = 9.0 Hz, 2H), 8.26 (d, *J* = 9.0 Hz, 2H) ppm. **$^{13}$C NMR** (126 MHz, $CDCl_3$): $\delta$ = 166.7, 150.6, 136.7, 131.0, 123.5 ppm. **IR** ($cm^{-1}$): 2979, 1739, 1604, 1521, 1427, 1350. **HRMS** (EI): *m/z* $(M+H)^+$ calcd. for $C_7H_5NO_4$ 168.0291, found 168.0292.

**Benzoic acid**[7] (**3f**)



Prepared according to *General procedure for aromatic benzoic acid synthesis (conditions **A**)*, using α-methylcinnamic acid **1p** (0.5 mmol, 81.1 mg), $V_2O_5$ (0.01 equiv., 1 mg), MeCN (5 mL), 30%$_{aq}$ $H_2O_2$ (28 equiv., 1.4 mL), reaction time 24 h. The product **3f** (55.0 mg, 90%) was obtained as a colorless solid after purification by column chromatography (EtOAc/heptane (2/1)).

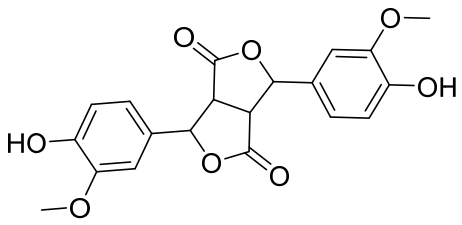
**4-nitrobenzoic acid**[7] (**3r**)



Prepared according to *General procedure for aromatic benzoic acid synthesis (conditions **A**)*, using methyl (2E)-3-(4-nitrophenyl)-2-propenoate **1r** (0.5 mmol, 110.6 mg), $V_2O_5$ (0.01 equiv., 1 mg), MeCN (5 mL), 30%$_{aq}$ $H_2O_2$ (28 equiv., 1.4 mL), reaction time 24 h. The product **3r** (74.4 mg, 89%) was obtained as a colorless solid after purification by column chromatography (EtOAc/heptane (2/1)).

**$^1$H NMR** (500 MHz, $CDCl_3$): $\delta$ = 8.31 (d, *J* = 9.0 Hz, 2H), 8.26 (d, *J* = 9.0 Hz, 2H) ppm. **$^{13}$C NMR** (126 MHz, $CDCl_3$): $\delta$ = 166.7, 150.6, 136.7, 131.0, 123.5 ppm. **IR** ($cm^{-1}$): 2979, 1739, 1604, 1521, 1427, 1350. **HRMS** (EI): *m/z* $(M+H)^+$ calcd. for $C_7H_5NO_4$ 168.0291, found 168.0292.

**3,6-bis(4-hydroxy-3-methoxyphenyl)tetrahydro-1H,4H-furo[3,4-c]furan-1,4-dione**[12] (**1a´**)




**$^{1}$H NMR** (500 MHz, $CDCl_3$): $\delta$ = 6.93 – 6.91 (m, 2H), 6.80 – 6.71 (m, 4H), 5.85 (s, 2H), 3.90 (s, 6H), 3.57 (s, 2H) ppm. **$^{13}$C NMR** (126 MHz, $CDCl_3$): $\delta$ = 175.0, 147.0, 146.3, 129.8, 117.4, 115.0, 107.5, 81.9, 56.1, 48.4 ppm. **HRMS** (EI): *m/z* $(M+H)^+$ calcd. for $C_{20}H_{18}O_8$ 387.1074, found 387.1063.

## 3. COPIES OF NMR SPECTRA

### Vanillin (2a)

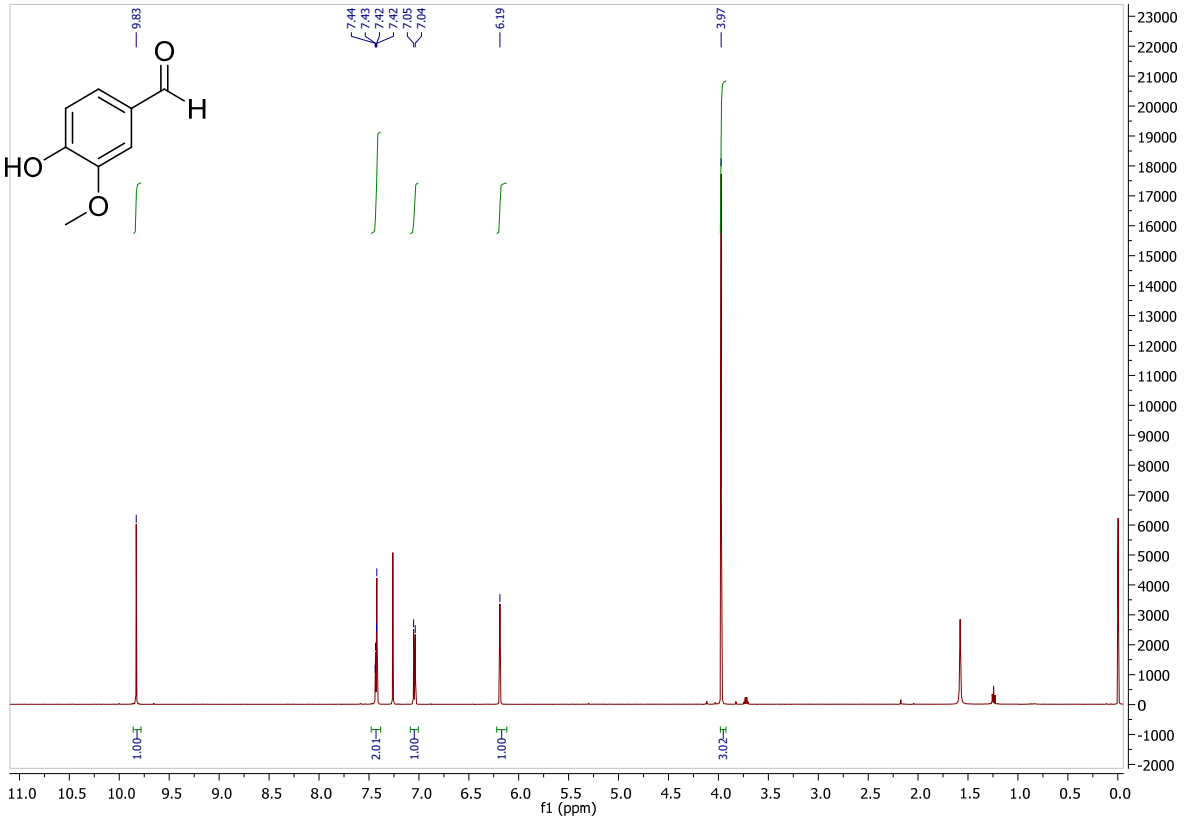



*Figure S3.1. $^{1}H$ NMR spectrum of vanillin **2a** in $CDCl_3$, 500 MHz.*

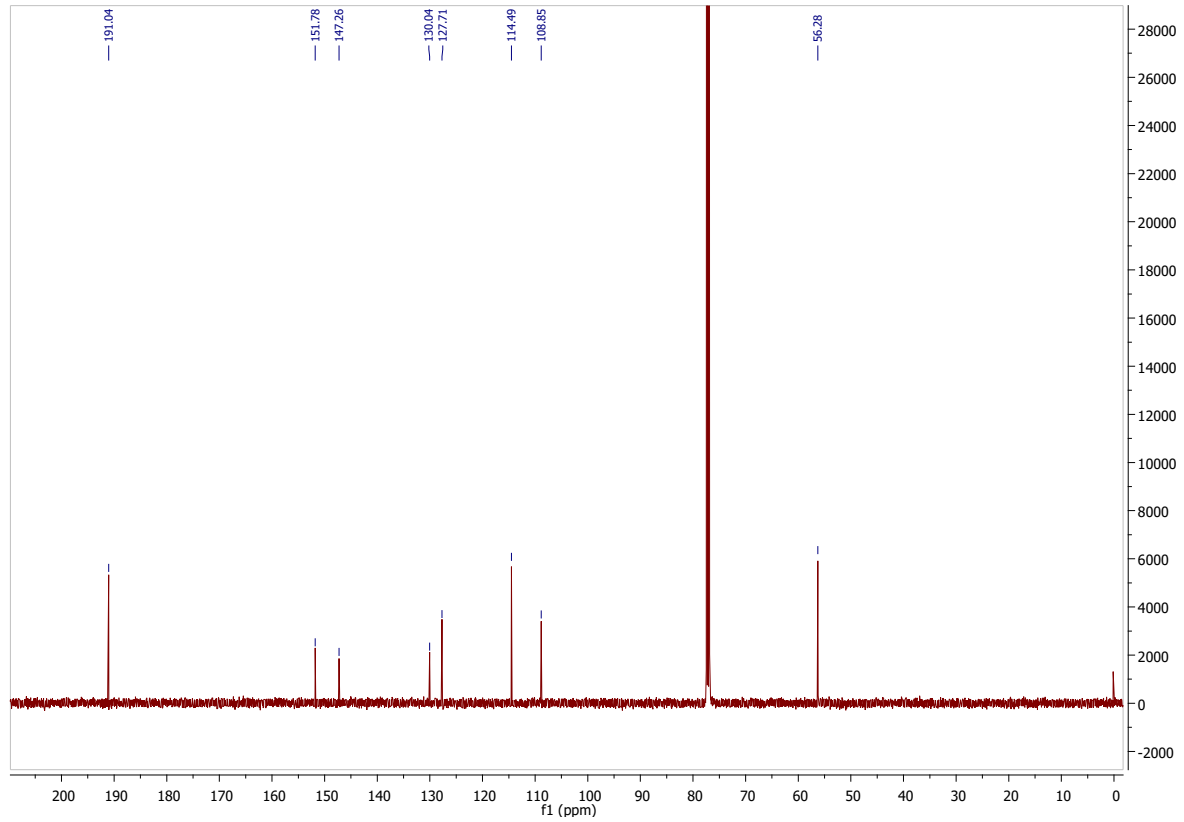



*Figure S3.2. $^{13}C$ NMR spectrum of vanillin **2a** in $CDCl_3$, 500 MHz.*

## 4-hydroxybenzaldehyde (2c)

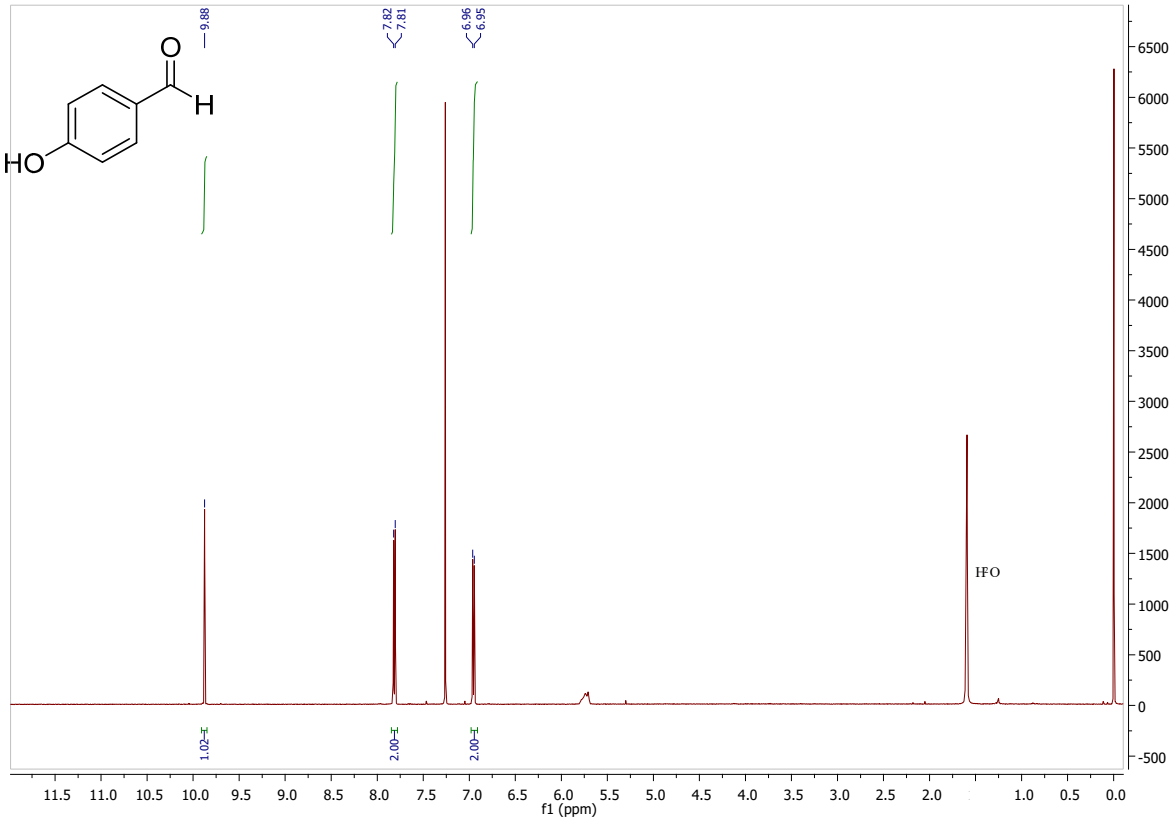



*Figure S3.3. $^{1}H$ NMR spectrum of 4-hydroxybenzaldehyde **2c** in $CDCl_3$, 500 MHz.*

