

## Electronic Supplementary Information (ESI)

### Sustainable oxidative cleavage of catechols for the synthesis of muconic acid and muconolactones including lignin upgrading

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## 1- General materials and instrumental information

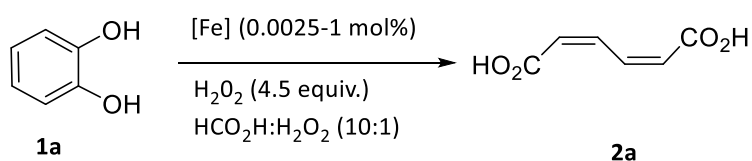
### Reagents

Solvents and chemicals including catechol substrates, metallic salts, hydrogen peroxide solutions, peracetic acid solution, acetic acid and formic acid were purchased from commercial suppliers and used without further purification. Hydrogenation batch reactions were pressurized under hydrogen atmosphere (*Airgas*, Ultra High Purity).

### Instrumental

$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR spectra were recorded either on a Bruker AVANCE III 400 or an Agilent DD2 400, at 25 °C (400 MHz for  $^1\text{H}$ , 100 MHz for  $^{13}\text{C}$ ). References for chemical shifts determination (in ppm) were solvent residual signals: DMSO- $d_6$ , 2.50 for  $^1\text{H}$  and 39.52 for  $^{13}\text{C}$ ;  $\text{CD}_3\text{OD}$ , 3.31 for  $^1\text{H}$  and 49.00 for  $^{13}\text{C}$ . FTIR spectra were recorded on a FTIR/Raman Thermo Nicolet 6700 apparatus. LCMS was performed on a Waters Xevo QToF high-resolution MS instrument. All hydrogenation reactions under  $\text{H}_2$  atmosphere were set-up in a 100 mL stainless-steel Parr reactor equipped with a mechanical stirrer. The loaded reactor was placed on a bench-top Parr stand equipped with a Parr 4843 reactor controller.

## 2- Table S1 – Evaluation of the activity of different metallic salts

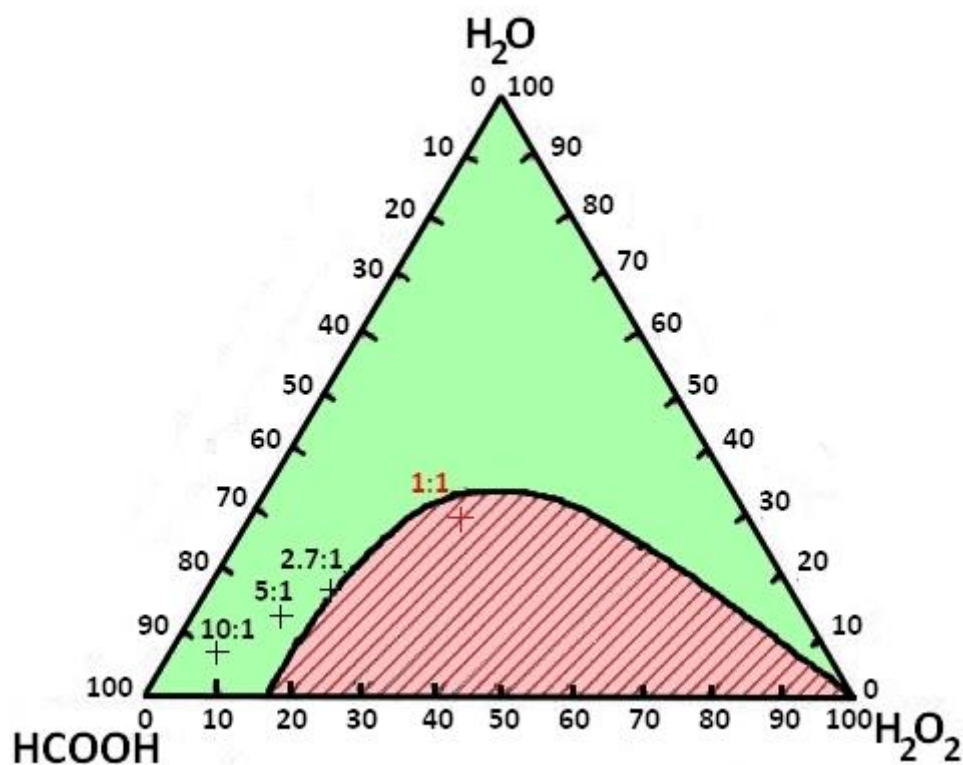


| Iron precursors   | Catalytic loading (mol%) | Yield <b>2a</b> (%) <sup>a</sup> |
|---|--------------------------|----------------------------------|
| $\text{Fe}_2\text{O}_3$   | 1                        | 2                                |
| $\text{Fe}_2\text{O}_3$   | 0.1                      | 5                                |
| $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$                                 | 0.1                      | 48                               |
| $\text{Na}[\text{Fe}(\text{EDTA})] \cdot 3\text{H}_2\text{O}$             | 0.1                      | 73                               |
| $\text{Fe}(\text{acac})_3$  | 0.1                      | 73                               |
| $\text{Fe}(\text{ClO}_4)_3 \cdot x \text{H}_2\text{O}$                    | 0.1                      | 74                               |
| $\text{K}_3[(\text{C}_2\text{O}_4)_3\text{Fe}] \cdot 3\text{H}_2\text{O}$ | 0.1                      | 75                               |
| $\text{Fe}_2(\text{SO}_4)_3 \cdot x \text{H}_2\text{O}$                   | 0.1                      | 76                               |
| $\text{FeCl}_2$   | 0.1                      | 76                               |
| $\text{FeCl}_3$ , anhydrous   | 0.1                      | 77                               |
| Ferric ammonium citrate   | 0.1                      | 78                               |
| $\text{Fe}(\text{CO})_5$  | 0.1                      | 78                               |
| $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$       | 0.1                      | 80                               |
| Iron, powder  | 0.1                      | 80                               |
| $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$                    | 0.1                      | 22                               |
| $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$       | 0.1                      | 23                               |
| $\text{CuCl}_2$   | 0.1                      | 32                               |
| $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$            | 0.1                      | 35                               |
| $\text{Fe}(\text{acac})_3$  | 0.01                     | 45                               |

|                                  |        |    |
|----------------------------------|--------|----|
| $K_3[(C_2O_4)_3Fe].3H_2O$        | 0.01   | 68 |
| $FeCl_3, \text{anhydrous}$       | 0.01   | 68 |
| $Fe_2(SO_4)_3 \cdot x H_2O$      | 0.01   | 72 |
| $Fe(ClO_4)_3 \cdot x H_2O$       | 0.005  | 40 |
| $FeCl_3, \text{anhydrous}$       | 0.005  | 47 |
| $K_3[(C_2O_4)_3Fe].3H_2O$        | 0.005  | 49 |
| Ferric ammonium citrate          | 0.005  | 49 |
| $FeCl_3, \text{anhydrous}$       | 0.005  | 62 |
| $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ | 0.005  | 66 |
| $Fe_2(SO_4)_3 \cdot xH_2O$       | 0.005  | 68 |
| $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ | 0.0025 | 10 |
| $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ | 0.0025 | 10 |
| Without iron precursor           | /      | 3  |

Reaction conditions: 10 mmol catechol added in 4.5 h, 4.5 equiv.  $H_2O_2$  (50 wt%),  $HCOOH:H_2O_2$  10:1 molar ratio, 20 °C, 20 h. <sup>a</sup> isolated yield (precipitated product filtration).

### 3- Explosivity range (red area) of the ternary system $HCOOH:H_2O_2:H_2O$



**Figure S1.** Explosivity range (red area) of the ternary system  $HCOOH:H_2O_2:H_2O$ , adapted from H. Klenk, P. H. Götz, R. Siegmeier and W. Mayr.<sup>[1]</sup> Displayed black points represent the different  $HCOOH:H_2O_2$  50 wt% ratio tested. The red point (1:1) falls into the explosivity range of the system and was thus not tested.

## **4- General experimental procedures**

### **4-1-Procedure for candlenut shell organosolv lignin extraction**

*Preparation of candlenut Shells:* Shells were washed in water to remove soil and debris then left to dry in air overnight. The shells were ground using an IKA MF 10 basic microfine grinder to a size smaller or equal to 0.5 mm. Moisture analyses on candlenut shells were performed routinely.

*Organosolv Lignin Extraction and Fractionation:* The procedure for extraction of candlenut shell organosolv lignin is identical to that reported by Anastas *et al.*<sup>[2]</sup> Representative procedure: Ground, cleaned and air-dried candlenut shells (153.05 g, 8 wt% moisture) were placed in a 2000 mL round bottom flask equipped with a Teflon coated stir bar. MeOH (500 mL) was added and the mixture was allowed to reflux overnight with stirring. Upon completion, the heterogeneous mixture was cooled and vacuum filtered. The retentate was rinsed with methanol, and the combined organic fractions were dried *in vacuo* until ~ 200 mL remained. The residue was poured in aliquots over stirred ice, inducing lignin to precipitate as an off-white solid. The ice-lignin mixture was vacuum filtered and allowed to dry on the filter. Once all the ice water was filtered, the retentate was collected as crude organosolv candlenut shell lignin (10.67 g, 7.8 wt% of candlenut shells). A portion (8.31 g, 1.38 wt% moisture) was placed in a 1000 mL round bottom flask equipped with a Teflon coated stir bar. Dichloromethane (DCM, 150 mL) was added to the flask and the mixture was allowed to stir at reflux for 12 hours. Upon completion, the mixture was cooled and vacuum filtered. The retentate was washed with DCM to yield purified organosolv candlenut shell lignin (8.24 g). Next, purified organosolv candlenut shell lignin was fractionated in ethyl acetate (EtOAc) by placing a portion (7.3 g) in EtOAc (400 mL) in a 1000 mL round bottom flask equipped with a Teflon coated stir bar and allowing to stir overnight at reflux. Upon completion, the mixture was vacuum filtered, and the retentate was washed with EtOAc. The combined organic fractions were concentrated *in vacuo* to yield EtOAc-soluble, purified organosolv candlenut shell lignin as a brown solid (3.21 g). The EtOAc-soluble organosolv candlenut shell lignin was acetylated then analyzed by NMR (Figures S54-S56, Section 6). Procedure for acetylation consisted in placing ~50 mg of EtOAc-soluble candlenut shell lignin to stir overnight, at room temperature, in a mixture of Ac<sub>2</sub>O:pyridine (2 mL, 1:1 v/v) before pouring the solution onto distilled water (200 mL) and filtering and rinsing the solid, acetylated EtOAc-soluble candlenut shell lignin. The non-acetylated EtOAc-soluble organosolv candlenut shell lignin was analysed by GPC (Table S2) as indicated.

*GPC:* Gel permeation chromatography (GPC) was performed at 40°C on a Shimadzu LC20AD instrument equipped with a Waters NR4E column using THF as solvent (1 mL/min) and UV detection at 254 nm and 280 nm with a Shimadzu SPD-M20A Photodiode array detector. Each lignin precipitate was dissolved fully in HPLC-grade THF (non-stabilized) and filtered through a 0.2 µm filter into sampling vials for analysis as indicated in the general experimental. Calibration was performed using polystyrene narrow standards in addition to eugenol (TCI) and synthesized 2-phenoxy-1-phenylethan-1-one. The polystyrene standards were analyzed at 254 nm while eugenol, 2-phenoxy-1-phenylethan-1-one and all lignin samples were analyzed at 280 nm. The log molecular weight vs retention time curve was fit using a linear or polynomial fit and was recorded with each batch of samples.

**Table S2:** GPC-determined Size of Organosolv Candlenut Shell EtOAc-soluble Lignin

| <b>Mp (g/mol)</b> | <b>Mw (g/mol)</b> | <b>Mn (g/mol)</b> | <b>Dispersity</b> |
|-------------------|-------------------|-------------------|-------------------|
| 730               | 997               | 1235              | 1.24              |

#### 4-2- Protocol for the candlenut shell EtOAc-soluble organosolv lignin depolymerization

Catalyst synthesis: The catalyst, a copper-doped porous metal oxide (Cu-PMO) was synthesized using an identical procedure as that reported in Anastas *et al.*<sup>[2]</sup> A solution of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (18.8 g, 0.05 mol, 1 equiv.), Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (30.76 g, 0.12 mol, 2.4 equiv.) and Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O (7.0g, 0.03 mol, 0.6 equiv.) in 300 mL distilled (DI) water was added dropwise to a stirring solution of Na<sub>2</sub>CO<sub>3</sub>·H<sub>2</sub>O (6.2 g, 0.05 mol, 1 equiv.) in 375 mL distilled water. The pH was kept constant at pH ~ 10 by adding aliquots of 1 M NaOH aqueous solution. Upon completion of the addition, the mixture is allowed to stir vigorously at room temperature overnight. The blue precipitate is collected by vacuum filtration and washed with 1.5 L distilled water. The filter cake is then suspended in a solution of Na<sub>2</sub>CO<sub>3</sub> solution (62 g, 0.5 mol, 10 equiv.) in DI H<sub>2</sub>O (250 mL, 2M) and allowed to stir at room temperature overnight. Upon completion, the precipitate is collected by vacuum filtration and washed with DI H<sub>2</sub>O (2.5 L). The filter is left to dry overnight in a 105 °C oven to obtain copper-doped hydrotalcite. The solid is ground by mortar and pestle and subjected to calcination at 460 °C in air for 24 h to obtain Cu-PMO as a green powder. The Cu-PMO was analyzed by XRPD and ICP-OES, showing the expected loss of hydrotalcite features and incorporation of metal ratios as reported in the literature.<sup>[2]</sup>

Depolymerization of candlenut shell EtOAc-soluble organosolv lignin towards catechols was performed using the procedure reported in Anastas *et al.*<sup>[2]</sup> Representative procedure: Dry EtOAc-soluble organosolv candlenut shell lignin (1.00 g) and catalyst Cu-PMO (500 mg) were placed a 100 mL stainless steel Parr reactor and MeOH (30 mL) was added. The reactor was sealed and placed on its stand and connected to a stirring and temperature controller. The heating mantle was lifted to the reactor and the reactor was pressurized with hydrogen (4 MPa) at room temperature. The reaction was started by turning stirring and heating on to the desired temperature, which constituted time t=0. The reaction was allowed to stir at 140 °C for 20 hours. Upon completion, the heating mantle was lowered and the stirring was stopped. The reactor was allowed to cool under a slow stream of water until it reached room temperature (~ 25 °C). The reactor was depressurized in a fume-hood (caution: flammable gas!), opened, and its contents were quantitatively filtered over a pre-tared medium porosity fritted filter. The solids were washed with methanol and the resulting filtrate was concentrated *in vacuo* in a pre-tared vial. The vial was left under high vacuum overnight prior to weighing to obtain the lignin oil mass (717.9 mg). The organic fraction was analyzed according to the procedures below by NMR (Figures S57-S59). In an instance, the lignin oil was used directly for substituted catechol cleavage (Section 4-3-11). In other instances, portions of the lignin oil were purified by column chromatography (silica gel, 20:1 DCM:MeOH then 9:1 DCM:MeOH) to obtain 4-propylcatechol **1i**, 4-(3-hydroxypropyl)catechol **1j** and 4-(3-methoxypropyl)catechol **1k** which were used as substrates in the substituted catechol cleavage individually (Sections 4-3-8 – 4-3-10).

**4-Propylcatechol 1i:** brown oil;  $R_f$  (silica gel, 20:1 DCM:MeOH): 0.44;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  6.66 – 6.54 (m, 2H), 6.45 (dd,  $J = 8.0, 2.1$  Hz, 1H), 2.40 (t,  $J = 7.6$  Hz, 2H), 1.55 (hex.,  $J = 7.4$  Hz, 2H), 0.88 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  144.53, 142.63, 134.03, 119.20, 115.08, 114.68, 37.02, 24.51, 12.61. Analytical data is identical to that reported in the literature.<sup>[2]</sup>

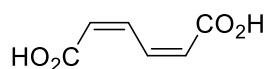
**4-(3-Hydroxypropyl)catechol 1j:** dark brown oil;  $R_f$  (silica gel, 9:1 DCM:MeOH): 0.28;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  6.64 (d,  $J = 8.0$  Hz, 1H), 6.60 (s, 1H), 6.48 (d,  $J = 8.0$  Hz, 1H), 3.60 – 3.47 (m, 2H), 2.50 (t,  $J = 7.7$  Hz, 2H), 1.82 – 1.69 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  144.65, 142.76, 133.52, 119.16, 115.06, 114.78, 60.88, 34.26, 30.98. Analytical data is identical to that reported in the literature.<sup>[2]</sup>

**4-(3-Methoxypropyl)catechol 1k:** dark brown oil;  $R_f$  (silica gel, 20:1 DCM:MeOH): 0.41;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  6.64 (d,  $J = 8.0$  Hz, 1H), 6.59 (s,  $J = 2.2$  Hz, 1H), 6.46 (dd,  $J = 8.0, 2.1$  Hz, 1H), 3.39 – 3.31 (m, 2H), 3.29 (s,  $J = 2.8$  Hz, 3H), 2.48 (t,  $J = 7.6$  Hz, 2H), 1.83 – 1.70 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  144.68, 142.83, 133.31, 119.20, 115.09, 114.80, 71.55, 57.30, 31.19, 31.07. Analytical data is identical to that reported in the literature.<sup>[2]</sup>

#### 4-3- Procedures for catechol cleavage

##### 4-3-1- Cleavage with *in situ* prepared performic acid, typical procedure

In a 25 mL round-bottomed flask, formic acid (10.40 g, 225.0 mmol) and  $\text{H}_2\text{O}_2$  (50 wt%, 3.06 g, 45.0 mmol, 4.5 equiv.) were stirred for 1 h at 20 °C to pre-form performic acid *in situ*. Then  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (3.9 mg, 0.1 mol%) was dissolved in the pre-mix, and catechol **1a** (1.10 g, 10.0 mmol) dissolved in 4 mL of  $\text{HCOOH}$  was added in 4h30 with a syringe pump. After the end of the addition, the mixture was stirred for 20 more hours to allow complete spontaneous peroxy decomposition (KI/starch test was negative at this time). Noticeably, NMR monitoring showed that no catechol remained in the reaction mixture only 1 h after the end of the addition. The obtained insoluble muconic acid **2a** was then filtered off, washed with a minimum amount of  $\text{H}_2\text{O}$ , and dried in a desiccator ( $\text{P}_2\text{O}_5$ ) (light grey solid, 1.19 g, 84% isolated yield). Purity was checked by  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ ). In a separate experiment, filtrate concentration followed by acetone washing allowed to recover 4% more muconic acid with 90% purity.



***cis,cis*-2,4-Hexadienedioic acid (*cis,cis*-Muconic acid) 2a:** Light grey solid (1.19 g, 84%);  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  12.73 (s, 2H), 7.80 – 7.65 (m, 2H), 6.08 – 5.91 (m, 2H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  166.81, 136.88, 125.36. NMR spectroscopic data ( $^1\text{H}$ ) are in accordance with previously published values.<sup>[3]</sup>

##### 4-3-2- Cleavage with *in situ* preparation of peracetic acid catalyzed by $\text{H}_2\text{SO}_4$ , typical procedure

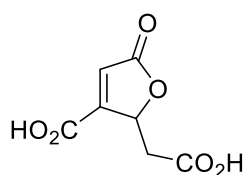
In a 25 mL round-bottomed flask, acetic acid (2.70 g, 45.0 mmol),  $\text{H}_2\text{O}_2$  (50 wt%, 3.06 g, 45.0 mmol, 4.5 equiv.) and concentrated  $\text{H}_2\text{SO}_4$  (0.057 g, 1 wt%) were stirred for 24 h at 20 °C to pre-form peracetic acid *in situ*. Then  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (3.9 mg, 0.1 mol%) was dissolved in the pre-mix, and catechol **1a** (1.10 g, 10.0 mmol) dissolved in 4 mL of  $\text{HCOOH}$  was added in 4h30 with a syringe pump. After the

end of the addition, the mixture was stirred for 20 more hours. The obtained insoluble muconic acid **2a** was then filtered off, washed with a minimum amount of H<sub>2</sub>O, and dried in a desiccator (P<sub>2</sub>O<sub>5</sub>) (light grey solid, 0.36 g, 25% isolated yield).

#### 4-4- Representative procedure for the substituted catechol cleavage:

##### 4-3-1- Protocatechuic acid **1h** cleavage – Representative procedure

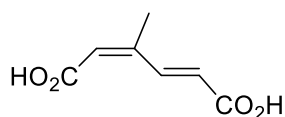
In a 25 mL round-bottomed flask, formic acid (5.20 g, 112.0 mmol) and H<sub>2</sub>O<sub>2</sub> (50 wt%, 1.53 g, 22.5 mmol) were stirred for 1 h at 20 °C to pre-form performic acid *in situ*. Then (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (2.0 mg, 0.1 mol %) was dissolved in the pre-mix, and protocatechuic acid **1h** (0.77 g, 5.0 mmol) was added portionwise in 2 h (note that depending on the substrate nature and solubility in HCOOH, it was either added portionwise or in solution in HCOOH). After the end of the addition, the mixture was stirred for 20 more hours, until all peroxides were spontaneously decomposed (KI/starch test negative). The medium was then concentrated *in vacuo* to leave a grey solid residue. Further purification by basic/acidic successive washings: the residue was stirred with 10 mL H<sub>2</sub>O and 10 mL AcOEt, and NaHCO<sub>3</sub> was added until no CO<sub>2</sub> was formed anymore (pH 8). The phases were separated, and the aqueous phase was extracted again with 2 x 10 mL AcOEt. Then the aqueous phase was acidified to pH 2 with HCl 12 M, extracted with 3 x 10 mL AcOEt, the organic extracts were combined, dried with MgSO<sub>4</sub>, filtered and concentrated *in vacuo* to leave leave **3h** as a grey solid residue (0.697 g, 68% at purity estimated at 90% by <sup>1</sup>H NMR).



**4-Carboxyl-5-carboxymethyl-2-furanone 3h:** Grey solid (0.627 g, 68%); IR: 2933, 2620, 1700, 1603, 1395, 1370, 1272, 1211, 1167, 1008, 932, 888, 862, 770, 680, 601, 455 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 12.94 (br s, 3H), 6.81 (d, *J* = 2.1 Hz, 1H), 5.53 (ddd, *J* = 8.0, 3.2, 2.1 Hz, 1H), 3.07 (dd, *J* = 16.6, 3.2 Hz, 1H), 2.63 (dd, *J* = 16.6, 8.0 Hz, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 171.01, 170.59, 162.29, 158.13, 126.09, 78.66, 36.73; HRMS (ESI) *m/z* calculated for C<sub>7</sub>H<sub>5</sub>O<sub>6</sub> [M-H]<sup>-</sup>: 185.0086, measured 185.0091. NMR spectroscopic data (<sup>1</sup>H, <sup>13</sup>C) are in accordance with previously published values.<sup>[4]</sup>

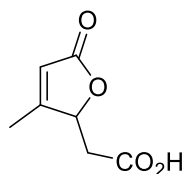
##### 4-3-2- 4-Methylcatechol **1b** cleavage

The reaction was performed as described above. At the end of the reaction, the formed, insoluble 3-methylmuconic acid was filtered off, washed with H<sub>2</sub>O and dried (13%). The filtrate was concentrated *in vacuo*, and the residue was purified by successive basic/acidic washings as described above. Further purification was performed by crystallization in EtOH.



**(2Z,4E)-3-Methyl-2,4-hexadienedioic acid (cis,trans-3-methylmuconic acid) 2b:** White powder (0.203 g, 13%); <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) δ 8.63 (d, *J* = 16.0 Hz, 1H), 6.19 (d, *J* = 16.0 Hz, 1H), 5.99 (s, 1H), 2.06

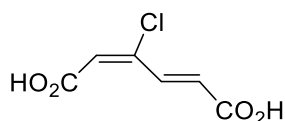
(d,  $J = 1.4$  Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  169.94, 168.60, 148.69, 141.82, 125.38, 125.03, 20.52.



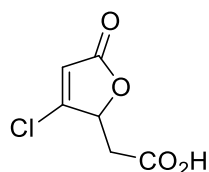
**4-Methyl-5-carboxymethyl-2-furanone 3b:** White crystals (1.106 g, 71%);  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  5.88 (m, 1H), 5.31 (m, 1H), 2.97 (dd,  $J = 16.3, 4.1$  Hz, 1H), 2.53 (dd,  $J = 16.3, 8.2$  Hz, 1H), 2.12 (dd,  $J = 1.6, 0.8$  Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  175.29, 172.69, 171.42, 117.57, 82.95, 37.71, 13.77. NMR spectroscopic data ( $^1\text{H}$ ,  $^{13}\text{C}$ ) are in accordance with previously published values.<sup>[5]</sup>

#### 4-3-3- 4-chlorocatechol 1c cleavage

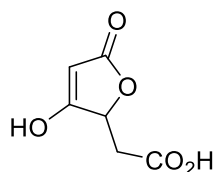
The reaction was performed as described above. At the end of the reaction, the insoluble *trans,trans*-3-chloromuconic acid **2c** formed was separated from the mixture by filtration (18%). The filtrate residue was concentrated and a mixture of two muconolactones, 4-chloro-5-carboxymethyl-2-furanone **3c-i** and 4-hydroxy-5-carboxymethyl-2-furanone **3c-ii**, was obtained in a 3:2 ratio (0.316 g, 45% and 30% resp.).



**(2E,4E)-3-Chloro-2,4-hexadienedioic acid (*trans,trans*-3-chloromuconic acid) 2c:** White solid (78 mg, 18%); IR: 3085, 2827, 2649, 2557, 1674, 1628, 1585, 1405, 1307, 1273, 1236, 1112, 986, 926, 891, 702, 670, 547, 516  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  13.16 (br s, 2H), 8.40 (d,  $J = 15.1$  Hz, 1H), 6.45 (s, 1H), 6.40 (d,  $J = 15.1$  Hz, 1H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{DMSO}-d_6$ )  $\delta$  166.37, 164.52, 143.04, 135.46, 128.59, 125.93; HRMS (ESI)  $m/z$  calculated for  $\text{C}_6\text{H}_4\text{ClO}_4$   $[\text{M}-\text{H}]^-$  174.9798, measured 174.9794.



**4-Chloro-5-carboxymethyl-2-furanone 3c-i:**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  6.59 (s, 1H), 5.43 (dd,  $J = 7.9, 3.5$  Hz, 1H), 2.98 (dd,  $J = 16.8, 3.5$  Hz, 1H), 2.63 (dd,  $J = 16.8, 7.9$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO}-d_6$ )  $\delta$  170.25, 169.76, 159.93, 118.19, 80.09, 35.89. NMR spectroscopic data ( $^1\text{H}$ ) are in accordance with previously published values.<sup>[6]</sup>



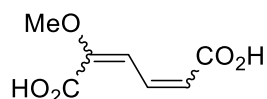
**4-Hydroxy-5-carboxymethyl-2-furanone 3c-ii:**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  5.04 (dd,  $J = 8.8, 3.3$  Hz, 1H), 4.92 (s, 1H), 2.84 (dd,  $J = 16.2, 3.3$  Hz, 1H), 2.41 (dd,  $J = 16.2, 8.8$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,



DMSO-*d*<sub>6</sub>)  $\delta$  181.28, 173.11, 170.91, 88.15, 75.38, 37.01. NMR spectroscopic data (<sup>1</sup>H) are in accordance with previously published values.<sup>[7]</sup>

#### 4-3-4- 3-Methoxycatechol cleavage 1d

The reaction was performed as described above. At the end of the reaction, one of the formed, insoluble 2-methoxy-2,4-hexadienedioic acid isomers (**a**) was filtered off, washed with H<sub>2</sub>O and dried (3%). The filtrate was concentrated *in vacuo*, and the residue was treated by successive basic/acidic washings as described above. The residue contained a mixture of the three other muconic acid analogue isomers (**b,c,d**), plus the muconolactone product (**3d**), in a **b:c:d:3d** ratio of 10:14:15:6 (total mass 0.676 g, 8%, 11%, 12%, 5%, considered they represent 90% of the products present) (cf <sup>1</sup>H NMR spectrum of the crude mixture, Figure S24). One of the muconic acid-structured isomer (**b**) was left as an insoluble solid by adding a small amount of AcOEt to the residue, and was then recovered by filtration and washed with a very small amount of AcOEt (3%). This new filtrate was concentrated again, and separation by silica gel chromatography (eluent AcOEt:AcOH 9:1) allowed to isolate another muconic acid-structured isomer (**c**, 3%). The last muconic acid analogue isomer (**d**) and the muconolactone (**3d**) could not have been isolated.



#### 2-Methoxy-2,4-hexadienedioic acid 2d

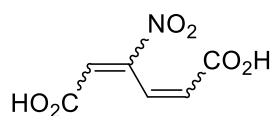
**Isomer a:** White powder (0.048 g, 3%); <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD)  $\delta$  7.61 (t, *J* = 11.5 Hz, 1H), 7.34 (d, *J* = 11.5 Hz, 1H), 5.67 (dd, *J* = 11.5, 1.1 Hz, 1H), 3.74 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>3</sub>OD)  $\delta$  169.96, 165.46, 153.74, 140.63, 118.29, 107.32, 56.36.

**Isomer b:** Light grey powder (0.050 g, 3%); <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD)  $\delta$  8.21 (dd, *J* = 15.3, 11.5 Hz, 1H), 6.07 (d, *J* = 11.5 Hz, 1H), 5.95 (d, *J* = 15.3 Hz, 1H), 3.74 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>3</sub>OD)  $\delta$  170.53, 168.04, 142.19, 135.17, 122.60, 109.38, 56.51.

**Isomer c:** Dark brown oil (0.049 g, 3%); <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD)  $\delta$  6.92 (dd, *J* = 9.9, 5.1 Hz, 1H), 6.08 (d, *J* = 9.9 Hz, 1H), 4.33 (d, *J* = 5.1 Hz, 1H), 3.40 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>3</sub>OD)  $\delta$  163.23, 145.23, 133.93, 121.76, 105.81, 65.35, 53.07.

#### 4-3-5- 4-Nitrocatechol 1e cleavage

The reaction and workup were performed as described above. The unreacted substrate **1e** was extracted with AcOEt after basification with an aqueous solution of NaHCO<sub>3</sub> (15% recovered). The product **2e** was then recovered with AcOEt after reacidification of the aqueous phase with HCl 5M. A mixture of three isomers was obtained in a ratio 20:11:7 in 39% yield.



#### 3-Nitro-2,4-hexadienedioic acid 2e

Dark yellow oil (369 mg, 39%). Mixture of three isomers **a**:**b**:**c**, ratio 20:11:7.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )

Isomer **a**:  $\delta$  8.33 (d,  $J$  = 6.0 Hz, 1H), 6.81 (dd,  $J$  = 6.0, 1.8 Hz, 1H), 6.00 (d,  $J$  = 1.8 Hz, 1H).

