

## Electronic Supplementary Information

### Laccase-catalyzed stereoselective oxidative ring opening of 2,5-dialkylfurans into 2-ene-1,4-diones using air as an oxidant

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## 1 General Methods

All starting materials were purchased from commercial suppliers (Sigma-Aldrich Chemical Co., Acros Organics, Alfa Aesar) and were used without further purification unless otherwise indicated. Solvents used for extraction and purification were distilled prior to use. THF was dried over sodium/benzophenone. TLC was performed on aluminium-backed plates coated with silicagel with F254 indicator (Merck). Compounds were visualised by UV light (254 nm) or with vanillin/H<sub>2</sub>SO<sub>4</sub> as a solution in ethanol. Flash Chromatography was carried out on silica gel 60 M, 230-400 mesh (Macherey & Nagel). <sup>1</sup>H (<sup>13</sup>C) NMR spectra were recorded at 300 (75) MHz on a Varian <sup>Unity</sup>Inova spectrometer with CDCl<sub>3</sub> ( $\delta = 7.26$  ppm in <sup>1</sup>H NMR spectra and  $\delta = 77.0$  ppm in <sup>13</sup>C NMR spectra) as internal standards.

## 2 Synthesis of 2,5-dialkylfurans 1

### 2.1. General procedure for the synthesis of 1b-g<sup>[1]</sup>

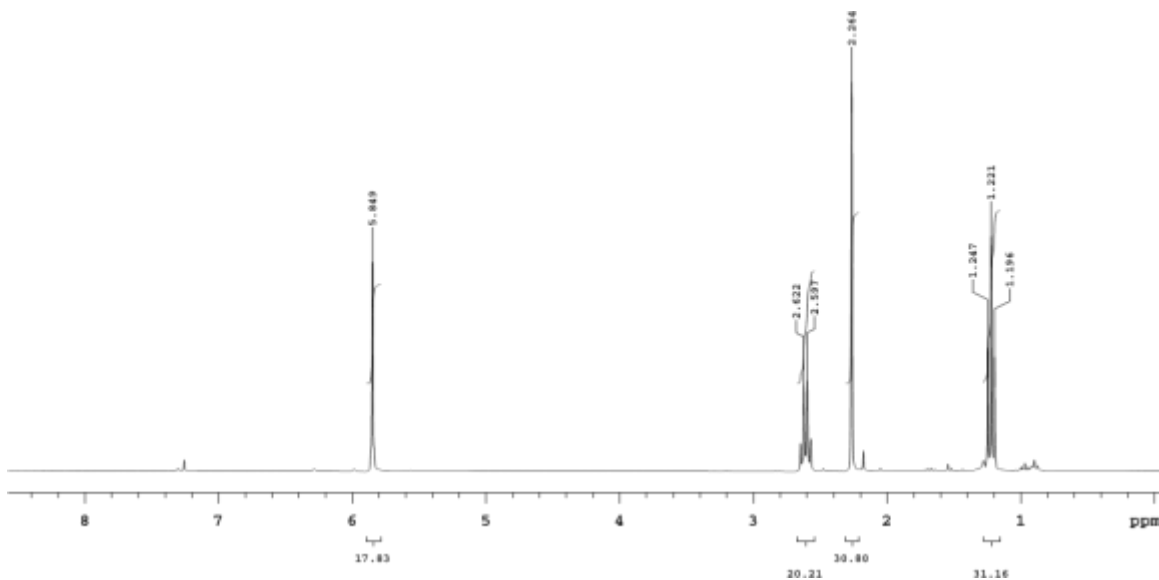
The 2-alkylfuran (20 mmol) was added dropwise to a stirred solution of *n*-BuLi (13.5 mL, 20 mmol, 1.6 M solution in hexanes) and dry THF (9 mL) under argon at -78 °C. The mixture was stirred for 24 h at rt. The alkyl iodide (20 mmol) was added dropwise and the mixture was stirred vigorously for another 24 h at rt. The reaction mixture was poured into 100 g ice water and extracted with diethylether (3 × 25 ml). The combined organic fractions were dried over Na<sub>2</sub>SO<sub>4</sub> and the solvents were removed under reduced pressure. The crude product was purified by flash chromatography on SiO<sub>2</sub> with *n*-pentane as eluent to provide the 2,5-dialkylfuran.

### 2.2. Synthesis and analytical data for 1b-g

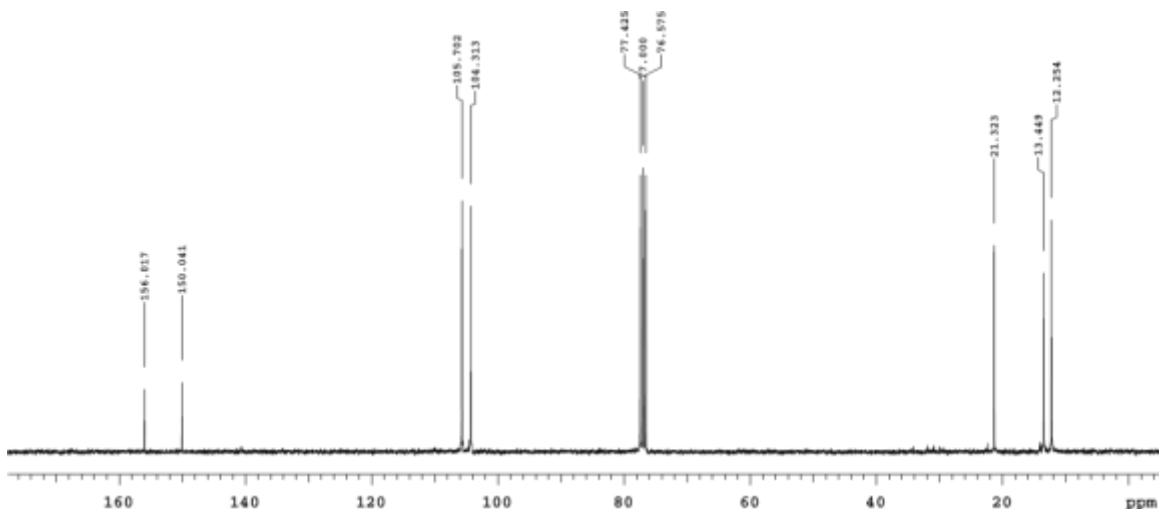
#### 2-Ethyl-5-methylfuran (1b)<sup>[1-3]</sup>

According to the general procedure, 2-methylfuran (1.8 mL, 20 mmol) was reacted with *n*-BuLi (13.5 mL, 20 mmol, 1.6 M solution in hexanes) and ethyl iodide (1.6 mL, 20 mmol). The crude product was purified by flash chromatography on SiO<sub>2</sub> with *n*-pentane as eluent to afford 2-ethyl-5-methylfuran (**1b**) (1.3 g, 61%) as colourless oil.

$R_f = 0.7$  (diethylether / *n*-pentane = 1:1);  $\delta_H$  (300 MHz;  $CDCl_3$ ) 1.22 (t,  $^3J_{2'-H, 1'-H} = 7.6$  Hz, 3H, 2'-H), 2.27 (s, 3H,  $CH_3$ ), 2.60 (q,  $^3J_{1'-H, 2'-H} = 7.5$  Hz, 2H, 1'-H), 5.85 (s, 2H, 4-H and 5-H) ppm;  $\delta_C$  (75 MHz;  $CDCl_3$ ) 12.25 (C-2'), 13.45 ( $CH_3$ ), 21.32 (C-1'), 104.31 (C-3), 105.70 (C-4), 150.04 (C-5), 156.01 (C-2) ppm.



**Fig. 1**  $^1H$  NMR spectrum of 2-ethyl-5-methylfuran (**1b**) (300 MHz,  $CDCl_3$ ).

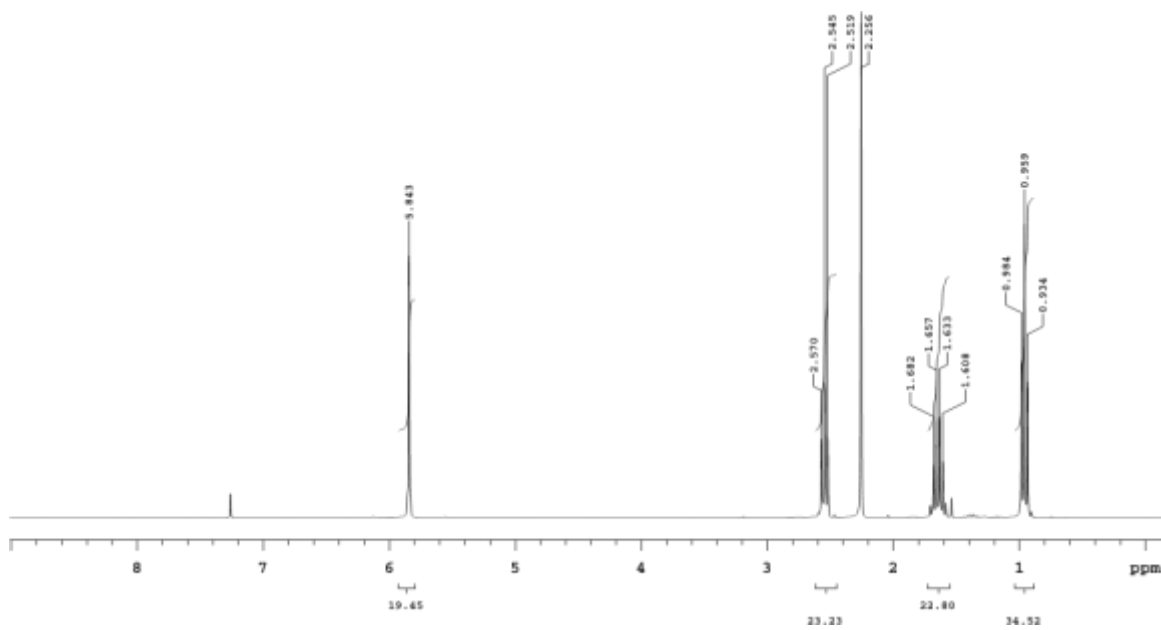


**Fig. 2**  $^{13}\text{C}$  NMR spectrum of 2-ethyl-5-methylfuran (**1b**) (75 MHz,  $\text{CDCl}_3$ ).

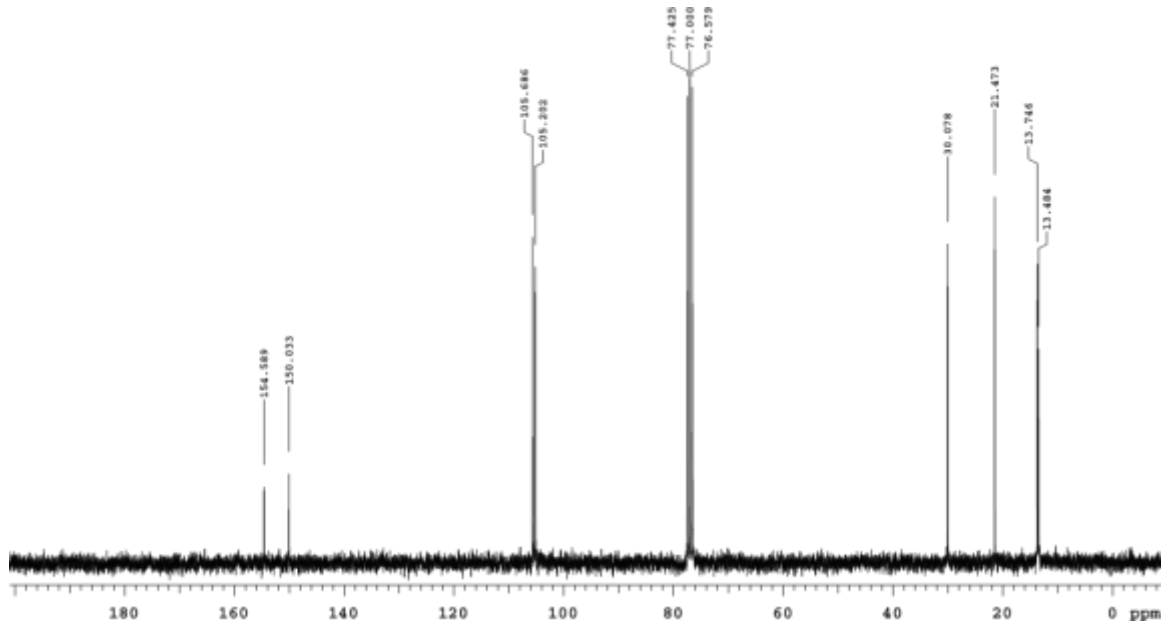
### 2-Methyl-5-propylfuran (**1c**)<sup>[1], [4]</sup>

According to the general procedure, 2-methylfuran (1.8 mL, 20 mmol) was reacted with *n*-BuLi (13.5 mL, 20 mmol, 1.6 M solution in hexanes) and *n*-propyl iodide (2 mL, 20 mmol). The crude product was purified by flash chromatography on  $\text{SiO}_2$  with *n*-pentane as eluent to afford 2-methyl-5-propylfuran (**1c**) (1.36 g, 55%) as colourless oil.