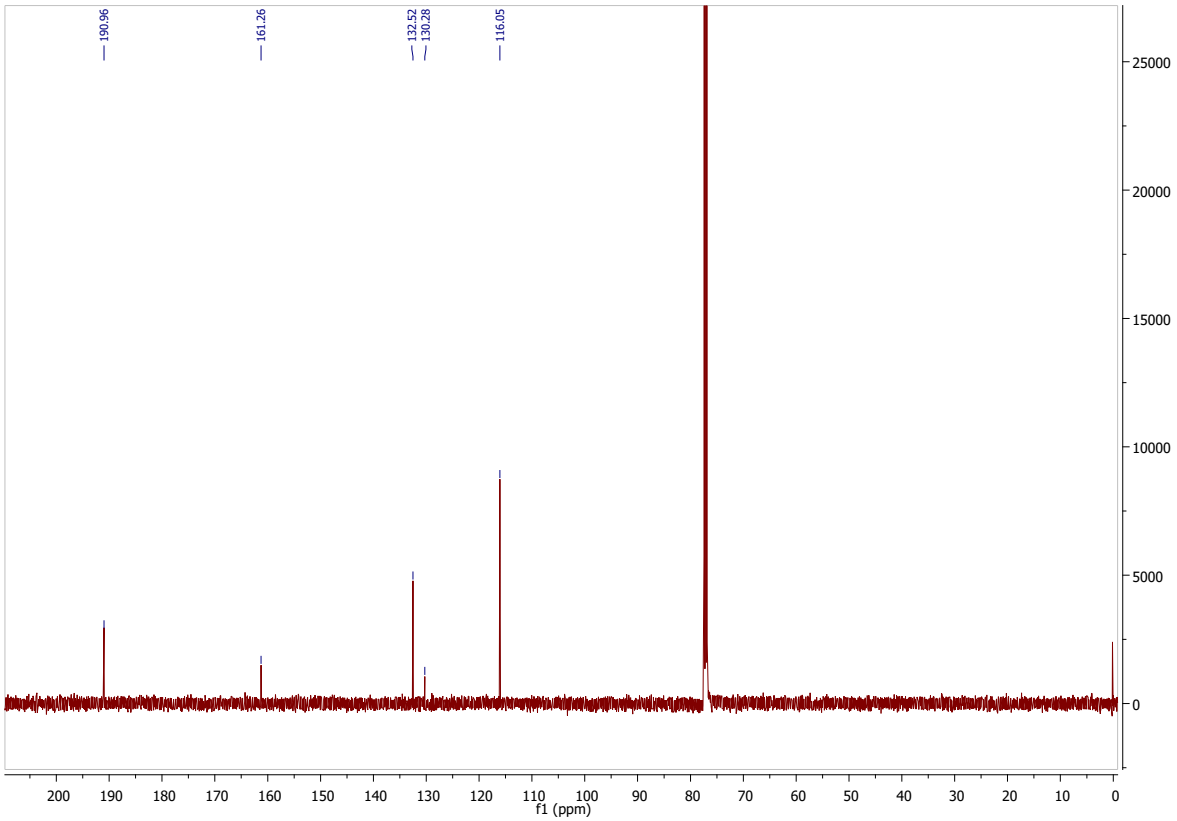



*Figure S3.4. $^{13}C$ NMR spectrum of 4-hydroxybenzaldehyde **2c** in $CDCl_3$, 500 MHz.*

## 2-methoxy-1,4-benzoquinone (4a)

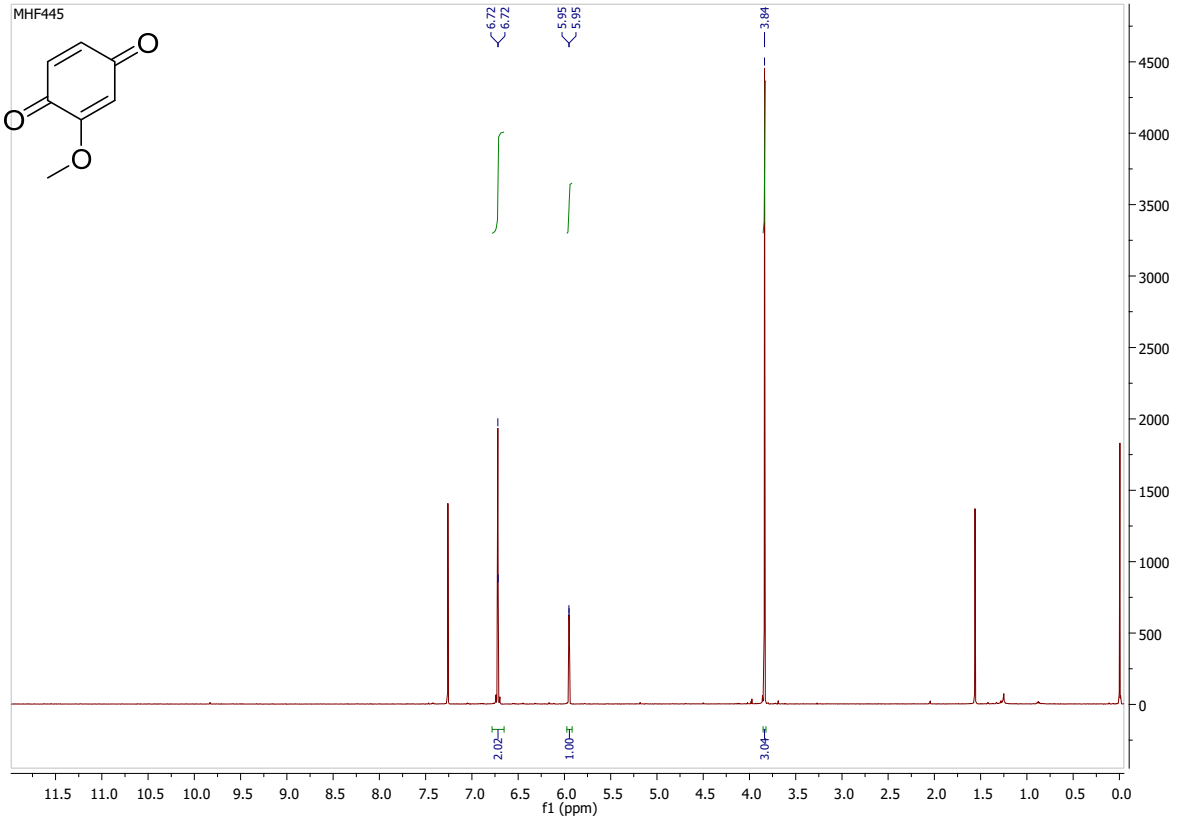



*Figure S3.5. $^{1}H$ NMR spectrum of 2-methoxy-1,4-benzoquinone **4a** in $CDCl_3$, 500 MHz.*

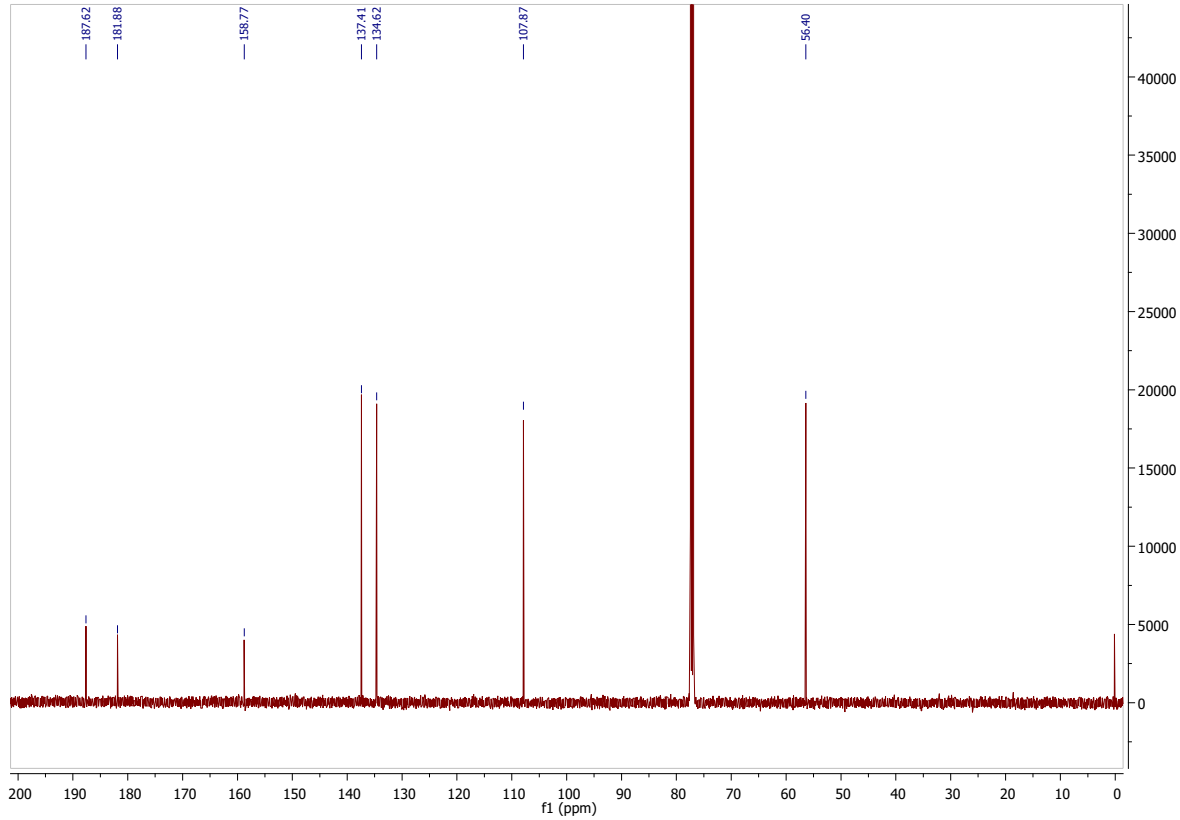



*Figure S3.6. $^{13}C$ NMR spectrum of 2-methoxy-1,4-benzoquinone **4a** in $CDCl_3$, 500 MHz.*

## 2,6-dimethoxy-1,4-benzoquinone (4d)

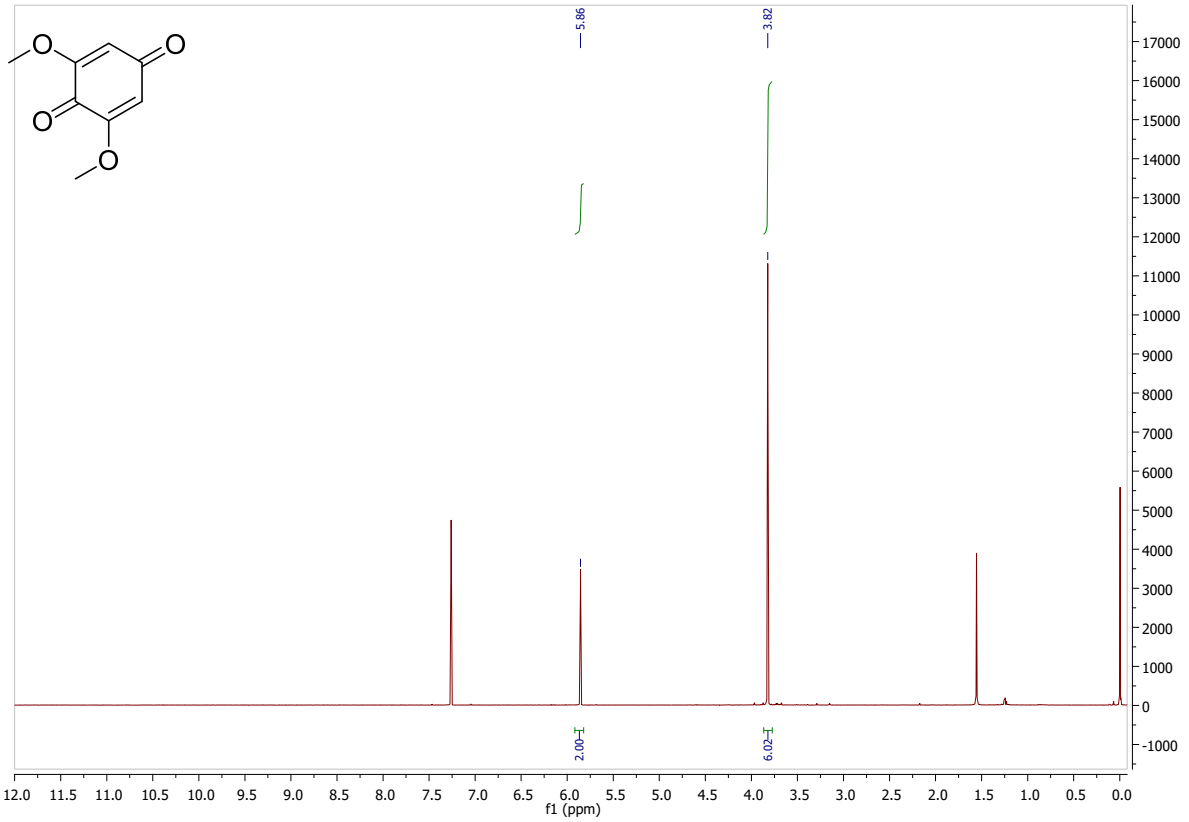



*Figure S3.7. $^{1}H$ NMR spectrum of 2,6-dimethoxy-1,4-benzoquinone **4d** in $CDCl_3$, 500 MHz.*