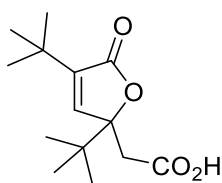
Isomer **b**:  $\delta$  7.76 (d,  $J$  = 9.1 Hz, 1H), 7.06 (d,  $J$  = 9.1 Hz, 1H), 6.27 (s, 1H).

Isomer **c**:  $\delta$  7.92 (d,  $J$  = 5.5 Hz, 1H), 6.75 (d,  $J$  = 5.5 Hz, 1H), 5.69 (s, 1H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, DMSO- $d_6$ ), mixture of 3 isomers **a**, **b** and **c**:  $\delta$  172.10, 168.16, 166.77, 168.85, 159.66, 155.66, 146.45 (**c**), 142.13 (**b**), 139.49, 134.03, 130.16 (**b**), 124.85 (**a**), 123.38 (**c**), 117.93 (**b**), 114.65 (**b**), 103.39 (**a**), 102.71 (**c**), 79.22.

#### 4-3-6- 3,5-Di-tert-butylcatechol **1f** cleavage

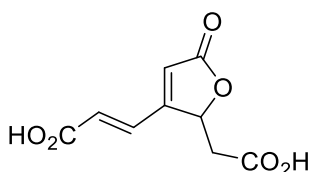
The reaction was performed as described above. At the end of the reaction, the medium was concentrated in vacuo, and the residue was purified by successive basic/acidic washings as described above. Further purification was performed by crystallization in EtOH.



**3,5-Di-tert-butyl-5-carboxymethylfuranone 3f**: White crystals (0.934 g 37%);  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  7.22 (s, 1H), 2.92 (d,  $J$  = 13.9 Hz, 1H), 2.85 (d,  $J$  = 13.9 Hz, 1H), 1.24 (s, 9H), 1.00 (s, 9H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  173.88, 172.88, 149.08, 144.14, 90.58, 38.66, 38.48, 32.47, 28.42, 25.63. NMR spectroscopic data ( $^1\text{H}$ ,  $^{13}\text{C}$ ) are in accordance with previously published values.<sup>[6]</sup>

#### 4-3-7- Caffeic acid **1g** cleavage

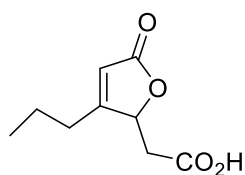
The reaction was performed as described above. At the end of the reaction time, the insoluble, unreacted caffeic acid **1g** left was then filtered off (37% recovered). Further purification of the product **3g** was performed by recrystallization in EtOH.



**4-(2-carboxyethenyl)-5-carboxymethyl-2-furanone 3g**: Red solid (634 mg, 58%); IR: 3105, 2662, 1694, 1516, 1395, 1272, 1166, 1012, 981, 945, 860, 821, 775, 666, 623, 602, 579, 504, 463  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  7.50 (d,  $J$  = 16.3 Hz, 1H), 6.44 (s, 1H), 6.42 (d,  $J$  = 16.3 Hz, 1H), 5.68 (dd,  $J$  = 8.3, 3.3 Hz, 1H), 3.07 (dd,  $J$  = 16.7, 3.3 Hz, 1H), 2.58 (dd,  $J$  = 16.7, 8.3 Hz, 1H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  172.32, 171.01, 166.74, 162.50, 132.29, 127.78, 120.76, 78.83, 37.40; HRMS (ESI)  $m/z$  calculated for  $\text{C}_9\text{H}_7\text{O}_6$  [ $\text{M}-\text{H}$ ] $^-$ : 211.0243, measured 211.0245.

#### 4-3-8- 4-*n*-propylcatechol **1i** cleavage

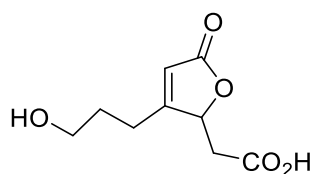
The reaction and workup were performed as described above.



**4-(Prop-1-yl)-5-carboxymethyl-2-furanone 3i:** Dark solid (11.7 mg, 73%); IR (cm<sup>-1</sup>): 3479, 2964, 2933, 2876, 1720, 1635, 1403, 1323, 1274, 1223, 1176, 1091, 1009, 932, 865, 839, 744, 659, 587, 455; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) δ 5.89 (d, *J* = 1.9 Hz, 1H), 5.34 (ddd, *J* = 8.2, 4.0, 1.9 Hz, 1H), 2.97 (dd, *J* = 16.3, 4.0 Hz, 1H), 2.52 (dd, *J* = 16.3, 8.2 Hz, 1H), 2.46 – 2.24 (m, 2H), 1.76 – 1.53 (m, 2H), 1.02 (t, *J* = 7.3 Hz, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>3</sub>OD) δ 175.57, 175.32, 172.74, 116.30, 82.35, 37.93, 30.86, 21.35, 14.06; HRMS (ESI) *m/z* calculated for C<sub>9</sub>H<sub>11</sub>O<sub>4</sub> [M-H]<sup>-</sup> 183.0657, measured 183.0647.

#### 4-3-9- 4-(3-Hydroxypropyl)catechol 1j cleavage

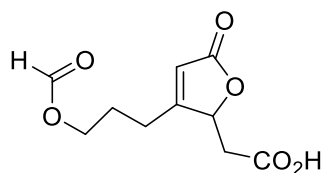
The reaction and workup were performed as described above. A mixture of two muconolactones was obtained, in a 5:2 ratio, one of them **3j-ii** resulting from the formylation of the expected muconolactone **3j-i** under the reaction conditions. The two compounds were not separated (28.6 mg, 60% **3j-ii** and 24% **3j-i**).



#### 4-(3-Hydroxyprop-1-yl)-5-carboxymethyl-2-furanone 3j-i

<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) δ 5.92 (d, *J* = 1.6 Hz, 1H), 5.37 (ddd, *J* = 8.1, 3.8, 1.6 Hz, 1H), 3.63 (t, *J* = 6.3 Hz, 2H), 2.99 (dd, *J* = 16.4, 3.8 Hz, 1H), 2.55 (dd, *J* = 16.4, 8.1 Hz, 1H), 2.61 – 2.37 (m, 2H), 1.90 – 1.80 (m, 2H). HRMS (ESI) *m/z* calculated for C<sub>9</sub>H<sub>11</sub>O<sub>5</sub> [M-H]<sup>-</sup> 199.0606, measured 199.0607.

<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>3</sub>OD) of the mixture (**3l**) + (**3n**): δ 175.38, 175.24, 175.07, 174.45, 172.71, 172.66, 162.85 (**3l**), 116.61, 116.37, 82.37, 82.29, 63.79 (**3l**), 61.84 (**3n**), 37.85, 37.78, 30.81 (**3n**), 27.00 (**3l**), 25.43, 25.40.

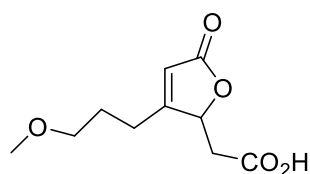


#### 4-(3-Formyloxyprop-1-yl)-5-carboxymethyl-2-furanone 3j-ii

<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) δ 8.10 (s, 1H), 5.94 (d, *J* = 1.7 Hz, 1H), 5.37 (ddd, *J* = 8.1, 3.8, 1.7 Hz, 1H), 4.24 (t, *J* = 6.3 Hz, 2H), 2.99 (dd, *J* = 16.4, 3.8 Hz, 1H), 2.55 (dd, *J* = 16.4, 8.1 Hz, 1H), 2.61 – 2.37 (m, 2H), 2.09 – 1.93 (m, 2H). HRMS (ESI) *m/z* calculated for C<sub>10</sub>H<sub>11</sub>O<sub>6</sub> [M-H]<sup>-</sup> 227.0556, measured 227.0578.

#### 4-3-10- 4-(3-methoxyprop-1-yl)catechol 1k cleavage

The reaction and workup were performed as described above.



**4-(3-methoxyprop-1-yl)-5-carboxymethyl-2-furanone 3k:** Dark solid (25.6 mg, 86%); IR (cm<sup>-1</sup>): 2930, 1717, 1637, 1398, 1174, 1099, 1009, 932, 865, 646, 592, 453; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) δ 5.91 (s, 1H), 5.36 (dd, *J* = 8.4, 3.8 Hz, 1H), 3.46 (t, *J* = 6.1 Hz, 2H), 3.33 (s, 3H), 2.98 (dd, *J* = 16.3, 3.8 Hz, 1H), 2.54 (dd, *J* = 16.3, 8.4 Hz, 1H), 2.57 – 2.41 (m, 2H), 1.94 – 1.82 (m, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>3</sub>OD) δ 175.27, 175.23, 172.68, 116.41, 82.35, 72.52, 58.83, 37.82, 28.02, 25.69; HRMS (ESI) *m/z* calculated for C<sub>10</sub>H<sub>13</sub>O<sub>5</sub> [M-H]<sup>-</sup> 213.0763, measured 213.0747.

#### 4-3-11- Cleavage of catechol mixture obtained from C-lignin depolymerisation

The reaction on the catechol mixture obtained from C-lignin depolymerization 4-(*n*-propyl)catechol **1i**, 4-(3-hydroxyprop-1-yl)catechol **1j** and 4-(3-methoxyprop-1-yl)catechol **1k** (in ratio 15:10:7) and workup were performed as described above. A mixture of 4 muconolactones **3i**, **3j-i**, **3j-ii** and **3k** as described above was obtained, in ratio 7:2:5:3.

#### 5- Determination of different green chemistry metrics values (Table S3)

| Metric                         | Unit   | Value based on PFA | Value based on H <sub>2</sub> O <sub>2</sub> |
|--------------------------------|--|--------------------|--|
| AE (atom economy)              | %  | 60.7               | 79.8   |
| RME (reaction mass efficiency) | % kg <sub>prod</sub> /kg <sub>reagents</sub> | 30.0               | 44.3   |
| MI (mass intensity)            | kg <sub>engaged</sub> /kg <sub>product</sub> | 15.6               | 15.6   |
| MI without H <sub>2</sub> O    | kg <sub>engaged</sub> /kg <sub>product</sub> | 14.3               | 14.3   |
| CE (carbon efficiency)         | %  | 75.0               | 100.0  |
| MP (mass productivity)         | % kg <sub>prod</sub> / kg <sub>engaged</sub> | 6.4                | 6.4  |
| MP without H <sub>2</sub> O    | % kg <sub>prod</sub> / kg <sub>engaged</sub> | 7.0                | 7.0  |
| E factor <sup>a</sup>          | kg <sub>waste</sub> /kg <sub>prod</sub>      | 2.0                | 2.0  |

a: Calculated considering that 90% of formic acid and water are recycled.

## 6- NMR spectra

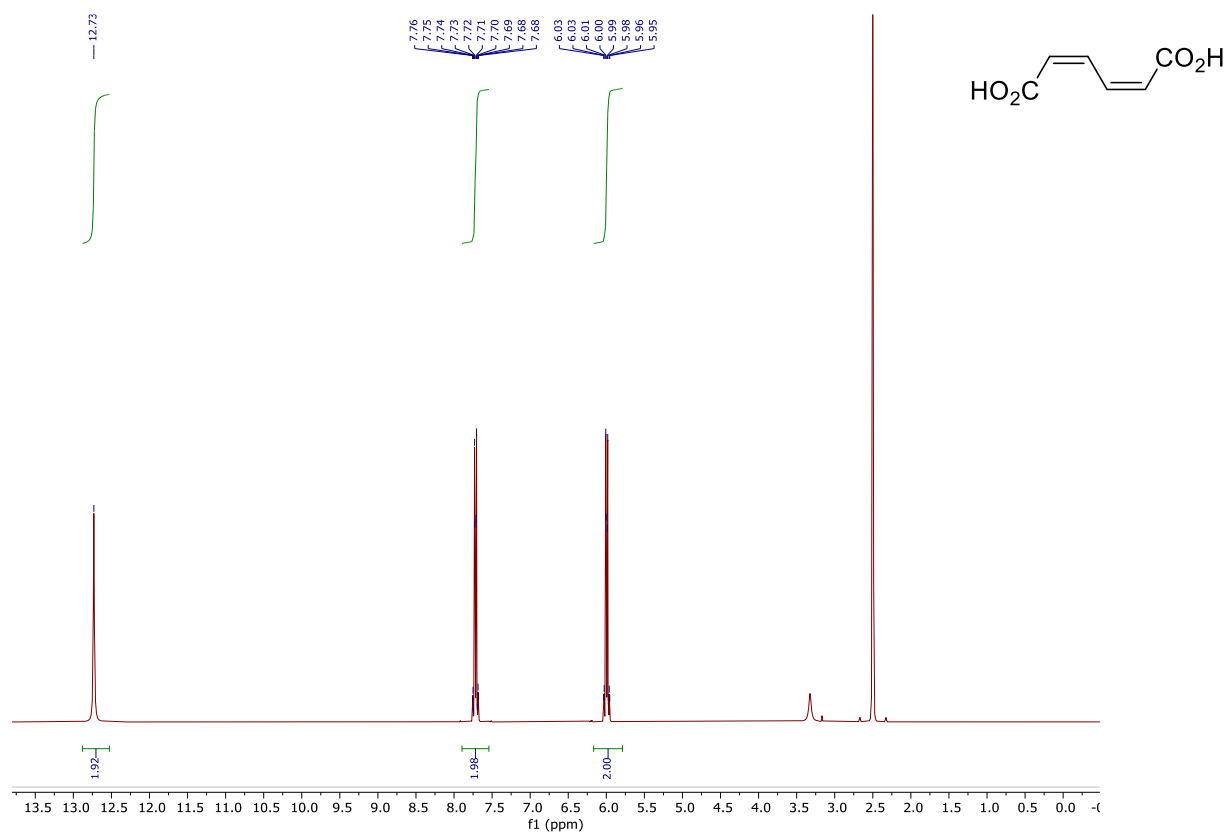


Figure S2. <sup>1</sup>H NMR spectrum of *cis,cis*-Muconic acid 2a.

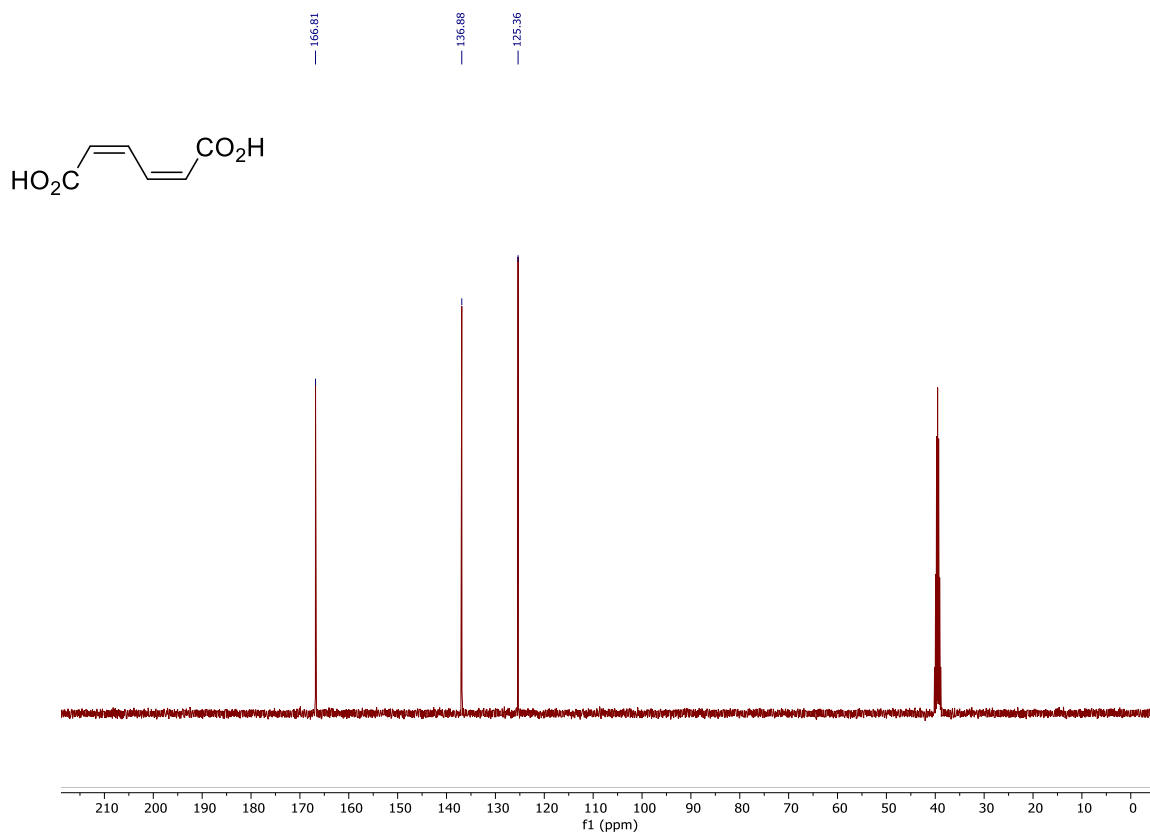


Figure S3. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of *cis,cis*-Muconic acid 2a.

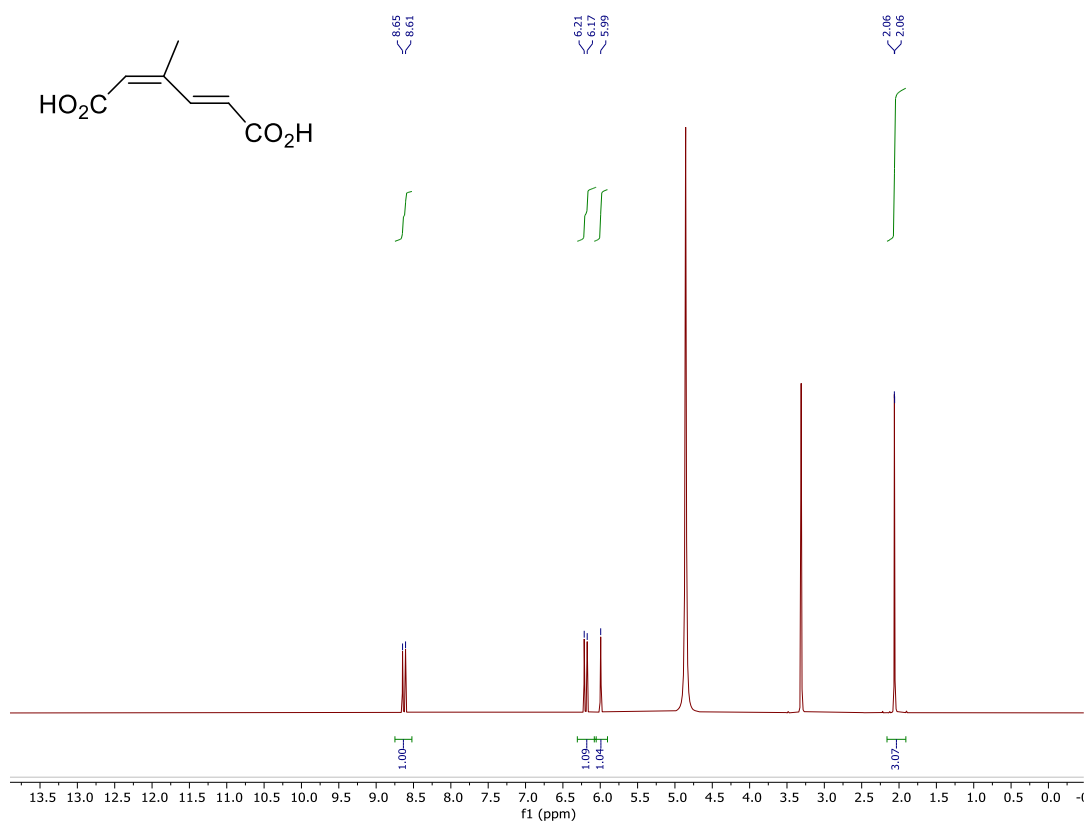


Figure S4.  $^1\text{H}$  NMR spectrum of *cis,trans*-3-Methylmuconic acid 2b.

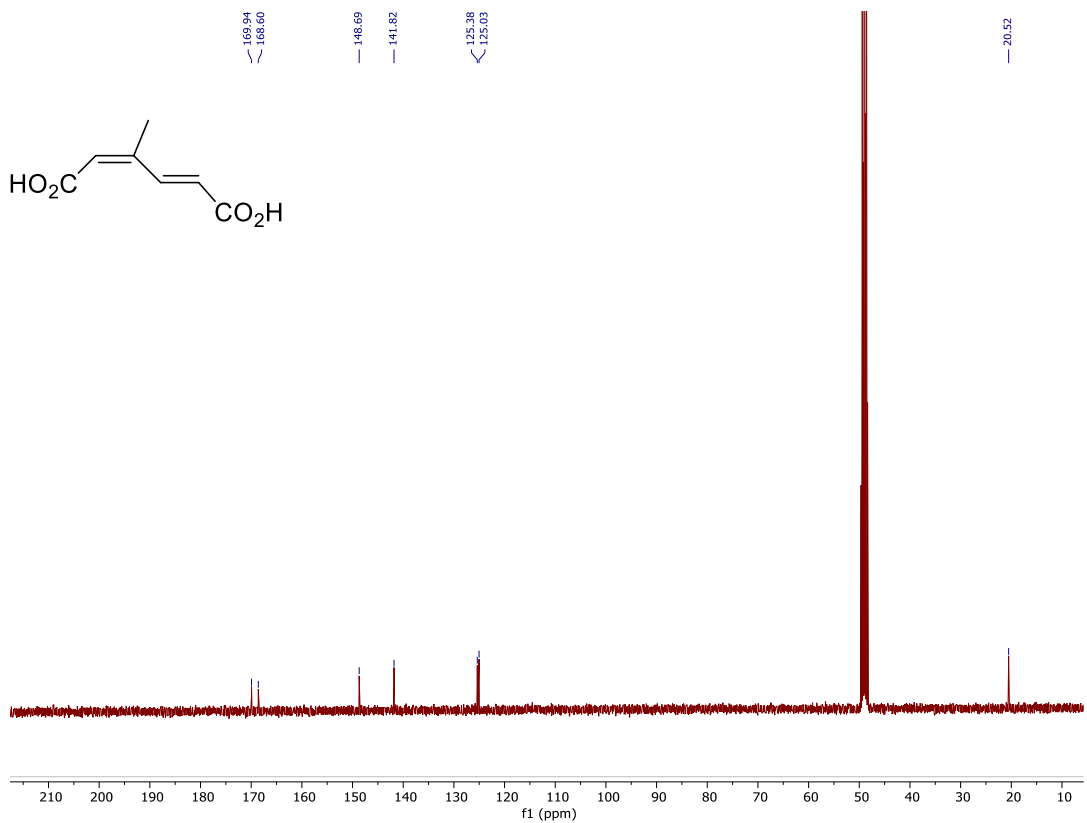


Figure S5.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of *cis,trans*-3-Methylmuconic acid 2b.

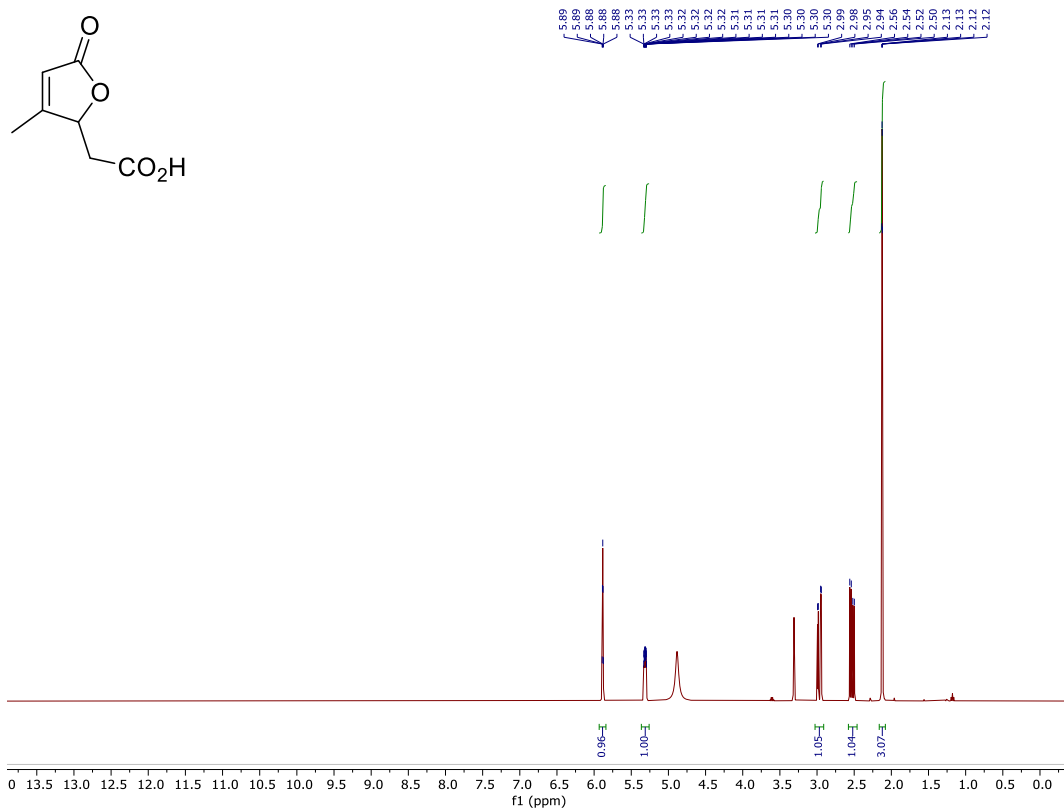


Figure S6. <sup>1</sup>H NMR spectrum of 4-Methyl-5-carboxymethyl-2-furanone 3b.

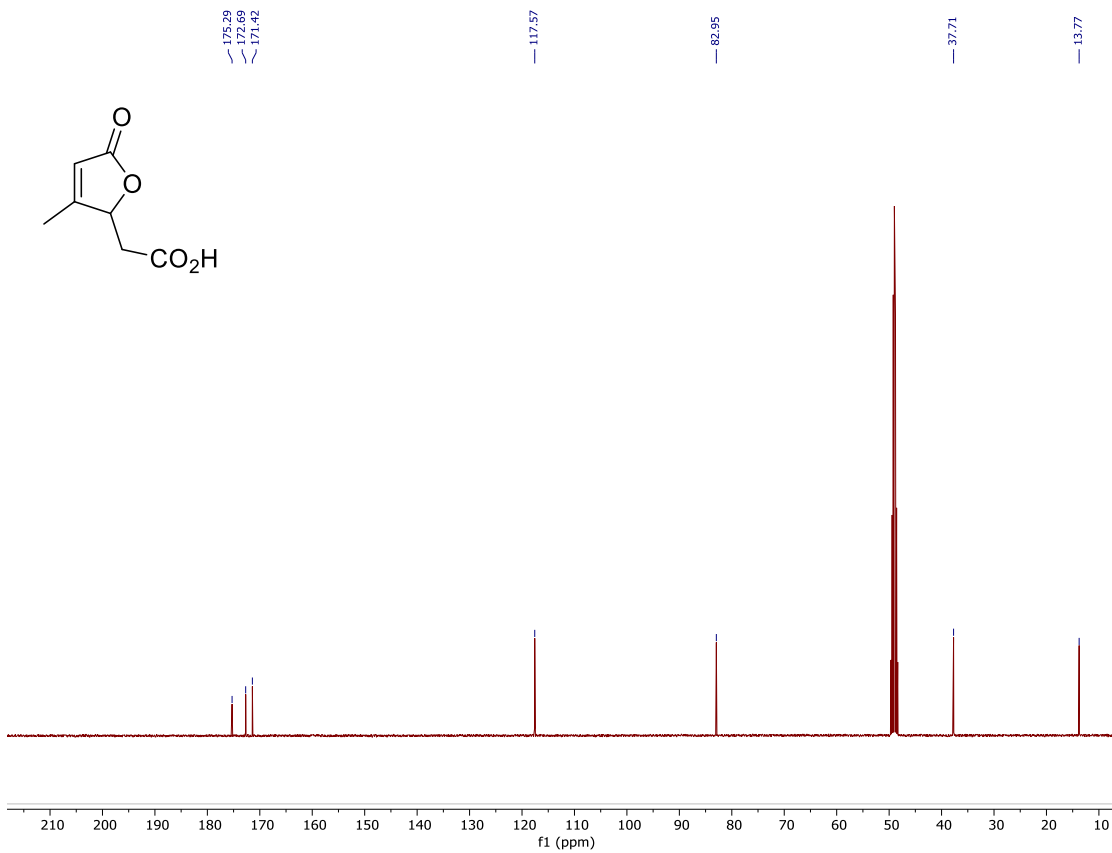


Figure S7. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 4-Methyl-5-carboxymethyl-2-furanone 3b.

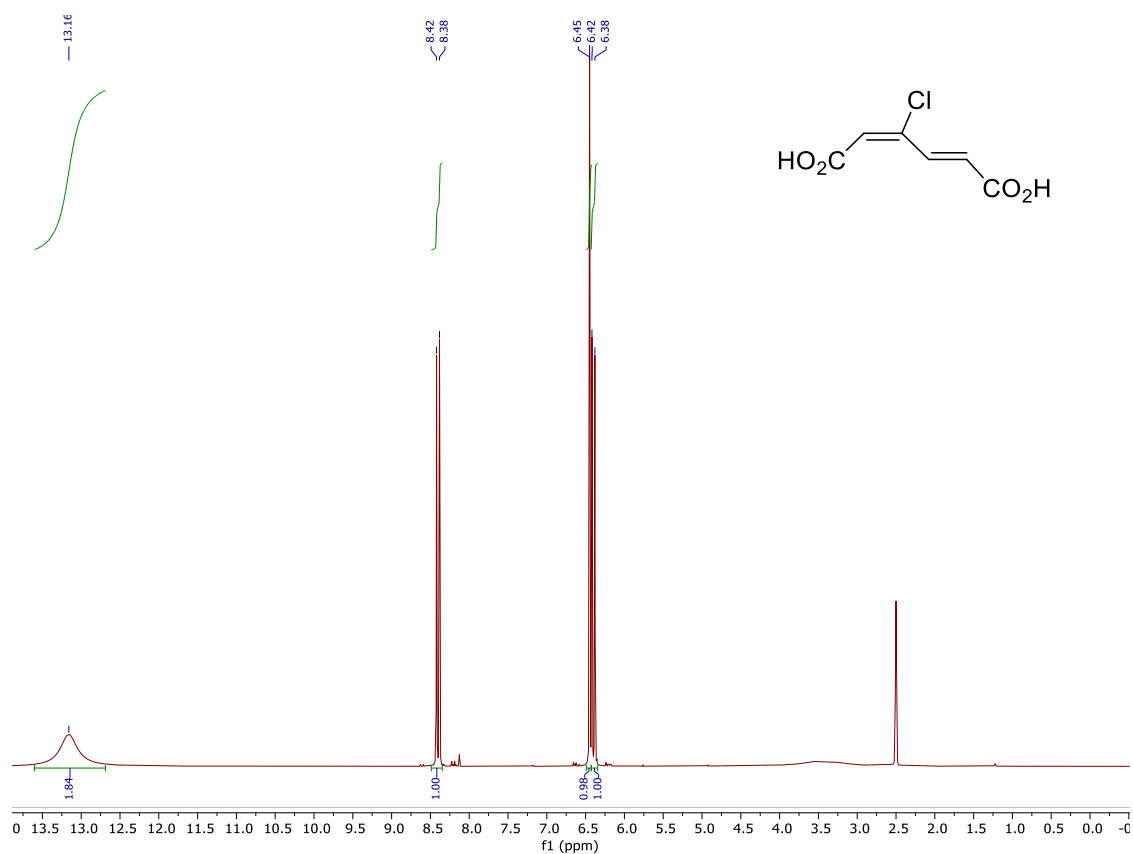


Figure S8.  $^1\text{H}$  NMR spectrum of *trans,trans*-3-chloromuconic acid **2c**.