$R_f = 0.7$  (diethylether / *n*-pentane = 1:1);  $\delta_{\text{H}}$  (300 MHz;  $\text{CDCl}_3$ ) 0.95 (t,  $^3J_{3\text{'-H}, 2\text{'-H}} = 7.32$  Hz, 3H, 3'-H), 1.64 (tq,  $^3J_{2\text{'-H}, 1\text{'-H}} = 7.0$  Hz,  $^3J_{2\text{'-H}, 3\text{'-H}} = 7.4$  Hz, 2H, 2'-H), 2.25 (s, 3H,  $\text{CH}_3$ ), 2.54 (t,  $^3J_{1\text{'-H}, 2\text{'-H}} = 7.49$  Hz, 2H, 1'-H), 5.84 (s, 2H, 4-H and 5-H) ppm;  $\delta_{\text{C}}$  (75 MHz;  $\text{CDCl}_3$ ) 13.48 (C-3'), 13.75 ( $\text{CH}_3$ ), 21.47 (C-2'), 30.07 (C-1'), 105.20 (C-3), 105.68 (C-4), 150.03 (C-5), 154.59 (C-2) ppm.



**Fig. 3** <sup>1</sup>H NMR spectrum of 2-methyl-5-propylfuran (**1c**) (300 MHz, CDCl<sub>3</sub>).

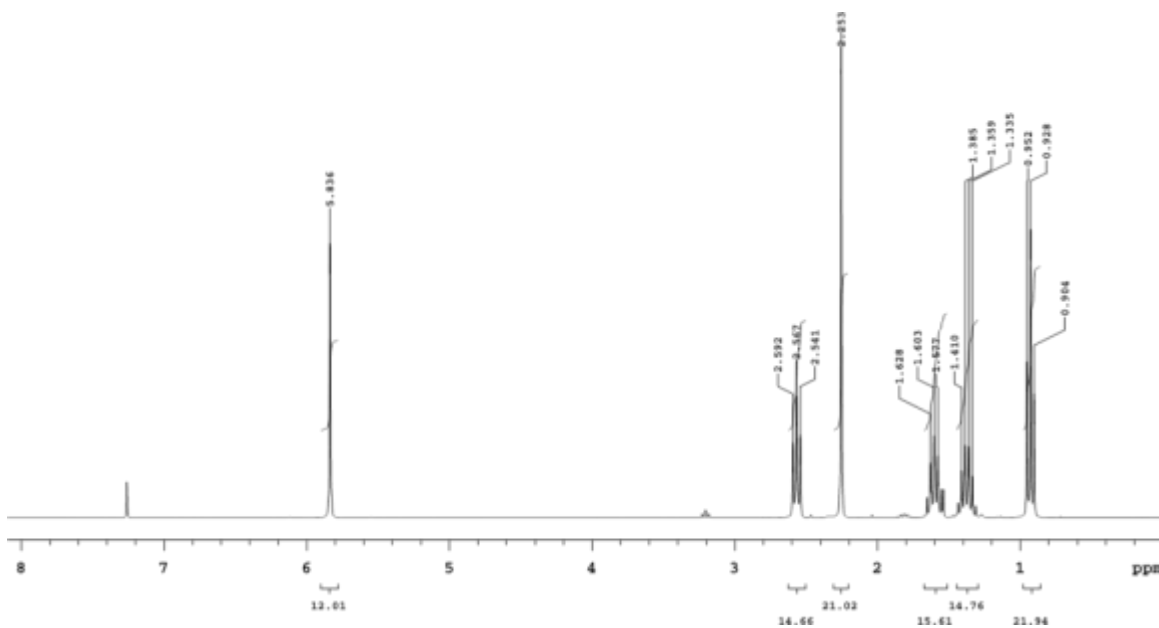


**Fig. 4** <sup>13</sup>C NMR spectrum of 2-methyl-5-propylfuran (**1c**) (75 MHz, CDCl<sub>3</sub>).

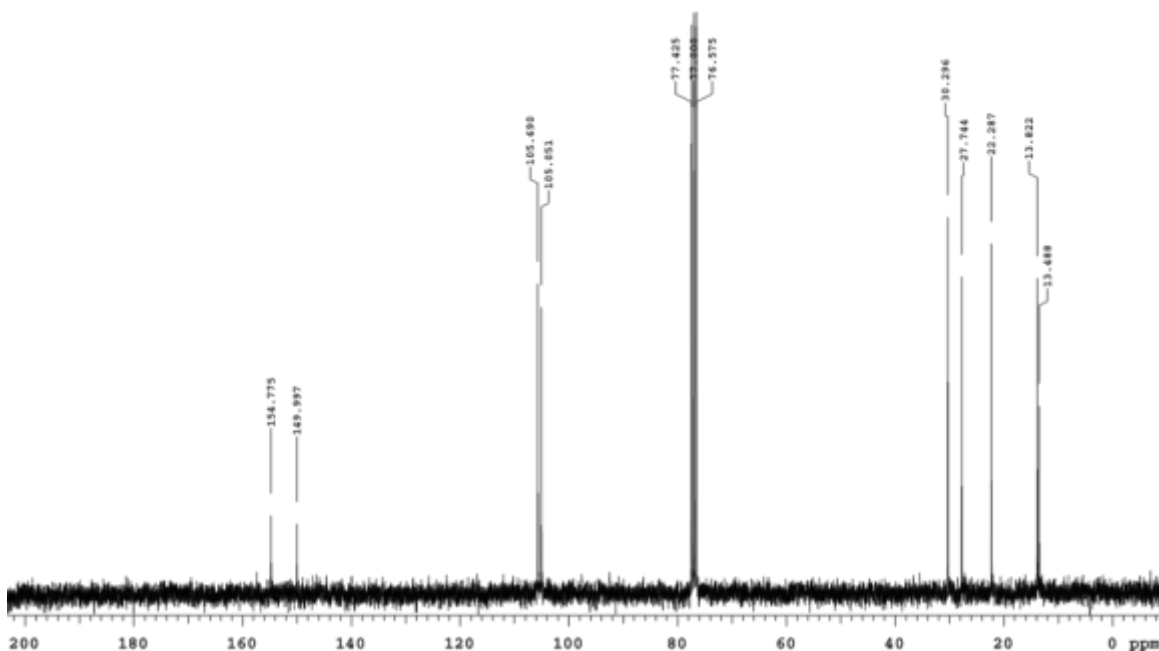
## 2-butyl-5-methylfuran (**1d**)<sup>[1], [5]</sup>

According to the general procedure, 2-methylfuran (1.8 mL, 20 mmol) was reacted with *n*-BuLi (13.5 mL, 20 mmol, 1.6 M solution in hexanes) and *n*-butyl iodide (2.3 mL, 20 mmol). The crude product was purified by flash chromatography on SiO<sub>2</sub> with *n*-pentane as eluent to afford 2-butyl-5-methylfuran (**1d**) (1.3 g, 61%) as colourless oil.

$R_f = 0.7$  (diethylether / *n*-pentane = 1:1);  $\delta_H$  (300 MHz; CDCl<sub>3</sub>) 0.93 (t,  $^3J_{4'-H, 3'-H} = 7.34$  Hz, 3H, 4'-H), 1.35-1.48 (m, 2H, 3'-H), 1.5-1.69 (m, 2H, 2'-H), 2.25 (s, 3H, CH<sub>3</sub>), 2.57 (t,  $^3J_{1'-H, 2'-H} = 7.62$  Hz, 2H, 1'-H), 5.84 (s, 2H, 4-H and 5-H) ppm;  $\delta_C$  (75 MHz; CDCl<sub>3</sub>) 13.48 (C-4'), 13.82 (CH<sub>3</sub>), 22.28 (C-3'), 27.74 (C-2'), 30.30 (C-1'), 105.05 (C-3), 105.70 (C-4), 149.99 (C-5), 154.77 (C-2) ppm.