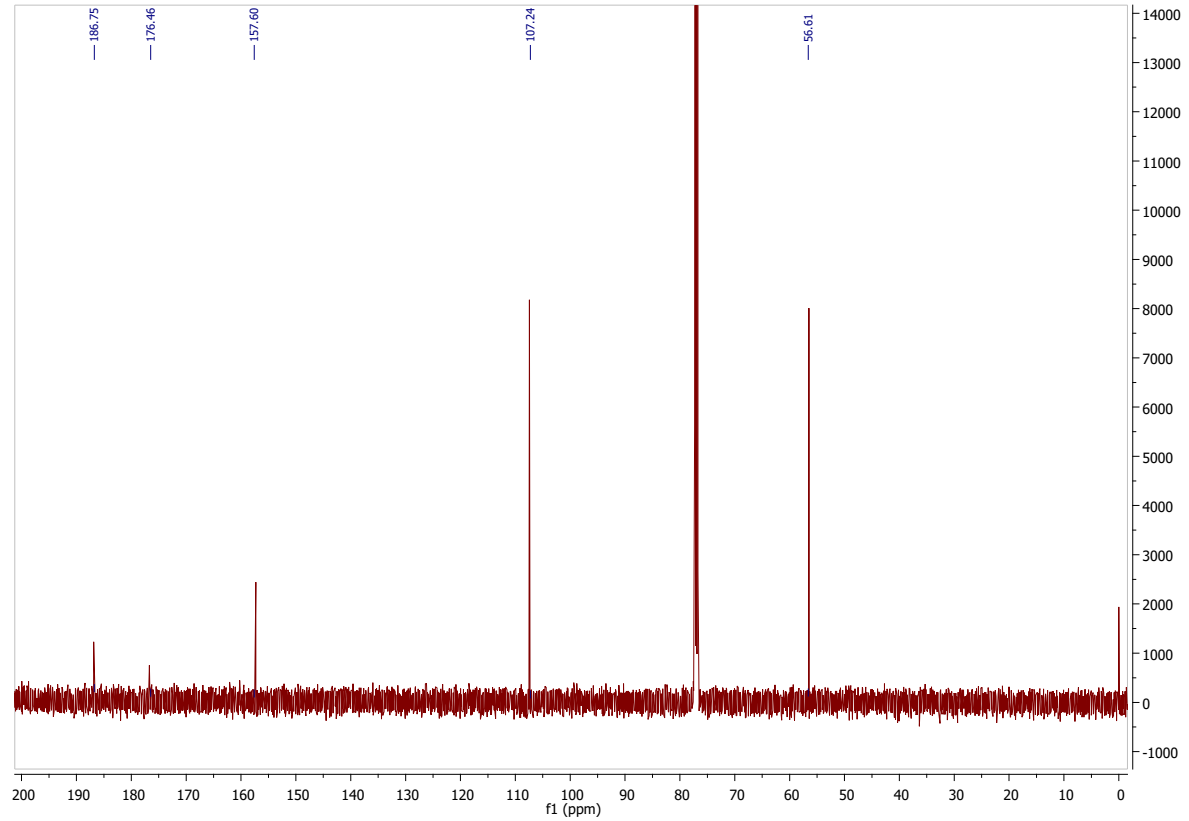



*Figure S3.8. $^{13}C$ NMR spectrum of 2,6-dimethoxy-1,4-benzoquinone **4d** in $CDCl_3$, 500 MHz.*

**Benzoic acid (3f)**

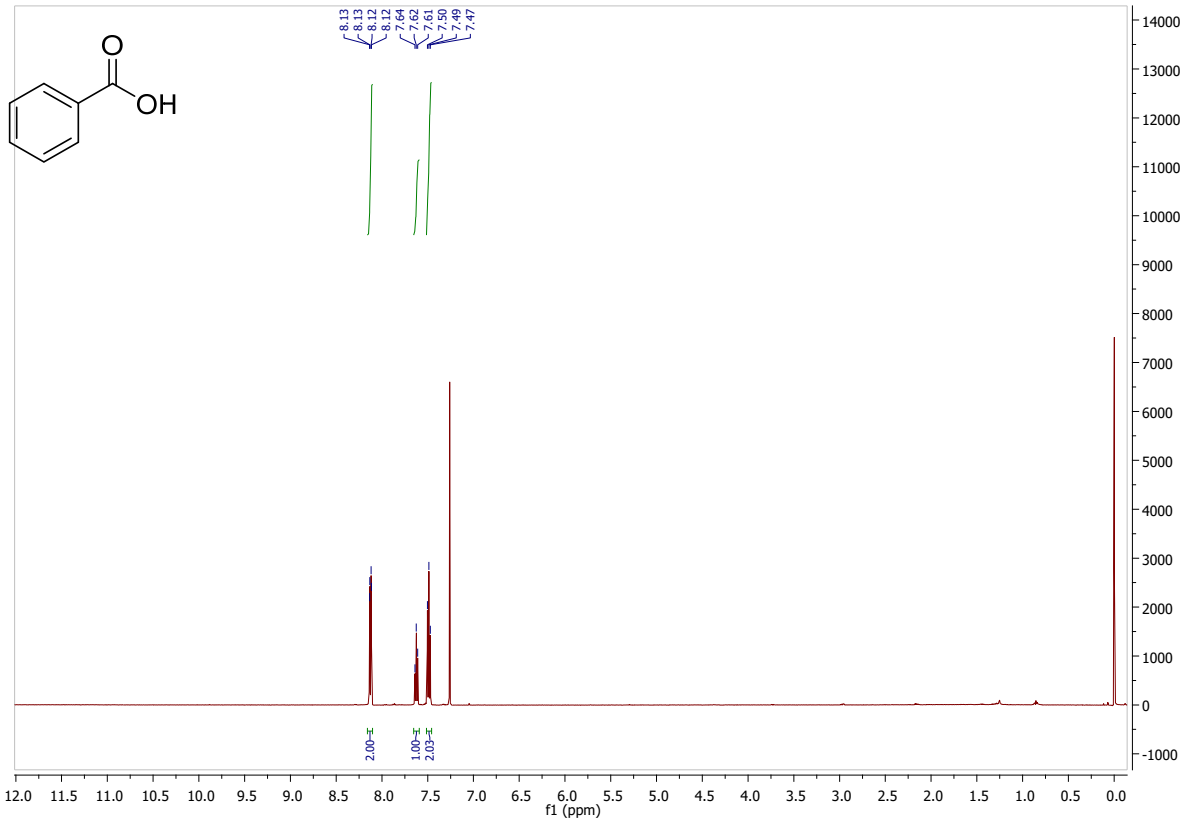



*Figure S3.9. $^{1}H$ NMR spectrum of benzoic acid **3f** in $CDCl_3$, 500 MHz.*

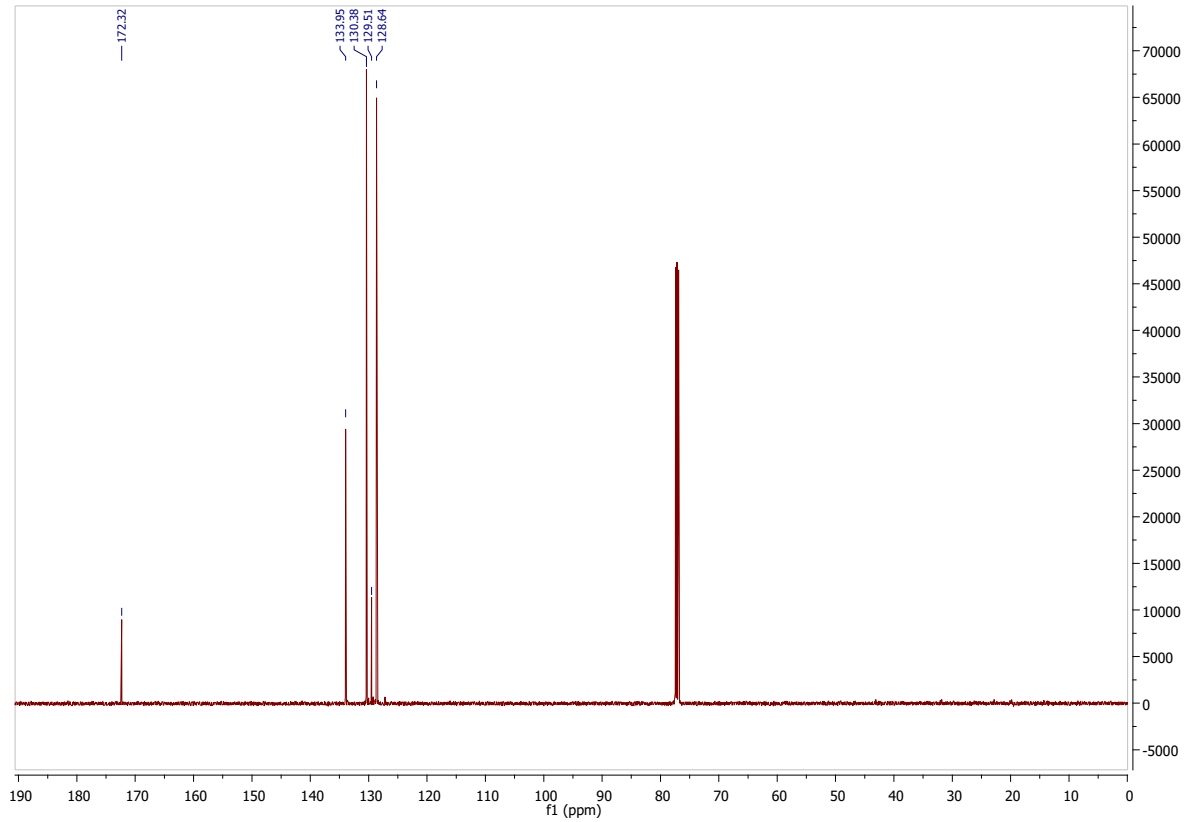



*Figure S3.10. $^{13}C$ NMR spectrum of benzoic acid **3f** in $CDCl_3$, 500 MHz.*

## 4-methylbenzoic acid (3g)

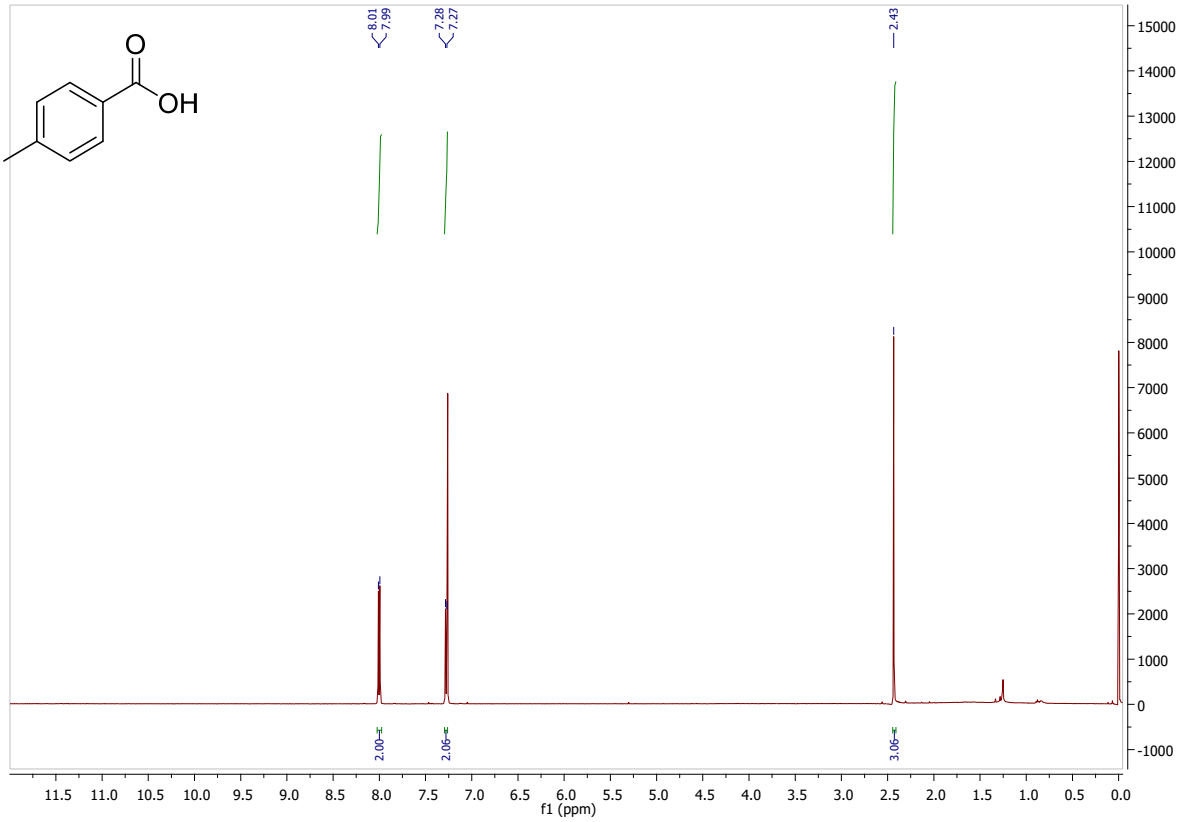



*Figure S3.11. $^{1}H$ NMR spectrum of 4-methylbenzoic **3g** acid in $CDCl_3$, 500 MHz.*