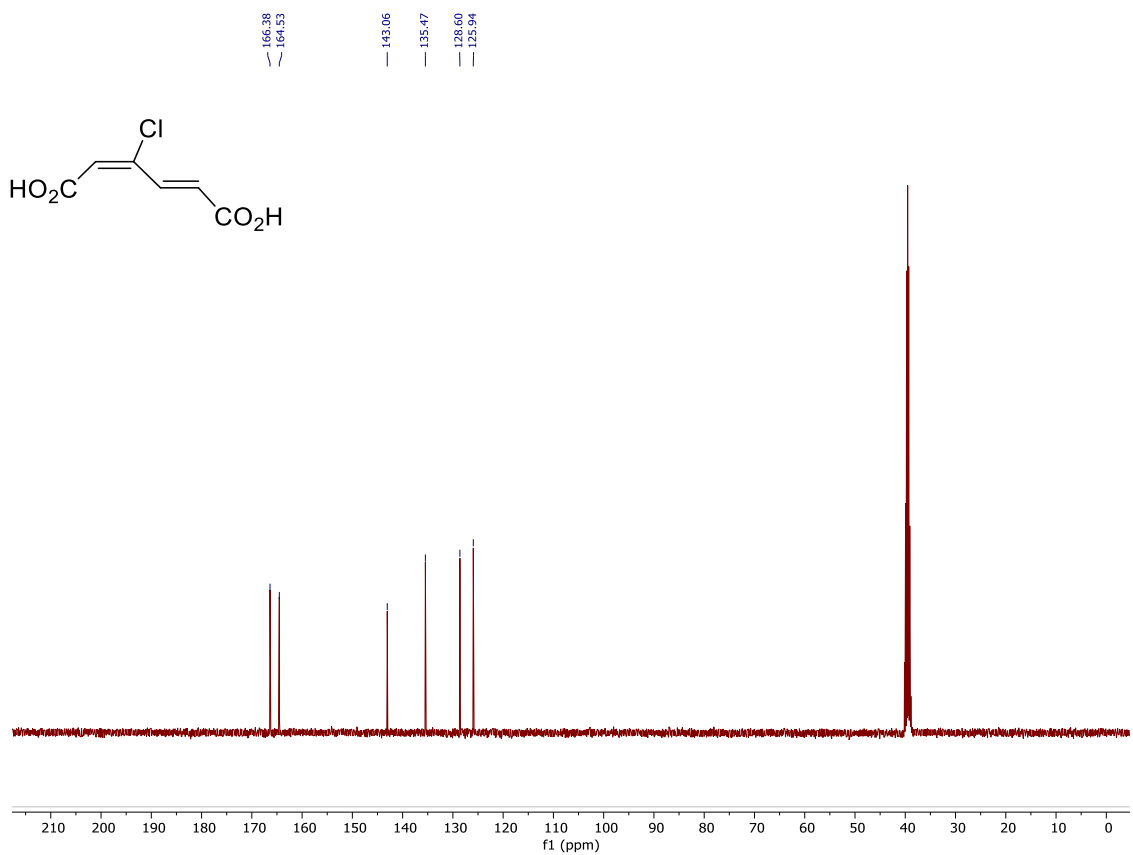


Figure S9.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of *trans,trans*-3-chloromuconic acid **2c**.



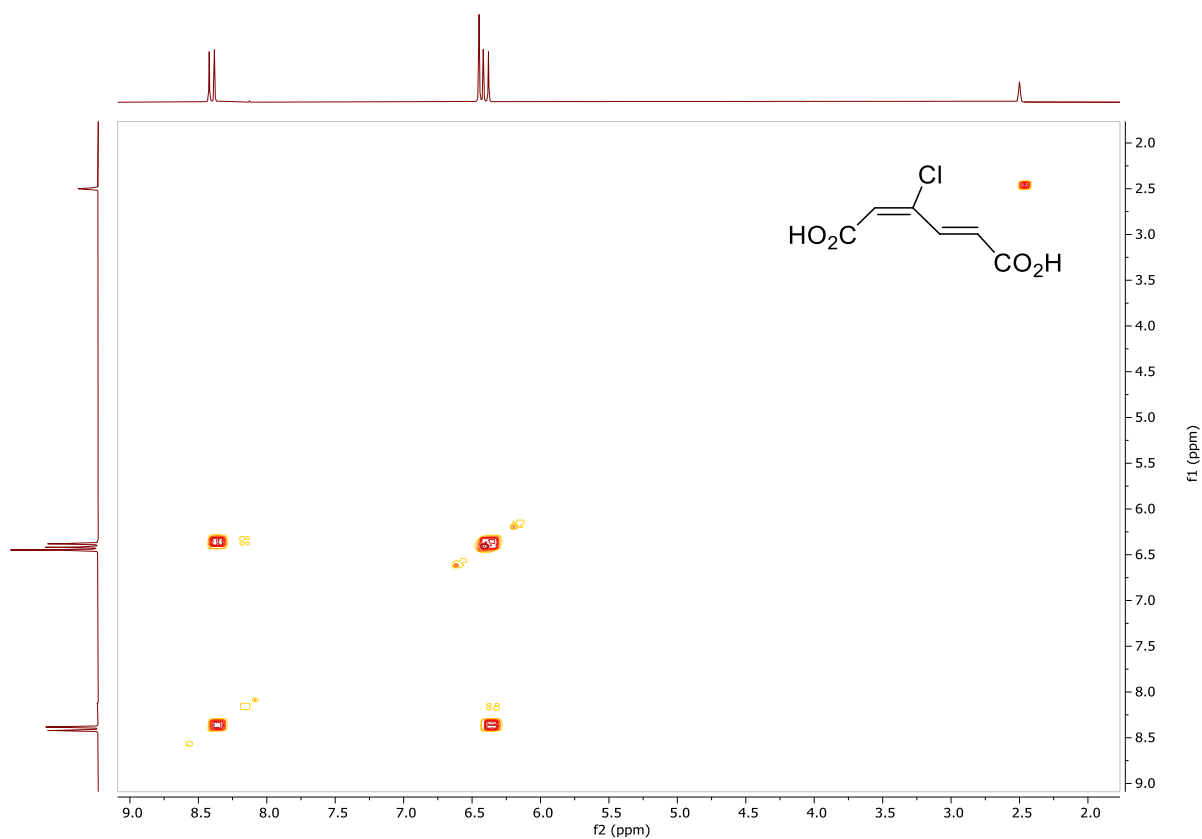


Figure S10. COSY NMR spectrum of *trans,trans*-3-chloromuconic acid 2c.

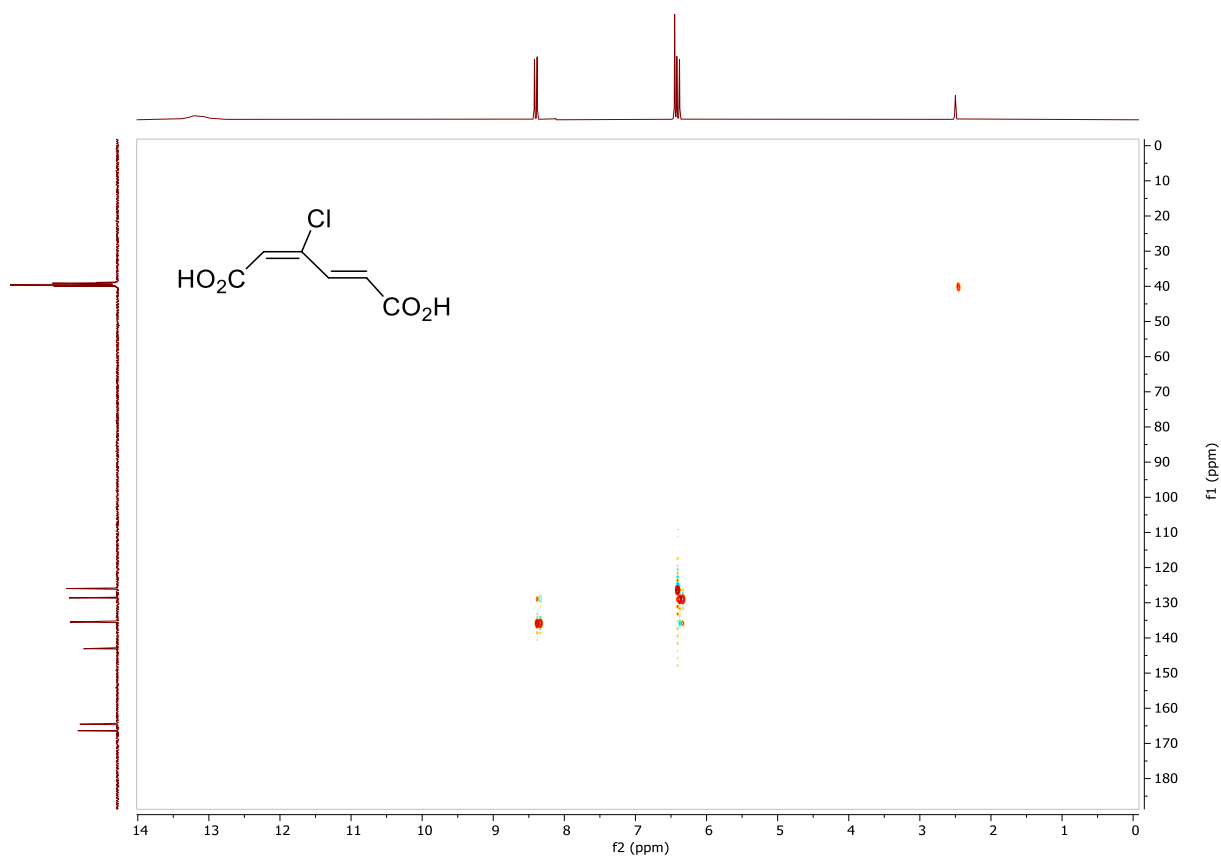


Figure S11. HSQC NMR spectrum of *trans,trans*-3-chloromuconic acid 2c.

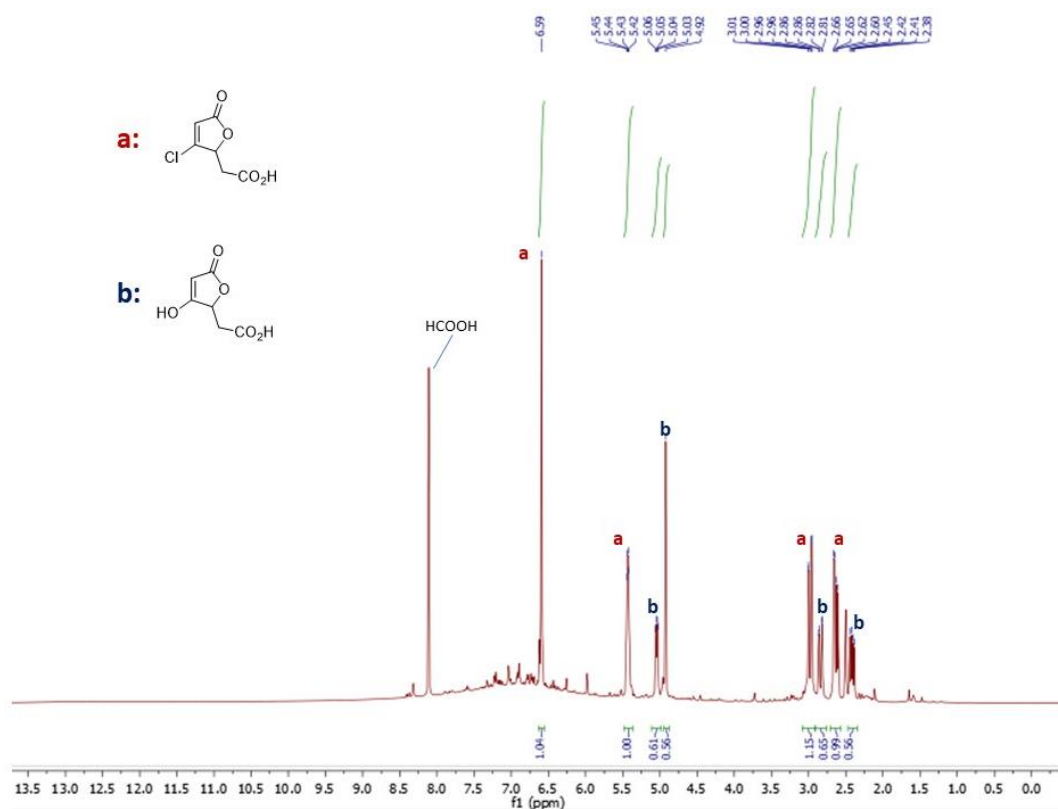


Figure S12.  $^1\text{H}$  NMR spectrum of the mixture of 4-chloro-5-carboxymethyl-2-furanone 3c-i and 4-hydroxy-5-carboxymethyl-2-furanone 3c-ii.

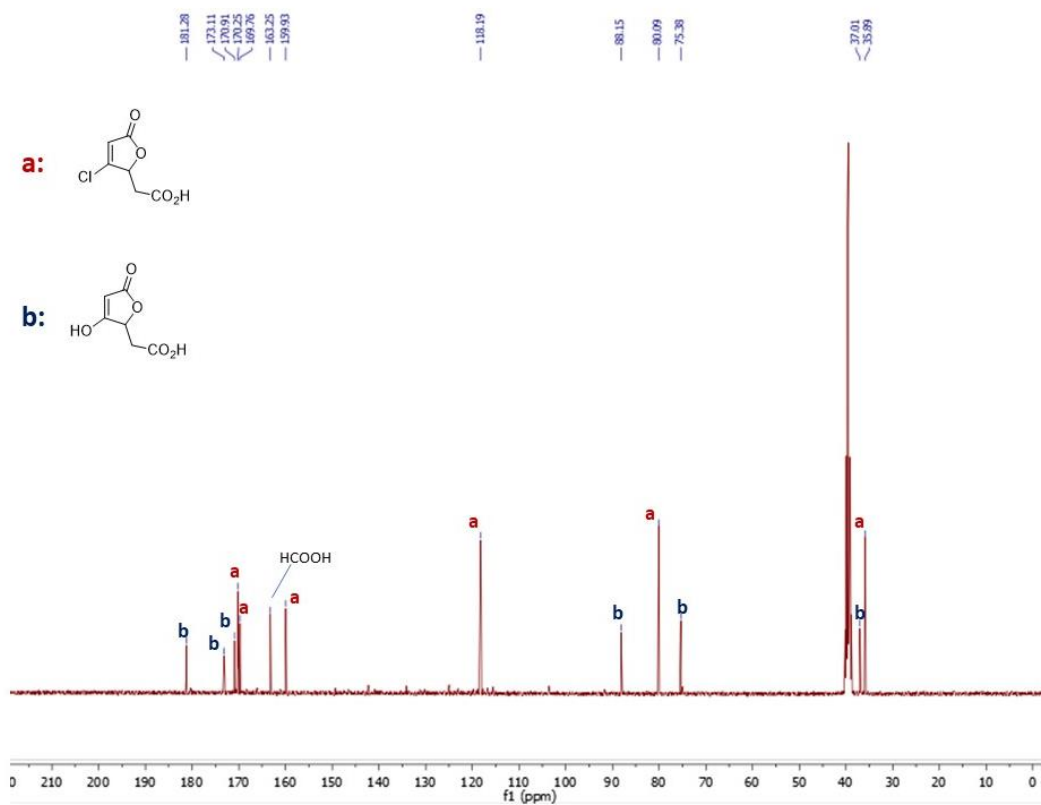
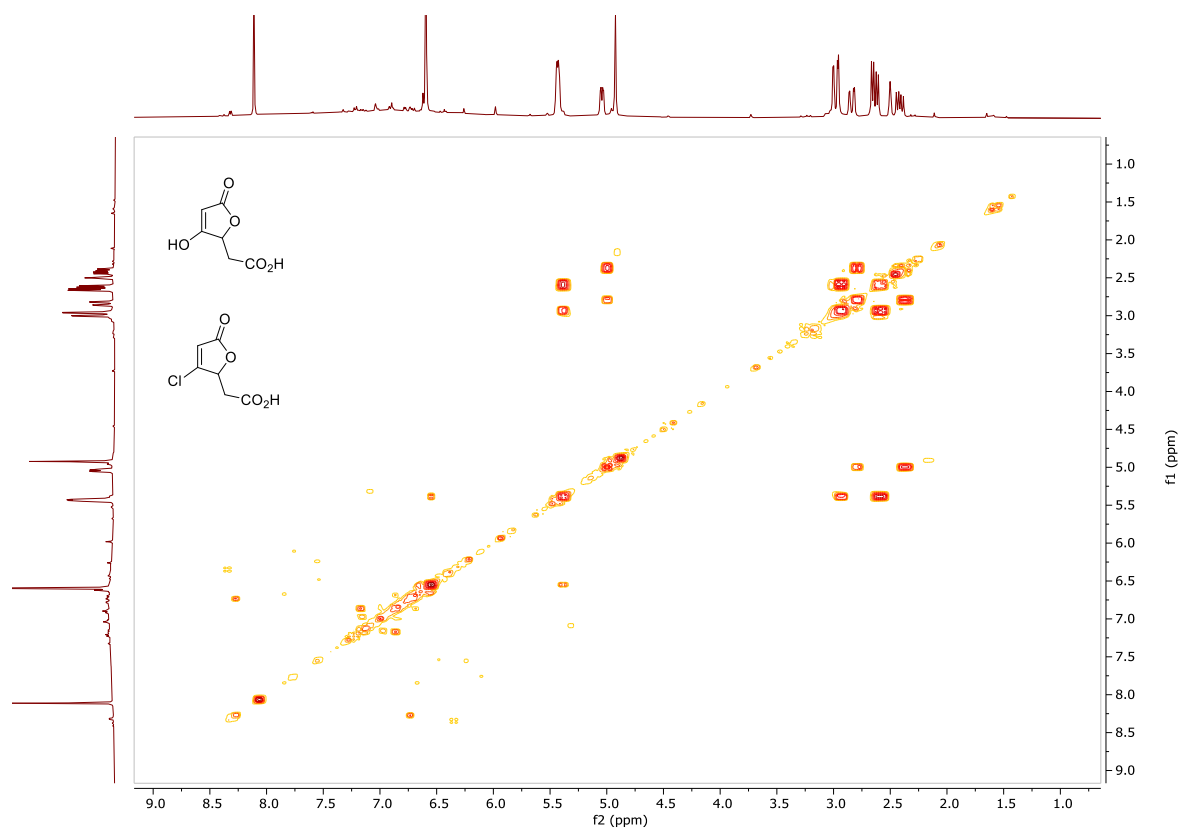
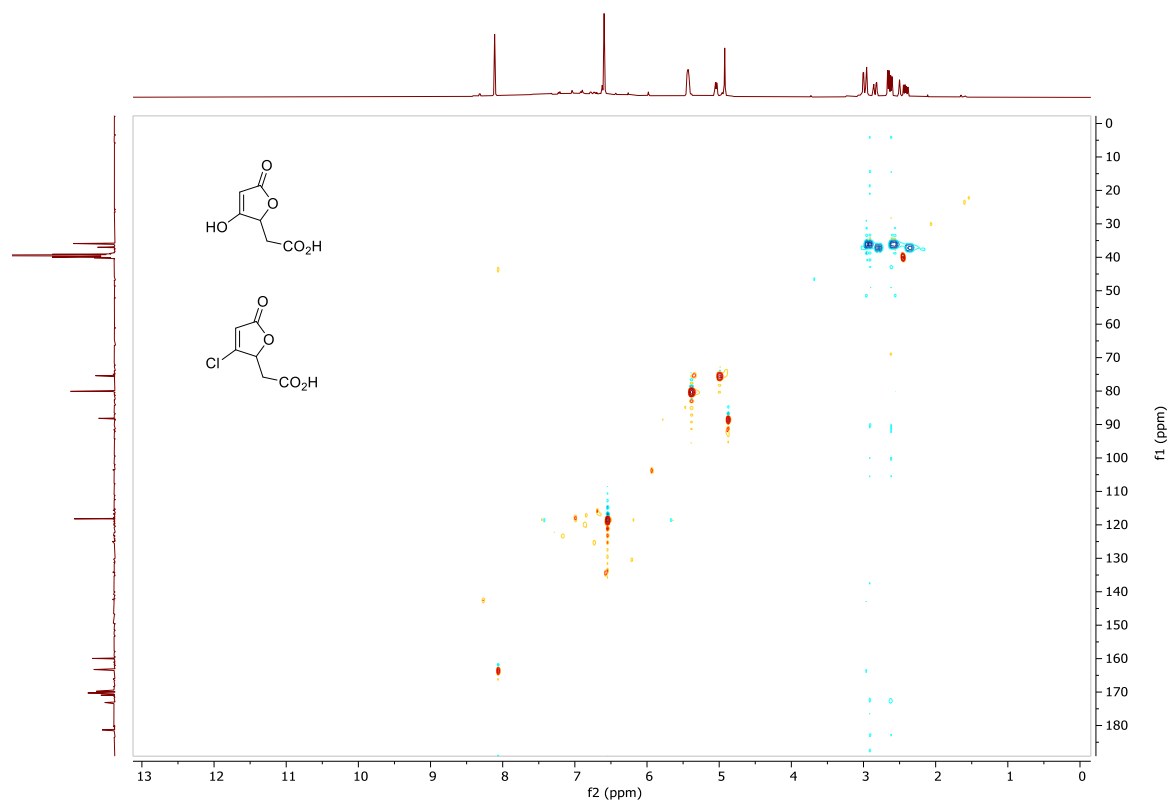


Figure S13.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of the mixture of 4-chloro-5-carboxymethyl-2-furanone 3c-i and 4-hydroxy-5-carboxymethyl-2-furanone 3c-ii.



**Figure S14. COSY NMR spectrum of the mixture of 4-chloro-5-carboxymethyl-2-furanone 3c-i and 4-hydroxy-5-carboxymethyl-2-furanone 3c-ii.**



**Figure S15. HSQC NMR spectrum of the mixture of 4-chloro-5-carboxymethyl-2-furanone 3c-i and 4-hydroxy-5-carboxymethyl-2-furanone 3c-ii.**

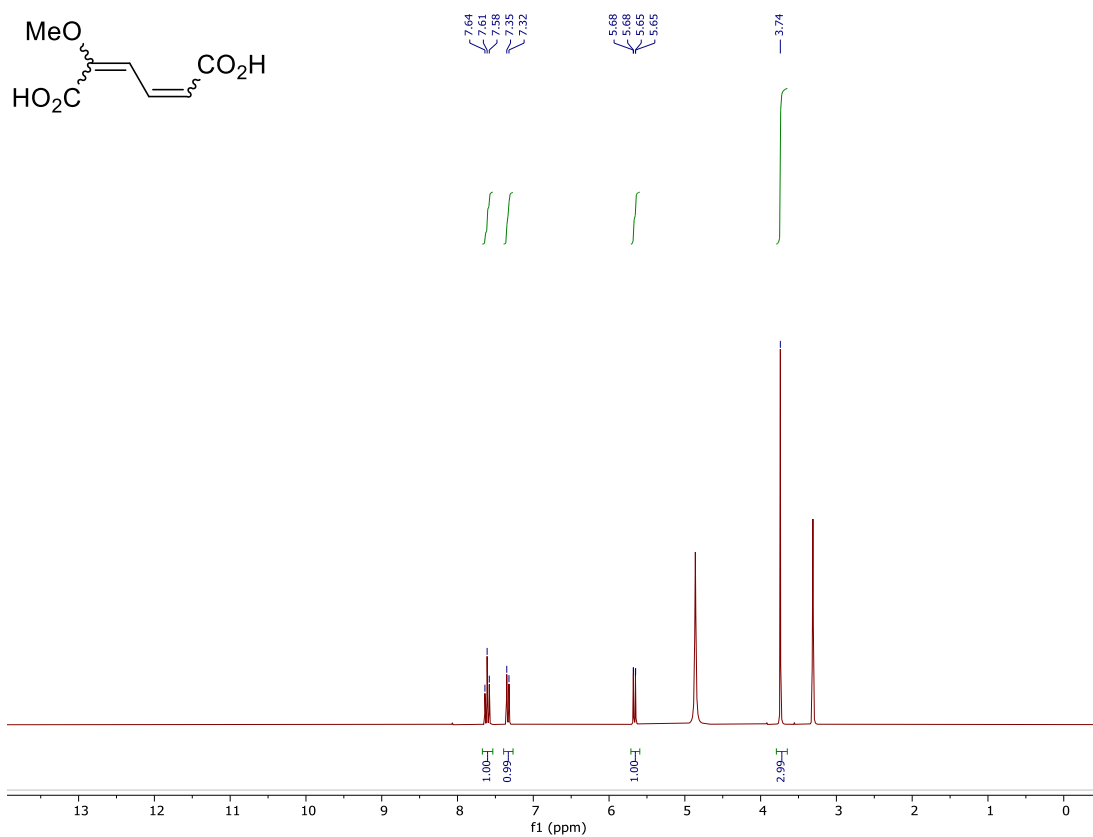


Figure S16.  $^1\text{H}$  NMR spectrum of 2-methoxy-2,4-hexadienedioic acid 2d, isomer a.

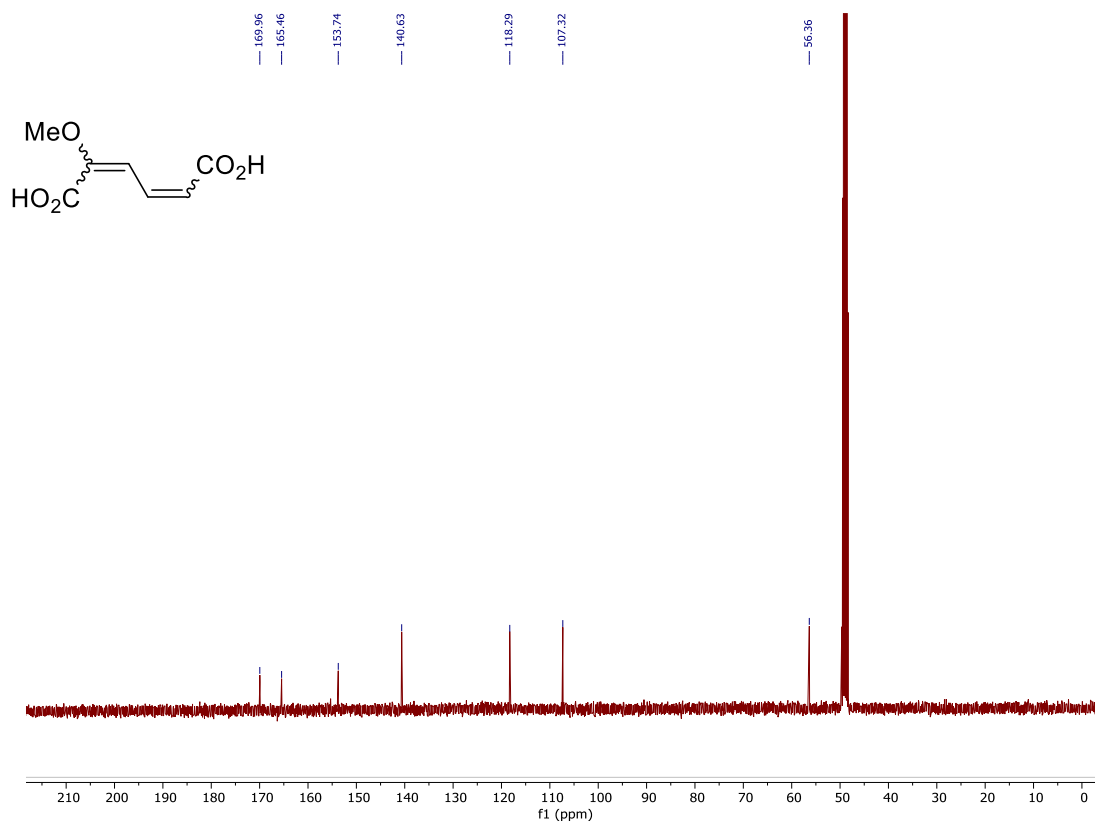


Figure S17.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 2-methoxy-2,4-hexadienedioic acid 2d, isomer a.