**Fig. 5** <sup>1</sup>H NMR spectrum of 2-butyl-5-methylfuran (**1d**) (300 MHz, CDCl<sub>3</sub>).

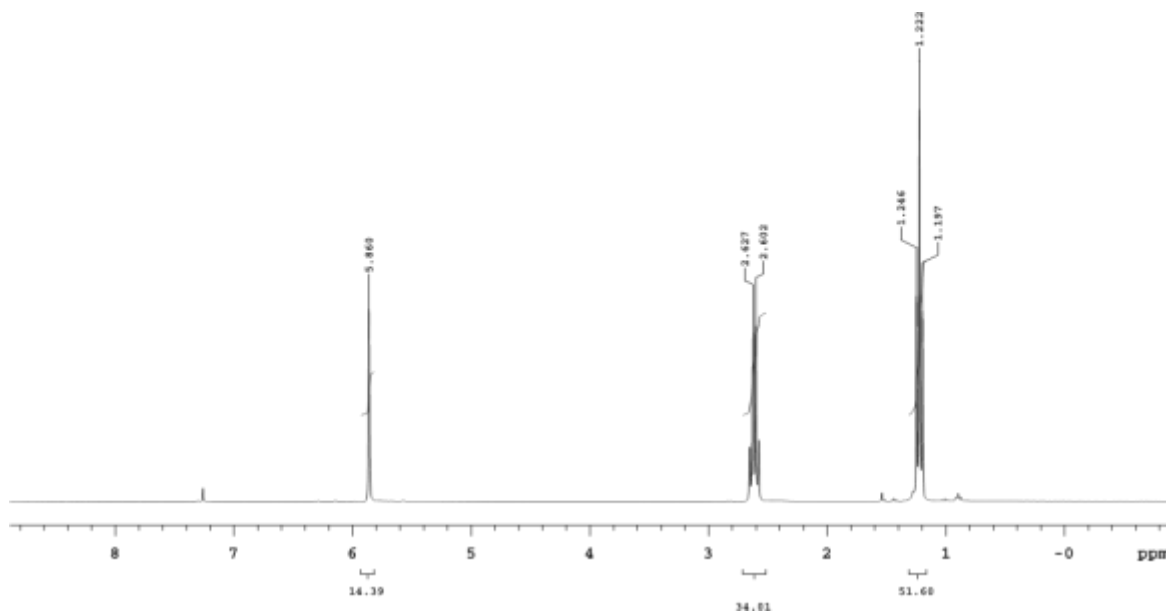


**Fig. 6**  $^{13}\text{C}$  NMR spectrum of 2-butyl-5-methylfuran (**1d**) (75 MHz,  $\text{CDCl}_3$ ).

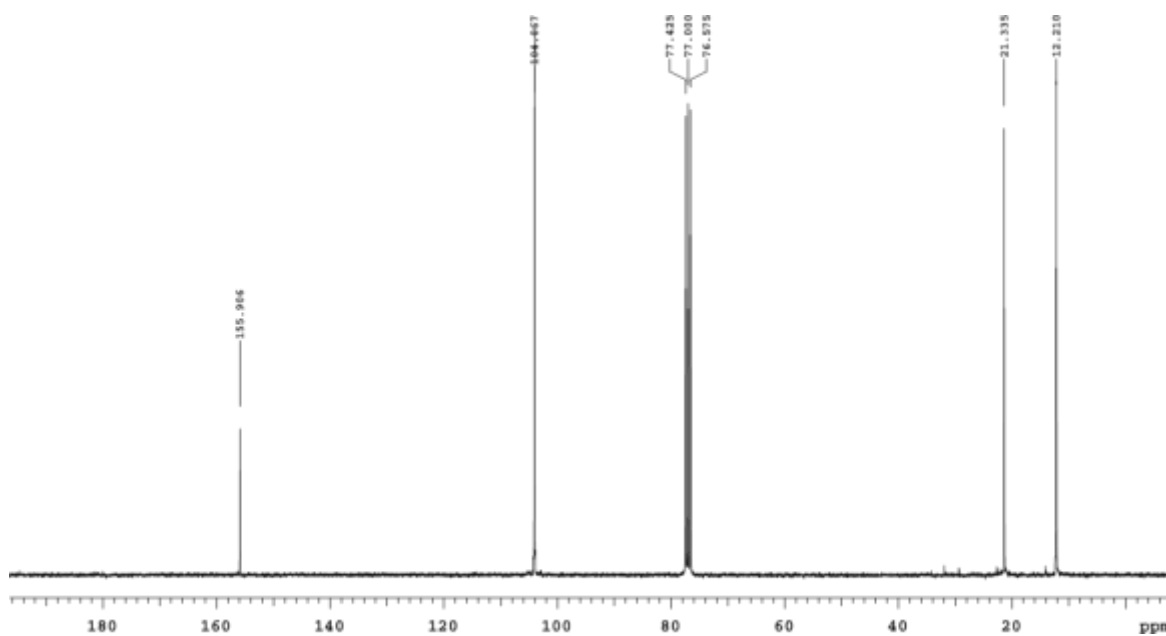
### 2,5-Diethylfuran (**1e**)<sup>[1]</sup>

According to the general procedure, 2-ethylfuran (2.1 mL, 20 mmol) was reacted with *n*-BuLi (13.5 mL, 20 mmol, 1.6 M solution in hexanes) and ethyl iodide (1.6 mL, 20 mmol). The crude product was purified by flash chromatography on  $\text{SiO}_2$  with *n*-pentane as eluent to afford 2,5-diethylfuran (**1e**) (1.49 g, 60%) as colourless oil.

$R_f = 0.7$  (diethylether/ *n*-pentane = 1:1);  $\delta_{\text{H}}$  (300 MHz;  $\text{CDCl}_3$ ) 1.22 (t,  $^3J_{2\text{-H}, 1\text{'-H}} = 7.5$  Hz, 6H, 2'-H), 2.61 (q,  $^3J_{1\text{'-H}, 2\text{'-H}} = 7.5$  Hz, 4H, 1'-H), 5.86 (s, 2H, 3-H and 4-H) ppm;  $\delta_{\text{C}}$  (75 MHz;  $\text{CDCl}_3$ ) 12.21 (C-2'), 21.34 (C-1'), 104.07 (C-3 and C-4), 155.91 (C-2 and C-5) ppm.



**Fig. 7** <sup>1</sup>H NMR spectrum of 2,5-diethylfuran (**1e**) (300 MHz, CDCl<sub>3</sub>).



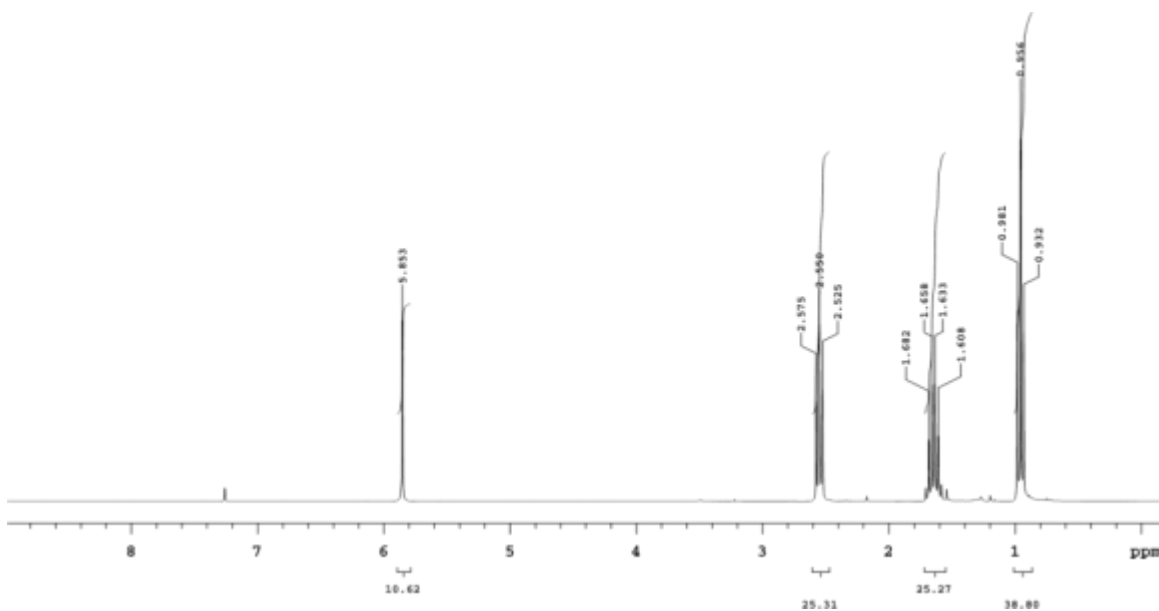
**Fig. 8** <sup>13</sup>C NMR spectrum of 2,5-diethylfuran (**1e**) (75 MHz, CDCl<sub>3</sub>).



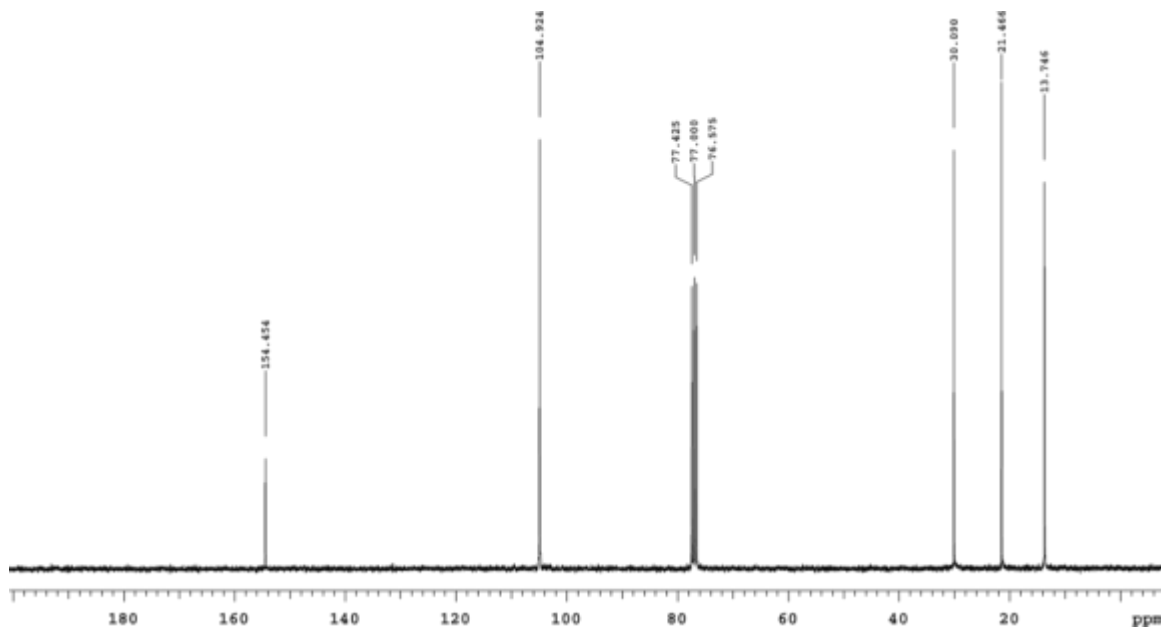
## 2,5-dipropylfuran (**1f**)<sup>[1]</sup>

According to the general procedure, furan (1.5 mL, 20 mmol) was reacted with *n*-BuLi (13.5 mL, 20 mmol, 1.6 M solution in hexanes) and *n*-propyl iodide (2 mL, 20 mmol). The crude product was purified by flash chromatography on SiO<sub>2</sub> with *n*-pentane as eluent to afford 2-propylfuran as colourless oil, which was reacted with *n*-BuLi (13.5 mL, 20 mmol, 1.6 M solution in hexanes) and *n*-propyl iodide (2 mL, 20 mmol) then purified by flash chromatography on SiO<sub>2</sub> with *n*-pentane as eluent to afford 2,5-dipropylfuran (**1f**) (1g, 33%) as colourless oil.

$R_f = 0.7$  (diethylether/ *n*-pentane = 1:1);  $\delta_H$ (300 MHz; CDCl<sub>3</sub>) 0.97 (t,  $^3J_{3'-H, 2'-H} = 7.5$  Hz, 6H, 3'-H), 1.64 (tq,  $^3J_{2'-H, 1'-H} = 7.4$  Hz,  $^3J_{2'-H, 3'-H} = 8$  Hz, 4H, 2'-H), 2.55 (t,  $^3J_{1'-H, 2'-H} = 7.5$  Hz, 4H, 1'-H), 5.85 (s, 2H, 3-H and 4-H) ppm;  $\delta_C$  (75 MHz; CDCl<sub>3</sub>) 13.75 (C-3'), 21.45 (C-2'), 30.09 (C-1'), 104.92 (C-3 and C-4), 154.45 (C-2 and C-5) ppm.