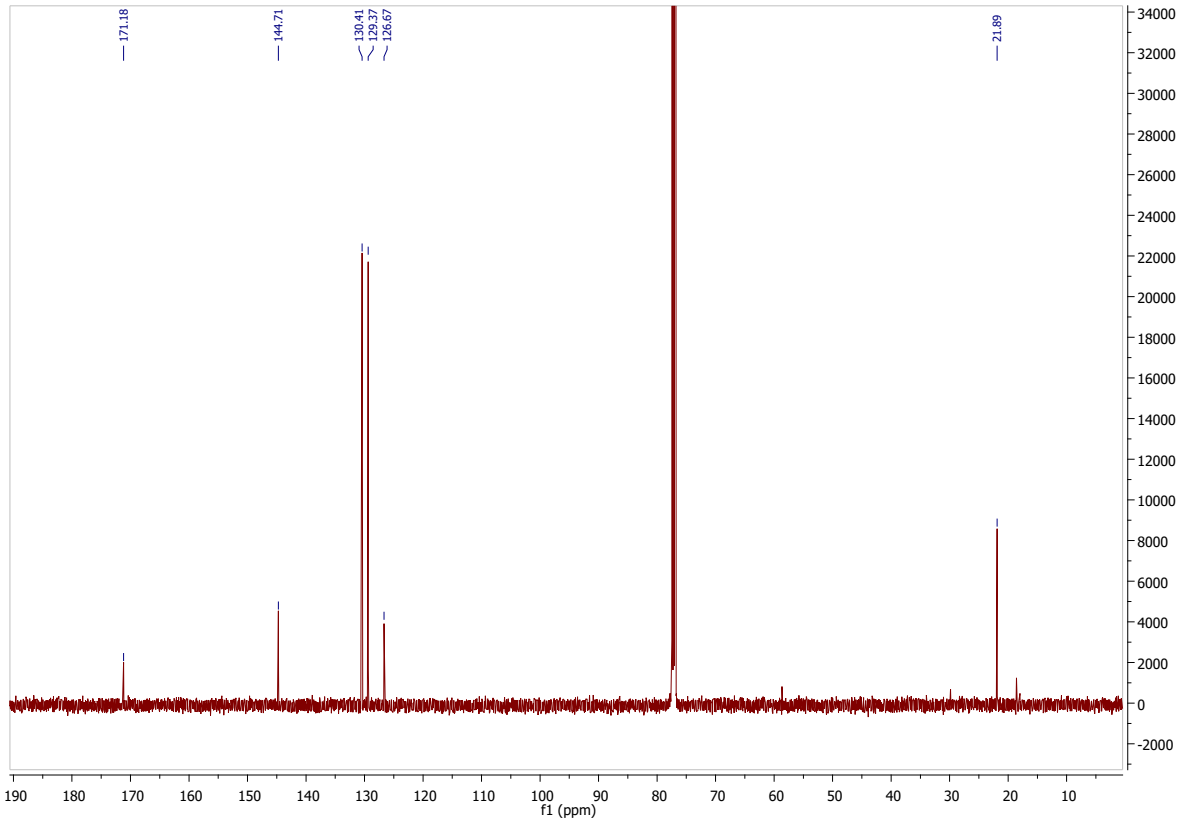



*Figure S3.12. $^{13}C$ NMR spectrum of 4-methylbenzoic acid **3g** in $CDCl_3$, 500 MHz.*

## 4-methoxybenzoic acid (3h)

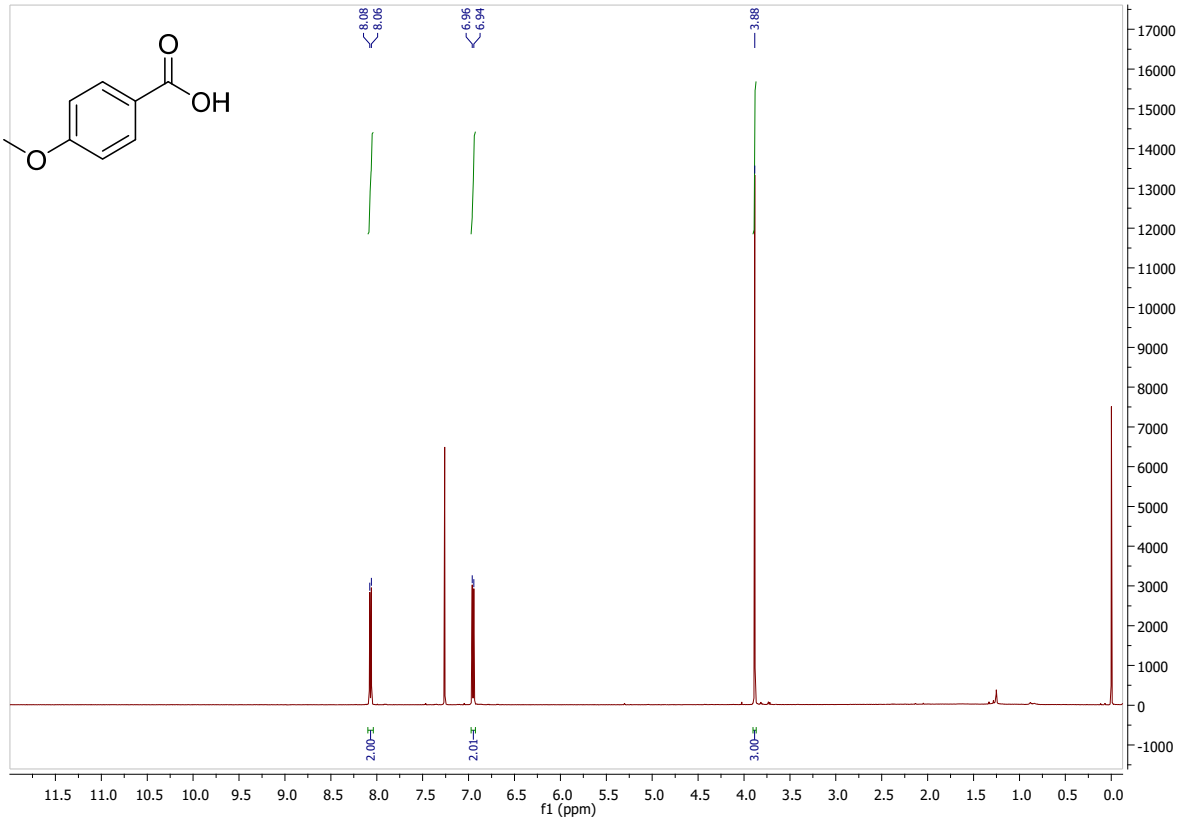



*Figure S3.13. $^{1}H$ NMR spectrum of 4-methoxybenzoic acid **3h** in $CDCl_3$, 500 MHz.*

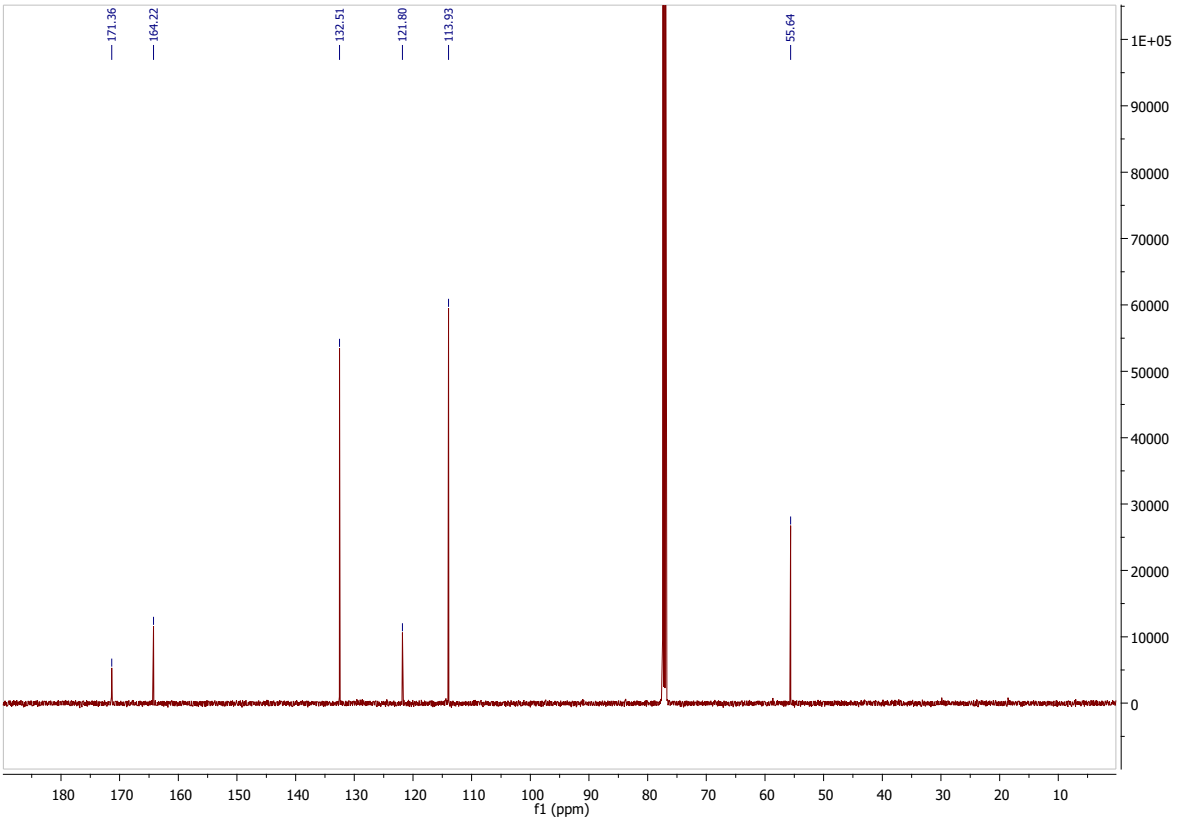



*Figure S3.14. $^{13}C$ NMR spectrum of 4-methoxybenzoic acid **3h** in $CDCl_3$, 500 MHz.*