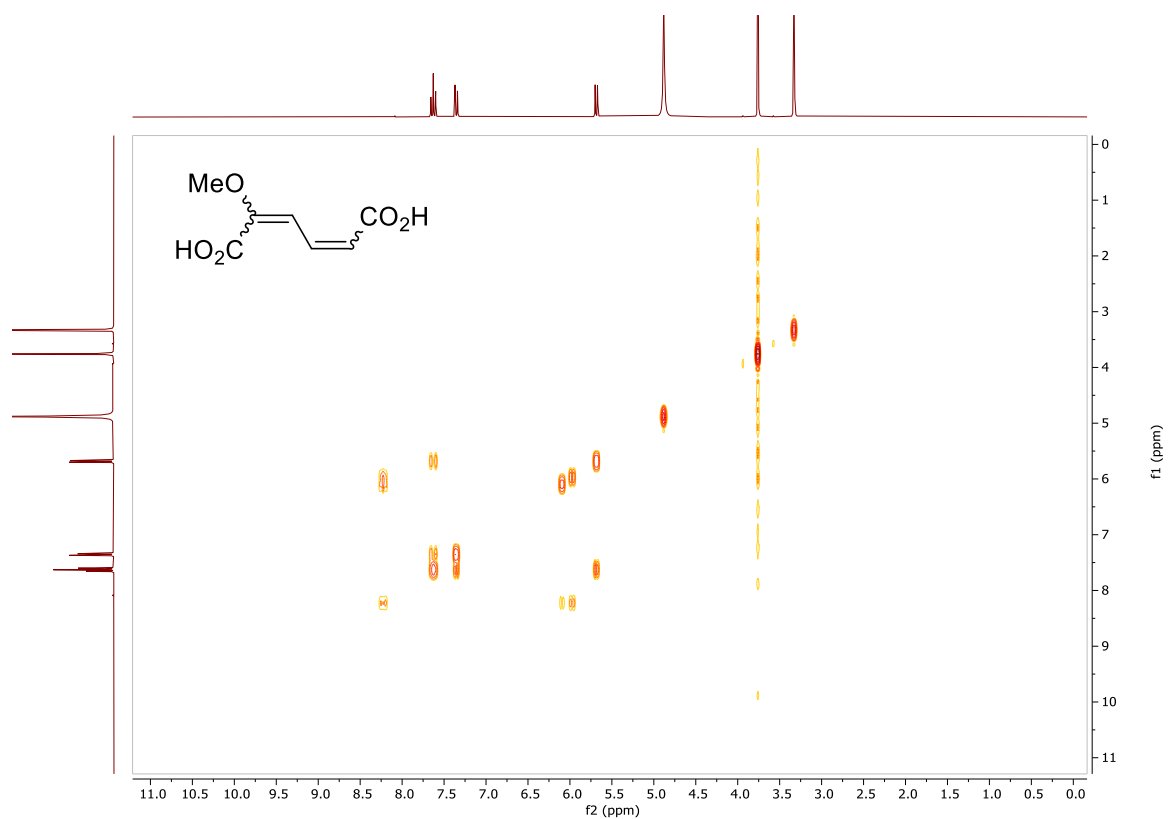


Figure S18. COSY NMR spectrum of 2-methoxy-2,4-hexadienedioic acid 2d, isomer a.

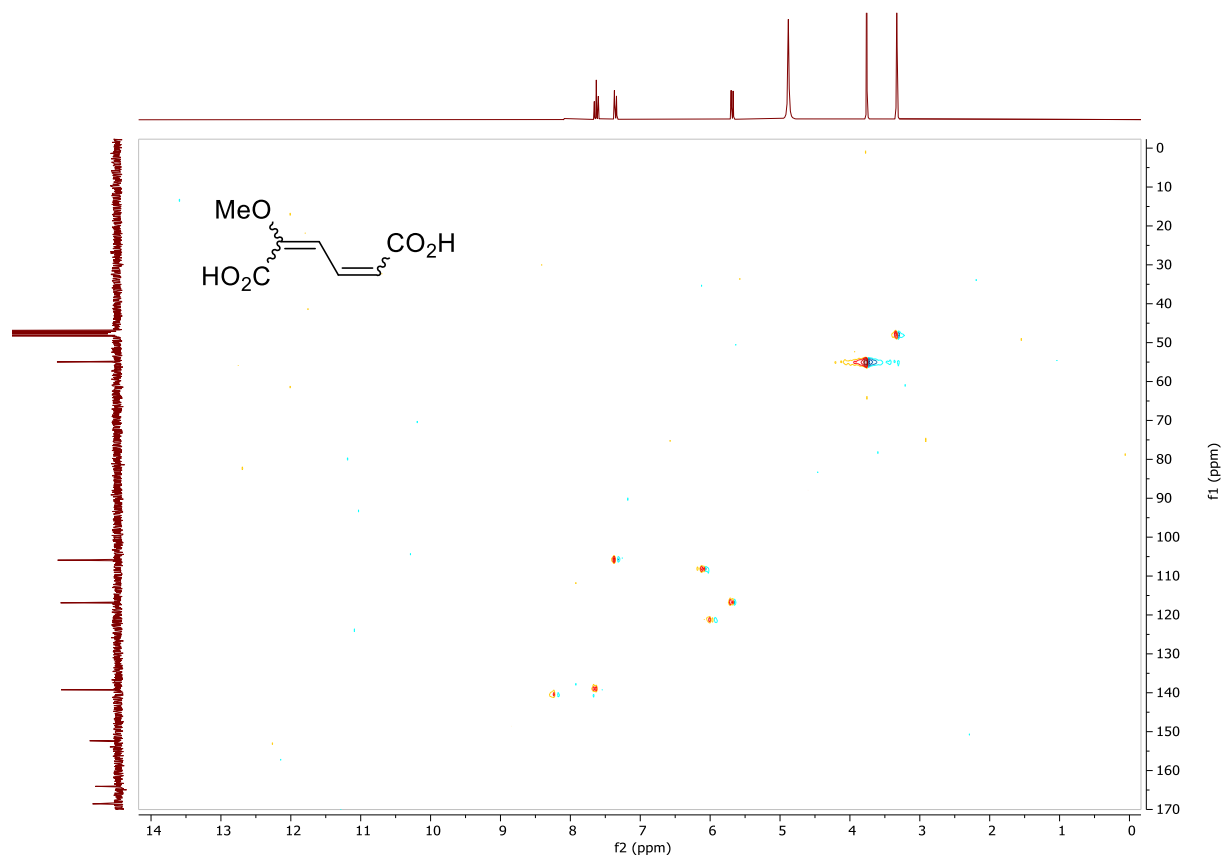


Figure S19. HSQC NMR spectrum of 2-methoxy-2,4-hexadienedioic acid 2d, isomer a.

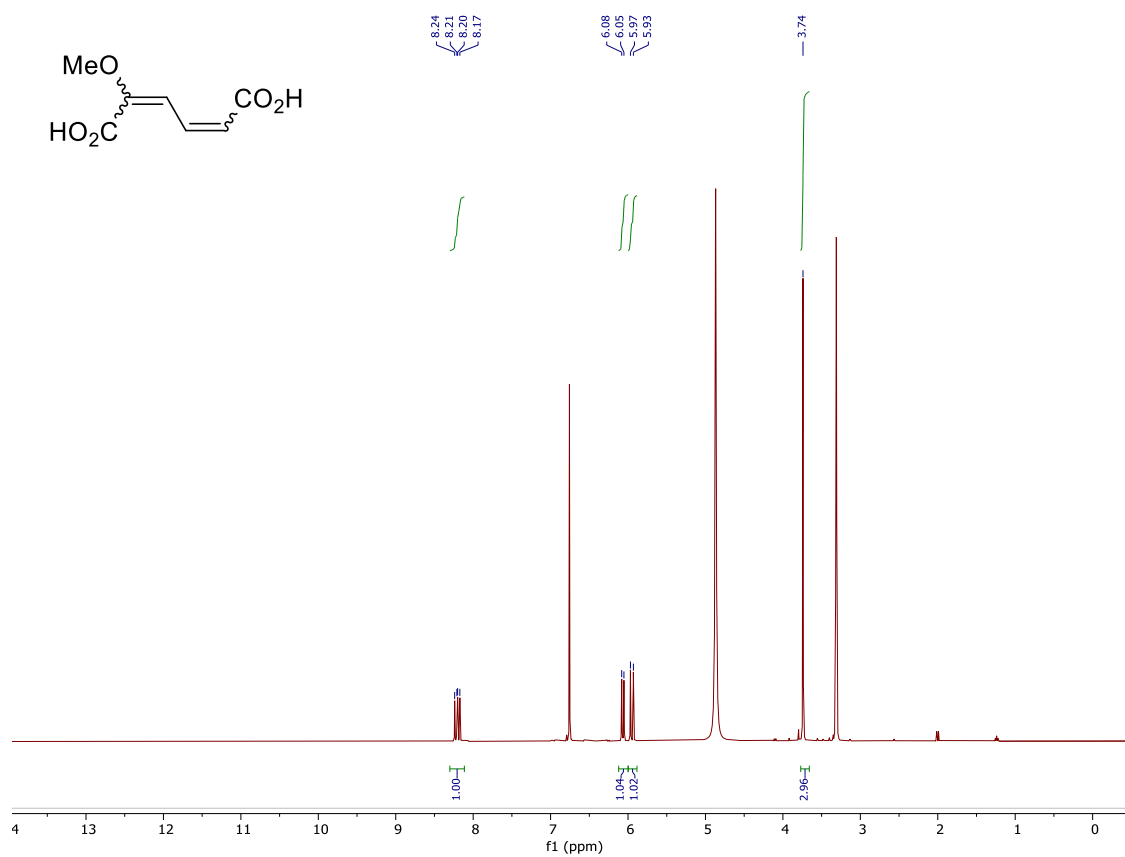


Figure S20. <sup>1</sup>H NMR spectrum of 2-methoxy-2,4-hexadienedioic acid 2d, isomer b.

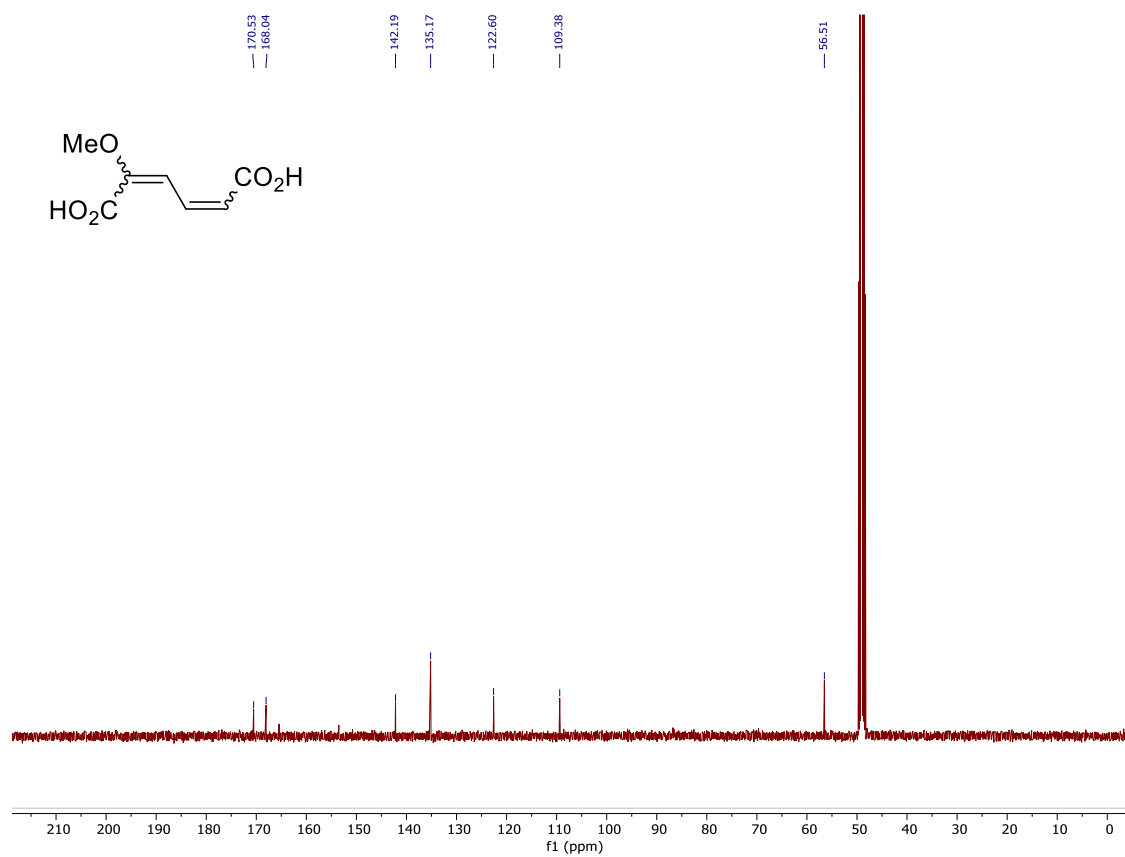


Figure S21. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 2-methoxy-2,4-hexadienedioic acid 2d, isomer b.

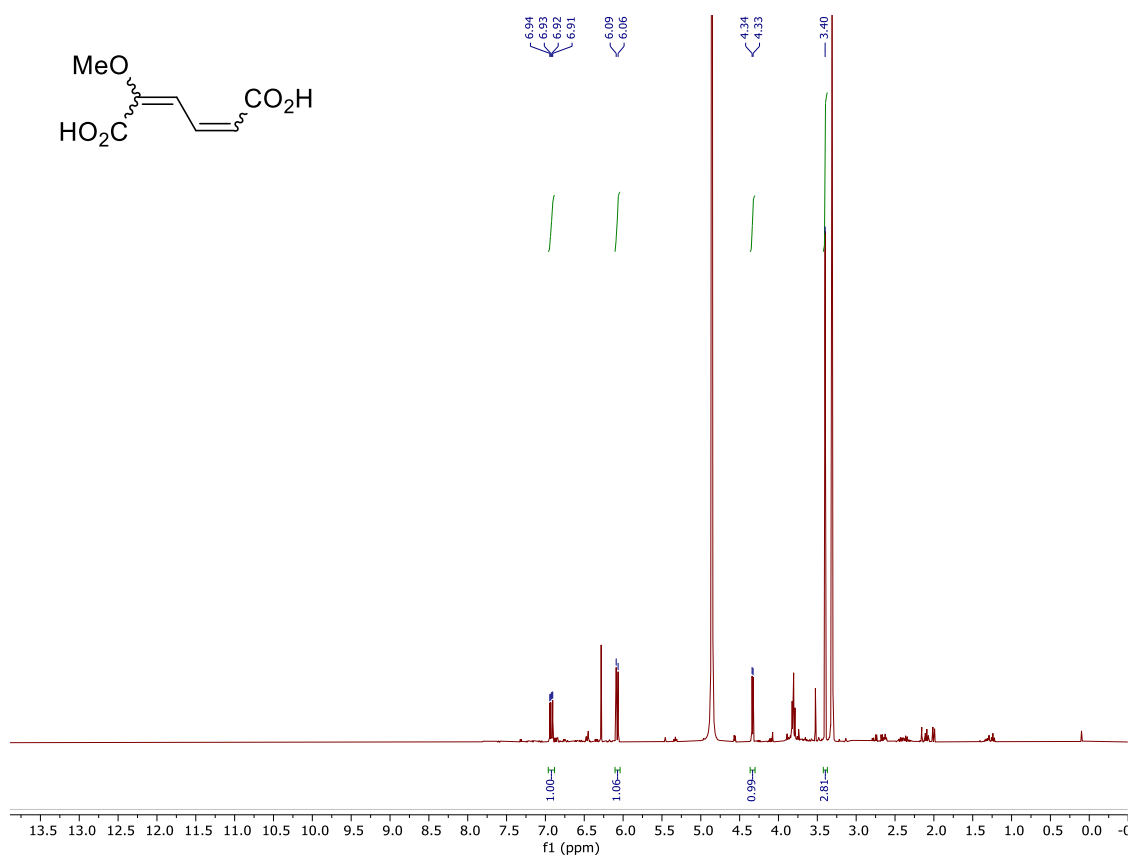


Figure S22. <sup>1</sup>H NMR spectrum of 2-methoxy-2,4-hexadienedioic acid 2d, isomer c.

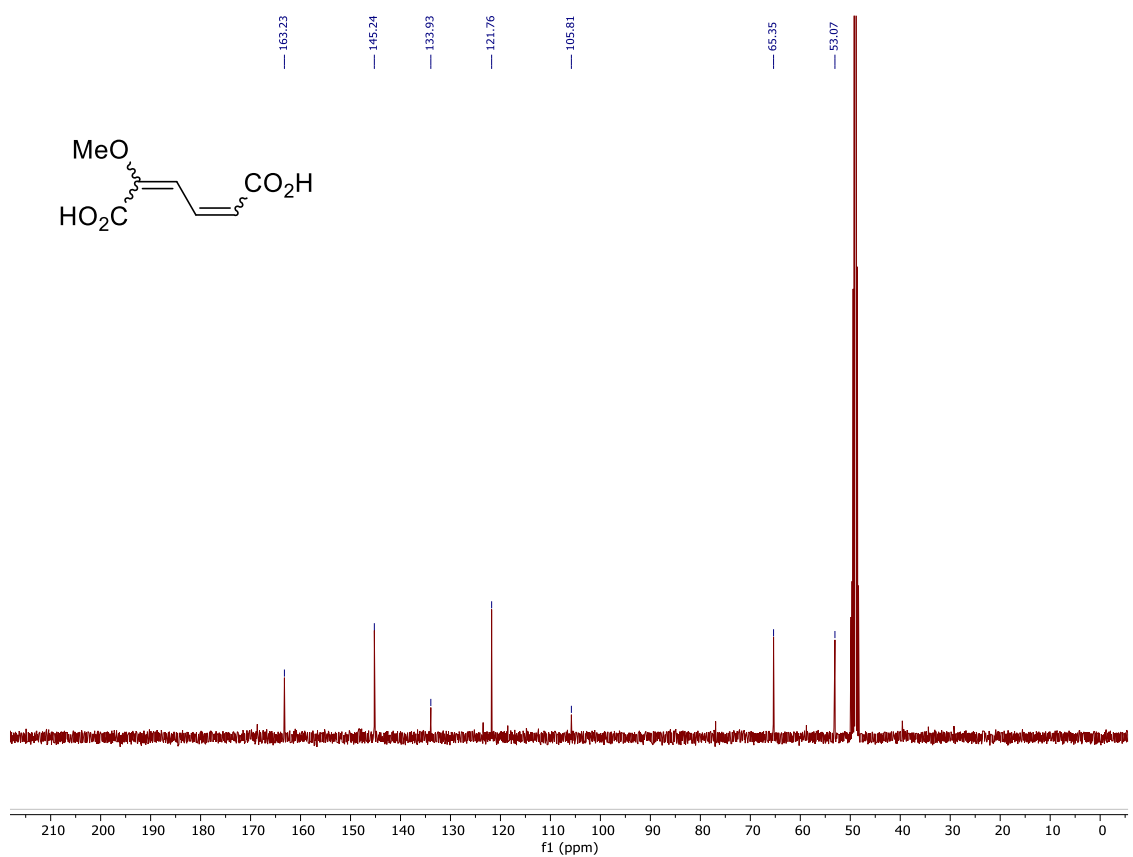


Figure S23. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 2-methoxy-2,4-hexadienedioic acid 2d, isomer c.

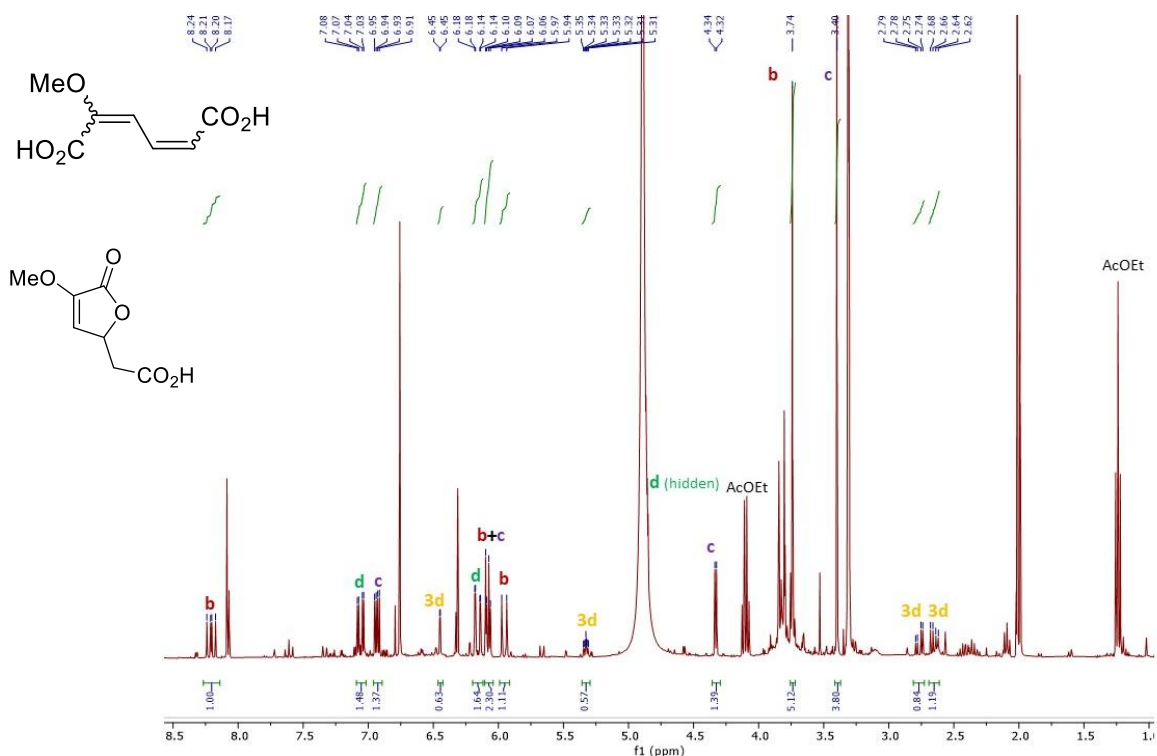


Figure S24.  $^1\text{H}$  NMR spectrum of the acidic extract containing the three 2-methoxy-2,4-hexadienedioic acid 2d isomers b,c,d, and the 3-methoxy-5-carboxymethyl-2-furanone 3d.

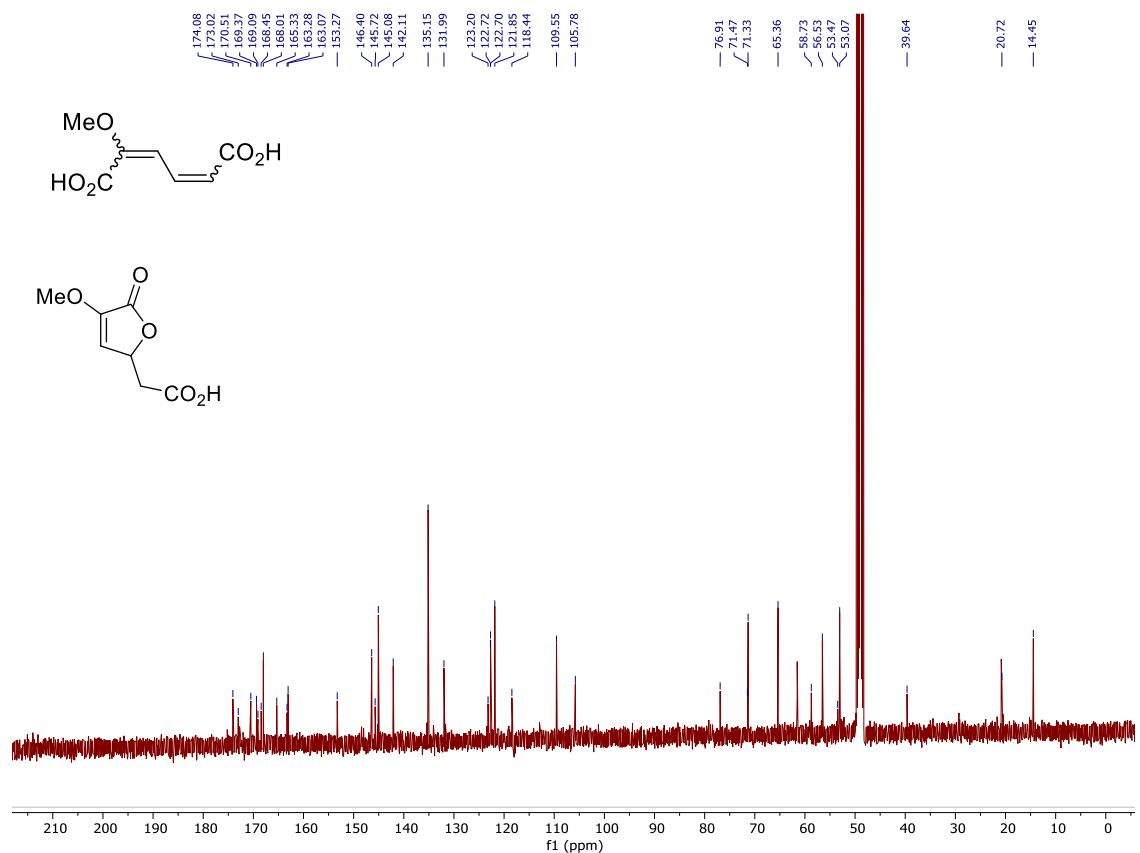


Figure S25.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of the acidic extract containing the three 2-methoxy-2,4-hexadienedioic acid 2d isomers b,c,d, and the 3-methoxy-5-carboxymethyl-2-furanone 3d.



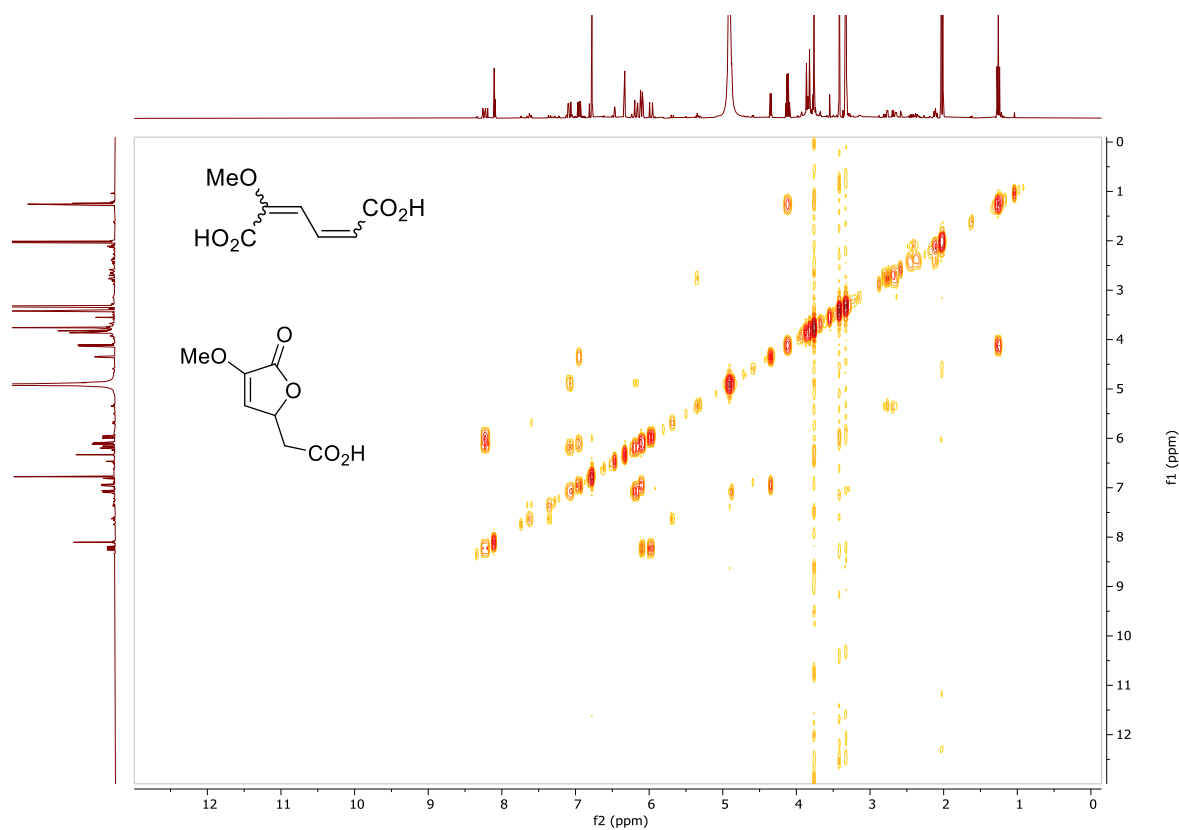


Figure S26. COSY NMR spectrum of the acidic extract containing the three 2-methoxy-2,4-hexadienedioic acid 2d isomers b,c,d, and the 3-methoxy-5-carboxymethyl-2-furanone 3d.

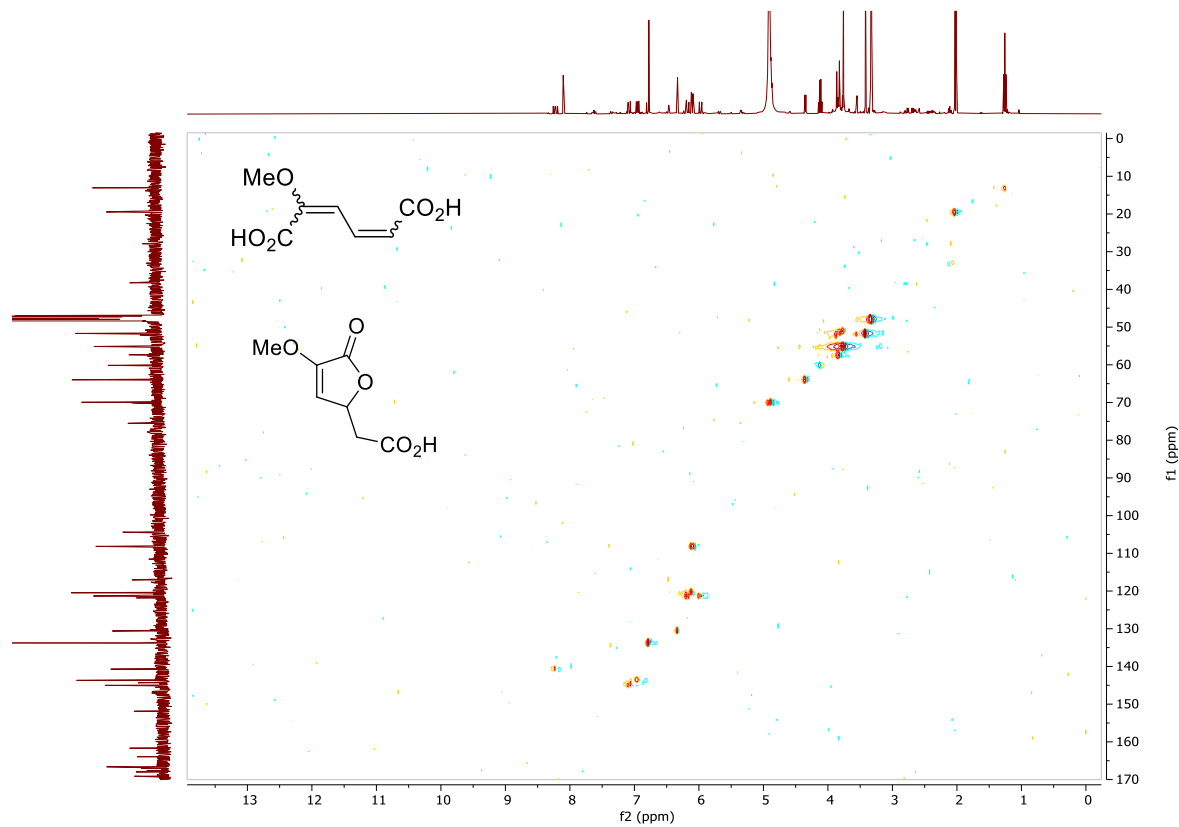


Figure S27. HSQC NMR spectrum of the acidic extract containing the three 2-methoxy-2,4-hexadienedioic acid 2d isomers b,c,d, and the 3-methoxy-5-carboxymethyl-2-furanone 3d.