**Fig 9:** <sup>1</sup>H NMR spectrum of 2,5-dipropylfuran (**1f**) (300 MHz, CDCl<sub>3</sub>).

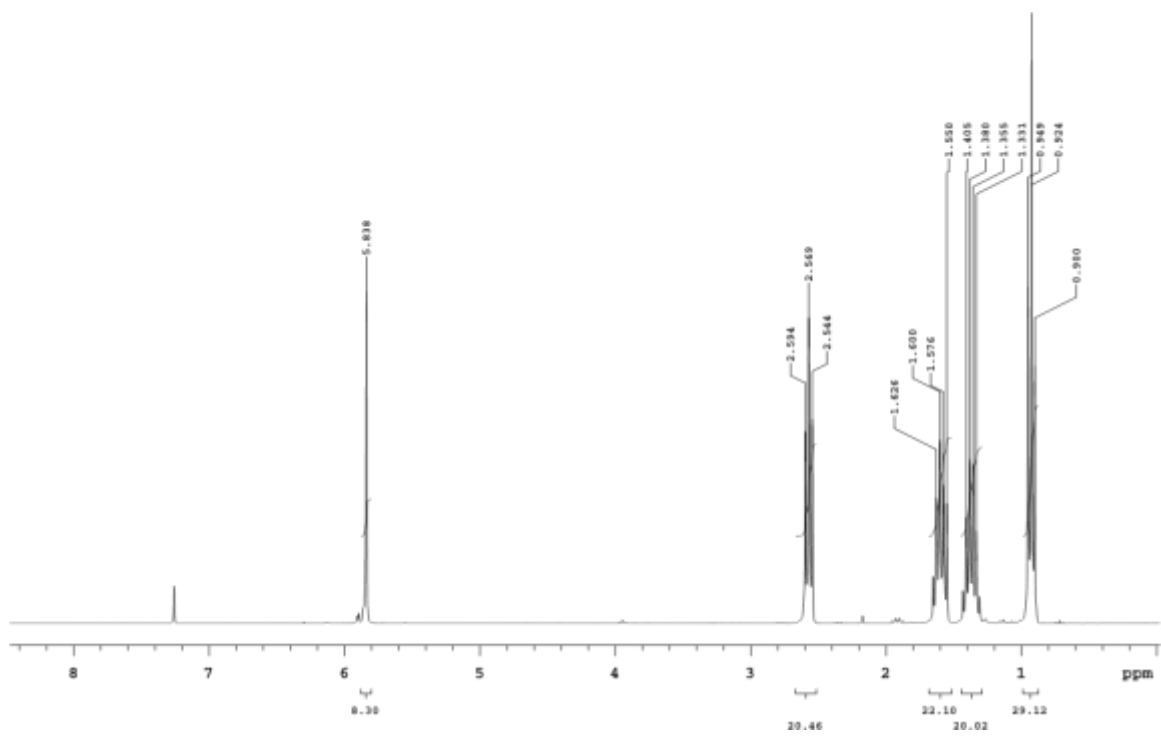


**Fig. 10**  $^{13}\text{C}$  NMR spectrum of 2,5-dipropylfuran (**1f**) (75 MHz,  $\text{CDCl}_3$ ).

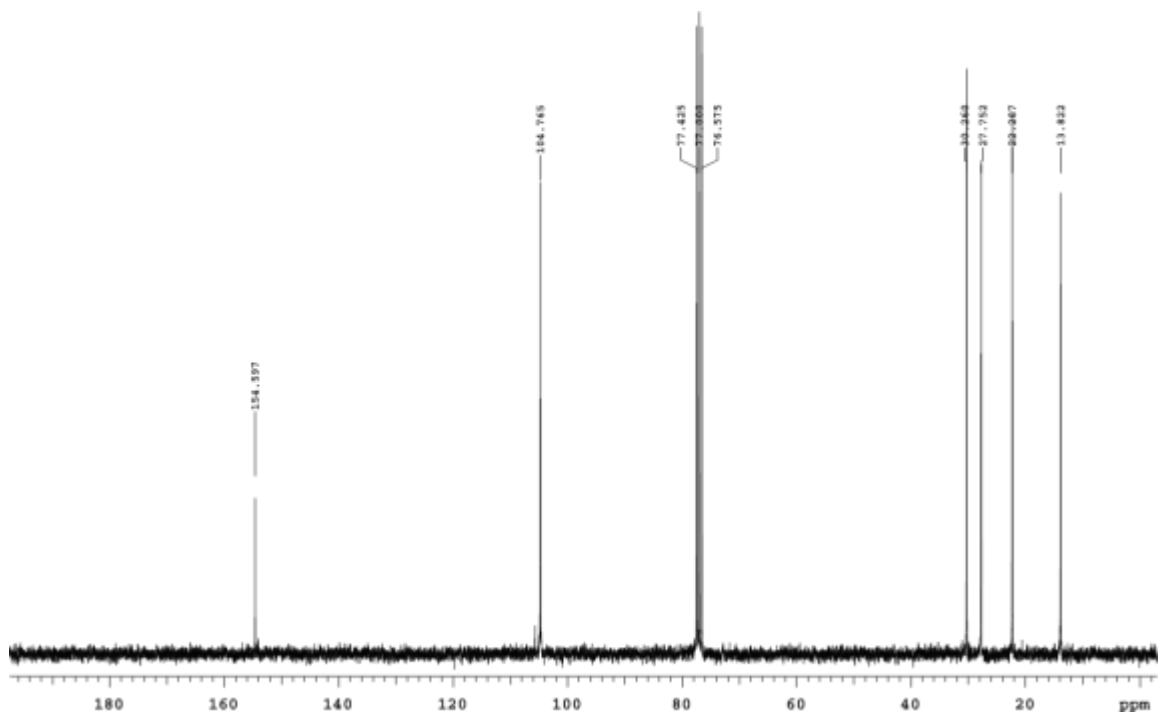
### 2,5-dibutylfuran (**1g**)<sup>[1]</sup>

According to the general procedure, 2-*n*-butylfuran (2.8 mL, 20 mmol) was reacted with *n*-BuLi (13.5 mL, 20 mmol, 1.6 M solution in hexanes) and *n*-butyl iodide (2.3 mL, 20 mmol). The crude product was purified by flash chromatography on  $\text{SiO}_2$  with *n*-pentane as eluent to afford 2,5-dibutylfuran (**1g**) (1.9 g, 61%) as colourless oil.

$R_f = 0.7$  (diethylether/ *n*-pentane = 1:1);  $\delta_{\text{H}}$  (300 MHz;  $\text{CDCl}_3$ ) 0.92 (t,  $^3J_{4'-\text{H}, 3'-\text{H}} = 7.3$  Hz, 6H, 4'-H), 1.34-1.47 (m, 4H, 3'-H), 1.57-1.70 (m, 4H, 2'-H), 2.57 (t,  $^3J_{1'-\text{H}, 2'-\text{H}} = 7.6$  Hz, 4H, 1'-H), 5.84 (s, 2H, 3-H and 4-H) ppm;  $\delta_{\text{C}}$  (75 MHz;  $\text{CDCl}_3$ ) 13.82 (C-4'), 22.29 (C-3'), 27.75 (C-2'), 30.26 (C-1'), 104.76 (C-3 and C-4), 154.60 (C-2 and C-5) ppm.



**Fig. 11** <sup>1</sup>H NMR spectrum of 2,5-dibutylfuran (**1g**) (300 MHz, CDCl<sub>3</sub>).



**Fig. 12** <sup>13</sup>C NMR spectrum of 2,5-dibutylfuran (**1g**) (75 MHz, CDCl<sub>3</sub>).

### 3 Oxidation of furans **1** to (Z)-enediones **2**

#### 3.1 General procedure for the oxidation of furans **1** to (Z)-enediones **2**

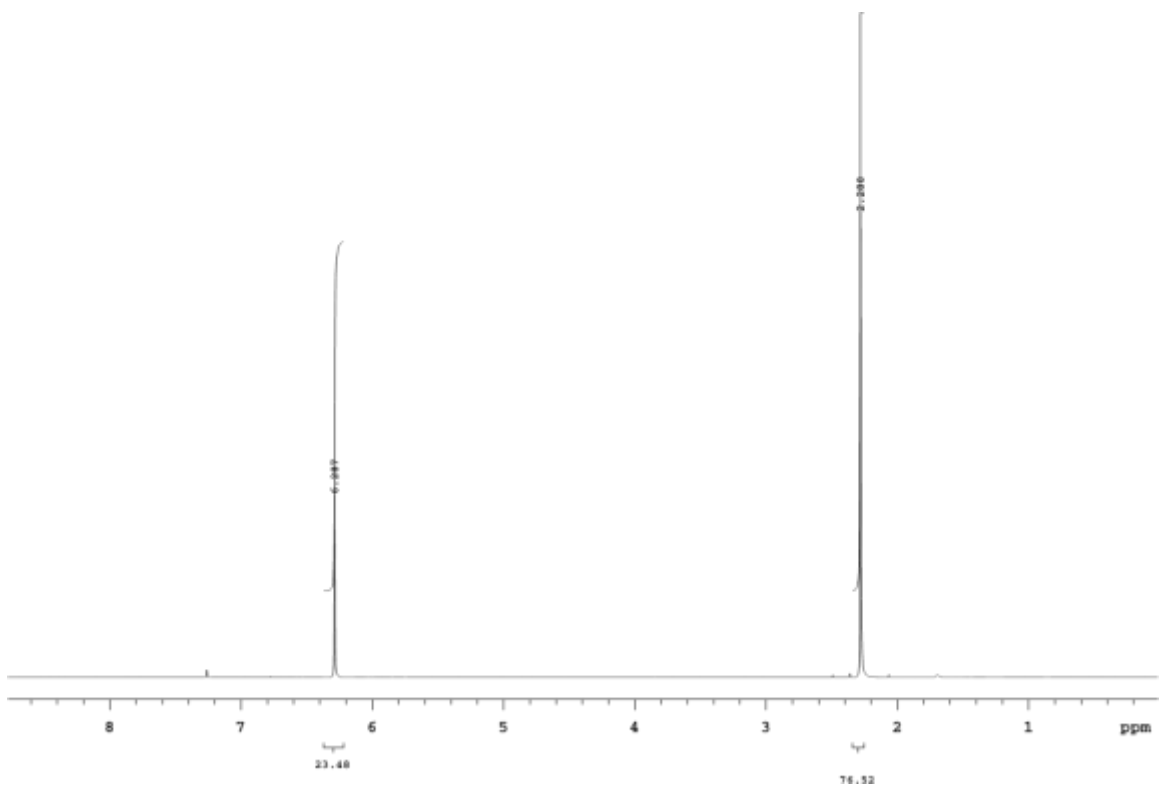
A 250 ml round bottomed flask was charged with 2,5-dialkylfuran (**1**) (2 mmol), *n*-octane (1 ml), 0.01 M acetate buffer pH 4.5 (10 mL), 4-hydroxy-TEMPO (**4b**) (34.5 mg, 0.2 mmol) and 350 U laccase (*Trametes versicolor*, FLUKA) and closed with a septum. The mixture was stirred at rt using a magnetic stirrer. The aqueous phase was saturated with NaCl (1 g) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (4×25 mL). The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvents in vacuo, the crude product was purified by flash chromatography on SiO<sub>2</sub>, diethylether / *n*-pentane = 1:1 to yield the (Z)-enedione **2**.