## 4-fluorobenzoic acid (3i)

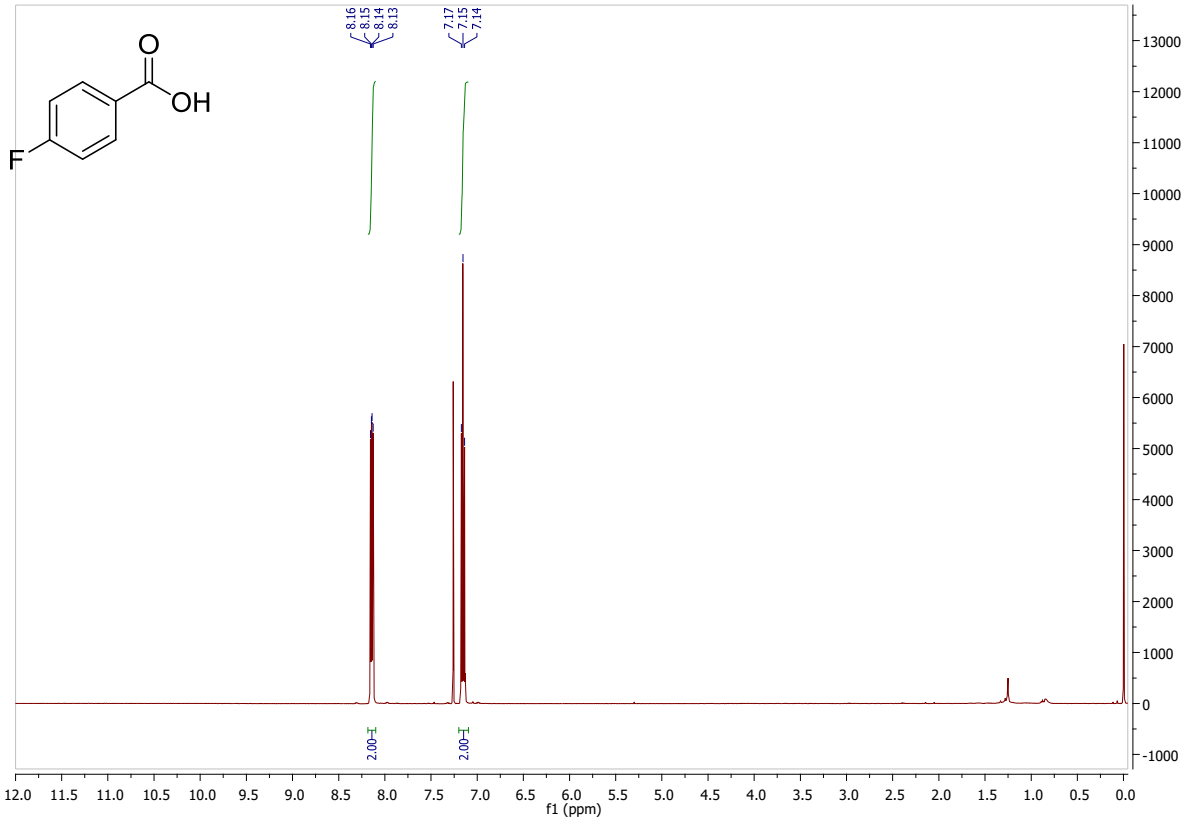



*Figure S3.15. $^{1}H$ NMR spectrum of 4-fluorobenzoic acid **3i** in $CDCl_3$, 500 MHz.*

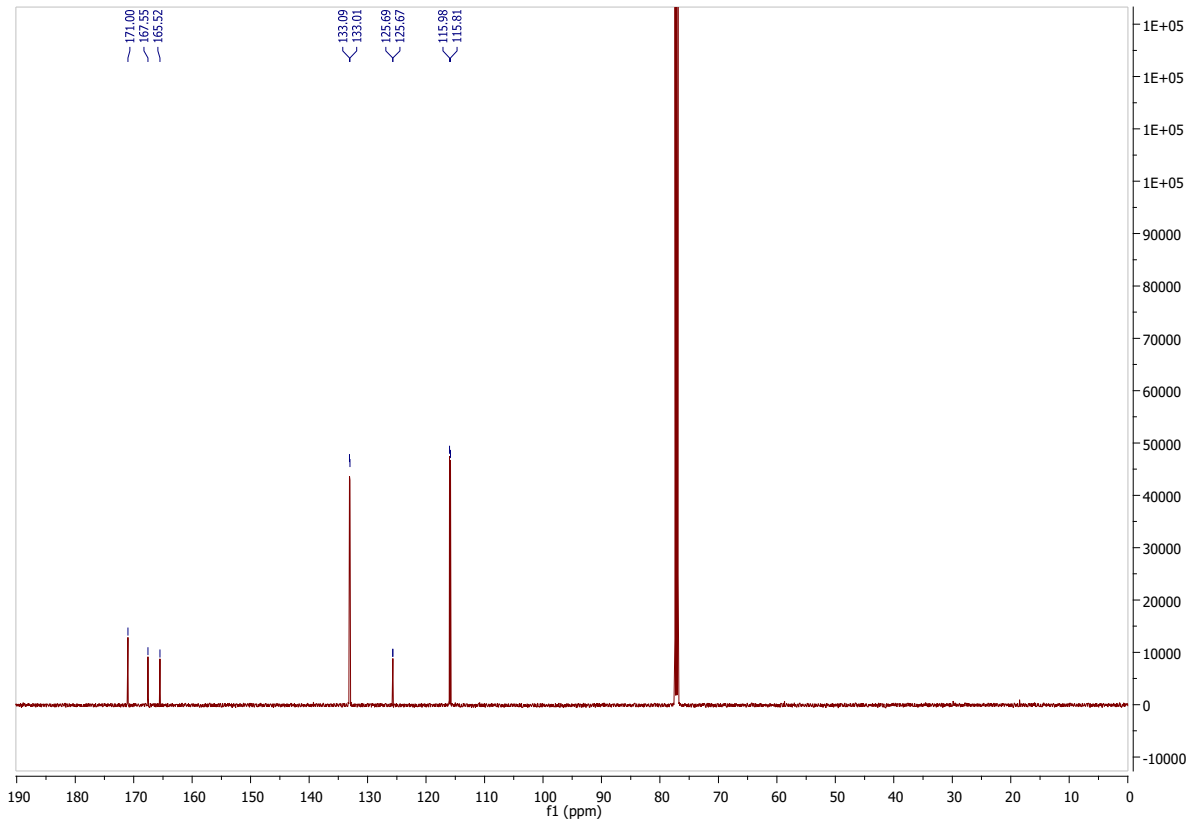



*Figure S3.16. $^{13}C$ NMR spectrum of 4-fluorobenzoic acid **3i** in $CDCl_3$, 500 MHz.*

## 3-chlorobenzoic acid (3j)

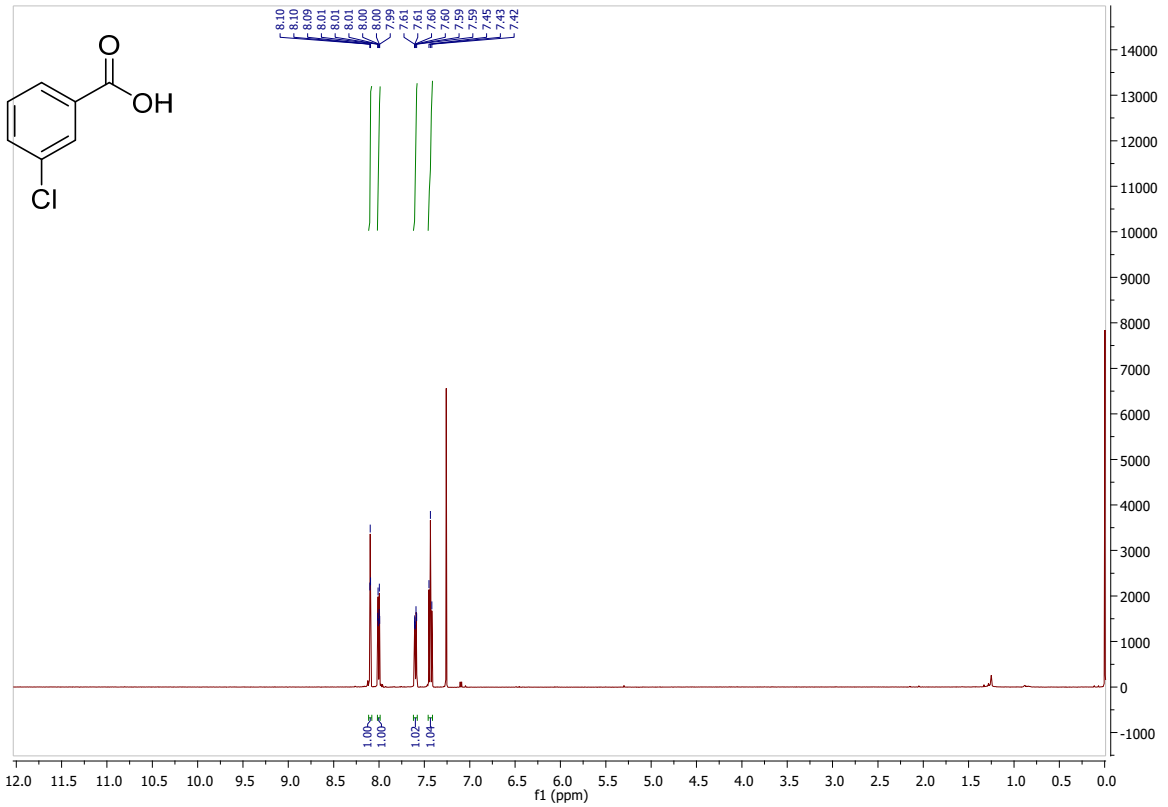



*Figure S3.17. $^{1}H$ NMR spectrum of 3-chlorobenzoic acid **3j** in $CDCl_3$, 500 MHz.*

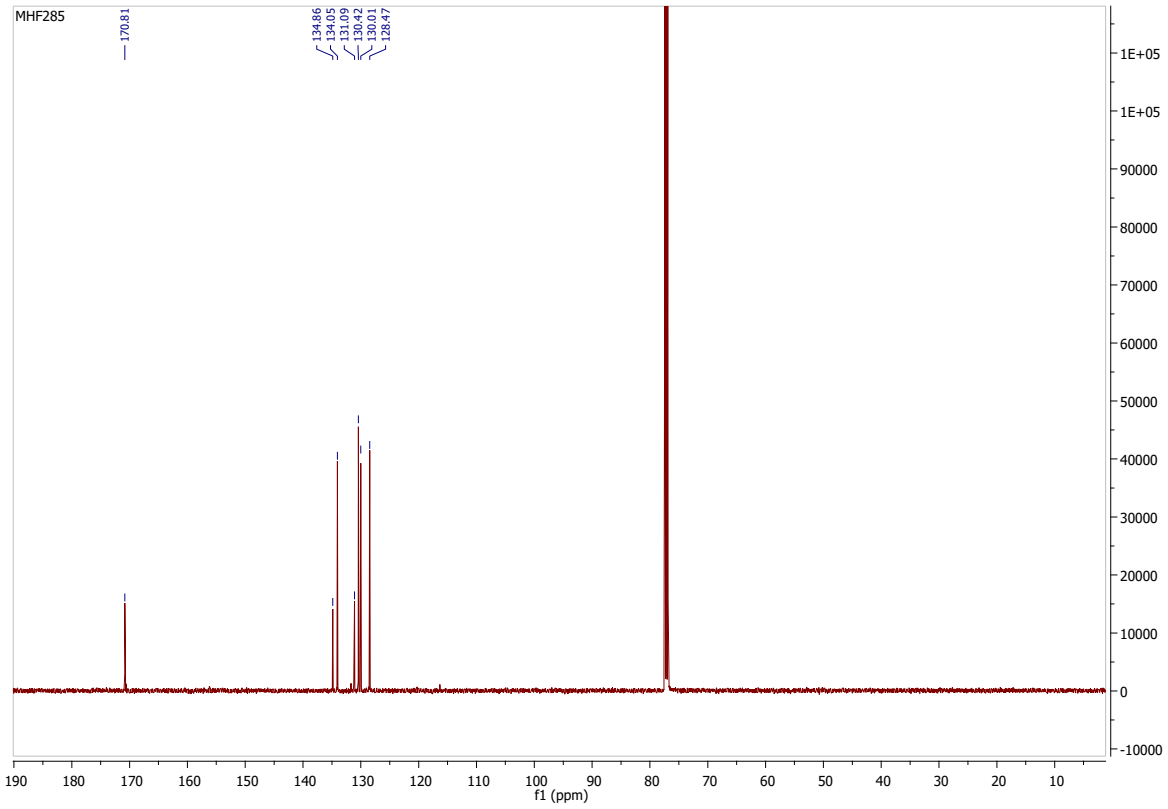



*Figure S3.18. $^{13}C$ NMR spectrum of 3-chlorobenzoic acid **3j** in $CDCl_3$, 500 MHz.*