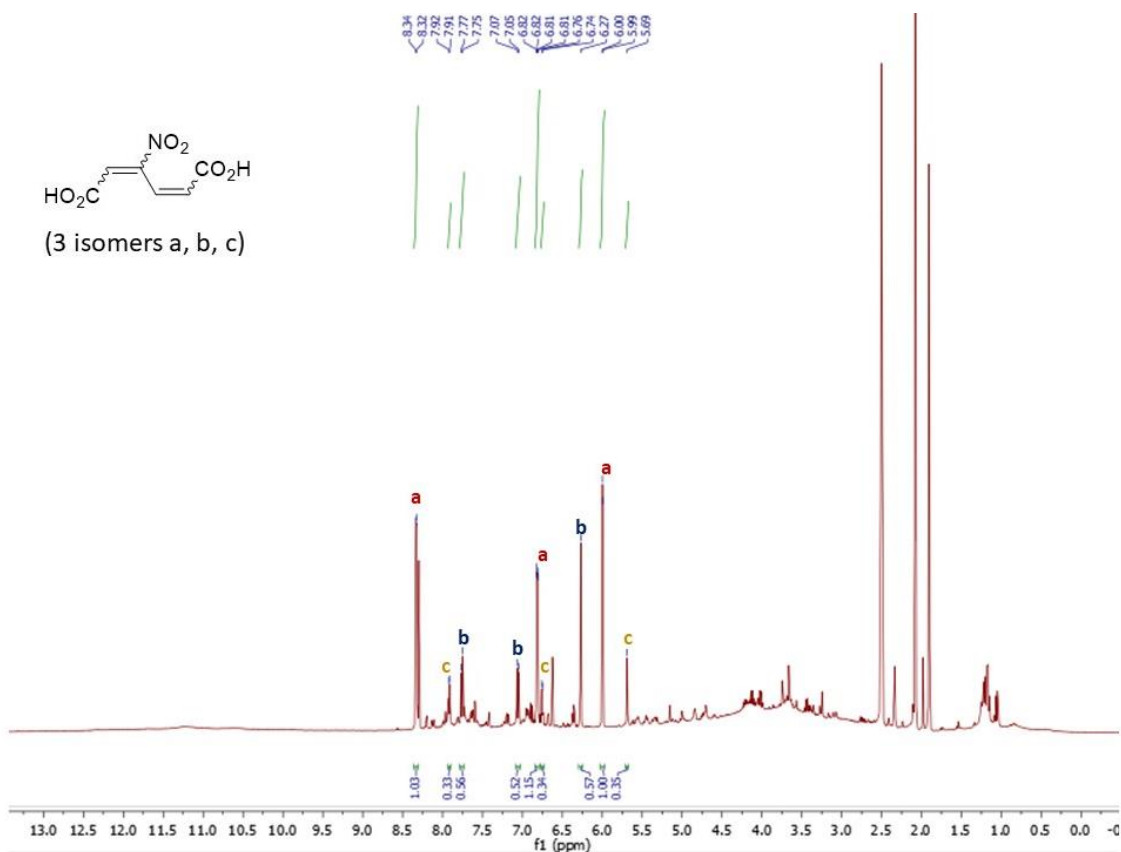


Figure S28.  $^1\text{H}$  NMR spectrum of the mixture of isomers of 3-nitro-2,4-hexadienedoic acid 2e.

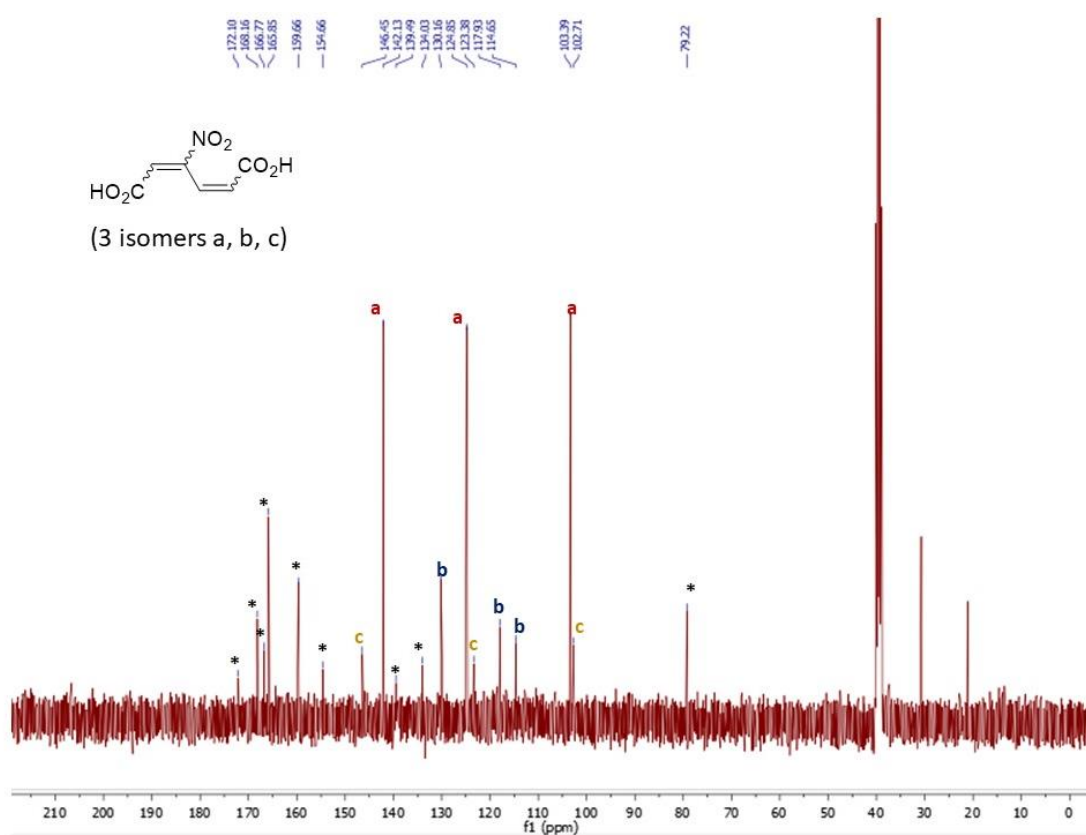


Figure S29.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of the mixture of isomers of 3-nitro-2,4-hexadienedoic acid 2e. Stars depict unattributed carbons.

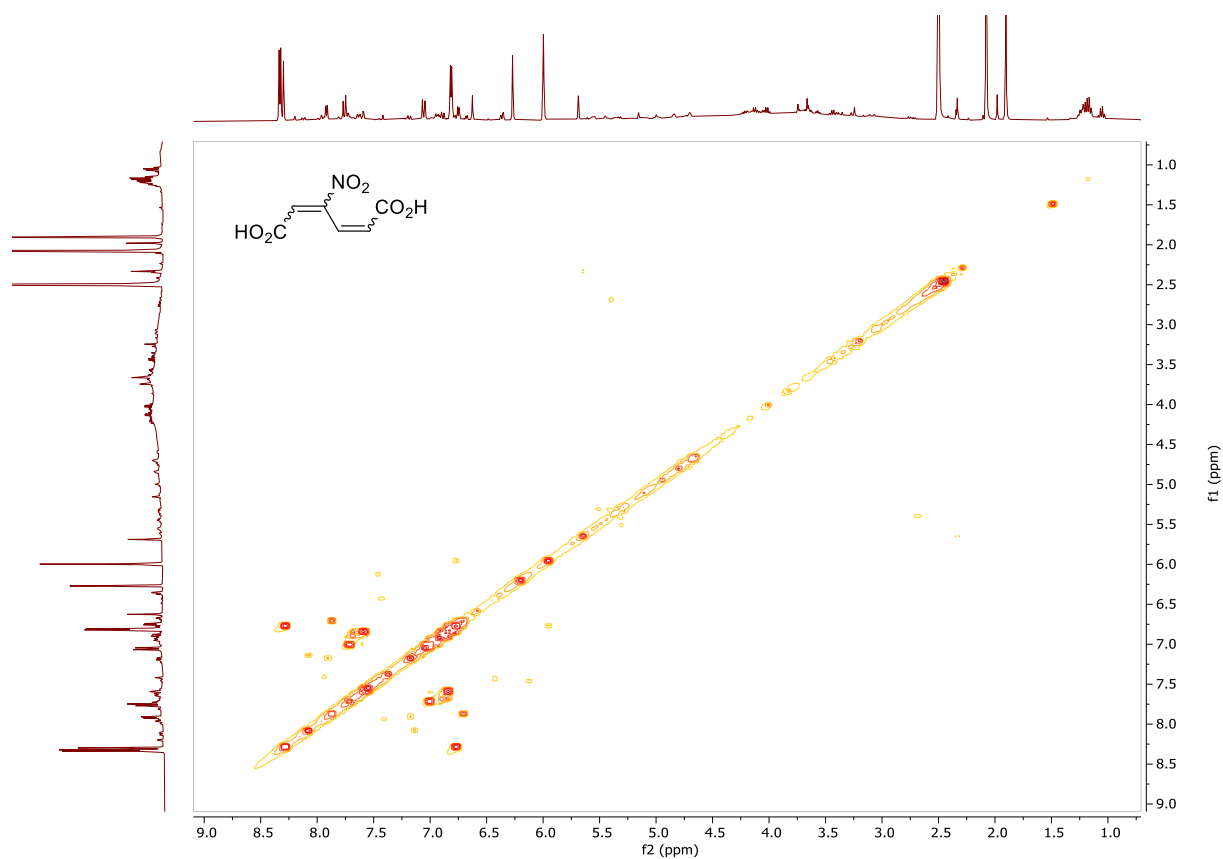


Figure S30. COSY NMR spectrum of the mixture of isomers of 3-nitro-2,4-hexadienedoic acid 2e.

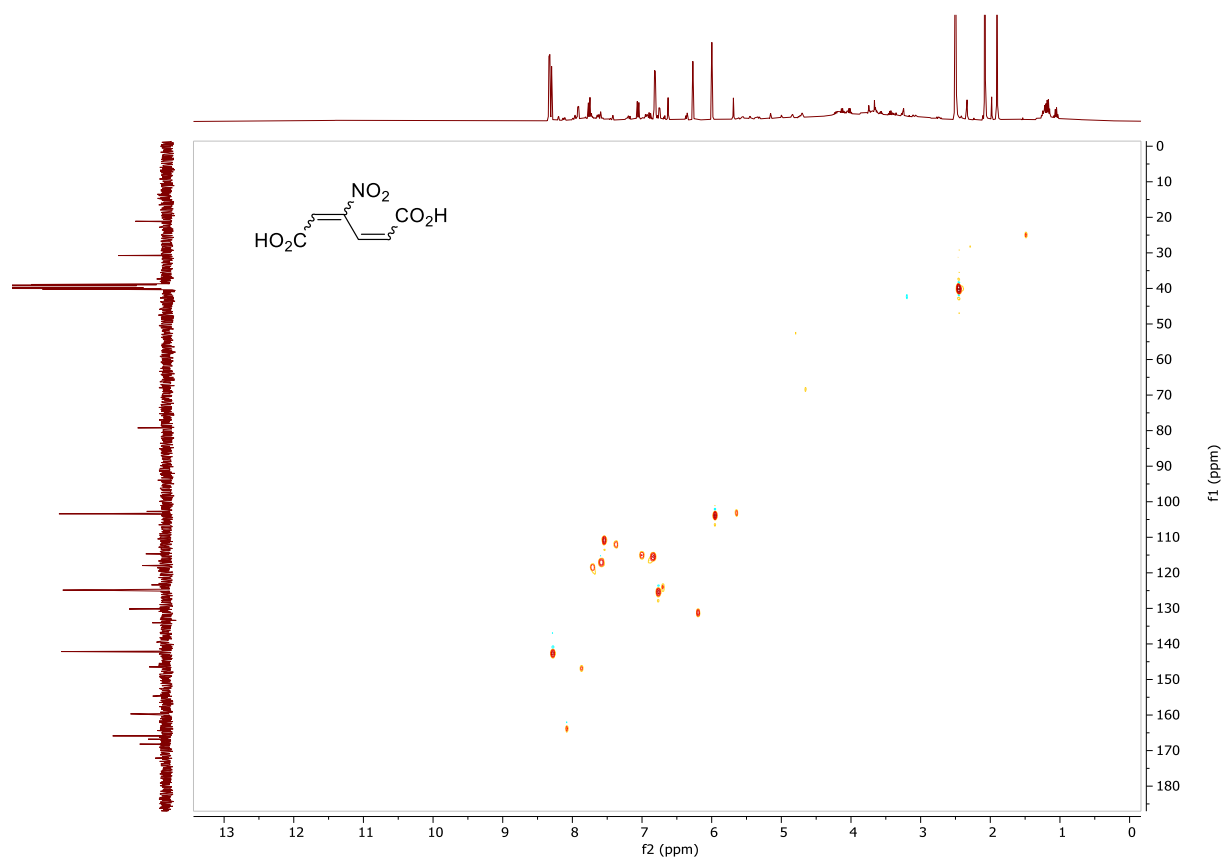


Figure S31. HSQC NMR spectrum of the mixture of isomers of 3-nitro-2,4-hexadienedoic acid 2e.

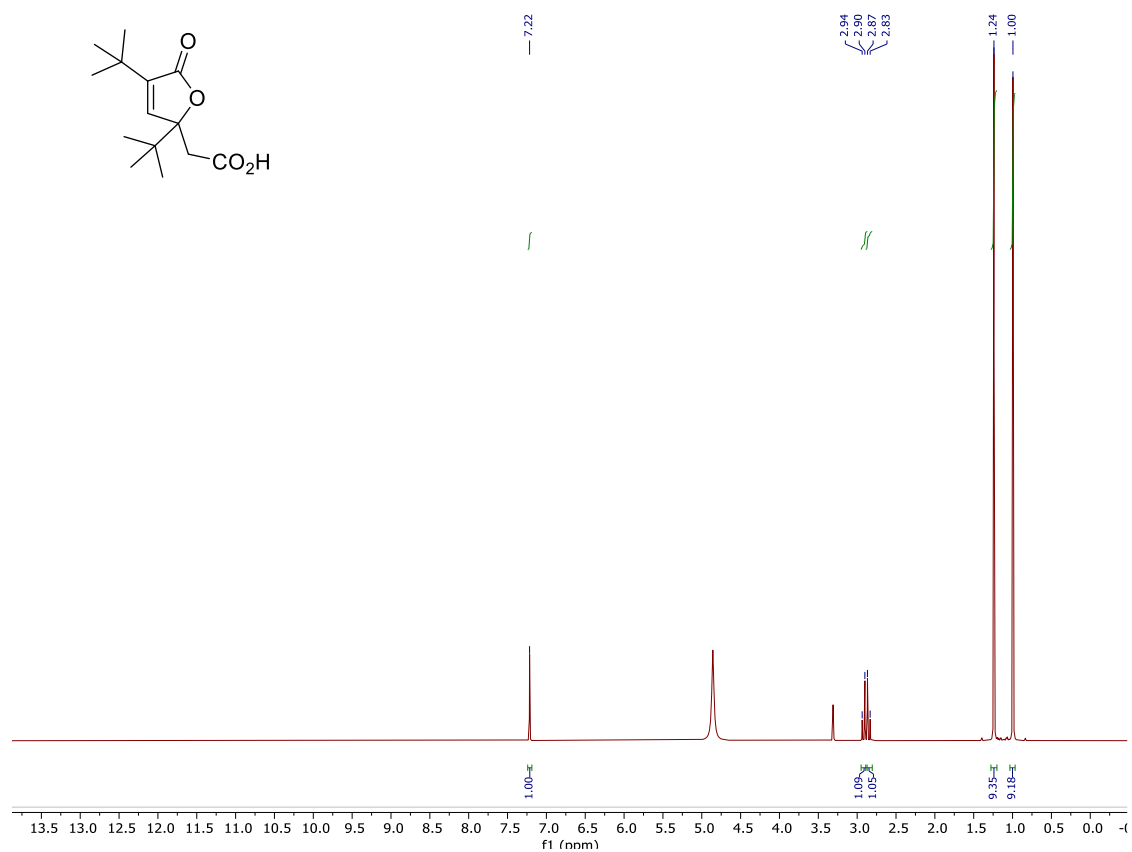


Figure S32.  $^1\text{H}$  NMR spectrum of 3,5-di-tert-butyl-5-carboxymethylfuranone 3f.

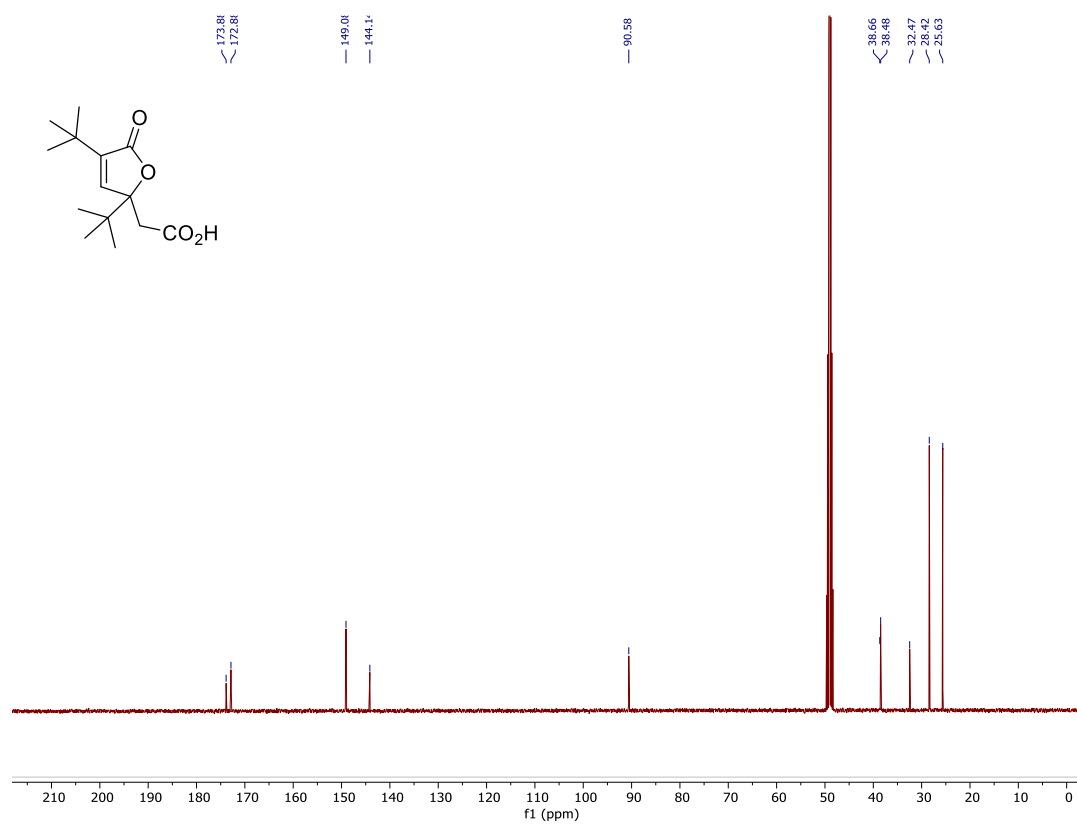


Figure S33.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 3,5-di-tert-butyl-5-carboxymethylfuranone 3f.

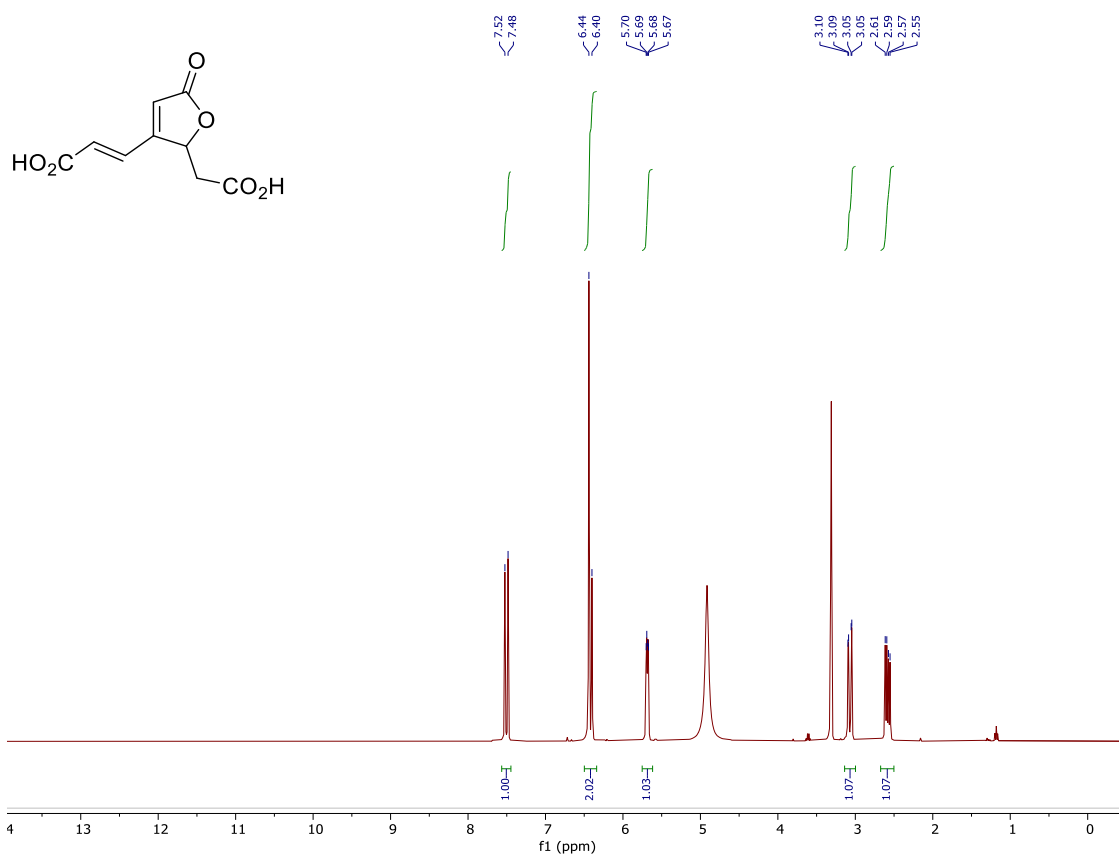


Figure S34. <sup>1</sup>H NMR spectrum of 4-(2-carboxyethenyl)-5-carboxymethyl-2-furanone 3g.

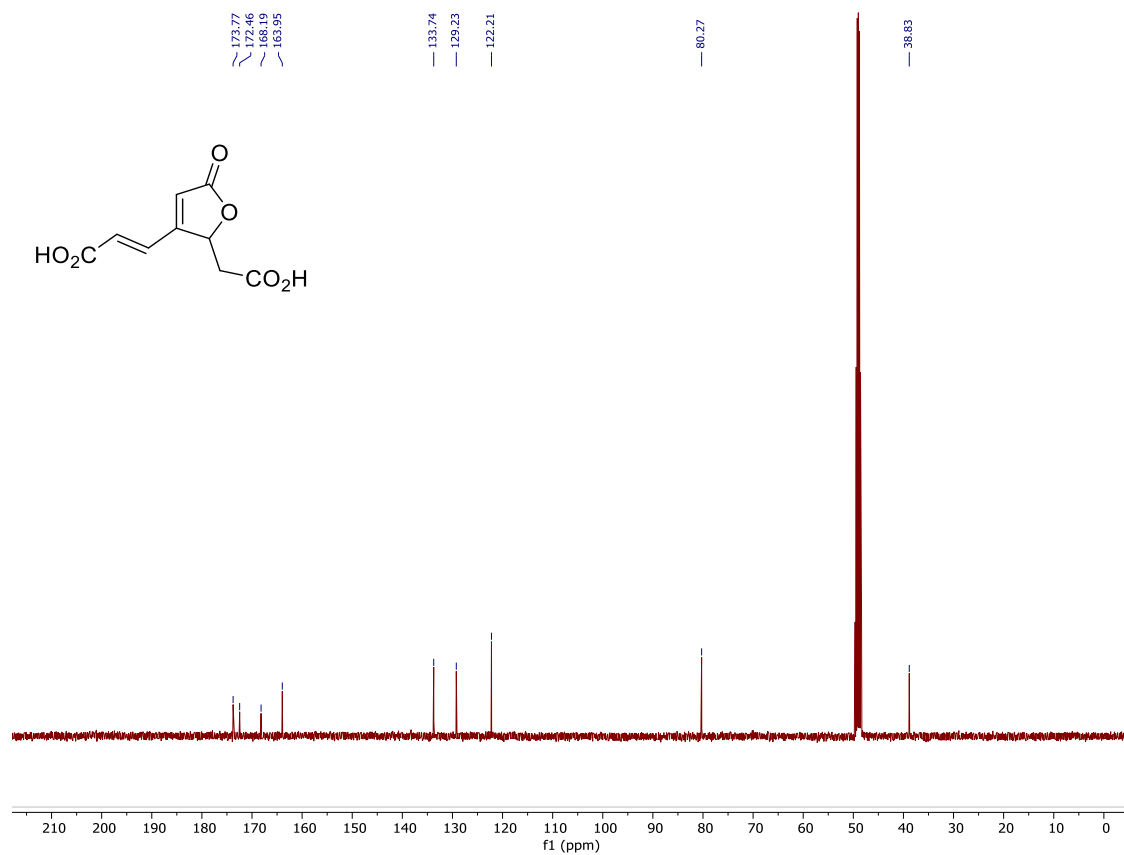


Figure S35. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 4-(2-carboxyethenyl)-5-carboxymethyl-2-furanone 3g.

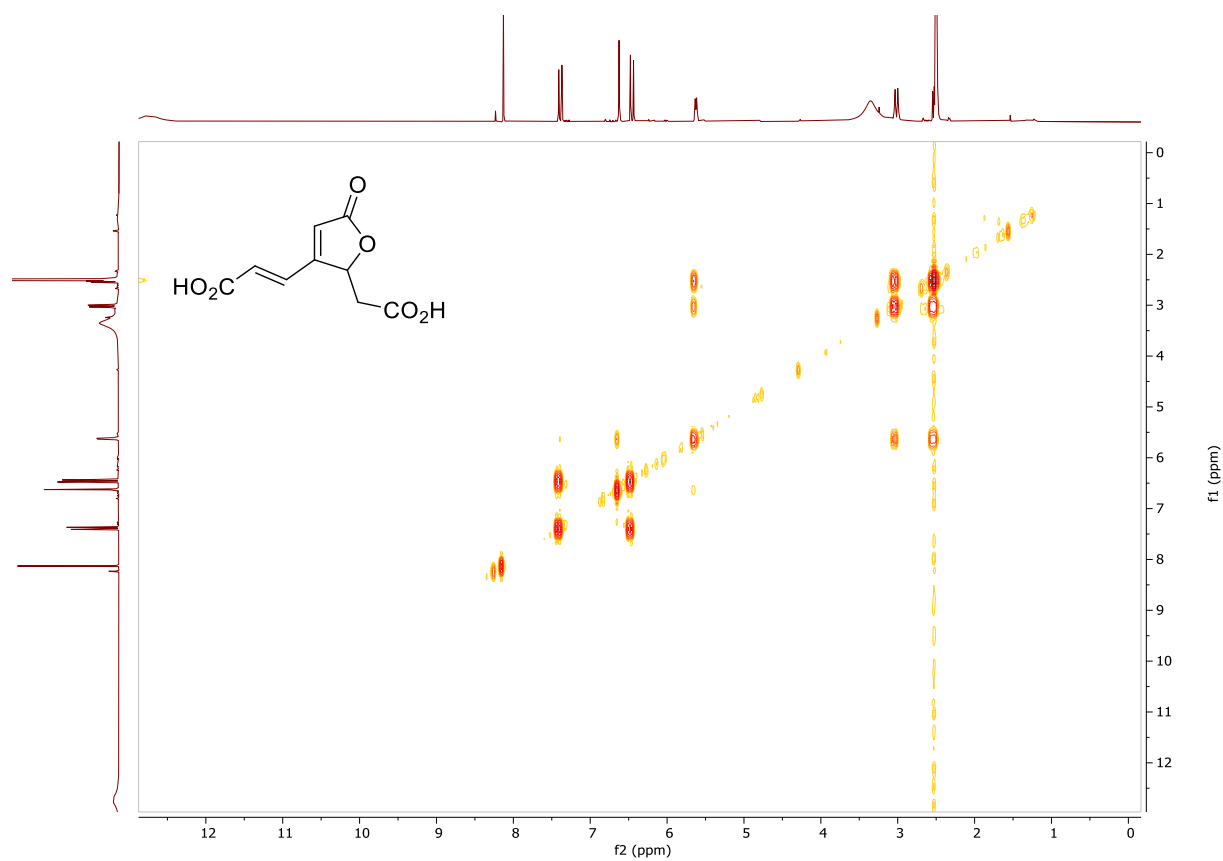


Figure S36. COSY NMR spectrum of 4-(2-carboxyethenyl)-5-carboxymethyl-2-furanone 3g.