#### 3.2 Synthesis and analytical data for **2a-g**

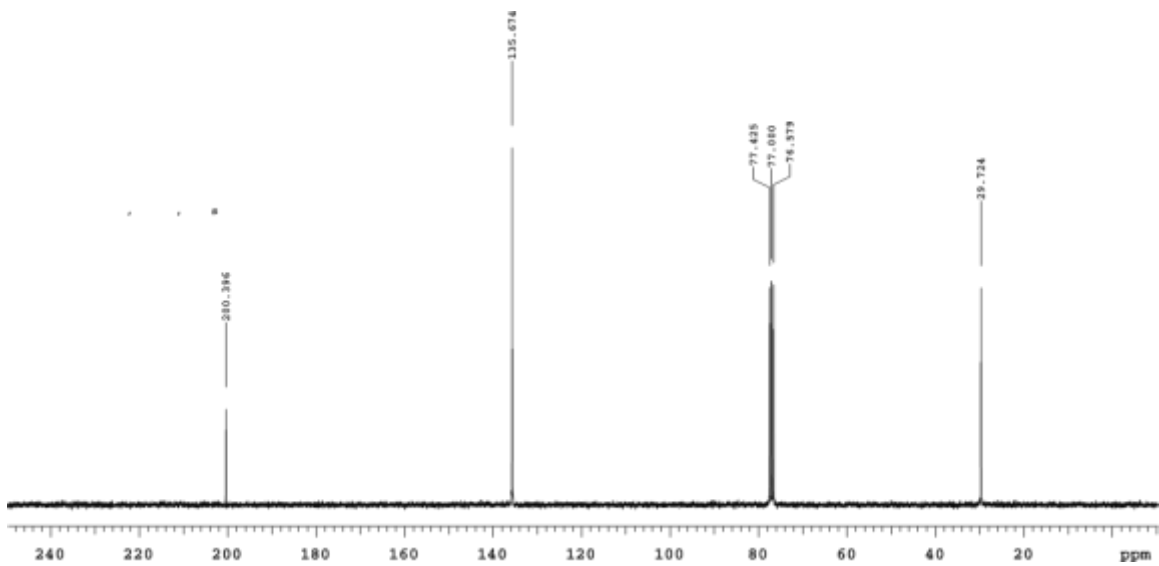
##### (Z)-3-Hexene-2,5-dione (**2a**)

According to the general procedure, 2,5-dimethylfuran (**1a**) (196 mg, 2 mmol) was reacted with **4b** (34.5 mg, 0.2 mmol) and 350 U laccase (*Trametes versicolor*, FLUKA) for 18 h. After purification of the crude product by flash chromatography on SiO<sub>2</sub> (diethylether / *n*-pentane = 1:1), (Z)-3-hexene-2,5-dione (**2a**) (177 mg, 79%) was obtained as yellow oil.

$R_f = 0.19$  (diethylether / *n*-pentane = 1:1),  $\delta_H$  (300 MHz; CDCl<sub>3</sub>) 2.28 (s, 6H, 1-H and 6-H), 6.29 (s, 2H, 3-H and 4-H);  $\delta_C$  (75 MHz; CDCl<sub>3</sub>) 29.72 (C-1 and C-6), 135.67 (C-3 and C-4), 200.40 (C-2 and C-5) ppm.



**Fig. 13** <sup>1</sup>H NMR spectrum of (Z)-3-hexene-2,5-dione (**2a**) (75 MHz, CDCl<sub>3</sub>).

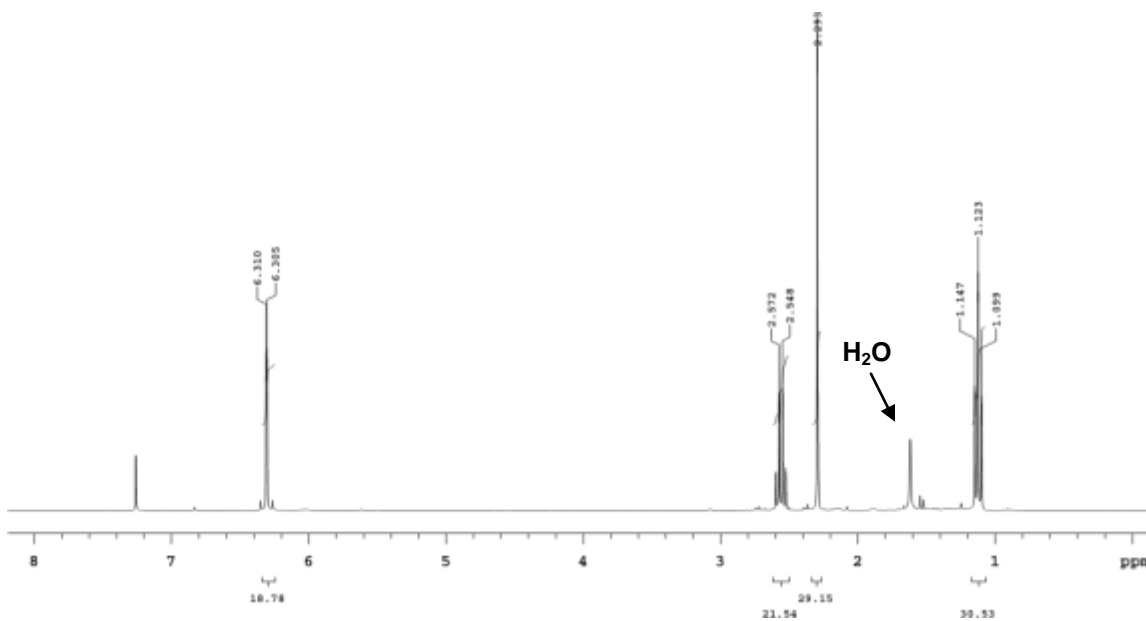


**Fig. 14** <sup>13</sup>C NMR spectrum of (Z)-3-hexene-2,5-dione (**2a**) (75 MHz, CDCl<sub>3</sub>).

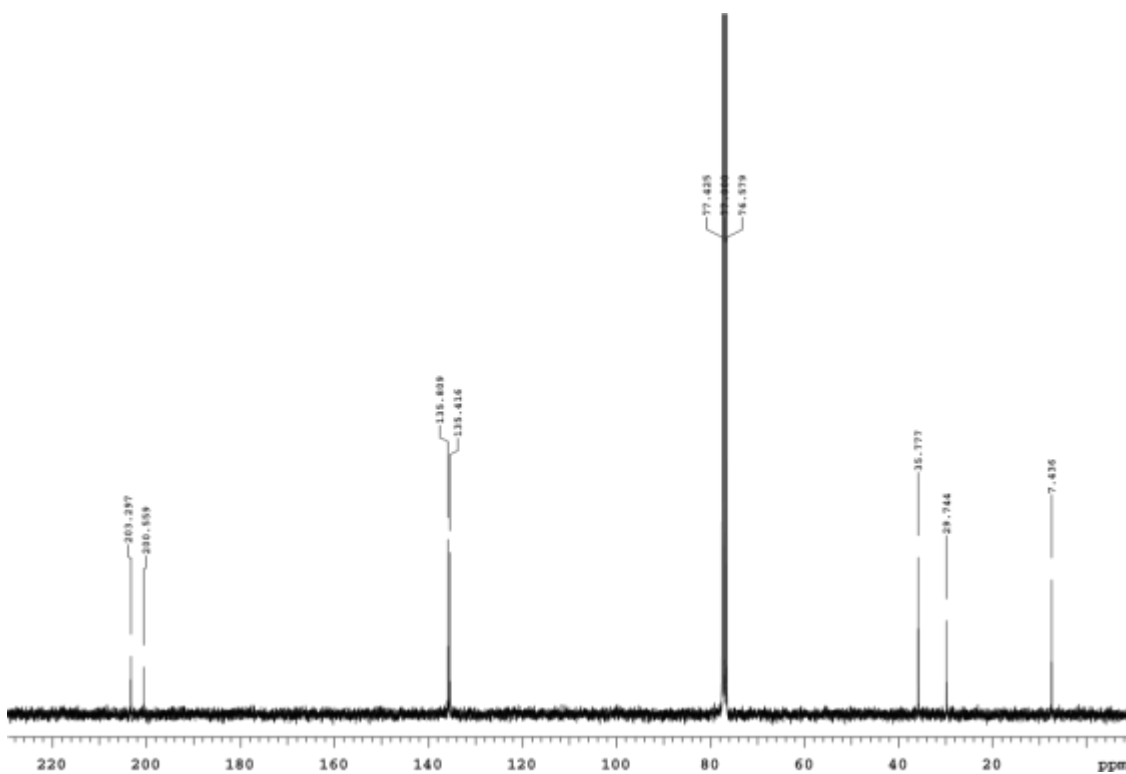
**(Z)-3-Heptene-2,5-dione (2b)**<sup>[6]</sup>

According to the general procedure, 2-ethyl-5-methylfuran (**1b**) (220 mg, 2 mmol) was reacted with **4b** (34.5 mg, 0.2mmol) and 350 U laccase (*Trametes versicolor*, FLUKA). After purification of the crude product by flash chromatography on SiO<sub>2</sub> (diethylether / *n*-pentane = 1:1), (*Z*)-3-heptene-2,5-dione (**2b**) (131 mg, 52%) was obtained as yellow oil.

$R_f = 0.28$  (diethylether / *n*-pentane = 1:1),  $\delta_H$  (300 MHz; CDCl<sub>3</sub>) 1.12 (t,  $^3J_{7-H, 6-H} = 7.3$  Hz, 3H, 7-H), 2.29 (s, 3H, 1-H), 2.55 (q,  $^3J_{6-H, 7-H} = 7.2$  Hz, 2H, 6-H), 6.30 (d,  $^3J_{3-H, 4-H} = 1.5$  Hz, 2H, 3-H and 4-H);  $\delta_C$  (75 MHz; CDCl<sub>3</sub>) 7.38 (C-7), 29.67 (C-1), 35, 71(C-6), 135.38 (C-3), 135.78 (C-4), 200.53 (C-2 or C-5), 203.27 (C-5 or C-2).