## 4-chlorobenzoic acid (3k)

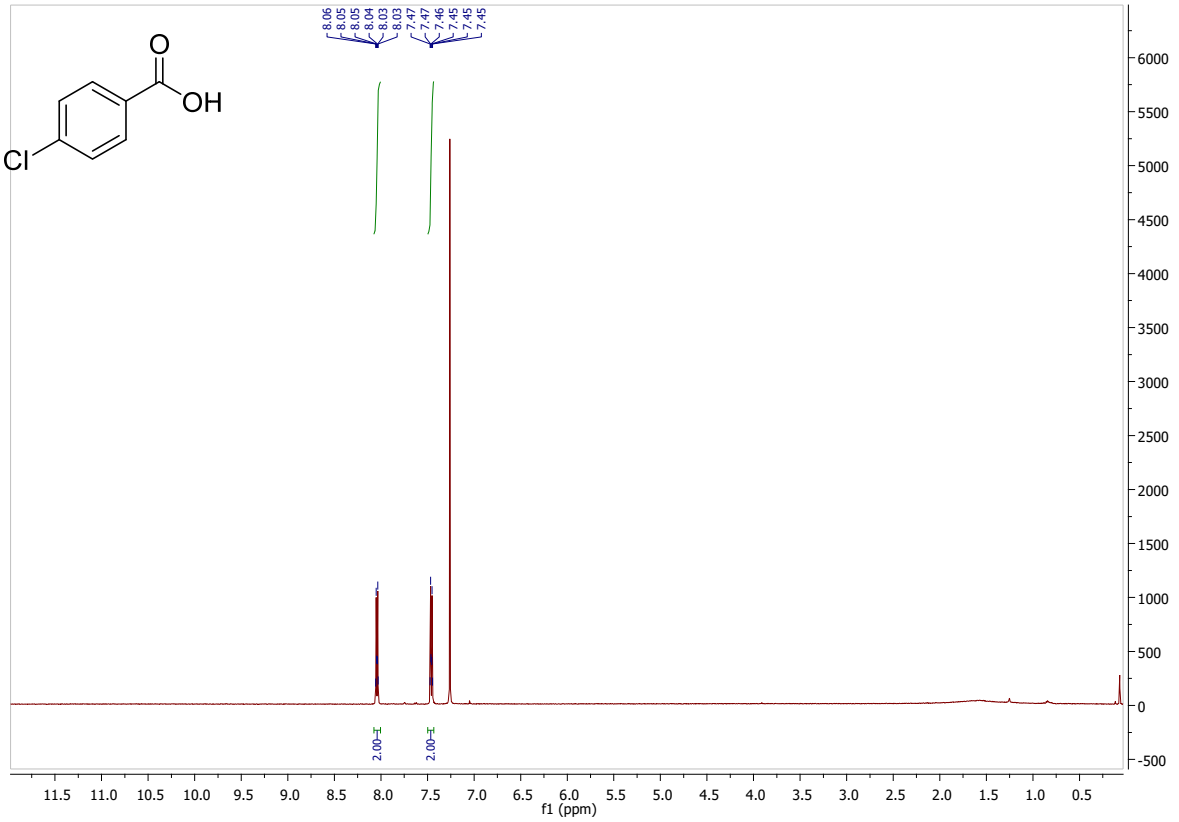



*Figure S3.19. $^{1}H$ NMR spectrum of 4-chlorobenzoic acid **3k** in $CDCl_3$, 500 MHz.*

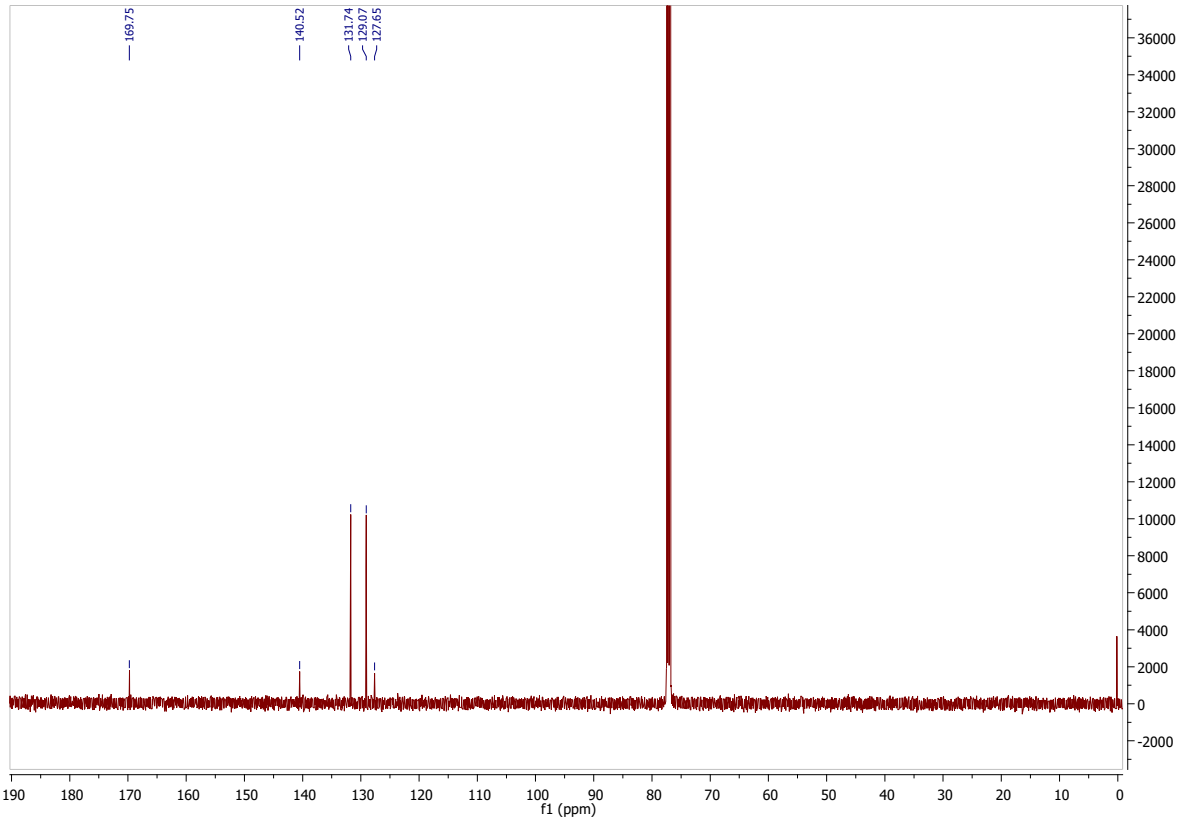



*Figure S3.20. $^{13}C$ NMR spectrum of 4-chlorobenzoic acid **3k** in $CDCl_3$, 500 MHz.*

## 2,4-dichlorobenzoic acid (3l)

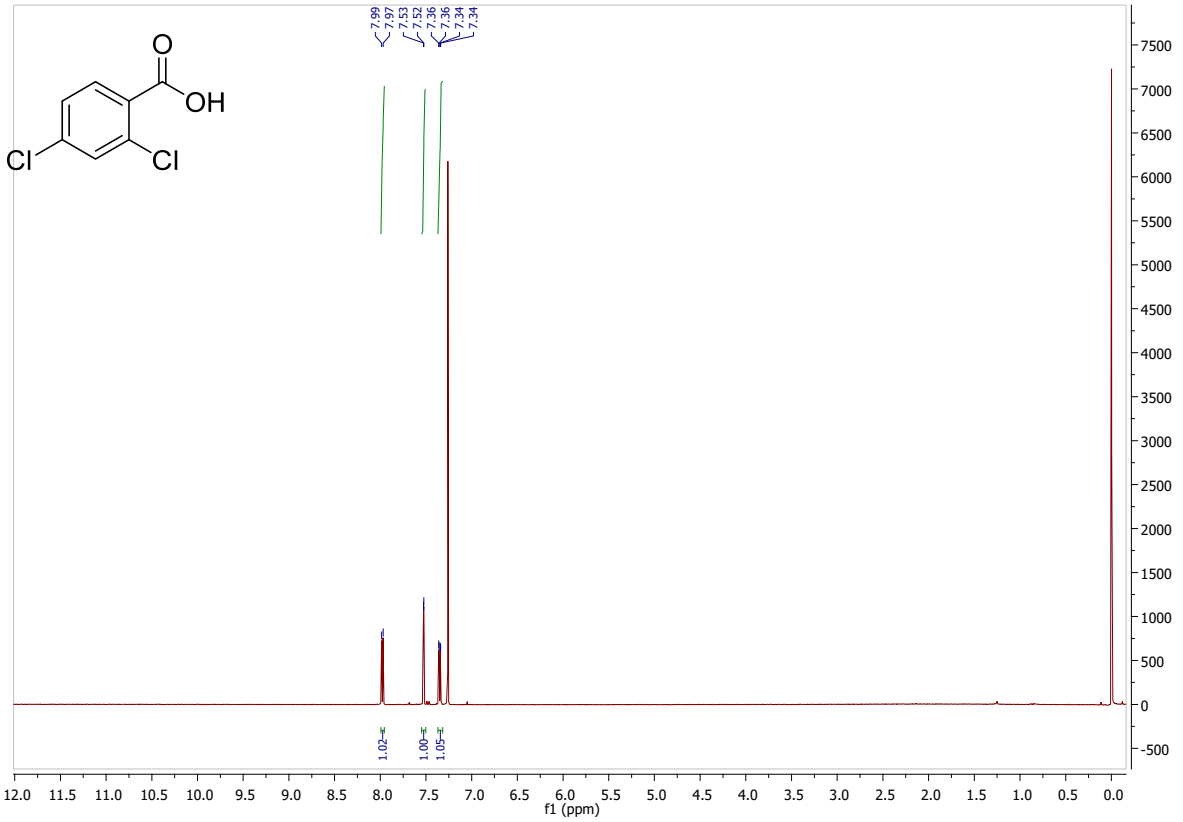



*Figure S3.21. $^{1}H$ NMR spectrum of 2,4-dichlorobenzoic acid **3l** in $CDCl_3$, 500 MHz.*

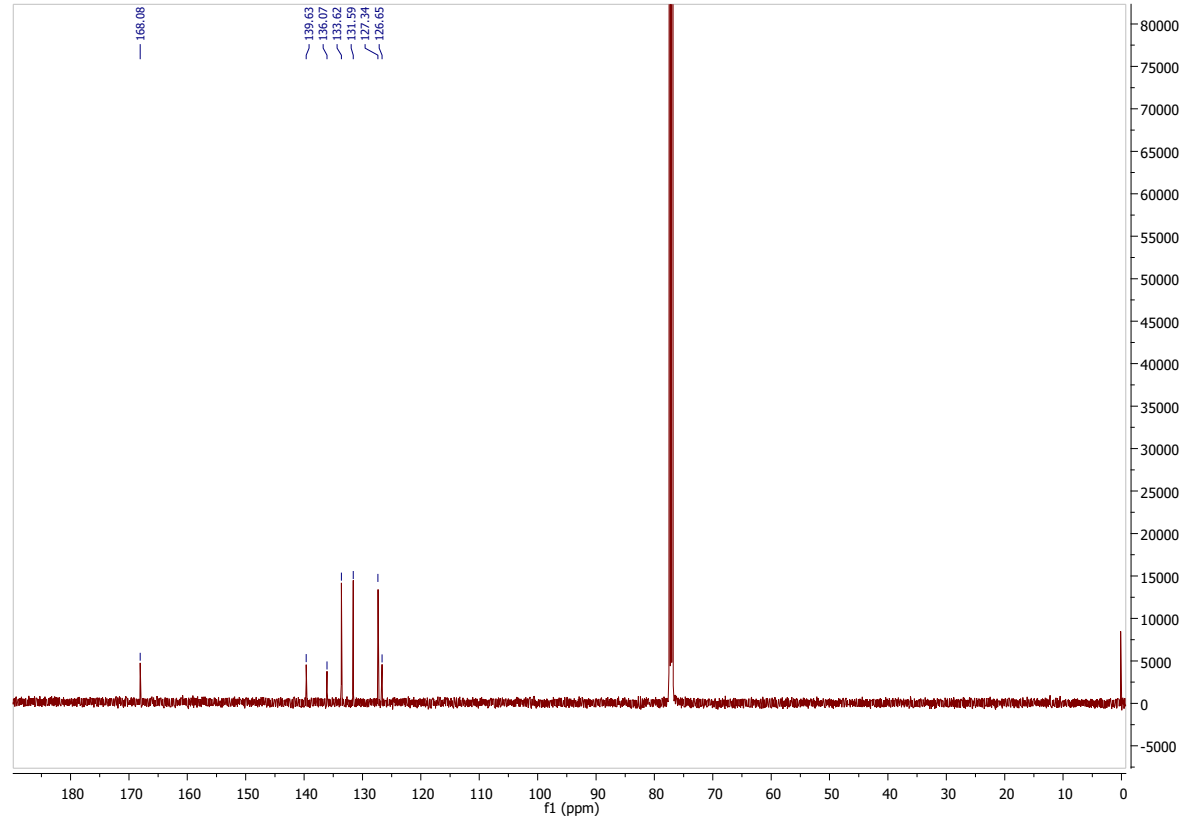



*Figure S3.22. $^{13}C$ NMR spectrum of 2,4-dichlorobenzoic acid **3l** in $CDCl_3$, 500 MHz.*