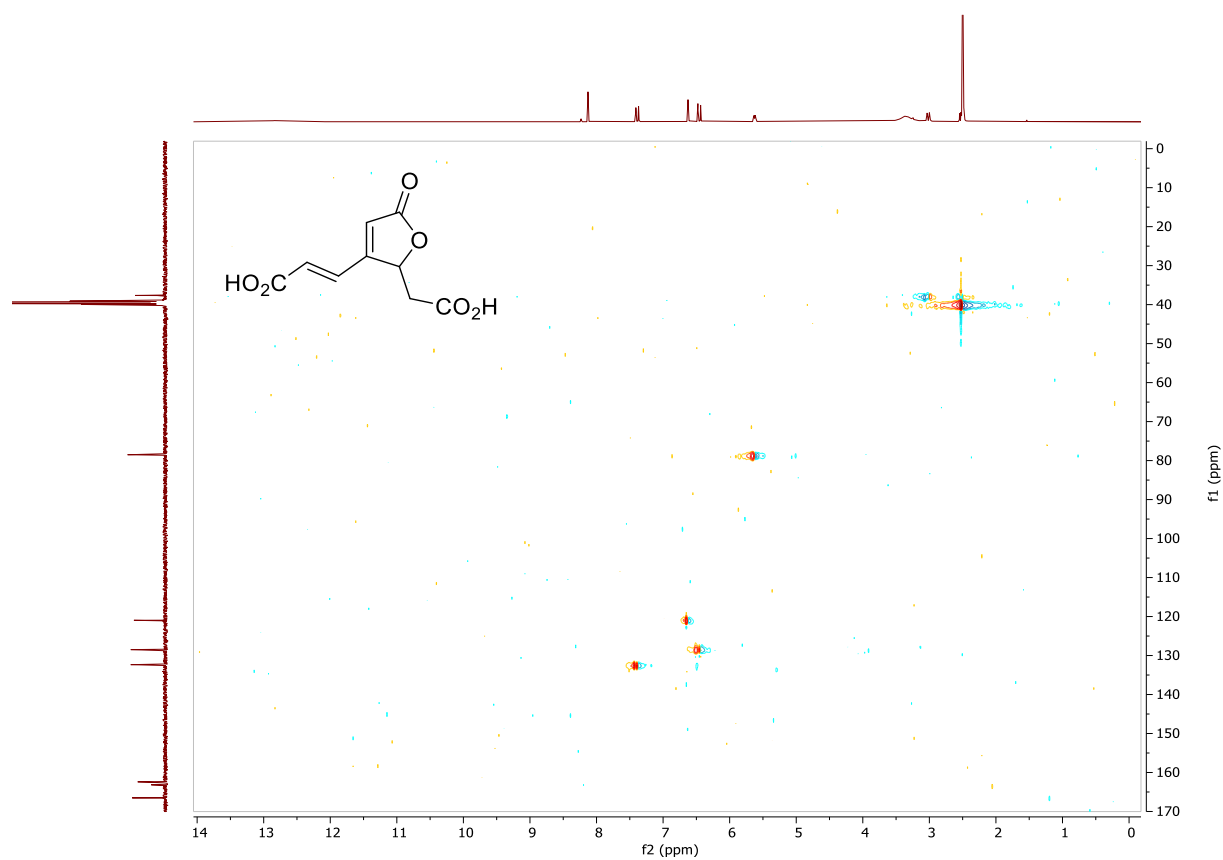


Figure S37. HSQC NMR spectrum of 4-(2-carboxyethenyl)-5-carboxymethyl-2-furanone 3g.

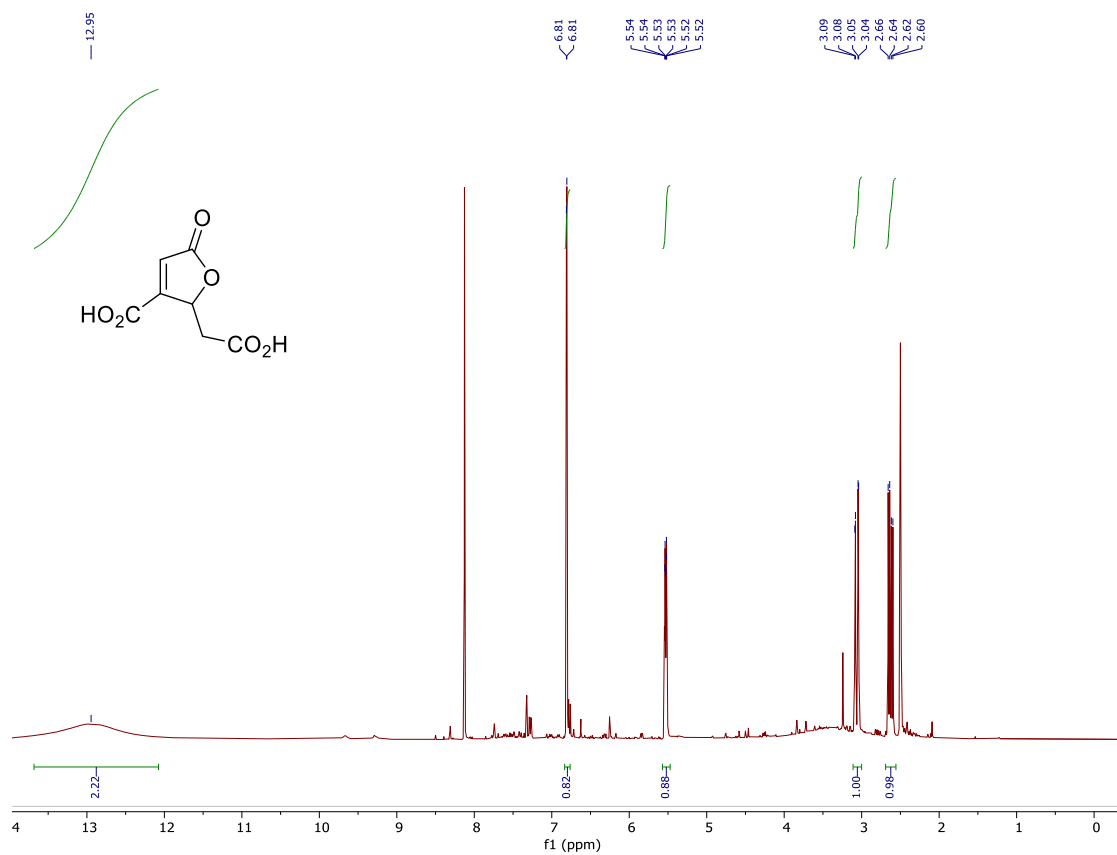


Figure S38. <sup>1</sup>H NMR spectrum of 4-carboxyl-5-carboxymethyl-2-furanone 3h.

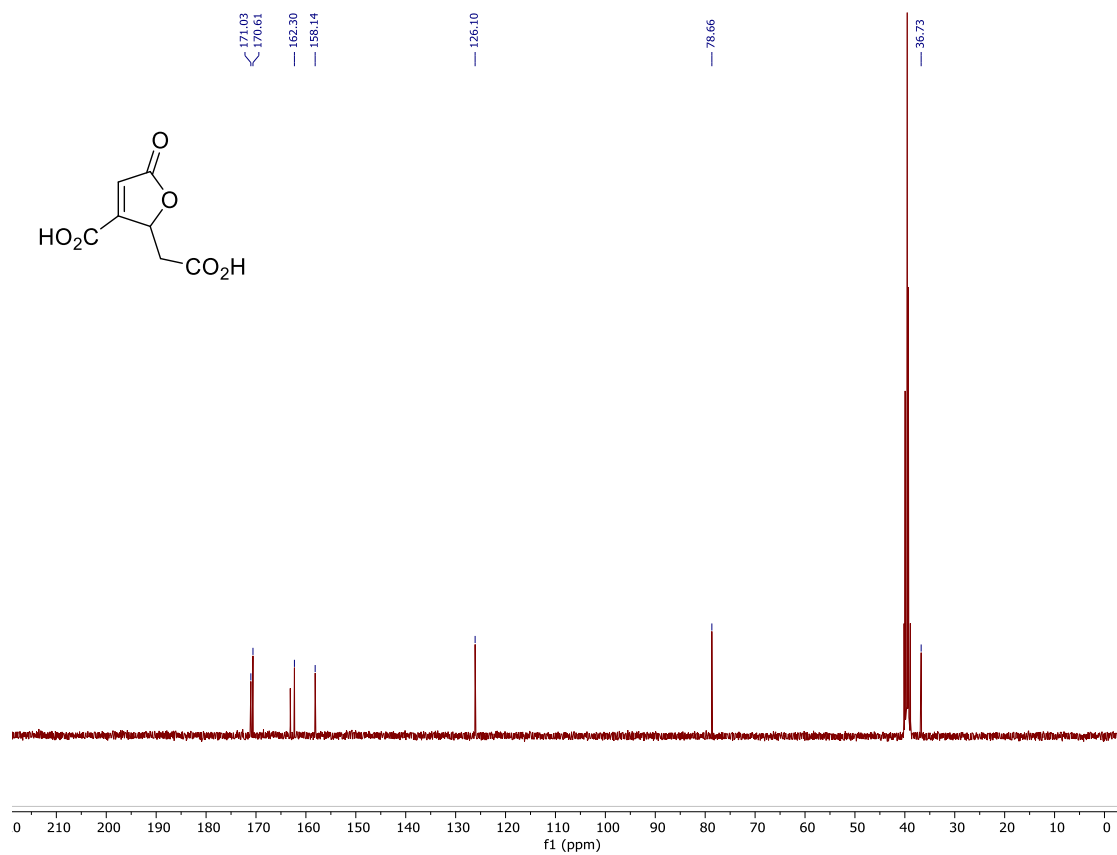


Figure S39. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 4-carboxyl-5-carboxymethyl-2-furanone 3h.

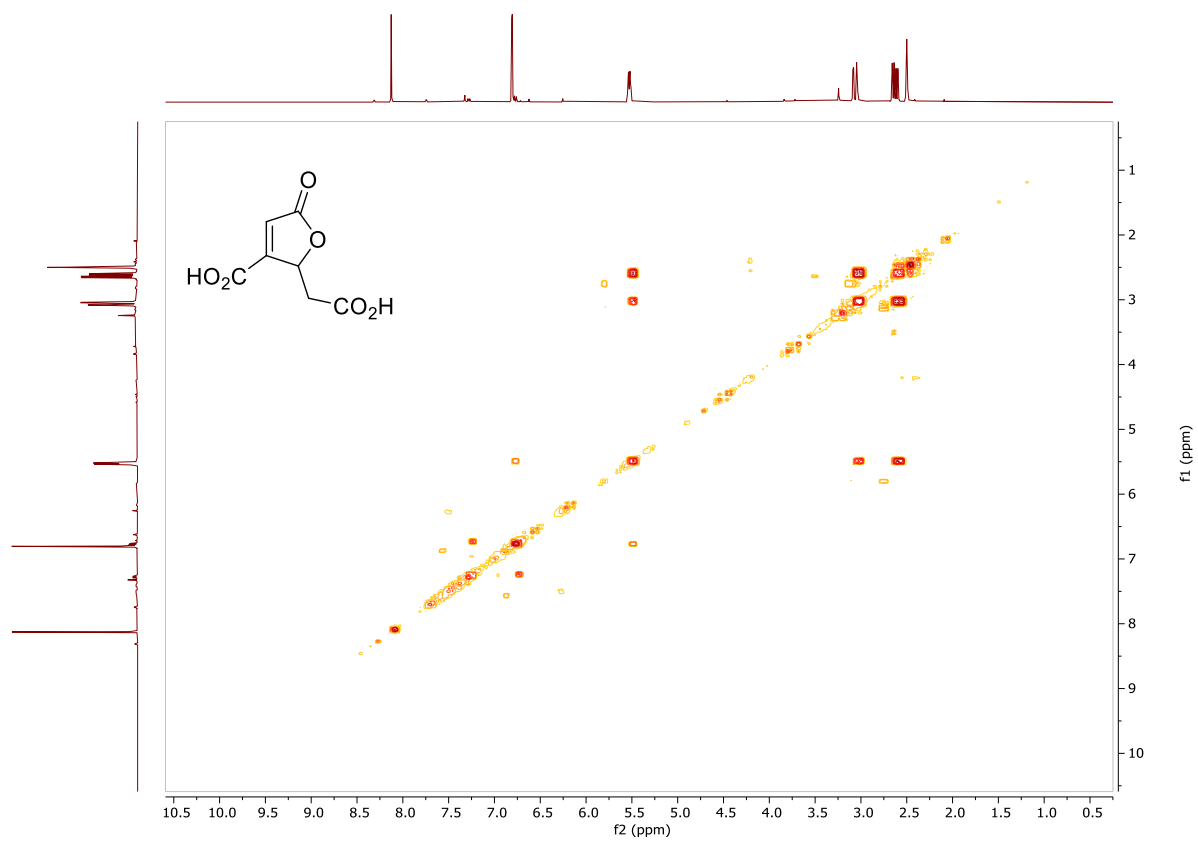


Figure S40. COSY NMR spectrum of 4-carboxyl-5-carboxymethyl-2-furanone 3h.

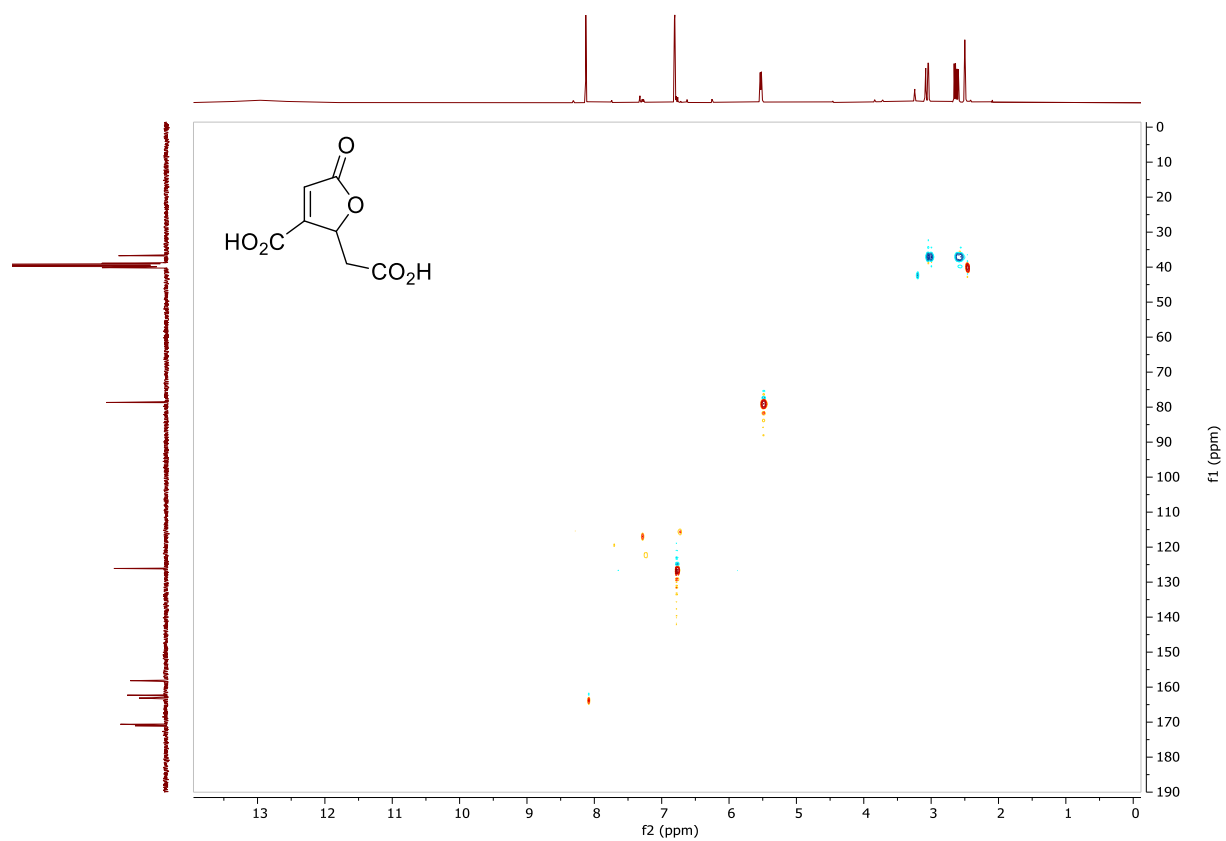


Figure S41. HSQC NMR spectrum of 4-carboxyl-5-carboxymethyl-2-furanone 3h.



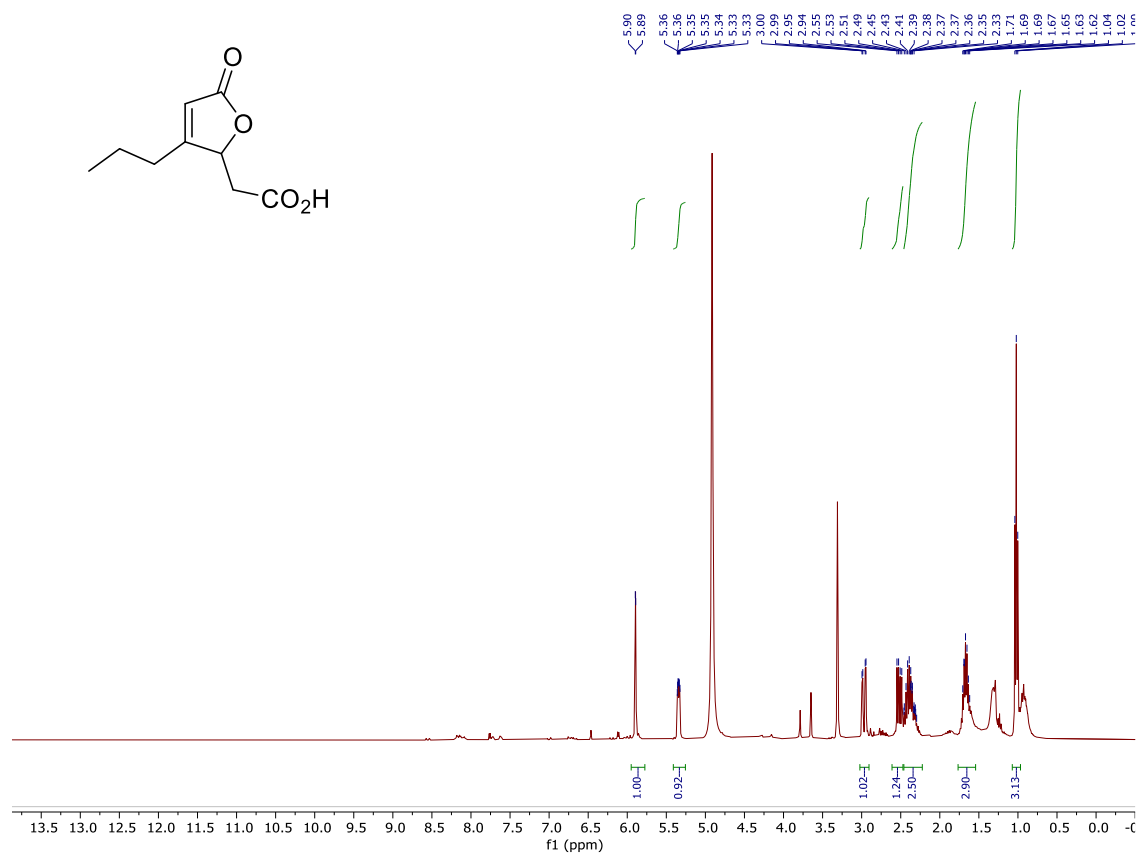


Figure S42. <sup>1</sup>H NMR spectrum of 4-(prop-1-yl)-5-carboxymethyl-2-furanone 3i.

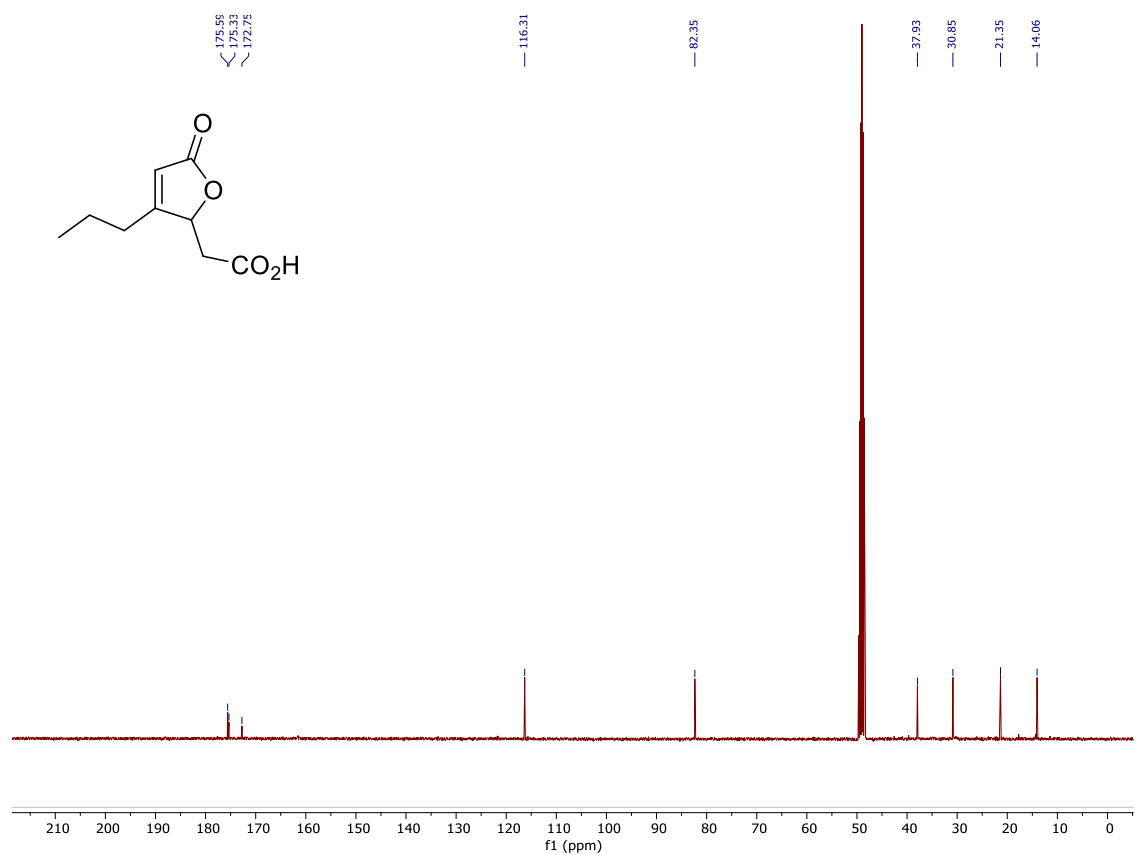


Figure S43. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 4-(prop-1-yl)-5-carboxymethyl-2-furanone 3i.

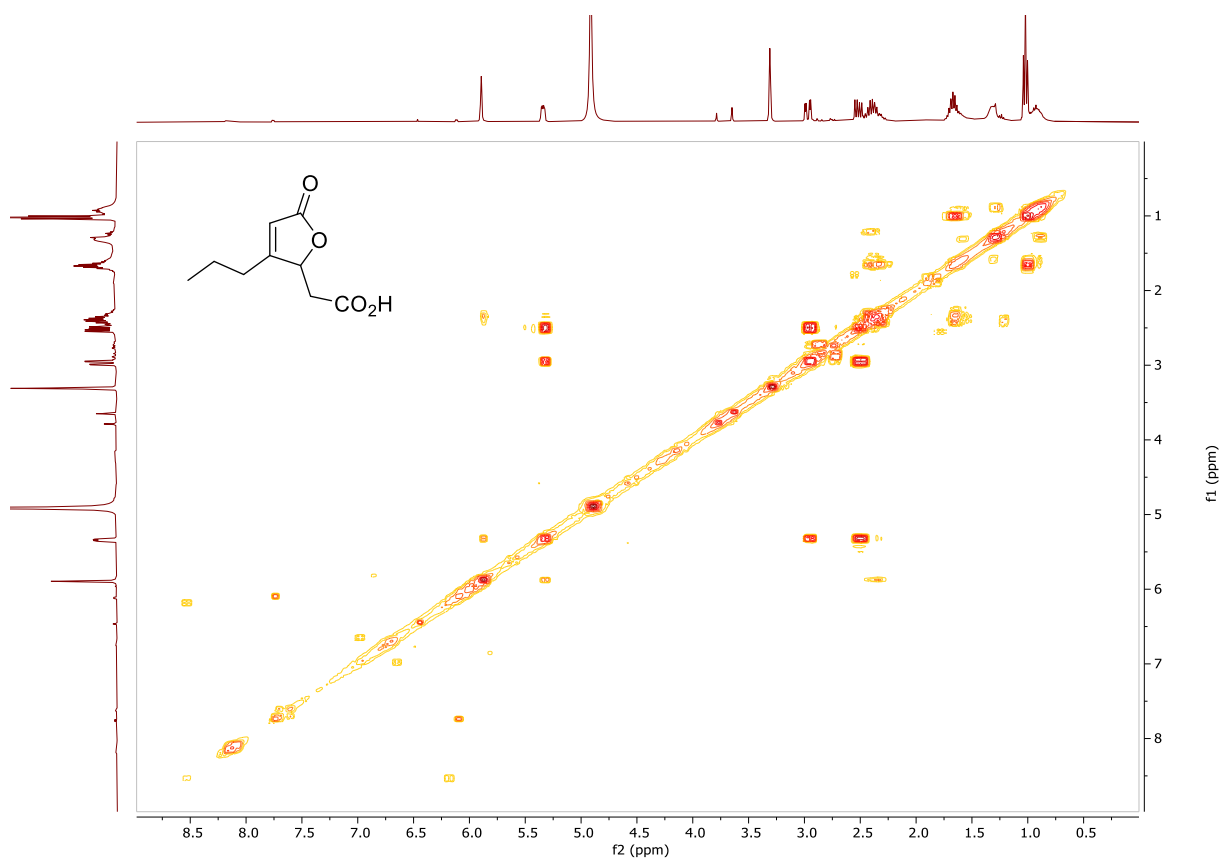


Figure S44. COSY NMR spectrum of 4-(prop-1-yl)-5-carboxymethyl-2-furanone 3i.

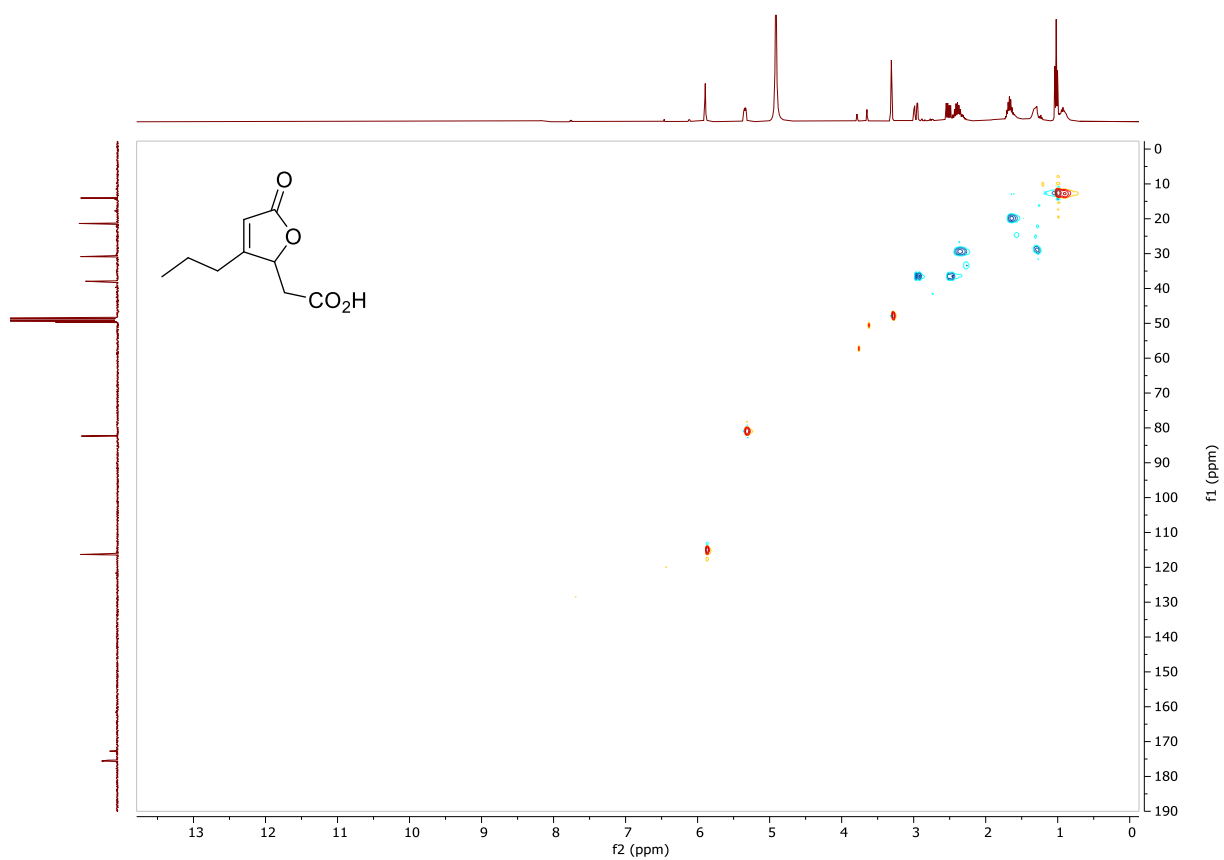


Figure S45. HSQC NMR spectrum of 4-(prop-1-yl)-5-carboxymethyl-2-furanone 3i.

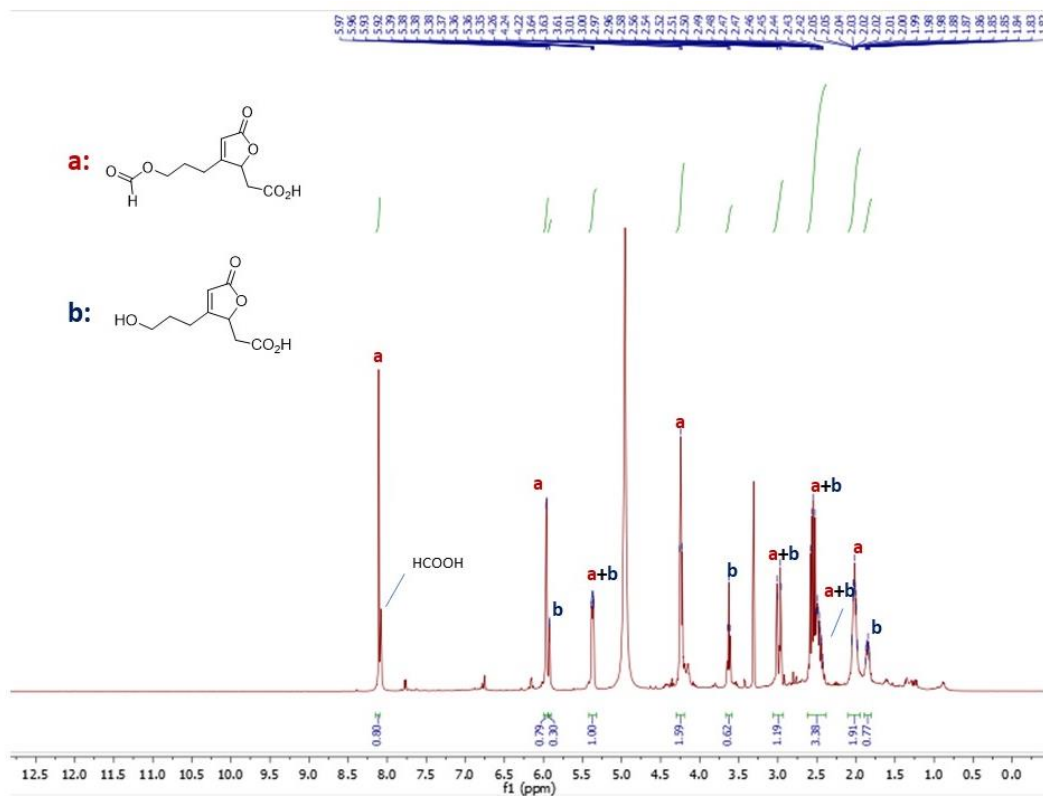


Figure S46.  $^1\text{H}$  NMR spectrum of the mixture of 4-(3-hydroxyprop-1-yl)-5-carboxymethyl-2-furanone **3j-i** and 4-(3-formyloxyprop-1-yl)-5-carboxymethyl-2-furanone **3j-ii**.