**Fig. 15** <sup>1</sup>H NMR spectrum of (*Z*)-3-heptene-2,5-dione (**2b**) (300 MHz, CDCl<sub>3</sub>).

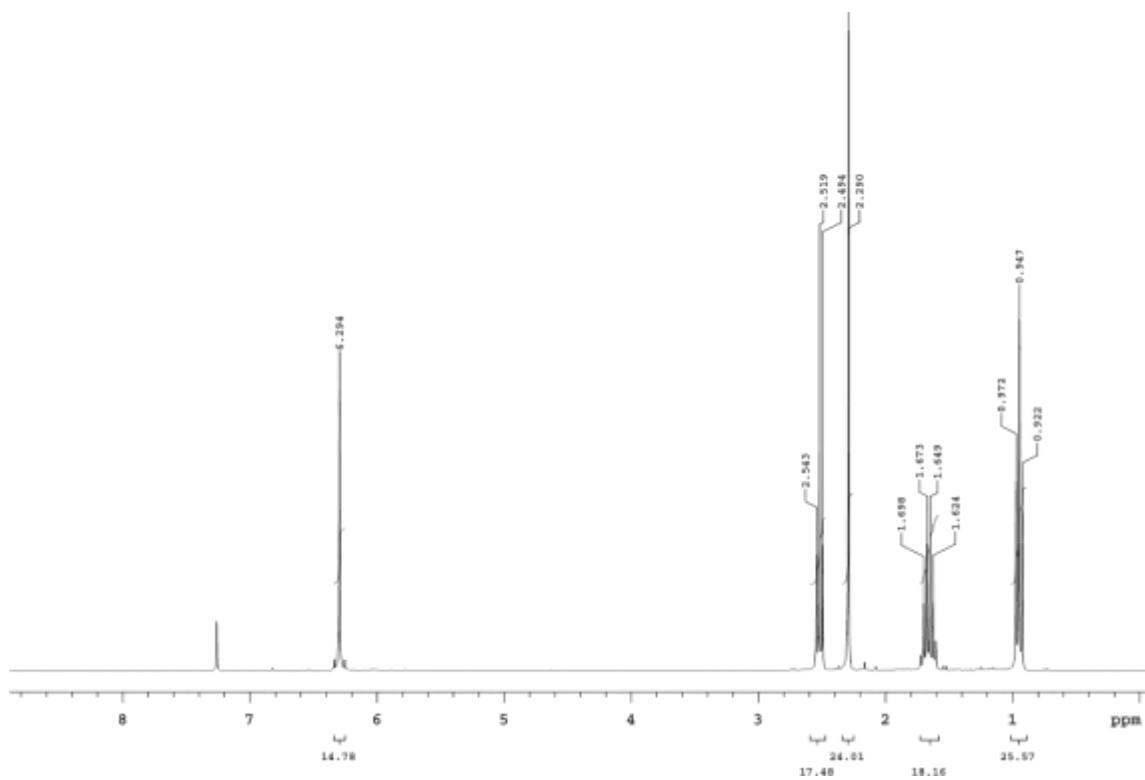


**Fig. 16** <sup>13</sup>C NMR spectrum of (Z)-3-heptene-2,5-dione (**2b**) (75 MHz, CDCl<sub>3</sub>).

### (Z)-3-Octene-2,5-dione (**2c**)<sup>[6]</sup>

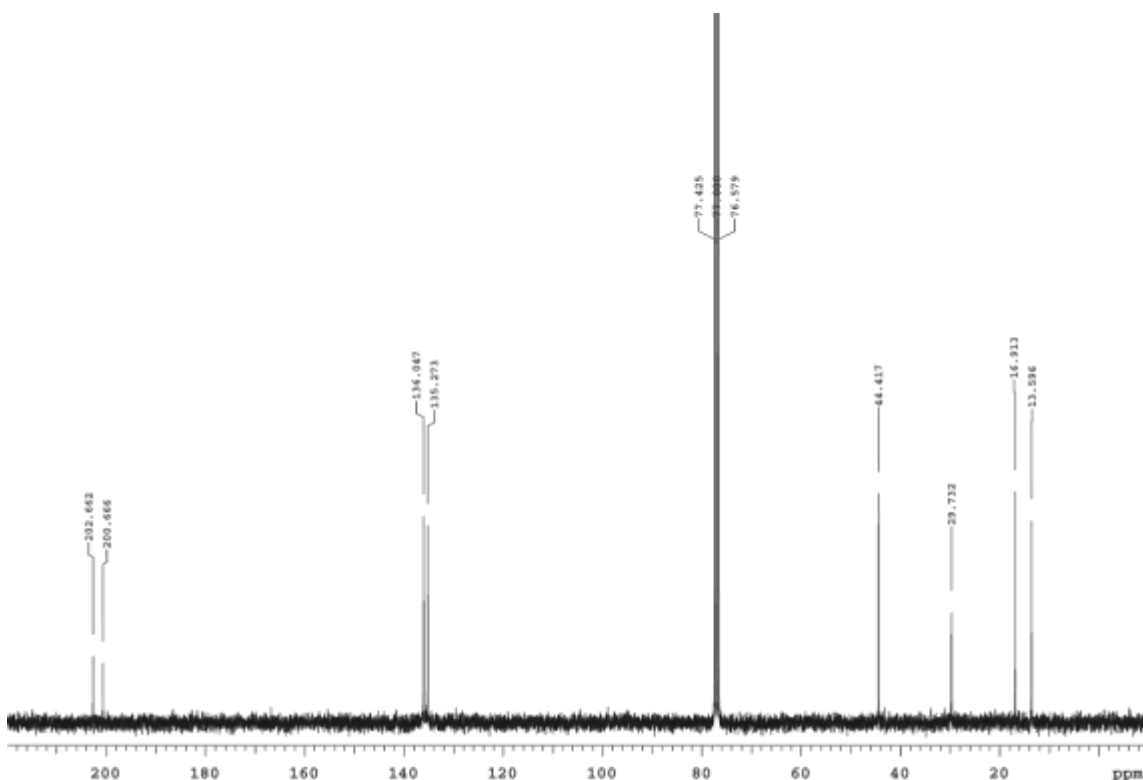
According to the general procedure, 2-methyl-5-propylfuran (**1c**) (248 mg, 2 mmol) was reacted with **4b** (34.5 mg, 0.2 mmol) and 350 U laccase (*Trametes versicolor*, FLUKA). After purification of the crude product by flash chromatography on SiO<sub>2</sub> (diethylether / *n*-pentane = 1:1), (Z)-3-octene-2,5-dione (**2c**) (165 mg, 59%) was obtained as yellow oil.

$R_f$  = 0.4 (diethylether / *n*-pentane = 1:1,  $\delta_H$  (300 MHz; CDCl<sub>3</sub>) 0.95 (t,  $^3J_{8-H, 7-H}$  = 7.4 Hz, 3H, 8-H), 1.66 (tq,  $^3J_{7-H, 6-H}$  = 7.5 Hz,  $^3J_{7-H, 8-H}$  = 7.8 Hz, 2H, 7-H), 2.29 (s, 3H, 1-H), 2.52 (t,  $^3J_{6-H, 7-H}$  = 7.4 Hz, 2H, 6-H), 6.31 (d,  $^3J_{3-H, 4-H}$  = 11.8 Hz, 1H, 3-H), 6.35 (d,  $^3J_{4-H, 3-H}$  = 11.8 Hz, 2H, 4-H) ppm;  $\delta_C$  (75 MHz; CDCl<sub>3</sub>) 13.60 (C-8), 16.91 (C-7), 29.73 (C-1), 44.42 (C-6), 135.27 (C-4), 136.05 (C-3), 200.53 (C-2 or C-5), 203.27 (C-5 or C-2) ppm.



**Fig. 17** <sup>1</sup>H NMR spectrum of (Z)-3-octene-2,5-dione (**2c**) (300 MHz, CDCl<sub>3</sub>).



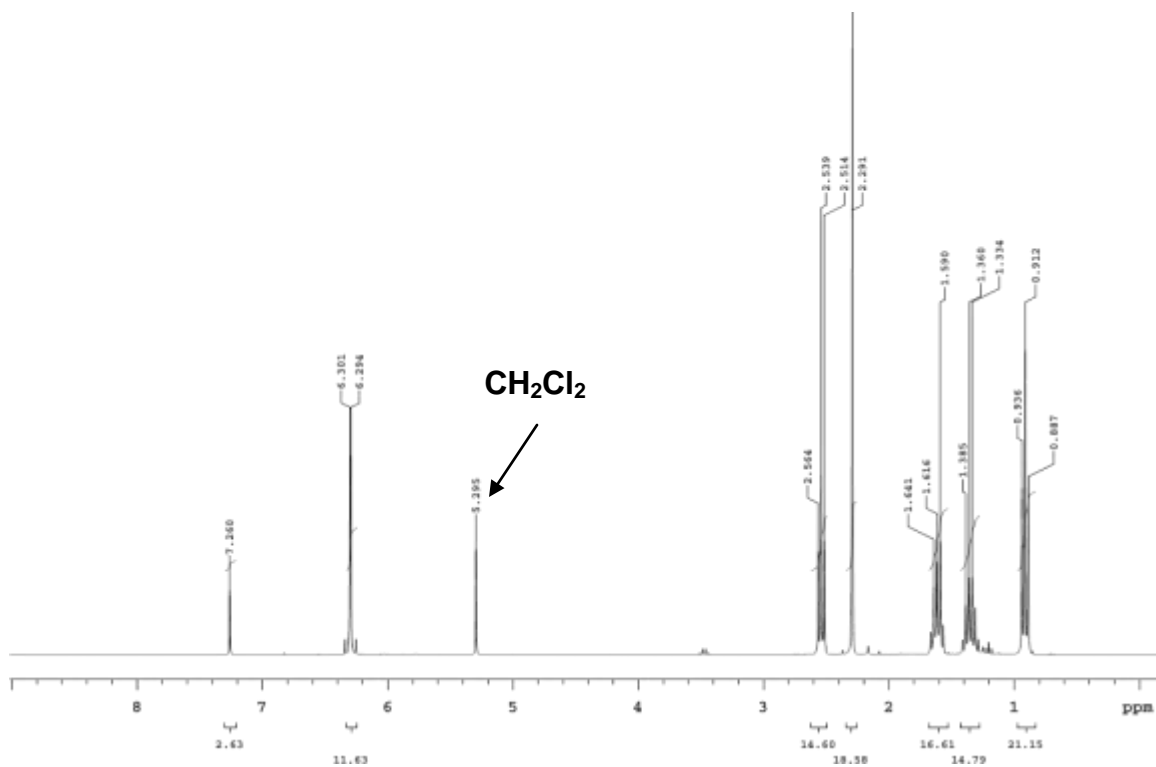


**Fig. 18**  $^{13}\text{C}$  NMR spectrum of (*Z*)-3-octene-2,5-dione (**2c**) (75 MHz,  $\text{CDCl}_3$ ).

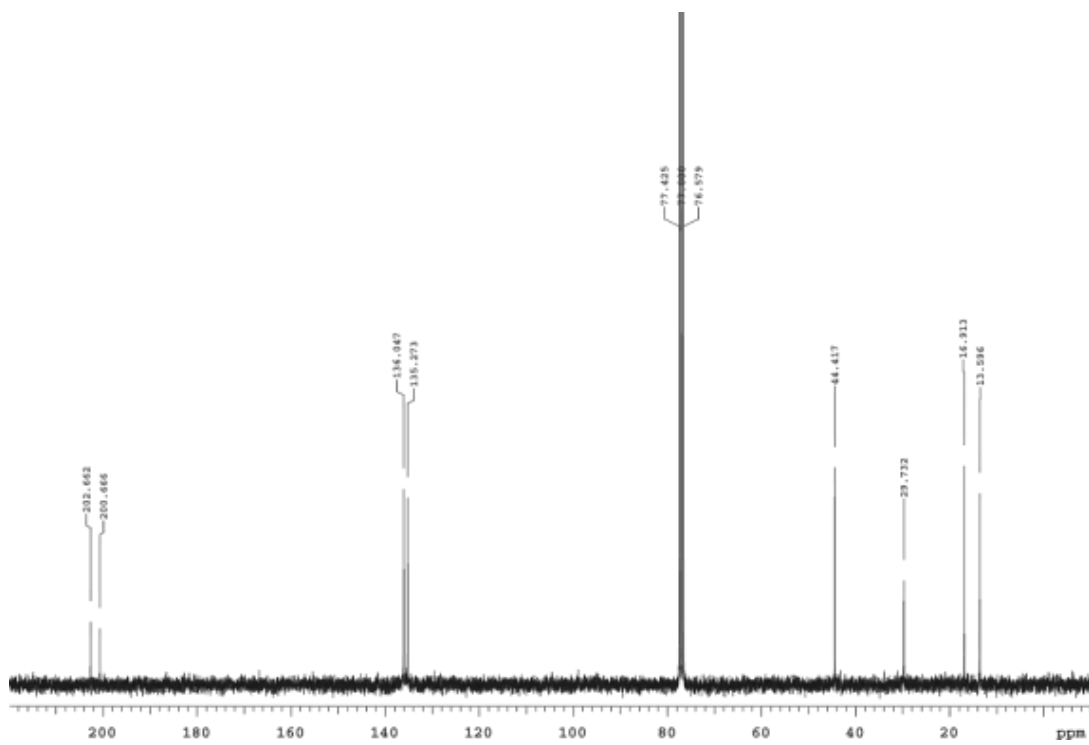
### (*Z*)-3-Nonene-2,5-dione (**2d**)<sup>[5]</sup>

According to the general procedure, 2-butyl-5-methylfuran (**1d**) (276 mg, 2 mmol) was reacted with **4b** (34.5 mg, 0.2 mmol) and 350 U laccase (*Trametes versicolor*, FLUKA). After purification of the crude product by flash chromatography on  $\text{SiO}_2$  (diethylether / *n*-pentane = 1:1), (*Z*)-3-nonene-2,5-dione (**2d**) (102 mg, 33%) was obtained as yellow oil.