## 4-bromobenzoic acid (3m)

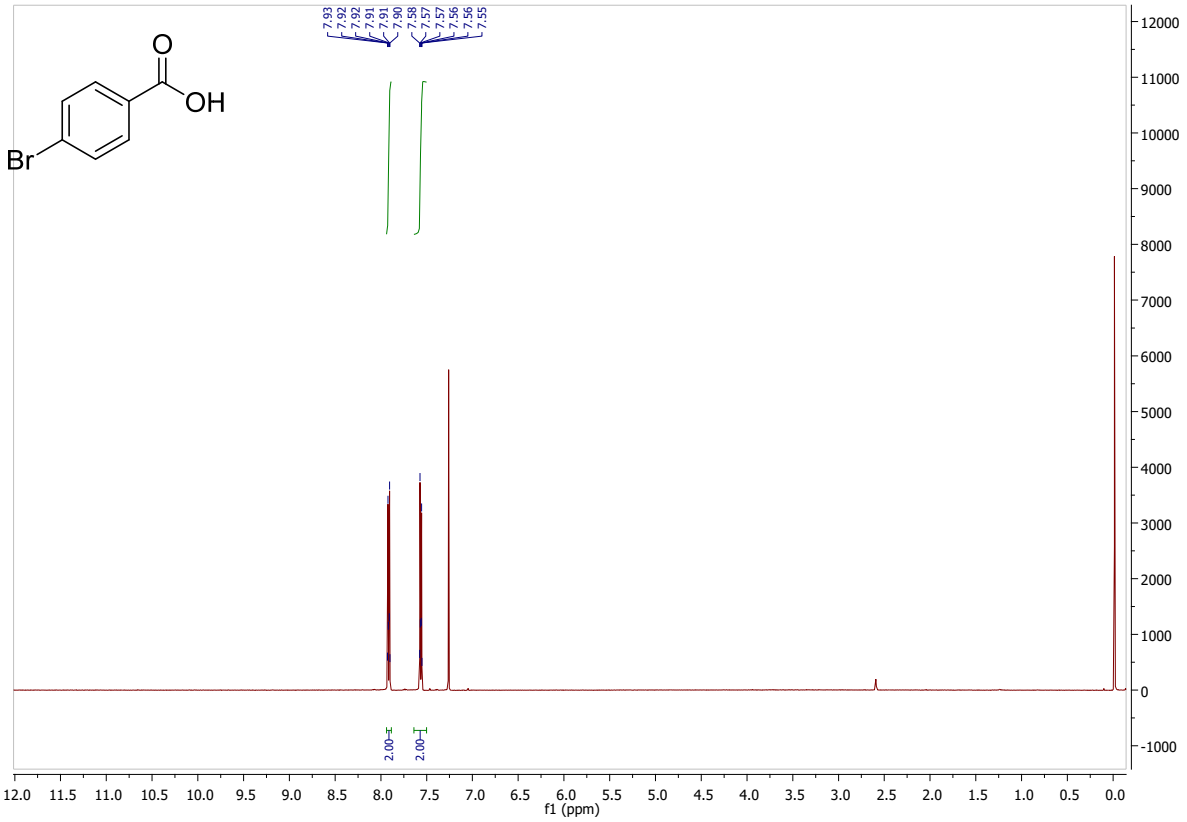



*Figure S3.23. $^{1}H$ NMR spectrum of 4-bromobenzoic acid **3m** in $CDCl_3$, 500 MHz.*

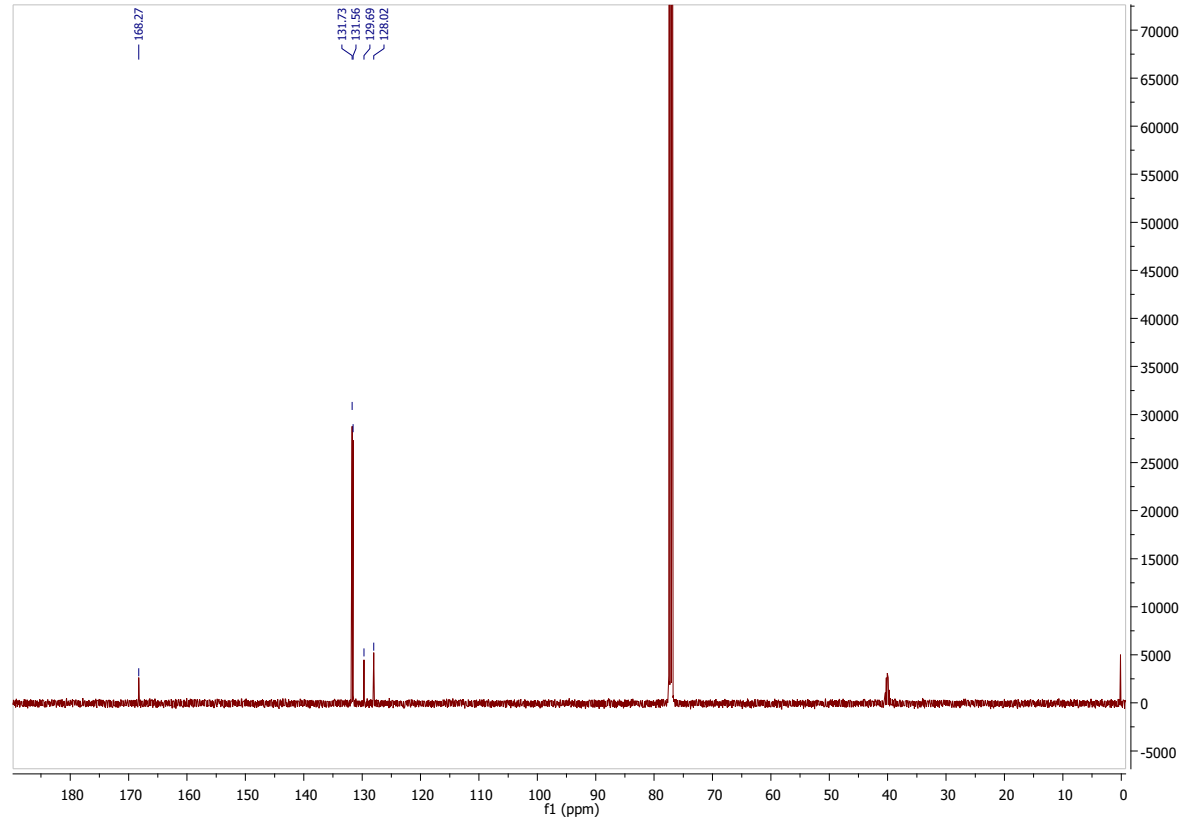



*Figure S3.24. $^{13}C$ NMR spectrum of 4-bromobenzoic acid **3m** in $CDCl_3$, 500 MHz.*

## 4-(trifluoromethoxy)benzoic acid (3n)

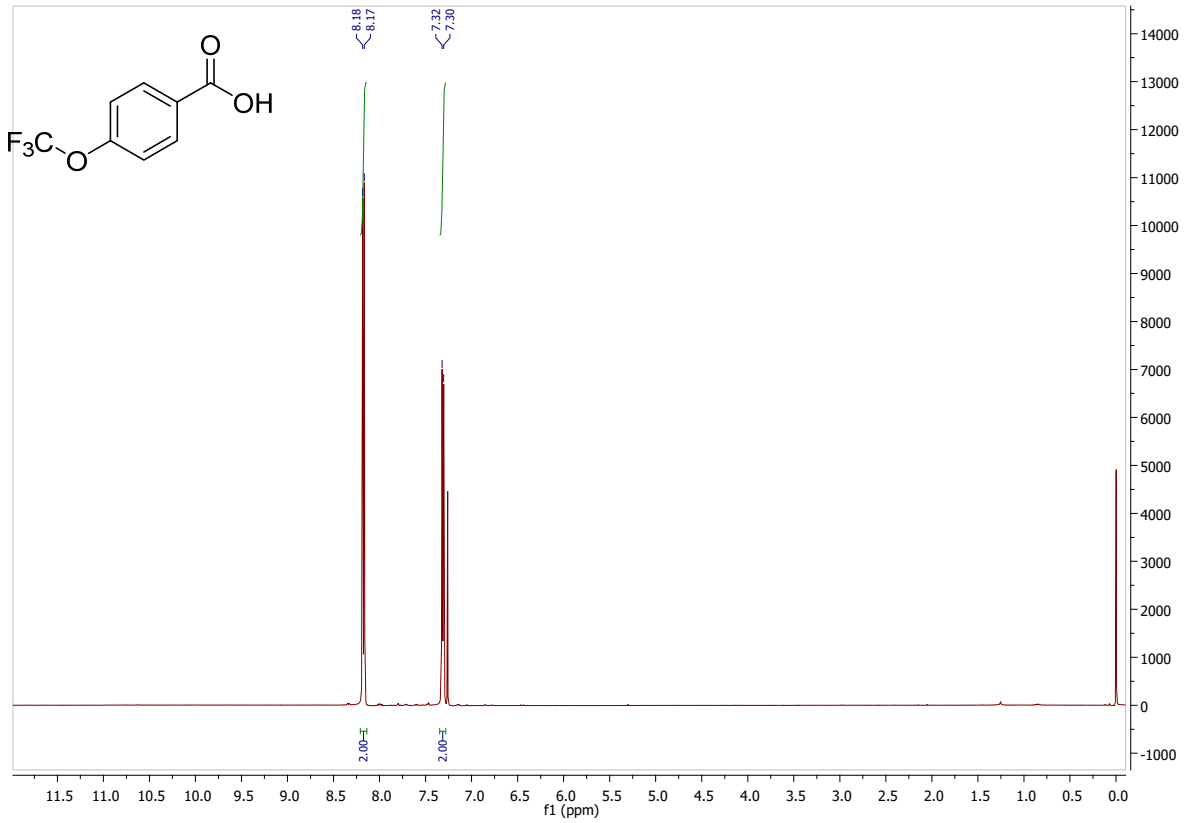



*Figure S3.25. $^{1}H$ NMR spectrum of 4-(trifluoromethoxy)benzoic acid **3n** in $CDCl_3$, 500 MHz.*

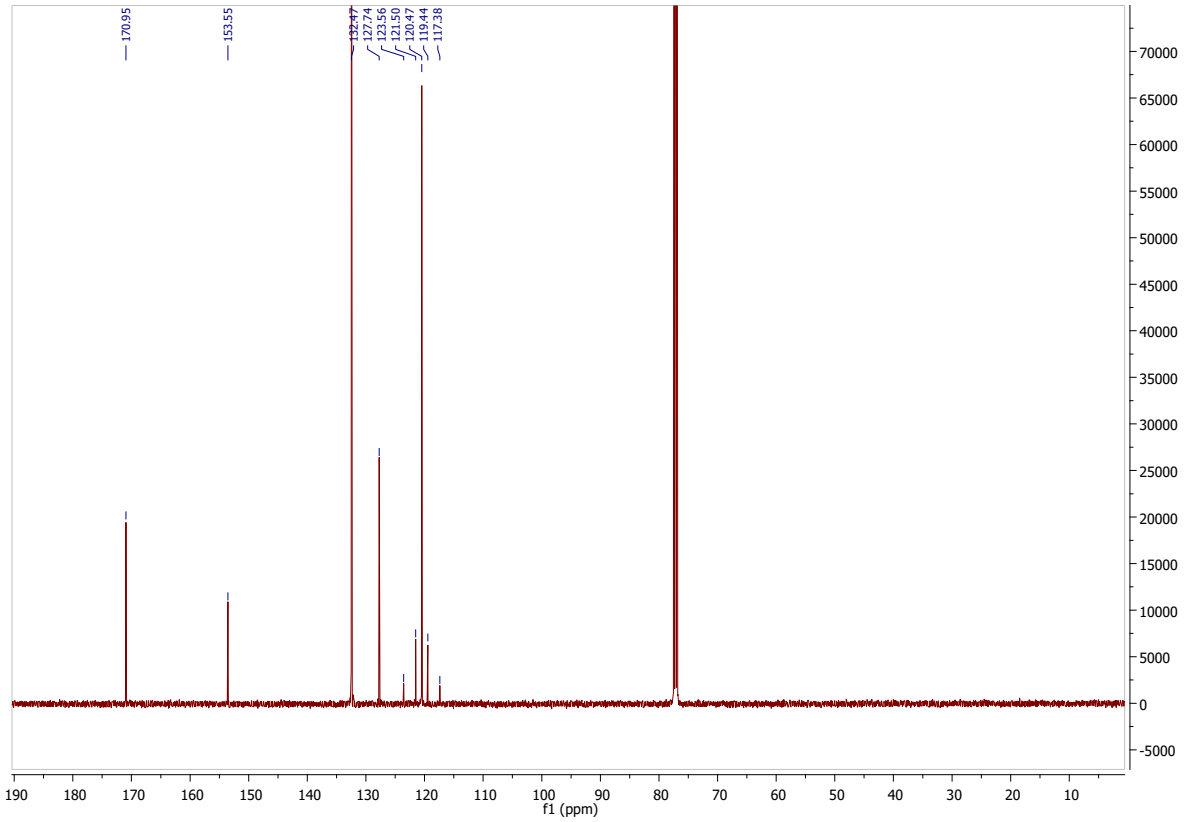



*Figure S3.26. $^{13}C$ NMR spectrum of 4-(trifluoromethoxy)benzoic acid **3n** in $CDCl_3$, 500 MHz.*