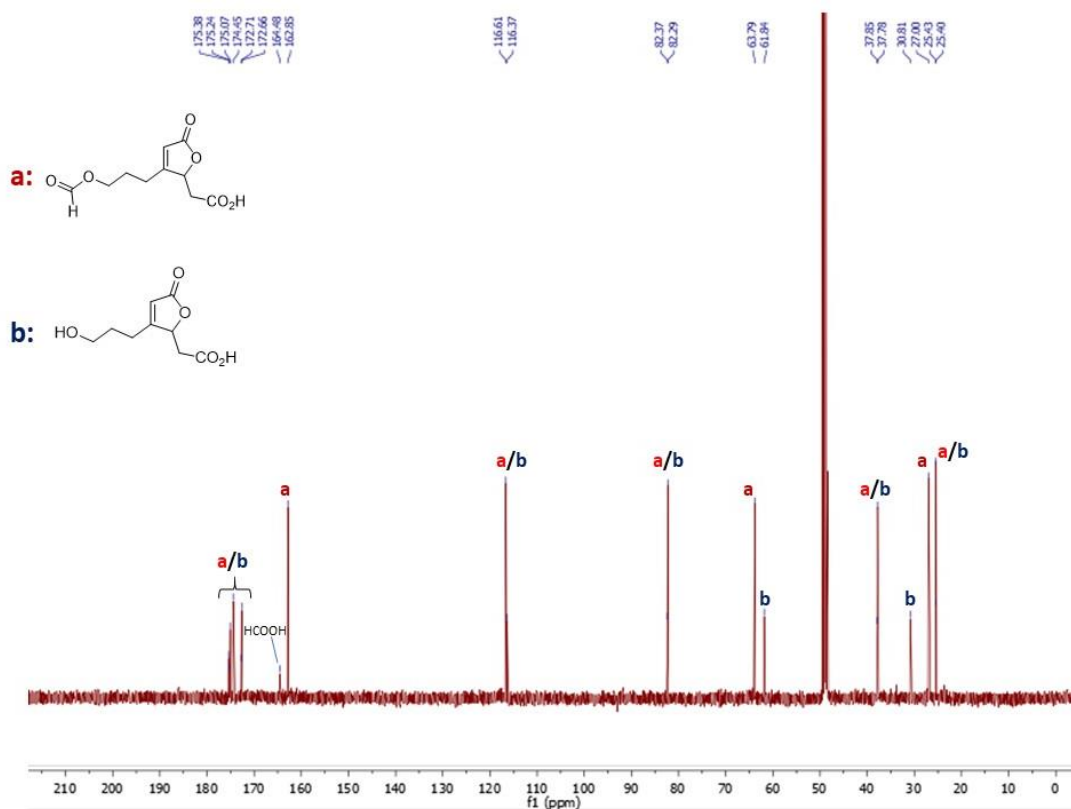
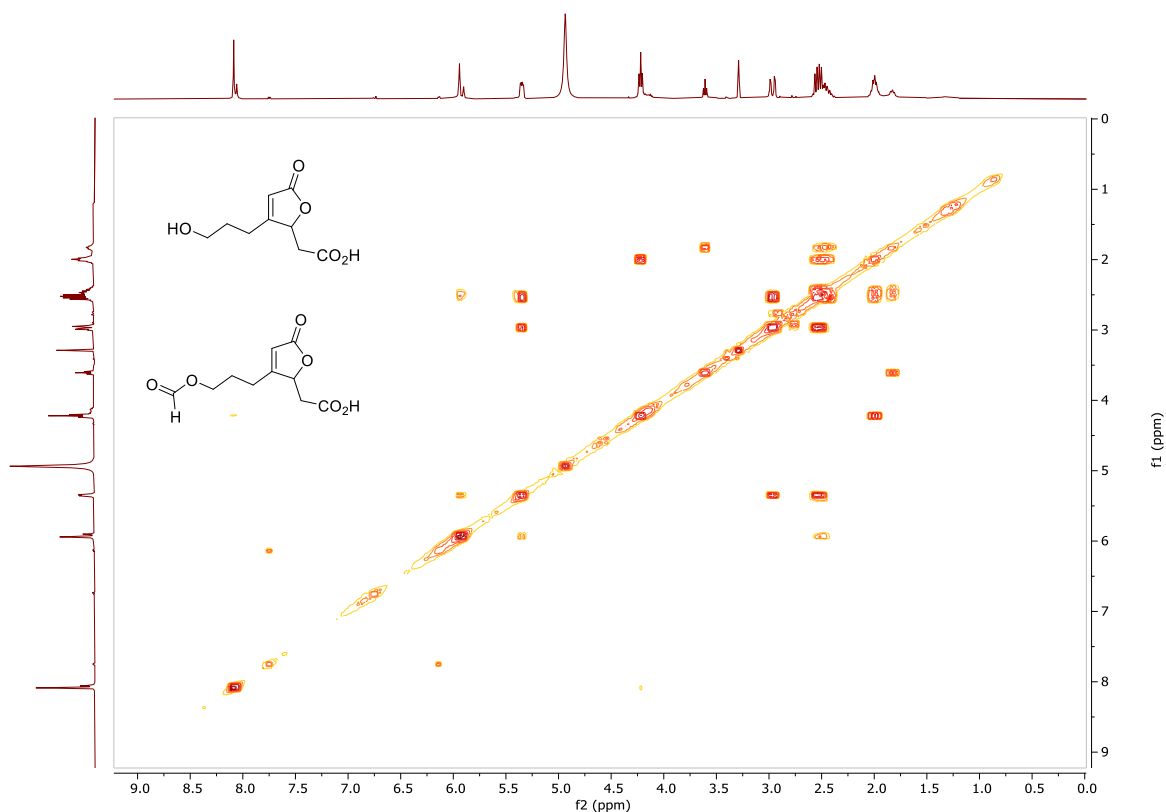
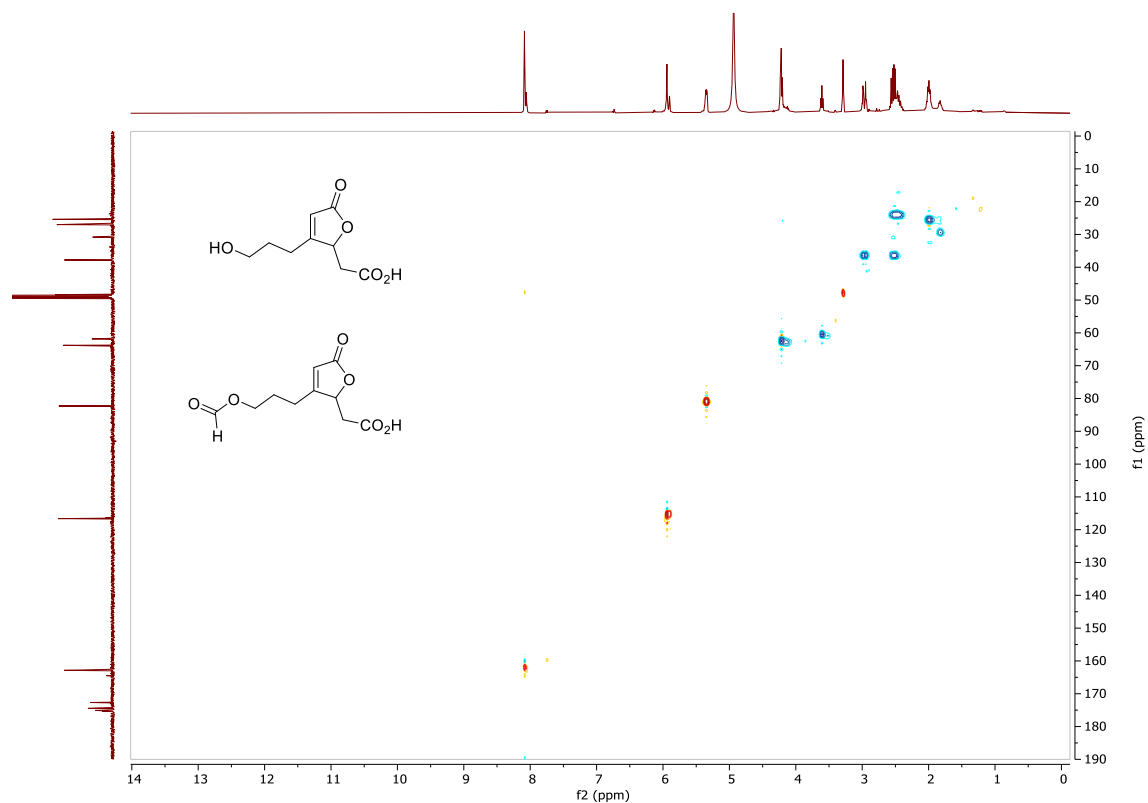


Figure S47.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of the mixture of 4-(3-hydroxyprop-1-yl)-5-carboxymethyl-2-furanone **3j-i** and 4-(3-formyloxyprop-1-yl)-5-carboxymethyl-2-furanone **3j-ii**.



**Figure S48. COSY NMR spectrum of the mixture of 4-(3-hydroxyprop-1-yl)-5-carboxymethyl-2-furanone 3j-i and 4-(3-formyloxyprop-1-yl)-5-carboxymethyl-2-furanone 3j-ii.**



**Figure S49. HSQC NMR spectrum of the mixture of 4-(3-hydroxyprop-1-yl)-5-carboxymethyl-2-furanone 3j-i and 4-(3-formyloxyprop-1-yl)-5-carboxymethyl-2-furanone 3j-ii.**

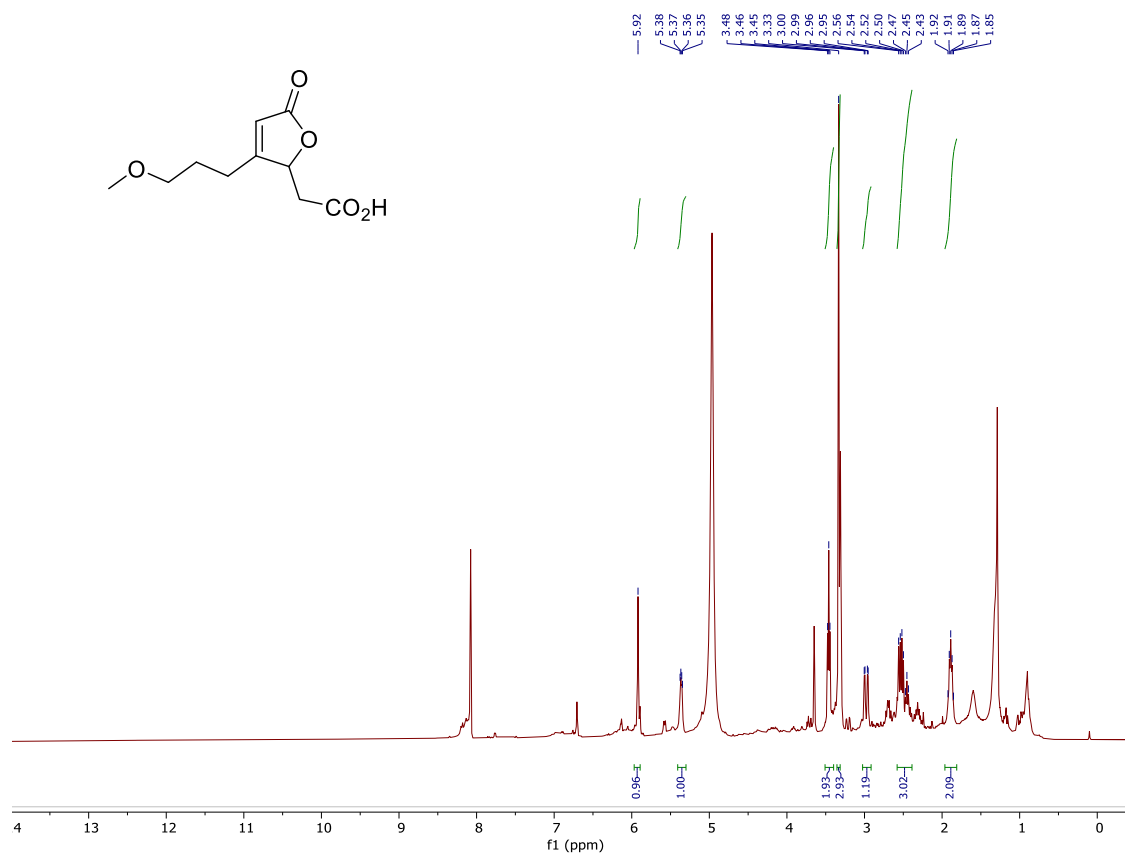


Figure S50. <sup>1</sup>H NMR spectrum of 4-(3-methoxyprop-1-yl)-5-carboxymethyl-2-furanone 3k.

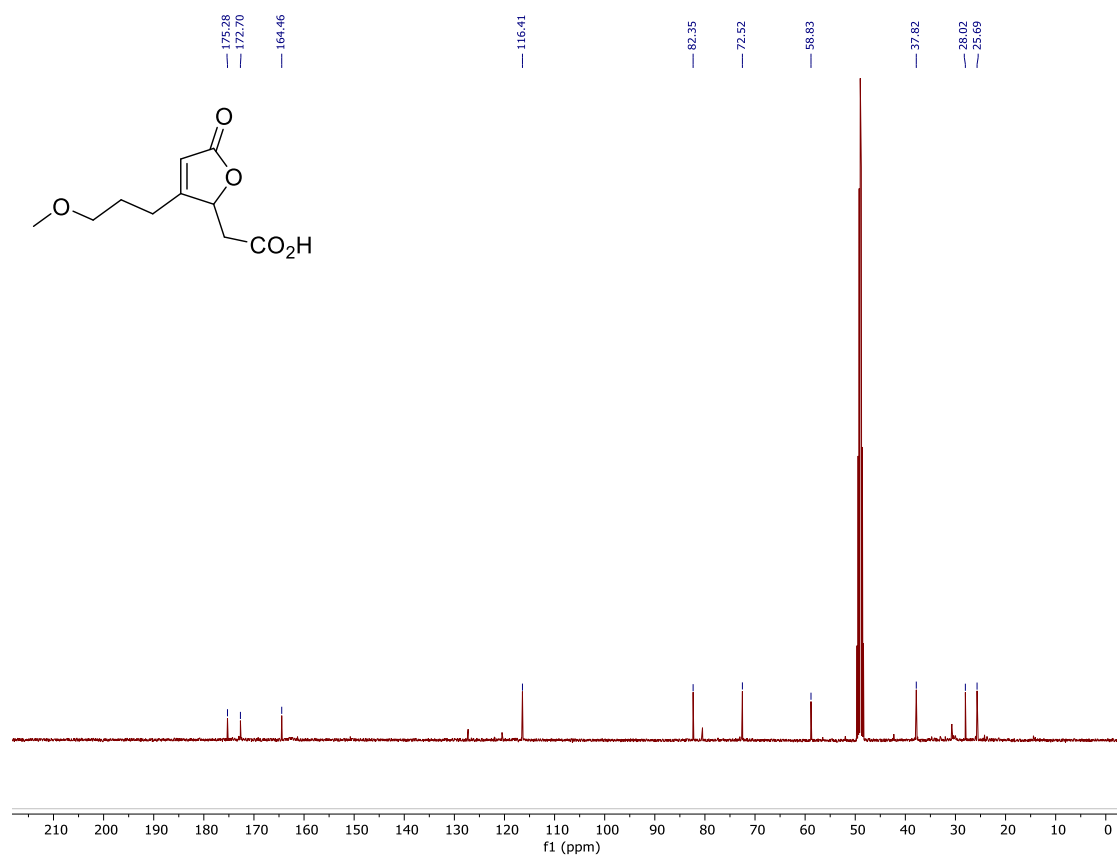


Figure S51. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 4-(3-methoxyprop-1-yl)-5-carboxymethyl-2-furanone 3k.

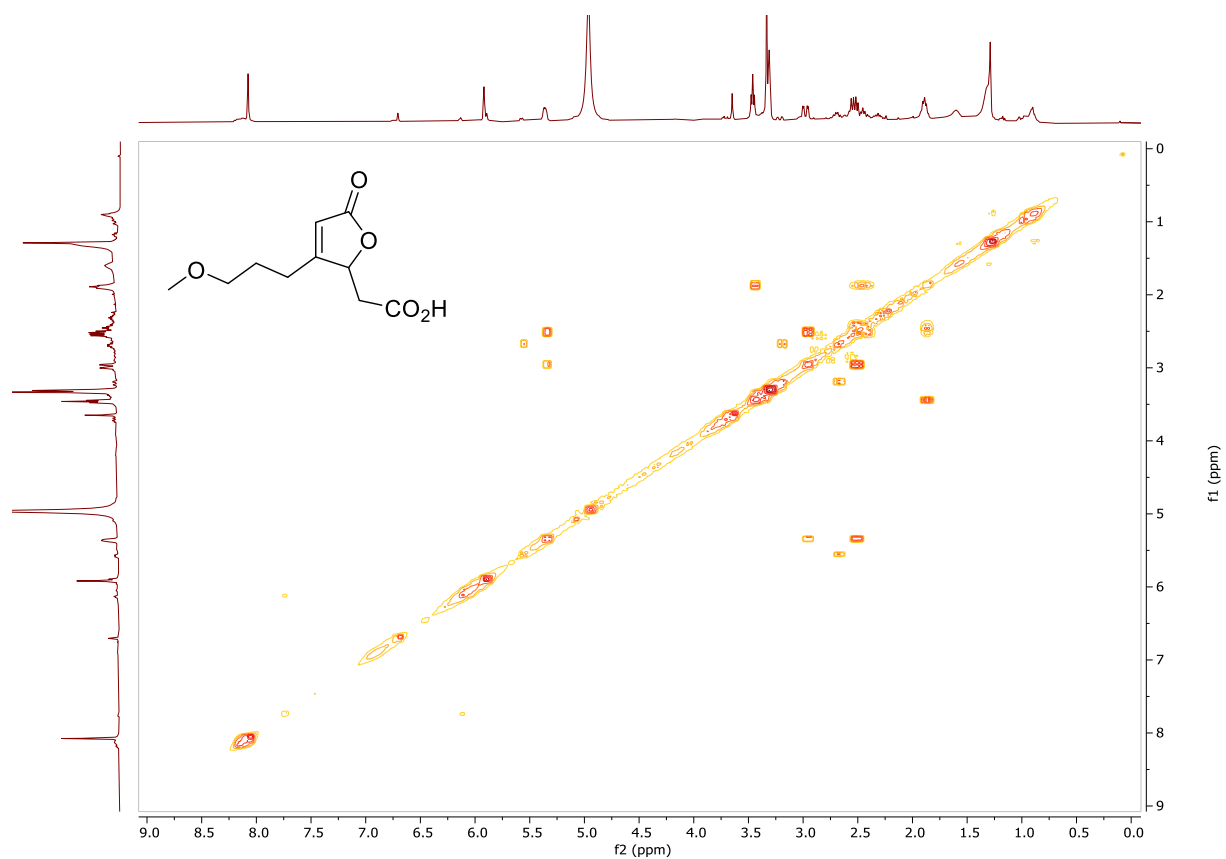


Figure S52. COSY NMR spectrum of 4-(3-methoxyprop-1-yl)-5-carboxymethyl-2-furanone 3k.

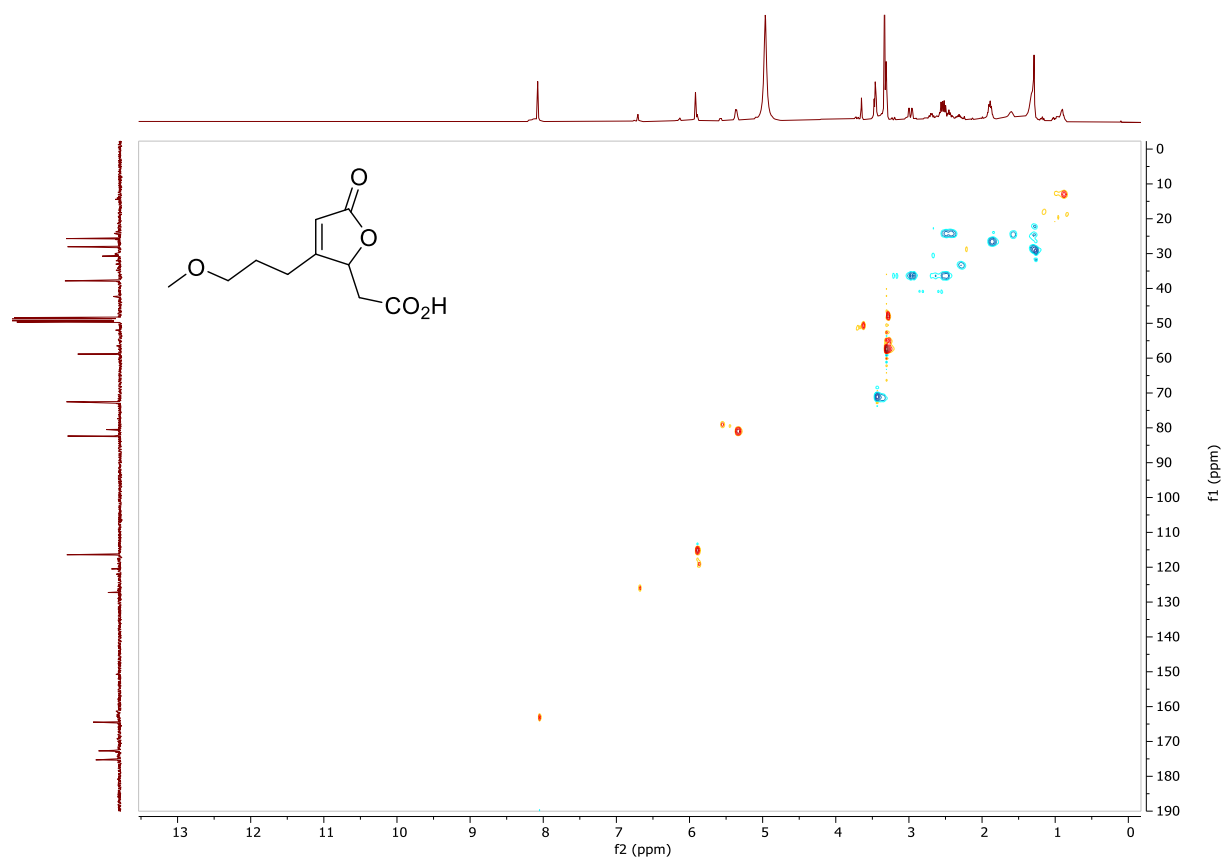


Figure S53. HSQC NMR spectrum of 4-(3-methoxyprop-1-yl)-5-carboxymethyl-2-furanone 3k.

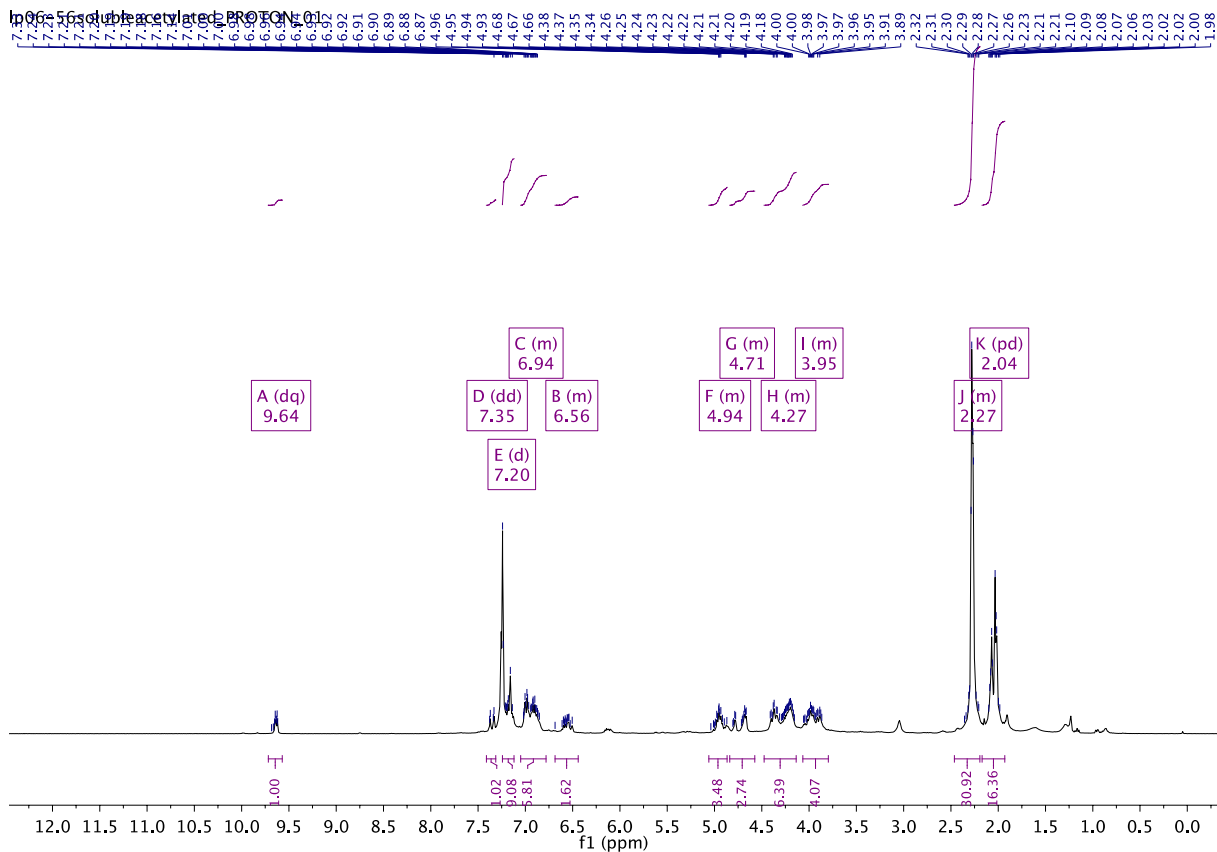


Figure S54. <sup>1</sup>H NMR of acetylated isolated EtOAc-soluble organosolv candlenut shell lignin in CDCl<sub>3</sub>

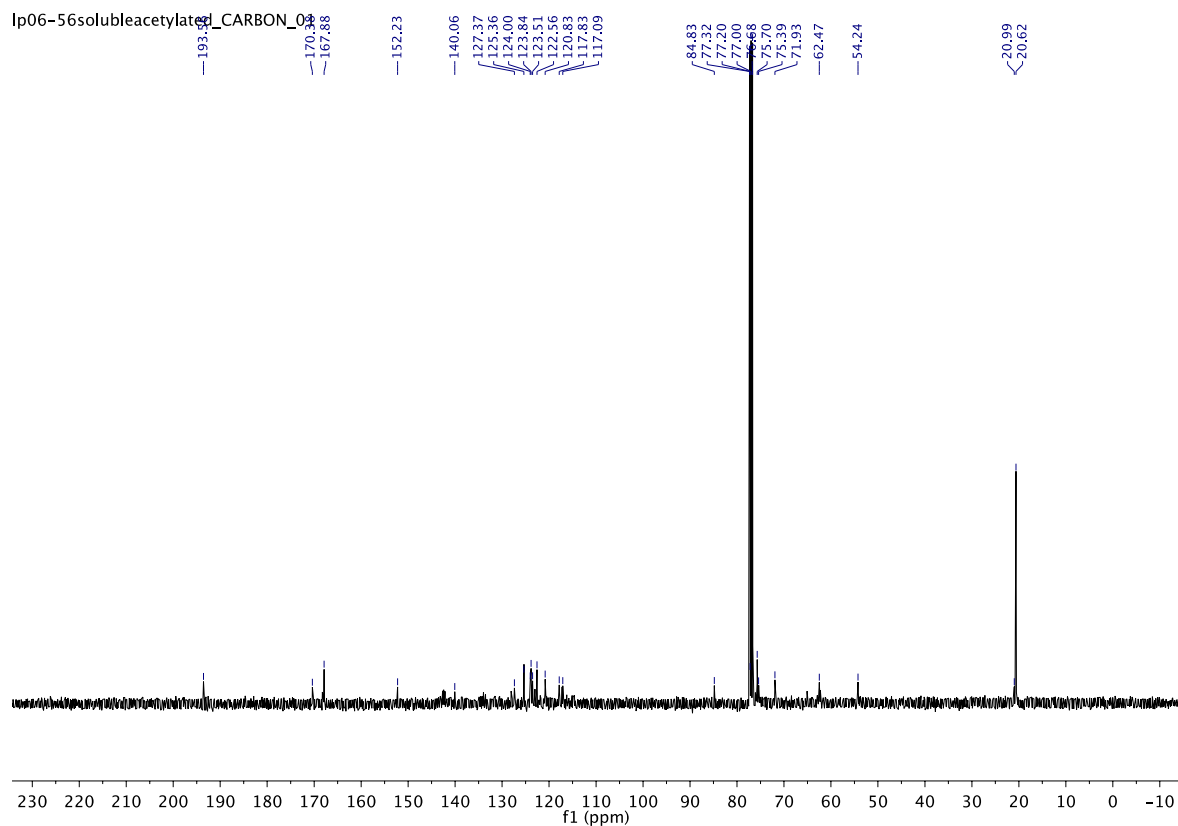


Figure S55. <sup>13</sup>C NMR of acetylated isolated EtOAc-soluble organosolv candlenut shell lignin in CDCl<sub>3</sub>