$R_f = 0.32$  (diethylether / *n*-pentane = 1:1),  $\delta_H$  (300 MHz;  $\text{CDCl}_3$ ) 0.91 (t,  $^3J_{9-H, 8-H} = 7.3$  Hz, 3H, 9-H), 1.31-1.46 (m, 2H, 8-H), 1.58-1.71 (m, 2H, 7-H), 2.29 (s, 3H, 1-H), 2.54 (t,  $^3J_{6-H, 7-H} = 7.4$  Hz, 2H, 6-H), 6.31 (d  $^3J_{3-H, 4-H} = 11.9$  Hz, 2H, 3-H), 6.35 (d  $^3J_{4-H, 3-H} = 11.9$  Hz, 2H, 4-H) ppm;  $\delta_C$  (75 MHz;  $\text{CDCl}_3$ ) 13.82 (C-9), 22.21 (C-8), 25.54 (C-7), 35.71 (C-6), 42.29 (C-1), 135.38 (C-4), 135.78 (C-3), 200.67 (C-2 or C-5), 202.78 (C-5 or C-2) ppm.



**Fig. 19**  $^1\text{H}$  NMR spectrum of (Z)-3-nonene-2,5-dione (**2d**) (300 MHz,  $\text{CDCl}_3$ ).

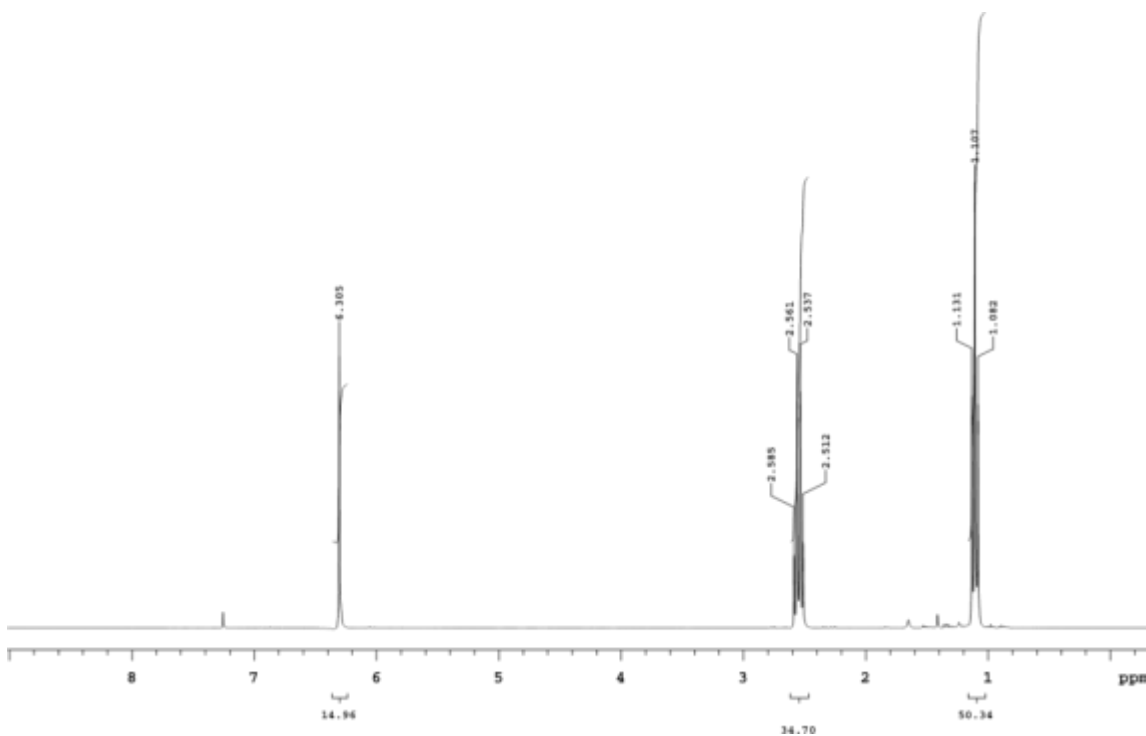


**Fig. 20**  $^{13}\text{C}$  NMR spectrum of (Z)-3-nonene-2,5-dione (**2d**) (75 MHz,  $\text{CDCl}_3$ ).

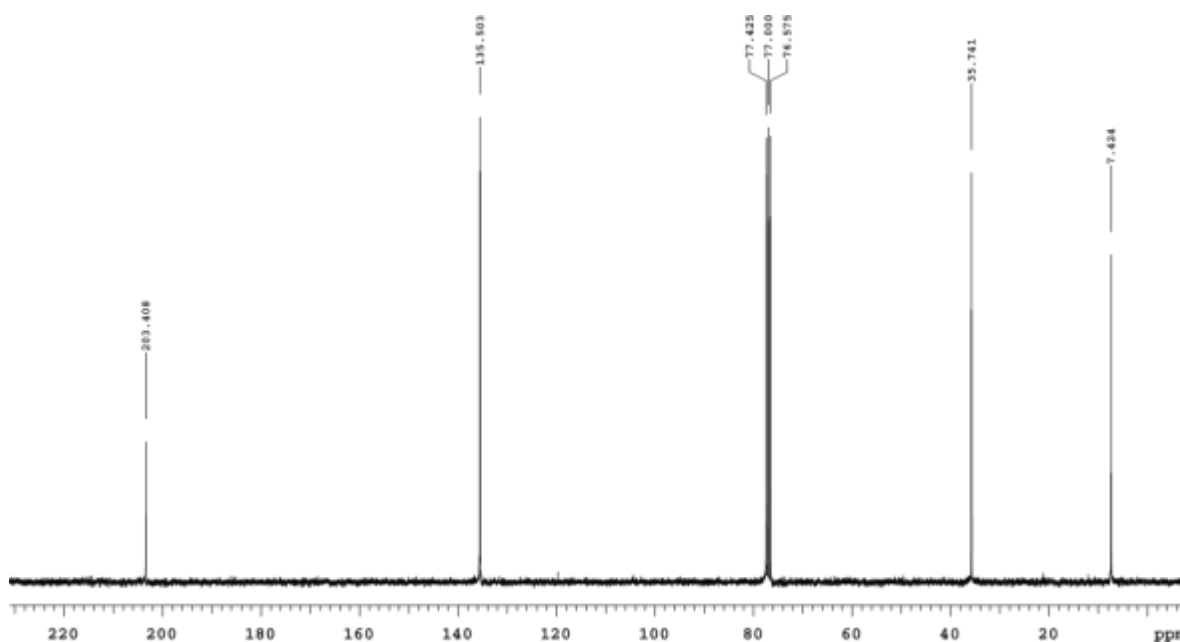
**(Z)-4-Octene-3,6-dione (2e)**<sup>[6]</sup>

According to the general procedure, 2,5-diethylfuran (**1e**) (248 mg, 2 mmol) was reacted with **4b** (34.5 mg, 0.2 mmol) and 350 U laccase (*Trametes versicolor*, FLUKA). After purification of the crude product by flash chromatography on SiO<sub>2</sub> (diethylether / *n*-pentane = 1:1), (Z)-4-octene-3,6-dione (**2e**) (182 mg, 65%) was obtained as yellow oil.

$R_f = 0.4$  (diethylether / *n*-pentane = 1:1),  $\delta_H$  (300 MHz; CDCl<sub>3</sub>) 1.11 (t,  $^3J_{1-H, 2-H} = ^3J_{7-H, 8-H} = 7.3$  Hz, 6H, 1-H and 8-H), 2.55 (q,  $^3J_{2-H, 1-H} = ^3J_{8-H, 7-H} = 7.2$  Hz, 4H, 2-H and 7-H), 6.31 (s, 2H, 4-H and 5-H) ppm;  $\delta_C$  (75 MHz; CDCl<sub>3</sub>) 7.42 (C-1 and C-8), 35.74 (C-2 and C-7), 135.50 (C-4 and C-5), 203.40 (C-3 and C-6) ppm.