**4-nitrobenzoic acid (3o)**

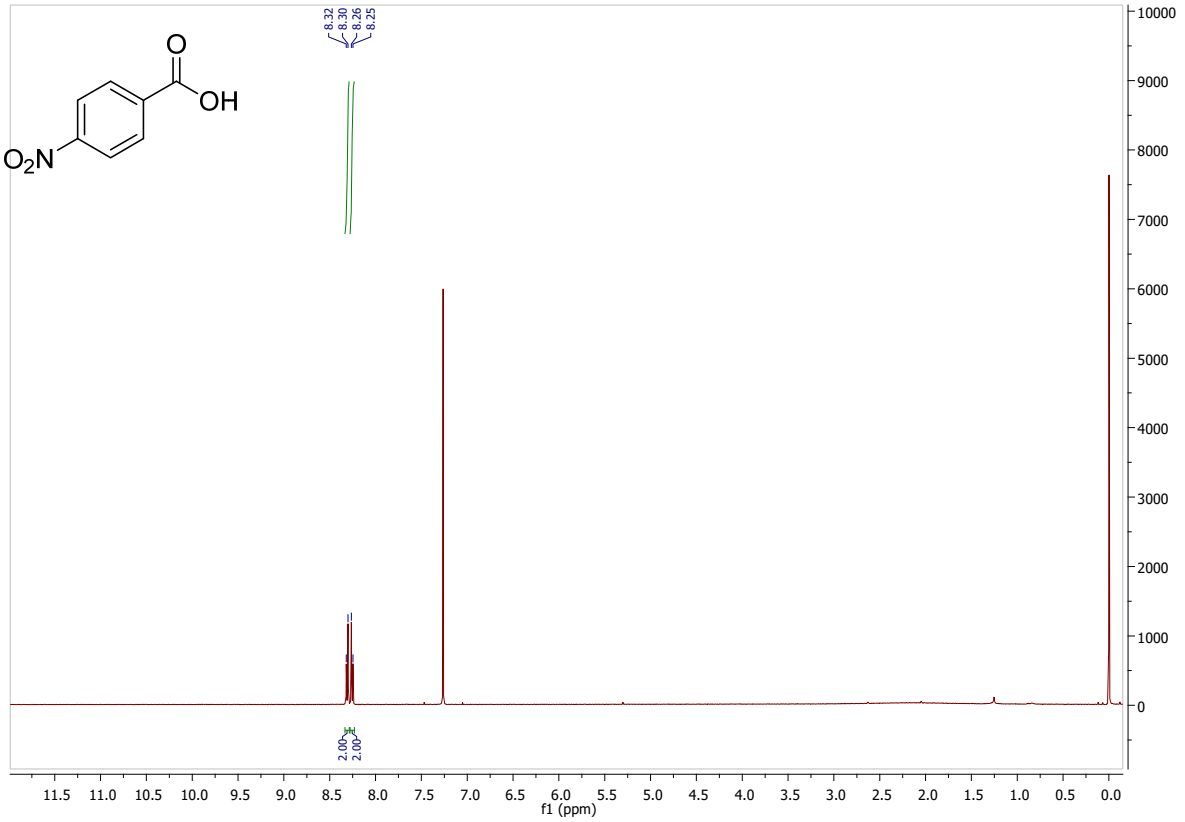



*Figure S3.27. $^{1}H$ NMR spectrum of 4-nitrobenzoic acid **3o** in $CDCl_3$, 500 MHz.*

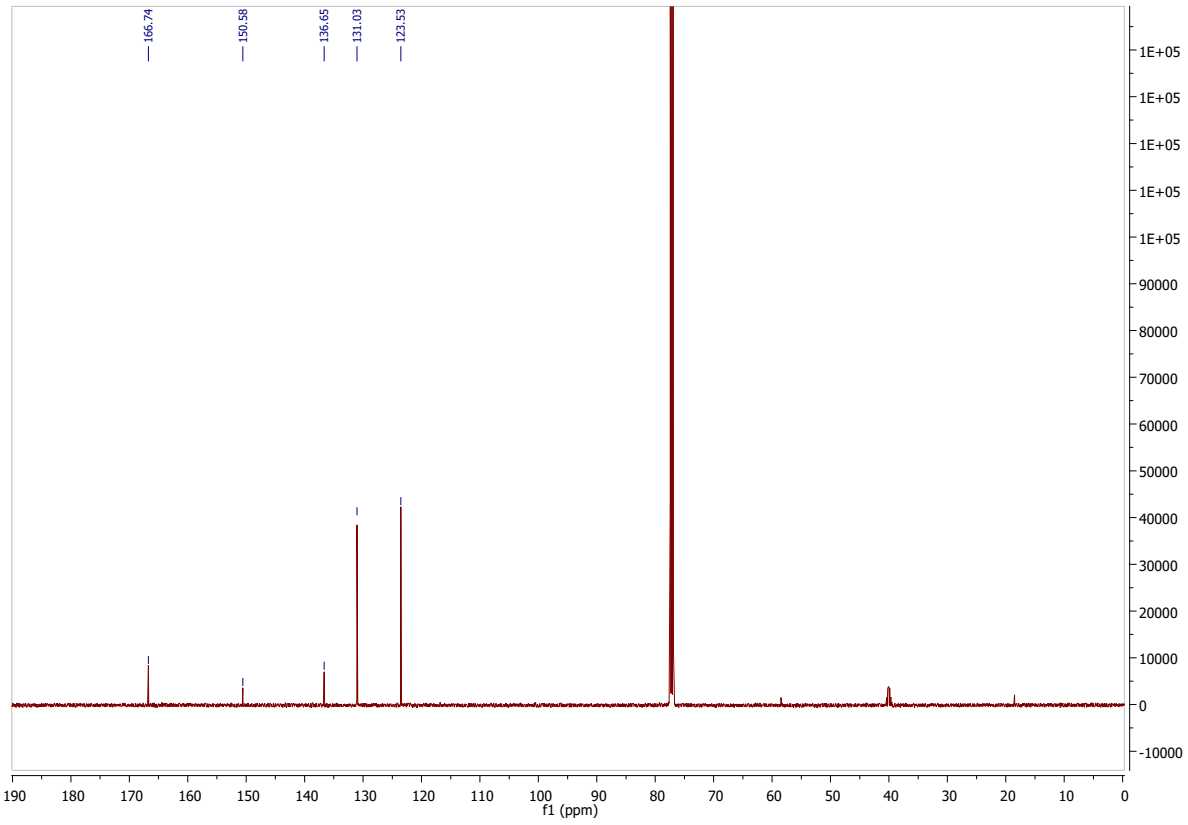



*Figure S3.28. $^{13}C$ NMR spectrum of 4-nitrobenzoic acid **3o** in $CDCl_3$, 500 MHz.*

**3,6-bis(4-hydroxy-3-methoxyphenyl)tetrahydro-1H,4H-furo[3,4-c]furan-1,4-dione (1a')**

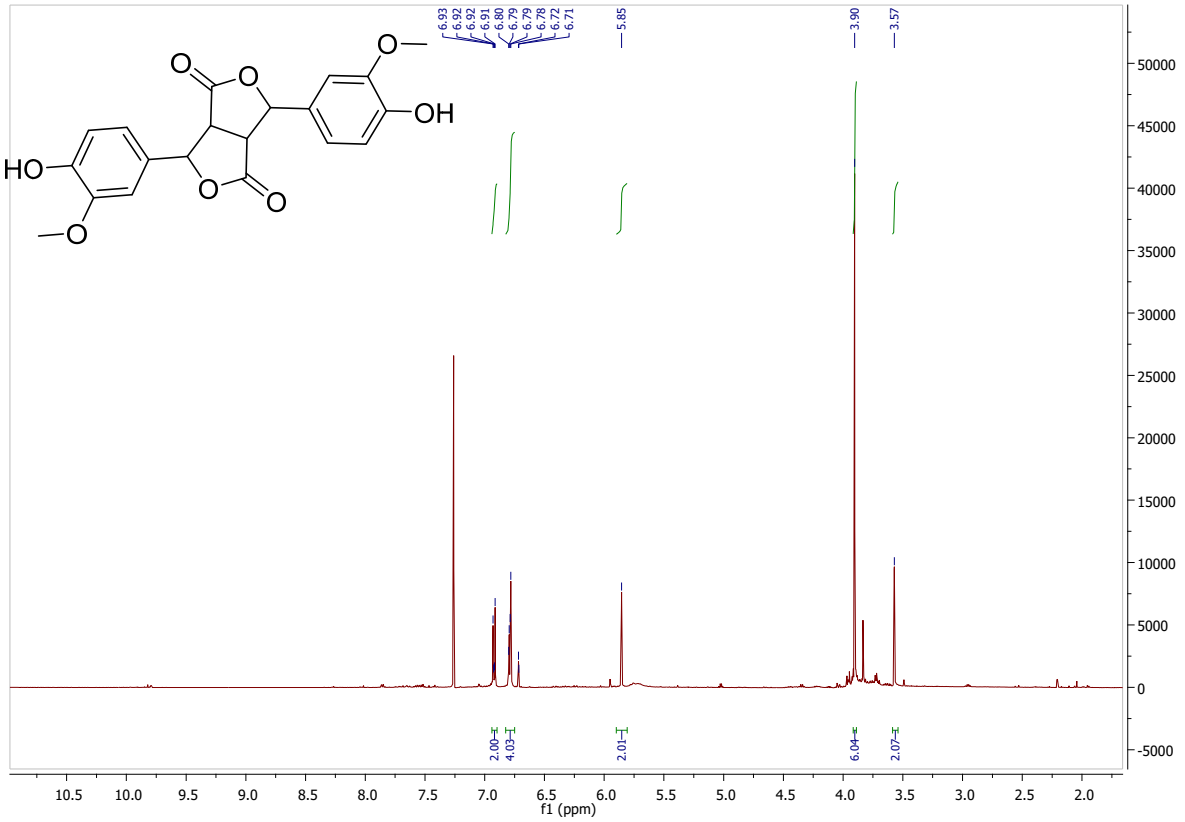



*Figure S3.29. $^{1}$H NMR spectrum of 3,6-bis(4-hydroxy-3-methoxyphenyl)tetrahydro-1H,4H-furo[3,4-c]furan-1,4-dione **1a'** in $CDCl_3$, 500 MHz.*

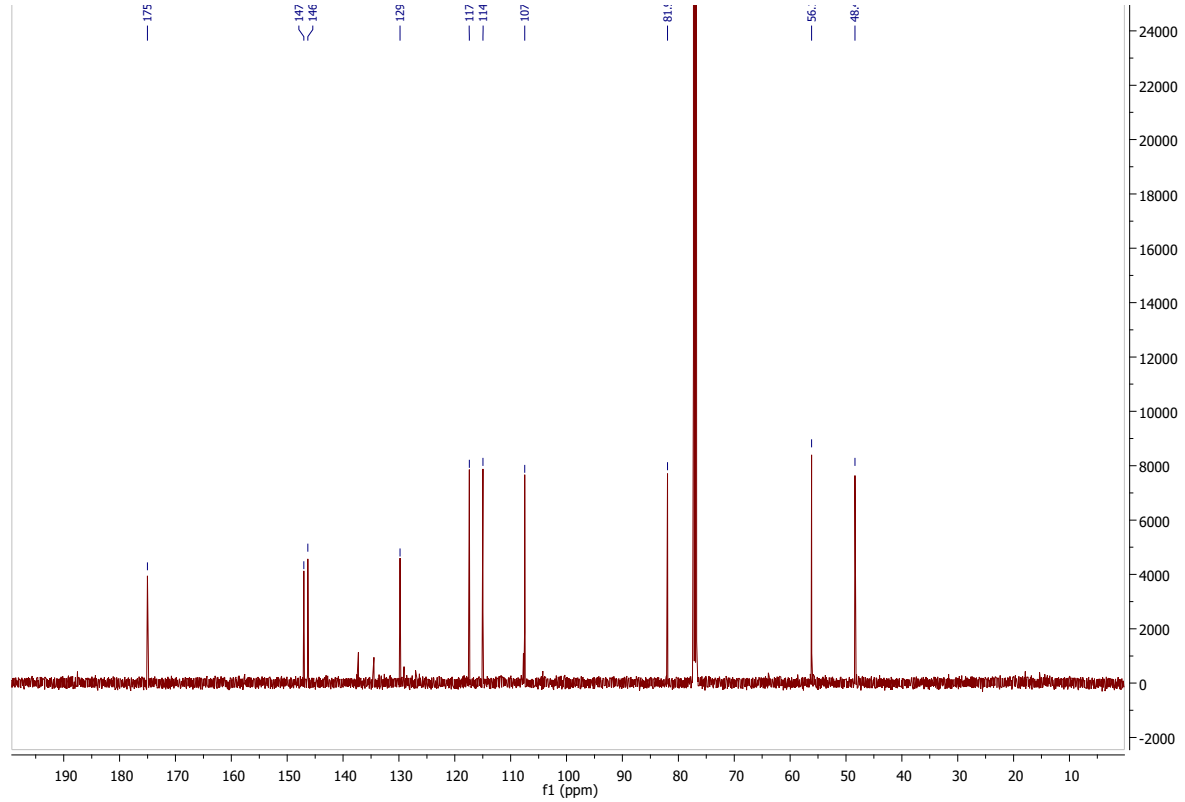



*Figure S3.30. $^{13}$C NMR spectrum of* 3,6-bis(4-hydroxy-3-methoxyphenyl)tetrahydro-1H,4H-furo[3,4-c]furan-1,4-dione **1a'** *in $CDCl_3$, 500 MHz.*

## 4. LITERATURE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