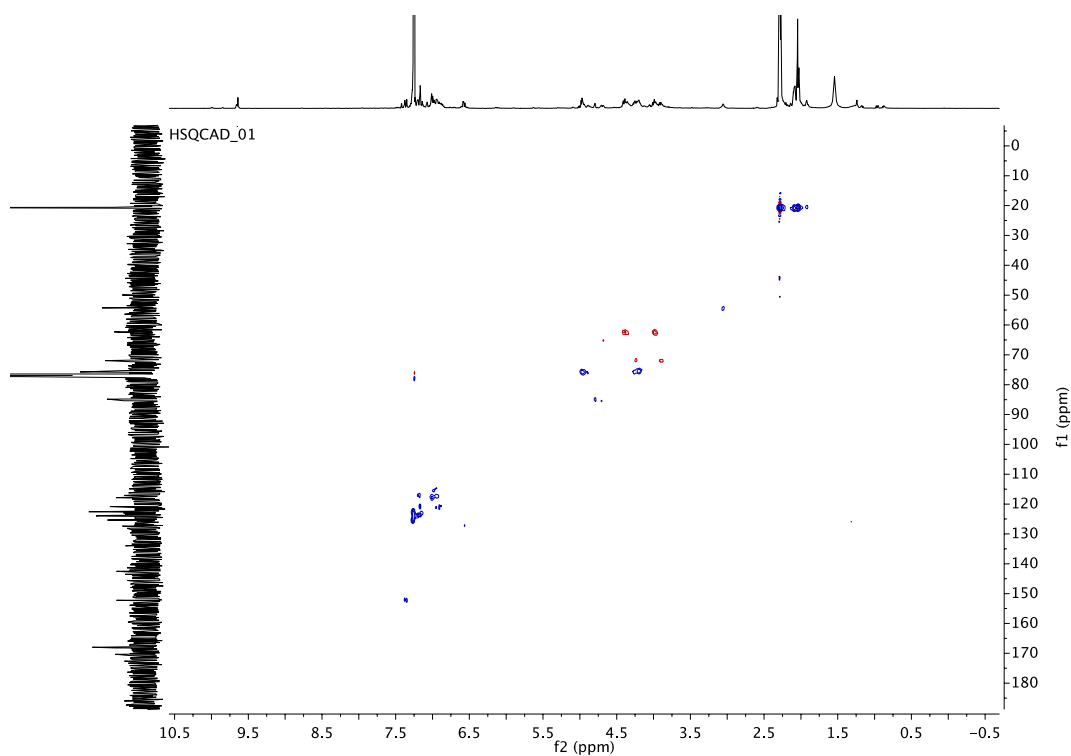


Figure S56. 2D HSQC NMR of acetylated isolated EtOAc-soluble organosolv candlenut shell lignin in  $\text{CDCl}_3$

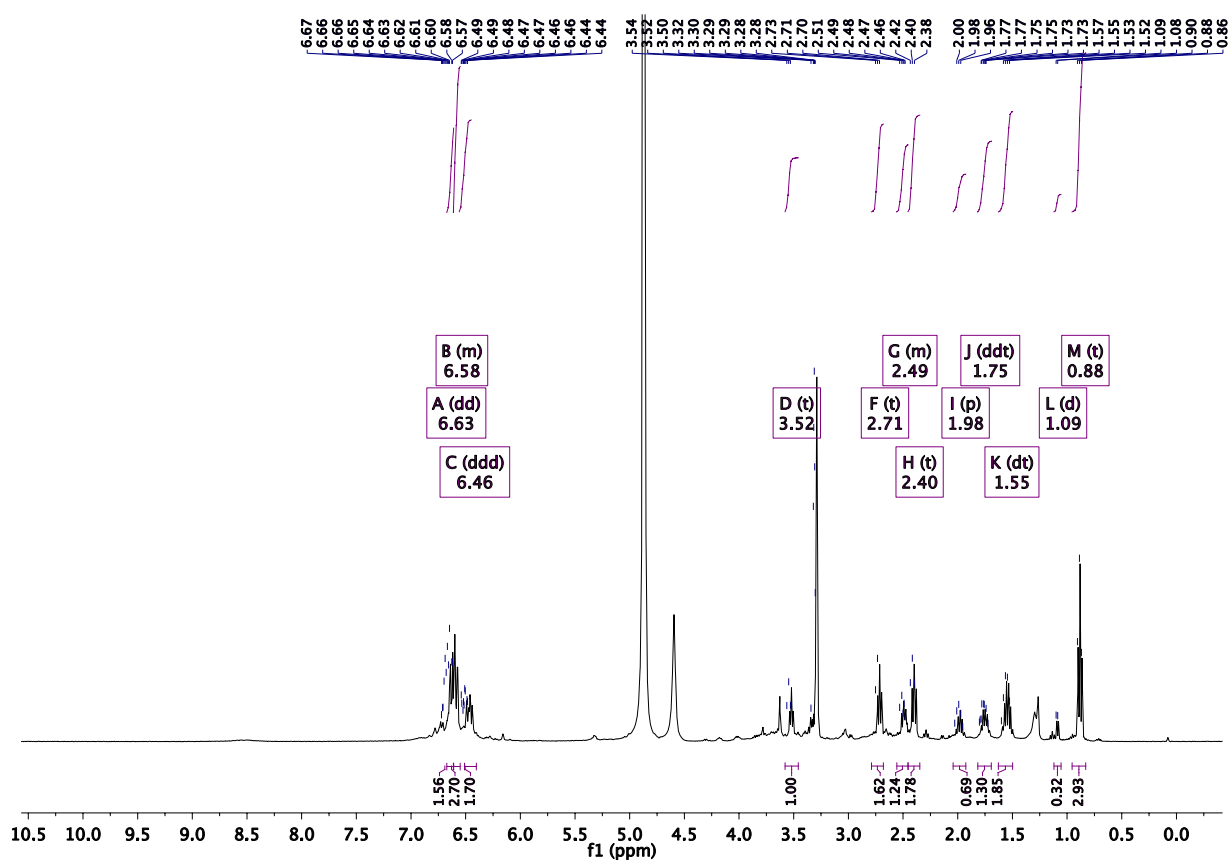


Figure S57.  $^1\text{H}$  NMR in MeOD of lignin oil following Cu-PMO catalysed reductive depolymerization of EtOAc-soluble organosolv candlenut shell lignin



CARBON\_01

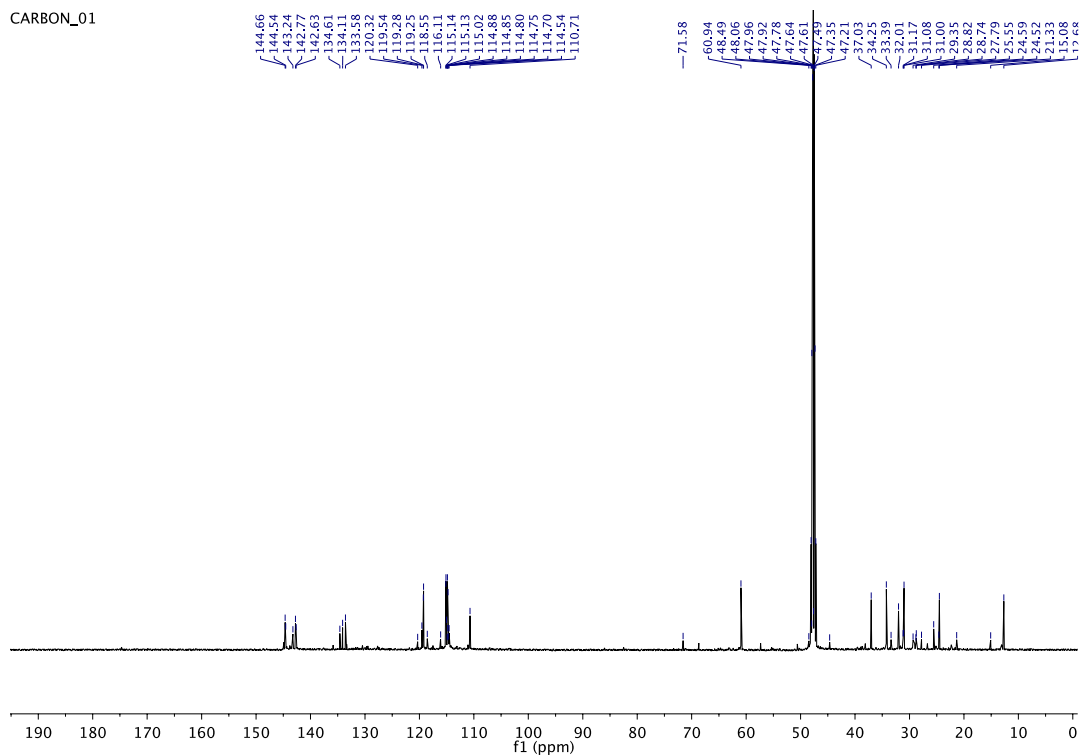


Figure S58.  $^{13}\text{C}$  NMR in MeOD of lignin oil following Cu-PMO catalysed reductive depolymerization of EtOAc-soluble organosolv candlenut shell lignin

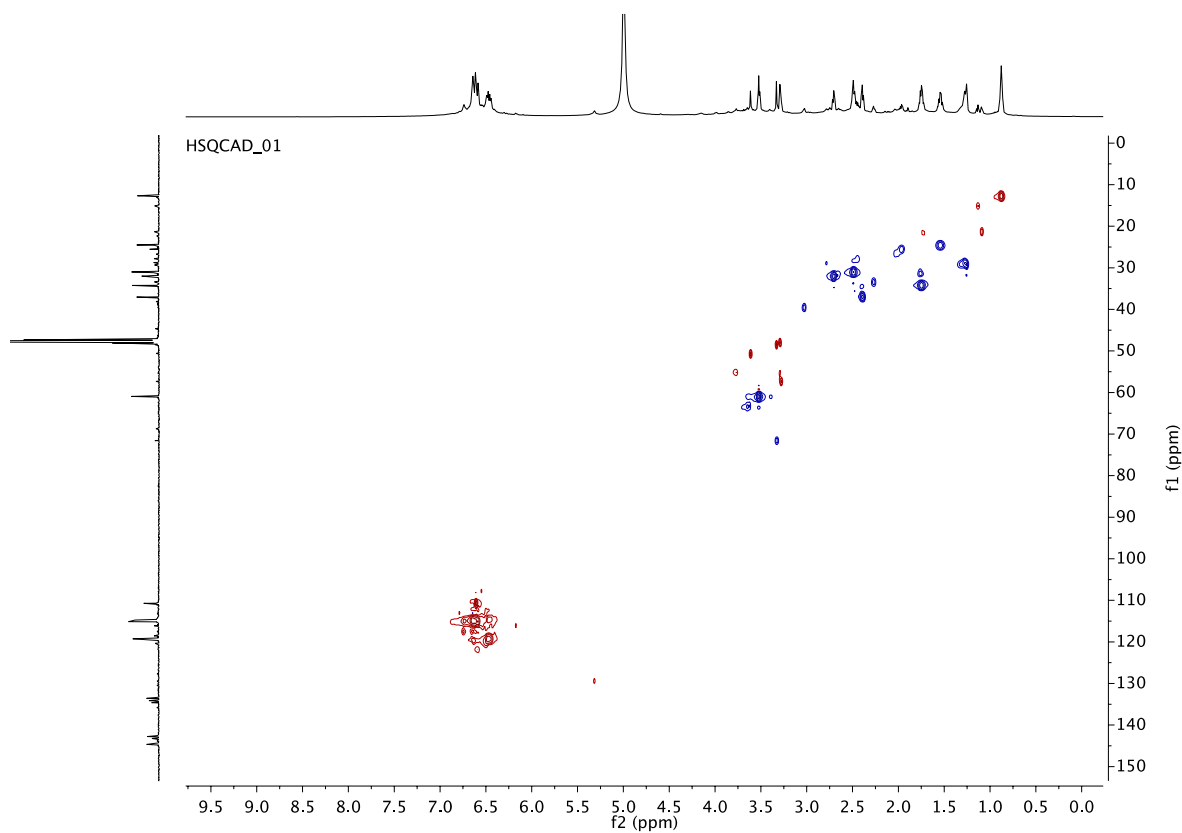


Figure S59. HSQC NMR in MeOD of lignin oil following Cu-PMO catalysed reductive depolymerization of EtOAc-soluble organosolv candlenut shell lignin

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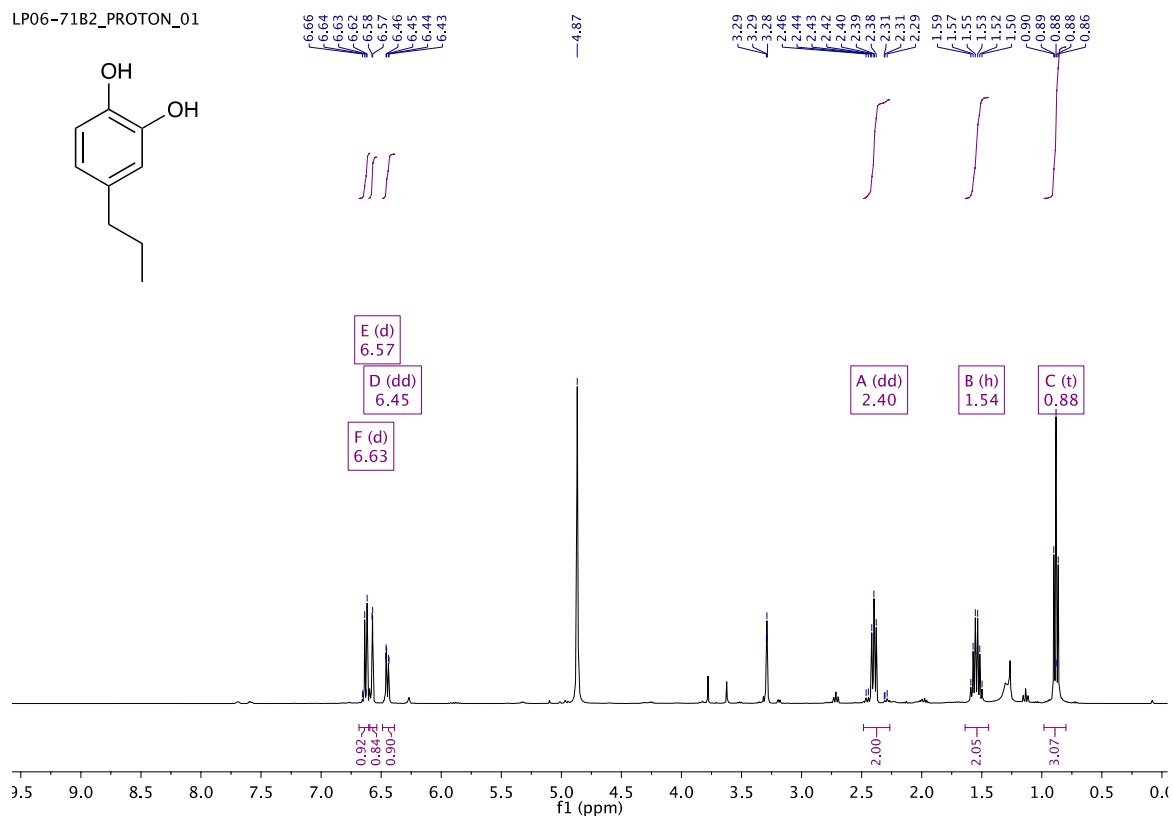


Figure S60.  $^1\text{H}$  NMR in MeOD of 4-propylcatechol **1i** isolated from Cu-PMO catalysed depolymerization of EtOAc-soluble candlenut shell lignin.

LP06-71B2\_CARBON\_01

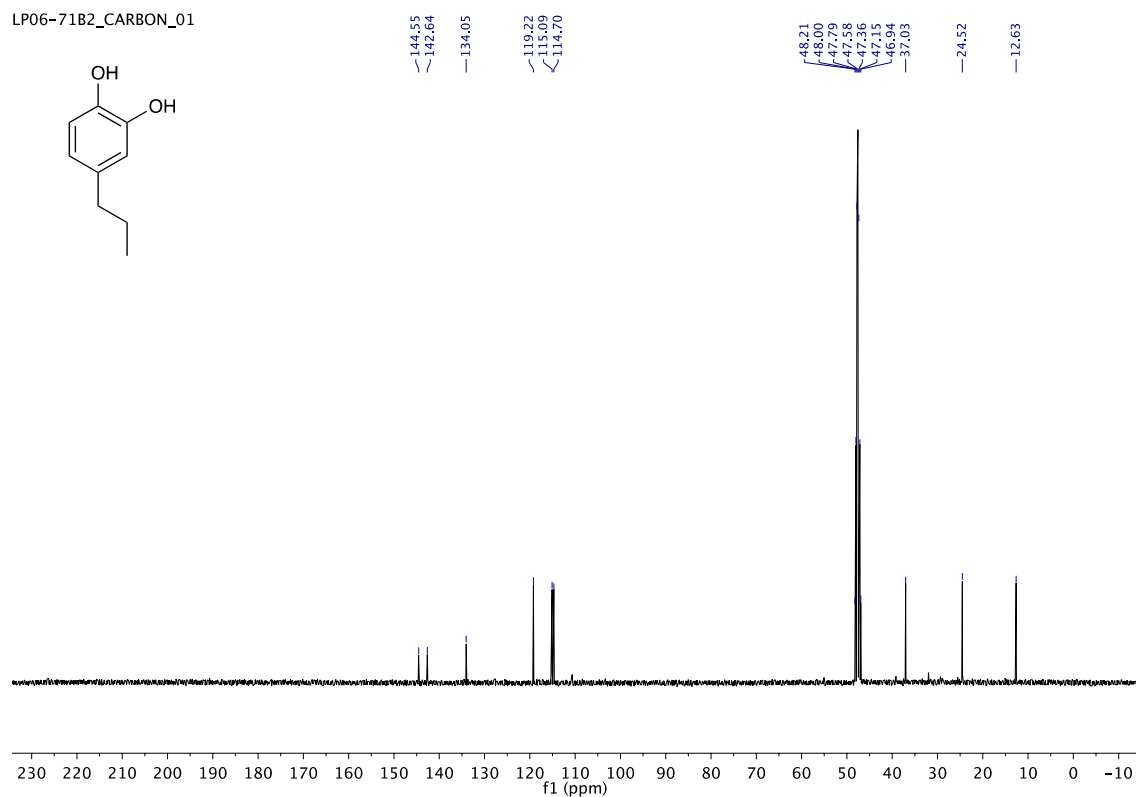


Figure S61.  $^{13}\text{C}$  NMR in MeOD of 4-propylcatechol **1i** isolated from Cu-PMO catalysed depolymerization of EtOAc-soluble candlenut shell lignin.

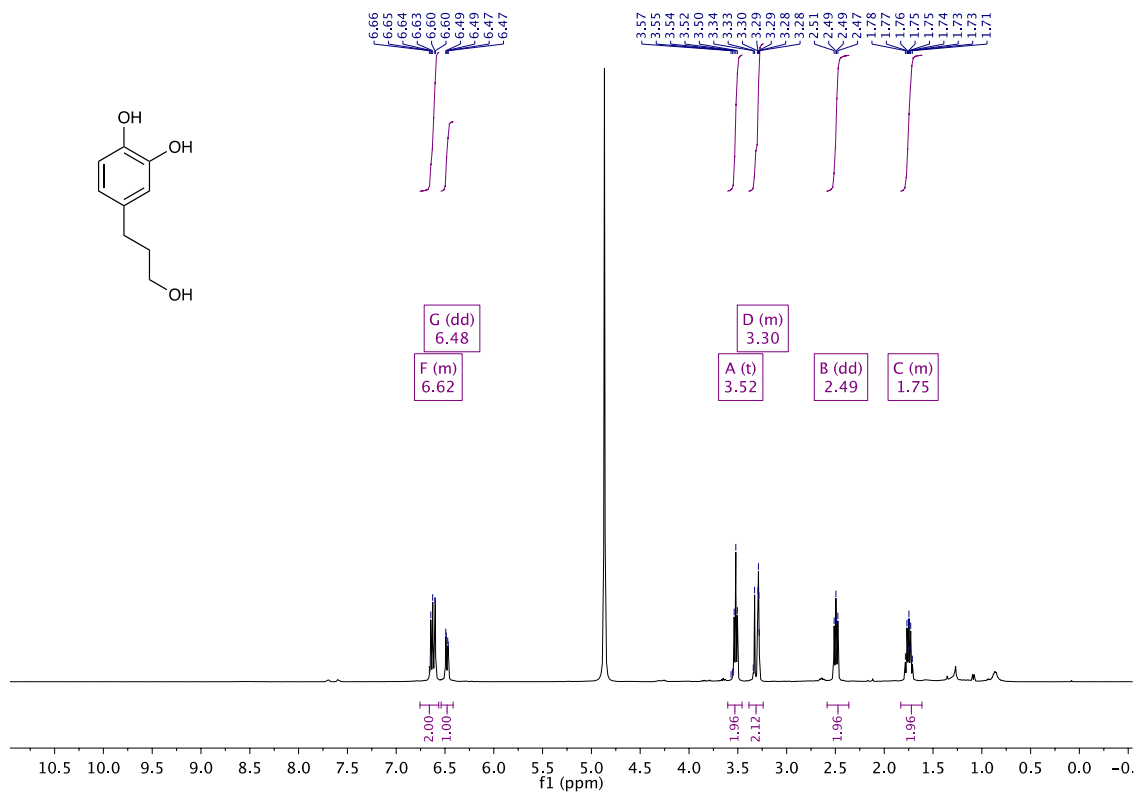


Figure S62. <sup>1</sup>H NMR in MeOD of 4-(3-hydroxypropyl)catechol **1j** isolated from Cu-PMO catalysed depolymerization of EtOAc-soluble candlenut shell lignin.

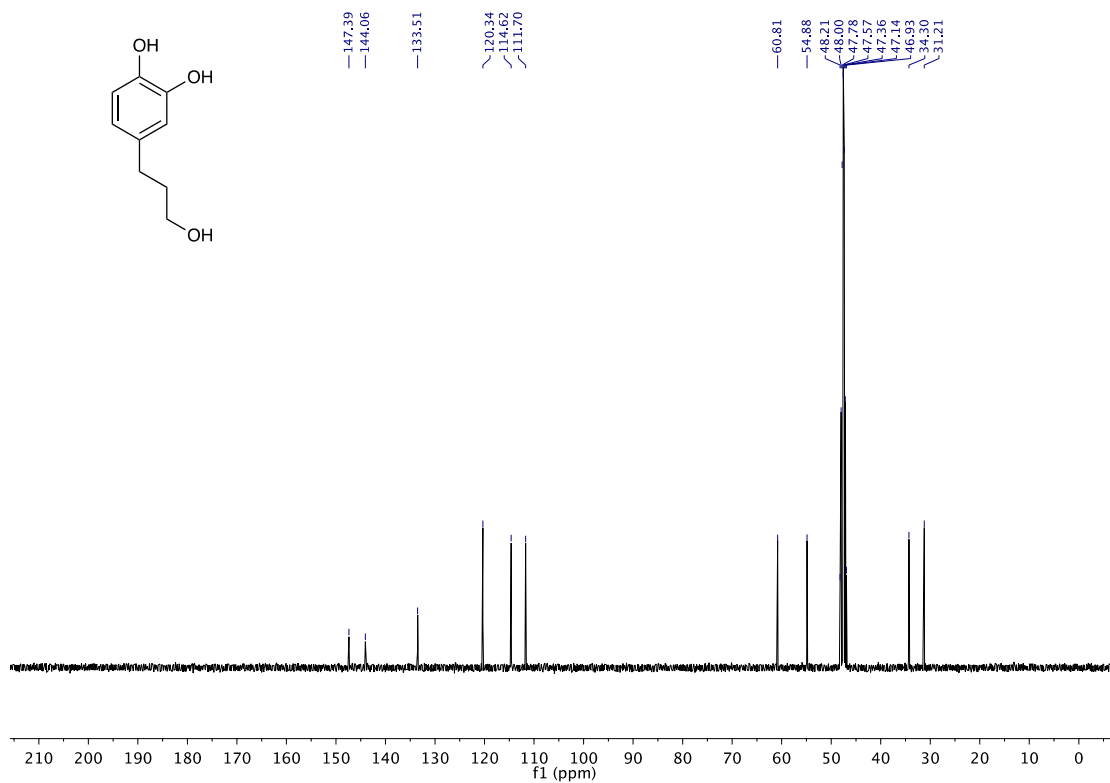


Figure S63. <sup>13</sup>C NMR in MeOD of 4-(3-hydroxypropyl)catechol **1j** isolated from Cu-PMO catalysed depolymerization of EtOAc-soluble candlenut shell lignin.

LP07-25pfd\_PROTON\_01

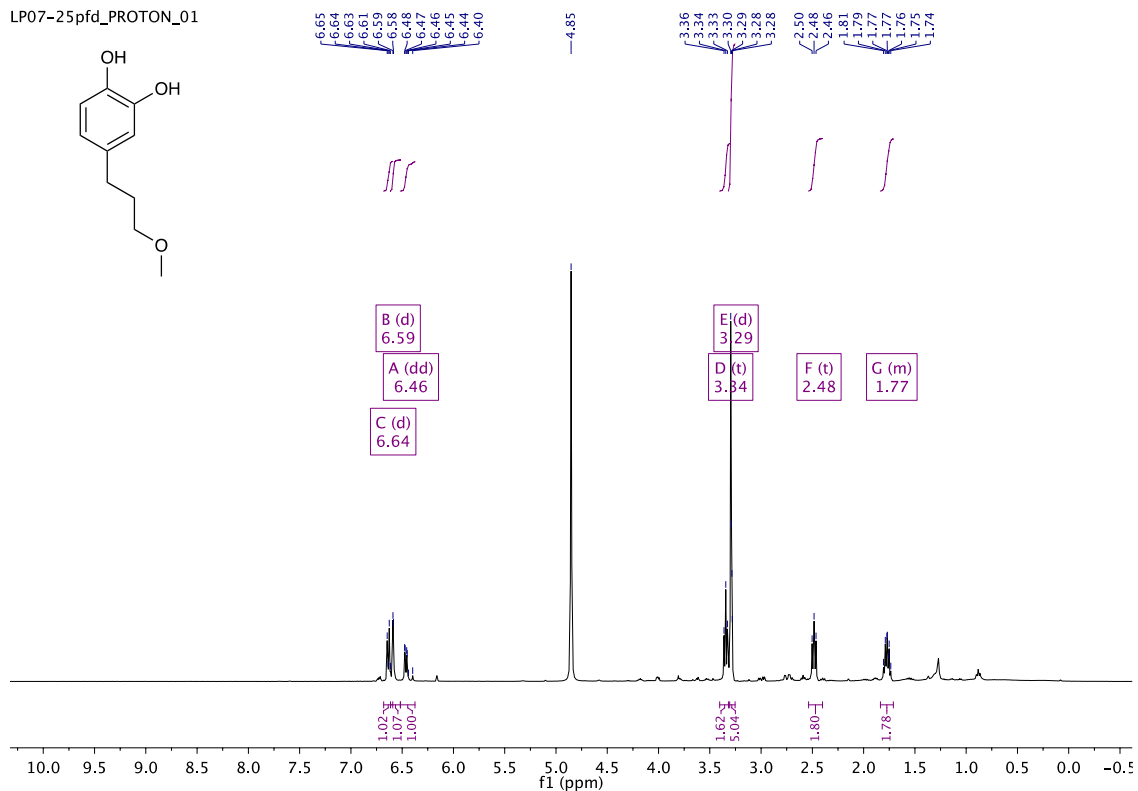


Figure S64.  $^1\text{H}$  NMR in MeOD of 4-(3-methoxypropyl)catechol 1k isolated from Cu-PMO catalysed depolymerization of EtOAc-soluble candlenut shell lignin.

LP07-25pfd\_CARBOON\_01

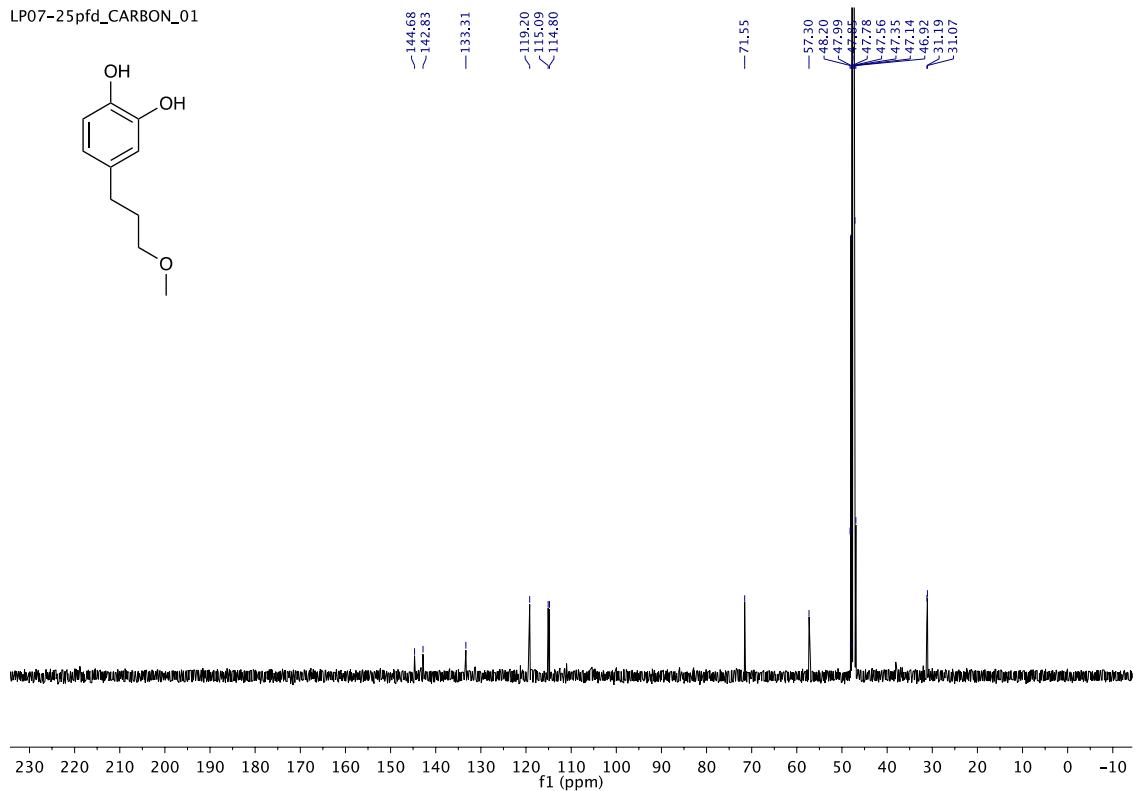


Figure S65.  $^{13}\text{C}$  NMR in MeOD of 4-(3-methoxypropyl)catechol 1k isolated from Cu-PMO catalysed depolymerization of EtOAc-soluble candlenut shell lignin.

## 7- References

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