**Fig. 21** <sup>1</sup>H NMR spectrum of (Z)-4-octene-3,6-dione (**2e**) (300 MHz, CDCl<sub>3</sub>).

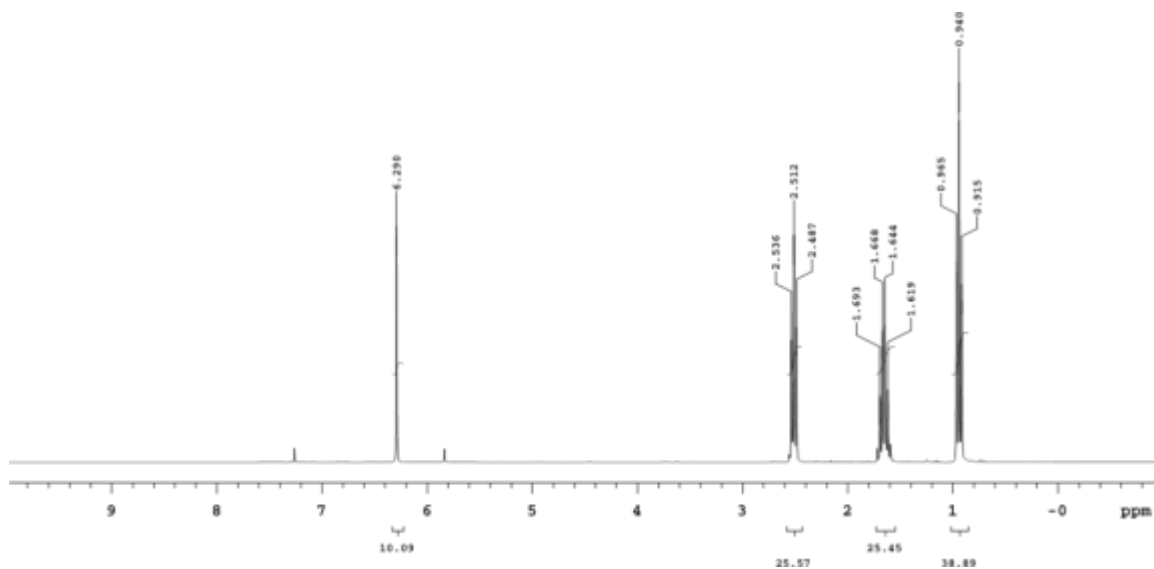


**Fig. 22**  $^{13}\text{C}$  NMR spectrum of (*Z*)-4-octene-3,6-dione (**2e**) (75 MHz,  $\text{CDCl}_3$ ).

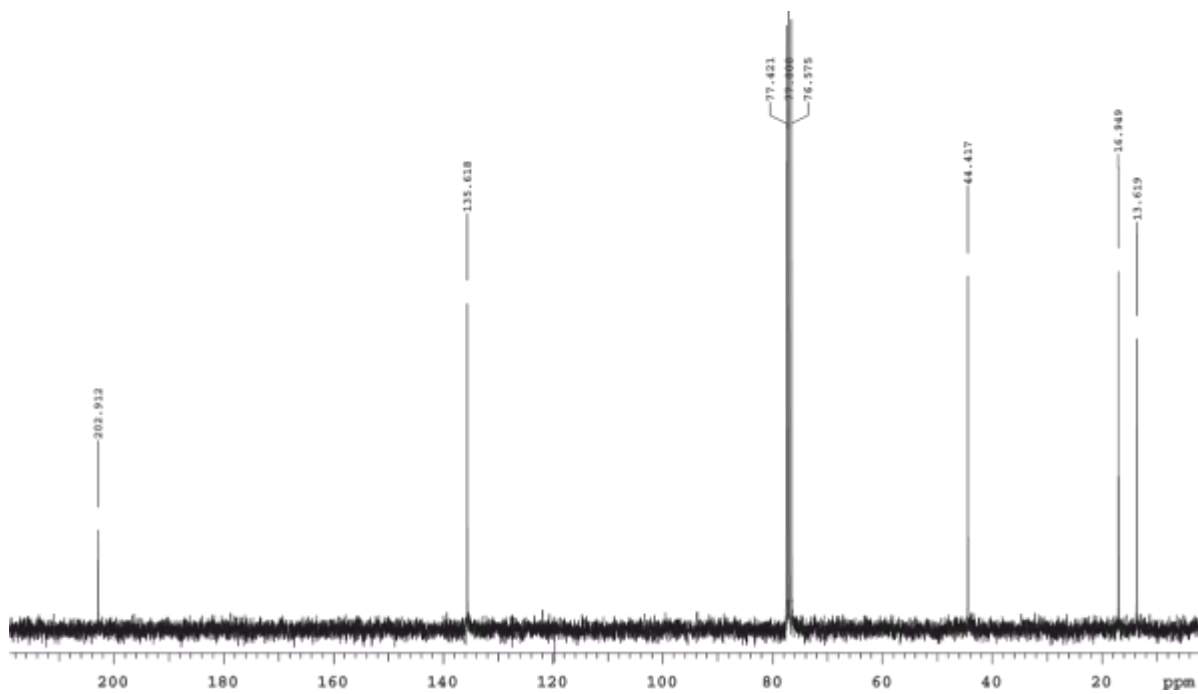
### (*Z*)-5-Decene-4,7-dione (**2f**)<sup>[6]</sup>

According to the general procedure, 2,5-dipropylfuran (**1f**) (304 mg, 2 mmol) was reacted with **4b** (34.5 mg, 0.2 mmol) and 350 U laccase (*Trametes versicolor*, FLUKA). After purification of the crude product by flash chromatography on  $\text{SiO}_2$  (diethylether / *n*-pentane = 1: 1), (*Z*)-5-decene-3,7-dione (**2f**) (74 mg, 22%) was obtained as yellow oil.

$R_f$  = 0.46 (diethylether / *n*-pentane = 1:1),  $\delta_{\text{H}}$  (300 MHz;  $\text{CDCl}_3$ ) 0.94 (t,  $^3J_{1\text{-H}, 2\text{-H}} = ^3J_{9\text{-H}, 10\text{-H}} = 7.4$  Hz, 6H, 1-H and 10-H), 1.65 (sextet,  $^3J_{2\text{-H}, 1\text{-H}} = ^3J_{2\text{-H}, 3\text{-H}} = ^3J_{9\text{-H}, 10\text{-H}} = ^3J_{9\text{-H}, 8\text{-H}} = 7.3$  Hz), 2.51 (t,  $^3J_{3\text{-H}, 2\text{-H}} = ^3J_{8\text{-H}, 9\text{-H}} = 7.3$  Hz, 4H, 3-H and 8-H), 6.29 (s, 2H, 5-H and 6-H) ppm;  $\delta_{\text{C}}$  (75 MHz;  $\text{CDCl}_3$ ) 13.62 (C-1 and C-10), 16.95 (C-2 and C-9), 44.42 (C-3 and C-8), 135.62 (C-5 and C-6), 202.91 (C-4 and C-7) ppm.



**Fig. 23** <sup>1</sup>H NMR spectrum of (*Z*)-5-decene-4,7-dione (**2f**) (300 MHz, CDCl<sub>3</sub>).



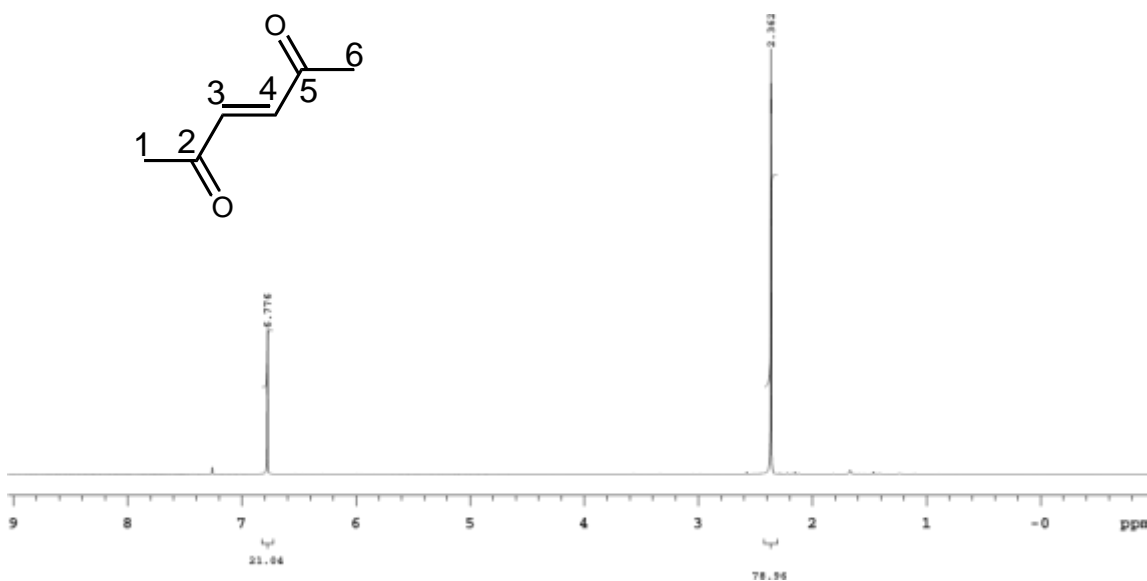
**Fig. 24** <sup>13</sup>C NMR spectrum of (*Z*)-5-decene-4,7-dione (**2f**) (75 MHz, CDCl<sub>3</sub>).

#### 4 Oxidation of furan **1a** to (*E*)-enedione **3a**

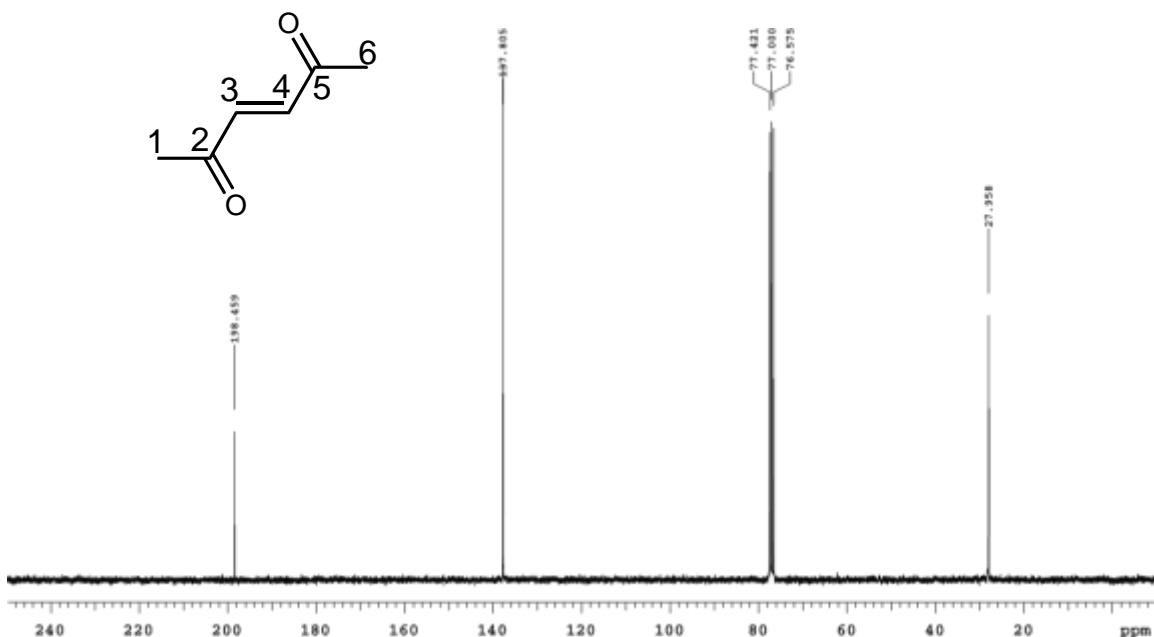
A 250 ml round bottomed flask was charged 2,5-dimethylfuran (**1a**) (192 mg, 2 mmol), *n*-octane (1 mL), 0.01 M acetate buffer pH 4.5 (10 mL), TEMPO (**4a**) (32 mg, 0.2 mmol) and 350 U laccase (*Trametes versicolor*, FLUKA), equipped with a magnetic magnetic stirrer and closed with a septum. The mixture was stirred for 18 h at rt. Then, violuric acid (**5**) (87.5 mg, 0.5 mmol) was added and the mixture was stirred at 50 °C for 6 h. The reaction mixture was saturated with NaCl (1 g) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (6×25 mL). The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvents in vacuo, the crude product was purified by flash chromatography on SiO<sub>2</sub> (diethylether / *n*-pentane = 1:1 to afford (*E*)-3-hexene-2,5-dione (**3a**) (157 mg, 70%) as a yellowish solid.

#### (*E*)-3-Hexene-2,5-dione (**3a**)

$R_f = 0.29$  (diethylether / *n*-pentane = 1:1),  $\delta_H$  (300 MHz; CDCl<sub>3</sub>) 2.36 (s, 1-H and 6-H), 6.78 (2H, 3-H and 4-H);  $\delta_C$  (75 MHz; CDCl<sub>3</sub>) 28.0 (C-1 and C-6), 137.81 (C-3 and C-4), 198.46 (C-2 and C-5) ppm.



**Fig. 25** <sup>1</sup>H NMR spectrum of (*E*)-3-hexene-2,5-dione (**3a**) (300 MHz, CDCl<sub>3</sub>).



**Fig. 26** <sup>13</sup>C NMR spectrum of (*E*)-3-hexene-2,5-dione (**3a**) (75 MHz, CDCl<sub>3</sub>).

## 5 Determination of the laccase activity <sup>[7],[8]</sup>

A 0.1 M solution of ABTS (0.3 mL) in 0.01 M acetate buffer (pH = 4.5) was diluted with 0.01 M acetate buffer (2.6 mL, pH = 4.5) and treated with a solution of laccase in the same buffer (0.1 mL). The change in absorption was followed *via* UV spectroscopy ( $\lambda = 414$  nm). One unit was defined as the amount of laccase (*Trametes versicolor*, Fluka) that converts 1 mmol of ABTS per minute at pH = 4.5 at rt.

## 6 References

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